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Structure of Dichlorobis(1,10-phenanthroline)iron(III) Tetrachloroferrate(III)

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Species with the empirical formula $FephenCl_3$ were first prepared by Simon, Morgenstern and Albrecht [1] and have since been studied by a number of groups [2–4]. The composition $[Fe(phen)_2Cl_2]$-$[FeCl_4]$ has been proposed on the basis of magnetic [5], conductimetric and spectrophotometric [2] and infrared spectral [4] data. On the other hand Berrett *et al.* [3] have proposed a chloro-bridged structure for the modifications they studied since their Mössbauer effect data were not consistent with the ionic formulation.

In the present work the species of composition $FephenCl_3$ was prepared by interaction of the base with $FeCl_3$ in acetone and crystals suitable for X-ray structural studies were obtained from an acetone/ether mixture. These studies show that the compound is $[Fe(phen)_2Cl_2]\,[FeCl_4]$.

Crystals of $C_{24}H_{16}Cl_6Fe_2N_4$, $M = 684.8$ are triclinic, spacegroup $P\bar{1}$ $a = 15.814(5)$, $b = 8.202(3)$, $c = 11.018(4)$ Å, $\alpha = 99.72(2)$, $\beta = 89.66(2)$, $\gamma = 103.26(2)^\circ$, $U = 1372.05$ Å^3, $D_c = 1.66$, $D_o = 1.60$ g cm^{-3}, $Z = 2$. The X-ray structure determination used 1490 reflections with $I \geqslant 3\sigma(I)$ measured with a Philips PW1100 four-circle diffractometer using MoKα radiation from a graphite crystal monochromator. Positional and thermal parameters for all non-hydrogen atoms (Fe and Cl anisotropic) were refined by full-matrix least squares procedures with the cation and anion in separate blocks ($R = 0.060$).

The structure consists of discrete anionic and cationic groups with no interionic contact of less than 3.49 Å. The $[FeCl_4]^-$ anion has the expected tetrahedral gometry, with an average Fe–Cl bond length of 2.19 Å. The $[Fe(phen)_2Cl_2]^+$ cation has octahedral coordination geometry with the expected *cis*-configuration [6] shown in Figure 1. The phenanthroline ligands are planar to within 0.1 Å and there are no significant differences in the chemically equivalent bond.

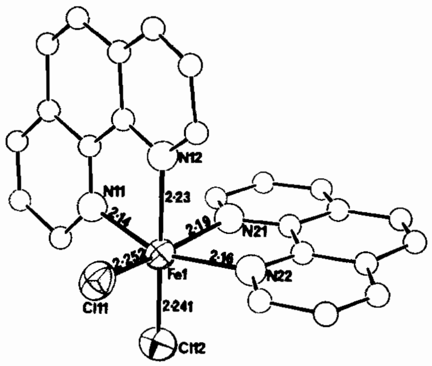

Fig. 1. The structure and principal bond lengths (Å) in the cation $[Fe(phen)_2Cl_2]^+$. E.s.d.'s average Fe–Cl 0.004, Fe–N 0.011 Å.

The sample has a magnetic moment at 303 K of 5.97 B.M. and the magnetism follows the Curie–Weiss law $\chi'_M = C/T - \theta$ with $\theta = -1$ K. It is thus magnetically dilute as is indicated by the structural data. The infrared spectrum shows bands arising from the Fe–Cl stretching mode at 375 cm^{-1} (for the anionic group) and at 325 cm^{-1} (for the cationic group) consistent with earlier data [4].

The high-spin nature of the complex shows that, as with iron(II), coordination of only two phenanthroline molecules will not normally effect spin-pairing in the metal. The iron–nitrogen distances observed in the present complex are significantly greater than those found for $[Fe(phen)_3]\,[ClO_4]_3$ [7] and this must arise, at least in part, from the different spin-state of the metal atom in the two complexes.

References

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