Ferrocenium μ-Oxo-bis[tribromoferrate(III)], a Product of Reaction of Ferrocene with Iron(III) Bromide†

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The μ-oxo anion $[(FeBr_3)_2O]^{2-}$ has been prepared as its ferrocenium salt. The crystal and molecular structure [orthorhombic, space group *Cmc*2, a = 13.739(2), b = 14.721(3), c = 14.302(2) Å] has been determined. The anion consists of two corner-sharing $FeBr_3O$ tetrahedra with parameters similar to those of the chloro-analogue. The cations are ferroceniums with eclipsed cyclopentadienyl rings. The magnetic susceptibility over a range of temperature is that expected for an intramolecular antiferromagnet. Both the cation and anion resonances in the Mössbauer spectrum are consistent with the structure as is the infrared spectrum. The crystal and molecular structure [orthorhombic, space group *Pmcn*, a = 9.036(3), b =12.137(2), c = 14.192(2) Å] of $[Fe(\eta\text{-}C_5H_5)_2][FeBr_4]$ has also been determined. This consists of a perfectly tetrahedral anion and a ferrocenium with eclipsed cyclopentadienyl rings.

Although six- and five-co-ordinate μ-oxo-diiron species are well known,[1] relatively few four-co-ordinate analogues have been characterized. Since its initial discovery,[2] the dinuclear oxo-bridged anion $[(FeCl_3)_2O]^{2-}$ containing tetrahedral iron(III) has been isolated with a variety of cations such as tetramethylammonium,[3] tetraethylammonium,[4] tetraphenylphosphonium,[5] tris(1,10-phenanthroline)iron(II),[6] ferrocenium[7,8] and $[\{(Ph_3P)_2CSe\}]^{2+}$.[9] A high-yield synthesis has been developed[10] in connection with possible uses of this ion as a precursor in the preparation of synthetic analogues of haemerythrin, an enzyme implicated in dioxygen transport in *Themiste dyscritum* and *Themiste zostericola*.[11]

The chemistry of systems containing the Fe–O–Fe unit is extensive.[12] It seemed to be worthwhile to develop a preparation of the bromo-species, $[Br_3Fe\text{–}O\text{–}FeBr_3]^{2-}$ with a view to studying its replacement reactions. Whilst a preparation of this anion as its benzyltriphenylphosphonium salt has been reported,[13] it is our intention to make a detailed investigation of its physical properties. The successful preparation of this ion as its ferrocenium salt is now described. We have also determined its crystal and molecular structure and recorded its paramagnetic susceptibility over a range of temperature (80–300 K) with a view to establishing its magnetic properties. It was of interest to compare its Mössbauer spectral parameters with those of the chloro-analogue: we therefore recorded its spectrum at 78 K. Small amounts of ferrocenium tetrahalogenoferrates are sometimes observed as secondary or minor products in preparations of these μ-oxo anions. The present preparation was no exception. Although analytically pure specimens were obtained by the procedures to be described, samples slowly recrystallized to yield crystals for X-ray analysis were observed to contain a minor phase which was shown to be ferrocenium tetrabromoferrate(III). There are relatively few reports of crystal structure determinations of ferrocenium salts with simple anions: we took the opportunity to solve the structure of this species also. This provided the basis for an accurate comparison of the Fe–Br bond distances in $[(FeBr_3)_2O]^{2-}$ and $[FeBr_4]^-$ and hence to assess the effect of Fe–O π bonding upon the other bond distances.

Table 1 Selected bond distances (Å) and angles (°) for $[Fe(\eta\text{-}C_5H_5)_2]_2[(FeBr_3)_2O]$ with estimated standard deviations (e.s.d.s) in parentheses

Br(1)–Fe(1)	2.354(3)	Fe(3)–C(32)	2.07(3)
Br(2)–Fe(1)	2.347(4)	Fe(3)–C(40)	2.09(3)
Br(3)–Fe(1)	2.341(3)	C(11)–C(12)	1.29(4)
Fe(1)–O	1.752(2)	C(20)–C(21)	1.41(2)
Fe(2)–C(10)	2.02(4)	C(21)–C(22)	1.41(3)
Fe(2)–C(22)	2.03(2)	C(30)–C(31)	1.42(4)
Fe(3)–C(30)	2.11(4)	C(31)–C(32)	1.53(4)
Fe(3)–C(31)	2.07(3)		
Br(1)–Fe(1)–Br(2)	110.3(1)	Br(2)–Fe(1)–O	109.4(2)
Br(1)–Fe(1)–Br(3)	109.6(1)	Br(3)–Fe(1)–O	111.5(5)
Br(1)–Fe(1)–O	109.6(4)	Fe–O–Fe	159.8(4)
Br(2)–Fe(1)–Br(3)	106.4(1)		

