Mononuclear, binuclear, trinuclear and tetranuclear iron complexes of the N(CH$_2$CH$_2$S)$_3$$^{3-}$ (NS$_3$) ligand with nitrosyl co-ligands

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Reaction of [Fe(acac)$_3$], (NEt$_4$)OAc and N(CH$_2$CH$_2$SH)$_3$ in MeCN in the presence of NO gives (NEt$_4$)[Fe(NS$_3$)(NO)] (**1**) [where NS$_3$ = N(CH$_2$CH$_2$S)$_3$]. Complex **1** reacts with metal chloride solvates, giving insoluble compounds of stoichiometry MFe$_2$(NO)$_2$(NS$_3$)$_2$, probably having the structure [M{Fe(NS$_3$)(NO)}$_2$-*S,S'*] [M = Fe (**2**), Co (**3**), Ni (**4**), Cu (**5**)], the nitrosyl analogues of known structurally characterised carbonyl compounds. **1** also reacts with HBF$_4$· Et$_2$O, giving the tetranuclear complex [{Fe(NO)$_2${Fe(NS$_3$)}-*S,S'*}$_2$-*S,S'*] (**6**), which adds small molecules, L, giving the binuclear complexes [Fe(NO)$_2${Fe(NS$_3$)(L)}-*S,S'*] [L = CO (**7**), CNMe (**8**), NO (**9**), CN$^-$ (**10**)]. Complexes **6**–**9** are more conveniently prepared by treatment of [Fe(NS$_3$)(L)]$^-$ precursors with half an equivalent of [{Fe(NO)$_2$}$_2$(μ-I)$_2$]. Reaction of (NEt$_4$)[Co(NS$_3$)(CN)] with half an equivalent of [{Fe(NO)$_2$}$_2$(μ-I)$_2$] gives [Fe(NO)$_2${Co(NS$_3$)(CN)}-*S,S'*] (**11**). Treatment of the [Fe(NS$_3$)L] precursors used to make **7**–**9** with one equivalent of [{Fe(NO)$_2$}$_2$(μ-I)$_2$] gives another series of complexes, [{Fe(NO)$_2$I}-*S*{Fe(NS$_3$)(L)}-*S',S''*{Fe(NO)$_2$}] [L = CO (**12**), CNMe (**13**), NO (**14**)]. Products were characterised by microanalyses, IR and Mössbauer spectra; X-ray crystal structure determinations were carried out on **1**, **6**, **7**, **9**, **10**, **13** and **14**. Magnetic measurements at room temperature showed evidence of spin pairing in all the polynuclear complexes.

Introduction

The chemistry of metals multiply ligated by sulfur atoms (plus other ligands) is of potential importance in understanding the mode of action of enzymes containing such structures at their active site, *e.g.* nitrogenase with its MoFe$_7$S$_9$ cofactor,[1] hydrogenase with two iron or nickel and iron atoms bridged by two sulfurs,[2] and nitrile hydratase with an iron or cobalt centre ligated by three cysteinyl sulfurs.[3] Recently, we have been developing the chemistry of the tripodal tetradentate nitrogen–sulfur donor ligand [N(CH$_2$CH$_2$S)$_3$]$^{3-}$ (NS$_3$) with a variety of metals. We have already reported or communicated some of our results for Mo,[4] V,[5] Fe[6,7] and Ni,[8] and this paper presents the synthesis, the structural and spectroscopic properties and some chemistry of Fe(NS$_3$) complexes containing nitrosyl co-ligands. The structures formed in some cases parallel those of Fe(NS$_3$) complexes containing carbonyl co-ligands,[6] but some completely new structures containing two, three or four iron atoms are also described.
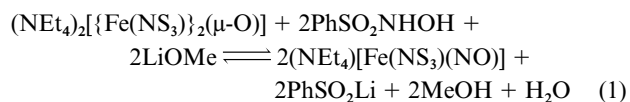
Results

Synthesis, spectra and structure of a mononuclear nitrosyl compound

We have already prepared the iron(II) carbonyl compound (NEt$_4$)[Fe(NS$_3$)(CO)][6] by the reaction of iron(III) acetylacetonate with tetraethylammonium acetate tetrahydrate and NS$_3$H$_3$ under an atmosphere of CO, so it seemed logical either to attempt a similar reaction under NO, or to displace the CO ligand by NO. Both approaches were successful, yielding brown crystals of (NEt$_4$)[Fe(NS$_3$)(NO)] (**1**) with ν(NO) at 1621 cm^{-1}. The reactions with NO were instantaneous and care was taken

not to expose the reaction mixtures to NO for longer than a few minutes [otherwise insoluble products whose IR spectra contained a multiplicity of bands between 1800 and 1600 cm^{-1} attributable to ν(NO) were obtained]. Subsequently, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald; Aldrich) was employed as a convenient source of NO; this reagent is principally known as a diazomethane precursor, but it has been used for many years as a nitrosylating reagent in inorganic and organometallic chemistry.[9] The reaction of [Fe(acac)$_3$], (NEt$_4$)OAc, Diazald and NS$_3$H$_3$ gave X-ray quality crystals of **1** in over 50% yield.

A further high-yield synthesis of **1** was carried out by displacing the bridging oxide ligand in the iron(III) complex (NEt$_4$)$_2$[{Fe(NS$_3$)}$_2$(μ-O)]·MeCN[10] using the NO$^-$-generating reagent *N*-hydroxybenzenesulfonamide (Piloty's acid[11]) in the presence of a base (lithium methoxide), according to eqn. (1).

$$(NEt_4)_2[\{Fe(NS_3)\}_2(\mu\text{-O})] + 2PhSO_2NHOH +$$
$$2LiOMe \rightleftharpoons 2(NEt_4)[Fe(NS_3)(NO)] +$$
$$2PhSO_2Li + 2MeOH + H_2O \quad (1)$$

The formal oxidation state of a metal ion in a complex containing a nitrosyl ligand is dependent upon whether the NO ligand is considered to be present as NO$^+$, neutral NO or NO$^-$. In the Enemark and Feltham notation,[12] **1** is a {FeNO}^{7} complex; ground spin states of $S = 3/2$ have been found in several {FeNO}^{7} complexes and biological systems, featuring either 5-coordinate (square pyramidal) or 6-coordinate ligation. This $S = 3/2$ state has been described as arising from the high-spin ferric ($S = 5/2$) state being antiferromagnetically coupled to NO$^-$ ($S = 1$).[13] However, it has also been argued from DFT calculations that {FeNO}^{7} centres of nitrosyl derivatives of

Table 1 Mössbauer parameters at 77 K (mm s^{-1}), with relative intensities and assignments

Complex	Fe(NS$_3$)			Fe(NO)$_2$			Other		
	i.s.	q.s.	Rel. int.	i.s.	q.s.	Rel. int.	i.s.	q.s.	Rel. int
1	0.37	0.68							
2	0.39	1.31	2				0.62	2.56	1 [a]
3	0.43	1.36							
4	0.38	1.29							
5	0.43	1.18							
6	0.40	1.28	1	0.18	0.60	1			
7	0.16	1.32	1	0.16	0.86	1			
8	0.24	1.68	1	0.18	0.74	1			
9	0.37	1.15	1	0.18	1.04	1			
10	0.28	2.08	1	0.17	0.43	1			
14	0.43	1.35	1	0.18	1.30	1	0.29	0.94	1 [b]

[a] Central Fe. [b] Fe(NO)$_2$I.

deoxyhemerythrin can experience strong valence delocalisation, leading to non-integral iron oxidation states.[14]

Experimental criteria for estimating the charge on an NO ligand include the M–N–O angle (160° or above for NO$^+$) and the value of v(NO) in the IR spectrum (1800–1900 cm^{-1} for NO$^+$ in a neutral complex and 1700–1800 cm^{-1} in an anion). In **1**, the Fe–N–O angle is 154.4(9)° and v(NO) is 1621 cm^{-1}; on these criteria the nitrosyl ligand is certainly not NO$^+$, but could be regarded as either neutral NO, NO$^-$ or a mixture of both (for which M–N–O angles down to 120° and v(NO) values down to 1500 cm^{-1} have been found[15]). Many {FeNO}^{7} $S = 3/2$ complexes described as containing high-spin ferric iron ($S = 5/2$) coupled to NO$^-$ ($S = 1$) have values of v(NO) much higher than in **1**.

The Mössbauer spectrum of **1** shows a symmetrical quadrupole-split doublet with an isomer shift (i.s.) of 0.37 mm s^{-1} and a quadrupole splitting (q.s.) of 0.68 mm s^{-1}. These parameters and the temperature independence of q.s. over the range 77–300 K are consistent with **1** containing high-spin iron(III) and being described as an {FeNO}^{7} complex.[13]

Mössbauer parameters, obtained by fitting the data with Lorentzian curves, for complexes **1**–**10** and **14**, with assignments, are given in Table 1.

