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Iron, cobalt and vanadium complexes of the $N(CH_2CH_2S)_3{}^{3-}$ ligand with chloride, azide, cyanide and carbonyl co-ligands

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Reaction of $[Fe(acac)_3]$, Et_4NCl and $N(CH_2CH_2SH)_3$ (NS_3H_3) in MeCN gave $[Et_4N][FeCl(NS_3)]$ **1** and metathesis the azide $[Et_4N][Fe(N_3)(NS_3)]$ **2**, but reaction of $[Fe(acac)_3]$, R_4NOAc and NS_3H_3 in MeCN gave $[R_4N][Fe_4(NS_3)_3]$ (R = Et, **3**; Me, **4**). Complex **1** is reduced under various conditions giving $R'[Fe(NS_3)]$ ($R' = Et_4N$, **5**; Tl, **6**; N_2H_5, **7**) which probably contain sulfur-bridged $[\{Fe(NS_3)\}_n]^{n-}$ anions. Under CO, **1** is reduced to the paramagnetic $[Et_4N][Fe(NS_3)(CO)]$ **8** from which $Tl[Fe(NS_3)(CO)]$ **9** may be made by metathesis. Compound **8** reacts with metal chlorides in acetonitrile giving trinuclear $[M\{Fe(NS_3)(CO)\}_2\text{-}S,S']$ (M = Fe, **10**; Co, **11**). The above complexes were characterised by microanalysis, IR and Mössbauer spectra and magnetic measurements; crystal structure determinations were carried out on **1**, **2**, **8**, **10**, and **11**. The properties of the anions of **1** and **8** and of the hypothetical anions $[Fe(NS_3)]^-$ and $[Fe(N_2)(NS_3)]^-$ have been investigated by density functional theory calculations. Compounds **8** and **10** have $\nu(CO)$ in the range 1960–1880 cm^{-1} and model aspects of carbon monoxide binding to the cofactor of nitrogenase. Related cyanide complexes $[Et_4N][M(NS_3)(CN)]$ (M = Co, **12**; V, **13**) have been characterised, **12** by X-ray analysis.

Introduction

The central Fe atoms in the cofactor FeMoco of the iron–molybdenum nitrogenase enzyme are coordinated by three sulfides in an approximately planar environment; the molybdenum atom is also coordinated to three sulfurs as well as two oxygens from homocitrate and one histidine nitrogen[1] and it is thought that the vanadium atom in vanadium nitrogenase[2] and one iron atom in the "iron-only" nitrogenase[3] are in similar environments. The chemistry of Fe, Mo and V carrying three sulfurs (plus other ligands) (MS_3 sites) is therefore of importance in understanding the mode of action of these enzymes. Tripodal sulfur-donor ligands such as $P\{C_6H_4S\text{-}2(Ph\text{-}3)\}_3{}^{3-}$ also feature in chemistry which aims to model the Fe–S structural units of hydrogenases and of nitrile hydratases.[4]

Recently a rich chemistry of the tripodal tetradentate nitrogen-donor ligand $[N(CH_2CH_2NSiMe_3)_3]^{3-}$ (NN_3) and its analogues has been developed, including the preparation of the tris(μ-dinitrogen) complex, $[Fe\{N_2Mo(NN_3)\}_3]$, as well as the monomer $[Mo(NN_3)(N_2)]$.[5,6] This prompted us to explore the chemistry of the related tripodal NS_3 ligand $[N(CH_2CH_2S)_3]^{3-}$ (NS_3), our aim being to investigate the ability of metal sites carrying this ligand to bind species on the route from N_2 to NH_3 such as N_2H, N_2H_2 and N_2H_4 and their derivatives or alternative substrates to dinitrogen such as CO, isocyanides, cyanide, and azide. We have already reported or communicated some of our results for Mo,[7] V,[8] Fe[9] and Ni;[10] this paper presents some data for Fe, particularly pertaining to mononuclear and trinuclear carbonyl complexes.

Results and discussion

Synthesis, spectra and structures

The starting point of our investigation was to synthesize suitable precursor complexes containing the intact NS_3 ligand which would allow introduction of the desired co-ligands into the coordination sphere. In our vanadium chemistry we[8] and others[11] have used the vanadium(V) starting material $[VO(OPr^i)_3]$ to synthesize $[VO(NS_3)]$ but an iron analogue of this is obviously inaccessible. Our molybdenum starting material was $[MoO_2(acac)_2]$[7] and following this we used for iron the very soluble $[Fe(acac)_3]$. Treatment of $[Fe(acac)_3]$ with NS_3H_3 in various solvents, however, gave materials of uncertain composition.

The vanadium(III) compound $[Et_4N][VCl(NS_3)]$ is easily prepared in high yield from $[VO(NS_3)]$[8] and we therefore attempted to synthesize its iron(III) analogue from $[Fe(acac)_3]$, Et_4NCl and NS_3H_3 in MeCN. X-Ray quality crystals of $[Et_4N][FeCl(NS_3)]$ **1** were formed in good yield. Presumably the mechanism of the formation of **1** involves displacement of two bidentate acetylacetonate ligands by one tetradentate NS_3 ligand, which leaves only one coordination site on the metal as the NS_3 ligand essentially forces five-coordination at iron, the third acetylacetone ligand being replaced by a monodentate chloride ligand.

It was found impossible to make the corresponding bromide, iodide or cyanide by this method, but the azide $[Et_4N][Fe(N_3)(NS_3)]$ **2** was made by metathesis. **1** and **2** appear indefinitely air-stable; they have magnetic moments and Mössbauer spectral parameters consistent with their being high-spin iron(III) complexes (see Experimental section).

Compound **1** is isostructural with its vanadium analogue[8] and has a structure, Fig. 1, typical of monomeric $M(NS_3)$ complexes. The iron atom is five-coordinate with essentially trigonal bipyramidal geometry. The three thiolate sulfur atoms form the equatorial plane and the amine N atom and the chloride ligand are in the apical sites. The iron atom is displaced 0.2540(4) Å from the plane of the three S atoms towards the chloride ligand. In this anion, as in many $M(NS_3)$ complexes, there is disorder in the N-methylene groups; they are arranged with S–C–C–N torsional angles of all either *ca.* +45° or all *ca.* −45°, mirrored about a crystallographic symmetry plane; the Fe, Cl and N atoms, one S atom and its bonded C atom all

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Table 1 Selected bond dimensions in the M(NS_3)Z complexes. Bond lengths are in Ångstroms, angles in degrees. E.s.d.s are in parentheses

