Refinement

Refinement on F
$R = 0.056$
$wR = 0.063$
$S = 1.48$
1351 reflections
111 parameters
$w = 2.20/[\sigma^2(F_o) + 0.00074F_o^2]$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 1.57$ e Å^{-3}
$\Delta\rho_{min} = -1.72$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) for Br and Rh and from *SHELX*76 (Sheldrick, 1976) for all other atoms

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Rh(1)	−0.1422 (1)	−0.0475 (1)	0.4439 (1)	1.56
Br(1)	−0.0116 (2)	0.0919 (1)	0.4447 (1)	4.30
Br(2)	−0.2772 (2)	0.0137 (2)	0.5479 (1)	4.05
Br(3)	−0.0083 (2)	−0.1126 (2)	0.3408 (1)	4.32
P(1)	−0.2531 (4)	−0.1694 (3)	0.4588 (3)	2.55
C(1)	−0.4157 (17)	−0.1602 (14)	0.4585 (12)	3.74
C(2)	−0.225 (2)	−0.2157 (16)	0.5558 (12)	5.40
C(3)	−0.2203 (16)	−0.2565 (11)	0.3878 (13)	3.83
P(2)	−0.2574 (4)	0.0000 (3)	0.3383 (3)	2.31
C(4)	−0.3955 (17)	0.0541 (12)	0.3680 (13)	3.76
C(5)	−0.1782 (18)	0.0797 (12)	0.2760 (12)	3.60
C(6)	−0.310 (2)	−0.0800 (14)	0.2638 (10)	4.29

Table 2. *Selected geometric parameters* (Å, °)

Br(1)—Rh(1)	2.601 (2)	Br(2)—Rh(1)	2.456 (2)
Br(3)—Rh(1)	2.462 (2)	P(1)—Rh(1)	2.266 (5)
P(2)—Rh(1)	2.273 (5)	C(1)—P(1)	1.790 (19)
C(2)—P(1)	1.779 (18)	C(3)—P(1)	1.825 (18)
C(4)—P(2)	1.801 (19)	C(5)—P(2)	1.829 (18)
C(6)—P(2)	1.841 (19)		
Br(2)—Rh(1)—Br(1)	90.2 (1)	Br(3)—Rh(1)—Br(1)	91.1 (1)
Br(3)—Rh(1)—Br(2)	178.6 (1)	P(1)—Rh(1)—Br(1)	173.4 (1)
P(1)—Rh(1)—Br(2)	85.7 (1)	P(1)—Rh(1)—Br(3)	92.9 (1)
P(2)—Rh(1)—Br(1)	92.2 (1)	P(2)—Rh(1)—Br(2)	94.0 (1)
P(2)—Rh(1)—Br(3)	86.5 (1)	P(2)—Rh(1)—P(1)	93.3 (2)
C(1)—P(1)—Rh(1)	117.9 (7)	C(2)—P(1)—Rh(1)	110.1 (8)
C(2)—P(1)—C(1)	102. (1)	C(3)—P(1)—Rh(1)	116.5 (6)
C(3)—P(1)—C(1)	104.7 (9)	C(3)—P(1)—C(2)	103 (1)
C(4)—P(2)—Rh(1)	114.4 (7)	C(5)—P(2)—Rh(1)	112.7 (6)
C(5)—P(2)—Rh(1)	103.6 (9)	C(6)—P(2)—Rh(1)	117.6 (6)
C(6)—P(2)—C(4)	103 (1)	C(6)—P(2)—C(5)	103 (1)

The crystal was mounted on a glass fibre with cyanoacrylate resin. The scan width and horizontal counter aperture were $(1.10 + 0.34\tan\theta)°$ and $(2.70 + 1.05\tan\theta)$ mm, respectively. The absorption correction was according to Coppens, Leiserowitz & Rabinovich (1965) and used $10\times12\times12$ sampling points with maximum and minimum corrections of 3.195 and 2.439, respectively. Data reduction and application of Lorentz, polarization and absorption corrections were carried out using the Enraf–Nonius *SDP* system (Frenz, 1985). The structure was solved by heavy-atom methods using *SHELX*76 (Sheldrick, 1976) and the solutions were extended by difference Fourier methods. H atoms were included at calculated sites with group isotropic displacement parameters and all other atoms were refined anisotropically. All calculations were carried out using *SHELX*76.

