expected, the extended conjugated ketoenolate ligand is nearly planar with the bulky isopropenyl group directed outwards from the plane. Surprisingly, no linear metal chain is formed in the solid state, but only dimeric entities are observed. The intermolecular Ir–Ir distance within the dimer is 3·29 Å, indicating a weak metal–metal interaction, and may be compared with the values for the one-dimensional metal chains in dicarbonyl(2,4-pentanedionato)iridium(I) (Ir–Ir 3·20 Å) (Pitt, Monteith, Ballard, Collman, Morrow, Roper & Ulkü, 1966) or in racemic dicarbonyl(3-trifluoroacetylcamphorato)iridium(I) (Ir–Ir 3·34 Å) (Pille, 1985). In contrast to racemic dicarbonyl(3-heptafluorobutanoylcamphorato)iridium(I) the dimers are not formed from homochiral complexes (*R*/*R* or *S*/*S*) but from heterochiral complexes (*R*/*S*). The reason for the failure of the title compound to undergo molecular stacking in the solid state is unknown at present.

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Structure of $Au_2[S_2CN(C_2H_5)_2]_2$, Bis(diethyldithiocarbamato)digold(I)

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Abstract. Bis(μ-*N*,*N*-diethyldithiocarbamato-*S*,*S*′)-digold(I), $[Au_2(C_5H_{10}NS_2)_2]$, $M_r = 690{\cdot}45$, tetragonal, $I4_1/a$, $a = 18{\cdot}060\ (3)$, $c = 22{\cdot}914\ (3)$ Å, $V = 7473{\cdot}1\ (18)$ Å^3, $D_x = 2{\cdot}45$ g cm^{-3}, $Z = 16$, λ(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 160{\cdot}8$ cm^{-1}, $F(000) = 5054$, $T = 295$ K, final $R = 0{\cdot}037$ and $wR = 0{\cdot}053$ using 163 parameters and 1951 reflections with $F_o > 3\sigma F_o$. The structure consists of discrete dimers each containing two Au atoms bridged by two diethyldithiocarbamate ligands. The intramolecular Au—Au distance is 2·782 (1) Å, with Au—S distances ranging from 2·28 to 2·30 Å. The packing of the dimeric units produces linear chains of Au atoms containing the shortest intermolecular Au—Au distance yet found in these dithiocarbamate digold(I) compounds [3·004 (1) Å].

Introduction. Our recent success in the preparation of dinuclear gold(II) ylide compounds containing thiolate ligands (Heinrich, 1987; Heinrich & Fackler, 1986) and in the preparation of a series of dinuclear Au^I and Au^{II} compounds bridged by 1,1-dicyano-2,2-ethylenedithiolate (i-mnt) (Khan, Fackler, King, Wang & Wang, 1988; Khan, Wang, Heinrich & Fackler, 1988) has prompted us to re-examine the chemistry of the dithiocarbamate dimers of gold(I). Dinuclear Au^I dithiocarbamate complexes have been studied in the past; the dipropyldithiocarbamate (Hesse & Jennische, 1972) and dibutyldithiocarbamate (Jennische, Anacker-Eickhoff & Wahlberg, 1975) complexes have been structurally characterized. In the solid state these compounds are found to stack so as to form linear gold chains with short intra- and intermolecular Au—Au distances. Although the structural characterization of a dinuclear Au^{II} system containing an Au—Au bond has not been achieved, Burmeister and co-workers have observed these species at low temperatures (Calabro, Harrison, Palmer, Moguel, Rebbert & Burmeister, 1981). As part of our studies we have been investigating the luminescence of Au systems which contain either Au—Au bonds or linear chains of Au atoms in

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the solid state (King, Wang, Khan & Fackler, 1989). A portion of this work has dealt with the dinuclear Au^I complex containing diethyldithiocarbamate, $Au_2[S_2CN(C_2H_5)_2]_2$. In this paper we report the structure of this compound, which has the shortest intermolecular Au—Au contact [3·004 (1) Å] yet characterized for an Au^I dithiocarbamate dimer.

