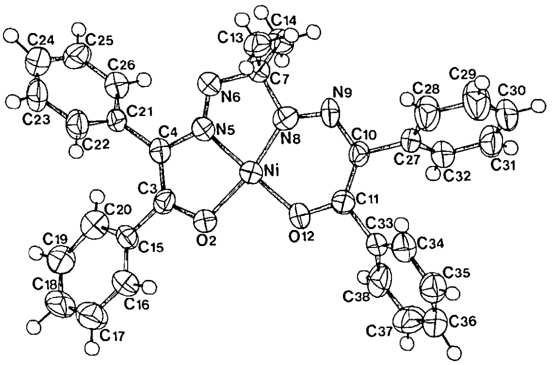

Fig. 1. Configuration de la molécule NiMMK.

Par rapport au plan moyen du macrocycle, les plans des groupements phényles sont inclinés de 34,6 (4), 59,0 (4), 62,5 (4) et 51,6 (4)° respectivement pour les groupes Ph1, Ph2, Ph3 et Ph4, ce qui limite la participation des phényles à la délocalisation électronique dans les cycles chélates. Les noyaux benzéniques sont peu perturbés, les distances C—C vont de 1,342 à 1,410 Å; les moyens distances C—C valent 1,38 (1), 1,38 (1), 1,37 (1) et 1,38 (1) Å respectivement pour Ph1, Ph2, Ph3 et Ph4. Les distances C—H sont comprises entre 0,81 (9) et 1,03 (7) Å. Il n'existe pas de contacts intermoléculaires importants, la plus courte distance intermoléculaire est de 3,39 (1) Å entre deux atomes de carbone benzéniques, toutes les autres distances sont supérieures à 3,5 Å. En outre, la distance entre atomes de nickel [5,586 (2) Å entre Ni reliés par le centre de symétrie] exclut toute interaction entre centres métalliques.

Des études radiocristallographiques sont en cours sur des composés homologues possédant des groupements moins encombrants que les phényles afin de vérifier, d'une part le mode de coordination et, d'autre part, la réactivité potentielle des fonctions carbonylées, la condensation de ces fonctions sur les hydrazones étant une voie d'accès à des entités polymétalliques polyaza.

Références

Bonfoey, D. B. & Melson, G. A. (1975). *Inorg. Chem.* **14**, 309–313.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Funke, L. A. & Melson, G. A. (1975). *Inorg. Chem.* **14**, 306–308.

Kerwin, C. M. & Melson, G. A. (1972). *Inorg. Chem.* **11**, 726–729.

Kerwin, C. M. & Melson, G. A. (1973). *Inorg. Chem.* **12**, 2410–2413.

Melson, G. A. (1974). *Inorg. Chem.* **13**, 994–996.

Nafisi-Movaghar, K. & Melson, G. A. (1975). *Inorg. Chem.* **14**, 2013–2016.

Peng, S. M., Gordon, G. C. & Goedken, V. L. (1978). *Inorg. Chem.* **17**, 119–126.

Prewitt, C. T. (1966). *SFLS5. A Fortran IV Full-Matrix Crystallographic Least-Squares Program.* Rapport ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Shalhoub, G. M., Reider, C. A. & Melson, G. A. (1982). *Inorg. Chem.* **21**, 1998–2002.

Acta Cryst. (1984). C**40**, 1357–1359

Tribromo(triethylphosphine)gold(III), $[AuBr_3\{P(C_2H_5)_3\}]$

By Drake S. Eggleston,*† Daniel F. Chodosh,† David T. Hill‡ and Gerald R. Girard‡

Smith Kline & French Laboratories, 1500 *Spring Garden Street, PO Box* 7929, *Philadelphia, PA* 19101, *USA*

(*Received* 16 *February* 1984; *accepted* 9 *April* 1984)

Abstract. $M_r = 554{\cdot}9$, monoclinic, $P2_1/n$, $a = 7{\cdot}871\ (3)$, $b = 14{\cdot}171\ (5)$, $c = 11{\cdot}734\ (3)$ Å, $\beta = 94{\cdot}41\ (3)°$, $V = 1304{\cdot}9$ Å^3, $Z = 4$, D_m(flotation in $CH_2I_2/C_3H_6I_2$) $= 2{\cdot}80\ (2)$, $D_x = 2{\cdot}824$ g cm^{-3}, Mo $K\alpha$, $\lambda(K\alpha_1) = 0{\cdot}70926$, $\lambda(K\alpha_2) = 0{\cdot}71354$ Å, $\mu = 204{\cdot}34$ cm^{-1}, $F(000) = 1000$, $T = 293$ K, $R = 0{\cdot}032$, $wR = 0{\cdot}031$ for 1470 observations. The coordination environment of Au^{III} is square planar. An appreciable lengthening of the gold–bromide bond *trans* to the phosphine is observed, with the Au—P bond length normal for this type of compound. The molecules exist as monomers and there are no unusually short intermolecular distances.

