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Dinuclear iron and vanadium complexes of the $N(CH_2CH_2S)_3{}^{3-}$ ligand with bridging oxide, nitride or cyanide

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Reaction of $Et_4N[Fe(NS_3)(CO)]$ [NS_3 is the ligand $N(CH_2CH_2S)_3$] with trimethylamine oxide in MeCN gives $(Et_4N)_2[\{Fe(NS_3)\}_2(\mu\text{-}O)]\cdot MeCN$ **1** with a symmetrical, bent Fe–O–Fe bridge while reaction of $Et_4N[V(NS_3)Cl]$ with sodium azide gives $Et_4N[\{V(NS_3)\}_2(\mu\text{-}N)]\cdot MeCN$ **2** with an unprecedented linear symmetrical V–N–V bridge. Reaction of $[V(NS_3)(NH_2NH_2)]$ with R_4NCN salts gives $R_4N[\{V(NS_3)\}_2(\mu\text{-}CN)]\cdot 2MeCN$ (**3**, R = Et; **4**, R = ^{n}Bu) while reaction of iron(III) acetylacetonate and Et_4NCN + Et_4NOAc with $N(SH)_3$ gives $(Et_4N)_2[\{Fe(NS_3)\}_2(\mu\text{-}CN)]\cdot MeCN$ **5**, which dissociates to $Et_4N[Fe(NS_3)(CN)]$ **6** and an uncharacterised species in methanol. The above complexes were characterised by microanalyses, IR and magnetic measurements and where appropriate by Mössbauer and ESR spectra; X-ray structural determinations were carried out on **1**, **2**, **4** and **6**.

Introduction

We have been exploring the chemistry of the tripodal NS_3 ligand $N(CH_2CH_2S)_3{}^{3-}$ (NS_3) in order to investigate the ability of metal sites carrying this ligand to mimic the behaviour of metal–sulfur sites in enzymes such as hydrogenases and nitrogenase. In the former study, some of us have shown that sulfur-bridged, dinuclear complexes containing the $\{Fe(\mu\text{-}NS_3)Ni\}$ unit model structural aspects of nickel–iron hydrogenase.[1] During the course of the latter study, we have prepared a range of mononuclear complexes containing the $M(NS_3)$ unit (M = Mo, V or Fe) that bind species on the route from N_2 to NH_3, or other small molecules such as CO or CNMe which may be inhibitors or alternative substrates to nitrogenase action.[2–4] We only obtained evidence for N_2 binding for M = V, where a transient species, possibly containing $[\{M(NS_3)\}_2(\mu\text{-}N_2)]$ was formed.[3]

Formation of dinuclear species, bridged either by the thiolate sulfurs of the NS_3 ligands,[1] by an atom such as sulfur[2] or by a small molecule such as N_2[3] is a feature of this type of system, and here we report four new dinuclear species, all anions, where two $M(NS_3)$ groups (M = V or Fe) are bridged by oxide, nitride or cyanide ligands.

Results and discussion

Oxide as the bridging ligand

Exposure to air or O_2 of the green acetonitrile or methanol solution of the iron(II) carbonyl compound $Et_4N[Fe(NS_3)(CO)]$, or of the yellow solution obtained by sodium amalgam reduction of $Et_4N[Fe(NS_3)Cl]$, results in an immediate colour change to red, and red crystals precipitate slowly. The reaction may be performed in a more controlled manner by adding dry trimethylamine *N*-oxide to an acetonitrile solution of the carbonyl compound, when X-ray quality crystals of $(Et_4N)_2[\{Fe(NS_3)\}_2(\mu\text{-}O)]$ **1** are formed in good yield; trimethylamine is generated [eqn. (1)]. Compound **1** may also be made from the reaction of the carbonyl compound with dimethyl sulfoxide, but forcing conditions (150 °C) are needed.

$$2Et_4N[Fe(NS_3)(CO)] + Me_3NO = (Et_4N)_2[\{Fe(NS_3)\}_2(\mu\text{-}O)] + 2CO + Me_3N \quad (1)$$

X-Ray analysis of **1** shows, in the anion, two $Fe(NS_3)$ units bridged by an oxo oxygen atom, with pseudo mirror symmetry relating the two units, Fig. 1. The iron atoms are five-coordinate with a distorted trigonal bipyramidal pattern having three sulfur atoms in the equatorial plane and the amino nitrogen *trans* to the bridging oxo atom in the apical sites. Selected dimensions in the anion are shown in Table 1 (together with corresponding dimensions from the other analyses). Both of the NS_3 ligands show disorder of the N-bonded methylene groups, with occupancies for the major sites of *ca.* 0.8 and 0.9 in the two units. The Fe–O distances in **1** are 1.791(2) and 1.801(2) Å and the Fe–O–Fe angle is 162.1(2)°. The major components of the two NS_3 ligands are in an eclipsed conformation relative to one another, in contrast to those in $[\{Mo(NS_3)\}_2(\mu\text{-}S)]$ which are staggered.[2]

