The complex anion is surrounded by six complex cations where the distances between oxonium ions and Th atoms are 7·78–8·38 Å. Besides Coulomb forces, there are van der Waals forces among complex anions and cations. The crystal is stabilized by these forces. The present structure suggests that the process of extraction of thorium(IV) from nitric acid solution with dicyclohexano-18-crown-6 isomer *A* in 1,2-dichloroethane is described as

$$Th^{4+} + 2(Ia) + 2H_3O^+ + 6NO_3^- = [(Ia)H_3O]_2Th(NO_3)_6.$$

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The Structure of the Palladium(II) and Zinc(II) Complexes of α,β,γ,δ-Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin

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Abstract. (I) $C_{76}H_{92}N_4O_4Pd.3C_6H_{12}$, $M_r = 1484{\cdot}49$, monoclinic, $C2/c$, $a = 28{\cdot}004\,(4)$, $b = 26{\cdot}871\,(7)$, $c = 21{\cdot}267\,(2)$ Å, $\beta = 131{\cdot}18\,(2)°$, $V = 12\,045\,(10)$ Å^3, $Z = 4$, D_m not measured, $D_x = 0{\cdot}819$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}186$ mm^{-1}, $F(000) = 3192$, $T = 293$ K. Final $R = 0{\cdot}086$ for 6308 reflections with $I \geq 3\sigma(I)$. (II) $C_{76}H_{92}N_4O_4Zn.4C_6H_{12}$, $M_r = 1527{\cdot}63$, monoclinic, $C2/c$, $a = 27{\cdot}966\,(7)$, $b = 26{\cdot}847\,(4)$, $c = 21{\cdot}275\,(2)$ Å, $\beta = 131{\cdot}09\,(3)°$, $V = 12\,038\,(11)$ Å^3, $Z = 4$, D_m not measured, $D_x = 0{\cdot}843$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}245$ mm^{-1}, $F(000) = 3320$, $T = 293$ K. Final $R = 0{\cdot}10$ for 4307 reflections with $I \geq 2\sigma(I)$. The structures are crystallographically isomorphous and have an unusual solvent of crystallization, cyclohexane, which is readily lost from the lattice, destroying the order. The structures also show excellent pseudo-orthorhombic symmetry which made the structure solution non-trivial.

Introduction. We have recently been investigating the chemistry of phenolic porphyrins and their metal complexes (Traylor, Nolan & Hildreth, 1983; Milgrom, 1983; Golder, Nolan, Povey & Milgrom, 1988), and have observed that the ease of oxidation of these complexes by air in basic solution is strongly dependent on the central metal cation. Hence, whereas cobalt(II), nickel(II), iron(III) and zinc(II) complexes of *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-porphyrin (H_2t^tbhpp) are readily oxidized in basified

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dichloromethane solution, the manganese(III) and palladium(II) complexes are resistant to oxidation under these conditions. Since we suspect that this behaviour depends on whether or not the porphyrin ligand in the complex is planar we decided to investigate the crystal structures of some of these metalloporphyrins. The crystal structure of the nickel complex has already been reported [Ni(t^tbhpp) Golder, Nolan, Povey & Traylor (1988)] and in this paper we describe the crystal and molecular structure of the palladium(II) and zinc(II) complexes.

Experimental. The preparation of H_2t^tbhpp and its zinc(II) complex have been reported (Traylor, Nolan & Hildreth, 1983) and the palladium(II) derivative was synthesized by insertion according to a literature method (Buchler, 1978). Suitable crystals of both (I) and (II) for X-ray studies were obtained by crystallization from a dichloromethane solution with cyclohexane carefully layered on top. The crystals so obtained were deep-red (I) and dark-purple (II) diamond-shaped prisms. In both cases the crystals were unstable due to loss of solvent and hence were mounted in capillaries by suction (by capillary action) from solution, a solvent atmosphere being maintained by incorporation of solvent-soaked tissue in the araldite-sealed capillary.

Accurate unit-cell parameters were measured on a CAD-4 diffractometer using 25 accurately centred reflections ($13 \leq \theta \leq 15°$) from crystals of dimensions 0·5 × 0·5 × 1·0 mm (I) and 0·5 × 0·5 × 0·6 mm (II). Structure (I) was collected in the *C*-centred monoclinic cell, $a = 26{\cdot}878$ (7), $b = 32{\cdot}016$ (4), $c = 19{\cdot}415$ (2) Å, $\beta = 133{\cdot}83$ (2)° and (II) in a different *C*-centred monoclinic cell, $a = 26{\cdot}847$ (4), $b = 27{\cdot}966$ (7), $c = 20{\cdot}907$ (3) Å, $\beta = 129{\cdot}92$ (1)°. These cells proved to be related to one another (see later).

