

Tableau 2. Distances interatomiques (Å) et angles (°)

Rh—Rh'	2,3829 (6)	O(1)—C(1)	1,260 (5)
Rh—O(1)	2,031 (3)	C(1)—C(2)	1,498 (7)
Rh—O(2)	2,043 (3)	C(1)—O(4')	1,266 (5)
Rh—O(3)	2,030 (3)	O(2)—C(3)	1,265 (5)
Rh—O(4)	2,038 (3)	C(3)—C(4)	1,495 (8)
Rh—N(13)	2,241 (4)	C(3)—O(3')	1,270 (5)
S(11)—C(12)	1,722 (4)	S(21)—C(22)	1,716 (5)
S(11)—C(15)	1,730 (5)	S(21)—C(25)	1,699 (7)
C(12)—N(13)	1,310 (5)	C(22)—C(23)	1,389 (7)
C(12)—N(28)	1,360 (6)	C(22)—C(26)	1,461 (7)
N(13)—C(14)	1,365 (6)	C(23)—C(24)	1,390 (8)
C(14)—C(15)	1,332 (7)	C(24)—C(25)	1,356 (9)
C(15)—N(16)	1,434 (6)	C(26)—O(27)	1,219 (6)
N(16)—O(17)	1,219 (6)	C(26)—N(28)	1,369 (6)
N(16)—O(18)	1,223 (6)		
C(30)—Cl(31)	1,753 (9)	C(30)—Cl(32)	1,753 (9)
Rh'—Rh—O(1)	88,52 (9)	O(1)—Rh—N(13)	90,9 (1)
Rh'—Rh—O(2)	88,50 (9)	O(2)—Rh—O(3)	175,9 (1)
Rh'—Rh—O(3)	87,54 (9)	O(2)—Rh—O(4)	89,3 (1)
Rh'—Rh—O(4)	87,66 (9)	O(2)—Rh—N(13)	93,0 (1)
Rh'—Rh—N(13)	178,4 (1)	O(3)—Rh—O(4)	91,6 (1)
O(1)—Rh—O(2)	90,0 (1)	O(3)—Rh—N(13)	90,9 (1)
O(1)—Rh—O(3)	88,8 (1)	O(4)—Rh—N(13)	92,9 (1)
O(1)—Rh—O(4)	176,1 (1)		
O(1)—C(1)—C(2)	117,8 (5)	C(4)—C(3)—O(3')	117,9 (5)
O(1)—C(1)—O(4')	125,7 (4)	Rh—O(1)—C(1)	118,8 (3)
C(2)—C(1)—O(4')	116,5 (5)	Rh—O(2)—C(3)	118,9 (3)
O(2)—C(3)—C(4)	117,8 (5)	Rh—O(3)—C(3)	120,5 (3)
O(2)—C(3)—O(3')	124,4 (4)	Rh—O(4)—C(1')	119,3 (3)
Rh—N(13)—C(12)	127,1 (3)	O(17)—N(16)—O(18)	125,2 (5)
Rh—N(13)—C(14)	122,6 (3)	C(22)—S(21)—C(25)	91,6 (3)
C(12)—S(11)—C(15)	86,5 (2)	S(21)—C(22)—C(23)	110,9 (4)
S(11)—C(12)—N(13)	116,3 (4)	S(21)—C(22)—C(26)	124,2 (4)
S(11)—C(12)—N(28)	123,2 (3)	C(23)—C(22)—C(26)	124,9 (5)
N(13)—C(12)—N(28)	120,5 (4)	C(22)—C(23)—C(24)	112,0 (5)
S(11)—C(15)—C(14)	112,6 (4)	C(23)—C(24)—C(25)	113,3 (6)
S(11)—C(15)—N(16)	121,4 (4)	C(24)—C(25)—S(21)	112,1 (5)
C(12)—N(13)—C(14)	110,2 (4)	C(22)—C(26)—O(27)	123,0 (4)
N(13)—C(14)—C(15)	114,3 (5)	C(22)—C(26)—N(28)	117,8 (4)
C(14)—C(15)—N(16)	125,9 (5)	O(27)—C(26)—N(28)	119,2 (5)
C(15)—N(16)—O(17)	118,2 (5)	C(12)—N(28)—C(26)	124,2 (4)
C(15)—N(16)—O(18)	116,6 (5)		
Cl(31)—C(30)—Cl(32)	103,0 (9)		

Code de symétrie: (i) 1 - x, 1 - y, 1 - z.