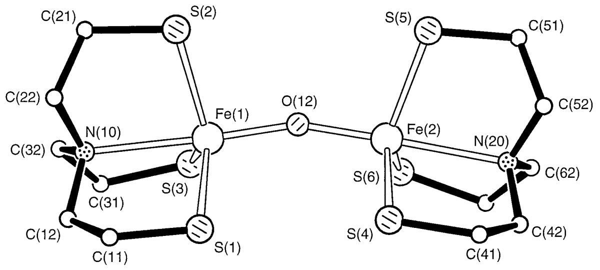

Fig. 1 The $[\{Fe(NS_3)\}_2(\mu\text{-}O)]^{2-}$ anion of complex **1**, showing the atom numbering scheme. Both NS_3 ligands are disordered in this complex; the major components are shown here. Hydrogen atoms in all the structures have been omitted for clarity.

To the best of our knowledge compound **1** is the first example of a species containing an oxo ligand bridging two iron(III) atoms in a trigonal bipyramidal configuration with each Fe ligated by three sulfurs. Several oxo-bridged dinuclear iron(III) compounds exist with square pyramidal five-coordination about the irons, rather than the trigonal bipyramidal

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Table 1 Selected molecular dimensions in the $M(NS_3)$ complexes. Bond lengths are in Ångstroms, angles in degrees. S.u's, or s.d's of mean values, are in parentheses

	In the $M(NS_3)$ moiety:			Also:				
	M–N(NS_3)	mean M–S	mean N–M–S	Z[a]	N–M–Z[a]	M–Z[a]	Other dimensions	
$(NEt_4)_2[\{Fe(NS_3)\}_2(\mu\text{-}O)]\cdot MeCN$, **1**	2.439(3)	2.344(6)	80.5(3)	O(12)	177.40(12)	1.801(2)	Fe(1)–O(12)–Fe(2)	162.1(2)
	2.440(3)	2.345(3)	80.8(2)		178.23(11)	1.791(2)		
$(NEt_4)[\{V(NS_3)\}_2(\mu\text{-}N)]\cdot MeCN$, **2**	2.253(9)	2.267(2)	84.1(2)	N(12)	178.6(3)	1.779(7)	V(1)–N(12)–V(2)	178.4(5)
	2.260(12)	2.277(1)	84.1(4)		178.1(4)	1.782(7)		
$(NBu_4)[\{V\{NS_3)\}_2(\mu\text{-}CN)]\cdot 2MeCN$, **4**	2.229(10)	2.287(8)	85.4(2)	C/N(1)	179.1(5)	2.09(2)	C/N(1)–C/N(2)	1.157(8)
	2.041(14)	2.289(10)	85.8(5)	C/N(2)	178.4(6)	2.08(2)	V(1)–C/N(1)–C/N(2)	175(2)
							V(2)–C/N(2)–C/N(1)	176(2)
$(NEt_4)[Fe(CN)(NS_3)]$, **6**	2.046(4)	2.1850(13)	88.5(2)	C(5)	179.2(3)	1.920(7)	C(5)–N(5)	1.095(8)
							Fe–C(5)–N(5)	178.7(8)

[a] Z is the apical, ligating atom, *trans* to the N atom of the NS_3 ligand.

coordination shown in **1**, including some with two ligating sulfurs per iron. These include $[\{(bme^*\text{-}daco)Fe\}_2(\mu\text{-}O)]$[5] ($H_2bme^*$-daco = *N,N′*-bis(2-methyl-2-mercaptopropane)-1,5-diazacyclooctane) (Fe–O distance 1.7798(10) Å, Fe–O–Fe angle 180°) and $[\{Fe(tsalen)\}_2(\mu\text{-}O)]$[6] ($H_2$tsalen = *N,N′*-ethylenebis(thiosalicylidineimine) (Fe–O distance 1.78(1) Å, Fe–O–Fe angle 159(3)°). There are also $(enH)_2[\{Fe(hedta)\}_2(\mu\text{-}O)]$[7,8] (en = ethylenediamine, hedta = *N*-hydroxyethylethylenediaminetriacetate) (Fe–O distances 1.79(1) and 1.80(1) Å, Fe–O–Fe angle 165.0(8)°) which **1** closely resembles (on account of the dinegative charge on the complex anion), and a series of compounds of the general formula $[\{Fe(salen)\}_2(\mu\text{-}O)]$ [salen = substituted 1,2-bis(salicylideneaminato)ethane(2−)].[9] The Fe–O distances and Fe–O–Fe angle in **1** are unremarkable compared to the values cited here.

