Notes

Reaction of Elemental Sulphur with (5*H*,14*H*-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecinato)iron(II): Synthesis and *X*-Ray Structure of a μ-Sulphido Iron(III) Complex†

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The reaction of (5*H*,14*H*-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecinato)-iron(II), [Fe(tmdbtd)] (**1**), with elemental sulphur under very mild conditions in tetrahydrofuran (thf) leads to quantitative formation of the corresponding μ-sulphido complex, [{Fe(tmdbtd)}$_2$-(μ-S)]·thf (**2**). Complex (**2**) has $\mu_{\text{eff.}}$ = 2.43 B.M. at 292 K, indicating an antiferromagnetic coupling between the two iron(III) high-spin centres. The *X*-ray analysis on complex (**2**) showed the typical 'saddle' shape for the macrocyclic ligand. The square-pyramidal co-ordination geometry and bond parameters indicate high-spin iron(III): the average displacement of the Fe^{III} from the N$_4$ donor plane is −0.698(2) Å, while the average Fe–N distance is 2.055 Å. The Fe–S–Fe angle is significantly narrower [126.3(1)°] than the corresponding value of Fe–O–Fe (142.75°) in [{Fe(tmdbtd)}$_2$(μ-O)]·MeCN.

The chemistry of elemental sulphur with metal chelates has received little attention,[1] despite the intrinsic interest in the reaction itself,[2] which has an important relationship with that of molecular oxygen.[3] Moreover, the final compounds promise interesting chemical and structural aspects like those involving electron-transfer processes.[4] In this context the reactivity of iron(II) complexes has significant relevance. Reaction with oxygen leads, usually, to the corresponding μ-oxo complexes containing the Fe–O–Fe bridge which has a relevant synthetic role, and is of interest for its magnetic behaviour[5] and biological importance.[4,6] The reaction of elemental sulphur with [Fe(salen)] [H$_2$salen = *NN'*-ethylenebis(salicylideneimine)] and [Fe(acacen)] [H$_2$acacen = *NN'*-ethylenebis-(acetylacetoneimine)] led to [{Fe(salen)}$_2$(μ-S)][7] and [{Fe-(acacen)}$_2$(μ-S)][8] respectively, which have magnetic and structural properties related to those of the corresponding μ-oxo complexes. Tetra-aza macrocyclic ligands are important supporting ligands for iron(II) in a wide variety of processes. We found that [Fe^{II}(tmdbtd)]·thf (H$_2$tmdbtd = 5*H*,14*H*-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecine, thf = tetrahydrofuran),[9] which forms [{Fe-(tmdbtd)}$_2$(μ-O)]·MeCN[10] with molecular oxygen, reacts with elemental sulphur to form the corresponding μ-sulphido complex, [{Fe(tmdbtd)}$_2$(μ-S)]·thf.

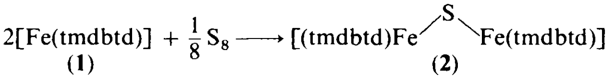
Results and Discussion

Reaction of elemental sulphur with [Fe(tmdbtd)] (**1**) was carried out at room temperature and gave, independently of the S:Fe molar ratio, exclusively complex (**2**), which crystallizes with a molecule of thf: equation (1).

Table 1. Selected bond distances (Å) and angles (°) for complex (**2**)*

Fe–S	2.196(3)	N(2)–C(6)	1.41(2)
Fe–N(1)	2.047(8)	N(2)–C(7)	1.34(2)
Fe–N(2)	2.053(8)	N(3)–C(9)	1.34(2)
Fe–N(3)	2.072(12)	N(3)–C(10)	1.44(2)
Fe–N(4)	2.048(10)	N(4)–C(15)	1.43(2)
N(1)–C(1)	1.41(2)	N(4)–C(16)	1.32(2)
N(1)–C(18)	1.32(1)		
N(3)–Fe–N(4)	78.7(4)	Fe–N(1)–C(1)	105.6(7)
N(2)–Fe–N(4)	139.1(4)	C(1)–N(1)–C(18)	125.0(10)
N(2)–Fe–N(3)	88.1(4)	Fe–N(2)–C(7)	129.1(9)
N(1)–Fe–N(4)	88.2(4)	Fe–N(2)–C(6)	105.3(7)
N(1)–Fe–N(3)	141.7(4)	C(6)–N(2)–C(7)	125.6(11)
N(1)–Fe–N(2)	78.7(4)	Fe–N(3)–C(10)	105.7(8)
S–Fe–N(4)	112.3(3)	Fe–N(3)–C(9)	125.9(10)
S–Fe–N(3)	105.3(3)	C(9)–N(3)–C(10)	128.1(12)
S–Fe–N(2)	108.5(3)	Fe–N(4)–C(16)	128.9(9)
S–Fe–N(1)	112.9(3)	Fe–N(4)–C(15)	107.3(7)
Fe–S–Fe′	126.3(1)	C(15)–N(4)–C(16)	122.9(11)
Fe–N(1)–C(18)	129.1(8)		

