C9	−0.3021 (12)	0.2016 (5)	0.0776 (5)	0.063 (4)
C10	−0.4075 (11)	0.1817 (6)	0.0112 (6)	0.068 (4)
C11	−0.4291 (12)	0.1165 (6)	−0.0028 (5)	0.065 (4)
C12	−0.3513 (10)	0.0720 (4)	0.0511 (5)	0.052 (3)
C13	−0.1910 (12)	−0.0150 (5)	0.1767 (5)	0.059 (4)
C14	−0.0874 (15)	−0.1228 (5)	0.2336 (6)	0.067 (5)
C15	−0.234 (2)	−0.1439 (5)	0.2629 (7)	0.117 (7)
C16	−0.083 (2)	−0.1536 (5)	0.1523 (7)	0.122 (7)
C17	0.0537 (15)	−0.1433 (5)	0.2940 (8)	0.141 (7)
C18	−0.2928 (14)	0.1557 (6)	0.3239 (7)	0.126 (7)
C19	−0.0617 (12)	0.1148 (5)	0.4552 (5)	0.088 (5)
C20	−0.2605 (12)	0.0260 (5)	0.3631 (6)	0.093 (6)
C21	0.1101 (13)	0.0643 (9)	0.0694 (6)	0.201 (11)
C22	0.336 (2)	0.0197 (7)	0.1941 (8)	0.177 (10)
C23	0.309 (2)	0.1483 (6)	0.1631 (8)	0.154 (9)

Table 2. *Selected geometric parameters* (Å, °)

P1—Ni	2.212 (3)	C22—P2	1.766 (14)
P2—Ni	2.206 (3)	C23—P2	1.780 (14)
N1—Ni	1.978 (6)	C13—O1	1.220 (12)
C1—Ni	1.930 (7)	C7—N1	1.411 (10)
C18—P1	1.804 (12)	C13—N1	1.366 (12)
C19—P1	1.816 (9)	C13—N2	1.379 (11)
C20—P1	1.798 (11)	C14—N2	1.475 (12)
C21—P2	1.754 (10)		
P1—Ni—P2	176.84 (12)	C20—P1—Ni	116.6 (4)
P1—Ni—N1	90.5 (2)	C21—P2—C22	102.1 (7)
P2—Ni—N1	92.4 (2)	C21—P2—C23	100.9 (7)
P2—Ni—C1	88.7 (3)	C21—P2—Ni	117.4 (4)
N1—Ni—C1	178.0 (3)	C22—P2—C23	99.9 (6)
C1—Ni—P1	88.4 (3)	C22—P2—Ni	115.7 (5)
C18—P1—C19	101.9 (5)	C23—P2—Ni	118.0 (5)
C18—P1—C20	100.3 (5)	C7—N1—C13	119.8 (7)
C18—P1—Ni	114.3 (4)	C7—N1—Ni	118.8 (5)
C19—P1—C20	100.5 (5)	C13—N1—Ni	121.4 (5)
C19—P1—Ni	120.2 (4)	C13—N2—C14	124.3 (8)

The ω-scan width was symmetrically over 1.2° about the $K\alpha_{1,2}$ maximum and the background was offset 1.0 and −1.0° in ω from the $K\alpha_{1,2}$ maximum. The scan speed was a variable 3–6° min^{-1} (depending upon intensity). The linear absorption coefficient was calculated using values from *International Tables for X-ray Crystallography* (1974). The structure was solved by the heavy-atom method from which the position of the Ni atom was obtained.

SHELXTL-Plus (Sheldrick, 1990) was used for cell refinement, data collection, data reduction, structure solution (direct methods) and molecular graphics. *SHELX76* (Sheldrick, 1976) was used for structure refinement (full-matrix least-squares).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1022). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis[bis(triphenylphosphoranylidene)ammonium] Bis[cyanodithiocarbimatogold(I)], $[PPN]_2[Au_2(S_2CNCN)_2]$

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Abstract

The title complex, bis[bis(triphenylphosphoranylidene)ammonium] bis[μ-cyanodithiocarbamato(2−)-S:S']-digold(I), $[(C_{18}H_{15}P)_2N]_2[Au_2(C_2N_2S_2)_2]$, displays a short Au···Au contact of 2.813 (1) Å, which is slightly longer than the value of 2.796 (1) Å found in the similar structure of the anionic $Au_2(i\text{-mnt})_2^{2-}$ dimer (*i*-mnt is 1,1-dicyano-2,2-ethenedithiolate). The complex oxidatively adds halogens to form green Au^{II} dimers which are unstable at room temperature.

