

closo-[IrCB₈] cluster (Alcock *et al.*, 1983) is supported by the present determination.

The cluster geometry is of standard *nido* form, corresponding to that of the parent borane, B₁₀H₁₄. However, the relatively low precision of the determination means that detailed comparisons of the cage dimensions cannot be made. One point should however be noted: the unusually long B(2)–B(7) distance of 2.04 (8) Å which is significantly different from the shorter cage bonds. This probably arises as a consequence of the distortions introduced by the C atom.

With the normal assumption of a +3 oxidation state for Ir, the title compound has 24 skeletal electrons, as expected for a *nido* cage. Three other [IrCB₈] cages have been characterized, none of which share this geometry. Two have 22 skeletal electrons and show the expected *closo* geometry (Alcock *et al.*, 1983; Crook, Greenwood, Kennedy & McDonald, 1983). However, the third, [μ -1,2-(MeCOO)-2-H-2,10(PPh₃)₂-*closo*-1,2-CIrB₈H₇] (Crook, Greenwood, Kennedy & McDonald, 1981), apparently also with 22 electrons, has *iso-nido* geometry, which is explained by postulating Ir^V rather than Ir^{III}. The importance compared with the present compound lies in the demonstration of alternative cage geometries. The difference can be correlated with the two bridging H atoms in the present structure and in B₁₀H₁₄. These provide 'support' for the open face of the cluster; in their absence the Ir moves inward, to span

five rather than *three* boron atoms, in the *iso-nido* geometry.

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[*N,N*-Bis(2-hydroxyethyl)dithiocarbamato-*S,S'*]dichlorogold(III)

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Abstract. [Au(C₅H₁₀NO₂S₂)Cl₂], *M_r* = 448.1, space group *P*2₁2₁2₁ (No. 19), *a* = 7.446 (2), *b* = 11.434 (4), *c* = 13.110 (3) Å, *V* = 1116.2 (5) Å³, *Z* = 4, *D_m* = 2.74 (5), *D_x* = 2.67 g cm⁻³, graphite-monochromatized Mo *K*α radiation, λ = 0.71069 Å, μ = 144.0 cm⁻¹, *F*(000) = 832.2, *T* = 298 K, *R* = 0.0432, *wR* = 0.0397 for 1974 unique reflections and 118 parameters. The gold atom is in a roughly square-planar environment, distorted as a result of the small

bite distance of the chelating dithiocarbamate ligand. Molecules pack in the crystal lattice such that there are linear ...S...Au...S... chains parallel to the *a* axis.

Introduction. We have been investigating the mutagenic activity and DNA binding of a series of Au^{III} square-planar compounds. Without exception the compounds were cytotoxic rather than mutagenic when tested in Ames assays of TA102 Salmonella bacteria

Table 1. *Positional parameters* ($\times 10^4$) and U_{eq} ($\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}(\text{\AA}^2)$
Au	5469.4 (6)	7735.3 (4)	-830.7 (3)	34.5
Cl(1)	5441 (6)	9738 (3)	-564 (3)	51
Cl(2)	5347 (5)	7914 (3)	-2597 (2)	55
S(1)	5622 (4)	7224 (3)	868 (2)	39
S(2)	5561 (5)	5736 (3)	-840 (2)	45
C(1)	5748 (7)	5809 (10)	456 (9)	37
N	5917 (13)	4897 (9)	1058 (8)	39
C(2)	6263 (17)	3714 (12)	586 (9)	42
C(3)	4562 (24)	3037 (12)	396 (11)	59
O(1)	3890 (17)	2492 (10)	1266 (8)	80
C(4)	6073 (20)	5016 (15)	2181 (10)	52
C(5)	4322 (24)	5270 (13)	2682 (10)	57
O(2)	3069 (16)	4389 (10)	2489 (8)	69

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

(Ames & Maron, 1983). Nevertheless, the effect of the title compound on the agarose gel electrophoretic mobility of PuC119 plasmid DNA differed from the other compounds which behaved identically. Since all the other compounds were planar we have investigated the structure of the title compound to examine the details of its non-planarity. The preparation of the complex will be described elsewhere.