Complex **1** crystallises isostructurally with several (NEt$_4$)-[M(NS$_3$)(L)] complexes, *e.g.* with M = V, L = Cl; M = Co, L = CN; M = Fe, L = Cl, CO, *etc.*, and is shown in Fig. 1. Principal dimensions of this and the other complexes described below,
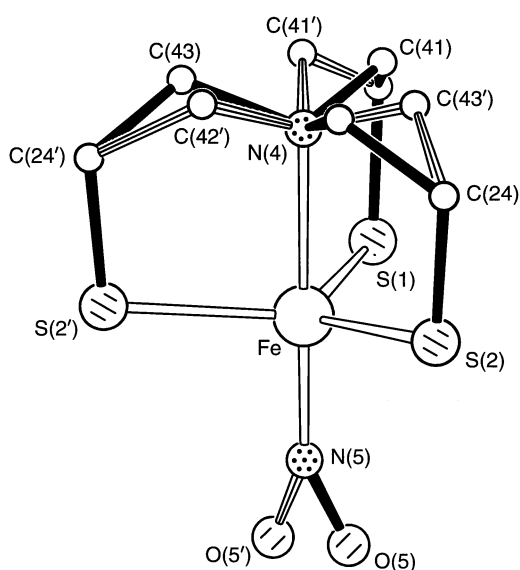
together with those of two 'parent' complexes, (NEt$_4$)[Fe(NS$_3$)-Cl] and (NEt$_4$)[Fe(NS$_3$)(CO)], are collated in Table 2.

The iron atom in complex **1** is five-coordinate, with trigonal bipyramidal geometry. Both cation and anion lie on elements of symmetry—the anion across a mirror plane and the cation on a twofold axis, giving rise to disorder in both ions. The O atom of the nitrosyl group is also disordered, with sites either side of the mirror plane and an Fe–N–O angle of 154.4(9)°. The iron atom is 0.228(1) Å out of the plane of the three sulfur atoms and the Fe–N(4) distance is 2.232(7) Å, typical of Fe(III) complexes.

The NO ligand in **1** has a *trans* effect nearer to that of the Cl ligand in the chloride (NEt$_4$)[Fe^{III}(NS$_3$)Cl] than that of the CO ligand in the carbonyl (NEt$_4$)[Fe^{II}(NS$_3$)(CO)] or the isocyanide ligand in the complex (NEt$_4$)[Fe^{II}(NS$_3$)(CNMe)],[7] as shown by a comparison of the Fe–N(NS$_3$) distances [2.276(3) Å in the chloride,[6] 2.035(7) Å in the carbonyl,[6] 2.049(2) Å in the isocyanide[7] and 2.232(7) Å in **1**]. The NO ligand, however, enforces spin pairing on **1** so that at 20 °C it has a spin state of $S = 3/2$, rather than the spin state of $S = 5/2$ in the chloride.

Complex **1** may be compared with a series of trigonal bipyramidal {FeNO}^{7} complexes with tripodal ligands derived from tris-(N-R-carbamoylmethyl)amine [R = isopropyl, cyclopentyl, 3,5-dimethylphenyl or n-(S)-(−)-(α)methylbenzyl].[16] In these complexes, the NO group is held within a cavity whose size is dependent on the size of R. N–O distances in these complexes fall in the range between 1.122(5) and 1.146(3) Å, similar to those in **1**, but the Fe–N–O angles, lying in the range 160.3(2) to 178.2(5)°, are much larger than the 154° found in **1**. As might be expected, the v(NO) values in the IR spectra of these complexes are also much higher at 1710–1750 cm^{-1} than v(NO) in the spectrum of **1**. All these complexes, like **1**, have $S = 3/2$ ground states, and Mössbauer spectra (measured at 4 K) containing simple doublets with isomer shifts ranging between 0.41 and 0.43 mm s^{-1} and quadrupole splittings ranging between 1.29 and 1.33 mm s^{-1}.

The structure of **1** may also be compared with that of the diamagnetic {MoNO}^{4} molybdenum compound [Mo(NS$_3$)-(NO)],[4] where the Mo–N–O angles are 176.4(2) and 176.1(2)° in the two virtually identical molecules in the crystal, considerably more linear than in **1**; the value of v(NO) in the spectrum of the molybdenum complex (1641 cm^{-1}) is, however, quite near to the 1621 cm^{-1} found in the spectrum of **1**.

Unlike its carbonyl analogue, **1** is indefinitely stable to air in the solid state and in acetonitrile solution. The nitrosyl ligand was displaced by reaction with sodium amalgam, and can be replaced by a carbonyl ligand if the reaction is carried out under CO, but the process is much slower than the displacement of the chloride ligand of (NEt$_4$)[Fe(NS$_3$)Cl].[6] We also tried displacing the NO ligand with a bridging oxo ligand by reaction with trimethylamine oxide, but could obtain no identifiable products, unlike when the carbonyl analogue was used to prepare (NEt$_4$)$_2$[{Fe(NS$_3$)}$_2$(μ-O)].[10]

Fig. 1 The anion of (NEt$_4$)[Fe(NO)(NS$_3$)], complex **1**, showing the disorder in the *N*-methylene groups and in the nitrosyl ligand. The atom numbering scheme is indicated. Hydrogen atoms have been omitted for clarity.

Table 2 Principal molecular dimensions in the Fe(NS₃)L complexes, bond lengths (Å) and angles (°). E.s.d.s are in parentheses. N.B. Fe⁵ and Fe⁴ refer to the five- and four-coordinate iron atoms, respectively

	Fe⁵–N(NS₃)	Fe⁵–S	N–Fe⁵–S	X, Fe⁵–X / Y, X–Y / Fe⁵–X–Y	Fe⁴–S / S–Fe⁴–S	Fe⁴–N / N–Fe⁴–N	N–O	Fe⁴–N–O	Other dimensions
(NEt₄)[Fe(NS₃)(NO)] (1)	2.232(7)	2.313(3) / 2.316(2)	84.2(2) / 84.40(12)	N(5), 1.721(8) / O(5), 1.143(12) / 154.4(9)	—	—	—	—	N(5)–Fe–N(4) 179.0(4)
[{Fe(NO₂){Fe(NS₃)}}₂] (6)	2.049(3)	2.2359(12)ᵃ / 2.2763(12)ᵃ / 2.2280(12)ᵃ	88.95(10) / 87.96(10) / 86.86(10)	S(23), 2.2186(11)	2.3039(13)ᵃ / 2.2975(13)ᵃ / 102.19(5)	1.682(4) / 1.676(4) / 118.0(2)	1.175(5) / 1.167(6)	168.5(4) / 172.0(5)	Fe(1)⋯Fe(2) 2.6779(9); Fe(1)⋯Fe(3) 2.7970(10); Fe(2)⋯Fe(1)⋯Fe(3) 137.43(3); Fe(1)–S(11)–Fe(3) 76.05(4); Fe(1)–S(12)–Fe(3) 75.40(4); Fe(2)–S(13)–Fe(1) 74.15(4); N(14)–Fe(1)–S(23) 168.33(11)
	2.041(4)	2.2251(12)ᵃ / 2.2658(12)ᵃ / 2.2250(11)ᵃ	89.31(10) / 88.28(10) / 86.52(10)	S(13), 2.2139(12)	2.3030(13)ᵃ / 2.2921(13)ᵃ / 102.32(4)	1.681(4) / 1.678(4) / 119.0(2)	1.181(5) / 1.174(6)	165.7(4) / 177.0(4)	Fe(2)⋯Fe(4) 2.7801(9); Fe(1)⋯Fe(2)⋯Fe(4) 138.45(3); Fe(2)–S(21)–Fe(4) 75.73(4); Fe(2)–S(22)–Fe(4) 75.17(4); Fe(1)–S(23)–Fe(2) 74.12(4); N(24)–Fe(2)–S(13) 168.15(10)
[Fe(NO₂){Fe(NS₃)(CO)}] (7)	2.0529(14)	2.2582(5)ᵃ / 2.2336(5)ᵃ / 2.1955(6)	88.23(4) / 88.53(4) / 88.13(4)	C(5), 1.770(2) / O(5), 1.140(2) / 178.7(2)	2.2925(6)ᵃ / 2.2741(6)ᵃ / 105.38(2)	1.679(2) / 1.665(2) / 119.96(10)	1.160(2) / 1.167(2)	168.5(2) / 175.4(2)	Fe(1)⋯Fe(2) 2.690(4); Fe(1)–S(1)–Fe(2) 72.13(2); Fe(1)–S(2)–Fe(2) 72.92(2); C(5)–Fe(1)–N(4), 177.20(8)
[Fe(NO₂){Fe(NS₃)(NO)}] (9)	2.231(2)	2.3547(9)ᵃ / 2.3089(9)ᵃ / 2.2305(8)	84.07(6) / 85.08(6) / 85.68(6)	N(5), 1.738(3) / O(5), 1.16(2)ᵇ / O(5a), 1.15(2)ᵇ / 145.3(12) / 151.8(9)	2.2913(9)ᵃ / 2.2976(9)ᵃ / 106.38(3)	1.672(3) / 1.660(3) / 117.32(13)	1.13(2)ᵇ / 1.23(2)ᵇ / 1.158(3)	161.6(13) / 170.1(9) / 173.3(3)	Fe(1)⋯Fe(2) 2.7660(6); Fe(2)–S(1)–Fe(1) 73.06(3); Fe(2)–S(2)–Fe(1) 73.80(3); N(5)–Fe(1)–N(4) 173.94(10)
(NEt₄)[Fe(NO₂){Fe(NS₃)(CN)}] (10)	2.067(6)	2.223(2)ᵃ / 2.214(2)ᵃ / 2.198(2)	87.6(2) / 88.4(2) / 88.0(2)	C(5), 1.890(8) / N(5), 1.156(8) / 177.7(8)	2.293(2)ᵃ / 2.293(2)ᵃ / 104.27(9)	1.661(6) / 1.657(7) / 116.6(3)	1.182(6) / 1.175(7)	162.1(6) / 178.0(7)	Fe(1)⋯Fe(2) 2.660(2); Fe(1)–S(1)–Fe(2) 72.16(7); Fe(1)–S(2)–Fe(2) 72.30(7); C(5)–Fe(1)–N(4) 176.2(3)
[{Fe(NO₂)I}{Fe(NS₃)(CNMe)}{Fe(NO₂)}] (13), Mol. 1	2.069(2)	2.2318(10)ᵃ / 2.2199(9)ᵃ / 2.2078(9)ᵃ	87.05(8) / 89.20(7) / 87.06(7)	C(15), 1.853(3) / N(15), 1.152(4) / 177.1(4)	2.2744(10) / 2.2645(10) / 105.22(4) / 2.3025(10)	1.654(3) / 1.667(3) / 116.8(2) / 1.666(4) / 1.671(4) / 114.6(2)	1.157(4) / 1.157(4) / 1.162(5) / 1.156(5)	167.3(4) / 172.0(4) / 166.9(5) / 170.5(5)	Fe(11)⋯Fe(12) 2.6552(7); Fe(11)⋯Fe(13) 2.8766(8); Fe(12)⋯Fe(11)⋯Fe(13) 137.17(2); Fe(11)–S(11)–Fe(12) 72.20(3); Fe(11)–S(12)–Fe(12) 72.61(3); Fe(11)–S(13)–Fe(13) 79.22(3); Fe(13)–I(2) 2.6605(7)
(13), Mol. 2	2.075(3)	2.2174(9)ᵃ / 2.2146(10)ᵃ / 2.2014(9)ᵃ	87.71(8) / 89.66(8) / 88.35(8)	C(25), 1.852(3) / N(25), 1.148(4) / 179.7(3)	2.2770(10) / 2.2558(10) / 104.43(4) / 2.2984(9)	1.675(3) / 1.661(3) / 116.8(2) / 1.674(3) / 1.660(3) / 111.8(2)	1.162(4) / 1.158(4) / 1.164(4) / 1.175(4)	167.5(3) / 172.7(4) / 164.0(3) / 168.4(3)	Fe(21)⋯Fe(22) 2.6639(7); Fe(21)⋯Fe(23) 2.7591(7); Fe(22)⋯Fe(21)⋯Fe(23) 152.20(2); Fe(21)–S(21)–Fe(22) 72.69(3); Fe(21)–S(22)–Fe(22) 73.15(3); Fe(21)–S(23)–Fe(23) 75.60(3); Fe(23)–I(2) 2.6438(6)
[{Fe(NO₂)I}{Fe(NS₃)(NO)}{Fe(NO₂)}] (14)	2.126(5)	2.282(2)ᵃ / 2.251(2)ᵃ / 2.263(2)ᵃ	86.5(2) / 87.9(2) / 85.9(2)	N(5), 1.768(8) / O(5), 1.123(8) / 168.5(7)	2.280(2) / 2.280(2) / 105.80(8) / 2.319(2)	1.658(7) / 1.647(7) / 120.2(3) / 1.669(7) / 1.690(8) / 110.3(3)	1.169(8) / 1.166(8) / 1.161(7) / 1.149(8)	169.6(7) / 175.8(7) / 162.1(7) / 165.2(7)	Fe(1)⋯Fe(2) 2.693(2); Fe(1)⋯Fe(3) 3.651(2); Fe(1)–S(1)–Fe(2) 72.37(7); Fe(1)–S(2)–Fe(2) 72.95(7); Fe(1)–S(3)–Fe(3) 105.65(8); Fe(3)–I(1) 2.5739(13)
(NEt₄)[Fe(NS₃)Cl]ᶜ	2.276(3)	2.3138(7) / 2.3193(10)	83.84(4) / 83.45(7)	Cl, 2.3113(11)	—	—	—	—	N(4)–Fe–Cl 178.95(7)
(NEt₄)[Fe(NS₃)(CO)]ᶜ	2.035(7)	2.281(3) / 2.271(2)	87.8(2) / 87.72(12)	C(5), 1.716(11) / O(5), 1.154(11) / 178.9(10)	—	—	—	—	C(5)–Fe–N(4) 179.9(4)

