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The Crystal and Molecular Structure of Diaqua(tetraphenylporphinato)-cobalt(III) Perchlorate

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The crystal structure of diaqua(meso-tetraphenylporphinato)cobalt(III) perchlorate, $[Co^{III}(tpp)(H_2O)_2]ClO_4$, has been determined by the X-ray method. The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions, $a=13.93(4)$ Å, $b=23.46(2)$ Å, $c=17.35(6)$ Å, and $\beta=129.4(2)°$. The Co(III) ion lies on the mean plane of the porphinato core, and is coordinated by the four porphinato nitrogen atoms and the two water oxygen atoms. The average Co–N distance is 1.964(4) Å, and the average Co–O(water) distance is 1.936(5) Å. The porphyrin plane is significantly ruffled and has an approximate S_4-$\bar{4}$ symmetry. The perchlorate anion is not bound directly to the cobalt(III) ion, and links the two adjacent $[Co^{III}(tpp)(H_2O)_2]^+$ cations by the hydrogen bonds with the aqua ligand oxygen atoms.

The structures of cobalt complexes with porphyrin have been of special interest because of their biological relevance to the hemoproteins[1] and vitamin B_{12} chemistry.[2] The stereochemistry of the cobalt porphinato complexes in the solid state has been reviewed by Scheidt,[1b] in which he states that the cobalt(III) derivatives are all low-spin complexes ($S=0$). Some cobalt complexes, however, have a paramagnetic nature in solution; chloro(tetraphenylporphinato)cobalt(III) complex, $[Co^{III}(tpp)Cl]$, shows a reversible paramagnetism with temperature in the inert solution,[3a] although it is the diamagnetic five coordinate complex in the solid state.[3b] Similar temperature dependence of magnetic conversion has been reported for several Co(III) complexes.[4] This paramagnetic state differs from that caused by the spin-state exchange of the metal ion as observed in the Co(II), Fe(III), or Ni(II) complexes,[5] and is considered to be arisen from the π-cation radical of the six-coordinated low-spin cobalt(III) complex, which is formed in the thermal equilibrium state.[3c].

We have, so far, studied on the structures and chemicophysical properties of several perchlorate metalloporphyrins[6] and found that diaqua(tetraphenylporphinato)cobalt(III) perchlorate, $[Co^{III}(tpp)(H_2O)_2]ClO_4$, shows the same magnetic behavior in the inert solution as observed in $[Co^{III}(tpp)Cl]$; the ^{1}H-NMR spectra of $[Co^{III}(tpp)(H_2O)_2]ClO_4$ in chloroform or benzene give the slight low-field shift and the line broadening of signals, while those spectra in the polar solvents exhibit diamagnetic properties.[6b] Thus the structure of this complex is of interest in relation to the anomalous magnetic properties. In this paper, the crystal structure of $[Co^{III}(tpp)(H_2O)_2]ClO_4$ is described, and the structural characteristics about the Co(III) ion will be discussed in comparison with those of the other metalloporphyrins.

Experimental

$[Co^{III}(tpp)(H_2O)_2]ClO_4$ was prepared by air-oxidation of $[Co^{II}(tpp)]$ in methanol containing hydroperchloric acid.[6b] Dark-violet, needle-like crystals were obtained by recrystallization using 10:1 mixture of benzene and acetone. A crystal with dimensions of 0.5 mm × 0.2 mm × 0.2 mm was used for the diffractometer experiment. Preliminary photographic examination established a monoclinic unit cell containing four chemical units of $[Co^{III}(tpp)(H_2O)_2]ClO_4\cdot(CH_3)_2C{=}O\cdot 3/2H_2O$. The systematic absences led to the space group $P2_1/c$. The least-squares refinement of setting angles of 20 reflections, measured on a Rigaku AFC-5 diffractometer using Mo $K\alpha$ radiation ($\bar{\lambda}=0.71073$ Å), led to the cell constants: $a=13.93(4)$ Å, $b=23.46(2)$ Å, $c=17.35(6)$ Å, and $\beta=129.4(2)°$. The calculated density of 1.35 g cm^{-3} agrees with the observed density of 1.33 g cm^{-3} by the floatation method in calcium chloride solutions.

Intensity data of 6953 reflections in the range $2\theta<50°$ were collected by the use of ω-2θ scanning technique, the scanning rate being 5° in ω per minute. During the course of data collection, three reflections were monitored every 60 reflections. The intensity data were converted to the F_o data in the usual manner. Absorption correction was not applied ($\mu=5.08$ cm^{-1} for Mo $K\alpha$). The standard deviations were estimated by counting statics. A total number of 4380 independent reflections with $F_o>3\sigma(F_o)$ were retained as observed, and employed in solving and refining the structure.