We gratefully acknowledge support from the Australian Research Council

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55822 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1014]

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Two Crystalline Polymorphs of Chloro-[tris(2-cyanoethyl)phosphine]gold(I), $[AuCl(C_9H_{12}N_3P)]$

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Abstract

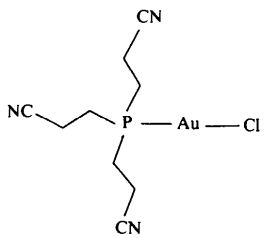
Polymorph (1) has Au—Cl and Au—P bond lengths of 2.295 (3) and 2.225 (3) Å, respectively, with a P—Au—Cl bond angle of 177.8 (1)°. Polymorph (2) has Au—Cl and Au—P bond lengths of 2.315 (2) and 2.243 (2) Å, respectively, with a P—Au—Cl bond angle of 177.1 (1)°. Polymorph (2) crystallizes with two of the C≡N groups alongside the Au^I center in the asymmetric unit.

Comment

We have been studying the coordination and reaction chemistry of complexes containing tris(2-cyanoethyl)phosphine (Khan, King, Fackler &

Winpenny, 1993). During our continued study of the bis[tris(2-cyanoethyl)phosphine]gold(I) cation (Assefa, Staples & Fackler, 1994) we isolated two crystalline polymorphs of the monomer chloro[tris(2-cyanoethyl)phosphine]gold(I).

Polymorph (1) is shown in Fig. 1 and polymorph (2) in Fig. 2.



(1), (2)

There have been several reports of chloro[triorganophosphine]gold(I) monomeric complexes. The Au—Cl and Au—P bond lengths in polymorph (1) are within the ranges observed previously (see Table 3). The Au—P bond length in polymorph (2) is at the long extreme of this range and the Au—Cl distance is slightly longer than those reported previously.

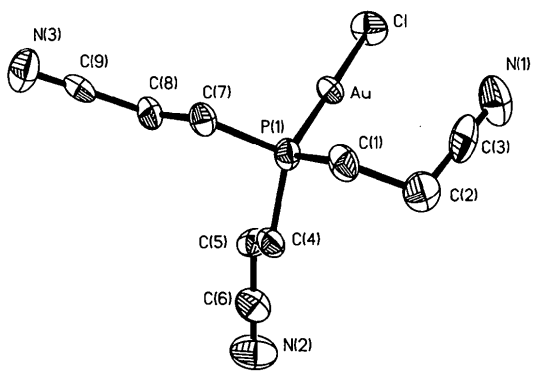


Fig. 1. A drawing of polymorph (1) of $[AuP(CH_2CH_2CN)_3Cl]$ showing the atomic labeling scheme with displacement ellipsoids drawn at 50% probability.

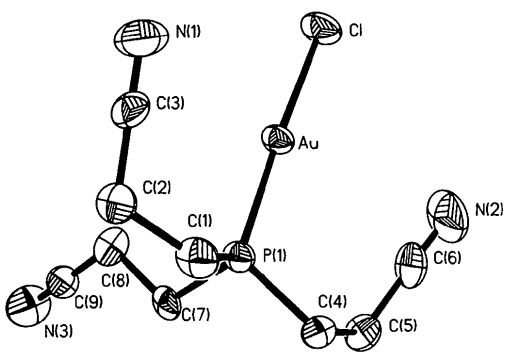


Fig. 2. A drawing of polymorph (2) of $[AuP(CH_2CH_2CN)_3Cl]$ showing the atomic labeling scheme with displacement ellipsoids drawn at 50% probability.

Only one other complex of this type with Au has been reported to give two crystalline polymorphs, chloro[tris(2-pyridyl)phosphine]gold(I) (Lock & Turner, 1987). Polymorph *A* of this complex packs with greater π–π interaction between the rings than polymorph *B*.

In our complexes, polymorph (2) seems to form with two of the C≡N groups positioned so as to block the Au^I center, whereas polymorph (1) has one in such a position. Fig. 3 shows the two forms when polymorph (2) is fitted to polymorph (1). The packing diagrams are shown in Figs. 4 and 5, and are viewed along the *b* axis. Reactions of both polymorphs in solution with acid results in decomposition to Au metal, unlike the behavior of chlorobis[tris(2-cyanoethyl)phosphine]gold(I) (Khan, King, Fackler & Winpenny, 1993).