Complex	M–N	M–S	N–M–S	Z, M–Z	Other dimensions
1 [Et_4N][FeCl(NS_3)]	2.276(3)	2.3138(7) 2.3193(10)	83.84(4) 83.43(7)	Cl, 2.3113(11)	
2 [Et_4N][Fe(N_3)(NS_3)]	2.250(4)	2.309(2) 2.309(2) 2.3148(14)	84.3(2) 84.8(2) 84.81(10)	N(5), 2.002(5)	N(5)–N(51) 1.143(9), Fe–N(5)–N(51) 126.4(5) N(51)–N(52a) 1.17(3), N(5)–N(51)–N(52a) 171(3) N(51)–N(52b) 1.12(4), N(5)–N(51)–N(52b) 163(4)
8 [Et_4N][Fe(NS_3)(CO)]	2.035(7)	2.281(3) 2.271(2)	87.8(2) 87.72(12)	C(5), 1.716(11)	C(5)–O(5) 1.154(11), Fe–C(5)–O(5) 178.9(10)
10 [Fe{Fe(NS_3)(CO)-*S*,*S*′}$_2$]	2.052(3)	2.2677(9) 2.2564(9) 2.2139(8)	88.28(7) 87.52(7) 88.51(7)	C(5), 1.765(4)	C(5)–O(5a) 1.131(12), Fe(1)–C(5)–O(5a) 168.8(6) C(5)–O(5b) 1.22(2), Fe(1)–C(5)–O(5b) 161.4(9) Fe(2)–S(1) 2.2775(9), Fe(2)–S(2) 2.2928(10) S(1)–Fe(2)–S(2) 106.21(3), S(1)–Fe(2)–S(1′) 121.89(6) S(1)–Fe(2)–S(2′) 105.93(3), S(2)–Fe(2)–S(2′) 110.50(6) Fe(1)–S(1)–Fe(2) 71.84(3), Fe(1)–S(2)–Fe(2) 71.76(3) Fe(1) · · · Fe(2) 2.6664(4), Fe(1) · · · Fe(2) · · · Fe(1′) 157.42(4)
11 [Co{Fe(NS_3)(CO)-*S*,*S*′}$_2$]	2.059(4)	2.272(2) 2.258(2) 2.215(2)	87.88(12) 87.39(12) 88.44(12)	C(5), 1.754(7)	C(5)–O(5) 1.136(7), Fe–C(5)–O(5) 177.5(6) Co–S(1) 2.242(2), Co–S(2) 2.285(2) S(1)–Co–S(2) 106.59(6), S(1)–Co–S(1′) 122.22(9) S(1)–Co–S(2′) 106.46(6), S(2)–Co–S(2′) 107.88(9) Fe–S(1)–Co 72.49(5), Fe–S(2)–Co 71.95(5) Fe · · · Co 2.6687(7), Fe · · · Co · · · Fe′ 155.05(5)
12 [Et_4N][Co(NS_3)(CN)]	1.992(4)	2.223(2) 2.2220(11)	89.09(14) 89.21(8)	C(5), 1.885(6)	C(5)–N(5) 1.149(8), Co–C(5)–N(5) 178.6(7)

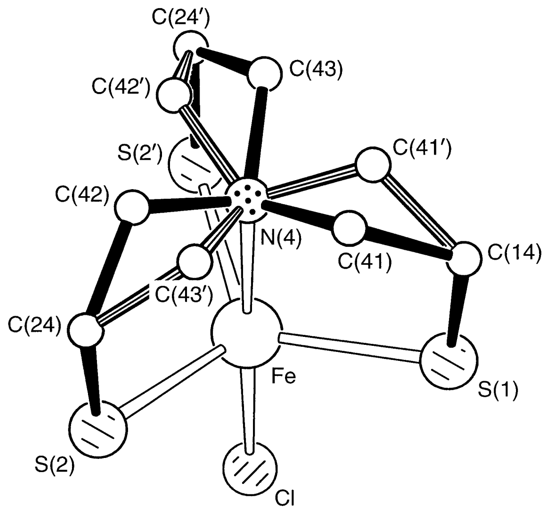


Fig. 1 View of an anion of [Et_4N][FeCl(NS_3)], **1**, showing the disorder in the N-methylene groups and the atom labelling scheme. The complexes [Et_4N][Fe(NS_3)(CO)], **8** and [Et_4N][Co(NS_3)(CN)], **12** are isostructural with **1** and have linear Fe–C–O and Co–C–N groups in place of Fe–Cl.

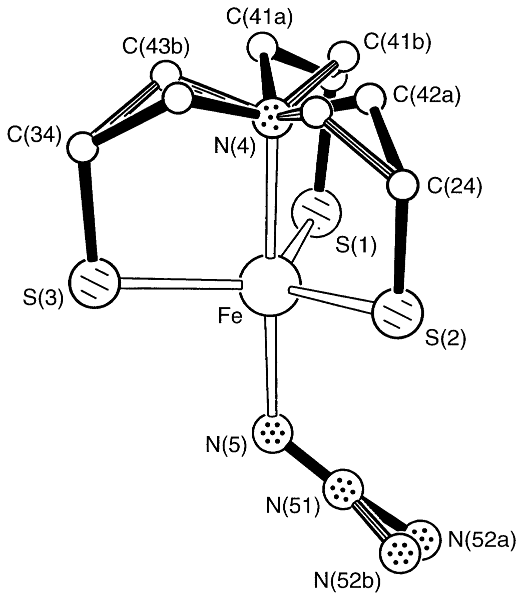


Fig. 2 The anion of the complex [Et_4N][Fe(N_3)(NS_3)], **2**.

lie in the mirror plane. Selected bond dimensions are listed in Table 1.

The anion of complex **2** has a very similar structure to that of **1**, with the same arrangement of disordered equal-occupancy methylene groups in the NS_3 ligand, but with no imposed crystallographic symmetry, Fig. 2. The azide ligand is an almost linear arrangement of three nitrogen atoms, but the outermost N was resolved into two distinct sites, 0.52(12) Å apart. The ligand is bent at the N atom next to Fe, with an Fe–N–N angle of 126.4(5)°.

We also tried the reaction of [Fe(acac)$_3$] and NS_3H_3 in MeCN in the presence of tetraethylammonium acetate. Small flaky microcrystals formed over a number of days. Several preparations had consistent microanalyses (C, H, N and Fe) and Mössbauer and IR spectra; on these bases we formulated this material as [Et_4N][$Fe_4(NS_3)_3$]·MeCN **3**, and its tetramethylammonium analogue as [Me_4N][$Fe_4(NS_3)_3$]·MeCN **4**. In this formulation all the Fe atoms in **3** and **4** are Fe^{II}, and it seems most likely that the reductant is NS_3H_3. (There was no sign in the infrared spectrum of S–H groups being present so it seems likely that any trithiolate ligands are still present in the trianionic NS_3 form.) Very large quadrupole splittings were found in the Mössbauer spectra of **3** and **4**, consistent with their formulation as iron(II) complexes, but the structure of their anions is unknown. These products could only be formed in acetonitrile; the crystals were unsuitable for X-ray analysis and attempts at recrystallisation failed.

Attempts were made to reduce complexes **1** and **2** in acetonitrile. They were not reduced by magnesium, but unlike its vanadium analogue the red **1** reacted with sodium amalgam to give a yellow solution. A yellow powder **5** (for which a satisfactory microanalysis could not be obtained) could be precipitated with diethyl ether from this yellow solution and another yellow powder of stoichiometry Tl[Fe(NS_3)] **6** could be obtained by adding thallium hexafluorophosphate to the yellow solution. These materials are very air-unstable and have identical Mössbauer spectra featuring a single doublet with a large quadrupole splitting, comparable to those of **3** and **4**. These large quadrupole splittings are consistent with the presence in **5** and **6** of similar structures containing high-spin Fe^{II}. It seems most unlikely that they are simple monomeric compounds and the most likely explanation is that both contain polymeric $[\{Fe(NS_3)\}_n]^{n-}$ anions, with Fe^{II} singly bonded *via* sulfurs to adjacent NS_3 groups (thus each iron atom is five-coordinate). **1** was also reduced by hydrazine hydrate in ethanol, giving in poor yield $[N_2H_5][Fe(NS_3)]\cdot EtOH$ **7**, which has a similar Mössbauer spectrum to those of **5** and **6**; samples of **7** were crystalline (and similar crystals could be made in methanol) but unsuitable for X-ray analysis.

