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The Crystal and Molecular Structure of Thiocyanatobis(thiourea)silver(I)

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The crystal structure of $Ag[SC(NH_2)_2]_2SCN$ was determined from three-dimensional diffractometer data and refined by least-squares to a conventional R factor of 0.044 for 1642 observed reflections. The compound is monoclinic (space group C2/c) with cell parameters a = 11.072(3), b = 13.838(4), c = 13.983(4) Å, $\beta = 111.65(3)°$, Z = 8, $d_c = 2.123$ g cm^{-3}, $d_m = 2.11$ g cm^{-3}.

Within one complex $Ag(tu)_2SCN$ unit, three S atoms of two thiourea molecules (Ag–S 2.482(2) and 2.462(2) Å) and of one SCN group (Ag–S 2.608(2) Å) are bonded to the central Ag with almost trigonal planar AgS_3 coordination. One of the two thiourea S atoms is weakly coordinated to a second Ag center (Ag–S 3.111(2) Å), forming a dimeric complex $[Ag(tu)_2SCN]_2$ unit with C_i symmetry and with a central planar four-membered Ag–S–Ag–S ring (Ag···Ag 3.097(1) Å, bond angles S–Ag–S 113.9(1)° and Ag–S–Ag 66.1(1)°). The orientation of the bridging thiourea molecule suggests the contribution of electron pairs in pπ carbon–sulfur MO's besides those in sulfur sp^2 orbitals to the Ag–S bonding system, all bridge bonds being two-electron two-center bonds.

Introduction

The preparation and structural investigation of metal thiourea complexes of a variety of transition and main group metals have proved the planar thiourea ligand to be very well suited as a geometric probe for the study of the metal–sulfur bonding in these soft donor ligand complexes[1]. Structural studies on thiourea (tu) complexes of Ag(I) and Cu(I) which include $Ag(tu)_2Cl$[2], $Ag(tu)_3ClO_4$[3], $Cu(tu)_2Cl$[4], $Cu(tu)_3ClO_4$[5], and $Cu(tu)_3BF_4$[1], have shown varying types of bonding, connected with different coordination characteristics and different degrees of condensation. Within different types of M–S–M bridges, sulfur sp^2 and pπ electrons participate in normal two-electron and in electron-deficient three-center two-electron bonds. To obtain more insight into the bonding characteristics of this class of compounds, we have investigated the crystal structure of thiocyanatobis(thiourea)silver(I), $Ag(tu)_2SCN$. This is our second study on a silver–thiourea complex after the previous one on the binuclear $[Ag(tu)_3{}^+]_2$ complex unit in $Ag(tu)_3ClO_4$[3].

Experimental

Thiocyanatobis(thiourea)silver(I), $Ag[SC(NH_2)_2]_2SCN$, was prepared by interacting silver nitrate, ammonium thiocyanate and thiourea in appropriate portions in water. Single crystals were obtained by slow evaporation of the aqueous solution containing the complex. *Anal.* Found, C 11.27, H 2.48, N 22.02, S 30.25, Ag 33.84%; required for $C_3H_8N_5S_3Ag$, C 11.33, H 2.52, N 22.00, S 30.24, Ag 33.92%.

