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

	(I)	(II)
Cu(1)—Cu(2)	2.793 (2)	2.835 (4)
Cu(1)—O(1)	1.916 (5)	1.879 (12)
Cu(1)—O(2)	1.912 (5)	1.880 (12)
Cu(1)—O(3)	2.056 (5)	2.054 (13)
Cu(1)—O(4)	2.178 (5)	2.173 (11)
Cu(1)—N(1)	2.096 (7)	2.066 (16)
Cu(2)—O(5)	2.111 (5)	2.145 (12)
Cu(2)—O(6)	2.055 (4)	2.059 (10)
Cu(2)—O(7)	1.905 (5)	1.927 (10)
Cu(2)—O(8)	1.909 (5)	1.885 (10)
Cu(2)—N(2)	2.094 (6)	2.083 (16)
Cu(2)—Cu(1)—O(1)	92.1 (1)	93.2 (4)
Cu(2)—Cu(1)—O(2)	84.7 (2)	85.2 (4)
Cu(2)—Cu(1)—O(3)	79.2 (1)	78.3 (4)
Cu(2)—Cu(1)—O(4)	70.0 (1)	68.8 (3)
Cu(2)—Cu(1)—N(1)	159.8 (2)	160.5 (5)
Cu(1)—Cu(2)—O(5)	72.5 (1)	71.0 (3)
Cu(1)—Cu(2)—O(6)	78.4 (1)	77.1 (3)
Cu(1)—Cu(2)—O(7)	83.9 (1)	83.8 (3)
Cu(1)—Cu(2)—O(8)	95.2 (1)	96.0 (3)
Cu(1)—Cu(2)—N(2)	166.6 (2)	166.5 (4)
O(1)—Cu(1)—O(2)	176.8 (2)	178.0 (5)
O(3)—Cu(1)—O(4)	148.7 (2)	146.7 (5)
O(3)—Cu(1)—N(1)	120.3 (2)	120.4 (6)
O(4)—Cu(1)—N(1)	90.9 (2)	92.9 (6)
O(5)—Cu(2)—O(6)	150.5 (2)	148.0 (4)
O(7)—Cu(2)—O(8)	179.1 (2)	179.8 (4)
O(5)—Cu(2)—N(2)	97.4 (2)	99.0 (5)
O(6)—Cu(2)—N(2)	112.2 (2)	113.0 (5)
Cu(1)—O(1)—C(1)	117.1 (5)	117.4 (10)
Cu(1)—O(2)—C(3)	123.7 (5)	124.6 (10)
Cu(1)—O(3)—C(5)	124.9 (5)	127.9 (12)
Cu(1)—O(4)—C(7)	134.3 (5)	134.6 (10)
Cu(2)—O(5)—C(1)	131.8 (5)	132.3 (10)
Cu(2)—O(6)—C(3)	125.6 (5)	126.7 (10)
Cu(2)—O(7)—C(5)	125.6 (5)	125.0 (12)
Cu(2)—O(8)—C(7)	115.7 (5)	113.9 (11)

Compound (I): $[Cu(Ph_3CCOO)_2(H_2O)]_2$ (Steward *et al.*, 1986) (1.0 g, 1.5 mmol) was dissolved in benzene (40 ml). On dropwise addition of 4-picoline (0.14 g, 1.5 mmol), the color of the solution changed from blue-green to green. Addition of petroleum ether (100 ml) yielded a green precipitate which was separated by filtration, washed with benzene-petroleum ether (30:70 *v*/*v*) and air dried. A crystal grown from toluene solution was coated with adhesive and cooled in a cold N_2 stream. The structure was solved by the Patterson-Fourier method. All non-H atoms were refined with anisotropic thermal parameters. *Compound* (II): Crystals were grown from a benzene solution. The density was measured by flotation in a tetrachloromethane-cyclohexane mixture. The crystal was coated with adhesive to prevent efflorescence. The atomic coordinates of (I) were utilized as initial parameters. The C and N atoms were refined isotropically to reduce the number of parameters.

Both structures were refined using *UNICS*III (Sakurai & Kobayashi, 1979) on a FACOM M-780/10 computer at Keio University. The relatively large *R* values [0.078 for (I) and 0.091 for (II)] may arise partly from the orientational disorder of the solvent molecules.

