# Iron complexes of the $N(CH_2CH_2S)_3{}^{3-}$ ligand; a paramagnetic, trigonal bipyramidal Fe(II) CO complex as a chelate ligand

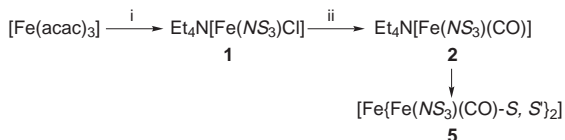**Sian C. Davies, David L. Hughes, Raymond L. Richards and J. Roger Sanders**

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The paramagnetic complex anions $[Fe(NS_3)Cl]^-$ $[NS_3 = N(CH_2CH_2S)_3{}^{3-}]$ and$[Fe(NS_3)(CO)]^-$ have been prepared and structurally characterised; with $FeCl_2$, $[Fe(NS_3)(CO)]^-$ gives the structurally characterised, linear, paramagnetic cluster complex $[Fe\{Fe(NS_3)(CO)\text{-}S,S'\}_2]$.

A number of metal sites in enzymes carry three sulfur-donor ligands. These include the low-spin Fe centre of nitrile hydratase,[1] which is bound to three cysteine sulfur and two amide nitrogen atoms, and the cofactor of molybdenum nitrogenase, FeMoco, an $MoFe_7S_9$ cluster in which the six central iron atoms are each coordinated by three sulfides.[2] The Mo atom in FeMoco is coordinated by three sulfides as well as two oxygens from homocitrate and one histidine nitrogen[2] and it is thought that the vanadium atom in vanadium nitrogenase[3] and one iron atom in the 'iron-only' nitrogenase[4] are in similar environments. We are particularly interested in models for the trigonally S-coordinated Fe centres in the central portion of FeMoco and the $S_3$-coordinated Mo, V or Fe centres at the histidine end of nitrogenase cofactor clusters. Following our investigation of the nitrogen chemistry of vanadium coordinating the tetradentate tripodal ligand $N(CH_2CH_2S)_3{}^{3-}$ $(NS_3)$,[5] we report iron chemistry of this ligand which, because its ligation involves three sulfur atoms, relates to the metal environments in the enzymes mentioned above. In the course of this work we have discovered a novel, paramagnetic carbonyl complex of iron which acts as a chelate ligand, as described below.

The starting point of our iron chemistry is the Fe(III) complex anion $[FeCl(NS_3)]^-$ **1**, obtained as shown in Scheme 1, which on reduction under CO gives the Fe(II) anion $[Fe(NS_3)(CO)]^-$ **2**. The $NEt_4$ salts of **1** and **2** {also the vanadium complex $NEt_4[VCl(NS_3)]$[5]} are isostructural; in both structures, the anion lies disordered about a crystallographic mirror plane.† Figs. 1 and 2 show the iron atoms to have trigonal bipyramidal geometry. In the solid state, both complexes are paramagnetic, The $NEt_4$ salt of **1** has $\mu_{eff} = 5.87\ \mu_B$, $S = 5/2$. Mössbauer data at 77 K, (rel. natural Fe), are; isomer shift (IS) 0.37 mm s⁻¹ and quadrupole splitting (QS) 1.00 mm s⁻¹. The $NEt_4$ salt of **2** has $\mu_{eff} = 2.79\ \mu_B$, $S = 1$; IS = 0.22, QS 0.99 mm s⁻¹. Comparison of the anions in Figs. 1 and 2 shows that in the carbonyl **2** the Fe–N distance [2.035(8) Å] and the average Fe–S distance [2.278(3) Å] are shorter than the corresponding distances in the chloride **1** [2.273(3) and 2.316(2) 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 **2**, and results in a relative distortion of the trithiolate ligand; the mean S–Fe–N angle contracts from 87.8(1)° in **2** to 83.6(2)° in **1**.
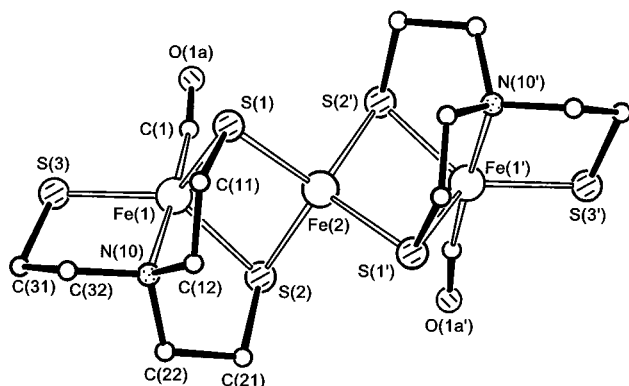
Paramagnetic CO complexes of iron are extremely rare and as far as we are aware only two other examples, $K[Fe\{N(CH_2\text{-}CONPr^i)_3\}(CO)]$[6] **3** and $Et_4N[Fe\{P[C_6H_3S\text{-}2(Ph\text{-}3)]_3\}(CO)]$[7] **4**, are known. Both have similar magnetic and Mössbauer properties to those of **2** but both have $v(CO)$ at 1940 cm⁻¹, a notably higher frequency than that of **2** (1885 cm⁻¹). Evidently the $FeNS_3{}^-$ site in **2** is more electron releasing to CO than are the corresponding iron sites in **3** and **4**.
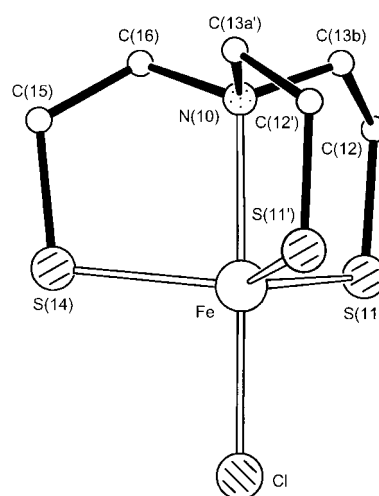


