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CRYSTAL AND MOLECULAR STRUCTURE OF FORMYLMETHYL(TETRAPHENYLPORPHINATO)COBALT(III)

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Summary

The crystal structure of formylmethyl(tetraphenylporphinato)cobalt(III) has been determined by the X-ray method. The complex crystallizes in the monoclinic space group *Pc* with two molecules in a unit cell of dimensions; *a* 13.132(9), *b* 12.747(5), *c* 13.443(8) Å, and β 129.83(4)°. The cobalt(III) ion is coordinated by the four porphinato nitrogen atoms and one carbon atom of the formylmethyl group, and is displaced by 0.14 Å from the mean plane of the four porphinato nitrogen atoms towards the axial formylmethyl ligand. A formylmethyl group is σ-bonded to the cobalt ion with the bond parameters: Co–C 1.976(7), C–C 1.426(14), C=O 1.216(10) Å, and Co–C–C 109.4(7)°, and the average Co–N bond distance is 1.969(29) Å. The C–C–Co–N torsion angle between the formylmethyl group and the porphyrin ring is 13.0°. The Co–C bond formation was interpreted by the attractive force between the Co d_{π}-orbital and the carbonyl carbon p_{π}-orbital of the formylmethyl group.

It is well known that the active site of vitamin B_{12} is the cobalt complex of the corrin ligand and that its coenzyme form and related alkylcobalamin are the novel organometallic compounds found in nature. Since the Co–C σ-bond in the vitamin B_{12} crystal was discovered by Hodgkin in 1961 [1], a large number of model compounds have been synthesized to elucidate the physico-chemical properties of the Co–C bond in square-planar macrocyclic systems [2], and the porphyrincobalt complexes [3] in them have particularly received attention because of the similarity of the tetrapyrrole macrocycles in porphyrin and corrin. The X-ray structures of porphyrincobalt(III) complexes including the Co–C σ-bond, however, have never been reported hitherto. Recently, Sugimoto et al. synthesized the title complex, formylmethyl(tetraphenylporphinato)cobalt(III), [Co^{III}(tpp)CH_2CHO], through the

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study on the electrophilic reaction of porphyrincobalt(III) complexes having weak counter-anions towards electron-rich olefins [4], and they obtained the single crystals suitable for the X-ray work. In this paper, the X-ray structure of this complex is described, and the coordination mode of the formylmethyl group bonded to the cobalt(III) ion is discussed in relation to a transition state in the complex formation.

Experimental

$[Co^{III}(tpp)CH_2CHO]$ was prepared by treatment of $[Co^{III}(tpp)CH_2CH(OC_2H_5)]$ with silica gel in CH_2Cl_2 [4]. Brown-red, needle-like single crystals were obtained by recrystallization from benzene solutions. Preliminary X-ray photographic examination established a monoclinic unit cell containing two chemical units of $[Co^{III}(tpp)CH_2CHO]$. The systematic absence of $h0l$ for $l = 2n + 1$ led to two possible space groups: $P2/c$ or Pc. The intensity statistics calculated after data collection indicated that the non-centrosymmetric space group Pc was correct. The crystal data are listed in Table 1.

The crystal with dimensions of $0.3 \times 0.3 \times 0.4$ mm^3 was mounted on a Rigaku AFC-5 diffractometer with graphite monochromatized Cu-K_α radiation ($\bar{\lambda}$ = 1.54178 Å). The intensity data of 2835 reflections in the range $2\theta < 120°$ were collected in the ω–2θ scan mode with a scan rate of 4° min^{-1}. During the course of data collection, three reflections were monitored every 56 reflections. The intensity data were converted to F_0 data in the usual manner. An absorption correction was applied in the cylindrical crystal approximation ($\mu R = 0.7$). The standard deviations, $\sigma(F_0)$, were estimated by counting statistics. A total number of 2531 independent reflections with $F_0 > 3\sigma(F_0)$ were retained as observed, and used in solving and refining the structure.