* Prime indicates atom at the position $\bar{x}, y, \frac{1}{2} - z$.



$$2[\text{Fe(tmdbtd)}] + \frac{1}{8}\text{S}_8 \longrightarrow [(\text{tmdbtd})\text{Fe}{-}\overset{\text{S}}{}{-}\text{Fe(tmdbtd)}] \qquad (1)$$

(**1**) (**2**)

Complex (**2**) was isolated as crystalline solid, relatively air-stable in the solid state, but sensitive to oxygen in solution, where it is converted into the corresponding μ-oxo complex, [{Fe(tmdbtd)}$_2$(μ-O)] (**3**).[10] The magnetic moment of (**2**) (2.43 B.M. at 292 K) is very close to that of (**3**) (1.96 B.M.). A similar antiferromagnetic coupling was observed in a wide variety of high-spin iron(III) μ-oxo complexes containing Schiff-base ligands,[5] and in the two μ-sulphido complexes [{Fe(salen)}$_2$(μ-S)] (**4**)[7] and [{Fe(acacen)}$_2$(μ-S)] (**5**).[8]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.
Non-S.I. unit employed: B.M. = 9.274×10^{-24} J T^{-1}.

Table 2. Structural and magnetic parameters for some related μ-oxo and μ-sulphido iron(III) complexes

Compound	Fe–X^a/Å	Fe–X–Fe/°	N–c$_t$^{b}/Å	Fe–N$_4$ (Fe–N$_2$O$_2$)^c/Å	Fe–N^d/Å	μ$_{eff.}$/B.M.	Ref.
[{Fe(acacen)}$_2$O]	1.775	150.7	—	0.048	2.050	1.80	8
(**5**) [{Fe(acacen)}$_2$S]	2.207	120.8	—	0.080	2.080	2.16	8
[{Fe(salen)}$_2$O]	1.780	144.6	—	0.400	2.097	1.87	17
(**4**) [{Fe(salen)}$_2$S]	2.170	121.8	—	—	2.116	2.06	7*c*
(**3**) [{Fe(tmdbtd)}$_2$O]·MeCN	1.793(1)	142.75	1.931	0.698	2.054	1.96	10
(**2**) [{Fe(tmdbtd)}$_2$S]·thf	2.196(3)	126.3(1)	1.934	0.698	2.055	2.43	*e*

^{a} Fe to bridging O or S ligand distance. ^{b} Ideal N to centre of macrocyclic core distance. ^{c} Distance of Fe from the equatorial plane defined by N_4 or N_2O_2 donor atoms. ^{d} Fe to N equatorial average distance. ^{e} This work.

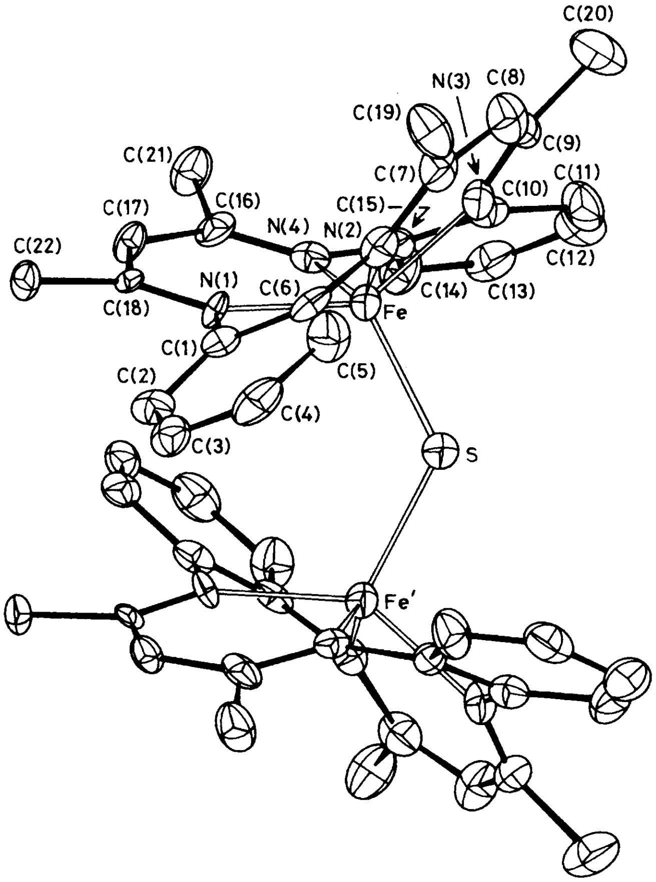
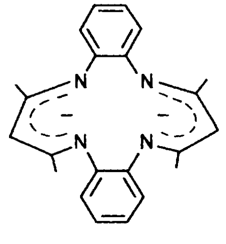