Treatment of the yellow solution formed by sodium amalgam reduction of complex **1** or **2** with dinitrogen or dihydrogen gas at pressures up to 10 atmospheres gave no reaction. It might be thought that this was due to competition from the solvent acetonitrile but no sign of this molecule coordinating to iron was observed in the IR spectra or in the microanalytical figures for **6**. We prefer to suggest that sulfur bridging effectively prevented these relatively weak ligands from coordinating to iron. It is noticeable that unlike NN_3 sites, our NS_3 sites are not sterically hindered which may contribute to their tendency to form sulfur bridges.

Treatment of the yellow solution with carbon monoxide gas immediately turns the solution green and from this green crystals of $[Et_4N][Fe(NS_3)(CO)]$ **8** can be obtained by layering with ether, or a green powder $Tl[Fe(NS_3)(CO)]$ **9** can be obtained by addition of $TlPF_6$. Complex **8** is more conveniently prepared in 70% yield and gave crystals suitable for X-ray studies by treating a solution containing $[Fe(acac)_3]$ and tetraethylammonium acetate with one containing a slight excess of NS_3H_3 under an atmosphere of CO. If the solutions are equilibrated with CO before mixing the CO uptake is quantitative for Fe and, if fast stirring is employed, is complete within 20 minutes, the rate being limited by dissolution of CO in the solvent. The reductant here is again NS_3H_3. Complex **8** is moderately air-sensitive in the solid state and reacts instantly with air or O_2 when in solution; it is readily soluble in MeCN or methanol. It has a strong band at 1910 cm^{-1} in its IR spectrum (in solution in acetonitrile) attributable to $\nu(CO)$. In the solid state this band occurs at 1885 (for **8**) and 1906 cm^{-1} (for **9**). The Mössbauer spectra of both **8** and **9** show one doublet and the magnetic moments are characteristic of an $S = 1$ state (see Experimental section). As far as we are aware there are two other examples of paramagnetic CO complexes of iron, $K[Fe\{N(CH_2CONPr^i)_3\}(CO)]$[12] and $[Et_4N][Fe\{P[C_6H_3S\text{-}2\text{-}(Ph\text{-}3)_3\}(CO)]$,[4] both of which have $S = 1$ but both have $\nu(CO)$ at 1940 cm^{-1}, considerably higher than that of **8**. The $Fe(NS_3)$ site in our complexes is more electron releasing to CO than are the corresponding iron sites in the other complexes.

Crystals of complex **8** are isostructural with those of **1** and the anions are as in Fig. 1 but with a linear Fe–C–O group in place of Fe–Cl. In the carbonyl **8** the iron atom is only 0.0893(11) Å out of the S_3 plane and the Fe–N distance (2.035(7) Å) and the average Fe–S distance (2.276(5) Å) are shorter than the corresponding distances in the chloride **1** (2.276(3) and 2.316(3) Å respectively), despite the higher formal oxidation state of the metal in **1**. This is probably a consequence of the higher spin state of **1** and electron withdrawal by CO in **8**. It results in a distortion of the NS_3 ligand; the mean S–Fe–N angle is 87.74(4)° in **8** and 83.7(2)° in **1**.

Evidence for sulfur bridging in our systems and for its positive use in a controlled synthesis comes from the interaction of complex **8** with iron(II) chloride solvates. This produces the dark green paramagnetic Fe_3S_4 linear cluster $[Fe\{Fe(NS_3)(CO)\text{-}S,S'\}_2]$ **10** which has a Mössbauer spectrum consistent with the presence of two different iron sites at a ratio of 2:1. The infrared spectrum in the solid state is also dependent on the solvent from which it is precipitated; from acetonitrile, $\nu(CO)$ occurs at 1961 and 1952 cm^{-1} while from dmso or dmf it occurs at 1937 cm^{-1}. All the iron atoms in **10** are formally in oxidation state 2, but it has $\mu_{eff} = 1.54\ \mu_B$ at 295 K, showing considerable electron coupling. Results of variable-temperature magnetic studies on **10** (as well as on **11**, see below), and on other trinuclear species containing nitrosyl or isocyanide co-ligands as well as NS_3 ligands, will be reported separately.

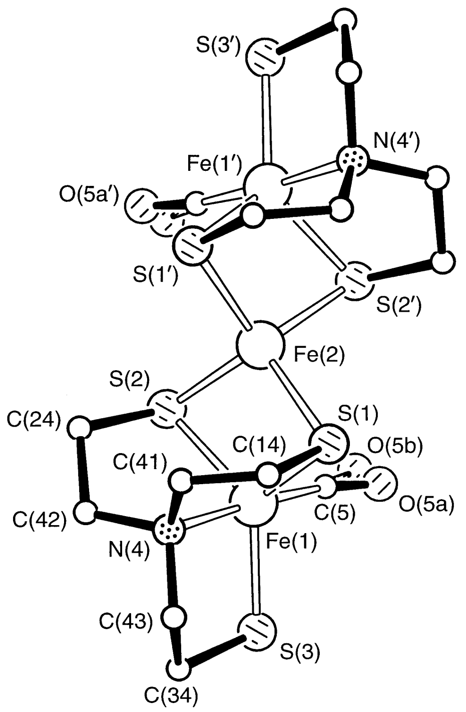


Fig. 3 The complex $[Fe\{Fe(NS_3)(CO)\text{-}S,S'\}_2]$, **10**, viewed down the twofold symmetry axis. Complex **11**, $[Co\{Fe(NS_3)(CO)\text{-}S,S'\}_2]$, is essentially identical with a cobalt atom replacing the central Fe; there is no disorder in the carbonyl ligands of **11**.

The discovery of complex **10** prompted us to search for analogues with other central metals. We found that **8** reacts with cobalt chloride solvates to give a cobalt–diiron analogue $[Co\{Fe(NS_3)(CO)\text{-}S,S'\}_2]$ **11** which has a Mössbauer spectrum consistent with the presence of only one iron site corresponding to the outer iron atoms in **10** and $\nu(CO)$ at 1938 cm^{-1}, almost exactly as for **10**. A corresponding nickel complex has been made by Dr D. J. Evans in our laboratory. However reactions of **8** with $CuCl_2$, $ZnCl_2$, VCl_2 and VCl_3 solvates under various conditions produced only the all-iron **10**, as shown by metal analyses and Mössbauer spectra. **8** is converted into **10** by treatment with acid and, by mixing methanol solutions of **8** and HBF_4, or **10** and LiOMe, in closed systems (see Experimental section) it is possible to show quantitative release or uptake of CO according to eqn. (1).

$$3[Et_4N][Fe(NS_3)(CO)] + 3HBF_4 \longrightarrow [Fe\{Fe(NS_3)(CO)\text{-}S,S'\}_2] + CO + 3Et_4NBF_4 + NS_3H_3 \quad (1)$$

Compound **8** is very sensitive to acids and the formation of **10** from reactions involving compounds of Zn, Cu or V may have been due to their acting as Lewis acids. Finally, **10** can also be made from $[Fe(acac)_3]$ and NS_3H_3 in MeCN, dmso or dmf in a CO atmosphere and two thirds of a mol of CO per mol of Fe is taken up in the process.