The structure was partially solved by the direct method with MULTAN [5]. The complete structure was elucidated through iterative applications of a Fourier synthesis method, and was refined by a block-diagonal least-squares method. Several cycles of the refinement including the anisotropic thermal parameters were carried out with the weighting scheme of $w^{-1} = (\sigma^2(F_0) + (0.023F_0)^2)$. Atomic scattering factors [6a]

(Continued on p. 389)

TABLE 1

CRYSTAL DATA

Formula	$CoC_{46}H_{31}N_4O$
Mol. wt	714 71
Crystal system	monoclinic
Space group	Pc
a	13 132(9) Å
b	12.747(5) Å
c	13.443(8) Å
β	129.83(4) °
V	1728 0(19) Å^3
Z	2
D_c	1.373 g cm^{-1}
D_x	1.37 g cm^{-1}
$F(000)$	734
μ(Cu-K_α)	43.573 cm^{-1}

TABLE 2

FINAL ATOMIC FRACTIONAL COORDINATES OF THE NON-HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x/a	y/b	z/c	B_{eq}
Co	0.0	0.2539(1)	0.0	2.92(4)
N(1)	0.0085(5)	0.1154(5)	0.0746(5)	3.39(22)
N(2)	−0.1179(5)	0.3028(4)	0.0362(6)	3.29(19)
N(3)	−0.0005(6)	0.3974(4)	−0.0490(6)	3.52(24)
N(4)	0.1367(5)	0.2113(4)	−0.0072(6)	3.04(20)
C(1)	0.0792(8)	0.0292(6)	0.0908(7)	4.11(31)
C(2)	0.0579(7)	−0.0599(5)	0.1382(8)	4.09(29)
C(3)	−0.0374(8)	−0.0304(6)	0.1449(9)	5.15(35)
C(4)	−0.0639(7)	0.0791(5)	0.1125(7)	3.58(27)
C(5)	−0.1523(7)	0.1345(5)	0.1083(8)	3.82(27)
C(6)	−0.1765(7)	0.2410(5)	0.0794(7)	3.47(26)
C(7)	−0.2714(7)	0.3018(7)	0.0716(8)	4.52(34)
C(8)	−0.2762(8)	0.3964(6)	0.0265(8)	4.24(31)
C(9)	−0.1864(6)	0.3991(5)	0.0044(7)	3.29(26)
C(10)	−0.1636(7)	0.4847(5)	−0.0411(7)	3.79(27)
C(11)	−0.0803(6)	0.4811(6)	−0.0672(7)	3.73(26)
C(12)	−0.0537(9)	0.5698(6)	−0.1180(9)	4.89(32)
C(13)	0.0297(7)	0.5366(6)	−0.1362(7)	3.97(30)
C(14)	0.0656(6)	0.4326(6)	−0.0886(7)	3.53(25)
C(15)	0.1572(6)	0.3719(6)	−0.0904(6)	3.47(28)
C(16)	0.1897(7)	0.2709(6)	−0.0475(7)	3.42(26)
C(17)	0.2813(7)	0.2095(5)	−0.0495(7)	3.47(25)
C(18)	0.2832(7)	0.1133(6)	−0.0085(8)	4.18(31)
C(19)	0.1904(8)	0.1143(6)	0.0175(8)	4.20(29)
C(20)	0.1715(6)	0.0290(5)	0.0688(7)	3.37(26)
C(21)	−0.2288(7)	0.0812(5)	0.1434(8)	3.80(27)
C(22)	−0.3328(7)	0.0210(6)	0.0595(8)	4.31(31)
C(23)	−0.4085(9)	−0.0295(8)	0.0885(11)	6.49(45)
C(24)	−0.3751(9)	−0.0077(8)	0.2036(10)	5.89(41)
C(25)	−0.2667(9)	0.0512(6)	0.2942(9)	4.93(32)
C(26)	−0.1944(10)	0.0944(6)	0.2646(9)	5.20(37)
C(27)	−0.2533(7)	0.5769(6)	−0.0834(8)	4.51(31)
C(28)	−0.2321(8)	0.6406(6)	0.0072(8)	4.88(35)
C(29)	−0.3206(12)	0.7327(7)	−0.0331(12)	6.79(47)
C(30)	−0.4119(9)	0.7528(7)	−0.1534(11)	6.52(47)
C(31)	−0.4284(9)	0.6859(8)	−0.2482(10)	6.41(41)
C(32)	−0.3431(8)	0.6031(7)	−0.2075(9)	5.31(37)
C(33)	0.2280(7)	0.4260(6)	−0.1281(7)	3.98(27)
C(34)	0.3395(8)	0.4922(7)	−0.0321(9)	5.26(35)
C(35)	0.4092(9)	0.5353(7)	−0.0660(9)	5.53(39)
C(36)	0.3720(9)	0.5204(8)	−0.1897(10)	5.91(41)
C(37)	0.2681(9)	0.4591(9)	−0.2760(9)	6.70(45)
C(38)	0.1948(8)	0.4062(8)	−0.2470(8)	5.13(35)
C(39)	0.2423(7)	−0.0731(5)	0.0915(8)	3.81(27)
C(40)	0.2220(10)	−0.1297(7)	−0.0117(11)	6.56(49)
C(41)	0.3028(11)	−0.2182(7)	0.0305(13)	7.45(46)
C(42)	0.4002(11)	−0.2481(7)	0.1634(14)	7.78(55)
C(43)	0.4188(10)	−0.1920(7)	0.2532(11)	6.58(49)
C(44)	0.3485(8)	−0.1018(6)	0.2238(9)	5.33(35)
C(45)	−0.1434(7)	0.2156(6)	−0.1831(7)	3.91(27)
C(46)	−0.2658(8)	0.2579(6)	−0.2249(8)	4.78(29)
O(1)	−0.3137(7)	0.3379(5)	−0.2885(7)	7.15(30)

