

Table 2. Bond lengths (Å) and angles (°) for (1) and (3)

	(1)	(3)		(1)	(3)		(1)	(3)
Rh(1)-Rh(2)	2.7610 (9)	2.7481 (6)	P(1)-C(5)	1.90 (1)	1.908 (5)	C(9)-C(11)	1.52 (2)	1.510 (9)
Rh(1)-P(1)	2.241 (2)	2.236 (1)	P(2)-C(9)	1.91 (1)	1.904 (6)	C(9)-C(12)	1.50 (1)	1.517 (9)
Rh(1)-P(2)	2.244 (2)	2.232 (1)	P(2)-C(13)	1.90 (1)	1.900 (6)	C(13)-C(14)	1.53 (1)	1.533 (9)
Rh(1)-C(17)	1.88 (1)	1.915 (7)	C(1)-C(2)	1.55 (1)	1.539 (8)	C(13)-C(15)	1.51 (2)	1.529 (9)
Rh(1)-C(18)	1.90 (1)	1.900 (7)	C(1)-C(3)	1.52 (1)	1.530 (8)	C(13)-C(16)	1.51 (1)	1.50 (1)
Rh(2)-P(1)	2.446 (2)	2.459 (1)	C(1)-C(4)	1.51 (1)	1.532 (8)	C(17)-O(1)	1.16 (1)	1.119 (7)
Rh(2)-P(2)	2.458 (2)	2.439 (1)	C(5)-C(6)	1.52 (1)	1.523 (8)	C(18)-O(2)	1.13 (1)	1.141 (7)
Rh(2)-C(19)	1.86 (1)	1.858 (6)	C(5)-C(7)	1.51 (2)	1.521 (8)	C(19)-O(3)	1.13 (1)	1.149 (7)
Rh(2)-C(20)	1.85 (1)	1.849 (7)	C(5)-C(8)	1.54 (2)	1.533 (8)	C(20)-O(4)	1.15 (1)	1.133 (8)
P(1)-C(1)	1.89 (1)	1.910 (5)	C(9)-C(10)	1.53 (2)	1.524 (9)			
Rh(2)-Rh(1)-P(1)	57.43 (6)	58.03 (4)	Rh(1)-P(1)-Rh(2)	72.02 (7)	71.49 (4)	C(6)-C(5)-C(7)	105 (1)	107.4 (5)
Rh(2)-Rh(1)-P(2)	57.73 (6)	57.53 (4)	Rh(1)-P(1)-C(1)	120.7 (3)	119.8 (2)	P(1)-C(5)-C(8)	108.5 (8)	110.0 (4)
P(1)-Rh(1)-P(2)	115.15 (9)	115.55 (5)	Rh(2)-P(1)-C(1)	114.0 (3)	114.6 (2)	C(6)-C(5)-C(8)	108 (1)	108.8 (5)
Rh(2)-Rh(1)-C(17)	125.7 (3)	123.7 (2)	Rh(1)-P(1)-C(5)	119.9 (3)	123.1 (2)	C(7)-C(5)-C(8)	110.0 (9)	109.6 (5)
P(1)-Rh(1)-C(17)	106.9 (3)	108.0 (2)	Rh(2)-P(1)-C(5)	112.7 (4)	111.7 (2)	P(2)-C(9)-C(10)	109.1 (8)	108.5 (5)
P(2)-Rh(1)-C(17)	108.9 (3)	107.0 (2)	C(1)-P(1)-C(5)	111.3 (4)	110.0 (2)	P(2)-C(9)-C(11)	112.3 (8)	115.3 (5)
Rh(2)-Rh(1)-C(18)	122.7 (3)	126.3 (2)	Rh(1)-P(2)-Rh(2)	71.74 (7)	71.94 (4)	C(10)-C(9)-C(11)	111 (1)	110.1 (7)
P(1)-Rh(1)-C(18)	107.7 (3)	109.6 (2)	Rh(1)-P(2)-C(9)	121.2 (4)	120.4 (2)	P(2)-C(9)-C(12)	107.8 (7)	107.1 (4)
P(2)-Rh(1)-C(18)	106.7 (3)	106.6 (2)	Rh(2)-P(2)-C(9)	112.5 (3)	111.8 (2)	C(10)-C(9)-C(12)	109 (1)	108.3 (6)
C(17)-Rh(1)-C(18)	111.6 (4)	109.9 (3)	Rh(1)-P(2)-C(13)	120.7 (3)	119.9 (2)	C(11)-C(9)-C(12)	108 (1)	107.3 (6)
Rh(1)-Rh(2)-P(1)	50.54 (5)	50.48 (3)	Rh(2)-P(2)-C(13)	113.8 (4)	115.9 (2)	P(2)-C(13)-C(14)	107.0 (7)	107.1 (4)
Rh(1)-Rh(2)-P(2)	50.53 (6)	50.54 (4)	C(9)-P(2)-C(13)	110.6 (4)	111.0 (3)	P(2)-C(13)-C(15)	108.5 (8)	108.0 (5)
P(1)-Rh(2)-P(2)	101.07 (8)	101.01 (5)	P(1)-C(1)-C(2)	108.5 (8)	107.5 (4)	C(14)-C(13)-C(15)	106 (1)	108.3 (6)
Rh(1)-Rh(2)-C(19)	134.4 (3)	134.6 (2)	P(1)-C(1)-C(3)	116.9 (8)	116.2 (4)	P(2)-C(13)-C(16)	116.8 (8)	116.2 (5)
P(1)-Rh(2)-C(19)	83.9 (3)	84.8 (2)	C(2)-C(1)-C(3)	107.8 (9)	108.4 (5)	C(14)-C(13)-C(16)	110 (1)	108.9 (6)
P(2)-Rh(2)-C(19)	173.5 (3)	170.4 (2)	P(1)-C(1)-C(4)	108.2 (6)	107.4 (4)	C(15)-C(13)-C(16)	109 (1)	108.1 (7)
Rh(1)-Rh(2)-C(20)	136.4 (3)	134.6 (2)	C(2)-C(1)-C(4)	107 (1)	108.5 (5)	Rh(1)-C(17)-O(1)	171 (1)	171.8 (6)
P(1)-Rh(2)-C(20)	170.9 (4)	172.0 (3)	C(3)-C(1)-C(4)	108 (1)	108.6 (5)	Rh(1)-C(18)-O(2)	170.5 (9)	171.6 (6)
P(2)-Rh(2)-C(20)	86.2 (3)	84.4 (2)	P(1)-C(5)-C(6)	108.3 (7)	107.1 (4)	Rh(2)-C(19)-O(3)	173.2 (9)	173.2 (5)
C(19)-Rh(2)-C(20)	89.2 (4)	90.7 (3)	P(1)-C(5)-C(7)	117.1 (8)	113.9 (4)	Rh(2)-C(20)-O(4)	173 (1)	173.3 (7)

