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## Structure of a Polymeric Cadmium Complex Containing Triply Bridging Monophenylphosphinate Ligands

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**Abstract.** Poly-aqua- $\mu$ -chloro- $\mu$ -monophenylphosphinato-cadmium(II), [Cd(C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>P)(Cl)(H<sub>2</sub>O)]<sub>x</sub>,  $M_r$  = 306.96, triclinic,  $P\bar{1}$ ,  $a$  = 12.855 (2),  $b$  = 13.501 (2),  $c$  = 5.8864 (6) Å,  $\alpha$  = 102.60 (1),  $\beta$  = 103.24 (1),  $\gamma$  = 110.235 (9)°,  $V$  = 882.3 (2) Å<sup>3</sup>,  $Z$  = 4,  $D_x$  = 2.311 g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.71069 Å,  $\mu$  = 29.1 cm<sup>-1</sup>,  $F(000)$  = 592,  $T$  = 294 K,  $R$  = 0.024 ( $wR$  = 0.029) for 9816 reflections with  $I \geq 3\sigma(I)$ . The crystal structure contains three independent cadmium ions, all of which have distorted octahedral coordinations. One Cd forms chains along  $c$  with double phosphinate bridges; the other two Cd ions form Cd(H<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub> units linked to each other along  $c$  by double Cl...H—O hydrogen bonds and to the phosphinate chains by O—Cd—O and Cl—Cd—Cl bridges and by (phosphinate)O...H—O hydrogen bonds, thus resulting in (1 $\bar{1}$ 0) polymeric sheets. The sheets are linked by van der Waals interactions between interleaving phenyl groups which are oriented perpendicular to the polymeric sheets. The phosphinate groups exhibit a triply bridging mode of coordination, not previously observed for organophosphinate complexes, in which one oxygen binds to two different metals and the second oxygen binds to a third metal.

**Introduction.** The potential of organophosphinate ligands to bind to metals in a variety of different ways has been realized for some time (Gillman, 1974; Gillman & Eichelberger, 1976); however, relatively few different bonding modes have, in fact, been identified by single-crystal X-ray diffraction. While there are some examples of monodentate phos-

phinate bonding (Betz & Bino, 1988; Du, Rettig, Thompson & Trotter, 1991), the most common mode is that of bidentate bridging in which each O atom of a phosphinate ligand binds to a different metal ion (Betz, Bino, Du, Lo & Thompson, 1990). The title compound provides the first example of an organophosphinate complex in which the phosphinate ligand exhibits a triply bridging mode of coordination whereby one O atom binds to two different metals and the second O atom binds to a third metal. A similar mode of phosphinate bonding has recently been reported for the inorganic phosphinate complex [CoCl(H<sub>2</sub>O)(H<sub>2</sub>PO<sub>2</sub>)]<sub>x</sub> (Marcos, Ibáñez, Amorós & Le Bail, 1991).

**Experimental.** Cadmium dichloride dihydrate (1.14 g) and monophenylphosphinic acid (0.71 g) were dissolved in 100 mL of distilled water in an open beaker. The beaker was loosely covered and its contents allowed to evaporate slowly. Crystals in the form of colourless prisms formed over a period of two weeks. The crystals were collected by filtration and air-dried. Analysis gives C 23.6 (calc. 23.5%), H 2.51 (calc. 2.63%). Colorless prism, 0.17 × 0.25 × 0.25 mm, Rigaku AFC6S diffractometer, lattice parameters from 25 reflections with  $\theta$  = 29.9–32.5°. Intensities for  $\theta < 45^\circ$ ,  $hkl$ : 0 to 25, -26 to 26, -11 to 11,  $\omega$ -2 $\theta$  scan,  $\omega$  scan width (1.10 + 0.35tan $\theta$ )° at 32° min<sup>-1</sup> (up to eight rescans), stationary backgrounds at each end of the scan counted 50% of the scan time, three standard reflections showed only small random fluctuations in intensity, Lp and absorption corrections (empirical, based on azimu-

