

Ligand Configuration and Coordination Geometry in Silver(I)–Thiosemicarbazide Complexes

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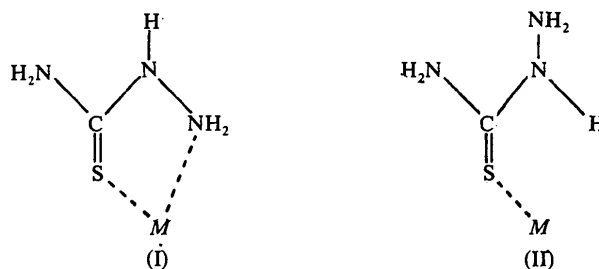
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Abstract. The crystal structures of four Ag^I–thiosemicarbazide [TSCZ = SC(NH₂)NHNH₂] complexes have been determined [MoK α ₁, λ = 0.709300 Å, T = 293 (1) K]: (1) [Ag₂(TSCZ)₆]Cl₂, M_r = 833.4, triclinic, $P\bar{1}$, a = 9.728 (3), b = 12.558 (3), c = 6.539 (1) Å, α = 97.20 (1), β = 102.07 (8), γ = 69.56 (2)°, V = 730.8 (4) Å³, Z = 1, D_x = 1.89 Mg m⁻³, μ = 1.96 mm⁻¹, $F(000)$ = 416, R_F = 0.0422, wR = 0.0456; (2) [Ag₂(TSCZ)₃Br₂]_n, M_r = 648.9, monoclinic, $P2_1$, a = 4.319 (1), b = 22.47 (4), c = 8.707 (4) Å, β = 96.62 (4)°, V = 839 (1) Å³, Z = 2, D_x = 2.57 Mg m⁻³, μ = 7.39 mm⁻¹, $F(000)$ = 616, R_F = 0.0718, wR = 0.0622; (3) [Ag₂(TSCZ)₄I₂]_n, M_r = 834.1, monoclinic, $C2/c$, a = 12.886 (3), b = 8.687 (1), c = 20.006 (16) Å, β = 105.36 (3)°, V = 2159 (2) Å³, Z = 4, D_x = 2.57 Mg m⁻³, μ = 5.02 mm⁻¹, $F(000)$ = 1568, R_F = 0.0447, wR = 0.0571; (4) [Ag(TSCZ)₂(NCS)]_n, M_r = 348.2, orthorhombic, $Pna2_1$, a = 11.495 (7), b = 15.049 (7), c = 6.601 (4) Å, V = 1142 (1) Å³, Z = 4, D_x = 2.03 Mg m⁻³, μ = 2.25 mm⁻¹, $F(000)$ = 688, R_F = 0.0560, wR = 0.0799. In all these compounds the S atom and the hydrazinic –NH₂ group have a planar *E* configuration relative to the C–N bond and the thiosemicarbazide behaves as a monodentate ligand through S. In (1) and (3) coordination about the metal is tetrahedral and there are centrosymmetric dimers formed by two coordination tetrahedra sharing an edge, with a direct Ag...Ag interaction [3.076 (1) Å in (1), 2.959 (2) Å in (3)]. In (1) the dimers are cations and the edge is formed by unsymmetrically bridging S atoms of two TSCZ molecules related by centrosymmetry, while the other TSCZ ligands are terminal and the Cl⁻ ions are not involved in coordination to the metal. In (3) the dimers are neutral molecules where I exhibits a quasisymmetrical bridging function and the TSCZ ligands are terminal. In (2) and (4) the structure is polymeric: in (2) tetrahedral Ag atoms, distorted to trigonal pyramids, are joined in pairs by sharing a long S...S edge whose S atoms join the pairs in chains; in (4) the Ag-coordination polyhedron is a distorted elongated trigonal bipyramid involving two S atoms from two

thiosemicarbazide molecules, one N atom from a thiocyanate group and two S atoms of two thiocyanate groups belonging to two adjacent coordination polyhedra shifted with respect to each other so as to form double chains with 2₁ symmetry. The TSCZ ligand does not show significant changes in its geometry when it is terminal or bridging, nor with respect to the uncomplexed molecule, excepting the S–C distance which is significantly longer when coordinating [av. 1.722 (3) Å] than in the uncomplexed state [1.707 (2) Å].

Introduction. Thiosemicarbazide, SC(NH₂)NHNH₂ (TSCZ), is a ligand able to exhibit a peculiar flexibility when coordinating in metal complexes (Domiano, Fava Gasparri & Nardelli, 1966; Fava Gasparri, Mangia, Musatti & Nardelli, 1968; Nardelli, 1979). In fact the S atom and the hydrazinic –NH₂ group assume the *Z* configuration (I) with respect to C–N when the ligand acts as an *S,N*-chelating agent, while their configuration is *E* when it behaves as a monodentate S-donor ligand. This behaviour can be related to the energy barrier to rotation about the C–N bond that can be overcome at the expense of chelation and lattice-packing energies.



The *E* configuration observed in the crystals of uncomplexed thiosemicarbazide (Andreotti, Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1970) and in the 1-phenyl (Czugler, Kálmán & Argay, 1973) and 4-phenyl (Kálmán, Argay & Czugler, 1972) derivatives, was found for the first time in the Ag^I complex, [Ag₄(TSCZ)₄Cl₄]_n (Fava Gasparri, Mangia, Musatti & Nardelli, 1968), and later in other Ag^I complexes, [Ag(TSCZ)₂(NCS)]_n (Calzolari Capacchi,

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Fava Gasparri, Ferrari & Nardelli, 1968a) and $[\text{Ag}_2(\text{TSCZ})_3\text{Br}_2]_n$ (Calzolari Capacchi, Fava Gasparri, Ferrari & Nardelli, 1968b), all characterized by polymeric structures in the crystal state. Therefore it was inferred (Nardelli, 1979) that in these polymeric structures there are no sites near enough to each other to be occupied by two atoms of the same organic ligand, so that thiosemicarbazide assumes the *E* configuration and coordinates through S as a monodentate ligand.