L'étude radiocristallographique a montré que la structure dinucléaire de l'acétate de rhodium(II) est conservée après réaction avec le ténonitrozole et que celui-ci est lié au rhodium par l'intermédiaire de l'atome d'azote N(13) du groupement thiazole. Cependant la conformation du ligand diffère de celle observée dans la molécule du ténonitrozole libre.

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A Luminescent Gold Complex: Bis- μ -[bis(dicyclohexylphosphino)ethane-*P,P'*]-digold Bis(hexafluorophosphate)

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Abstract. $[\text{Au}_2(\text{C}_{26}\text{H}_{48}\text{P}_2)_2](\text{PF}_6)_2$, $M_r = 1529.1$, tetragonal, $P4n2$, $a = 15.917$ (5), $c = 12.448$ (1) Å, V

$= 3154$ (1) Å³, $Z = 2$, $D_x = 1.61$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 50.1$ cm⁻¹, $F(000) = 1528$, room temperature (297 K), $R = 0.064$ for 3525 reflections with $F_o^2 > 0$, 0.038 for 2440 with $F_o^2 > 3\sigma(F_o^2)$. This

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compound shows a strong luminescence in the solid state at 77 K. The cation consists of two Au atoms joined by two bis(dicyclohexylphosphino)ethane links, with one Au atom and one half of a link being the asymmetric unit. The Au—Au distance [2.936 (1) Å] is only slightly longer than the 2.884 Å found in gold metal, indicative of substantial metal-metal bonding.

Introduction. Several gold dimers have been reported to luminesce in the solid state (Khan, Fackler, King, Wang & Wang, 1988; Che, Wong, Lai & Kwong, 1989; King, Wang, Khan & Fackler, 1989) with emission maxima from 456 to 593 nm and excited-state lifetimes from 0.1 to 24 μs. At least two of these dimers have been reported to emit at room temperature in solution (Che *et al.*, 1989; King *et al.*, 1989); the title compound {Au[bis-1,2-dicyclohexylphosphino)ethane]}₂(PF₆)₂ was made in order to investigate the role of the Au—Au interaction in the dimer photophysics. The compound luminesces (489 nm) in the solid state at 77 K but not at room temperature; it appears that the emission is a property of the AuP₂ monomeric unit, with the Au—Au interaction playing a lesser role. We are continuing this work with other gold dimers and related monomeric complexes.

Experimental. This material was synthesized by adding one equivalent of the chelating phosphine ligand to 50 ml of argon-purged CH₃CN containing 150 mg of (Cl)Au(tetrahydrothiophene), which was prepared according to the literature procedure (Uson, Laguna & Vicente, 1977). After stirring for 1 h the solvent was removed under reduced pressure. Metathesis to the PF₆⁻ salt was accomplished by dissolving the Cl⁻ salt in 30 ml of a 70/30 mixture of MeOH/H₂O and then adding excess NH₄PF₆ to precipitate the PF₆ salt. The white PF₆ salt was collected by vacuum filtration; crystals for X-ray diffraction were grown by recrystallization from CH₃CN/Et₂O.

Crystal: square prism with cross section 0.26 × 0.26 mm, 0.3 mm long with skewed ends. CAD-4 diffractometer; ω scans; cell dimensions from 25 reflections with 39 < 2θ < 43°; no absorption correction (μ_rmax = 1.2, two data sets merged satisfactorily); (sin θ/λ)_{max} = 0.66 Å⁻¹; data collected to 2θ = 56°, h from 0 to 21, k from 0 to 21, l from -16 to 16; three standard reflections, 230, 140 and 22̄, showed no variations greater than expected from counting statistics; 8221 reflections measured, 3805 independent; goodness of fit for merging 1.08 {GOF_{hkl} = [Σ_nw(F_o²(hkl) - F_{av}²(hkl))²/(n - 1)]^{1/2} for n observations of reflection hkl; GOF_{merge} = [Σ_mw(GOF_{hkl})²/m]^{1/2}, for m reflections with more than one contributor}; R_{merge} (point group, 4̄m2) for 3386 reflections with exactly two observations = 0.042; all reflections used