A quarter sphere of reciprocal space was measured [$0 \leq h \leq 30$, $0 \leq k \leq 36$, $-22 \leq l \leq 22$ (I), $0 \leq h \leq 30$, $0 \leq k \leq 32$, $-23 \leq l \leq 23$ (II)]; θ limit 24°, ω–2θ scan, scan speed 5° min^{-1}; 222 (I) and 0,16,0 and 4,12,2 (II) reflections monitored hourly. Variation of intensity reflections was corrected, 4·4 (I), –4·1% (II) and after data reduction from 9424 (9425) unique reflections, 6308 (3670) had $I \geq 3\sigma(I)$. Intensity statistics indicated a centric distribution and systematic absences determined the space group as $C2/c$ in both cases.

The solution of the structure was not straightforward. The initial cells for (I) and (II) as collected were different but Delaunay reduction indicated they were related *via* an *F* orthorhombic cell, $a = 26{\cdot}871$, $b = 32{\cdot}015$, $c = 28{\cdot}004$ Å. The final solution to both structures proved to be a third *C*-centred monoclinic cell also related to this orthorhombic cell. The symmetry-equivalent reflections after data reduction and rotation to the *F* orthorhombic cell showed very few discrepancies of any note. Photographic data were sought but the mounting technique did not allow for orientation of the crystals and the only set obtained was in the monoclinic cell measured for (I) with the crystal axis along **c**, disguising the pseudo-orthorhombic symmetry.

Structure (I) was solved and refined, albeit with difficulty, in the original setting. The Pd atom was located in the Patterson map at $0\frac{1}{8}\frac{1}{4}$. A Fourier map phased on this gave the positions of the atoms of the porphyrin ring, a C atom of a phenyl ring and one O atom. Attempted refinement of these positions failed but with structure-factor calculations and subsequent Fourier syntheses, the remaining atoms were located. With the 44 unique atoms located, full-matrix anisotropic refinement was possible ($R = 0{\cdot}11$) and a solvent molecule, cyclohexane, was found. Further work failed to improve the refinement and the solvent positions would not refine.

(I) was then solved in the *F* orthorhombic cell, the zonal data indicating *F*2*dd* (non-standard *Fdd*2, No. 43) as the space group. All but three atoms were located in the contoured Patterson map with the Pd atom at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$, and gradual refinement seemed successful. With all atoms anisotropic, and the inclusion of one cyclohexane molecule R was reduced to 0·12.

Neither of the refinements of (I) was good; the e.s.d.'s of bonds and angles were high and the geometry was poor. Attempted refinement of (II) both in the original *C*-centred and in the orthorhombic cell gave similar results. Inspection of lattice drawings indicated that a third monoclinic cell could be obtained, this being related to the two original cells *via* the *F* orthorhombic one. From the results obtained above it was concluded that the structures were isomorphous so this third cell was investigated and found to give a solution with well behaved and reasonable final geometry and e.s.d.'s.

The collected data were corrected for decay and a semi-empirical absorption correction applied to (I), minimum and maximum correction for the latter being 0·958 and 1·0, respectively. Data were rotated to the monoclinic cell given in the *Abstract*, using matrices $-1,0,-2; -1,0,0; \frac{1}{2},\frac{1}{2},1$ (I) and $0,-1,0; -1,0,0; -\frac{1}{2},\frac{1}{2},-1$ (II). The structure was solved by Patterson and Fourier methods in $C2/c$ with the metal located on the twofold axis ($0y\frac{1}{4}$, $y = 0{\cdot}375$). Three cyclohexane solvent molecules were located in (I) and four in (II). H atoms were added in calculated positions ($d_H = 1{\cdot}0$ Å) to the porphyrin molecule and an absorption correction by *DIFABS* (Walker & Stuart, 1983) applied, with minimum and maximum corrections 0·478 and 1·533 (I), 0·385 and 1·530 (II) respectively. Cyclohexane molecules were refined isotropically but the geometry became poor so they were fixed in original positions with an averaged $B_{\rm iso} = 20$ Å^2. Full-matrix anisotropic refinement on F first on heavy atoms, then for all porphyrin non-H atoms, converged at $R = 0{\cdot}086$, $wR = 0{\cdot}113$, $S = 1{\cdot}03$ for 6308 reflections

$[F_o \geq 3{\cdot}0\sigma(F)]$, using a Cruickshank weighting scheme for (I) and $R = 0{\cdot}100$, $wR = 0{\cdot}099$, $S = 1{\cdot}64$ for 4307 reflections $[F_o \geq 2{\cdot}0\sigma(F)]$, using a Cruickshank weighting scheme for (II). The effects of various weighting schemes, chiefly polynomials in F, on refinement were investigated assuming a normal distribution of errors over the whole range of F values. The quantity S, the e.s.d. of an observation with unit weight, which should ideally be 1·0, was the criterion for best fit – the fit in the case of the zinc structure was poor but could not be improved.