The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. The locations of the crystal water and acetone molecules were determined by the difference Fourier syntheses. The hydrogen atoms were placed at the theoretically calculated positions (C–H=1.00 Å). After several cycles of refinement, the hydrogen atoms of the aqua ligand were revealed on the difference Fourier map. The further refinement was carried to convergence with the weighting scheme of $w=1/\sigma(F_o)^2$ including the hydrogen atoms in the structure factor calculation. The final R value was 0.077. Atomic scattering factors were obtained from the International Table for X-Ray Crystallography IV.[7] All computations were performed on a FACOM M-190 computer in the Data Processing Center of Kyoto University by using the program system KPAX.

Results and Discussion

The atomic parameters are listed in Table 1.[8] The structure of $[Co^{III}(tpp)(H_2O)_2]^+$ cation is shown in Fig. 1, and the crystal structure in Fig. 2. The atomic numbering scheme is given in Figs. 1 and 3.

Bond distances and bond angles are listed in Table 2. The average bond distances and bond angles for the four crystallographically nonequivalent pyrrole rings

TABLE 1. POSITIONAL AND THERMAL PARAMETERS FOR THE ATOMS OF $[Co^{III}(tpp)(H_2O)_2]ClO_4 \cdot (CH_3)_2C{=}O \cdot 3/2H_2O$

Estimated standard deviations in the least significant figure(s) are give in parentheses. B_{eq} is the equivalent isotropic temperature factor defined by Hamilton.[9]

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Co	0.2840(1)	0.3064(1)	0.1576(1)	3.07	C_7	0.5275(7)	0.1368(3)	0.2226(5)	3.84
N_1	0.1109(5)	0.3291(2)	0.0529(4)	3.38	C_8	0.5734(8)	0.1170(3)	0.1755(6)	4.74
N_2	0.2650(5)	0.2444(2)	0.0725(4)	3.64	C_9	0.6365(8)	0.0656(3)	0.2028(6)	5.24
N_3	0.4583(5)	0.2849(2)	0.2606(4)	3.33	C_{10}	0.6550(8)	0.0336(3)	0.2771(6)	5.24
N_4	0.3045(5)	0.3673(2)	0.2452(4)	3.37	C_{11}	0.6138(8)	0.0524(4)	0.3255(6)	5.47
C_{1A}	0.0446(6)	0.3685(3)	0.0619(5)	3.71	C_{12}	0.5497(8)	0.1038(4)	0.2988(6)	5.17
C_{1B}	−0.0754(7)	0.3781(3)	−0.0343(6)	4.33	C_{13}	0.6440(7)	0.3998(3)	0.4583(5)	4.03
C_{1C}	−0.0792(7)	0.3449(3)	−0.0995(5)	4.17	C_{14}	0.6630(8)	0.4551(3)	0.4442(6)	5.00
C_{1D}	0.0334(6)	0.3135(3)	−0.0465(5)	3.82	C_{15}	0.7689(8)	0.4850(4)	0.5192(7)	5.92
C_{1M}	0.0596(6)	0.2699(3)	−0.0860(5)	3.77	C_{16}	0.8572(8)	0.4602(4)	0.6101(6)	5.94
C_{2A}	0.1655(7)	0.2366(3)	−0.0281(5)	3.91	C_{17}	0.8377(8)	0.4059(4)	0.6265(6)	5.92
C_{2B}	0.1819(7)	0.1834(3)	−0.0593(5)	4.64	C_{18}	0.2328(8)	0.3760(3)	0.5524(6)	5.01
C_{2C}	0.2874(7)	0.1590(3)	0.0208(6)	4.60	C_{19}	−0.0014(7)	0.4381(3)	0.1427(6)	4.24
C_{2D}	0.3411(7)	0.1979(3)	0.1029(5)	3.87	C_{20}	−0.0785(9)	0.4196(4)	0.1623(8)	6.90
C_{2M}	0.4574(7)	0.1914(3)	0.1949(5)	3.75	C_{21}	−0.1651(10)	0.4559(5)	0.1498(10)	8.87
C_{3A}	0.5150(6)	0.2364(3)	0.2637(5)	3.39	C_{22}	−0.1741(9)	0.5115(4)	0.1208(8)	7.65
C_{3B}	0.6469(7)	0.2390(3)	0.3444(5)	3.86	C_{23}	−0.0953(9)	0.5298(4)	0.1055(8)	6.59
C_{3C}	0.6698(7)	0.2906(3)	0.3876(5)	4.05	C_{24}	−0.0086(8)	0.4940(4)	0.1160(7)	5.47
C_{3D}	0.5528(6)	0.3185(3)	0.3393(5)	3.54	Cl	0.4016(3)	0.1661(1)	0.4395(2)	7.62
C_{3M}	0.5332(7)	0.3669(3)	0.3740(5)	3.67	O_1	0.4244(9)	0.2006(5)	0.3898(7)	13.86
C_{4A}	0.4149(6)	0.3852(3)	0.3336(5)	3.34	O_2	0.2770(8)	0.1553(5)	0.3911(8)	13.60
C_{4B}	0.3864(7)	0.4248(3)	0.3805(5)	4.15	O_3	0·4478(10)	0.1919(5)	0.5316(8)	14.45
C_{4C}	0.2637(7)	0.4300(3)	0.3221(6)	3.93	O_4	0.4723(13)	0.1173(6)	0.4689(11)	18.78
C_{4D}	0.2106(7)	0.3959(3)	0.2347(5)	3.48	C_{A1}	0.0604(13)	0.1255(6)	0.0628(10)	10.36
C_{4M}	0.0869(7)	0.3979(3)	0.1482(6)	3.84	C_{A2}	−0.0378(16)	0.1028(6)	−0.0350(13)	14.13
C_1	−0.0368(7)	0.2545(3)	−0.1934(5)	4.06	C_{A3}	0.1639(16)	0.0927(7)	0.1473(13)	13.12
C_2	−0.1522(8)	0.2343(4)	−0.2291(6)	5.40	O_A	0.0564(8)	0.1780(3)	0.0744(6)	10.08
C_3	−0.2405(8)	0.2176(4)	−0.3279(7)	6.43	O_{w1}	0.3299(5)	0.3591(2)	0.0997(4)	4.32
C_4	−0.2136(9)	0.2200(4)	−0.3913(6)	6.58	O_{w2}	0.2308(5)	0.2567(2)	0.2129(4)	4.10
C_5	−0.0999(9)	0.2388(4)	−0.3579(6)	5.75	O_{w3}	0.5515(14)	0.4162(7)	0.1923(10)	20.82
C_6	−0.0114(8)	0.2563(4)	−0.2595(6)	4.97	O_{w4}	0.5335(25)	0.4900(13)	0.0734(20)	18.86

