Chemical Communications

(The Journal of The Chemical Society, Section D)

NUMBER 7/1970 8 APRIL

The Crystal Structure of an Eight-co-ordinated Iron(II) Complex: Tetrakis-(1,8-naphthyridine)iron(II) Perchlorate[†]

By A. CLEARFIELD and P. SINGH

(Department of Chemistry, Ohio University, Athens, Ohio 45701)

and IVAN BERNAL[*]

(Department of Chemistry, Brookhaven National Laboratory, Upton, Long Island, New York 11973)

Summary The crystal structure of the title compound has been determined from three-dimensional *X*-ray diffractometry measurements: the iron atom is surrounded by four bidentate ligands.

RECENTLY, Hendricker and Bodner[1,2] reported the synthesis of a series of first-row transition-metal complexes of the type $M(L)_4(ClO_4)_2$, where M is a transition metal and L = 1,8-naphthyridine. Since composition is not necessarily a good index of the co-ordination number of the central metal ion, we decided to determine the structures of the salts of this series of metal complexes since their spectral characteristics are very different from those of known examples of four- and six-co-ordinated species.[1,2] Single crystals of the iron salts were the easiest to prepare and the least sensitive to atmospheric attack. Preliminary *X*-ray data indicate that all the perchlorates of the 3*d* transition series from $M = Mn^{2+}$ to $M = Zn^{2+}$ are isomorphous.

Crystal data. Single crystals suitable for *X*-ray diffraction studies were grown from methanol solutions of the perchlorate salts. Red, prismatic, crystals of the $Fe(ClO_4)_2$-$C_8H_6N_2$ salt were found to be triclinic with the following cell dimensions: $a = 9{\cdot}163(3)$, $b = 9{\cdot}315(3)$, $c = 20{\cdot}116(8)$ Å, $\alpha = 99{\cdot}66(8)$, $\beta = 77{\cdot}37(8)$, $\gamma = 91{\cdot}20(8)°$; $Z = 2$, $V = 1652$ (Å)^3 $D_m = 1{\cdot}57$; $D_c = 1{\cdot}56$ g. cm^{-3}. The space group is $P\bar{1}$, verified by structure solution and refinement. The intensity data were collected with Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å) using a manually-operated Picker four-circle goniometer. In all 1969 non-zero, independent reflections were obtained for which the value of $|F^2| \geqslant 3\sigma$.

The structure was solved by standard Patterson methods using an unsharpened three-dimensional function. Initial solution proceeded *via* co-ordinates for the iron and the two independent chlorine atoms. An electron-density map based on phases obtained from these atoms immediately revealed the approximate positions of many of the non-hydrogen atoms in the asymmetric unit. The remaining atoms were found in successive Fourier and difference Fourier syntheses.

The most interesting feature of the cation is the co-ordination of the Fe^{II} atom. Refinement of the structure with anisotropic perchlorate ions and Fe atoms while constraining the atoms of naphthyridine molecules to isotropic motion gave $R_1 = 10{\cdot}5\%$ and $R_2 = 14{\cdot}5\%$. The iron–nitrogen distances at that stage of refinement are given in the Table. The co-ordination polyhedron is a distorted dodecahedron, the distortions of which are the result of the rather rigid constraints introduced by a planar, inflexible ligand having a small "bite" and by ligand–ligand repulsions.

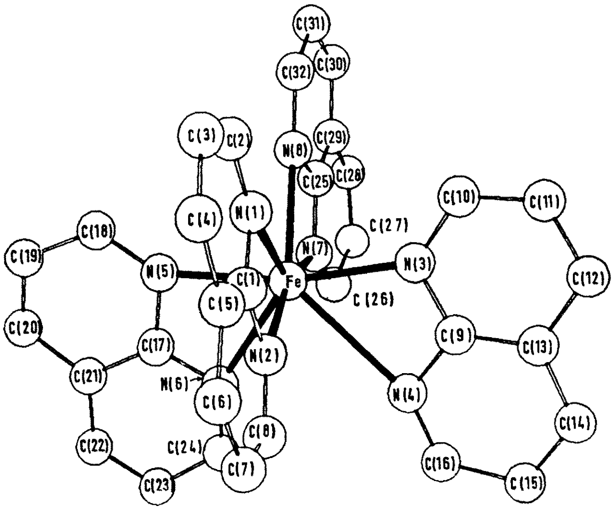
The arrangement of the eight nitrogen atoms around the Fe^{II} ion is shown in the Figure. Their disposition can be described as follows: one nitrogen of each naphthyridine ligand occupies the A positions of the dodecahedron[3] while the second is constrained to occupy the B positions. The Fe–N bond of the latter set is shorter. Simple packing considerations dictate that the naphthyridine complex would be somewhat crowded and it appears that both steric hindrance and ligand–ligand repulsions are relieved by the distortion of the ligand which contains N(4).

When 2,7-dimethyl-1,8-naphthyridine is used as the ligand, the products are always the tris-derivatives.[5] Using their spectra as standards, Hendricker and Bodner[5] have shown that when tetrakis-(1,8-naphthyridine)Fe^{II} derivatives are placed in solutions saturated with ligand, the

---

[†] Work performed under the auspices of the U.S. Atomic Energy Commission.

only detectable product is tris-(1,8-naphthyridine)Fe^{II}. This result is in line with our structural observation that one of the four ligands is less tightly bound and, therefore, probably the more labile.



FIGURE

TABLE[a]

Parameters describing the inner co-ordination sphere around the iron ion: estimated standard deviations in the Fe–N *bond lengths* = 0·010 Å; *in the angles at the* Fe = 1·0°

Fe–N(1) = 2·464 Å
Fe–N(2) = 2·201
Fe–N(3) = 2·178
Fe–N(4) = 2·756
Fe–N(5) = 2·255
Fe–N(6) = 2·350
Fe–N(7) = 2·197
Fe–N(8) = 2·400

N(1)–Fe–N(2) = 56·9°
N(3)–Fe–N(4) = 54·1
N(5)–Fe–N(6) = 58·4
N(7)–Fe–N(8) = 57·6
N(1)–C(1)–N(2) = 112·0
N(3)–C(9)–N(4) = 114·3
N(5)–C(17)–N(6) = 114·2
N(7)–C(25)–N(8) = 111·0

[a] Compare average Fe–N bond length (2·29 Å) with that found[4] in tris(pyridine)iron(III) cation (2·27 Å).

The distortions of the binuclear ligand rings due to the presence of the two nitrogens at the 1,8-positions are evident from the values of the angles at the C(1), C(9), C(17), and C(25) sites (see Table). The average value of this quantity is approximately 113°, which is significantly smaller than the ideal value of 120° for a hexagonal ring.

(*Received, February 2nd,* 1970; *Com.* 159.)

[1] D. G. Hendricker and R. L. Bodner, *Inorg. Nuclear Chem. Letters*, in the press.
[2] D. G. Hendricker and R. L. Bodner, personal communication.
[3] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235.
[4] R. L. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, **88**, 4847.
[5] D. G. Hendricker and R. L. Bodner, *Inorg. Chem.*, 1970, **9**, 273.