The largest shift/e.s.d. was 0·72 (I), 0·43 (II), associated with the metal atom and the highest peak in a difference map was 0·38 (I), 0·27 (II) e Å^{-3} – associated with the cyclohexane molecules. Atomic scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Refinement using *SDP Plus* (Frenz, 1983).

Discussion. The molecular structure of $\mathrm{Pd^{II}(t^tbhpp)}$ [$\mathrm{Zn^{II}(t^tbhpp)}$ is isomorphous] is shown in Fig. 1 and two packing diagrams, the first of which includes solvent molecules, in Figs. 2 and 3. Atomic coordinates and some relevant bond distances and angles (averaged assuming fourfold symmetry, individual values do not differ significantly from this) are listed in Tables 1 and 2, respectively.*

Each complex contains a planar porphyrin core, with maximum deviation of 0·01 (2) (I) and 0·02 (2) Å (II) from the least-squares plane (see deposition footnote) and the phenyl rings are ±67 [illegible] (5) (I), ±66·9 (5)° (II) to this plane. The metal ion is accurately centred in the plane of the porphyrin core with normal M—N distances, Pd—N = 2·022 (7) Å [*cf.* 2·009 (9) Å in the puckered Pd(tpp) (Fleischer, Miller & Webb, 1964)] and Zn—N = 2·041 (8) Å [*cf.* 2·037 (2) Å average value in Zn(tpp) (Scheidt *et al.*, 1986)]. The bond distances and angles in the porphyrin core do not differ significantly from those expected for an unexpanded core (Scheidt, 1978), and those in the substituents and solvent are also normal. The planar core is in contrast to the very puckered core in $\mathrm{Ni^{II}(t^tbhpp)}$ (Golder, Nolan, Povey & Taylor, 1988) which shows approximate S_4 symmetry, with the *meso*-C atoms displaced ±0·54 Å from the least-squares plane of the core.

The complexes contain intermolecular hydrogen bonds between the phenolic groups giving a two-dimensional sheet structure having O···O distances of

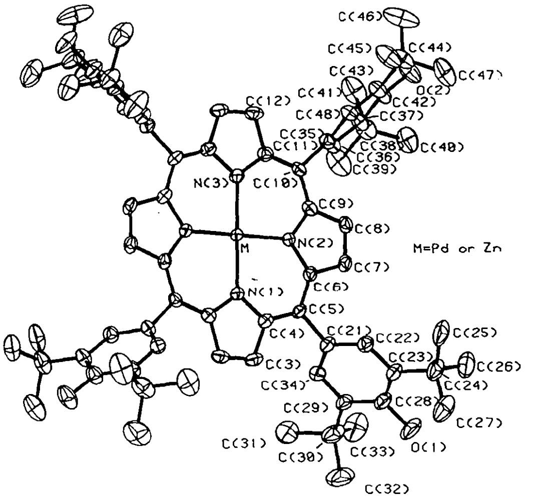

Fig. 1. *ORTEP* (Johnson, 1965) view of $\mathrm{Pd^{II}(t^tbhpp)}$ showing the atomic numbering scheme; 30% probability ellipsoids.

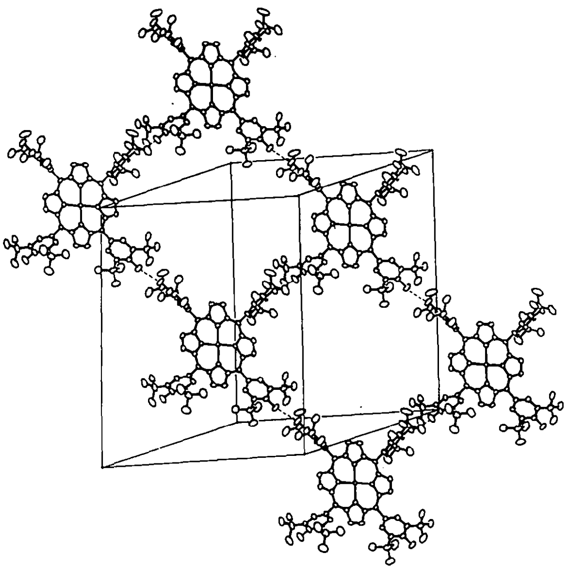

Fig. 2. Packing diagram of $\mathrm{Pd^{II}(t^tbhpp)}$, showing the hydrogen-bonded sheets (H bonds are indicated with a dotted line). **a** horizontal, **b** vertical, **c** into plane of paper.

