Five-co-ordinate Cobalt(III): Crystal and Molecular Structure of Corrole-(triphenylphosphine)cobalt(III) †

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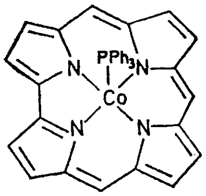
An X-ray structural analysis of the title compound (I) has converged at R 0.080 based on 1 332 reflections measured by diffractometer. The cobalt atom has square pyramidal co-ordination and is 0.38 Å above the plane of the corrole ligand which is disordered in the crystal. There is an intermolecular contact of 3.0 Å from a hydrogen atom of a phenyl ring to the vacant sixth co-ordination site of the cobalt. The structure was determined by the heavy-atom method. Crystals are monoclinic, space group $P2_1/n$, with $Z = 4$, in a cell of dimensions: $a = 21.432(9)$, $b = 13.513(6)$, $c = 10.005(5)$ Å, $\beta = 95.20(2)°$.

In general, transition-metal complexes where the metal atom has a d^6 configuration tend to be octahedrally co-ordinated, and in the case of Co^{III} this is almost always true. However, certain five-co-ordinate complexes of Co^{III} are known [1] and in one case [2] a crystal structure determination has been carried out. It has been shown by Johnson *et al.*[3] that the preparation of a corrole ring by a cyclisation reaction in the presence of cobalt(II) acetate and triphenylphosphine results in a product characterised by them as a five-co-ordinate corrole(triphenylphosphine)cobalt(III) complex (I). In order to confirm this characterisation and to provide further structural information on five co-ordinate cobalt(III), the crystal structure of this complex has been determined.



(I)

EXPERIMENTAL

Crystal Data.—$C_{37}H_{26}CoN_4P$, $M = 616.6$, Monoclinic, $a = 21.432(9)$, $b = 13.513(6)$, $c = 10.005(5)$ Å, $\beta = 95.20(2)°$, $U = 2\,885.6$ Å^3, $Z = 4$, $D_c = 1.42$ g cm^{-3}, $F(000) = 1\,272$. Mo-K_α radiation, $\lambda(\text{Mo-}K_{\alpha 1}) = 0.709\,26$ Å; $\mu(\text{Mo-}K_\alpha) = 7.1$ cm^{-1}. Space group $P2_1/n$ (No. 14) from systematic absences of $h0l$ for $h + l$ odd, and $0k0$ for k odd.

A crystal of dimensions *ca.* 0.3 × 0.2 × 0.2 mm was used for data collection. Preliminary cell dimensions were derived from Weissenberg and precession films. The crystal was then transferred to a Hilger and Watts Y 290 four-circle diffractometer and accurate cell dimensions derived by least-squares treatment of 2θ values for 12 reflections. Intensity data for the unique quadrant with $\theta < 20°$ were measured by the ω–2θ step scan technique with Mo-K_α radiation (graphite-crystal monochromator). The peak scan was carried out in 100 steps of 1 s with 50 s background counts at either end of the scan. Three standard reflections remeasured after every 100 reflections showed no significant variation with time. Data were corrected for Lorentz and polarisation effects but not for absorption. Of a total of 1 590 independent reflections, those having $I < 3\sigma(I)$ were considered unobserved, leaving 1 332 independent observed reflections which were used in the structure analysis.

The positions of the Co and P atoms were derived from a Patterson synthesis and subsequent difference-Fourier maps were interpreted as showing atoms C(1)—C(19) and C(21)—C(38), corresponding to a complex of a corrole ligand as expected. Full-matrix least-squares refinement of this model with the Co and P atoms anisotropic converged at R 0.094. However, the geometry of the model showed some rather unlikely dimensions, particularly a very long C(1)–C(19) bond, and a difference-Fourier map showed a peak of height 1.5 eÅ^{-3} at a position between C(1) and C(19) and several other peaks at heights of *ca.* 1 eÅ^{-3}. It was, therefore, assumed that the corrole ligand had a two-fold disorder across the line C(5) · · · C(15) and a new atom position C(20) was included. Although this would not give exact overlap of the other atoms from the two orientations, none of the peaks in an observed Fourier map could be resolved into two positions and no attempt was made to allow for this in the model. At this point, the weighting scheme was changed from unit weights to empirical weights (w) defined as $w = 1/[1 + (F_o - 50/80)^2]$. Hydrogen atoms for the phenyl rings were included at calculated positions with temperature factors of B 6.5 Å^2 and were not refined. No attempt was made to include the hydrogen atoms of the disordered corrole ring. Continued refinement allowing the occupancy of sites C(10) and C(20) to vary converged at R 0.080 with occupancies of 0.8 for C(10) and 0.7 for C(20). This might indicate a higher degree of disorder about a four-fold axis along the line Co–P and the refinement was continued with all atoms given full occupancies in the hope that the relative temperature factors of C(5), C(10), C(15), and C(20) might help to resolve the question. At convergence (R 0.080) the positions of all atom sites showed no significant change from the previous refinement and are listed in Table 1. A final difference-Fourier synthesis had a peak of 0.85 eÅ^{-3} at a position (0.263,0.395,0.410) and one of 0.66 eÅ^{-3} at (0.283,0.350, 0.500) both of which are near C(17) and C(18); all other peaks were <0.5 eÅ^{-3}. The maximum shift-to-error in the least-squares refinement was 0.1 and σ for an observation of unit weight was 1.8.

