

Complexes of vanadium(IV) oxide difluoride with neutral N- and O-donor ligands

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Abstract

A convenient new synthesis for complexes of VOF_2 with N-donor ligands is via the reaction of VF_4 with the ligand in water, either under reflux or using hydrothermal conditions. The complexes, *mer*- $[\text{VOF}_2(\text{terpy})]\cdot 3\text{H}_2\text{O}$ (terpy = 2,2',6',2'''-terpyridyl), $[\text{VOF}_2(\text{bipy})(\text{H}_2\text{O})]$, $[\text{VOF}_2(\text{phen})(\text{H}_2\text{O})]$, $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})]$, $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})]\cdot \text{H}_2\text{O}$, $[\text{V}_2\text{O}_2\text{F}_4(\text{py})_4]$ and $[\text{pyH}]_2[\text{V}_2\text{O}_2\text{F}_6(\text{H}_2\text{O})_2]$, along with the O-donor, pyridine N-oxide (pyNO) complex, $[\text{V}_2\text{O}_2\text{F}_4(\text{H}_2\text{O})_2(\text{pyNO})_2]$, have been isolated and characterised. The controlled hydrolysis of VF_4 in water produces the hydrate $[\text{VOF}_2(\text{H}_2\text{O})_2]\cdot \text{H}_2\text{O}$. The complex $[\text{VOF}_2(\text{Me}_3\text{tacn})]$ (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) was prepared by the reaction of $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})]$ and Me_3tacn in MeCN. The new complexes have been characterised by microanalysis and single crystal X-ray diffraction. Powder X-ray diffraction (PXRD) data were recorded for the bulk samples and compared with the PXRD patterns simulated from the single crystal data to confirm that the latter were representative of the bulk products. All the complexes contain six-coordinate vanadium(IV), with extensive H-bonding and (in the pyridyl ligand complexes) π -stacking interactions present. IR and UV-visible spectroscopic data and magnetic measurements are also reported and discussed. Attempts to obtain phosphine oxide or ether complexes by similar routes were unsuccessful. Unless the temperature is carefully controlled, the hydrothermal route yields mixtures of V^{IV} and V^{V} complexes.

1. Introduction

The oxide halides of the early d-block elements in higher oxidation states are strong Lewis acids and have an extensive coordination chemistry [1], although the strong $\text{O}(\pi) \rightarrow \text{M}(\text{d})$ donation increases the electron density on the metal, making the oxide halide a less strong acceptor than the corresponding binary halide. While numerous oxide-fluoride anions are known [2,3], complexes of the oxide fluorides with neutral ligands have been neglected until relatively recently [4]. This reflects the commercial unavailability of most metal oxide fluorides, coupled with more challenging syntheses. Vanadium(V) oxide trifluoride reacts directly with many ligands in MeCN solution to form

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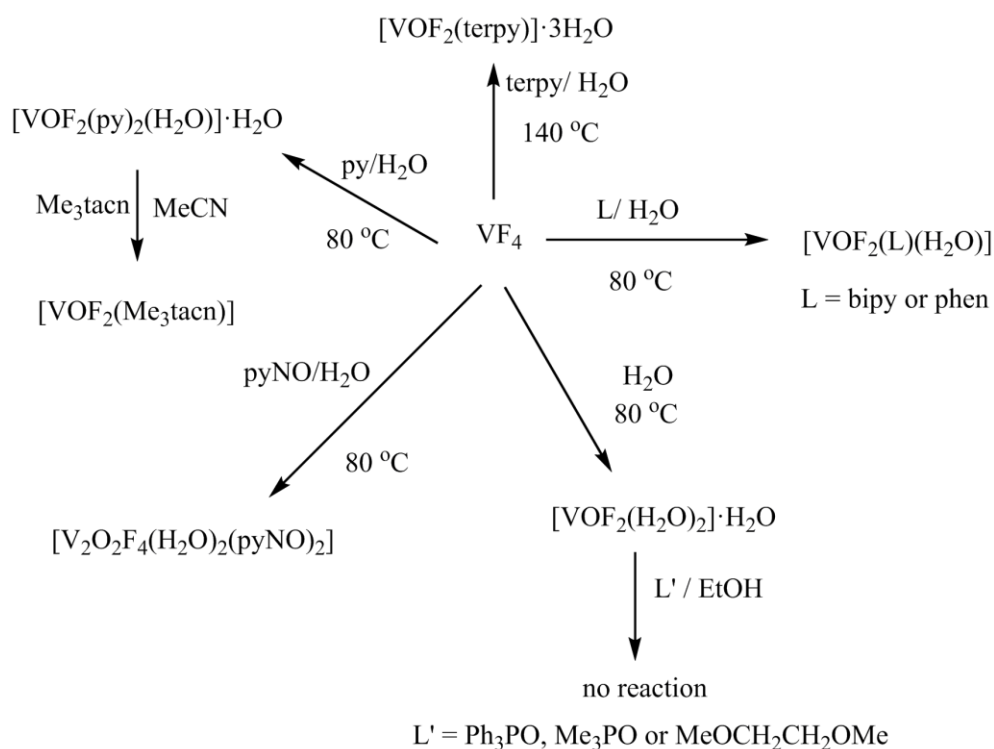
[VOF₃(L)_n] (L = bipy, phen, py, OPR₃, tmeda, *etc.*; [5], and a few examples of WOF₄ complexes have been obtained similarly [6-9]. However, these are the exceptions. Most oxide fluorides, e.g. MoO₂F₂, WO₂F₂, VO₂F, NbOF₃, are strongly polymerised and unreactive. In the latter cases, alternative approaches are required, typically involving O/F exchange, by reaction of the corresponding fluoride complexes with a siloxane, such as (Me₃Si)₂O, or Cl/F exchange from the corresponding oxide chlorides using Me₃SnF [10-13]. The strong fluoride bridges in the oxide fluorides also limit the neutral ligand coordination chemistry, in that weak donor ligands may be displaced from the metal centre, while the coordination number is maintained by formation of (stronger) M–F–M bridges [4]. Anhydrous VOF₂ was reported in 1911, as a yellow powder formed from VOBBr₂ and HF at red-heat and is insoluble in water and organic solvents [14]. Its structure is unknown and its reaction chemistry remains unexplored. Green and blue hydrates, VOF₂·xH₂O, of unknown structure(s) are reported to form from reaction of VO₂ and aqueous HF, or from vanadyl salts and HF in aqueous solution [15,16]. There have been scattered reports of complexes with diimine ligands [16-18], but with poor (or no) spectroscopic characterisation; the only crystallographically characterised example, [VOF₂(phen)(H₂O)], had no associated spectroscopy [19]. It does not appear possible to establish if the complexes with the same ligand in different reports are all the same complex. A blue [VOF₂(tacn)]·2H₂O (tacn = 1,4,7-triazacyclononane) complex was formed by air-oxidation of [VF₃(tacn)] in methanol/H₂O [20]. Very recently, a series of oxido-fluorido cations, *cis*-[VOF(R₂bipy)₂]⁺ (R₂bipy = 2,2'-bipy, 4,4'-Me₂-2,2'-bipy, 4,4'-ⁱBu₂-bipy), have been obtained by reaction of VOSO₄, the diimine and KF in aqueous solution [21]. X-ray crystal structures were determined for *cis*-[VOF(2,2'-bipy)₂][SbF₆] and *cis*-[VOF(4,4'-ⁱBu₂-bipy)₂][BF₄]. Oxido-fluorido-vanadate(IV) anions are well known and a large variety of structural motifs have been characterised [3,22-25].

Here we report the preparation and characterisation of a series of neutral nitrogen- and oxygen-donor ligand complexes of VOF₂, together with their spectroscopic and structural characterisation.

2. Results and Discussion

2.1 Synthesis

We explored a number of possible routes to N-donor complexes of VOF₂, including reduction of the corresponding VOF₃ adducts [5] by refluxing in EtOH, refluxing with excess ligand in MeCN, or with SO₂ in MeCN, all of which were unsuccessful. The attempted F/O exchange between VF₄ and (Me₃Si)₂O in MeCN also failed, with the insoluble VF₄ mostly recovered unchanged. We note in passing that the commercial samples of VF₄ used in this work were dull brown powders, due to surface hydrolysis [26], rather than the lime-green of the pure product [27]. However, noting that the VF₄ turned blue slowly on exposure to air and immediately in water, we developed a general synthesis for N-base complexes of VOF₂ using the reaction of VF₄ with the ligands in water under hydrothermal conditions (Scheme 1).



Scheme 1 Synthesis of the VOF_2 complexes.

Hydrothermal or solvothermal preparations have been used to prepare oxido-fluorido-vanadates(IV) in the presence of appropriate cations and some HF [22-25].

2.2 $[VOF_2(H_2O)_2] \cdot H_2O$

Either refluxing VF_4 in water, or heating the mixture in a hydrothermal bomb, gave a clear blue solution, from which blue crystals were obtained by allowing the water to evaporate. Performing the reactions in PTFE hydrothermal vessels is convenient and avoids the production of fluorosilicate impurities, which were sometimes observed in reactions performed in borosilicate glass vessels. The crystals were identified as $[VOF_2(H_2O)_2] \cdot H_2O$ by X-ray structure determination. The structure (Fig. 1a) consists of square pyramidal $VOF_2(H_2O)_2$ units weakly linked via the apical $V=O$ into chains, with asymmetric $V \cdots O=V$ bridges. The basal F/H_2O donors are disordered. A PXRD pattern of the bulk powder was in excellent agreement with the pattern simulated using the single crystal X-ray data, confirming the crystal was representative of the bulk product (Fig. 1b). The $[VOF_2(H_2O)_2] \cdot H_2O$ is a useful synthon for other complexes and is a likely intermediate in the hydrothermal syntheses.

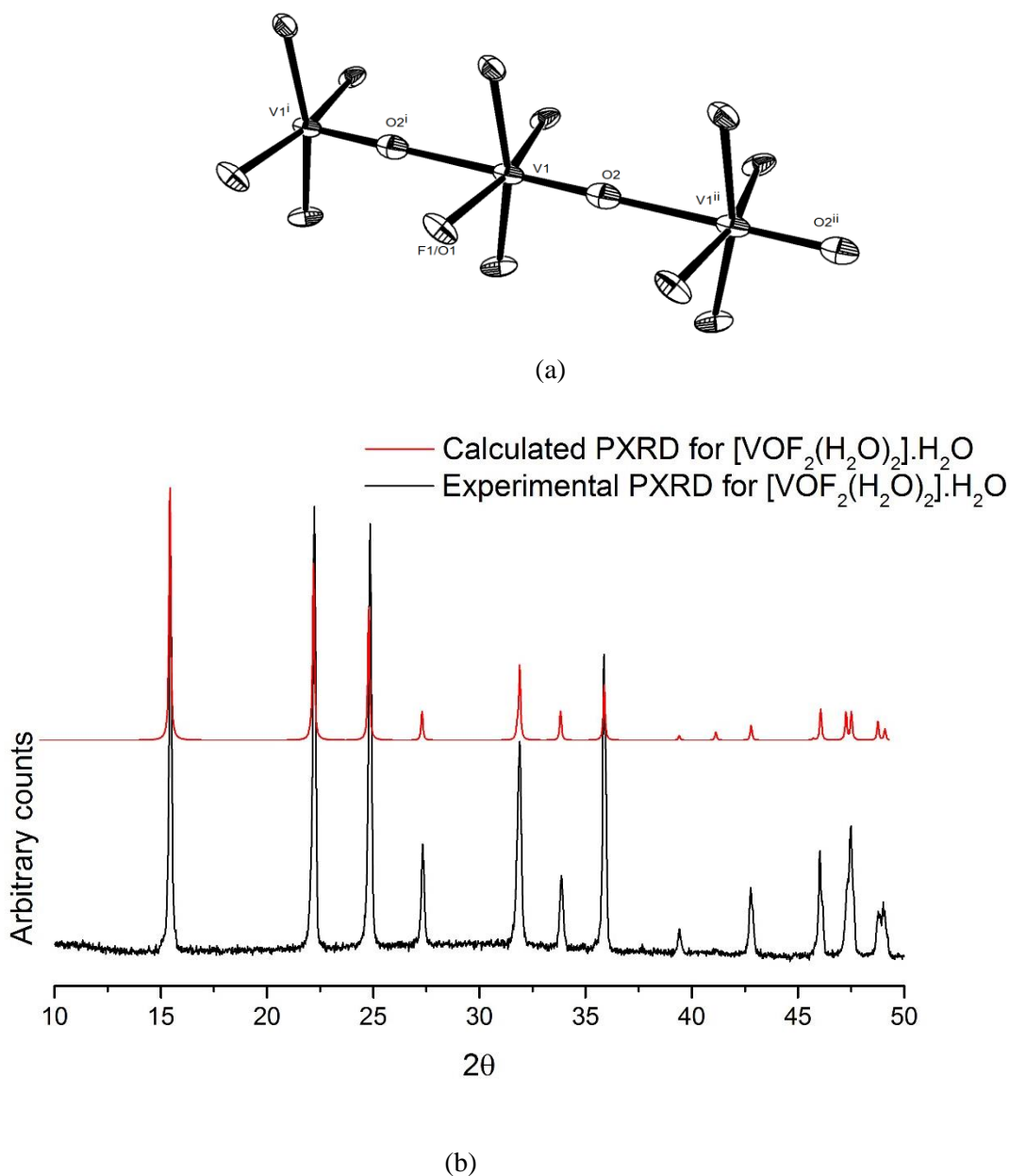


Figure 1 (a) Part of the chain structure of $[\text{VOF}_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Lattice water and hydrogen atoms are omitted for clarity. The $\text{H}_2\text{O}/\text{F}$ in the basal plane are disordered. Selected bond lengths (\AA) and angles ($^\circ$): $\text{V1-F1/O1} = 1.95(1)$, $\text{V1-O2} = 1.71(1)$, $\text{V1-O2}^i = 2.20(1)$, $\text{O2-V1-O2}^i = 180.0$. Symmetry operation: $i = x, y, z+1$. (b) The experimental PXRD pattern obtained from the bulk sample of $[\text{VOF}_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ and the simulated PXRD calculated from the single crystal X-ray data.