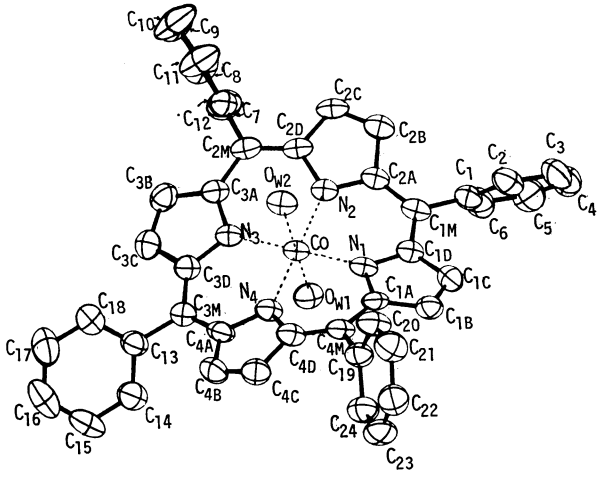

Fig. 1. Computer-drawn perspective model of $[Co^{III}(tpp)(H_2O)_2]^+$.

are given in Fig. 4. The cobalt(III) ion occupies the center of the octahedron formed by the four porphinato nitrogen atoms and the two aqua oxygen atoms, and it lies on the mean plane of the porphinato core; the displacement is 0.004 Å out of the plane defined by the four nitrogen atoms toward the O_{w2} atom and 0.006 Å out of the porphinato mean plane.

