CHEMISTRY LETTERS, pp. 1235-1238, 1972. Published by the Chemical Society of Japan

THE CRYSTAL STRUCTURE OF BIS(IMIDAZOLE)OCTAETHYLPORPHINATOIRON(III) PERCHLORATE

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The crystal structure of bis(imidazole)octaethylporphinatoiron(III) perchlorate has been determined by the X-ray method. The monoclinic unit-cell dimensions are a=10.50, b=26.10, c=9.65 Å and β=103.6°. The space group is $P2_1/m$ and there are two formula units and four chloroform molecules in the unit cell. The iron atom is strictly coplanar with the four porphinato nitrogen atoms, and these four and two imidazole nitrogen atoms form an approximately regular octahedron. The complex cations contact with the perchlorate anions at their non-coordinated imidazole nitrogen atoms.

The stereochemistry of the iron porphyrins has contributed to the comprehension of the subtle biological function of the hemoproteins. In high-spin ferric porphyrins, it has been commonly observed that the iron atom deviates by 0.4-0.5 Å from the plane of four porphinato nitrogen atoms to result in the square-pyramidal five-coordinated structure[1-4]. When the sixth ligand coordinates to the ferric atom in the low-spin ground state, the iron atom might be expected to be coplanar with the four porphinato nitrogen atoms, and this was confirmed for bis(imidazole)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III) chloride[5] recently. The four phenyl groups at the methine carbon atoms of tetraphenylporphine may exert some steric effect on the macrocyclic conjugation of the porphinato core. To provide stereochemical information in the more analogous system to the naturally occurring iron porphyrins,

the crystal structure of bis(imidazole)octaethylporphinatoiron(III) perchlorate was determined by the X-ray method.

The crystals*, obtained from a chloroform solution, were reddish brown and plate-like, which contain four molecules of the solvent per cell. A specimen was sealed in capillary with the mother liquor to prevent the degradation of the crystal.

Crystal data; $C_{42}H_{52}N_8O_4FeCl \cdot 2CHCl_3$, F.W.=1063.0 , monoclinic, space group $P2_1/m$, a=10.50(4), b=26.10(2), c=9.65(4) Å, β=103.6(5)°, D_m=1.31 g·cm^{-3} , D_x=1.37 g·cm^{-3} , Z=2 .

The observed density shows about 20 % loss of the solvent molecules. Equi-inclination Weissenberg photographs about the c axis were taken using Fe-filtered Co Kα radiation. Intensities of 2680 independent reflections were measured by TV densitometer[6,7], of which 1228 were too weak to be observable. Interlayer scales were obtained by the use of the (0kl) and (1kl) precession photographs taken with Zr-filtered Mo Kα radiation. The structure was solved by Patterson and Fourier techniques and refined by the block-diagonal least-squares method, anisotropic thermal motions for all the non-hydrogen atoms being applied. The occupancy for the three oxygen atoms in perchlorate anion was assigned a half, because each of them took two equivalent orientations about the mirror plane at y=1/4, on which the chlorine and the remaining one oxygen atoms were located. The convergence was slow and the final R factor was 0.149, presumably because of absorption effects and of imperfections in the crystal structure owing to the partial loss of the solvent molecules. The standard deviations in positional parameters are about 0.02 Å for the porphinato-core atoms.

The figure shows the crystal structure viewed down the c axis. The iron atom is strictly coplanar with the four porphinato nitrogen atoms, and these four and two imidazole nitrogen atoms are coordinated to the central iron atom to complete an approximately regular octahedron. The three independent Fe-N distances (average 2.01 Å) are in agreement with those found in bis(imidazole)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III) chloride[5] within the standard deviations, and the bond angles around the iron atom are very close to 90°. The planar imidazole rings are nearly parallel to the plane containing the N51 atom and the equatorial Fe-N2 bond; the dihedral angle between these planes is only 7°, while the corresponding angles in the related compound [5] mentioned above are 18 and 39°. Some interactions between the N2 atom and the hydrogen atom attached to the C51 atom and between N2 and that