TABLE 3

BOND DISTANCES (Å) AND BOND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Bond distances					
Co–N(1)	1.998(7)	C(16)–C(17)	1.450(14)	C(24)–C(25)	1 361(11)
Co–N(2)	1.997(9)	C(18)–C(19)	1.467(18)	C(25)–C(26)	1.359(21)
Co–N(3)	1.943(6)	C(2)–C(3)	1.364(17)	C(26)–C(21)	1.394(17)
Co–N(4)	1.936(8)	C(7)–C(8)	1.333(13)	C(27)–C(28)	1.336(15)
Co–C(45)	1.976(7)	C(12)–C(13)	1.335(18)	C(28)–C(29)	1.489(14)
C(45)–C(46)	1.426(14)	C(17)–C(18)	1.338(11)	C(29)–C(30)	1.279(15)
C(46)–O(1)	1.216(10)	C(1)–C(20)	1.420(16)	C(30)–C(31)	1.430(19)
N(1)–C(1)	1.363(11)	C(4)–C(5)	1 329(14)	C(31)–C(32)	1.372(14)
N(1)–C(4)	1.414(14)	C(5)–C(6)	1.392(9)	C(32)–C(27)	1.329(12)
N(2)–C(6)	1.457(13)	C(9)–C(10)	1.374(12)	C(33)–C(34)	1.449(10)
N(2)–C(9)	1.416(9)	C(10)–C(11)	1.347(16)	C(34)–C(35)	1.372(20)
N(3)–C(11)	1.403(11)	C(14)–C(15)	1.443(13)	C(35)–C(36)	1.414(19)
N(3)–C(14)	1.353(14)	C(15)–C(16)	1.363(11)	C(36)–C(37)	1.338(12)
N(4)–C(16)	1.356(14)	C(19)–C(20)	1.392(13)	C(37)–C(38)	1.419(19)
N(4)–C(19)	1.355(10)	C(5)–C(21)	1.517(16)	C(38)–C(33)	1 384(15)
C(1)–C(2)	1.415(13)	C(10)–C(27)	1.495(11)	C(39)–C(40)	1.429(18)
C(3)–C(4)	1.437(10)	C(15)–C(33)	1.483(15)	C(40)–C(41)	1.396(14)
C(6)–C(7)	1.413(14)	C(20)–C(39)	1.513(10)	C(41)–C(42)	1.430(18)
C(8)–C(9)	1.389(17)	C(21)–C(22)	1.324(9)	C(42)–C(43)	1.285(22)
C(11)–C(12)	1.474(15)	C(22)–C(23)	1.432(19)	C(43)–C(44)	1.365(13)
C(13)–C(14)	1.415(11)	C(23)–C(24)	1.340(20)	C(44)–C(39)	1.437(11)
(b) Bond angles					
N(1)–Co–N(2)	87.5(3)	C(5)–C(6)–C(7)	126.1(10)		