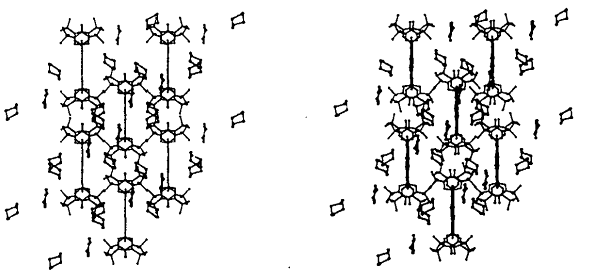

Fig. 3. Stereoview of packing, viewed down **b**, and including cyclohexane solvent molecules.

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* Lists of observed and calculated structure factors, anisotropic temperature factors, calculated hydrogen positions and a complete list of bond lengths and angles and a selection of least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51116 (79 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses and* B_{eq} *thermal parameters* (Å^2)

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	Zn$^{\rm II}$(t$^{\rm t}$bhpp)				Pd$^{\rm II}$(t$^{\rm t}$bhpp)			
	x	y	z	$B_{\rm eq}$	x	y	z	$B_{\rm eq}$
Zn/Pd	0·500	0·37504 (7)	0·750	2·80 (4)	0·500	0·37504 (3)	0·750	2·44 (1)
O(1)	0·2873 (3)	0·1485 (3)	0·3293 (4)	6·9 (3)	0·2874 (3)	0·1493 (2)	0·3286 (3)	7·4 (2)
O(2)	0·2922 (3)	0·6007 (3)	0·3295 (4)	6·9 (3)	0·2918 (3)	0·6012 (3)	0·3300 (3)	7·6 (2)
N(1)	0·500	0·2989 (4)	0·750	2·7 (3)	0·500	0·2996 (3)	0·750	3·2 (2)
N(2)	0·4364 (3)	0·3754 (4)	0·6227 (3)	2·7 (2)	0·4369 (2)	0·3750 (2)	0·6235 (2)	3·0 (1)
N(3)	0·500	0·4510 (4)	0·750	3·1 (3)	0·500	0·4500 (3)	0·750	3·2 (2)
C(3)	0·4797 (5)	0·2171 (4)	0·7082 (5)	4·5 (3)	0·4791 (3)	0·2182 (2)	0·7088 (4)	4·6 (2)
C(4)	0·4658 (4)	0·2683 (4)	0·6812 (5)	3·3 (3)	0·4654 (2)	0·2688 (2)	0·6808 (3)	3·7 (1)
C(5)	0·4246 (4)	0·2844 (4)	0·5983 (4)	3·1 (3)	0·4244 (2)	0·2845 (2)	0·5987 (3)	3·2 (1)
C(6)	0·4125 (3)	0·3340 (4)	0·5733 (4)	3·1 (2)	0·4114 (2)	0·3335 (2)	0·5723 (3)	3·2 (1)
C(7)	0·3683 (4)	0·3493 (4)	0·4871 (5)	3·6 (3)	0·3686 (3)	0·3506 (3)	0·4878 (3)	3·9 (2)
C(8)	0·3685 (4)	0·4004 (4)	0·4872 (5)	3·8 (3)	0·3695 (3)	0·3996 (3)	0·4874 (3)	3·9 (2)
C(9)	0·4103 (3)	0·4164 (4)	0·5726 (5)	2·9 (3)	0·4110 (2)	0·4164 (2)	0·5722 (3)	3·3 (1)
C(10)	0·4245 (4)	0·4660 (4)	0·5988 (5)	3·3 (3)	0·4244 (2)	0·4655 (2)	0·5989 (3)	3·5 (1)
C(11)	0·4661 (4)	0·4809 (4)	0·6813 (5)	3·8 (3)	0·4655 (2)	0·4807 (2)	0·6804 (3)	3·5 (1)
C(12)	0·4791 (5)	0·5319 (4)	0·7088 (5)	4·5 (3)	0·4792 (3)	0·5318 (2)	0·7079 (4)	4·7 (2)
C(21)	0·3905 (4)	0·2464 (4)	0·5308 (5)	3·0 (3)	0·3902 (3)	0·2456 (3)	0·5309 (3)	3·9 (2)
C(22)	0·4024 (4)	0·2418 (4)	0·4767 (5)	4·0 (3)	0·4040 (3)	0·2418 (3)	0·4787 (3)	4·1 (2)
C(23)	0·3705 (4)	0·2098 (4)	0·4106 (5)	3·9 (3)	0·3707 (3)	0·2099 (3)	0·4107 (3)	4·5 (2)
C(24)	0·3851 (5)	0·2074 (5)	0·3533 (6)	6·0 (4)	0·3848 (3)	0·2081 (4)	0·3527 (4)	6·0 (2)
C(25)	0·4361 (5)	0·2448 (6)	0·3782 (6)	8·5 (4)	0·4359 (4)	0·2463 (5)	0·3777 (4)	8·1 (3)
C(26)	0·3272 (5)	0·2202 (6)	0·2649 (6)	7·1 (4)	0·3267 (4)	0·2203 (5)	0·2638 (4)	8·0 (3)
C(27)	0·4085 (5)	0·1562 (6)	0·3563 (6)	7·2 (4)	0·4094 (4)	0·1553 (5)	0·3564 (5)	8·4 (3)
C(28)	0·3228 (4)	0·1804 (4)	0·3973 (5)	4·5 (3)	0·3229 (3)	0·1809 (3)	0·3971 (4)	4·9 (2)
C(29)	0·3097 (4)	0·1824 (4)	0·4500 (5)	4·0 (3)	0·3088 (3)	0·1835 (3)	0·4499 (3)	4·4 (2)
C(30)	0·2576 (4)	0·1503 (5)	0·4361 (6)	6·2 (4)	0·2545 (3)	0·1526 (4)	0·4316 (5)	6·8 (2)
C(31)	0·2565 (5)	0·1567 (6)	0·5051 (7)	8·6 (4)	0·2556 (3)	0·1570 (4)	0·5061 (5)	8·7 (3)