Results and Discussion

Crystal and Molecular Structure of $[Fe(\eta\text{-}C_5H_5)_2]_2[(FeBr_3)_2O]$.—The unit cell is shown in Fig. 1 and the atom numbering schemes for the cations and anion in Figs. 2 and 3, respectively. Selected bond lengths and angles are given in Table 1. The cell contains four molecules. There are two crystallographically independent ferrocenium cation sets and one set of $[(FeBr_3)_2O]^{2-}$ anions. These consist of two corner-sharing $FeBr_3O$ tetrahedra with molecular parameters similar to those of the chloro-analogue. Although the space group and lattice are different from those of the chloro-species, the distribution of atoms relative to the mirror planes is similar. In this compound, both ferroceniums are eclipsed and disordered as against just one in the chloro-compound. The Fe–O bond length [1.752(2) Å], like that in $[(FeCl_3)_2O]^{2-}$ [1.757(2) Å], is

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

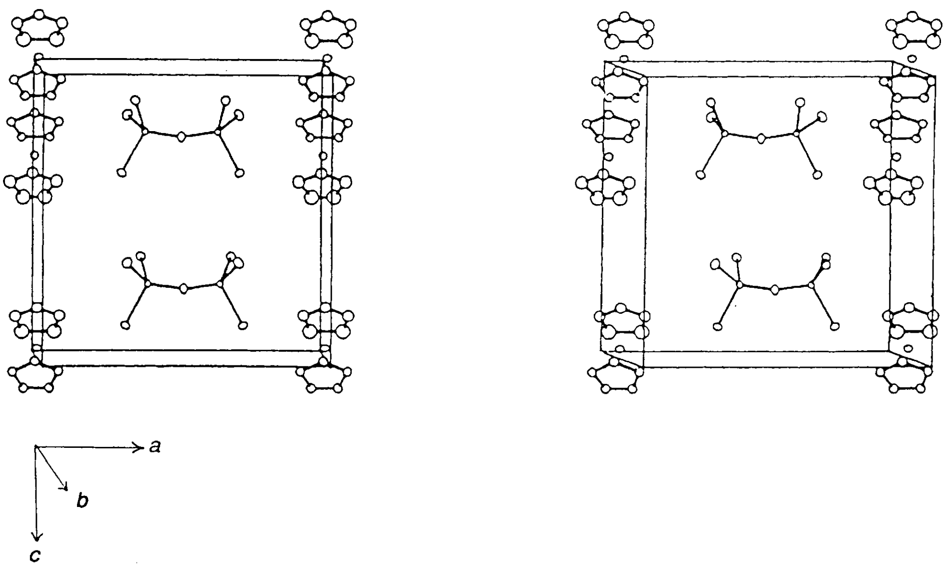

Fig. 1 Unit cell of ferrocenium μ-oxo-bis[tribromoferrate(III)]

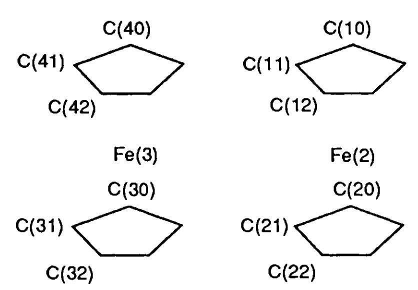

Fig. 2 Atom numbering scheme for the ferrocenium cations

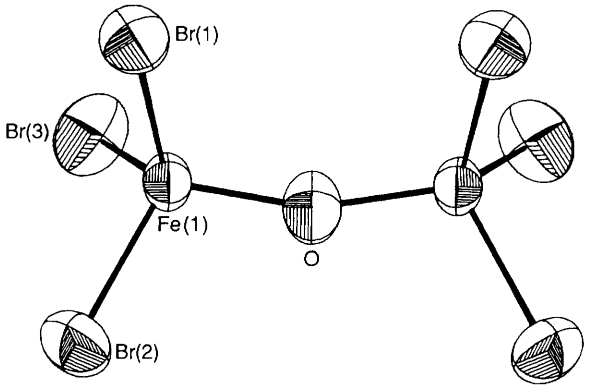

Fig. 3 An ORTEP[14] drawing of the $[(FeBr_3)_2O]^{2-}$ anion showing the atom numbering scheme