Experimental. Density of crystals obtained by suspension in $\text{CHCl}_3/\text{CHBr}_3$ solution. Crystal chosen for diffraction; needle, $0.10 \times 0.15 \times 0.50$ mm. Space group $P2_12_12_1$, origin as in *International Tables for Crystallography* (Hahn, 1983). Unit-cell parameters refined by least-squares fit of positional angles for 15 strong independent reflections, $19^\circ < 2\theta < 29^\circ$, on Nicolet *P3* diffractometer at 298 K, monochromated $\text{Mo K}\alpha$ radiation, 2259 reflections measured for $2\theta < 50^\circ$. Intensities $0 \leq h \leq 8$, $0 \leq k \leq 13$, $-15 \leq l \leq 15$, measured by θ - 2θ scan technique. Range of scan rates 5.0 to $29.3^\circ \text{ min}^{-1}$ in 2θ . The ratio of total background time to scan time is 1:1. Two standard reflections measured every 48 reflections (052 , 1.7%; $40\bar{5}$, 1.6%) showed no instrument instability or crystal decay. Zonal reflections averaged to give 1974 independent reflections, $R_{\text{int}} = 0.011$. Reflections with $3\sigma_I > I > -3\sigma_I$ were treated by the method of French & Wilson (1978). L_p and absorption corrections were made [absorption correction factors 3.148–9.818, correction applied with use of the program *PSISCAN* (Calabrese & Burnett, 1980)]. Structure solved by Patterson method. Anisotropic full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma_F^2 + 0.0004F_o^2)^{-1}$. Scale, positional and anisotropic temperature factors for non-hydrogen atoms refined, 118 parameters. H atoms were included but not refined. The H atom attached to O(2) was not located. Final $R = 0.0432$, $wR = 0.0397$, $S = 1.4539$. Chosen enantiomeric solution of the structure justified by alternate refinement of $-x, -y, -z$ coordinates for every atom to $R = 0.0581$, $wR = 0.0572$, $S = 2.1962$. Secondary-extinction correction unnecessary and not

applied. Refinement ended when $(\Delta/\sigma)_{\text{max}} = 0.097$. Final difference map revealed electron density max. 1.9 e \AA^{-3} located near the gold atom, min. -2.0 e \AA^{-3} . Scattering factors for atoms from Cromer & Waber (1974). Corrections for anomalous dispersion were made for Au, S and Cl (Cromer & Ibers, 1974). Calculations employed *XTAL* (Stewart & Hall, 1983), *SHELX* (Sheldrick, 1976), *MOLGEOM* (Stephens, 1973) and *SNOOPI* (Davies, 1983) program systems on VAX 8600 computer. Atomic positional parameters and U_{eq} for non-hydrogen atoms are given in Table 1.

Discussion. The molecule is shown in Fig. 1 and interatomic distances and angles are listed in Table 2.* The geometry of the Au atom is square planar, distorted as a result of the typical restricting chelate angle $[\text{S}-\text{Au}-\text{S } 75.5(1)^\circ]$ of the dithiocarbamate ligand (Beurskens, Blaauw, Cras & Steggerda, 1968; Beurskens, Cras & Steggerda, 1968; Klug, 1966; Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965). The main portion of the molecule is roughly planar. There are small distortions of the square plane towards square-pyramidal geometry such that the Au atom lies roughly 0.01 \AA out of the ligand atom plane. The S(1), S(2), C(1), N plane lies at $3.6(3)^\circ$ to the square plane and the C(1), N, C(2), C(4) plane is bent a further $4.0(4)^\circ$ away from the square plane, although a slight twist has developed such that the dihedral angle between S(1), S(2), C(1), N and C(1), N, C(2), C(4) is $5.3(5)^\circ$ rather than $4.0(4)^\circ$. The N- CH_2 - CH_2 planes are almost at right angles to these planes and are arranged such that the CH_2OH units lie on the same