The IR spectrum of the crystals shows broad features at $3600\text{--}3200$ and 1650 cm^{-1} due to the water, $\nu(\text{V}=\text{O})$ at 945 cm^{-1} and a sharp $\nu(\text{V-F})$ at 505 cm^{-1} , the latter suggesting the VF_2 unit may have a *trans* geometry. A new $\text{V}_2\text{O}_2\text{F}_4(\text{H}_2\text{O})_2\cdot\text{H}_2\text{O}$ complex made serendipitously during solvothermal synthesis of vanadium selenites, has a fluoride-bridged 2D layer structure [28], rather different to the chain structure reported here.

2.3 Nitrogen and oxygen donor ligands

The reactions of VF₄ with 2,2'-bipyridyl, 1,10-phenanthroline or 2,2',6',2''-terpyridyl in a hydrothermal bomb were explored as a function of time, temperature, and ratio of reagents. It was found that temperature was the key control parameter. At high temperatures (~ 180 °C) decomposition occurred and some V^V products were isolated, whereas high yields of pure VOF₂ adducts, *mer*-[VOF₂(terpy)]·3H₂O, [VOF₂(bipy)(H₂O)] and [VOF₂(phen)(H₂O)], were isolated at lower temperatures (typically ~ 80 °C; see Experimental section). Crystals of the complexes were grown by evaporation of the mother liquor, after removal of any insoluble residues.

The VF₄/pyridine/H₂O system proved to be quite complicated and four distinct compounds were identified, [VOF₂(py)₂(H₂O)], [VOF₂(py)₂(H₂O)]·H₂O, [V₂O₂F₄(py)₄] and [pyH]₂[V₂O₂F₆(H₂O)₂]. The reaction of VF₄ with a large excess of pyridine in water at 80 °C, gave, on cooling, some pale blue-purple crystals; the mother liquor was then taken to dryness *in vacuo* and afforded more blue-purple crystals that were identified as [VOF₂(py)₂(H₂O)]. Concentration of the mother liquor from a similar reaction by slow evaporation at ambient temperatures gave blue crystals of the monohydrate, [VOF₂(py)₂(H₂O)]·H₂O. A few green crystals of [V₂O₂F₄(py)₄] were obtained from the reaction of VF₄ and pyridine in a 1 : 3 mol. ratio in water at 150 °C for 5 h. The [pyH]₂[V₂O₂F₆(H₂O)₂] was obtained from a VF₄ : pyridine ratio of 1 :2 in water heated to 80 °C for 5 h.

Attempts to prepare [VOF₂(Me₃tacn)] (Me₃tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) by the hydrothermal route using VF₄, Me₃tacn and H₂O, gave unidentified sticky green solids. However, the reaction of Me₃tacn with [VOF₂(py)₂(H₂O)] in MeCN produced a high yield of blue [VOF₂(Me₃tacn)].

Green crystals of [V₂O₂F₄(H₂O)₂(pyNO)₂] were obtained by a solvothermal route using a mixture of H₂O and MeCN, but attempts to make complexes of Ph₃PO, Me₃PO or MeOCH₂CH₂OMe either hydrothermally, or by reaction of [VOF₂(H₂O)₂]·H₂O with the ligand in ethanol, were unsuccessful, with the [VOF₂(H₂O)₂]·H₂O recovered following work-up.

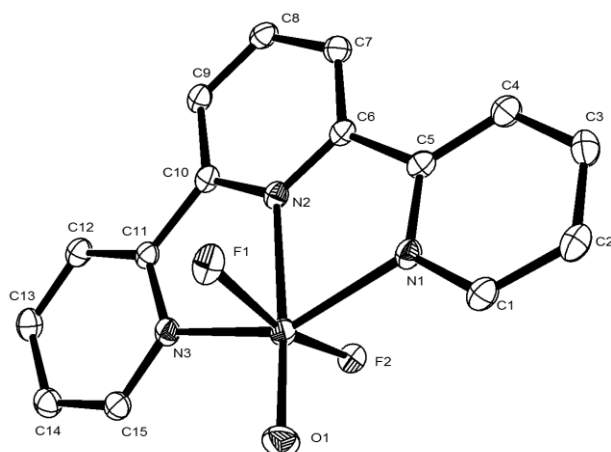
2.4 X-ray crystal structures

Single crystal X-ray diffraction provided key data on the new VOF₂ adducts, but before discussing these results it is necessary to explicitly consider some possible complications:

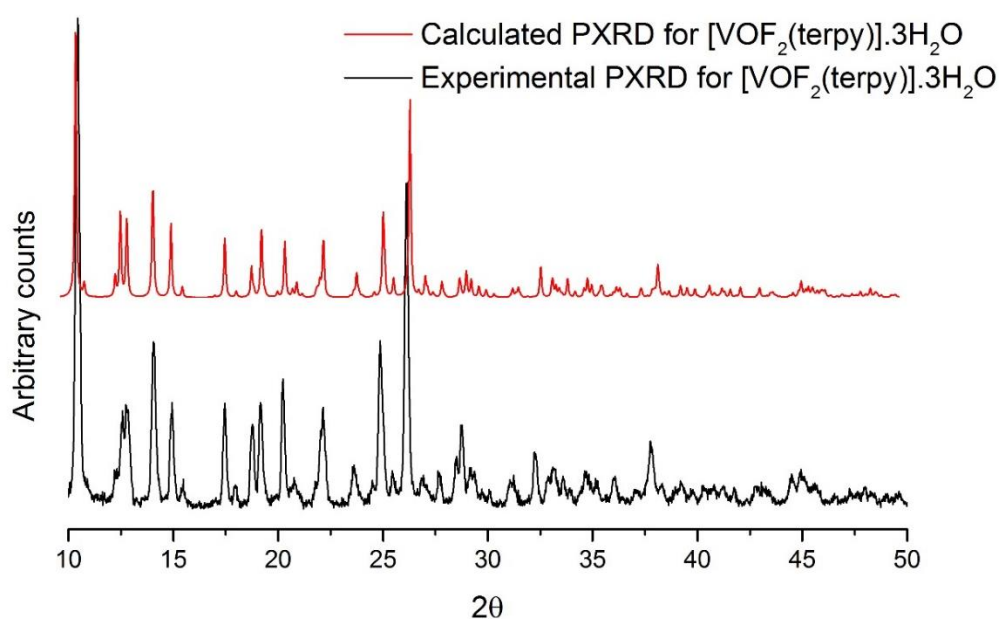
1. O/F disorder. This is relatively common in many early d-block oxide-fluoride species [5,10-12] and whilst V=O and V–F should be distinguishable by their different bond lengths, distinction of V–O–V from V–F–V is much more difficult. Bond lengths intermediate between those expected for terminal V=O and V–F should raise the question of possible disorder, even if the thermal ellipsoids are not apparently elongated along the bond axis.

2. For a metal like vanadium, which can readily switch its oxidation state, co-crystallisation of V^{IV} and V^V complexes is likely. For example, the literature shows that three crystal structures were reported for “[VO₂Cl(py)₂]”, one yellow and two green forms, which had slightly different geometries and different H-bonding. It was concluded [11] that the yellow form was pure [VO₂Cl(py)₂], whereas the green forms were co-crystallised [VO₂Cl(py)₂] and (blue) [VOCl₂(py)₂] in differing ratios – an example of the erroneous concept of ‘distortional isomerism’ [29]. As discussed by Parkin, [29] ‘distortional isomerism’ can be surprisingly difficult to identify even with good quality X-ray diffraction data, and careful consideration of the spectroscopic data is often necessary.

In view of the easy interconversions between V^{IV} and V^V complexes, and the production of mixtures under some conditions, it was important to establish that the crystal structures determined were truly representative of the bulk products. To confirm this, PXRD patterns were recorded from the bulk products and compared to the patterns simulated from the single crystal X-ray data.



(a)



(b)

Figure 2. (a) The structure of *mer*-[VOF₂(terpy)]·3H₂O with ellipsoids drawn at the 50% probability level. The lattice water and H-atoms have been omitted. Selected bond lengths (Å) and angles (°): V1–O1 = 1.618(2), V1–F1 = 1.923(1), V1–F2 = 1.911(1), V1–N1 = 2.127(2), V1–N2 = 2.179(2), V1–N3 = 2.124(2); O1–V1–F1 = 92.72(7), O1–V1–F2 = 99.07(7), O1–V1–N1 = 109.47(7), O1–V1–N2 = 176.35, O1–V1–N3 = 103.36(8), F1–V1–F2 = 164.13(6); (b) The experimental PXRD pattern of the bulk sample and the pattern simulated from the single crystal X-ray data.

The structures of *mer*-[VOF₂(terpy)]·3H₂O and [VOF₂(bipy)(H₂O)] are shown in Figures 2 and 3. The structure of [VOF₂(phen)(H₂O)] gave bond lengths of V=O = 1.608(2) Å, V–F = 1.919(1), 1.933(1) Å, V–N = 2.141(2), 2.323(2) Å and V–OH₂ = 2.007(2) Å, which are not significantly different from the published structure [19] (see Supplementary Information). The experimental and simulated PXRD patterns for *mer*-[VOF₂(terpy)]·3H₂O are shown in Figure 2(b) and the PXRD patterns for the two diimine complexes are in the Supplementary Information. The structures have similar distorted octahedral geometries with *trans*-VF₂ units bent away from the V=O, and with V–F ~1.9 Å, V=O ~1.6 Å and V–OH₂ ~2.0 Å. The different V–N distances (~0.15 Å) reflect the high *trans* influence of the V=O group compared to the V–OH₂.

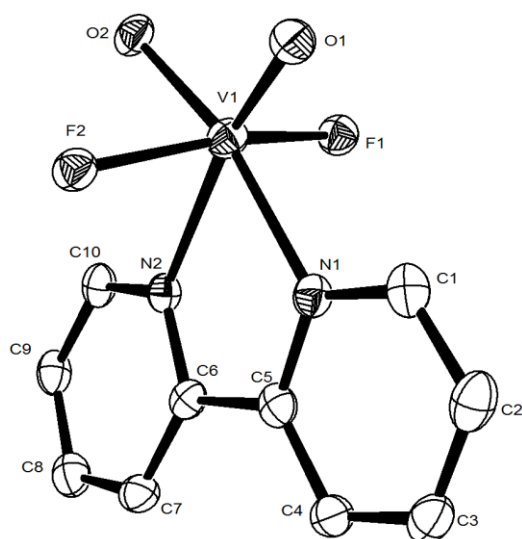


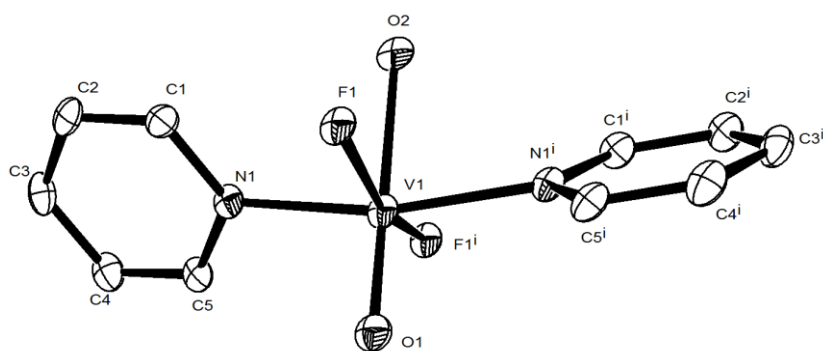
Figure 3. The structure of [VOF₂(bipy)(H₂O)] with ellipsoids drawn at the 50% probability level, and with H-atoms omitted. Selected bond lengths (Å) and angles (°): V1–O1 = 1.640(3), V1–O2 = 2.008(3), V1–F1 = 1.912(3), V1–F2 = 1.902(3), V1–N1 = 2.120(4), V1–N2 = 2.273(4); O1–V1–O2 = 104.1(2), O1–V1–F1 = 100.4(1), O1–V1–F2 = 98.7(2), F2–V1–F1 = 160.5(1), O1–V1–N1 = 92.5(2), O2–V1–F1 = 85.8(1), O2–V1–F2 = 85.8(1), F1–V1–N1 = 91.3(1), F1–V1–N2 = 82.6(1), F2–V1–N1 = 91.8(1), F2–V1–N2 = 79.9(1).

