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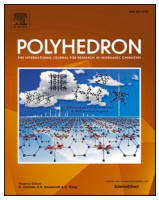

Structure of a dinickel(II)-dithiolate bridged macrocyclic complex synthesised via a novel solvent-assisted disulfide cleavage reaction

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ABSTRACT

The reaction of 2,6-diformyl-4-methylphenyl disulfide with $[Ni(tn)_3]Cl_2$ (tn = 1,3-diaminopropane), in methanol and in the presence of $NaBPh_4$ resulted in the isolation of $[Ni_2(L1)](DMF)_2(BPh_4)_2$ (**I**), (L1 = $1^5,9^5$-dimethyl-3,7,11,15-tetraaza-1,9(1,3)-dibenzenacyclohexadecaphane-2,7,10,15-tetraene-$1^2,9^2$-bis(thiolate). This reaction represents a 2-electron solvent assisted reduction of the disulfide bond to form two thiolate ligands where methanol is converted to formaldehyde and the two nickel centres remained in the + 2 oxidation state. The crystal structure of **I** showed the two nickel(II) atoms are bridged by two thiolates in a binuclear Ni_2S_2 core inside of a macrocyclic framework. The IR spectrum showed a band at 1625 cm^{-1}, assigned to the imine ν(C =N) stretch of the macrocyclic ligand, and bands at 734, 706 cm^{-1}, are assigned to the tetraphenylborate counter ions. This is the first example of solvent assisted S—S bond cleavage being used to prepare a dicompartmental macrocyclic complex.

1. Introduction

The synthesis and study of binuclear nickel-containing thiolate complexes has attracted attention [1] since the publication of the structures of the active sites of nickel-iron hydrogenase [2] and acetyl CoA synthase (ACS) [3]. However, there are synthetic difficulties associated with the coordination chemistry of thiolate containing ligands since the anionic sulfur can potentially participate in redox reactions and act as non-innocent ligands. Disulfides have been studied as a way of masking the thiolate donors to protect them from being oxidized and can coordinate to a redox active metal via a oxidative addition step, but the use of a disulfide reagent to synthesise thiolate complexes has not been widely extended [4]. However, recent advances in smart polymers have used aromatic disulfide bridges in new materials such as self-healing elastomers and epoxy vitrimer composites that show mechanochromic activity [5].

Eichhorn et al. have reported a novel Schiff-base semi-template synthetic strategy for nickel(II), copper(II) and iron(III) complexes with mixed N/S donating chelates in which a disulfide reagent was used as the source of thiolate donors [6]. This method involves the reaction of the metal complex containing coordinated primary amines chelates with 2,2′-dithiodibenzaldehyde, which has both disulfide and aldehyde functionalities, in methanol via a mechanism involving concomitant Schiff-base condensation and solvent-assisted S—S bond cleavage [6]. This is a rare example of where a disulfide group is used to introduce thiolate donors without affecting the oxidation state of the metal ions. The identity of the terminal reductant in this reaction has not been identified, but the reactions only occur in MeOH suggesting that the solvent is the reductant [7]. The cleavage is believed to proceed when the disulfide is attacked by a nucleophile, in this case the alcoholic solvent, and for cleavage to occur the LUMO orbital of the disulfide must be antibonding character with respect to the S—S bond. The attack of a nucleophile onto a disulfide bond can be catalysed by a metal, where the metal can act as an electrophile binding to the disulfide. This leaves the disulfide with some density of positive charge, enhancing attack by the nucleophile. In the case of an alcohol acting as the nucleophile, the intermediate nucleophile-sulfenyl compound can readily decompose into the thiolate and the oxidised alcohol, which for methanol would give rise to the formation of formaldehyde [7]. It has also been suggested that the metal, depending on the donor set, can help to cleave the disulfide by transferring charge density via π-back bonding into the vacant S—S σ antibonding orbital [8]. In addition, this method has been successfully used to synthesise mononuclear nickel(II) complexes that model the active site of nickel superoxide dismutase (NiSOD) [9] forming a