ᵃ The sulfur atom bridges two iron atoms. ᵇ The oxygen atom is disordered. ᶜ From ref. 6.
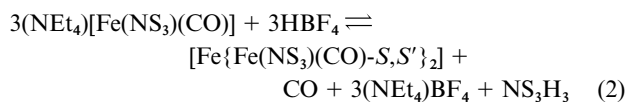
Trinuclear complexes

Following the chemistry of the carbonyl analogue of **1**, we tried to use **1** as a basis for building up multinuclear structures. The interaction of **1** with iron chloride solvates produced a dark brown insoluble compound, **2**, of stoichiometry $Fe_3(NO)_2$-$(NS_3)_2$ which has $\nu(NO)$ at 1710 and 1680 cm^{-1}, a Mössbauer spectrum containing two doublets of relative intensities 2 : 1, and a μ_{eff} of 2.90 μ_B at 295 K. We have not been able to grow crystals of this compound, but it probably has the structure $[Fe\{Fe(NS_3)(NO)\}_2\text{-}S,S']$, *i.e.* it is the nitrosyl analogue of the structurally characterised $[Fe\{Fe(NS_3)(CO)\}_2\text{-}S,S']$[6] and $[Fe\{Fe(NS_3)(CNCy)\}_2\text{-}S,S']$.[7] In both these compounds, as in **2**, $\nu(CO)$ and $\nu(CN)$ are raised approximately 50–100 cm^{-1} from their values in the anions $[Fe(NS_3)(CO)]^-$ and $[Fe(NS_3)\text{-}(CNCy)]^-$; again as in **2**, they show Mössbauer spectra containing two doublets of relative intensities 2 : 1, assigned to the two outer iron atoms and one central high-spin iron(II) atom respectively.

Complex **1** reacts with other metal chloride solvates, giving dark brown paramagnetic insoluble compounds of stoichiometry $MFe_2(NO)_2(NS_3)_2$ [M = Co (**3**), Ni (**4**), Cu (**5**)], all with $\nu(NO)$ near 1700 cm^{-1}, and Mössbauer spectra containing one doublet at a position near to that of the doublet corresponding to the outer iron atoms in the Mössbauer spectrum of **2**. Again, we were unable to grow crystals of these compounds, but they probably have the structures $[M\{Fe(NS_3)(NO)\}_2\text{-}S,S']$. Therefore **3** would be the nitrosyl analogue of the structurally characterised $[Co\{Fe(NS_3)(CO)\}_2\text{-}S,S']$,[6] and **4** that of the nickel complex $[Ni\{Fe(NS_3)(CO)\}_2\text{-}S,S']$.[17]

Complexes containing Fe(NO)$_2$ groups

In the carbonyl series, mononuclear and trinuclear carbonyls are interconverted by acid or base and, in closed systems, it is possible to show quantitative release or uptake of CO according to eqn. (2).

$$3(NEt_4)[Fe(NS_3)(CO)] + 3HBF_4 \rightleftharpoons$$
$$[Fe\{Fe(NS_3)(CO)\text{-}S,S'\}_2] +$$
$$CO + 3(NEt_4)BF_4 + NS_3H_3 \quad (2)$$

We therefore treated **1** with $HBF_4 \cdot Et_2O$ in acetonitrile in an attempt to prepare compound **2**, but the black crystals, **6**, that we obtained had the stoichiometry $Fe_2(NO)_2(NS_3)$, different from the expected $Fe_3(NO)_2(NS_3)_2$ of **2**. An X-ray study (Fig. 2)
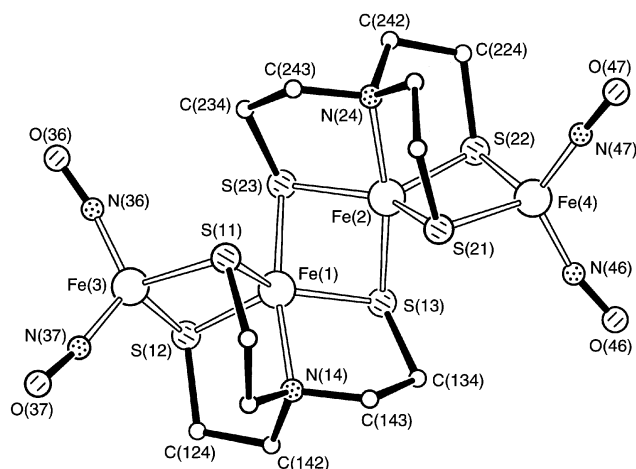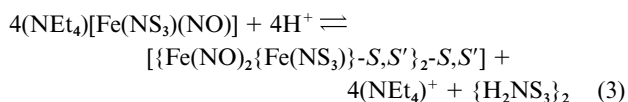

Fig. 2 A molecule of $[\{Fe(NO)_2\{Fe(NS_3)\}\text{-}S,S'\}_2\text{-}S,S']$, complex **6**.

revealed that **6** has the tetranuclear structure $[\{Fe(NO)_2\{Fe\text{-}(NS_3)\}\text{-}S,S'\}_2\text{-}S,S']$, where all the sulfurs are used in bridging between iron atoms.