**Fig. 1** The molecular structure of anion **1**. The disorder about the mirror symmetry plane is not shown; the atoms C(13a′), C(13b) and C(16) have half occupancy of the sites shown. Selected molecular dimensions: Fe–N(10) 2.273(3), Fe–Cl 2.3120(14), Fe–S(11) 2.3143(9), Fe–S(14) 2.3193(12) Å; N(10)–Fe–Cl 179.00(9), N(10)–Fe–S(average) 83.6(2)°.
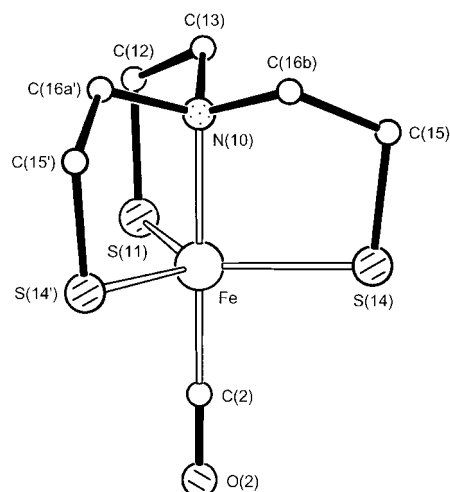


**Fig. 2** The molecular structure of anion **2** which has disorder similar to that described in Fig. 1. Selected molecular dimensions: Fe–N(10) 2.035(8), Fe–C(2) 1.720(14), C(2)–O(2) 1.154(14), Fe–S(11) 2.281(3), Fe–S(14) 2.272(2) Å; N(10)–Fe–C(2) 179.7(5), N(10)–Fe–S(av.) 87.8(1)°.



**Scheme 1** *Reagents and conditions*: i, $N(SH)_3$ + $Et_4NCl$ in MeCN; ii, Na/CO in MeCN; iii, $FeCl_2$ (0.5 mol ratio) in MeCN or $Me_2SO$.

