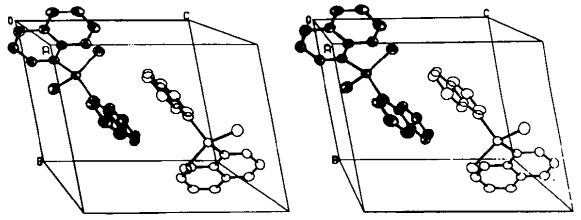

Fig. 2. Stereoview of the molecular packing.

Table 3. *The unit-cell parameters of the isomorphous compounds of the type MQ_2X_2*

	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)
CoQ_2Cl$_2$	8·789(2)	9·554(2)	11·026(2)	80·26(2)	72·19(2)	71·83(2)
CoQ_2Br$_2$	8·689(3)	9·652(2)	11·238(3)	80·74(2)	74·83(3)	73·26(2)
ZnQ_2Cl$_2$	8·822(2)	9·552(2)	11·028(2)	80·33(2)	72·36(2)	71·69(2)
ZnQ_2Br$_2$	8·677(1)	9·646(3)	11·276(3)	80·85(2)	74·51(4)	73·27(3)
NiQ_2Cl$_2$	8·703(1)	9·511(1)	11·075(1)	81·36(1)	73·12(1)	72·01(1)

The unit-cell parameters have been determined by least-squares methods as described in the text for all five compounds.

the octahedrally coordinated pyridine analogue [average Co—Cl = 2·50 Å: Dunitz (1957)]. The Co—N distances, 2·061 (3) and 2·037 (5) Å, are nearly the same as the corresponding distances in the analogous tetrahedral compound of γ-picoline (Co—N = 2·06 and 2·03 Å), and slightly shorter than those in the pyridine complex cited above, where the average Co—N distance is 2·14 Å. The angles range from 106·2 (1) to 114·5 (1)° within the coordination tetrahedron.

The bond-length and angle ranges in the quinoline ligands are in agreement with the corresponding ranges observed in other related structures, *e.g.* tetra-*n*-butylammonium tribromo(quinoline)nickelate(II) (Horrocks, Templeton & Zalkin, 1968) and bis(acetylacetonato)-bis(6-methylquinoline)cobalt(II) (Hursthouse & Malik, 1978). The quinoline ligands are planar. The maximum deviations of the atoms from the corresponding mean planes of the ligands are 0·029 and 0·026 Å, and the average deviations are 0·019 and 0·016 Å. The interplanar angle between the two independent ligands is 66·2 (5)°.

The title compound is isomorphous with the analogous complexes CoQ_2Br$_2$, ZnQ_2Cl$_2$, ZnQ_2Br$_2$ and NiQ_2Cl$_2$ (blue isomer), as shown by the comparison of their unit-cell parameters (Table 3).

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The Structure of μ-(1,1-Dicyanoethylene-2,2-dithiolato-S,S')-bis(triphenylphosphine)digold(I) Diethyl Ether Solvate

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Abstract. $[Au_2(C_4N_2S_2)(C_{18}H_{15}P)_2].C_4H_{10}O$, $M_r = 1132·82$, monoclinic, $C2/c$, $a = 23·556$ (3), $b = 14·655$ (4), $c = 16·138$ (3) Å, $\beta = 128·95$ (1)°, $V = 4332·3$ (14) Å^3, $D_x = 1·73$ g cm^{-3}, $Z = 4$, $\mu = 71·4$ cm^{-1}, λ(Mo $K\alpha$) = 0·71073 Å, $F(000) = 2184$, $T = 298$ K. Convergence to final conventional R values of $R = 0·0344$ and $wR = 0·0367$ was obtained using 195 variable parameters and 2260 reflections with $|F_o|^2 > 3\sigma(|F_o|^2)$. The structure consists of two units of AuPPh$_3$ bridged by a 1,1-dicyanoethylene-2,2-dithio-

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lato (imnt) ligand, which coordinates through the S atoms, and a molecule of diethyl ether solvate. The Au(1)—Au(1)′ distance is 3·156 (1) Å, the Au—S distance is 2·313 (2) Å, and the C—S distance is 1·729 (7) Å.