At *ca.* 2.440 Å, the Fe–N distances in the $Fe(NS_3)$ groups of **1** are the longest we have observed in any $M(NS_3)$ complexes, and the N–Fe–S angles, in the range of 80.02(8)–81.05(8)°, are the smallest we have seen. These distortions, and the conformation of the two NS_3 ligands, do not appear to be the result of non-bonded repulsive interactions between the two NS_3 ligands, as the shortest $S \cdots S$ distance is 3.770(1) Å, larger than the sum of van der Waals radii (3.7 Å). In contrast, it has been concluded that the conformations of the series of square-pyramidal $[\{Fe(salen)\}_2(\mu\text{-}O)]$ compounds cited above, where the Fe–O–Fe angle was varied by introducing bulky substituents on to the salen rings, are determined largely by non-bonded repulsions amongst half-dimers and bridging atoms.[9]

The infrared spectrum of **1** is almost identical to that of the chloride $Et_4N[Fe(NS_3)Cl]$[4] except that (a) in the spectrum of **1** a band is found that may be assigned to ν(CN) of the acetonitrile of solvation and (b) a sharp band at 783 cm^{-1} in the spectrum of the chloride appears to be broadened and strengthened in the spectrum of **1** with its centre now at 789 cm^{-1}. If this latter band is assigned to the asymmetric Fe–O–Fe stretching frequency then its position fits reasonably well into the correlation of these stretching frequencies against the Fe–O–Fe bond angle established by Sanders-Loehr *et al.*[10] We were unable to identify any band in the IR spectrum that could be assigned to the symmetric Fe–O–Fe stretching frequency. Such a band might be expected to occur near 400 cm^{-1} but to be very weak.[10]

The Mössbauer spectrum of **1** shows a single sharp doublet in a position close to that found in the spectrum of the chloride $Et_4N[Fe(NS_3)Cl]$;[5] there is a slightly higher isomer shift (0.37 against 0.26 mm s^{-1}) and a slightly lower quadrupole splitting (0.90 against 0.98 mm s^{-1}). The magnetic moment of **1** (1.83 μ_B per Fe) corresponds to only a single unpaired electron on each iron atom at 20 °C suggesting considerable antiferromagnetic coupling through the oxygen bridge. This situation resembles that in the compounds cited above; the magnetic moment in $[\{(bme^*\text{-}daco)Fe\}_2(\mu\text{-}O)]$ is 1.32 μ_B per Fe at 20 °C and in $[\{Fe(tsalen)\}_2(\mu\text{-}O)]$ it is 1.90 μ_B per Fe. In $(enH)_2[\{Fe(hedta)\}_2(\mu\text{-}O)]$[7,8] it is 1.9 μ_B per Fe and in the $[\{Fe(salen)\}_2(\mu\text{-}O)]$ series of compounds the coupling shows a small increase as the Fe–O–Fe angle increases.

Nitride as bridging ligand

Treatment of the chloride $Et_4N[Fe(NS_3)Cl]$ with an excess of sodium azide gave a metathetical reaction yielding the corresponding azide $Et_4N[Fe(NS_3)(N_3)]$[4] [eqn. (2)]. However, applying the same treatment to its vanadium analogue $Et_4N[V(NS_3)(Cl)]$ yielded the bridging nitride $Et_4N[\{V(NS_3)\}_2(\mu\text{-}N)]\cdot MeCN$ **2** [eqn. (3)]. In acetonitrile, compound **2** reacts instantly and quantitatively with HCl to give the V^{III} salt $Et_4N[V(NS_3)(Cl)]$ and the V^{V} complex $[V(NS_3)(NH)]$ [eqn. (4)].

$$Et_4N[Fe(NS_3)(Cl)] + NaN_3 = Et_4N[Fe(NS_3)(N_3)] + NaCl \quad (2)$$

$$2Et_4N[V(NS_3)(Cl)] + 2NaN_3 = Et_4N[\{V(NS_3)\}_2(\mu\text{-}N)] + 2NaCl + N_2 + Et_4NN_3 \quad (3)$$

$$Et_4N[\{V(NS_3)\}_2(\mu\text{-}N)] + HCl = Et_4N[V(NS_3)(Cl)] + [V(NS_3)(NH)] \quad (4)$$

The anion of complex **2** has an almost linear central V–N–V angle of 178.4(5)°, and V–N distances of 1.779(7) and 1.782(7) Å. It is, as far as we are aware, the first structurally characterised symmetrical μ-nitrido complex of vanadium (Fig. 2), though $[\{V(C_{22}H_{22}N_4)\}_2(\mu\text{-}N)]BPh_4$ has been reported[11] ($C_{22}H_{22}N_4$ = dibenzotetramethyltetraaza[14]annulene). Several unsymmetrically bridged V–N–V compounds, *e.g.* the polymeric $[V(\mu\text{-}N)Cl_2(py)_2]_n$,[12] $[VBr_2(N_3)(dmpe)(\mu\text{-}N)VBr(dmpe)_2]$[13] (dmpe = 1,2-dimethylphosphinoethane) and $[VCl_3(tmeda)(\mu\text{-}N)VCl_2(tmeda)]$[14] (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) are known.

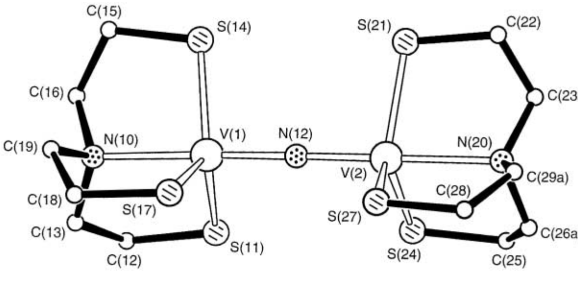

Fig. 2 The $[\{V(NS_3)\}_2(\mu\text{-}N)]^-$ anion of complex **2**. The ligand of N(20) is disordered; only the major component is shown here.