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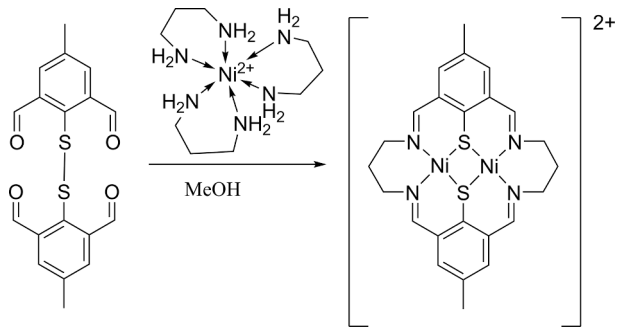

Scheme 1. The reaction of $[Ni(tn)_3]Cl_2$ with 2,6-diformyl-4-methyl disulfide in methanol.

tridentate N_2S ligand from 2,20-dithiodibenzaldehyde and N,*N*-dimethylethylenediamine [10]. This route has been further expanded to include an example of a main-group metal complex with the isolation of the indium(III) complex of the N,N'-ethylenebis(thiosalicylideneimine) ligand [11].

This semi-template method offers an alternative route for the synthesise of bicompartmental macrocyclic complexes using the 2,6-diformyl-4-methylphenyl disulfide reagent with the amine precoordinated to the metal. The *S*-(2,6-diformyl-4-methylphenyl) dimethylthiocarbamate compound has been successfully used for the synthesis of thiolate containing dicompartmental macrocyclic complexes [12]. However, the basic conditions used to cleave the thiocarbamoyl *in-situ* can lead to the generation of undesired metal hydroxides and the conversion of the thiocarbamoyl into the disulfide derivative provides a strategy for protecting the thiolate prior to reaction with the metal, which can avoid these problems. The 2,6-diformyl-4-methylphenyl disulfide reagent has been previously reported [13] although its chemistry is less well developed, but it has been used for the synthesis of a tetracopper(II) thiolate complex [13]. Here we report the synthesis of the binuclear $[Ni_2(L1)](DMF)_2(BPh_4)_2$ (**I**) compound using 2,6-diformyl-4-methylphenyl disulfide following the concomitant Schiff-base condensation and solvent-assisted S—S bond cleavage method, see Scheme 1. This is the first example of this method being used to prepare a [2+2] dicompartmental macrocyclic ligand containing a Ni_2S_2 core.

2. Experimental

2.1. General experimental

Elemental analysis has been obtained from the MicroAnalytical Laboratory at the University of Manchester, X-ray crystallography was carried out at the EPSRC National crystallography service in the Department of Chemistry at Southampton University. UV-vis spectra have been recorded on a Perkin Elmer instrument, Lambda 40 UV/VIS spectrometer. IR spectra were recorded in a KBr matrix (pellets) on a Nicolet Nexus FT-IR™ spectrometer and ^1H NMR spectra have been acquired using a 250 MHz Jeol JNM-GSX 270 spectrometer.

Methanol was dried over magnesium and 2-propanol was dried over calcium oxide. Hexane, dichloromethane, DMF and all chemical reagents have been used as purchased. Tris(1,3-diaminopropane)nickel(II) chloride, $[Ni(tn)_3]Cl_2$, [14] and *S*-(2,6-diformyl-4-methylphenyl) dimethylthiocarbamate [15] were prepared by methods previously described in the literature, with modifications [16].

2.2. X-ray crystallography

Single dark red block-shaped crystals of $[Ni_2(L1)](DMF)_2(BPh_4)_2$ recrystallised by slow vapour diffusion of methanol into a solution of the compound in DMF. A suitable crystal with dimensions 0.10×0.10×0.04 mm^3 was selected and mounted on a glass fibre with silicon oil on a Bruker Nonius FR591 – HF diffractometer. The crystal was kept at a steady $T = 120(2)$ K during data collection. The structure was solved with the ShelXT [17] solution program using dual methods and by using Olex2 1.5-alpha [18] as the graphical interface. The model was refined with ShelXL 2016/6 [19] using full matrix least squares minimisation on F^2.

