

The Structure of (5,10,15,20-Tetraphenylporphinato)gold(III) Tetrachloroaurate(III)

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Abstract. $[\text{Au}(\text{C}_{44}\text{H}_{28}\text{N}_4)][\text{AuCl}_4]$, $M_r = 1148.5$, triclinic, $P\bar{1}$, $a = 9.0697$ (23), $b = 10.0030$ (15), $c = 11.9912$ (18) Å, $\alpha = 70.600$ (11), $\beta = 80.544$ (16), $\gamma = 71.485$ (16)°, $V = 970.91$ (31) Å³, $Z = 1$, $D_x = 1.95$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 80.2$ cm⁻¹, $F(000) = 546$, $T = 298$ K, $R = 0.0248$ for 1906 observed reflections. The X-ray analysis indicates that (5,10,15,20-tetraphenylporphinato)gold(III) is a planar four-coordinate complex. The porphyrin Au atom is located at an inversion center with Au–N bond distances of 2.004 (6) and 2.029 (7) Å and N(1)–Au(1)–N(2) bond angles of 89.9 (3) and 90.1 (3)°. The square-planar tetrachloroaurate counteranion is non-bonding. The Cl atoms are positioned 3.520 and 4.058 Å from the porphinato Au center. Additionally, the porphyrin ring does not display any significant out-of-plane ruffling of individual C atoms.

Introduction. The structure of four-coordinate (5,10,15,20-tetraphenylporphinato)metal complexes of the first-row transition elements Cr through Zn and second-row metals Pd and Ag have been previously reported (Kirner, Reed & Scheidt, 1977; Collman, Hoard, Kim, Lang & Reed, 1975; Madura & Scheidt, 1976; Fleischer, Miller & Webb, 1964; Scheidt, Kastner & Hatano, 1978; Scheidt & Reed, 1978; Scheidt, Mondal, Eigenbrot, Adler, Radanovich & Hoard, 1986). The metal ions of all of these derivatives, except MnTPP (TPP = 5,10,15,20-tetraphenylporphinato), lie in the plane of the porphinato core. The present paper reports the structure of a four-coordinate third-row transition-metal porphyrin, $[\text{Au}^{\text{III}}\text{TPP}][\text{AuCl}_4]$. The Au^{III} atom of this complex lies in the plane of the porphyrin ring and the tetrachloroaurate counter anion is not located within bonding distance of the gold porphyrin.

Experimental. $[\text{Au}^{\text{III}}\text{TPP}][\text{AuCl}_4]$ was synthesized as previously reported (Fleischer & Laszlo, 1968). A thin burnt-orange crystal plate (0.31 × 0.17 × 0.04 mm) was obtained by recrystallization from benzene. The data were collected on a Syntex P3/F diffractometer. The cell dimensions were determined by least-squares fit of 2θ for 25 reflections ($40 \leq 2\theta \leq 46.4^\circ$). Four standard reflections, 204, $0\bar{2}3$, $\bar{2}\bar{2}2$, $22\bar{2}$, were measured every 100 reflections with no significant fluctuation.

Intensities were obtained for $3 \leq 2\theta \leq 50^\circ$, $-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-15 \leq l \leq 15$, $\theta/2\theta$ scans, with max. $[(\sin\theta)/\lambda] = 0.595$ Å⁻¹. A scan speed of 2° min⁻¹ and a scan range of 0.9–1.1° were used. 5680 reflections were measured, with 2796 unique reflections. $R_{\text{merge}} = 0.013$. For $F > 6\sigma(F)$, there were 1906 observed reflections. Empirical laminar absorption corrections from ψ scans were applied using 360 ψ -scan data points measured for 10 reflections with a diffraction vector increment of 10° (36 scans reflection⁻¹). The principal face was (0,0,1). The internal merging R for the ψ scans improved from 0.103 to 0.028. Min. and max. transmission coefficients were 0.827 and 0.252.

The Au atoms were located using Patterson methods (0,0,0 and $0, \frac{1}{2}, 0$). The model was then expanded by Fourier methods and refined using blocked cascade diagonal least-squares calculations minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, where $w = 1.0 / \{\sigma^2(F_o) + 0.0002(F_o^2)\}$. There were 184 least-squares parameters. Positional and anisotropic parameters were refined for all non-H atoms, except for the disordered phenyl C atoms. The H atoms were not included in the final model, although several were observed in the final difference map. The initial difference map revealed satellite peaks near the phenyl C atoms, indicating disorder of the phenyl groups. In all further refinements, this disorder was modeled using rigid groups with partial occupancy. For the observed reflections, $R = 0.0248$, $wR = 0.0325$ and $S = 1.711$. For all data, $R = 0.0421$ and $wR = 0.0363$. $(\Delta/\sigma)_{\text{av}} = 0.004$ and $(\Delta/\sigma)_{\text{max}} = -0.017$ in final cycle. $(\Delta\rho)_{\text{max}} = 0.88$ (0.9 Å from the porphyrin Au atom) and $(\Delta\rho)_{\text{min}} = -0.45$ e Å⁻³. Neutral-atom scattering factors were used (*International Tables for X-ray Crystallography*, 1974). *SHELXTL* programs were employed for structure solution, refinement and plotting (Sheldrick, 1985).*

* Lists of structure factors, anisotropic thermal parameters, deviations from the least-squares plane and full lists of coordinates and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44094 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The $[\text{Au}^{\text{III}}\text{TPP}][\text{AuCl}_4]$ numbering sequence and molecular structure appear in Figs. 1 and 2. The 'prime' notation indicates atoms which are generated by crystallographic inversion centers located at each of the Au atoms. The final atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are given in Table 1 (the H atoms were not located in this structure). Important bond lengths and bond angles are given in Table 2.