Experimental. $Au_2[S_2CN(C_2H_5)_2]_2$ is prepared in tetrahydrofuran by the reaction of (tht)AuCl (tht = tetrahydrothiophene) with $KS_2CN(C_2H_5)_2$. Single crystals suitable for X-ray crystallographic analysis were obtained from $CHCl_3$ by slow evaporation. A light-red crystal with dimensions 0·12 × 0·13 × 0·80 mm was selected and mounted on a glass fiber with epoxy. Data were collected at room temperature using the $\theta/2\theta$ 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 graphite-monochromated Mo $K\alpha$ radiation. The initial orientation matrix was obtained from ten centered reflections selected from a rotation photograph. Tetragonal symmetry was suggested from the axial lengths and inter-axial angles, and was confirmed by comparison of symmetry-related reflections. 25 reflections ($25 < 2\theta < 30°$) were used to determine the final lattice parameters and orientation matrix. Intensities were measured for 2878 over $0 \le h \le 21$, $0 \le k \le 21$, $0 \le l \le 27$ and $3 < 2\theta < 47°$. The scan rate was variable (2·02–29·30° min^{-1}) with scan ranges −1·0° from $K\alpha_1$ to +1·0° from $K\alpha_2$. Backgrounds were estimated from a 96-step peak profile. Three standard reflections (040, 440, 428) were measured every 97 reflections and showed only small (<4%) random variations. Data were also corrected for absorption, Lorentz and polarization effects. Corrections for absorption were applied empirically on the basis of 8 reflections spanning a range of 2θ values from 12·6 to 29·6° (minimum and maximum transmission was 0·065 and 0·092, respectively). Crystal structure solution and refinement were carried out using the *SHELXTL* collection of crystallographic software (version 4.1) (Sheldrick, 1981) using a Data General Eclipse S140 minicomputer. The systematic absences [hkl, $h + k + l = 2n + 1$; $hk0$, $h(k) = 2n + 1$; $00l$, $l = 4n$] observed are consistent with the space group $I4_1/a$, which was confirmed by the successful solution and refinement of the structure. The coordinates of the unique Au atoms were determined from a Patterson map. All remaining non-H atoms were obtained from subsequent difference Fourier maps. H atoms were placed in calculated positions (C—H = 0·960 Å) with thermal parameters fixed at 1·2 times that of the atom to which they were attached. All non-H atoms were refined anisotropically. Refinements were based on minimizing $\sum w(|F_o| - |F_c|)^2$ with weights of the form $w^{-1} = (\sigma^2|F_o| + |g|F_o^2)$, where g had a value of 0·00167 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 scattering factors, including terms for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974). Convergence to conventional R values of $R = 0·037$ and $wR = 0·053$ was obtained using 163 variable parameters and 1951 reflections with $F_o > 3\sigma F_o$. In the final cycle of refinement the maximum shift/e.s.d. was 0·018, with a goodness-of-fit indicator = 1·111. The maximum and minimum residual electron density on the final difference Fourier map was +1·22 and −1·38 e $Å^{-3}$ with the largest residual electron density located 1·54 Å from an S atom and 1·84 Å from an Au atom.

Discussion. A perspective drawing of the complex $Au_2[S_2CN(C_2H_5)_2]_2$ can be found in Fig. 1. The final positional and thermal parameters are given in Table 1.* Selected interatomic distances and angles are listed in Table 2. The dimer consists of two independent Au atoms bridged by two diethyl dithiocarbamate ligands (dtc = dithiocarbamate). The gold(I) atoms have the expected two-coordinate linear coordination geometry, with bonds to one S atom of each dithiocarbamate bridge. The C atoms C(1) and C(2), as well as nitrogen atoms N(1) and N(2), are planar. The eight-membered ring consisting of $Au_2(CSC)_2$ is not planar due to the twist in the orientation of the dithiocarbamate ligands. A similar twist has been observed in both the dipropyl and dibutyl dithiocarbamate gold(I) complexes. This twist results in short intramolecular Au—Au distances (dipropyl = 2·76 Å; dibutyl = 2·78 Å). The Au—Au distance found in the title compound is 2·782 (1) Å. The Au—S distances in $Au_2[S_2CN(C_2H_5)_2]_2$ of 2·285 (3)–2·300 (3) Å are very