The unit cell dimensions of the monoclinic crystals obtained from Weissenberg and precession photographs are reported earlier[6]. They were refined by least-squares from diffractometer coordinates of 15 high angle reflections to be (at 20 °C; including σ's): a = 11.072(3), b = 13.838(4), c = 13.983(4) Å, β = 111.65(3)°, V = 1991 Å^3. From the two possible space groups (Cc and C2/c) indicated by the systematic absences hkl: h+k ≠ 2n and h0l: l ≠ 2n, the centrosymmetric one C2/c–C_{2h}^6 (No. 15) was shown to be the correct choice from the statistical distribution of the normalized structure factors and from the successful completion of the structure analysis. With Z = 8 $Ag(tu)_2SCN$ the X-ray density d_c = 2.123 g cm^{-3} is in good agreement with the experimental value d_m = 2.11 ± 0.02 g cm^{-3} (by flotation). A complete set of 1983 independent reflections in the range $\sin\Theta/\lambda < 0.64$ Å^{-1} was measured with Zr-filtered Mo-Kα radiation on a computer controlled Hilger–Watts four-circle diffractometer ($\lambda(K\alpha_1)$ 0.70926 Å, ω– 2Θ mode, scintillation counter, pulse height discrimination), using a prismatic crystal with the dimensions 0.09 × 0.12 × 0.10 mm^3. Measuring conditions were: 240 sec scan time per reflection (0.96° in Θ, take-off angle 3°), stationary background counts (48 sec) at both sides, a standard reflection every 30 reflections, source to crystal and crystal to counter distances 21 cm and 30 cm (receiving aperture 3.5 mm in diameter). The mosaic spread was normal as judged by a narrow-source opencounter peak width of ~0.10° for an average reflection. Considering the low linear absorption coefficient (25.3 cm^{-1}), no absorption correction was applied. Data reduction was done in the usual way, applying Lorentz and polarization corrections and including a Wilson plot.

Determination and Refinement of the Structure

The structure could be solved from the three-dimensional Patterson function. Approximate coordinates for the Ag and S atoms were located from the Patterson map, the C and N positions being obtained from subsequent difference Fourier maps. After full-matrix least-squares refinement of the positional and anisotropic thermal parameters, the coordinates of the H atoms could be obtained from a subsequent ΔF synthesis and were included in the refinement with isotropic temperature factors. Atomic scattering factors for Ag, S, C and N were used as given in the International Tables[7], the values for hydrogen were taken from Stewart, Davidson and Simpson[8]. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$. The weighting scheme was based on the variance of the structure factors derived from counting statistics. It was shown to be adequate from an analysis of the residuals. For 341 out of the total of 1983 reflections the measured net intensity I was below 2 $\sigma(I)$. They were treated as being unobserved and were assigned zero weight ($w = 0$). No spurious peaks were found in the final difference map. The standard error of an observation of unit weight was 1.67*. The final R values after completion of the full-matrix refinement were (in parentheses: including zero reflections): $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o| = 0.044$ (0.057), $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.046$ (0.053). The positional and ther-

TABLE I. $Ag(tu)_2SCN$: Coordinates of the Atoms in the Unit Cell.[a]

	x	y	z
Ag	0.01175(4)	0.45784(3)	0.10567(4)
S1	0.11057(13)	0.62061(9)	0.11817(11)
S2	0.14413(13)	0.31118(9)	0.16540(12)
S3	−0.22409(14)	0.45440(11)	0.10494(12)
C1	0.0033(5)	0.7092(4)	0.1220(4)
C2	0.0422(5)	0.2148(4)	0.1458(4)
C3	−0.3076(5)	0.4967(4)	−0.0122(5)
N1	0.0397(6)	0.7997(4)	0.1311(5)
N2	−0.1158(5)	0.6884(4)	0.1145(4)
N3	0.0905(6)	0.1280(4)	0.1737(5)
N4	−0.0857(5)	0.2243(4)	0.1045(4)
N5	−0.3686(6)	0.5244(4)	−0.0930(5)

[a] Estimated standard deviations are given in all tables in parentheses in units of the last significant digits.

