The packing diagram is shown in Fig. 2. The molecules are packed so that the molecular planes of the phen ligand are almost parallel to the *ab* plane. It is interesting that only the acetate-*A* group, with its molecular plane almost in the *ac* plane and perpendicular to that of the phen molecule, has the greatest degree of mobility among the acetate groups in the crystal. From the thermal ellipsoids of O1*A* and C2*A*, it is apparent that the acetate-*A* group is dangling only within its molecular plane. The other chemically equivalent acetate, acetate-*C*, shows no such thermal motion. The ligand may be fixed in the crystal by the packing mode.

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Structure of Chloro($\alpha,\beta,\gamma,\delta$-tetraphenylporphinato)manganese(III) Toluene Solvate

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Abstract. $[Mn(C_{44}H_{28}N_4)Cl].C_7H_8$, $M_r = 795.27$, monoclinic, $P2_1/m$, $a = 9.918\ (2)$, $b = 15.395\ (3)$, $c = 13.453\ (2)$ Å, $\beta = 103.68\ (1)°$, $V = 1995.8\ (6)$ Å^3, $Z = 2$, $D_x = 1.323$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 3.91$ cm^{-1}, $F(000) = 824$, $T = 294$ K, final $R = 0.034$ for 3049 reflections. The manganese complex and the toluene molecule lie on a crystallographic mirror plane. The Mn atom is coordinated by a chloro ligand and a tetraphenylporphinato ligand in an approximate square-pyramidal arrangement with the latter ligand deformed to give a saddle conformation. The Mn—Cl and Mn—N(av.) bond lengths are 2.345 (1) and 2.015 Å, respectively. The toluene molecule lies perpendicular to the plane of the porphinato ligand and makes its closest contacts with pyrrole atoms.

Introduction. Manganese porphyrin complexes have been the subject of much study because of their biological and photochemical importance. During a study of the spectroelectrochemistry of derivatives of Mn^{III} porphyrin complexes, we isolated the title compound and determined its structure. The structure of the complex has been determined previously as the acetone solvate (Tulinsky & Chen, 1977) but the present study is more precise and reveals a number of small but significant differences in the geometry about the Mn atom.

Experimental. A crystal was mounted on a glass fibre with epoxy resin. Data were collected on an Enraf–Nonius CAD-4 automatic diffractometer using graphite-monochromated Mo $K\alpha$ radiation. 25 independent reflections with $2 < 2\theta < 30°$ were used for least-squares determination of cell constants. Intensities of three reflections were monitored, and indicated less than 1.0% decomposition. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least squares using *SHELX*76 (Sheldrick, 1976). Non-H atoms were refined with anisotropic thermal parameters. The positions of H atoms were calculated assuming planar or tetrahedral geometry with a constrained C—H distance of 0.97 Å and their thermal parameters were refined isotropically either individually or in groups. At convergence, all shifts were $< 0.1\sigma$. Maximum excursions in a final difference map were 0.2 and -0.2 e Å^{-3}. Data reduction and application of corrections for absorption were carried out using the *Enraf–Nonius SDP-Plus Structure Determination Package* (Frenz, 1985). All other calculations were performed using the program *SHELX*76 (Sheldrick, 1976). A drawing of the title complex was produced using the program *ORTEP* (Johnson, 1965). Scattering factors and anomalous-dispersion terms for Mn (treated as neutral Mn) were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The values supplied in *SHELX*76 were used for all other atoms.

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Table 1. *Summary of data-collection and processing parameters*

Crystal dimensions (mm)	0.40 × 0.37 × 0.30
Crystal faces	$\bar{1}02$, $\bar{1}\bar{2}\bar{1}$, 011, $43\bar{2}$, $1\bar{1}0$, $\bar{1}10$
Data-collection range	$2 < 2\theta < 50°$
Scan width (°)	$1.00 + 0.34\tan\theta$
Horizontal counter aperture (mm)	$2.70 + 1.05\tan\theta$
Scan type	ω–θ
Absorption correction*	
Number of sampling points	14 × 10 × 10
Maximum correction	1.405
Minimum correction	1.107
Range of *hkl*	*h* −11 to 11, *k* 0 to 18, *l* 0 to 16
$R_{\rm int}$	0.019
Total data collected	3818
Number of unique reflections	3440
Data with $I > 2.5\sigma(I)$	3049
Total variables	283
Function minimized	$\sum w(F_o - F_c)^2$
R	0.034
wR	0.040
Weights, *w*	$2.23/[\sigma^2(F_o) + 0.00021F_o^2]$

* Coppens, Leiserowitz & Rabinovich (1965).