In the formation of **6**, one of the iron atoms loses its NS$_3$ ligand and an NO ligand migrates to it. A possible equation for

this reaction is shown as eqn. (3)—it involves the release of $\{H_2NS_3\}_2$. The driving force in the preparation of **6** is presumably the very stable nature of the Fe(NO)$_2$ unit, which features prominently in iron–sulfur cluster chemistry.[18]

$$4(NEt_4)[Fe(NS_3)(NO)] + 4H^+ \rightleftharpoons$$
$$[\{Fe(NO)_2\{Fe(NS_3)\}\text{-}S,S'\}_2\text{-}S,S'] +$$
$$4(NEt_4)^+ + \{H_2NS_3\}_2 \quad (3)$$

We decided to synthesise **6** rationally by a method not involving NO migration from iron to iron and not involving wastage of half the NS$_3$ ligand. Accordingly, the yellow solution obtained by reducing $(NEt_4)[Fe(NS_3)Cl]$ with sodium amalgam,[6] which is thought to contain the anion $[Fe(NS_3)]_n^{n-}$, was treated with half an equivalent of $[\{Fe(NO)_2\}_2(\mu\text{-}I)_2]$[19] [*i.e.* a ratio of one Fe(NO)$_2$ group per Fe(NS$_3$) group]; from this reaction, **6** was isolated in good yield.

It is possible to split the central Fe–S bonds between the two $\{Fe(NO)_2Fe(NS_3)\}$ fragments of compound **6** with small molecules like CO. X-Ray quality crystals of $[Fe(NO)_2\text{-}\{Fe(NS_3)(CO)\}\text{-}S,S']$ (**7**) (Fig. 3) were obtained from the reac-
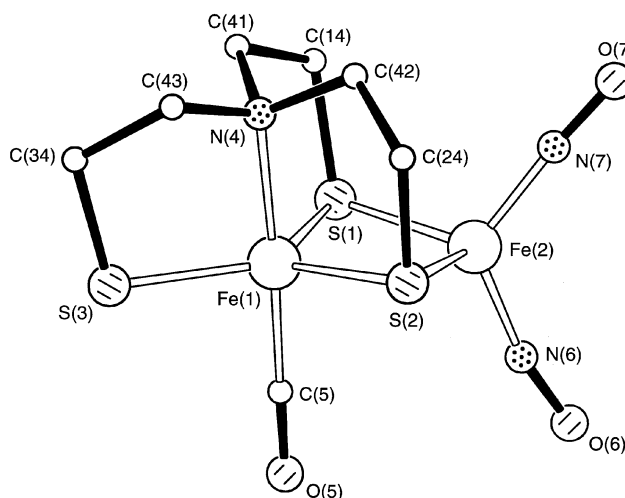

Fig. 3 A molecule of $[Fe(NO)_2\{Fe(CO)(NS_3)\}\text{-}S,S']$, complex **7**.

tion of **6** with CO, but yields were low, possibly because of the insolubility of **6**. Compound **7** can also be prepared from **1** by reaction with $HBF_4 \cdot Et_2O$ under CO, where formation of the insoluble **6** is prevented; attempts to recrystallise **7** from MeCN under an atmosphere of N$_2$ resulted in the loss of the CO ligand, **6** being formed.

To obtain high yields of **7**, we used an approach similar to that outlined above for **6**, involving treating $(NEt_4)[Fe(NS_3)\text{-}(CO)]$ with half an equivalent of $[\{Fe(NO)_2\}_2(\mu\text{-}I)_2]$, giving a 70% yield of **7**. In similar reactions, we prepared $[Fe(NO)_2\text{-}\{Fe(NS_3)(L)\}\text{-}S,S']$ [L = CNMe (**8**), NO (**9**)] from $(NEt_4)\text{-}[Fe(NS_3)(L)]$. We also isolated **9** (Fig. 4) in moderate yield from the reaction between **1** and *N*-hydroxybenzenesulfonamide (Piloty's acid—see above), which provides an extra NO group for reaction. $(NEt_4)[Fe(NO)_2\{Fe(NS_3)(CN)\}\text{-}S,S']$ (**10**) (Fig. 5) was obtained from the reaction of **6** with $(NEt_4)CN$, but yields were very low, and $[Fe(NO)_2\{Co(NS_3)(CN)\}\text{-}S,S']$ (**11**) was synthesised *via* the reaction of $(NEt_4)[Co(NS_3)(CN)]$ with half an equivalent of $[\{Fe(NO)_2\}_2(\mu\text{-}I)_2]$, but was not obtained analytically pure (see Experimental section).

We also treated $(NEt_4)[Fe(NS_3)(L)]$ with one equivalent of $[\{Fe(NO)_2\}_2(\mu\text{-}I)_2]$ [*i.e.* a ratio of two Fe(NO)$_2$ groups per Fe(NS$_3$) group] and isolated complexes with the structure $[\{Fe(NO)_2I\}\text{-}S\{Fe(NS_3)(L)\}\text{-}S',S''\{Fe(NO)_2\}]$ [L = CO (**12**), CNMe (**13**) (Fig. 6), NO (**14**) (Fig. 7)]. Complexes **12–14** are more soluble than complexes **7–9**, so it was necessary to employ exact stoichiometric ratios of reactants to obtain them.
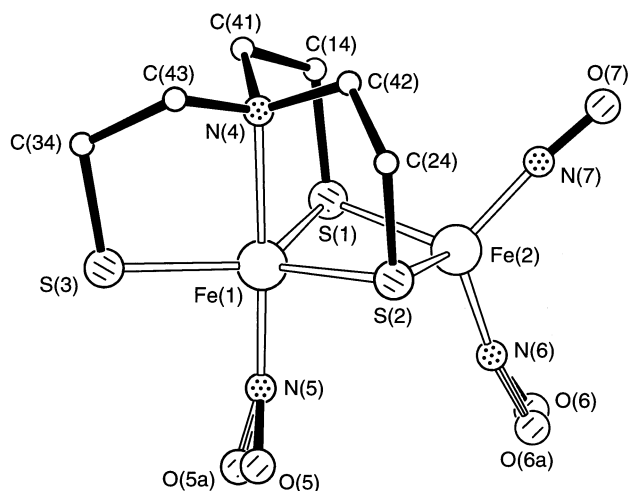
Fig. 4 A molecule of $[Fe(NO)_2\{Fe(NO)(NS_3)\}\text{-}S,S']$, complex **9**, showing disorder in two of the nitrosyl groups.
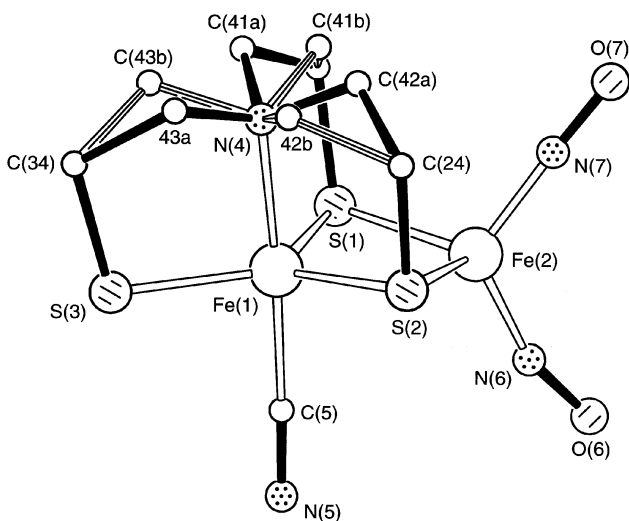
Fig. 5 The anion of $(NEt_4)[Fe(NO)_2\{Fe(CN)(NS_3)\}\text{-}S,S']$, complex **10**, showing the two possible orientations of the NS_3 ligand.

Complexes **6–11** show two bands in their IR spectra assigned to $\nu(NO)$ of the $Fe(NO)_2$ group and, in addition, bands assigned to $\nu(CO)$ (**7**), $\nu(CN)$ (**8**), $\nu(NO)$ (**9**) and $\nu(CN)$ (**10** and **11**) from the ligands on the $Fe(NS_3)$ or $Co(NS_3)$ sites. Comparison of the spectra of the isoelectronic **10** and **11** shows that the positions of both $\nu(CN)$ and $\nu(NO)$ are raised by about 80 cm^{-1} on going from the anion **10** to the neutral complex **11**.

The IR spectrum of complex **14** shows five bands in the 1800–1690 cm^{-1} region assignable to $\nu(NO)$, corresponding to the five nitrosyl groups, which are all in different environments. Complexes **12** and **13** were obtained in very low yields; their IR spectra show traces of contamination with **14**, and a crystal selected from the sample of **12** for X-ray study in fact turned out to be a crystal of **14**. It seems likely that the carbonyl ligand in **12** is even more labile than that in **7**, as it is replaced easily by extra NO groups, presumably from the $[\{Fe(NO)_2\}_2(\mu\text{-}I)_2]$ reagent. Attempts to employ excess $[\{Fe(NO)_2\}_2(\mu\text{-}I)_2]$ or temperatures above ambient in the preparation of **12** resulted in isolation of **14**.