* Lists of structure factors, anisotropic temperature factors, H-atom positions and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51222 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

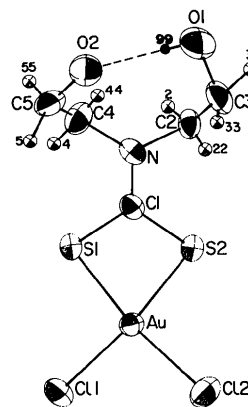


Fig. 1. A molecule of the title complex showing the atom numbering. H atoms are shown by affixes only in small print.

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

Au—Cl(1)	2.316 (3)	Au—Cl(2)	2.325 (3)
Au—S(1)	2.305 (3)	Au—S(2)	2.287 (3)
S(1)—C(1)	1.71 (1)	S(2)—C(1)	1.71 (1)
C(1)—N	1.31 (2)	N—C(2)	1.51 (2)
N—C(4)	1.48 (2)	C(2)—C(3)	1.51 (2)
C(4)—C(5)	1.49 (2)	C(3)—O(1)	1.39 (2)
C(5)—O(2)	1.40 (2)	O(1)—H(99)	0.87 (1)
Au...S(1')	3.610 (3)	Au...S(1'')	3.838 (3)
O(1)...O(2)	2.77 (2)	O(2)...Cl(1)	3.35 (1)
O(1)—H(99)	0.87	H(99)...O(2)	2.04
Cl(1)—Au—Cl(2)	93.6 (1)	Cl(1)—Au—S(1)	96.0 (1)
Cl(1)—Au—S(2)	171.5 (1)	Cl(2)—Au—S(1)	170.4 (1)
Cl(2)—Au—S(2)	94.8 (1)	S(2)—Au—S(1)	75.5 (1)
Au—S(1)—C(1)	86.4 (4)	Au—S(2)—C(1)	87.0 (4)
S(1)—C(1)—S(2)	110.9 (7)	S(1)—C(1)—N	125 (1)
S(2)—C(1)—N	125 (1)	C(1)—N—C(2)	119 (1)
C(1)—N—C(4)	122 (1)	C(2)—N—C(4)	118 (1)
N—C(2)—C(3)	113 (1)	N—C(4)—C(5)	113 (1)
C(2)—C(3)—O(1)	113 (1)	C(4)—C(5)—O(2)	111 (1)
Au...S(1)...Au	177.3 (1)	C(3)—O(1)...2	101.7 (1)
C5—O2...Cl(1)	99.4 (1)	O(1)—H(99)...O(2)	141

side of the square plane. They are arranged in this manner because of an intramolecular hydrogen bond [O(1)...O(2), 2.77 (2); O(1)—H(99), 0.87; H(99)...O(2), 2.04 Å; O(1)—H(99)...O(2), 141; C(3)—O(1)...O(2), 101.7 (4)°]. The asymmetry introduced here is responsible for the twist mentioned above. Thus the C atoms of the —CH₂OH groups lie 0.88 (2) [C(3)] and 1.11 Å [C(5)] and the oxygen atoms 1.43 (1) [O(1)] and 2.06 (1) Å [O(2)] out of the square plane, such that overall the molecule is markedly non-planar.

The Au—Cl bonds are relatively long but this is because of the *trans* influence of the S atoms. The strong *trans* influence of a ligand S atom compared with Cl has been shown in the structure of trichloro(thianthrene)gold(III) (Alcock, Ang, Mok & Tan, 1978) where the Au—Cl distance *trans* to the thianthrene ligand is 2.31 (2) Å and that *trans* to the Cl atom is 2.27 (4) Å. The Au—Cl and Au—S bond lengths agree well with those observed in similar Au^{III} structures (Mazid, Razi & Sadler, 1981; Beurskens, Blaauw, Cras & Steggerda, 1968; Beurskens, Cras & Steggerda, 1968).

