EXAFS STUDIES OF SOME TRANSITION METAL SYSTEMS

A Thesis Submitted for the Degree of
Doctor of Philosophy

by Paul Stephen Western

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ACKNOWLEDGMENTS

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An especial "Thankyou" to all the many denizens, past and present, of the 6th floor, for three years' assistance, friendship and misspent lunchtimes around the pool table at 'The Brook'. 
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Using the technique of extended X-ray absorption fine structure (EXAFS) spectroscopy, it is possible to examine the atomic structures of even non-crystalline samples. The information is obtained as a view of the structure around the atoms of a particular element. In this work, studies of a variety of transition metal systems are reported.

Surface anchored clusters offer the promise of catalysts that combine the advantages of homogeneous and heterogeneous systems. The metal framework of the tethered hexanuclear rhodium cluster Rh$_6$(CO)$_{16}$PPh$_2$(CH$_2$)$_2$-SILICA was found to be structurally identical to its molecular precursor, Rh$_6$(CO)$_{16}$. This is evidence that the cluster is held at a distance from the silica surface, with no direct interaction between the cluster and the oxide.

Mixed metal clusters are of interest both as a potential source of stereoselective catalysts and as models of heterogeneous alloy catalysts. The EXAFS results for the clusters H$_2$Ru$_4$(CO)$_{12}$(MPPPh)$_2$ (M=Cu, Au; 1,2 respectively) compared reasonably well with crystallographic data. An unidentified carbonyl cluster, a minor product of the reaction of (1) with carbon monoxide, contains carbon atoms bound to copper at a distance of 2.03Å. These are taken as evidence of carbonyl units forming a semi-bridging link between copper and ruthenium atoms in the cluster.

Polyoxometalate anions are believed to provide soluble models for the heterogeneous metal oxides that are so often used as catalyst supports. EXAFS spectra, including solution spectra, of several polyoxometalates were recorded. The structures of [V$_2$W$_4$O$_{13}$]$_2^-$ and [V$_2$W$_4$O$_{13}$]$_3^-$, in particular, were resolved in almost as much detail in solution as in the solid state, with atoms up to 5Å from each tungsten atom being detectable. There is thus an obvious potential to monitor structural changes resulting from, or even during, reactions involving polyoxometalate complexes.
### ABBREVIATIONS

<table>
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<tr>
<td>15C5</td>
<td>15-crown-5 crown ether</td>
</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
</tr>
<tr>
<td>Cy</td>
<td>cyclohexanyl</td>
</tr>
<tr>
<td>E</td>
<td>non-metal atom</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>L</td>
<td>ligand</td>
</tr>
<tr>
<td>M</td>
<td>metal atom</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>Py</td>
<td>pyridyl</td>
</tr>
<tr>
<td>R</td>
<td>alkyl; alkyl or aryl</td>
</tr>
<tr>
<td>X</td>
<td>undefined atom</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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</thead>
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<tr>
<td>EDAX</td>
<td>Energy Dispersive Analysis of X-rays</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>i.r.</td>
<td>infra-red</td>
</tr>
<tr>
<td></td>
<td>(classification of i.r. signals: s strong m medium w weak sh shoulder)</td>
</tr>
<tr>
<td>JANET</td>
<td>Joint Academic Network</td>
</tr>
<tr>
<td>MAS</td>
<td>Magic Angle Spinning</td>
</tr>
<tr>
<td>nmr</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>SEPT</td>
<td>Skeletal Electron Pair Theory</td>
</tr>
<tr>
<td>SRS</td>
<td>Synchrotron Radiation Source</td>
</tr>
<tr>
<td>uv/vis</td>
<td>ultra-violet/visible</td>
</tr>
<tr>
<td>WGSR</td>
<td>Water Gas Shift Reaction</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near Edge Structure</td>
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INTRODUCTION
Introduction

The studies reported in this work address three areas of transition metal chemistry. Each one is connected, to a greater or lesser degree, with research into catalysis; especially, but not exclusively, involving transition metal carbonyl clusters.

**Transition Metal Clusters**

Transition metal clusters represent metal particles of uniform size and established geometries. Their properties are intermediate between those of metal atoms and crystallites. The close proximity of coordination sites allows for interactions not possible in mononuclear systems.

A generally accepted definition of a transition metal cluster is 3 or more metal atoms in a discrete compound containing M-M bonds, stabilised by surrounding ligands. The class can be divided into those compounds which have high-valent metal atoms, exemplified by halide clusters like Nb₆Cl₁₂, and those containing low-valent metals, stabilised by \( \pi \)-acceptor ligands such as carbonyls, isocyanides and phosphines. All clusters contain triangular or square faces, and the majority represent fragments of close-packed metal atoms. Transition metal cluster structures have been reviewed by Raithby².

The synthesis of these compounds runs ahead of the theoretical understanding of the structures so produced. Nevertheless, the well-known effective atomic number rule (18 electron rule) is good for binary carbonyls with up to four atoms³. Wade's skeletal electron pair theory (SEPT)⁴, as applied to metal clusters by Mingos⁵, provides some insight into the structures of clusters with four to six metal atoms⁶-¹².
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Interest in Transition Metal Clusters

In addition to being studied for their own sake\(^\text{14}\), it is thought that transition metal clusters provide insights into the properties of metal surfaces\(^\text{15–20}\). In particular, they may throw light upon:

i) preferential binding modes of small molecules with various metal atom arrangements,

ii) interconversion energies between bonding modes,

iii) the chemical activity at a surface, e.g. during catalysis.

Important differences must always be borne in mind, however. For instance, clusters tend to have lower metal-metal coordination numbers, with correspondingly higher metal-ligand coordination. Compare the large anion \([\text{Pt}_{18}\text{H}_6\text{(CO)}_{24}]^-\) with a typical flat metal surface: the M-M coordination number at the surface of the metal will be 6-9 against 6 in the cluster, whilst the M-CO coordination of surface atoms is less than one for the metal surface, 1.66 in the cluster. What is more, metal surface atoms are not saturated, which can lead to a difference in the stereochemistry of bound molecules and fragments, e.g. 'CH\(_3\)':

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{M} \\
\text{M} & \quad \text{M}
\end{align*}
\]

Cluster

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{M} \\
\text{M} & \quad \text{M}
\end{align*}
\]

Metal

(Ni (111))

The resemblance between clusters and metal surfaces is greatest when comparing large clusters with small metal crystallites:

i) both have enclosed M atoms,

ii) both show transmission of electronic effects via L-M-M-CO linkages,

iii) the higher work function for small metal particles indicates that they are electron deficient; this is also true of clusters, but they are shielded by ligands or anionic charge,
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iv) the enthalpy of the M-CO bond in clusters is similar to the enthalpy of CO chemisorption on metal particles; the M-M bond enthalpy in clusters resembles the heat of vapourisation of metal crystallites,
v) both have similar M-M distances, and arrangements of metal atoms,
vii) the behaviour of both under vigorous catalytic conditions is thought to be similar. Changes in nuclearity and packing like those that occur in clusters are thought to take place at a lesser pace in crystallites, such as in superficial carbide layers in Fischer-Tropsch hydrocarbon production.

Clusters and Catalysis

Transition metals are prevalent in catalysis for several reasons:
i) valence orbitals are available for $\sigma$- and $\pi$-bonding,
ii) there is a wide choice of ligands,
iii) they have variable oxidation states,
iv) there are wide ranges of ligand effects and stereochemistries,
v) ligands can be orientated and activated by coordination.

Clusters of transition metal atoms have their role to play within the field of catalysis research.

On one hand, they can be used to model the mode of coordination, stereochemistry, and reaction mechanisms of molecules or fragments attached to sites like those on surfaces. For example, the Os$_3$ triangle in H$_2$Os$_3$(CO)$_6$ supports alkene hydrogenation. Those clusters with interstitial or semi-interstitial C or N atoms model bulk or surface carbides and nitrides.

Clusters can also be used in actual catalytic systems.

When used in heterogeneous catalysis, they can produce metal particles of very even size if the ligands are removed, or 'heterogenised' homogeneous catalysts if not.
In homogeneous catalysis, clusters can be used as a source of reactive mononuclear species. It is also thought that clusters can be active in catalysing reactions in their own right, e.g. in the hydroformylation of olefins with Rh₆(CO)₁₂ or Rh₆(CO)₁₄. It is by no means certain that the cluster itself is the catalytically active species. In fact it is generally difficult to establish this. The criteria by which the cluster is judged the actual catalyst have been set out by Laine (see chapter three).

**Extended X-Ray Absorption Fine Structure (EXAFS) Spectroscopy**

EXAFS spectroscopy is an X-ray absorption spectroscopy technique which provides information on the type, number and distances of the atoms surrounding the X-ray absorbing element under study. The usual source of the X-rays is synchrotron radiation, for reasons mentioned in the next chapter. An important advantage of EXAFS spectroscopy is that the material under study may be in any form, including amorphous powders or solutions. The theory and practice of EXAFS spectroscopy are described in chapter one.

Although the phenomenon of EXAFS has been known of for nearly seventy years, the practical applications of EXAFS spectroscopy have only emerged within the last two decades. The technique first came to attention as a tool in bioinorganic chemistry, as described in a review by Cramer and Hodgson. EXAFS sees molecules with neither the scope nor the detail that X-ray crystallography does, but it does act as a probe into the local structure around the atoms of a particular element. This is important in, say, protein chemistry because the process mediated by the macromolecule usually takes place at a small number of sites centred upon a heavy metal atom or atoms. To solve a structure using protein crystallography requires that a large number of atomic positions be refined, a process which can take a very long time, given that a good-quality crystal of the compound under study can be produced in the first place.

Recent examples of work in this area include two separate studies of the carbon monoxide dehydrogenase enzyme from the bacterium *Clostridium thermoaceticum*, which establish that there is a nickel
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site in the enzyme in which the nickel atom is ligated by four sulphur atoms at a distance of 2.16Å. Comparison with model compounds indicates that the geometry is square planar. EXAFS spectroscopy was also used to characterise the sulphur ligation in the enzymes chloroperoxidase and oxygenated cytochrome P-450-CAM®. Here, the spectrum reveals an Fe-S bond of 2.37Å which, by analogy with model compounds, suggests a thiolate donor ligand. Iron-sulphur interactions have also been studied in the nitrogenase iron protein from Azobacter vinelandii®.

EXAFS has been used to locate the non-bonded and bridging atoms in binuclear iron centres®®, and also to distinguish bridged and non-bridged centres®®. The application of EXAFS, and other synchrotron X-ray techniques, to metal based drugs and their metabolites has been reviewed by Elder and Eidsness®. An unusual EXAFS study on a single crystal, pending a detailed X-ray crystallographic analysis, has been reported®.

There are many examples of EXAFS spectroscopy being used to obtain structural information from samples that are in some way 'difficult' and unsuitable for a crystallographic study. For instance, the technique was used to determine the Fe-Cl and Fe-P distances in the unstable FeIV complex [Fe(α-C6H4(PMe2)2)2Cl2][BF4]2®. Other types of structure that might yield information upon EXAFS examination include intrazeolite complexes®®, intercalation compounds®®, polymers®® and Chevrel phases®®.

Structural information is often deduced by comparing the EXAFS spectrum of a compound with that of an analogous one. An example is the determination of the Re-Re and Re-F bond lengths in Re2Fe2-®®, which extended the results already obtained by crystallography for Re2Br4-® and Re2Cl4-®. Another case is that of the electride and rubidide, Rb⁺(15C5)2, e⁻ and Rb⁺(15C5)2, Rb⁻ respectively. These, by their EXAFS spectra, have local structures around Rb⁺ similar to Rb⁺(15C5)2, Na⁻, whose X-ray structure is known®. The high-temperature form of Sr2Co2O6 has been found to be isostructural with Sr2Fe2O6®®.

Sometimes the EXAFS spectrum cannot provide a complete answer to structural questions. In a study of titanium alkoxides®®, it was possible to distinguish monomers and trimers, but evidence from a second
technique was needed to determine the exact geometry of the trimers. In another case, the EXAFS spectrum of the peroxo-dicopper complex

\[
\begin{array}{ccc}
\text{N} & \text{Cu}^2+ & \text{N} \\
\text{O} & \text{(O}_2\text{)} & \text{Cu}^2+ \\
\text{py} & \text{py} & \text{py}
\end{array}
\]

allowed the experimenters to rule out \(\mu-1\)-bridging coordination of oxygen,

\[
\begin{array}{ccc}
\text{Cu} & \text{Cu}
\end{array}
\]

because of the long Cu-Cu distance of 3.31Å. This still left \(\mu-1,2\)-bridging and non-bridging modes, with the Raman spectrum of the complex indicating the former\(^{\text{52}}\).

EXAFS spectra can be taken of species in solution, but the concentration of the X-ray absorbing element within the beam is necessarily lower than in the solid state, so that the spectra are usually significantly poorer.

Silver(I) solvation in nitrogen-donor solvents has been studied\(^{\text{83}}\). Silver(I) is surrounded by four solvent molecules in liquid NH\(_3\), pyridine and acetonitrile solutions, with Ag–N bond lengths of 2.31Å, 2.29Å and 2.24Å respectively. Although acetonitrile is the weakest donor of the three, backbonding to cyanide \(\pi\)-orbitals is thought to account for the shorter bond.

In light petroleum solution, the carbonyl cluster Fe\(_5\)(CO)\(_{12}\) adopts mainly an all-terminal carbonyl coordination. In frozen CH\(_3\)Cl\(_2\) solution, however, there is a substantial population of bridging sites\(^{\text{54}}\).
EXAFS spectroscopy has proved especially valuable in the field of heterogeneous catalysis. Using it, it has been possible to examine the local structure around the metal centres of either active catalysts or their precursors.

In a study of the products of the adsorption of $\text{Ru}_{2}(\text{CO})_{2}$ onto $\gamma$-$\text{Al}_2\text{O}_3$, the Ru-Ru bonds in the small metal clusters that had been formed initially were disrupted upon adsorption of CO, to produce Ru($\text{CO})_n$ species. The ultra-dispersed ruthenium clusters are recovered on desorption of CO. The change from ruthenium to carbon and oxygen near-neighbours is observed in the EXAFS spectrum.

Studies of an ultra-dispersed Rh/Al$_2$O$_3$ catalyst have revealed the existence of small rhodium crystallites on the surface, apparently interacting with the surface via an ion-induced dipole Rh-O bond of 2.7Å length. Upon adsorption of CO, the crystallites break up into discrete Rh($\text{CO})_n$ units, attached to the surface via three oxygen atoms.

Copper and ruthenium EXAFS spectra have been taken of a silica supported ruthenium-copper catalyst. The ruthenium in the bimetallic clusters was found to be coordinated primarily to other ruthenium atoms, whilst the copper atoms' nearest neighbours were equally distributed among copper and ruthenium atoms. This was seen to indicate that the catalyst took the form of ruthenium-copper clusters in which the copper was present at the surface.

In a study of a silica supported dispersed cobalt-manganese catalyst, EXAFS evidence was found that the manganese was present in an oxidised state, whereas the cobalt was found in both metallic and oxidised forms. Furthermore, an increase in the manganese content was accompanied by an increase in the proportion of cobalt that was metallic, in turn associated with higher catalytic activity. The experimenters propose that the Mn atoms scavenge any traces of oxygen, allowing the cobalt to remain metallic.

The application of EXAFS to the study of binary metallic clusters on surfaces has been reviewed by Sinfelt.

There are many examples of metal carbonyl clusters remaining essentially intact on reaction with a supporting oxide. Although it has been established that EXAFS can be used to characterise large metal
carbonyl clusters$^{54}$, this process becomes less clear when the cluster is grafted to an oxide surface. Osmium EXAFS studies of a trinuclear cluster have suggested both structures (1)$^{62}$ and (2)$^{62}$ below, whilst other spectroscopic evidence indicates a third structure, (3)$^{64}$.

\[
\begin{align*}
(1) & \quad Os(CO)_4 \quad (CO)Os \quad Os(CO)_4 \\
(2) & \quad (CO)Os \quad Os(CO)_4 \quad (CO)Os \\
(3) & \quad Os(CO)_4 \quad Os(CO)_4 \quad Os(CO)_4
\end{align*}
\]

The EXAFS spectrum of the analogous ruthenium complex implied that one or both of species analogous to (1) and (3) above were present$^{64}$.

The cluster \(\{Ru_3(\mu-H)_6(CO)_9(\mu_3-PCH_2CH_2Si(OEt)_3)\}\), derived from Ru$_3$(CO)$_{12}$, has been tethered to alumina and characterised by i.r., uv/vis, $^{31}$P cross polarisation MAS nmr and EXAFS spectroscopy$^{65}$. The EXAFS spectra of the precursor and the tethered cluster reveal two Ru-Ru distances, as expected of an isosceles metal triangle (one edge is hydrogen bridged). The EXAFS helps to establish that the metal carbonyl part of the complex is preserved unaltered when tethered to the oxide.

Low oxidation state transition metal species supported on oxides such as silica and alumina have attracted most attention, but are not the only heterogeneous systems to be studied. EXAFS has identified isolated VO$_4$ species on the surface of photoactive V$_2$O$_5$/SiO$_2$ catalysts$^{66}$. The technique has also been used to analyse the changes in the local structure around nickel ions in Nickel Y Zeolite$^{67}$.

**Aims of this Work**

Surface anchored clusters offer the promise of catalysts that combine the advantages of homogeneous and heterogeneous systems. Chapter two describes an EXAFS (see below) investigation of the tethered hexanuclear rhodium cluster Rh$_6$(CO)$_{15}$PPh$_2$(CH$_2$)$_2$-SILICA.
Introduction

Mixed metal clusters are of interest both as a potential source of stereoselective catalysts and as models of heterogeneous alloy catalysts. The EXAFS results for the clusters HgRu₄(CO)₁₂(MPPh₂) (M=Cu,Au; 1,2 respectively) are compared with crystallographic data. Initially unidentified minor products of the reaction of (1) and (2) with carbon monoxide are also examined.

Polyoxometalate anions are believed to provide soluble models for the heterogeneous metal oxides that are so often used as catalyst supports. EXAFS spectra, including solution spectra, of several polyanions were recorded. The potential of EXAFS to detail these complex structures is examined.

General Experimental

Infra-red spectra were recorded as nujol mulls on a Perkin-Elmer 580B with model 3500 data station, or on a Perkin-Elmer 1710 with 3600 data station. A Perkin-Elmer 554 was used for uv/vis spectra. ¹⁷O and ³¹V nmr spectra were taken with a Bruker AM-360, externally referenced to H₂O and VOCl₃, respectively.

References

2. P.R. Raithby; in reference 1, chapter 2, p5.
5. K. Wada; New Scientist, 62 (1972), 615.
Introduction

Introduction

CHAPTER ONE

EXAFS SPECTROSCOPY¹,²
1.1 X-RAY ABSORPTION

The X-ray absorption of a compound tends to decrease smoothly with increasing energy. However, this decline is punctuated by steep "edges" (fig. 1.1), which occur whenever the incoming photon has sufficient energy to eject a core electron from an atom. The edges are characteristic of each element, and are labelled according to the core state of the electron before absorption. Thus, a 1s electron gives rise to a K edge, a 2s electron to an L\text{I}, a 2p electron to L\text{II} and L\text{III} edges, and so on.

The area around the edge contains fine structure characteristic of the chemical environment of the absorbing atom. Superimposed upon the edge itself are transitions of core electrons to vacant energy levels below the continuum. This is the X-ray absorption near edge structure, or XANES. Out to several hundred eV past the edge there is an oscillation in the absorption, the extended X-ray absorption fine structure, or EXAFS.

Fig. 1.1: Vanadium metal K edge.
1.2 EXPERIMENTAL PROCEDURE

The quantity measured in an absorption experiment is the absorbance, $A$, as a function of photon energy, $E$, as defined by

$$ A = \ln\left(\frac{I_0}{I}\right) = \mu(E)x, $$

where $I_0$ is the incident flux, $I$, the transmitted flux, $x$ the sample thickness and $\mu(E)$ the absorption coefficient of the sample. Since the sample's absorbance is superimposed on the energy-dependent spectrometer background, what is measured is a relative absorbance. This is no problem, however, as it is the modulation of the absorbance that is of interest. In addition, the extraction of the modulation from the other components leads to the sample thickness cancelling itself out (see section 1.3), so that $x$ does not have to be measured precisely.

What is needed, then, is a source of X-ray light, and the apparatus to measure its attenuation by a sample.

1.2.1 The X-ray Source

All the EXAFS spectra in this work were recorded on the Synchrotron Radiation Source (SRS) at the SERC's Daresbury Laboratory, in Cheshire. Synchrotron radiation is emitted by charged particles being accelerated around a curved path at relativistic speeds. The radiation is swept forward into a narrow cone in front of the circulating particles and comes off tangentially to their path. At Daresbury the radiation is produced by bunches of electrons held at an energy of 2 GeV in a circular storage ring (fig. 1.2). The advent of synchrotron radiation has revolutionised many areas of science, not least X-ray absorption spectroscopy.

As a source of X-rays, synchrotron radiation has several key advantages over conventional X-ray sources:
Chapter 1: EXAFS

High Intensity - from $10^4$ to $10^6$ times that of a rotating anode generator, the most powerful laboratory source. A useful EXAFS spectrum can be obtained for a concentrated sample using conventional sources in a day or so. With synchrotron radiation, spectra can be recorded in about an hour, and on dilute samples.

![Plan of the SRS, Daresbury](image)

**Collimation** - the beam is highly collimated, its angular divergence in the plane of the ring being only 0.01-0.02°. Thus a high intensity can be brought to bear on a small sample.

**Tuneability** - a wide band of wavelengths is available (fig. 1.3). A low energy limit of 3.2Å is set by the beryllium windows used in the beam lines, whilst the upper limit is set by the performance of the accelerator. This limit is currently about 0.1Å. Furthermore, the spectrum is not broken by the emission lines characteristic of laboratory sources.

Table 1.1 lists the absorption edges covered by this work. Note that $L_\alpha$ and $L_{\beta,\gamma}$ edges are often so close that their spectra overlap, and are rarely examined.
### Table 1.1: Selected X-ray Absorption Edges

<table>
<thead>
<tr>
<th>Element</th>
<th>Edge</th>
<th>λ/Å</th>
<th>Energy/keV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium</td>
<td>K</td>
<td>2.269</td>
<td>5.464</td>
</tr>
<tr>
<td>Copper</td>
<td>K</td>
<td>1.380</td>
<td>8.992</td>
</tr>
<tr>
<td>Zinc</td>
<td>K</td>
<td>1.283</td>
<td>9.661</td>
</tr>
<tr>
<td>Tungsten</td>
<td>L_{III}</td>
<td>1.215</td>
<td>10.202</td>
</tr>
<tr>
<td>Gold</td>
<td>L_{III}</td>
<td>1.040</td>
<td>11.918</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>K</td>
<td>0.560</td>
<td>22.121</td>
</tr>
<tr>
<td>Rhodium</td>
<td>K</td>
<td>0.534</td>
<td>23.228</td>
</tr>
</tbody>
</table>

**Fig. 1.3:** Spectrum of radiation available at the SRS. The wiggler is a series of superconducting magnets inserted into the ring that literally 'wiggles' the beam to produce a path with tighter curvature. The effect of this is to shift the spectrum to higher energies.