In the present paper, the crystal structures of two more Ag^{I} complexes, $[\text{Ag}_2(\text{TSCZ})_6]\text{Cl}_2$ and $[\text{Ag}_2(\text{TSCZ})_4\text{I}_2]$,* are described in which thiosemicarbazide exhibits monodentate behaviour with the *E* configuration, even though these crystal structures are dimeric rather than polymeric; this indicates that additional factors, such as the nature of the metal and co-ligands, are relevant in determining the ligand behaviour. In this respect it is worth noting that in all the thiosemicarbazide- Ag^{I} complexes whose crystal structure is known the thiosemicarbazide is monodentate.

In addition the crystal structures of $[\text{Ag}_2(\text{TSCZ})_3\text{Br}_2]_n$ and $[\text{Ag}(\text{TSCZ})_2(\text{NCS})]_n$ have been redetermined using new diffractometer data and a full account of them is now reported.

Experimental. The crystals were prepared as already described (Nardelli, Fava Gasparri & Chierici, 1965). All data were collected on a Philips PW 1100 diffrac-

tometer using $\text{MoK}\alpha$ radiation, $\lambda = 0.7069 \text{ \AA}$ and an $\omega-2\theta$ scan mode; they are summarized in Table 1. The intensity data for compounds (2) and (4) were of a quality poorer (owing to the poorer quality of the crystals) than the data for the other two compounds; consequently, the accuracy obtained from the corresponding analyses is lower. All the intensity data were corrected for Lorentz and polarization effects, but only those of (2) and (4) were corrected for absorption using the empirical method of Walker & Stuart (1983).

The new structures were solved by Patterson and Fourier methods and refinement was by anisotropic full-matrix least squares (on *F*) for all the structures. In the case of compound (4) anisotropic thermal motion was considered only for the heaviest atoms (*Ag*, *S* and only one *N* atom), while for compound (2) all the non-H atoms, excepting three *N* and two *C* atoms, were treated anisotropically. This treatment was also applied to all the non-H atoms of compounds (1) and (3). In all cases the H atoms were located from Fourier difference maps, but only in the case of compounds (1) and (3) were the coordinates refined isotropically.

In the case of compound (4) a particularly high anisotropic thermal coefficient along the *z* axis was found for *Ag*; it probably corresponds to some disorder of this atom in that direction. In compound (1) the *N*(8) atom has been found to be disordered over two positions with occupancy factors 0.78 and 0.22, and only the H atoms attached to the *N* with the higher occupancy factor were considered.

The polymeric structures of the bromine and thiocyanate derivatives are polar, so it was necessary to define their structural chiralities. This was done by comparing the *wR* factors of the enantiomeric distri-

* A preliminary account on these structures have been communicated at the XII Congresso della Associazione Italiana di Cristallografia, Firenze, 7-9 October, 1981.

Table 1. *Experimental data for the crystallographic analyses*

	$[\text{Ag}_2(\text{TSCZ})_6]\text{Cl}_2$	$[\text{Ag}_2(\text{TSCZ})_3\text{Br}_2]_n$	$[\text{Ag}_2(\text{TSCZ})_4\text{I}_2]$	$[\text{Ag}(\text{TSCZ})_2(\text{NCS})]_n$
Lattice-parameter measurement				
No. of reflections	21	21	22	22
θ range ($^\circ$)	8-23	10-21	13-29	14-26
Crystal size (mm)	0.10 × 0.13 × 0.22	0.16 × 0.08 × 0.08	0.16 × 0.22 × 0.40	0.10 × 0.08 × 0.15
Absorption correction				
Min.	—	0.7936	—	1.000
Max.	—	1.5267	—	1.166
Extinction correction	—	0.6374-1.0461	—	—
Scan speed ($^\circ \text{ s}^{-1}$)	0.050	0.050	0.050	0.075
Scan width ($^\circ$)	0.65 + 0.20 tan θ	1.0 + 0.20 tan θ	0.70 + 0.20 tan θ	1.20 + 0.20 tan θ
θ range ($^\circ$)	3-30	3-30	3-30	3-30
<i>h</i> range	-13→13	-6→6	-18→18	0-15
<i>k</i> range	-17→17	0-32	0-13	0-20
<i>l</i> range	0-9	0-12	0-28	0-9
Standard reflection	231	771	312	351
No. of measured reflections	4290	2643	3405	1675
Conditions for observed reflections	$l \geq 3\sigma(l)$	$l \geq 2\sigma(l)$	$l \geq 3\sigma(l)$	$l \geq 3\sigma(l)$
No. of reflections used in the refinement	2298	1066	2313	758
$(\Delta/\sigma)_{\text{max}}$	0.06	0.01	0.22	0.30
Min., max. $\Delta\rho$ (e \AA^{-3})	-0.16, 0.19	-0.34, 0.37	-0.53, 0.77	-0.67, 0.21
No. of parameters refined	205	151	149	82
<i>R</i>	0.0422	0.0718	0.0447	0.0560
<i>wR</i>	0.0456	0.0622	0.0571	0.0799
<i>S</i>	1.4757	1.5508	1.6686	1.2384
$g, w = [\sigma^2(F_o) + gF_o^{2-1}]^{-1}$	0.000000	0.000284	0.000676	0.002942

butions by means of Hamilton's (1965) significance test. The following results were obtained:

$$[\text{Ag}_2(\text{TSCZ})_3\text{Br}_2]_n: \quad wR(x,y,z)/wR(\bar{x},\bar{y},\bar{z}) = 1.130, \\ \mathcal{R}_{1,915,0.005} = 1.004,$$

$$[\text{Ag}(\text{TSCZ})_2(\text{NCS})]_n: \quad wR(x,y,z)/wR(\bar{x},\bar{y},\bar{z}) = 1.005, \\ \mathcal{R}_{1,676,0.005} = 1.006,$$