The V–N distances and N–V–S angles within the $V(NS_3)$ groups in **2** (Table 1), whilst unremarkable among $M(NS_3)$ groups generally, have V–N distances much shorter than the Fe–N distances, and N–V–S angles larger than the N–Fe–S angles within the $Fe(NS_3)$ groups in **1**. The NS_3 ligands in **2**, even though they are eclipsed with respect to each other (as in **1** but not as in [{Mo(NS$_3$)}$_2$(μ-S)]), are not pushed back from each other nearly as much as they are in **1**. Because the V–N–V bridge in **2** is almost linear the shortest S $\cdots$ S distance between S atoms in different NS$_3$ ligands in **2** is 3.884(5) Å, rather longer than in **1**.

We cannot unequivocally identify a band in the IR spectrum of **2** that can be assigned to the asymmetric V–N–V stretch. For other nitride-bridged species[15] this band falls within the range 1050–1120 cm^{-1}. In the spectrum of Et$_4$N[V(NS$_3$)(Cl)] there are three fairly strong bands within this range but none of them is significantly enhanced, nor does a strong new band appear, when **2** is formed. Neither the asymmetric nor the symmetric (Fe–N–Fe) stretching bands have been detected in the IR spectra of several compounds containing symmetric linear Fe–N–Fe cores, *e.g.* [{L(Cl$_4$-cat)Fe^{IV}}$_2$(μ-N)]Br (L = 1,4,7-trimethyl-1,4,7-triazacyclononane),[16] [{(tpp)Fe}$_2$(μ-N)]ClO$_4$ (tpp = tetraphenylporphinate)[17] and [{(pc)Fe}$_2$(μ-N)]ClO$_4$ (pc = phthalocyaninate).[18]

Both vanadium atoms in the anion of **2** are formally vanadium(IV). The magnetic moment of **2** at room temperature is consistent with the presence of one unpaired electron per vanadium atom and there is no evidence of delocalisation of these electrons between vanadium atoms. The ESR spectrum of this complex in the solid state confirmed the presence of one unpaired spin per vanadium atom, *i.e.* two unpaired spins per molecule.

This situation resembles that in the symmetrical linear oxo-bridged complex of vanadium(IV) [{V(salen)OV(salen)}$_2$-(μ-O)][BF$_4$]$_2$·MeCN,[19] which contains a symmetrical linear V$_4$O$_3$ chain, in which all the vanadium atoms are formally vanadium(IV). The central V–O–V angle is 180° and the V–O distances are 1.763(1) Å, very much as in **2**, and characteristic of a V–O (or V–N) bond order of approximately 3/2. Such complexes are expected to hold the unpaired electrons in a d$_{xy}$ orbital at right-angles to the V–N–V or V–O–V chain.[20]

The M(NS$_3$) site is thus able to form dinuclear complexes with either oxygen (**1**), nitrogen (**2**) or sulfur[2] acting as a single bridging atom. It is noticeable that there are no dinuclear complexes with a single bridging atom in the Mo, V or Fe chemistry of the related nitrogen-donor tripodal ligands such as N(CH$_2$-CH$_2$NSiMe$_3$)$_3$$^{3-}$ which are designed to accommodate a metal atom in cavities formed by three bulky trimethylsilyl groups.[21]

Cyanide as bridging ligand

Treatment of [V(NS$_3$)(N$_2$H$_4$)] with tetraethylammonium cyanide gives a product whose nature depends on the proportions of reagents used. At a ratio of 1 : 1 [eqn. (5)] the product is Et$_4$N[V(NS$_3$)(CN)][3] with a straightforward IR spectrum and magnetic moment, but at a ratio of 2 : 1 [eqn. (6)] the product is Et$_4$N[{V(NS$_3$)}$_2$(μ-CN)]·2MeCN, **3**. The corresponding reaction using Bu$_4$NCN at a ratio of 2 : 1 (a ratio of 1 : 1 would be expected to give Bu$_4$N[V(NS$_3$)(CN)] but this was not done) gives Bu$_4$N[{V(NS$_3$)}$_2$(μ-CN)]·2MeCN, **4**, whose X-ray crystal structure was determined.

$$[\mathrm{V(NS_3)(N_2H_4)}] + \mathrm{NEt_4CN} = \mathrm{Et_4N[V(NS_3)(CN)]} + \mathrm{N_2H_4} \quad (5)$$

$$2[\mathrm{V(NS_3)(N_2H_4)}] + \mathrm{NEt_4CN} = \mathrm{Et_4N[\{V(NS_3)\}_2(\mu\text{-}CN)]} + 2\mathrm{N_2H_4} \quad (6)$$