### 1.22 The Experimental Station

**The 'Hutch'**

The experimental equipment is contained within a radiation-proofed 'hutch'. The X-ray beam from the synchrotron has to pass through a shutter which cannot be opened until the hutch has been cleared of experimenters and sealed.
Chapter 1: EXAFS

Fig. 1.4: Set-up for recording an EXAFS spectrum using transmission and fluorescence modes.

**Monochromators**

The energy range is scanned by passing the white X-ray light through a monochromator that is rotated in small steps to bring successive photon energies onto the sample. As the monochromator moves through a scan, the beam is displaced slightly, so a sample holder wide enough to accommodate this drift needs to be used.

The entrance to the monochromator is a variable slit whose size is used to define the resolution of the monochromator. The exit slit is usually wider; it is intended to collect scatter from the entrance slit that has bypassed the monochromator.

(a) Si(111) Channel Cut Crystal Monochromator

This consists of a silicon crystal, with a channel cut into it aligned with the (111) crystal plane. White X-ray flux enters the channel, whilst only the wavelength determined by the Bragg equation.
Emerges. The radiation is contaminated with harmonics \((n = 2, 3, 4, \ldots)\) in the Bragg equation which can lead to a loss of fine structure.

(b) Si(220) Order-sorting Monochromator

Two silicon crystals, cut to expose (220) faces, are aligned so as to provide a path for the X-ray beam similar to the channel cut crystal. The first crystal, however, is kept slightly out of parallel with the second. This misalignment results in a much greater loss in intensity for the harmonics than for the fundamental. The degree of misalignment is varied throughout a scan to maintain a constant degree of harmonic rejection.

Fig. 1.5: Monochromator types, (a) Channel cut crystal; (b) Order-sorting monochromator.
Detection Systems

(a) Transmission

Ionisation detectors are placed in front of and behind the sample to record $I_0$ and $I_1$. These are filled to 1 atm pressure with a mixture of rare gases with different X-ray absorption coefficients (typically He/Ar), such that the front chamber absorbs ~20% of the light and the rear chamber, ~80%.

For a good spectrum, the absorbance needs to be as high as possible whilst keeping the contribution of electronic noise in the rear ion chamber to a minimum. In practice this means achieving a change in absorbance across the edge of about 1-3. This can be achieved with ~1-2mm thickness of a sample in which the concentration of the relevant element is about 10 atom%.

Solid samples are ground to a homogeneous powder. If they are too concentrated in the element under study, they can be diluted with boron nitride powder. If the sample is too dilute, the thickness can be increased - but one will eventually reach the point where the absorption by the rest of the sample is so great that no useful signal reaches the back detector.

(b) Fluorescence

Samples in solution (even saturated ones) and metal clusters dispersed on an oxide surface are usually too dilute to study using transmission mode: the edge is just a small superimposition on the background.

In this case, the sample is placed in the beam at an angle of 45° and the fluorescence from it is measured by a number of scintillation detectors (NaI or T1I). Scattered radiation can be filtered out using a metal foil of 5-15μm thickness. The foil is chosen so that its K edge is at a higher energy than that of fluorescence, which usually means using a Z-1 filter (Z is the atomic number of the element under study).

For thin or dilute samples, the fluorescence intensity is a direct measure of the absorption probability². Exactly the same information is contained in the fluorescence EXAFS as in a transmission spectrum.
One thrust of the work at the SRS aims towards recording the whole absorption spectrum at a go. The full X-ray bandwidth is dispersed into a fan with a curved silicon crystal. The sample intercepts a slice of this radiation and the transmitted X-rays are recorded by a detector (fig. 1.6). Fig. 1.7 shows the spectrum of K\textsubscript{2}V\textsubscript{2}W\textsubscript{6}O\textsubscript{19}(aq), recorded in only 30s using a photodiode array.

With the introduction of superior detectors (such as charged coupled devices), it should become possible to record useful spectra on short timescales. This would open up the possibility of using time resolved EXAFS to follow structural changes during the course of a reaction.

![Energy dispersive EXAFS apparatus](image)

Fig. 1.6: Energy dispersive EXAFS apparatus. The sample must be wide enough to cover the energy range of interest.
Fig. 1.7: X-ray absorption spectrum of $K_xV_yW_zO_{3x+y} (aq)$, recorded in energy dispersive mode. Some XANES and the early part of the EXAFS can be made out.
Chapter 1: EXAFS

1.3 THEORY OF EXAFS

The absorbance, \( \mu(E)x \), recorded in an X-ray absorption experiment can be divided into several components:

\[
\mu(E)x = \mu(E)_o + \mu(E)_m + \mu(E)_0 + \mu(E)_{\text{EXAFS}}x,
\]

where \( \mu(E)_o \) is the sloping spectrometer baseline, \( \mu(E)_m \) the absorption due to the matrix that the absorbing atom is embedded in, \( \mu(E)_0 \) the absorption that would be seen for a free atom and \( \mu(E)_{\text{EXAFS}} \) the modulation in the absorption about \( \mu(E)_0 \).

The modulation, denoted \( \chi(E) \), is isolated by subtracting the background components and normalising relative to the free atom absorption. Thus

\[
\chi(E) = \frac{\mu(E)_{\text{EXAFS}}}{\mu(E)_0} = \frac{\mu'(E)}{\mu(E)_0} - 1.
\]

\( \mu'(E) \) is the absorption attributable to the edge under consideration, i.e. \( \mu(E)_0 + \mu(E)_{\text{EXAFS}} \). The sample thickness cancels out.

Although the first observations of EXAFS were reported in 1920\(^{10,11} \), it is only within the last two decades that the theories explaining it have been formulated in a useful way. Major breakthroughs on these lines were made by Sayers, Stern and Lytle\(^{12-14} \), who were the first to demonstrate how structural information could be obtained directly from an EXAFS spectrum.

1.31 Plane Wave Theory\(^{12-15} \)

The oscillation in the absorption arises because the probability of the X-ray photon being absorbed depends upon the interaction of the initial- and final-state wave functions of the excited electron. The initial state is a core level localised near the atomic nucleus and is essentially invariant. The final state is the wave function of the ejected electron, whose frequency depends on the energy of the absorbed
photon, and which is affected by backscattering from neighbouring atoms (fig. 1.8).

**Fig. 1.8; Schematic representation of the EXAFS mechanism. The symbols are explained within the text.**

When the backscattered wave returns to the absorbing atom in phase with the outgoing wave, absorption is enhanced, and *vice versa*. Thus, as the frequency of the electron wave rises with increasing photon energy, the backscattered wave arrives at the absorbing atom successively in and out of phase, leading to a modulation of the absorption coefficient that can be expressed in the equation:

\[
\chi(k) = \frac{1}{k} \sum_{n} N_{s} \frac{|f_{s}(\pi, k)|}{R_{as}^{2}} \exp(-2\sigma_{as}^{2}k^{2}) \exp(-2R_{as}/\lambda) \sin(2kR_{as}+2\delta_{s}+\alpha_{s}).
\]

Where:

- \( k \) - photoelectron wavenumber, \( k = \sqrt{(2m_{e}/\hbar^{2})(E_{0})} \)
- \( m_{e} \) - electron rest mass
- \( E_{0} \) - threshold energy for the release of a photoelectron
- \( N_{s} \) - number of equivalent scatterers
- \( R_{as} \) - separation between the absorber and scatterer
- \( f_{s}(\pi, k) \) - backscattering amplitude of the scattering atom
- \( \sigma_{as}^{2} \) - mean square variation of \( R_{as} \)
- \( \lambda \) - elastic mean free path of the electron
- \( \delta_{s} \) - phaseshift due to the passage of the photoelectron through the potential of the emitting atom
- \( \alpha_{s} \) - phaseshift at the scattering atom
Chapter 1: EXAFS

Note that in practice the oscillation is not expressed as a function of photon energy, but of the photoelectron wavenumber.

Compare this equation with a simple sine wave: \( y = A \sin(\omega t + \phi) \).

Each shell of equivalent atoms produces its own modulation: a damped sine wave. Structural information is available because the frequency of this wave depends on the interatomic distance. Its absolute phase depends upon the atomic phase shifts. The amplitude is governed by the number of scatterers and the inverse square of the interatomic radius. Finally, the envelope of the wave is shaped by the backscattering amplitude (in turn characteristic of the atom's atomic number), the deviation in the distance between the absorber and scatterer, and the mean free path of the electron. The EXAFS spectrum is a summation over all atoms in the neighbourhood of the absorber.

**Factors Influencing the EXAFS**

**Phaseshifts and Backscattering Amplitudes**

The potential through which the photoelectron passes is assumed to be a series of muffin-tin potentials\(^{16}\), spherically symmetrical about each atom and non-overlapping. An allowance for the ionisation of the central atom is made when calculating its potential (see also section 1.4). Between the atoms there is a level potential in which the electron moves as a free wave. The backscattering amplitude and phaseshifts experienced by the electron at the scattering atom can then be calculated from the overall potential\(^{16,18}\).

The usefulness of EXAFS is to a large extent dependent on the transferability of the parameters between chemical systems. The phaseshifts and backscattering amplitudes are dominated by the strongly bound inner shell electrons, which are chemically insensitive. It has been shown that for photoelectron energies above 5Å\(^{-1}\), the phaseshifts are essentially independent of the chemical environment\(^{19}\).
Debye-Waller Factors

The atoms in a backscattering shell may not all be at the same distance from the centre atom, giving rise to an element of static disorder. In addition, the distances are time dependent due to thermal motion. Thus there is a deviation in $R_{nn}$, and the EXAFS signal is averaged over the mean square configuration of the atoms. This leads to a damping of the signal which is described by the term $\exp(-2\sigma_n^2k^2)$, which is known as a Debye-Waller factor.

It is the relative motion between two atoms that is important. Atoms close to the central atom are more likely to be moving in sympathy with the centre atom than more distant ones. These will therefore tend to have smaller Debye-Waller factors, whilst the more remote atoms will have more heavily damped signals.

Mean Free Path

The expanding photoelectron wave loses energy to its environment (through processes such as Auger electron emission), and so has a limited lifetime and path length. For instance, if $k=12\AA^{-1}$, the penetration of the electron is no more than $30\AA$. This energy loss means that the longer the electron's 'round trip', the less interaction the backscattered wave can have with the outgoing wave, which in turn causes a loss in EXAFS signal. This is accounted for in the term $\exp(-2R_{nn}/\lambda)$, where $\lambda$ is the mean free path of the electron.

Core Hole Lifetime

If the original hole created by X-ray absorption disappears before the return of the backscattered electron wave, it can prevent the coherent interference of the outgoing and reflected waves, reducing the EXAFS signal. Holes in K shells of light elements have long lifetimes, but these become shorter with increasing atomic number, impairing the EXAFS spectrum.
Multiple Excitations

The photoelectron is not emitted cleanly. Rather, its energy is shared to some extent with other electrons in the atom, reducing the EXAFS amplitude. When another electron is promoted to an excited state this is known as 'shake-up'. These transitions occur within 4Å⁻¹ of the absorption edge. If an electron is elevated to the continuum, this is 'shake-off'. Shake-off transitions have a wide phase spread and tend to cancel out. The effects of these amplitude reductions appear to saturate within 6-7Å⁻¹ of the edge.

The amplitude reduction depends upon the type of absorbing atom, but the chemical environment of the central atom is only of slight significance. The loss of EXAFS amplitude to multiple excitations is accounted for in practice by a scaling factor (typically 0.6-0.8) that depends on the absorbing atom only.

The derivation of the EXAFS equation assumes that the size of the backscattering atom is small compared with the distance from the centre atom, i.e. that the incoming electron can be treated as a plane wave. This simplification is valid for high photoelectron energies, but at lower energies the curvature of the spherical wave cannot be ignored and this expression is invalid.

Much of the structural information, however, is contained within the low energy region of the spectrum. This is particularly so for the more distant atoms (because of the R⁻² dependence, finite electron path length and higher Debye-Waller factors), and for light atoms such as C, N or O (because only low energy electrons are strongly scattered by such atoms).

Additionally, for coordination spheres outside the first, there is an alteration in phase shifts and amplitudes caused by scattering of the photoelectron wave from intervening atoms. The plane wave theory makes no allowance for this multiple scattering.
1.32 Curved Wave Theory

An exact theory incorporating the spherical shape of the photoelectron, allowing the analysis of the low energy part of the spectrum ($k<7\AA^{-1}$), was derived by Lee and Pendry.\(^{22}\)

Briefly, the absorption coefficient of the free atom, $\mu_0$, may be written

$$\mu_0 \propto \sum_{m_0} \sum_{lm} |\langle lm|e.\mathcal{E}|l_0m_0\rangle|^2,$$

within the dipole approximation. The symbols are

- $l_0m_0$: angular momentum quantum numbers of the initial state wavefunction,
- $lm$: angular momentum quantum numbers of the final state wavefunction (i.e. the emitted electron),
- $e$: polarisation vector of the X-ray's electric field,
- $\mathcal{E}$: magnitude of the electric field vector.

In the case of an isolated atom the matrix element is real.

When one considers the (background subtracted) absorption of an atom in a condensed sample, $\mu'$, account must be taken of the scattering of the photoelectron wave. Here, the final state function becomes

$$|f\rangle = \sum_{LM} \langle I+Z_{l',m',L'}|LM\rangle,$$

and the X-ray absorption coefficient is

$$\mu' \propto \sum_{m_0} \sum_{l'm'} \langle l_0m_0|e.\mathcal{E}|I+Z_{l',m',L'}\rangle \langle LM|l_0m_0\rangle \langle l_0m_0|l_{0m_0}|e.\mathcal{E}|l_{0m_0}\rangle.$$

Remembering that

$$\chi(E) = \mu'(E)/\mu_0(E) - 1,$$
and that the matrix elements are real, the EXAFS function may be written to first order in the scattering Z matrix as

\[ \chi(E) = \frac{1}{\mu_0} \sum_{m_0} \sum_{l m} \langle l_0 m_0 | \mathbf{e} \cdot \mathbf{r} | l m \rangle <2 \text{ Re } Z_{l m, l'm'} \rangle < l'm'| \mathbf{e} \cdot \mathbf{r} | l_0 m_0 \rangle. \]

All the effects of the scattering atoms are contained in the matrix Z, and so the EXAFS function is known once Z is known. Lee and Pendry's theory gives an exact expression for Z. All the factors discussed under the plane wave theory are incorporated into this expression, albeit in mathematically different forms; by making the appropriate approximations the curved wave theory can be reduced to the plane wave form. Computations using this theory are, however, very time-consuming.

The majority of samples for which structural determination by EXAFS is of relevance are either polycrystalline or amorphous. With such samples, an average has to be performed over the angular positions of the scattering atoms relative to the X-ray beam direction (or equivalently of the beam direction relative to an interatomic distance in the sample). This angle averaging has been performed analytically by Gurman, Binsted and Ross\textsuperscript{23} to produce a simpler, quicker version of the theory which still treats the outgoing wave exactly. It is this version of the curved wave theory (up to forty times faster computationally than the original) that has been used in the analysis of all the results presented in this work.

1.33 Multiple Scattering

Multiple scattering occurs when the photoelectron hits more than one scattering atom before returning to the central one. Fig. 1.9 shows the first, second and third order scattering pathways for a three atom system. The EXAFS corresponding to the distance A-C is the sum of these three terms.
Multiple scattering only affects the EXAFS of those atoms with another atom between themselves and the absorber. The pathways tend to be long, therefore, giving rise to rapidly oscillating waves which tend to cancel out. These waves are significantly attenuated by the $R_{n}^{-2}$ dependence of the EXAFS, and so are most important in the early part of the spectrum. Early EXAFS analyses dealt with multiple scattering by ignoring it and only using the spectrum above 4Å⁻¹.

However, multiple scattering cannot really be ignored when the atoms are approximately colinear. At high electron energies scattering is strong in the forward direction and weak otherwise — so the middle atom in a linear array forward-scatters the photoelectron onto the second atom. This causes an amplitude enhancement and a change of phase. The EXAFS signal is modified by the intervening atom for bond angles from 180° to ~75°. For bond angles greater than 150°, the relative importance of the scattering orders is 3rd>2nd>1st. Below this value the effect drops off sharply and the priorities are reversed to 1st>2nd>3rd.

The curved wave theory of EXAFS can be extended to higher orders of scattering, at a substantial cost in computing time. If only the most important multiple scattering pathways are considered, calculations using the rapid version of the theory are manageable. Results of such calculations are presented in the appropriate sections later.
1.4 DATA ANALYSIS

A suite of fortran programs is available in the SRS Program Library at Daresbury, covering every stage of the analysis of experimental data. The programs are run on the Daresbury Laboratory's Hitachi NAS 7000 IBM compute-alike, which is accessible to any terminal linked to the JANET network.

1.41 Calibration

The experimental data is recorded in the form of ion chamber, or fluorescence detector, readings against monochromator angle. One converts this to a spectrum of absorption versus photon energy with the calibration program EXCALIB. Spectra can be averaged at this stage to improve signal-to-noise, and instrumental artefacts (‘glitches’) can be smoothed out (fig. 1.10). These artifacts can arise from stray reflections in the monochromator when the Bragg condition is fulfilled for more than one crystal plane at a time, or from electronic quirks in the recording equipment.

1.42 Extracting the EXAFS Spectrum

This is accomplished using one or other variant of the program EXBACK (fig. 1.10).

Firstly, the threshold energy $E_\theta$ (for which $k = 0\text{Å}^{-1}$) is chosen, customarily the energy where the edge’s gradient is at a maximum. The pre-edge is fitted with a 1st or 2nd order polynomial, which is then extrapolated beyond the edge to model the sloping background ($\mu(E) = \mu(E)_\theta$ in section 1.31). The background is subtracted from the spectrum. To
Fig. 1.10: From absorption spectrum to EXAFS spectrum, showing (a) the unedited X-ray absorption spectrum, (b) the spectrum without 'glitches' and with the spectrometer background function, (c) the background-subtracted spectrum with post-edge polynomial, (d) the unweighted EXAFS plotted vs. energy, (e) the $k^2$ weighted EXAFS spectrum and (f) the $k^3$ EXAFS vs. $k$. 
model the free atom absorption, a second polynomial is fitted to the post-edge region. Although potentially of 1st to 6th order, this function is typically 4th or 5th order in practice. The experimenter determines the shape of the function by selecting the absorption at $E_q$ (extrapolating the post-edge back to $E_q$), a reference point in the early region of the spectrum and a weighting factor to compensate for the smaller EXAFS amplitude at higher energies. The spectrum is normalised relative to this polynomial and the pre-edge ($k<0\text{Å}^{-1}$) discarded, leaving the EXAFS spectrum.

Determining this second polynomial is the most critical and arbitrary step in the data processing. The EXAFS amplitude envelope should obviously be roughly evenly distributed on either side of the baseline, and the background polynomial has to be adjusted by trial and error until this is achieved.

The EXAFS spectrum is multiplied by $k^2$ to offset the attenuation of the signal. Before the spectrum is analysed the first 20-50eV are edited out to remove any XANES and shake-up transitions. The signal at the high $k$ end of the spectrum may be completely invisible under $k^2$ weighted noise: if this is the case, then this end of the spectrum is also discarded.

**1.43 Fourier Analysis**

In $k$-space the EXAFS can be expressed as a sum of sine waves. Sayers, Stern and Lytle showed that Fourier transformation of the EXAFS from $k$- ($\text{Å}^{-1}$) to R-space (Å) yields a function similar to a radial distribution. The Fourier transform of $\chi(k)$

$$
\phi(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{\text{min}}}^{k_{\text{max}}} k^2 \chi(k) \exp(2i\kappa R) \, dk,
$$

shows peaks corresponding to the distances $R_{nm}$, but shifted by an average phaseshift $\omega_f$. This provides a means of visualising the
individual interatomic distances giving rise to a particular EXAFS pattern (fig. 1.11).

In plane wave theory the phase shift is corrected for by assuming that the first shell's phase shift is dominant and using this as the basis for correcting the whole spectrum. The curved wave theory employs a similar approach with the Fourier transform being corrected for the energy dependent phase shifts to give peaks close to the true interatomic distances.

The finite length of the EXAFS spectrum causes side lobes to appear with all the main peaks in the FT. These truncation induced ripples are reduced by combining the Fourier transform with a Gaussian window function, the cost being some broadening of the main peaks.

**Fourier Filtration**

The quality of an EXAFS spectrum can be greatly improved by obtaining the Fourier transform, marking off the distance range of chemical interest and backtransforming to produce a clean EXAFS signal (fig. 1.12). This procedure removes any residual uneveness in the baseline (which shows up at low R values in the FT) and the bulk of the noise (found at high R values in the FT). Note that Fourier filtering a spectrum does not provide a panacea for a badly selected baseline: such a baseline will produce amplitude and phase distortions in the part of the Fourier transform that is retained.

**1.44 Curve-fitting Analysis**

The essence of curve-fitting analysis is to propose a model structure, from which a theoretical spectrum is calculated, and then to adjust the parameters of the model until a match between the theoretical and experimental spectra is found.

The program EXCURVE and its variants allow the experimenter to produce a theoretical EXAFS spectrum (based on the fast version of the
Fig. 1.11: (top) EXAFS spectrum of gold metal and (bottom) its Fourier transform, showing the atomic shells around each atom.
Fig. 1.12: Fourier filtration - (a) untreated EXAFS spectrum, (b) Fourier transform, with region to be retained marked out, and (c) the filtered EXAFS spectrum.
curved wave theory) by defining a set of structure dependent parameters. The program will then refine these parameters, searching for a minimum discrepancy between the theoretical spectrum and the experimental results being analysed.

The model structure is composed of a series of shells, each set of identical atoms at the same distance from the absorber constituting a shell. If atoms of the absorbing element exist in more than one environment, the EXAFS will be an average over these environments. The parameters of the model will need to be similarly averaged.

The chief parameters are as follows:

- **E₀** - The value of the photoelectron threshold energy used for the theory spectrum, relative to that defined in the experimental spectrum (see below).
- **VPI** - A constant imaginary potential used in the curved wave theory to describe the lifetime of the electron. Generally kept constant between compounds of the same element.
- **AFAC** - A scaling factor, independent of photon energy, to compensate for multiple excitations. Should be kept the same for spectra at the same edge.
- **E_{min}** - Relative to the edge defined in the experimental spectrum, the minimum energy used for calculations and plots (adjustable by the experimenter, but not refineable).
- **E_{max}** - The maximum energy used for calculations or plots (not refineable).
- **Nn** - Number of atoms in shell n.
- **Rn** - Radius in Å of shell n.
- **An** - Debye-Waller factor for shell n.