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2)

$$B_{\text{eq}} = \frac{1}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i, \mathbf{a}_j).$$

	x	y	z	B_{eq}
$[\text{Ag}_2(\text{TSCZ})_6]\text{Cl}_2$				
Ag	-22 (1)	3950.8 (4)	3519 (1)	3.40 (2)
Cl	3700 (2)	-1631 (1)	3215 (3)	3.53 (5)
S(1)	91 (2)	2093 (1)	4974 (2)	2.94 (5)
S(2)	923 (2)	3521 (1)	70 (2)	2.85 (4)
S(3)	2384 (2)	4398 (1)	6168 (2)	2.66 (4)
C(1)	-846 (6)	1460 (5)	2922 (9)	2.48 (17)
C(2)	2520 (6)	2373 (4)	509 (9)	2.40 (17)
C(3)	3220 (6)	4600 (5)	4235 (8)	2.25 (16)
N(1)	-1543 (6)	814 (5)	3399 (9)	3.35 (19)
N(2)	-2272 (9)	227 (6)	1824 (10)	3.84 (22)
N(3)	-857 (8)	1552 (6)	963 (10)	4.43 (25)
N(4)	2833 (5)	1741 (4)	2125 (8)	2.68 (15)
N(5)	4183 (6)	820 (5)	2498 (10)	3.37 (18)
N(6)	3473 (7)	2093 (6)	-795 (10)	3.83 (21)
N(7)	2640 (6)	5541 (4)	3163 (8)	2.97 (16)
N(9)	4450 (6)	3820 (4)	3788 (9)	3.16 (17)
N(8A)	3352 (8)	5655 (6)	1606 (12)	3.74 (14)
N(8A)	5180 (23)	3858 (17)	2162 (32)	2.50 (37)
$[\text{Ag}_2(\text{TSCZ})_3\text{Br}_2]_n$				
Ag(1)	-1795 (7)	841	-974 (3)	3.80 (9)
Ag(2)	-1760 (7)	2275 (2)	-1467 (3)	2.90 (8)
Br(1)	-692 (8)	36 (2)	1219 (4)	2.73 (10)
Br(2)	-214 (7)	3209 (2)	430 (3)	2.03 (9)
S(1)	-5799 (15)	1612 (4)	-457 (9)	1.72 (20)
S(2)	-792 (23)	592 (4)	-3593 (10)	2.88 (26)
S(3)	-589 (21)	2438 (4)	-4108 (9)	2.50 (24)
N(1)	-6353 (62)	1249 (11)	2410 (28)	2.39 (73)
N(2)	-3837 (67)	2129 (13)	2273 (28)	3.39 (87)
N(3)	-5999 (64)	1301 (19)	3990 (32)	3.70 (91)
N(4)	1815 (65)	-278 (13)	-4919 (29)	2.94 (86)
N(5)	2678 (60)	-287 (12)	-2304 (28)	2.39 (76)
N(7)	2119 (62)	3279 (16)	-5560 (32)	3.80 (92)
C(3)	1685 (77)	3058 (12)	-4245 (32)	1.62 (82)
N(6)	4686 (59)	-807 (11)	-2360 (27)	1.85 (48)
N(8)	2782 (58)	3360 (11)	-2963 (28)	1.85 (51)
N(9)	4759 (60)	3840 (11)	-3050 (27)	1.99 (50)
C(1)	-5273 (60)	1691 (11)	1527 (32)	1.04 (53)
C(2)	1364 (73)	-65 (13)	-3634 (36)	1.96 (64)
$[\text{Ag}_2(\text{TSCZ})_4]\text{I}_2$				
Ag	290 (1)	4951 (1)	-667.5 (3)	3.19 (2)
I	538.2 (4)	2305 (1)	174.9 (2)	3.09 (1)
S(1)	-1062 (2)	4909 (2)	-1870 (1)	2.80 (4)
S(2)	2128 (1)	5702 (2)	-894 (1)	2.46 (4)
N(1)	-934 (5)	1897 (6)	-1711 (3)	2.63 (15)
N(2)	-999 (7)	350 (7)	-1931 (4)	3.18 (18)
N(3)	-1440 (6)	2735 (8)	-2830 (3)	3.20 (16)
N(4)	2071 (5)	8722 (7)	-811 (3)	2.90 (15)
N(5)	1822 (7)	10252 (7)	-1050 (3)	3.02 (18)
N(6)	1296 (5)	7758 (7)	-1895 (3)	2.87 (15)
C(1)	-1141 (5)	3047 (7)	-2158 (3)	2.30 (15)
C(2)	1803 (5)	7528 (7)	-1236 (3)	2.18 (14)
$[\text{Ag}(\text{TSCZ})_2(\text{NCS})]_n$				
Ag	2341 (1)	324 (1)	3392	9.39 (10)
S(1)	2696 (3)	1920 (2)	3578 (18)	2.22 (7)
S(2)	3900 (3)	-791 (2)	3501 (23)	2.70 (9)
S(3)	-1987 (3)	-208 (2)	3564 (23)	3.42 (11)
N(1)	358 (9)	2027 (7)	3384 (57)	3.10 (39)
N(2)	1366 (8)	3328 (6)	3759 (34)	1.80 (20)
N(3)	313 (9)	3805 (6)	3828 (31)	1.98 (21)
N(4)	2048 (8)	-1845 (6)	3842 (27)	1.40 (18)
N(5)	3819 (8)	-2550 (6)	3468 (37)	1.81 (16)
N(6)	1395 (8)	-2652 (6)	3814 (32)	1.77 (20)
N(7)	445 (11)	-190 (7)	3397 (39)	2.96 (23)
C(1)	1355 (9)	2436 (7)	3494 (46)	1.67 (18)
C(2)	3209 (10)	-1802 (7)	3351 (42)	1.90 (23)
C(3)	-547 (11)	-184 (7)	3770 (42)	1.89 (23)