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71058 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1031]

This work was supported by a Grant in Aid of Scientific Research from the Japanese Ministry of Education, Science and Culture.

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Chloro(trimesitylphosphine)gold(I)

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(*Received* 28 *September* 1992; *accepted* 3 *December* 1992)

Abstract

Chloro(trimesitylphosphine)gold(I), $[AuCl(C_9H_{11})P_3]$, has approximate threefold symmetry in the solid state [dihedral angles between the mesityl ring planes and the relevant Au—P—C planes are 47.0 (1), 48.0 (1) and 48.5 (1)°]. The Au atom has a linear coordination geometry with Au—Cl and Au—P bond lengths of 2.2716 (19) and 2.2634 (15) Å, respectively, and a P—Au—Cl bond angle of 178.01 (8)°. The C_{ar}—C_{ar} bond lengths are in the range 1.360 (10) to 1.424 (8) Å, while the range of C_{ar}—C_{sp^3} distances lies between 1.499 (10) and 1.529 (9) Å.

Comment

The structural chemistry of monophosphine gold(I) halides continues to attract considerable attention and there have been several crystallographic studies reported. Our interest in complexes of this general type stems from our continuing study of the electronic and steric effects that bulky phosphines exert on the metal atoms to which they are bonded (Alyea, Ferguson, Malito & Ruhl, 1989; Ferguson, Alyea, Roberts & Khan, 1978).

Chloro(trimesitylphosphine)gold(I) has approximate threefold symmetry in the solid state (Fig. 1) [the dihedral angles between the mesityl ring planes and the relevant Au—P—Cn1 (n = 1 to 3) planes are 47.0 (1), 48.0 (1) and 48.5 (1)° for planes C11-C19, C21-C29 and C31-C39, respectively].

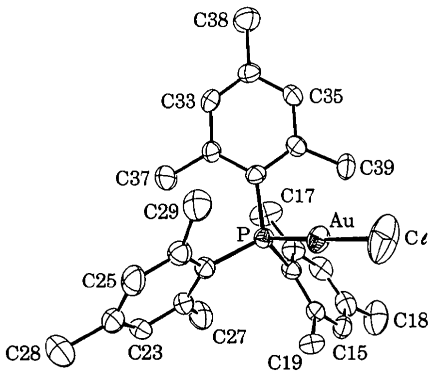

Fig. 1. View of the molecule showing the general conformation and numbering scheme. The non-H atoms have thermal ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

The three mesityl moieties of the bulky trimesitylphosphine ligand have very similar geometries (Fig. 2). The P atom is displaced 0.34 Å from the aromatic plane and the immediately adjacent methyl C atoms are displaced in the opposite direction (C17 −0.19, C19 −0.14 Å). There is clearly some interaction between the Au atom and the immediately adjacent mesityl methyl groups (C19, C29 and C39) (mean contacts Au···C 3.229 Å and Au···H 2.40 Å). Examination of the mesityl geometry would indicate that this is an attractive interaction (as opposed to just a mere contact); thus, the mean P—Cn1—Cn6 angle [117.3 (6)°] (where n = 1, 2, 3) is 6.7° less than the mean P—Cn1—Cn2 angle [124.0 (6)°], the mean P···Cn9 distance [3.138 (7) Å] is 0.2 Å shorter than the mean P···Cn7 distance [3.340 (6) Å] and the mean Au—P—C angle [107.6 (2)°] is 3.6° less than the mean C—P—C angle [111.2 (3)°]. Metal···H interactions of this type have been described as 'remote agostic' by Brookhart, Green & Wong (1988).

A search of the January 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) for structures containing the P—Au—Cl fragment (P = monophosphine), revealed several structures of this type, shown in Table 2 with the relevant Au—Cl and Au—P bond lengths and P—Au—Cl angles for

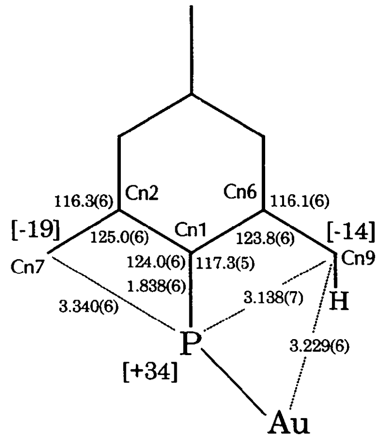

Fig. 2. Schematic drawing showing selected dimensions averaged over the three mesityl rings. Deviations of the atoms (Å × 10^2) from the aromatic plane are enclosed in square brackets [ ].