thal scans for four reflections, transmission factors 0.59–1.00), 14 959 reflections measured, 14 513 independent ( $R_{\text{merge}} = 0.016$ ), 9816 with  $I \geq 3\sigma(I)$ ,  $\sigma^2(F_o^2) = [S^2(C + 4B) + (0.02F_o^2)^2]/Lp^2$ ,  $S =$  scan speed,  $C =$  scan count,  $B =$  background count. Structure by Patterson and Fourier syntheses, full-matrix least squares on  $w(\Delta F)^2$ ,  $w = 4F_o^2/\sigma(F_o^2)$ , phosphorus- and oxygen-bound H atoms refined with isotropic thermal parameters, other H atoms fixed in calculated positions ( $C-H = 0.98 \text{ \AA}$ ,  $B_H = 1.2B_{\text{bonded atom}}$ ), scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–102, 149), *TEXSAN* crystallographic software (Version 5.1; Molecular Structure Corporation, 1989), final  $R = 0.024$ ,  $wR = 0.029$  for 9816 reflections,  $S = 1.32$ , 245 parameters,  $R = 0.064$  for all 14 513 reflections,  $\Delta/\sigma_{\text{max}} = 0.17$ , maximum final difference density  $-0.48$  to  $+0.88 \text{ e \AA}^{-3}$ .

**Discussion.** Final positional and equivalent isotropic thermal parameters are given in Table 1, geometrical data appear in Table 2 and hydrogen-bonding parameters in Table 3. Stereoviews of the asymmetric unit, showing atom numbering, and the polymeric sheet structure of poly-aqua- $\mu$ -chloro- $\mu$ -monophenylphosphinato-cadmium(II) are shown in Figs. 1 and 2.\* Although the coordinates in Table 1 {Cd(1) at approximately  $(\frac{1}{4}, \frac{1}{4}, 0)$  and relationships between coordinates:  $\text{Cl}(2) \equiv [\frac{1}{2} - \text{Cl}(1), \frac{1}{2} - \text{Cl}(1), -\text{Cl}(1)]$ ;  $\text{P}(2) \equiv [\frac{1}{2} - \text{P}(1), \frac{1}{2} - \text{P}(1), 1 - \text{P}(1)]$ ; *etc.*} suggest a pseudocentre of symmetry at the Cd(1) position, no transformation to a higher symmetry unit cell was found.

The crystal structure contains three independent Cd atoms, all three of which are six-coordinated. Cd(1), in a general position, coordinates to four different monophenylphosphinate ligands in a square-planar array and to two chlorines above and below the plane. This cadmium is linked by double phosphinate bridges forming Cd(1)-bis(phosphinate) chains extending along the  $c$  axis [ $\text{Cd}(1)\cdots\text{Cd}(1) = 5.8864(6) \text{ \AA}$ ]. There are only minor differences between Cd(2) and Cd(3) which lie on centres of symmetry at  $(0, 0, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  respectively. These Cd atoms are bonded to two *trans*-chloro ligands which in turn are bonded to Cd(1) atoms thus forming  $\text{Cl}-\text{Cd}(2,3)-\text{Cl}$  bridges between the Cd(1)-bis(phosphinate) chains with  $\text{Cd}(1)\cdots\text{Cd}(2) = 3.7249(8)$  and  $\text{Cd}(1)\cdots\text{Cd}(3) = 3.7252(6) \text{ \AA}$ . In addi-

Table 1. *Final atomic coordinates (fractional) and  $B_{\text{eq}}$  values ( $\text{\AA}^2$ )*

$$B_{\text{eq}} = (8/3)\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

	$x$	$y$	$z$	$B_{\text{eq}}$
Cd(1)	0.25001 (1)	0.249981 (9)	0.02041 (2)	1.313 (2)
Cd(2)	0	0	0	1.562 (3)
Cd(3)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1.564 (3)
Cl(1)	0.19950 (3)	0.03914 (3)	-0.09281 (7)	1.761 (8)
Cl(2)	0.30046 (3)	0.46084 (3)	0.16849 (7)	1.757 (8)
P(1)	0.10740 (3)	0.26467 (3)	0.45162 (6)	1.231 (7)
P(2)	0.39260 (3)	0.23533 (3)	0.57957 (6)	1.243 (7)
O(1)	0.1007 (1)	0.1952 (1)	0.2019 (2)	1.55 (2)
O(2)	0.1112 (1)	0.2098 (1)	0.6508 (2)	1.87 (3)
O(3)	0.3993 (1)	0.3049 (1)	0.4067 (2)	1.58 (2)
O(4)	0.3887 (1)	0.2903 (1)	0.8301 (2)	1.85 (3)
O(5)	-0.0732 (1)	0.0491 (1)	-0.3219 (2)	2.30 (3)
O(6)	0.5733 (1)	0.4515 (1)	0.2022 (2)	2.33 (3)
C(1)	-0.0095 (1)	0.3089 (1)	0.4202 (3)	1.60 (3)
C(2)	-0.0838 (2)	0.2948 (2)	0.1912 (3)	2.13 (4)
C(3)	-0.1663 (2)	0.3396 (2)	0.1786 (4)	2.68 (5)
C(4)	-0.1748 (2)	0.3986 (2)	0.3947 (5)	2.88 (6)
C(5)	-0.1028 (2)	0.4109 (2)	0.6214 (4)	2.84 (6)
C(6)	-0.0195 (2)	0.3667 (2)	0.6366 (3)	2.22 (4)
C(7)	0.5092 (1)	0.1911 (1)	0.6207 (3)	1.59 (3)
C(8)	0.5194 (2)	0.1329 (2)	0.7886 (3)	2.27 (4)
C(9)	0.6026 (2)	0.0884 (2)	0.8125 (4)	2.80 (5)
C(10)	0.6755 (2)	0.1016 (2)	0.6726 (4)	2.89 (5)
C(11)	0.6666 (2)	0.1603 (2)	0.5057 (4)	2.68 (5)
C(12)	0.5839 (2)	0.2051 (2)	0.4803 (3)	2.13 (4)