Comment

While gold(I) complexes often display short Au···Au contacts, ranging from 2.7 to 3.3 Å, little is known about the dependence of this interaction on the ligand bound to the Au-atom center. Neutral and anionic bridged dinuclear dithiocarbamate (Heinrich, Wang & Fackler, 1990) and 1,1-dithiolate gold(I) complexes (Khan, Wang & Fackler, 1989) are known to contain some of the shortest Au···Au distances. In addition, both the neutral (Calabro *et al.*, 1981) and the anionic 1,1-dithiolate (Khan, Wang & Fackler, 1989) species are known to add halides oxidatively to form Au^{II} dimers. As a consequence of better σ donation, the oxidative addition product formed with the dianionic 1,1-dithiolate ligand is more stable than the neutral dithiocarbamate dimer product. Compared with *i*-mnt (1,1-dicyano-2,2-

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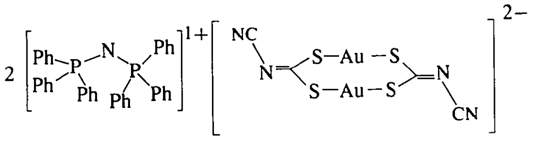
ethenedithiolate), the cyanodithiocarbimate (cdc) ligand (Coucouvanis & Fackler, 1967) has been reported to have a reduced σ-donating ability. In order to investigate how this reduced σ-donating ability of the cdc ligand influences the Au···Au interaction and the stability of the oxidative addition products, we have undertaken the synthesis and crystal-structure determination of $[PPN]_2[Au_2(S_2CNCN)_2]$, (I) [PPN is the bis(triphenylphosphoranylidene)ammonium cation]. Fig. 1 shows the $[Au_2(S_2CNCN)_2]$ dianion of (I) with the atomic labeling scheme.



(I)

The Au···Au separation in (I) is only slightly longer than that found [2.796 (1) Å] in a similar structure reported for the $Au_2(i\text{-mnt})_2^{2-}$ dimer (Khan, Wang & Fackler, 1989). Moreover, the Au—S distances and the S—Au—S angles in (I) are almost identical to those of the $Au_2(i\text{-mnt})_2^{2-}$ dimer, showing that the differences in the σ-donating ability of the two ligands (*i*-mnt *versus* cdc) alter the Au···Au contact slightly. The N1—C2 bond distance in (I) (Table 2) is short and almost identical to the C1—N1 distance and indicates delocalization in the π system of the ligand.

Compound (I) oxidatively adds halogens to form a green Au^{II} dimer, which is stable indefinitely if kept at temperatures below 253 K. At room temperature, however, decomposition to Au^{III} and Au^{I} products occurs more readily than found with the $Au_2(i\text{-mnt})_2^{2-}$ complex (Khan, Wang & Fackler, 1989).

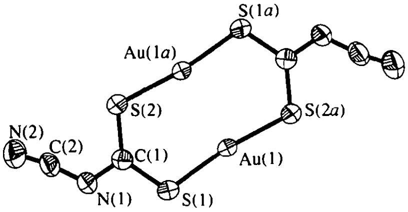


Fig. 1. Drawing with 50% probability ellipsoids of the dianion $[Au_2(S_2CNCN)_2]$, showing the atom-labeling scheme.

Experimental

To a suspension of AuCN (Aldrich Chemical Company) in acetone, one equivalent of $K_2(S_2CNCN)$, prepared from KNCN (Aldrich) and CS_2, was added. After stirring for 2 h, the solution was filtered and the solvent removed by vacuum suction. The white residue was then dissolved in CH_2Cl_2 and two equivalents of PPNCl were added. A colorless crystalline product was obtained after precipitating with Et_2O.