Introduction. Although a wide variety of complexes for both transition metals (Coucouvanis, 1979; Burns, McCullough & McAuliffe, 1980) and non-transition metals (Coucouvanis, 1979) containing 1,1-dithiolate ligands have been reported, only a few examples of this chemistry with gold has been reported. In recent years some gold complexes containing bridging dithiolate ligands (Shaw & Beery, 1986) and chelating thioglucose ligands (Mirabelli, Johnson, Hill, Fancette, Girard, Kuo, Sung & Crooke, 1986) have proved to be active as anti-tumor and anti-arthritic agents analogous to auranofin (Sutton, McGusty, Walz & DiMartino, 1972). The synthesis and structural characterization of gold–dithiolate complexes is of importance to many research groups because of its significance as related to biological studies.

In addition to monomeric complexes of Au^I (Chiari, Piovesana, Tarantelli & Zanazzi, 1985) and Au^{III} (Schmidbaur & Dash, 1982; Beurskens, Cras & Steggerda, 1968), dimeric systems of bis(dithiocarbamato)digold(I), $[Au^I(dtc)]_2$ (Hesse & Jennische, 1972) have been structurally characterized. The Au^{II} complex $[Au^{II}(dtc)]_2Br_2$ has been observed at low temperatures upon oxidation of $[Au^I(dtc)]_2$ with Br_2 (Calabro, Harrison, Palmer, Moguel, Rebbert & Burmeister, 1981). Our focus has been directed at dinuclear Au^I complexes containing the 1,1-dicyanoethylene-2,2-dithiolato (imnt) ligand and the oxidative addition reactions which give structurally characterizable Au^{II} dimer complexes (Wang, Khan, Fackler & Heinrich, 1988). In this paper we report the structure of the dinuclear Au^I complex containing two triphenylphosphine ligands and one bridging imnt ligand, $[(AuPPh_3)_2(imnt)]$.

Experimental. *Synthesis.* $[AuPPh_3]NO_3$ was synthesized by a reaction of $AuPPh_3Cl$ and $AgNO_3$ in a mixed-solvent system of CH_3OH/CH_2Cl_2. To a stirred solution of $[AuPPh_3]NO_3$ (0·05 g, 0·096 mmol) in CH_2Cl_2 was added K_2(imnt) (0·011 g, 0·048 mmol) [obtained using modified preparation of Gompper & Topel (1962)] in one portion at room temperature. The resultant yellow solution was allowed to stir overnight, after which time a white solid (KNO_3) was separated by filtration. The filtrate was evaporated to dryness giving $[(AuPPh_3)_2(imnt)]$ as a very light-yellow solid (0·051 g, 95%). The crude product was purified by recrystallization from CH_2Cl_2 with Et_2O. IR $\nu_{max} = 2200\ cm^{-1}$ (C≡N of imnt); $^{13}C\{H\}$ NMR ($CDCl_3$) 117 p.p.m. (C≡N of imnt); $^{31}P\{H\}$ NMR ($CDCl_3$) 36·20 p.p.m. (*s*).