C(32)	0·2658 (6)	0·0954 (6)	0·4303 (8)	9·5 (5)	0·2624 (5)	0·0971 (5)	0·4261 (7)	11·9 (4)
C(33)	0·1913 (5)	0·1668 (7)	0·3546 (8)	10·3 (6)	0·1902 (4)	0·1684 (6)	0·3525 (6)	9·6 (4)
C(34)	0·3441 (4)	0·2162 (4)	0·5160 (5)	4·1 (3)	0·3437 (3)	0·2167 (3)	0·5157 (3)	4·1 (2)
C(35)	0·3899 (4)	0·5037 (4)	0·5303 (5)	3·4 (3)	0·3903 (2)	0·5042 (3)	0·5305 (3)	3·7 (2)
C(36)	0·3249 (4)	0·5084 (4)	0·4769 (5)	3·7 (3)	0·3254 (2)	0·5080 (3)	0·4790 (3)	4·0 (2)
C(37)	0·2902 (4)	0·5401 (4)	0·4099 (5)	3·9 (3)	0·2905 (3)	0·5403 (3)	0·4103 (3)	4·3 (2)
C(38)	0·2186 (5)	0·5422 (5)	0·3533 (6)	6·0 (4)	0·2177 (3)	0·5419 (3)	0·3520 (4)	6·0 (2)
C(39)	0·1925 (5)	0·5050 (6)	0·3793 (7)	8·3 (5)	0·1923 (3)	0·5042 (5)	0·3788 (5)	8·3 (3)
C(40)	0·1872 (5)	0·5291 (6)	0·2642 (7)	6·9 (5)	0·1869 (4)	0·5288 (5)	0·2636 (5)	7·6 (3)
C(41)	0·1976 (5)	0·5933 (6)	0·3568 (7)	7·3 (4)	0·1976 (4)	0·5942 (5)	0·3576 (6)	9·1 (3)
C(42)	0·3245 (4)	0·5696 (4)	0·3969 (5)	4·3 (3)	0·3241 (3)	0·5690 (3)	0·3963 (4)	5·1 (2)
C(43)	0·3909 (4)	0·5680 (4)	0·4497 (5)	4·1 (3)	0·3910 (3)	0·5665 (3)	0·4495 (4)	4·5 (2)
C(44)	0·4279 (5)	0·5997 (5)	0·4355 (7)	6·6 (4)	0·4270 (3)	0·5984 (3)	0·4320 (4)	6·6 (2)
C(45)	0·4989 (5)	0·5926 (6)	0·5047 (8)	9·4 (5)	0·5001 (4)	0·5923 (4)	0·5045 (5)	8·4 (3)
C(46)	0·4154 (6)	0·6543 (6)	0·4309 (8)	9·5 (6)	0·4143 (5)	0·6526 (5)	0·4266 (8)	12·0 (5)
C(47)	0·4120 (5)	0·5816 (7)	0·3530 (7)	9·8 (5)	0·4132 (4)	0·5811 (5)	0·3542 (5)	9·8 (3)
C(48)	0·4219 (4)	0·5340 (4)	0·5154 (5)	4·1 (3)	0·4221 (2)	0·5338 (3)	0·5158 (3)	3·9 (2)
C(110)	0·333 (1)	0·443 (2)	0·285 (2)	20·0*	0·702	0·192	0·776	20·0*
C(111)	0·329 (1)	0·389 (2)	0·263 (2)	20·0*	0·691	0·140	0·772	20·0*
C(112)	0·359 (1)	0·383 (2)	0·224 (2)	20·0*	0·609	0·134	0·710	20·0*
C(113)	0·302 (1)	0·409 (1)	0·134 (2)	20·0*	0·724	0·474	0·315	20·0*
C(114)	0·317 (1)	0·466 (1)	0·157 (2)	20·0*	0·675	0·445	0·227	20·0*
C(115)	0·289 (1)	0·471 (2)	0·205 (2)	20·0*	0·593	0·001	0·519	20·0*
C(210)	0·682 (1)	0·133 (2)	0·762 (2)	20·0*	0·567	−0·042	0·478	20·0*
C(211)	0·613 (1)	0·123 (2)	0·712 (2)	20·0*	0·544	−0·050	0·392	20·0*
C(212)	0·571 (1)	0·161 (1)	0·636 (2)	20·0*	0·510	−0·010	0·342	20·0*
C(213)	0·582 (1)	0·212 (1)	0·652 (2)	20·0*	0·521	0·040	0·366	20·0*
C(214)	0·655 (1)	0·215 (2)	0·697 (2)	20·0*	0·567	0·050	0·461	20·0*
C(215)	0·696 (1)	0·184 (2)	0·784 (2)	20·0*	0·571	0·166	0·630	20·0*
C(310)	0·513 (1)	0·033 (1)	0·364 (2)	20·0*	0·591	0·219	0·660	20·0*
C(311)	0·520 (1)	−0·023 (1)	0·355 (2)	20·0*	0·664	0·224	0·699	20·0*
C(312)	0·549 (1)	−0·050 (1)	0·437 (2)	20·0*	0·671	0·390	0·235	20·0*
C(313)	0·586 (1)	−0·023 (1)	0·508 (2)	20·0*	0·643	0·385	0·285	20·0*
C(314)	0·593 (1)	0·023 (1)	0·509 (2)	20·0*	0·689	0·411	0·373	20·0*
C(315)	0·558 (1)	0·059 (2)	0·434 (2)	20·0*	0·683	0·464	0·344	20·0*
C(410)	0·666 (1)	0·284 (1)	0·503 (2)	20·0*				
C(411)	0·679 (1)	0·232 (1)	0·511 (2)	20·0*				
C(412)	0·620 (1)	0·198 (2)	0·434 (2)	20·0*				
C(413)	0·596 (1)	0·223 (1)	0·358 (2)	20·0*				
C(414)	0·572 (1)	0·275 (1)	0·348 (2)	20·0*				
C(415)	0·641 (1)	0·297 (1)	0·416 (2)	20·0*				