tion, each Cd(2) and Cd(3) atom is bonded to two *trans*-aqua ligands and to two O atoms which come from different phosphinates on adjacent Cd(1)-bis(phosphinate) chains. This latter interaction gives rise to O—Cd(2,3)—O bridges between the Cd(1)-bis(phosphinate) chains. The aqua ligands are bonded to Cd(2) and Cd(3) and are each involved in two types of hydrogen bonding (see Table 3). O—H $\cdots$ Cl hydrogen bonding forms double bridges between adjacent Cd(2,3) atoms along the  $c$  axis and O—H $\cdots$ O hydrogen bonds involving the phosphinate O(2) or O(4) atoms, which are bonded to one Cd(1) atom only, form additional O $\cdots$ H—O—Cd(2,3)—O—H $\cdots$ O linkages between Cd(1)-bis(phosphinate) chains. The overall structure is that of an infinite (1 $\bar{1}$ 0) sheet. The phenyl rings are oriented perpendicular to the plane of the sheet. The sheets are linked by van der Waals interactions between inter-leaving phenyl groups.

There are two crystallographically independent phosphinate groups in this structure which in fact differ very little from each other. This discussion which concerns the phosphinate containing P(1) applies equally to the other phosphinate group. The phosphinate O(2) atom is bonded to just one Cd atom and the Cd(1)—O(2) distance of 2.291 (1)  $\text{\AA}$  agrees well with the sum of the ionic radii involved, 2.30  $\text{\AA}$  (Shannon, 1976). The other phosphinate O atom, O(1), is bonded to two Cd atoms at longer distances: Cd(1)—O(1) = 2.382 (1) and Cd(2)—O(1) = 2.367 (1)  $\text{\AA}$ . Differences between the P—O bond lengths are also a consequence of different bonding

\* Lists of anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H atoms, torsion angles, intermolecular contacts, least-squares planes, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54966 (69 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0583]