X-ray data collection, solution and refinement. A colorless crystal of $[(AuPPh_3)_2(imnt)]$ was grown from a solvent mixture of CH_2Cl_2/Et_2O. A suitable crystal with dimensions 0·20 × 0·20 × 0·40 mm was mounted on a glass fiber with epoxy. Data collection was carried out at room temperature using the Wyckoff ω scanning technique in bisecting geometry. Diffraction experiments were performed on a Nicolet $R3m$/E four-circle diffractometer controlled by a Data General Nova 4 minicomputer using Mo $K\alpha$ radiation. The initial orientation matrix was obtained from 20 machine-centered reflections selected from a rotation photograph. Monoclinic symmetry was suggested from interaxial angles and confirmed by Delaunay reduction. Axial lengths were confirmed by comparison with interlayer spacings observed in axial photographs. 24 reflections ($18 < 2\theta < 33°$) were used to determine the final lattice parameters and orientation matrix. Intensities were measured for 6129 unique reflections of which 2260 were observed for $|F_o|^2 > 3\sigma(|F_o|^2)$ over $0 \leq h \leq 25$, $0 \leq k \leq 15$, $-18 \leq l \leq 18$ and $2 < 2\theta < 45°$. The scan rate was variable (3·10–29·30° min^{-1}). Backgrounds were estimated from a 96-step peak profile. Three standard reflections ($\bar{6}02$, $\bar{8}04$, $\bar{1}32$) were measured every 97 reflections. The data were corrected for decay (~0·10) by scaling on the three standards (all of which decayed similarly). Data were also corrected for absorption, Lorentz and polarization effects. Corrections for absorption were applied empirically on the basis of eight reflections spanning a range of 2θ values from 5·06 to 36·63° (minimum and maximum transmission was 0·179 and 0·340, respectively). Crystal structure solution and refinement were carried out using the *SHELXTL* collection of crystallographic software (version 4.1) (Sheldrick, 1981) on a Data General Eclipse S140 minicomputer.

The systematic absences hkl, $h + k = 2n + 1$ and $h0l$, $h + l = 2n + 1$ ($l = 2n + 1$), observed for this compound are consistent with the space groups $C2/c$ and Cc. Structure solution was initiated by assuming the space group $C2/c$ (No. 15, *International Tables for X-ray Crystallography,* 1974). This choice was confirmed by the successful solution and refinement of the structure. The coordinates of the unique Au atom were determined from 126 reflections ($E \geq 1·60$) phased by application of direct-methods procedures [*SOLV*, a program adapted from MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978)]. All remaining non-hydrogen atoms were obtained from subsequent difference Fourier maps. All phenyl rings were refined as rigid bodies with fixed C—C distances of 1·39 Å and C—C—C angles of 120°. The molecule possesses a twofold axis upon which carbon atoms C(1) and C(2) lie. Both C(1) and C(2) were refined with structure occupancy factors (SOF) of 50%. A diethyl ether solvent molecule was located with O(1) on the center of symmetry of the lattice and was refined with

SOF of 50%. In addition, the C atom bonded to O(1) showed disorder and was refined as C(4) and C(4)′, both with SOF of 50%. Atoms heavier than H were refined anisotropically except for the disordered diethyl ether molecule. The positions of H atoms on the phenyl rings were calculated by using a fixed C—H distance, 0·96 Å. Refinements were based on F with weights of the form $w^{-1} = (\sigma^2|F_o| + |g|F_o^2)$, where g had a value of 0·00119 and was refined by fitting $(F_o - F_c)^2$ to $[\sigma^2(F) + gF^2]/k$ (k = scale factor) to put the weights on an approximately absolute scale. Neutral-atom scattering factors, including terms for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974). Convergence to conventional R values of $R = 0{\cdot}0344$ and $wR = 0{\cdot}0367$ was obtained using 195 variable parameters and 2260 reflections with $|F_o|^2 > 3\sigma(|F_o|^2)$. In the final cycle the maximum shift/e.s.d. was 0·001, with a goodness-of-fit indicator = 1·116. The maximum and minimum residual electron density on the final difference Fourier map were +1·235 and −1·242 e Å^{-3} with the largest residual electron density located 1·28 Å from the Au atom.