2.3. Synthesis of 2,6-diformyl-4-methylphenyl disulfide.

2 mmol (502 mg) of *S*-(2,6-diformyl-4-methylphenyl) dimethylthiocarbamate and 2 mmol (80 mg) of sodium hydroxide were dissolved in dry propan-2-ol (120 mL). The mixture was refluxed for 5 h then cooled to room temperature and filtered. A solution of iodine (5 mmol, 1.26 g) dissolved in dry propan-2-ol (100 mL) was added to the filtrate until the red colour of the thiolate solution became yellow. The solution was taken to dryness under vacuo and the resulting residue was dissolved in dichloromethane (100 mL), the solution was washed with water (2×100 mL) and both aliquots of water were washed with dichloromethane (1×100 mL). All the dichloromethane aliquots were combined and dried with anhydrous sodium sulfate. Once dried, the sodium sulfate was filtered off and the solution was reduced in volume (10 mL) to give a concentrated orange solution. The final product was precipitated by adding *n*-hexane (100 mL) to the concentrated dichloromethane solution of the disulfide. The yellow solid was filtered and dried under vacuo. Yield 143 mg, 20 %. IR (KBr) Characteristic peaks are (cm^{-1}): 3055, 2923, 2857, 1690, 1558, 1406, 1383, 1277, 1221, 9225, 699, 540, 520. ^1H NMR (250 MHz, CD_2Cl_2): δ (ppm): s 10.3 (s 4H), 7.9 (s, 4H), 2.6 (s, 6H).

2.4. Synthesis of $[Ni_2(L1)](DMF)_2(BPh_4)_2$.

To a solution of 0.2 mmol (70.4 mg) of tris(propane-1,3-diamine) nickel(II) chloride in methanol (50 mL) under a nitrogen atmosphere, 0.1 mmol (35.8 mg) of 2,6-diformyl-4-methylphenyl disulfide was added. This mixture was refluxed for 4 h, the colour of the solution changed from purple to red, the reaction mixture was cooled to room temperature and 0.2 mmol (68.4 mg) of sodium tetraphenylborate was added. The mixture was allowed to stand for 1 h and the resulting red precipitate was filtered. Yield 49.4 mg, 41 %. Single crystals were obtained by slow vapour diffusion of methanol into a solution of the compound in DMF. IR (KBr) (cm^{-1}): 3053, 3033, 2998, 2982, 2923, 2855, 1625, 1579, 1538, 1478, 1427, 1372, 1320, 1266, 1183, 1101, 1070, 1032, 947, 865, 846, 734, 706, 612. Anal. Calcd. for $C_{78}H_{80}B_2N_6Ni_2O_2S_2$: C, 70.09; H, 6.03; N, 5.29. Found: C 70.85; H 5.54; N 5.10.

3. Results and discussion

The previously reported synthesis of the 2,6-diformyl-4-methylphenyl disulfide derivative involved the initial isolation of the free thiol [13] but the synthesis was revised using an *in-situ* disulfide formation method in propan-2-ol. This route had the advantage that the unprotected thiolate reagent was not exposed to potential oxidation and the use of propan-2-ol reduced the tendency for acetal formation at the formyl groups [16]. However, yields of the 2,6-diformyl-4-methylphenyl disulfide product were still low, ~20 % since this compound was highly soluble in most of the common organic solvents and difficult to recrystalise. The reaction of iodine with the thiolate was followed by a colour change, where the reaction mixture changes from red, due to the RS^- anion, to yellow, indicating that the addition of iodine can be stopped since complete oxidation of the thiolate ions had occurred leading to the formation of the disulfide group. The product was isolated as a yellow powder by adding hexane to a concentrated dichloromethane solution of 2,6-diformyl-4-methylphenyl disulfide. The IR spectrum was similar to the previous reported spectrum showing an aldehyde νC = O band at 1690 cm^{-1} and the ^1H NMR spectrum showed

