cobaloximes having a chlorine and a N-donor ligand in *trans* relation. It follows that the Co—Cl distance is rather insensitive towards changes in the structure of the *trans* N-donor ligand. The values, ranging from 2·235 to 2·261 Å with an average of 2·249 (10) Å, are, however, significantly smaller than those reported (Marzilli, Toscano, Ramsden, Randaccio & Bresciani-Pahor, 1982) for chloro-cobaloximes with a *trans* P-donor ligand. In the latter complexes the range of Co—Cl is from 2·277 to 2·294 Å.

Turning to the Co—N(axial) distances (Table 4) one immediately notices much more variation. If only steric interactions were responsible, one would expect the Co—N to increase in the series $\mathrm{Co(Hdmg)_2Cl}Y$ with $Y = \mathrm{NH_3} < \mathrm{NH_2}R < \mathrm{NH}R_2$. Indeed, the smallest Co—N is observed for $Y = \mathrm{NH_3}$ but all other complexes fall in the same range. At first sight one concludes that none of the listed ligands is sterically demanding. A more detailed analysis, however, shows that local crowding around the central $\mathrm{Co^{III}}$ exists and has consequences for the structures examined. *cis* effects are in operation as revealed by two indicators. The first indicator is the shift (d) of the $\mathrm{Co^{III}}$ out of the least-squares plane through the four N atoms of the two Hdmg ligands; d is taken as positive when Co is shifted towards the axial N ligand, or in an alternative way of thinking when the *cis*-ligand plane (the Hdmg ligands) is pushed away from the axial N ligand. Examination of Table 4 shows that d is significantly larger for secondary amines than for primary amines or the $\mathrm{NH_3}$ molecule. With primary amines or $\mathrm{NH_3}$ as an axial ligand d is practically zero. The second indicator is the angle α between the two Hdmg moieties, all of which can be considered planar as judged by the small values (0–4°) of the torsion angle $\varphi(\mathrm{N{=}C{-}C{=}N})$. Crowding will increase α. Table 4 shows that α is small (*ca* 2°) for small axial ligands such as $\mathrm{NH_3}$ and $\mathrm{NH(CH_3)_2}$, but that α is roughly three times larger for the more bulky ligands, irrespective of whether this is a secondary or a primary amine. We conclude that *cis* effects are operative in cobaloximes.

The title compound has two short hydrogen bridges, *viz* O(1B)···O(2A) at 2·45 (1) Å and O(1A)···O(2B) at 2·42 (1) Å. The accuracy of the data did not permit us to locate H atoms in these O···O bridges, nor could we infer information about the hydrogen positions from a comparison of Co—N(equatorial) and N—O bond lengths as indicated by Palenik, Sullivan & Naik (1976) and by Bresciani-Pahor, Calligaris & Randaccio (1978). Therefore the question whether the complex is truly $\mathrm{Cl(Hdmg)_2CoNH(CH_3)_2}$ or should be formulated as $\mathrm{Cl(dmg)(H_2dmg)CoNH(CH_3)_2}$ remains to be answered.

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Structure of (5,10,15,20-Tetraphenyl-21*H*,23*H*-porphinato)platinum(II), $\mathrm{C_{44}H_{28}N_4Pt}$

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Abstract. $M_r = 807{\cdot}8$, tetragonal, $I\bar{4}2d$, $a = 15{\cdot}073$ (1), $c = 13{\cdot}988$ (1) Å, $V = 3178{\cdot}0$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}688$ (3) Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 8{\cdot}632$ (1) mm^{-1}, $F(000) = 1592$, room temperature. Final $R = 0{\cdot}012$ for 1051 observed reflexions. The porphine nucleus is slightly ruffled, with N alternately 0·025 (3) Å above and below the plane. Pt—N is 2·008 (2) Å. The pyrrole ring is tilted at an

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angle of 12·0° with the (001) plane and the phenyl group an angle of 79·6°, the angle between these rings being 89·5°. The crystal is isomorphous with the corresponding Fe, Co, Ni, Cu and Pd complexes.