The average axial Co(III)–OH_2 bond distance of 1.936(5) Å is comparable with the sum of ionic radii of Co(III) (0.53 Å) and 0 (1.40 Å),[10] and close to the Co(III)–OCH_3 distance, 1.92 Å, observed in $[Co^{III}(OCH_3)(tpp)(py)]$.[11] The average Co–N distance of 1.964(6) Å is within the range of reported distances (1.958—1.982 Å).[1b] The Co(III)–N and Co(III)–O distance are in good agreement with those of the low-spin Co(III) ion in which d_{z^2} and $d_{x^2-y^2}$ orbitals are vacant.[1b]

Deviations of atoms from the least-squares plane of the porphinato core are given in Fig. 5. The porphinato core has a ruffled conformation with an approximate S_4-$\bar{4}$ symmetry. The four pyrrole rings are all swiveled about the metal-nitrogen bond; the dihedral angles between the pyrrole ring and the porphinato mean plane are 14, 16, 18 and 16°. Similar conformations have been observed in Ni- and Co-

Table 2. Bond distances and angles for $[Co^{III}(tpp)(H_2O)_2]ClO_4 \cdot (CH_3)_2C{=}O$
Estimated standard deviations are in parentheses.

(a) Bond distances (l/Å)

Co-N_1	1.959(9)	C_{3A}-C_{3B}	1.440(11)	C_{3M}-C_{13}	1.500(10)	C_3-C_4	1.370(21)
Co-N_2	1.967(7)	C_{3C}-C_{3D}	1.433(12)	C_{4M}-C_{19}	1.504(14)	C_4-C_5	1.369(18)
Co-N_3	1.958(9)	C_{4A}-C_{4B}	1.447(14)	C_1-C_2	1.388(15)	C_9-C_{10}	1.367(15)
Co-N_4	1.970(7)	C_{4C}-C_{4D}	1.436(12)	C_1-C_6	1.399(18)	C_{10}-C_{11}	1.357(19)
Co-O_{w1}	1.939(8)	C_{1B}-C_{1C}	1.346(15)	C_7-C_8	1.398(18)	C_{15}-C_{16}	1.370(12)
Co-O_{w2}	1.932(8)	C_{2B}-C_{2C}	1.351(10)	C_7-C_{12}	1.387(14)	C_{16}-C_{17}	1.370(14)
N_1-C_{1A}	1.384(12)	C_{3B}-C_{3C}	1.351(10)	C_{13}-C_{14}	1.377(11)	C_{21}-C_{22}	1.375(16)
N_1-C_{1D}	1.382(10)	C_{4B}-C_{4C}	1.328(12)	C_{13}-C_{18}	1.394(11)	C_{22}-C_{23}	1.352(22)
N_2-C_{2A}	1.389(9)	C_{1M}-C_{1D}	1.402(13)	C_{19}-C_{20}	1.386(20)	Cl-O_1	1.359(15)
N_2-C_{2D}	1.372(10)	C_{1M}-C_{2A}	1.383(10)	C_{19}-C_{24}	1.373(12)	Cl-O_2	1.390(12)
N_3-C_{3A}	1.367(10)	C_{2M}-C_{2D}	1.383(10)	C_2-C_3	1.388(13)	Cl-O_3	1.424(14)
N_3-C_{3D}	1.392(8)	C_{2M}-C_{3A}	1.403(10)	C_5-C_6	1.389(12)	Cl-O_4	1.380(15)
N_4-C_{4A}	1.378(9)	C_{3M}-C_{3D}	1.391(12)	C_8-C_9	1.387(11)	C_{A1}-O_A	1.255(16)
N_4-C_{4D}	1.375(13)	C_{3M}-C_{4A}	1.387(13)	C_{11}-C_{12}	1.393(13)	C_{A1}-C_{A2}	1.445(20)
C_{1A}-C_{1B}	1.445(10)	C_{4M}-C_{4D}	1.393(10)	C_{14}-C_{15}	1.387(11)	C_{A1}-C_{A3}	1.462(19)
C_{1C}-C_{1D}	1.420(11)	C_{4M}-C_{1A}	1.394(13)	C_{17}-C_{18}	1.377(11)		
C_{2A}-C_{2B}	1.435(12)	C_{1M}-C_1	1.493(11)	C_{20}-C_{21}	1.377(20)		
C_{2C}-C_{2D}	1.438(12)	C_{2M}-C_7	1.493(11)	C_{23}-C_{24}	1.385(18)		

(b) Bond angles (ϕ/°)