which indicate that, while for the $^{\text{Br}}$ derivative the coordinates quoted in Table 2 can be accepted as corresponding to the correct chirality at the 0.005 confidence level, for the thiocyanate derivative the enantiomeric structure cannot be rejected at the same confidence level, *i.e.* the accuracy of the analysis is not enough to remove the ambiguity.

The atomic scattering factors and the anomalous-scattering coefficients are from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates with the equivalent isotropic thermal parameters B_{eq} for non-H atoms are quoted in Table 2.* The calculations were carried out on the Gould-SEL 32/77 computer of the 'Centro di Studio per la Strutturistica Diffraattometrica del CNR (Parma)', using *SHELX* (Sheldrick, 1976), *LQPARM* (Nardelli, 1978), *PARST* (Nardelli, 1983), *ABSORB* (Ugozzoli, 1983), *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell, 1976).

Throughout the paper an average value is a weighted mean with weights equal to the reciprocal of the squares of the e.s.d.'s, and, when two values are compared, the ratio between their difference and the e.s.d. of the difference, Δ/σ , is considered.

Discussion. $[\text{Ag}_2(\text{TSCZ})_6]\text{Cl}_2$. The Cl^- ion does not exert any direct interaction on the metal, whose coordination sphere only involves S atoms of the monodentate TSCZ ligands. As shown in Fig. 1, the metal coordination is distorted tetrahedral and involves two kinds of TSCZ ligands, S(1) and S(2) terminal and S(3) asymmetrically bridging two metal atoms, so that centrosymmetric dimeric cations are formed. Relevant

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and hydrogen-bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43362 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

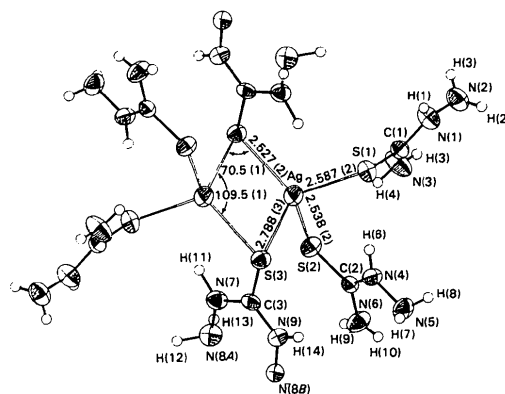


Fig. 1. ORTEP (Johnson, 1965) drawing of the centrosymmetric dimeric $[\text{Ag}_2(\text{TSCZ})_6]^{2+}$ cation (thermal ellipsoids at 50% probability).

data on the geometry of these dimers and on the orientation of the ligands with respect to the metal centres are collected in Table 3.

The angle Ag—S—Ag is much smaller than the tetrahedral one, the deformation being imposed by the requirements of the metal-coordination geometry which impose a tetrahedral value for the S—Ag—S angle. The Ag...Ag distance of 3.076 (1) Å is indicative of some direct interaction between the two metal centres.

The Cl⁻ anions interact with the dimeric cations through the N—H...Cl hydrogen bonds shown in Fig. 5.

[Ag₂(TSCZ)₃Br₂]_n. The structure is polymeric, being made up by chains of crystallographically non-equivalent pairs of Ag atoms each tetrahedrally coordinated by a terminal halogen, a terminal TSCZ ligand and two bridging TSCZ ligands. The coordination tetrahedra are distorted to trigonal pyramids, one bond being much longer than the others, as shown by the data in Table 3 and Fig. 2. The chains, which run along the shortest crystallographic [100] direction, have approximate C_s symmetry and a polar character due essentially to the remarkable difference between the Ag—S(1) and Ag—S(1') distances. S(1) is asymmetrically bound to four Ag atoms.

As observed for the dimers in the Cl derivative, in the Br complex the Ag—S—Ag angles are also much narrower than the tetrahedral one, but, in contrast to the Cl compound, a sensible narrowing is also observed for the S—Ag—S angles. The Ag...Ag distance is longer than in the previous compound indicating that the metal-metal interaction is markedly reduced.

[Ag₂(TSCZ)₄I₂]. Like the Cl derivative, the crystals of the I complex contain centrosymmetric dimers formed by pairs of coordination tetrahedra sharing an edge (Fig. 3), but now the halogen is involved in coordination to the metal and exerts a bridging function. From the data of Table 3, it appears that the I bridge is nearly symmetric and that the increase of the Ag—I distances with respect to the Ag—S ones produces an enlargement of the I—Ag—I angle and a narrowing of Ag—I—Ag. The geometry of the Ag—I—Ag—I ring is influenced by the Ag...Ag interaction which is stronger than in the previous compounds.