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 which is larger or smaller than the central hole, but also from packing forces. The structure of PtTPP (TPP = 5,10,15,20-tetraphenylporphinato) has been studied in connexion with current metal (^{113}Cd, ^{195}Pt, ^{205}Pb) NMR studies (Jakobsen, Ellis, Inners & Jensen, 1982) of metallotetraphenylporphyrins 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. Tetragonal bipyramidal crystal, bounded by {101} and dimensions such that the distance of the faces from the centre was 0·09 mm, mounted on a Picker FACS-1 diffractometer. Cell dimensions determined from setting angles of 14 reflexions, $13 \leq \theta \leq 26°$. Intensities measured out to $(\sin\theta/\lambda)_{\max} = 0{\cdot}56$ Å^{-1} using an ω–2θ scan and Ni-filtered Cu $K\alpha$ radiation, scan width $(3{\cdot}0 + 0{\cdot}36\tan\theta)°$, step length 0·04°. Reflexions with $0 \leq h \leq 16$, $0 \leq k \leq 16$, and $-14 \leq l \leq 14$ measured giving 1127 independent reflexions, $R_{\rm int} = 0{\cdot}015$, of which 1051 had $I > 3\sigma(I)$. Bijvoet pairs were not averaged except for the classes of reflexions to which Pt does not contribute. Reflexions 620 and 008 monitored every 60 reflexions, overall fall-off in intensity 2·4%. Data corrected for absorption, transmission factors ranging from 0·30 to 0·50. Least-squares refinement (on F) carried out using atomic coordinates of the isomorphous Co compound as starting parameters. All non-H atoms refined anisotropically. H atoms located from a difference map but during refinement placed at fixed positions calculated assuming C—H = 0·95 Å. Anomalous-dispersion corrections were included for Pt, the imaginary term was included as $\eta f''$ (Rogers, 1981) and η was refined to 0·98 (3). An isotropic extinction factor was refined giving $g = 1{\cdot}02\,(4) \times 10^{-4}$ which corresponds to a minimum value of $I/I_{\rm corrected}$ of 0·59. Weighting scheme $w = 1/\sigma(F)$ where $\sigma(F) = [\sigma_{\rm CS}(F^2) + 1{\cdot}02F^2]^{1/2} - |F|$ where $\sigma_{\rm CS}(F^2)$ is the standard deviation of F^2 from counter statistics. Final $R = 0{\cdot}012$, $wR = 0{\cdot}017$, $S = 1{\cdot}156$, $(\Delta/\sigma)_{\max} = 0{\cdot}0002$, $\Delta\rho = -0{\cdot}37\,(6)$ to $0{\cdot}34\,(6)$ e Å^{-3}. Bond distances were corrected for thermal vibration assuming the porphyrin skeleton and the phenyl group to be

Table 1. *Fractional coordinates* (×10^5) *and equivalent isotropic thermal parameters* (×10^4) *for the non*-H *atoms with e.s.d.'s in parentheses*

	x	y	z	$U_{\rm eq}$*(Å^2)
Pt	0	0	0	293 (1)
N	11471 (16)	6733 (17)	−176 (23)	323 (13)
C(1)	19772 (21)	3251 (22)	1646 (31)	359 (19)
C(2)	26123 (23)	10431 (22)	1610 (29)	444 (21)
C(3)	21714 (22)	17916 (21)	−615 (39)	456 (20)
C(4)	12429 (24)	15703 (22)	−1423 (28)	380 (21)
C(5)	5691 (23)	21804 (21)	−2806 (26)	330 (20)
C(6)	8187 (21)	31134 (22)	−5360 (26)	360 (19)
C(7)	13069 (27)	48273 (24)	−10239 (32)	542 (25)
C(8)	10286 (28)	33185 (25)	−14648 (28)	500 (23)
C(9)	12715 (35)	41726 (29)	−17178 (34)	631 (28)
C(10)	8510 (32)	37744 (28)	1489 (30)	557 (25)
C(11)	10967 (32)	46307 (26)	−1053 (34)	605 (25)

* $U_{\rm eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Table 2. *Molecular geometry*

(*a*) Bond lengths, *l*, and their standard deviations (Å) and the values, $l_{\rm corr}$, corrected for thermal libration

	l	$l_{\rm corr}$		l	$l_{\rm corr}$
Pt—N	2·005 (2)	2·008	C(5)—C(6)	1·499 (5)	1·503
N—C(1)	1·380 (4)	1·382	C(6)—C(8)	1·373 (6)	1·391
N—C(4)	1·371 (4)	1·373	C(6)—C(10)	1·383 (5)	1·398
C(1)—C(2)	1·445 (5)	1·447	C(7)—C(9)	1·385 (6)	1·401
C(1)—C(5$^{\rm iii}$)	1·392 (5)	1·394	C(7)—C(11)	1·356 (6)	1·374
C(2)—C(3)	1·346 (5)	1·348	C(8)—C(9)	1·384 (6)	1·388
C(3)—C(4)	1·443 (5)	1·445	C(10)—C(11)	1·389 (6)	1·393
C(4)—C(5)	1·384 (5)	1·386			

(*b*) Bond angles (°)

N—Pt—N$^{\rm ii}$	90·009 (2)	N—Pt—N$^{\rm i}$	178·6 (2)
Pt—N—C(1)	125·9 (2)	Pt—N—C(4)	126·3 (2)
N—C(1)—C(5$^{\rm iii}$)	126·1 (3)	N—C(4)—C(5)	126·6 (3)
C(1$^{\rm ii}$)—C(5)—C(4)	123·3 (3)	C(1)—N—C(4)	107·6 (3)
N—C(1)—C(2)	108·4 (3)	N—C(4)—C(3)	108·7 (3)
C(1)—C(2)—C(3)	107·6 (3)	C(4)—C(3)—C(2)	107·7 (3)
C(2)—C(1)—C(5)	125·5 (3)	C(3)—C(4)—C(5)	124·7 (3)
C(1$^{\rm ii}$)—C(5)—C(6)	118·5 (3)	C(4)—C(5)—C(6)	118·2 (3)
C(5)—C(6)—C(8)	119·7 (3)	C(5)—C(6)—C(10)	121·3 (3)
C(6)—C(8)—C(9)	120·8 (4)	C(6)—C(10)—C(11)	120·1 (4)
C(8)—C(9)—C(7)	119·6 (4)	C(10)—C(11)—C(7)	120·5 (4)
C(8)—C(6)—C(10)	119·0 (3)	C(9)—C(7)—C(11)	119·9 (3)