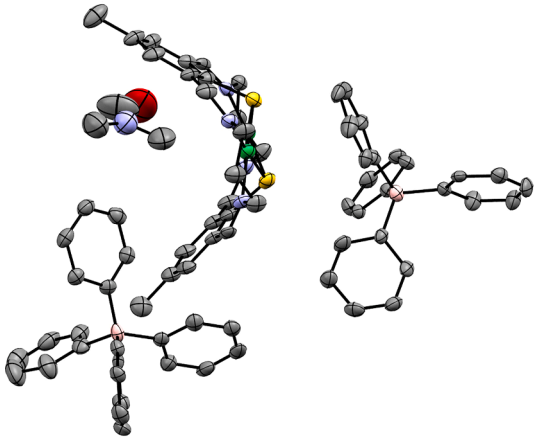

Fig. 1. ORTEP view (ellipsoids drawn to 50 % of probability) of $[Ni_2(L1)](BPh_4)_2{\cdot}DMF$.

the expected resonance peaks at 10.3 ppm, 7.9 ppm and 2.6 ppm for the aldehyde, aryl and methyl protons respectively.

The reaction of $[Ni(tn)_3]Cl_2$ with the 2,6-diformyl-4-methylphenyl disulfide in a 2:1 ratio, using methanol as solvent in the presence of $NaBPh_4$, see Scheme 1, resulted in the formation of a red solution. This indicated that the cleavage of the disulfide had taken place via the reduction of the S—S bond by two electrons from the oxidation of the methanol to formaldehyde and the resulting thiolates bonding to two nickel(II) ions in a Ni_2S_2 core. The crude product was isolated from the reaction mixture as a dark red air stable powder with tetraphenylborate present as the counter anions, which showed low solubility in most common organic solvents except DMF. The IR spectrum of the product exhibited an imine ν(C═N) band at 1625 cm^{-1}, resulting from a Schiff-base condensation between the aldehyde groups of 2,6-diformyl-4-methylphenyl disulfide and the precoordinated amine groups in $[Ni(tn)_3]Cl_2$ to form the [2+2] dicompartmental macrocyclic ligand via a novel semi-template reaction. The bands at 734, 706 cm^{-1} were assigned to the tetraphenylborate counter anions due to the mono-substituted aromatic out-of-plane C—H bending motions of the phenyl rings. The UV-vis spectrum showed a S(3pπ) → Ni(3d) charge transfer band at 523 nm and the position of this band was consistent with the value reported for the similar dinuclear Ni_2S_2 complexes [16,20] and elemental analysis of the product confirmed the $C_{78}H_{80}B_2N_6Ni_2O_2S_2$ formula of the compound.

Red crystals suitable for single crystal X-ray diffraction were obtained by slow vapour diffusion of methanol into a solution of **I** in DMF and the dark red block crystals belonged to the triclinic crystal system in the *P*-1 (# 2) space group [21]. The crystal structure revealed that the Schiff-base macrocycle has been formed where two thiolate groups bridged two nickel(II) ions with two BPh_4^- anions and two molecules of DMF present, although one of the molecules is too disordered and has been masked using PLATON/SQUEEZE protocols, see Fig. 1. All non-hydrogen atoms were refined anisotropically, hydrogen atom positions were calculated geometrically and refined using the riding model.

