

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

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A μ -Bis(phosphino)ethane Gold(I) Dimer

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Abstract. Bis(bromo,cyano)- μ -[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) Å³, $Z = 4$, $D_x = 2.01$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 111.2$ cm⁻¹, $F(000) = 1774$, 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⁻ or CN⁻ 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)- μ -[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; ω scans; cell dimensions from 25 reflections with $29 < 2\theta < 41^\circ$; empirical absorption correction based on ψ scans of six reflections, relative transmission factors 0.618 to 1.307; $(\sin\theta/\lambda)_{\text{max}} = 0.48$ Å⁻¹; h from 0 to 9, k from -14 to 14, l from -20 to 20; standard reflections 01 $\bar{5}$, 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_{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⁻ ions on Au, difference maps suggested partial occupancy by CN⁻. Atoms of the CN⁻ groups could not be refined, so they were introduced at fixed positions with fixed isotropic thermal parameters and their populations refined. The CN⁻ 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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(0.0147)². In the final least-squares cycle, maximum shift to e.s.d. < 0.01; final difference map had peaks of 1.25 e Å⁻³ and holes of 0.89 e Å⁻³; all large peaks are in the vicinities of the Au and Br atoms. Atomic scattering factors taken from Cromer & Waber (1974), dispersion corrections from Cromer (1974). Programs used were those of the *CRYM* crystallographic computing system (Duchamp, 1964) and *ORTEPII* (Johnson, 1976).

Discussion. Final parameters are given in Table 1, with selected distances and angles in Table 2.* Fig. 1 shows a view of the molecule, with the Br⁻ and CN⁻ ions both shown on both Au atoms. The three atoms of these ions are so close together that they could not be refined simultaneously, and even when the location of the Br atom was fixed, the C—N distance became unrealistic. Thus our model for the cyanide is idealized and its inadequacies may explain the relatively large peaks in the final difference map that we note in the vicinity of the Au and Br atoms. The geometry of the remainder of the structure is well determined, however, and has no surprises. The Au—P distances, 2.264 (3) and 2.254 (3) Å, are only slightly shorter than the average of 2.300 Å reported for non-chelating Au—P distances (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989) and the Au—Br distances, even though perhaps influenced by the presence of the cyanide ligands, are 2.405 (2) Å, close to the 2.413 (28) Å average reported in the same survey. The P—Au—Br angles full-matrix least-squares refinement; H atoms positioned by calculation (C—H 0.95 Å) and included as constant contributions to the structure factors; H-atom parameters not refined but repositioned once near conclusion of refinement; H-atom thermal parameters based on U_{eq} of bonded C atom. Positional and anisotropic displacement parameters for all non-H atoms, population parameters for Br1 and Br2, and a scale factor refined; a secondary-extinction parameter refined to zero, so it was not included in the final calculations. For 2747 reflections with $F_o^2 > 0$, R on $F = 0.042$, wR on $F^2 = 0.0033$, and goodness of fit = 1.53 for 2862 reflections and 291 parameters. Variances [$\sigma^2(F_o^2)$] derived from counting statistics plus an additional term, (0.0147)²; variances of the merged data by propagation of error plus another additional term,

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

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{eq}
Au1	1033 (0.5)	514 (0.3)	2767 (0.2)	412 (1)
Br1	-390 (3)	1800 (2)	2699 (1)	829 (11)
P1	2421 (3)	-676 (2)	2985 (1)	380 (8)
C3	1926 (12)	-1655 (7)	2471 (5)	487 (33)
C4	418 (11)	-1660 (7)	2048 (4)	433 (31)
C11	2406 (10)	-1079 (6)	3810 (4)	338 (30)
C12	925 (11)	-1289 (7)	3868 (5)	505 (36)
C13	878 (13)	-1629 (8)	4542 (6)	628 (37)
C14	1522 (14)	-1015 (9)	5072 (5)	678 (41)
C15	2992 (13)	-772 (8)	5012 (5)	632 (41)
C16	3061 (11)	-440 (7)	4346 (5)	527 (37)
C21	4234 (11)	-455 (7)	2913 (4)	440 (31)
C22	5298 (11)	-1151 (7)	3225 (5)	446 (34)
C23	6716 (12)	-990 (9)	3055 (5)	599 (41)
C24	7251 (13)	-82 (9)	3239 (5)	615 (36)
C25	6173 (15)	621 (8)	2962 (6)	691 (40)
C26	4743 (12)	461 (8)	3121 (5)	522 (35)
Au2	1600 (0.5)	112 (0.3)	1362 (0.2)	359 (1)
Br2	3068 (2)	1370 (1)	1365 (1)	582 (7)
P2	238 (3)	-1084 (2)	1278 (1)	367 (8)
C31	-1640 (11)	-850 (7)	985 (4)	431 (34)
C32	-2140 (12)	-80 (8)	1330 (5)	571 (35)
C33	-3627 (13)	158 (9)	1003 (6)	698 (45)
C34	-4584 (12)	-628 (10)	983 (5)	749 (55)
C35	-4088 (12)	-1407 (9)	655 (6)	724 (56)
C36	-2595 (11)	-1638 (8)	978 (5)	574 (48)
C41	663 (11)	-1872 (6)	691 (5)	361 (31)
C42	2073 (12)	-2323 (7)	919 (5)	542 (35)
C43	2370 (13)	-2941 (8)	402 (6)	646 (39)
C44	2233 (13)	-2527 (8)	-260 (6)	667 (42)
C45	824 (13)	-2105 (7)	-478 (5)	585 (37)
C46	539 (11)	-1457 (7)	18 (5)	528 (35)