[Ag(TSCZ)₂(NCS)]_n. The metal coordination in this complex is trigonal and involves two monodentate TSCZ ligands, coordinating through S, and one thiocyanate group coordinating through N (Fig. 4). The system is practically planar, the Ag atom being only 0.066 (1) Å out of the plane defined by the ligand atoms. It is important to consider that, owing to the high anisotropic thermal motion (or disorder) of Ag, all distances involving this atom are affected by errors probably higher than the values that can be inferred from their e.s.d.'s. The two TSCZ ligands nearly lie in the coordination plane [N(7)—Ag—S(2)—C(2) = 4.9 (9)°, N(7)—Ag—S(1)—C(1) = -4.5 (9)°], but their orien-

Table 3. Comparison of bond distances (Å) and angles (°) in the metal coordination sphere

	(1)	(2)	(3)	(4)
Ag—S terminal	2.538 (2)	2.436 (10)	2.570 (2)	2.439 (3)
Ag—S bridge	2.587 (2)	2.438 (9)	2.610 (2)	2.456 (3)
	2.527 (2)	2.525 (9)	—	—
	2.788 (3)	2.528 (9)	—	—
	—	3.017 (8)	—	—
	—	3.106 (8)	—	—
Ag—X	—	2.633 (5)	2.818 (1)	2.312 (12)
	—	2.706 (6)	2.889 (1)	—
Ag...Ag	3.076 (1)	3.252 (7)	2.959 (2)	—
Ag—S—Ag	70.5 (1)	64.1 (3)	—	—
	—	80.1 (3)	—	—
Ag—X—Ag	—	—	62.43 (3)	—
S—Ag—S ring	109.5 (1)	99.7 (3)	—	—
	—	102.0 (3)	—	—
X—Ag—X	—	—	117.6 (1)	—
Ag—S—C bridge	97.0 (2)	103.6 (10)	—	—
	110.7 (2)	105.8 (10)	—	—
Ag—S—C terminal	104.3 (2)	111.4 (11)	99.3 (2)	105.4 (4)
	104.6 (2)	111.7 (10)	107.1 (2)	107.0 (4)
Ag—S—C—NH terminal	-150.5 (5)	-12.2 (28)	26.8 (6)	174.4 (12)
	16.2 (6)	4.9 (28)	96.8 (5)	-20.1 (16)
Ag—S—C—NH bridge	73.3 (5)	-74.8 (22)	—	—
	1.4 (5)	-158.1 (19)	—	—
Ag—S—C—NH ₂ terminal	32.0 (6)	173.6 (23)	—	1.0 (22)
	-164.3 (5)	-167.9 (24)	—	-176.9 (14)
Ag—S—C—NH ₂ bridge	-106.5 (5)	102.9 (26)	—	—
	-178.3 (4)	19.5 (28)	—	—

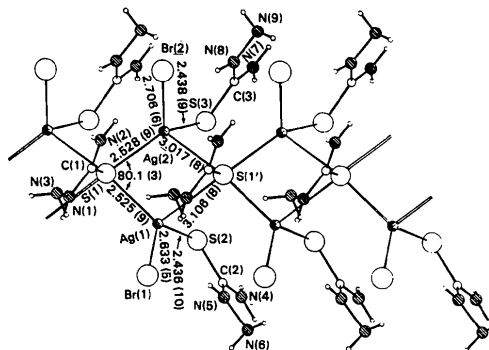


Fig. 2. Polymeric [Ag₂(TSCZ)₃Br₂]_n chain.

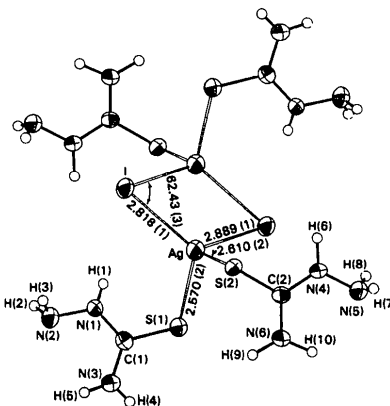
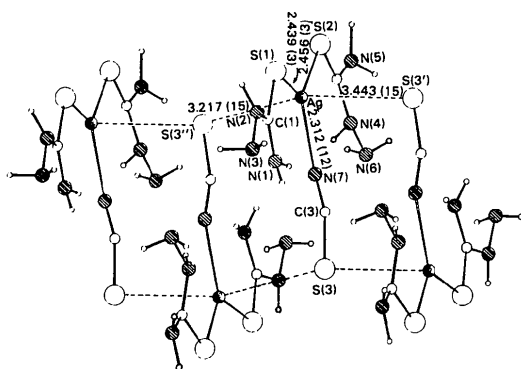


Fig. 3. ORTEP (Johnson, 1965) drawing of the centrosymmetric [Ag₂(TSCZ)₄I₂] dimer (thermal ellipsoids at 50% probability).

Fig. 4. Polymeric $[Ag(TSCZ)_2(NCS)]_n$ chain.

tation is not the same, one ligand [S(1)C(1)N(1)-N(2)N(3)] directing its $-N(1)H_2$ amide group towards the metal [$N(1)\cdots Ag = 3.430(11)$, $H(11)\cdots Ag = 2.84(5)$ Å], the other [S(2)C(2)N(5)N(4)N(6)] being oriented in such a way that the N atom of the N(4)H imine group is nearest to the metal [$N(4)\cdots Ag = 3.294(9)$, $H(4)\cdots Ag = 2.73(4)$ Å]. Consequently, the two N-Ag-S angles are not exactly equal [$N(7)-Ag-S(2) = 117.3(3)$, $N(7)-Ag-S(1) = 119.2(3)^\circ$], both being narrower than the S(1)-Ag-S(2) angle of $123.3(1)^\circ$. This behaviour of the TSCZ ligands is probably influenced by the hydrogen bonds formed by $N(4)-H(4)$ and $N(1)-H(11)$ with the thiocyanate N(7) atom.