For these three complexes the X-ray structural data shows no evidence of O/F disorder.

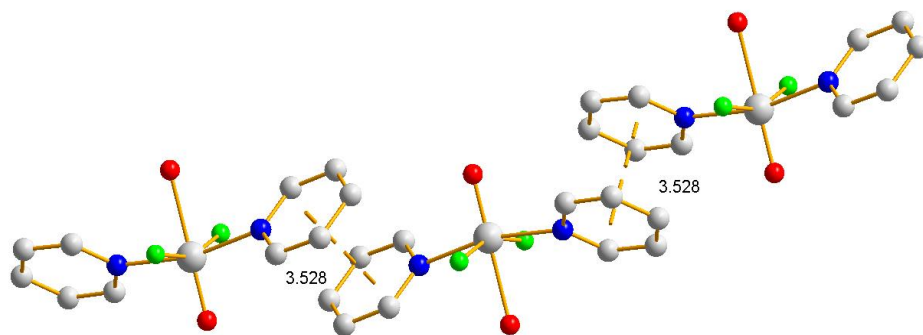
Several batches of blue crystals of [VOF₂(Me₃tacn)] were obtained by allowing MeCN solutions of the complex to evaporate, and X-ray data sets were collected on several crystals. These showed the expected octahedral structure composed of κ³-Me₃tacn and a VOF₂ unit, but all showed extensive

disorder both of O/F and within the aza-macrocyclic ring. A satisfactory model was not developed ([VOF₂(Me₃Tacn)]·4H₂O: orthorhombic, *Pbca*, *a* = 8.8759(3), *b* = 13.4689(6), *c* = 26.885(1) Å, $\alpha = \beta = \gamma = 90^\circ$, *Z* = 8, *R*₁ [*I*_o > 2σ(*I*_o)] = 0.047, *R*₁ (all data) = 0.062).

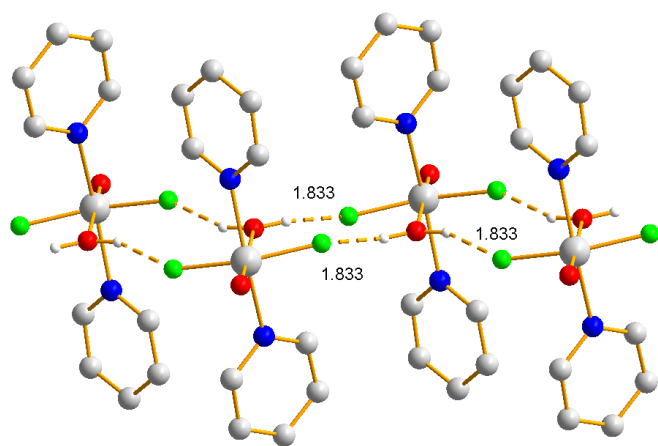
The structure of [VOF₂(py)₂(H₂O)] (*C2/c*) is shown in Figure 4(a). The bond lengths, V=O = 1.608(3), V–F = 1.921(2), V–N = 2.140(3) and V–OH₂ = 2.201(3) Å, are much as expected by comparison with the diimine structures discussed previously, and the longer V–OH₂ bond (which is *trans* V=O), compared to V–OH₂ in [VOF₂(bipy)(H₂O)] (which is *trans* V–N) (2.008(3) Å) is again evidence for the high *trans* influence of the vanadyl group. The structure shows both π -stacking of the pyridine rings (Figure 4(b)) and significant H-bonding between the coordinated water and fluoride ligands on neighbouring molecules (Figure 4(c)).



(a)



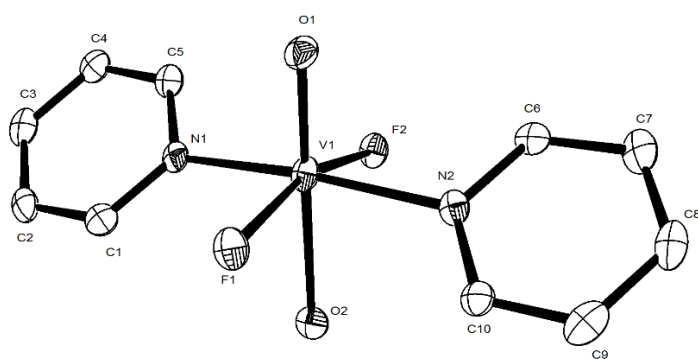
(b)



(c)

Figure 4 (a) The structure of $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})]$ with ellipsoids drawn at the 50% probability level. The hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): $\text{V1-O1} = 1.608(3)$, $\text{V1-F1} = 1.921(2)$, $\text{V1-N1} = 2.140(3)$, $\text{V1-O2} = 2.201(3)$, $\text{O1-V1-F1} = 99.99(6)$, $\text{F1-V1-O2} = 80.0(1)$, $\text{F1-V1-F1} = 160.0(1)$, $\text{O1-V1-N1} = 96.6(1)$, $\text{F1-V1-N1} = 89.7(1)$, $\text{F1-V1-N1} = 88.0(1)$; (b) the π -stacking of the pyridine rings; (c) the H-bonding between the coordinated water and fluoride ligands.

As described above, different work-up of the reaction products resulted in isolation of blue crystals of the monohydrate $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ ($P2_1$) (Figure 5). There are small differences in bond lengths and angles between the $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})]$ and $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$, but the most obvious differences are that in the latter the pyridine rings are almost co-planar, whilst in the former they lie at 78° to each other. There are also significant differences in the H-bonding and π -stacking within the structures, in that the lattice water in $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ is H-bonded to both the coordinated V–F and V=O.



(a)

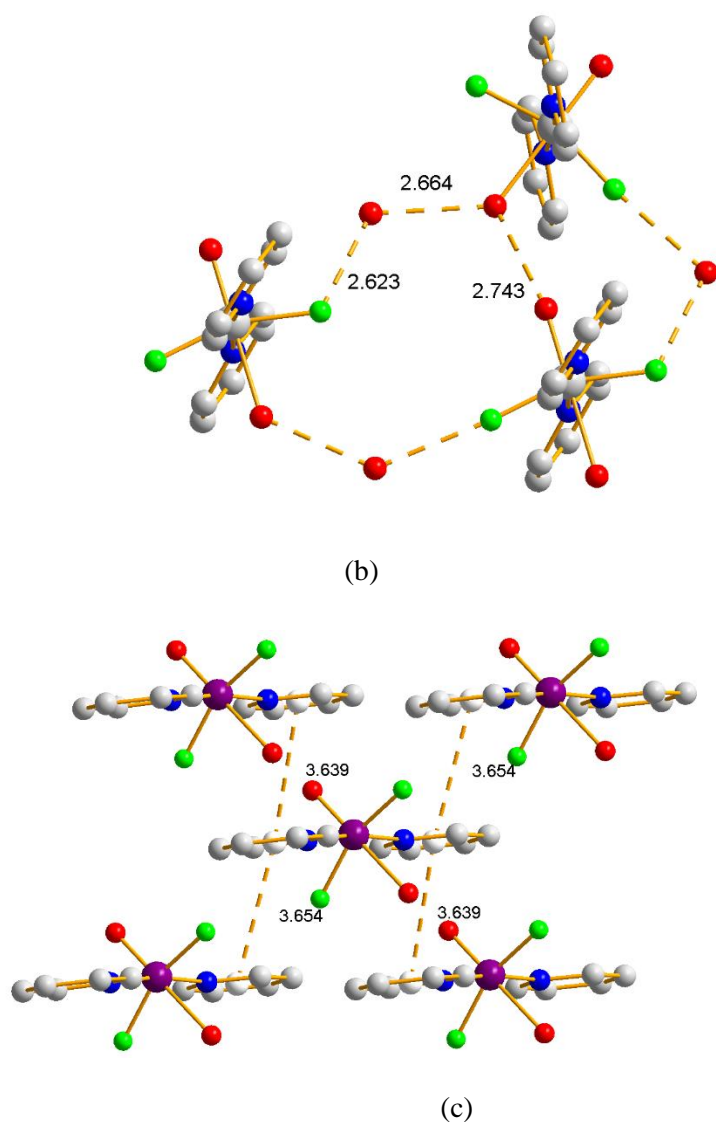


Figure 5 (a). The structure of $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ with ellipsoids drawn at the 50% probability level. The hydrogen atoms and lattice water are omitted. Selected bond lengths (\AA) and angles ($^\circ$): $\text{V1-O1} = 1.656(4)$, $\text{V1-O2} = 2.168(5)$, $\text{V1-F1} = 1.856(4)$, $\text{V1-F2} = 1.896(3)$, $\text{V1-N1} = 2.129(4)$, $\text{V1-N2} = 2.130(4)$; $\text{O1-V1-F1} = 101.3(2)$, $\text{O1-V1-F2} = 98.6(2)$, $\text{F1-V1-O2} = 79.0(2)$, $\text{O1-V1-N1} = 93.3(2)$, $\text{O1-V1-N2} = 93.4(2)$, $\text{F1-V1-F2} = 160.1(2)$; (b) the H-bonding involving the lattice water; (c) the π -stacking of the pyridine rings in $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$.

The small number of green crystals, isolated as a by-product of the reaction of VF_4 , pyridine and water at 150°C , proved to be a dimer, $[\text{V}_2\text{O}_2\text{F}_4(\text{py})_4]$ (Figure 6), formally derived by replacing the coordinated water in $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})]$ with a bridging fluoride.

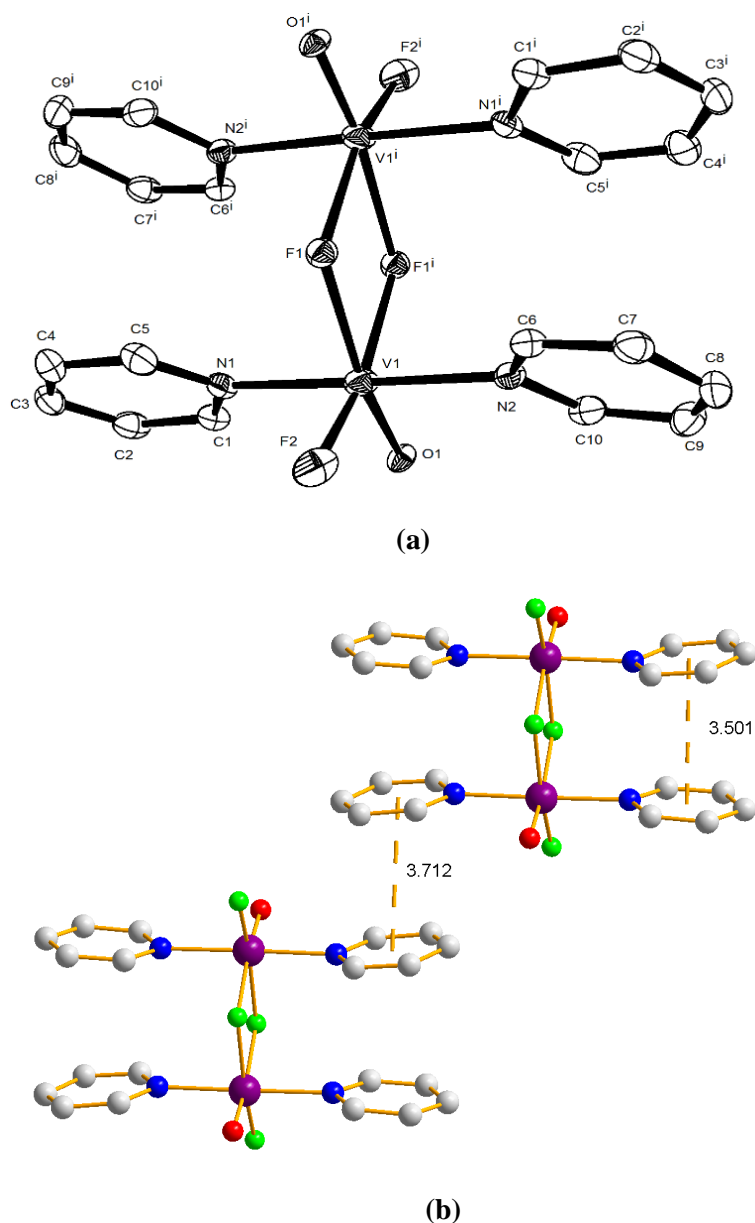
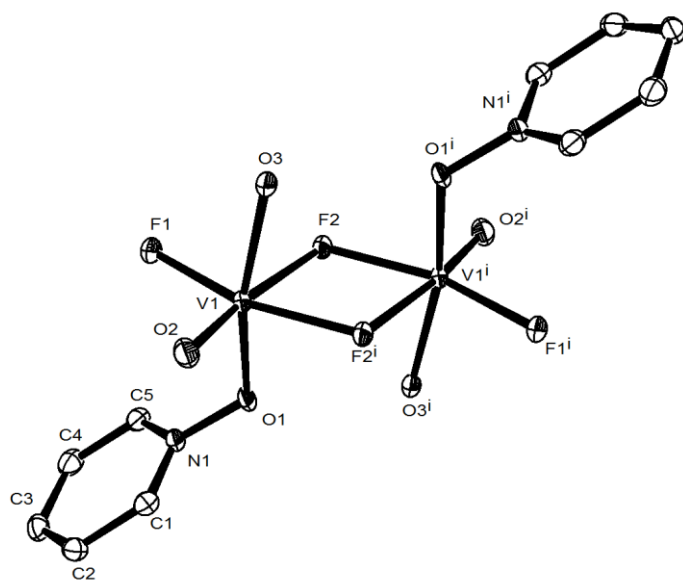