* Position [for Pd$^{\rm II}$(t$^{\rm t}$bhpp)] and isotropic temperature factor fixed.

2·849 (7) (I), 2·852 (10) Å (II). In order to accommodate this hydrogen bonding the phenyl rings are rotated by ±22° from the perpendicular reducing the steric interactions between the bulky *tert*-butyl groups of different molecules. An unusual feature of the structure is the presence of cyclohexane as a solvent of crystallization, which occupies the large voids in the structure between the sheets. However, the cyclohexane is not merely trapped but actually holds the sheets together, presumably by rather weak dispersion forces. The closest contact (Tables 3 and 4) between a solvent-molecule atom, C(214) [C(410), (II)], and a

Table 2. *Selected average bond lengths* (Å) *and angles* (°) *and comparison of* $\mathrm{Ni^{II}}$(*t*^{t}*bhpp*), $\mathrm{Pd^{II}}$(t^t*bhpp*) *and* $\mathrm{Zn^{II}}$(t^t*bhpp*) *structures*

			Ni*	Pd	Zn
M		N	1·913 (3)	2·022 (7)	2·041 (8)
N		C_α	1·379 (4)	1·384 (6)	1·366 (12)
C_α		C_β	1·429 (5)	1·432 (7)	1·440 (14)
C_β		C_β	1·340 (5)	1·329 (8)	1·35 (2)
C_α		C_m	1·382 (5)	1·380 (8)	1·392 (14)
C_m		C_p	1·497 (4)	1·509 (8)	1·491 (13)
C		O	1·389 (4)	1·379 (9)	1·377 (12)
M		C_α	2·961 (6)	3·058 (5)	3·052 (9)
M		C_m	3·367 (9)	3·431 (6)	3·441 (9)
N†		N′	2·706 (6)	2·860 (7)	2·886 (11)
N		N″	3·826 (8)	4·041 (10)	4·082 (11)
N	*M*	N′	90·0 (1)	90·0 (2)	90·0 (3)
N	*M*	N″	179·1 (1)	180·0 (2)	179·8 (4)
M	N	C_α	127·4 (2)	126·5 (4)	126·6 (5)
C_α	N	$C_{\alpha'}$	105·2 (3)	106·9 (5)	107·8 (9)
N	C_α	C_β	110·1 (3)	108·3 (5)	108·7 (8)
N	C_α	C_m	125·3 (3)	125·7 (5)	126·6 (9)
C_α	C_b	C_β	107·3 (3)	108·2 (5)	107·3 (9)
C_α	C_m	C_m	121·3 (3)	125·5 (5)	124·5 (9)
C_β	C_α	C_α	124·3 (3)	126·0 (5)	124·6 (8)

