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Preferential Coordination of Iron(III) over Iron(II) by Facultative Tetradentate Thioether Ligands

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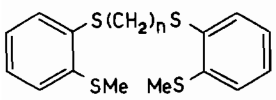
We have recently been examining the donor properties of facultative (open-chain) tetradentate chelating ligands containing thioether groups.[1,2] We have shown that ligands of types (I) and (II) readily complex with heavy transition metal ions such as palladium(II), platinum(II) and rhodium(III).

$MeS(CH_2)_nS(CH_2)_nSMe$

$n = m = 2$ (2,2,2) $n = m = 3$ (3,3,3)
$n = 2, m = 3$ (2,3,2) $n = 3, m = 2$ (3,2,3)

(I)



(II)

However, their complexing properties towards 'hard' acceptors of the first transition series, *e.g.* cobalt(II) and nickel(II) is dependent on symbiotic effects;[2] iodo complexes form more readily than do the chloro and bromo analogues, the latter being difficult to isolate and apparently not forming in many cases. We now find that ligands of type I exhibit an unexpected preference for Fe^{3+} over Fe^{2+}.

Although iron(III) complexes of sulphur ligands are well known[3] and currently receiving much attention as biological models,[4,5] these usually contain negatively charged sulphur donors. We know of no thioether ligands which complex to iron other than those which also contain a second donor atom such as nitrogen. An example is the bidentate ligand 2-ethylthiomethylpyridine (NS) which forms high-spin iron(II) complexes of the type $Fe(NS)_2X_2$ (X = Cl or NCS) on reaction with either iron(II) or iron(III) salts.[6] In contrast, thioethers of types I or II do not appear to react with iron(II) nor do those of type II react with iron(III). However, when methylene chloride solutions of type I ligands are treated with $FeCl_3$ or $FeBr_3$ in diethylether under anhydrous conditions dark red solutions are formed from which solid complexes may be isolated in many cases.

The complexes are exceedingly moisture sensitive and are insoluble in solvents in which they do not decompose (chlorinated hydrocarbons, benzene). Elemental analyses indicate the stoichiometry $Fe_2(ligand)X_6$ (X = Cl, Br). They are formulated as high-spin iron(III) salts of the type $[Fe(ligand)X_2]$-FeX_4 on the following evidence.

Mössbauer spectra of two members of the series consist of an overlapping doublet and a somewhat broadened singlet (see Table). Isomer shifts and quadrupole splittings are consistent with high-spin iron(III).[7] The singlet is assigned to the tetrahedral $[FeCl_4]^-$ anion and the quadrupole split doublet to the six-coordinate cation. The magnetic moment of $Fe_2(2,2,2)Cl_6$ at 293K was found to be 5.91 B.M. indicative of an S = 5/2 ground state of both iron atoms. The other complexes which are more moisture sensitive gave non-reproducible moments between 5.0 and 5.9 B.M. This is attributed to partial decomposition during packing of the Gouy tube. Mössbauer spectra of several of the complexes similarly indicated partial decomposition during the course of the experiments. In all cases mull infrared spectra showed strong bands at 385 cm^{-1} (chlorides) or 289 cm^{-1} (bromides) attributable to ν(Fe–X) of the tetrahaloferrate(III) anions.[8]

The complexes are formally similar to $[Fe(diphos)_2Cl_2]FeCl_4$ and $[Fe(diars)_2Cl_2]FeCl_4$ but

TABLE. Analytical, Physical and Spectral Data.

Complex	Color	%C [a]	%H [a]	%Halogen [a]	ν(M–X) (cm^{-1})	Electronic Spectra (kK)	Mössbauer Parameters [b]	
							δ (mm s^{-1})	ΔE_Q (mm s^{-1})
$Fe_2(2,2,2)Cl_6$	dark red	16.9(16.9)	3.2(3.2)	36.8(37.6)	378	22.5, 19.6sh, 15.2sh	0.65±0.02 0.06±0.02	0.72±0.02
$Fe_2(2,3,2)Cl_6$	dark red	18.5(18.6)	3.8(3.5)	35.4(36.7)	378	23.2, 17.9sh	0.40±0.03 0.19±0 03	0.38±0.03
$Fe_2(3,2,3)Cl_6$	dark green	20.0(20.2)	3.6(3.7)	35.8(35.9)	375	22.8, 17.5sh		
$Fe_2(2,2,2)Br_6 \cdot CH_2Cl_2$	dark red	12.8(12.8)	2.5(3.2)	50.5(52.3)	286	22.4, 17.4sh		
$Fe_2(2,3,2)Br_6 \cdot CH_2Cl_2$	dark red	12.8(12.6)	2.8(3.0)	55.5(57.5)	290	21.5, 17.4sh		

[a] Calculated (Found). [b] 293K, relative to natural iron.

differ in that in the latter the metal of the complex cation has an S = 1/2 ground state.[9,10] The ready formation of thioether complexes with high-spin iron(III), generally regarded as among the 'hardest' of the transition metals acceptors, is unexpected. This is particularly so in view of the fact that the thioethers, unlike the phosphines and arsines, do not, apparently, complex with iron in the +2 oxidation state. This ferric–thioether coordination may be stabilized by the lattice effects of the $[FeLX_2][FeX_4]$.

Experimental

The ligands were prepared as previously reported.[1]

The complexes were prepared under rigorously moisture-free conditions. The ligand (2 mmol) was dissolved in dichloromethane (35 ml) and added to a stirred solution of anhydrous ferric halide (4 mmol) in anhydrous diethyl ether (15 ml) under nitrogen. The mixture was stirred for 15 min and the precipitate was filtered, washed well with anhydrous dichloromethane and dried *in vacuo*. Yields, 40–60%. The complexes were stored in ampoules *in vacuo* and handled in a glove box where possible during physical measurements. The Mössbauer spectra and other measurements were obtained as previously described.[9]

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