Introduction. The biological activity of gold compounds has attracted considerable interest over the past fifty years. In particular, the use of gold complexes in the treatment of rheumatoid arthritis has been studied extensively (Sadler, 1976; Shaw, 1978; Brown & Smith, 1980). The immunopharmacology of gold complexes

---

* Author to whom correspondence should be addressed.

† Department of Analytical, Physical and Structural Chemistry.

‡ Department of Medicinal Chemistry.

0108-2701/84/081357-03$01.50

Table 1. *Positional and thermal parameters*

	x	y	z	B_{eq}(Å^2)*
Au	0·01091 (5)	0·02469 (3)	0·20800 (3)	3·42 (1)
Br(1)	0·1883 (2)	0·1232 (1)	0·3361 (1)	6·48 (3)
Br(2)	−0·1743 (2)	−0·07786 (9)	0·0917 (1)	6·26 (3)
Br(3)	0·2410 (2)	−0·0937 (1)	0·2090 (1)	7·61 (4)
P	−0·2010 (3)	0·1387 (2)	0·2150 (2)	3·08 (5)
C(1)	−0·117 (1)	0·2550 (7)	0·1926 (8)	3·9 (2)
C(2)	−0·382 (1)	0·1245 (8)	0·1143 (9)	5·0 (3)
C(3)	−0·277 (1)	0·1366 (8)	0·3568 (9)	4·5 (2)
C(12)	−0·043 (1)	0·2683 (7)	0·0802 (9)	5·1 (3)
C(22)	−0·504 (1)	0·2070 (10)	0·1050 (10)	7·0 (4)
C(32)	−0·321 (2)	0·0388 (9)	0·3968 (9)	6·0 (3)

* $B_{eq} = \frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

and their interactions with certain biomacromolecules such as proteins has been reviewed (Lewis & Walz, 1982). Recently, several gold(III) compounds were reported to bind DNA suggesting their possible utility as antineoplastic agents (Mirabelli, Sung, Bartus & Crooke, 1983). Although the mechanism by which gold(III) species bind to DNA is not known it is likely that the process involves labilization of one or more ligands from the gold(III) coordination sphere. Thus, detailed structural information on gold(III) compounds is of interest and the structure of tribromo(triethylphosphine)gold(III) was determined in order to ascertain the influence of the phosphine on the bonding of the coordinated bromides.

Experimental. Tribromo(triethylphosphine)gold(III) prepared as described (Mann & Purdie, 1940) and recrystallized from toluene to give red-orange prisms, m.p. 402–404 K. Crystal 0·08 × 0·15 × 0·50 mm mounted in a capillary with longest dimension parallel to φ. Enraf–Nonius CAD-4 diffractometer, graphite monochromator; systematic absences $0k0$ for k odd, $h0l$ for $h+l$ odd; cell constants from least-squares analysis of 25 reflections with $30 \leq 2\theta(\mathrm{Mo}) \leq 35°$ measured on the diffractometer. Intensity data collected in ω–θ scan mode, as suggested by peak-shape analysis; 2465 measured reflections, $2\theta \leq 50°$, $0 \leq h \leq 9$, $0 \leq k \leq 16$, $-14 \leq l \leq 14$; Lorentz-polarization correction, absorption correction based on ψ scans of nine reflections with $80 \leq \chi \leq 90°$, min. correction factor = 0·8955, max. correction factor = 0·9973; no systematic fluctuations in reflections $\bar{5}\bar{6}2$, $41\bar{7}$, 186 monitored at beginning, end and each 3 h during data collection (27 times); max. deviations in F 1·8, 2·0 and 1·8%, respectively; mean values of F 92·0 (5), 152·3 (9) and 107·0 (7), respectively. Programs in CAD-4 structure determination package with local modifications; position of gold atom located from Patterson map, remaining non-hydrogen atoms from difference Fourier map; anisotropic least-squares refinement (on F) of positions led to wR 0·043; weights $4F_o^2/\sigma^2(I)$; subsequent difference Fourier syntheses revealed positions for all 15 H atoms; methyl H atoms assigned fixed isotropic values of 7·0 Å^2, otherwise all parameters allowed to vary in five final cycles of least-squares refinement; weighting scheme above with $\sigma(I)$ as defined by Corfield, Doedens & Ibers (1967) with $p = 0·03$, $wR = 0·031$, $S = 1·20$, 1470 observations with $I \geq 3·0\sigma(I)$, 152 variables; extinction parameter included in later stages refined to 7·4 (1) × 10^{-8}; in final least-squares cycle max. Δ/σ 0·41; final difference Fourier map contained several peaks of heights 0·60 to 1·0 e Å^{-3} within 1 Å of gold atom, which presumably reflect a slight inefficiency in modeling thermal motion of this atom. Neutral-atom scattering factors and effects of anomalous dispersion for nonhydrogen atoms from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965).