N_1-Co-N_2	90.3(3)	N_1-C_{1D}-C_{1C}	109.7(8)	C_{3M}-C_{3D}-C_{3C}	125.6(6)	C_5-C_6-C_1	120.6(11)
N_2-Co-N_3	89.6(3)	N_2-C_{2A}-C_{2B}	108.5(6)	C_{3M}-C_{4A}-C_{4B}	125.2(6)	C_7-C_8-C_9	121.0(10)
N_3-Co-N_4	89.7(3)	N_2-C_{2D}-C_{2C}	109.6(6)	C_{4M}-C_{4D}-C_{4C}	125.1(9)	C_{11}-C_{12}-C_7	120.6(12)
N_4-Co-N_1	90.5(3)	N_3-C_{3A}-C_{3B}	110.6(6)	C_{1D}-C_{1M}-C_{2A}	123.1(7)	C_{13}-C_{14}-C_{15}	121.3(7)
N_1-Co-N_3	178.5(3)	N_3-C_{3D}-C_{3C}	109.4(7)	C_{2D}-C_{2M}-C_{3A}	121.2(7)	C_{17}-C_{18}-C_{13}	121.1(8)
N_2-Co-N_4	178.8(2)	N_4-C_{4A}-C_{4B}	108.1(7)	C_{3D}-C_{3M}-C_{4A}	122.0(6)	C_{19}-C_{20}-C_{21}	120.4(11)
N_1-Co-O_{w1}	87.9(3)	N_4-C_{4D}-C_{4C}	108.8(6)	C_{4D}-C_{4M}-C_{1A}	122.1(9)	C_{23}-C_{24}-C_{19}	119.6(12)
N_2-Co-O_{w1}	90.8(3)	C_{1A}-C_{1B}-C_{1C}	106.3(8)	C_{1D}-C_{1M}-C_1	118.7(6)	C_2-C_3-C_4	120.0(11)
N_3-Co-O_{w1}	90.7(3)	C_{1B}-C_{1C}-C_{1D}	108.5(6)	C_{2A}-C_{1M}-C_1	118.0(8)	C_4-C_5-C_6	120.1(13)
N_4-Co-O_{w1}	90.2(3)	C_{2A}-C_{2B}-C_{2C}	108.1(7)	C_{2D}-C_{2M}-C_7	120.9(6)	C_8-C_9-C_{10}	119.9(12)
N_1-Co-O_{w2}	89.5(3)	C_{2B}-C_{2C}-C_{2D}	107.0(7)	C_{3A}-C_{2M}-C_7	117.9(6)	C_{10}-C_{11}-C_{12}	120.6(10)
N_2-Co-O_{w2}	90.9(3)	C_{3A}-C_{3B}-C_{3C}	106.5(7)	C_{3D}-C_{3M}-C_{13}	118.6(8)	C_{14}-C_{15}-C_{16}	120.5(9)
N_3-Co-O_{w2}	92.0(3)	C_{3B}-C_{3C}-C_{3D}	107.7(6)	C_{4A}-C_{3M}-C_{13}	119.4(8)	C_{16}-C_{17}-C_{18}	120.9(7)
N_4-Co-O_{w2}	88.2(3)	C_{4A}-C_{4B}-C_{4C}	108.0(7)	C_{4D}-C_{4M}-C_{19}	119.5(8)	C_{20}-C_{21}-C_{22}	120.8(16)
O_{w1}-Co-O_{w2}	176.8(3)	C_{4B}-C_{4C}-C_{4D}	107.8(10)	C_{1A}-C_{4M}-C_{19}	118.1(6)	C_{22}-C_{23}-C_{24}	122.0(10)
Co-N_1-C_{1A}	126.4(5)	N_1-C_{1A}-C_{4M}	126.5(6)	C_{1M}-C_1-C_2	120.6(10)	C_3-C_4-C_5	120.4(8)
Co-N_1-C_{1D}	127.7(6)	N_1-C_{1D}-C_{1M}	124.3(6)	C_{1M}-C_1-C_6	121.4(9)	C_9-C_{10}-C_{11}	120.3(8)
Co-N_2-C_{2A}	126.3(5)	N_2-C_{2A}-C_{1M}	126.3(8)	C_{2M}-C_7-C_8	123.0(8)	C_{15}-C_{16}-C_{17}	118.9(7)
Co-N_2-C_{2D}	126.6(5)	N_2-C_{2D}-C_{2M}	125.8(7)	C_{2M}-C_7-C_{12}	119.4(10)	C_{21}-C_{22}-C_{23}	118.4(12)
Co-N_3-C_{3A}	127.0(4)	N_3-C_{3A}-C_{2M}	126.1(6)	C_{3M}-C_{13}-C_{14}	120.4(6)	O_1-Cl-O_2	115.5(7)
Co-N_3-C_{3D}	127.0(5)	N_3-C_{3D}-C_{3M}	124.3(7)	C_{3M}-C_{13}-C_{18}	122.3(7)	O_1-Cl-O_3	109.7(8)
Co-N_4-C_{4A}	126.3(6)	N_4-C_{4A}-C_{3M}	126.6(8)	C_{4M}-C_{19}-C_{20}	121.2(8)	O_1-Cl-O_4	109.2(12)
Co-N_4-C_{4D}	126.3(4)	N_4-C_{4D}-C_{4M}	125.5(8)	C_{4M}-C_{19}-C_{24}	120.1(11)	O_2-Cl-O_3	104.9(9)
C_{1A}-N_1-C_{1D}	105.6(6)	C_{4M}-C_{1A}-C_{1B}	123.6(8)	C_2-C_1-C_6	117.9(7)	O_2-Cl-O_4	113.4(9)
C_{2A}-N_2-C_{2D}	106.8(6)	C_{1M}-C_{1D}-C_{1C}	125.8(6)	C_8-C_7-C_{12}	117.6(8)	O_3-Cl-O_4	103.3(9)
C_{3A}-N_3-C_{3D}	105.7(6)	C_{1M}-C_{2A}-C_{2B}	124.7(6)	C_{14}-C_{13}-C_{18}	117.3(6)	O_A-C_{A1}-C_{A2}	116.4(11)
C_{4A}-N_4-C_{4D}	107.1(7)	C_{2M}-C_{2D}-C_{2C}	124.4(8)	C_{20}-C_{19}-C_{24}	118.7(10)	O_A-C_{A1}-C_{A3}	118.2(11)
N_1-C_{1A}-C_{1B}	109.8(8)	C_{2M}-C_{3A}-C_{3B}	123.2(8)	C_1-C_2-C_3	121.0(12)	C_{A2}-C_{A1}-C_{A3}	125.4(13)