This type of dicompartmental macrocyclic complex with a Ni_2S_2 core has been previously reported, by Schröder et al. with hexafluorophospate counter anions [20], and Brooker et al with perchlorate counter anions [16], synthesied using transmetallation of the zinc macrocycle and a template reaction with nickel(II) ions respectively. This dithiophenolate-bridged macrocyclic complex has also been prepared with perchlorate anions from the reaction of Ni(pftp) (pftp = *N,N*-Propane-1,3-diyl(6-formyl-4-methyl-2 methyliminatothiophenolato) with 1 equivalent of $Ni(ClO_4)_2$ and 1,3-diaminopropane in methanol/DMF [22]. However, this is the first example where this type of macrocyclic complex has been prepared from the solvent assisted cleavage of a disulfide and crystallised with tetraphenylborate counter

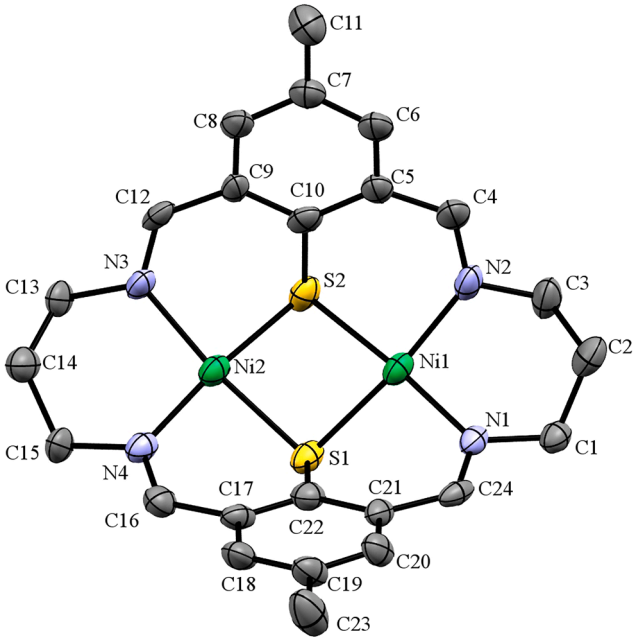

Fig. 2. ORTEP view of $[Ni_2(L1)]^{2+}$ (ellipsoids drawn to 50 % of probability) with numbering scheme. Selected bond lengths (Å) and angles (°): Ni1-N1, 1.925(5); Ni1-N2, 1.924(7); Ni2-N3, 1.898(5); Ni2-N4, 1.920(6); Ni1-S2, 2.159(2); Ni1-S1, 2.170(2); Ni2-S1, 2.158(2); Ni2-S2, 2.162(2); S1-C22, 1.768 (6); S2-C10, 1.789(8); N1-C24, 1.284(9); N2-C4, 1.29(1); N3-C12, 1.29(1); N4-C16, 1.281(8); N4-C15, 1.487(9); N1-Ni1-N2, 94.4(2); N1-Ni1-S2, 174.2(2); N2-Ni1-S2, 91.4(2); N1-Ni1-S1, 92.3(2), N2-Ni1-S1, 173.2(2); S2-Ni1-S1, 81.94 (7); N3-Ni2-N4, 93.9(2); S1-Ni2-S2, 82.15(7); Ni2-S1-Ni1, 92.93(8); C10-S2-Ni1, 100.5(2); C10-S2-Ni2, 100.4(2); Ni1-S2-Ni2, 93.14(7).

Table 1
A comparison of selected distances (Å) and angles (°) for the dinickel macrocycles $[Ni_2(L1)]^{2+}$.

	$[Ni_2(L1)](DMF)_2(BPh_4)_2$	$[Ni_2(L1)](DMF)_2(PF_6)_2$	$[Ni_2(L1)](ClO_4)_2$
Ni-S	2.158(2)-2.170(2)	2.171–2.181	2.150–2.168
Ni-N	1.898(5)-1.925(5)	1.906–1.927	1.891–1.918
C—S—Ni	100.4(2)-101.9(2)	99.3–101.6	101.3–102.2
Ni · · ·Ni	3.138(1)	3.163	3.141–3.150
S · · ·S	2.838(3)	2.87	2.83–2.85
Ni · · ·O	4.940(6)	2.64	2.71
	7.104(6)		2.76

anions. The structure showed that both nickel(II) ions were in a square planar geometry surrounded by two bridging thiolates and two imine *N*-donors with the nickel atoms being 0.016(2) and 0.039(3) Å out of the N_2S_2 plane, see Fig. 2. The macrocyclic ligand displayed a distinctive bowed shape analogous to the previously reported structures [16,20], where the planes of the phenyl rings intersect each other at 76.6(2)°, and the N_2S_2 planes intersect at an angle of 146.24(11)°.