among the shortest known indicating strong π bonding. This is consistent with the observed lengthening of the mean Fe–Br distance [2.347(3) Å] relative to the mean value in the $[FeBr_4]^-$ anion [2.329(12) Å]. The Fe–O–Fe bond angle is 159.8(4)° and the bromides are eclipsed.

Vibrational Spectrum.—The IR spectrum is dominated by a strong absorption at 850 cm^{-1} which is assigned to an asymmetric Fe–O mode. The relatively high wavenumber is consistent with strong π bonding. Absorption due to Fe–Br stretching modes is observed at 295 and 280 cm^{-1} compared with Fe–Cl stretching modes at 363 and 315 cm^{-1} for the chloro-analogue.

Magnetic Properties.—The magnetic moment of this compound varies with temperature (μ_{eff}, Table 2). If it is assumed that the ferrocenium cation has a temperature-independent magnetic moment of 2.4 then the anion moment varies with temperature as indicated. This is as expected for a moderately strongly coupled antiferromagnet. The assumptions made in extracting the magnetic moment for the anion do not justify the calculation of an exchange integral.

Table 2 Variation with temperature of experimental (μ_{eff}) and calculated (μ_{calc}) magnetic moments for ferrocenium μ-oxo-bis-[tribromoferrate(III)]

μ_{eff}[a]	μ_{calc}[b]	T/K
3.47	2.51	295.0
3.41	2.42	263.0
3.35	2.34	231.0
3.29	2.25	198.5
3.22	2.15	166.5
3.16	2.06	135.5
3.07	1.92	104.5

[a] Calculated using relative molecular mass = 489.6. [b] Magnetic moment per iron atom of anion calculated assuming μ_{eff} for the ferrocenium cation is 2.4, independent of temperature.

Mössbauer Spectrum.—The spectrum (Fig. 4) is consistent with the formulation of the compound as $[Fe(\eta\text{-}C_5H_5)_2]^+{}_2$-$[(FeBr_3)_2O]^{2-}$. Whilst there is no obvious sign of $[FeBr_4]^-$ as a minor impurity, small amounts of this species, if present, would be masked by the ferrocenium resonance which is the central broad peak at $\delta = 0.511$ mm s^{-1}. The quadrupole doublet at $\delta = 0.341$ mm s^{-1} with $\Delta E_Q = 1.313$ mm s^{-1} is due to the μ-oxy anion.

Crystal and Molecular Structure of $[Fe(\eta\text{-}C_5H_5)_2][FeBr_4]$.—The $[FeBr_4]^-$ ion has nearly perfect tetrahedral geometry with a mean Fe–Br distance of 2.329(12) Å. The atom numbering scheme is shown in Fig. 5. Selected bond lengths and angles are given in Table 3. The cyclopentadienyl rings lie across the mirror plane and are in the eclipsed configuration. The average C–C bond distance is 1.387(48) Å and the mean distance of Fe(2) from the carbon atoms is 2.05(1) Å.

The preparation of the new μ-oxo species $[(FeBr_3)_2O]^{2-}$ was based on our earlier identification of its chloro-analogue as a product of reaction of iron(III) chloride with ferrocene. Accordingly, we used the reaction (1). It proved convenient to prepare the iron(III) bromide *in situ* from iron(II) bromide and