The anion of **4** is shown in Fig. 3 and has two V(NS$_3$) units bridged essentially linearly by a CN ligand. The atoms of the bridging group might lie in either direction; the sites could not be differentiated or further resolved and both are *ca.* 2.09(2) Å from the vanadium atoms. The V–N(amine) distances are however significantly different from each other, at 2.041(14) and 2.229(10) Å. The shorter of these two distances is similar to the Fe–N(amine) distance [2.046(4) Å] in Et$_4$N[Fe(NS$_3$)(CN)], compound **6** (see below) and to the Co–N(amine) distance [1.992(4) Å] in Et$_4$N[Co(NS$_3$)(CN)];[4] the V(NS$_3$) group in **4**, therefore, with this short V–N(amine) distance may be that ligated by the carbon atom of the bridging cyanide group.

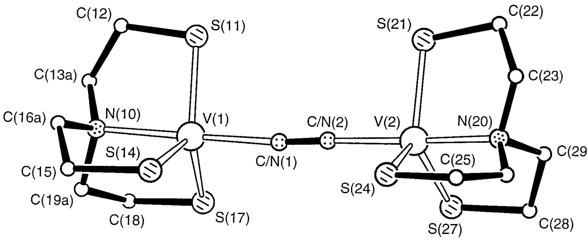

Fig. 3 The [{V(NS$_3$)}$_2$(μ-CN)]$^-$ anion of complex **4**. The ligand of N(10) is disordered; one of the two equally occupied arrangements is shown here.

The IR spectra of **3** and **4** each contain five bands in the 2300–2000 cm^{-1} region that can be assigned to CN stretching. Of these bands the two highest are attributable to the acetonitrile molecules, leaving three in the 2120–2000 cm^{-1} region to be assigned to the C–N stretch in the bridging cyanide ligand. One of these is very slightly higher than the frequency in the terminal cyanide (as is predicted[22]) but two are considerably lower. The multiplicity of bands is probably a solid state effect; it was impossible to be sure of this because **3** and **4** could not be recrystallised from methanol, acetonitrile, dichloromethane or dimethylformamide, and it was suspected that dissolution in these solvents involved dissociation, as found for compound **5** (see below).

Unlike the bridging nitride in **2**, the cyanide in **3** has a low magnetic moment at 20 °C of 2.14 μ_B (1.52 μ_B per V) indicating spin-pairing even though the M–N and M–C bonds are only formally single. Both vanadium atoms in **3** are vanadium(III) with unpaired electrons in orbitals which can interact along the chain.

In contrast to the position with vanadium, the product of the reaction between [Fe(acac)$_3$], Et$_4$NCN (with or without added Et$_4$NOAc) and N(SH)$_3$ in MeCN does not depend on the relative concentrations of cyanide and N(SH)$_3$. The only pure product isolated under various ratios of starting reagents was (Et$_4$N)$_2$[{Fe(NS$_3$)}$_2$(μ-CN)]·MeCN **5** which was obtained crystalline but the crystals were always too small for study by X-ray diffraction. Recrystallisation attempts from dichloromethane–ether and dmso–ether failed, while recrystallisation from MeOH–ether yielded a mixture of crystals and non-crystalline material. From one of these mixtures, an individual crystal suitable for an X-ray study was picked; it proved to be Et$_4$N[Fe(NS$_3$)(CN)], **6**. Attempts to make **5** (or **6**) using the reaction between [Fe(acac)$_3$], Et$_4$NCN and N(SH)$_3$ in MeOH yielded no pure products.

The formulation of **5** as stated above is based on the following data:

(a) the elemental analysis;

(b) the IR spectrum (in the solid state) which shows two bands attributable to ν(CN), one associated with the acetonitrile molecule of solvation and the other with the bridging cyanide ligand;

(c) the Mössbauer spectrum which shows two doublets (one near the position for the single doublet in Et$_4$N[Fe(NS$_3$)Cl]);

(d) the magnetic moment which at 7.47 μ_B (5.28 μ_B per Fe) is consistent with a 1 : 1 mixture of atoms of spins 5/2 (high-spin iron(III), 5.9 μ_B) and 2 (high-spin iron(II), 4.85 μ_B) with no spin-delocalisation. The iron(II) and iron(III) atoms at either end of the cyanide bridge do not exchange electrons.

The anion of **5** may be regarded as [(NS$_3$)Fe^{III}CNFe^{II}(NS$_3$)]$^{2-}$ *i.e.* a complex in which an {(NS$_3$)Fe^{III}CN)} group is acting as an N-donor ligand to an Fe^{II}(NS$_3$) site, and does not generate a strong enough ligand field to enforce spin-pairing on the iron(II) atom. This is consistent with the dissociation of **5** to **6** and an unspecified polymeric material, with the nominal empirical formula $Et_4N[Fe(NS_3)]$. The alternative formulation for the anion of **5** is $[(NS_3)Fe^{II}CNFe^{III}(NS_3)]^{2-}$ *i.e.* an $\{(NS_3)Fe^{II}(CN)\}$ group is acting as a ligand on an $Fe^{III}(NS_3)$ site; in that case the carbon-bound CN group might be expected to enforce spin-pairing on the iron(II) atom, as happens in the compound $Et_4N[Fe(NS_3)(CO)]$[4] and in the isoelectronic $Et_4N[Co(NS_3)(CN)]$.[4]

Crystal analysis of **6** shows it to have a monomeric anion, and to be isostructural with a number of $Et_4N[M(NS_3)L]$ complexes, *e.g.* for M = Fe, L = Cl, CO; M = V, L = Cl; M = Co, L = CN. In all these complexes, the anion lies across a crystallographic mirror plane and the NS_3 ligand is thus disordered in two inverted orientations. The cations, too, are disordered over several orientations about a two-fold symmetry axis.