Figure 6 (a) The structure of $[\text{V}_2\text{O}_2\text{F}_4(\text{py})_4]$ with ellipsoids drawn at the 50% probability level, and with hydrogen atoms omitted. Selected bond lengths (\AA) and angles ($^\circ$): $\text{V1-F1} = 2.061(1)$, $\text{V1-F1}^i = 2.061(1)$, $\text{V1-F2} = 1.813(1)$, $\text{V1-O1} = 1.721(1)$, $\text{V1-N1} = 2.145(2)$, $\text{V1-N2} = 2.134(2)$; $\text{O1-V1-F1}^i = 92.39(6)$, $\text{O1-V1-F2} = 104.96(7)$, $\text{N2-V1-N1} = 178.98(7)$, $\text{F2-V1-F1} = 91.26(5)$, $\text{O1-V1-N1} = 90.02(6)$, $\text{O1-V1-N2} = 90.99(6)$, $\text{F2-V1-F1} = 91.26(5)$, $\text{F2-V1-N1} = 89.46(7)$, $\text{F2-V1-N2} = 90.77(5)$, $\text{F1-V1-N1} = 90.20(6)$, $\text{F1-V1-N2} = 88.80(5)$. Symmetry operation: $i = -x+1, -y+1, -z+1$; (b) the π -stacking of the pyridine rings. Note there is some disorder involving F2/O1.

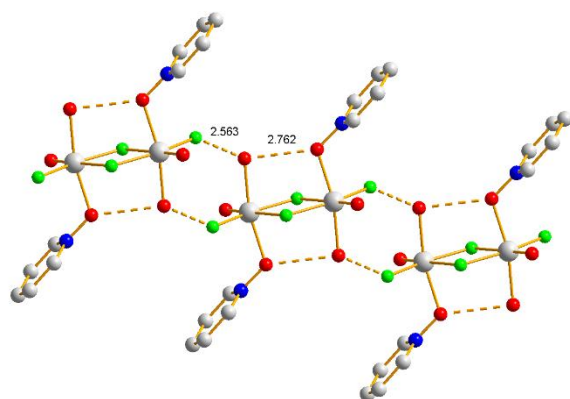
Whilst the structure is consistent with V^{IV} , the bond lengths suggest disorder in the terminal $\text{V}=\text{O}/\text{V}-\text{F}$. Notably the $\text{V}-\text{F}$ bridge distances are the same, despite one fluoride being *trans* to $\text{V}=\text{O}$ and the second *trans* to $\text{V}-\text{F}$, whilst the “ $\text{V}=\text{O}$ ” at $1.721(1) \text{ \AA}$ is rather longer than expected and “ $\text{V}-\text{F}$ (terminal)” at $1.813(1) \text{ \AA}$ shorter. The ellipsoids do not appear to be elongated, but as stated above, this is not unequivocal evidence of the absence of disorder. There is some (small) residual electron density which could not be modelled near to the $\text{V}=\text{O}$ group. π -Stacking of the pyridine rings is again present. The oxido-fluorido-vanadate(IV) anion in $[\text{pyH}]_2[\text{V}_2\text{O}_2\text{F}_6(\text{H}_2\text{O})_2]$ has been structurally

characterised with various cations [3,22-25], although not with $[\text{pyH}]^+$. The structure is included in the Supplementary Information.

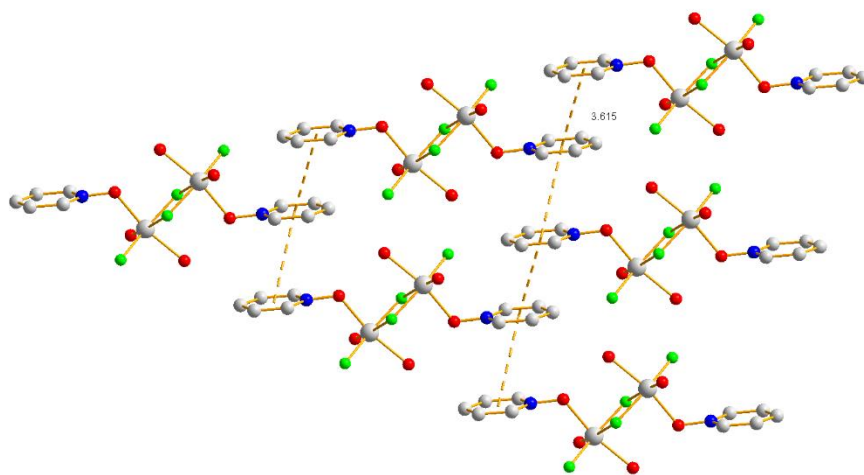
The structure of the blue dimeric pyNO complex, $[\text{V}_2\text{O}_2\text{F}_4(\text{H}_2\text{O})_2(\text{pyNO})_2]$, is shown in Figure 7.



(a)



(b)



(c)

Figure 7 (a) The structure of $[V_2O_2F_4(H_2O)_2(pyNO)_2]$ showing the atom numbering, with ellipsoids drawn at the 50% probability level, and with H-atoms omitted. Selected bond lengths (Å) and angles (°): V1–O1 = 2.026(1), V1–O2 = 1.600(1), V1–O3 = 2.059(1), V1–F1 = 1.905(1), V1–F2 = 2.140(1), V1–F2ⁱ = 1.9502(9); O1–V1–O2 = 97.24(6), O1–V1–F1 = 91.30(5), O1–V1–F2 = 80.97(4), O1–V1–F2ⁱ = 86.09(4), O2–V1–O3 = 97.68(6), O2–V1–F1 = 100.67(5), O2–V1–F2ⁱ = 100.56(5), O3–V1–F1 = 91.43(4), O3–V1–F2 = 83.58(4), O3–V1–F2ⁱ = 85.69(4). Symmetry operation: $i = -x+1, -y, -z+1$; (b) the H-bonding network; (c) the π -stacking of the pyridine-N-oxide rings.

The bond lengths in this complex are consistent with the absence of O/F disorder.

2.5 Spectroscopic and Magnetic Data

Selected IR and UV/visible spectroscopic data are collected in Table 1. All the complexes show room temperature magnetic moments in the range 1.7–1.95 B.M., typical of simple d^1 systems in molecular coordination complexes. The antiferromagnetic interactions seen in some extended lattice oxide-fluoride materials. The IR spectra exhibit strong broad absorptions in the range 945–975 cm^{-1} , assigned as $\nu(V=O)$, which are similar to those in $[VOF(diimine)_2]^+$ [21]. The V^V complexes, $[VOF_3L_n]$ mostly have $\nu(V=O)$ at rather higher frequency [5], although there is some overlap – not unexpected given the different geometries and sometimes different *trans* ligands. The antisymmetric stretch of the *trans*-VF₂ units in the V^{IV} complexes occurs as a sharp band $\sim 500\text{ cm}^{-1}$, whilst in $[VOF_2(Me_3tacn)]$, the *cis*-VF₂ group exhibits two bands of similar intensity at 542, 519 cm^{-1} .

The UV-visible spectra of VO^{2+} complexes have been studied in great detail over more than sixty years [30,31], and have produced much dispute over assignments. The V=O unit is the major influence on the d-orbital energies and although the actual point group symmetries of the complexes are lower due to mixed donor sets, assignments for six-coordinate complexes are usually based upon C_{4v} symmetry, with the V=O on the z-axis, leading to a B_2 ground state (with the single electron in d_{xy}). Typically, three d-d transitions are observed at $\sim 12\,000$, $\sim 17\,000$ and $\sim 25\,000\text{ cm}^{-1}$, although the last band is sometimes partially or totally obscured by the tails from the higher energy, intense charge

transfer bands. The complexes in Table 1 and Figure 8 generally conform to this pattern, although some show evidence of splitting of the first band, which may reflect the lower symmetry present. Hence we assign the three bands in order of increasing energy as ${}^2B_2 \rightarrow {}^2E$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$.

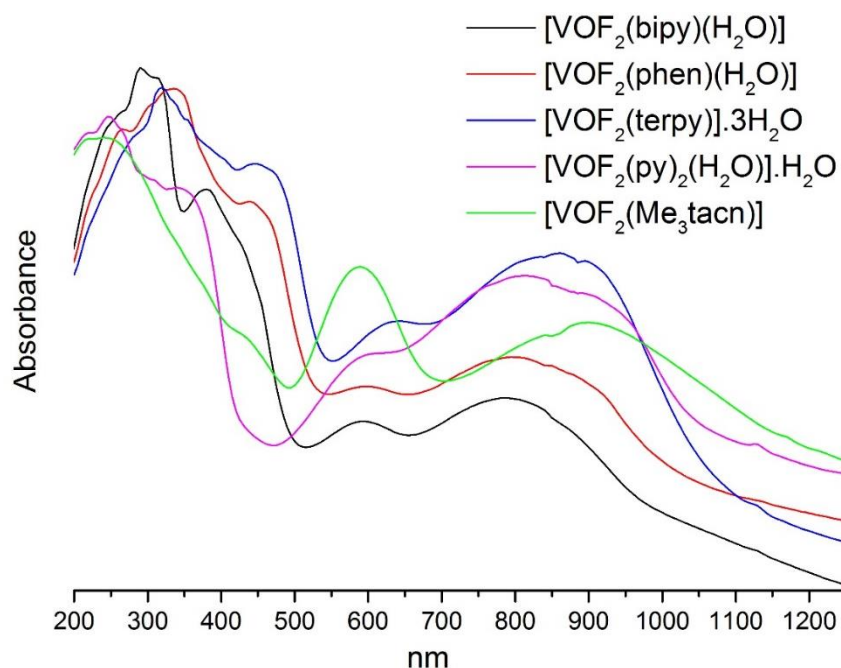


Figure. 8 UV-visible spectra of the vanadyl fluoride complexes in the solid state.

Higher energy bands (above $\sim 27\,000\text{ cm}^{-1}$) are ligand \rightarrow V charge transfer transitions. For $[\text{VOF}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ and $[\text{VOF}_2(\text{Me}_3\text{tacn})]$ the lowest energy charge transfer band is $\sim 41\,000\text{ cm}^{-1}$ and is likely to be $\text{O}_{\text{H}_2\text{O}} \rightarrow \text{V}$ and $\text{N}_{\text{Me}_3\text{tacn}} \rightarrow \text{V}$, respectively, with the $\text{F} \rightarrow \text{V}$ and $\text{O}_{\text{V}=\text{O}} \rightarrow \text{V}$ at even higher energy and not observed. For those complexes containing pyridyl ligands, $\pi \rightarrow \pi^*$ transitions associated with the aromatic rings will also be present in the near ultra-violet region, in addition to $\text{N} \rightarrow \text{V}$ charge transfers from the imines.

Table 1 Selected spectroscopic data

Compound	$\nu(\text{V}=\text{O})/\text{cm}^{-1}$ ^a	$\nu(\text{V}-\text{F})/\text{cm}^{-1}$ ^a	UV-vis/ cm^{-1} ^b	$\mu_{\text{eff}}/\text{B.M.}$ ^c
$[\text{VOF}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	945	505	42 550, 25 900, 16 610, 11 930	-
$[\text{VOF}_2(\text{terpy})] \cdot 3\text{H}_2\text{O}$	951	503	35 460(sh), 31 350, 22 320, 15 580, 11 905	1.83
$[\text{VOF}_2(\text{bipy})(\text{H}_2\text{O})]$	968	500	38 460(sh), 34 480, 26 385, 16 860, 12 770.	1.77
$[\text{VOF}_2(\text{phen})(\text{H}_2\text{O})]$	963	494	37 600(sh), 33 330, 22 880, 16 780, 12 595	1.76
$[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})]$	969	505	40 650, 29 410, 16 695, 12 300.	1.80
$[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	949	548	40 000, 27 700, 17 400, 12 500.	1.80
$[\text{VOF}_2(\text{Me}_3\text{tacn})]$	951	542, 519	41 660, 23 470(sh), 17 000, 11 100	1.93
$[\text{V}_2\text{O}_2\text{F}_4(\text{H}_2\text{O})_2(\text{pyNO})_2]$	972	522, 317	45 045, 37 880, 28 650(sh), 16 455, 12 050.	1.74 per V
$[\text{V}_2\text{O}_2\text{F}_4(\text{py})_4]$	968	480, 434	n.d.	n.d. ^d

a. Nujol mull; b. diffuse reflectance; c. 295 K, ± 0.05 B.M; d. n.d. = not determined (due to lack of sufficient bulk sample).