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Structure of (5,10,15,20-Tetraphenylporphinato)cadmium(II)

BY ALAN HAZELL

Institute of Chemistry, Århus University, DK-8000 Århus C, Denmark

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Abstract. $[\text{Cd}(\text{C}_{44}\text{H}_{28}\text{N}_4)]$, $M_r = 781.2$, triclinic, $P\bar{1}$, $a = 14.697$ (7), $b = 10.096$ (4), $c = 14.784$ (6) Å, $\alpha = 56.31$ (2), $\beta = 68.76$ (2), $\gamma = 62.43$ (2)°, $V = 1601$ (1) Å³, $Z = 2$, $D_x = 1.620$ (1) Mg m⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.7255$ (6) mm⁻¹, $F(000) = 736$, $T = 294$ K, $R(F) = 0.042$ for 3905 reflexions [$I > 3\sigma(I)$] and 443 variables. The porphine skeleton is

non-planar, Cd being 0.578 (6) Å out of the plane of the N atoms and only 2.845 (5) Å from an α -carbon of a pyrrole group of the centrosymmetrically related molecule. The mean Cd-N distance is 2.187 (2) Å, the mean N-C-N angles are 86.0 (1) and 149.3 (1)°. Although chemically equivalent bonds and angles do not differ significantly the molecule is flexible and

deviates significantly from fourfold symmetry. The molecules pack in layers with N_4 almost parallel to the twin plane (010).