Discussion. The positional parameters, along with their standard deviations as estimated from the inverse matrix, are listed in Table 1.* The structure of a single molecule is displayed in Fig. 1. The molecules exist as discrete monomers in the crystal lattice consisting of one gold(III) atom coordinated by three bromides and a phosphine ligand. As such, this molecule is quite similar to the square-planar complex Me_3PAuBr_3 which has been reported previously (Perutz & Weisz, 1946). The Au—Br bond lengths range from 2·407 (1) to 2·468 (1) Å and are comparable to bond lengths in

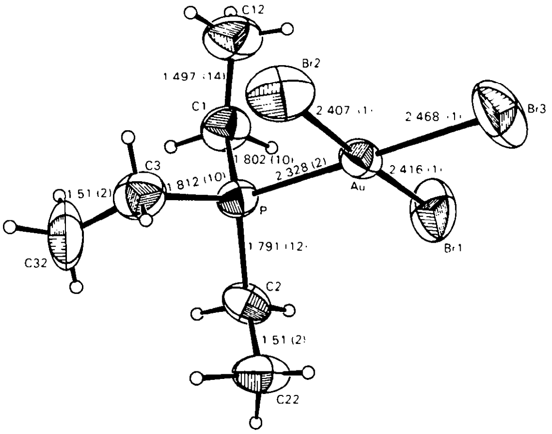

Fig. 1. View of a single molecule of tribromo(triethylphosphine)-gold(III) showing the labeling scheme employed. Thermal ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary size. (Distances in Å.)

---

* Lists of structure factors, H-atom positions, thermal parameters, bond distances and angles involving H atoms and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39382 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

other gold complexes containing coordinated bromide ligands (Bennett, Hoskins, Kneen, Nyholm, Hitchcock, Mason, Robertson & Towl, 1971; Komiya, Huffman & Kochi, 1977; Perutz & Weisz, 1946; Strähle & Bärnighausen, 1971). The two Au—Br bonds *trans* to one another, Au—Br(1) [2·416 (1) Å] and Au—Br(2) [2·407 (1) Å] are equivalent. By comparison the Au—Br(3) bond *trans* to the phosphine is lengthened considerably [2·468 (1) Å]. This observation is expected, however, owing to the strong *trans* influence of the coordinated phosphine (Cotton & Wilkinson, 1980). An analogous observation was reported for the crystal structure of trichloro(triphenylphosphine)gold(III) (Bandoli, Clemente, Marangoni & Catalini, 1973). The Au^{III}—P bond length of 2·328 (2) Å is quite normal for bonds of this type (Bandoli, Clemente, Marangoni & Catalini, 1973; Baker & Pauling, 1969).

The angles subtended at the gold atom are indicative of its square-planar coordination environment (see Table 2). Slight deviations from the ideal value of 90° in the P—Au—Br(1) [87·61 (7)°] and the P—Au—Br(2) [91·99 (7)°] angles are probably attributable to subtle adjustments owing to steric constraints of the phosphine ligand. The square-planar arrangement of atoms is further exemplified by the least-squares plane through the five atoms Au, Br(1), Br(2), Br(3), P, from which no atom deviates by more than 0·043 (1) Å.