The Fe_3 and Fe_2Co trinuclear complexes, **10** and **11**, are isostructural and essentially identical. In each, two $Fe(NS_3)(CO)$ units are ligands to the central metal atom, M, which is Fe in **10**, Co in **11**. The atom M lies on a twofold symmetry axis and the two ligands bind, each through two thiolate sulfur atoms, in a distorted tetrahedral arrangement, Fig. 3. Principal dimensions are in Table 1; the only significant differences in the dimensions of **10** and **11** are in the M–S distances (the Co–S distances are slightly longer than the corresponding Fe–S lengths) and in some of the angles about M. The two carbonyl ligands, one on each outer iron atom, may be described as

Table 2 Optimised geometries for the truncated $[FeX(SH)_3(NH_3)]^-$ anions

	X absent,[a] $S = 1$	X absent,[a] $S = 2$	X = Cl, $S = 3/2$	X = Cl, $S = 5/2$	X = CO, $S = 1$	X = CO, $S = 2$	X = N_2, $S = 1$	X = N_2, $S = 2$
Fe–N(NH_3)/Å	2.051	2.198	2.035	2.244	2.025	2.201	2.002	2.207
N–H/Å	1.021	1.019	1.021	1.019	1.021	1.020	1.022	1.019
Fe–S/Å	2.439	2.449	2.439	2.454	2.436	2.508	2.447	2.471
S–H/Å	1.383	1.382	1.376	1.377	1.380	1.382	1.381	1.383
Fe–X/Å	—	—	2.289	2.356	1.769	2.097	1.810	2.590
C–O or N–N/Å	—	—	—	—	1.187	1.174	1.148	1.132
S–Fe–X/°	84.4	83.6	96.2	98.8	94.0	90.7	93.8	87.1
H–S–Fe/°	97.8	97.8	97.0	96.9	103.9	100.0	101.9	98.7
H–N–Fe/°	105.3	104.9	106.3	105.5	106.6	104.6	106.5	104.4
H–S–Fe–S′/°	−27.1	−31.6	−100.2	−104.9	−79.7	−45.1	−73.9	−35.3
H–N–Fe–S/°	12.5	14.2	60.6	60.0	36.8	14.5	34.6	12.4
Relative energy[b]/kJ mol^{-1}	+106	G.S.[c]	+34	G.S.	G.S.	+37	+18	G.S.

[a] Here X is a dummy atom for the purpose of definition of angles. [b] Neglecting zero-point energy corrections. [c] Ground state.

gauche, with C–Fe···Fe–C torsion angles of 84.9(2)° in **10**, 86.3(3)° in **11**. The geometry and dimensions in the $Fe(NS_3)(CO)$ ligand units are very similar to those in the monomer, **8**, except that there is no disorder of the methylene groups in the trinuclear species; disorder was observed in the carbonyl groups of **10**, however, with two O atom sites resolved, 0.60(2) Å apart, with an approximately 60/40 occupancy ratio. The shapes of **10** and **11** are reminiscent of those of the linear trinuclear complexes $[Et_4N]_3[Fe_3S_4(SPh)_4]$[13] and $[Et_4N]_3[VFe_2S_4Cl_4]$.[14]

The shift of 30–50 cm^{-1} in ν(CO) in going from complex **8** to **10** may simply reflect the different electronic structures of an anion (**8**) and a neutral molecule (**10**). However the C–O stretching frequencies in the IR spectra of **8** and **10** are in the region of several frequencies observed in stopped-flow FTIR studies of CO complexes of *Klebsiella pneumoniae* nitrogenase.[15] Under stoichiometric FeMo cofactor : CO conditions (lo-CO) a single band at 1904 cm^{-1} is seen but in the presence of a 10-fold excess of CO (hi-CO) additional peaks at 1936, 1958 and 1880 cm^{-1} appear (these are shifted downwards by the calculated amount if ^{13}CO is used).

It is still unclear where CO (and N_2) binds to this cofactor. The lo-CO band has been suggested to be either due to binding of one CO to one of the formally coordinatively unsaturated central Fe atoms of the cofactor or as a bridge between two of them.[16] The values of 1885–1910 cm^{-1} shown for ν(CO) of **8** lend support to the former suggestion. In the case of the hi-CO bands it is suggested that two CO molecules bind as terminal ligands to different iron ions separated by one or two sulfur bridges, and the values of 1937–1961 cm^{-1} found in the spectrum of **10** lend support to this interpretation.

DFT calculations

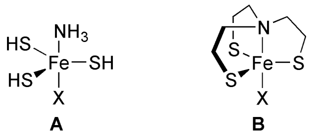
In order to understand better the characteristics of CO and N_2 binding at the $[Fe(NS_3)]^-$ site, we carried out quantum calculations on selected species using density functional theory (DFT). In order to reduce computational costs, studies of this type routinely use truncated forms of the complexes, in which atoms outside the immediate coordination environment are replaced by hydrogens as appropriate. We adopted this approach for our initial studies; however, the $[Fe(X)(NS_3)]^-$ anion (X = CO, N_2 or nothing) is itself sufficiently small that we were able to carry out some calculations on the whole anions also. We discuss the results for the truncated systems first. The general form of the model is shown in Scheme 1**A**.

For each species, geometry optimisations were carried out on both high- and low-spin models, and the results are shown in Table 2. The calculations correctly predict the ground states of complexes **1** and **8** as $S = 5/2$ and 1 respectively, and there is generally good agreement between the calculated and observed geometries. Of particular note is the predicted lengthening of the Fe–NH_3 bond from *ca.* 2.0 to 2.2 Å for all of the complexes in going from low-spin to high-spin configurations; this is confirmed experimentally in the Fe–N(4) values of complexes **8** and **1** (2.035(7) and 2.276(3) Å respectively). The predicted ν(CO) for $[Fe(CO)(SH)_3(NH_3)]^-$ ($S = 1$) is 1911 cm^{-1}, in excellent agreement with the experimental value. The calculated CO binding energy is −75 kJ mol^{-1}, or −58 kJ mol^{-1} including zero-point energy (ZPE) corrections, which is probably at the lower limit for a stable complex.

Table 3 Optimised geometries for the $[FeX(NS_3)]^-$ anions[a]

	X absent, $S = 1$	X absent, $S = 2$	X = CO, $S = 1$	X = N_2, $S = 2$
Fe–N/Å	2.034	2.236	2.037	2.280
C–N/Å	1.512	1.509	1.514	1.508
C–C/Å	1.538	1.539	1.532	1.538
C–S/Å	1.912	1.911	1.908	1.906
Fe–S[b]/Å	2.425	2.430	2.418	2.447
C–H/Å	1.098	1.099	1.098	1.099
Fe–X/Å	—	—	1.777	2.356
C–O or N–N/Å	—	—	1.185	1.133
Fe–N–C/°	107.9	107.9	108.8	108.2
N–C–C/°	113.3	112.9	112.7	113.0
C–C–S/°	111.9	112.2	110.5	112.2
Fe–N–C–C/°	54.6	38.9	57.0	40.6
S–C–C–N/°	−49.2	−61.6	−48.1	−61.2
Relative energy/kJ mol^{-1}	+107	G.S.	G.S.	G.S.

