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The Crystal and Molecular Structure of Aquachloro(*meso*-tetraphenylporphyrinato)cobalt(III)

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The crystal and molecular structure of the title compounds, [Co^{III}Cl(tpp)(H_2O)], has been determined by means of X-ray diffraction techniques. The compound crystallizes in the monoclinic system; space group $P2_1/c$. The unit cell has a=13.542(2), b=25.760(2), c=10.423(1) Å, β=99.33(2)°, and Z=4. The cobalt atom is coordinated by four porphyrinato nitrogen atoms, one chlorine atom, and one oxygen atom of water, and is displaced by 0.039(2) Å from the mean plane defined by the four porphyrinato nitrogen atoms towards the axial chlorine atom. The average Co–N(tpp) distance is 1.955(2) Å. The Co–Cl distance is 2.216(1), and the Co–O(water) distance, 1.979(3) Å. The porphyrinato core is significantly ruffled and has an approximate $\bar{4}$ symmetry. The [Co^{III}Cl(tpp)(H_2O)] molecules are stacked along the c axis by O–H···Cl hydrogen bonds.

In our investigation of chloro (*meso*-tetraphenylporphyrinato)cobalt(III), [Co^{III}Cl(tpp)], its characteristic phenomena, behavior, or properties have been found by the use of optical absorption, NMR, and ESR spectral techniques.[1)] The crystallization of the complex from common solvents gives crystals of various external forms: obelisk, pyramid, prism, and/or bulky shapes from a dichloromethane or chloroform solution, and only obelisks from a methanol solution. A previous X-ray diffraction study[2)] of the obelisk crystals isolated from a dichloromethane or chloroform solution demonstrated that the complex can be represented as a five-coordinate cobalt complex of tpp having square-pyramid structure with a chlorine atom at the apex. However, a subsequent X-ray diffraction study[3)] of the pyramid crystals obtained from a dichloromethane or chloroform solution suggested that there is an unidentified atom in the sixth axial position. The possibility of the partial coordination of water at the sixth ligand position was considered, because it has been well known that the cobalt(III) complex is stable in the case of six-coordination.[4)] Presumably, water in the atmosphere contaminated the solution being crystallized. However, an IR examination of the crystals did not find any OH stretchings. In order to elucidate the coordination of a water molecule as the sixth ligand, crystals of species with one water molecule, [Co^{III}Cl(tpp)(H_2O)], were prepared from a solution of dichloromethane saturated with water and then analyzed by means of X-ray diffraction. The result shows that when the water molecule coordinates at the sixth axial position, the crystal and molecular structure is completely different from that of [Co^{III}Cl(tpp)]. The present paper will deal with the structure of [Co^{III}Cl(tpp)(H_2O)].

Experimental

Materials. The chloro(*meso*-tetraphenylporphyrinato)cobalt(III), [Co^{III}Cl(tpp)], was prepared by the method previously reported.[2)] The complex was dissolved in a solution of dichloromethane saturated with water and evaporated spontaneously; metallic lustrous reddish-purple prismatic crystals were thus obtained.

Found: C, 72.71; H, 4.07; Cl, 4.90; Co, 8.37; N, 7.75; O, 2.40%. Calcd for $C_{44}H_{30}ClCoN_4O$ ([Co^{III}Cl(tpp)(H_2O)]): C, 72.88; H, 4.17; Cl, 4.89; Co, 8.13; N, 7.73; O, 2.21%.