There are no unusual intermolecular contacts within the crystal lattice. The closest Au–Au contact is 4·921 (1) Å while the closest intermolecular contact with Au is 3·910 (1) Å between Au and Br(2) of a molecule related by the crystallographic inversion center.

Table 2. *Bond angles* (°)

Br(1)—Au—Br(2)	176·05 (5)	Au—P—C(1)	111·0 (4)
Br(1)—Au—Br(3)	90·07 (5)	Au—P—C(2)	115·8 (5)
Br(1)—Au—P	87·61 (7)	Au—P—C(3)	108·1 (4)
Br(2)—Au—Br(3)	90·26 (5)	C(1)—P—C(2)	106·7 (6)
Br(2)—Au—P	91·99 (7)	C(1)—P—C(3)	107·4 (5)
Br(3)—Au—P	177·43 (7)	C(2)—P—C(3)	107·5 (6)
P—C(1)—C(12)	114·6 (7)	P—C(3)—C(32)	113·5 (8)
P—C(2)—C(22)	116·0 (10)		

References

BAKER, R. W. & PAULING, P. J. (1969). *J. Chem. Soc. Chem. Commun.* p. 745.

BANDOLI, G., CLEMENTE, D. A., MARANGONI, G. & CATALINI, L. (1973). *J. Chem. Soc. Dalton Trans.* pp. 886–889.

BENNETT, M. A., HOSKINS, K., KNEEN, W. R., NYHOLM, R. S., HITCHCOCK, P. B., MASON, R., ROBERTSON, G. B. & TOWL, A. D. C. (1971). *J. Am. Chem. Soc.* **93**, 4592–4594.

BROWN, D. H. & SMITH, W. E. (1980). *Chem. Soc. Rev.* **8**, 217–240.

CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.

COTTON, F. A. & WILKINSON, G. (1980). *Advanced Inorganic Chemistry*, 4th ed. New York: John Wiley.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 72. Birmingham: Kynoch Press.

KOMIYA, S., HUFFMAN, J. C. & KOCHI, J. K. (1977). *Inorg. Chem.* **16**, 1253–1255.

LEWIS, A. J. & WALZ, D. J. (1982). *Prog. Med. Chem.* **19**, 1–58.

MANN, F. G. & PURDIE, D. (1940). *J. Chem. Soc.* pp. 1235–1239.

MIRABELLI, C. K., SUNG, C. M., BARTUS, H. E. & CROOKE, S. T. (1983). *Proc. Am. Assoc. Cancer Res.* **24**, Abstract 1157.

PERUTZ, M. F. & WEISZ, O. (1946). *J. Chem. Soc.* pp. 438–442.

SADLER, P. J. (1976). *Struct. Bonding (Berlin)*, **29**, 171–219.

SHAW, C. F. (1978). *Inorg. Perspect. Biol. Med.* **2**, 287–355.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

STRÄHLE, J. & BÄRNIGHAUSEN, H. (1971). *Z. Kristallogr.* **134**, 471–472.

Acta Cryst. (1984). C**40**, 1359–1362

Structure of Tris(1,10-phenanthroline)cobalt(II) Diperchlorate Monohydrate, $[Co(C_{12}H_8N_2)_3](ClO_4)_2.H_2O$

BY D. BOYS, C. ESCOBAR AND O. WITTKE

Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 5487, *Santiago, Chile*

(*Received* 5 *January* 1984; *accepted* 24 *April* 1984)

Abstract. $M_r = 816{\cdot}48$, monoclinic, $C2/c$, $a = 36{\cdot}366$ (12), $b = 15{\cdot}854$ (2), $c = 12{\cdot}341$ (1) Å, $\beta = 102{\cdot}83$ (2)°, $V = 6938$ (2) Å^3, $Z = 8$, $D_m = 1{\cdot}547$ (5), $D_x = 1{\cdot}563$ (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}74$ mm^{-1}, $F(000) = 3336$, $T = 295$ K, final $R = 0{\cdot}086$ for 3849 independent observed reflections. The metal ion is coordinated to the six N atoms of the bidentate chelates in a distorted octahedral arrangement with average Co—N length of 2·127 (14) Å and average N—Co—N within each phenanthroline of 78·1 (4)°, where the standard deviations are based on the spread in values. This coordination is different from the tetragonally octahedral coordination present in the isostructural Cu^{II} analogue.

0108-2701/84/081359-04$01.50