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† No reprints available.

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TABLE 1

Final atom positional ($\times 10^4$) and thermal ($\times 10^3$) parameters, with estimated standard deviations in parentheses

	x	y	z	U_{iso}/Å^2
Co	1 644(1)	2 028(2)	1 484(2)	*
P	0 921(2)	3 162(3)	0 952(5)	*
N(1)	1 208(6)	1 238(10)	2 566(14)	45(4)
N(2)	1 487(7)	1 112(11)	0 067(14)	46(4)
N(3)	2 301(7)	2 568(10)	0 578(14)	48(4)
N(4)	1 980(7)	2 682(11)	3 040(16)	57(4)
C(1)	1 163(9)	1 393(15)	3 922(21)	58(4)
C(2)	0 747(11)	0 697(17)	4 456(24)	83(7)
C(3)	0 529(9)	0 157(15)	3 460(21)	65(6)
C(4)	0 792(9)	0 425(15)	2 212(21)	64(6)
C(5)	0 751(10)	0 074(16)	0 984(23)	68(6)
C(6)	1 052(10)	0 346(15)	−0 031(22)	63(6)
C(7)	1 072(11)	−0 122(18)	−1 347(24)	87(7)
C(8)	1 485(11)	0 378(18)	−1 929(24)	84(7)
C(9)	1 769(11)	1 128(18)	−1 147(23)	74(7)
C(10)	2 177(14)	1 721(23)	−1 439(30)	115(10)
C(11)	2 422(10)	2 342(16)	−0 704(23)	71(6)
C(12)	2 943(10)	3 059(19)	−0 993(23)	85(7)
C(13)	3 073(20)	3 553(20)	−0 022(27)	98(8)
C(14)	2 707(10)	3 295(17)	1 104(23)	77(7)
C(15)	2 754(11)	3 650(19)	2 282(28)	93(8)
C(16)	2 462(12)	3 425(18)	3 242(26)	88(7)
C(17)	2 403(12)	3 659(19)	4 695(26)	91(8)
C(18)	2 026(16)	3 154(26)	5 251(34)	141(11)
C(19)	1 767(13)	2 586(20)	4 203(30)	101(9)
C(20)	1 447(14)	2 055(27)	4 645(31)	128(10)
C(21)	0 382(8)	3 440(13)	2 193(17)	41(5)
C(22)	0 223(8)	4 423(13)	2 550(18)	49(5)
C(23)	−0 233(9)	4 545(15)	3 410(21)	66(6)
C(24)	−0 550(9)	3 763(16)	3 904(21)	69(6)
C(25)	−0 412(9)	2 806(15)	3 571(19)	59(5)
C(26)	0 056(8)	2 666(12)	2 716(17)	41(5)
C(27)	1 283(8)	4 328(14)	0 604(18)	50(5)
C(28)	1 308(10)	4 672(16)	−0 677(21)	67(6)
C(29)	1 651(12)	5 570(19)	−0 863(26)	97(8)
C(30)	1 937(12)	6 061(19)	0 213(27)	93(8)
C(31)	1 913(10)	5 732(16)	1 480(23)	76(7)
C(32)	1 572(9)	4 863(14)	1 728(19)	56(6)
C(33)	0 386(7)	2 884(14)	−0 508(16)	41(4)
C(34)	−0 262(8)	2 883(14)	−0 459(17)	45(5)
C(35)	−0 647(9)	2 675(14)	−1 631(19)	56(5)
C(36)	−0 399(9)	2 520(14)	−2 809(20)	64(6)
C(37)	0 231(9)	2 517(14)	−2 890(20)	62(6)
C(38)	0 626(8)	2 677(13)	−1 736(19)	52(5)