[a] Angular variables involving hydrogens omitted. [b] Not a specified variable but included as a derived parameter for comparison.



Scheme 1 The structures of the anions examined by DFT calculations.

Comparing $[Fe(CO)(SH)_3(NH_3)]^-$ with $[Fe(N_2)(SH)_3(NH_3)]^-$, there is an obvious difference, namely the change in the ground spin state from $S = 1$ to 2. The predicted ν(NN) is at 2248 cm^{-1} and the N_2 binding energy is just −15 kJ mol^{-1} (−12 kJ mol^{-1} including zero-point correction), moreover the Fe–N distance suggests a van der Waals contact only. Hence these calculations predict that this iron site has a very low affinity for N_2, consistent with the experimental non-isolation of a dinitrogen complex.

We will now consider the results for the more sophisticated model calculations, in which the whole of the NS_3 ligand was included (Scheme 1**B**). The results are shown in Table 3. Calculations on the $[Fe(NS_3)]^-$ ion in both $S = 1$ and 2 spin states confirmed the high-spin ground state, with an energy difference very similar to that of the simpler model. The predicted ν(CO) for the carbonyl complex is now slightly higher, at 1926 cm^{-1}; it is well known that systematic errors generally lead to a small overestimation of calculated infrared frequencies, which are probably fortuitously cancelled out in the simpler model. The CO binding energy is rather higher, −102 kJ mol^{-1} (−88 kJ mol^{-1} including the ZPE). For the hypothetical dinitrogen complex, ν(NN) is 2222 cm^{-1} and the N_2 binding energy is −29 kJ mol^{-1} (−26 kJ mol^{-1} including the ZPE). Although these binding energies are higher than those obtained with the simple model, the dinitrogen complex should still be far too labile to permit its isolation. Most likely the entropy of the system would further lower the affinity of the iron site for dinitrogen. Relating our experimental and theoretical results to nitrogenase, we may say that if the trigonal iron sites of FeMoco are indeed similar to the [Fe(NS_3)] site, then dinitrogen binding at the former will be at best transient.

The DFT calculations also suggest that iron(II) bound to NS_3 groups will exist in a high- rather than a low-spin configuration unless the fifth coordination position is filled by a strong field ligand such as CO; this is consistent with the large quadrupole splittings in the Mössbauer spectra of the presumed polynuclear anions in **3**, **4**, **5** and **6**.

Cyanide complexes

The fact that the Fe(NS_3) site is able to bind CO (though not N_2) with biologically relevant values of ν(CO) strengthens its credibility as a structural model for a single metal site in FeMoco of nitrogenase. We therefore searched for interactions of this site with other small molecules able to function as alternative substrates for dinitrogen, and have developed chemistry of isocyanides and of nitric oxide on this site which will be reported in the near future. Cyanide is another possible alternative substrate; we have been unable to isolate a complex with a simple monodentate cyanide ligand on the Fe(NS_3) site but have made analogous compounds of cobalt and vanadium. Treatment of [Co(acac)$_3$] with Et_4NCN and NS_3H_3 gives [Et_4N][Co(NS_3)(CN)] **12**, while treatment of [V(N_2H_4)(NS_3)][8] with [Et_4N]CN affords [Et_4N][V(NS_3)(CN)] **13**, These are straightforward complexes with strong bands near 2100 cm^{-1} ν(CN) in their infrared spectra and spin states of $S = 1$. Compound **12** is isoelectronic with **8** and unsuccessful attempts have been made to make trinuclear complexes analogous to **10** with the Co(NS_3)(CN) group acting as a ligand.

Compound **12** is isostructural with **1** and **8**, with both anion and cation lying on symmetry elements and showing disorder as described previously. The Co atom has trigonal bipyramidal coordination (as Fig. 1), but the dimensions around the metal (Table 1) are all slightly different from those in compound **8**, *viz* the Co–S and Co–N distances are shorter than the corresponding ones around the Fe atom, and the Co atom is displaced 0.0321(6) Å from the S_3 plane. The apical Co–C–N group is essentially linear.

Attempted hydration of acetonitrile

The active site of nitrile hydratase has iron(III) bound to three (cysteine) sulfurs, and will support an azide group.[17,18] In some respects it therefore resembles an Fe(NS_3) site, though the geometry at iron is very different, and we have attempted to use complexes **2** and **8** to catalyse the hydration of acetonitrile to acetamide, but found no enhancement of hydration rates over those produced by general base catalysis.

Conclusion

The Fe(NS_3) site is able to support a number of co-ligands including carbon monoxide. The tendency of this site to form bridging structures with additional iron–sulfur bonds can be an obstacle to isolation of mononuclear complexes, but can be turned to account in the synthesis of extended trinuclear complexes in which the [Fe(NS_3)(CO)]$^-$ ion can function as a ligand.

Experimental

General

All operations were carried out under a dry dinitrogen atmosphere, using standard Schlenk techniques. All the 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[7,19–21] *via* tris(2-chloroethyl)amine hydrochloride. **CAUTION**: vesicant; this work was carried out in enclosed Schlenk apparatus while wearing heavy duty gloves and a face mask. The [$FeCl_2$(MeCN)$_2$] and [$FeCl_2$(dmso)$_3$] starting materials and their cobalt analogues were made by heating the anhydrous metal chlorides in MeCN or dmso until they dissolved and crystallising the products by adding diethyl ether. Infrared spectra were recorded on Perkin-Elmer 883 or Shimadzu FTIR-8101M instruments in Nujol mulls. Mössbauer parameters (isotopic shift, IS and quadrupole splitting, QS) were determined at 77 K (on an ES-Technology MS105 spectrometer using a 925 MBq ^{57}Co source in a rhodium matrix at ambient temperature, referenced against a 25 μm iron foil at 295 K) by Dr David Evans or Mrs Elaine Barclay of this laboratory. Magnetic moment determinations at 20 °C were in the solid state, using a Johnson-Matthey Göuy balance. Microanalyses were by Mr A. Saunders of the University of East Anglia (CHN), or by Southern Science, Falmer Laboratories, East Sussex (metals).

Preparations

[Et_4N][FeCl(NS_3)] 1. [Fe(acac)$_3$] (3.53 g, 10 mmol) and $Et_4NCl\cdot H_2O$ (1.80 g, 10 mmol) were stirred in MeCN (80 ml) and NS_3H_3 (2 g, 10 mmol) in MeCN (20 ml) was added. The dark red solution was heated at reflux for 30 minutes then filtered hot leaving a small residue. Diethyl ether (100 ml) was added to the cooled filtrate which was kept at −20 °C overnight. The resulting red X-ray quality crystals (2.9 g, 70%) were filtered off, washed with diethyl ether and dried in a vacuum. Found: C, 40.2; H, 7.7; N, 6.7. $C_{14}H_{32}ClFeN_2S_3$ requires C, 40.4; H, 7.7; N, 6.7%. $\mu_{eff} = 5.88$ μ_B ($S = 5/2$). Mössbauer: IS 0.258, QS 0.982 mm s^{-1}.