Introduction. Porphyrins have been studied extensively because of the diversity of their complexes, which are used as enzyme models, as catalysts, or as photosensitizers. The porphyrin skeletons are not usually planar but are distorted either by 'doming' or by 'ruffling' [the structures of a large number of porphyrins are discussed by Hoard (1975)]. The distortions can come from the molecule trying to accommodate a central atom that is larger or smaller than the central hole, but also from packing forces. The structures of PtTPP (Hazell, 1984) and of CdTPP (TPP = 5,10,15,20-tetraphenylporphinato) have been studied in connexion with current metal (^{113}Cd , ^{195}Pt , ^{205}Pb) NMR studies (Jakobsen, Ellis, Inners & Jensen, 1982) of metallo-tetraphenylporphyrins in both the solid and the liquid state. Of particular interest in this connexion is the position of the metal atom relative to the porphyrin ring.

Experimental. CdTPP is difficult to recrystallize from solution unless solvents are used with which it forms an adduct. The sample used for the NMR measurements (Jakobsen *et al.*, 1982) was recrystallized as the pyridine adduct, the pyridine being removed by heating to give a fine powder quite unsuitable for single-crystal work. Small single crystals, all twinned, were obtained by sublimation *in vacuo* at 380 K for several months. Comparison with powder photographs later showed these crystals to belong to a different phase from those used in the solid-state NMR measurements. Crystal mounted on a Picker FACS-1 diffractometer. Cell dimensions determined from setting angles of 30 reflexions, $6.1 < \theta < 10.7^\circ$. Intensities measured to $2\theta_{\text{max}} = 50^\circ$ using $\omega-2\theta$ scan and Nb-filtered $\text{Mo } K\alpha$ radiation, scan width $(3.0 + 0.692 \tan \theta)^\circ$, step length 0.04° , 2 s step^{-1} . Reflexions with $-17 \leq h \leq 15$, $-11 \leq k \leq 0$, $-17 \leq l \leq 14$ measured giving 5622 independent reflexions of which 4054 had $I > 3\sigma(I)$. Reflexions $\bar{2}30$ and 004 monitored every 60 reflexions, overall fall-off in intensity of 16%. Crystal was a triplet, two parts of which had the same orientation. 76 strong reflexions measured for both twins, 2 s step^{-1} for larger and 4 s step^{-1} for smaller; $0\bar{2}0$ and $0\bar{3}0$, common to both, monitored as standards. The smaller twin contributes 10.4 (1)% of the scattering. For scans showing two well resolved peaks that closest to the centre of the scan was accepted, completely overlapped reflexions were corrected for using the known ratio of the two twins. Number of significant reflexions thus reduced to 3905. Reflexions integrated using Nelmes's (1975) method. Data corrected for absorption (crystal $0.17 \times 0.14 \times 0.11$ mm), transmission factors ranged from 0.916 to 0.935. Structure solved by Patterson and

Fourier methods, hydrogen atoms located on difference synthesis, but during refinement positions kept fixed at those calculated assuming C—H = 0.95 Å. Hydrogens given isotropic temperature factors 10% larger than U_{eq} for carbon to which they were attached. All non-hydrogen atoms refined anisotropically. Isotropic extinction factor refined giving $g = 0.28 (6) \times 10^{-4}$, which corresponds to a minimum value of $I/I_{\text{corr.}}$ of 0.90, $w = 1/\sigma(F)$, where $\sigma(F) = \{[\sigma_c(F^2) + 1.03F^2]\}^{1/2} - |F|$, where $\sigma_c(F^2)$ is the standard deviation of F^2 from counting statistics. Final R^* (on F) = 0.042, $wR = 0.048$, $S = 1.255$, $(\Delta/\sigma)_{\text{max}} = 0.035$, $\Delta\rho = -0.5 (1)$ to $0.6 (1) \text{ e } \text{Å}^{-3}$. Fractional coordinates are listed in Table 1, bond distances and angles in Table 2. Computations carried out on a VAX 11/780 with following programs: *DATAP* and *DSORTH* (State University of New York, Buffalo)—data processing; modified *ORFLS* (Busing, Martin & Levy, 1962)—least-squares refinement; *ORTEP* (Johnson, 1965)—drawings. Scattering curves: Cromer & Mann (1968) for Cd, N and C; Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion corrections for Cd from Cromer & Liberman (1970).