Angles within the dithiocarbamate group are consistent with an *sp*² hybridization scheme for C(1) [S(1)—C(1)—S(2) 110.9 (7), S(1)—C(1)—N 125 (1), S(2)—C(1)—N 125 (1)°]. The shortness of the C(1)—N bond length [1.31 (2) Å] compared with the other C—N bond lengths [1.51 (2), 1.48 (2) Å] suggests considerable double-bond character in the C(1)—N bond as reported in crystallographic and infrared studies of a diethylthiocarbamate nickel(II) complex (Bonamico *et al.*, 1965).

A stereoview of the packing is shown in Fig. 2. The molecules related by the 2₁ axis parallel to *a* are arranged such that the square planes are coplanar with *bc* and stack one above the other in the *a* direction. The result is that the Au atom in one molecule lies directly

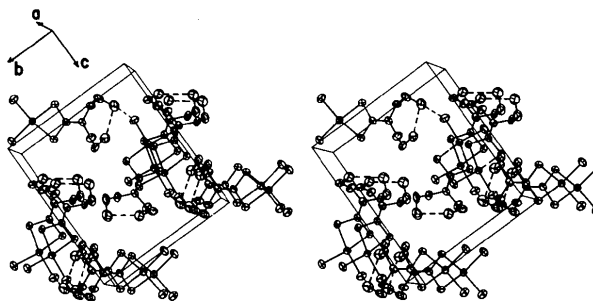


Fig. 2. The packing of the molecules within the unit cell. Hydrogen bonds are shown by broken lines.

above and below S(1) of adjacent molecules. If there is an Au...S interaction it is extremely weak as Au...S(1) distances [3.610 (6), 3.838 (6) Å] are greater than the sum of van der Waals radii (approximately 3.5 Å) (Bondi, 1964). The S(1)...Au...S(1') chain is rectilinear [S(1)...Au...S(1') 177.9 (1)°]. Within a given chain, pairs of —CH₂OH units project in the same direction from the main planes of the molecules and are hydrogen bonded to Cl(1) [through O(2)...Cl(1), 3.35 (1) Å] in molecules in an adjacent chain in which the —CH₂OH units project from the main planes in the opposite direction. The resultant hydrogen-bonded molecules form a helix generated by the 2₁ axis in the *c* direction and are the source of chirality in the structure.

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Structure of *rac*-Bromo(1,4,7,11,14-pentaazacycloheptadecane)cobalt(III) Tetrabromozincate(II)

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Abstract. $[\text{CoBr}(\text{C}_{12}\text{H}_{29}\text{N}_5)][\text{ZnBr}_4]$, $M_r = 767.25$, monoclinic, $P2_1/n$, $a = 8.399$ (2), $b = 18.784$ (3), $c = 14.688$ (3) Å, $\beta = 103.12$ (2)°, $V = 2256.7$ (14) Å³, $Z = 4$, $D_x = 2.26$, $D_m = 2.250$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 106$ cm⁻¹, $F(000) = 1472$, room temperature, $R = 0.033$ for 3189 reflections. The structure consists of an octahedral cobalt(III) cation with five nitrogens of the macrocycle and a Br⁻ ion in the coordination sphere and an unexceptional tetrahedral tetrabromozincate anion. The macrocycle is coordinated to the Co^{III} with the 6,5,6 arrangement of chelate rings in the plane of the four N atoms and the configuration of the chiral N centres is *1RS*, *7SR*, *11RS*, *14RS*.