When refining a set of parameters, EXCURVE seeks for a minimum in a function known as the fit index (FI), which is a measure of the closeness of the match between theory and experiment. For $k^2$ weighted data,

$$FI = \sum_i (k_i)^2 (\chi_i^t - \chi_i^e)^2,$$

where there are i individual points in the experimental spectrum. More advanced versions of EXCURVE also calculate a discrepancy index, $R$,

$$R = \frac{\int |\chi^t(k) - \chi^e(k)| k^2 \, dk}{\int |\chi^e(k)| k^2 \, dk} \times 100\%$$
R is independent of the way the spectrum is sampled, or of its absolute magnitude. It is therefore more meaningful when comparing fits from different spectra.

Statistical errors and correlation coefficients for the refined parameters are calculated using standard techniques employing numerical estimates of the partial derivatives at the minimum. The variances can only be regarded as crude estimates in view of the strong correlations between some of the variables. In general EXAFS spectroscopy can provide accurate and precise interatomic distances, but is less effective at determining and defining the parameters that affect the amplitude of the EXAFS signal, i.e. the co-ordination numbers and Debye-Waller factors. However, the Debye-Waller factors can be used to rule out spurious fits with the data. Any shell whose Debye-Waller factor is outside the chemically feasible range (0.05 to 0.25 Å⁻², as a rule of thumb) can probably be rejected as unreasonable.

**VPI and AFAC**

The theoretical basis of these parameters is not well enough understood for them to be calculated. What is known is that they are not greatly affected by the chemical environment of the absorbing atom. Generally, a reference compound is chosen for each edge (the pure element if possible). During the analysis of the EXAFS spectrum, VPI and AFAC are refined along with the other parameters; the values obtained are then kept for all other samples. Some experimenters do argue that because the two constants are not thoroughly understood, they should be refined for each sample.

In the work presented here, the former approach is the norm, with only one or two exceptions. These are noted where they occur.

**Phaseshifts**

Although it is possible to determine phaseshifts empirically (as discussed in reference 1), calculated phaseshifts are used in data analysis at Daresbury (section 1.3).
The use of ab initio phaseshifts requires that $E_0$ be included as an adjustable parameter. This is to compensate for systematic errors at low $k$ arising from some of the simplifications made in calculating the shifts. The positioning of $E_0$ affects the phaseshifts mainly at low $k$, whilst at higher $k$ they are determined primarily by the shell radius. Because they take effect in different parts of the spectrum, there is little risk of the flexibility in $E_0$ producing an artificially good fit with incorrect radii.

In the calculations, the outgoing photoelectron wave is decomposed into components with different quanta of angular momentum, $L=0,1,2,3...$, when it leaves the absorbing atom. As $L$ increases, the wave consists of more nodes and backscattering becomes weaker. Experience has shown that for each atom pair, thirteen phaseshifts (up to $L=12$) are plenty.

EXCURVE offers two options for dealing with the central atom. The wavefunction for an atom with a core hole (1s or 2p as appropriate) and an extra screening electron in the valence shell approximates a fully relaxed atom, the most relevant model for low photoelectron energies. Using a $Z+1$ ($Z$=centre atom atomic number) phaseshift represents the incomplete screening and relaxation of the central atom found at higher electron energies. In practice, the first option gives the better result, and was chosen for all the data analyses presented here.

**Multiple Scattering**

The inclusion of multiple scattering effects in the theoretical spectrum allows accurate modelling of the early part of the EXAFS spectrum, where much of the structural information and the best signal-to-noise is to be found. EXCURVE allows the experimenter to assign the shells of atoms to multiple scattering 'units', for which the second and third order multiple scattering may be calculated. Because of the increased demand on computing time, only those units whose multiple scattering will be significant are defined. This generally means looking at shells whose atoms are roughly colinear with the absorbing atom.

The angular dependance of the multiple scattering contribution has allowed the calculation of bond angles from EXAFS spectra, to accuracies of a few degrees. The inclusion of angular parameters creates
a further increase in the computing time required for multiple scattering calculations. Since, in the compounds covered in this study, the relevant bond angles were either known or could be assumed to this degree of accuracy, the angle in the multiple scattering unit was usually left as a fixed parameter.
1.5 REFERENCES

CHAPTER TWO

EXAFS STUDIES OF AN OXIDE-SUPPORTED RHODIUM CARBONYL CLUSTER
2.1 INTRODUCTION

Rhodium combines an extensive range of compounds with a high degree of catalytic activity. It features in heterogeneous systems, in the so-called hybrid catalysts (see below) that are currently arousing a great deal of interest, and in many other kinds of chemical environment as well.

Where the rhodium compound is dispersed upon a surface, structural characterisation presents considerable problems. X-ray crystallography is obviously impossible, and information from other methods is made more difficult to obtain. It is here that EXAFS, with its ability to extract structural information from irregular, dilute systems in any phase, can be of use.

As described in the introduction, there is also specific interest in the catalytic potential of metal clusters. In this study, EXAFS has been used to examine the structure of a hexanuclear rhodium cluster attached to a silica surface, comparing it with molecular analogues.

The EXAFS analysis of the product of an attempt to create a similar system with \([\text{Rh}_7\text{S}_2(\text{CO})_{22}]^{2-}\) and \(\gamma\)-alumina is briefly discussed.
2.21 Homogeneous vs. Heterogeneous Catalysis

On the whole, homogeneous catalysts are better understood than their heterogeneous counterparts, and on paper are the most useful category. Their advantages include syntheses that are generally easily reproducible, the possession of a specific active site (which is controllable by varying the ligand, and could be chiral) and the fact that essentially all molecules of the catalyst are available for reaction. Because they are more selective, their kinetics tend to be simpler, and so easier to study. On the other hand, energetically more demanding processes - like the hydrogenation of N₂ and CO, or the activation of C-H and C-C bonds - tend to have low activity in homogeneous systems. In addition, one is limited to solvents that will dissolve the catalyst and generally to moderate temperatures. Finally, homogeneous catalysts are difficult to separate from the other reactants.

Heterogeneous catalysts are less easy to synthesise reproducibly, are active at the surface only and are, due to side reactions at alternative reactive sites, typically non-specific. Their great advantages, however, are their greater stability in the more vigorous conditions required by industry and the ease of removing them from the reaction mixture. In commercial practice, these factors are usually overriding.

2.22 'Hybrid' Catalysts

The desire to combine the specificity of homogeneous catalysts with the separability of heterogeneous systems has driven the search for so-called 'hybrid' catalysts'^7. The main approach has been to attempt to
heterogenise homogeneous catalysts, i.e. to immobilise them on a solid support that can easily be removed from a reaction. The mode of immobilisation can either be inclusion within a solid matrix (e.g. graphite intercalation compounds), or support by the surface of a solid. Inclusion catalysts have fewer reactive sites available to the reactants; the latter approach is therefore by far the most common, and there are essentially two ways of classifying these compounds.

For a start, the method of surface support can be either physisorption, direct binding to the surface via atoms such as O, S, Sn, etc., or the tethering of the metal complex to the surface via a bifunctional ligand (a 'pendant' or 'anchoring' ligand). Given that physisorbed species are not likely to survive industrial conditions, the spotlight falls on catalysts that are more or less firmly attached to a surface.

Secondly, the nature of the support may also vary. Both organic and inorganic compounds are used, usually polymers and metal oxides respectively. The combination of the two as an oxide-mounted polymer support has also been prepared.

Polymer supports are potentially multifunctional, and ion exchange resins can immobilise charged species. They have the disadvantage, even when they have been stiffened by cross-linking, that their flexibility leads to chelation, multi-coordination, intermolecular reactions between the supported species and variable support geometry. These effects lead to deactivation and a loss in selectivity. Inorganic supports, on the other hand, are more stable at high temperatures, more controllable and reproducible, and able to hold higher catalyst concentrations due to their rigidity. They are often catalytically active themselves, giving rise to side reactions, which may be an advantage for complex processes - but is obviously a potential disadvantage as well.

Focussing on inorganic supports, one has to answer the question as to whether direct binding of, or tethering of, the metal complex is preferable. Directly bound species are more resistant to heat and to leaching. The strong attachment to the surface also tends to fix the stereochemistry and electronic environment of the catalyst, which prevents fine tuning of its properties. In fact, these complexes are not actually very different from straightforward heterogeneous catalysts.
Chapter 2: Supported Rhodium Cluster

Though the flexibility of pendant ligands may allow the supported complex to come into destructive contact with the surface, one is more free to fine-tune the stereochemistry and electronic structure of the catalyst, which is a great advantage.

2.23 Pendant Ligand Anchoring

Tethering a metal complex to a surface relies upon the use of a bifunctional ligand that can react with both the complex and the hydroxyl groups on the oxide surface. Fig. 2.1 illustrates the two main classes of such ligands. The Si-O-Si linkage is more resistant to hydrolytic and thermolytic cleavage than Si-O-C, and so is the more frequently used. (EtO)₂Si(CH₃)₂PPh₂ is a common choice.

Fig. 2.1: Anchoring ligands, classified by the surface-reactive functional group: (a) substituted alcohol, (b) substituted alkyl silane. L = complexing function; X = Cl, OR, OCOOR'.
There are two main synthetic approaches to tethering, each with their advantages and disadvantages. One method is to attach the ligand to the oxide surface, and then introduce the metal. This has the advantage of allowing more severe conditions to be used in the first stage, increasing the concentration of ligand on the surface. However, tightly packed 'islands' of ligand may form on the surface, which may cause chelation of the metal complex.

The second route is obviously to ligate the metal complex first, and then to attach the whole thing to the oxide surface. This allows intermediate purification of the catalyst, increasing one's ability to tune and control the system. If the anchoring reaction is not stoichiometric, however, then the unattached compound may decompose to give other catalytically active species.

Some potential drawbacks of this type of catalyst need to be borne in mind: destructive reactions of the complex with the surface, reversal of the anchoring reaction by trace water, and enhancement of poisoning compared with the homogeneous complex arising from trace species being absorbed by the support.

2.24 The Supporting Oxide

Recent work within this research group has focussed on three inorganic oxides: silica, γ-alumina and titania.

Silica

Silicas range from the macroporous porous glasses, through the microporous silica gels to the non-porous aerosils. Aerosils are usually chosen as catalyst supports because they are more pure, uniform and i.r. transparent. A certain amount of water is introduced during manufacture. The surface is generally fairly acidic and its chemistry revolves around hydroxyl groups. Before use, aerosils are dried under vacuum at high
temperature (~200°) to remove absorbed water (whilst retaining full hydroxylation). Three groups predominate on the surface:

```
     O    HO·····HO    OH
     / \  |    |    |
    Si  Si  Si    Si  Si
```

with the last being the most reactive.

**Alumina**

Alumina is more reactive to electron donating molecules, presumably because it possesses sites of Lewis acid character (as well as hydroxyl groups), which can give this oxide catalytic potential in its own right.

**Titania**

Generally similar to silica, though more complex and less well understood, the titania surface is amphoteric with some Lewis acid sites.
2.3 IMMOBILISATION OF Rh₆(CO)₁₆

2.31 Catalysis by Rh₆(CO)₁₆

Rh₆(CO)₁₆ has featured as the homogeneous catalyst source in the water gas shift reaction (WGSR)\(^{12,19}\), the reduction of nitrobenzene to aniline\(^{14,15}\) and NO to N₂O and ammonia\(^{16}\), and in catalytic oxidations\(^{17}\). This area of research has been reviewed by Basset\(^{18}\).

The adsorption of Rh₆(CO)₁₆ on an oxide surface, followed by decomposition to give '100%' dispersed metal particles is claimed to provide the ideal heterogeneous catalyst.

Rh₆(CO)₁₆ has been anchored to phosphinated polymers and to charged resins\(^{19,20}\). Tethering to inorganic supports has tended to employ the first method mentioned in the previous section, i.e. pre-treating the surface, and then adding the cluster. Recent research within this group made use of the alternative approach of attaching the anchoring ligand to the cluster first, as summarised in the next section.

2.32 Tethering of Rh₆(CO)₁₆ to inorganic oxides\(^{11}\)

Reaction with Phosphines

Depending upon the reaction conditions it is possible to substitute from one to six carbonyl ligands with phosphines. Stirring Rh₆(CO)₁₆ in CH₂Cl₂ at room temperature with one equivalent of PPh₂Et produces Rh₆(CO)₁₆PPh₂Et, whose identity was confirmed by \(^{13}C\) and \(^{31}P\) nmr measurements.

Surface Anchoring Experiments

Once the initial chemistry was established, the rhodium cluster was functionalised by reaction with (OEt)₃Si(CH₂)₂PPh₂. Pre-treated silica, alumina or titania was then added to the cluster in CCl₄, under an
overpressure of CO. That anchoring of the intact cluster had occurred was supported by the solid state \(^{31}\)P nmr results. The stability of the product depended upon the oxide in the order SiO\(_2\) >> TiO\(_2\) > Al\(_2\)O\(_3\), with the decomposition products including Rh\(^+\)(CO)\(_2\) units, metal crystallites and adsorbed Rh\(_x\)(CO)\(_y\) on the surface. There was also \(^{31}\)P nmr evidence for the following structure:

\[
\begin{align*}
\text{Rh}^+\text{(CO)}_2 \\
\text{O(CH}_2\text{)}_2\text{(Ph}_2\text{P)} & \quad \text{O} \\
\text{Si} & \quad \text{Si} \\
\end{align*}
\]

No detailed structural information was obtained on the anchored cluster.
Chapter 2: Supported Rhodium Cluster

2.4 EXPERIMENTAL

Rh K edge EXAFS spectra were recorded for the rhodium carbonyl cluster Rh₆(CO)₁₆, its substituted analogue Rh₆(CO)₁₆PPh₂Et and an oxide-tethered form Rh₆(CO)₁₆PPh₂(CH₂)₂-SILICA. Two spectra were recorded for each sample, using fluorescence detection for the oxide-tethered sample, and then averaged.

In the data analysis, the initial values for the parameters VPI and AFAC were taken to be -4eV and 0.6, from previous experience²¹. The theoretical basis for these parameters is not solid, and so they are only ever evaluated empirically. They are to some degree arbitrary. What happens most often is that their values are determined for a reference sample, such as a pure metal, and these values are then kept fixed for all other spectra on a given edge. Some experimenters will, however, refine VPI and AFAC for each EXAFS spectrum. For these rhodium spectra, they were treated as refineable parameters.

The only X-ray crystallographic data for any of these systems is a short paper concerning Rh₆(CO)₁₆.¹⁷ This provided the comparison data for all three samples.

The samples were prepared by R.J. Crowte and R.J. Price.

Rh₆(CO)₁₆ was prepared by literature methods²². Mixing of CH₂Cl₂ solutions of Rh₆(CO)₁₆ and PPh₂Et under N₂ at room temperature for 30mins produced a mixture of products with a varying degree of substitution of the carbonyls by phosphines. The mono-substituted derivative predominates and can be separated by column chromatography employing 1:1 petroleum ether/dichloromethane as the eluant.

Replacing PPh₂Et by (OEt)₃Si(CH₂)₃PPh₂ produced the functionalised cluster, which was anchored to silica by adding the oxide to a CCl₄ solution of the cluster under an overpressure of CO (maintained by a party balloon) and stirring overnight. The solution was filtered and the product dried under vacuum.
Chapter 2: Supported Rhodium Cluster

2.5 Rh₆(CO)₁₂ AND DERIVATIVES

The structure of Rh₆(CO)₁₂, as determined by X-ray crystallography^1, is illustrated in fig. 2.2. Each rhodium atom is equivalent and, seen in terms of backscattering shells, its environment can be described as follows.

Firstly, there are two carbon atoms from the terminally bound carbonyls at 1.864Å, with two more from the bridging carbonyls at 2.168Å. Beyond this at 2.776Å are four rhodium atoms, with the two oxygens from the terminally bound carbonyls at 3.019Å. In the bridging carbonyls, the average Rh-C-O angle is 132°, the C-O bond is 1.201Å long, from which the Rh-O non-bonded distance was calculated to be 3.103Å. The Rh-Rh distance across the octahedral framework of the cluster has not been published, but it will be 3.925Å if the octahedron is assumed to be regular. Beyond 4Å there are several shells due to the remaining carbonyl ligands. Because of the drop-off in EXAFS intensity with shell radius, these shells will give weak signals and so be difficult to resolve. For this reason they were not included in the data analysis.

Fig. 2.2: Structure of the cluster Rh₆(CO)₁₂.
**2.5.1 Results**

Rh(CO)$_6$

The Rh K edge spectrum was Fourier filtered between 1.53Å and 3.90Å. A six shell theoretical model taking the six radii noted above as its starting point, with all Debye-Waller factors set to 0.01Å$^2$ at first, was refined against the experimental data. Multiple scattering within the terminal carbonyls (shells 1 and 4) and the bridging carbonyls (shells 2 and 5) was included in the calculations. The initial Rh-C-O angles were 180° and 132° respectively.

The two Rh-O shells contain the same number of the same type of scattering atom at roughly the same distance. This means that the non-multiple scattering EXAFS signals for these shells will be essentially impossible to resolve. EXCURVE allows the parameters for any two (or more) shells to be linked, and in this case the radii and Debye-Waller factors of the two oxygen shells were both set to their average values and refined together.

The theoretical parameters were refined until a minimum fit index (FI) was obtained between theory and experiment, producing the results summarised in table 2.1. The EXAFS spectra and their Fourier transforms are shown in fig. 2.3.

<table>
<thead>
<tr>
<th>Shell No.</th>
<th>Atoms</th>
<th>Element</th>
<th>RadiusÅ (EXAFS)</th>
<th>RadiusÅ (Crystal)</th>
<th>Debye-Waller FactorÅ$^2$</th>
<th>% Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>C</td>
<td>1.903(8)</td>
<td>1.864</td>
<td>0.014</td>
<td>2.09</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>C</td>
<td>2.187(11)</td>
<td>2.168</td>
<td>0.014</td>
<td>0.86</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>Rh</td>
<td>2.747(2)</td>
<td>2.776</td>
<td>0.009</td>
<td>-1.04</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>O</td>
<td>3.063(5)</td>
<td>3.019</td>
<td>0.007</td>
<td>1.66</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>O</td>
<td>3.063(5)</td>
<td>3.103*</td>
<td>0.007</td>
<td>-1.10</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>Rh</td>
<td>3.873(9)</td>
<td>3.926*</td>
<td>0.011</td>
<td>-1.35</td>
</tr>
</tbody>
</table>

*calculated from other distances
$\theta_{\text{Rh-C-0,terminal}}=175^\circ$; $\theta_{\text{Rh-C-0,bridging}}=136^\circ$.
FI=1.1437; R=18.5461.
Fig. 2.3: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for Rh₆(CO)₆(s).
It is clear that there is good agreement between the EXAFS spectrum and the X-ray structure.

**Rh₆(CO)₆PPh₂Et**

The Rh K edge spectrum was Fourier filtered between 1.55Å and 4.00Å. As with Rh₆(CO)₆, a six shell model was used, again with the oxygen shells linked. Since one of the six rhodium atoms has only one terminal CO ligand attached, the occupancy of the CO_TERMINAL shells was reduced to 1.83. Attempts were made to model the presence of phosphorus (0.17 P atoms per Rh atom, on average), but its contribution to the EXAFS spectrum was too small to allow it to be modelled realistically.

The results obtained at minimum FI are given in table 2.2, where the percentage discrepancy mentioned is that between the EXAFS results and the X-ray structure of Rh₆(CO)₆. The EXAFS spectra and their Fourier transforms are shown in fig. 2.4.

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>( R_{\text{EXAFS}} / \AA )</th>
<th>( R_{\text{Crystal}} / \AA )</th>
<th>Debye-Waller % Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.83</td>
<td>C</td>
<td>1.882(6)</td>
<td>1.864</td>
<td>0.012</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>C</td>
<td>2.169(7)</td>
<td>2.188</td>
<td>0.012</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>Rh</td>
<td>2.752(1)</td>
<td>2.776</td>
<td>0.011</td>
</tr>
<tr>
<td>4</td>
<td>1.83</td>
<td>O</td>
<td>3.061(4)</td>
<td>3.019</td>
<td>0.007</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>O</td>
<td>3.061(4)</td>
<td>3.103*</td>
<td>0.007</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>Rh</td>
<td>3.852(12)</td>
<td>3.926*</td>
<td>0.017</td>
</tr>
</tbody>
</table>

*calculated from other distances
\( \angle \text{Rh-C-O} \text{terminal}=173^\circ; \angle \text{Rh-C-O} \text{bridging}=136^\circ. \)

\( \text{FI}=0.55915; R=16.5288. \)

Quite obviously, Rh₆(CO)₆PPh₂Et has essentially the same structure as Rh₆(CO)₆.
Fig. 2.4: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for Rh\textsubscript{3}(CO)\textsubscript{12}PPh\textsubscript{3}Et(s).
Chapter 2: Supported Rhodium Cluster

$\text{Rh}_2(\text{CO})_5\text{PPh}_3(\text{CH}_3)_2\cdot\text{SILICA}$

The quality of the Rh K edge spectrum deteriorates badly at high values of $k$, fig. 2.5 (top). In the Fourier transform of this spectrum (fig. 2.5 (bottom)) there is a fairly strong signal at around 2.25 Å (which was at first assigned to phosphorus) and another at ~3.5 Å which did not tally with any expected atomic shell. One obvious ground for suspicion is that if phosphorus could not be resolved in the spectrum of $\text{Rh}_2(\text{CO})_5\text{PPh}_3\text{Et}$, then it should not be detectable in the current spectrum. In fact, the presence of so much $k^2$-weighted noise was giving rise to spurious signals. When the experimental data were truncated to remove the noisiest part, these disappeared; see fig. 2.6.

The spectrum was filtered between 1.59 Å and 4.49 Å and the same initial model as for $\text{Rh}_2(\text{CO})_5\text{PPh}_3\text{Et}$ refined against the experimental EXAFS spectrum. Once again, the phosphorus contribution was not included.

The parameters obtained at minimum FI are tabulated in Table 2.3, and the spectra illustrated in fig. 2.6.

<table>
<thead>
<tr>
<th>Shell</th>
<th>No.</th>
<th>Atoms</th>
<th>Element</th>
<th>Radius Å (EXAFS)</th>
<th>Radius Å (Crystal)</th>
<th>Debye-Waller Factor Å$^2$</th>
<th>% Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.83</td>
<td>C</td>
<td>1.868(7)</td>
<td>1.864</td>
<td>0.020</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>C</td>
<td>2.160(9)</td>
<td>2.168</td>
<td>0.020</td>
<td>-0.37</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>Rh</td>
<td>2.739(1)</td>
<td>2.776</td>
<td>0.012</td>
<td>-1.33</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.83</td>
<td>O</td>
<td>3.028(2)</td>
<td>3.013</td>
<td>0.006</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>O</td>
<td>3.028(2)</td>
<td>3.103*</td>
<td>0.006</td>
<td>-2.42</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>Rh</td>
<td>3.879(5)</td>
<td>3.926*</td>
<td>0.013</td>
<td>-1.20</td>
<td></td>
</tr>
</tbody>
</table>

*calculated from other distances
\(\angle \text{Rh-C-O}_{\text{terminal}}=180^\circ\); \(\angle \text{Rh-C-O}_{\text{bridging}}=134^\circ\).