Discussion. The molecule (Fig. 1) is non-planar; Cd is 0.578 (6) Å out of the plane of the nitrogen atoms. The mean Cd—N distance is 2.187 (2) Å, which is considerably less than the value in octahedrally coordinated Cd complexes, *e.g.* 2.367 (5) Å in bis(thiosemicarbazide)Cd sulfate (Larsen & Trinderup, 1975). The mean distance between C_t , the centre of the nitrogens, and N is 2.109 (2) Å, which is the upper limit suggested by Collins & Hoard (1970) for C_t —N. Bond distances in the porphyrin skeleton are very similar to those for other TPP complexes, the main difference between the angles in CdTPP and a 'ruffled' complex such as PtTPP is that the angle C(1)—C(5)—C(4') is opened out by 3.5° .

The pyrrole groups are not coplanar with the nitrogen atoms but tilted out of the N_4 plane by τ° and twisted by φ° about an axis that is the projection of Cd—N onto the pyrrole. The values of τ and φ are 16.6 (1), $-1.3 (3)$; $-1.9 (2)$, 1.8 (3); 9.4 (1), $-1.3 (3)$; 6.2 (3), 1.4 (6) $^\circ$ for rings 1 to 4. A positive τ means that a pyrrole is on the opposite side of N_4 to Cd. The twists, which are small, are such that neighbouring groups are twisted towards each other. Porphyrins with pyramidal coordination at the metal atom are usually referred to as 'dome-shaped', but in this case 'floppy-hat' would seem to be a better description. The phenyl

* Lists of structure factors, anisotropic thermal parameters, coordinates for hydrogen atoms and a detailed description of the crystal shape and dimensions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42632 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

groups make dihedral angles of 55.6 (3), 60.6 (3), 88.9 (3) and 56.3 (3) $^\circ$ with the planes defined by C(5) and the neighbouring α -carbons of the pyrroles. Phenyl group 3, which is almost perpendicular to the porphyrin skeleton, exhibits considerable thermal vibration, the major principal axis of its libration tensor being 154 (10) $^\circ$.

Rodesiler, Griffith, Ellis & Amma (1980) report the crystal structure of CdTPP(dioxane)₂ which they find to be nearly planar with Cd only 0.03 (1) Å out of the plane of the nitrogens, a mean Cd–N distance of 2.14 Å, and C–N of 2.14 Å. Their ORTEP drawing of the molecule shows the thermal ellipsoid for Cd to be very elongated perpendicular to N₄ suggesting that the apparent planarity might arise from disorder.

Table 1. Fractional atomic coordinates ($\times 10^5$ for Cd, $\times 10^4$ for N and C) and U_{eq} ($\text{\AA}^2 \times 10^{-4}$ for Cd, $\text{\AA}^2 \times 10^{-3}$ for N and C)