Table 2. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Cd(1)—Cl(1)	2.5816 (5)	P(2)—O(3)	1.526 (1)
Cd(1)—Cl(2)	2.5819 (5)	P(2)—O(4)	1.520 (1)
Cd(1)—O(1)	2.382 (1)	P(2)—C(7)	1.784 (2)
Cd(1)—O(2)	2.291 (1)	C(1)—C(2)	1.393 (2)
Cd(1)—O(3)	2.384 (1)	C(1)—C(6)	1.399 (2)
Cd(1)—O(4')	2.289 (1)	C(2)—C(3)	1.387 (3)
Cd(2)—Cl(1)	2.6429 (5)	C(3)—C(4)	1.394 (3)
Cd(2)—O(1)	2.367 (1)	C(4)—C(5)	1.377 (4)
Cd(2)—O(5)	2.253 (1)	C(5)—C(6)	1.391 (3)
Cd(3)—Cl(2)	2.6432 (6)	C(7)—C(8)	1.401 (2)
Cd(3)—O(3)	2.366 (1)	C(7)—C(12)	1.395 (2)
Cd(3)—O(6)	2.252 (1)	C(8)—C(9)	1.392 (3)
P(1)—O(1)	1.528 (1)	C(9)—C(10)	1.374 (3)
P(1)—O(2)	1.518 (1)	C(10)—C(11)	1.399 (3)
P(1)—C(1)	1.786 (2)	C(11)—C(12)	1.390 (3)
Cl(1)—Cd(1)—Cl(2)	175.44 (1)	Cd(1)—Cl(1)—Cd(2)	90.96 (2)
Cl(1)—Cd(1)—O(1)	80.58 (3)	Cd(1)—Cl(2)—Cd(3)	90.93 (2)
Cl(1)—Cd(1)—O(2')	87.58 (4)	O(1)—P(1)—O(2)	115.45 (7)
Cl(1)—Cd(1)—O(3)	96.22 (3)	O(1)—P(1)—C(1)	111.18 (7)
Cl(1)—Cd(1)—O(4')	95.77 (4)	O(2)—P(1)—C(1)	109.49 (7)
Cl(2)—Cd(1)—O(1)	96.19 (3)	O(3)—P(2)—O(4)	115.33 (7)
Cl(2)—Cd(1)—O(2')	95.69 (4)	O(3)—P(2)—C(7)	111.23 (7)
Cl(2)—Cd(1)—O(3)	80.57 (3)	O(4)—P(2)—C(7)	109.54 (7)
Cl(2)—Cd(1)—O(4')	87.53 (3)	Cd(1)—O(1)—Cd(2)	103.35 (4)
O(1)—Cd(1)—O(2')	90.62 (4)	O(1)—O(1)—P(1)	123.35 (6)
O(1)—Cd(1)—O(3)	90.97 (4)	Cd(2)—O(1)—P(1)	129.20 (6)
O(1)—Cd(1)—O(4')	176.13 (4)	Cd(1 <sup>iv</sup> )—O(2)—P(1)	133.48 (7)
O(2)—Cd(1)—O(3)	176.08 (4)	Cd(1)—O(3)—Cd(3)	103.28 (4)
O(2)—Cd(1)—O(4')	87.97 (4)	Cd(1)—O(3)—P(2)	123.27 (6)
O(3)—Cd(1)—O(4')	90.67 (4)	Cd(3)—O(3)—P(2)	129.40 (6)
Cl(1)—Cd(2)—Cl(1 <sup>iv</sup> )	180.00	Cd(1 <sup>iv</sup> )—O(4)—P(2)	133.47 (7)
Cl(1)—Cd(2)—O(1)	79.58 (3)	P(1)—C(1)—C(2)	122.4 (1)
Cl(1)—Cd(2)—O(1 <sup>iv</sup> )	100.42 (3)	P(1)—C(1)—C(6)	117.5 (1)
Cl(1)—Cd(2)—O(5)	91.45 (4)	C(2)—C(1)—C(6)	119.9 (2)
Cl(1)—Cd(2)—O(5 <sup>iv</sup> )	88.55 (4)	C(1)—C(2)—C(3)	119.8 (2)
O(1)—Cd(2)—O(1 <sup>iv</sup> )	180.00	C(2)—C(3)—C(4)	120.1 (2)
O(1)—Cd(2)—O(5)	83.84 (5)	C(3)—C(4)—C(5)	120.2 (2)
O(1)—Cd(2)—O(5 <sup>iv</sup> )	96.16 (5)	C(4)—C(5)—C(6)	120.3 (2)
O(5)—Cd(2)—O(5 <sup>iv</sup> )	180.00	C(1)—C(6)—C(5)	119.7 (2)
Cl(2)—Cd(3)—Cl(2 <sup>iv</sup> )	180.00	P(2)—C(7)—C(8)	117.7 (1)
Cl(2)—Cd(3)—O(3)	79.63 (3)	P(2)—C(7)—C(12)	122.6 (1)
Cl(2)—Cd(3)—O(3 <sup>iv</sup> )	100.37 (3)	C(8)—C(7)—C(12)	119.5 (2)
Cl(2)—Cd(3)—O(6)	91.42 (4)	C(7)—C(8)—C(9)	120.0 (2)
Cl(2)—Cd(3)—O(6 <sup>iv</sup> )	88.58 (4)	C(8)—C(9)—C(10)	120.4 (2)
O(3)—Cd(3)—O(3 <sup>iv</sup> )	180.00	C(9)—C(10)—C(11)	120.1 (2)
O(3)—Cd(3)—O(6)	84.11 (5)	C(10)—C(11)—C(12)	120.1 (2)
O(3)—Cd(3)—O(6 <sup>iv</sup> )	95.89 (5)	C(7)—C(12)—C(11)	119.9 (2)
O(6)—Cd(3)—O(6 <sup>iv</sup> )	180.00		