Table 1. Final refined parameters (x, y, z and U_{eq} × 10⁴)

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

	x	y	z	U _{eq} (Å ²)
Au	652 (3)	5652	2500	439 (1)
P1	1058 (1)	5593 (1)	717 (1)	481 (4)
C1	458 (4)	4959 (5)	-262 (5)	681 (20)
C10	2116 (6)	5166 (6)	635 (8)	533 (24)
C11	2128 (7)	4273 (5)	1132 (7)	810 (27)
C12	3017 (9)	3932 (6)	1106 (9)	1030 (35)
C13	3626 (7)	4503 (8)	1673 (9)	1052 (35)
C14	3624 (6)	5342 (8)	1209 (9)	951 (33)
C15	2746 (5)	5736 (6)	1198 (8)	768 (26)
C20	1107 (5)	6670 (5)	219 (6)	597 (20)
C21	300 (9)	7167 (7)	439 (10)	894 (37)
C22	407 (6)	8091 (6)	119 (9)	1006 (34)
C23	697 (8)	8193 (6)	-994 (9)	1077 (36)
C24	1465 (9)	7702 (8)	-1196 (11)	1442 (48)
C25	1372 (6)	6772 (6)	-934 (7)	907 (27)
P2	3292 (3)	8292	2500	899 (8)
F1	3128 (8)	8509 (8)	1366 (5)	2497 (54)
F2	3924 (9)	8924	2500	3533 (72)
F3	2639 (8)	7639	2500	2385 (44)
F4	3854 (8)	7670	2050 (8)	2838 (63)

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

Au—Au	2.935 (1)	P1—C10	1.819 (10)
Au—P1	2.314 (2)	P1—C20	1.825 (8)
P1—C1	1.848 (7)	C1—C1	1.463 (9)
P1—Au—P1	160.6 (1)	C20—P1—C10	107.0 (4)
Au—P1—C1	120.7 (2)	C1—C1—P1	117.8 (5)
Au—P1—C10	109.1 (3)	C11—C10—P1	109.4 (6)
Au—P1—C20	107.4 (2)	C15—C10—P1	111.2 (6)
C10—P1—C1	103.8 (4)	C21—C20—P1	112.8 (6)
C20—P1—C1	108.2 (3)	C25—C20—P1	115.9 (6)

in solution and refinement of the structure. Au-atom coordinates found from Patterson map, remainder of structure by successive structure factor-Fourier calculations; full-matrix least-squares refinement using F² values. H atoms placed by calculation 0.95 Å from their C atoms, with isotropic B's of 10.0 Å², H-atom coordinates not refined but adjusted once near conclusion of refinement; 165 parameters refined, including scale factor, all refinable coordinates of non-H atoms and their anisotropic U_{ij}'s. w = 1/σ²(F_o²), final R 0.064 (wR on F² = 0.005) for 3525 reflections with F_o² > 0, 0.038 (wR on F² = 0.004) for 2440 reflections with F_o² > 3σ(F_o²), final goodness of fit, S = 1.46. The absolute configuration for the structure which we describe here was confirmed by refining both alternatives; the incorrect one gives R = 0.087 compared to R = 0.064 for the correct one. Variances [σ²(F_o²)] derived from counting statistics plus an additional term, (0.014I)², variances of the merged data by propagation of error plus another additional term, (0.014I)²; ratio of maximum shift to e.s.d. in final least-squares cycle, 0.07 for cation, 0.36 for F atoms of PF₆⁻ anion; one peak 2.7 e Å⁻³ between the two Au atoms, another 1.8 e Å⁻³, 0.3 Å from Au atom, all other peaks less

than $|1.5| e \text{ \AA}^{-3}$, most negative peaks in vicinity of PF_6^- ion. Atomic scattering factors and dispersion corrections taken from Cromer & Waber (1974). Programs used were those in *CRYM* (Duchamp, 1964) and *ORTEP* (Johnson, 1976). Final parameters are given in Table 1* and selected distances and angles in Table 2.