There is little to tell between these parameters and those of the two molecular species.
Fig. 2.5: Unfiltered (top) EXAFS spectrum and (bottom) its Fourier transform, for Rh$_8$(CO)$_{15}$PPh$_3$(CH$_3$)$_3$-SILICA.
Chapter 2: Supported Rhodium Cluster

Fig. 2.6: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for Rh$_6$(CO)$_{16}$PPh$_3$(CH$_2$)$_2$-SILICA.
2.52 Conclusions

That the Rh₆(CO)₁₅⁻ unit could be anchored intact to an oxide surface was supported by previous ³¹P nmr experiments. The EXAFS spectrum provides confirmation that this is so, and that the cluster is structurally unaltered when anchored. In fact, no shell radius varies by more than 1.8% across the three compounds examined. The conformity of structure between the anchored species and its molecular analogues is a demonstration that the cluster is held at a remove from the surface by the intervening ligand. A direct interaction with the oxide (or, indeed, with other anchored clusters) would produce structural distortions detectable in the EXAFS.
Transition metal clusters with encapsulated atoms form a recognised cluster sub-class. The interstitial atom has a tendency to stabilise the cluster through strong M-E bonding. Unlike normal clusters, these species are often anionic (as the more stable framework can hold extra electrons).

Clusters are often thought of as fragments of a metal lattice - both have a similar drive to maximise the amount of bonding. Extending the analogy, clusters with heteroatoms can be thought of as fragments of an alloy structure, potentially modelling compounds such as the binary metal carbides. Note, however, that the shapes of clusters are not confined to the regular forms needed to build a lattice, and that the steric and electronic effects of ligands can produce less symmetric, and non-close-packed, structures.

The higher stability of heteroatomic clusters means that they are more likely to withstand the rigours of catalytic conditions - indeed, if the elements are present, these clusters are sometimes the thermodynamic product under these conditions. The anionic cluster \([\text{Rh}_7\text{S}_2\text{CO}_3]^{2-}\) is both stable and active, and so has been contemplated as a subject for immobilisation on a surface.

Earlier studies in this group have shown that this cluster can be anchored intact to alumina and (apparently) titania, but not to silica. Catalysis using the product of reaction with silica is inconsistent with normal metal crystallites: the sulphur in the starting material could be acting as a poison.

\subsection*{Experimental}

A sample of \((\text{Ph}_3\text{P})_2\text{Ni}_3\text{Rh}_7\text{S}_2\text{CO}_3\text{CN}(\text{CH}_2)_2\text{Si}(\text{OEt})_3\) prepared by R.J. Crowte was stirred with dry \(\gamma\)-\(\text{Al}_2\text{O}_3\) overnight in \(\text{CH}_2\text{Cl}_2\) under \(\text{N}_2\). The grey-pink solid so produced was filtered out and dried under vacuum. This sample was prepared at the last minute and no tests of its identity were possible before travelling to the SRS.
Chapter 2: Supported Rhodium Cluster

The functionalised cluster had been made by adding the isocyanide to a stirred solution of the cluster in 1,2-dichloroethane. CN(CH₂)₃Si(OEt)₃ was produced from commercial 3-aminopropyltriethoxysilane using a literature synthesis. Preparation of the cluster followed the method of Vidal and coworkers.

Two Rh K edge EXAFS spectra of the supposed oxide-supported cluster were recorded using fluorescence detection and averaged. A model for the theoretical spectrum was prepared from the crystallographic results of Vidal etc. The preparation of such a model is described in more detail in chapter 3. The major shells out to 4Å are presented in table 2.4.

Table 2.4: Averaged Atomic Shells Around Rh in [Rh₅S₅(CO)₉]²⁻

<table>
<thead>
<tr>
<th>Element</th>
<th>Number</th>
<th>Radius/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.8</td>
<td>1.952</td>
</tr>
<tr>
<td>Rh</td>
<td>4.7</td>
<td>2.867</td>
</tr>
<tr>
<td>O</td>
<td>2.8</td>
<td>2.990</td>
</tr>
<tr>
<td>C</td>
<td>2.4</td>
<td>3.561</td>
</tr>
<tr>
<td>Rh</td>
<td>2.4</td>
<td>3.829</td>
</tr>
<tr>
<td>C</td>
<td>1.9</td>
<td>4.000</td>
</tr>
</tbody>
</table>

2.6.2 Results

The experimental spectrum was only usable over a short range of k-space, fig. 2.7 (top). In the Fourier transform, fig. 2.7 (bottom), the large Rh shell at 2.9Å is conspicuous by its absence. In fact, all attempts to match up the experimental spectrum with the anticipated set of atomic shells were a failure. In addition, a three shell model (carbonyl carbon, surface oxygen and carbonyl oxygen), inspired by the possibility of cluster fragmentation to Rh₅(CO)₉ (n=2 or 3) units on the surface, failed to match the experimental EXAFS spectrum (the best R value obtained was 61.7).

The i.r. spectrum of the original sample was taken, revealing that no carbonyl ligands were present - so there had in fact been serious decomposition of the sample. A third approach was adopted, in which it was assumed that rhodium was scattered over the surface, primarily as
Fig. 2.7: Unfiltered (top) EXAFS spectrum and (bottom) its Fourier transform, for the 'Rh_{17} cluster' on an alumina surface.
single atoms or in very small clusters, each atom being hydroxylated through contact with the air. Although there would have been sulphur atoms present, they would be relatively few, and were not considered. In the starting model, each rhodium was coordinated to a triangle of surface oxygen atoms and had three hydroxyl ligands, and was in addition involved in a dimer. The numbers of atoms in each shell were refined with the other parameters. The match between experiment and such a model is illustrated in fig. 2.8, while the parameters obtained at minimum FI are listed in table 2.5.

Table 2.5: EXAFS Results for the Rh\textsubscript{5} cluster decomposed on a γ-alumina Surface

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Debye-Waller Factor/Å\textsuperscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>0</td>
<td>2.059(2)</td>
<td>0.011</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>Rh</td>
<td>2.665(4)</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Spectrum Fourier filtered from 0.83Å to 2.88Å, FI=0.45767.

The EXAFS results support the notion that the cluster has oxidised and decomposed over the alumina surface. There is evidence that some of the Rh-Rh bonds remain intact even so.
Chapter 2: Supported Rhodium Cluster

Fig. 2.8: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for the Rh$_7$ cluster decomposed on an alumina surface.
Chapter Three

EXAFS Studies of Some Mixed Metal Clusters
3.1 INTRODUCTION

Although the syntheses of mixed metal clusters are now more or less systematic, their reactivity is not so well understood. As there is great interest in the potential of heterometallic clusters in catalysis, both in their own right and as analogues to heterogeneous bimetallic catalysts, there is a need for greater understanding of their basic chemistry. Recent work by this group investigated the reactivity of, and catalysis by, $\text{H}_2\text{Ru}_4(\text{CO})_2(\text{MFPPh}_3)$ ($\text{M}=\text{Cu},\text{Au}; \text{1,2}$ respectively) compared with $\text{H}_2\text{Ru}_4(\text{CO})_2$ \(^1\).

In particular, the activation towards alkene isomerisation caused by introducing a gold centre into $\text{H}_2\text{Ru}_4(\text{CO})_2$ \(^2\) was investigated in greater depth. The addition of the heterometal was discovered to lead to easier cluster fragmentation, in turn promoting the activation of the cluster towards alkene isomerisation. The heterometallic mechanism differed from the homometallic; evidence was found that the catalytic species was bimetallic and included $\text{MPR}_3$ ($\text{M}=\text{Cu},\text{Au}$).

The EXAFS spectra of the clusters (1) and (2) were recorded with a view to comparing them with the X-ray crystallographic data for each. In addition, investigations into the reactivity of these clusters produced two partially characterised mixed metal species \(^1\). The EXAFS spectra of these were also recorded, in the hope that the structural data so obtained would allow the new compounds to be clearly identified.
Chapter 3: Mixed Metal Clusters

3.2 HETEROMETALLIC CARBONYL CLUSTERS

The first mixed metal cluster to be produced was \( \text{[FeCo}_{3}(\text{CO})_{2}]^{-} \) in 1959. Over the intervening years many hundreds more have been made, with the syntheses gradually becoming more systematic.

3.2.1 Catalysis

Although no intact cluster has yet been firmly identified as the active species in a catalysis, the criteria for establishing that cluster catalysis has occurred have been thought out\(^2\). Briefly these are:

1. The turnover frequency increases with increasing catalyst concentration.

2. The selectivity is different for the cluster precursor, or the catalysis mechanism is not explainable in terms of mononuclear species.

3. A mixed metal combination enhances or changes the selectivity of a reaction normally catalysed by one or both of the metals alone.

4. Conditions that favour M-M bond formation also increase the catalytic activity.

5. A framework-chiral cluster is active in asymmetric catalysis.

Because of the last criterion above, particular efforts have been made to obtain an inherently chiral cluster (i.e. the chirality is a property of the metal framework)\(^3\).

Another source of the interest in heterometallic clusters are heterogeneous alloy catalysts, which have the potential to alter reaction selectivity\(^4\). Catalysts derived from the combination of metals from groups 8-10 and group 11, such as ruthenium-copper, have been studied in detail\(^6-7\). Some of these combinations have been studied using EXAFS.
Chapter 3: Mixed Metal Clusters

providing some insight into the clusters that the metals form on the supporting surface, as mentioned in the introduction.

Although several studies have been made, no heterometallic cluster has been firmly established as an active catalytic species. Heterosite reactivity has been found, however, in Ru₂₄Co₃(CO)₁₃⁹ and HRuCo₃(CO)₁₂⁹.
Chapter 3: Mixed Metal Clusters

3.3 EXPERIMENTAL

The EXAFS spectra of four mixed metal compounds, two already identified and two not, along with some samples chosen for comparison purposes, were recorded. See table 3.1 for a list.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Edge(s) Examined</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper Foil</td>
<td>Cu</td>
<td></td>
</tr>
<tr>
<td>Gold Foil</td>
<td>Au</td>
<td></td>
</tr>
<tr>
<td>Cu(MeCN)$_2$BF$_4$</td>
<td>Cu</td>
<td>-</td>
</tr>
<tr>
<td>Au(PPh$_3$)$_2$Cl</td>
<td>Au</td>
<td>-</td>
</tr>
<tr>
<td>H$_3$Ru$_4$(CO)$_3$(CuPPh$_3$)</td>
<td>Cu &amp; Ru</td>
<td>12, 13</td>
</tr>
<tr>
<td>H$_3$Ru$_4$(CO)$_3$(AuPPh$_3$)</td>
<td>Au</td>
<td>14, 15</td>
</tr>
<tr>
<td>&quot;Cu$_2$Ru$_2$F$_2&quot;&quot;</td>
<td>Cu</td>
<td>1</td>
</tr>
<tr>
<td>&quot;Ru$_2$Au$_2$F&quot;&quot;</td>
<td>Au</td>
<td>1</td>
</tr>
</tbody>
</table>

* Cl$^-$ counter ion

* \(PCy_3\) instead of PPh$_3$

* (CuPMePh$_3$) instead of (CuPPh$_3$)

3.31 Preparations

The foils were used off the shelf. All other samples were provided by A.C. Street.

H$_3$Ru$_4$(CO)$_3$(CuPPh$_3$) is prepared by reacting [N(PPh$_3$)$_2$]H$_2$Ru$_4$(CO)$_3$ with [Cu(MeCN)$_2$]PF$_6$/PPh$_3$ under nitrogen, followed by recrystallisation from CH$_2$Cl$_2$/petroleum ether. H$_3$Ru$_4$(CO)$_3$(AuPPh$_3$) is made by an analogous process employing AuPPh$_3$Cl.

The reaction of H$_3$Ru$_4$(CO)$_3$(CuPPh$_3$) with CO (in octane at 60° for 24 hours), to produce a mixture of half a dozen well-characterised
cluster compounds, also yields "\text{Cu}_5\text{Ru}_5\text{P}_2" as a partially characterised side product.

This compound is a black powder, sparingly soluble in polar solvents. The quoted stoichiometry is implied by EDAX analysis. CHN analysis indicates the presence of 42.0% carbon and 3.2% hydrogen. The $^1$H nmr spectrum contains signals corresponding to aromatic protons and a hydride singlet. The latter is apparently due to just one atom, though

![Fig. 3.1: Solid state i.r. spectrum of "\text{Cu}_5\text{Ru}_5\text{P}_2" (carbonyl stretching region).](image)
the signal is too small to be sure. There are two roughly equal signals in the $^{31}$P nmr spectrum, at 23.65 and 8.60 ppm (referenced to 85% $\text{H}_3\text{PO}_4$). Comparison with the structurally characterised cluster $\text{H}_2\text{Ru}_2\text{Cu}_2\text{P}((\text{CO})_2\text{PPh}_3\text{COMe})$ ($^{31}$P nmr 26.4 and 2.7 ppm) implies that one phosphorus is bound to a ruthenium atom, and the other to a copper. The nujol mull i.r. spectrum of this compound (fig. 3.1) contains these eight bands in the carbonyl stretching region: 2033 (s); 2010 (s); 1995 (s); 1969 (sh), 1957 (s), 1939 (sh), 1929 (sh) and 1915 cm$^{-1}$ (m). Assuming that the species is monomeric, this points to a carbonyl cluster with a molecular formula something like $\text{H}_x\text{Ru}_2\text{Cu}_2\text{P}((\text{CO})_2\text{PPh}_3\text{COMe})$, where $x$ is small (say 1 to 4), $y$ is 0 or 1 and $z$ is at least eight.

Reaction of $\text{H}_2\text{Ru}_4((\text{CO})_2\text{AuPPh}_3)$ with CO in the manner described for its copper analogue also produces an unidentified minor product, $\text{Ru}_2\text{Au}_2\text{P}^\text{II}$.

This very dark brown powder is insoluble in both cyclohexane and dichloromethane. The 4:2:1 stoichiometry was suggested by an EDAX analysis. A solid state i.r. spectrum of this compound contains no signals due to carbonyl stretching.

3.32 EXAFS Experiments

The metal spectra were recorded in transmission mode using 10µm foils. The other samples were ground to fine powder and spectra of the transmission through a 1-2mm thickness were recorded. The [Cu(MeCN)$_4$]BF$_4$ sample was diluted with an equal mass of boron nitride powder to reduce the concentration of copper to roughly 10% by weight.

Theoretical models for the elemental samples were generated automatically using an option provided in one of the versions of the EXCURVE data analysis program.

For those compounds whose X-ray structure was known, the atomic coordinates and unit cell data were fed into the program XANADU$^{17}$, which was then used to generate all the interatomic distances within the unit cell. For all the samples under consideration in this chapter, the atoms
are distributed within a unit cell such that the region accessible to EXAFS falls entirely within it. By inspection, then, of the output from XANADU, it is possible to select those atom pairs that have the EXAFS absorbing atom as one partner. For instance, in $\text{H}_2\text{Ru}_4(\text{CO})_9(\text{AuPPh}_3)$, we have

$$\text{Au-Ru: 2.766, 2.766, 3.851, 4.797Å}$$
$$\text{Au-P: 2.305Å}$$
$$\text{Au-H: 3.298, 3.422Å}$$
$$\text{Au-O: 3.337, 3.667, 3.752, 4.067Å}$$

Hydrogen atoms are very poor backscatterers, so they can be discounted. Taking the other atom types in turn, one progresses through the atom to atom distances, averaging those for like atoms which are separated by less than 0.1Å (a good EXAFS resolution). This gives the following backscattering shells around each gold atom:

<table>
<thead>
<tr>
<th>Atom</th>
<th>No.</th>
<th>Radius/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1</td>
<td>2.306</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>2.660</td>
</tr>
<tr>
<td>Ru</td>
<td>2</td>
<td>2.766</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>3.051</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>3.304</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>3.343</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>3.500</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>3.710</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>3.779</td>
</tr>
<tr>
<td>Ru</td>
<td>1</td>
<td>3.851</td>
</tr>
<tr>
<td>O</td>
<td>1</td>
<td>4.067</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>4.568</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>4.786</td>
</tr>
<tr>
<td>Ru</td>
<td>1</td>
<td>4.797</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>4.913</td>
</tr>
</tbody>
</table>
Chapter 3: Mixed Metal Clusters

Obviously, this is far too complex a model for practical use. It does, however, provide a starting point. The model can be simplified as far as is necessary in the light of the experimental spectrum, by averaging adjacent shells of the same element, or by discarding small shells containing weakly backscattering atoms.

For many of the compounds, the crystallographic structure of a related compound had to be used, meaning that some of the calculated shell radii are only estimates. As it happens, the discrepancies were all confined to atoms removed from the X-ray absorbing atom; often the estimated shells were not even observed in the EXAFS spectrum.
3.4 REFERENCE MATERIALS

3.41 Gold Foil

This element has a cubic close packed structure. Detail is visible in the Fourier transform of its spectrum out to 6 Å. Within this range there are four backscattering shells. The attempt to fit a four shell model to the experimental data produced the numerical results in table 3.2. The result for shell 1 is rather poor for an innermost shell. It is possible that the theoretical backscattering phaseshift for gold is not quite accurate. As can be seen in fig. 3.2, the visual fit for the outer two shells is also disappointing.

Table 3.2: EXAFS Results for Gold Foil

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller Factor/Å²</th>
<th>% Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>Au</td>
<td>2.822(3)</td>
<td>2.824</td>
<td>0.016</td>
<td>-2.15</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>Au</td>
<td>4.015(14)</td>
<td>4.078</td>
<td>0.024</td>
<td>-1.54</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>Au</td>
<td>4.865(16)</td>
<td>4.995</td>
<td>0.038</td>
<td>-2.60</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>Au</td>
<td>5.892(14)</td>
<td>5.767</td>
<td>0.022</td>
<td>2.17</td>
</tr>
</tbody>
</table>

F1=2.15906; R=27.4204. Spectrum Fourier filtered from 1.95Å to 5.97Å.

Inclusion of the multiple scattering contribution between the colinear first and fourth shells makes the theoretical fourth shell appear too intense in the Fourier transform, rather than too weak as above. The fit index is a little worse. Since the experimental spectrum is rather short, extending only to k=13Å⁻¹, with some noise in the last
Fig. 3.2: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for gold foil.
third, it is not surprising that a shell over 5Å from the absorbing atom cannot be modelled precisely.

### 3.42 Copper Foil

Copper is also a cubic close packed element. Again, structure out to 6Å can be seen in the EXAFS, which in this case means five shells. The first and fourth shells are colinear. When the multiple scattering between them was included, a slight overestimation of the fourth shell's radius was exchanged for a similar underestimate. The shape of the spectrum and the fit index were, however, greatly improved. Table 3.3 gives the results obtained with multiple scattering included, which are illustrated in fig. 3.3.

**Table 3.3: EXAFS Results for Copper Foil**

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>$R_{(EXAFS)}$</th>
<th>$R_{(Crystal)}$</th>
<th>Debye-Waller Factor/A²</th>
<th>% Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>Cu</td>
<td>2.514(1)</td>
<td>2.555</td>
<td>0.015</td>
<td>-1.54</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>Cu</td>
<td>3.535(5)</td>
<td>3.615</td>
<td>0.024</td>
<td>-2.21</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>Cu</td>
<td>4.370(3)</td>
<td>4.427</td>
<td>0.023</td>
<td>-1.29</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>Cu</td>
<td>5.064(3)</td>
<td>5.112</td>
<td>0.023</td>
<td>-0.94</td>
</tr>
<tr>
<td>5</td>
<td>24</td>
<td>Cu</td>
<td>5.660(8)</td>
<td>5.716</td>
<td>0.034</td>
<td>-0.98</td>
</tr>
</tbody>
</table>

FI=1.54567; R=9.0764,
Spectrum Fourier filtered from 1.52Å to 5.71Å.

### 3.43 Au(CPPh₃)Cl

The chlorine atom and phosphine ligand sit opposite each other, with the gold atom in between.
Fig. 3.3: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for copper foil, multiple scattering included.
Chapter 3: Mixed Metal Clusters

The usable part of the EXAFS spectrum was relatively short. The fitting of a five shell model was attempted; however, the outer shells became lost in Fourier transformed noise. Some apparently good results were obtained with a less ambitious three shell model (see fig. 3.4 and table 3.4). In fact, during the refinement the parameters for the first two shells proved to be extremely highly correlated, correlation coefficients exceeding 0.9 in some cases. This means that the values for the phosphorus and chlorine shells are in a sense invalid: their correspondence with the crystallographic results could be largely coincidental. This is undoubtedly because the backscattering properties of phosphorus and chlorine are similar, and the shell radii are comparable.

Table 3.4: EXAFS Results for Au(PPh₃)Cl

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller Factor/Å²</th>
<th>% Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>P</td>
<td>2.237(2)</td>
<td>2.242</td>
<td>0.007</td>
<td>-0.22</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>Cl</td>
<td>2.274(2)</td>
<td>2.279</td>
<td>0.007</td>
<td>-0.22</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>C</td>
<td>3.418(6)</td>
<td>3.374</td>
<td>0.014</td>
<td>1.30</td>
</tr>
</tbody>
</table>

F1=0.14222; R=16.1299, Fourier filtered from 1.45Å to 3.18Å.

3.44 [Cu(MeCN)BF₄]

Only the cation of this compound lies within the volume of space accessible to EXAFS. This is a tetrahedral arrangement of linear N≡C=CH₂ ligands around the central copper atom.

A good quality spectrum was obtained, and was Fourier filtered from 0.94Å to 4.42Å. When multiple scattering along the linear ligand is
Fig. 3.4: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for Au(PPh₃)Cl (s).
not considered, the results are only really satisfactory for the first shell (fig. 3.5 and table 3.5).

Table 3.5: EXAFS Results for solid [Cu(MeCN)]BF,

<table>
<thead>
<tr>
<th>Shell</th>
<th>No, Atoms</th>
<th>Element</th>
<th>Radius Å (EXAFS)</th>
<th>Radius Å (Crystal)</th>
<th>Debye-Waller % Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>N</td>
<td>1.951(4)</td>
<td>1.983</td>
<td>0.011</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>C</td>
<td>3.192(6)</td>
<td>3.100</td>
<td>0.003</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>C</td>
<td>4.666(26)</td>
<td>4.566</td>
<td>0.009</td>
</tr>
</tbody>
</table>

$E_0=27.4(8)$ eV; $E_{n,m}=53.55$ eV; $E_{n,m,m}=786.61$ eV; $\varphi I=-4.0$; $AFAC=0.6$.