TABLE II. Coefficients of the Anisotropic Temperature Factors.[a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ag	3.14(2)	2.30(2)	5.94(3)	0.28(2)	1.50(2)	0.48(2)
S1	2.07(5)	1.90(5)	3.39(6)	0.15(4)	1.13(5)	−0.19(5)
S2	1.97(5)	2.08(6)	3.94(7)	0.21(4)	0.93(5)	0.19(5)
S3	2.53(6)	2.58(6)	4.23(7)	0.02(5)	1.53(5)	−0.04(5)
C1	2.43(21)	1.82(20)	2.29(21)	0.36(17)	0.84(17)	0.14(16)
C2	2.69(22)	1.86(21)	2.73(22)	0.11(17)	1.09(17)	−0.28(17)
C3	2.55(24)	2.06(22)	4.81(33)	−0.22(19)	1.36(24)	−0.81(23)
N1	3.07(24)	2.16(21)	6.94(35)	0.19(19)	2.44(25)	−0.08(22)
N2	2.35(20)	2.79(22)	5.38(28)	−0.13(17)	1.95(20)	−0.90(20)
N3	3.09(25)	2.16(21)	4.69(27)	0.39(19)	0.81(22)	−0.08(19)
N4	2.50(20)	1.95(19)	4.19(24)	−0.21(17)	1.02(18)	−0.43(18)
N5	3.46(25)	3.54(27)	5.84(35)	0.40(21)	0.52(24)	0.33(24)

[a] The anisotropic temperature factors are expressed in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

TABLE III. Experimental Coordinates and Temperature Factors of the Thiourea Hydrogen Atoms.

	x	y	z	B
H11	−0.014(6)	0.847(5)	0.138(4)	3.6(14)
H12	0.100(6)	0.812(5)	0.122(5)	3.8(17)
H21	−0.175(7)	0.737(5)	0.108(5)	4.9(17)
H22	−0.138(8)	0.606(7)	0.117(6)	7.7(22)
H31	0.035(8)	0.076(6)	0.158(6)	6.7(21)
H32	0.165(6)	0.124(4)	0.203(4)	1.7(12)
H41	−0.134(5)	0.175(5)	0.098(4)	2.6(13)
H42	−0.114(7)	0.298(6)	0.098(5)	6.3(19)

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* The calculations were done on a PDP 10 computer using, besides own programs, local versions of the programs FORDAP (A. Zalkin), ORFLS and ORFFE (W.R. Busing, K.O. Martin, H.A. Levy), SADIAN (W.H. Baur), DATAP (M. Dobler).

mal parameters, including the least-squares standard deviations, are given in Tables I, II and III. A table of observed and calculated structure factors is available from the Editor upon request.

Results and Discussion

The structure consists of complex $Ag(tu)_2SCN$ units which are associated through weak Ag–S bonds to form centrosymmetric dimers. The configuration of the binuclear complex molecule is shown in Figure 1. The arrangement of the dimers in the unit cell is pictured in Figure 2. Table IV gives the bond distances and angles.

The Ag atoms are coordinated by two thiourea sulfur atoms (S1 and S2, bond distances 2.482 and 2.462 Å) and one S atom of a thiocyanate ligand (Ag–S3 2.608 Å), the three ligands forming an almost planar arrangement together with the central Ag. The silver atom is displaced only 0.29 Å from the S1–S2–S3 plane towards S1(a). This fourth sulfur atom S1(a) (see Figure 1), which is much more weakly bonded (Ag–S1(a) 3.111 Å), completes a highly distorted tetrahedral coordination polyhedron around the silver atom and acts as a bridge to the second half of the centrosymmetric dimer $[Ag(tu)_2SCN]_2$. The Ag· · ·Ag distance across the exactly planar asymmetric four-membered Ag_2S_2 ring is 3.097 Å.

The dimensions of the thiourea molecules (mean S–C and C–N bond lengths: 1.712 Å and 1.315 Å, respectively) are not significantly different from those of the free molecule which are 1.720(9) and 1.340(6) Å (corrected for rotational oscillations)[9] from X-ray data and 1.709(8) and 1.333(3) Å (uncorrected; after correction: 1.746 and 1.349 Å)[10] from neutron diffraction. In $[Ag(tu)_2SCN]_2$ the bond distances of the bridging thiourea group are only slightly different from those for the terminal one (see below). Within the limits of error, the thiourea molecules are exactly