[Et_4N][Fe(N_3)(NS_3)] 2. [Et_4N][FeCl(NS_3)] (1.66 g, 4.0 mmol) and sodium azide (2.6 g, 40 mmol) were heated at reflux in MeCN (40 ml) overnight, then the resulting mixture was filtered hot leaving a white residue. The filtrate volume was reduced to 20 ml, ether (20 ml) added, and the solution kept at −20 °C overnight. Red X-ray quality crystals (1.08 g, 64%) were filtered off, washed with ether and dried in a vacuum. Found: C, 39.9; H, 7.9; N, 16.8. $C_{14}H_{32}FeN_5S_3$ requires C, 39.8; H, 7.6; N, 16.6%. $\mu_{eff} = 5.80$ μ_B ($S = 5/2$). Mössbauer: IS 0.352, QS 0.731 mm s^{-1} IR: 2048 cm^{-1} ($\nu(N_3)$).

[Et_4N][$Fe_4(NS_3)_3$]·MeCN 3. [Fe(acac)$_3$] (1.42 g, 4 mmol) and $Et_4NOAc\cdot 4H_2O$ (1.30 g, 5 mmol) were heated at reflux in MeCN (32 ml) and NS_3H_3 (1 g, 5 mmol) in MeCN (8 ml) was added. The dark red solution was heated at reflux for 20 minutes, then filtered hot from a little dark deposit and cooled overnight. Red flaky microcrystals (0.23 g, 24%) were filtered off, washed with MeCN and ether and dried in a vacuum. Found: C, 34.9; H, 6.0; Fe, 22.9; N, 7.1. $C_{28}H_{59}Fe_4N_5S_9$ requires C, 34.4; H, 6.1; Fe, 22.8; N, 7.2%. Mössbauer: IS 0.835, QS 3.357 (78%) and IS 0.737, QS 2.944 mm s^{-1} (22%).

[Me_4N][$Fe_4(NS_3)_3$]·MeCN 4. This was made similarly in 27% yield starting from Me_4NOAc. Found: C, 31.3; H, 5.5; N, 6.9.

$C_{24}H_{51}Fe_4N_5S_9$ requires C, 31.3; H, 5.6; N, 7.6%. Mössbauer: IS 0.815, QS 3.075 (80%) and IS 0.850, QS 3.639 mm s^{-1} (20%).

Reduction of complex 1. $[Et_4N][FeCl(NS_3)]$ (0.84 g, 2.0 mmol) was treated with sodium amalgam (100 g, 0.5% Na) in MeCN (20 ml). After 20 minutes the solution became yellow; it was filtered through Celite and diethyl ether (20 ml) immediately added. Yellow crystals (0.25 g) precipitated and were filtered off, washed with ether and dried in a vacuum. A satisfactory microanalysis could not be obtained, but on the basis of a Mössbauer spectrum which was very similar to those of **6** and **7** below the crystals are given the formulation $[Et_4N]_n[\{Fe(NS_3)\}_n]$ **5**. Found: C, 40.3; H, 7.4; N, 7.9. $C_{14}H_{32}FeN_2S_3$ requires C, 44.2; H, 8.5; N, 7.4%. Mössbauer: IS 0.830, QS 3.145 mm s^{-1}. In a separate experiment $TlPF_6$ (0.36 g, 1 mmol) in MeCN (5 ml) was added immediately to the yellow filtrate from Celite. Yellow crystals (0.35 g, 77%) of $Tl_n[\{Fe(NS_3)\}_n]$ **6** were filtered off, washed with ether and dried in a vacuum. Found: C, 15.3; H, 2.4; N, 3.1. $C_6H_{12}FeNS_3Tl$ requires C, 15.8; H, 2.7; N, 3.1%. Mössbauer: IS 0.800, QS 3.060 mm s^{-1}.

$[N_2H_5]_2[\{Fe(NS_3)\}_2]\cdot EtOH$ 7. $[Et_4N][FeCl(NS_3)]$ (0.21 g, 0.50 mmol) and hydrazine monohydrate (0.5 g, 10 mmol) were stirred in ethanol for 30 minutes then filtered from a small residue. After 4 days a few brown crystals (approx. 0.02 g, 7%) deposited; they were filtered off, washed with ether and dried in a vacuum. Found: C, 27.9; H, 6.8; N, 13.2. $C_{14}H_{40}Fe_2N_6OS_6$ requires C, 27.5; H, 6.6; N, 13.7%. Mössbauer: IS 0.832, QS 3.181 mm s^{-1}.

$[Et_4N][Fe(NS_3)(CO)]$ 8. $[Fe(acac)_3]$ (2.84 g, 8 mmol) and $Et_4NOAc\cdot 4H_2O$ (2.61 g, 10 mmol) were stirred in MeCN (60 ml) under CO. NS_3H_3 (2.4 g, 12 mmol) in MeCN (15 ml) was added; the solution turned dark red but within 20 minutes became dark green while 190 ml (approx. 7.9 mmol at 20 °C) of CO was absorbed. The solution was then filtered leaving a small residue which was washed with MeCN (5 ml) then ether (240 ml) was added to the filtrate. Green X-ray quality crystals (2.4 g, 72%) grew overnight; they were filtered off, washed with ether and dried in a vacuum. Found: C, 44.1; H, 8.1; N, 7.5. $C_{15}H_{32}FeN_2OS_3$ requires C, 44.1; H, 7.9; N, 6.9%. $\mu_{eff} = 2.78\ \mu_B$ ($S = 1$). Mössbauer: IS 0.222, QS 0.992 mm s^{-1}. IR: 1885 (ν(CO)) (solid), 1910 cm^{-1} (MeCN solution).

$Tl[Fe(NS_3)(CO)]$ 9. $[Et_4N][FeCl(NS_3)]$ (0.42 g, 1.0 mmol) was treated with sodium amalgam (100 g, 0.5% Na) in MeCN (20 ml). After 20 minutes the solution became yellow; it was filtered through Celite and exposed to CO gas when it immediately became dark green. Addition of ether to this solution gave the product **8** above; addition of $TlPF_6$ (0.35 g) gave a green powder in essentially quantitative yield which was filtered off, washed with ether and dried in a vacuum. Found: C, 17.4; H, 2.5; N, 3.1. $C_7H_{12}FeNOS_3Tl$ requires C, 17.4; H, 2.5; N, 2.9%. Mössbauer: IS 0.217, QS 1.221 mm s^{-1}. IR: 1906 cm^{-1} (ν(CO)).