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and isotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52671 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

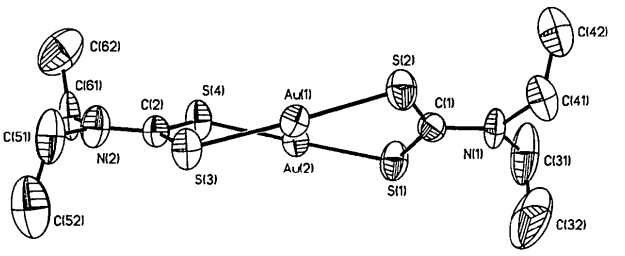

Fig. 1. A perspective view of the $Au_2[S_2CN(C_2H_5)_2]_2$ dimer. Thermal ellipsoids have been drawn at the 50% probability level.

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

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Au(1)	2800 (1)	4914 (1)	1934 (1)	38 (1)
Au(2)	2635 (1)	4771 (1)	732 (1)	39 (1)
S(1)	2467 (2)	3516 (2)	821 (2)	61 (1)
S(2)	3237 (2)	3721 (2)	2012 (2)	55 (1)
S(3)	2401 (2)	6117 (2)	1896 (1)	48 (1)
S(4)	2828 (2)	6009 (2)	593 (1)	53 (1)
C(1)	2880 (7)	3216 (7)	1467 (5)	46 (4)
C(2)	2612 (7)	6508 (6)	1235 (5)	37 (4)
N(1)	2918 (6)	2466 (5)	1510 (5)	54 (4)
N(2)	2618 (6)	7238 (6)	1185 (5)	57 (4)
C(31)	2661 (14)	1923 (9)	1051 (8)	109 (10)
C(32)	1863 (15)	1799 (12)	1062 (11)	168 (15)
C(41)	3261 (9)	2086 (8)	2021 (7)	71 (6)
C(42)	4050 (11)	1943 (10)	1940 (9)	111 (10)
C(51)	2443 (10)	7683 (8)	1685 (7)	76 (7)
C(52)	1621 (12)	7826 (9)	1771 (7)	95 (9)
C(61)	2764 (9)	7623 (7)	635 (6)	65 (6)
C(62)	3565 (10)	7809 (11)	567 (8)	108 (9)

Table 2. *Bond distances* (Å) *and angles* (°)

Au(1)—Au(2)	2·782 (1)	Au(1)—S(2)	2·300 (3)
Au(1)—S(3)	2·291 (3)	Au(1)—Au(2*a*)	3·004 (1)
Au(2)—S(1)	2·297 (3)	Au(2)—S(4)	2·285 (3)
Au(2)—Au(1*a*)	3·004 (1)	S(1)—C(1)	1·742 (13)
S(2)—C(1)	1·675 (13)	S(3)—C(2)	1·713 (12)
S(4)—C(2)	1·769 (12)	C(1)—N(1)	1·360 (15)
C(2)—N(2)	1·323 (15)	N(1)—C(31)	1·511 (21)
N(1)—C(41)	1·494 (19)	N(2)—C(51)	1·433 (18)
N(2)—C(61)	1·464 (17)	C(31)—C(32)	1·459 (36)
C(41)—C(42)	1·460 (25)	C(51)—C(52)	1·519 (28)
C(61)—C(62)	1·492 (25)		