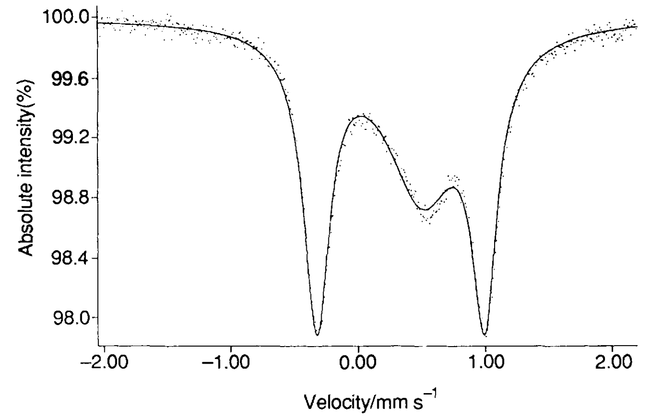

Fig. 4 Mössbauer spectrum of ferrocenium μ-oxo-bis[tribromo-ferrate(III)]

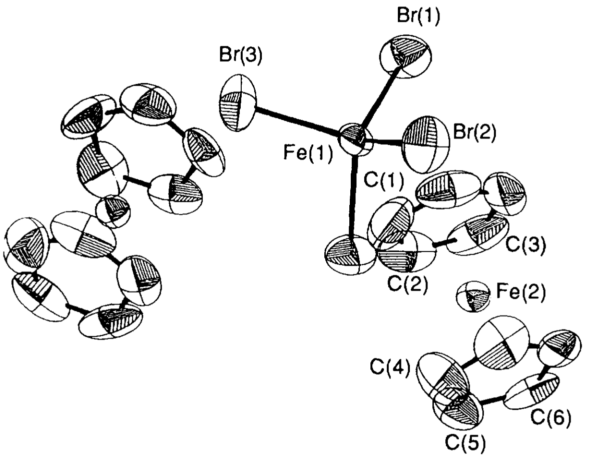

Fig. 5 Atom numbering scheme for ferrocenium tetrabromoferrate(III)

Table 3 Selected bond distances (Å) and angles (°) for [Fe(η-$C_5H_5)_2$][$FeBr_4$] with e.s.d.s in parentheses

Fe(1)–Br(1)	2.316(4)	Fe(2)–C(5)	2.06(2)
Fe(1)–Br(2)	2.333(3)	Fe(2)–C(6)	2.050(15)
Fe(1)–Br(3)	2.338(3)	C(1)–C(2)	1.31(2)
Fe(2)–C(1)	2.05(3)	C(2)–C(3)	1.37(3)
Fe(2)–C(2)	2.03(2)	C(4)–C(5)	1.37(2)
Fe(2)–C(4)	2.05(3)	C(5)–C(6)	1.42(2)
Br(1)–Fe(1)–Br(2)	109.8(1)	Br(2)–Fe(1)–Br(3)	109.6(1)
Br(1)–Fe(1)–Br(3)	108.5(2)		

$$FeBr_3 + [Fe(\eta\text{-}C_5H_5)_2] \longrightarrow [Fe(\eta\text{-}C_5H_5)_2]_2[(FeBr_3)_2O] \qquad (1)$$

Br_2. The method was successful and gave yields in the region of 70%. Like its chloro-analogue, the structure of this μ-oxo bromo-compound is very closely related to that of the corresponding tetrahalogenoferrate in that the μ-oxo compound is theoretically derived from it by replacing halogen by oxygen. Microscopic examination of crystals of the μ-oxo compound as recrystallized for X-ray analysis revealed the presence of [Fe(η-$C_5H_5)_2$][$FeBr_4$] as a minor impurity. The crystal and molecular structure of this were solved as part of this study.

Experimental

Magnetic measurements were carried out over the temperature region 80–300 K using the Gouy method on a magnetic balance supplied by Newport Instruments, Newport Pagnell. The calibrant was Hg[Co(NCS)$_4$] and the magnetic susceptibility of [Fe(η-$C_5H_5)_2]_2[(FeBr_3)_2O]$ was found to be independent of field strength. Mössbauer spectra were recorded on a micro-processor-based constant-acceleration spectrometer supplied by Cryophysics (UK). It was calibrated using iron foil. Spectral results were fitted using a least-squares program and chemical isomer shifts are given relative to the centre of the natural iron spectrum.