In the anion of **6**, (Fig. 4), with Fe^{III} at the centre, the Fe–N and Fe–S distances are amongst the shortest on record, and very similar to the corresponding dimensions in $Et_4N[Co(NS_3)(CN)]$;[4] the N–Fe–S angles, as in the Co complex but in contrast to those in complex **1**, are close to 90°.

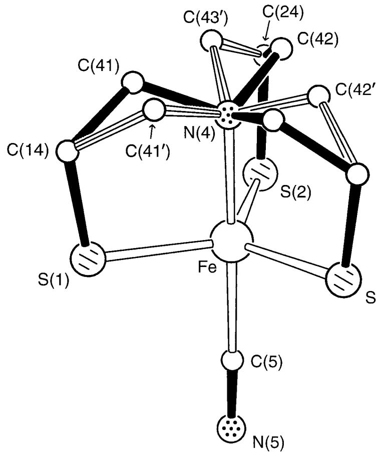

Fig. 4 The $[Fe(CN)(NS_3)]^-$ anion of complex **6**. The two arrangements of the anion, disordered about a mirror plane of symmetry, are shown.

Experimental

General

All operations were carried out under a dry dinitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled under dinitrogen from the appropriate drying agents prior to use. Starting materials were obtained from the Aldrich Chemical Co. and used without further purification unless stated otherwise. NS_3H_3 was made by a modification of the literature method[23–25] *via* tris(chloroethyl)amine hydrochloride. **CAUTION—VESICANT**: this work was carried out in enclosed Schlenk apparatus while wearing heavy duty gloves and a face mask. IR and Mössbauer spectra and magnetic measurements were made as described.[4] ESR measurements were made on a Bruker ER 200 D-SRC instrument with an Oxford Instruments ESR 910 continuous flow cryostat.

Syntheses

$(Et_4N)_2[\{Fe(NS_3)\}_2(\mu\text{-}O)]\cdot MeCN$ 1. *(Method A).* Green crystals of $Et_4N[Fe(NS_3)(CO)]$[4] (1.23 g, 3 mmol) were dissolved in MeCN (80 ml). Trimethylamine oxide (0.5 g, 6.7 mmol) in MeCN (20 ml) was added. There was effervescence and the solution turned dark red; it was kept at −20 °C overnight to give red X-ray quality crystals which were filtered off, washed with cold MeCN and diethyl ether and dried in a vacuum (1.66 g, 67%). Found: C, 43.9; H, 8.2; N, 8.7. $C_{30}H_{67}Fe_2N_5OS_6$ requires C, 44.1; H, 8.3; N, 8.6%. Mössbauer; IS 0.37, QS 0.90 mm s^{-1}. $\mu_{eff} = 2.60\ \mu_B$ (1.83 μ_B per Fe). IR 2234 [ν(CN)], 789 [ν(FeOFe)] cm^{-1}.

(Method B). $Et_4N[Fe(NS_3)(Cl)]$ (0.41 g, 1 mmol) in MeCN (20 ml) was treated with sodium amalgam (0.5%, 50 ml) giving a yellow solution which was filtered through Celite and exposed briefly to air. The solution turned red immediately and over a week a few crystals of **1** formed.

$Et_4N[\{V(NS_3)\}_2(\mu\text{-}N)]\cdot MeCN$ 2. $Et_4N[V(NS_3)Cl]$[3] (1.64 g, 4 mmol) and sodium azide (2.6 g, 40 mmol) were heated at reflux overnight in MeCN (40 ml) giving a yellow solution which was filtered hot from a white residue and gave dark needles when kept at −20 °C overnight. These were filtered off, washed with cold MeCN and diethyl ether and dried in a vacuum (0.54 g, 40%). Found: C, 39.3; H, 7.0; N, 10.3. $C_{22}H_{47}N_5S_6V_2$ requires C, 39.1; H, 7.0; N, 10.4%. $\mu_{eff} = 2.58\ \mu_B$ (1.82 μ_B per Fe). IR 2240 cm^{-1} [ν(CN)].