The thiocyanate group [S(3)-C(3) = 1.661(13), C(3)-N(7) = 1.167(19) Å] deviates significantly from linearity [S(3)-C(3)-N(7) = $163(2)^\circ$], and is oriented in such a way as to form an Ag-N(7)-C(3) angle of $157(1)^\circ$ and to lie nearly in the coordination plane [N(7), C(3), S(3)-N(7), Ag, S(2)S(1) = $3.4(7)^\circ$], with S(3) between two Ag atoms in the [001] direction at distances $Ag\cdots S(3)(\bar{x}, y, z - \frac{1}{2}) = 3.217(15)$ and $Ag\cdots S(3)(\bar{x}, y, z + \frac{1}{2}) = 3.443(15)$ Å, corresponding to weak interactions. Considering these contacts, the Ag coordination becomes distorted trigonal bipyramidal with zigzag chains of coordination polyhedra running along the [001] direction with an S(3')-Ag-S(3'') angle of $164.7(2)^\circ$. The asymmetry of these long Ag \cdots S contacts is related to the polar character of the 2₁ axis. The looseness of these Ag \cdots S(3) interactions can be justified by the particularly high anisotropic thermal motion (or disorder) along this direction.

Thiosemicarbazide ligands. As observed in the *Introduction*, in all these compounds the thiosemicarbazide molecules always have the S and the hydrazinic $-NH_2$ group in an *E* configuration and behave as monodentate-terminal or S-bridging ligands. In all cases they do not deviate significantly from planarity, nor show significant differences in the corresponding bond distances and angles in the different compounds or when they are terminal or bridging. So the averaged values quoted in Table 4 are

Table 4. Comparison of bond distances (Å) and angles ($^\circ$) in the thiosemicarbazide ligand

	(1)	(2)	(3)	(4)	Av.	TSCZ†
S-C	1.730 (6)	1.748 (31)	1.712 (7)	1.728 (11)		
	1.712 (4)	1.717 (31)	1.734 (6)	1.719 (12)		
	1.730 (6)	1.725 (29)	—	—		
av.	1.720 (6)	1.730 (17)	1.725 (11)	1.724 (8)	1.722 (3)	1.707 (2)
C-NH ₂	1.304 (8)	1.253 (41)	1.324 (9)	1.302 (15)		
	1.320 (9)	1.281 (41)	1.324 (8)	1.328 (14)		
	1.315 (7)	1.298 (37)	—	—		
av.	1.313 (4)	1.279 (23)	1.324 (6)	1.316 (13)	1.316 (3)	1.316 (3)
C-NH	1.323 (9)	1.326 (38)	1.320 (8)	1.354 (14)		
	1.324 (8)	1.345 (36)	1.327 (8)	1.374 (16)		
	1.330 (7)	1.370 (37)	—	—		
av.	1.326 (5)	1.347 (41)	1.324 (6)	1.363 (11)	1.329 (4)	1.326 (2)
N-N	1.402 (8)	1.460 (37)	1.410 (8)	1.407 (14)		
	1.413 (6)	1.384 (35)	1.420 (8)	1.428 (13)		
	1.393 (11)*	1.371 (37)	—	—		
av.	1.406 (5)	1.404 (27)	1.415 (6)	1.418 (10)	1.412 (3)	1.411 (2)
S-C-NH ₂	123.9 (5)	118.6 (24)	120.7 (5)	125.1 (9)		
	119.9 (4)	121.4 (24)	122.3 (5)	120.1 (9)		
	120.1 (4)	125.4 (22)	—	—		
av.	121.3 (11)	122.0 (17)	121.5 (8)	122.6 (25)	121.3 (6)	122.0 (1)
S-C-NH	117.4 (4)	118.4 (23)	120.2 (5)	115.7 (8)		
	121.7 (4)	120.1 (22)	117.9 (5)	118.4 (8)		
	121.1 (4)	118.3 (21)	—	—		
av.	119.7 (12)	118.9 (13)	119.1 (11)	117.1 (14)	119.5 (6)	119.2 (2)
N-C-N	118.6 (6)	122.7 (29)	119.1 (6)	118.9 (10)		
	118.4 (5)	118.2 (28)	119.8 (6)	117.4 (10)		
	118.8 (5)	116.3 (25)	—	—		
av.	118.6 (3)	118.8 (16)	119.4 (4)	118.2 (7)	118.8 (2)	118.8 (2)
C-N-N	121.2 (5)	117.9 (24)	121.6 (6)	120.1 (9)		
	120.5 (5)	120.5 (24)	121.2 (5)	123.2 (9)		
	119.2 (5)*	119.7 (24)	—	—		
av.	120.9 (3)	119.4 (14)	121.4 (4)	121.6 (15)	121.1 (3)	121.1 (2)

* Starred values involve disordered atoms and are not considered in the averages.

† Andreotti, Domiano, Fava Gasparri, Nardelli & Sgarabotto (1970).

justified. Comparing them with the corresponding values in uncomplexed thiosemicarbazide (Andreotti, Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1970), it appears that only the S-C distance is significantly longer ($\Delta/\sigma = 4.2$) when TSCZ is coordinating to a metal. All the other distances and angles are not significantly different and the averaged values for coordinated TSCZ are practically the same as the corresponding values for the uncoordinated ligand.

If the Ag-S-C and Ag-S-C-N angles in Table 3 are considered, it appears that the ligand tends to assume the same orientation as that observed in metal-thiourea and metal-ethylenethiourea (Battaglia, Bonamartini Corradi & Nardelli, 1984) complexes, indicating that the electronic interactions responsible for coordination involve similar orbitals of these ligands. The S bridging is of the same kind as that found in bis(thiourea)-silver(I) chloride (Vizzini & Amma, 1966) and in bis(thiourea)copper(I) chloride (Spofford & Amma, 1968), which has been interpreted as resulting from a three-centre electron-deficient bond.