Table 4 Final atomic coordinates with e.s.d.s in parentheses for [Fe(η-$C_5H_5)_2]_2[(FeBr_3)_2O]$

Atom	*x*	*y*	*z*
Br(1)	0.3444(2)	0.1844(1)	0.8685(2)
Br(2)	0.2965(2)	0.2856(2)	0.6241(2)
Br(3)	0.3077(2)	0.4404(1)	0.8324(2)
Fe(1)	0.3745(2)	0.3080(1)	0.7682(2)
Fe(2)	1.000	0.4449(2)	0.0325(3)
Fe(3)	1.000	0.1341(2)	0.6769(3)
O	0.500	0.319(1)	0.750
C(10)	1.000	0.451(2)	0.174(2)
C(11)	0.921(2)	0.489(2)	0.147(2)
C(12)	0.942(2)	0.558(1)	0.096(2)
C(20)	1.000	0.312(2)	−0.019(2)
C(21)	0.917(1)	0.360(1)	−0.051(1)
C(22)	0.953(1)	0.435(1)	−0.102(1)
C(30)	1.000	0.007(2)	0.610(3)
C(31)	0.918(2)	0.059(2)	0.584(2)
C(32)	0.960(3)	0.143(2)	0.537(2)
C(40)	1.000	0.114(2)	0.821(2)
C(41)	0.916(1)	0.167(1)	0.794(1)
C(42)	0.949(1)	0.247(1)	0.747(1)

Crystallography.—Crystal data for [Fe(η-$C_5H_5)_2]_2[(FeBr_3)_2O]$. $C_{20}H_{20}Br_6Fe_4O$, $M = 979.2$, orthorhombic, space group *Cmc*2 (no. 36), $a = 13.739(2)$, $b = 14.721(3)$, $c = 14.302(2)$ Å, $U = 2893$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections), $Z = 4$, $D_c = 2.25$ g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, $F(000) = 1848$, deep violet prism, 0.33 × 0.3 × 0.3 mm, $\mu = 101.9$ cm^{-1}.

The crystals were grown from ethyl methyl ketone. X-Ray intensities were recorded on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation at 292–294 K. 1529 Unique reflections were recorded ($1 \leqslant \theta \leqslant 28°$) of which 851 were statistically significant with $I \geqslant 3\sigma(I)$. The intensities were corrected for Lorentz and polarization factors and a linear decay of 22%.

Determination of structure. Systematic absences do not differentiate between *Cmcm*, *Cmc*2$_1$ or *C*2*cm* (non-standard *Aam*2) but the Patterson method, by virtue of revealing no significant peak at 00*z* (indicating a mirror plane perpendicular to *c*), uniquely defined the space group as *Cmc*2$_1$. Full-matrix least-squares refinement of the heavy atoms (Fe,Br,O) found and subsequent Fourier calculations completed the structure. The ferrocenium irons and the oxygen atoms lie on the mirror planes (at $x = 0$ and 0.5 respectively). Disorder (shown by high thermal parameters) prevented full refinement and no hydrogen atoms were included. An absorption correction, using DIFABS,[15] was applied (minimum 0.736, maximum 1.389, average 1.006). Final *R* and *R'* values were 0.047, 0.054 and $S = 1.202$ using a weighting scheme $w^{-1} = 17.34 - 0.219F + 0.014F^2$. Final atomic coordinates are given in Table 4.

Crystal data for [Fe(η-$C_5H_5)_2$][$FeBr_4$]. $C_{10}H_{10}Br_4Fe_2$, $M = 561.5$, orthorhombic, space group *Pmcn* (non-standard no. 62), $a = 9.036(3)$, $b = 12.137(2)$, $c = 14.192(2)$ Å, $U = 1556.6$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections), $Z = 4$, $D_c = 2.40$ g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, $F(000) = 1048$.

The crystals were grown as a second phase in the crystallization described above. They separated as deep violet plates

Table 5 Final atomic coordinates with e.s.d.s in parentheses for $[Fe(\eta\text{-}C_5H_5)_2][FeBr_4]$