* Data from Golder, Nolan, Povey & Traylor (1988).
† N—N′, adjacent N atoms; N—N″, opposite N atoms.

tert-butyl C atom, C(32) [C(46)], is 3·79 Å (3·77 Å). The structural role of cyclohexane is indicated by the fact that the crystals no longer diffract when allowed to dry out – photographs taken of a crystal mounted on a fibre showed the appearance of powder rings prior to diffraction ceasing entirely. This must be due to the loss of cyclohexane since no dichloromethane was found in the crystal structure. A search of the Cambridge Structural Database (Allen *et al.*, 1979) revealed 26 structures reported with cyclohexane as the solvent of crystallization, at least two of which are unstable by loss of solvent (Brock & Webster, 1976; Masamune, Hanzawa & Williams, 1982).

In view of the very low calculated densities [0·819 (I), 0·843 (II) Mg m^{-3}], more solvent molecules than were found were expected to be present in the lattice. The solvent molecules located, however, were not disordered significantly, the isotropic temperature factors were high and only one chair form was present at each location. The density could not be measured experimentally to determine the actual number of solvent molecules present because of the very rapid loss of solvent from the lattice. A density similar to that calculated for $\mathrm{Ni^{II}}$(t^{t}bhpp) [$D_x = 1{\cdot}01$ Mg m^{-3} (Golder, Nolan, Povey & Traylor, 1988)] is obtained with 7 cyclohexane molecule per asymmetric unit or 28 per unit cell.

The fact that the $\mathrm{Pd^{II}}$ complex is planar while the $\mathrm{Ni^{II}}$ complex is highly puckered is due largely to the different ionic radii of the metal ions. A planar metalloporphyrin is estimated to have a hole radius of 2·01 Å (Hoard, 1975) and in order to retain planarity the metal radius should not be less than 1·96 Å. Therefore, while the ionic radius of $\mathrm{Pd^{II}}$ is compatible with porphyrin planarity the much smaller ionic radius of $\mathrm{Ni^{II}}$ causes severe ruffling of the porphyrin core. This structural difference may account for the contrasting behaviour of these complexes towards aerial oxidation in basified solutions (Golder, Nolan, Povey & Milgrom, 1987). In the $\mathrm{Ni^{II}}$ complex the *meso* substituents may achieve a degree of overlap with the porphyrin π system and facilitate oxidation. In the $\mathrm{Pd^{II}}$ complex, on the other hand, the planarity of the porphyrin ligand prevents this from occurring. Although the $\mathrm{Zn^{II}}$ and $\mathrm{Pd^{II}}$ complexes are structurally similar, the chemical reactivity of the former complex resembles that of $\mathrm{Ni^{II}}$. It may well be, however, that in the presence of hydroxide ion (the added base) $\mathrm{Zn^{II}}$ becomes pentacoordinate, causing the porphyrin to become nonplanar. This is consistent with previously reported structures of $\mathrm{Zn^{II}}$–porphyrins in the presence of added ligands (Bobrik & Walker, 1980; Collins & Hoard, 1970; Cullen & Meyer, 1976).

Table 3. *Close contacts* (< 4·0 Å) *for* $\mathrm{Pd^{II}}$(t^t*bhpp*) (Å)

E.s.d.'s are 0·007–0·010 Å.

C6	C31	3·800	C7	C31	3·569	C7	C45	3·888
C7	C110	3·966	C7	C111	3·982	C8	C31	3·904
C8	C45	3·546	C9	C45	3·775	C12	C213	3·901
C27	C41	3·798	C31	C111	3·923	C32	C214	3·793
C32	C213	3·970	C36	C213	3·987	C46	C114	3·868
C46	C115	3·912	C214	C310	3·916	C313	C313	3·554

Table 4. *Close contacts* (< 4·0 Å) *for* $\mathrm{Zn^{II}}$(t^t*bhpp*) (Å)

E.s.d.'s are 0·010–0·015 Å.