Figure. ORTEP drawing for complex (**2**) (30% probability ellipsoids)



tmdbtd

The structure of (**2**) (Figure) reveals two five-co-ordinate macrocyclic units, joined by a bridging sulphur atom, with a Fe–S–Fe angle of 126.3(1)°, and a Fe–S distance of 2.196(3) Å (Table 1). The dimer has C_2 symmetry, with the C_2 axis passing through the sulphur atom. The iron(III) atom is displaced from the N_4 mean plane by a distance of −0.698(2) Å. The macrocyclic ligand in both halves of the dimer has the usual saddle shape previously reported.[9–11] Examination of the structure reveals that the bond distances and angles of the macrocyclic ligand are essentially identical with chemically equivalent parameters in other complexes of the same ligand.[9–11] There is a significant asymmetry in the two halves of the tmdbtd ligand because of some compression imposed by the sulphur bridge having a relatively small Fe–S–Fe angle. The planes N(1), C(1), C(6), N(2) and N(3), C(10), C(15), N(4) form a dihedral angle of 28.5(4)° and with the N_4 plane, dihedral angles of 15.4(5)° and 13.1(4)° respectively. Bonding patterns describing the 16 π-electron ring system, which is not delocalized, are maintained since the N(1)–C(1), N(2)–C(6), N(3)–C(10), and N(4)–C(15) bonds have single-bond character.

Parameters characterizing the Fe–S–Fe bridge are of considerable interest.[7c,8] The Fe–S distance [2.196(3) Å] and the Fe–S–Fe angle [126.3(1)°] are similar to those found for complexes (**4**) (2.170 Å, 121.8°) and (**5**) (2.207 Å, 120.8°), despite the fact that the three ligands differ significantly in their rigidity and bulkiness. The important narrowing of the Fe–X–Fe angle from X = O to X = S (142.75 *vs.* 126.3°) is a general trend also observed in the acacen and salen complexes.[7c,8] This is due to the lower Fe(*d*π)–S(*p*π) orbital interaction in comparison with the μ-oxo complex.

Table 2 lists structural and magnetic parameters for some related μ-oxo and μ-sulphido iron(III) dimers containing a five-co-ordinate square-pyramidal iron(III). There is a macrocyclic expansion by which there is an increase of the N–c$_t$ distance (N–c$_t$ = ideal N to centre of macrocyclic core distance) from 1.910 Å in [Fe(tmdbtd)Cl]·MeCN (**6**),[11a] to 1.931 Å in (**3**)[10] and 1.934 Å in (**2**). The ring expansion and the torsional angle distribution indicate a larger and very close radius for iron(III) in (**2**) and (**3**).[10] Consequently the Fe–N distances increase from 2.002 Å in (**6**) to 2.054 Å in (**3**) and they are in the range 2.047(8)—2.072(12) Å in complex (**2**). The increase in the displacement of Fe from the N_4 plane is in agreement with the increase of the iron radius from (**6**) (0.600 Å) to (**3**) (0.698 Å) and (**2**) (0.698 Å). The Fe–N bond distances in complex (**2**) are markedly longer than those found for the low-spin [Fe(tmdbtd)Ph] (1.908 Å)[12] and [Fe(tmdbtd)(NO)] [1.944(7) Å][13] and conclusively support the high-spin d^5 formulation. Examination of Table 2 reveals that for a decrease in the Fe–X–Fe angle an increase of the magnetic moment is observed in agreement with the decrease of Fe–X multiple bonding moving from S to O. For complex (**2**) we observed the disappearance of the Fe–O bands at 890 and 882 cm^{-1},[10] but we are unable to assign the new Fe–S band.