X-Ray Measurements. The crystal used was 0.25×0.31×0.75 mm in size. The preliminary Weissenberg photographs showed that the crystal belongs to the monoclinic system. The systematic absences ($h0l$ for l odd and $0k0$ for k odd) led to the space group $P2_1/c$. The least-squares refinement of the setting angles of 24 reflections, measured on a Rigaku AFC-4 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å), gave the following cell constants: a=13.542(2), b=25.760(2), c=10.423(1) Å, and β=99.33(2)°. The calculated density (1.342 g cm^{-3}) agreed with the observed value (1.345 g cm^{-3}) obtained by the floatation method in a tetrachloromethane-methylcyclohexane mixture. Intensity data within the range ($\sin\theta/\lambda$<0.75598 Å^{-1}) were collected by the use of the ω scan (2θ<30°) and ω-2θ scan methods ($2\theta\geqq30°$), with a scan speed of 4° min^{-1} in ω. The three standard reflections ($\bar{2}$ 2 1, 0 2 5, and 6 10 0), measured every 100 reflections, showed no significant deterioration. The ordinary Lorentz and polarization corrections and absorption correction were applied. The absorption coefficient for Mo$K\alpha$ radiation was 5.899 cm^{-1}. The minimum and maximum transmission coefficients were 0.83 and 0.87 respectively. 13597 reflections were measured, and 5873 unique reflections obtained with $F_o\geqq3.0\,\sigma\,(F_o)$. 7114 reflections were unobserved with the criterion of $F_o<3.0\,\sigma\,(F_o)$.

Structure Analysis

The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. Difference Fourier syntheses gave the positions of all the hydrogen atoms. In the final stage, the structure was refined by the full-matrix least-squares method, based on $|F_o|$, with isotropic and anisotropic temperature factors for hydrogen and non-hydrogen atoms respectively. The function minimized was $\sum w(|F_o|-|F_c|)^2$, where w=1.0. The final R and R_w values were 0.055 and 0.054 respectively. In the final cycle of refinement, the largest shift/error was 0.931 for B_{33} of the C(9C) atom. The maximum and minimum heights in the final difference synthesis were 0.57 and -0.61 e Å^{-3} respectively. Calculations were carried out on the FACOM M-380 computer of this Institute using the UNICS III program system[5] and the best-plane calculation with the BP70 program.[6] The atomic-scattering factors, including anomalous scattering corrections, were taken from the International Tables for X-Ray Crystallography.[7]

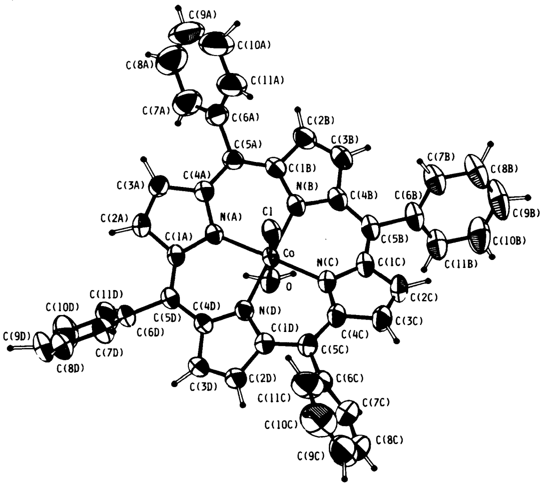

Fig. 1. The molecular structure.
The thermal ellipsoids are at 50% probabillity for non-hydrogen atoms (hydrogen atoms are arbitrarily scaled).

Results and Discussion

The atomic coordinates except hydrogen atoms are listed in Table 1.[8] The molecular structure of [Co^{III}Cl(tpp)(H$_2$O)] is shown in Fig. 1, along with the atomic numbering and the thermal ellipsoids. The intramolecular bond distances(Å) are listed in Table 2, while the crystal structure projected along the a axis is shown in Fig. 2.

The coordination around the cobalt atom is

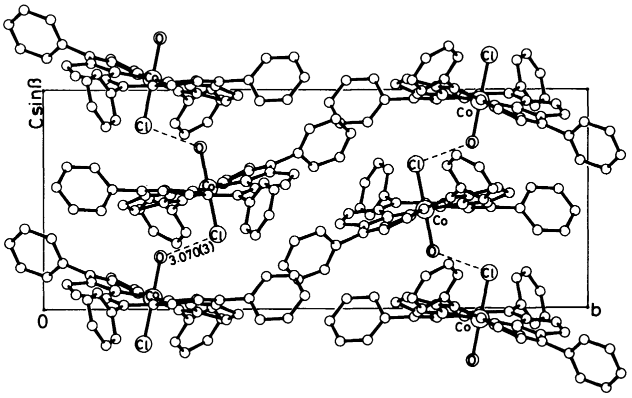

Fig. 2. The crystal structure projected along the a axis. Hydrogen atoms are omitted for clarity. Broken lines show the O-H···Cl hydrogen bonds (distances in Å).