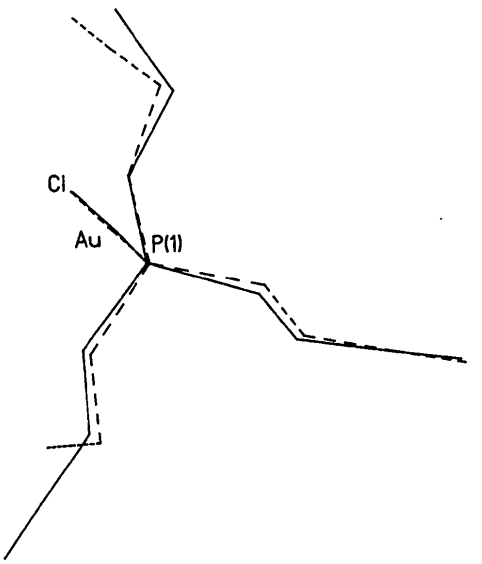


Fig. 3. Drawing showing the best fit between the molecule as it is observed in polymorph (2) (dotted lines) and in polymorph (1).

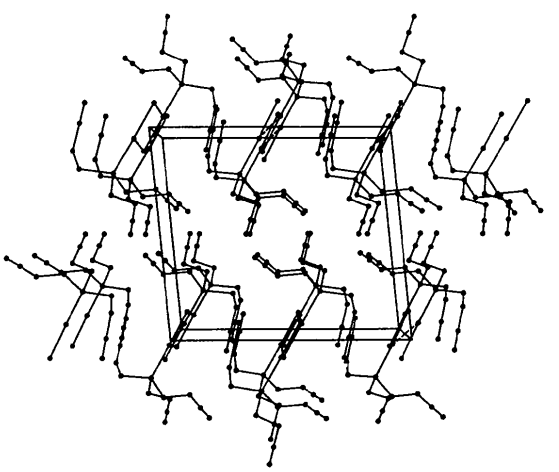


Fig. 4. Packing diagram of polymorph (1) viewed along the *b* axis.

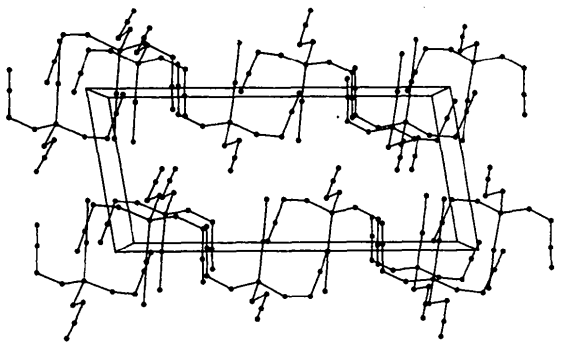


Fig. 5. Packing diagram of polymorph (2) viewed along the b axis.

Experimental

The title complex was prepared by displacement of tetrahydrothione (THT) from Au(THT)Cl in dichloromethane. Polymorph (1) was formed by refluxing [AuCl($C_9H_{12}N_3P$)] in toluene prior to crystallization. Crystals of polymorphs (1) and (2) were grown by diffusion of diethyl ether into a dichloromethane solution.

Polymorph (1)

Crystal data

[AuCl($C_9H_{12}N_3P$)]
M_r = 425.44
Monoclinic
$P2_1/c$
a = 11.761 (4) Å
b = 7.988 (2) Å
c = 13.416 (3) Å
β = 95.75 (2)°
V = 1254.3 (6) Å^3
Z = 4
D_x = 2.25 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 12.02 mm^{-1}
T = 298 K
Colorless

Data collection

R3m/E diffractometer
Wyckoff scans (2–30° min^{-1})
Absorption correction: empirical
T_{min} = 0.298, T_{max} = 0.894
1954 measured reflections
1644 independent reflections
1298 observed reflections [$F_o^2 > 3\sigma(F_o^2)$]
R_{int} = 0.0315
θ_{max} = 22.5°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 9$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 97 reflections
intensity variation: none

Refinement

Refinement on F
R = 0.0345
wR = 0.0342
S = 1.25
1298 reflections
136 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.00059F_o^2]$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −1.20 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Polymorph (2)

Crystal data

[AuCl($C_9H_{12}N_3P$)]
M_r = 425.44
Monoclinic
$P2_1/c$
a = 8.556 (6) Å
b = 7.970 (6) Å
c = 19.03 (1) Å
β = 99.82 (6)°
V = 1278 (2) Å^3
Z = 4
D_x = 2.21 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 11.79 mm^{-1}
T = 298 K
Colorless

Data collection

R3m/E diffractometer
Wyckoff scans (2–30° min^{-1})
Absorption correction: empirical
T_{min} = 0.461, T_{max} = 0.921
1953 measured reflections
1642 independent reflections
1299 observed reflections [$F_o^2 > 3\sigma(F_o^2)$]
R_{int} = 0.0284
θ_{max} = 22.5°
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 20$
3 standard reflections monitored every 97 reflections
intensity variation: none