**Fig. 3** The molecular structure of **5**, viewed down the twofold symmetry axis through Fe(2). Selected molecular dimensions: Fe(1)–N(10) 2.052(3), Fe(1)–C(1) 1.765(4), C(1)–O(1a) 1.13(1) (major component in disordered carbonyl group), C(1)-O(1b) 1.22(2), Fe(1)–S(1) 2.2677(10), Fe(1)–S(1) 2.2563(10), Fe(1)–S(3) 2.2139(9), Fe(2)–S(1) 2.2774(9), Fe(2)–S(2) 2.2928(10), Fe(1)⋯Fe(2) 2.6663(5) Å; N(10)–Fe(1)–C(1) 175.67(13), N(10)–Fe(1)–S(av.) 88.1(5), Fe(1)–S(1)–Fe(2) 71.84(3), Fe(1)–S(2)–Fe(2) 71.76(3), S(1)–Fe(1)–S(2) 107.79(3), S(1)–Fe(2)–S(2) 106.21(3), S(1)–Fe(2)–S(2') 105.93(3), S(1)–Fe(2)–S(1') 121.89(6), S(2)–Fe(2)–S(2') 110.50(6)°.

The latter sites are sterically hindered and **3** and **4** are made by CO addition to trigonal pyramidal iron-complex precursors. We have not been able to isolate the monomeric precursor to **2**, $[Fe(NS_3)]^-$. Instead, we obtain as yet uncharacterised products which appear to be multinuclear, probably because sulfur acts as a bridging group in them. However, the bridging ability of its sulfur ligands allows **2** itself to function as a ligand in a controlled way. Thus treatment of **2** with $FeCl_2$ (Scheme 1) affords the novel green, paramagnetic, linear $Fe_3S_4$ carbonyl cluster $[Fe\{Fe(NS_3)(CO)\text{-}S,S'\}_2]$ **5** [$\nu$(CO) 1937 cm$^{-1}$]. Mössbauer consistent with two different iron(II) sites: IS = 0.60, QS = 1.96 (intensity 1); IS = 0.22, QS = 1.17 mm s$^{-1}$ (intensity 2)].

The structure of **5** (Fig. 3)† shows that this complex is made up from two trigonal bipyramidal Fe($NS_3$)(CO) units, each of which bridges through two of its sulfur atoms to a central Fe, which thus has distorted tetrahedral geometry and lies on a crystallographic twofold symmetry axis. Within the Fe($NS_3$)-(CO) units, the Fe-S distances involving the four bridging S atoms are 2.256(1) and 2.268(1)Å, but those to the non-bridging S atoms are shorter [2.214(1) Å]. The Fe-S distances about the central Fe are 2.277(1) Å and 2.293(1) Å. All the iron atoms can be regarded as formally in oxidation state two, but solid **5** has $\mu_{eff}$ = 1.54 $\mu_B$ per molecule at 20 °C showing considerable electron coupling. The molecule is disordered with two distinct sites for the O atoms of the CO ligands; the C–O distances are 1.131(12) and 1.22(2) Å, with corresponding Fe–C–O angles of 168.8(6) and 161.4(9)°.

We note that the C–O stretching frequencies in the IR spectra of **2** (1885 cm$^{-1}$) and **5** (1937 cm$^{-1}$) are in the region of several frequencies observed in stopped-flow FTIR studies of CO complexes of *Klebsiella pneumoniae* nitrogenase (1880, 1906, 1936 and 1958 cm$^{-1}$).[8]

We also point out that treatment of the NEt$_4$ salt of **1** with NaN$_3$ gives NEt$_4$[Fe($NS_3$)N$_3$], which has relevance to azide inhibition of the iron site in nitrile hydratase.[1] This and other complexes of inhibitors of nitrile hydratase are under investigation, although MeCN appears to bind very weakly to the Fe$NS_3^-$ site.

The shape of our iron cluster is reminiscent of those of the linear trinuclear complexes [Et$_4$N]$_3$[Fe$_3$S$_4$(SPh)$_4$][9] and [Et$_4$N]$_3$[VFe$_2$S$_4$Cl$_4$].[10] We anticipate in our future work that **2** and related complex anions such as $[Fe(NS_3)(CNR)]^-$ will function as ligands to allow assembly of a range of multi-nuclear complexes of iron with other metals. Already, we have obtained the analogue of **5**, $[Fe_3(NS_3)_2(CNC_6H_{11})_2]$, [from Fe(acac)$_3$, $NS_3H_3$, and CNC$_6$H$_{11}$,[11] and [Fe$_2$Co($NS_3$)$_2$(CO)$_2$] (by use of CoCl$_2$ in place of FeCl$_2$ in step iii of Scheme 1).

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## Notes and references

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