Table 1. Atomic Coordinates with Estimated Standard Deviations in Parentheses. Positional Parameters Are Multiplied by 10^4. B_{eq} Values Are Equivalent Isotropic Temperature Factors

$$B_{eq} = \frac{4}{3}\sum_i \sum_j B_{ij} \boldsymbol{a}_i \cdot \boldsymbol{a}_j$$

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
CO	1661.8(4)	1992.3(2)	513.4(5)	2.7	C(9B)	48(6)	−621(2)	3019(7)	8.1
Cl	1321.3(8)	1821.6(4)	−1596.1(9)	3.7	C(10B)	825(6)	−346(2)	3677(6)	7.4
O	1984(2)	2135(1)	2400(3)	3.6	C(11B)	1081(5)	137(2)	3228(5)	5.4
N(A)	1090(2)	2686(1)	238(3)	2.8	C(1C)	1799(3)	869(1)	1247(4)	3.8
N(B)	358(2)	1721(1)	764(3)	3.1	C(2C)	2429(4)	424(2)	1150(5)	4.9
N(C)	2254(2)	1302(1)	841(3)	3.3	C(3C)	3227(4)	583(2)	671(5)	4.8
N(D)	2978(2)	2277(1)	357(3)	3.1	C(4C)	3147(3)	1137(1)	507(4)	3.7
C(1A)	1595(3)	3145(1)	194(3)	2.9	C(5C)	3886(3)	1457(2)	182(4)	3.9
C(2A)	898(3)	3551(1)	−256(4)	3.5	C(6C)	4835(3)	1235(2)	−136(6)	5.1
C(3A)	−16(3)	3337(2)	−501(4)	3.5	C(7C)	5506(5)	976(2)	757(9)	7.6
C(4A)	87(3)	2802(1)	−143(3)	3.1	C(8C)	6406(6)	793(3)	434(15)	11.1
C(5A)	−696(3)	2466(2)	−49(4)	3.4	C(9C)	6634(7)	881(3)	−737(15)	11.3
C(6A)	−1740(3)	2651(2)	−489(5)	4.7	C(10C)	5988(7)	1135(4)	−1650(11)	10.1
C(7A)	−2132(4)	3071(3)	53(7)	6.5	C(11C)	5077(5)	1314(3)	−1359(7)	7.2
C(8A)	−3107(6)	3246(3)	−446(10)	8.4	C(1D)	3817(3)	1999(2)	211(4)	3.6
C(9A)	−3634(5)	2997(5)	−1451(11)	9.9	C(2D)	4653(3)	2341(2)	225(5)	4.5
C(10A)	−3271(6)	2573(4)	−2004(9)	9.5	C(3D)	4323(3)	2822(2)	404(5)	4.2
C(11A)	−2330(4)	2403(3)	−1514(6)	6.8	C(4D)	3270(3)	2789(1)	445(4)	3.2
C(1B)	−547(3)	1971(2)	483(4)	3.6	C(5D)	2625(3)	3209(1)	404(4)	3.2
C(2B)	−1312(4)	1659(2)	905(5)	4.4	C(6D)	3025(3)	3750(1)	462(4)	3.9
C(3B)	−876(4)	1231(2)	1428(4)	4.4	C(7D)	3496(4)	3950(2)	−506(6)	5.3
C(4B)	162(3)	1249(1)	1307(4)	3.5	C(8D)	3834(5)	4460(2)	−440(8)	7.1
C(5B)	842(3)	845(1)	1571(4)	3.8	C(9D)	3708(5)	4770(2)	581(9)	8.2
C(6B)	528(4)	345(2)	2113(4)	4.4	C(10D)	3231(6)	4577(2)	1516(9)	8.1
C(7B)	−280(4)	63(2)	1486(5)	5.3	C(11D)	2881(4)	4069(2)	1476(6)	5.7
C(8B)	−516(6)	−419(2)	1924(6)	6.8					