The structures of various tetraphenylporphyrins have been previously reported (Scheidt, 1977). The bond lengths and angles associated with the porphyrin ring of the structure are in good agreement with previous studies. Similarly, the Au—N bond distances of 2.029 (7) and 2.004 (6) Å compare closely to those reported for $\text{Au}^{\text{III}}\text{TPP}\text{Cl}$ (2.00 Å) (Timkovich & Tulinsky, 1977) as well as the Au—N bond lengths (1.969–2.142 Å) in other mononuclear gold(III) compounds (Melnik & Parish, 1986). Least-squares-plane calculations indicate that the Au atom lies in the plane

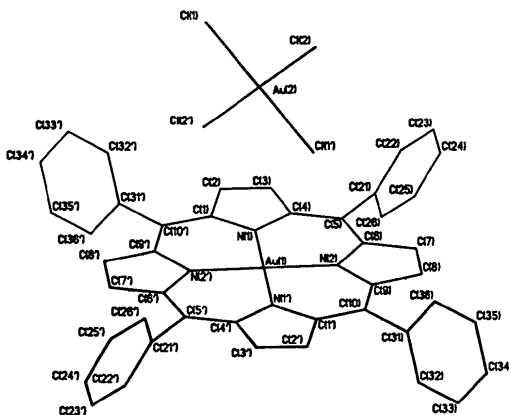


Fig. 1. Numbering scheme for the gold porphyrin.

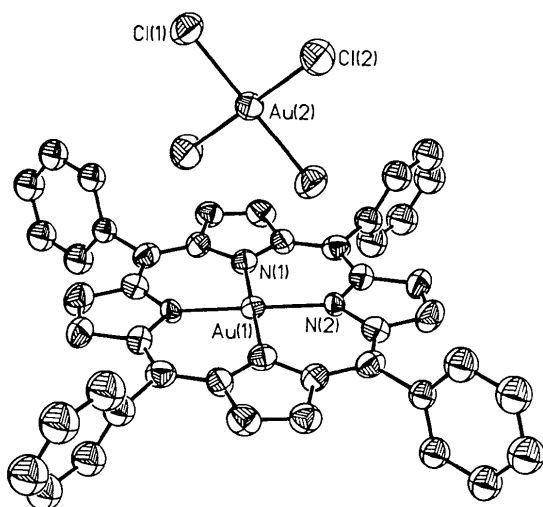


Fig. 2. Molecular structure of $[\text{Au}^{\text{III}}\text{TPP}][\text{AuCl}_4]$.

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Au(1)	0	0	0	34 (1)*
Au(2)	0	5000	0	44 (1)*
Cl(1)	-1109 (3)	6705 (3)	1000 (2)	66 (1)*
Cl(2)	1924 (3)	6125 (3)	-770 (2)	71 (1)*
N(1)	-2057 (7)	1289 (6)	-701 (5)	41 (2)*
N(2)	1054 (7)	304 (6)	-1633 (5)	35 (2)*
C(1)	-3453 (9)	1658 (8)	-70 (7)	41 (3)*
C(2)	-4623 (10)	2637 (8)	-871 (8)	50 (3)*
C(3)	-3890 (10)	2819 (9)	-1987 (8)	53 (4)*
C(4)	-2308 (10)	1992 (8)	-1857 (7)	44 (3)*
C(5)	-1226 (10)	1946 (8)	-2815 (7)	48 (3)*
C(6)	379 (10)	1149 (8)	-2687 (7)	45 (3)*
C(7)	1517 (10)	1103 (9)	-3684 (8)	53 (4)*
C(8)	2926 (10)	217 (10)	-3203 (8)	60 (4)*
C(9)	2604 (10)	-284 (8)	-1921 (7)	46 (3)*
C(10)	-1192 (8)	3759 (9)	-1173 (7)	46 (3)*
C(21)	-1765 (17)	2885 (12)	-4002 (9)	52 (4)
C(22)	-1327	4175	-4590	62 (4)
C(23)	-1754	4978	-5742	69 (5)
C(24)	-2620	4493	-6307	78 (6)
C(25)	-3058	3204	-5720	78 (6)
C(26)	-2630	2400	-4568	74 (5)
C(31)	5348 (8)	-1816 (8)	-1661 (8)	41 (3)
C(32)	5764	-3237	-1771	52 (3)
C(33)	7251	-3833	-2234	62 (4)
C(34)	8322	-3007	-2587	70 (4)
C(35)	7906	-1586	-2477	65 (4)
C(36)	6419	-991	-2014	61 (4)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Selected bond lengths (Å) and bond angles (°)