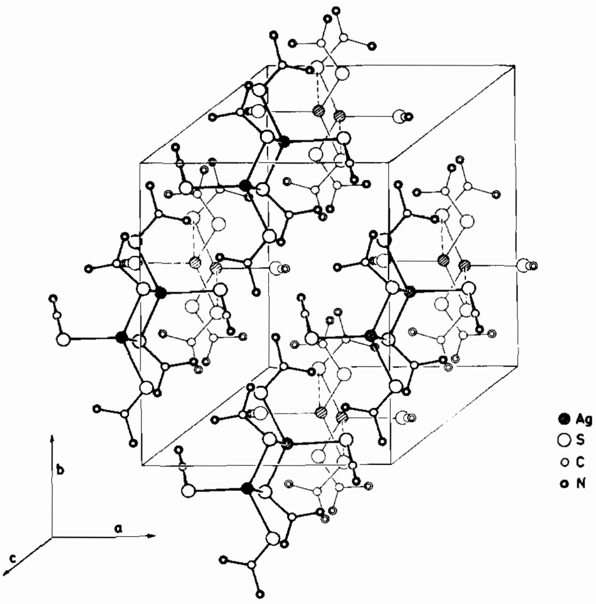

Figure 2. Unit cell of the $Ag(tu)_2SCN$ crystal structure.

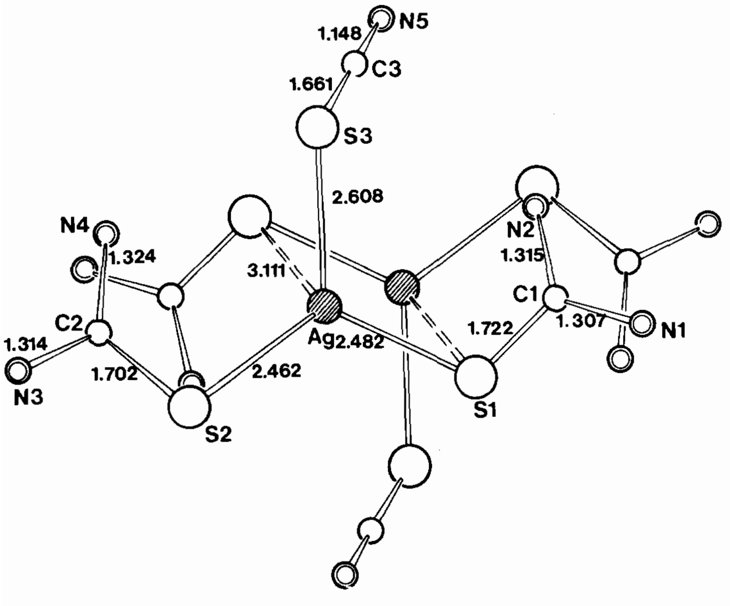

Figure 1. Structure of the binuclear complex $[Ag(tu)_2SCN]_2$ in the crystal with numbering of the atoms. The two halves of the complex are related by a center of inversion. H atoms are omitted.

TABLE IV. Interatomic Distances and Bond Angles within the $Ag(tu)_2SCN$ Complex.

Ag Coordination			
Ag–S1	2.482(2) Å	S1–Ag–S2	122.2(1)°
Ag–S2	2.462(2)	S1–Ag–S3	115.6(1)
Ag–S3	2.608(2)	S2–Ag–S3	117.1(1)
Ag–S1(a)[a]	3.111(2)	S1–Ag–S1(a)	113.9(1)
Ag···Ag(a)	3.097(1)	S1(a)–Ag–S2	92.1(1)
		S1(a)–Ag–S3	85.8(1)
		Ag–S1–Ag(a)	66.1(1)
Thiourea Molecules			
S1–C1	1.722(6) Å	S2–C2	1.702(6) Å
C1–N1	1.307(8)	C2–N3	1.314(8)
C1–N2	1.315(8)	C2–N4	1.324(8)
S1–C1–N1	119.5(5)°	S2–C2–N3	119.7(5)°
S1–C1–N2	121.7(4)	S2–C2–N4	122.1(5)
N1–C1–N2	118.8(5)	N3–C2–N4	118.2(5)
Ag–S1–C1	110.9(2)	Ag–S2–C2	108.4(2)
Ag(a)–S1–C1	103.3(2)		
SCN^- Ion			
S3–C3	1.661(7) Å		
C3–N5	1.148(9)		
S3–C3–N5	177.9(6)°		
Ag–S3–C3	100.9(2)		

[a] The index (a) refers to the centrosymmetric equivalent to the atom (transformation –x, 1–y, –z).

planar. The deviations of the C, N, and S atoms from the best least-squares planes through the SCN_2 skeletons are below 0.005 Å ($<0.8\sigma$), the deviations of the hydrogens are below 0.16 Å ($<1.9\sigma$).