C6	C31	3·846	C7	C31	3·602	C7	C45	3·923
C7	C215	3·909	C8	C31	3·915	C8	C45	3·601
C9	C45	3·831	C12	C114	3·892	C27	C41	3·811
C31	C215	3·815	C32	C313	3·936	C32	C114	3·896
C45	C110	3·912	C46	C410	3·766	C112	C415	3·779
C113	C415	3·858	C211	C312	3·932	C211	C311	3·995
C212	C312	3·963	C311	C311	3·837	C414	C414	3·400

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Structures of Tetranitratobis(tripyrrolidinophosphine oxide)uranium(IV) and Tetranitratobis(triphenylphosphine oxide)uranium(IV)

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Abstract. (1) $[U(NO_3)_4(C_{12}H_{24}N_3OP)_2]$, $M_r = 1000\cdot7$, tetragonal, $P4_12_12$, $a = 10\cdot607\ (11)$, $c = 33\cdot497\ (4)$ Å, $V = 3769\ (1)$ Å^3, $Z = 4$, $D_x = 1\cdot76$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0\cdot71069$ Å, $\mu = 4\cdot42$ mm^{-1}, $F(000) = 1984$, $T = 243\ (3)$ K, final $wR = 0\cdot050$ ($R = 0\cdot070$) for 1883 independent observed reflections. (2) $[U(NO_3)_4(C_{18}H_{15}OP)_2]$, $M_r = 1042\cdot7$, monoclinic, $P2_1/n$, $a = 13\cdot996\ (1)$, $b = 17\cdot461\ (3)$, $c = 16\cdot438\ (2)$ Å, $\beta = 91\cdot13\ (1)°$, $V = 4016\ (1)$ Å^3, $Z = 4$, $D_x = 1\cdot72$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0\cdot71069$ Å, $\mu = 3\cdot99$ mm^{-1}, $F(000) = 2096$, $T = 295$ K, $wR = 0\cdot053$ ($R = 0\cdot094$) for 5969 observed reflections. The uranium(IV) is ten-coordinated in both complexes, with the U—O distances for the phosphoryl groups [mean = $2\cdot234\ (9)$ Å] significantly shorter than the U—O distances for the nitrate groups [mean = $2\cdot470\ (12)$ Å].

Introduction. The thermal decomposition of $[U(NO_3)_4L_2]$ where L = tris(dimethylamino)phosphine oxide (tdpo), triphenylphosphine oxide (tppo) and trispyrrolidinophosphine oxide (tpyrp) has been investigated (Strydom & van Vuuren, 1986). From the observed enthalpy of the decomposition reaction an order of the stability of the complexes was proposed as:

$$[U(NO_3)_4(tppo)_2] > [U(NO_3)_4(tdpo)_2] > [U(NO_3)_4(tpyrp)_2].$$

Crystal-structure determinations of uranium nitrate complexes are mainly concerned with the structures of uranyl nitrato complexes, and no structure determinations of a uranium(IV) nitrato complex could be found in the Cambridge Structural Database (see Allen, Kennard & Taylor, 1983). This may be a result of the apparent instability of some of the uranium(IV) nitrates in X-rays: it is not yet possible to obtain X-ray-stable crystals of the $[U(NO_3)_4(tdpo)_2]$ complex, and usable diffraction data for the $[U(NO_3)_4(tpyrp)_2]$ complex had to be obtained at low temperature. It was of interest to obtain structural data for these complexes in order to gain a better understanding of the related solid-state chemistry, and in this paper we present the first crystal structures of uranium(IV) nitrato complexes, that of $[U(NO_3)_4(tpyrp)_2]$ (1) and $[U(NO_3)_4(tppo)_2]$ (2).

Experimental. Crystals obtained from the slow evaporation from methylene chloride solutions in a petroleum ether atmosphere for both (1) and (2). Crystal sizes: (1) $0\cdot17 \times 0\cdot20 \times 0\cdot26$, (2) $0\cdot30 \times 0\cdot23 \times 0\cdot12$ mm. Lattice parameters refined using 25 reflections in the ranges (1) $7 \le \theta \le 17$ and (2) $7 \le \theta \le 19°$, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω–2θ scans in range $3 \le \theta \le 25°$, scan angle (1) $(0\cdot53 + 0\cdot34\tan\theta)$, (2) $(0\cdot57 + 0\cdot34\tan\theta)°$. Scan rate variable (1) $0\cdot05°$ s^{-1}, max. time 50 s refl^{-1}, (2) $0\cdot092°$ s^{-1}, max. time 50 s refl^{-1}. Range of hkl: (1) $0 \le h \le 12$, $0 \le k \le 12$, $0 \le l \le 40$, (2) $0 \le h \le 16$, $0 \le k \le 20$, $-19 \le l \le 19$. For (1) 2031 reflections measured, 1704 observed $[I > 2\sigma(I)]$, for (2) 7310 reflections measured, 4495 observed $[I > 2\sigma(I)]$. Stan-

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