As noted in chapter 1, the calculation of multiple scattering effects requires a great deal of computing time. The program EXCURVE is only equipped to deal with the simplest (and most significant) case, namely, multiple scattering within a three atom unit. This is fine for the second shell in this model, but it only includes some of the possible scattering pathways involving the third shell, as fig. 3.6 shows. Obviously, the distance of this carbon shell from the absorbing copper atom means that these pathways will each have a relatively insignificant effect on the EXAFS spectrum. On the other hand, the number of pathways and the fact that the atoms are in line could produce a combined effect that is significant. When the multiple scattering paths containing three atoms are included in the EXCURVE calculations, there is an improvement in the results for the second shell, both in terms of the shape of the theoretical Fourier transform and the accuracy of the shell radius, but not for the third (fig. 3.7 and table 3.6).
Fig. 3.5: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for [Cu(MeCN)]$_2$BF$_4$. Multiple scattering is not considered.
Chapter 3: Mixed Metal Clusters

2nd Order

\[
\text{Cu} - \text{N} - \text{C} - \text{C}
\]

3rd Order

\[
\text{Cu} - \text{N} - \text{C} - \text{C}
\]

4th Order

\[
\text{Cu} - \text{N} - \text{C} - \text{C}
\]

5th Order

\[
\text{Cu} - \text{N} - \text{C} - \text{C}
\]

Fig. 3.6: Multiple scattering pathways within a four atom colinear unit, EXCURVE is not equipped to deal with those pathways that include each of the four atoms (shown below the dotted line).

Table 3.6: EXAFS Results for [Cu(MeCN)]BF₄ (multiple scattering included)

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius Å (EXAFS)</th>
<th>Radius Å (Crystal)</th>
<th>Debye-Waller Factor Å²</th>
<th>% Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>N</td>
<td>1.970(3)</td>
<td>1.983</td>
<td>0.011</td>
<td>-0.66</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>C</td>
<td>3.104(5)</td>
<td>3.100</td>
<td>0.018</td>
<td>0.13</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>C</td>
<td>4.588(16)</td>
<td>4.568</td>
<td>0.039</td>
<td>2.37</td>
</tr>
</tbody>
</table>

E₀=22.4(4) eV; Eₐₐₐ=53.55 eV; Eₑₑₑₑₑ=786.61 eV; VPI=-4.0; AFAC=0.6

F₁=0.61787; R=29.4491.
Fig. 3.7: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for [Cu(MeCN)]_2BF_4, multiple scattering effects included.
3.5 THE KNOWN CLUSTERS

3.5.1 H$_2$Ru$_4$(CO)$_8$(CuPPh$_3$)

The structure of this complex is illustrated in fig. 3.8. The copper atom bridges a ruthenium triangle.

**Fig. 3.8: Crystallographically determined structure of H$_2$Ru$_4$(CO)$_8$(CuPPh$_3$),**

![Structure of H$_2$Ru$_4$(CO)$_8$(CuPPh$_3$)](image)

**Ru edge Spectrum**

This was a good quality spectrum, and the six shells within 3.5 Å of the central atom were modelled. The results are presented in table 3.7 and fig. 3.9. Because of multiple scattering within the Ru-C-O units, the contribution of the oxygen shell to the EXAFS signal is comparable to that of the heavy metal atoms. The contribution of the sixth, carbon, shell is less significant, so the figures for this shell should be considered a little less reliable. In addition, the parameters for the second and third shells are quite highly correlated.
Chapter 3: Mixed Metal Clusters

Beyond 3.5Å the atomic shells are too weakly scattering, too numerous and too close together to be resolved.

Table 3.7: EXAFS Results for \( \text{H}_2\text{Ru}_5(\text{CO})_{12}(\text{CuPPh}_3)_2 \), Ru edge Spectrum

\[
\begin{array}{ccccccc}
\text{Shell} & \text{No. Atoms} & \text{Element} & \text{Radius Å} & \text{Radius Å} & \text{Debye-Waller % Discrepancy} \\
& & & \text{(EXAFS)} & \text{(Crystal)} & \text{Factor Å}^2 \\
1 & 3 & \text{C} & 1.918(2) & 1.845 & 0.004 & 3.96 \\
2 & 0.8 & \text{Cu} & 2.730(33) & 2.738 & 0.003 & -0.29 \\
3 & 1.5 & \text{Ru} & 2.758(29) & 2.791 & 0.008 & -1.18 \\
4 & 1.5 & \text{Ru} & 2.974(5) & 2.966 & 0.008 & 0.27 \\
5 & 3 & \text{O} & 3.094(16) & 3.038 & 0.026 & 1.84 \\
6 & 1.5 & \text{C} & 3.205(26) & 3.221 & 0.001 & -0.50 \\
\end{array}
\]

\( F_r=1.05962; R=17.8910 \),
Spectrum Fourier filtered from 1.25Å to 3.15Å,

\textbf{Cu edge Spectrum}

Despite the EXAFS spectrum being fairly noisy (because only a small sample was available), reasonable results, with no high correlations between shells, were obtained for a model based on the four innermost shells around the copper atom (table 3.8 and fig. 3.10). The discrepancy in the copper-ruthenium distance between the copper and ruthenium edges is 1.65%.

The prospects for modelling the spectrum out to about 5Å with a ten shell model looked promising at first, but EXCURVE was unable to refine the model to a minimum. In addition, there were several large correlation coefficients (greater than 0.9) between parameters.
Fig. 3.9: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for solid $H_2Ru_4(CO)_{12}(CuPPh_3)_2$. Ru edge.
Fig. 3.10: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for H$_2$Ru$_4$(CO)$_{12}$(CuPPh$_3$)$_2$, Cu edge.
Table 3.8: EXAFS Results for H₃Ru₄(CO)₁₂(CuPPh₃), Cu edge Spectrum

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius Å (EXAFS)</th>
<th>Radius Å (Crystal)</th>
<th>Debye-Waller Factor Å²</th>
<th>% Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>P</td>
<td>2.18(2)</td>
<td>2.197</td>
<td>0.004</td>
<td>-0.64</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>Ru</td>
<td>2.68(2)</td>
<td>2.798</td>
<td>0.021</td>
<td>-1.94</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>C</td>
<td>2.81(12)</td>
<td>2.896</td>
<td>0.028</td>
<td>-2.90</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>C</td>
<td>3.41(23)</td>
<td>3.397</td>
<td>0.028</td>
<td>0.65</td>
</tr>
</tbody>
</table>

E₀=21.3(4) eV; Eₘₘₜₜ=33.11 eV; Eₘₘₜₜ=615.39 eV; VPI=-0.4; AFAC=-0.5.

Fig. 3.11 illustrates the structure of this cluster. In contrast to the copper cluster, the gold atom bridges a ruthenium-ruthenium edge.

3.52. H₃Ru₄(CO)₁₂(AuPPh₃)

Fig. 3.11; Structure of H₃Ru₄(CO)₁₂(AuPPh₃).
Chapter 3: Mixed Metal Clusters

Au edge Spectrum

Only a very small sample was available for study and, as can be seen in fig. 3.12, a very poor spectrum was obtained. As well as a great deal of noise, there is a 'lump' in the EXAFS between 12 000eV and 12 050eV, which appears to be too long and large to be a genuine oscillation.

![Absorption vs Energy](image)

Fig. 3.12: Gold L\(_{\text{III}}\) edge X-ray absorption spectrum of H\(_3\)Ru\(_4\)(CO)\(_8\)(AuPPh\(_3\)).

Using a background subtraction that takes no account of this feature produces an EXAFS spectrum with a high degree of low frequency distortion, from which no useful information can be derived. In order to extract any information from this spectrum, it was necessarily to, firstly, discard the latter part, which consisted mainly of noise. Then the background subtraction polynomial was weighted heavily towards the middle portion of the data. This produced a spectrum that was reasonably balanced in its central portion. Even so, this part of the spectrum contained a fair amount of distortion (fig. 3.13).
Chapter 3: Mixed Metal Clusters

Fig. 3.13: Unfiltered EXAFS spectrum of H₃Ru₄(CO)₁₂(AuPPh₃), and its Fourier transform.
The data was Fourier filtered from 1.83Å to 2.94Å to isolate the main signal, which was modelled as a single ruthenium shell. The results are presented in table 3.9 and fig. 3.14.

Table 3.9: EXAFS Results for H$_2$Ru$_x$(CO)$_y$(AuPPh$_3$)$_z$, Au edge Spectrum

<table>
<thead>
<tr>
<th>Shell No.</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius (Å) (EXAFS)</th>
<th>Radius (Å) (Crystal)</th>
<th>Debye-Waller Factor (Å$^2$)</th>
<th>% Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>Ru</td>
<td>2.689(2)</td>
<td>2.765</td>
<td>0.012</td>
<td>-2.78</td>
</tr>
</tbody>
</table>

$E_0=21.3(5)$eV; $E_{in}=213.85$eV; $E_{ex}=546.93$eV; $\Delta E=4.0$; $\beta=1.5$, $\alpha=0.6$. 
$FI=0.10278$; $R=11.0835$. 

- 93 -
Fig. 3.14: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for H$_2$Ru$_4$(CO)$_{12}$(AuPPh$_3$)$_2$. 
3.6 THE 'UNKNOWN' SAMPLES

3.61 "Ru-Au.P" - Gold Edge EXAFS Spectrum

The analysis of an EXAFS spectrum usually begins with a theoretical model proposed in the light of other chemical experiments. The aim is to find evidence supporting the proposed model (or disproving it), and to derive some numerical results should the theory be backed up. The problem here is that almost nothing is known about the sample under study, leaving one to try to determine the structure using EXAFS data alone.

The positions of the signals in the Fourier transform of a spectrum are determined mainly by the shell radii and the phaseshifts. The former are the unknowns that we wish to determine, whilst the latter are reasonably defined and well known from atom type to atom type. This means that it is possible to get a good idea of which types of atoms are present in a sample, and of the distances involved.

The amplitudes, however, are determined primarily by the numbers of atoms in the shells and the Debye-Waller factors. The Debye-Waller factors, which represent both the thermal motion of the atoms and their static disorder, cannot be determined theoretically, though they can be estimated from experience. They are normally treated as refineable parameters, with the numbers of atoms fixed according to some probable model. The two cannot be refined at the same time, since they are generally highly correlated. If the numbers of atoms are not known, they can be estimated if estimates of the Debye-Waller factors are made. In a sample such as this, then, the analysis of the structure is hindered by the inability to be precise as to the number of atoms in a shell.

The useable part of the EXAFS spectrum is very short. Although the Fourier transform of the gold L\textsubscript{III} edge spectrum of "Ru-Au.P" seems to contain structure out to around 4.5\AA{} (fig. 3.15), the outer shells are certainly contaminated with noise, and were not seriously examined.
Chapter 3: Mixed Metal Clusters

Fig. 3.15: Unfiltered EXAFS spectrum of "Ru_{x}Au_{y}P" and its Fourier transform.
Chapter 3: Mixed Metal Clusters

The main signals were isolated by Fourier filtration from 1.96Å to 3.35Å. Although the Fourier transform in this region clearly has two peaks, it was modelled successively by a gold and a ruthenium shell, then by both together. The Debye-Waller factors were fixed at an arbitrary value of 0.012Å², allowing the numbers of atoms per shell to be refined. Table 3.10 contains the results.

Table 3.10: EXAFS Results for "Au,Ru-P", first metal shell

<table>
<thead>
<tr>
<th>Shell</th>
<th>No.</th>
<th>Atoms</th>
<th>Element</th>
<th>Radius Å (EXAFS)</th>
<th>Radius Å (Crystal)</th>
<th>Debye-Waller Factor Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au shell only</td>
<td>1</td>
<td>3(1)</td>
<td>Au</td>
<td>2.767(4)</td>
<td>-</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>E₀=14.9(7) eV; FI=0.24835; R=29.1630.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru shell only</td>
<td>1</td>
<td>1.8(1)</td>
<td>Ru</td>
<td>2.933(6)</td>
<td>-</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>E₀=4.1(1) eV; FI=0.50197; R=46.6221.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au and Ru shells</td>
<td>1</td>
<td>1.4(0)</td>
<td>Ru</td>
<td>2.864(2)</td>
<td>-</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>E₀=8.0(2) eV; FI=0.02205; R=8.7037.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.5(0)</td>
<td>Au</td>
<td>2.854(3)</td>
<td>-</td>
<td>0.012</td>
</tr>
</tbody>
</table>

The spectra and their transforms are illustrated in figs. 3.16-18. It seems clear that the gold atoms are coordinated to both ruthenium and other gold atoms.

Note how the shape of the Fourier transform is affected by the changes in E₀. As mentioned in the discussion of curve-fitting analysis (section 1.44), the positioning of E₀ affects the phaseshifts mainly at low k values. All of this spectrum is at low k, giving the threshold energy an undue influence, with high correlations between it and the radii. This means that the values for the radii need to be treated with a little caution. The correlations in the two shell model are lower (0.8 compared with 0.9), so it must be assumed that these values are more reliable.
Fig. 3.16: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for "Ru,Au", Au shell only.
Fig. 3.17: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for \( \text{Ru}_{x} \text{Au}_{1-x} \). Ru shell only.
Fig. 3.18: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for “RuAu2”, Au and Ru shells.
Using a slightly longer Fourier filtration window, from 1.35Å to 3.35Å, a phosphorus shell was added to the model, with the results presented in Table 3.11 and Fig. 3.19. Since the phosphorus atom will be closer to the central atom, a slightly lower Debye-Waller factor was chosen. There were high correlation coefficients (above 0.9) between R1 and R2, and R2 and R3.

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius Å (EXAFS)</th>
<th>Radius Å (Crystal)</th>
<th>Debye-Waller Factor Å²</th>
<th>Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5(0)</td>
<td>P</td>
<td>2.221(7)</td>
<td>-</td>
<td>0.008</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1.9(1)</td>
<td>Ru</td>
<td>2.366(5)</td>
<td>-</td>
<td>0.012</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>2.6(1)</td>
<td>Au</td>
<td>2.371(6)</td>
<td>-</td>
<td>0.012</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.11: EXAFS Results for "Ru,Au,P", 3 shell model

Beyond the fact that there is both gold and ruthenium coordinated to the 'average' gold atom, there is little that can be said. It is worth noting that even the shortest gold-ruthenium distance above is nearly 0.2Å greater than that found in the parent cluster, implying that the metal atoms are impeded from packing as closely as is possible. Bearing in mind the insolubility of the sample, one might suggest that the compound has some kind of extended metal framework, containing interstitial phosphorus and carbon from the parent compound.

3.62 "Cu-Ru,P" - Copper Edge EXAFS Spectrum

A great deal more supporting information was available about this compound. In particular, there is a carbonyl signal in the i.r., suggesting that we may have a distinct cluster with a definite structure. The EXAFS spectrum was Fourier filtered from 1.40Å to 2.86Å to isolate the main signals.
Chapter 3: Mixed Metal Clusters

Fig. 3.19: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for "RuAuP", 3 shell model.
Chapter 3: Mixed Metal Clusters

The starting material from which "Cu₂Ru₂P₂" is made is based upon a trigonal bipyramidal Ru₄Cu framework. A reasonable first proposal would be that one of the ruthenium atoms is substituted by a copper atom (bringing with it a phosphine ligand). This could occur to produce either a trans- or a cis- arrangement of copper atoms, as illustrated in fig. 3.20.

![Diagram of possible frameworks](image)

**Fig. 3.20:** (a) heavy atom framework of H₂Ru₄(CO)₁₂(CuPPh₃); (b) & (c) possible frameworks arising from the replacement of a ruthenium atom by copper.

Attempts to base a theoretical EXAFS spectrum on the trans-configuration of copper atoms (i.e. with only ruthenium and phosphorus bound directly to the central copper atom) were unsuccessful. It was
discovered that the shape of the EXAFS signal could not be rendered with a ruthenium shell alone.

There is, in fact, a precedent for the cis- arrangement of copper atoms, in the compound \( \text{Cu}_2\text{Ru}_6\mu_3-\text{H}_2\mu_2(\text{CO})_3\mu_2(\text{PPh}_3)_2 \) (\( R = \text{CHMe}_2 \) or \( \text{Ph} \))\(^a\), in which a copper atom is bound to an Ru-Cu triangle. A model based on framework (c) in fig. 3.20 above (consisting of phosphorus, copper and ruthenium shells) gave a promising result. To produce a good fit between theory and experiment, however, it proved necessary to introduce a carbon shell at approximately 2\( \AA \). Shells containing one, two and three atoms were tried; only the last of these produced an acceptable Debye-Waller factor. This four shell model is illustrated in table 3.12 and fig. 3.21. Remember that the \( ^{31}\text{P} \) nmr spectrum showed that one of the PPh\(_3\) units was bound to a ruthenium atom, hence there is only half an atom in the phosphorus shell. Although it produces a comparatively weak signal, removal of the phosphorus shell does produce a worse result. Thus it is deemed a valid contribution to the model.

Table 3.12: EXAFS Results for "Cu,Ru,P"  

<table>
<thead>
<tr>
<th>Shell No.</th>
<th>Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller Factor/Å(^2)</th>
<th>Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>C</td>
<td>2.028(4)</td>
<td>-</td>
<td>0.010</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>P</td>
<td>2.286(8)</td>
<td>-</td>
<td>0.005</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>Cu</td>
<td>2.509(4)</td>
<td>-</td>
<td>0.013</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>Ru</td>
<td>2.630(5)</td>
<td>-</td>
<td>0.028</td>
<td>-</td>
</tr>
</tbody>
</table>

Discussion

Although the results above are not inconsistent with the metal framework shown in fig. 3.20 (c), they cannot be taken as firm evidence of that structure. It would be possible to change the numbers of atoms in the shells, especially in the ruthenium shell, and still obtain a reas-
Fig. 3.21: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for "Cu₃Ru₃P₆".
onable fit. All that is clear is that copper atoms are bound to both ruthenium and copper atoms within the metal framework of the compound. Roughly half the copper atoms have a phosphine ligand.

The i.r. spectrum contains eight carbonyl signals: so the compound is a carbonyl cluster of some description. The carbon atoms bound to copper are at a distance somewhat greater than that for a typical terminal copper carbonyl (which is roughly 1.8Å\textsuperscript{19,20}). This indicates that some of the carbonyl ligands are bridging, a notion borne out by the fairly low carbonyl stretching frequencies in the i.r. spectrum. Bridging carbonyls would certainly be needed to stabilise a copper atom with no other ligands. It is also possible that there is an interstitial carbon atom within the metal framework.

It must be remembered that the Cu\textsubscript{2}Ru\textsubscript{4}P\textsubscript{2} formula only indicates the stoichiometry of this compound. It may actually be a larger cluster based upon a multiple of this unit.
3.7 CONCLUSIONS

The results in this chapter demonstrate how the EXAFS technique can extract some information from the most unpromising of situations - a tiny sample producing a poor spectrum can still be made to yield a bond distance, as was the case with H$_2$Ru$_4$(CO)$_{12}$(AuPPh$_3$). With better data, as was obtained for H$_2$Ru$_4$(CO)$_{12}$(CuPPh$_3$), quite a lot of information about the metal framework can be obtained. Table 3.13 compares the EXAFS distances obtained for the cluster above with those found in "Cu$_2$Ru$_3$P$_2"$, and with those in a silica supported 1:1 Ru$_x$Cu alloy catalyst$^{21}$. There are longer bond lengths in the Ru$_x$Cu cluster because each triangular Ru$_x$Cu face is capped by a hydrogen atom.

Table 3.13: EXAFS M-M Bond Lengths in 3 Ruthenium-Copper Compounds

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Bond</th>
<th>Distance/Å</th>
<th>Supported Catalyst</th>
<th>H$_2$Ru$<em>4$(CO)$</em>{12}$(CuPPh$_3$)</th>
<th>&quot;Cu$_2$Ru$_3$P$_2&quot;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru edge</td>
<td>Cu-Ru</td>
<td>2.595</td>
<td>2.730</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Cu edge</td>
<td>Cu-Ru</td>
<td>2.636</td>
<td>2.685</td>
<td>2.620</td>
<td></td>
</tr>
<tr>
<td>Cu edge</td>
<td>Cu-Cu</td>
<td>2.582</td>
<td>-</td>
<td>2.599</td>
<td></td>
</tr>
<tr>
<td>Ru edge</td>
<td>Ru-Ru</td>
<td>2.653</td>
<td>2.755,2.974</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

To describe structures in detail, it is clear that the data obtained from an EXAFS analysis should be supported by information derived from other techniques, so that a structure may be proposed. The EXAFS spectrum can then act as a test of this proposal. Here, it is only possible to conclude that the compound "Cu$_2$Ru$_3$P$_2"$ is a carbonyl cluster, also containing phosphine ligands, in which some bonding between carbonyl ligands and copper atoms is present. Within the metal framework, copper is bound to both ruthenium and other copper atoms. Only some very general speculation about the nature of "Ru$_x$Au$_y$P" could be made. It would obviously have been desirable to have Ru edge spectra of both of the unknowns. This was precluded, however by a shutdown of the SRS for refurbishment.
Chapter 3: Mixed Metal Clusters

3.8 REFERENCES

15. J. Evans, A.C. Street & M. Webster; Organometallics, 6 (1987), 794.
16. J. Evans & P.M. Stroud, unpublished results.
CHAPTER FOUR

EXAFS STUDIES OF POLYOXOMETALATES
4.1 INTRODUCTION

Polyoxometalate anions form a structurally distinct class of metal-oxygen complexes based primarily on quasi-octahedrally coordinated metal atoms. They are formed by the group 5 and 6 metals (except chromium), and mixtures thereof, in their highest ($d^0$ or $d^1$) oxidation states. They have the general formulas

$$\text{[M}_n\text{O}_y\text{]}^{x^-}$$ isopolyanions

$$\text{[X}_x\text{M}_m\text{O}_y\text{]}^{z^-} (x \leq m)$$ heteropolyanions

where M stands for the metal or metals (the addenda atoms) and X is the so-called heteroatom. Around seventy elements, from all groups of the Periodic Table except the noble gases, have been found in the latter role. All in all, there are hundreds, if not thousands, of polyoxometalates.

Composed as they are of arrays of $\text{MO}_6$ octahedra, many polyoxoanions resemble fragments of metal oxides, and their surfaces mimic those of heterogeneous metal oxides. Because of this, it is believed that the study of organometallic derivatives of polyanions may provide insights into the properties of oxide-supported catalysts, or even uncover new catalytic materials. As supports for organometallic centres, soluble polyoxometalates have the advantages that they can often be crystallised for $X$-ray crystallography experiments and that their solubility makes detailed nmr studies possible.

Furthermore, the EXAFS technique opens up the potential for confirming and characterising solution structures, for determining interatomic distances in compounds whose structure is only known by analogy or by indirect means (e.g. nmr) and for monitoring structural changes resulting from chemical reactions.