illustrated in Fig. 3. The cobalt atom is coordinated by four porphyrinato nitrogen atoms, one chlorine atom, and one oxygen atom of water. The axial Co–Cl distance of 2.216(1) Å is shorter than those of $[Co^{III}Cl(tpp)(py)]$ (2.251(3) Å)⁹⁾ and $[Co^{III}Cl(NH_3)_5]Cl_2$ (2.286(2) Å),¹⁰⁾ and it is close to the sum of the covalent radii¹¹⁾ of Co(III)(1.22 Å) and Cl(0.99 Å). Another axial Co–O distance of 1.979(3) Å is longer than those of $[Co^{III}(tpp)(H_2O)_2]ClO_4$ (1.936(5) Å),¹²⁾ $[Co^{III}(CH_3O)(tpp)(py)]$(1.92 Å),¹³⁾ and $[Co^{III}(H_2O)(NH_3)_5]_2(S_2O_6)_3 \cdot 2H_2O$ (1.954(1) Å);¹⁴⁾ furthermore, it is longer than the sum of the covalent radii of Co(III) and O(0.66 Å) and comparable with that of the ionic radii of Co(+3) (0.63 Å) and O(−2)(1.40 Å).

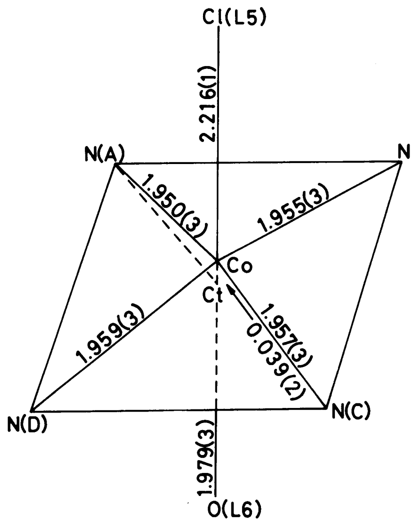

Fig. 3. Perspective diagram of the six-coordination around the cobalt(III) atom.
Ct represents the center of four porphyrinato nitrogen atoms.

The cobalt atom is displaced by 0.039(2) Å from the mean plane defined by four porphyrinato nitrogen atoms (4N plane) towards the axial chlorine atom, as is shown in Fig. 3. The displacement of the cobalt atom is common in five-coordinate complexes,²,¹⁵,¹⁶⁾ but is observed only for the present complex among the six-coordinate complexes.⁹,¹³,¹⁷⁻¹⁹⁾ A small displacement (0.013(2) Å) of the cobalt atom is observed for $[Co^{III}(NO_2)(tpp)(lut)]$,²⁰⁾ but it is buried in the mean 4N plane(±0.04(2) Å). The displacement of the metal atom has been well-known in iron porphyrin complexes, depending on its oxidation state and spin state.²¹⁾ In the present complex, the Co–Cl distance is short, while that of Co–O is long; hence a rather strong coordination of the chloride ligand to the cobalt atom and a weak coordination of the water ligand. Therefore, the displacement of cobalt in the present complex may result from a compromise between (1) the necessity for the best σ-overlapping of the chlorine and oxygen atoms of axial ligands with the cobalt atom and (2) the planarity for the optimum π-bonding of the porphyrinato ligand.

The average distance between cobalt and the porphyrinato nitrogen atom (Co–N(tpp)) is 1.955(2)