Crystal data

$(C_{36}H_{30}NP_2)_2[Au_2(C_2N_2S_2)_2]$
$M_r = 1703.43$
Triclinic
$P\overline{1}$
$a = 11.416\,(1)$ Å
$b = 11.749\,(1)$ Å
$c = 14.501\,(1)$ Å
$\alpha = 105.08\,(1)°$
$\beta = 109.83\,(1)°$
$\gamma = 95.33\,(1)°$
$V = 1731.1\,(4)$ Å^3
$Z = 1$
$D_x = 1.624$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–15°$
$\mu = 4.49$ mm^{-1}
$T = 293$ K
Block
0.4 × 0.2 × 0.1 mm
Colorless

Data collection

*R*3*m*/*E* diffractometer
Wyckoff scans
Absorption correction: ψ scans of 6 reflections (North, Phillips & Mathews, 1968)
$T_{min} = 0.698$, $T_{max} = 0.957$
4989 measured reflections
4167 independent reflections
3924 observed reflections $[F_o^2 > 3\sigma(F_o^2)]$
$R_{int} = 0.0165$
$\theta_{max} = 22.5°$
$h = 0 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 97 reflections intensity decay: <1%

Refinement

Refinement on *F*
$R = 0.0290$
$wR = 0.0380$
$S = 1.014$
3924 reflections
415 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.00093F_o^2]$
$(\Delta/\sigma)_{max} = -0.016$
$\Delta\rho_{max} = 0.834$ e Å^{-3}
$\Delta\rho_{min} = -1.56$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	U_{eq}
Au(1)	0.5137 (1)	0.8899 (1)	0.0195 (1)	0.043 (1)
S(1)	0.4882 (2)	0.9483 (1)	0.1734 (1)	0.052 (1)
S(2)	0.4570 (2)	1.1924 (2)	0.1301 (1)	0.068 (1)
P(1)	0.0036 (1)	0.8859 (1)	0.2361 (1)	0.031 (1)
P(2)	−0.1414 (1)	0.6570 (1)	0.2232 (1)	0.034 (1)
N(1)	0.4287 (4)	1.1245 (4)	0.2822 (3)	0.050 (2)
N(2)	0.3848 (7)	1.3220 (6)	0.3507 (5)	0.091 (4)
N(3)	−0.1133 (4)	0.7905 (4)	0.2224 (3)	0.038 (2)
C(1)	0.4559 (5)	1.0914 (5)	0.1984 (4)	0.042 (2)
C(2)	0.4063 (6)	1.2327 (6)	0.3137 (5)	0.059 (3)
C(10)	0.0275 (4)	0.8698 (4)	0.1175 (4)	0.035 (2)
C(11)	0.1237 (5)	0.9459 (5)	0.1120 (4)	0.047 (2)
C(12)	0.1388 (6)	0.9314 (6)	0.0197 (5)	0.056 (3)
C(13)	0.0598 (7)	0.8411 (6)	−0.0674 (5)	0.062 (3)
C(14)	−0.0377 (7)	0.7685 (6)	−0.0648 (5)	0.070 (3)
C(15)	−0.0533 (6)	0.7822 (5)	0.0293 (4)	0.056 (3)
C(20)	−0.0288 (5)	1.0343 (4)	0.2780 (4)	0.036 (2)
C(21)	0.0694 (5)	1.1333 (5)	0.3291 (4)	0.049 (2)
C(22)	0.0421 (7)	1.2469 (5)	0.3544 (5)	0.063 (3)
C(23)	−0.0802 (7)	1.2611 (6)	0.3297 (5)	0.062 (3)

C(24)	−0.1781 (6)	1.1636 (5)	0.2799 (5)	0.061 (3)
C(25)	−0.1528 (5)	1.0499 (5)	0.2534 (5)	0.047 (3)
C(30)	0.1513 (5)	0.8852 (5)	0.3330 (4)	0.039 (2)
C(31)	0.2561 (5)	0.8587 (6)	0.3100 (5)	0.061 (3)
C(32)	0.3679 (6)	0.8608 (8)	0.3884 (7)	0.086 (4)
C(33)	0.3773 (7)	0.8852 (7)	0.4854 (6)	0.087 (4)
C(34)	0.2731 (8)	0.9127 (6)	0.5126 (5)	0.083 (4)
C(35)	0.1606 (6)	0.9114 (6)	0.4346 (4)	0.060 (3)
C(40)	−0.2321 (5)	0.5554 (4)	0.0955 (4)	0.038 (2)
C(41)	−0.2184 (6)	0.4372 (5)	0.0659 (4)	0.051 (3)
C(42)	−0.2942 (7)	0.3603 (6)	−0.0324 (5)	0.066 (3)
C(43)	−0.3806 (7)	0.4032 (6)	−0.0988 (5)	0.071 (3)
C(44)	−0.3969 (6)	0.5206 (6)	−0.0706 (5)	0.067 (3)
C(45)	−0.3217 (5)	0.5954 (5)	0.0280 (4)	0.050 (3)
C(50)	−0.2390 (4)	0.6491 (5)	0.2971 (4)	0.037 (2)
C(51)	−0.2552 (5)	0.7514 (5)	0.3580 (4)	0.049 (3)
C(52)	−0.3292 (6)	0.7440 (7)	0.4154 (5)	0.066 (3)
C(53)	−0.3884 (6)	0.6341 (7)	0.4101 (5)	0.071 (3)
C(54)	−0.3722 (6)	0.5314 (7)	0.3476 (5)	0.069 (3)
C(55)	−0.2986 (5)	0.5358 (6)	0.2903 (4)	0.052 (3)
C(60)	−0.0022 (5)	0.6014 (4)	0.2798 (4)	0.045 (2)
C(61)	0.0762 (6)	0.5680 (6)	0.2264 (6)	0.065 (3)
C(62)	0.1914 (6)	0.5375 (6)	0.2769 (7)	0.076 (4)
C(63)	0.2273 (6)	0.5432 (6)	0.3784 (7)	0.076 (4)
C(64)	0.1528 (7)	0.5768 (6)	0.4314 (6)	0.079 (4)
C(65)	0.0385 (5)	0.6064 (5)	0.3830 (5)	0.055 (3)