3. Experimental

VF_4 was obtained from Alfa and used as received. Me_3tacn was made by the literature route [32]. The other ligands were obtained from Sigma Aldrich and used as received. Hydrothermal preparations were conducted in a 23 mL Teflon reactor vessel placed in a Parr stainless steel autoclave. Infrared spectra were recorded by a Perkin-Elmer Spectrum 100 spectrometer in the range $4000\text{--}200\text{ cm}^{-1}$, and samples prepared as Nujol mulls between two CsI plates. UV/visible spectra were recorded as powdered solids, using the diffuse reflectance mode of a Perkin Elmer 750S spectrometer. Magnetic measurements were made on Johnson Matthey magnetic balance. Microanalyses were performed by London Metropolitan University. Solvents were dried by distillation from CaH_2 (MeCN or CH_2Cl_2) or Na/benzophenone ketyl (diethyl ether, toluene, n-hexane).

CARE Small amounts of HF are inevitably generated in the syntheses - due care should be taken to avoid skin contact.

3.1 X-ray experimental:

Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum ($\lambda = 0.71073$) rotating anode generator with VHF Varimax optics (70 micron focus) with the crystal held at 100 K

(N₂ cryostream). Details of the X-ray crystallographic data are given in Table 2. Structure solution and refinement were performed using SHELX(S/L)97, SHELX-2014/7 and were straightforward [33,34] H atoms were added and refined with a riding model. Crystallographic data in cif format have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and given numbers 1503653-1503661. The individual code numbers are CCDC 1503653 [VOF₂(bipy)(H₂O)]; CCDC 1503654 [VOF₂(py)₂(H₂O)]H₂O; CCDC 1503655 [V₂O₂F₄(pyNO)₂(H₂O)₂]; CCDC 1503656 [VOF₂(phen)(H₂O)]; CCDC 1503657 [VOF₂(terpy)].3H₂O; CCDC 1503658 [VOF₂(H₂O)₂].H₂O; CCDC 1503659 [VOF₂(py)₂(H₂O)]; CCDC 1503660 [V₂O₂F₄(H₂O)][pyH]₂; CCDC 1503661 [V₂O₂F₄(py)₄]. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366033, e-mail: deposit@ccdc.cam.ac.uk or on the web at <http://www.ccdc.cam.ac.uk>.

Powder X-ray diffraction (PXRD) data were collected using a Bruker D2 diffractometer with Cu-K_α radiation with the simulated PXRD patterns generated using the Bruker software [35] and the results plotted using *Origin* [36].

3.2 [VOF₂(H₂O)₂].H₂O

VF₄ (0.13 g, 1.0 mmol) was placed in a PTFE container and de-ionised water (*ca.* 5 mL) added. The PTFE container was placed in the hydrothermal autoclave and heated to 80 °C for 2 h. After cooling, the autoclave was opened and the blue solution transferred to a plastic beaker and allowed to evaporate in air. Blue solid. Yield: 0.14 g. 89%. IR (Nujol/cm⁻¹): 3600–3200, 1650 (H₂O), 945s (V=O), 505s (V–F). UV-vis (diffuse reflectance, E_{max}/cm⁻¹): 42 555, 25 900, 16 610, 11 930.

3.3 [VOF₂(2,2',6',2''-terpyridyl)]·3H₂O

VF₄ (0.195 g, 1.53 mmol), terpy (0.375 g, 1.61 mmol) and deionised water (7mL) were placed in the PTFE container to form a green solution. The container was placed inside the hydrothermal autoclave and heated at 140 °C for 5 h. After cooling, the green solid deposited was filtered off, washed with cold ⁱPrOH (5 mL), followed by diethyl ether (5 mL) and dried *in vacuo*. Green powder. Yield: 0.35 g, 67%. Required for C₁₅H₁₇F₂N₃O₄V (392.25): C, 45.91; H, 4.37; N, 10.71. Found: C, 46.02; H, 4.30; N, 10.63%. IR (Nujol/cm⁻¹): 3370–3200, 1640 (H₂O), 951s (V=O), 503s (V–F). UV-vis (diffuse reflectance, E_{max}/cm⁻¹): 35 460(sh), 31 350, 22 320, 15 580, 11 905. μ_{eff} = 1.83 B.M.

3.4 [VOF₂(2,2'-bipyridyl)(H₂O)]

VF₄ (0.127g, 1.00 mmol), bipy (0.156 g, 1.00 mmol) and deionised water (10mL) were placed in the PTFE container, which was placed inside the hydrothermal autoclave and heated at 80 °C for 12 h. After cooling a green solution and some green solid were present. The solution was evaporated in air, the residue washed with cold ⁱPrOH (5 mL), followed by diethyl ether (5 mL) and dried *in vacuo*. Green solid. Yield: 0.237 g, 85.7%. Required for C₁₀H₁₀F₂N₂O₂V (279.12): C, 43.03; H, 3.61; N,

10.04. Found: C, 42.95; H, 3.41; N, 9.92%. IR (Nujol/cm⁻¹): 3550–3400, 1606 (H₂O), 968s (V=O), 500s (V–F). UV-vis (diffuse reflectance, E_{max}/cm⁻¹): 38 460(sh), 34 480, 26 385, 16 860, 12 770. μ_{eff} = 1.77 B.M.

3.5 [VOF₂(1,10-phenanthroline)(H₂O)]

VF₄ (0.205 g, 1.615 mmol), 1,10-phenanthroline (0.291 g, 1.615 mmol) and deionised water (7 mL) was added to a PTFE container. The reaction mixture's colour was green. The Teflon container was loaded into an autoclave and then put in the oven at 140 °C for 5 hours. There was a solid at the bottom of the Teflon container which was separated from the solvent, washed with cold ⁱPrOH (5 mL) and diethyl ether (5 mL), and dried *in vacuo* resulting in a green product. Yield: 0.44g, 55 %. Required for C₁₂H₁₀F₂N₂O₂V (303.14): C, 47.55; H, 3.32; N, 9.24. Found: C, 46.02; H, 3.50; N, 8.86%. IR (Nujol/cm⁻¹): 3300br, 1620 (H₂O), 963s (V=O), 494s (V–F). UV-vis (diffuse reflectance, E_{max}/cm⁻¹): 37 600(sh), 29 670, 22 880, 16 780, 12 595. μ_{eff} = 1.76 B.M.

3.6 [VOF₂(pyridine)₂(H₂O)]·H₂O

VF₄ (0.22 g, 2.0 mmol), pyridine (4 mL) and deionised water (2 mL) were added to the PTFE container in the autoclave. The autoclave was placed in an oven at 80 °C for 1.5 h. After cooling, the solution was blue and some blue crystals had formed. The solution was transferred to a plastic beaker and allowed to evaporate in air at room temperature, whereupon more blue crystals formed. The solvent was decanted from the crystals, which were then rinsed with cold ⁱPrOH (2 mL), followed by diethyl ether (5 mL), and dried *in vacuo*. Yield: 0.155 g, 70%. Required for C₁₀H₁₄F₂N₂O₃V (299.17): C, 40.15; H, 4.72; N, 9.36. Found: C, 40.09; H, 4.53; N, 9.27%. IR (Nujol/cm⁻¹): 3390br, 1650 (H₂O), 949s (V=O), 548s, (V–F). UV-vis (diffuse reflectance, E_{max}/cm⁻¹): 40 000, 27 700, 17 400, 12 500. μ_{eff} = 1.80 B.M.

3.7 [VOF₂(pyridine)₂(H₂O)]

VF₄ (0.22 g, 2.0 mmol) was placed in a PTFE container, pyridine (4 mL) and de-ionised water (2 mL) were added and the contained was placed in the autoclave. This was then put in an oven and heated to 80 °C for 1.5 h. After cooling, the solution was blue and some blue crystals formed. The solution was transferred to a plastic beaker and dried *in vacuo*. The residue was then washed with cold EtOH (2 mL), followed by diethyl ether (5 mL). The blue solid was dried *in vacuo*. Yield: 0.155 g, 70%. IR (Nujol/cm⁻¹): 3170br, 1637 (H₂O), 969s (V=O), 504s (V–F). UV-vis (diffuse reflectance, E_{max}/cm⁻¹): 40 650, 29 410, 16 695, 12 300.

3.8 [V₂O₂F₄(pyridine)₄]

A small number of green crystals were obtained from the reaction of VF₄ (0.10 g, 0.9 mmol), pyridine (0.23 g, 2.8 mmol) and water (5 mL) at 150 °C for 5 h. These were identified by their X-ray crystal

structure as the dimer. IR (Nujol, cm^{-1}): 968s (V=O), 480s, 434m (V–F). The bulk product was a mixture.

3.9 $[\text{pyH}]_2[\text{V}_2\text{O}_2\text{F}_6(\text{H}_2\text{O})_2]$

VF_4 (0.13 g, 1.0 mmol), pyridine (0.17 g, 2.1 mmol) and deionised water (10 mL) were placed in the PTFE container, and the autoclave heated at 80 °C for 5 h. After cooling, the blue solution was transfer to a PTFE beaker and evaporated in air. The solid was washed with cold $i\text{PrOH}$ (5 mL), followed by diethyl ether (5 mL), the washings removed, and the blue solid dried in air. Yield: 0.18 g, 82%. IR (Nujol, cm^{-1}): 974 (V=O), 528sh, 485s, 435m (V–F). UV-vis (diffuse reflectance, $E_{\text{max}}/\text{cm}^{-1}$): 39 525, 34 720 (sh), 23 150, 15 480, 11 990. Pale blue crystals grew from evaporating the mother liquor.

3.10 $[\text{VOF}_2(\text{Me}_3\text{tacn})]$

$[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})]$ (0.07 g, 0.25 mmol) was dissolved in dry MeCN (5 mL) and Me_3tacn (0.05 mL, 0.25 mmol) added with stirring. The solution darkened and after about 10 mins. became deep blue. The solvent was removed in *vacuo* giving a blue solid, which was rinsed with diethyl ether (5 mL). Yield: 0.055 g, 83%. Required for $\text{C}_9\text{H}_{21}\text{F}_2\text{N}_3\text{OV}$ (276.22): C, 39.13; H, 7.66; N, 15.21. Found: C, 38.55; H, 8.80; N, 15.09%. IR (Nujol/ cm^{-1}): 951s (V=O), 541, 519 (V–F). UV-vis (diffuse reflectance, $E_{\text{max}}/\text{cm}^{-1}$): 41 495, 23 530, 16 980, 11 100. $\mu_{\text{eff}} = 1.93$ B.M.

3.11 $[\text{V}_2\text{O}_2\text{F}_4(\text{H}_2\text{O})_2(\text{pyNO})_2]$

VF_4 (0.13 g, 1.0 mmol), pyridine-N-oxide (0.57 g, 6.0 mmol), MeCN (9 mL) and deionised water (1 mL) were added to the PTFE container. The autoclave was heated at 80 °C overnight. After cooling, a green solution and blue crystals were present. The blue crystals were collected, rinsed with MeCN (2 mL) and dried *in vacuo*. Yield: 0.17 g, 79%. Required for $\text{C}_{10}\text{H}_{14}\text{F}_4\text{N}_2\text{O}_6\text{V}_2$ (436.10): C, 27.54; H, 3.24; N, 6.42. Found: C, 27.49; H, 3.35; N, 6.33%. IR (Nujol/ cm^{-1}): 3370, 1623 (H_2O), 1206 (PyO), 972 (V=O), 522s, 317m (V–F). $\mu_{\text{eff}} = 1.74$ B.M per V. UV-vis (diffuse reflectance, $E_{\text{max}}/\text{cm}^{-1}$): 45 045, 37 880, 28 650(sh), 16 455, 12 050.

4 Conclusions

A convenient synthesis for neutral nitrogen-donor ligand complexes of VOF_2 , by controlled hydrolysis of VF_4 in the presence of the ligand, has been developed. Seven examples of such N-donor complexes have been thoroughly characterised, along with one O-donor example containing pyNO. The failure to isolate complexes with other O-donors by this route probably results from their inability to compete with the water present for coordination to the vanadium centre. The hydrate, $[\text{VOF}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, has also been fully characterised for the first time. Careful control of the temperature during the hydrothermal syntheses is essential to avoid formation of V^{V} complexes or mixtures, but provided this control is applied, this is a suitable route to a range of VOF_2 complexes. It is possible that with

controlled amounts of water in an organic solvent, the route could be extended to allow complexes with O-donor ligands, or possibly even soft S- or P-donor ligands, to be isolated. This will be explored in the future.