Table 2. Intramolecular Bond Distances with e.s.d.'s in Parentheses

Type	l/Å	Type	l/Å	Type	l/Å
Co–Cl	2.216(1)	(Cβ–Cβ')		C(10A)–C(11A)	1.367(10)
Co–O	1.979(3)	C(2A)–C(3A)	1.340(6)	C(11A)–C(6A)	1.383(8)
		C(2B)–C(3B)	1.327(7)		
Co–N(A)	1.950(3)	C(2C)–C(3C)	1.326(8)	C(6B)–C(7B)	1.387(7)
Co–N(B)	1.955(3)	C(2D)–C(3D)	1.341(6)	C(7B)–C(8B)	1.378(8)
Co–N(C)	1.957(3)			C(8B)–C(9B)	1.368(9)
Co–N(D)	1.959(3)	(Cα–Cm)		C(9B)–C(10B)	1.358(10)
		C(4A)–C(5A)	1.386(6)	C(10B)–C(11B)	1.394(8)
(N–Cα)		C(5A)–C(1B)	1.391(6)	C(11B)–C(6B)	1.384(7)
N(A)–C(1A)	1.371(5)	C(4B)–C(5B)	1.387(6)		
N(A)–C(4A)	1.385(5)	C(5B)–C(1C)	1.392(7)	C(6C)–C(7C)	1.366(9)
N(B)–C(1B)	1.375(5)	C(4C)–C(5C)	1.381(6)	C(7C)–C(8C)	1.397(12)
N(B)–C(4B)	1.386(5)	C(5C)–C(1D)	1.400(6)	C(8C)–C(9C)	1.326(22)
N(C)–C(1C)	1.374(5)	C(4D)–C(5D)	1.388(5)	C(9C)–C(10C)	1.353(15)
N(C)–C(4C)	1.379(6)	C(5D)–C(1A)	1.386(6)	C(10C)–C(11C)	1.396(12)
N(D)–C(1D)	1.372(5)			C(11C)–C(6C)	1.382(10)
N(D)–C(4D)	1.375(5)	(Cm–Cp)			
		C(5A)–C(6A)	1.491(6)	C(6D)–C(7D)	1.377(8)
(Cα–Cβ)		C(5B)–C(6B)	1.495(6)	C(7D)–C(8D)	1.391(8)
C(1A)–C(2A)	1.436(5)	C(5C)–C(6C)	1.492(7)	C(8D)–C(9D)	1.361(12)
C(3A)–C(4A)	1.429(5)	C(5D)–C(6D)	1.492(5)	C(9D)–C(10D)	1.349(13)
C(1B)–C(2B)	1.436(7)			C(10D)–C(11D)	1.388(8)
C(3B)–C(4B)	1.432(7)	(Phenyl group)		C(11D)–C(6D)	1.378(7)
C(1C)–C(2C)	1.442(6)	C(6A)–C(7A)	1.368(9)		
C(3C)–C(4C)	1.440(6)	C(7A)–C(8A)	1.412(10)		
C(1D)–C(2D)	1.432(6)	C(8A)–C(9A)	1.332(14)		
C(3D)–C(4D)	1.436(6)	C(9A)–C(10A)	1.362(15)		

Å. This distance is located near the lower end of the range of distances (1.948—1.985 Å) of the reported Co^{III}(tpp) complexes.[2,9,12,13,15–20] It is shorter than the Co–NH$_3$ distances of [Co^{III}(NH$_3$)$_6$][Co^{III}(CN)$_6$] (1.972(1) Å),[22] [Co^{III}Cl(NH$_3$)$_5$]Cl$_2$ (1.976 Å), and [Co^{III}(H$_2$O)(NH$_3$)$_5$]$_2$(S$_2$O$_6$)$_3$·2H$_2$O (1.961 Å).

The average distances of other chemically analogous types are: N–Cα=1.377(6), Cα–Cβ=1.435(4), Cβ–Cβ'=1.334(8), Cα–Cm=1.389(6), and Cm–Cp=1.492(2) Å, where Cα and Cβ (Cβ') denote α and β carbon atoms in pyrrole rings; Cm, methine carbon atoms; and Cp, phenyl carbon atoms. The figure in parentheses is the standard deviation. Except for Cm–Cp, these distances are very similar to those of the reported Co^{III}(tpp) complexes.

The intramolecular bond angles are listed in Table 3. The average value of four N–Co–N angles is 90.0(2)° (max. —min.: 90.3(1)—89.4(1)°); the cobalt atom is surrounded by a square-planar array of pyrrole nitrogen atoms. The average angles of the other chemically analogous types are: Co–N–Cα=126.8(2), Cα–N–Cα=106.0(2), N–Cα–Cβ=109.5(2), N–Cα–Cm=125.5(2), Cm–Cα–Cβ=124.8(3), Cα–Cβ–Cβ'=107.5(2), Cα–Cm–Cα=122.1(2), and Cα–Cm–Cp=118.7(5)°. These angles are comparable to those of [Co^{III}(NO$_2$)(tpp)(lut)] and [Co^{III}(tpp)(H$_2$O)$_2$]$^+$ in that the porphyrinato cores are ruffled, but differ somewhat from those of [Co^{III}Cl(tpp)] in that the core is planar.