	x	y	z	U_{eq}^*
Cd	7332 (3)	13777 (6)	-15126 (3)	302 (2)
N(1)	-815 (3)	2129 (6)	-1830 (3)	32 (3)
N(2)	-52 (3)	2112 (5)	-202 (3)	29 (2)
N(3)	1981 (3)	2085 (5)	-1615 (3)	29 (2)
N(4)	1227 (3)	2107 (6)	-3259 (3)	32 (3)
C(11)	-1037 (4)	2393 (7)	-2747 (4)	29 (3)
C(12)	-2154 (4)	2918 (8)	-2656 (5)	39 (3)
C(13)	-2573 (4)	2970 (8)	-1692 (5)	40 (3)
C(14)	-1730 (4)	2450 (7)	-1161 (4)	29 (3)
C(15)	-1840 (4)	2402 (7)	-151 (4)	29 (3)
C(16)	-2922 (4)	2781 (7)	458 (4)	32 (3)
C(18)	-3336 (4)	4104 (8)	702 (5)	42 (3)
C(19)	-4332 (5)	4472 (9)	1247 (5)	57 (4)
C(17)	-4922 (5)	3525 (10)	1567 (6)	61 (5)
C(111)	-4544 (5)	2245 (9)	1300 (6)	56 (4)
C(110)	-3538 (4)	1843 (8)	749 (5)	42 (4)
C(21)	-1050 (4)	2148 (7)	317 (4)	29 (3)
C(22)	-1157 (4)	2047 (7)	1375 (4)	34 (3)
C(23)	-244 (4)	1984 (7)	1446 (4)	34 (3)
C(24)	453 (4)	2035 (7)	459 (4)	28 (3)
C(25)	1470 (4)	2095 (7)	174 (4)	29 (3)
C(26)	1845 (4)	2146 (7)	967 (4)	33 (3)
C(28)	2736 (4)	880 (8)	1425 (5)	41 (4)
C(29)	3097 (5)	906 (9)	2160 (5)	53 (4)
C(27)	2582 (6)	2235 (11)	2418 (5)	58 (5)
C(211)	1709 (6)	3473 (9)	1969 (5)	51 (4)
C(210)	1345 (5)	3434 (8)	1244 (5)	44 (4)
C(31)	2145 (4)	2170 (7)	-808 (4)	30 (3)
C(32)	3123 (4)	2487 (8)	-1157 (4)	38 (3)
C(33)	3511 (4)	2549 (8)	-2144 (5)	40 (4)
C(34)	2804 (4)	2293 (7)	-2446 (4)	31 (3)
C(35)	2901 (4)	2342 (7)	-3450 (4)	34 (3)
C(36)	3845 (4)	2666 (8)	-4276 (4)	36 (3)
C(38)	3811 (5)	4286 (9)	-5023 (5)	53 (4)
C(39)	4651 (6)	4626 (11)	-5804 (6)	76 (5)
C(37)	5534 (5)	3331 (13)	-5843 (6)	72 (6)
C(311)	5589 (6)	1725 (13)	-5099 (7)	88 (6)
C(310)	4747 (5)	1342 (10)	-4299 (6)	66 (5)
C(41)	2184 (4)	2244 (7)	-3818 (4)	31 (3)
C(42)	2287 (4)	2421 (8)	-4885 (4)	37 (3)
C(43)	1407 (4)	2365 (7)	-4939 (4)	37 (3)
C(44)	724 (4)	2225 (7)	-3927 (4)	31 (3)
C(45)	-321 (4)	2320 (7)	-3687 (4)	30 (3)
C(46)	-736 (4)	2410 (7)	-4511 (4)	29 (3)
C(48)	-1179 (4)	1204 (8)	-4191 (4)	38 (3)
C(49)	-1555 (5)	1265 (9)	-4942 (5)	47 (4)
C(47)	-1492 (5)	2476 (10)	-6027 (5)	54 (4)
C(411)	-1061 (5)	3657 (9)	-6359 (5)	49 (4)
C(410)	-700 (4)	3643 (8)	-5604 (5)	41 (3)