A few words about absorption, which we expected might be a problem ($\mu r_{\text{max}} = 1.2$). While the crystal

* Tables 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 54393 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

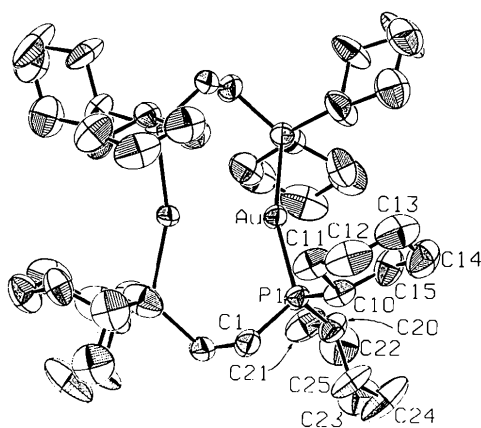


Fig. 1. An *ORTEP* (Johnson, 1976) view of the cation with 50% probability ellipsoids showing the numbering system. H atoms are not shown.

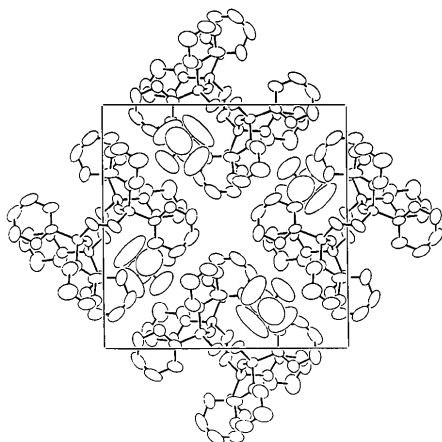


Fig. 2. An *ORTEP* (Johnson, 1976) drawing of four cations and four anions viewed perpendicular to the *ab* plane. The unit cell is outlined; atoms are shown at the 50% probability level with H atoms omitted.

was not far from cube-shaped, its morphology did not match its point group, and some of the bounding faces appeared to be complicated; a few were hidden in the cement. Our attempts to apply absorption corrections on the basis of our measurements of the crystal faces, or on the basis of ψ -scan measurements, were unsuccessful, in that they led to somewhat larger values of the goodness-of-fit for merging (the range of calculated transmission coefficients was 0.25–0.37 and the relative transmissions for three reflections used for the ψ scans were 0.85–1.10). We believe that the excellent GOF we obtained for averaging the two uncorrected data sets – 1.08 – suggests that absorption was not a serious problem, but we caution that our final U_{ij} values may include some absorption effects.

Discussion. The cation in this compound is positioned at a point of 222 symmetry; thus one quarter of the cation is the asymmetric unit. An *ORTEP* drawing of the cation showing the numbering system is given in Fig. 1. Fig. 2 is a view perpendicular to the *ab* plane. The two Au atoms are 2.935 (1) Å apart, 0.05 Å farther than in Au (metal) but indicative of a substantial Au–Au interaction. Fig. 1 shows the cation with the Au atoms apparently pulled toward each other by this bonding. The average length of Au–Au bonds in 123 dimers listed in the Cambridge Structural Database (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989) is 2.87 Å, with actual distances ranging from 2.55 to 3.29 Å. Thus the distance observed here is slightly longer than average and within normal limits. The Au–P distance is 2.314 (2) Å, somewhat shorter than the value of 2.400 (13) Å given for eight compounds of 1,2-bis(diphenylphosphino)ethane with gold (Orpen *et al.*, 1989), the closest match to the ligand used in this work. Other bond distances and angles are normal. The PF_6^- anion packs near the Au–Au group but at van der Waals distances or further away. The F atoms of this ion have large (apparent) thermal motions, reaching 0.8 Å r.m.s. deviation for F2. A model with disordered F atoms might have been used, but we considered it unlikely to improve the overall results significantly.