The deviations of 24 atoms from the least-squares plane of the porphyrinato core are shown in Fig. 4. The porphyrinato core is considerably ruffled. The ruffled core has an approximate $\bar{4}$ symmetry. As is usual, a local flatness (within 0.02 Å) is maintained in

Table 3. Intramolecular Bond Angles with e.s.d.'s in Parentheses

Type	ϕ/°	Type	ϕ/°	Type	ϕ/°
Cl–Co–O	179.0(1)	N(D)–C(4D)–C(3D)	109.3(3)	C(4C)–C(5C)–C(6C)	120.7(4)
Cl–Co–N(A)	91.24(9)			C(1D)–C(5C)–C(6C)	116.7(4)
Cl–Co–N(B)	90.84(9)	(N–Cα–Cm)		C(4D)–C(5D)–C(6D)	120.3(4)
Cl–Co–N(C)	90.4(1)	N(A)–C(1A)–C(5D)	126.3(3)	C(1A)–C(5D)–C(6D)	117.9(3)
Cl–Co–N(D)	92.2(1)	N(A)–C(4A)–C(5A)	124.8(3)		
		N(B)–C(1B)–C(5A)	125.6(4)	(Cm–Cp–Cp')	
O–Co–N(A)	89.7(1)	N(B)–C(4B)–C(5B)	125.0(4)	C(5A)–C(6A)–C(7A)	122.6(4)
O–Co–N(B)	89.5(1)	N(C)–C(1C)–C(5B)	126.3(4)	C(5A)–C(6A)–C(11A)	119.3(5)
O–Co–N(C)	88.7(1)	N(C)–C(4C)–C(5C)	125.3(4)	C(5B)–C(6B)–C(7B)	121.7(4)
O–Co–N(D)	87.5(1)	N(D)–C(1D)–C(5C)	125.5(4)	C(5B)–C(6B)–C(11B)	120.2(4)
		N(D)–C(4D)–C(5D)	125.0(4)	C(5C)–C(6C)–C(7C)	122.6(6)
N(A)–Co–N(B)	90.1(1)			C(5C)–C(6C)–C(11C)	119.4(5)
N(B)–Co–N(C)	90.3(1)	(Cm–Cα–Cβ)		C(5D)–C(6D)–C(7D)	121.8(4)
N(C)–Co–N(D)	90.1(1)	C(5D)–C(1A)–C(2A)	123.8(3)	C(5D)–C(6D)–C(11D)	119.5(4)
N(D)–Co–N(A)	89.4(1)	C(5A)–C(4A)–C(3A)	125.4(4)		
		C(5A)–C(1B)–C(2B)	124.8(4)	(Phenyl group)	
N(A)–Co–N(C)	178.3(1)	C(5B)–C(4B)–C(3B)	126.0(4)	C(6A)–C(7A)–C(8A)	120.2(6)
N(B)–Co–N(D)	177.0(1)	C(5B)–C(1C)–C(2C)	124.5(4)	C(7A)–C(8A)–C(9A)	119.1(8)
		C(5C)–C(4C)–C(3C)	125.3(4)	C(8A)–C(9A)–C(10A)	122.3(8)
(Co–N–Cα)		C(5C)–C(1D)–C(2D)	123.9(4)	C(9A)–C(10A)–C(11A)	118.6(8)