* Anisotropic temperature factors* (Å^2 × 10^4), in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	302(13)	401(14)	486(15)	008(14)	−024(10)	057(16)
P	311(27)	323(31)	456(31)	−020(23)	−002(23)	−004(25)

TABLE 2

Proposed hydrogen atom co-ordinates ($\times 10^3$)

	x	y	z
H(22)	047	503	217
H(23)	−034	528	372
H(24)	−092	391	455
H(25)	−066	218	398
H(26)	017	193	246
H(28)	109	426	−151
H(29)	142	593	−173
H(30)	218	675	003
H(31)	217	611	227
H(32)	154	462	275
H(34)	−046	302	047
H(35)	−115	264	−160
H(36)	−070	240	−370
H(37)	043	240	−386
H(38)	112	262	−176

Scattering factors for neutral atoms and dispersion corrections for Co and P were taken from ref. 4. Final observed and calculated structure factors are deposited as Supplementary Publication No. SUP 21736 (11 pp. 1 microfiche).* The structure solution and refinement were carried out using the '*X*-Ray' program system[5] on an ICL 1906A computer at the Atlas Computer Laboratory. Hydrogen atom positions are listed in Table 2, bond distances and angles in Table 3.

TABLE 3

Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Bonds			
Co–P	2.210(5)	Phenyl rings C–C	
P–C(21)	1.81(2)	Mean	1.39
P–C(27)	1.80(2)	Min.	1.35(4)
P–C(33)	1.81(2)	Max.	1.43(4)
(*b*) Angles			
P–Co–N(1)	99.3(5)	Phenyl rings C–C–C	
P–Co–N(2)	101.6(5)	Mean	120
P–Co–N(3)	98.8(5)	Min.	117(2)
P–Co–N(4)	94.7(5)	Max.	123(2)

DISCUSSION

The corrole ring can be described as a porphyrin framework with one of the methine groups bridging the C_4N rings missing. In this case, the temperature factors of the various atom sites indicate that the structure is disordered so that the missing methine group is approximately equally at the sites C(10) and C(20) and also perhaps to a small extent at positions C(5) and C(15). Both the drawing of the molecule (Figure 1) showing the atom numbering scheme and the packing diagram (Figure 2) show all the atom sites. Figure 3 shows the apparent distances and angles between the atom sites in the plane of the macrocycle together with our suggestion as to the principal nature of the disorder. The atom sites are obviously averaged over quite widely different positions in some cases and the distances and angles are quoted only to support our interpretation of the disorder. The nature of the disordering precludes any detailed discussion of the geometry of the corrole ligand but the observed arrangement is compatible with that observed in 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole[6] allowing for averaging over positions related by the disorder. The cobalt atom can be seen to be formally five-coordinate. The carbon framework of the corrole ligand is nearly planar (Table 4) with the nitrogen atoms displaced above the ring by *ca.* 0.1 Å and the cobalt atom displaced 0.38 Å above the plane as is usually observed for square-pyramidal complexes of first row transition metals.[1,7]

The mean Co–N distance (1.87 Å) is similar to those in cobalt–corrin complexes[8] and slightly shorter than those

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

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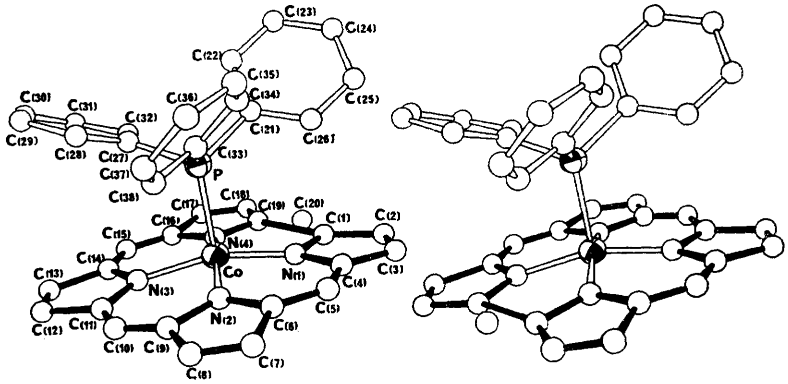