Discussion. A thermal-ellipsoid diagram showing the molecular structure of $[(AuPPh_3)_2(imnt)]$ is shown in Fig. 1. A stereoview packing diagram for the molecule is shown in Fig. 2. The final positional and thermal parameters are given in Table 1.* Selected interatomic distances and angles are listed in Table 2. The molecule consists of two units of $AuPPh_3$ bridged by an imnt ligand. The imnt ligand is bound to each Au center through a single S atom. The bond distance for Au(1)—S(1) of 2·313 (2) Å is normal. The Au(1)—Au(1)′ distance of 3·156 (1) Å indicates the presence of significant non-bonding interactions between the two Au atoms. The steric interaction of the triphenylphosphine ligands is significant, however, since the separation of the Au atoms is greater than the S—C—S bite of 1,1-dicyanoethylene-2,2-dithiolato (3·02 Å). The slight bending of angle P(1)—Au(1)—S(1) from linearity, 172·1 (1)°, could also be attributed to the steric interaction of the two bulky triphenylphosphine ligands. In the lattice the molecules are staggered with respect to each other (Fig. 2). The shortest intermolecular Au—Au

Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å$^2 \times 10^3$)

	x	y	z	U/U_{eq}
Au(1)	696 (1)	5426 (1)	2562 (1)	46 (1)*
P(1)	1420 (1)	4211 (2)	3477 (2)	46 (1)*
S(1)	88 (2)	6750 (2)	1643 (2)	66 (2)*
C(1)	0	7311 (8)	2500	50 (7)*
C(2)	0	8245 (8)	2500	54 (8)*
C(3)	141 (5)	8758 (7)	1892 (9)	70 (7)*
N(1)	255 (6)	9160 (8)	1413 (10)	108 (10)*
C(11)	2243 (2)	4001 (5)	5688 (4)	60 (6)*
C(12)	2319	3912	6614	79 (7)*
C(13)	1701	3891	6552	76 (7)*
C(14)	1007	3958	5564	92 (8)*
C(15)	932	4046	4638	77 (7)*
C(16)	1550	4068	4700	49 (5)*
C(21)	859 (3)	3120 (4)	1727 (4)	65 (6)*
C(22)	615	2307	1149	75 (7)*
C(23)	587	1512	1599	77 (7)*
C(24)	803	1530	2625	74 (8)*
C(25)	1047	2343	3203	62 (6)*
C(26)	1075	3138	2754	43 (5)*
C(31)	2654 (4)	5201 (4)	4226 (6)	70 (7)*
C(32)	3348	5342	4533	85 (8)*
C(33)	3714	4627	4477	86 (8)*
C(34)	3386	3771	4115	83 (8)*
C(35)	2691	3629	3808	71 (7)*
C(36)	2325	4344	3863	50 (5)*
O(1)	2500	2500	0	145 (5)
C(4)	1984 (22)	2924 (32)	166 (34)	179 (15)
C(6)	2884 (18)	2932 (25)	1140 (26)	141 (11)
C(5)	2317 (13)	3312 (17)	1081 (19)	194 (9)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

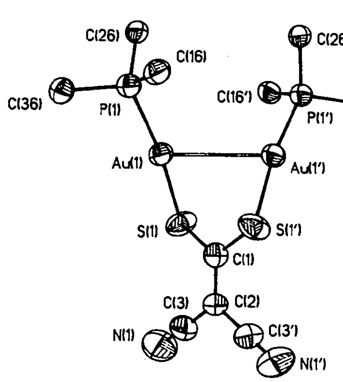

Fig. 1. A perspective view of the $[(AuPPh_3)_2(imnt)]$ structure. Thermal ellipsoids have been drawn at the 50% probability level. Phenyl rings are omitted for clarity.