The considerable number of structurally characterized thiourea complexes of metals such as Co(II), Ni(II), Pd(II), Cu(I), Cu(II), Ag(I), Zn(II), Cd(II), Pb(II), Te(IV) show similar bond lengths and angles in the tu molecules. They include the recently determined structures of $Ag(tu)_2Cl$[2], $Ag(tu)_3ClO_4$[3], $Cu(tu)_2Cl$[4], $Cu(tu)_3Cl$[11], $Cu(tu)_3ClO_4$[5], $Cu(tu)_3BF_4$[1,12], $Cu(bipy)_2tu(ClO_4)_2$[13] and $Cu(pib)tu(ClO_4)_2$[13] (bipy = 2,2'-bipyridyl; pib = N,N'-tetramethylenebis-(2-pyridinaldimine)). A survey on the available structural data on thiourea molecules in complexes shows that, due to various reasons (*e.g.* large bond distance errors, uncertain rotational oscillation corrections, effects of intermolecular hydrogen bonding), significant correlations between bonding and bond dimensions in different free and ligand thiourea molecules cannot yet be derived (see also ref. 14). In the present case of $Ag(tu)_2SCN$ a rigid body model for the tu molecules was found not to be satisfactory. Bond length corrections for C–S and C–N are estimated to be around +0.02 Å.

It is well known that silver(I) is quite variable in the geometries of its sulfur coordination which can vary between linear (c.n.2), trigonal-planar (c.n.3), tetrahedral (c.n.4) and higher, including intermediate stages (see *e.g.* ref. 15). In contrast to the tetrahedral AgS_4 and CuS_4 geometries in $Ag(tu)_3ClO_4$[3], $Cu(tu)_3Cl$[11], $Cu(tu)_3ClO_4$[5] and $Cu(tu)_3BF_4$[1], the essentially trigonal-planar coordination with an additional more weakly bonded "axial" ligand realized in $[Ag(tu)_2SCN]_2$ has similarly been found in the $Ag(tu)_2Cl$[2] and $Cu(tu)_2Cl$[4] structures. In these compounds trigonal almost planar AgS_3 and CuS_3 groups (Ag–S 2.433–2.588 Å) are linked through corners to form endless chains, the essentially ionic chlorines being in the axial positions. The novel feature of the present complex is this type of coordination existing in an isolated molecular unit. The two shorter Ag–S bonds of 2.462 and 2.482 Å are to be considered as the normal single covalent bond lengths for trigonal coordination, being somewhat shorter than the sum of the tetrahedral covalent radii (about 2.56 Å[16]). The third bond to the thiocyanate sulfur atom (2.608 Å) is significantly longer (the Ag–S bond length in AgSCN with c.n.2 of the silver is 2.428 Å[17]), but is still to be considered as close to a single bond. The very much weaker axial Ag–S bond (3.111 Å) can be related to the nature of the Ag–S1–Ag(a) bridge bond (*vide infra*). The dimensions of the thiocyanate ligand are within normal limits for SCN^- ions or S-coordinated SCN ligands[18]. Similar silver thiocyanato complexes include AgSCN · 2tris(cyclohexylphosphine)[19] (3-coordinated Ag), AgSCN · P(n-propyl)$_3$[20,21] and $NH_4SCN \cdot AgSCN$[22] (4-coordinated Ag).