Introduction. Isolation and characterization of cobalt(III) complexes of a series of pentaazamacrocyclic ligands has been described (Curtis, Osvath & Weatherburn, 1987). The ligand 1,4,7,11,14-pentaazacycloheptadecane is unusual in that two isomeric forms can be isolated. The α -isomer was identified by ¹³C NMR as one of two possible *meso* isomers of the form of the complex with the 6,5,6 arrangement of chelate rings in the plane of the four N atoms (Hay, Bembi, McLaren & Moodie, 1984; Bombieri, Forsellini, Del Pra, Cooksey, Humanes & Tobe, 1982). The other isomer isolated could not be identified on the basis of its ¹³C NMR spectrum so a crystal structure analysis was undertaken. The complex has the same arrangement of the macrocyclic ligand about the Co as the α -isomer but is the racemate.

Experimental. Preparation of the complex as reported (Curtis, Osvath & Weatherburn, 1987). Triangular

Table 1. Positional parameters and their e.s.d.'s

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)
Br(1)	-0.11164 (7)	0.05330 (3)	0.61745 (4)	3.65 (1)
Br(2)	0.06483 (7)	0.27052 (3)	1.10292 (4)	3.02 (1)
Br(3)	-0.24131 (7)	0.10708 (3)	1.07073 (4)	3.24 (1)
Br(4)	-0.05811 (8)	0.18181 (3)	1.31853 (4)	3.66 (1)
Br(5)	0.22479 (7)	0.07796 (3)	1.17852 (5)	3.99 (1)
Zn	0.00281 (8)	0.15851 (3)	1.16872 (5)	2.86 (1)
Co	0.10484 (8)	0.11254 (3)	0.72495 (5)	2.09 (1)
N(1)	0.2469 (5)	0.0246 (2)	0.7418 (3)	3.2 (1)
N(2)	0.1995 (5)	0.1491 (2)	0.6203 (3)	2.75 (9)
N(3)	-0.0267 (5)	0.2014 (2)	0.7072 (3)	2.49 (9)
N(4)	0.0027 (5)	0.0828 (2)	0.8270 (3)	2.50 (9)
N(5)	0.2796 (5)	0.1540 (2)	0.8240 (3)	2.30 (9)
C(1)	0.2775 (7)	-0.0098 (3)	0.6545 (5)	4.2 (1)
C(2)	0.3527 (7)	0.0406 (3)	0.5953 (4)	4.3 (1)
C(3)	0.2388 (7)	0.0986 (3)	0.5501 (4)	3.8 (1)
C(4)	0.0890 (7)	0.2060 (3)	0.5716 (4)	3.3 (1)
C(5)	0.0388 (7)	0.2501 (3)	0.6447 (4)	3.2 (1)
C(6)	-0.0550 (7)	0.2416 (3)	0.7897 (4)	3.2 (1)
C(7)	-0.1421 (6)	0.1971 (3)	0.8504 (4)	3.0 (1)
C(8)	-0.1565 (6)	0.1184 (3)	0.8283 (4)	2.9 (1)
C(9)	0.1215 (6)	0.0864 (3)	0.9186 (4)	3.0 (1)
C(10)	0.2386 (7)	0.1473 (3)	0.9180 (4)	2.9 (1)
C(11)	0.4344 (6)	0.1175 (3)	0.8201 (4)	3.2 (1)
C(12)	0.4039 (7)	0.0389 (3)	0.8127 (4)	3.7 (1)

The equivalent isotropic displacement parameter B_{eq} is: $\frac{1}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

prismatic crystals, 0.35 × 0.17 × 0.15 mm, density by flotation in CH₂Br₂/CCl₄; preliminary examination and data collection performed on an Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo *K*α radiation. Accurate unit-cell dimensions and an orientation matrix by least-squares fit of diffracting positions of 25 reflections (21 ≤ 2θ ≤ 27°). Data collected using the θ/2θ technique to a maximum 2θ of 54.9°, ω scan ranges (0.6 + 0.35tanθ)°. Gradual decrease in intensities of four representative reflections monitored every 60 min of X-ray exposure. Loss of intensity reached