$Et_4N[\{V(NS_3)\}_2(\mu\text{-}CN)]\cdot 2MeCN$ 3. $[V(NS_3)(NH_2NH_2)]$[3] (1.04 g, 3.75 mmol) and Et_4NCN (0.32 g, 2 mmol) were heated at reflux in MeCN (80 ml) for 1 h giving a yellow precipitate which was filtered off hot (0.86 g, 63%). A further crop of crystals was collected from the filtrate after cooling overnight (0.18 g, 13%); both fractions were washed with cold MeCN and diethyl ether and dried in a vacuum. Found: C, 41.3; H, 6.8; N, 12.0. $C_{25}H_{50}N_6S_6V_2$ requires C, 41.2; H, 6.9; N, 11.5%. $\mu_{eff} = 2.14\ \mu_B$ (1.52 μ_B per Fe). IR 2288, 2250, 2109, 2061, 2008 cm^{-1} [ν(CN)].

$Bu_4N[\{V(NS_3)\}_2(\mu\text{-}CN)]\cdot 2MeCN$ 4. $[V(NS_3)(NH_2NH_2)]$ (0.45 g, 1.5 mmol) and $Bu^n{}_4NCN$ (0.2 g, 0.8 mmol) were heated at reflux in MeCN (50 ml) for 1 h; the solution was filtered hot, reduced to 10 ml and kept at −20 °C overnight. A few yellow X-ray quality crystals were filtered off, washed with cold MeCN and diethyl ether and dried in a vacuum (0.05 g, 8%). Found: C, 46.7; H, 7.8; N, 9.5. $C_{33}H_{66}N_6S_6V_2$ requires C, 47.1; H, 7.9; N, 10.0%. IR 2292, 2247, 2110, 2064, 2013 cm^{-1} [ν(CN)].

$(Et_4N)_2[\{Fe(NS_3)\}_2(\mu\text{-}CN)]\cdot MeCN$ 5. $[Fe(acac)_3]$ (0.71 g, 2 mmol), Et_4NCN (0.32 g, 2 mmol) and $Et_4NOAc\cdot 4H_2O$ (0.65 g, 2.5 mmol) were dissolved in acetonitrile (25 ml). NS_3H_3 (0.6 g, 3 mmol) was added giving a dark red solution which was filtered after 10 min and kept at −20 °C for 1 week to give red crystals which were filtered off, washed with MeCN and diethyl ether and dried in a vacuum (0.50 g, 60%). Found: C, 44.5; H, 7.9; N, 10.0. $C_{31}H_{67}FeN_6S_6$ requires C, 45.0; H, 8.2; N, 10.2%. Mössbauer; IS 0.33, QS 1.14 mm s^{-1} (intensity 1) IS 0.47, QS 0.56 mm s^{-1} (intensity 1) or IS 0.27, QS 0.99 mm s^{-1} (intensity 1) IS 0.55, QS 0.69 mm s^{-1} (intensity 1). $\mu_{eff} = 7.47\ \mu_B$ (5.28 μ_B per Fe). IR 2292, 1922 cm^{-1} [ν(CN)].

$Et_4N[Fe(NS_3)(CN)]$ 6. Compound **5** (0.1 g) was dissolved with stirring in methanol (5 ml), then filtered and diethyl ether (20 ml) was added to the filtrate. After 3 h a few crystals had formed, intimately mixed with some non-crystalline material. From one such mixture, a crystal was separated manually; it was washed with methanol–ether, then ether, and dried in a vacuum.

Crystal structure analyses

We describe below the crystal structure analysis of $Et_4N[\{V(NS_3)\}_2(\mu\text{-}N)]\cdot MeCN$, complex **2**; the procedures for the other crystals were very similar. Crystal data and experimental details for complexes **1**, **2**, **4** and **6** are collated in Table 2.

A crystal was mounted on a glass fibre, in air. After preliminary photographic examination, this was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated

Table 2 Crystal data and crystallographic experimental details for the complexes analysed[a]