Symmetry operations: (i)  $x, y, z - 1$ ; (ii)  $-x, -y, -z$ ; (iii)  $1 - x, 1 - y, 1 - z$ ; (iv)  $x, y, 1 + z$ .

modes: P(1)—O(2) = 1.518 (1) and P(1)—O(1) = 1.528 (1) Å. The latter distance, in particular, is significantly longer than, for example, the P—O distances in poly-bis(acetamide)tris( $\mu$ -phenylphosphinato)manganese(II) where P—O = 1.510 (1) and 1.512 (1) Å (Du, Rettig, Thompson, Trotter, Betz & Bino, 1992). In this latter compound both phosphinate O atoms are involved in coordination to one metal ion only.

Triply bridging modes of coordination similar to that observed here were reported previously for the related phosphinate ligands in Cu(F<sub>2</sub>PO<sub>2</sub>)<sub>2</sub> (Begley, Dove, Hibbert, Logan, Nunn & Sowerby, 1985) and [CoCl(H<sub>2</sub>O)(H<sub>2</sub>PO<sub>2</sub>)<sub>2</sub>]<sub>x</sub> (Marcos, Ibáñez, Amorós & Le Bail, 1991). In the former case very asymmetrical

Table 3. Hydrogen-bond geometry (Å, °)

Interaction	O—H	H...Cl/O	O...Cl/O	O—H...Cl/O
O(5)—H(3)—O(2)( $x, y, z - 1$ )	0.94 (3)	1.77 (3)	2.668 (2)	159 (3)
O(5)—H(4)—Cl(1)( $-x, -y, -z - 1$ )	0.96 (3)	2.32 (3)	3.199 (1)	152 (2)
O(6)—H(5)—Cl(2)( $1 - x, 1 - y, -z$ )	1.02 (3)	2.31 (3)	3.197 (1)	144 (3)
O(6)—H(6)—O(4)( $x, y, z - 1$ )	0.73 (3)	1.94 (3)	2.670 (2)	175 (3)

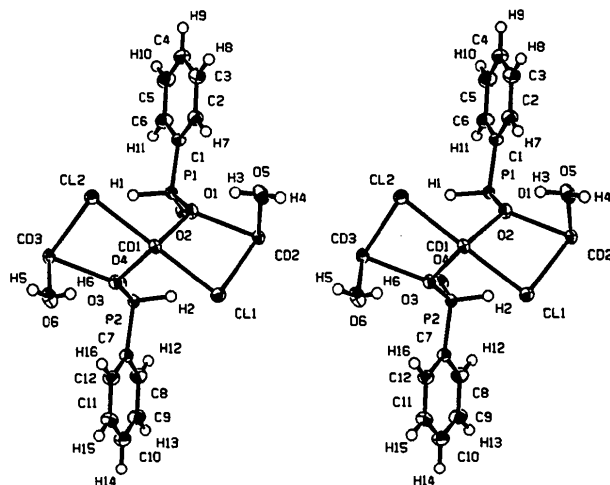


Fig. 1. Stereoview of the asymmetric unit and atom-numbering scheme for poly-aqua- $\mu$ -chloro- $\mu$ -phenylphosphinato-cadmium(II); 50% probability thermal ellipsoids are shown for the non-H atoms.

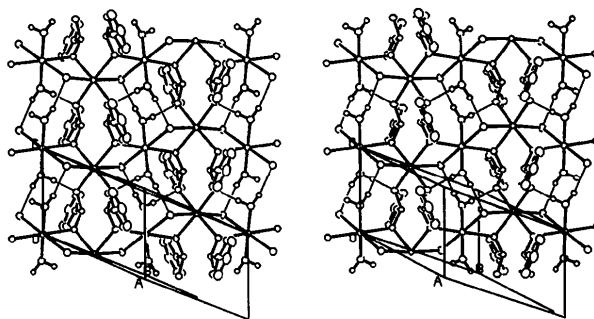


Fig. 2. Stereoview of the polymeric sheet structure of poly-aqua- $\mu$ -chloro- $\mu$ -phenylphosphinato-cadmium(II). Fine lines represent hydrogen bonds.