To explore this potential, several polyoxometalates were synthesised and their EXAFS spectra recorded. The quality and amount of structural information obtained from these spectra is examined, and the role of EXAFS in the study of polyanions is discussed.
Chapter 4: Polyoxometalates

4.2 POLYOXOMETALATES

4.2.1 General Chemistry

As a class, polyoxoanions can be viewed as one intermediate between discrete metal oxoanions and aquocations, in a series linked by a series of hydrolysis reactions:

Aquocations \( \{\text{Fe(H}_2\text{O)}_6\}^{3+} \)
Oh⁻⁺ \( \leftrightarrow \) H⁺
(Poly)oxo/Hydroxocations \( \{\text{VO(H}_2\text{O)}_2\}^{3+}, \{\text{Pb}_4\text{(OH)}_4\}^{4+} \)
Oh⁻⁺ \( \leftrightarrow \) H⁺
Oxides/Hydroxides \( \text{CrO}_3, \text{MnO(OH)} \)
Oh⁻⁺ \( \leftrightarrow \) H⁺
Polyoxo/Hydroxoanions \( \{\text{V}_{10}\text{O}_{28}\}^{6-}, \{\text{Mo}_6\text{O}_{24}(\text{OH})_2\}^{6-} \)
Oh⁻⁺ \( \leftrightarrow \) H⁺
Oxo/Hydroxoanions \( \text{WO}_4^{2-}, \{\text{Sb(OH)}_6\}^{3-} \).

Which compound will be formed by a particular element in a particular oxidation state depends upon the ability of the metal to form strong bonds with oxygen. The extremes of this series can be linked conceptually by the general equilibrium:

\[ M^{z+} + \text{OH}_2 \leftrightarrow M^{-\text{OH}^{(z-1)}} + \text{H}^+ \leftrightarrow M^{z-2} + 2\text{H}^+ \]

where \( M^{z+} \) is some metal cation. \( \text{Zn}^{2+} \), for example, has a low charge, a relatively large ionic radius and no vacant orbitals suitable for forming a \( d\pi-p\pi \) bond with oxygen: it forms an aquocation. \( \text{Mn}^{2+} \), on the other hand, with high charge and low radius, would immediately and strongly polarise any coordinating water molecules. It is also a good acceptor of oxygen \( p\sigma \) electrons. In aqueous solution \( \text{Mn}^{2+} \) exists as \( \text{MnO}_4^{2-} \) — species like this are the anions of very strong acids and resist protonation and polymerisation.

Between these extremes are those metal centres that can form discrete oxoanions in sufficiently alkaline conditions, but which can be protonated in more acid conditions. The protonated species can polymerise, with the elimination of water, e.g.:
Chapter 4: Polyoxometalates

\[
\begin{align*}
\text{Cr}^{4+} \text{O}_n^m & \quad \rightarrow \quad \text{CrO}_n \left< \text{OH} \right>^m \quad \text{CrO}_n \left< \text{OH} \right>^m \quad \text{Cr}_2\text{O}_n^m + \text{H}_2\text{O}.
\end{align*}
\]

For chromium, the process cannot proceed much further than this because the relatively small \(\text{Cr}^{4+}\) cation can only accommodate tetrahedral oxygen coordination. Polychromate chemistry is thus limited to a few compounds based on corner sharing \(\text{CrO}_4\) tetrahedra.

The other group 5 and 6 \(d^0\) cations are large enough to expand from tetrahedral to octahedral coordination. They are able to form extended structures based on \(\text{MO}_6\) units. To give just three examples,

\[
\begin{align*}
7\text{MoO}_4^{2-} + 8\text{H}^+ & \rightarrow (\text{Mo}_7\text{O}_{24})^{3-} + 4\text{H}_2\text{O}, \\
2\text{V}_2\text{O}_5^+ + 4\text{WO}_4^{2-} + 6\text{H}^+ & \rightarrow [\text{V}_2\text{W}_6\text{O}_{19}]^{4+} + 3\text{H}_2\text{O} \\
12\text{WO}_4^{2-} + \text{HPO}_4^{2-} + 23\text{H}^+ & \rightarrow [\text{PW}_{12}\text{O}_{49}]^{3-} + 12\text{H}_2\text{O}.
\end{align*}
\]

Three typical such extended structures are illustrated in fig. 4.1.

In all polyanion structures, the metal ion is displaced towards the surface of the anion: approaching either one corner or an edge of its coordination polyhedron. Each metal atom thus forms one or two short metal-oxygen bonds, implying the existence of significant \(\pi\)-bonding. These short bonds are directed towards the exterior of the anion, forming a layer of surface oxygens that are strongly inwardly polarised. Terminal oxygens (i.e. those bound to only one metal atom, denoted \(\text{OM}\)) are the most affected, followed by atoms bridging two metals (\(\text{OM}_2\)) and, where they occur, triply bridging oxygens (\(\text{OM}_3\)). The displacement of the metal atoms towards the vertices and edges of the anion is undoubtedly reinforced by the mutual repulsion of the positive metal centres, in turn enhancing the electron withdrawing effect of the \(\pi\)-\(\pi\) interactions.

The resulting uneven removal of surface electron density has been correlated successfully with \(^{17}O\) nmr chemical shifts. Where protonation occurs, it is at the bridging rather than the terminal oxygens. However, these atoms are essentially non-basic and discourage extensive protonation and further polymerisation. It is this effect that halts the aggregation process before insoluble anions or oxides are produced, so giving polyanions their solution stability.

It is possible for one or two of the oxygen atoms to be substituted by some other atom. This has been done with sulphur, giving, as an example \(\text{NbW}_4\text{O}_{12}\text{S}^{2-}\) and \(\text{TaW}_4\text{O}_{12}\text{S}^{2-}\), and nitrogen in \(\text{[n-But}_4\text{N}]_2\text{[Mo}_6\text{O}_{19}\text{(WNNMePh)}]\).
Fig. 4.1: Structure of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ (the 'a-Keggin' structure) in (a) bond and (b) polyhedral representations. The a-Keggin structure is the most common polyanion structure. Structure of $[\text{V}_{12}\text{O}_{40}]^{3-}$: (c) atomic positions, (d) approximately space-filling model. The so-called hexametalate structure is also very common. The oxygens lie in an essentially cubic close packed formation, with the metal cations in octahedral holes, a structure reminiscent of metal oxides. The vanadium atoms are cis- to each other. Structure of $[\text{V}_{12}\text{O}_{40}]^{3-}$ illustrated (e) as VO₆ polyhedra.
The organometallic derivatives of polyanions can be roughly divided into two classes. Firstly, there are those compounds in which an organometallic fragment is incorporated into a vacancy in the framework of a polyanion. For example, \((\eta^5-C_5H_5)Ti^{4+}\) in \([\text{CpTi}M_6O_{12}]^{3-}\) \((M=Mo \text{ or } W; \text{ see fig. 4.2})^2\), or in \([\text{CpTi}PW_{11}O_{39}]^{12-}\)^13.14.

More important, from the viewpoint of modelling oxide surfaces, are those complexes in which the organometallic unit is supported by the polyanion, i.e. is attached to a \(\eta^2-\text{O}\) site on the anion surface. Several

---

**Fig. 4.2:** A comparison of the structures of (a) \([\text{MoO}_3]^{2-}\) and (b) \([\text{CpTi}M_6O_{12}]^{3-}\), illustrating how \((\text{CpTi}^{IV})^{2+}\) has replaced \((0=\text{M}^{VI})^{4+}\) in the anion framework, \(M=\text{Mo} \text{ or } W\).
such compounds have been made and are listed in table 4.1. The second example contains both an incorporated and a supported moiety.

**Table 4.1: Polyoxoanion-supported Organometallic Species**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>((n\text{-Bu}^N)_3[[\text{OC}]<em>3\text{M} (\text{Nb}<em>x\text{W}</em>{y}\text{O}</em>{z})]) (M=Mn or Re)</td>
<td>15, 16</td>
</tr>
<tr>
<td>((n\text{-Bu}^N)_2[[\text{CpTi}]_2\text{Mn(CO)}_3])</td>
<td>17</td>
</tr>
<tr>
<td>((n\text{-Bu}^N)<em>2[[\text{C}</em>{3}\text{Me}_5]\text{Rh(Nb}_x\text{W}<em>y\text{O}</em>{z})])</td>
<td>18</td>
</tr>
<tr>
<td>((n\text{-Bu}^N)<em>3[[\text{C}</em>{3}\text{Me}_5]\text{Rh(Si}_x\text{W}_y\text{Nb}<em>z\text{O}</em>{w})])</td>
<td>19</td>
</tr>
<tr>
<td>((n\text{-Bu}^N)_2[[\text{CpTi}]_2\text{SiW}_x\text{P}<em>y\text{O}</em>{z}])</td>
<td>8</td>
</tr>
<tr>
<td>((n\text{-Bu}^N)<em>3[[\text{C}</em>{3}\text{Me}_5]\text{Rh-P}_x\text{W}_y\text{Nb}<em>z\text{O}</em>{w}])</td>
<td>20</td>
</tr>
<tr>
<td>((n\text{-Bu}^N)<em>3[[\text{C}</em>{3}\text{Me}_5]\text{Rh-P}_x\text{W}_y\text{Nb}<em>z\text{O}</em>{w}])</td>
<td>20</td>
</tr>
</tbody>
</table>

Fig. 4.3 depicts the structures of these compounds, which were determined either directly from X-ray crystallography or by analogy and deduction from ir and nmr studies. All of the compounds were created in CH_2Cl_2 or MeCN solution. Note the use of the \((n\text{-Bu}^N)^+\) counter-ion to make organic solvent soluble forms of the polyanions.

Fig. 4.3: (a) The organometallic units Mn(CO)_3^+ and Rh(C_3Me_5)^2+ fit onto the \([\text{Nb}_x\text{W}_y\text{O}_{z}]^{4-}\) ion as shown. All orientations of the anion are found to some extent.
Chapter 4: Polyoxometalates

Fig. 4.3 (contd.); (b) The organometallic units \( \text{Rh(C}_6\text{H}_5\text{Me}_3)^{2-} \) and \( \text{CpTi}^{2+} \) fit onto the \( [\text{SiW}_{10}\text{MoO}_{40}]^{7-} \) ion as shown (M'=Nb or V respectively). This is the only anion orientation found; (c) The structure of \((n-\text{Bu}_4\text{N})_7[(\text{C}_6\text{H}_5\text{Me}_3)\text{Rh}^2\text{W}_{16}\text{Nb}_9\text{O}_{62}^-] \) is analogous. In both illustrations, the vanadium or niobium polyhedra are shaded.
In the light of the ideas noted above, concerning the surface electron density of polyanions, there are a couple of predictable features to this chemistry. In each case the supported moiety is coordinated by three $\text{OM}_2$ oxygen atoms, avoiding the inwardly polarised terminal oxygens, with the anion effectively forming a 6e$^-$ donor. What is more, for mixed addenda anions, the face with the least electron withdrawing trio of metals beneath it is preferred.

Some analogous compounds derived from the $[\text{P}_2\text{O}_9]^{2-}$ anion have been prepared for comparison purposes\textsuperscript{21}.

A few examples of polyoxoanion coordination via single oxygen atoms (including terminal ones) have been reported, always in sterically bulky systems\textsuperscript{22-24}.
4.3 EXPERIMENTAL

The EXAFS spectra for a series of polyoxometalate compounds were recorded, along with those of a few miscellaneous compounds chosen for comparison. Table 4.2 gives the details.

Table 4.2: Complexes included in this Chapter

<table>
<thead>
<tr>
<th>Compound</th>
<th>Edge(s) Examined</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Synthesis</td>
</tr>
<tr>
<td>Vanadium Foil</td>
<td>V</td>
<td>-</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>V</td>
<td>-</td>
</tr>
<tr>
<td>(NH$_4$)$_3$V$_2$O$_7$</td>
<td>V$^a$</td>
<td>26</td>
</tr>
<tr>
<td>K$_4$V$_2$W$<em>4$O$</em>{19}$</td>
<td>V$^a$</td>
<td>28</td>
</tr>
<tr>
<td>(n-Bu$_3$N)$_3$VW$<em>6$O$</em>{19}$</td>
<td>V$^a$</td>
<td>28</td>
</tr>
<tr>
<td>(n-Bu$_3$N)$_3$NbW$<em>6$O$</em>{19}$</td>
<td>V$^a$</td>
<td>23</td>
</tr>
<tr>
<td>(n-Bu$_3$N)$_3$ZnW$<em>3$O$</em>{40}$</td>
<td>V$^a$ &amp; Zn</td>
<td>30</td>
</tr>
<tr>
<td>Zn(OH)$_2$$_4$(NO$_3$)$_2$</td>
<td>Zn</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Solution spectra also recorded.
$^b$ Structure of (V$_2$W$_6$O$_{19}$)$^{14-}$ used as a guideline.
$^c$ Structure of (P$_2$W$_{12}$O$_{40}$)$^{32-}$ used as a guideline.

Although the [NbW$_6$O$_{19}$]$^{3-}$ anion has been incorporated into an organometallic polyoxo complex$^{23}$, these prototypical samples were chosen mainly for ease of synthesis, or for amenability to study by EXAFS, or both; rather than for having been used as organometallic supports.

Most of the polyanions held out the promise of examining the structures from two perspectives. This was especially true of the vanado-tungsten compounds, because the metals each form a significant percentage by mass in the complexes, and because both these metals have accessible absorption edges. As it turned out, unfortunately, the SRS closed down for refurbishment before vanadium spectra could be obtained for (n-Bu$_3$N)$_3$VW$_6$O$_{19}$ and K$_4$V$_2$W$_4$O$_{19}$.
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4.31 Preparations

Off-the-shelf samples of the non-polyanion compounds were used. The syntheses employed for the polyanions are outlined below. Unless otherwise indicated, spectral data referred to can be found in the same paper as the synthesis.

\((\text{NH}_4)_6\text{V}_4\text{O}_{23}\) was prepared by adding ammonia solution to an aqueous slurry of \(\text{V}_2\text{O}_5\). After filtering out the unreacted oxide, the orange solution was treated with acetone to precipitate the product, which is pure enough to use crude.

Its identity was confirmed by comparison of its \(^{17}\text{O}\) and \(^{51}\text{V}\) nmr spectra with literature results\(^{23}\). The i.r. spectrum of the solid has distinguishing bands at 972 (s), 948 (s), 813 (s), ~735 (s), 590 (m), 530 (m), 450 (m), 400 (m) and 330 cm\(^{-1}\) (w,sh), similar to other decavanadate salts\(^{24}\).

Note the approach used: whilst most polyanions are produced by aggregating oxoanions in increasingly acid conditions, they can be made by fragmenting a metal oxide in alkali, as here.

\(\text{K}_{x}\text{V}_2\text{W}_4\text{O}_{19}\cdot8\text{H}_2\text{O}\) was made by acidification (with acetic acid) of a solution of \(\text{K}_2\text{WO}_4\) and \(\text{KVO}_3\). The solution was reduced and cooled to produce orange-yellow crystals of the product, which was used crude.

\(\lambda_{max}\) for the main signal in the anion's uv/vis spectrum was at ~370nm, which is indicative of the protonated \([\text{HV}_2\text{W}_4\text{O}_{19}]^{3-}\) anion. This suggests that the acid reaction solution was concentrated a little too much. The protonation was confirmed by its i.r. spectrum.

The \(^{51}\text{V}\) nmr resonance of this compound occurs at ~510.45 ppm. Since the \(\text{V}^{5+}\) centres are pseudo-octahedral, the resonance is narrow for a quadrupolar nucleus (half-width: ~100Hz).

\(\text{KVO}_3\) was obtained by stirring together \(\text{K}_2\text{CO}_3\) and \(\text{V}_2\text{O}_5\) in hot aqueous solution/suspension and adding \(\text{H}_2\text{O}_2\) to help dissolve the oxide. After reducing and cooling the solution, red rhomboedral crystals of the product were retrieved and dried.
(n-Bu\textsubscript{4}N\textsubscript{6})\textsubscript{2}VW\textsubscript{6}O\textsubscript{18} was synthesised by using aqueous H\textsubscript{2}SO\textsubscript{4} to acidify a solution of Na\textsubscript{2}WO\textsubscript{4}·2H\textsubscript{2}O and NaVO\textsubscript{3}. Treating the resultant yellow solution with n-Bu\textsubscript{4}NBr produced a yellow precipitate, which was purified by recrystallisation from boiling methanol. The product's identity was checked by its i.r. spectrum.

NaVO\textsubscript{3} was prepared as a yellow powder by a method analogous to that for KVO\textsubscript{3}.

(n-Bu\textsubscript{4}N\textsubscript{6})\textsubscript{3}NbW\textsubscript{6}O\textsubscript{19} was made by converting a solution of K\textsubscript{5}HNbO\textsubscript{3} in water to a peroxide with H\textsubscript{2}O\textsubscript{2} to stabilise it, and then adding Na\textsubscript{2}WO\textsubscript{4}. This solution was acidified with H\textsubscript{2}SO\textsubscript{4} and subsequently treated with n-Bu\textsubscript{4}NBr to give a pale yellow precipitate, which was purified by recrystallisation from boiling acetonitrile.

The identity of the compound was checked by elemental analysis (observed: C-27.8%, H-5.1%, N-1.9%; calc.: C-28.2%, H-5.3%, N-2.1%), by its i.r. spectrum and by comparison of the \textsuperscript{17}O nmr spectrum with the literature result\textsuperscript{5}.

The preparation of K\textsubscript{5}HNbO\textsubscript{3} \textsuperscript{5} involved adding Nb\textsubscript{2}O\textsubscript{5} to a melt of potassium hydroxide pellets. After cooling, the melt was dissolved in 100ml of degassed water and filtered. White needle-shaped crystals of the product were obtained from the reduced solution.

"(n-Bu\textsubscript{4}N\textsubscript{6})\textsubscript{2}HZnW\textsubscript{12}O\textsubscript{40}" was prepared by free adaptation from the results of Brown and Mair\textsuperscript{20}. Na\textsubscript{2}WO\textsubscript{4}·2H\textsubscript{2}O (11.24g, 34.1 mmole) in 80ml of water and 40ml of 1M aqueous HNO\textsubscript{3} were heated together to the boiling point. After cooling to 80°, excess Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (2g, 6.7 mmole) in 100ml of water was added, and the resulting solution stirred at 80° for two hours. The solution was filtered hot, evaporated to 50ml, cooled and acidified to pH<1.

The acid H\textsubscript{2}ZnW\textsubscript{12}O\textsubscript{40} was obtained using the 'etherate' method\textsuperscript{25}. The acidified reactants were shaken with 75ml of diethyl ether, giving two layers: an oily lower layer (aqueous/etherate) and an upper, ether layer. The lower layer was run into a further 75ml of ether and shaken. The resulting lower layer was again run off. It was then diluted with 100ml
of water to decompose the etherate, and reduced to 50ml (incidentally removing residual ether). 5.5g (17 mmole) of n-Bu₄NBr in 25ml H₂O were added to precipitate a white solid which was stirred for 30 minutes to coagulate it. The crude product was recrystallised from boiling MeCN to give colourless, block-like, isotropic crystals of the product. The crystals lose solvent rapidly in the open air, leaving opaque white particles. The best yield obtained was 7.8g (65% in tungsten).

The solid state i.r. spectrum of the product is presented in fig. 4.4. EDAX analysis indicates a Zn:W ratio of 1:11, which is accurate within experimental error (1:12 expected). Elemental analysis of the vacuum-dried product gives the result C-21.6%, H-5.1% and N-1.2% (calc. for (n-Bu₄N)₅WO₆: C-23.3%, H-4.4% and N-1.7%; for the (n-Bu₄N)₅H₂W₂O₆ salt: C-19.8%, H-3.8% and N-1.4%). The precipitated salt thus retains one or two protons.

4.3.2 EXAFS Experiments

The vanadium metal spectrum was recorded in transmission mode on a 10µm foil. The other solids were ground to a fine powder. In most cases the transmission through a 1-2mm thickness was recorded, with the sample diluted if necessary with boron nitride to keep the metal of interest to around 10% by weight. The spectra of V₂O₅ and (NH₄)₅V₂O₇, however, were recorded using thin (<0.1mm) films of the undiluted powder. Zn is only 1.5% by weight in (n-Bu₄N)₆ZnW₁₂O₄₀, so the Zn-edge spectrum could only be obtained in fluorescence mode, and then only in the solid state. Solution spectra were taken of saturated solutions using fluorescence detection (aqueous solution for Na⁺ and K⁺ counter-ions, MeCN for (n-Bu₄N)⁺).

As noted in chapter 3, the results expected from the metal foils can be obtained from the EXCURVE analysis program. Where X-ray data existed, this was converted to series' of shells around the absorbing atom as described in chapter 3, except in the case of V₂O₅. The program XANADU can only find interatomic distances within a unit cell, but in
V₂O₅ the unit cell is long and thin, so the EXAFS effect extends into neighbouring cells.

This problem was overcome by using the University of Washington's Molecular Graphics Program\textsuperscript{26} running on a microcomputer. Eighteen unit cells were butted together and the program used to find all atoms.
within 5Å of a chosen atom (see plate 1). These results were then combined into a set of atomic shells by hand, as with the other systems.

Plate 1 (over); unit cell of V$_2$O$_6$ (top), and (bottom) 18 unit cells combined. The atom from which all others within 5Å were found is arrowed.
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4.4 REFERENCE SAMPLES

4.41 Zn(OH)$_6$(NO$_3$)$_2$

The structure of this compound, as seen from a zinc centre, consists of a Zn$^{2+}$ cation within an octahedron of coordinating water molecules. Beyond this are nitrate anions and then further zinc centres, etc. As Table 4.3 indicates, however, the backscattering shells outside the coordination sphere form a messy group - lots of small shells containing weak scatterers, each at least 3.8Å away. Fig. 4.5 shows the theoretical Fourier transform of an unrefined model based on the crystal data (with the unfiltered experimental FT for comparison), and illustrates how the nine shells from 3.8Å to 5Å produce only a very weak signal.

![Fig. 4.5: Fourier transform of the experimental (solid line) and theoretical (dashed line) EXAFS spectrum for Zn(OH)$_6$(NO$_3$)$_2$.](image-url)
Thus, the zinc K edge experimental spectrum was Fourier filtered from 1.23\(\AA\) to 2.03\(\AA\), and a model based only on the coordinating six oxygens refined against the experimental spectrum. A Zn-O distance of 2.047\(\AA\) was found. Table 4.3 lists the detailed results, whilst fig. 4.6 illustrates the spectra and Fourier transforms.

Because no previous zinc results were available, it was necessary to determine the optimum values of VPI and AFAC. Once the theoretical model had been refined to give a minimum fit index (FI) using the default values of -4 and 0.8 respectively, a map of the FI over the 'rule-of-thumb' chemically reasonable ranges of these two parameters was produced (0.6 to 0.8 for AFAC; -2 to -4 for VPI). The lowest FI value is given by a VPI of -2 and an AFAC of 0.6. These values were selected for the final refinement.