Supplementary Data

The X-ray crystal structures of $[\text{VOF}_2(1,10\text{-phen})(\text{H}_2\text{O})]$ and $[\text{pyH}]_2[\text{V}_2\text{O}_2\text{F}_6(\text{H}_2\text{O})_2]$, and PXRD data for the complexes described in the main text. IR spectra for each of the new complexes.

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[35] Bruker AXS. DIFFRAC.EVA 2.1, Bruker AXS 2010-2012.

[36] *Origin*, OriginLab Corporation (2016), Northampton, MA 01060, U.S.A.

Table 2 X-ray crystallographic data ^{a,b}

Compound	[VOF ₂ (OH ₂) ₂]·H ₂ O	[VOF ₂ (py) ₂ (H ₂ O)]
Formula	F ₂ H ₆ O ₄ V	C ₁₀ H ₁₂ F ₂ N ₂ O ₂ V
Formula weight	156.97	281.16
Crystal system	Tetragonal	Monoclinic
Space group	<i>P4/n</i> (85)	<i>C2/c</i> (15)
<i>a</i> / Å	7.7624(1)	13.1275(13)
<i>b</i> / Å	7.7624(1)	10.5430(10)
<i>c</i> / Å	3.9085(1)	8.0936(4) 8.2083(5)
α / deg	90	90
β / deg	90	94.253(6)
γ / deg	90	90
<i>U</i> / Å ³	235.51(1)	1132.9(2)
<i>Z</i>	2	4
μ (Mo-K α)/mm ⁻¹	2.068	0.893
<i>F</i> (000)	154	572
Total no. reflections	3740	2895
Unique reflections	235	1108
<i>R</i> _{int}	0.033	0.050
No. of parameters, restraints	19, 0	80, 0
<i>R</i> ₁ ^b [<i>I</i> _o > 2σ(<i>I</i> _o)]	0.058	0.048
<i>R</i> ₁ (all data)	0.058	0.062
w <i>R</i> ₂ ^b [<i>I</i> _o > 2σ(<i>I</i> _o)]	0.134	0.093
w <i>R</i> ₂ (all data)	0.134	0.010

^a Common items: temperature = 100 K; wavelength (Mo-K α) = 0.71073 Å; θ (max)= 27.5°;

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$

Table 1 Continued

Compound	[VOF ₂ (terpy)] · 3H ₂ O	[VOF ₂ (bipy)(H ₂ O)]
Formula	C ₁₅ H ₁₇ F ₂ N ₃ OV	C ₁₀ H ₁₀ F ₂ N ₂ O ₂ V
Formula weight	392.26	279.14
Crystal system	Monoclinic	Monoclinic
Space group (no)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i> / Å	10.369(3)	8.4634(5)
<i>b</i> / Å	9.639(3)	7.0925(4)
<i>c</i> / Å	16.122(5)	19.638(1)
α / deg	90	90
β / deg	100.077(6)	98.842(5)
γ / deg	90	90
<i>U</i> / Å ³	1586.5(8)	1164.8(1)
<i>Z</i>	4	4
μ (Mo-K α)/mm ⁻¹	0.674	0.868
<i>F</i> (000)	804	564
Total no. reflections	9783	11405
Unique reflections	3103	2043
<i>R</i> _{int}	0.044	0.049
No. of parameters, restraints	223, 0	155, 0
<i>R</i> ₁ ^b [<i>I</i> _o > 2 σ (<i>I</i> _o)]	0.035	0.065
<i>R</i> ₁ (all data)	0.045	0.079
w <i>R</i> ₂ ^b [<i>I</i> _o > 2 σ (<i>I</i> _o)]	0.086	0.119
w <i>R</i> ₂ (all data)	0.091	0.123

Table 1 Continued

Compound	[VOF ₂ (py) ₂ (H ₂ O)].H ₂ O	[V ₂ O ₂ F ₄ (py) ₄]
Formula	C ₁₀ H ₁₄ F ₂ N ₂ O ₃ V	C ₂₀ H ₂₀ F ₄ N ₄ O ₂ V ₂
Formula weight	299.17	526.28
Crystal system	Monoclinic	Monoclinic
Space group (no)	<i>P</i> 2 ₁ (4)	<i>P</i> 2 ₁ / <i>c</i> (14)
<i>a</i> / Å	7.2724(3)	7.0183(4)
<i>b</i> / Å	11.2664(4)	9.9954(4)
<i>c</i> / Å	8.0936(4)	15.2215(8)
α / deg	90	90
β / deg	115.839(5)	96.333(5)
γ / deg	90	90
<i>U</i> / Å ³	596.84(5)	1061.28(9)
<i>Z</i>	2	2
μ (Mo-K α)/mm ⁻¹	0.859	0.941
<i>F</i> (000)	306	532
Total no. reflections	6546	9612
Unique reflections	2109	3488
<i>R</i> _{int}	0.041	0.037
No. of parameters, restraints	173, 1	145, 0
<i>R</i> ₁ ^b [<i>I</i> _o > 2 σ (<i>I</i> _o)]	0.043	0.035
<i>R</i> ₁ (all data)	0.049	0.046
w <i>R</i> ₂ ^b [<i>I</i> _o > 2 σ (<i>I</i> _o)]	0.101	0.084
w <i>R</i> ₂ (all data)	0.105	0.090

Table 1 Continued

Compound	[V ₂ O ₂ F ₄ (H ₂ O) ₂ (pyNO) ₂]
Formula	C ₁₀ H ₁₄ F ₄ N ₂ O ₆ V ₂
Formula weight	436.11
Crystal system	Triclinic
Space group (no)	<i>P</i> -1 (2)
<i>a</i> / Å	7.1260(3)
<i>b</i> / Å	7.1626(4)
<i>c</i> / Å	8.6624(4)
α / deg	82.772(4)
β / deg	79.918(4)
γ / deg	60.977(5)
<i>U</i> / Å ³	380.21(4)
<i>Z</i>	1
μ (Mo-K α)/mm ⁻¹	1.306
<i>F</i> (000)	218
Total no. reflections	6525
Unique reflections	1485
<i>R</i> _{int}	0.029
No. of parameters, restraints	110, 0
<i>R</i> ₁ ^b [<i>I</i> _o > 2σ(<i>I</i> _o)]	0.022
<i>R</i> ₁ (all data)	0.025
w <i>R</i> ₂ ^b [<i>I</i> _o > 2σ(<i>I</i> _o)]	0.056
w <i>R</i> ₂ (all data)	0.057

SUPPLEMENTARY INFORMATION

Complexes of vanadium(IV) oxide difluoride with neutral N- and O-donor ligands

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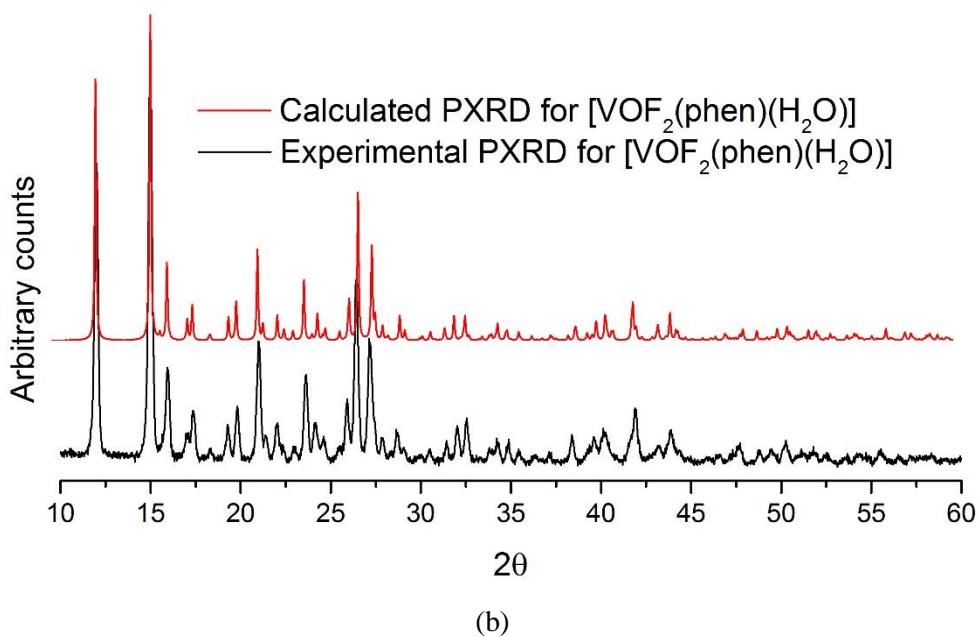
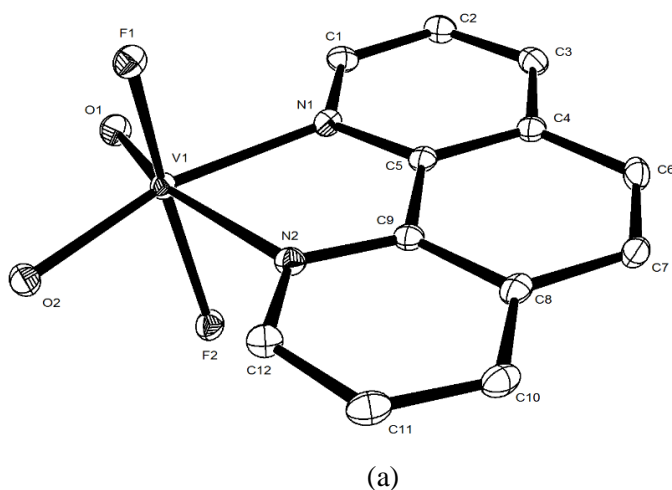


Figure S1 (a) The structure of [VOF₂(phen)(H₂O)] showing the atom numbering scheme, and

with H-atoms omitted. Selected bond lengths (Å) and angles (°): V1–O1 = 1.608(2), V1–O2 = 2.007(2), V1–F1 = 1.919(1), V1–F2 = 1.933(1), V1–N1 = 2.141(2), V1–N2 = 2.323(2); F1–V1–F2 = 158.97(5), O1–V1–O2 = 105.37(7). The structure is the same as that reported [15], but of higher precision; (b) the experimental PXRD pattern of the bulk sample and the pattern simulated from the single crystal X-ray data.

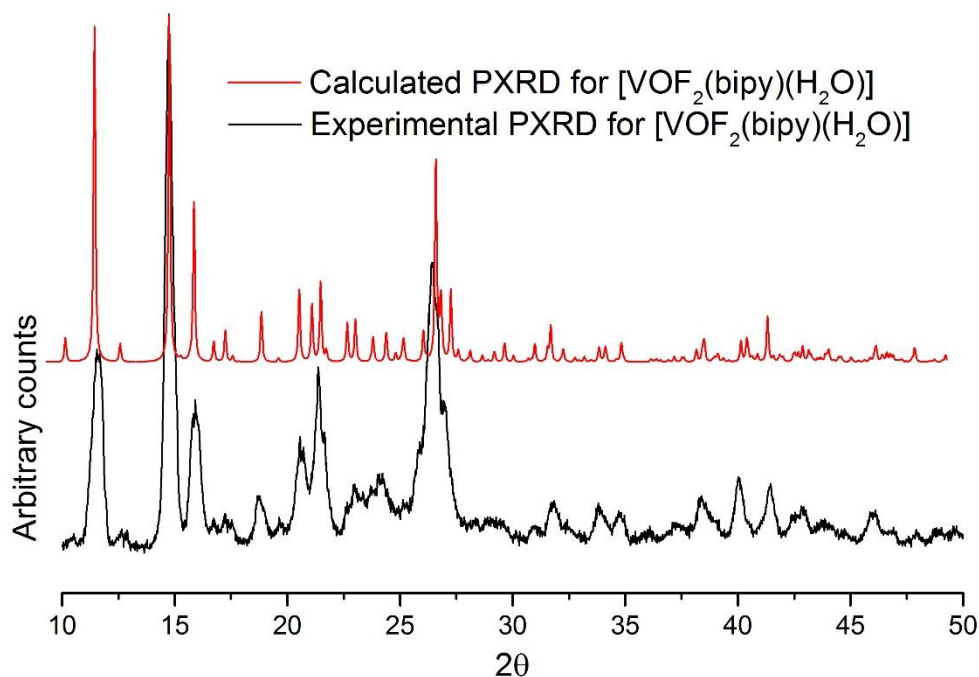


Figure S2 The experimental PXRD pattern of the bulk sample of $[\text{VOF}_2(\text{bipy})(\text{H}_2\text{O})]$ and the pattern simulated from the single crystal X-ray data. The broad lines in the experimental pattern suggest poor crystallinity, but indicate the bulk and single crystal sample are the same.