The Mössbauer spectra of complexes **6–10** show two doublets of relative intensity 1 : 1, which we assign to the $Fe(NS_3)$ sites and the $Fe(NO)_2$ groups, respectively (Table 1). In each complex, the doublet with lower i.s. is assigned to the $Fe(NO)_2$ iron atom. The i.s. of this atom, as expected, does not change significantly with variation of the ligand at the $Fe(NS_3)$ site. The spectrum of complex **14** shows three overlapping doublets

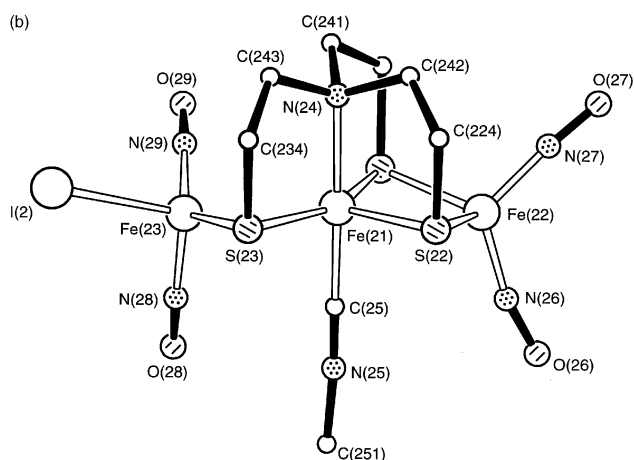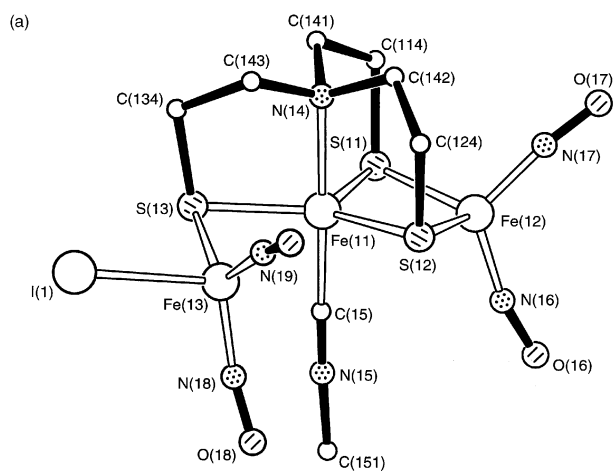**Fig. 6** The two independent molecules of $[\{Fe(NO)_2I\}\text{-}S\{Fe(NS_3)\text{-}(CNMe)\}\text{-}S',S''\{Fe(NO)_2\}]$, complex **13**.
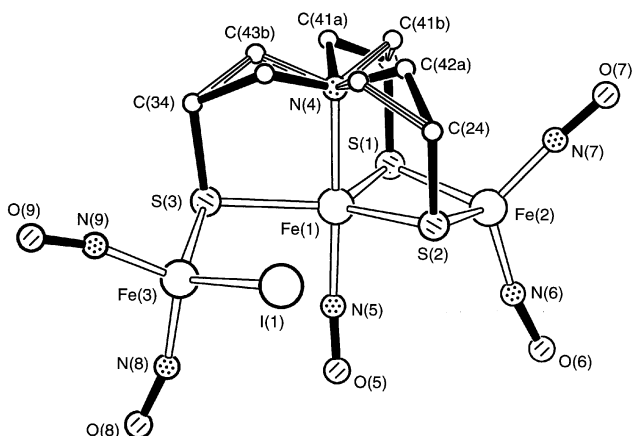
Fig. 7 A molecule of $[\{Fe(NO)_2I\}\text{-}S\{Fe(NS_3)(NO)\}\text{-}S',S''\{Fe(NO)_2\}]$, complex **14**, showing the disorder in the NS_3 ligand.

of relative intensity 1 : 1 : 1 (i.s. = 0.18, 0.29, 0.43; q.s. = 1.30, 0.94, 1.35 mm s^{-1}) which are assigned to the $Fe(NO)_2$, $Fe(NO)_2I$ and $Fe(NS_3)(NO)$ fragments, respectively.

Structures of polynuclear complexes

The molecule of compound **6** shows pseudo-twofold symmetry about a line normal to the projection plane shown in Fig. 2. The central pair of iron atoms are the typical five-coordinate atoms of $Fe(NS_3)L$ groups, where L, in an apical site, here is a sulfur of the other $Fe(NS_3)$ group. There is more distortion in this complex from the normal trigonal bipyramidal pattern found in $[Fe(NS_3)L]$ complexes; the *trans* N–Fe–S angles are 168.33(11) and 168.15(10)°, compared with, for example, 179.0(4)° found

for N–Fe–N in complex **1**. All the Fe–S distances are shorter than in complex **1**, even though all the sulfur atoms bridge two Fe atoms. The Fe–N(amine) distances, 2.049(3) and 2.041(4) Å, are indicative of Fe^{II}. Each of the outer pair of iron atoms has an approximately tetrahedral coordination pattern, with two (bridging) thiolate ligands and two terminal nitrosyl groups. From a room temperature study, one of the nitrosyl groups is disordered, with its O atom having two equally likely sites; the corresponding O atom on the opposite iron atom has large thermal parameters but was not resolved into two sites. The results from the low-temperature dataset reported here show both these O atoms refined with relatively large U values at single sites. The Fe–N–O angles must therefore be considered with caution, but those nitrosyl groups with no disorder and little thermal motion have Fe–N–O angles of *ca* 166°, not a linear arrangement.

The central quartet of atoms in **6** forms a distorted tetrahedron rather than a square, with angles of 81.47(4), 74.15(4), 81.64(4) and 74.12(4)° at Fe(1), S(13), Fe(2) and S(23), respectively. The distance between the two central iron atoms is 2.6779(9) Å, remarkably similar to the Fe–Fe distance of 2.6664(4) Å in the trinuclear complex [Fe{Fe(NS₃)(CO)}₂-S,S′].[6]

Crystal structure analysis of complex **7** shows a dinuclear molecule containing the Fe(NS₃)Fe(NO)₂ moiety found in complex **6** above, with a carbonyl ligand occupying the fifth, apical site on the five-coordinate iron atom of the Fe(NS₃) group, Fig. 3. Without the bridging constraints found in complex **6**, the *trans* N–Fe–C angle in **7** is almost linear at 177.20(8)°. The Fe(1)–N(4) distance of 2.0529(14) Å suggests this iron is Fe^{II}. The second Fe resembles the outer iron atoms of complex **6**, having tetrahedral coordination. The two nitrosyl ligands on this Fe are slightly bent, with Fe–N–O angles of 168.5(2) and 175.4(2)°.

Molecules of complex **9** appear very similar to those of complex **7**, with a five-coordinate Fe(NS₃)(NO) moiety linked through two thiolate sulfur atoms to a tetrahedral FeS₂(NO)₂ unit, Fig. 4. There are, however, distinct differences in the molecular dimensions: the two Fe atoms are almost 0.1 Å closer in complex **7**; the Fe(1)–S distances are all significantly shorter in **7**; Fe(1)–N(4) is nearly 0.2 Å shorter in **7**. The dimensions about Fe(1) indicate that this atom is Fe^{III} in complex **9**. The dimensions about Fe(2) in complexes **7** and **9** are very similar and we propose that these tetrahedral irons are Fe^{III} in both complexes. The dimensions of the nitrosyl ligands, all slightly bent (including the disordered groups), are consistent with their being NO^{-} ligands.

The anion of complex **10** is shown in Fig. 5 and is very similar to complexes **7** and **9**. In **10**, however, the *N*-methylene groups of the NS₃ ligand are disordered, with an occupancy ratio of 0.760 : 0.240. The other ligands, an apical CN^{-} group on Fe(1) and the two nitrosyl ligands on Fe(2), show no sign of disorder. The cyanide and one of the nitrosyl ligands are essentially linear, but the second nitrosyl group has the more usual bent conformation.

In all the complexes containing the tetrahedral FeS₂(NO)₂ group, we note that the S–Fe–S angle (in the range 102.2 to 106.4°) is rather sharper than the regular tetrahedral angle, and that the opposing N–Fe–N angle is correspondingly wider (116.6 to 120.0°).

There are two independent and distinctly different molecules in crystals of complex **13**. Fig. 6 shows these molecules, with the Fe₂S₂ four-member rings aligned as for complexes **7** and **9** in Fig. 3 and 4. In this view, the right-hand side of the molecules have very similar conformations. The third thiolate S atom, and indeed the whole of the NS₃ ligand in molecule 1 of **13**, look very similar to the arrangements found in the previous structures and the FeI(NO)₂ group is bonded to that thiolate, S(13). The iron atom Fe(13) is tetrahedrally coordinated and arranged with the Fe–I bond roughly *trans* to S(13)–Fe(11). The Fe(11)–

S(13)–Fe(13) angle is acute at 79.22(3)° and the FeI(NO)₂ group comes out of the plane of the page towards the viewer.

In contrast, the NS₃ group in molecule 2 of **13** is uniquely distorted from the normal pseudo-threefold symmetrical arrangement. The S–C–C–N torsion angles in the three arms of this ligand are 42.7(4), 46.8(4) and −46.6(3)°, and the the S–Fe(21)–S angles, at 107.86(4), 153.85(4) and 97.95(4)°, deviate greatly from the usual values, *e.g.* 107.92(2), 125.19(2) and 126.63(2)° in complex **7**; there is some distortion from these values in molecule 1 of **13**, where the corresponding angles are 108.20(4), 115.37(4) and 135.97(4)°. The distortions in molecule 2 presumably arise to accommodate the FeI(NO)₂ group on the opposite side of the molecule, with the S(23)–Fe(23) bond projecting away from the viewer. The Fe(21)–S(23)–Fe(23) angle, at 75.60(3)°, is again acute (even more so than in molecule 1) and the Fe(23)–I bond is essentially *trans* to the S(23)–Fe(21) bond.