FIGURE 1 A stereopair of the molecule showing all atom sites. The two major orientations of the disordered corrole ring are indicated by the shaded bonds

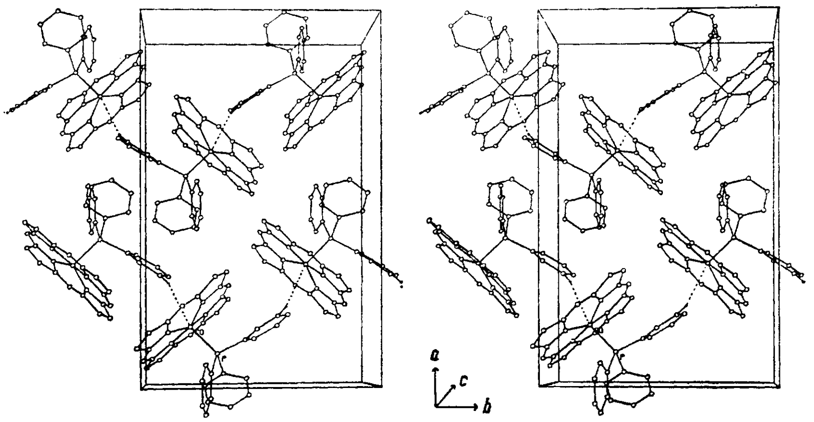

FIGURE 2 A stereopair of the crystal packing showing all atom sites. The dotted line indicates a 3.0 Å intermolecular contact of the cobalt atom with an adjacent phenyl hydrogen atom

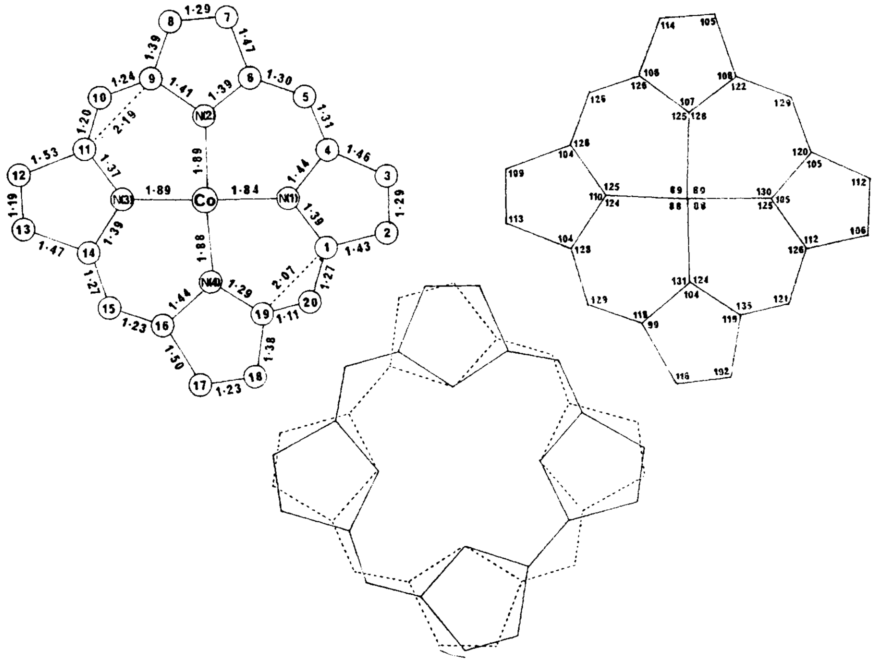

FIGURE 3 Distances (Å) and angles (°) for averaged atom sites in the plane of the disordered corrole ring together with our interpretation of the disorder

in cobalt–prophyrins (*ca.* 1.98 Å),[9] presumably owing to the decrease in macrocycle size. One would expect non-equivalent Co–N bonding but in this structure only the average distance is available. The cobalt–phosphorus bond length (2.210 Å) is in good agreement with those observed in other complexes.[10] It has been shown,[9] in some five- and six-co-ordinate cobalt–porphyrin complexes, that on changing from $\mathrm{Co^{III}}$ to $\mathrm{Co^{II}}$ the Co–N(porphyrin) distances remain constant at *ca.* 1.98 Å but the Co–N(axial) distance increases from *ca.* 2.0 to 2.4 Å, due presumably to the extra electron in the $\mathrm{Co^{II}}$ case (t_{2g}^6,e_g^1) being in the d_{z^2} orbital in the axial direction. Thus, a five-co-ordinate cobalt(II)–porphyrin (or corrole) would be expected to have an axial Co–P distance of *ca.* 2.60 Å. This effectively rules out the possibility of this structure being a cobalt(II) porphyrin. In addition, of course, the apparent distances and angles within the macrocycle are much more compatible with a disordered corrole structure, and the chemical evidence originally adduced was very strong.