comparison with the present structural determination. The Au—Cl bond length [2.2716 (19) Å] and P—Au—Cl bond angle [178.01 (8)°] in our present study are comparable with those reported in the other structural studies. The Au—P bond length of 2.2634 (15) Å in chloro(trimesitylphosphine)gold(I) is longer than all other reported Au—P distances [2.214 (4) to 2.243 (2) Å], presumably as a result of the steric bulk of the ligand and the remote agostic interaction between the Au and the adjacent methyl groups already mentioned. There are no short Au···Au contacts in the lattice [the closest distance is 7.762 (1) Å; the shortest intermolecular Au···Cl distance is 6.519 (2) Å].

The structure which most resembles chloro(trimesitylphosphine)gold(I) is that of chloro(tri-o-tolylphosphine)gold(I) (Table 2). This molecule also has approximate threefold symmetry with the o-tolyl rings oriented so that the methyl groups are adjacent to the Au atom. The Au···C(methyl) distances are in the range 3.352 to 3.382 Å (mean 3.366 Å) but there is no evidence from the molecular-geometry details of any remote agostic interaction.

Experimental

Crystal data

[AuCl($C_{27}H_{33}P$)]	D_x = 1.66 Mg m^{-3}
M_r = 620.95	Mo $K\alpha$ radiation
Monoclinic	λ = 0.70930 Å
$P2_1/c$	Cell parameters from 25 reflections
a = 8.2306 (10) Å	θ = 9.0–20.5°
b = 22.4835 (19) Å	μ = 6.08 mm^{-1}
c = 13.5614 (13) Å	T = 293 K
β = 97.906 (9)°	Block
V = 2485.7 (4) Å^3	0.50 × 0.25 × 0.25 mm
Z = 4	Colourless

Data collection

Nonius CAD-4 diffractometer	$R_{int} = 0.030$
$\omega/2\theta$ scans	$\theta_{max} = 26.91°$
Absorption correction: empirical	$h = -10 \rightarrow 10$
$T_{min} = 0.1741$, $T_{max} = 0.2865$	$k = 0 \rightarrow 28$
5775 measured reflections	$l = 0 \rightarrow 17$
5413 independent reflections	3 standard reflections
3337 observed reflections	frequency: 60 min
$[I_{net} > 3.0\sigma(I_{net})]$	intensity variation: 2.5% decay

Refinement

Refinement on F	$\Delta\rho_{max} = 0.65$ e Å^{-3}
Final $R = 0.032$	$\Delta\rho_{min} = -0.79$ e Å^{-3}
$wR = 0.032$	Extinction correction: Larson (1970)
$S = 1.13$	Extinction coefficient: 671 (209)
3337 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)
272 parameters	
C—H 0.95 Å; H riding	
$w = 1/[\sigma^2(F) + 0.0002F^2]$	
$(\Delta/\sigma)_{max} = 0.001$	

Data collection: Enraf-Nonius CAD-4 software. Cell refinement: Enraf-Nonius CAD-4 software. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *NRCVAX*; *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES*.