bonding is involved. O atoms involved in bonding to two Cu atoms exhibit one short Cu—O bond in the range 1.98 to 1.99 Å and one longer bond in the range 2.48 to 2.62 Å. This contrasts sharply with the situation for the cadmium compound reported here where the two Cd—O bond lengths involving the bidentate O atoms differ by only 0.015 Å. The closely related [CoCl(H<sub>2</sub>O)(H<sub>2</sub>PO<sub>2</sub>)<sub>2</sub>]<sub>x</sub> structure also consists of two-dimensional polymeric layers and contains  $\mu$ -Cl ligands and similarly bridging phosphinate ligands, but is not isostructural with the present cadmium compound. There is only one type of Co atom in [CoCl(H<sub>2</sub>O)(H<sub>2</sub>PO<sub>2</sub>)<sub>2</sub>]<sub>x</sub>, six-coordinated

by a square-planar array of phosphinate O atoms and axial chloride and aqua ligands.

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## A $\mu$ -Bis(phosphino)ethane Gold(I) Dimer

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**Abstract.** Bis(bromo,cyano)- $\mu$ -[bis(dicyclohexylphosphino)ethane-*P,P'*]-digold,  $[\text{Au}_2(\text{C}_{26}\text{H}_{48}\text{P}_2)\{\text{Br}_{1.16}(\text{CN})_{0.84}\}]$ ,  $M_r = 931.09$ , monoclinic,  $P2_1/n$ ,  $a = 9.772$  (3),  $b = 15.366$  (4),  $c = 20.973$  (5) Å,  $\beta = 102.53$  (2)°,  $V = 3074.2$  (15) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.01$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu = 111.2$  cm<sup>-1</sup>,  $F(000) = 1774$ , room temperature (297 K),  $R = 0.029$  for 2255 reflections with  $F_o > 3\sigma(F_o^2)$ . A bis(dicyclohexylphosphino)ethane ligand bonds one Au atom at each P atom. The Au atoms are further bonded to Br<sup>-</sup> or CN<sup>-</sup> ions in a disordered manner, with the bromide populations being 0.532 (5) on Au1 and 0.628 (5) on Au2.

**Introduction.** We are currently investigating properties of gold(I) phosphine complexes. The compound bis(bromo,cyano)- $\mu$ -[bis(dicyclohexylphosphino)ethane]-digold was synthesized in an attempt to produce compounds that would give benchmark spectra, to elucidate the nature of the emission in previously synthesized compounds (Henling, Flanagan, McCleskey & Gray, 1992; Schaefer, Marsh, McCleskey & Gray, 1991). However, the title compound shows no luminescence in solution or as a solid.

**Experimental.** The title compound was synthesized by irradiating a mixture of  $[\text{Au}_2(\text{dcpe})_3]^{2+}[\text{Au}$

$(\text{CN})_2]^-$  and bromobenzene in acetonitrile with 366 nm light from a mercury lamp for 1 h. Crystals for X-ray diffraction were grown by vapor diffusion of ether into the acetonitrile. Crystal: a pale yellow needle elongated along **a**,  $0.15 \times 0.21 \times 0.42$  mm. CAD-4 diffractometer;  $\omega$  scans; cell dimensions from 25 reflections with  $29 < 2\theta < 41^\circ$ ; empirical absorption correction based on  $\psi$  scans of six reflections, relative transmission factors 0.618 to 1.307;  $(\sin\theta/\lambda)_{\text{max}} = 0.48$  Å<sup>-1</sup>;  $h$  from 0 to 9,  $k$  from -14 to 14,  $l$  from -20 to 20; standard reflections 0 $\bar{1}$ 5, 2 $\bar{3}$ 1 and 1 $\bar{1}$ 6 showed no significant variations; 6469 reflections measured, 2862 independent; goodness of fit for merging 1.19 ( $R_{\text{merge}}$  for 2260 reflections with exactly two observations = 0.028); all reflections used in solution and refinement of the structure; coordinates of one Au atom found from Patterson map, remaining heavy atoms found by successive structure factor-Fourier calculations. At convergence with only Br<sup>-</sup> ions on Au, difference maps suggested partial occupancy by CN<sup>-</sup>. Atoms of the CN<sup>-</sup> groups could not be refined, so they were introduced at fixed positions with fixed isotropic thermal parameters and their populations refined. The CN<sup>-</sup> groups were repositioned once, such that the Au—C—N group was linear and the Au—C vector was collinear with the Au—Br vector. The population parameters for Br refined to 0.532 (5) for Br1 and 1-0.532 for C1 and N1, 0.628 (5) for Br2 and 1-0.628 for C2 and N2. Values of  $F^2$  (positive and negative) used in

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