coordination plane are given by the torsion angles in Table 2. The planes defined by the *trans* nitro groups make angles with one another of 87.4° about Pd(1) and 73.3° about Pd(2). The K atoms are coordinated by eight O atoms, forming a distorted square antiprism about each K atom. In each case, one nitro group only is chelated to K. No K···O contacts other than those given are shorter than 3.23 Å. The structure appears to be similar to that of $K_2Pt(NO_2)_4$ (Porai-Koshits, Kukina & Nikolaev, 1978).

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Structure of Bis(thiourea)gold(I) Bromide, $[Au\{SC(NH_2)_2\}_2]Br$

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Abstract. $[Au(CH_4N_2S)_2]Br$, $M_r = 429.20$, monoclinic, $C2/c$, $a = 8.703$ (2), $b = 16.025$ (8), $c = 6.799$ (2) Å, $\beta = 100.83$ (2)°, $V = 931.3$ (6) Å^3, $Z = 4$, $D_x = 3.060$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 20.394$ mm^{-1}, $F(000) = 776$, $T = 298$ K, $R = 0.0632$ and $wR = 0.0929$, obtained for 48 variable parameters and 609 averaged reflections with $F > 0\sigma(F)$. The asymmetric unit consists of one half of a centrosymmetric bis(thiourea)gold(I) molecule with thiourea ligands coordinating in a monodentate fashion through the S atom [Au(1)—S(1) = 2.291 (4) Å]. The thiourea groups are essentially planar but are twisted by an angle of 21.0° about the S—C atoms. The Au atoms in adjacent molecules are separated by a distance of 3.400 Å and the Br^- counterions are located in the cavities formed by the terminal amine groups of the thiourea ligands.

Introduction. The ability of thiourea to form stable adducts with a variety of transition metals is well established and the structures of several of these have been determined [see, for example, Girling, Chatterjee & Amma (1973)]. A number of interesting structural features such as twisting and tilting of the thiourea ligands have been observed, although whether or not this can be attributed to back-bonding interactions between filled metal *d* orbitals and ligand π^* orbitals remains to be established; such observations appear to be largely independent of the transition metal involved.

Crystallographic data concerning the structures of Au–thiourea complexes are scarce, although there is currently much interest in these complexes since thiourea may prove to be important as an alternative to the use of cyanide in the extraction of gold from ores. Raman and solution infrared studies have been carried out and provide evidence for the existence of S-bound species in thiourea complexes of Au^I and Au^{III}, and suggest that the N-bound species may also be formed initially with Au^0 (Freeman, Baglin, Wilkes & MacDougall, 1986; Marcotrigiano, Peyronel & Battistuzzi, 1972). Although linkage

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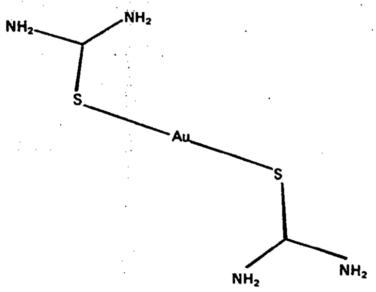
isomerization in solution is possible, S-atom bonding in thiourea complexes of gold can be expected to be much more important. Recently, the crystal structure of a bis(thiourea)gold(I) complex containing perchlorate counterions was described (Lin, Liu & Yong, 1990). In this paper we report the X-ray crystal-structure determination of bis(thiourea)gold(I) with bromide counterions.



(I)

Experimental. Bis(thiourea)gold(I) bromide was prepared by adding $K[Au^{III}Br_4]$ to an aqueous solution of thiourea. Recrystallization from methanol led to numerous single well formed regularly shaped colourless crystals. A small crystal of approximate dimensions 0.6 × 0.3 × 0.6 mm was selected and mounted on the end of a glass fiber in a random orientation. Monoclinic symmetry was suggested on the basis of the interaxial angles and confirmed by axial rotation photographs. Assignment to the *C*2/*c* space group was based on an inspection of the systematically absent reflections ($h + k = 2n + 1$; $k, 0, l = 2n + 1$). Refined cell parameters were obtained from the setting angles of 20 reflections with $30 < 2\theta < 54°$. Data collection was carried out at ambient temperature on a Nicolet *R*3*m*/*E* diffractometer (graphite-monochromated Mo *Kα* radiation) using the *ω*-scan technique in bisecting geometry; scan rate variable, 2–30° $\min^{-1}$; scan range 1.8° in *ω*. Intensities were measured for 654 reflections ($+h$, $+k$, $\pm l$; $h_{\max} = 9$, $k_{\max} = 17$, $l_{\max} = 7$) with $0 < 2\theta < 45°$ [$(\sin\theta)/\lambda_{\max} = 0.538$ Å^{-1}] and averaged to give 613 unique reflections ($R_{\text{int}} = 0.0413$). Three standards ($\bar{1}50$, $\bar{1}10$, 112) measured every 100 data showed no significant variation (< 1%) over the period of data collection. The data were corrected for absorption, Lorentz and polarization effects. Absorption corrections were applied empirically on the basis of azimuthal scans of nine reflections spanning a range of 2θ values (minimum and maximum transmission factors 0.110 and 0.237, respectively). Structure solution was carried out using the *SHELXTL* collection of crystallographic software and refined using the *SHELXTL-PC* software package (Sheldrick, 1978, 1990). The Au-atom position was determined from a sharpened Patterson map; remaining non-H atoms were located on difference Fourier maps. H atoms associated with N groups were placed in idealized positions (N—H = 0.90 Å) with fixed isotropic $U = 0.080$ Å^2. All non-H atoms were refined anisotropically. Scattering factors, including terms for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Refinement was based on *F* using weights of the form $w^{-1} = [\sigma^2(F) + 0.0074(F^2)]$. An empirical correction for extinction of the form $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$ where $\chi = 0.0016$ (3) was used. This resulted in a substantial improvement in the model; however, several intense low-angle reflections still appeared to suffer from some form of extinction and were therefore omitted during the final stages of the refinement. Convergence to conventional *R* values of $R = 0.0632$ and $wR = 0.0929$ was obtained used 48 variable parameters and 609 reflections with $F > 0\sigma(F)$. For the final cycle, maximum $\Delta/\sigma = 0.000$ with minimum and maximum residual electron densities of -2.21 and 2.25 e Å^{-3} in the vicinity of the Au atom.