$[Fe\{Fe(NS_3)(CO)\text{-}S,S'\}_2]$ 10. *Method (A).* Solutions of $[Fe(acac)_3]$ (0.71 g, 2.0 mmol) in dmso (20 ml) and NS_3H_3 (0.6 g, 3 mmol) in dmso (20 ml) were stirred under a CO atmosphere then mixed giving a dark green solution and an uptake of CO of 33.2 ml (approx. 1.38 mmol at 20 °C) in 20 minutes. The mixture was then filtered under CO leaving a dark green precipitate (0.24 g, 59%). Found: C, 27.4; H, 3.9; N, 4.6. $C_{14}H_{24}Fe_3N_2O_2S_6$ requires C, 27.5; H, 4.0; N, 4.6%. Mössbauer: IS 0.616, QS 1.931 (intensity 1), IS 0.210, QS 1.182 mm s^{-1} (intensity 2). IR: 1937 cm^{-1} (ν(CO)). $\mu_{eff} = 1.54\ \mu_B$ at 295 K. A similar reaction in MeCN gave 0.41 g of product (100%), not quite pure and with 1961 and 1952 cm^{-1} (ν(CO)) but identical Mössbauer parameters.

Method (B). Solutions of $[Fe(acac)_3]$ (0.18 g, 0.5 mmol) in dmso (20 ml) and NS_3H_3 (0.1 g, 0.5 mmol) in dmso (5 ml) were mixed giving a dark red solution in a 250 ml flask. The flask was evacuated and filled with a CO atmosphere without stirring. The solution slowly turned green from the top; after a week it was filtered under CO leaving behind some X-ray quality crystals which were filtered off, washed with ether and dried in a vacuum.

Method (C). $HBF_4\cdot Et_2O$ (0.10 g, 0.6 mmol) was added to $[Et_4N][Fe(NS_3)(CO)]$ (0.20 g, 0.05 mmol) in MeCN (10 ml). Black crystals (0.10 g, 75% based on Fe) were filtered off.

Method (D). $[Et_4N][Fe(NS_3)(CO)]$ (0.41 g, 0.1 mmol) in MeCN was added to $[FeCl_2(MeCN)_2]$ (0.11 g, 0.5 mmol) in MeCN or to $[FeCl_2(dmso)_3]$ (0.18 g, 0.5 mmol) in dmso. Black crystals (80%) were filtered off.

$[Co\{Fe(NS_3)(CO)\text{-}S,S'\}_2]$ 11. $[Et_4N][Fe(NS_3)(CO)]$ (0.41 g, 1 mmol) in MeCN (40 ml) was added to $[CoCl_2(MeCN)_2]$ (0.11 g, 0.5 mmol) in MeCN (10 ml). Black crystals (0.23 g, 60%) gradually formed; they were filtered off, washed with ether and dried in a vacuum. Found: C, 27.7; H, 3.7; Co, 9.5; Fe, 19.1; N, 4.7. $C_{14}H_{24}CoFe_2N_2O_2S_6$ requires C, 27.3; H, 3.9; Co, 9.6; Fe, 18.2; N, 4.6%. Mössbauer: IS 0.211, QS 1.285 mm s^{-1}. IR: 1938 cm^{-1} (ν(CO)).

$[Et_4N][Co(NS_3)(CN)]$ 12. $[Co(acac)_3]$ (0.80 g, 2.25 mmol) and Et_4NCN (0.40 g, 2.5 mmol) were heated at reflux in MeCN and NS_3H_3 (0.5 g, 2.5 mmol) in MeCN (5 ml) was added. After 10 minutes the dark green solution was filtered hot and cooled overnight. Dark green X-ray quality crystals (0.70 g, 76%) were filtered off, washed with ether and dried in a vacuum. Found: C, 43.9; H, 7.7; N, 10.2. $C_{15}H_{32}CoN_3S_3$ requires C, 44.0; H, 7.8; N, 10.3%. $\mu_{eff} = 2.83\ \mu_B$ ($S = 1$). IR: 2104 cm^{-1} (ν(CN)).

$[Et_4N][V(NS_3)(CN)]$ 13. $[V(NH_2NH_2)(NS_3)]$ (2.08 g, 7.5 mmol) and Et_4NCN (1.25 g, 8.0 mmol) were heated at reflux in MeCN (150 ml) for 20 minutes and the mixture was then filtered hot. The volume of the cooled solution was reduced to 100 ml when yellow crystals (1.66 g, 55%) precipitated. They were filtered off, washed with ether and dried in a vacuum. Found: C, 45.1; H, 8.1; N, 10.5. $C_{15}H_{32}N_3S_3V$ requires C, 44.9; H, 8.0; N, 10.5%. $\mu_{eff} = 2.67\ \mu_B$ ($S = 1$). IR: 2095 cm^{-1} (ν(CN)).

Release and uptake of CO from solutions of complexes 8 and 10

Solutions of complex **8** (0.41 g, 1 mmol) in methanol (20 ml) and of $HBF_4\cdot Et_2O$ (1.8 mmol) in methanol (5 mmol) were made up in separate arms of an inverted U-shaped apparatus and allowed to come to thermal equilibrium at 20 °C under an atmosphere of CO. The solutions were mixed in one side of the apparatus; there was an immediate release of 8.0 ml (0.33 mmol at atmospheric pressure) of CO, and a black suspension of **10** formed. A similar experiment starting with a suspension of **10** (0.33 mmol) in methanol and a solution of LiOMe (5 mmol) and NS_3H_3 (0.5 mmol) in methanol resulted in the uptake of CO (7.8 ml, 0.32 mmol at atmospheric pressure) over 20 minutes and the conversion of the black suspension into a blue solution of **8**.

Crystal structure analyses

The analyses followed standard procedures; all data were measured at room temperature. Details for complex **1** are given; the other compounds were treated similarly. Crystal and refinement data are collated in Table 4.

Crystals of complex **1** are black irregular shaped prisms. One was mounted, examined photographically, then diffraction data were measured on an Enraf-Nonius CAD4 diffractometer (Mo-Kα radiation). Corrections were applied for Lorentz-polarisation effects, slight 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 automated Patterson routines in the

Table 4 Crystallographic and refinement data for the M(NS$_3$) complexes

	[Et$_4$N][FeCl(NS$_3$)] **1**	[Et$_4$N][Fe(N$_3$)(NS$_3$)] **2**	[Et$_4$N][Fe(NS$_3$)(CO)] **8**	[Fe{Fe(NS$_3$)(CO)-*S*,*S*′}$_2$] **10**	[Co{Fe(NS$_3$)(CO)-*S*,*S*′}$_2$] **11**	[Et$_4$N][Co(NS$_3$)(CN)] **12**
Elemental formula	$C_8H_{20}N$, $C_6H_{12}ClFeNS_3$	$C_8H_{20}N$, $C_6H_{12}FeN_4S_3$	$C_8H_{20}N$, $C_7H_{12}FeNOS_3$	$C_{14}H_{24}Fe_3N_2O_2S_6$	$C_{14}H_{24}CoFe_2N_2O_2S_6$	$C_8H_{20}N$, $C_7H_{12}CoN_2S_3$
Molecular weight, *M*	415.9	422.5	408.5	612.3	615.3	409.5
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Tetragonal	Tetragonal	Orthorhombic
Space group (no.)	*Pbcm* (no. 57)	$C222_1$ (no. 20)	*Pbcm* (no. 57)	$I4_1cd$ (no. 110)	$I4_1cd$ (no. 110)	*Pbcm* (no. 57)
a/Å	8.7922(9)	15.905(2)	8.8530(7)	13.5324(4)	13.5277(5)	8.8650(11)
b/Å	14.3189(11)	14.254(2)	14.1800(11)	13.5324(4)	13.5277(5)	14.1311(14)
c/Å	15.9028(14)	18.458(3)	15.869(2)	24.499(2)	24.414(5)	15.757(2)
Cell volume, V/Å^3	2002.1(3)	4184.8(10)	1992.1(3)	4486.4(3)	4467.7(9)	1973.9
No. of formula units/cell, *Z*	4	8	4	8	8	4
μ(Mo-Kα)/cm^{-1}	12.0	10.3	10.7	24.9	25.9	11.9
Total reflections measured (not including absences)	2736	2732	2384	3240	2931	2336
Total unique reflections	2504	2534	1111	1668	1252	2229
R_{int} for equivalents	0.027	0.011	0.053	0.020	0.029	0.019
Final R_1 (all data)	0.054	0.071	0.082	0.029	0.042	0.101
wR_2 (all data)	0.112	0.127	0.123	0.046	0.052	0.123
R_1 for 'observed' data	0.040	0.047	0.046	0.023	0.030	0.046
No. 'observed' reflections ($I > 2\sigma_I$)	1870	1620	678	1453	1010	1153