$$* U_{eq} = \frac{1}{3} \sum_{i=1}^3 U_{ii} a_i^* a_i^* a_i^*$$

Table 2. Molecular geometry

	Ring 1	Ring 2	Ring 3	Ring 4	Mean
(a) Bond distances (Å) and their standard deviations					
Cd–N	2.181 (4)	2.195 (4)	2.188 (4)	2.182 (4)	2.187 (2)
N–C(1)	1.361 (6)	1.382 (6)	1.353 (6)	1.375 (6)	1.368 (3)
N–C(4)	1.371 (6)	1.378 (6)	1.375 (6)	1.362 (6)	1.372 (3)
C(1)–C(2)	1.452 (7)	1.463 (7)	1.462 (7)	1.443 (7)	1.455 (4)
C(3)–C(4)	1.440 (7)	1.437 (7)	1.435 (7)	1.441 (7)	1.438 (4)
C(2)–C(3)	1.353 (7)	1.354 (7)	1.337 (7)	1.353 (7)	1.349 (4)
C(4)–C(5)	1.418 (7)	1.419 (7)	1.413 (7)	1.414 (7)	1.416 (4)
C(5)–C(1 ^h)	1.415 (7)	1.415 (7)	1.410 (7)	1.424 (7)	1.416 (4)
C(5)–C(6)	1.505 (7)	1.497 (7)	1.507 (7)	1.492 (7)	1.500 (4)
C(6)–C(8)	1.381 (8)	1.393 (8)	1.363 (8)	1.415 (7)	1.390 (4)
C(8)–C(9)	1.381 (8)	1.387 (8)	1.376 (8)	1.371 (8)	1.379 (4)
C(9)–C(7)	1.363 (9)	1.392 (10)	1.363 (11)	1.377 (9)	1.374 (5)
C(7)–C(11)	1.370 (10)	1.365 (10)	1.345 (11)	1.375 (9)	1.365 (5)
C(11)–C(10)	1.398 (8)	1.385 (8)	1.398 (9)	1.398 (8)	1.392 (4)
C(10)–C(6)	1.401 (7)	1.374 (8)	1.387 (9)	1.391 (7)	1.389 (4)
Cd–C(21 ^h)	2.845 (5)				
(b) Bond angles ($^\circ$)					
Cd–N–C(1)	125.4 (3)	123.8 (3)	125.6 (3)	124.9 (3)	124.9 (2)
Cd–N–C(4)	126.4 (3)	124.3 (3)	125.5 (3)	126.0 (3)	125.5 (2)
C(1)–N–C(4)	108.3 (4)	108.5 (4)	108.5 (4)	108.3 (4)	108.4 (2)
N–C(1)–C(2)	108.4 (4)	107.4 (4)	108.1 (4)	108.1 (4)	108.0 (2)
N–C(4)–C(3)	108.7 (4)	108.5 (4)	108.2 (4)	108.6 (4)	108.5 (2)
C(1)–C(2)–C(3)	107.3 (5)	107.5 (4)	107.2 (5)	107.4 (4)	107.3 (2)
C(2)–C(3)–C(4)	107.3 (5)	108.1 (4)	108.1 (4)	107.5 (5)	107.8 (2)
N–C(4)–C(5)	126.0 (5)	125.2 (4)	125.5 (5)	125.9 (5)	125.0 (5)
N–C(1)–C(5 ^h)	126.8 (4)	125.3 (4)	127.1 (4)	125.9 (5)	126.3 (2)
C(4)–C(5)–C(1 ^h)	127.0 (4)	125.8 (5)	128.0 (5)	126.5 (5)	126.8 (2)
C(3)–C(4)–C(5)	125.2 (5)	126.2 (5)	126.2 (4)	126.3 (5)	126.0 (2)
C(5 ^h)–C(1)–C(2)	124.7 (5)	127.0 (5)	124.7 (5)	125.8 (5)	125.7 (2)
C(4)–C(5)–C(6)	117.1 (4)	116.9 (4)	117.0 (5)	117.5 (4)	117.1 (2)
C(6)–C(5)–C(1 ^h)	115.8 (4)	117.2 (4)	114.8 (5)	116.0 (4)	116.1 (2)
C(5)–C(6)–C(8)	120.3 (5)	119.7 (5)	119.6 (5)	120.0 (5)	119.9 (3)
C(6)–C(8)–C(9)	120.6 (6)	120.6 (6)	121.2 (7)	120.6 (5)	120.7 (3)
C(8)–C(9)–C(7)	120.7 (6)	119.8 (6)	120.0 (7)	121.0 (6)	120.4 (3)
C(9)–C(7)–C(11)	119.8 (6)	119.4 (6)	119.7 (6)	119.6 (5)	119.6 (3)
C(7)–C(11)–C(10)	120.7 (6)	120.6 (6)	121.6 (8)	120.3 (6)	120.7 (3)
C(11)–C(10)–C(6)	119.2 (6)	121.0 (6)	118.4 (7)	121.0 (6)	120.0 (3)
C(10)–C(6)–C(8)	118.9 (5)	118.5 (5)	119.1 (5)	117.5 (5)	118.5 (3)
C(10)–C(6)–C(5)	120.7 (5)	121.8 (5)	121.2 (6)	122.4 (5)	121.6 (3)

(c) Angles round Cd

	N(2)	N(3)	N(4)	C(21 ^h)
N(1)	86.2 (2)	149.4 (2)	86.1 (2)	95.0 (2)
N(2)		84.9 (2)	149.3 (2)	101.1 (2)
N(3)			86.7 (2)	115.4 (2)
N(4)				109.1 (2)

Symmetry code: (i) $-x, -y, -z$; (ii) neighbouring ring.