A perspective drawing of the structure illustrating the atomic numbering scheme is given in Fig. 1; in Fig. 2 is shown a stereoview packing diagram of the complex. Atomic positional parameters and equivalent isotropic thermal parameters for all non-H atoms are presented in Table 1.† Bond distances and angles are summarized in Table 2.

Discussion. The asymmetric unit of this structure consists of one half of a centrosymmetric molecule with the Au atom located at the cell origin. The Br^- counterions are located in the cavities formed by the terminal amine groups and the Au atoms are oriented along the crystallographic *c* axis to form chains with an intermolecular separation of 3.400 Å. The Au atoms in this structure are two-coordinate linear and form bonds to the S atoms of the thiourea ligands [Au(1)—S(1) = 2.291 (4) Å]. The S, C and N atoms of the thiourea groups are essentially coplanar (mean deviation of 0.0228 Å) and these ligands are twisted by 21.1° about the C—S direction. We find the C—S bond length in this complex [1.771 (13) Å] to be longer than the 1.720 (9) Å C—S bond length reported in the X-ray crystal structure determination of free thiourea (Truter, 1967) and the 1.746 (9) Å C—S bond length determined from a neutron diffraction study (Elcombe & Taylor, 1968). Notable deviations from 2/*m* symmetry are also evident in the

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† Lists of structure factors, anisotropic thermal parameters and H-atom positional parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55163 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0577]

interaxial angles associated the S—C—N atoms, as well as the C—N bond lengths associated with the two crystallographically independent amine groups. Angles associated with the two sets of S—C—N atoms differ by approximately 10° [114.4 (9) and 125.2 (9)° for S(1)—C(1)—N(1) and S(1)—C(2)—N(2), respectively], and bonds to the amine groups vary by 0.14 (2) Å [N(1)—C(1) = 1.263 (16), N(2)—C(2) = 1.404 (17) Å].

Similar patterns in bond lengths are observed in the structures of other bis(thiourea) complexes. In the structure of bis(thiourea)iodine(I) iodide, asymmetry in the observed C—N bond lengths was interpreted in terms of contributions from the various resonance forms of thiourea (Lin & Hope, 1972). In the structure described here, however, we find that the halide counterion, Br(1), is not located symmetrically with respect to the terminal amine groups in the thiourea ligands, but is instead considerably closer to N(2) than to N(1) [Br(1)—N(1) = 5.524, Br(1)—N(2) = 3.500 Å]. In other complexes only minor variations in the C—N bond lengths are observed as, for example, in the structure of bis(thiourea)nickel(II) thiocyanate (Nardelli, Gasparri, Battistini & Domiano, 1966). These differences may reflect variations in packing motif that facilitate dipole-induced distortions or permit weak hydrogen-bonding interactions between the H atoms associated with one of the N atoms of the terminal amine groups and the Br^- counterions.

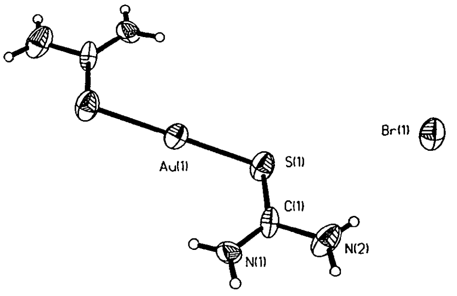

Fig. 1. A perspective view of the bis(thiourea)gold(I) bromide adduct illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level.

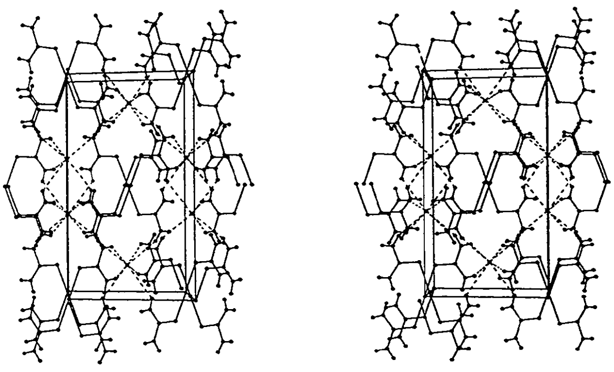

Fig. 2. A stereoview packing diagram projected along the crystallographic *c* axis.