Table 2. Selected distances (Å) and angles (°)

Au—Br1	2.403 (3)	Br—Au1—P1	172.0 (1)
Au1—P1	2.264 (3)	Br2—Au2—P2	175.5 (1)
Au1—C1	1.976	Au1—C1—N1	179.3
P1—C3	1.851 (11)	Au2—C2—N2	179.6
P1—C11	1.842 (10)	Au1—P1—C3	118.0 (4)
P1—C21	1.843 (11)	Au1—P1—C11	109.6 (3)
C3—C4	1.547 (15)	Au1—P1—C21	112.3 (4)
Au2—Br2	2.406 (2)	Au2—P2—C4	112.7 (3)
Au2—P2	2.254 (3)	Au2—P2—C31	113.3 (3)
Au2—C2	1.966	Au2—P2—C41	112.0 (3)
P2—C31	1.841 (11)	C11—P1—C3	102.7 (5)
P2—C41	1.837 (10)	C21—P1—C3	103.7 (5)
P2—C4	1.816 (10)	C21—P1—C11	110.1 (5)
C1—N1	1.127	C4—C3—P1	115.7 (7)
C2—N2	1.119	P2—C4—C3	113.8 (7)

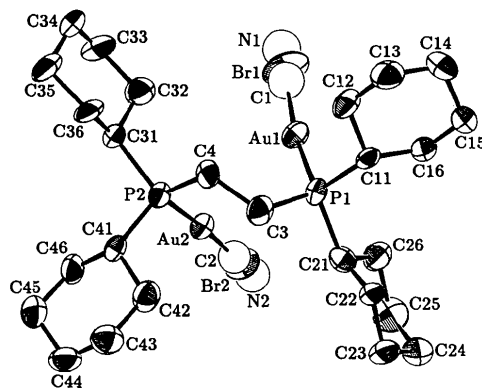


Fig. 1. An *ORTEPII* (Johnson, 1976) drawing of the molecule with 50% probability ellipsoids showing the numbering system. Br and CN groups are not both present at the same position in a given molecule. H atoms are not shown.

* Lists of anisotropic displacement parameters, complete distances and angles, observed and calculated structure factors and assigned H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54987 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0581]

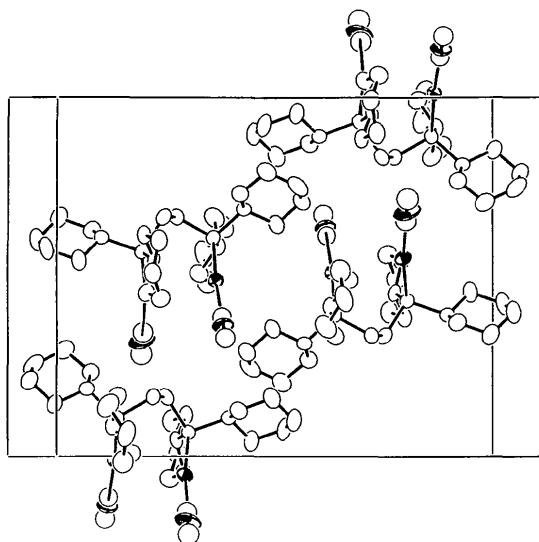


Fig. 2. An ORTEP (Johnson, 1976) projection perpendicular to the *bc* plane showing the contents of one unit cell, with a unit cell outlined. The *c* axis is horizontal. Au and Br atoms are shown shaded; H atoms are not shown.

are close to linear [172.0 (1) and 175.5 (1)°], appropriate for the +1 oxidation state of the Au. All four cyclohexyl rings are in the chair conformation, with average C—C distance of 1.517 (11) Å and average C—C—C angle of 111.5 [11]°.

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Structure of *trans*-Bis[*dimethylglyoximato*(1-)-*N,N'*]bis(*pyridine-N*)cobalt(III) Tetrachloroferrate(III)

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Abstract. [Co(C₄H₇N₂O₂)₂(C₅H₅N)₂][FeCl₄], *M_r* = 645.1, triclinic, *P* $\bar{1}$, *a* = 9.306 (3), *b* = 16.247 (3), *c* = 8.972 (2) Å, α = 104.72 (2), β = 96.38 (2), γ = 80.44 (2)°, *V* = 1290.4 (7) Å³, *Z* = 2, *D_m* = 1.67, *D_x* = 1.660 g cm⁻³, λ (Mo *K* α) = 0.71069 Å, μ = 16.93 cm⁻¹, *F*(000) = 654, room temperature, *R* = 0.062 for 4566 observed reflections. The crystal consists of cobaloxime cations and FeCl₄⁻ anions. Two crystallographically independent cobaloxime cations occupy the individual centres of symmetry. The cobaloxime cations exhibit a distorted octahedral

The molecules pack in the crystal more or less extended in the *z* direction. There are a few contacts shorter than van der Waals distances; the two shortest (3.10, 3.23 Å) involve cyclohexyl C atoms and N atoms of the cyanide groups, so they are not present in all unit cells. All other intermolecular distances are greater than 3.7 Å.

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coordination with the four oxime N donors at the equatorial positions and two pyridyl N donors at the axial sites. The tetrahedral FeCl₄⁻ anion is stabilized by the large cobaloxime cation in the crystal.

Introduction. Recently the complexes of LCo(DH)₂R, where *L* = neutral amine ligand, *R* = alkyl group and DH = monoanion of dimethylglyoxime, have been extensively studied as a simple molecular model of the vitamin B₁₂ system (Bresciani Pahor, Forcolin, Randaccio, Marzilli, Summers & Toscano, 1985).