porphyrins.[12,13c] As compared with these complexes, the lengthening of the metal–N bond accompanied by increasing the C_A–N–C_A angle and decreasing the N–C_A–C_B angle seems to relieve the ruffling. The phenyl rings attached to C_M are tilted from the core plane, because of repulsions between the hydrogen atoms. The dihedral angles of each phenyl ring with the porphinato mean plane are 59, 65, 60, and 81°; their average value being 66°. As seen in Fig. 6, these angles have a linear relationship for the C_M–C_P bond distances; the C_M–C_P bond distance of 1.498(5) Å is very close to the value of 1.497(3) Å observed for the central C–C bond of planar biphenyl molecule.[14] Thus, the C_M–C_P bond has a little π-conjugation character, in spite of the steric hindrance. Although the π-conjugate system of the porphinato

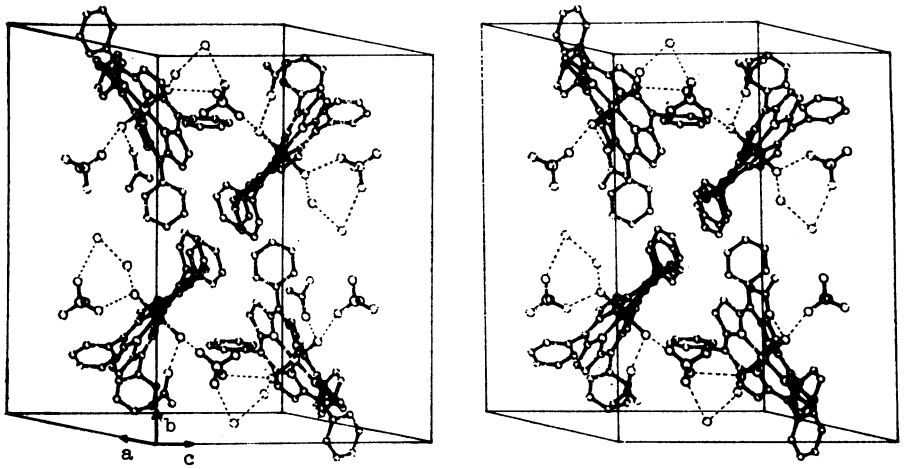

Fig. 2. Stereoscopic view of the contents in the unit cell of $[Co^{III}(tpp)(H_2O)_2]ClO_4 \cdot (CH_3)_2C{=}O \cdot 3/2H_2O$ crystal.