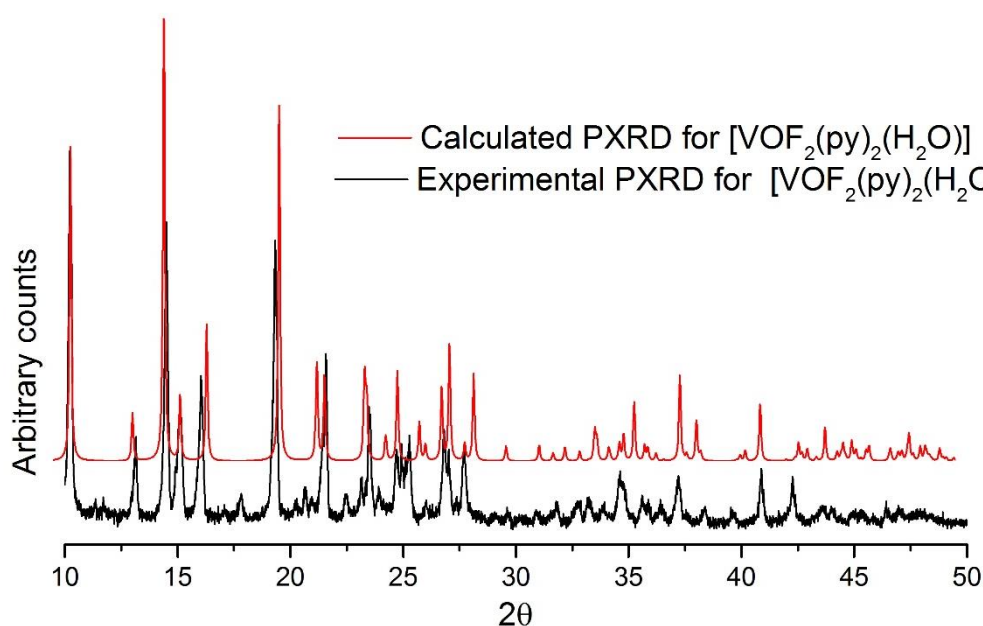


Figure S3 The experimental PXRD pattern of the bulk sample of $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})]$ and the pattern simulated from the single crystal X-ray data.

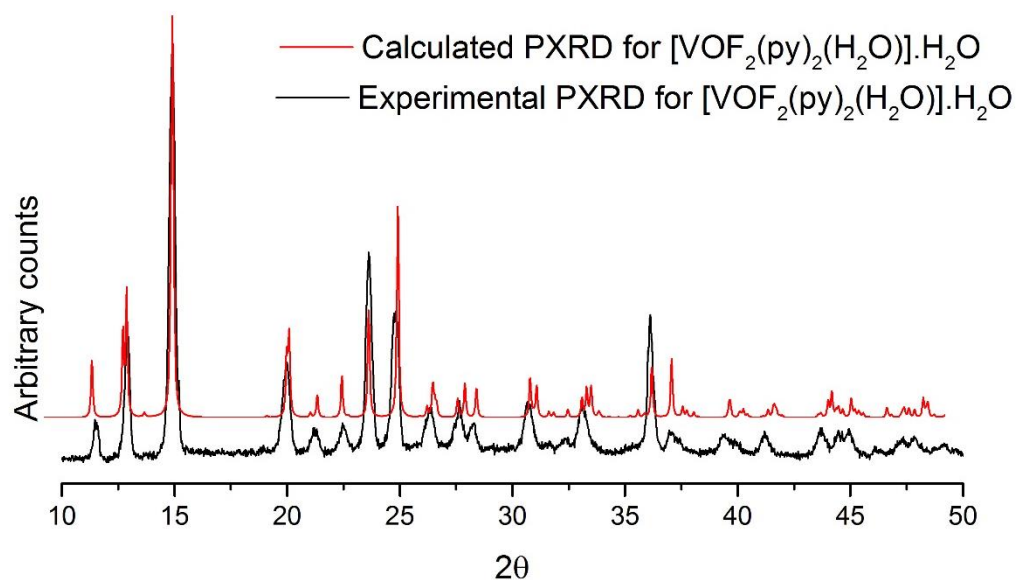


Figure S4 The experimental PXRD pattern of the bulk sample of $[\text{VOF}_2(\text{py})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ and the pattern simulated from the single crystal X-ray data.

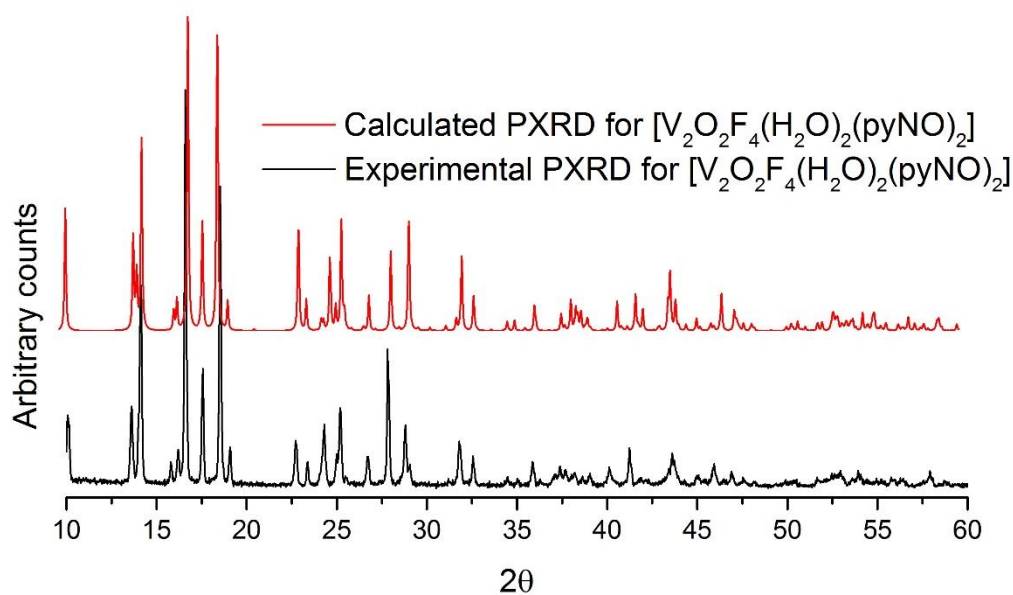
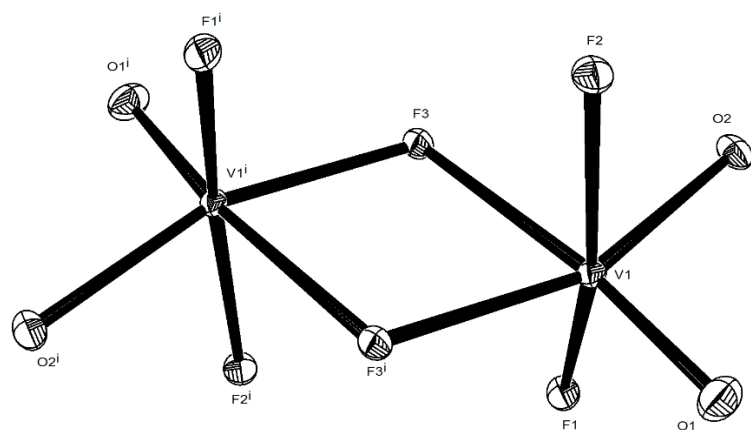
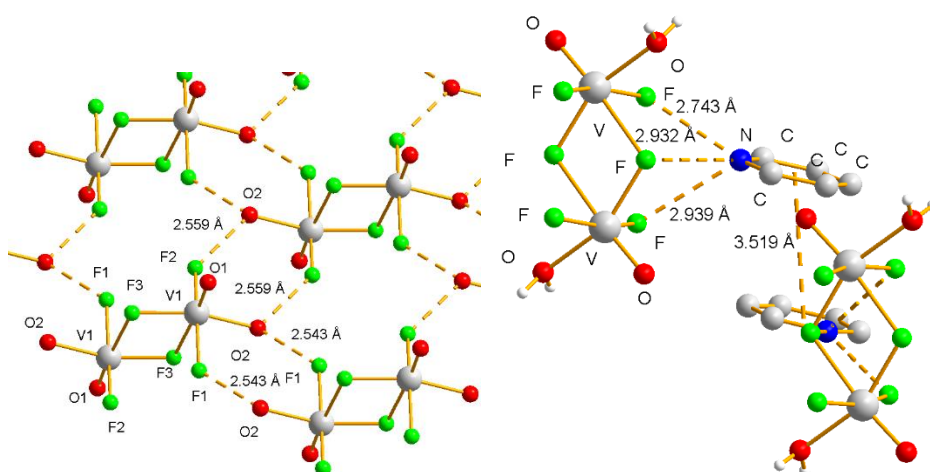


Figure S5 The experimental PXRD pattern of the bulk sample of $[\text{V}_2\text{O}_2\text{F}_4(\text{pyNO})_2(\text{H}_2\text{O})_2]$ and the pattern simulated from the single crystal X-ray data.



(a)



(b)

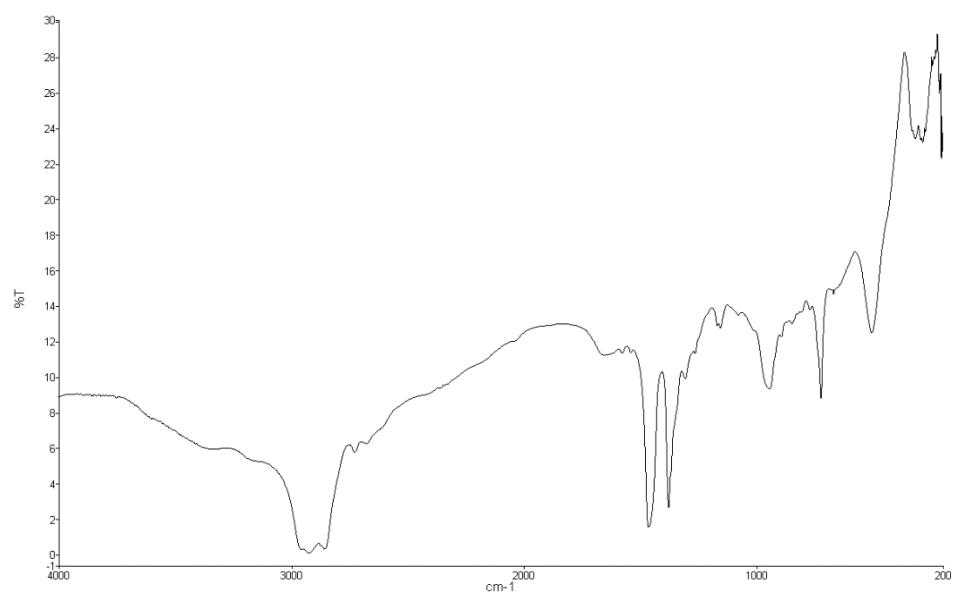
Figure S6 (a) The structure of the anion in $[\text{pyH}]_2[\text{V}_2\text{O}_2\text{F}_6(\text{H}_2\text{O})_2]$ showing the atom numbering scheme, and with H-atoms omitted. Selected bond lengths (Å) and angles (°): $\text{V1-O1} = 1.596(2)$, $\text{V1-O2} = 2.019(2)$, $\text{V1-F1} = 1.939(1)$, $\text{V1-F2} = 1.920(1)$, $\text{V1-F3} = 2.228(1)$, $\text{V1-F3}^i = 1.948(1)$; $\text{O1-V1-O2} = 102.63(8)$, $\text{F1-V1-F2} = 161.65(6)$, $\text{F3-V1-F3}^i = 73.37(5)$. Symmetry operation: $i = 1-x, -y, 1-z$; (b) the hydrogen bonding network in $[\text{pyH}]_2[\text{V}_2\text{O}_2\text{F}_6(\text{H}_2\text{O})_2]$ showing (left) the anion interactions and (right) the anion-cation interactions and the π -stacking.