Hydrogen bonding and packing. Packing and hydrogen bonding are illustrated in Figs. 5-8. If an exception is made for the thiocyanate complex, where the situation of the thiosemicarbazide ligands is rather unusual, in all the other complexes the TSCZ molecules form an intramolecular N-H \cdots N hydrogen bond [av. N-H = 0.88 (4), N \cdots N = 2.697 (9), H \cdots N =

2.34 (2) Å, N—H...N = 102 (2)°] equal to that in the uncomplexed ligand [N—H = 0.86 (2), N...N = 2.690 (2), H...N = 2.34 (2) Å, N—H...N = 105 (1)°] (Andreotti, Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1970). In the case of the disordered N(8) atom of the chlorine complex, the geometry of the intraligand hydrogen bond cannot be described as the H atoms have not been localized, but the N(8A)...N(9) distance of 2.637 (10) Å is also indicative of hydrogen bonding.

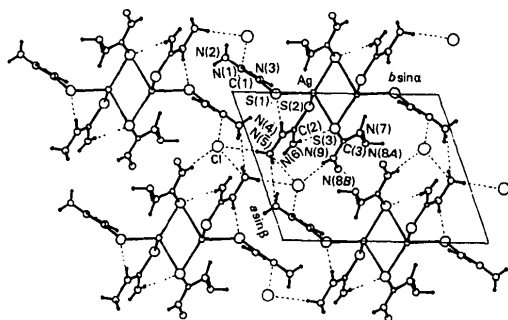


Fig. 5. Packing and hydrogen bonding in $[Ag_2(TSCZ)_6]Cl_2$.

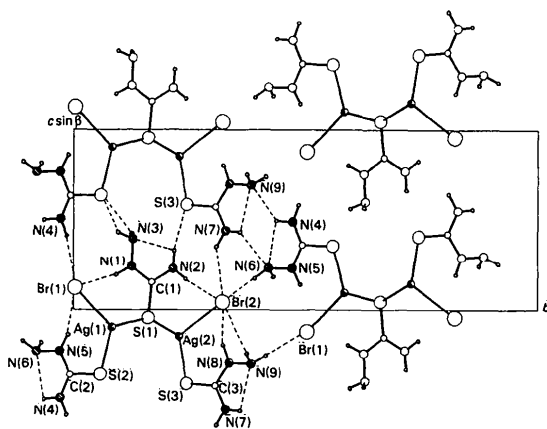


Fig. 6. Packing and hydrogen bonding in $[Ag_2(TSCZ)_3Br_2]_n$.

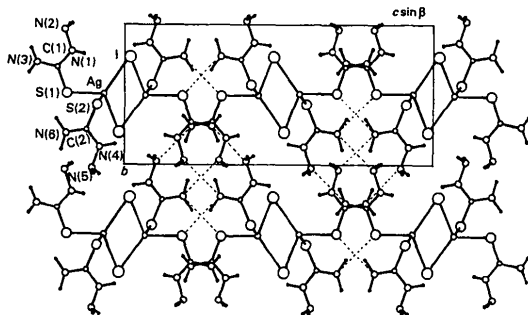


Fig. 7. Packing and hydrogen bonding in $[Ag_2(TSCZ)_4]_2$.

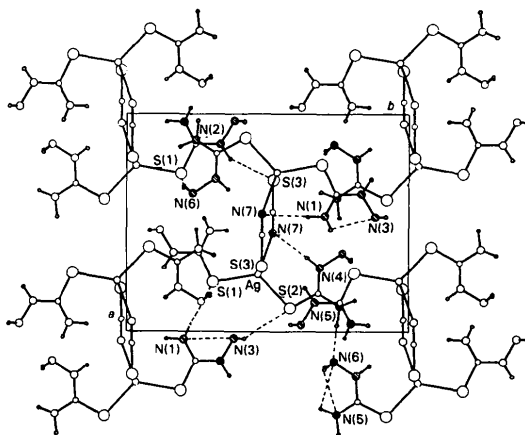


Fig. 8. Packing and hydrogen bonding in $[Ag(TSCZ)_2(NCS)]_n$.

In the thiocyanate complex, the two thiosemicarbazide molecules are oriented in such a way as to interact by hydrogen bonding with the N atom of the thiocyanate group, one through the imine nitrogen N(4)—H(4)...N(7), the other through the amide N(1)—H(11)...N(7) group. It is worth noticing the particular situation of the N(6) hydrazide [N(6)—H(61)...N(5), N(6)—H(62)...N(5)] and N(1) amide groups of this compound. The first directs its H(51) atom towards N(5), while N(5) fits its H atoms towards N(6) between H(61) and H(62): in the second N(1) directs its H(12) atom towards N(3) and S(1) at $x - \frac{1}{2}, \frac{1}{2} - y, z$ forming asymmetric bifurcated contacts as shown in Fig. 8.

In all cases the packing is mainly due to N—H...halogen and N—H...S contacts with the following mean geometries:

N...Cl = 3.321 (4) Å	H...Cl = 2.53 (3) Å	N—H...Cl = 155 (8)°
N...Br = 3.43 (2)	H...Br = 2.53 (3)	N—H...Br = 166 (3)
N...S = 3.41 (2)	H...S = 2.60 (3)	N—H...S = 150 (4)

A number of intermolecular N—H...N hydrogen bonds are also present.