Table 2. *Final atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters* $B_{\rm eq}$ (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$B_{\rm eq}$
Mn(1)	0.5745 (1)	0.2500	0.8122 (1)	2.04
Cl(1)	0.7565 (1)	0.2500	0.7282 (1)	3.49
N(1)	0.5540 (2)	0.1213 (1)	0.8219 (1)	2.36
N(2)	0.6848 (2)	0.2500	0.9596 (2)	2.36
N(3)	0.4068 (2)	0.2500	0.6913 (2)	2.43
C(1)	0.4861 (2)	0.0682 (1)	0.7431 (2)	2.64
C(2)	0.5367 (2)	−0.0188 (1)	0.7613 (2)	3.17
C(3)	0.6325 (2)	−0.0190 (1)	0.8508 (2)	3.07
C(4)	0.6411 (2)	0.0675 (1)	0.8908 (1)	2.37
C(5)	0.7173 (2)	0.0923 (1)	0.9874 (1)	2.44
C(6)	0.7275 (2)	0.1783 (1)	1.0208 (2)	2.57
C(7)	0.7890 (2)	0.2065 (1)	1.1228 (2)	3.15
C(8)	0.2180 (2)	0.2065 (1)	0.5673 (2)	3.50
C(9)	0.3372 (2)	0.1785 (1)	0.6428 (2)	2.68
C(10)	0.3780 (2)	0.0927 (1)	0.6618 (2)	2.70
C(11)	0.7910 (2)	0.0234 (1)	1.0577 (2)	2.58
C(12)	0.9340 (2)	0.0283 (2)	1.0986 (2)	3.56
C(13)	1.0021 (3)	−0.0385 (2)	1.1589 (2)	4.69
C(14)	0.9307 (3)	−0.1098 (2)	1.1799 (2)	4.63
C(15)	0.7903 (3)	−0.1143 (2)	1.1418 (2)	3.92
C(16)	0.7204 (2)	−0.0483 (1)	1.0815 (2)	3.09
C(17)	0.2994 (2)	0.0228 (1)	0.5950 (2)	3.10
C(18)	0.2135 (3)	−0.0322 (2)	0.6321 (2)	4.45
C(19)	0.1429 (3)	−0.0981 (2)	0.5709 (2)	5.48
C(20)	0.1582 (3)	−0.1097 (2)	0.4743 (2)	5.46
C(21)	0.2428 (3)	−0.0554 (2)	0.4366 (2)	5.43
C(22)	0.3121 (3)	0.0118 (2)	0.4961 (2)	4.50
C(23)	0.4137 (5)	0.2500	0.3001 (5)	7.08
C(24)	0.2772 (6)	0.2500	0.2904 (6)	8.42
C(25)	0.1858 (7)	0.2500	0.1910 (8)	10.24
C(26)	0.2430 (13)	0.2500	0.1083 (6)	10.73
C(27)	0.3847 (14)	0.2500	0.1229 (9)	11.99
C(28)	0.4669 (9)	0.2500	0.2191 (7)	9.32
C(29)	0.5133 (8)	0.2500	0.4033 (6)	11.67

Data collection and refinement parameters are in Table 1. Final positional parameters and bond lengths and angles are listed in Tables 2 and 3.*

Table 3. *Bond lengths* (Å) *and angles* (°)