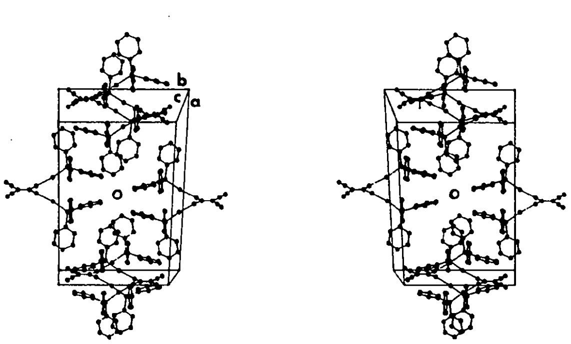

Fig. 2. Unit-cell stereoview packing diagram for $[(AuPPh_3)_2(imnt)]$ along the c axis. A disordered $(C_2H_5)_2O$ molecule, with oxygen (O) at the center of symmetry and disordered CH_2 groups (50% each position), is not drawn into the figure.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44660 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic bond distances* (Å) *and angles* (°)

Au(1)—S(1)	2·313 (2)	Au(1)—P(1)	2·257 (2)
Au(1)···Au(1′)	3·156 (1)	S(1)—C(1)	1·729 (7)
P(1)—C(16)	1·809 (6)	P(1)—C(26)	1·817 (6)
P(1)—C(36)	1·817 (9)	C(1)—C(2)	1·37 (2)
C(2)—C(3)	1·43 (2)	C(3)—N(1)	1·13 (2)
S(1)—Au(1)—P(1)	172·1 (1)	S(1)—Au(1)—Au(1′)	76·1 (1)
P(1)—Au(1)—Au(1′)	111·7 (1)	Au(1)—S(1)—C(1)	102·9 (3)
Au(1)—P(1)—C(16)	110·2 (2)	Au(1)—P(1)—C(26)	114·4 (2)
Au(1)—P(1)—C(36)	112·4 (2)	P(1)—C(16)—C(11)	121·9 (2)
P(1)—C(16)—C(15)	118·1 (2)	P(1)—C(26)—C(21)	117·5 (2)
P(1)—C(26)—C(25)	122·5 (2)	P(1)—C(36)—C(31)	117·6 (2)
P(1)—C(36)—C(35)	122·5 (2)	S(1)—C(1)—C(2)	118·4 (4)
S(1)—C(1)—S(1′)	123·2 (7)	C(1)—C(2)—C(3)	121·7 (6)
C(3)—C(2)—C(3′)	117· (1)	C(2)—C(3)—N(1)	180· (1)

distance is 8·138 Å. The S(1)—C(1) bond length of 1·729 (7) Å and the C(2)—C(3) bond length of 1·43 (2) Å indicate partial multiple-bonding electron delocalization in the imnt ligand. The imnt ligand is planar as expected. The Au(1)—P(1) bond length of 2·257 (2) Å is within the normal range for an Au—P bond. The P—C bond distances in the molecule are similar and range from 1·809 (8) to 1·817 (9) Å. Other than being disordered, the diethyl ether molecule is unremarkable.

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Di-μ-chloro-bis[(aza-4 azonia-1 bicyclo[2.2.2]octane)dichloromanganèse(II)]

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(*Reçu le* 28 *juillet* 1987, *accepté le* 4 *janvier* 1988)

Abstract. $[Mn_2Cl_6(C_6H_{13}N_2)_2]$, $M_r = 548{\cdot}96$, monoclinic, $P2_1/n$, $a = 7{\cdot}157\ (2)$, $b = 12{\cdot}378\ (3)$, $c = 12{\cdot}047\ (1)$ Å, $\beta = 96{\cdot}90\ (1)°$, $V = 1059{\cdot}6\ (7)$ Å^3, $Z = 2$, $D_m = 1{\cdot}76\ (2)$, $D_x = 1{\cdot}721$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu = 1{\cdot}91$ mm^{-1}, $F(000) = 556$, $T = 294\ (1)$ K, $R = 0{\cdot}023$ for 2015 independent reflections. The molecule has a centre of symmetry. Its two halves are linked together by two Mn—Cl—Mn bridges. The coordination polyhedron of the Mn atom is a bipyramid constituted of four Cl atoms and an N atom from the organic ligand. The apical Mn—Cl distance is significantly greater than the same equatorial distances. In a rough estimate, the plane of the two Mn—Cl—Mn bridges is a plane of symmetry for the molecule which

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