The most interesting feature of the structure is the bonding in the central Ag_2S_2 ring of the dimer. In the similar bridge systems of previously investigated thiourea complexes the usually sharp Ag–S–Ag bridge angle (*ca.* 64–83°) was rationalized by different bonding mechanisms: (1): two-center two-electron Ag–S bonds, utilizing (a) electrons form the (delocalized) $p\pi$ S–C orbital (in terms of a more general MO description: the highest filled approximately nonbonding π–MO with symmetry designation a_1'[4]), and/or (b) normally non-bonding electrons from sp^2 orbitals of the thiourea S atoms or (2): a new type of electron-deficient three-center two-electron bond, using the thiourea $p\pi$ S–C MO with its electrons or a sulfur sp^2 electron pair in a three-center M–S–M system (M = Ag(I) or Cu(I)). Examples are: $Ag(tu)_2Cl$[2]: (1) + (2); $Ag(tu)_3ClO_4$[3]: (1); $Cu(tu)_2Cl$[4]: (1) + (2); $Cu(tu)_3BF_4$[1]: (1); $Cu(tu)_3ClO_4$[5]: (2); $Cu_4(tu)_9(NO_3)_4$[23]: (2).

For $Ag(tu)_2SCN$ the following data clearly indicate that the bridge bonding has to be described as a system of two-center bonds: the Ag–S1–C1 and Ag(a)–S1–C1 bond angles (Figure 1) are 110.9 and 103.3°, respectively; dihedral angles are: Ag–S1–Ag(a)–S1(a)/Ag–S1–S2–S3 86.9°; Ag–S1–Ag(a)–S1(a)/S1–C1–N1–N2 95.5°; Ag–S1–S2–S3/S1–C1–N1–N2 12.1°; S1–C1–N1–N2/Ag–S1–C1 1.8°; S1–C1–

TABLE V. Hydrogen Bond System in the $Ag(tu)_2SCN$ Structure.[a]

H Donor	N–H Distance, Å	H Acceptor	N···N or N···S Distance, Å	H···N or H···S Bridge Distance, Å	N–H···N or N–H···S Angle
N1–H11	0.92(7)	N5(b)	3.009(9)	2.15(7)	155(5)°
N1–H12	0.74(8)	S3(c)	3.502(7)	2.84(8)	150(7)°
N2–H21	0.92(8)	S2(d)	3.443(6)	2.63(8)	148(6)°
N2–H22	1.17(9)	S3	3.438(6)	2.28(9)	169(7)°
N3–H31	0.91(9)	N5(e)	3.117(9)	2.22(9)	166(8)°
N3–H32	0.77(6)	S1(f)	3.511(7)	2.80(6)	154(5)°
N4–H41	0.85(7)				
N4–H42	1.05(9)	S3	3.535(5)	2.51(9)	164(6)°
Average:	0.92				

[a] The additional indices refer to the following transformations of the coordinates given in Table I:
(b): $-x-1/2, -y+3/2, -z$; (c): $x+1/2, y+1/2, z$; (d): $x-1/2, y+1/2, z$; (e): $-x-1/2, -y+1/2, -z$; (f): $-x+1/2, y-1/2, -z+1/2$.

N1–N2/Ag(a)–S1–C1 64.7°. It follows that the Ag–S1 bond which is approximately in the S1–C1–N1–N2 thiourea molecular plane, can be regarded as of type (1b) (see above). The Ag(a)–S1 bond, being roughly perpendicular to the thiourea plane, must be assumed to be a two-center bond of type (1a), utilizing the electron pair from the thiourea $p\pi$ orbital. The Ag–S2 bond (bond angle C2–S2–Ag 108.4°; dihedral angle Ag–S1–S2–S3/S2–C2–N3–N4 13.3°) can be interpreted as a normal two-center bond using electrons from a nonbonding sulfur sp^2 orbital (type (1b)).

Within the crystal the binuclear $[Ag(tu)_2SCN]_2$ complexes are in contact with each other, besides normal van der Waals contacts, through an extensive N–H···S and N–H···N hydrogen bond system. The relevant data are given in Table V which also contains the experimental bond distances involving the hydrogen atoms.

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