Complex **14** has the same general formula as **13**, [{Fe-(NO)₂I}-S{Fe(NS₃)(L)}-S′,S″{Fe(NO)₂}], differing only in the L ligand; CNMe for **13**, NO for **14**. The coordination patterns for the three iron atoms are similar in the two complexes. The molecule in **14** shows no evidence of gross distortion of the NS₃ ligand from pseudo-threefold symmetry, but there is the more frequently found disorder in that ligand, as found in complex **1**, with an occupancy ratio 0.741(12) : 0.259 for the two components. In **14**, the FeI(NO)₂ group projects forward from the NS₃ ligand, with the major NS₃ component aligned in Fig. 7 as in Fig. 4 and 6(a). Now the Fe(3)–I(1) bond is *cis* to the S(3)–Fe(1) bond. The Fe(1)–S(3)–Fe(3) angle is 105.65(8)° and the close interaction that I(1) makes with S(2) [3.813(2)Å] suggests that a more acute angle at S(3), as found in **13**, is not feasible here. The Fe(1) ⋯ Fe(3) distance is correspondingly longer than those in **13**.

Discussion and conclusions

The [Fe(NO)₂Fe(NS₃)-S,S′] and [{Fe(NO)₂I}-S{Fe(NS₃)}-S′,S″{Fe(NO)₂}] neutral sites may, thus, be ligated by some of the same small molecules L (L = CO, CNMe and NO), as may the anionic [Fe(NS₃)]⁻ site.[6] In view of this ability of the Fe(NS₃) site to ligate small molecules, whether or not it is coordinated to the Fe(NO)₂ group and the Fe(NO)₂I group, it is probably justifiable to assume that the formal oxidation state of the iron atom in the Fe(NS₃) site does not change on ligation of this site, either as a bidentate chelating ligand to one Fe(NO)₂ group or as a bridging tridentate ligand between Fe(NO)₂ and Fe(NO)₂I groups. Thus, the oxidation state of the Fe(NS₃) iron atom is 2+ in complexes **6**, **7**, **8**, **10**, **12** and **13**, and probably 3+ in **9** and **14** (as in the parent nitrosyl complex **1**).

Comparison of the IR spectra of the complexes **7**, **8**, **12** and **13** with the spectra of the parent complexes reinforces the above conclusion. Thus, v(CO) for **7** is at 1948 cm⁻¹, very near the value of 1937 cm⁻¹ found for the trinuclear [Fe{Fe(NS₃)(CO)}₂-S,S′] and, allowing for the change from an anion to a neutral complex, approximately equivalent to the 1910 cm⁻¹ observed for (NEt₄)[Fe(NS₃)(CO)].[6] The value of v(CO) for **12** is 1973 cm⁻¹, slightly higher than that of **7**, which presumably reflects the slight increase in positive charge on the Fe(NS₃) site on coordination to the Fe(NO)₂I group (and also reflects the increase in lability of the CO ligand). Similarly, the value of v(CN) for **8** (2152 cm⁻¹) is near that found for the trinuclear [Fe{Fe(NS₃)(CNMe)}₂-S,S′] (2101 cm⁻¹) and, again allowing for the change from an anion to a neutral complex, approximately equivalent to v(CN) for (NEt₄)[Fe(NS₃)(CNMe)][7] (2061 cm⁻¹). v(CN) for **13** is at the slightly higher value of 2171 cm⁻¹.

If a similar comparison is carried out of the IR spectra of **1**, **9** and **14**, the lowest wavenumber band in the 1600–1800 cm⁻¹ region (at 1621, 1654 and 1695 cm⁻¹ in the spectra of **1**, **9** and **14**, respectively) can be assigned to the nitrosyl ligand on the Fe(NS₃) sites. The 1695 cm⁻¹ absorbance in the spectrum of

14 appears as a weak band or shoulder in the spectra of **12** and **13** (which contain **14** as an impurity).

There is very little difference between the *trans* effect of a CO ligand in the anion of $(NEt_4)[Fe(NS_3)(CO)]$,[6] where the Fe–N distance in the $Fe(NS_3)$ system is 2.035(7) Å, and the *trans* effect of a CO ligand in **7**, where the Fe–N distance in the $Fe(NS_3)$ system is 2.0529(14) Å. Similarly, there is very little difference between the *trans* effect of an NO ligand in the anion of **1**, where the Fe–N distance in the $Fe(NS_3)$ system is 2.232(7) Å, and the *trans* effect of an NO ligand in **9**, where the Fe–N distance in the $Fe(NS_3)$ system is 2.231(2) Å. This is consistent with the hypothesis proposed above that the oxidation state of the iron in the $Fe(NS_3)$ group is essentially unchanged upon its ligation to the $Fe(NO)_2$ group.

The Fe–Fe distance in $[\{Fe(NO)_2(SEt)\}_2]$[20] is 2.72 Å; this compound is diamagnetic, either because of the presence of a metal–metal bond or through superexchange magnetic interactions through the sulfur bridges. The Fe–Fe distance compares with the distances between the irons of the $Fe(NS_3)$ and $Fe(NO)_2$ groups of 2.7970(10) and 2.7801(9) Å in the $\{Fe(NO)_2Fe(NS_3)\}$ fragments of **6**, of 2.6790(4) Å in **7**, of 2.7660(6) Å in **9** and of 2.660(2) Å in **10**. The values of the Fe–Fe distances in the structures of **6–10** also fall within the ranges of Ni–Fe distances in selected dichalcogenide $Fe(NO)_2$ compounds compiled by Liaw *et al*,[21] *e.g.* $[(ON)Ni\{\mu\text{-}S(CH_2)_2\text{-}S(CH_2)_2S\}Fe(NO)_2]$, where the Ni–Fe distance is 2.8001(6) Å, and $Ni(L)Fe(NO)_2$ (L = N,N'-diethyl-3,7-diazanonane-1,9-dithiolate), where it is 2.797(1) Å.[22] As might be expected from these short Fe–Fe distances, the magnetic moments of the complexes **2–10** and **14** are low at 20 °C, like those of $[M\{Fe(NS_3)(CO)\}_2\text{-}S,S']$[6] (M = Fe, Co) (see Experimental section). Temperature-dependent magnetic studies on selected complexes will be reported separately.

The $Fe(NO)_2$ group is a very common feature of FeS clusters with NO ligands, ranging from the dinuclear $[Fe_2S_2(NO)_4]^{2-}$ [23] to large clusters like $[Fe_7S_6(NO)_{10}]^-$.[24] Several compounds with $Fe(NO)_2$ groups ligated by nickel thiolates through two sulfurs, and one compound with an $Fe(NO)_2$ group ligated by a CO ligand together with a nickel thiolate through a single sulfur, have also been described.[21] Favoured reagents for introducing the $Fe(NO)_2$ group into complexes are the nitrite anion (used to make Roussin salts[23]), the dicarbonyl dinitrosyl reagent $[Fe(CO)_2(NO)_2]$[21,22] and salts of the $[Fe(NO)_2(SePh)_2]^-$ anion.[21] The use of $[\{Fe(NO)_2\}_2(\mu\text{-}I)_2]$, which can be made extremely pure because it sublimes *in vacuo* at 100 °C, is a little-explored alternative means for building up cluster compounds without oxidation or reduction of the parent starting materials. Complexes **12–14** are the first known compounds with an $Fe(NO)_2$ fragment ligated both by an iodine ligand and a metal-containing thiolate ligand.

Finally, following Liaw *et al*,[21] we note that the $Fe(NO)_2$ fragment is isolobal with the $Fe(CO)(CN)_2$ fragment established to be present in hydrogenases,[2] and may serve as an acceptable alternative model fragment in modelling studies of these enzymes.

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 Aldrich Chemical Co. and used without further purification, unless otherwise stated. NS_3H_3 was prepared by a modification of the literature method[25] *via* tris(chloroethyl)amine hydrochloride. $[FeCl_2(MeCN)_2]$ and $[FeCl_2(dmso)_3]$ and their cobalt, nickel and copper analogues were made by heating the anhydrous metal chlorides in MeCN or dmso until they dissolved and

crystallising by adding diethyl ether. $[\{Fe(NO)_2\}_2(\mu\text{-}I)_2]$ was made from Fe, I_2 and NO.[19] Spectroscopic and magnetic measurements were made as described previously.[6]

CAUTION: tris(chloroethyl)amine hydrochloride is a vesicant. Reactions involving this reagent were carried out in enclosed Schlenk apparatus while wearing heavy-duty gloves and a face mask.

Syntheses

$(NEt_4)[Fe(NS_3)(NO)]$ (1). *Method A.* Iron(III) acetylacetonate (2.84 g, 8 mmol), $(NEt_4)OAc\cdot4H_2O$ (2.62 g, 10 mmol) and Diazald (*N*-nitroso *N*-methyl-*p*-toluenesulfonamide) (1.76 g, 8 mmol) were stirred in MeCN (30 mL), and NS_3H_3 (2.4 g, 12 mmol) in MeCN (10 mL) was added, giving a dark brown solution. This was filtered from some sticky residue after 2 h; the residue was washed with MeCN (10 mL), and diethyl ether (150 mL) was added as a layer to the combined filtrate and washings. Brown crystals (1.86 g, 57%) grew overnight—they were filtered off and washed with a mixture of MeCN and diethyl ether (1 : 3), and then diethyl ether, and dried in a vacuum. Found: C, 40.7; H, 7.7; N, 10.1; $C_{14}H_{32}FeN_3OS_3$ requires: C, 41.0; H, 7.8; N, 10.2%. IR: 1621 cm^{-1} [ν(NO)]. $\mu_{eff} = 3.74 \mu_B$ (S = 3/2).

Method B. $(NEt_4)[Fe(NS_3)(CO)]$ (0.41 g, 1 mmol) in MeCN (40 mL) was stirred under NO gas for 10 min. The green solution turned brown with gas being evolved. The volume was reduced to 10 mL, and diethyl ether (40 mL) was added as a layer, giving 0.34 g (74%) of brown needles.

