π-Effects in Thioether Macrocyclic Complexes: the Stabilisation and Structure of the Low-Spin Fe$^{\rm III}$ Thioether Complex [Fe([9]aneS$_3$)$_2$]$^{3+}$

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Oxidation of [Fe([9]aneS$_3$)$_2$]$^{2+}$ to [Fe([9]aneS$_3$)$_2$]$^{3+}$ leads to an *elongation* of the Fe–S bonds from 2.251(1), 2.241(1), 2.259(1) Å in the 2+ cation to 2.280(3), 2.2846(25), 2.276(3) Å in the 3+ cation giving, for the first time, direct structural evidence for the π-acceptor properties of thioether crowns.

In general, thioether ligands are regarded as poor σ-donors to metal ion centres.[1] However, a wide range of stable transition metal complexes with thioether crowns has now been reported[2—4] and this has led to much discussion of the π-properties of these ligands.[3] In principle, the S-donor in co-ordinated thioethers can act either as a π-acceptor using empty d-orbitals on sulphur, or as a π-donor *via* donation of the available lone-pair on sulphur.[1] On the basis of electronic and redox data, most attention has been focused on potential π-acceptor effects of thioether crowns,[3,4] although the ability of thioethers to stabilise relatively high metal oxidation states such as Pd$^{\rm III}$, Pt$^{\rm IV}$,[2] Mo$^{\rm IV}$,[5] and Nb$^{\rm V}$[6] suggests that π-donor capability is possible in the presence of particular metal centres.

We were interested in obtaining direct structural data of relevance to the question of the potential π-effects of co-ordinated thioether crowns, and report herein the stabilisation and a structural study of the low-spin Fe$^{\rm III}$ complex [Fe([9]aneS$_3$)$_2$]$^{3+}$.

Wieghardt and co-workers have reported the synthesis of the low-spin d^6 Fe$^{\rm II}$ complex [Fe([9]aneS$_3$)$_2$]$^{2+}$.[7] This species shows an Fe$^{\rm II/III}$ couple in MeCN at +0.982 V *vs.* Fc$^+$/Fc (Fc = ferrocene). The complex [Fe([9]aneS$_3$)$_2$]$^{3+}$ is a powerful oxidant and has been shown by magnetic susceptibility measurements and by electronic and Mössbauer spectroscopy to be a low-spin Fe$^{\rm III}$ complex.[8] Further study of this complex was hampered severely by its high reactivity and decomposition even in the solid state. We have found previously that oxidised complexes of [9]aneS$_3$ such as [Pd([9]aneS$_3$)$_2$]$^{3+}$ are stabilised in highly acidic media[9] and argued that a similar stabilisation of [Fe([9]aneS$_3$)]$^{3+}$ might be achieved under these conditions.

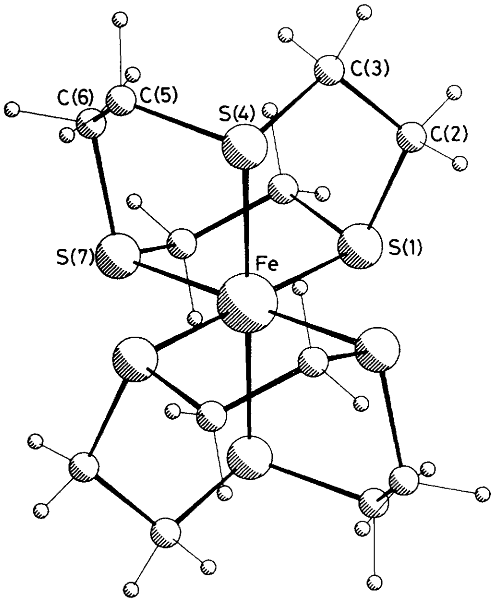
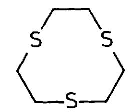


Figure 1. Structure of [Fe([9]aneS$_3$)$_2$]$^{3+}$ with numbering scheme adopted.