Table 2. *Selected geometric parameters* (Å, °)

Au(1)—S(1)	2.288 (2)	S(2)—C(1^{ii})	1.733 (7)
Au(1^{i})—S(2)	2.285 (2)	C(1)—N(1)	1.326 (8)
Au(1)···Au(1^{i})	2.813 (1)	N(1)—C(2)	1.314 (8)
S(1)—C(1)	1.727 (6)	C(2)—N(2)	1.138 (10)
S(1)—Au(1)—S(2^{i})	172.3 (1)	S(1)—C(1)—N(1)	113.0 (5)
S(1)—Au(1)···Au(1^{i})	94.7 (1)	S(2^{i})—C(1)—N(1)	118.5 (4)
S(2^{i})—Au(1)···Au(1^{i})	92.9 (1)	N(1)—C(2)—N(2)	171.3 (9)
Au(1)—S(1)—C(1)	111.0 (2)	C(1)—N(1)—C(2)	120.3 (6)
S(1)—C(1)—S(2^{i})	128.5 (4)		

Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $1 - x, -y, -z$.

The *SHELXTL-Plus* program package (Sheldrick, 1991) was used for crystallographic computations.

Support from the National Science Foundation (CHE 9300107), the Robert A. Welch Foundation and the Texas Advanced Research Program is gratefully acknowledged.

Lists of structure factors, H-atom coordinates, complete geometry and structure of the $[(C_{18}H_{15}P)_2N]_2$ cation have been deposited with the IUCr (Reference: BK1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(1-methylcytosinium) Tetrachlorocuprate(II)

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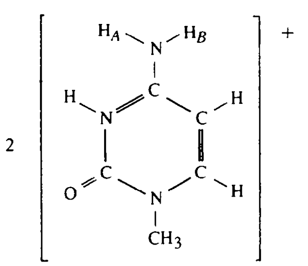
Abstract

The structure consists of discrete $C_5H_8N_3O^+$ (4-amino-1-methyl-2-oxo-1,2-dihydropyrimidinium) and $CuCl_4^{2-}$ ions. The coordination about the Cu atom is distorted tetrahedral with an average *trans* Cl—Cu—Cl angle of 127.7 (1)°.

Comment

The title compound, (I), has been found to exhibit a band maximum in the near IR spectrum at *ca* 9100 cm^{-1}. According to an established correlation (Halvorson, Patterson & Willet, 1990), this would correspond to an average *trans* Cl—Cu—Cl angle of about 130°, markedly different from the value of 139.2 (1)° observed in the closely related compound biscytosinium tetrachlorocuprate, (II) (Ogawa, Nishitani, Fujiwara, Shirotake & Tomita, 1979). To explain this difference, the present crystal structure analysis was undertaken.



(I)

The structure consists of discrete $C_5H_8N_3O^+$ and $CuCl_4^{2-}$ ions. There are no intermolecular Cu···Cl contacts less than 4 Å. Each cation is hydrogen bonded to one anion through N(3)H and N(4)H(*A*) and to two $C_5H_8N_3O^+$ units related by translation through

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† Deceased.