N(2)–Co–N(3)	87.4(3)	C(8)–C(9)–C(10)	124.9(7)		
N(3)–Co–N(4)	92.8(3)	C(10)–C(11)–C(12)	124.6(8)		
N(4)–Co–N(1)	91.2(3)	C(13)–C(14)–C(15)	122.3(9)		
N(1)–Co–N(3)	171.6(3)	C(15)–C(16)–C(17)	122.7(10)		
N(2)–Co–N(4)	171 1(2)	C(18)–C(19)–C(20)	123.4(8)		
N(1)–Co–C(45)	96.3(3)	C(4)–C(5)–C(6)	124.6(10)		
N(2)–Co–C(45)	96.4(4)	C(9)–C(10)–C(11)	122.3(7)		
N(3)–Co–C(45)	91.0(3)	C(14)–C(15)–C(16)	122.5(9)		
N(4)–Co–C(45)	92.5(4)	C(19)–C(20)–C(1)	123.3(7)		
Co–C(45)–C(46)	109.4(7)	C(4)–C(5)–C(21)	118.9(7)		
C(45)–C(46)–O(1)	122.6(12)	C(6)–C(5)–C(21)	116.5(9)		
Co–N(1)–C(1)	127.3(7)	C(9)–C(10)–C(27)	116 8(9)		
Co–N(1)–C(4)	129.5(5)	C(11)–C(10)–C(27)	120.1(8)		
Co–N(2)–C(6)	128.2(5)	C(14)–C(15)–C(33)	117.9(7)		
Co–N(2)–C(9)	129.7(7)	C(16)–C(15)–C(33)	119.3(8)		
Co–N(3)–C(11)	128.0(7)	C(19)–C(20)–C(39)	119.4(10)		
Co–N(3)–C(14)	106.0(7)	C(1)–C(20)–C(39)	117.1(8)		
Co–N(4)–C(16)	126.3(5)	C(5)–C(21)–C(22)	121.5(10)		
Co–N(4)–C(19)	126.7(7)	C(5)–C(21)–C(26)	121.7(7)		
C(1)–N(1)–C(4)	103.0(7)	C(10)–C(27)–C(28)	118.5(7)		
C(6)–N(2)–C(9)	101.2(7)	C(10)–C(27)–C(32)	121.7(10)		
C(11)–N(3)–C(14)	106.0(7)	C(15)–C(33)–C(34)	117.6(9)		
C(16)–N(4)–C(19)	106.8(9)	C(15)–C(33)–C(38)	120.5(7)		
N(1)–C(1)–C(2)	114.1(10)	C(20)–C(39)–C(40)	122.0(7)		
N(1)–C(4)–C(3)	109.8(9)	C(20)–C(39)–C(44)	116.9(8)		
N(2)–C(6)–C(7)	109.9(6)	C(22)–C(21)–C(26)	116 8(11)		
N(2)–C(9)–C(8)	112 1(7)	C(28)–C(27)–C(32)	119 4(8)		
N(3)–C(11)–C(12)	107.0(9)	C(34)–C(33)–C(38)	121.7(11)		
N(3)–C(14)–C(13)	112.1(8)	C(40)–C(39)–C(44)	120.2(8)		