SHELXS program[22] and refined by full-matrix least-squares methods, on F^2, in SHELXL.[23] There is disorder in both the cation and anion. The non-hydrogen atoms of the anion and the common N atom of the various disordered cations were refined with anisotropic thermal parameters; the disordered C atoms of the cation were refined isotropically. Hydrogen atoms were included in both anion and cation, in idealised positions, with all parameters set to ride on those of the parent carbon atoms. In the final difference map the highest peaks (to *ca.* 0.4 e Å^{-3}) were in the cation region. Scattering factors for neutral atoms were taken from reference 24. Computer programs used in this analysis have been noted above or in Table 4 of reference 25, and were run on our DEC-AlphaStation 200 4/100 computer.

In compound **2** there are two cation sites, each lying on two-fold symmetry axes; one cation is well ordered, the other disordered with two distinct orientations. This complex crystallises in the polar space group $C222_1$, and the Flack parameter, x, refined to 0.20(5), suggesting that the absolute structure is probably correct; for the inverted structure, $x = 0.36(5)$. In **8** a single, distinct orientation of the cation was identified. The final difference map, however, suggests that there might be minor, alternative, unresolved orientations for the cation. The Flack parameter, x, in the isostructural complexes **10** and **11** is 0.005(18) and 0.003(26), indicating that the correct absolute structure has been determined for both structures.

CCDC reference number 186/2238.

See http://www.rsc.org/suppdata/dt/b0/b006591i/ for crystallographic files in .cif format.

DFT Calculations

All quantum calculations were carried out using the GAUSSIAN 98W suite of programs.[26] Becke's three parameter hybrid functional using the correlation functional of Lee, Yang and Parr (B3LYP[27]) was used in conjunction with the LanL2DZ basis set, which uses Dunning/Huzinaga full double zeta (D95) basis functions on first row atoms[28] and Los Alamos effective core potentials plus double zeta basis functions[29] on other atoms. For all species, geometries were optimised using z-matrix methods within C_3 symmetry; thus, the N–Fe–C–O and N–Fe–N–N moieties were linear by definition. The variables used for models **A** and **B** in Scheme 1 are given in Tables 2 and 3 respectively; in addition, model **B** used a generic C–H bond length but the H–C–C angles were allowed to vary independently; the dihedral angles defined by the H–C^A–C^B and X–C^A–C^B planes (X = S or N) were constrained to ideal values (±120°).

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References

1 D. C Rees, M. K. Chan and J. Kim, *Adv. Inorg. Chem.*, 1993, **40**, 89.
2 R. R. Eady, *Chem. Rev.*, 1996, **96**, 3013 and references therein.
3 R. N. Pau, in *Biology and Biochemistry of Nitrogen Fixation*, eds. M. J. Dilworth and A. R. Glenn, Elsevier, Oxford, 1991, p. 37.
4 D. H. Nguyen, H.-F. Hsu, M. Millar, S. A. Koch, C. Achim, E. L. Bominaar and E. Münck, *J. Am. Chem. Soc.*, 1996, **118**, 8963.
5 M. B. O'Donoghue, N. C. Zanetti, W. M. Davis and R. R. Schrock, *J. Am. Chem. Soc.*, 1997, **119**, 2753.
6 M. B. O'Donoghue, W. M. Davis, R. R. Schrock and W. M. Reiff, *Inorg. Chem.*, 1999, **38**, 243.
7 S. C. Davies, D. L. Hughes, R. L. Richards and J. R. Sanders, *J. Chem. Soc., Dalton Trans.*, 2000, 719.
8 S. C. Davies, D. L. Hughes, Z. Janas, L. Jerzykiewicz, R. L. Richards, J. R. Sanders and P. Sobota, *Chem. Commun.*, 1997, 1261.
9 S. C. Davies, D. L. Hughes, R. L. Richards and J. R. Sanders, *Chem. Commun.*, 1998, 2699.
10 S. C. Davies, D. J. Evans, D. L. Hughes, S. Longhurst and J. R. Sanders, *Chem. Commun.*, 1999, 1935.

11 K. K. Nanda, E. Sinn and A. W. Adamson, *Inorg. Chem.*, 1996, **35**, 1.

12 M. Ray, A. P. Golombek, M. P. Hendrich, V. G. Young, Jr. and A. S. Borovik, *J. Am. Chem. Soc.*, 1996, **118**, 6084.

13 K. S. Hagen, A. D. Watson and R. H. Holm, *J. Am. Chem. Soc.*, 1983, **105**, 3905.

14 Y. Do, E. D. Simhon and R. H. Holm, *Inorg. Chem.*, 1985, **24**, 4635.

15 S. J. George, G. A. Ashby, C. W. Wharton and R. N. F. Thorneley, *J. Am. Chem. Soc.*, 1997, **119**, 6450.

16 H.-I. Lee, L. M. Cameron, B. J. Hales and B. M. Hoffman, *J. Am. Chem. Soc.*, 1997, **119**, 10121.

17 W. Huang, J. Jia, J. Cummings, M. Nelson, G. Schneider and Y. Lundquist, *Structure*, 1997, **5**, 691.

18 S. Nagashima, M. Nakasako, N. Dohmae, M. Tsujimura, K. Takio, M. Odaka, M. Yohda, N. Kamiya and I. Endo, *Nature Struct. Biol.*, 1998, **5**, 347.

19 K. Ward, *J. Am. Chem. Soc.*, 1935, **57**, 914.

20 J. Harley-Mason, *J. Chem. Soc.*, 1947, 320.

21 P. Barbaro, C. Bianchini, G. Scapacci, D. Masi and P. Zanello, *Inorg. Chem.*, 1994, **33**, 3180.

22 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

23 G. M. Sheldrick, SHELXL, Program for crystal structure refinement, University of Göttingen, 1993.

24 *International Tables for X-Ray Crystallography*, Kluwer Academic Publishers, Dordrecht, 1992, vol. C, pp. 193, 219 and 500.

25 S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.

26 Gaussian 98, Revision A.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

27 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

28 T. H. Dunning Jr. and P. J. Hay, in *Modern Theoretical Chemistry*, ed. H. F. Schaefer, III, Plenum, New York, 1976, vol. 3, p. 1.

29 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270; W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284; P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.