The distances and angles around the coordinated nickel(II) ions are very similar to the previously reported macrocyclic complexes [16,20]. The nickel(II)-sulfur distances are between the distances observed in the previous two structures (2.158(2)-2.170(2) Å for $[Ni_2(L1)](DMF)_2(BPh_4)_2$, 2.171–2.181 Å for $[Ni_2(L1)](DMF)_2(PF_6)_2$ and 2.150–2.168 Å for $[Ni_2(L1)](ClO_4)_2$). The nickel(II)-nitrogen distances and the C—S—Ni angles are similar to those previously reported in the structures of $[Ni_2(L1)](DMF)_2(PF_6)_2$ [20] and $[Ni_2(L1)](ClO_4)_2$ [16], see Table 1. However, the nickel-nickel distance was shorter for $[Ni_2(L1)](DMF)(BPh_4)_2$ (3.138(1) Å, while for $[Ni_2(L1)](DMF)_2(PF_6)_2$ it is 3.163 Å and for $[Ni_2(L1)](ClO_4)_2$ it is 3.141–3.150 Å). Whilst these distances are short, they are too long to be considered for any weak direct metal-

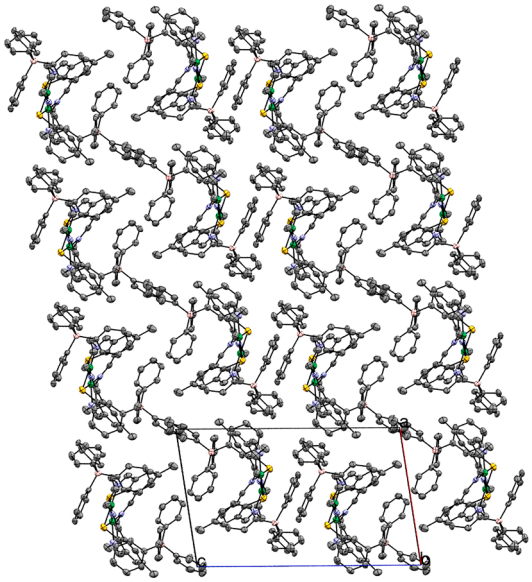

Fig. 3. View down the b crystallographic axis, DMF molecules have been removed for clarity.

metal interaction to exist between the d^8 metal atoms [23]. The sulfur-sulfur distance also lies between the distances reported for the other complexes, see Table 1. The structures of both the $[Ni_2(L1)](DMF)_2(PF_6)_2$ and $[Ni_2(L1)](ClO_4)_2$ compounds showed a weakly bound fifth axial ligand coordinating to the nickel(II) ions, either as one oxygen from a DMF molecule [20], or as one oxygen from a perchlorate [16]. A key difference in the structure for $[Ni_2(L1)](DMF)_2(BPh_4)_2$ was that the oxygen from the DMF solvent molecule was too far from the nickel(II) to be considered as a coordinating ligand (Ni-O = 4.996 Å and 7.173 Å for the non-disordered DMF molecule) and square planar geometry was observed at both nickel(II) centres in the crystal structure. In addition, a three-dimensional supramolecular framework in the crystal lattice was formed where the cationic complex molecules form a channel in the solid state with tetraphenylborate intercalated between them, see Fig. 3.

In summary, the reaction of 2,6-diformyl-4-methylphenyl disulfide with $[Ni(tn)_3]Cl_2$ resulted in the isolation of $[Ni_2(L1)](DMF)_2(BPh_4)_2$ as a red crystalline product. This is the first example of a [2+2] dicompartmental macrocyclic complex with a Ni_2S_2 core synthesised using the novel concomitant Schiff-base condensation with solvent-assisted S—S bond cleavage method.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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