[9]ane S_3

Oxidation of $[Fe([9]aneS_3)_2]^{2+}$ using $NOBF_4$ in the presence of concentrated acids such as $HClO_4$, H_2SO_4 and CF_3SO_3H generates the green Fe^{III} complex quantitatively. Importantly, solutions of $[Fe([9]aneS_3)_2]^{3+}$ are stable indefinitely under these conditions and on cooling $HClO_4$ solutions, dark green crystals of the oxidised product can be isolated. These crystals are highly unstable outside the mother liquor, reducing to the parent Fe^{II} complex in air. Crystals of the Fe^{III} complex and $HClO_4$ mother liquor were sealed together in a Lindemann glass capillary tube and transferred to a Stoë STADI-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[10] The crystal was cooled to 173 ± 0.1 K and this temperature was maintained during data collection. The single crystal *X*-ray structure† shows a centrosymmetric $[Fe([9]aneS_3)_2]^{3+}$ cation (Figure 1) with bond lengths Fe–S(1) 2.280(3), Fe–S(4) 2.2846(25), Fe–S(7) 2.276(3) Å, and bond angles S(1)–Fe–S(4) 90.04(9), S(1)–Fe–S(7) 90.16(9), S(1)–Fe–S(7) 89.65(9)°. Significantly, these bond lengths are longer than for the parent Fe^{II} complex $[Fe([9]aneS_3)_2]^{2+}$ which shows Fe–S 2.251(1), 2.241(1), and 2.259(1) Å.[7] The elongation in Fe–S bonds on going from $t_{2g}{}^6$ Fe^{II} to $t_{2g}{}^5$ Fe^{III} gives, for the first time, direct structural evidence for the π-acceptor properties of thioether crowns. Thus, loss of an electron from a formally bonding t_{2g} orbital leads to a decrease in π-back-bonding from Fe→S and to a lengthening of the Fe–S bond lengths. A similar trend has been noted for $[Ru(NH_3)_5pz]^{2+/3+}$ (pz = pyrazine) in which the Ru–N(pz) bond length is 2.006(6) Å for Ru^{II} but 2.076(8) Å for Ru^{III}.[11] In the absence of π-effects, increasing the cation charge (from 2+ to 3+) and decreasing the ionic radius of the metal centre (from 0.61 Å for Fe^{II} to 0.55 Å for Fe^{III} [12]) would be expected to decrease the Fe–S bond lengths on oxidation of $[Fe([9]aneS_3)_2]^{2+}$ to $[Fe([9]aneS_3)_2]^{3+}$. Interestingly, the low-spin complexes $[Fe([9]aneN_3)_2]^{2+}$ and $[Fe(9]aneN_3)_2]^{3+}$ show Fe–N bond lengths of 2.03(1) and 1.99(1) Å respectively.[13]

Although the complexes $[M([9]aneS_3)_2]^{2+}$ can be prepared readily when M = Fe, Co, Ni, Cu and Zn, the synthesis of the Mn^{II} complex has not yet been achieved. The above results suggest that the M–S bond lengths for low-spin d^5 $[Mn([9]aneS_3)_2]^{2+}$ should be greater than for $[Fe([9]aneS_3)_2]^{3+}$ due to the overall decrease in the charge of the cation from 3+ to 2+. This would be expected to weaken and labilise the Mn–S bonds in $[Mn([9]aneS_3)_2]^{2+}$ thereby explaining the difficulty in synthesising this cation and related bis-sandwich complexes of metal ions to the left of Fe.

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† *Crystal data*: $C_{12}H_{24}S_6Fe^{3+}\cdot 3ClO_4{}^-\cdot 2(H_3O^+\cdot ClO_4{}^-)\cdot 2HCl\cdot HClO_4$, $M = 1125.07$, monoclinic, space group $P2_1/c$, with $a = 10.6220(19)$, $b = 8.9929(20)$, $c = 19.157(4)$ Å, $\beta = 94.905(18)°$, $U = 1823.2$ Å^3, $D_c = 2.049$ g cm^{-3} [from 2θ values of 34 reflections measured at ±ω (2θ = 24 → 26°, $\lambda = 0.71073$ Å)], $Z = 2$; $F(000) = 1142$, μ(Mo-K_α) = 14.2 cm^{-1}. Data collection and processing; Stoë STADI-4 diffractometer, Mo-K_α *X*-radiation, $T = 173$ K, ω-2θ scans with ω scan width (1.50 + 0.347tanθ)°, 2642 reflections measured ($2\theta_{max.} = 45°$), 2022 unique ($R_{int} = 0.082$), giving 1486 with $F \geqslant 4\sigma(F)$. Linear isotropic crystal decay (*ca.* 28%) corrected for during data reduction. Structure analysis and refinement; intensity statistics suggested the location of the Fe on an inversion centre and iterative rounds of least-squares refinement and difference Fourier synthesis[14] located all remaining non-H atoms. Anisotropic thermal parameters were refined for all non-H atoms; methylene H atoms were included in fixed, calculated positions or, in the case of the H_3O^+ ions, as part of a rigid group.[14] The weighting scheme $w^{-1} = \sigma^2(F) + 0.001030F^2$ gave satisfactory analyses. At convergence, $R, R_w = 0.0553$ and 0.0687 respectively for 261 parameters, $S = 1.106$. The maximum and minimum residues in the final ΔF synthesis were +0.65 and −0.64 eÅ^{-3} respectively. Illustrations were prepared using PLUTO,[15] molecular geometry calculations utilised CALC,[16] and scattering factor data were taken from ref. 17. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.