Method C. $(NEt_4)_2[\{Fe(NS_3)\}_2(\mu\text{-}O)]\cdot MeCN$ (0.2 g, 0.25 mmol) and lithium methoxide (0.5 mL, 1 M solution in methanol) were stirred in MeCN (5 mL) and *N*-hydroxybenzenesulfonamide (0.09 g, 0.5 mmol) was added, giving a brown solution. Next day this was filtered and diethyl ether (20 mL) was added, giving brown crystals (0.12 g, 60%).

$[Fe\{Fe(NS_3)(NO)\}_2\text{-}S,S']$ (2). $[FeCl_2(MeCN)_2]$ (0.15 g, 0.75 mmol) in MeOH (15 mL) was added to $(NEt_4)[Fe(NS_3)(NO)]$ (0.62 g, 1.5 mmol) in MeOH (30 mL). There was an immediate brown precipitate (0.33 g, 71%) which was filtered off and washed with methanol and diethyl ether. Found: C, 23.2; H, 3.5; N, 9.0; Fe, 27.8; $C_{12}H_{24}Fe_3N_4O_2S_6$ requires: C, 23.4; H, 3.9; N, 9.1; Fe, 27.3%. IR: 1701 cm^{-1} [ν(NO)]. $\mu_{eff} = 2.90 \mu_B$ (293 K).

$[Co\{Fe(NS_3)(NO)\}_2\text{-}S,S']$ (3). Compound **3** was prepared similarly to **2** in 80% yield from $[CoCl_2(dmso)_3]$. Found: C, 23.2; H, 4.0; N, 8.8; Fe, 17.2; Co, 10.7; $C_{12}H_{24}CoFe_2N_4O_2S_6$ requires: C, 23.3; H, 3.9; N, 9.1; Fe, 18.1; Co, 9.5%. IR: 1693 cm^{-1} [ν(NO)]. $\mu_{eff} = 3.83 \mu_B$ (293 K).

$[Ni\{Fe(NS_3)(NO)\}_2\text{-}S,S']$ (4). Compound **4** was prepared similarly to **2** in 55% yield from $[NiCl_2(dmso)_3]$. Found: C, 23.9; H, 4.1; N, 8.7; Fe, 18.7; Ni, 10.7; $C_{12}H_{24}Fe_2N_4NiO_2S_6$ requires: C, 23.3; H, 3.9; N, 9.1; Fe, 18.1; Ni, 9.2%. IR: 1679 cm^{-1} [ν(NO)]. $\mu_{eff} = 4.70 \mu_B$ (293 K).

$[Cu\{Fe(NS_3)(NO)\}_2\text{-}S,S']$ (5). Compound **5** was prepared similarly to **2** in 48% yield from $[CuCl_2(dmso)_2]$. Found: C, 23.5; H, 4.1; N, 8.2; Fe, 17.7; $C_{12}H_{24}CuFe_2N_4O_2S_6$ requires: C, 23.1; H, 3.8; N, 9.0; Fe, 17.9%. IR: 1692 cm^{-1} [ν(NO)]. $\mu_{eff} = 4.28 \mu_B$ (293 K).

$[\{Fe(NO)_2\{Fe(NS_3)\}\text{-}S,S'\}_2\text{-}S,S']$ (6). *Method A.* Compound **1** (0.21 g, 0.5 mmol) in MeCN (10 mL) and $HBF_4\cdot Et_2O$ (0.08 g, 0.5 mmol) in MeCN(10 mL) were mixed. Black microcrystals (0.06 g, 64% of Fe) precipitated; they were filtered off after 1 h, washed with MeCN and diethyl ether, and dried in a vacuum. Found: C, 19.9; H, 3.0; N, 11.3; $C_{12}H_{24}Fe_4N_6O_4S_6$ requires: C, 19.7; H, 3.3; N, 11.5%. IR: 1708, 1680 cm^{-1} [ν(NO)]. $\mu_{eff} = 3.26 \mu_B$ (293 K).

Method B. (NEt$_4$)[Fe(NS$_3$)Cl] (0.84 g, 2 mmol) in MeCN (60 mL) was shaken with sodium amalgam (0.5% Na, 100 g) until the red colour disappeared, then the MeCN layer was filtered through Celite and [{Fe(NO)$_2$}$_2$(μ-I)$_2$] (0.49 g, 1 mmol) in MeCN (20 mL) was added to the orange filtrate. There was an immediate dark precipitate, which was filtered off after 30 min, washed with MeCN and diethyl ether, and dried in a vacuum. It was identified from its IR spectrum as being identical to the product obtained *via* method A. Yield: 0.46 g, 63%.

[Fe(NO)$_2${Fe(NS$_3$)(CO)}-*S*,*S'*] (7). *Method A.* Compound **6** (0.14 g, 0.18 mmol) was warmed to 40 °C in MeCN (2 mL) under a CO atmosphere for 20 min, giving a bright red solution which was filtered from a little residue and cooled at −20 °C overnight. Small black square crystals (0.01 g, 0.02 mmol, approx 5%) were isolated by decantation of the supernatant, washed with MeCN and diethyl ether, and dried in a vacuum.

Method B. Compound **1** (0.52 g, 1.25 mmol) in MeCN (15 mL) and HBF$_4$·Et$_2$O (0.21 g, 1.25 mmol) in MeCN (5 mL) were mixed and stirred under CO. There was no precipitation, and a slow uptake of CO occurred. After 1 h, the solution was warmed to 40 °C for 30 min, filtered under CO and left to cool overnight. Small square crystals (0.02 g, approximately 5% of Fe, IR spectrum identical to that of the product from method A) were isolated by decantation of the solvent under CO, washed with MeCN and diethyl ether, and dried in a vacuum.

Method C. (NEt$_4$)[Fe(NS$_3$)(CO)] (0.41 g, 1 mmol) in MeCN (15 mL) was filtered from a small amount of residue and [{Fe(NO)$_2$}$_2$(μ-I)$_2$] (0.25 g, 0.5 mmol) in MeCN (5 mL) was added to the green filtrate. There was an immediate change to a dark colour, and small square crystals (0.20 g, 0.51 mmol, 51%) precipitated overnight. They were filtered off, washed with MeCN and diethyl ether, and dried in a vacuum. Found: C, 21.6; H, 3.0; N, 10.8; C$_7$H$_{12}$Fe$_2$N$_3$O$_3$S$_3$ requires: C, 21.3; H, 3.0; N, 10.7%. IR: 1948 [ν(CO)], 1769, 1722 cm^{-1} [ν(NO)]. μ_{eff} = 2.91 μ_B (293 K).

[Fe(NO)$_2${Fe(NS$_3$)(CNMe)}-*S*,*S'*] (8). This was made similarly to **7** by method C from (NEt$_4$)[Fe(NS$_3$)(CNMe)] and [{Fe(NO)$_2$}$_2$(μ-I)$_2$] in 18% yield. Found: C, 23.6; H, 3.6; N, 13.6; C$_8$H$_{15}$Fe$_2$N$_4$O$_2$S$_3$ requires: C, 23.6; H, 3.7; N, 13.8%. IR: 2152 [ν(CN)], 1738, 1693 cm^{-1} [ν(NO)]. μ_{eff} = 2.37 μ_B (293 K).

[Fe(NO)$_2${Fe(NS$_3$)(NO)}-*S*,*S'*] (9). *Method A.* Compound **1** (0.21 g, 0.5 mmol) and PhSO$_2$NHOH (0.08 g, 0.5 mmol) were heated at reflux in MeCN (20 mL), then cooled to 20 °C overnight. The resulting crystals (0.07 g, 60% of Fe) were filtered off, washed with MeCN and diethyl ether, and dried in a vacuum. Found: C, 18.3; H, 3.0; N, 14.0; C$_6$H$_{12}$Fe$_2$N$_4$O$_3$S$_3$ requires: C, 18.2; H, 3.0; N, 14.1%. IR: 1789, 1736, 1654 cm^{-1} [ν(NO)]. μ_{eff} = 2.81 μ_B (293 K).

Method B. Compound **9** was also prepared in a similar way to **7** (method C) in 75% yield starting from (NEt$_4$)[Fe(NS$_3$)(NO)] and [{Fe(NO)$_2$}$_2$(μ-I)$_2$].

(NEt$_4$)[Fe(NO)$_2${Fe(NS$_3$)(CN)}-*S*,*S'*] (10). Compound **6** (0.14 g, 0.18 mmol) and (NEt$_4$)CN (0.06 g, 0.37 mmol, dried *in vacuo* at 140 °C) were heated in MeCN (2 mL) at reflux for 20 min giving a bright red solution which was filtered from a little residue and cooled at −20 °C overnight. Small black, square crystals (0.02 g, 0.04 mmol, approx 10%) were isolated by decantation of the solvent, washed with MeCN and diethyl ether, and dried in a vacuum. Found: C, 34.4; H, 6.0; N, 13.4; C$_{15}$H$_{32}$Fe$_2$N$_5$O$_2$S$_3$ requires: C, 34.5; H, 6.1; N, 13.4%. IR: 2060 [ν(CN)], 1717, 1672 cm^{-1} [ν(NO)].