References

- ANDREOTTI, G. D., DOMIANO, P., FAVA GASPARRI, G., NARDELLI, M. & SGARABOTTO, P. (1970). *Acta Cryst.* B26, 1005–1009.
- BATTAGLIA, L. P., BONAMARTINI CORRADI, A. & NARDELLI, M. (1984). *Croat. Chem. Acta*, 57, 545–563.
- CALZOLARI CAPACCHI, L., FAVA GASPARRI, G., FERRARI, M. & NARDELLI, M. (1968a). *Chem. Commun.* pp. 910–911.
- CALZOLARI CAPACCHI, L., FAVA GASPARRI, G., FERRARI, M. & NARDELLI, M. (1968b). *Ric. Sci.* 38, 974–975.
- CZUGLER, M., KÁLMÁN, A. & ARGAY, G. (1973). *Cryst. Struct. Commun.* 2, 655–658.
- DOMIANO, P., FAVA GASPARRI, G. & NARDELLI, M. (1966). *Ric. Sci.* 36, 744–745.
- FAVA GASPARRI, G., MANGIA, A., MUSATTI, A. & NARDELLI, M. (1968). *Acta Cryst.* B24, 367–374.
- HAMILTON, W. C. (1965). *Acta Cryst.* 18, 502–510.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99–149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KÁLMÁN, A., ARGAY, G. & CZUGLER, M. (1972). *Cryst. Struct. Commun.* **1**, 375–378.
- MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- NARDELLI, M. (1978). *LQPARM*. Program for least-squares refinement of lattice parameters. Univ. of Parma, Italy.
- NARDELLI, M. (1979). Proc. 5th Eur. Crystallogr. Meet. Copenhagen, 13–17 August, Abstracts, p. 262.
- NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
- NARDELLI, M., FAVA GASPARRI, G. & CHERICI, I. (1965). *Ric. Sci.* **35**(11-A), 480–481.
- SHELDRIK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
- SPOFFORD, W. A. & AMMA, E. L. (1968). *Chem. Commun.* pp. 405–407.
- UGOZZOLI, F. (1983). *ABSORB*. Program for Walker and Stuart's absorption correction. Univ. of Parma, Italy.
- VIZZINI, E. A. & AMMA, E. L. (1966). *J. Am. Chem. Soc.* **88**, 2872–2873.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1987). **C43**, 413–416

Structure of Monomethylammonium Tetrachlorocuprate at 297 and 100 K

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Abstract. $[\text{CH}_3\text{NH}_3]_2[\text{CuCl}_4]$, $M_r = 269.48$, monoclinic, $P2_1/a$, $Z = 2$, $F(000) = 270$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$. $T = 297 (1) \text{ K}$: $a = 7.268 (4)$, $b = 7.367 (4)$, $c = 9.971 (3) \text{ \AA}$, $\beta = 110.89 (1)^\circ$, $V = 498.8 (9) \text{ \AA}^3$, $D_x = 1.794 \text{ Mg m}^{-3}$, $\mu = 3.21 \text{ mm}^{-1}$, $R_F = 0.042$ for 879 observed independent reflections. $T = 100 (2) \text{ K}$: $a = 7.155 (4)$, $b = 7.424 (4)$, $c = 9.814 (3) \text{ \AA}$, $\beta = 109.18 (7)^\circ$, $V = 492.4 (3) \text{ \AA}^3$, $D_x = 1.818 \text{ Mg m}^{-3}$, $\mu = 3.26 \text{ mm}^{-1}$, $R_F = 0.040$ for 862 observed independent reflections. The crystal structure is monoclinic in the whole temperature range from 100 to 297 K in contrast to earlier results [Steijger, Frikkee, de Jongh & Huiskamp (1984). *Physica B*, **123**, 284–290] that suggested orthorhombic symmetry at 297 K and a phase transition to monoclinic symmetry at lower temperatures. The Cu^{2+} cations are coordinated by six Cl^- ions with four short and two long Cu–Cl bond distances in a Jahn–Teller distorted octahedron. The methylammonium groups are connected to chloride by hydrogen bonds.

Introduction. Compounds with the general formula $(\text{CH}_3\text{NH}_3)_2\text{MCl}_4$, where M is a divalent metal ($M = \text{Mn}, \text{Cd}, \text{Cu}$ etc.), have been extensively studied in recent years with respect to their magnetic properties and interesting structural phase transitions. The crystal structure may be described as two-dimensional layers of corner-sharing MCl_6 units. The alkylammonium entities are situated between the layers and connected by hydrogen bonds to the Cl^- ions. The crystal structure and the structural phase transitions of $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$ (Chapuis, Arend & Kind, 1975; Chapuis, Kind & Arend, 1976) and of the analogous

manganese compound (Heger, Mullen & Knorr, 1975) were studied in great detail. The analogous compound $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ was studied by X-ray and neutron diffraction powder methods; Steijger, Frikkee, de Jongh & Huiskamp (1984a) reported several structural phase transformations and determined its magnetic properties at low temperatures (Steijger, Frikkee, de Jongh & Huiskamp, 1984b). They found a tetragonal high temperature phase above 348 (1) K and an orthorhombic structure at room temperature. Between 250 and 170 K a coexistence of the orthorhombic room temperature structure and of a low temperature monoclinic phase was derived from the data. These authors confirm the monoclinic phase as stable below 170 K. The present work was undertaken in order to solve the crystal structure of $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ in its different phases and to elucidate the nature of the coexistence of two structures in the same temperature region by single-crystal X-ray diffraction.

Experimental. Brown crystals were obtained by slow evaporation of an aqueous solution of stoichiometric amounts of $\text{CH}_3\text{NH}_3\text{Cl}$ and $\text{CuCl}_2 \cdot \text{H}_2\text{O}$. The first two crystals examined showed orthorhombic symmetry by precession photographs and on an automatic diffractometer. The structure determination and the refinement (*XRAY* system, Stewart, Kruger, Ammon, Dickinson & Hall, 1972) revealed, however, a domain structure and suggested that the true symmetry is monoclinic and the domains give rise to orthorhombic pseudo-symmetry.

Finally a one-domain crystal of size $0.4 \times 0.9 \times 1.0 \text{ mm}$ of good optical quality was selected and used