Co–N(A)–C(1A)	127.4(3)	C(5D)–C(4D)–C(3D)	125.1(4)	C(10A)–C(11A)–C(6A)	121.8(7)
Co–N(A)–C(4A)	126.1(2)			C(11A)–C(6A)–C(7A)	118.1(5)
Co–N(B)–C(1B)	126.7(3)	(Cα–Cβ–Cβ')			
Co–N(B)–C(4B)	127.3(3)	C(1A)–C(2A)–C(3A)	107.5(3)	C(6B)–C(7B)–C(8B)	121.6(5)
Co–N(C)–C(1C)	126.9(3)	C(4A)–C(3A)–C(2A)	107.4(4)	C(7B)–C(8B)–C(9B)	119.4(6)
Co–N(C)–C(4C)	126.0(3)	C(1B)–C(2B)–C(3B)	107.3(4)	C(8B)–C(9B)–C(10B)	120.3(6)
Co–N(D)–C(1D)	126.6(3)	C(4B)–C(3B)–C(2B)	108.3(4)	C(9B)–C(10B)–C(11B)	120.7(6)
Co–N(D)–C(4D)	127.5(3)	C(1C)–C(2C)–C(3C)	108.0(4)	C(10B)–C(11B)–C(6B)	119.9(5)
		C(4C)–C(3C)–C(2C)	107.4(4)	C(11B)–C(6B)–C(7B)	118.1(4)
(Cα–N–Cα)		C(1D)–C(2D)–C(3D)	106.8(4)		
C(1A)–N(A)–C(4A)	106.0(3)	C(4D)–C(3D)–C(2D)	107.7(4)	C(6C)–C(7C)–C(8C)	120.8(9)
C(1B)–N(B)–C(4B)	106.0(3)			C(7C)–C(8C)–C(9C)	120.4(9)
C(1C)–N(C)–C(4C)	106.4(3)	(Cα–Cm–Cα)		C(8C)–C(9C)–C(10C)	120.7(10)
C(1D)–N(D)–C(4D)	105.8(3)	C(4A)–C(5A)–C(1B)	122.5(4)	C(9C)–C(10C)–C(11C)	120.0(11)
		C(4B)–C(5B)–C(1C)	122.2(4)	V(10C)–C(11C)–C(6C)	120.2(7)
(N–Cα–Cβ)		C(4C)–C(5C)–C(1D)	122.5(4)	C(11C)–C(6C)–C(7C)	118.0(6)
N(A)–C(1A)–C(2A)	109.5(3)	C(4D)–C(5D)–C(1A)	121.6(3)		
N(A)–C(4A)–C(3A)	109.5(3)			C(6D)–C(7D)–C(8D)	120.3(6)
N(B)–C(1B)–C(2B)	109.6(4)	(Cα–Cm–Cp)		C(7D)–C(8D)–C(9D)	120.7(7)
N(B)–C(4B)–C(3B)	108.7(4)	C(4A)–C(5A)–C(6A)	118.4(4)	C(8D)–C(9D)–C(10D)	119.0(6)
N(C)–C(1C)–C(2C)	108.9(4)	C(1B)–C(5A)–C(6A)	119.0(4)	C(9D)–C(10D)–C(11D)	121.7(8)
N(C)–C(4C)–C(3C)	109.2(4)	C(4B)–C(5B)–C(6B)	120.0(4)	C(10D)–C(11D)–C(6D)	119.7(6)
N(D)–C(1D)–C(2D)	110.3(3)	C(1C)–C(5B)–C(6B)	117.6(4)	C(11D)–C(6D)–C(7D)	118.6(4)