TABLE 3 (continued)

N(4)–C(16)–C(17)	110.4(7)	C(21)–C(22)–C(23)	123.1(11)
N(4)–C(19)–C(18)	109.3(8)	C(22)–C(23)–C(24)	116.8(9)
N(1)–C(1)–C(20)	123.6(8)	C(23)–C(24)–C(25)	121.9(14)
N(1)–C(4)–C(5)	125.6(7)	C(24)–C(25)–C(26)	119.2(12)
N(2)–C(6)–C(5)	123.7(9)	C(25)–C(26)–C(21)	121.9(8)
N(2)–C(9)–C(10)	123.0(9)	C(27)–C(28)–C(29)	119.3(8)
N(3)–C(11)–C(10)	128.4(8)	C(28)–C(29)–C(30)	120.0(13)
N(3)–C(14)–C(15)	125.5(7)	C(29)–C(30)–C(31)	119.5(10)
N(4)–C(16)–C(15)	126.6(9)	C(30)–C(31)–C(32)	119.0(9)
N(4)–C(19)–C(20)	127.2(11)	C(31)–C(32)–C(27)	122.4(11)
C(1)–C(2)–C(3)	105.2(7)	C(33)–C(34)–C(35)	116.5(10)
C(2)–C(3)–C(4)	107.6(10)	C(34)–C(35)–C(36)	122.4(8)
C(6)–C(7)–C(8)	108.2(11)	C(35)–C(36)–C(37)	119.4(13)
C(7)–C(8)–C(9)	108.7(9)	C(36)–C(37)–C(38)	122.3(12)
C(11)–C(12)–C(13)	107.9(7)	C(37)–C(38)–C(33)	117.6(8)
C(12)–C(13)–C(14)	106.8(9)	C(39)–C(40)–C(41)	113.1(10)
C(16)–C(17)–C(18)	106.5(10)	C(40)–C(41)–C(42)	124.2(14)
C(17)–C(18)–C(19)	106.9(8)	C(41)–C(42)–C(43)	120.3(10)
C(20)–C(1)–C(2)	122.3(8)	C(42)–C(43)–C(44)	120.7(10)
C(3)–C(4)–C(5)	124.4(10)	C(43)–C(44)–C(39)	120.9(10)

and anomalous dispersion terms [6b] were taken from the International Tables for X-Ray Crystallography, Vol. IV. Hydrogen atoms were included as a fixed contribution in the last cycle; their positions were assumed to be in accordance with the idealized geometry (C–H 1.00 Å), and their temperature factors were assumed to be isotropic (B 8.00 Å). The final R and R_w values were 0.057 and 0.072. The final difference Fourier maps showed no peak greater than 0.4 e/Å^3; most of the largest peaks were around the cobalt atom. All computations were performed on a FACOM M-382 computer at the Data Processing Center of Kyoto University by using the program system KPAX. The positional parameters of the non-hydrogen atoms are given in Table 2 [7,8].

Results and discussion

The crystal structure of the [Co^{III}(tpp)CH_2CHO] complex consists of neutral molecules in which the trivalent cobalt cation is penta-coordinated by the four nitrogen atoms of the divalent tpp anion and one carbon atom of the univalent formylmethyl anion (Fig. 1).

The numbering of the atoms used in this paper is given in Fig. 1. Individual bond distances and bond angles are listed in Table 3. The values agree well with those of the corresponding bonds in the other cobalt porphyrins [9] within experimental error. The porphinato core is planar within 0.10 Å, as expected from the usual porphyrincobalt(III) [9].