Au(2)—Au(1)—S(2)	91·5 (1)	Au(2)—Au(1)—S(3)	90·9 (1)
S(2)—Au(1)—S(3)	177·1 (1)	Au(2)—Au(1)—Au(2*a*)	171·1 (1)
S(2)—Au(1)—Au(2*a*)	93·6 (1)	S(3)—Au(1)—Au(2*a*)	84·2 (1)
Au(1)—Au(2)—S(1)	91·0 (1)	Au(1)—Au(2)—S(4)	91·8 (1)
S(1)—Au(2)—S(4)	176·8 (1)	Au(1)—Au(2)—Au(1*a*)	176·8 (1)
S(1)—Au(2)—Au(1*a*)	91·6 (1)	S(4)—Au(2)—Au(1*a*)	85·6 (1)
Au(2)—S(1)—C(1)	109·0 (4)	Au(1)—S(2)—C(1)	108·7 (4)
Au(1)—S(3)—C(2)	110·8 (4)	Au(2)—S(4)—C(2)	110·4 (4)
S(1)—C(1)—S(2)	129·0 (7)	S(1)—C(1)—N(1)	113·1 (9)
S(2)—C(1)—N(1)	118·0 (10)	S(3)—C(2)—S(4)	125·0 (7)
S(3)—C(2)—N(2)	119·3 (9)	S(4)—C(2)—N(2)	115·7 (9)
C(1)—N(1)—C(31)	125·5 (11)	C(1)—N(1)—C(41)	122·4 (11)
C(31)—N(1)—C(41)	112·1 (10)	C(2)—N(2)—C(51)	119·2 (11)
C(2)—N(2)—C(61)	123·3 (10)	C(51)—N(2)—C(61)	117·4 (10)
N(1)—C(31)—C(32)	113·0 (17)	N(1)—C(41)—C(42)	112·8 (14)
N(2)—C(51)—C(52)	114·6 (13)	N(2)—C(61)—C(62)	111·7 (13)

similar to those found in the other $Au_2(dtc)_2$ structures (2·28–2·30 Å). The main structural feature of these compounds is the short Au—Au inter- and intramolecular distances. These arise from the stacking of dimer units so that long chains of Au—Au interactions result. A unit-cell projection of the eight-membered $Au_2(SCS)_2$ ring is shown in Fig. 2 and illustrates these interactions. The Au—Au distances between dimer units vary significantly from structure to structure. The intermolecular Au—Au separation is 3·40 Å in bis(dipropyldithiocarbamato)digold(I) and 3·02 Å in bis(dibutyldithiocarbamato)digold(I). The present structure contains the shortest intermolecular distance yet observed in this class of Au^I compounds at 3·004 (1) Å. This separation is comparable to the intramolecular distance observed in a series of gold(I) dimers with phosphine ylide bridges (Basil *et. al.*, 1985; Heinrich, 1987). Although the Au(2)—Au(1)—Au(2*a*) angle of 171·1 (1)° is not rigorously linear, it does fall in the range observed for other Au dimer systems.

Although the intermolecular distance in $Au_2[S_2CH(C_2H_5)_2]_2$ is larger than the metal–metal bond distance in elemental gold (2·884 Å), the occurrence of several complexes with a variety of dithiocarbamate ligands all having crystal structures with short intermolecular distances suggests an Au—Au interaction may be important in these complexes. The intermolecular distance of 3·004 Å in $Au_2[S_2CN(C_2H_5)_2]_2$ is more than 0·02 Å shorter than the Au—Au distances in other compounds such as $[Au(dmg)_2]^+[AuCl_2]^-$ (3·26 Å, dmgH = dimethylglyoxime] (Rundle, 1954), [AuCl(piperidine)] (3·30 Å) (Guy, Jones, Mays & Sheldrick, 1977), $Na_3[Au(S_2O_3)_2].H_2O$ (3·30 Å) (Ruben, Zalkin, Faltens & Templeton, 1974) and [ClAuS(Ph)CH_2CH_2S(Ph)AuCl] (3·20 Å) (Drew & Riedl, 1973) where metal–metal interactions have been reported. The dithiophosphate dimers of gold, $Au_2[S_2P(OR)_2]_2$, which have nearly indentical inter- and intramolecular distances of ~3·04 Å, are considered to be polymeric chains with significant metal–metal interactions (Lawton, Rohrbaugh & Kokotailo, 1972). Since the van der Waals radius of gold is 1·70 Å, Au—Au distances of ~3·0 Å suggest some interaction is taking place, possibly in order to stabilize the short intramolecular Au—Au interactions.