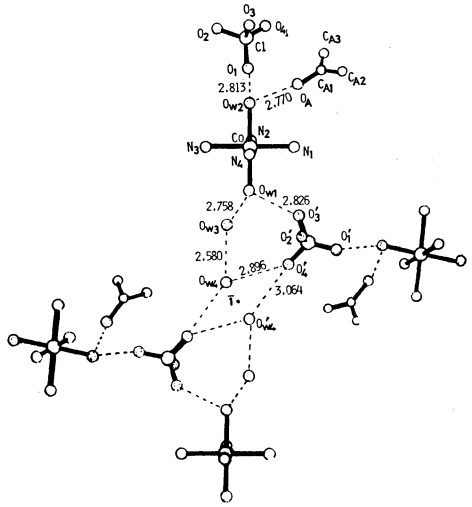

Fig. 3. Hydrogen-bonding scheme among the $[Co^{III}(tpp)(H_2O)_2]^+$ cations, the perchlorate anions, the water molecules, and the acetone molecules. The dotted lines represent hydrogen bonds. The tetraphenylporphine atoms other than the nitrogen atoms are omitted for clarity.

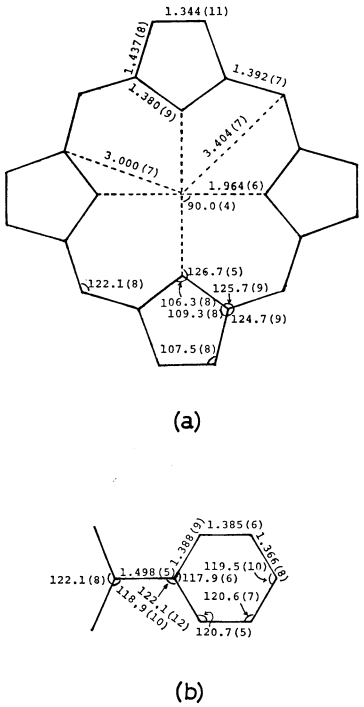

Fig. 4. Average bond distances (l/Å) and angles (ϕ/°) for the porphine skeleton of the $Co^{III}(tpp)^+$ cation (a) and for the peripheral phenyl groups (b).

core might be weakened because of its ruffled conformation, the π-conjugate system may be slightly delocalized over the phenyl rings through the C_M–C_P bond.

The crystal structure consists of the discrete $[Co^{III}(tpp)(H_2O)_2]^+$ cations, the perchlorate anions, the acetone molecules, and the water molecules other than the aqua ligands. As shown in Fig. 3, the aqua ligand O_{w1} atom forms the two hydrogen bonds with the perchlorate O_3 and water O_{w3} atoms, while the ligand O_{w2} atom forms the two hydrogen bonds with the perchlorate O_1 and acetone O_A atoms. Thus, the two $[Co^{III}(tpp)(H_2O)_2]^+$ cations are linked together by the perchlorate anion through the $O_{w1}\cdots O_3$ and $O_{w2}\cdots O_1$ hydrogen bonds. The water O_{w4} atom occupies the two positions with the half occupancy near the inversion center. This oxygen atom is hydrogen-bond to the two adjacent perchlorate anions and the water O_{w3} atom. The perchlorate O_1 atom exists near the porphinato nitrogen N_3 atom at 3.241 Å and the Co(III) atom at 4.026 Å, and it seems to have weak interactions with the central Co(III) atom because of their interorbital overlapping between the π-orbital of Co–N bond and the σ-orbital of O_1 atom. This crystal structure may, therefore, suggest that the perchlorate anion, bound directly to the Co(III) atom in the inert solvent, might be replaced by the water molecule in the crystallization process, since the water molecule acts as a little stronger ligand for the Co(III) ion than the perchlorate anion. The diamagnetic properties of $[Co^{III}(tpp)(H_2O)_2]ClO_4$ in ethanol or pyridine are considered to be caused by the strong coordination of the polar solvent molecules as the fifth and/or sixth axial ligands.

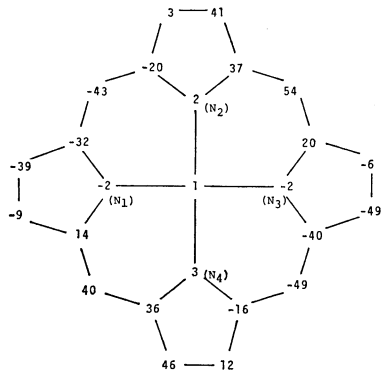

Fig. 5. Ruffling of the porphinato core. Perpendicular distances of the atoms from the porphinato mean plane are in a unit of 0.01 Å.