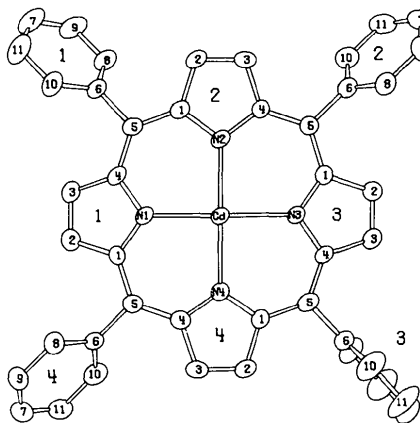


Fig. 1. Numbering of atoms and rings. The chemical symbol for the carbon atoms has been omitted. The full symbol contains first the ring number and then the atom number, e.g. C(16) is atom 6 of ring 1. Hydrogen atoms have the same numbers as the carbons to which they are attached.

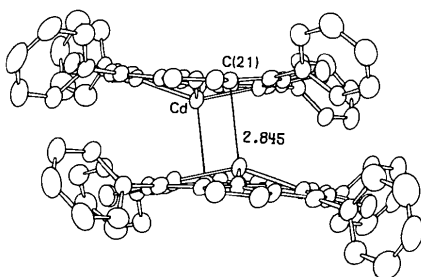


Fig. 2. A centrosymmetrically related pair of molecules showing the short Cd...C(21) distance.

The molecules pack in layers at $y \pm \sim 0.2$ with N_4 almost parallel to (010) which is the twin plane. Pyrrole 2 is tilted towards a centrosymmetrically related molecule, so that an α -carbon, C(21), is only 2.845 (5) Å from cadmium, Fig. 2. The molecules pack more tightly than in PtTPP; although Cd–N is some 9% longer than Pt–N the volume of CdTPP is less than 1% larger than that of PtTPP. Rodesiler *et al.* (1980) find that NMR spectra in dilute solutions show a concentration dependence that they say is not unexpected for a system that can undergo intermolecular stacking interactions. Similar effects are also reported for ZnTPP (Abraham, Pearson & Smith, 1976). These compounds are almost insoluble in, for example, $CHCl_3$,

unless a donor molecule such as pyridine is added which dissociates the aggregates.

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Structure of (Di-2-pyridylamine)(*N*-phenylsalicylideneaminato)copper Perchlorate

BY M. T. GARLAND AND J. Y. LE MAROUILLE

Laboratoire de Chimie du Solide et Inorganique Moléculaire, UA au CNRS n° 254, Campus de Beaulieu, 35042 Rennes CEDEX, France

AND E. SPODINE

Facultad de Ciencias Basicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile

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Abstract. $[Cu(C_{13}H_{10}NO)(C_{10}H_9N_3)]ClO_4$, $M_r = 530.42$, triclinic, $P\bar{1}$, $a = 10.631(3)$, $b = 11.010(2)$, $c = 11.347(4)$ Å, $\alpha = 104.16(2)^\circ$, $\beta = 113.98(3)^\circ$, $\gamma = 96.50(2)^\circ$, $V = 1142.7(6)$ Å³, $Z = 2$, $D_x = 1.542$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 11.162$ cm⁻¹, $F(000) = 542$, $T = 291$ K. Final $R = 0.044$ for 2960 observed reflections. The coordination sphere of Cu is partially tetrahedral, the dihedral angle CuN(2)N(4)–CuN(1)O(5) being 49.4° . The three Cu–N bond lengths are nearly the same, 1.961(2), 1.964(2) and 1.987(2) Å, while that of Cu–O is quite different, 1.874(2) Å. The crystal packing is mainly stabilized by hydrogen bonds and van der Waals forces.

Introduction. Several reviews contain abundant structural data related to metal complexes of Schiff bases (Casellato, Vigato & Vidali, 1977; Holm, Everett & Chakravorty, 1966; Holm & O'Connor, 1971; Maslen & Waters, 1975). However, further studies continue since these complexes have diverse applications; biological models and transition-metal-ion extraction being some of the important ones (Cimerman, Deljac & Štefanac, 1980; Leussing, 1976).

All the structures studied correspond to neutral bis-chelate complexes of copper(II). We were interested in studying an N_3O chromophore, that is a mixed complex with one salicylideneamine molecule and a