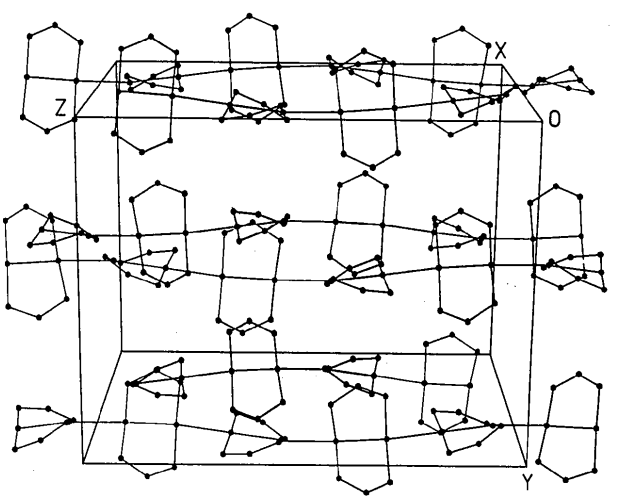

Fig. 2. A view of the unit cell of $Au_2[S_2CN(C_2H_5)_2]_2$ showing the $Au_2(SCS)_2$ rings and the Au—Au chains.

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Structure of Bis(diphenylboron-dimethylglyoximato)nickel(II)*

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Abstract. $[Ni(C_{32}H_{32}B_2N_4O_4)]$, $M_r = 616{\cdot}96$, triclinic, $P\bar{1}$, $a = 8{\cdot}385\ (2)$, $b = 14{\cdot}068\ (3)$, $c = 14{\cdot}234\ (3)$ Å, $\alpha = 75{\cdot}20\ (2)$, $\beta = 72{\cdot}74\ (2)$, $\gamma = 72{\cdot}53\ (2)°$, $V = 1503{\cdot}8$ Å^3, $Z = 2$, $D_m = 1{\cdot}36$, $D_x = 1{\cdot}37$ g cm^{-3}, Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å), $\mu = 6{\cdot}91$ cm^{-1}, $F(000) = 1148$, room temperature, $R = 0{\cdot}042$ for 4366 observed reflections. The macrocyclic ligand has a pronounced saddle-shaped conformation. In this four-coordinate complex, the coordination geometry around the Ni^{II} atom is a distorted square pyramid and the Ni^{II} atom deviates from the coordination plane by 0·14 Å as is found in five-coordinate square pyramidal Ni^{II} complexes.

Introduction. Ordinarily the coordination geometry around the Ni^{II} atom is square planar in four-coordinate low-spin complexes, but larger deviations from exact coplanarity may occur in unsymmetrical complexes (Wells, 1984). A number of papers have reported larger tetrahedral distortion owing to steric interference between the ligands (Braun & Lingafelter, 1967; Cotton, DeBoer & Pipal, 1970). The present work describes a novel square-pyramidal distortion in a four-coordination Ni^{II} complex.

Experimental. The complex was prepared by mixing stoichiometric amounts of $NiCl_2.6H_2O$, dimethylglyoxime and sodium tetraphenylboron in a chloroform–ethanol solution. The solution was refluxed for 12 h. After the reaction mixture had cooled to room temperature, the resulting white precipitate was separated by filtration, then reddish crystals suitable for X-ray analysis were formed by evaporation at 343 K. D_m was determined by flotation (CCl_4–C_6H_6). A well shaped crystal with dimensions 0·20 × 0·30 × 0·28 mm was mounted on an Enraf–Nonius CAD-4 diffractometer. Unit-cell parameters were determined by least-squares fit of 2θ values of 25 higher-order reflections ($20 \le 2\theta \le 28°$). Intensity data were collected by the ω–2θ scan using graphite-monochromated Mo $K\alpha$ radiation, the scan width was $\Delta\omega$

* {Bis-μ-[2,3-butanedionedioximato(2−)-*O*,*O*′]-bis(diphenylborio-*N*,*N*′,*N*″,*N*‴)}nickel(II).

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