The map generated did not contain a true minimum FI. The effects of changing AFAC and VPI on the theoretical spectrum are highly correlated. It is often the case for simple spectra that the mathematically closest fit between experiment and theory can be achieved with a combination of AFAC and VPI which is impossible in reality (e.g. AFAC greater than 1.0 implies that over 100\% of the X-ray absorption events contribute to the EXAFS signal).

It must be remembered that the experimental spectrum will contain a degree of error and distortion which it could be possible to reproduce exactly if the theoretical parameters were allowed to take any combination of values. This is especially true of relatively arbitrary and highly correlated parameters such as VPI and AFAC, which should be confined to reasonable values by the experimenter.

### 4.4.2 Vanadium Foil

The EXAFS results obtained for the vanadium K edge spectrum of a 10\(\mu\)m thick foil are tabulated in table 4.4, and illustrated in fig. 4.7. The settings of VPI and AFAC were determined as described above.
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The ripple in the Fourier transform at around 3.6Å does not correspond with any expected shell. In the absence of a clear alternative, it is assumed to be a truncation effect.

Table 4.3: EXAFS Results for Zn(OH₃)(NO₃)

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller % Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>O</td>
<td>2.047(2)</td>
<td>2.056</td>
<td>0.016</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>O</td>
<td>-</td>
<td>3.794</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>O</td>
<td>-</td>
<td>4.056</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>O</td>
<td>-</td>
<td>4.201</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>N</td>
<td>-</td>
<td>4.330</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>O</td>
<td>-</td>
<td>4.484</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>N</td>
<td>-</td>
<td>4.590</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>O</td>
<td>-</td>
<td>4.727</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>O</td>
<td>-</td>
<td>4.913</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>N</td>
<td>-</td>
<td>4.993</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.4: EXAFS Results for Vanadium Metal Foil

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller % Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>V</td>
<td>2.604(3)</td>
<td>2.620</td>
<td>0.015</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>V</td>
<td>2.974(5)</td>
<td>3.026</td>
<td>0.020</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>V</td>
<td>4.257(9)</td>
<td>4.281</td>
<td>0.027</td>
</tr>
<tr>
<td>4</td>
<td>24</td>
<td>V</td>
<td>4.981(6)</td>
<td>4.784</td>
<td>0.021</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>V</td>
<td>5.376(19)</td>
<td>5.240</td>
<td>0.021</td>
</tr>
</tbody>
</table>

The vanadium K edge spectrum was Fourier filtered from 1.34Å to 5.44Å. The Fourier filtered from 1.00Å to 4.27Å. In the Fourier transform strong signals are apparent all the way out to over 4Å (fig. 4.8). Such a volume encompasses around a dozen atomic shells (table 4.5). With a radius and a Debye-Waller factor for
Fig. 4.8: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for Zn(OH)₆(NO₃)₂.
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Fig. 4.7: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for vanadium foil.
each shell, plus $E_0$, this implies at least 25 parameters in the theoretical model. The EXCURVE analysis program can only cope with 20 refinable parameters, however.

![Unfiltered Fourier transform of the EXAFS spectrum of V2O8, showing the grouping of the shells.](image)

**Fig. 4.8** Unfiltered Fourier transform of the EXAFS spectrum of V$_2$O$_8$, showing the grouping of the shells.

**Table 4.5: Expected Atomic Shells for V$_2$O$_8$**

<table>
<thead>
<tr>
<th>Element</th>
<th>Number</th>
<th>Radius/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>1</td>
<td>1.542</td>
</tr>
<tr>
<td>O</td>
<td>1</td>
<td>1.771</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>1.874</td>
</tr>
<tr>
<td>O</td>
<td>1</td>
<td>2.024</td>
</tr>
<tr>
<td>O</td>
<td>1</td>
<td>2.827</td>
</tr>
<tr>
<td>V</td>
<td>2</td>
<td>3.075</td>
</tr>
<tr>
<td>V</td>
<td>1</td>
<td>3.420</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>3.499</td>
</tr>
<tr>
<td>V</td>
<td>2</td>
<td>3.562</td>
</tr>
<tr>
<td>O</td>
<td>9</td>
<td>3.950</td>
</tr>
<tr>
<td>O</td>
<td>9</td>
<td>4.400</td>
</tr>
<tr>
<td>V</td>
<td>4</td>
<td>4.450</td>
</tr>
</tbody>
</table>
As can be seen from fig. 4.8, the shells fall fairly neatly into three groups. In order to reduce the number of parameters, the Debye-Waller factors for all the shells in each of the two outermost groups were kept equal and refined as just two parameters. Nevertheless, on trying to refine this model, it was found that there were a large number of pairs of parameters with unacceptably high correlation coefficients (i.e. with a value above 0.8). There is always a danger with a very complex model that the various parameters will interact with each other in this way, preventing the experimenter from defining any of them with precision.

To overcome this problem, the spectrum was subdivided into three using Fourier filtration. Theoretical parameters were then fitted to each part of the spectrum separately. It should be remembered that Fourier filtration introduces a certain amount of distortion into the FT, so this kind of approach should not be used routinely.

The Three-Section Approach

The first section of the spectrum covers the radii from 0.98Å to 2.25Å. Using the first four shells from table 4.5 as a starting point, the theoretical model was refined against experiment with little success. The correlation coefficient between the two radii R2 and R3 was 0.939, indicating that EXCURVE was unable to resolve these two shells. Consequently, their theoretical parameters were averaged to give one shell of three oxygens at 1.840Å. The results for this part of the spectrum are listed in table 4.6 and illustrated in fig. 4.9.

Table 4.6: EXAFS Results for V2O5 from 0.98Å to 2.25Å

<table>
<thead>
<tr>
<th>Shell No.</th>
<th>Atoms</th>
<th>Element (EXAFS)</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller Factor/Å²</th>
<th>% Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1.578(4)</td>
<td>1.542</td>
<td>0.007</td>
<td>2.33</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0</td>
<td>1.843(5)</td>
<td>1.840</td>
<td>0.016</td>
<td>0.16</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0</td>
<td>2.012(12)</td>
<td>2.024</td>
<td>0.011</td>
<td>-0.59</td>
</tr>
</tbody>
</table>

F1=1.01192; R=48.0789,
Fig. 4.9: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for V$_2$O$_5$, inner shells.
As in vanadium metal, the first large signal is accompanied by a (presumably) truncation induced ripple. If this feature is removed from consideration by Fourier filtering from 0.98 Å to 1.91 Å, the results outlined in table 4.7 and fig. 4.10 are obtained - essentially the same, but with a better fit index.

Table 4.7: EXAFS Results for V,0, from 0.98 Å to 1.91 Å

<table>
<thead>
<tr>
<th>Shell</th>
<th>No, Atoms</th>
<th>Element</th>
<th>Radius Å (EXAFS)</th>
<th>Radius Å (Crystal)</th>
<th>Debye-Waller Factor Å²</th>
<th>% Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1.583(3)</td>
<td>1.542</td>
<td>0.007</td>
<td>2.56</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0</td>
<td>1.849(4)</td>
<td>1.840</td>
<td>0.016</td>
<td>0.49</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0</td>
<td>2.026(3)</td>
<td>2.024</td>
<td>0.011</td>
<td>0.10</td>
</tr>
</tbody>
</table>

F1=0.79013; R=42.7704.

Between 2.25 Å and 3.31 Å, there are five shells expected under one peak in the Fourier transform, which necessarily makes it difficult to resolve the different shell radii. In fact, EXCURVE was not able to locate a defined minimum in the fit index with so many variable parameters. The radii and Debye-Waller factors for the two shells closest in radius - shells six and seven - were linked together to restrict the theoretical model a little. This enabled the program to locate a minimum in the fit index, giving the results shown in table 4.8 and fig. 4.11. Even so, the results are not particularly good, especially for the two shells that were linked together. It might have been wise to devise an even more approximate model, with even fewer parameters. Note that as E0 is largely defined by the early part of the EXAFS spectrum which in turn mostly contains information about the inner shells, E0 was set to the value determined by these innermost shells (19.3 eV), and not refined further.
Fig. 4.10: Alternative theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for $V_8O_{16}$, inner shells.
The final region of the FT lies between 3.31 Å and 4.30 Å. Although the weakest area of the FT in intensity, the backscattering shells are sufficiently separated to allow all three to be reasonably accurately located. The results obtained are presented in Table 4.9 and Fig. 4.12.

Table 4.9: EXAFS Results for V-O, from 3.31 Å to 4.30 Å

<table>
<thead>
<tr>
<th>n</th>
<th>13</th>
<th>12</th>
<th>11</th>
<th>10</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>χ</td>
<td>0</td>
<td>V</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>θ</td>
<td>2,082(2)</td>
<td>2,827</td>
<td>0,007</td>
<td>-4,03</td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>0,015</td>
<td>3,075</td>
<td>0,015</td>
<td>-0,59</td>
<td></td>
</tr>
<tr>
<td>η</td>
<td>0,023</td>
<td>3,420</td>
<td>0,023</td>
<td>-7,13</td>
<td></td>
</tr>
<tr>
<td>ζ</td>
<td>0,023</td>
<td>3,499</td>
<td>0,023</td>
<td>-9,23</td>
<td></td>
</tr>
<tr>
<td>θ</td>
<td>0,041</td>
<td>3,562</td>
<td>0,041</td>
<td>-2,47</td>
<td></td>
</tr>
</tbody>
</table>

\( F_I=0,03520; R=14,8046, \)

The composite spectrum derived from these results is illustrated in Fig. 4.13. Considering the complexity of the structure being modelled and the necessarily less than perfect modelling approach used, there is a good match between the experimental and theoretical spectra.
Fig. 4.11: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for V$_2$O$_5$, middle range of the Fourier transform.
Fig. 4.12: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for $\text{V}_2\text{O}_5$, outer range of the Fourier transform.
Fig. 4.13: Composite theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for V₂O₅.
4.5 THE DECAVANADATE ANION, \([\text{V}_5\text{O}_{28}]^6^-\)

4.51 Solid-state Spectrum

The vanadium K edge spectrum was Fourier filtered from 0.86\(\text{Å}\) to 4.42\(\text{Å}\). An eight shell theoretical model was used. Though complex, it was possible to refine it as one unit. During refinement, the Debye-Waller factors for the first and third shells began to get unrealistically low and high respectively. Because of this, they were held at respective values of 0.05\(\text{Å}^2\) and 0.025\(\text{Å}^2\). The EXAFS results are tabulated in table 4.10 and illustrated in fig. 4.14. Note how the weaker backscattering shells are a little less well defined, having larger standard deviations.

Table 4.10: EXAFS Results for the solid-state Decavanadate ion

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller Factor/Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2</td>
<td>O</td>
<td>1.617(3)</td>
<td>1.639</td>
<td>0.005</td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
<td>O</td>
<td>1.842(4)</td>
<td>1.911</td>
<td>0.018</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
<td>O</td>
<td>2.072(20)</td>
<td>2.239</td>
<td>0.025</td>
</tr>
<tr>
<td>4</td>
<td>4.8</td>
<td>V</td>
<td>3.109(3)</td>
<td>3.127</td>
<td>0.012</td>
</tr>
<tr>
<td>5</td>
<td>3.6</td>
<td>O</td>
<td>3.273(4)</td>
<td>3.407</td>
<td>0.005</td>
</tr>
<tr>
<td>6</td>
<td>1.2</td>
<td>O</td>
<td>3.554(26)</td>
<td>3.616</td>
<td>0.012</td>
</tr>
<tr>
<td>7</td>
<td>1.4</td>
<td>V</td>
<td>4.263(22)</td>
<td>4.439</td>
<td>0.019</td>
</tr>
<tr>
<td>8</td>
<td>2.5</td>
<td>O</td>
<td>4.428(8)</td>
<td>4.491</td>
<td>0.011</td>
</tr>
</tbody>
</table>

4.52 Solution Spectrum

The experimental spectrum was Fourier filtered from 0.99\(\text{Å}\) to 4.57\(\text{Å}\) and in this case was rather poor (fig. 4.15). Nevertheless, a reasonable result was obtained for all but the outermost atomic shells (see fig. 4.16). The Debye-Waller factor for the eighth shell is low, suggesting that there are actually more atoms in that region than are
Fig. 4.14: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for the solid-state decavanadate anion.
being modelled for. It is possible that backscattering from oxygen atoms in the solvent water is being superimposed upon the signal due to the polyanion. The results are tabulated in table 4.11.

![EXAFS spectrum of aq. \(\left[V_{10}O_{28}\right]^{4-}\).](image)

Fig. 4.15: Unfiltered EXAFS spectrum of aq. \(\left[V_{10}O_{28}\right]^{4-}\).

### Table 4.11: EXAFS Results for the Aqueous Decavanadate Anion

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller Factor/Å²</th>
<th>% Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2</td>
<td>O</td>
<td>1.691(4)</td>
<td>1.639</td>
<td>0.005</td>
<td>3.17</td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
<td>O</td>
<td>1.938(5)</td>
<td>1.911</td>
<td>0.019</td>
<td>1.05</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
<td>V</td>
<td>2.206(8)</td>
<td>2.239</td>
<td>0.008</td>
<td>-1.52</td>
</tr>
<tr>
<td>4</td>
<td>4.8</td>
<td>V</td>
<td>3.081(6)</td>
<td>3.127</td>
<td>0.020</td>
<td>-1.47</td>
</tr>
<tr>
<td>5</td>
<td>3.6</td>
<td>O</td>
<td>3.234(16)</td>
<td>3.407</td>
<td>0.014</td>
<td>-5.08</td>
</tr>
<tr>
<td>6</td>
<td>1.2</td>
<td>O</td>
<td>3.555(24)</td>
<td>3.616</td>
<td>0.008</td>
<td>-1.41</td>
</tr>
<tr>
<td>7</td>
<td>1.4</td>
<td>V</td>
<td>4.305(26)</td>
<td>4.439</td>
<td>0.016</td>
<td>-3.02</td>
</tr>
<tr>
<td>8</td>
<td>9.6</td>
<td>O</td>
<td>4.447(8)</td>
<td>4.481</td>
<td>0.005</td>
<td>-0.76</td>
</tr>
</tbody>
</table>

\(E_0=23.1(8)\)eV; \(E_{	ext{ex}}=45.0\)eV; \(E_{\text{max}}=538.6\)eV; \(\text{AFAC}=0.6\); \(\text{VPI}=-1\).

FI=1.06606.
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Fig. 4.16: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for the aqueous decavanadate ion.
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4.6 THE 12-TUNGSTOZINCATE ANION, \([\text{ZnW}_{12}O_{40}]^{3-}\)

4.6.1 Solid-state Spectra

No X-ray structure determination has been reported for \([\text{ZnW}_{12}O_{40}]^{3-}\), so for comparison the backscattering shells expected for \([\text{PW}_{12}O_{40}]^{3-}\) were determined. The \(\alpha\)-Keggin structure of this latter anion can be seen in fig. 4.1 (p. 113). The crystal radii in the tables below refer to this anion. Although the figure does not have the same meaning as for the other spectra, the discrepancy between EXAFS and crystallography has still been calculated.

W Edge

This is probably the poorest tungsten spectrum taken on a day when the detectors at the SRS were performing erratically, so much so that the 8 shells derived from the crystallographic data (table 4.12) could not possibly all be resolved.

<table>
<thead>
<tr>
<th>Element</th>
<th>Number</th>
<th>Radius/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>1</td>
<td>1.757</td>
</tr>
<tr>
<td>O</td>
<td>4</td>
<td>1.961</td>
</tr>
<tr>
<td>O</td>
<td>1</td>
<td>2.507</td>
</tr>
<tr>
<td>W</td>
<td>2</td>
<td>3.512</td>
</tr>
<tr>
<td>O</td>
<td>1</td>
<td>3.645</td>
</tr>
<tr>
<td>Zn</td>
<td>1</td>
<td>3.659</td>
</tr>
<tr>
<td>W</td>
<td>2</td>
<td>3.803</td>
</tr>
<tr>
<td>O</td>
<td>6</td>
<td>4.015</td>
</tr>
</tbody>
</table>

Through examining the contributions of the separate shells to the theoretical spectrum, it was decided not to include the 5th shell because it was very weak, and also to average the first two shells. On attempting to refine this model against the experimental data, however, the correlations between the shells were still unacceptably high. What is
more, EXCURVE could not distinguish between the three metal shells, tending to 'swap' their relative positions in the model.

All six inner oxygens were combined into one averaged shell, whilst the metal shells were treated as one signal arising from five tungsten atoms - admittedly a very rough approximation. Refining this model produced the results illustrated in fig. 4.17 and listed in table 4.13.

**Table 4.13: EXAFS Results for [ZnW₆O₄₀]⁻**

<table>
<thead>
<tr>
<th>Shell</th>
<th>No, Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller % Discrepancy* Factor/Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>O</td>
<td>1.783(7)</td>
<td>2.018</td>
<td>0.039</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>W</td>
<td>3.472(32)</td>
<td>3.658</td>
<td>0.049</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>O</td>
<td>3.765(15)</td>
<td>4.015</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Experimental spectrum Fourier filtered from 0.00Å to 3.85Å, FI=1.44188; R=33.7726,

* compared with [PV₃O₁₀]³⁻.

Taken literally these results would imply that the 12-tungstozincate anion is considerably shrunken when compared with its phosphorus counterpart. At 74pm, the Zn²⁺ ion is 39pm larger than "Pu⁺⁺", so this conclusion is unlikely. The E₀ value for these results is atypically high for a polyanion spectrum: among the samples covered by this work, no other polyanion spectrum, particularly no other tungsten edge spectrum, not even the solution W edge spectrum of this anion, has an E₀ outside the 5-25eV range. Starting with E₀ within these limits and repeating the refinement reproduced the results above, so it was decided to try arbitrarily fixing E₀ at 12.5eV (a typical value for a polyanion) and refining the model once more. The results of this approach are to be found in table 4.14 and fig. 4.18. Although the FI is worse, they are more in line with what is expected of this sample (see below for more discussion).
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Fig. 4.17: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for [ZnW$_{13}$O$_{40}$]$^{3-}$. 
Table 4.14: EXAFS Results for \([\text{ZnW}_4\text{O}_{10}]^{6-}\) (alternative model)

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius Å (EXAFS)</th>
<th>Radius Å (Crystal)</th>
<th>Debye-Waller % Discrepancy*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>W</td>
<td>1.893(6)</td>
<td>2.018</td>
<td>0.051</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>W</td>
<td>3.666(8)</td>
<td>3.658</td>
<td>0.020</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>O</td>
<td>4.103(11)</td>
<td>4.015</td>
<td>0.014</td>
</tr>
</tbody>
</table>

F\(l=2.41972; R=65.9599; \)

* compared with \([\text{PW}_4\text{O}_{10}]^{3-}\)

Zn Edge

The theoretical model for this edge is relatively simple because of the symmetry about the zinc centre; which is fortunate, since this spectrum was usable for only 400eV or so past the edge. The refined five shell shell model for this spectrum is tabulated in table 4.15 below, and illustrated in fig. 4.19.

Table 4.15: EXAFS Results for the 12-tungstozincate ion (Zinc Edge)

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius Å (EXAFS)</th>
<th>Radius Å (Crystal)</th>
<th>Debye-Waller % Discrepancy*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>0</td>
<td>1.900(4)</td>
<td>-</td>
<td>0.009</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>0</td>
<td>3.346(12)</td>
<td>3.465</td>
<td>0.0025</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>W</td>
<td>3.486(5)</td>
<td>3.659</td>
<td>0.0017</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>0</td>
<td>4.134(17)</td>
<td>4.051</td>
<td>0.0020</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>0</td>
<td>4.931(10)</td>
<td>5.390</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Spectrum Fourier filtered from 0.85Å to 5.13Å, \(F\(l=8.06193; R=32.4739; \)

* compared with \([\text{PW}_4\text{O}_{10}]^{3-}\)

Although values for VPI and AFAC of \(-2\) and \(0.6\) respectively had been established for \(\text{Zn(\text{OH})}_2^{2-}\), these values are not used here. Because of the poor quality of the spectrum and the rather arbitrary nature of these parameters, the effect of refining VPI and AFAC was investigated.
Fig. 4.18: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for \([\text{ZnW}_{18}O_{40}]^{18-}\), alternative model.
Fig. 4.19: Five-shell theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for the 12-tungsto-zincate anion, Zn edge.
Although the effect on the radii was not great, the EXCURVE default values of -4 and 0.8 produced the best fit. These values were accepted.

During refinement the Zn-O distance tended towards 1.53Å, which would be shorter than the P-O distance in [PW_{12}O_{40}]^{3-} (1.571Å). The radii R3 and R4 were simultaneously apparently much larger than in the phosphorus analogue. A map of R1 against $E_o$ was used to locate a more convincing value for R1, which was then used to find minima for R3 and R4 (fig. 4.20). The straying parameters were reset into these minima and refinement continued. The Debye-Waller factors were not allowed outside the range 0.005 to 0.025Å².

The fifth shell is rather a poor fit, probably due to the effect of noise on the spectrum. If it is simply not included, a much better fit index can be obtained, as shown in table 4.16 and fig. 4.21.

### Table 4.16: EXAFS Results for 12-tungstozincate (Zinc Edge)

<table>
<thead>
<tr>
<th>Shell No.</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius Å (EXAFS)</th>
<th>Radius Å (Crystal)</th>
<th>Debye-Waller F Discrepancy*</th>
<th>Factor Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>O</td>
<td>1.900(3)</td>
<td>-</td>
<td>0.008</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>O</td>
<td>3.353(9)</td>
<td>3.465</td>
<td>0.025</td>
<td>-3.23</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>W</td>
<td>3.48(4)</td>
<td>3.659</td>
<td>0.017</td>
<td>-4.78</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>O</td>
<td>4.144(12)</td>
<td>4.051</td>
<td>0.025</td>
<td>2.30</td>
</tr>
</tbody>
</table>

Spectrum Fourier filtered from 0.86Å to 3.94Å, FF=3.77537; R=23.3190.
* compared with [PW_{12}O_{40}]^{3-}

### 4.62 Solution Spectrum

**W Edge**

This was another poor spectrum, with only 250eV post-edge being usable. In terms of the number and occupancy of shells, the theoretical model was based on the three shell model used for the solid-state...
Fig. 4.20: Maps illustrating the relationship between pairs of parameters in the 12-tungstozincate model. Contour lines link points of equal fit index, (a) $E_0$ vs. $R_1$; (b) $R_1$ vs. $R_3$; (c) $R_1$ vs. $R_4$.

The absorption fine structure was particularly weak, so the Debye-Waller factors were allowed to take on the high values tabulated below.
Fig. 4.21: Four-shell theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for 12-tungstozincate.
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There were strong correlations between each of the radii and $E_o$. The results are illustrated in fig. 4.22 below, tabulated in table 4.17.

