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Seven-Coordinate Complexes of Iron(II) with Pentadentate Macrocyclic Ligands

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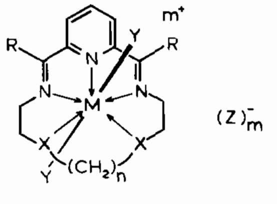
Following our earlier reports[1] of the first pentagonal bipyramidal complexes of iron(III) with a planar pentadentate macrocyclic ligand we have extended the investigation to the synthesis of complexes of other metal ions and other macrocyclic ligands. Such compounds are important in two respects. Firstly, they are among the first examples of (approximate) D_{5h} symmetry in transition metal chemistry and, secondly, they constitute a class of compound having obvious structural similarities to many naturally occurring metal macrocycles yet with the difference that the macrocycle is pentadentate rather than tetradentate. Of particular interest are the ways in which the higher co-ordination number may influence properties, and the capacity of different metal ions to accommodate this geometry.

Using the appropriate pyridine dialdehyde, linear tetramine (or diamine), and metal salt, template synthesis has yielded the series of complexes indicated below. Physical properties and X-ray structural analyses of selected members of the series indicate that they also have 7-co-ordinate (approximately D_{5h} structures.[2]



M = Fe(III), Mn(II), Zn
R = H, CH_3
X = NH, O
n = 2, 3
m = 0, 1
Y = Cl, Br, NCS, N_3
Z = ClO_4, PF_6, BF_4, BPh_4, NO_3, $FeCl_4$, $FeBr_4$

Despite repeated attempts we have so far been unsuccessful in isolating compounds of this class by template synthesis except with metal ions having symmetrically occupied d shells. Similarly, template synthesis of the related series of macrocycles, in which N and X are linked by *o*-phenylene bridges, is so far known only for Fe(III)[2] and Mn(II) and Zn[3]. This may be fortuitous or it may mean that ions having unsymmetrically occupied *d*-shells cannot accommodate so readily to the particular stereochemical constraints imposed by the template process. It seemed to us that an alternative route to iron(II) complexes might be reduction of corresponding iron(III) compounds; once formed, the macrocycle is likely to remain intact.

Cyclic voltammetry and coulometry revealed that the iron(III) complexes in acetonitrile solution undergo reversible one-electron reductions at +0.5 to –0.4 V *vs.* SCE. Dithionite reduction in aqueous solution in the presence of excess Y^- yielded deep blue or green crystals of Fe(macrocycle)$Y_2 \cdot nH_2O$ (Y = Cl, Br, NCS, CN; n = 0, 1) stable for long periods in the solid state and in solution in the absence of oxygen. They are non-electrolytes in acetonitrile and, except for the cyanides which are diamagnetic, have magnetic moments of 5.0 - 5.2 B.M. (90 - 360 °K). Mössbauer isomer shifts and quadrupole splittings at 77 K, relative to natural iron, fall in the ranges 1.0 - 1.2 mm s^{-1} and 2.4 - 2.8 mm s^{-1} (Y = NCS) and 0 - 0.3 mm s^{-1} and 0.1 - 0.3 mm s^{-1} (Y = CN). Single crystal X-ray structures of FeB$(NCS)_2$ and FeC$(NCS)_2$ (where for B, R = CH_3, X = NH, n = 2 and for C, R = CH_3, X = NH, n = 3) have been determined to R = 0.060 and 0.069 respectively. Crystal data for FeB$(NCS)_2$: Triclinic, $P\bar{1}$, Z = 2, *a* = 12.911(11), *b* = 7.200(9), *c* = 11.711(8) Å, α = 92.99(11), β = 90.85(11), γ = 110.00(12)°, 1078 refined intensities; for FeC$(NCS)_2$: Monoclinic, P2/c, Z = 4, *a* = 7.746(8), *b* = 11.747(12), *c* = 24.367(18) Å, β = 102.08(12)°, 1131 refined intensities. The pentagonal bipyramidal structure found[1,2,4] for the parent Fe(III) complexes is retained, the maximum deviations of a ring nitrogen from the least squares planes containing the metal being 0.12 and 0.30 Å, respectively.

The diamagnetism of the cyanide complexes precludes their formulation as pentagonal bipyramidal complexes. Moreover, the infrared spectra show significant differences from those of the paramagnetic derivatives. However, the macrocycle must still be intact since treatment with an excess of thiocyanate ion yielded the known Fe(macrocycle)$(NCS)_2$ complexes. Thus, it appears that a strong field anionic ligand can induce the metal to impose a new conformation on the macrocycle. The gain in CFSE accompanying the magnetic change-over may be sufficient to distort the complexes, *e.g.* by ring folding, towards a geometry, possibly 6-coordinate, in which the degeneracy of d_{xy} and $d_{x^2-y^2}$ is lifted to an extent exceeding the pairing energy.

An interesting property of several of the iron(III) complexes is that they undergo photoreduction to Fe(II) species in the solid state, the sensitivity to light depending on the nature both of the coordinated anion Y and the counter anion Z.

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