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

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

	x	*y*	*z*	U_{eq}
Au(1)	0	0	0	34 (1)
Br(1)	0	3716 (1)	2500	46 (1)
S(1)	886 (5)	1346 (2)	0	43 (1)
N(1)	3143 (12)	716 (7)	2901 (18)	37 (4)
N(2)	2849 (16)	2148 (9)	2887 (19)	53 (5)
C(1)	2384 (17)	1350 (7)	2159 (19)	29 (5)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Au(1)—S(1)	2.291 (4)	S(1)—C(1)	1.771 (13)
N(1)—C(1)	1.263 (16)	N(2)—C(1)	1.404 (17)
S(1)—Au(1)—S(1*A*)	180.0 (1)	Au(1)—S(1)—C(1)	101.4 (4)
S(1)—C(1)—N(1)	125.2 (9)	S(1)—C(1)—N(2)	114.4 (9)
N(1)—C(1)—N(2)	119.8 (12)		

The linear chain-like arrangement of the Au atoms in this complex is an interesting structural feature. Close intermolecular contacts (< 3.6 Å) have been observed in other neutral Au^I complexes and the propensity for many of the heavier elements such as Au, Pt and Hg to adopt this type of arrangement in the solid state may reflect some kind of weak relativistic interaction (Wang & Fackler, 1990; Wang, Fackler, King & Wang, 1988). Such relativistic stabilizations reach a maximum for Au and result in a weak interaction between the formally non-bonded Au centers (Pitzer, 1979; Pykkö & Desclaux, 1979).

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Structures of Chromium(III) Cyclam Complexes. 3. Structure of *trans*-Dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) Bromide

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Abstract. [CrCl$_2$(C$_{10}$H$_{24}$N$_4$)]Br, $M_r = 403.1$, triclinic, $A\bar{1}$, $a = 6.440$ (3), $b = 16.608$ (1), $c = 7.641$ (2) Å, $\alpha = 86.61$ (2), $\beta = 89.21$ (2), $\gamma = 105.13$ (3)°, $V = 787.4$ (3) Å^3, $Z = 2$, $D_x = 1.70$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54184 Å, $\mu = 122.3$ cm^{-1}, $F(000) = 410$, room temperature, $R = 0.032$ for 1461 observed reflections and 113 parameters. The X-ray analysis indicates that the cyclam moiety exists in a chair conformation located on a crystallographic centre of symmetry. The equatorial nitrogen ligands and the central Cr ion are coplanar.

Introduction. A number of salts of the complex ion *trans*-[Cr(cyclam)Cl$_2$]$^+$, where cyclam = 1,4,8,11-tetraazacyclotetradecane, have been prepared. The electronic spectra of these compounds should be similar especially in the region around 200–600 cm^{-1} from the electronic origin where the intramolecular vibrational modes are expected. In practice, the electronic spectra that have been measured for different salts differ in detail and spectral resolution. The complexity of some of the spectra would seem to indicate the existence of multiple sites. We present the structure of *trans*-[Cr(cyclam)Cl$_2$]Br as part of our investigation into the roles of exact site symmetry and the field due to neighbouring counterions in determining the form of the electronic spectra of these compounds. Structures bearing *cis* forms of the cations of the title compound have been reported by House & McKee (1984) and Forsellini, Parasassi, Bombieri, Tobe & Sosa (1986): (−)-*cis*-dichloro-[(*R*,*R*,*R*,*R*)-1,4,8,11-tetraazacyclotetradecane]chromium(III) perchlorate and *cis*-dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) chloride, respectively.

Experimental. Crystals from slowly cooled warm methanolic solution. Red rectangular prisms 0.42 × 0.10 × 0.21 mm used for data collection. Preliminary Weissenberg and precession photographs yielded approximate cell dimensions. Space group $A1$ or $A\bar{1}$ indicated from systematic absences (hkl, $k + l = 2n$), $A\bar{1}$ confirmed by structure analysis. Enraf–Nonius CAD-4 diffractometer; 25 high-angle reflections ($20 < \theta < 40°$) used to obtain accurate cell dimensions by least-squares fit. ω–2θ scan width $(0.85 + 0.14\tan\theta)°$ in ω, vertical aperture 4 mm; 3250 reflections measured ($-7 \leq h \leq 7$, $-20 \leq k \leq 20$, $0 \leq l \leq 9$; $0 < \theta < 70°$); three intensity standards ($0\bar{5}1$, 002, $0\bar{4}0$) monitored at intervals of 100 reflections showed no significant variations during data collection; intensity data corrected for Lorentz–polarization factors. Merging equivalent reflections gave 1491 unique intensities, 1461 with $I > 3\sigma(I)$ with $R_{\text{int}} = 0.024$. The

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