[Fe(NO)$_2${Co(NS$_3$)(CN)}-*S*,*S'*] (11). (NEt$_4$)[Co(NS$_3$)(CN)] (0.41 g, 1 mmol) in MeCN (40 mL) was filtered from a small amount of residue and [{Fe(NO)$_2$}$_2$(μ-I)$_2$] (0.25 g, 0.5 mmol) in MeCN (5 mL) was added to the green filtrate. After 3 days, the dark brown mixture was filtered; there was only a very small amount of precipitate, so the filtrate was taken to reflux for 20 min, then cooled at −20 °C for 6 days. This gave a brown precipitate which was filtered off, washed with diethyl ether, and dried in a vacuum. Yield 0.18 g, 0 45 mmol, 45%. A poor elemental analysis was obtained: found: C, 22.7; H, 3.3; N, 13.3; C$_7$H$_{12}$CoFeN$_4$O$_2$S$_3$ requires: C, 21.2; H, 3.0; N, 14.2%. IR: 2141 [ν(CN)], 1782, 1728 cm^{-1} [ν(NO)].

[{Fe(NO)$_2$I}-*S*{Fe(NS$_3$)(CO)}-*S'*,*S''*{Fe(NO)$_2$}] (12). (NEt$_4$)-[Fe(NS$_3$)(CO)] (0.21 g, 0.5 mmol) in MeCN (10 mL) was filtered from a small residue and [{Fe(NO)$_2$}$_2$(μ-I)$_2$] (0.25 g, 0.5 mmol) in MeCN (6 mL) was added to the green filtrate. There was an immediate change to a dark colour, but no precipitate. After 3 days, the solution volume was reduced to approximately 5 mL, whereupon some precipitation was seen; it was then filtered and dark blue needles (0.04 g, 0.06 mmol, 12%) crystallised overnight from the filtrate. They were filtered off, washed with MeCN and diethyl ether and dried in a vacuum. Found: C, 12.9; H, 2.0; N, 11.6; C$_7$H$_{12}$Fe$_3$I N$_5$O$_5$S$_3$ requires: C, 13.2; H, 1.9; N, 11.0%. IR: 1973 [ν(CO)] 1797, 1771, 1749, 1722, 1690(sh) cm^{-1} [ν(NO)].

[{Fe(NO)$_2$I}-*S*{Fe(NS$_3$)(CNMe)}-*S'*,*S''*{Fe(NO)$_2$}] (13). Compound **13** was synthesised similarly to **12** from (NEt$_4$)[Fe(NS$_3$)-(CNMe)] (0.16 g, 0.33 mmol) and [{Fe(NO)$_2$}$_2$(μ-I)$_2$] (0.16 g, 0.33 mmol) in a yield of 10%. Found: C, 15.0; H, 2.3; N, 12.9; C$_8$H$_{15}$Fe$_3$I N$_6$O$_4$S$_3$ requires: C, 14.8; H, 2.3; N, 13.0%. IR: 2172 [ν(CN)], 1784, 1753, 1738, 1713, 1699(w) cm^{-1} [ν(NO)].

[{Fe(NO)$_2$I}-*S*{Fe(NS$_3$)(NO)}-*S'*,*S''*{Fe(NO)$_2$}] (14). Compound **14** was prepared similarly to **12** from (NEt$_4$)[Fe(NS$_3$)-(NO)] (0.21 g, 0.5 mmol) and [{Fe(NO)$_2$}$_2$(μ-I)$_2$] (0.36 g, 0.75 mmol), in MeCN (5 mL). The solution was briefly heated to reflux temperature, filtered and allowed to cool to room temperature, whereupon long dark blue needles (0.18 g, 0.28 mmol, 56%) crystallised. Found: C, 11.4; H, 1.7; N, 13.0; C$_6$H$_{12}$Fe$_3$-I N$_6$O$_5$S$_3$ requires: C, 11.3; H, 1.9; N, 13.1. IR: 1797, 1778, 1753, 1724, 1697 cm^{-1} [ν(NO)]. μ_{eff} = 2.81 μ_B (293 K).

Crystal structure analyses

Diffraction data for twinned crystals of compound **6** were kindly provided by Dr M. Ruf of Bruker AXS, Inc., Madison, WI, from measurements at 173 K on a Bruker SMART 6000 CCD diffractometer using monochromated Cu-Kα radiation.

Crystals of the other complexes, after preliminary photographic examination, were mounted on our Nonius CAD4 diffractometer, equipped with a scintillation counter and using Mo-Kα radiation, for determination of accurate cell parameters and measurement of diffraction intensities.

Semi-empirical absorption corrections were applied to all datasets, structures were determined by direct methods in the SHELXS program[26] and refined, by full-matrix least-squares methods on F^2 in SHELXL.[27] Crystal data and details and results of all the crystallographic analyses are collated in Table 3. Scattering factors for neutral atoms were taken from ref. 28. Computer programs used in the analyses are noted above or listed in ref. 29, and were run on our DEC-Alpha Station 200 4/100 computer or in the laboratories of Bruker AXS, Inc.

CCDC reference numbers 178000–178006.

See http://www.rsc.org/suppdata/dt/b2/b200694b/ for crystallographic data in CIF or other electronic format.

Table 3 Crystallographic and refinement data for the Fe(NS₃) complexes

Compound	(NEt₄)[Fe(NO)(NS₃)]	[{Fe(NO)₂{Fe(NS₃)}}₂]	[Fe(NO)₂{Fe(CO)(NS₃)}]	[Fe(NO)₂-{Fe(NO)(NS₃)}]	(NEt₄)[Fe(NO)₂-{Fe(CN)(NS₃)}]	[{Fe(NO)₂I}{Fe(NS₃)}-(CNMe)}{Fe(NO)₂}]	[{Fe(NO)₂I}{Fe(NS₃)}-(NO)}{Fe(NO)₂}]
Compound no.	**1**	**6**	**7**	**9**	**10**	**13**	**14**
Elemental formula	C₈H₂₀N, C₆H₁₂FeN₂OS₃	C₁₂H₂₄Fe₄N₆O₄S₆	C₇H₁₂Fe₂N₃O₃S₃	C₆H₁₂Fe₂N₄O₃S₃	C₈H₂₀N, C₇H₁₂Fe₂N₄O₂S₃	C₈H₁₅Fe₃IN₆O₄S₃	C₆H₁₂Fe₃IN₆O₅S₃
Molecular weight	410.5	732.1	394.1	396.1	522.3	649.9	638.8
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$Pbcm$ (no. 57)	$P\bar{1}$ (no. 2)	$F2/d$ (equiv. to no. 15^b)	$C\bar{1}$ (equiv. to no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	8.8770(11)	9.9285(7)	18.092(2)	8.1707(6)	10.6164(11)	15.111(2)	8.6016(9)
b/Å	14.2422(14)	10.9103(8)	13.4423(13)	14.314(2)	17.184(2)	14.233(2)	9.670(2)
c/Å	15.919(2)	11.9760(8)	22.510(3)	12.1054(12)	12.649(2)	10.0102(11)	12.678(2)
α/°	90	98.430(2)	90	82.108(10)	90	98.701(9)	108.594(13)
β/°	90	109.149(2)	98.454(9)	91.536(7)	97.229(10)	110.566(8)	98.556(12)
γ/°	90	90.726(2)	90	83.088(9)	90	94.203(8)	101.865(11)
V/Å³	2012.6(4)	1209.7(2)	5414.8(10)	1390.9(3)	2289.2(5)	1973.9(4)	951.6(2)
Z	4	2	16	4	4	4	2
Density (calc.)/g cm⁻³	1.355	2.010	1.934	1.89	1.516	2.187	2.230
$F(000)$	876	740	3184	800	1092	1264	618
Absorption coefficient/mm⁻¹	1.065	24.001	2.606	2.54	1.56	4.082	4.236
Temperature/K	293(1)	173(2)	293(1)	293(1)	293(1)	293(1)	293(1)
Wavelength/Å	0.71069	1.54180	0.71069	0.71069	0.71069	0.71069	0.71069
Reflections measured (not including absences)	1841	6818	4636	3474	4483	12066	3714
Unique reflections	1296	3806	3946	3341	3190	11451	3332
'Observed' reflections ($I > 2\sigma_I$)	716	3285	3429	2236	1488	8036	1920
Goodness-of-fit on F^2, S	1.018	1.011	1.084	0.99	1.010	1.054	0.991
Final R_1 (all data)	0.098	0.043	0.032	0.057	0.127	0.057	0.085
Final wR_2	0.116	0.094	0.073	0.070	0.111	0.085	0.084
R_1 (observed data)	0.048	0.039	0.027	0.031	0.053	0.035	0.040
Reflections weighted ^{a}, $w=$	$[\sigma^2(F_o^2) + (0.0315P)^2]^{-1}$	$[\sigma^2(F_o^2) + (0.0531P)^2]^{-1}$	$[\sigma^2(F_o^2) + (0.0276P)^2 + 6.2789P]^{-1}$	$\sigma^{-2}(F_o^2)$	$[\sigma^2(F_o^2) + (0.0178P)^2]^{-1}$	$[\sigma^2(F_o^2) + (0.0268P)^2 + 0.407P]^{-1}$	$\sigma^{-2}(F_o^2)$
Largest diff. peak and hole/e Å⁻³	0.33 and −0.28	0.70 and −0.74	0.45 and −0.42	0.26 and −0.31	0.38 and −0.42	1.16 and −1.14	0.51 and −0.50

^{a} $P = (F_o^2 + 2F_c^2)/3$. ^{b} In the standard setting of space group $C2/c$, the β angle is 123.6° and the alternative I-cell has $\beta = 102.6°$. The space group $F2/d$ was selected as having the most orthogonal cell and, therefore, the most appropriate for the refinement procedure.

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