Table 3. Fractional atomic co-ordinates (× 10^4) for complex (**2**)

Atom	*X/a*	*Y/b*	*Z/c*
Fe	46(1)	1 555(1)	1 255(1)
S	0(0)	2 070(2)	2 500(0)
N(1)	−285(6)	525(4)	1 222(6)
N(2)	−1 231(6)	1 562(6)	377(6)
N(3)	389(8)	2 327(5)	485(8)
N(4)	1 330(6)	1 264(5)	1 284(6)
C(1)	−1 204(9)	505(7)	1 207(8)
C(2)	−1 590(9)	33(6)	1 650(8)
C(3)	−2 481(11)	95(7)	1 611(9)
C(4)	−3 033(9)	630(8)	1 134(10)
C(5)	−2 625(10)	1 129(7)	707(10)
C(6)	−1 724(9)	1 073(6)	720(8)
C(7)	−1 550(10)	1 927(7)	−382(9)
C(8)	−1 039(10)	2 412(7)	−655(9)
C(9)	−150(11)	2 588(6)	−277(10)
C(10)	1 337(10)	2 458(7)	887(8)
C(11)	1 754(11)	3 129(7)	967(10)
C(12)	2 660(11)	3 172(8)	1 421(10)
C(13)	3 132(10)	2 604(8)	1 875(9)
C(14)	2 733(10)	1 971(7)	1 825(10)
C(15)	1 850(9)	1 886(6)	1 329(8)
C(16)	1 631(9)	646(7)	1 141(8)
C(17)	1 093(9)	39(6)	1 095(8)
C(18)	204(9)	−22(5)	1 146(7)
C(19)	−2 475(10)	1 797(7)	−995(10)
C(20)	265(11)	3 111(7)	−807(9)
C(21)	2 520(9)	541(6)	947(9)
C(22)	−168(8)	−748(5)	1 034(7)
C(1S)*	−30(42)	5 096(25)	2 936(36)
C(2S)*	34(28)	4 593(23)	3 485(27)
C(3S)*	164(33)	4 005(23)	3 220(31)
C(4S)*	374(31)	4 018(23)	2 318(36)
C(5S)*	338(46)	4 816(37)	2 397(67)

* The site occupation factor for atoms from C(1S)—C(5S) is 0.5.

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The synthesis of ligand H_2tmdbtd was carried out as reported,[14] while that of [Fe(tmdbtd)] can be carried out either by the published procedure[9] or by a significant modification.[15] Crystalline sulphur was used as purchased from Aldrich. Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer and magnetic susceptibilities determined using a Faraday balance.

Synthesis of [{Fe(tmdbtd)}$_2$(μ-S)] (**2**).—A thf (50 cm^3) solution of S_8 (0.28 g, 1.09 mmol) was added to a thf (100 cm^3) solution of [Fe(tmdbtd)]·thf (1.75 g, 3.72 mmol). A few seconds later a black solid crystallized (1.10 g). Crystals suitable for *X*-ray analysis formed from the mother-liquor cooled at −15 °C (Found: C, 63.8; H, 5.60; N, 11.95; S, 3.40. Calc. for $C_{48}H_{52}Fe_2N_8OS$: C, 63.90; H, 5.75; N, 12.40; S, 3.50%); $\mu_{\text{eff.}}$ = 2.43 B.M. at 292 K.

Crystal-structure Determination of Complex (**2**).—*Crystal data.* $C_{44}H_{44}Fe_2N_8S{\cdot}C_4H_8O$, $M = 900.7$, monoclinic, $a = 15.440(3)$, $b = 19.274(4)$, $c = 15.560(3)$ Å, $\beta = 106.59(2)°$, $U = 4\,438(2)$ Å^3, $Z = 4$, $D_c = 1.348$ g cm^{-3}, $F(000) = 1\,888$, Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 7.42 cm^{-1}, space group *C*2/*c*, crystal dimensions 0.28 × 0.35 × 0.45 mm.

The intensity data [3 147 reflections, 1 169 with $I > 3\sigma(I)$, $3 < \theta < 23°$, at 295 K] were measured on a Philips PW 1100 diffractometer (graphite-monochromatized Mo-K_α radiation). Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 computer using SHELX 76.[16] Lorentz and polarization corrections[16] were applied. The crystal quality was tested by ψ scans showing that crystal absorption effects could be neglected. The structure was solved by the heavy-atom method. Refinement was first carried out isotropically, then anisotropically for non-hydrogen atoms, by blocked full-matrix least squares down to $R = 0.057$ ($R' = 0.054$).* The *X*-ray analysis revealed the presence of a thf molecule of crystallization, disordered around a two-fold axis. All H atoms except those associated with thf were located in difference maps and introduced in the subsequent refinement as fixed contributors with isotropic *U* values fixed at 0.10 Å^2.

Final atomic co-ordinates are listed in Table 3. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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* $R = \Sigma|\Delta F|/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}|\Delta F|/\Sigma w^{\frac{1}{2}}|F_o|$, and $w = 1.2419/[\sigma^2(F_o) + 0.000155F_o^2]$.

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