Complex	$(NEt_4)_2[\{Fe(NS_3)\}_2(\mu\text{-}O)]\cdot MeCN$, **1**	$(NEt_4)[\{V(NS_3)\}_2(\mu\text{-}N)]\cdot MeCN$, **2**	$(NBu_4)[\{V(NS_3)\}_2(\mu\text{-}CN)]\cdot 2MeCN$, **4**	$(NEt_4)[Fe(CN)(NS_3)]$, **6**
Elemental formula	$2(C_8H_{20}N)\cdot C_{12}H_{24}Fe_2N_2OS_6\cdot C_2H_3N$	$C_8H_{20}N\cdot C_{12}H_{24}N_3S_6V_2\cdot C_2H_3N$	$C_{16}H_{36}N\cdot C_{13}H_{24}N_3S_6V_2\cdot 2(C_2H_3N)$	$C_8H_{20}N\cdot C_7H_{12}FeN_2S_3$
Formula weight	818.0	675.9	841.2	406.5
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_1/c$ (no. 14)	*Pnaa* (equiv. to no. 56)	$P2_1$ (no. 4)	*Pbcm* (no. 57)
a/Å	16.929(2)	15.587(8)	11.6163(14)	8.9215(9)
b/Å	11.2912(10)	17.728(2)	17.384(2)	14.1773(14)
c/Å	22.060(2)	24.016(2)	11.3268(13)	15.7017(13)
α/°	90	90	90	90
β/°	92.207(7)	90	100.518(10)	90
γ/°	90	90	90	90
Cell volume/Å^3	4213.7(7)	6636(4)	2248.9(4)	1986.0(3)
Z	4	8	2	4
Density (calculated)/Mg m^{-3}	1.29	1.353	1.242	1.36
F(000)	1752	2848	896	868
μ(Mo-Kα)/mm^{-1}	1.02	0.96	0.72	1.08
Crystal colour, shape	Reddish-brown square and hexagonal prisms	Large, black needles, some slightly curved	Dark orange-brown plates	Dark brown needles
Crystal size/mm	0.38 × 0.29 × 0.12	0.55 × 0.10 × 0.14	0.33 × 0.21 × 0.12	0.55 × 0.14 × 0.10
Crystal mounting	on glass fibre, coated in epoxy resin	on a glass fibre	on a glass fibre, coated in epoxy resin	on glass fibre, coated in epoxy resin
On the diffractometer:				
θ for centred reflections/°	10–11	9–10	10–11	10–11
θ range for data collection/°	1.5–25	1.5–22	1.5–20	1.5–25.0
Ranges of *h*, *k*, *l* indices	−1/20, −1/13, −26/26	−1/16, −1/18, −1/25	−11/10, 0/16, 0/10	−1/10, −1/16, −1/18
Crystal degradation (%)	11.0	21.3	6	1.3
Total reflections accepted (not including absences)	8213	4531	2819	2209
Total no. of unique reflections	7390 (R_{int} = 0.014)	4061 (R_{int} = 0.026)	2167 (R_{int} = 0.018)	1821 (R_{int} = 0.021)
Observed reflections, $I > 2\sigma(I)$	4389	1740	1677	1031
Absorption:				
Transmission factor range	0.987–0.993	0.51–0.57	0.094–0.112	0.174–0.209
Structure determined by	Direct methods, SHELXS	Direct methods, SHELXS	Direct methods, SHELXS	Isostructural with Co analogue[4]
Refinement:[b]				
Data/restraints/parameters	7390/0/419	4060/1/338	2167/14/428	1821/0/145
Goodness-of-fit, *S*, on F^2	1.06	0.966	1.082	1.021
Final *R*'s (all data),				
wR_2	0.110	0.224	0.103	0.123
R_1	0.081	0.146	0.050	0.089
Final R_1 for observed data	0.042	0.066	0.037	0.046
Reflections weighted, w^b	$[\sigma^2(F_o^2) + (0.036P)^2 + 1.15P]^{-1}$	$[\sigma^2(F_o^2) + (0.1094P)^2]^{-1}$	$[\sigma^2(F_o^2) + (0.054P)^2 + 0.473P]^{-1}$	$[\sigma^2(F_o^2) + (0.051P)^2]^{-1}$
Absolute structure parameter, *x*	—	—	−0.02(9)	—
Final difference map:				
Highest peak and hole/e Å^{-3}	0.32, −0.25	0.47, −0.26	0.30, −0.20	0.52, −0.27
Location of highest peak	close to S(6)	in disordered cations	close to cation	close to the NS_3 ligand

[a] For all analyses: temperature, $T = 293(2)$ K; wavelength, $\lambda = 0.71069$ Å. [b] Refinement of each structure: by full-matrix least-squares methods, on F_o^2, in SHELXL: in the weighting $P = (F_o^2 + 2F_c^2)/3$.

radiation) for determination of accurate cell parameters (from the settings of 25 reflections, each centred in four orientations) and for measurement of diffraction intensities.

During processing, corrections were applied for Lorentz-polarisation effects, crystal deterioration, absorption (by semi-empirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods). The structure was determined by the direct methods routines in the SHELXS program[26] and refined by full-matrix least-squares methods, on F^2's, in SHELXL.[27] Disorder was found in one of the NS_3 ligands and also in the two cation units (one of which lies about a two-fold symmetry axis, the other about an inversion centre) and in the solvent molecule. Hydrogen atoms were included in idealised positions on the ordered $N(CH_2CH_2S)_3$ ligand and on the major component of the disordered ligand; the isotropic thermal parameters of the hydrogen atoms were set to ride on the U_{eq} values of the parent carbon atoms. The non-hydrogen atoms in sites of more than 50% occupancy were refined with anisotropic thermal parameters; those in other sites were refined isotropically. Final *R*-factors are included in Table 2.

N.B. Crystals of complex **4** diffracted less strongly than the others, and the useful data were limited to $\theta_{max} = 20°$; for **4**, therefore, the ratio of the number of reflections to parameters is rather low, but we believe that the results are reliable (within the error limits specified).

Scattering factors for neutral atoms were taken from reference 28. Computer programs used in this analysis have been noted above or in Table 4 of reference 29, and were run on a DEC-AlphaStation 200 4/100.

CCDC reference numbers 169282–169285.

See http://www.rsc.org/suppdata/dt/b1/b107399k/ for crystallographic data in CIF or other electronic format.

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