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

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

	x	y	z	U_{eq}
Au	0.18923 (3)	0.665975 (13)	0.127845 (17)	0.03968 (13)
P	0.39466 (19)	0.64898 (7)	0.25368 (11)	0.0302 (8)
Cl	−0.0191 (3)	0.68596 (13)	0.00430 (15)	0.0858 (15)
C11	0.3022 (8)	0.6256 (3)	0.3632 (4)	0.033 (3)
C12	0.3439 (8)	0.6512 (3)	0.4588 (4)	0.043 (4)
C13	0.2390 (10)	0.6424 (3)	0.5289 (5)	0.050 (4)
C14	0.1002 (9)	0.6079 (3)	0.5106 (5)	0.050 (4)
C15	0.0709 (8)	0.5776 (3)	0.4206 (5)	0.045 (4)
C16	0.1691 (7)	0.5863 (3)	0.3476 (4)	0.035 (3)
C17	0.4975 (11)	0.6860 (4)	0.4906 (5)	0.065 (5)
C18	−0.0199 (11)	0.6035 (5)	0.5856 (6)	0.087 (6)
C19	0.1266 (8)	0.5491 (3)	0.2536 (5)	0.046 (4)
C21	0.5330 (7)	0.5916 (3)	0.2142 (4)	0.033 (3)
C22	0.5855 (8)	0.5413 (3)	0.2702 (5)	0.038 (4)
C23	0.6725 (8)	0.4974 (3)	0.2283 (5)	0.043 (4)
C24	0.7142 (7)	0.5022 (3)	0.1331 (5)	0.048 (4)
C25	0.6682 (8)	0.5536 (4)	0.0812 (5)	0.050 (4)
C26	0.5811 (8)	0.5983 (3)	0.1186 (4)	0.039 (3)
C27	0.5618 (9)	0.5303 (3)	0.3775 (5)	0.056 (4)
C28	0.8089 (10)	0.4545 (4)	0.0876 (7)	0.075 (6)
C29	0.5490 (9)	0.6538 (3)	0.0560 (5)	0.052 (4)
C31	0.5000 (7)	0.7202 (3)	0.2779 (4)	0.031 (3)
C32	0.6726 (7)	0.7283 (3)	0.2835 (4)	0.033 (3)
C33	0.7327 (7)	0.7860 (3)	0.2829 (4)	0.037 (4)
C34	0.6376 (7)	0.8354 (3)	0.2834 (4)	0.037 (3)
C35	0.4711 (7)	0.8275 (3)	0.2869 (4)	0.035 (3)
C36	0.4025 (7)	0.7711 (3)	0.2845 (4)	0.033 (3)
C37	0.7982 (8)	0.6789 (3)	0.2962 (6)	0.053 (4)
C38	0.7089 (10)	0.8969 (3)	0.2841 (6)	0.059 (5)
C39	0.2196 (8)	0.7692 (3)	0.2942 (5)	0.047 (4)

Table 2. *Summary of dimensions* (Å, °) *for chloro(monophosphine)gold*(I) *complexes*

Structure	Au—Cl	Au—P	Cl—Au—P	Reference
$(Mesityl)_3PAuCl$	2.2716 (19)	2.2634 (15)	178.01 (8)	(i)
Ph_3PAuCl	2.279 (3)	2.235 (3)	179.6 (1)	(ii)
Ph_2(2-pyridyl)PAuCl	2.286 (4)	2.234 (4)	178.0 (2)	(iii)
$(Cyclohexyl)_3PAuCl$	2.279 (5)	2.242 (4)	177.0 (2)	(iv)
$(Ethyl)_3PAuCl$	2.305 (8)	2.232 (9)	178.5 (3)	(v)
	2.306 (8)	2.231 (8)	178.9 (3)	
(2-Pyridyl)$_3$PAuCl	2.277 (5)	2.214 (4)	179.5 (1)	(vi)
	2.272 (5)	2.218 (4)	176.5 (2)	
	2.274 (1)	2.220 (1)	178.9 (1)	
$Ph(Me_2C_4H_2)PAuCl$	2.288 (2)	2.227 (2)	176.1 (1)	(vii)
(*o*-Tolyl)$_3$PAuCl	2.281 (3)	2.243 (2)	179.4 (1)	(viii)
(*m*-Tolyl)$_3$PAuCl	2.288 (2)	2.235 (2)	175.1 (1)	(ix)
Ph(cyclohexyl)$_2$PAuCl	2.281 (3)	2.234 (2)	178.3 (1)	(x)

References: (i) this work; (ii) Baenziger, Bennett & Soboroff (1976); (iii) Alcock, Moore, Lampe & Mok (1982); (iv) Muir, Muir, Pulgar, Jones & Sheldrick (1985); (v) Tiekink (1989); (vi) Lock & Turner (1987); (vii) Attar, Bearden, Alcock, Alyea & Nelson (1990); (viii) Harker & Tiekink (1990); (ix) Harker & Tiekink (1991); (x) Muir, Cuadrado & Muir (1991).

The compound was synthesized by stirring trimesitylphosphine with (dimethyl sulfide)gold(I) chloride in dichloromethane at ambient temperature for 30 min. The yield obtained was 75-80% (depending on the purity of the starting material). The colourless crystals were grown from 1:10 *v*/*v* dichloromethane/*n*-hexane and are stable for months in either the solid state or in solution. The melting point is 433-436 K (decomposition) and the results of elemental analysis were: calculated C 52.23, H 5.36, Cl 5.71%; found C 52.36, H 5.18, Cl 7.99%.