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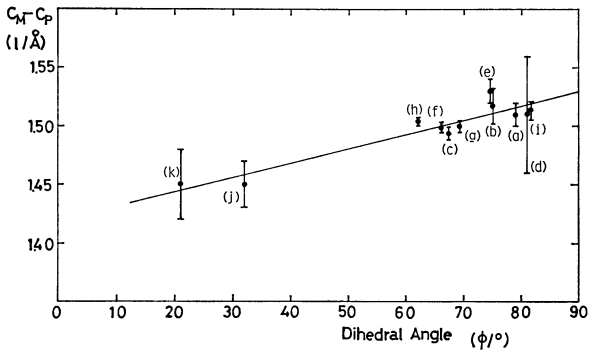

Fig. 6. The C_M–C_P bond distances (l/Å) *vs.* the dihedral angles (ϕ/°) of the phenyl groups for the porphinato mean plane. Seven Co^{III}(tpp) complexes[3b,11,13a–d] and four metal-free porphyrins (three tpp compounds[13e,f,15] and one tetrapyridylporphyrin compound[15]), as shown below, are plotted:
(a): Ref. 13a, (b): Ref. 3b, (c): Ref. 13b, (d): Ref. 11, (e): Ref. 13c, (f): this work, (g): Ref. 13d, (h): Ref. 13e, (i): Ref. 13f, (j): Ref. 15, and (k): Ref. 15.

References

1) a) E. B. Fleischer, *Acc. Chem. Res.*, **3**, 105 (1969); b) W. R. Scheidt, *ibid.*, **10**, 339 (1977); c) J. L. Hoard, "Porphyrins and Metalloporphyrins," ed by K. M. Smith, Elsevier, Amsterdam (1975), p. 317; d) J. L. Hoard, *Ann. N.Y. Acad. Sci.*, **206**, 18 (1973).

2) J. M. Pratt, "The Inorganic Chemistry of Vitamin B_{12}," Academic Press, New York (1972).

3) a) K. Yamamoto, J. Uzawa, and T. Chijimatsu, *Chem. Lett.*, **1979**, 89; b) T. Sakurai, K. Yamamoto, H. Naito, and N. Nakamoto, *Bull. Chem. Soc. Jpn.*, **49**, 3042 (1976); c) K. Yamamoto, M. Kohno, and H. Ohya-Nishiguchi, *Chem. Lett.*, **1981**, 255.

4) a) M. Gerloch, B. M. Higson, and E. D. McKenjie, *J. Chem. Soc., Chem. Commun.*, **1971**, 1149; b) C. R. Ollis, D. Y. Jeter, and W. E. Hatfield, *J. Am. Chem. Soc.*, **93**, 547 (1971).

5) L. Sacconi, *Pure Appl. Chem.*, **27**, 161 (1971).

6) a) H. Masuda, T. Taga, K. Osaki, H. Sugimoto, Z. Yoshida, and H. Ogoshi, *Inorg. Chem.*, **19**, 950 (1980); b) H. Sugimoto, M. Nagano, Z. Yoshida, and H. Sugimoto, *Chem. Lett.*, **1980**, 521; c) H. Ogoshi, H. Sugimoto, and Z. Yoshida, *Biochim. Biophys. Acta*, **621**, 19 (1980).

7) "International Tables for X-Ray Crystallography," ed by J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, England (1974), Vol. IV, p. 99.

8) The anisotropic thermal parameters and complete lists of the $|F_o|$ and $|F_c|$ values are deposited as Document No. 8203 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

9) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

10) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, New York, N. Y. (1975), p. 259.

11) C. Riche, A. Chiaroni, M. Perree-Fauvet, and A. Goudemer, *Acta Crystallogr., Sect. B*, **34**, 1868 (1978).

12) D. L. Cullen and E. F. Meyer, Jr., *J. Am. Chem. Soc.*, **96**, 2095 (1974).

13) a) J. W. Lauher and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4447 (1974); b) W. R. Scheidt, J. A. Cunningham, and J. L. Hoard, *ibid.*, **95**, 8289 (1973); c) T. Sakurai, K. Yamamoto, N. Seino, and M. Katsura, *Acta Crystallogr., Sect. B*, **31**, 2514 (1975); d) J. A. Kaduk and W. R. Scheidt, *Inorg. Chem.*, **13**, 1875 (1974); e) S. J. Silvers and A. Tulinsky, *J. Am. Chem. Soc.*, **89**, 3331 (1967); **86**, 927 (1964); f) M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, **86**, 1938 (1964).

14) G. B. Robertson, *Nature*, **191**, 593 (1961).

15) a) E. B. Fleischer and A. L. Stone, *J. Chem. Soc., Chem. Commun.*, **1967**, 332; b) A. L. Stone and E. B. Fleischer, *J. Am. Chem. Soc.*, **90**, 2735 (1968).