Figure 2 presents a perspective diagram of the environment of the cobalt(III) ion. The cobalt ion is displaced by 0.14 Å from the plane defined by the four porphinato nitrogen atoms towards the axial ligand. The small displacement of the Co atom above the basal plane can be explained in terms of the participation of the cobalt electrons in the π-orbitals of the conjugate system of the porphyrin ring. A

square-planar pyramid complex represents perhaps the best condition for efficient π-back-bonding as compared with a distorted pyramid complex. The average Co–N bond distance, 1.969(29) Å, is normal for the trivalent cobalt ion [9], while the Co–C(45) bond distance, 1.976(7) Å, is shorter than the sum of the covalent radii of cobalt(III) (1.28 Å) and of the sp^3-hybridized carbon (0.77 Å). The σ-bond distances observed hitherto range from 1.89 to 1.97 Å [10] for Co–C(sp^2) and from 1.99 to 2.10 Å [11] for Co–C(sp^3). The Co–C(45) bond distance exists in the intermediate range in the sp^2 and sp^3 cases. The Co–C(45)–C(46) bond angle is 109.4(7)°. The geometry around the cobalt(III) atom seems to be due to a compromise between the necessity of planarity for optimum π-bonding and the best σ-overlap of the Co–C bond.

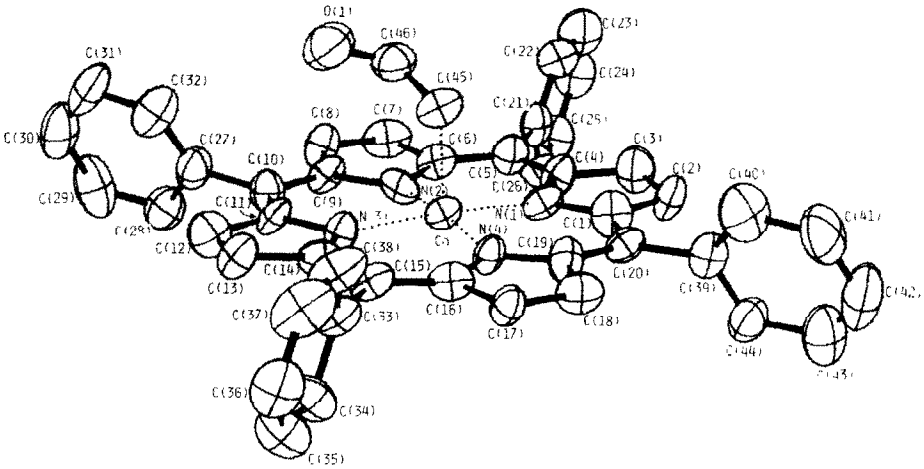

Fig. 1. Computer-drawn model in perspective of the [Co^{III}(tpp)CH_2CHO] complex. The vibrational ellipsoids are drawn at the 50% probability level. The labelling scheme used for the atoms in the complex is also shown.

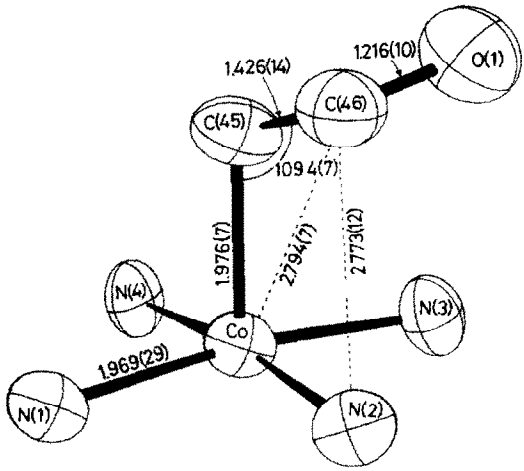

Fig. 2. The square-pyramidal coordination group in the [Co^{III}(tpp)CH_2CHO] complex.