Atom	x	y	z
Br(1)	0.250	0.3829(2)	0.2714(2)
Br(2)	0.0390(2)	0.1127(2)	0.2540(1)
Br(3)	0.250	0.2254(3)	0.0420(2)
Fe(1)	0.250	0.2081(3)	0.2060(2)
Fe(2)	0.750	0.2492(2)	0.4918(2)
C(1)	0.750	0.348(3)	0.375(2)
C(2)	0.868(2)	0.369(1)	0.425(1)
C(3)	0.828(2)	0.407(1)	0.513(1)
C(4)	0.750	0.086(2)	0.454(2)
C(5)	0.875(2)	0.108(2)	0.505(1)
C(6)	0.830(2)	0.147(1)	0.595(1)

and the one chosen for data collection measured 0.6 × 0.7 × 0.3 mm. X-Ray intensities were measured as above. 1987 Unique reflections were recorded ($1 \leqslant \theta \leqslant 28°$) of which 951 were statistically significant with $I \geqslant 3\sigma(I)$. The intensities were corrected for Lorentz and polarization factors and a linear decay of 5.5%. Least-squares refinement was carried out with the SDP package[16] with atomic scattering factors as supplied with the program.

Determination of structure. Systematic absences combined with the intensity distribution uniquely define the space group. The Patterson map clearly indicated an iron tetrabromide unit sited on a mirror plane. Subsequent Fourier calculations completed the structure. Isotropic refinement converged at $R = 0.16$ and an absorption correction was applied using the program DIFABS (minimum 0.547, maximum 1.580, average 0.944). Anisotropic refinement with hydrogen atoms in fixed geometrically calculated positions converged at $R = 0.078$ and $R' = 0.099$, $S = 1.335$ using a weighting scheme $w^{-1} = 17.34 - 0.219F + 0.014F^2$. Final atomic coordinates are given in Table 5. For both structures, all calculations were performed on a DEC PDP 11/73 computer using the SDP suite of crystallographic programs.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Preparation of $[Fe(\eta\text{-}C_5H_5)_2]_2[(FeBr_3)_2O]$.—Hydrated iron(II) bromide (1.75 g, 8.1 mmol) was ground in a mortar with diethyl ether (3 × 20 cm^3) and filtered. Bromine (0.6 g, 3.75 mmol) and ferrocene (1.85 g, 10 mmol) were added to the filtrate and stirred for 30 min. The volume was reduced to not less than 40 cm^3 after which the mixture was subjected to a stream of oxygen for about 9 h. The product was filtered off, washed with ethanol followed by ethyl methyl ketone and then soaked in diethyl ether to remove ferrocene before being washed with CCl_4. The yield was 1.1 g (30%) (Found: C, 24.40; H, 1.95; Br, 50.30. $C_{20}H_{20}Br_6Fe_4O$ requires C, 24.55; H, 2.05; Br, 49.0%).

References

1 K. S. Murray, *Coord. Chem. Rev.*, 1974, **12**, 1.
2 M. G. B. Drew, V. McKee and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1978, 80.
3 E. W. Neuse and M. G. Merim, *Transition Met. Chem.*, 1984, **9**, 205.
4 E. D. Simon and R. H. Holm, *Inorg. Chem.*, 1983, **22**, 3809.
5 K. Dehnicke, H. Prinz, W. Massa, J. Pebler and R. Schmidt, *Z. Anorg. Allg. Chem.*, 1983, **499**, 20.
6 W. M. Reiff, E. H. Witter, K. Mottle, T. E. Breannan and A. K. Garafalo, *Inorg. Chim. Acta*, 1983, **77**, L83.
7 G. J. Bullen, B. J. Howlin, J. Silver, B. W. Fitzsimmons, I. Sayer and L. F. Larkworthy, *J. Chem. Soc., Dalton Trans.*, 1986, 1937.
8 P. Carty, K. C. Clare, J. R. Creighton, E. Metcalfe, E. S. Raper and H. M. Dawes, *Inorg. Chim. Acta*, 1986, **112**, 113.
9 H. Schmidbauer, C. E. Zybill and D. Neugebauer, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 156.
10 W. H. Armstrong, A. Spool, G. C. Papaefthymiou and S. J. Lippard, *J. Am. Chem. Soc.*, 1984, **106**, 3653.
11 J. B. Vincent, G. L. Olivier-Lilley and B. A. Averill, *Chem. Rev.*, 1990, **90**, 1447.
12 D. M. Kurtz, *Chem. Rev.*, 1990, **90**, 585.
13 D. Petridis and A. Terzis, *Inorg. Chim. Acta*, 1986, **118**, 129.
14 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, TN, 1971.
15 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 159.
16 B. A. Frenz, Enraf-Nonius Structure Determination Package, SDP; Enraf Nonius, Delft, 1987.

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