Cl(1)—Mn(1)	2.345 (1)	N(1)—Mn(1)	2.000 (2)
N(2)—Mn(1)	2.026 (2)	N(3)—Mn(1)	2.033 (2)
C(1)—N(1)	1.381 (2)	C(4)—N(1)	1.383 (2)
C(6)—N(2)	1.382 (2)	C(9)—N(3)	1.379 (2)
C(2)—C(1)	1.431 (3)	C(10)—C(1)	1.391 (3)
C(3)—C(2)	1.346 (3)	C(4)—C(3)	1.431 (3)
C(5)—C(4)	1.393 (3)	C(6)—C(5)	1.395 (3)
C(11)—C(5)	1.493 (3)	C(7)—C(6)	1.431 (3)
C(7)—C(7')	1.338 (4)	C(9)—C(8)	1.431 (3)
C(8)—C(8^{i})	1.341 (5)	C(10)—C(9)	1.386 (3)
C(17)—C(10)	1.497 (3)	C(12)—C(11)	1.396 (3)
C(16)—C(11)	1.384 (3)	C(13)—C(12)	1.383 (3)
C(14)—C(13)	1.371 (4)	C(15)—C(14)	1.367 (4)
C(16)—C(15)	1.380 (3)	C(18)—C(17)	1.376 (3)
C(22)—C(17)	1.376 (3)	C(19)—C(18)	1.388 (3)
C(20)—C(19)	1.355 (4)	C(21)—C(20)	1.364 (4)
C(22)—C(21)	1.387 (3)	C(24)—C(23)	1.330 (7)
C(28)—C(23)	1.317 (8)	C(29)—C(23)	1.501 (8)
C(25)—C(24)	1.427 (9)	C(26)—C(25)	1.363 (10)
C(27)—C(26)	1.372 (12)	C(28)—C(27)	1.357 (12)
N(1)—Mn(1)—Cl(1)	97.6 (1)	N(2)—Mn(1)—Cl(1)	100.0 (1)
N(2)—Mn(1)—N(1)	88.6 (1)	N(3)—Mn(1)—Cl(1)	101.0 (1)
N(3)—Mn(1)—N(1)	88.6 (1)	N(3)—Mn(1)—N(2)	159.0 (1)
C(1)—N(1)—Mn(1)	125.1 (1)	C(4)—N(1)—Mn(1)	125.5 (1)
C(4)—N(1)—C(1)	105.9 (2)	C(6)—N(2)—Mn(1)	127.0 (1)
C(9)—N(3)—Mn(1)	127.0 (1)	C(2)—C(1)—N(1)	109.6 (2)
C(10)—C(1)—N(1)	126.0 (2)	C(10)—C(1)—C(2)	124.3 (2)
C(3)—C(2)—C(1)	107.5 (2)	C(4)—C(3)—C(2)	107.5 (2)
C(3)—C(4)—N(1)	109.5 (2)	C(5)—C(4)—N(1)	125.2 (2)
C(5)—C(4)—C(3)	125.2 (2)	C(6)—C(5)—C(4)	122.9 (2)
C(11)—C(5)—C(4)	118.2 (2)	C(11)—C(5)—C(6)	118.9 (2)
C(5)—C(6)—N(2)	125.3 (2)	C(7)—C(6)—N(2)	109.3 (2)
C(7)—C(6)—C(5)	125.4 (2)	C(6)—N(2)—C(6')	106.0 (2)
C(8)—C(9)—N(3)	109.4 (2)	C(10)—C(9)—N(3)	125.5 (2)
C(10)—C(9)—C(8)	125.0 (2)	C(9)—N(3)—C(9^{i})	106.0 (2)
C(9)—C(10)—C(1)	122.8 (2)	C(17)—C(10)—C(1)	118.1 (2)
C(17)—C(10)—C(9)	119.0 (2)	C(12)—C(11)—C(5)	120.7 (2)
C(16)—C(11)—C(5)	121.0 (2)	C(16)—C(11)—C(12)	118.3 (2)
C(13)—C(12)—C(11)	120.0 (2)	C(14)—C(13)—C(12)	120.8 (2)
C(15)—C(14)—C(13)	119.5 (2)	C(16)—C(15)—C(14)	120.6 (2)
C(15)—C(16)—C(11)	120.8 (2)	C(18)—C(17)—C(10)	120.2 (2)
C(22)—C(17)—C(10)	121.1 (2)	C(22)—C(17)—C(18)	118.7 (2)
C(19)—C(18)—C(17)	120.2 (2)	C(20)—C(19)—C(18)	120.7 (3)
C(21)—C(20)—C(19)	119.6 (2)	C(22)—C(21)—C(20)	120.5 (3)
C(21)—C(22)—C(17)	120.3 (3)	C(28)—C(23)—C(24)	121.1 (7)
C(29)—C(23)—C(24)	121.5 (7)	C(29)—C(23)—C(28)	117.4 (7)
C(25)—C(24)—C(23)	119.9 (6)	C(26)—C(25)—C(24)	118.1 (7)
C(27)—C(26)—C(25)	119.5 (9)	C(28)—C(27)—C(26)	120.0 (10)
C(27)—C(28)—C(23)	121.4 (8)		

Symmetry code: (i) x, $0.5 - y$, z.