The C(45)–C(46) and C(46)–O(1) bond distances in the formylmethyl group are 1.426(14) and 1.216(10) Å, respectively. The C(45)–C(46)–O(1) valence angle is 122.6(12)°. The C(45)–C(46) bond distance is significantly shorter than the normal C–C single bond distance (1.51 Å) [12] in C–C=O type compounds. The short C–C bond distance implies its partial double-bond character. The C(45)–C(46) bond rotates around the Co–C(45) bond only by 13.0° from an ideal eclipsed form for the Co–N(2) bond (Fig. 3(a)). As shown in Fig. 3(b), the Van der Waals energy calculated by changing the rotation angle, ϕ, around Co–C(45) has a minimum at an angle of 45°, which is usually expected. The small rotation angle observed here suggests the possibility that the attractive force acts between the Co d_{π}-orbital (d_{xz}

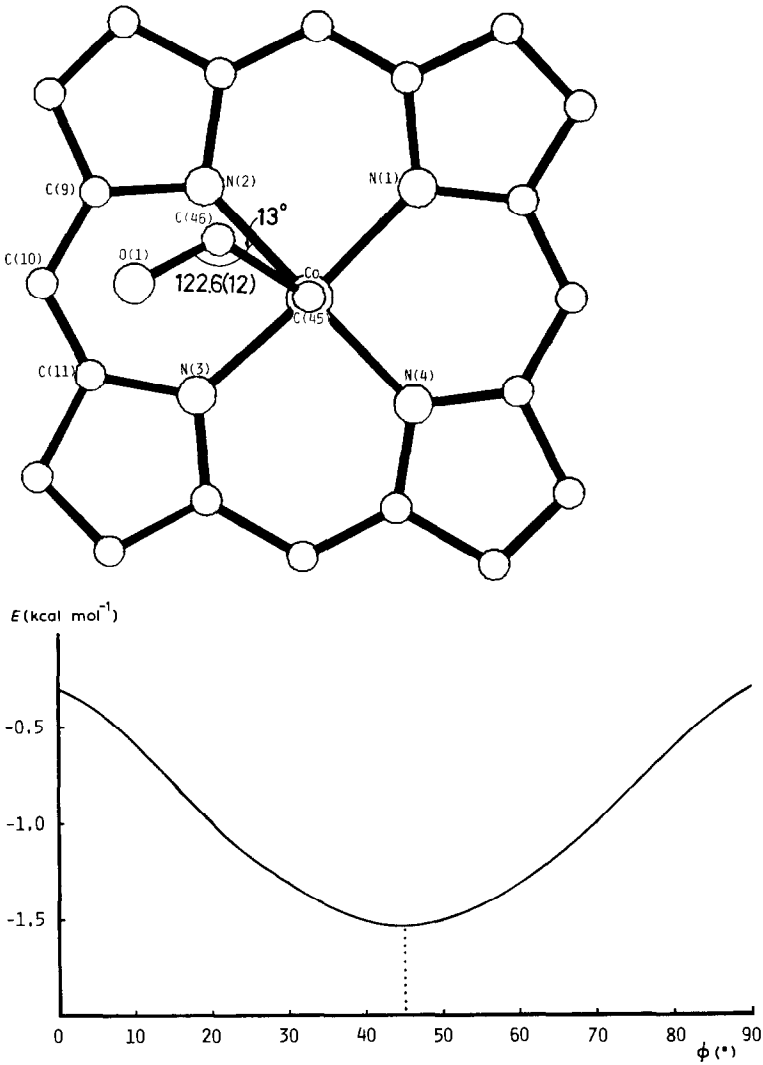

Fig. 3. (a) Projection of the complex to the mean plane of the four nitrogen atoms of tetraphenylporphyrin. (b) The variation of Van der Waals energy, E, with the rotation angle, ϕ, around Co–C(45), $[Co^{III}(tpp)CH_2CHO]$ being fixed. The axial ligand is rotated counter-clockwise from the position in which the dihedral angle of N(2)–Co–C(45)–C(46) is zero.

or d_{yz}) and the C(46) p_{π}-orbital. The C(46) atom must approach the N(2) atom (2.773(12) Å) on account of this attractive force against the interatomic Van der Waals repulsion between them. Sugimoto et al. suggested a π-complex, base-off penta-coordinated and cationic complex, as an intermediate complex [4] in the electrophilic reaction between $Co(tpp)(H_2O)_2ClO_4$ and $CH_2{=}CH{-}O{-}CH_2CH_3$. The established structure seems to support this proposal.

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