Table S1 X-ray crystallographic parameters

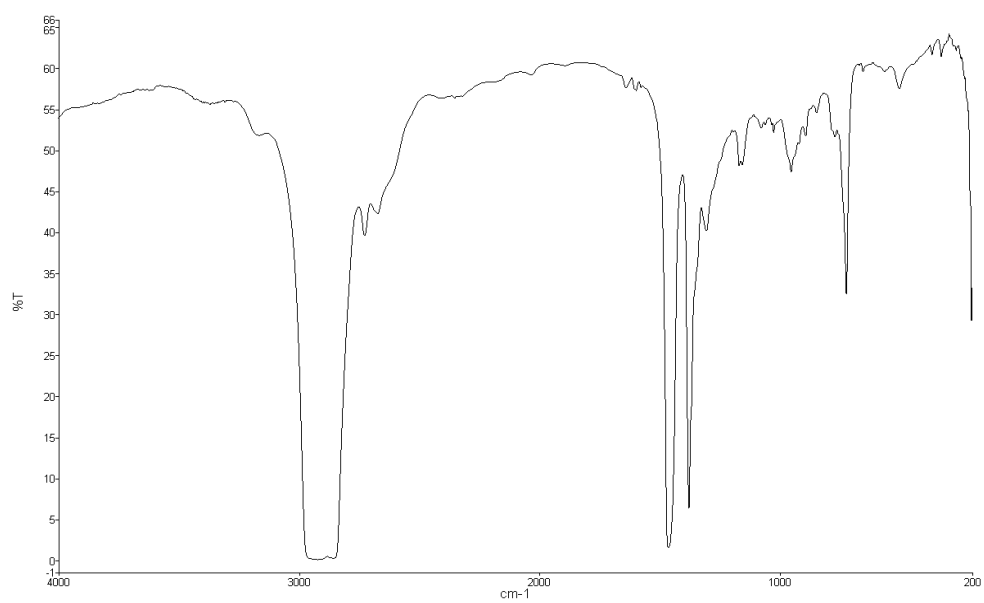
Compound	[pyH] ₂ [V ₂ O ₂ F ₆ (H ₂ O) ₂]	[VOF ₂ (phen)(H ₂ O)]
Formula	C ₁₀ H ₁₆ N ₂ F ₆ O ₄ V ₂	C ₁₂ H ₁₀ F ₂ N ₂ O ₂ V
Formula weight	444.13	303.16
Crystal system	Monoclinic	Monoclinic
Space group	C2/c (15)	<i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i> / Å	12.6567(6)	8.439(2)
<i>b</i> / Å	7.4961(4)	7.193(2)
<i>c</i> / Å	16.3739(7)	19.208(5)
α / deg	90	90
β / deg	98.839(4)	100.772(4)
γ / deg	90	90
<i>U</i> / Å ³	1535.0(1)	1145.4(5)
<i>Z</i>	4	4
μ (Mo-K α)/mm ⁻¹	1.304	0.891
<i>F</i> (000)	888	612
Total no. reflections	6660	7860
Unique reflections	1506	2240
<i>R</i> _{int}	0.039	0.050
No. of parameters, restraints	118, 0	180, 0
<i>R</i> ₁ ^b [<i>I</i> _o > 2 σ (<i>I</i> _o)]	0.031	0.030
<i>R</i> ₁ (all data)	0.048	0.041
<i>wR</i> ₂ ^b [<i>I</i> _o > 2 σ (<i>I</i> _o)]	0.068	0.073
<i>wR</i> ₂ (all data)	0.074	0.078

^a common items as in Table 1

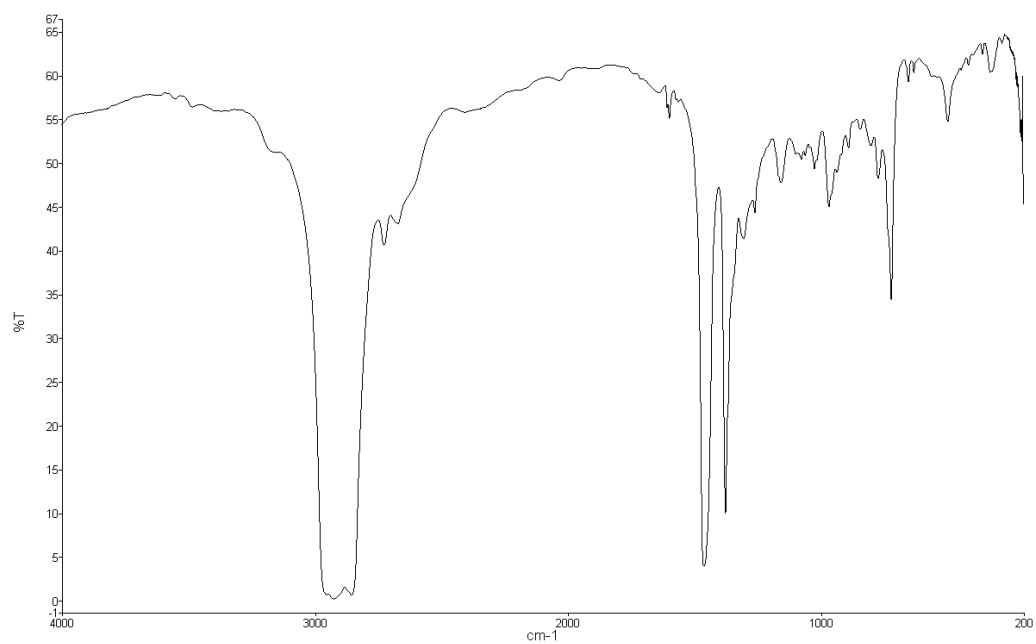
IR spectra for the new compounds (Nujol).



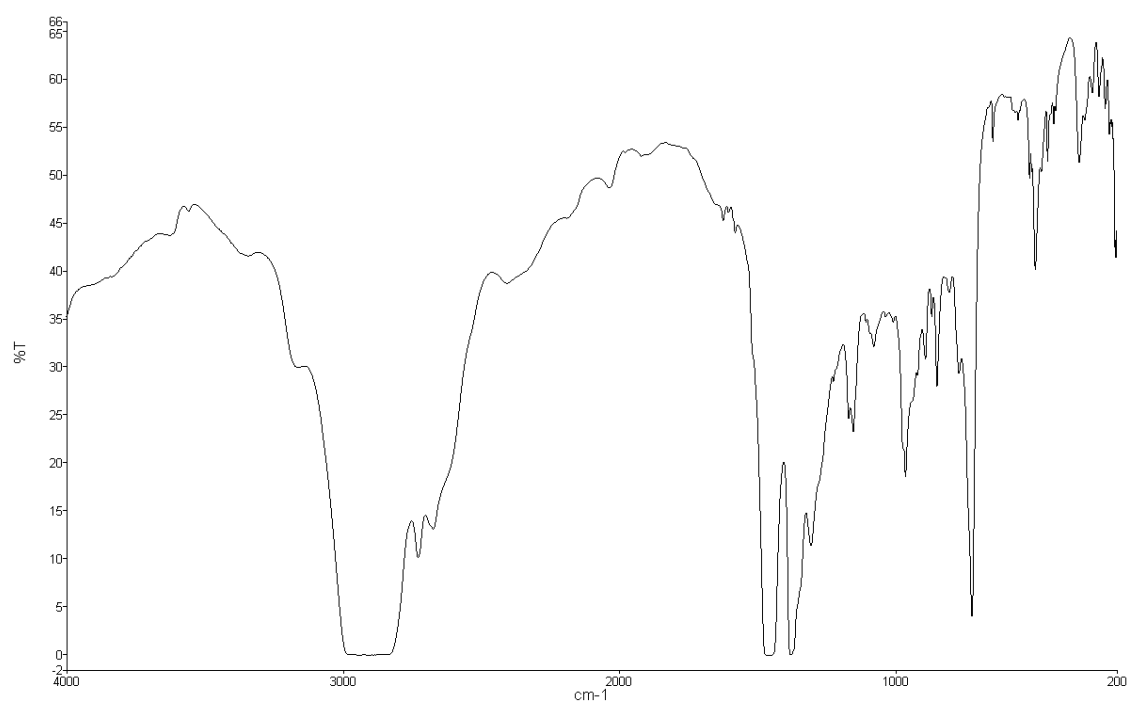
$[\text{VOF}_2(2,2',6',2''\text{-terpyridyl})]\cdot 3\text{H}_2\text{O}$



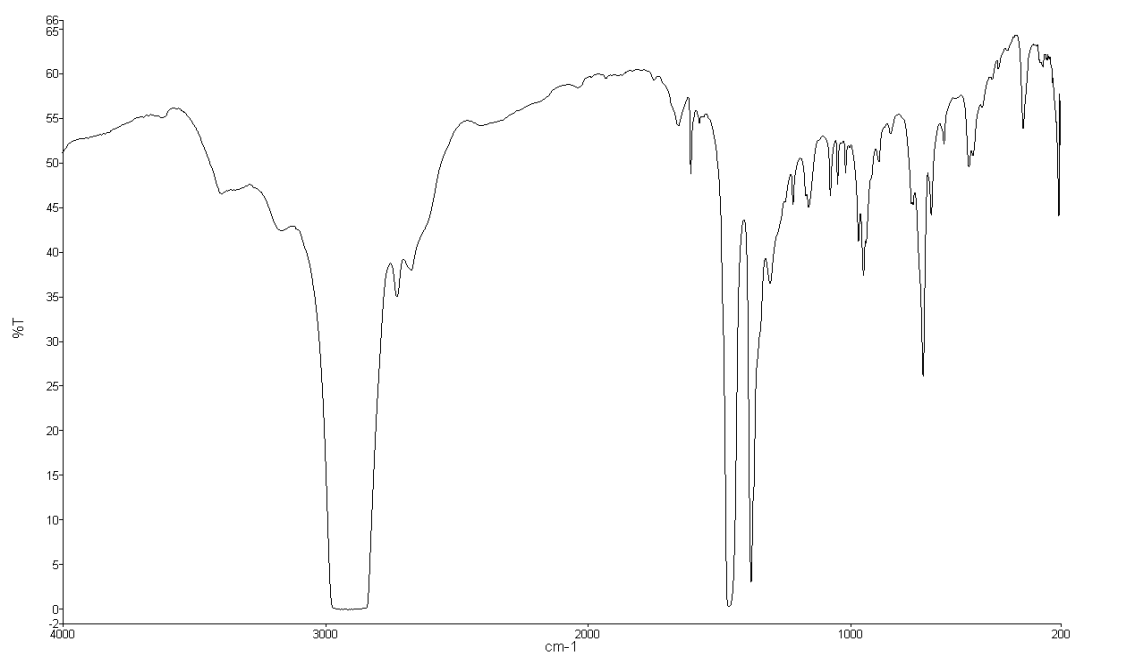
$[\text{VOF}_2(2,2'\text{-bipyridyl})](\text{H}_2\text{O})$



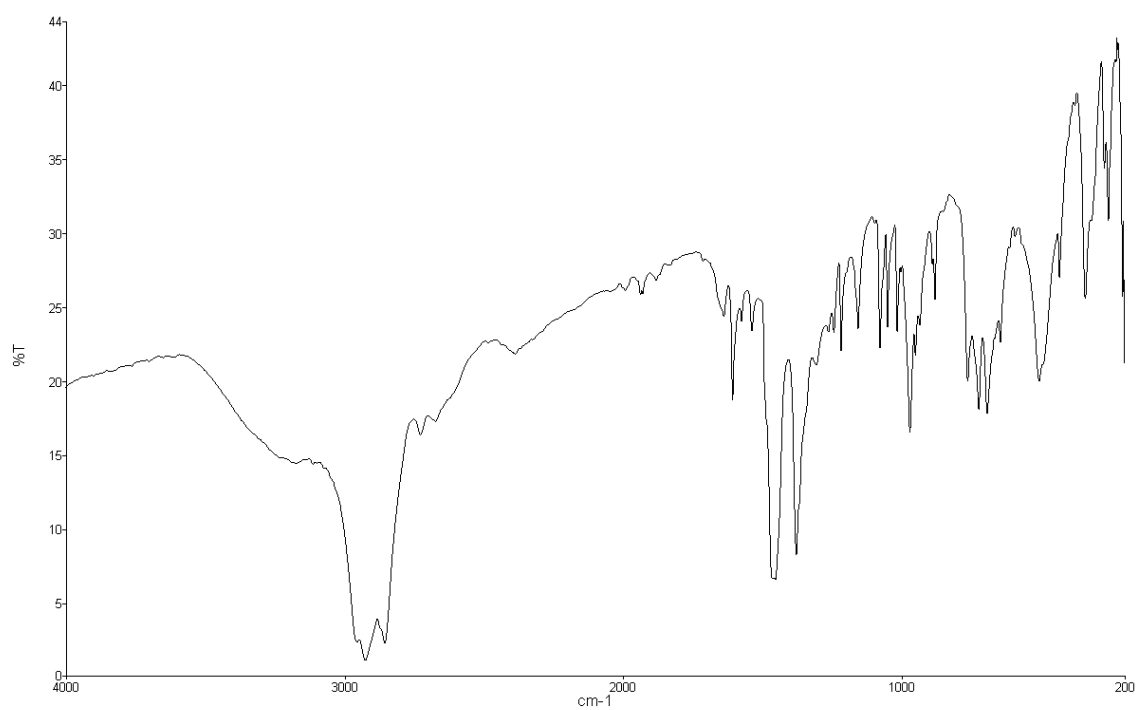
$[\text{VOF}_2(1,10\text{-phenanthroline})(\text{H}_2\text{O})]$



$[\text{VOF}_2(\text{pyridine})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$



$[\text{VOF}_2(\text{pyridine})_2(\text{H}_2\text{O})]$



$[\text{V}_2\text{O}_2\text{F}_4(\text{pyridine})_4]$