Discussion. The title structure consists of the complex (Fig. 1) and a solvated toluene molecule, both of which lie on the mirror plane at $y = 1/4$. The Mn, Cl and two of the N atoms of the porphinato ligand lie on the mirror plane that bisects two of the pyrrole rings. The porphinato ligand is thus perpendicular to the mirror plane and to the toluene molecule which makes only van der Waals contacts with the periphery of the pyrrole rings, the shortest of these contacts being 3.57 Å. This is in contrast to the coplanar arrangement of the toluene and porphinato moieties in [Mn($\alpha,\beta,\gamma,\delta$-tetraphenylporphinato)] toluene in which the toluene–pyrrole contacts are as short as 3.04 Å (Kirner, Reed & Scheidt, 1977). The atoms of the toluene molecule have large thermal parameters and most of the motion is in the plane of the molecule.

The geometry about the Mn atom is best described as square pyramidal with the chloro ligand occupying the apical site and the Mn atom lying 0.32 Å above the mean plane defined by the four N

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55571 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0291]

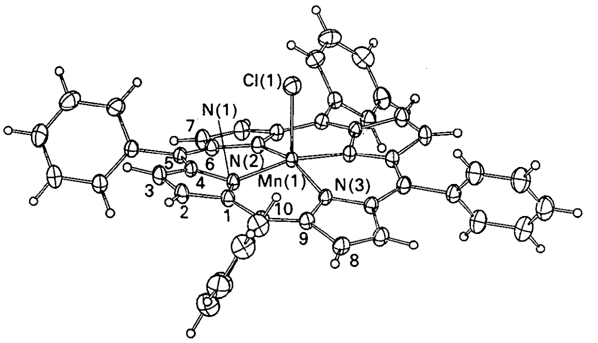

Fig. 1. *ORTEP* plot (Johnson, 1965) of the complex showing the atomic labels used (30% thermal ellipsoids). Atoms not otherwise designated are C atoms.

atoms. The porphinato ligand is deformed into a saddle conformation with pairs of opposing pyrrole rings disposed either up or down. This leads to the four N atoms being non-coplanar and to a distortion of the coordination geometry towards trigonal pyramidal. The bond lengths from the Mn atom to the two N atoms distorted further away from the chloro ligands are longer: 2.026 (2) and 2.033 (2) Å compared with 2.000 (2) Å. A similar result is seen in the structure of the acetone solvate (Tulinsky & Chen, 1977) though in that case it is of marginal significance. The average Mn—N bond lengths in the two structures are not significantly different. The Mn atom in the present structure lies further from the N_4 plane than it does in the acetone solvate: 0.32 compared with 0.27 Å; as a probable consequence of this, the Mn—Cl bond length is found to be significantly shorter: 2.345 (1) compared with 2.363 (2) Å. The porphinato group is also more deformed from planarity in the present structure, the largest deviation being 0.58 Å compared with 0.49 Å in the acetone solvate. All of this suggests a degree of plasticity in the coordination geometry.

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cis-[Diaquabis(1-aminocyclohexanecarboxylato)nickel(II)]–Water (1/1)

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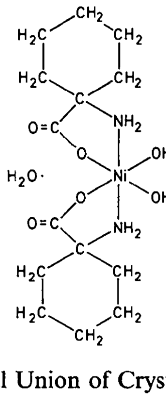
Abstract. (α-6-22)-Diaquabis[(1-amino-κN)cyclohexanecarboxylato-κO]nickel(II) hydrate, $[Ni(C_7H_{12}NO_2)_2(H_2O)_2].H_2O$, $M_r = 397.0$, monoclinic, Cc, $a = 27.073\,(7)$, $b = 6.145\,(2)$, $c = 11.605\,(4)$ Å, $\beta = 107.24\,(3)°$, $V = 1844\,(1)$ Å^3, $Z = 4$, $D_x = 1.43$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.09$ mm^{-1}, $F(000) = 848$, $T = 293\,(1)$ K, $R = 0.032$ for 1831 reflections. The single Ni atom is hexacoordinated by two bidentate ligands, through the amino N atoms and the carboxylate O atoms, and by O atoms of two water molecules. The N atoms are in *trans* positions and the water molecules are in *cis* positions. The third water molecule is not coordinated but participates in a hydrogen-bonding network. The nickel–ligand distances are 2.059 (4) for Ni—O(carboxyl), 2.095 (4) and 2.098 (4) for Ni—O(water), and 2.054 (7) and 2.082 (7) Å for Ni—N.

Introduction. The structure analysis of the title compound is a continuation of the investigation of the metal complexes of aromatic and heterocyclic amino acids (Boudreau & Haendler, 1992; Haendler, 1989).



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