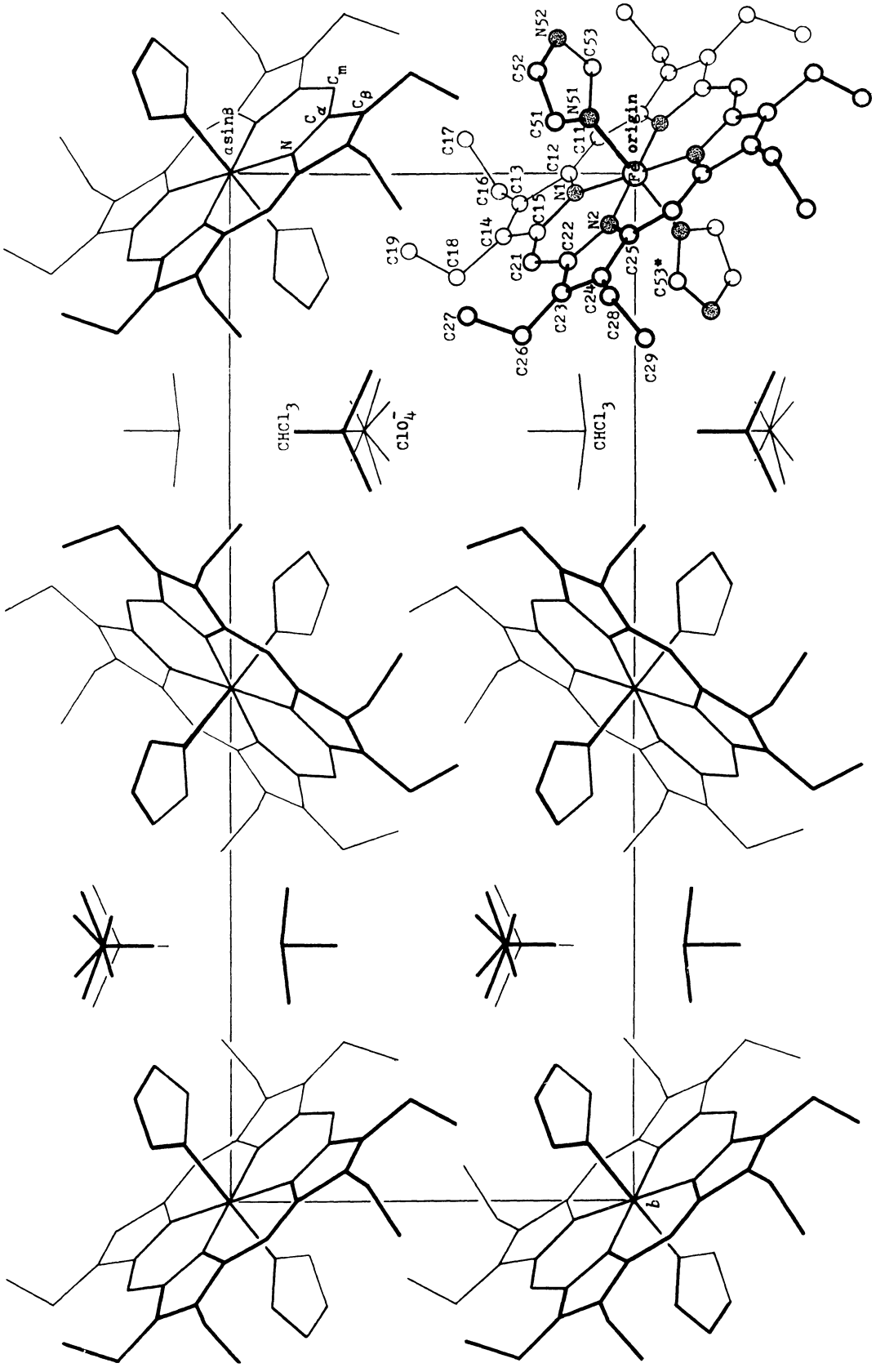

Figure The crystal structure viewed down the c axis.

to C53* may be suggested from their interatomic distances (N2···H(C51)=2.34 Å and N2···H(C53*)=2.45 Å). Although the porphinato core except for the ethyl groups is nearly planar within 0.06 Å, it shows the slight ruffling of the ring. The average bond distances are : C_m-C_α 1.36; C_α-C_β 1.48; C_β-C_β 1.31; C_α-N 1.38 Å, and the average bond angles are : C_α-C_m-C_α 124; C_m-C_α-C_β 126; C_m-C_α-N 128; C_β-C_α-N 108; C_α-C_β-C_β 108; C_α-N-C_α 108; C_α-N-Fe 126°, where C_α, C_β and C_m represent the three chemically and structurally different type of carbon atoms in the system (see the Figure). These averages are in agreement with those reported previously[8]. Two ethyl groups attached to one of the two independent pyrrole rings orient upward and downward from the pyrrole plane, while the two ethyl groups to the other ring lie in the same side. The former two participate in van der Waals contacts with those in the adjacent complex cations.

The complex cations, related by the mirror plane to each other, contact with the perchlorate anion at their non-coordinated imidazole nitrogen atoms, N52, presumably by forming hydrogen bonds; the hydrogen atom attached to the N52 atom is expected to exist between the lines, from the N52 atom to the non-disordered oxygen atom and from N52 to one of the disordered oxygen atoms. The solvent molecules on the mirror plane occupy the cavity between the two porphinato planes and the perchlorate anions. The temperature factors of one of the two solvent molecules are remarkably large, suggesting the partial elimination of it.

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* For the synthesis and properties of this substance, see H. Ogoshi, E. Watanabe, Z. Yoshida, J. Kincaid and K. Nakamoto, J. Amer. Chem. Soc., to be published.

(Received October 13, 1972)