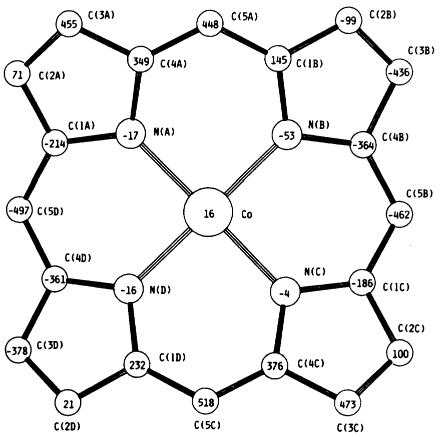

Fig. 4. A diagram of the porphyrinato core showing displacement of atoms, in units of 0.001 Å, from the mean plane at the 24 atom core.

the pyrrole rings. The four pyrrole rings are swiveled about the Co–N(tpp) bond; the dihedral angles between the pyrrole rings and the porphyrinato mean plane are 17.0, 14.9, 17.0, and 16.6°. Similar conformations have been observed for [$Co^{III}Cl(tpp)(py)$], [$Co^{III}(CH_3O)(tpp)(py)$], [$Co^{III}(NO_2)(tpp)(lut)$], and [$Co^{III}(tpp)(H_2O)_2$]$^+$. Recently, by comparing various Co^{III}(tpp) complexes, we found[23] a linear relationship between the ruffling of the porphyrinato core and the Co–N(tpp) distance; the porphyrinato core is ruffled as the Co–N(tpp) distance decreases.

The two oppisite phenyl groups are above, and the two other phenyl groups are below, the porphyrinato core, as is shown in Fig. 2. The dihedral angles between the mean plane of the porphyrinato core and the plane of the four phenyl groups are 59.9(2), 52.5(2), 61.5(2), and 62.2(2)°, their average value being 59°. In general, the angles smaller than 60° are precluded by steric interactions between the pyrrole hydrogen and phenyl hydrogen atoms.[9] The dihedral angle of 52.5° obtained from the present study is the smallest among those of Co^{III}(tpp) complexes thus far reported. Masuda et al.[12] have pointed out a linear relationship between the dihedral angles and the Cm–Cp distance. The average Cm–Cp distance of the present complex is 1.492(3) Å. This distance is the shortest among those reported of the Co^{III}(tpp) complexes; also it is close to that observed for the central C–C bond of the planar biphenyl molecule.[24] Through the short distance of Cm–Cp, the π-conjugate system of the porphyrinato core may be slightly delocalized over the phenyl rings, although the π-conjugate system might be weakened because of its ruffled conformation.[12]

The short C···C intermolecular van der Waal's contacts are shown in Table 4. Two less than 3.55 Å are observed between phenyl-carbon and pyrrole-carbon atoms. The shortest phenyl carbon–phenyl carbon distance (3.322(8) Å) is between C(7B) and $C(7B)^{V}$ atoms; the shortest pyrrole carbon–pyrrole carbon distance (3.411(6) Å) is between C(3A) and $C(3B)^{IV}$ atoms.

Table 4. The Short Intermolecular van der Waal's Contacts

Symmetry Code:
I $1+x, y, z$ II $-1+x, y, z$
III $1+x, y, 1+z$ IV $x, -y+1/2, z-1/2$
V $-x, -y, -z$ VI $1-x, -y, -z$
VII $-x, y+1/2, -z+1/2$

Type	l/Å
Pyrrole carbon ··· phenyl carbon	
C(2A) ··· $C(9B)^{VII}$	3.550(9)
C(2D) ··· $C(9A)^{I}$	3.549(12)
C(3A) ··· $C(9B)^{VII}$	3.732(8)
C(3D) ··· $C(9A)^{I}$	3.650(11)
C(2D) ··· $C(10A)^{III}$	3.696(9)
C(2B) ··· $C(9C)^{II}$	3.626(11)
C(1C) ··· $C(8B)^{V}$	3.665(7)
C(2C) ··· $C(9C)^{VI}$	3.643(10)
Pyrrole carbon ··· pyrrole carbon	
C(3A) ··· $C(3B)^{IV}$	3.411(6)
C(3A) ··· $C(4B)^{IV}$	3.539(6)
Phenyl carbon ··· phenyl carbon	
C(7B) ··· $C(7B)^{V}$	3.322(8)
C(11C)··· $C(11D)^{IV}$	3.568(8)

The porphyrinato core is almost vertical to the bc plane, as seen from the crystal structure shown in Fig. 2. The Co–Cl bond makes an angle of 16.6° from the c axis. The porphyrin molecule is transferred by the c glide operation and is stacked along the c axis. The hydrogen bond between an axial water molecule of a [$Co^{III}Cl(tpp)(H_2O)$] molecule and an axial chlorine atom of the neighbor [$Co^{III}Cl(tpp)(H_2O)$] molecule is zigzagged along the c axis direction. The hydrogen-bond distance, O–H···Cl, is 3.070(3) Å.

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