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

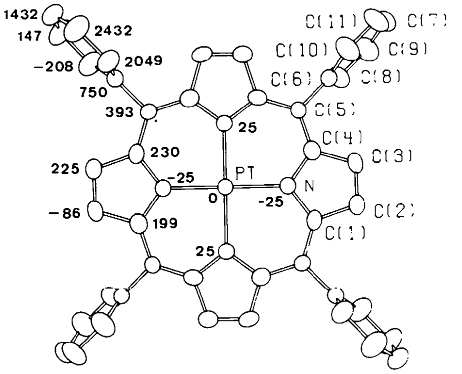

Fig. 1. A perspective drawing of the molecule showing the numbering of the atoms and their deviations (Å ×10^3) from the (001) plane through Pt. E.s.d.'s are 0·003 Å for N and 0·004–0·005 Å for C.

Table 3. *Libration tensors and their e.s.d.'s in deg² for the phenyl groups of some isomorphous MTPP complexes*

L is relative to the molecular axes with *x* parallel to C(5)—C(6) and *z* perpendicular to the ring.

	L_{11}	L_{22}	L_{33}	L_{12}	L_{13}	L_{23}
PtTPP[a]	93·0 (7·8)	9·2 (3·9)	8·8 (3·4)	−5·9 (4·1)	−0·2 (4·9)	1·6 (3·0)
CoTPP[b]	74·0 (5·3)	8·1 (2·6)	7·2 (2·4)	−10·2 (2·7)	−3·0 (3·3)	−1·4 (2·2)
FeTTP[c]	88·7 (8·9)	6·9 (4·3)	7·8 (3·0)	−13·1 (4·8)	−1·2 (5·6)	−0·1 (3·6)

(*a*) This work. (*b*) Madura & Scheidt (1976). (*c*) Coalman *et al.* (1975). The data for the Cu and Pd compounds could not be analysed in terms of rigid-body libration of the phenyl groups.

independent rigid bodies. Computations carried out on a VAX-VMS computer with the following programs: *PROFILE, DATAP* and *DSORT* (State University of New York, Buffalo)–data processing; modified *ORFLS* (Busing, Martin & Levy, 1962)–least-squares refinement; *TLS* (Schomaker & Trueblood, 1968)–thermal-vibration analysis; *ORTEP* (Johnson, 1965)–drawings. Scattering curves those of *International Tables for X-ray Crystallography* (1974) for Pt, Cromer & Mann (1968) for N and C, Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion corrections for Pt from Cromer & Liberman (1970).

Discussion. Atomic parameters are listed in Table 1,* bond distances and angles in Table 2. The atom-numbering scheme is shown in Fig. 1.

The molecules are situated on fourfold inversion axes which means that they must be ruffled or planar but cannot be domed. The porphine nucleus is slightly ruffled, with N alternately 0·025 (3) Å above and below the (001) plane (Fig. 1), so that the angle N—Pt—N is 90·009 (2)°. Pt—N is 2·008 (2) Å which is similar to the Pd—N distance of 2·009 (9) Å in PdTPP (Fleischer, Miller & Webb, 1964). These results are at variance with those of Stong, Spiro, Kubaska & Shupack (1980), who report resonance Raman frequencies for a series of tetraphenylporphinato complexes and find for planar, or ruffled, complexes a correlation between certain marker frequencies and the radius (*Ct*—N) of the porphyrin core. From their measurements they predict that PtTPP has a *Ct*—N distance of only 1·984 Å and furthermore suggest that PtTPP might be domed.

Bond distances C(4)—C(5) and C(5)—C(1) are almost identical as are C(1)—N and C(4)—N indicating almost complete delocalization of π-electrons around the porphyrin ring.

The pyrrole ring is tilted at an angle of 12·0° with the (001) plane and the phenyl group an angle of 79·6°, the angle between these rings being 89·5°.

PtTPP is isomorphous with the corresponding Co (Madura & Scheidt, 1976), Cu, Ni, and Pd (Fleischer *et al.*, 1964), and Fe (Coalman, Hoard, Kim, Lang & Reed, 1975) complexes, and with the tetragonal form of H_2TPP (Hoard, Hamor & Hamor, 1963). There is a correlation between *Ct*—N and the length of *a*; however, the spread is too large for it to be useful for estimating *Ct*—N distances from the cell dimensions of any other members of the isomorphous series. The thermal motion of the phenyl groups is very large and can be interpreted as a libration about C(5)—C(6) with a mean-square amplitude of 93 (8)$^{\circ 2}$ which is similar to the values obtained (Table 3) for those of the isomorphous compounds for which the thermal parameters could be interpreted in terms of rigid-body libration of the phenyl groups.

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* Observed and calculated structure factors, anisotropic thermal parameters and coordinates for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39159 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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