Refinement

Refinement on F
R = 0.0314
wR = 0.0324
S = 1.25
1299 reflections
131 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.00072F_o^2]$
$(\Delta/\sigma)_{max}$ = 0.009
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −1.37 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for polymorphs* (1) *and* (2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Polymorph (1)				
Au	0.0657 (1)	0.2663 (1)	0.0494 (1)	0.032 (1)
Cl	−0.1023 (3)	0.1926 (4)	−0.0420 (3)	0.053 (1)
P(1)	0.2272 (3)	0.3300 (4)	0.1424 (2)	0.032 (1)
N(1)	−0.0822 (9)	0.5077 (16)	0.2111 (8)	0.065 (5)
N(2)	0.3918 (13)	0.7282 (16)	−0.1146 (10)	0.076 (6)
N(3)	0.5011 (10)	−0.1806 (14)	0.1328 (8)	0.054 (4)
C(1)	0.2094 (9)	0.4105 (14)	0.2677 (7)	0.037 (4)
C(2)	0.1341 (11)	0.5649 (16)	0.2717 (9)	0.051 (5)
C(3)	0.0120 (12)	0.5313 (15)	0.2367 (8)	0.049 (5)
C(4)	0.3135 (10)	0.4865 (14)	0.0853 (8)	0.037 (4)
C(5)	0.3019 (11)	0.4771 (13)	−0.0304 (9)	0.044 (5)
C(6)	0.3538 (12)	0.6176 (18)	−0.0769 (9)	0.051 (5)
C(7)	0.3205 (9)	0.1497 (14)	0.1733 (8)	0.032 (4)
C(8)	0.3588 (10)	0.0613 (14)	0.0839 (8)	0.040 (4)
C(9)	0.4384 (10)	−0.0771 (15)	0.1117 (9)	0.040 (4)
Polymorph (2)				
Au	1.0468 (1)	0.2561 (1)	0.4077 (1)	0.031 (1)
Cl	1.3107 (3)	0.3321 (4)	0.4385 (1)	0.049 (1)
P(1)	0.7947 (3)	0.1721 (3)	0.3746 (1)	0.030 (1)
N(1)	0.9784 (12)	0.2388 (11)	0.5848 (5)	0.065 (4)
N(2)	1.1509 (14)	0.0640 (16)	0.2597 (6)	0.089 (5)

N(3)	0.4933 (14)	0.7409 (10)	0.3425 (5)	0.065 (4)
C(1)	0.7145 (11)	0.0542 (11)	0.4437 (5)	0.041 (4)
C(2)	0.7026 (11)	0.1425 (11)	0.5133 (5)	0.038 (3)
C(3)	0.8573 (12)	0.1974 (12)	0.5532 (5)	0.040 (3)
C(4)	0.7661 (11)	0.0272 (11)	0.2989 (4)	0.038 (3)
C(5)	0.8425 (12)	0.0825 (13)	0.2352 (5)	0.046 (4)
C(6)	1.0178 (15)	0.0718 (14)	0.2503 (6)	0.055 (4)
C(7)	0.6526 (10)	0.3416 (11)	0.3442 (4)	0.033 (3)
C(8)	0.6867 (12)	0.5017 (11)	0.3877 (5)	0.044 (4)
C(9)	0.5748 (11)	0.6359 (11)	0.3621 (5)	0.038 (2)

Table 2. *Selected geometric parameters* (Å, °) *for polymorphs* (1) *and* (2)