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Structure of β -Mo₂(SCN)₄[(2*S*,3*S*)-2,3-bis(diphenylphosphino)butane]₂ Nitromethane Solvate

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Abstract. Bis- μ -[(2*S*,3*S*)-2,3-bis(diphenylphosphino)butane-*P,P'*]-bis[bis(thiocyanato)molybdenum](*Mo—Mo*) nitromethane solvate, [Mo₂(SCN)₄(C₂₈H₂₈P₂)₂].CH₃NO₂, *M*_r = 1338.2, orthorhombic, *P*2₁2₁2, *a* = 15.890 (3), *b* = 17.532 (3), *c* = 24.745 (3) Å, *V* = 6893 (2) Å³, *Z* = 4, *D*_x = 1.29 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 6.0 cm⁻¹, *F*(000) = 2736, *T* = 298 K, *R* = 0.067 for 3341 unique observed reflections. The asymmetric unit consists of two half molecules of the title complex, each residing on a twofold axis. The Mo—Mo quadruple bond [2.172 (3) and 2.154 (3) Å] is bridged by an *S,S*-dppb ligand, and each Mo atom is *N*-coordinated to two thiocyanate groups. The intraligand P—Mo—Mo—P torsion angles (φ) are 25.8 (3) and 21.9 (3)°.

Introduction. Compounds of the structural type β-Mo₂X₄(PP)₂ have been intensively studied in the recent past (Agaskar, Cotton, Fraser, Manojlovic-Muir, Muir & Peacock, 1986). When the Mo₂X₄P₄ core is twisted about the Mo—Mo axis, an inherently dissymmetric Mo₂⁴⁺ chromophore results (Peacock, 1987). In order to observe the optical activity of this chromophore, it is necessary to stabilize one conformer of the Mo₂P₂C₂ ring by using a chiral diphosphine such as (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane, (*S,S*-dppb). One of us has previously reported the structures of β-Mo₂X₄(*S,S*-dppb) (*X* = Cl, Br) (Agaskar *et al.*, 1986), and herein we detail the structure of the thiocyanate derivative.

Experimental. The title complex was synthesized as follows. (NH₄)₄[Mo₂(SCN)₈].6H₂O (0.08 g) and a

slight excess of *S,S*-dppb (0.09 g) were refluxed in methanol (35 ml) under nitrogen atmosphere. The colour of the solution changed from green to yellow-brown during the course of the reaction. Removal of the methanol, followed by chromatography on alumina, using toluene as an eluant afforded a yellow band. The product was recrystallized from nitromethane. Analysis, calculated for C₆₀H₅₆Mo₂N₄P₄S₄: C 56.4, H 4.42, N 4.39%; found C 56.00, H 4.37, N 4.41%. A yellow-green prism, *ca* 0.5 × 0.4 × 0.15 mm, was mounted in a general position on a glass fibre; systematic absences: *h* = 2*n* + 1 in *h*00, *k* = 2*n* + 1 in 0*k*0; the reflections *l* = 2*n* + 1 in 00*l* were systematically weak; Enraf-Nonius CAD-4F diffractometer; graphite monochromator; θ/2θ scan mode; cell parameters refined by least-squares methods on basis of 25 independent θ values, 11 < θ < 13°; intensities measured to θ = 25.0° over *hkl* range 0 to 18, 0 to 20, 0 to 29; 402 and 042 measured every 2 h and showed a decay of *ca* 3% over data collection; 6990 data measured, 6935 independent data with 3341 having *I* > 2.0σ(*I*) considered observed and used in structure determination and refinement: *R*_{int} = 0.034; corrected for decomposition, Lorentz-polarization effects and absorption (*DIFABS*; Walker & Stuart, 1983), max. and min. values of applied absorption correction 1.40 and 0.77; solved by direct methods (*MITHRIL*; Gilmore, 1984) for heavy atoms, and subsequent full-matrix least squares; anisotropic thermal parameters for all non-H atoms except aryl C atoms and solvent atoms; phenyl groups refined as rigid groups with idealized geometry, C—C 1.395, C—H 1.0 Å; aliphatic C—H atoms included at calculated positions, C—H 1.0 Å, fixed contributions to structure factors for all H atoms, with *U* =

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