### Table 4.17: EXAFS Results for solvated $\text{t}_2\text{tunostozincate (Tungsten Edge)}$

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller % Discrepancy* Factor/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>O</td>
<td>1.919(6)</td>
<td>2.018</td>
<td>0.071</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>W</td>
<td>3.637(8)</td>
<td>3.588</td>
<td>0.023</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>O</td>
<td>4.136(14)</td>
<td>4.015</td>
<td>0.024</td>
</tr>
</tbody>
</table>

Spectrum Fourier filtered from 0.37Å to 3.87Å, FI=0.28909,

* compared with $[\text{PW}_{12}\text{O}_{40}]^{3-}$

### 4.63 Discussion

One would expect the $[\text{ZnW}_{12}\text{O}_{40}]^{6-}$ anion to be essentially similar to $[\text{PW}_{12}\text{O}_{40}]^{3-}$. The main difference would be a longer Zn-O distance due to the weaker positive charge on the zinc atom. This would lead to a corresponding reduction in some W-O distances.

It is difficult to say that the EXAFS results categorically support this hypothesis, as the assumptions required to produce an analysis of the results were necessarily guided by the expected outcome. This is, of course, true of all scientific experiments to a greater or lesser extent. Here, however, more manipulation than usual was required, especially of the W-edge solid state results, because the data was poor. One can say that the EXAFS spectrum is consistent with the expected structure.
Fig. 4.22: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for the solvated 12-tungstoazincate anion (W edge).
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4.7 THE HEXAMETALATE ANIONS

All the spectra in this section were recorded at the tungsten L\textsubscript{III} edge. For many of the samples a vanadium spectrum would have provided a useful alternative viewpoint on the structure. However, because of the shutdown of the SRS, there was no time available to take these spectra.

Refer back to fig. 4.1 (p. 113) for the structure of these polyanions.

4.71 K.V.W.O\textsubscript{3}

Solid-state Spectrum

A good quality spectrum was obtained, with structure visible in the Fourier transform out to around 4.5\AA. Unfortunately, the description of the anion in terms of atomic shells is quite complex. Bearing in mind that the two tungsten to metal radii each have to be represented by two shells (one for tungsten, one for vanadium), there are ten shells to be modelled. What is more, because there are three atoms lying along a straight line, it was decided to include the contribution of the multiple scattering effect across the centre of the anion. In order to do this it was necessary to split the third shell (representing the central oxygen atom) into two components - one for each opposite metal atom. EXCURVE allows two theoretical shells to have their parameters kept equal, so this did not mean that one of the shells finished up with two radii.

Despite the complexity of the model, the parameters refined to a well-defined minimum. At first the oxygen shells 7 and 10 had radii that were larger than expected, against a general tendency to underestimate the radii of oxygen shells. By using maps it was possible to locate shell ten more satisfactorily, but the seventh shell remained stubbornly inaccurate. The results are tabulated and illustrated in table 4.18 and fig. 4.23 respectively.
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Table 4.18: EXAFS Results for the \([V_2W_6O_{18}]^{4-}\) anion

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller Factor/Å²</th>
<th>% Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>O</td>
<td>1.721(3)</td>
<td>1.684</td>
<td>0.003</td>
<td>2.20</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>W</td>
<td>2.228(5)</td>
<td>2.309</td>
<td>0.007</td>
<td>-3.51</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>O</td>
<td>3.272(2)</td>
<td>3.252</td>
<td>0.011</td>
<td>0.62</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>W</td>
<td>3.344(17)</td>
<td>3.252</td>
<td>0.027</td>
<td>2.83</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>V</td>
<td>3.461(3)</td>
<td>3.478</td>
<td>0.003</td>
<td>-0.49</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>O</td>
<td>4.212(26)</td>
<td>4.558</td>
<td>0.024</td>
<td>-7.59</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>W</td>
<td>4.549(30)</td>
<td>4.596</td>
<td>0.014</td>
<td>-1.02</td>
</tr>
<tr>
<td>8</td>
<td>0.5</td>
<td>W</td>
<td>4.452(108)</td>
<td>4.596</td>
<td>0.019</td>
<td>-3.13</td>
</tr>
<tr>
<td>9</td>
<td>0.5</td>
<td>V</td>
<td>4.600(59)</td>
<td>4.703</td>
<td>0.026</td>
<td>-2.19</td>
</tr>
</tbody>
</table>

The raw spectrum was Fourier filtered from 0.85Å to 5.09Å, FI=0.58054.

Extended Multiple Scattering Treatment

By including more of the multiple scattering paths within the anion, it was hoped to improve the accuracy of the analysis. Fig. 4.24 is a plan view of one of the anion's equatorial planes, showing the triplets of atomic shells within which second and third order multiple scattering was considered. There are other possible scattering paths to choose from, but those shown represent the practical limit of the EXCURVE program at the time of analysis. The multiple scattering units selected have either a straight-line arrangement (which is the most important, as discussed in chapter one), or include a metal atom.

Fig. 4.24: MS Pathways in the \([V_2W_6O_{18}]^{4-}\) Anion

x=oxygen; *=absorbing tungsten atom; O=other metal atom.
Fig. 4.23: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for \([\text{V}_3\text{W}_4\text{O}_{19}]^{2-}\).
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To save computing time, the angles within the multiple scattering units were set at 135° and 180° as appropriate and were not refined. Nevertheless, the refinement of this model took an order of magnitude more computing time than for the previous model with only one multiple scattering pathway. The results are given in table 4.19 and fig. 4.25. There is a considerable improvement in the agreement between EXAFS and crystallography for the seventh shell, i.e. the oxygen shell involved in the new multiple scattering units.

Table 4.19: EXAFS Results for Hexa-2-vanadotungstate, using extended multiple scattering.

<table>
<thead>
<tr>
<th>Shell</th>
<th>No.</th>
<th>Atoms</th>
<th>Radius (Å)</th>
<th>Element</th>
<th>Radius (Å)</th>
<th>Debye-Waller Factor (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>EXAFS</td>
<td>Crystal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>O</td>
<td>1.729(4)</td>
<td>1.684</td>
<td>0.003</td>
<td>2.67</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>O</td>
<td>1.908(4)</td>
<td>1.864</td>
<td>0.012</td>
<td>2.36</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>O</td>
<td>2.217(9)</td>
<td>2.309</td>
<td>0.009</td>
<td>-3.98</td>
</tr>
<tr>
<td>4</td>
<td>2,5</td>
<td>W</td>
<td>3.273(3)</td>
<td>3.252</td>
<td>0.009</td>
<td>0.65</td>
</tr>
<tr>
<td>5</td>
<td>1,5</td>
<td>V</td>
<td>3.245(8)</td>
<td>3.252</td>
<td>0.009</td>
<td>-0.22</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>O</td>
<td>3.412(11)</td>
<td>3.478</td>
<td>0.005</td>
<td>-1.90</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>O</td>
<td>4.524(4)</td>
<td>4.558</td>
<td>0.015</td>
<td>-0.75</td>
</tr>
<tr>
<td>8</td>
<td>0,5</td>
<td>W</td>
<td>4.653(137)</td>
<td>4.596</td>
<td>0.023</td>
<td>1.24</td>
</tr>
<tr>
<td>9</td>
<td>0,5</td>
<td>V</td>
<td>4.626(65)</td>
<td>4.586</td>
<td>0.011</td>
<td>0.65</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>O</td>
<td>4.814(7)</td>
<td>4.703</td>
<td>0.006</td>
<td>2.36</td>
</tr>
</tbody>
</table>

The spectrum was Fourier filtered from 0.85Å to 5.09Å, FI=0.868331 R=22.20Å8.

Solution Spectrum

Although the raw EXAFS spectrum (fig. 4.26) is considerably poorer for the solution spectrum, as compared to the solid state spectrum, results almost as good were obtained after Fourier filtration. Only one fewer shells were resolved. The results are in table 4.20 and fig. 4.27.
Fig. 4.25: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for the hexa-2-vanadotungstate anion.
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Fig. 4.26: Unfiltered EXAFS spectra of the \((\text{V}_5\text{W}_4\text{O}_{19})^{12-}\) anion (top) in the solid state (absorption spectrum) and (bottom) in aqueous solution (fluorescence spectrum).
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Table 4.20: EXAFS Results for the Aquated Hexa-2-vanadotungstate Anion

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius/$\AA$ (EXAFS)</th>
<th>Radius/$\AA$ (Crystal)</th>
<th>Debye-Waller Factor/$\AA^2$</th>
<th>% Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>O</td>
<td>1.762(5)</td>
<td>1.684</td>
<td>0.008</td>
<td>4.63</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>W</td>
<td>1.939(5)</td>
<td>1.864</td>
<td>0.024</td>
<td>4.02</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>O</td>
<td>2.264(4)</td>
<td>2.309</td>
<td>0.004</td>
<td>-1.95</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>W</td>
<td>3.250(3)</td>
<td>3.252</td>
<td>0.012</td>
<td>0.06</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>V</td>
<td>3.298(9)</td>
<td>3.252</td>
<td>0.017</td>
<td>1.11</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>O</td>
<td>3.446(11)</td>
<td>3.478</td>
<td>0.015</td>
<td>-0.92</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>O</td>
<td>4.452(39)</td>
<td>4.558</td>
<td>0.025</td>
<td>-1.45</td>
</tr>
<tr>
<td>8</td>
<td>0.5</td>
<td>W</td>
<td>4.538(27)</td>
<td>4.596</td>
<td>0.015</td>
<td>-1.26</td>
</tr>
<tr>
<td>9</td>
<td>0.5</td>
<td>V</td>
<td>4.575(111)</td>
<td>4.596</td>
<td>0.025</td>
<td>-0.46</td>
</tr>
</tbody>
</table>

Spectrum Fourier filtered from 1.04Å to 4.74Å, $F_i=0.63230$.

4.72. (n-Bu$_3$N)$_4$VW$_6$O$_{19}$

No X-ray crystallographic structure exists for this compound, so the structure of the hexa-2-vanadotungstate ion was used as the starting point for the theoretical model, and for comparison purposes.

Solid-state Spectrum

The EXAFS spectrum for this compound is much the same as for $[\text{V}_2\text{W}_6\text{O}_{19}]^{13-}$, with the obvious proviso that the tungsten shells are more intense, whilst the vanadium signals are correspondingly weaker. Table 4.21 lists the 9 shells that were resolved without any contribution from multiple scattering being considered. The results are illustrated in fig. 4.28.

In order to create a strictly representative model of the multiple scattering across the centre of the anion, it would be necessary to split the third oxygen shell into two shells with 0.8 and 0.2 atoms respectively, to correspond with the metal shells (8 and 9). 0.2 of an oxygen atom is essentially invisible to EXAFS - so it was necessary instead to consider the two metal shells as one, containing one W atom. Probably because of this approximation, the results obtained when
Fig. 4.27: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for \( [\text{VW}_2\text{O}_{19}]^{14-} \) in aqueous solution.
Fig. 4.23: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for Hexa-i-vanadotungstate in the solid state.
multiple scattering is used are not really any better, as table 4.22 and fig. 4.29 reveal.

### Table 4.21: EXAFS Results for solid-state Hexa-1-vanadotungstate

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius/A (EXAFS)</th>
<th>Radius/A (Crystal)</th>
<th>Debye-Waller % Discrepancy* Factor/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>O</td>
<td>1.718(5)</td>
<td>1.684</td>
<td>0.005</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>O</td>
<td>1.911(3)</td>
<td>1.864</td>
<td>0.009</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>O</td>
<td>2.244(13)</td>
<td>2.309</td>
<td>0.014</td>
</tr>
<tr>
<td>4</td>
<td>3,2</td>
<td>W</td>
<td>3.286(5)</td>
<td>3.252</td>
<td>0.010</td>
</tr>
<tr>
<td>5</td>
<td>0,8</td>
<td>V</td>
<td>3.307(19)</td>
<td>3.252</td>
<td>0.009</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>O</td>
<td>3.450(14)</td>
<td>3.478</td>
<td>0.008</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>O</td>
<td>4.722(37)</td>
<td>4.558</td>
<td>0.017</td>
</tr>
<tr>
<td>8</td>
<td>0,8</td>
<td>W</td>
<td>4.560(9)</td>
<td>4.596</td>
<td>0.005</td>
</tr>
<tr>
<td>9</td>
<td>0,2</td>
<td>V</td>
<td>4.573(81)</td>
<td>4.596</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Fourier filtered from 1.01Å to 5.12Å, \( \beta = 9443 \), compared with \([V_{2}W_{4}O_{13}]^{2-}\)

### Table 4.22: EXAFS Results for the Hexa-1-vanadotungstate Anion, with multiple scattering included

<table>
<thead>
<tr>
<th>Shell</th>
<th>No. Atoms</th>
<th>Element</th>
<th>Radius/A (EXAFS)</th>
<th>Radius/A (Crystal)</th>
<th>Debye-Waller % Discrepancy* Factor/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>O</td>
<td>1.722(4)</td>
<td>1.684</td>
<td>0.005</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>O</td>
<td>1.914(3)</td>
<td>1.864</td>
<td>0.010</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>O</td>
<td>2.234(14)</td>
<td>2.309</td>
<td>0.015</td>
</tr>
<tr>
<td>4</td>
<td>3,2</td>
<td>W</td>
<td>3.276(2)</td>
<td>3.252</td>
<td>0.009</td>
</tr>
<tr>
<td>5</td>
<td>0,8</td>
<td>V</td>
<td>3.289(10)</td>
<td>3.252</td>
<td>0.009</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>O</td>
<td>3.441(6)</td>
<td>3.478</td>
<td>0.007</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>O</td>
<td>4.557(35)</td>
<td>4.558</td>
<td>0.025</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>W</td>
<td>4.613(11)</td>
<td>4.596</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Spectrum Fourier filtered from 1.01Å to 5.12Å, \( \beta = 1,31833 \), compared with \([V_{2}W_{4}O_{13}]^{2-}\)
Chapter 4: Polyoxometalates

Fig. 4.29: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for $\text{VW}_6\text{O}_{18}\text{I}_{3^-}$, multiple scattering included.
Solution Spectrum

The results are much the same as for the solid state sample. However, it was not possible to resolve the outermost metal shells at all; they had to be considered as one (tungsten) shell. This meant that multiple scattering could be included without detriment to the results, which are presented in fig. 4.30 and table 4.23.

### Table 4.23: EXAFS Results for solvated Hexa-1-vanadotungstate

<table>
<thead>
<tr>
<th>Shell</th>
<th>No, Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller X Discrepancy* Factor/Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>O</td>
<td>1.696(9)</td>
<td>1.684</td>
<td>0.023</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>O</td>
<td>1.315(4)</td>
<td>1.864</td>
<td>0.023</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>W</td>
<td>2.251(4)</td>
<td>2.309</td>
<td>0.006</td>
</tr>
<tr>
<td>4</td>
<td>3.2</td>
<td>W</td>
<td>3.252(5)</td>
<td>3.252</td>
<td>0.023</td>
</tr>
<tr>
<td>5</td>
<td>0.8</td>
<td>V</td>
<td>3.258(5)</td>
<td>3.252</td>
<td>0.007</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>O</td>
<td>3.413(7)</td>
<td>3.478</td>
<td>0.017</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>O</td>
<td>4.330(14)</td>
<td>4.558</td>
<td>0.025</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>W</td>
<td>4.606(10)</td>
<td>4.596</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Fourier filtered from 0.85Å to 4.83Å,
FI=0.39191.
* compared with [V_2W_4O_7]^{4-}

### 4.73 (n-Bu)_4N[NbW_6O_19]

No X-ray structure was available for this compound, so, as with the previous example, the EXAFS results were compared with the crystallographic structure of [V_2W_4O_7]^{4-}.

Solid-state Spectrum

It was not possible to differentiate between the two smaller metal shells. On the other hand, the oxygen shell beyond these was found in this spectrum. The contribution of multiple scattering across the centre of the anion was included. See fig. 4.31 and table 4.24 for the results.
Fig. 4.30: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for [VW_{6}O_{19}]^{2-} in acetonitrile solution.
Table 4.24: EXAFS Results for the Hexa-1-niobotunostate anion

<table>
<thead>
<tr>
<th>Shell No.</th>
<th>Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller % Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>O</td>
<td>1.722(6)</td>
<td>1.684</td>
<td>0.010</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>O</td>
<td>1.906(4)</td>
<td>1.884</td>
<td>0.016</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>O</td>
<td>2.317(5)</td>
<td>2.309</td>
<td>0.005</td>
</tr>
<tr>
<td>4</td>
<td>3,2</td>
<td>W</td>
<td>3.294(3)</td>
<td>3.252</td>
<td>0.011</td>
</tr>
<tr>
<td>5</td>
<td>0,8</td>
<td>Nb</td>
<td>3.356(15)</td>
<td>3.252</td>
<td>0.011</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>O</td>
<td>3.383(7)</td>
<td>3.478</td>
<td>0.008</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>O</td>
<td>4.263(20)</td>
<td>4.538</td>
<td>0.025</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>W</td>
<td>4.597(5)</td>
<td>4.596</td>
<td>0.006</td>
</tr>
<tr>
<td>9</td>
<td>4</td>
<td>O</td>
<td>4.689(10)</td>
<td>4.703</td>
<td>0.006</td>
</tr>
</tbody>
</table>

The spectrum was Fourier filtered from 0,91Å to 4,71Å

FI=0,81910; R=23,9600.
*a compared with IV₃W₄O₁₉J⁻*

**Solution Spectrum**

As has been found to be typical, the solution spectrum of this anion is considerably poorer than its solid state counterpart. In the experimental spectrum, the signal beyond about 4Å is indistinguishable from the baseline. Only the shells within this radius were considered, resulting in the six-shell model presented below. There are no multiple scattering units to take into consideration.

Table 4.25: EXAFS Results for Hexa-1-niobotunostate in acetonitrile solution

<table>
<thead>
<tr>
<th>Shell No.</th>
<th>Atoms</th>
<th>Element</th>
<th>Radius/Å (EXAFS)</th>
<th>Radius/Å (Crystal)</th>
<th>Debye-Waller % Discrepancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>O</td>
<td>1.659(12)</td>
<td>1.684</td>
<td>0.019</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>O</td>
<td>1.876(7)</td>
<td>1.864</td>
<td>0.016</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>O</td>
<td>2.285(4)</td>
<td>2.309</td>
<td>0.004</td>
</tr>
<tr>
<td>4</td>
<td>3,2</td>
<td>W</td>
<td>3.212(6)</td>
<td>3.252</td>
<td>0.009</td>
</tr>
<tr>
<td>5</td>
<td>0,8</td>
<td>Nb</td>
<td>3.396(16)</td>
<td>3.252</td>
<td>0.009</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>O</td>
<td>3.279(6)</td>
<td>3.478</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Data Fourier filtered from 0,56Å to 4,73Å,

FI=0,21441; R=12,2591.
*a compared with IV₃W₄O₁₉J⁻*
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Fig. 4.31: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for solid state Hexa-i-niobotungstate.
Fig. 4.32: Theoretical (dashed line) and experimental (solid line) (top) EXAFS spectra and (bottom) Fourier transforms for the Hexa-l-niobotungstate anion in MeCN.
Whilst observing structure out to 5Å in the EXAFS results for a pure metal foil is not unusual, these samples show that, with good spectra, such resolution can be achieved in samples of compounds. What is more, if a concentrated solution of the sample can be obtained, it can be possible to resolve as many shells in the solution spectrum as in the solid state, as is the case with $[\text{V}_{10}\text{O}_{28}]^{6-}$. Failing that, it is conceivable to get within one shell of the solid state spectrum, as was achieved with $[\text{VW}_{6}\text{O}_{19}]^{2-}$ and $[\text{V}_{2}\text{W}_{4}\text{O}_{19}]^{3-}$. There appear to be no consistent differences in the structural parameters of the solid state and solvated anions.

With this kind of resolution, there is an obvious potential for monitoring the products of a reaction in situ. It has to be borne in mind, of course, that EXAFS spectroscopy cannot be used to determine unknown or new structures on its own. In order to propose a structural model, information from another source or sources is required. Nmr spectroscopy has proved an extremely powerful method of probing the structures of polyanions in solution. $^{51}$V studies have been reported$^{23,29}$, but the most prevalent nuclei are $^{17}$O $^{5,6,12,13,15-18,23,24,37,38}$ and $^{185}$W $^{8,11,12,20,39-47}$. A combination of nmr and EXAFS spectra could provide a very detailed characterisation of a polyanion compound.

When looking beyond the first shell in the complex, lattice-like structures that the polyanions possess, the backscattered electron is bound to undergo a certain amount of multiple scattering. Taking account of the more important pathways can improve the accuracy of the model for those shells involved, at a cost in the amount of computing power required to calculate the theoretical model.
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4.9 REFERENCES

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35. M.T. Pope; op. cit., p. 16.
CONCLUSIONS
Previously, the results of EXAFS studies have tended to be limited to situations in which a relatively simple theoretical model, say two to four shells, is matched to the spectrum. These results show that EXAFS spectroscopy can resolve detail in complex structures up to 5Å from the absorbing atom, even in solution. As many as ten shells can be modelled. At a cost in computing power, detailed multiple scattering calculations can be used to enhance the results obtained.

It is clear from the studies on mixed metal compounds that, firstly, some information can be extracted even from poor data. More importantly, it is not really possible to 'solve' a structure using EXAFS in the way that it is with X-ray crystallography. Precise information on bond angles is hard to obtain, and there is too much leeway in the parameters that determine the spectrum's amplitude (i.e. the Debye-Waller factor and number of atoms in the shell). This means that it is virtually impossible to fix unambiguously on a theoretical model without supporting evidence from other techniques.

EXAFS spectroscopy is useful, however, for establishing and characterising a structure postulated from other evidence, or for disproving a proposed structure. It can be employed, for instance, to test theoretical models based on analogies with known structures (as was the case with many of the spectra reported herein), or on the results of other techniques such as nmr spectroscopy.

**Future Work**

Many of the compounds studied have an 'alternative viewpoint' as far as EXAFS is concerned. A useful extension of this work would be to examine them from this viewpoint. That is to say, analyse the ruthenium spectra of $\text{H}_3\text{Ru}_4(\text{CO})_8(\text{AuPPPh}_3)_2$, "Au$_4$Ru$_2$P" and "Cu$_2$Ru$_2$P$_2"; and the vanadium spectra of the vanado-tungstate anions. Having two spectra of the unknowns might make it possible to propose their structures.
Conclusions

Some of the solid state spectra presented earlier were of high quality throughout the energy range examined. This suggests that they could be taken again, extending the length of the post-edge region, to achieve even greater accuracy and resolution.

A longer term aim would be to extend the three threads examined here into the realm of actual catalysis. One might examine how the structure of the tethered rhodium clusters, and similar compounds, stood up to catalytic conditions. Likewise for the mixed metal complexes. Finally, the changes in the EXAFS spectra of polyanions when an organometallic fragment is attached to them, and when the resulting compound were used in catalysis, would also be worthy of study.