TABLE 4

Distances (Å) of atoms from the mean planes through the corrole and phenyl rings. The equations to the mean planes are defined as $PX + QY + RZ = S$, where X, Y, and Z are the co-ordinates in Å with respect to the axes a, b, c *

Plane (a): Corrole ring

$$-0.6927X + 0.6605Y - 0.2897Z = -1.3399$$

[C(1) −0.03, C(2) −0.16, C(3) −0.09, C(4) 0.06, C(5) 0.08, C(6) 0.09, C(7) −0.06, C(8) −0.09, C(9) −0.02, C(10) −0.02, C(11) −0.01, C(12) −0.07, C(13) −0.06, C(14) 0.01, C(15) −0.01, C(16) 0.00, C(17) −0.02, C(18) −0.04, C(19) 0.07, C(20) −0.01, N(1) 0.07, N(2) 0.10, N(3) 0.08, N(4) 0.11, Co* 0.38]

Plane (*b*): Phenyl ring A

$$-0.6168X + 0.0481Y - 0.7856Z = -1.8748$$

[C(21) 0.00, C(22) 0.00, C(23) −0.01, C(24) 0.01, C(25) 0.00, C(26) −0.01, P* 0.17]

Plane (*c*): Phenyl ring B

$$0.8446X - 0.5302Y - 0.0739Z = -0.8748$$

[C(27) 0.01, C(28) 0.01, C(29) −0.01, C(30) 0.00, C(31) 0.02, C(32) −0.02, P* 0.14]

Plane (*d*): Phenyl ring C

$$-0.0096X + 0.9788Y - 0.2047Z = 3.9021$$

[C(33) 0.02, C(34) 0.00, C(35) −0.02, C(36) 0.01, C(37) 0.01, C(38) −0.03, P* 0.06]

Angles (°) between normals to mean planes: (*a*)–(*b*) 47, (*a*)–(*c*) 24, (*a*)–(*d*) 45.

* Atom not included in calculation of plane.

From Table 5, it can be seen that there is a short intermolecular contact of 3.0 Å between the cobalt atom and a hydrogen atom on a phenyl ring of an adjacent molecule related by the 2_1 screw axis along *b* (see Figure 2). This contact effectively fills the vacant sixth co-ordination site of the cobalt atom but, although short, it seems unlikely to represent a bonding interaction.

TABLE 5

Intermolecular distances (Å) less than the sum of contact radii *

$\mathrm{C(25)\cdots H(36^{I})}$	2.90	$\mathrm{H(31)\cdots Co^{III}}$	3.00
$\mathrm{C(20)\cdots H(37^{I})}$	2.80	$\mathrm{H(30)\cdots C(20^{III})}$	2.96
$\mathrm{H(25)\cdots H(36^{I})}$	2.35	$\mathrm{H(30)\cdots N(4^{III})}$	2.82
$\mathrm{C(2)\cdots H(37^{I})}$	2.97	$\mathrm{H(30)\cdots C(17^{III})}$	2.74
$\mathrm{C(24)\cdots H(29^{II})}$	2.76	$\mathrm{H(30)\cdots C(19^{III})}$	2.58
$\mathrm{C(31)\cdots H(35^{II})}$	2.76	$\mathrm{H(31)\cdots N(4^{III})}$	2.83
$\mathrm{C(23)\cdots H(28^{II})}$	3.00	$\mathrm{H(30)\cdots C(16^{III})}$	2.91
$\mathrm{C(23)\cdots H(29^{II})}$	2.99	$\mathrm{H(30)\cdots C(18^{III})}$	2.58
$\mathrm{C(30)\cdots H(35^{II})}$	2.89		

Roman numeral superscripts denote the following equivalent positions: I $x, y, 1 + z$; II $\bar{x}, 1 - y, \bar{z}$; III $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$

* Defined as 2.1 for Co and P, 1.7 for C and N, and 1.3 Å for H.

We thank Professor A. W. Johnson for the sample of crystals used, and Professor R. Mason for the use of *X*-ray facilities.

[5/2182 *Received*, 10*th November*, 1975]

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