The space group was determined unambiguously from the systematic absences ($h0l$ absent if $l = 2n + 1$, $0k0$ absent if $k = 2n + 1$) and successful refinement as $P2_1/c$ (No. 14). The H atoms attached to the C atoms were visible in difference maps (the methyl H atoms were disordered over two orientations). All H atoms were positioned geometrically (C—H 0.95 Å) and included as riding atoms in the structure-factor calculations.

ECA and GF thank NSERC Canada for Research Grants.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55957 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1050]

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Acta Cryst. (1993). C**49**, 1476–1479

Structure of a Mixed-Valence Copper Complex with 1,10-Phenanthroline and Pseudohalogenide Ligands

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(*Received* 7 *August* 1992; *accepted* 19 *January* 1993)

Abstract

The reaction of $Cu(NO_3)_2$, NH_4OH, 1,10-phenanthroline (phen), KSCN and KSeCN in the molar ratio 1:10:2:2:2 in a water–ethanol solution gives a new mixed-valence compound, μ-cyano-$1\kappa N$:$2\kappa C$-(seleno,thio)cyanato-$2\kappa N$-tris(1,10-phenanthroline)-$1\kappa^4 N,N'$;$2\kappa^2 N,N'$-dicopper(I,II) (seleno,thio)cyanate semiethanolate, for which the X-ray structure analysis reveals the composition $[Cu^{II}Cu^{I}(phen)_3(CN)(SeCN)_{0.65}(SCN)_{0.35}]^+(SeCN)^-_{0.45}(SCN)^-_{0.55}.0.5C_2H_5OH$. The $[Cu^{II}(phen)_2]^{2+}$ and $[Cu^{I}(phen)\{(Se,S)CN\}]$ moieties are bridged by CN^-, giving rise to a binuclear cation with deformed trigonal-bipyramidal and deformed tetrahedral coordination for the bivalent and monovalent Cu atoms, respectively.

Comment

This work is part of a project aimed at exploring the structural and chemical properties of mixed-valence copper complexes with organic and inorganic ligands. In this report we describe the crystal structure of a compound which was obtained by mixing $Cu(NO_3)_2$, NH_4OH, phen, KSCN and KSeCN in the molar ratio 1:10:2:2:2 in a water–ethanol solution. The $SeCN^-$ anion serves both as a ligand and as a reducing agent in the reaction. Thus, although the cyanide anion was not added to the reaction mixture, it appears in the system as a consequence of the following redox and protolytic reactions:

$$2Cu^{II}(solv.) + 2SeCN^- \rightleftarrows (CN)_2 + 2Cu^{I} + Se_2$$

$$(CN)_2 + H_2O \rightleftarrows HCN + HCNO$$

Several other bi- and polynuclear-ligand(s) bridged copper(I) and copper(II) compounds are known to be prepared by similar reactions (Dunaj-Jurčo, Ondrejovič, Melník & Garaj, 1988, and references therein).

The crystal structure was found to consist of discrete $[Cu^{II}Cu^{I}(phen)_3(CN)\{(Se,S)CN\}]^+$ cations, $[(Se,S)CN]^-$ anions and solvated ethanol molecules. One of the two crystallographically independent complex cations, which are nearly centrosymmetrically related, is shown in Fig. 1. The CN^- anion linearly bridges the Cu^{II} and Cu^{I} ions and the coordination environments around Cu^{II} and Cu^{I} are distorted trigonal bipyramidal and tetrahedral, respectively. The bridging cyanide ion is coordinated to Cu^{II} through its N atom and occupies an equatorial position. The axial Cu—N(11) and Cu—N(102) bonds are slightly but significantly longer than the corresponding in-plane bonds and almost linear, with an N(11)—Cu—N(102) angle of 177.3 (5)°. Similar stereochemical features for Cu^{II} have been observed previously in the compounds $[Cu^{II}(phen)_3CN]NO_3$ (Anderson, 1975) and $[Cu^{II}(bipy)_2CN]NO_3.2H_2O$ (Harrison & Hathaway, 1980). As suggested by Harrison & Hathaway (1980), the type and extent of distortion of the trigonal-bipyramidal geometry around Cu^{II} can best be