Au(1)—N(1)	2.029 (7)	Au(1)—N(2)	2.004 (6)
Au(2)—Cl(1)	2.287 (5)	Au(2)—Cl(2)	2.279 (5)
N(1)—C(1)	1.373 (10)	N(1)—C(4)	1.350 (10)
N(2)—C(6)	1.380 (9)	N(2)—C(9)	1.376 (10)
C(1)—C(2)	1.434 (11)	C(2)—C(3)	1.375 (13)
C(3)—C(4)	1.414 (11)	C(4)—C(5)	1.386 (12)
C(5)—C(6)	1.426 (11)	C(5)—C(21)	1.482 (13)
C(5)—C(41)	1.520 (14)	C(6)—C(7)	1.448 (12)
C(8)—C(7)	1.391 (12)	C(8)—C(9)	1.460 (12)
C(9)—C(10)	1.375 (11)	C(10)—C(31)	1.484 (11)
C(10)—C(1')	1.415 (11)		
N(1)—Au(1)—N(2)	89.9 (3)	N(2)—Au(1)—N(1')	90.1 (3)
Cl(1)—Au(2)—Cl(2)	89.3 (2)	Cl(2)—Au(2)—Cl(1')	90.7 (2)

of the porphyrin core and also that the entire porphyrin ring itself is planar. The deviations of Au, N and C atoms from the least-squares plane do not exceed 0.03 Å,* which, with error considerations, are negligible (Stout & Jensen, 1968, p. 424). Similar planarity has been reported for ZnTPP, Co^{III}TPP and several other TPP derivatives (Scheidt, Kastner & Hatano, 1978; Madura & Scheidt, 1976).

The square-planar AuCl_4^- counteranion is not located within bonding distance of the porphyrin center. The Au(1)—Au(2) distance is over 4 Å. The Au(1)—Cl contacts are 3.520 Å for Cl(1') and 4.058 Å for Cl(2'). The Au—Cl bond lengths of 2.287 (5) and 2.279 (5) Å

* See deposition footnote.

are similar to those reported for other AuCl₄⁻ anions (2.28 Å).

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Structure of Dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II) Dichloromethane Solvate

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Abstract. [NiCl₂(C₂₆H₂₄P₂)]·CH₂Cl₂, *M_r* = 612.95, monoclinic, *P*2₁/*c*, *a* = 12.248 (3), *b* = 15.388 (3), *c* = 15.290 (4) Å, β = 104.77 (2)°, *U* = 2787 (1) Å³, *Z* = 4, *D_x* = 1.461 g cm⁻³, *Mo Kα*, λ = 0.71073 Å, μ = 12.1 cm⁻¹, *F*(000) = 1256, *T* = 295 K, *R* = 0.056 for 3610 observed reflections with *I* > 2.5σ(*I*). The square-planar geometry about Ni is defined by the two P and two Cl atoms to which it is bonded. The P–Ni–P bite angle of the chelating Ph₂PCH₂CH₂PPh₂ ligand is 86.93 (6)° and the Cl–Ni–Cl angle is 95.47 (6)°. Distances to the coordinating ligands are Ni–Cl 2.205 (2) and 2.195 (2) Å, Ni–P 2.157 (2) and 2.145 (2) Å.

Introduction. In the course of investigations on the coordinating properties of chlorosulfine ligands, it was shown that metals can insert into the C–Cl bond of the chlorosulfine (Alper, 1975; Gosselink, van Koten, Vrieze, Zwanenburg & Lammerink, 1979; Gotzfried & Beck, 1980; Gosselink, Brouwers, van Koten & Vrieze, 1982; Gosselink, Bulthuis & van Koten, 1982). We have

examined the reaction of chlorosulfines with nickelbis(1,5-cyclooctadiene) in the presence of 1,2-bis(diphenylphosphino)ethane (dppe). The initial adduct of the chlorosulfine with the nickel dppe species readily decomposes to NiCl₂dppe, the crystal structure of which is presented here.

Experimental. Orange-brown crystal (0.20 × 0.20 × 0.50 mm) glued on top of a glass fiber with the longest dimension approximately parallel to the φ axis. Enraf-Nonius CAD-4F diffractometer, Zr-filtered Mo *Kα* radiation. 8436 reflections scanned, ω/2θ scan; Δω = (0.60 + 0.35 tan θ)°; 1.33 < θ < 30.0°; *h* –17→16, *k* 0→21, *l* 0→21. Three reference reflections (504: e.s.d. 0.8%; 463: e.s.d. 0.8%; 346: e.s.d. 0.8%); linear decay of 16% during 140 h of X-ray exposure time. Cell dimensions from the setting angles of 16 reflections (10 < θ < 11.5°). Space group *P*2₁/*c* from the observed extinctions (0*k*0: *k* = 2*n* + 1; *h*0*l*: *l* = 2*n* + 1). Correction for Lp and linear decay but not for absorption. [A 360° ψ scan for the close to axial reflection 013 did not show a variation higher than 6% in the intensity.] 8108 unique reflections of which

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