Polymorph (1)			
Au—Cl	2.295 (3)	Au—P(1)	2.225 (3)
P(1)—C(1)	1.832 (11)	P(1)—C(4)	1.827 (12)
P(1)—C(7)	1.833 (11)	N(1)—C(3)	1.143 (18)
N(2)—C(6)	1.132 (20)	N(3)—C(9)	1.125 (16)
C(1)—C(2)	1.522 (17)	C(2)—C(3)	1.490 (19)
C(4)—C(5)	1.546 (16)	C(5)—C(6)	1.449 (18)
C(7)—C(8)	1.500 (16)	C(8)—C(9)	1.473 (16)
Cl—Au—P(1)	177.8 (1)	Au—P(1)—C(1)	115.2 (4)
Au—P(1)—C(4)	113.6 (4)	C(1)—P(1)—C(4)	105.3 (5)
Au—P(1)—C(7)	113.9 (4)	C(1)—P(1)—C(7)	100.9 (5)
C(4)—P(1)—C(7)	106.7 (5)	P(1)—C(1)—C(2)	115.9 (8)
C(1)—C(2)—C(3)	112.9 (10)	N(1)—C(3)—C(2)	178.8 (14)
P(1)—C(4)—C(5)	113.0 (8)	C(4)—C(5)—C(6)	113.3 (10)
N(2)—C(6)—C(5)	178.2 (14)	P(1)—C(7)—C(8)	114.2 (7)
C(7)—C(8)—C(9)	112.7 (9)	N(3)—C(9)—C(8)	178.5 (13)
Polymorph (2)			
Au—Cl	2.315 (2)	Au—P(1)	2.243 (2)
P(1)—C(1)	1.842 (10)	P(1)—C(4)	1.830 (9)
P(1)—C(7)	1.843 (8)	N(1)—C(3)	1.154 (13)
N(2)—C(6)	1.124 (18)	N(3)—C(9)	1.112 (13)
C(1)—C(2)	1.518 (13)	C(2)—C(3)	1.475 (12)
C(4)—C(5)	1.536 (14)	C(5)—C(6)	1.480 (16)
C(7)—C(8)	1.522 (12)	C(8)—C(9)	1.463 (13)
Cl—Au—P(1)	177.1 (1)	Au—P(1)—C(1)	114.1 (3)
Au—P(1)—C(4)	113.8 (3)	C(1)—P(1)—C(4)	102.9 (4)
Au—P(1)—C(7)	114.9 (3)	C(1)—P(1)—C(7)	107.0 (4)
C(4)—P(1)—C(7)	102.9 (4)	P(1)—C(1)—C(2)	118.3 (6)
C(1)—C(2)—C(3)	113.5 (8)	N(1)—C(3)—C(2)	179.3 (9)
P(1)—C(4)—C(5)	114.9 (6)	C(4)—C(5)—C(6)	112.6 (8)
N(2)—C(6)—C(5)	177.9 (13)	P(1)—C(7)—C(8)	112.9 (6)
C(7)—C(8)—C(9)	112.2 (7)	N(3)—C(9)—C(8)	178.0 (11)

Table 3. *Comparison of bond lengths and angles* (Å, °) *for mononuclear gold*(I) *triorganophosphine chloride complexes*

Phosphine	Au—Cl	Au—P	P—Au—Cl	References
PPh_3	2.279	2.235	179.6	Baenziger, Bennet & Soboroff (1976)
$(o\text{-MePh})_3P$	2.281	2.243	179.4	Harker & Tiekink (1990)
$(m\text{-MePh})_3P$	2.288	2.235	175.1	Harker & Tiekink (1991)
Cy_2PhP	2.281	2.234	178.3	Muir, Cuadrado & Muir (1991)
$(2\text{-pyridyl})_3P$ (*A*)	2.277	2.214	179.4	Lock & Turner (1987)
(*B*)	2.272	2.218	176.5	Lock & Turner (1987)
Cy_3P	2.279	2.242	177.0	Muir, Muir, Pulgar, Jones & Sheldrick (1985)
Et_3P	2.305	2.232	178.5	Tiekink (1989)
	2.306	2.231	178.9	
CEP (1)	2.295	2.225	177.8	This work
(2)	2.315	2.243	177.1	This work
Average for all	2.289	2.2232	178.0	

A small colorless crystal was mounted on a glass fiber in a random orientation. Monoclinic symmetry of both polymorphs was suggested on the basis of symmetry in axial photographs. Data were corrected for Lp factors. The Au atom was found by direct methods; the remaining non-H atom positions were located by Fourier techniques. H atoms were placed in idealized positions (C—H 0.96 Å) and the isotropic displacement parameters were fixed as $1.2\times U_{eq}$ of the parent C atom. All computation was carried out using the *SHELXTL* crystallographic program package (Sheldrick, 1986).

These studies were supported by the Welch Foundation and the National Science Foudation (grant CHE-8708625).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1000). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BK1000]

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Acta Cryst. (1994). C**50**, 1023–1026

μ_4-Oxo-hexakis(μ-3,5-dimethylpyrazolato-*N*,*N*′)tetracobalt(II)

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Abstract

The title compound, $[Co_4O(C_5H_7N_2)_6]$, consists of a central O atom coordinated by four Co^{II} atoms which are themselves bridged in a pairwise fashion by six exobidentate 3,5-dimethylpyrazolate ligands. The coordination geometry about each Co^{II} atom is that of a distorted tetrahedron.