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The Crystal and Molecular Structure of Tris(thiourea)silver(I) Perchlorate

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Tris(thiourea)silver(I) perchlorate, $Ag[SC(NH_2)_2]_3ClO_4$, is monoclinic with cell parameters $a = 19.537(8)$, $b = 13.436(6)$, $c = 10.791(5)$ Å, $\beta = 103.57(5)°$. The space group is C2/c with $Z = 8$, $d_c = 2.102$ g. cm^{-3} and $d_m = 2.090$ g.cm^{-3}. The crystal structure was determined from three-dimensional diffractometer data and refined by least-squares methods with anisotropic thermal parameters to a conventional R factor of 0.048 for 2202 observed reflections.

The structure is ionic and consists of binuclear complexes $(Ag_2[SC(NH_2)_2]_5)^{2+}$ with C_2 symmetry and perchlorate anions. The sulphur atoms of four thiourea molecules form a distorted coordination tetrahedron (S-Ag-S angles range from 100.5(1) to 115.9 (1)°) around each Ag. Two of the six sulphur atoms of the binuclear complex cation act as bridging ligands in a four-membered Ag-S-Ag-S ring (bridge bond lengths 2.663(2) and 2.684(2) Å), the remaining four are terminal (Ag-S bond lengths 2.524(2) and 2.570 (2) Å). The bond angle Ag-S-Ag is 64.3(1), the Ag... Ag distance in the binuclear complex is 2.845(1) Å.

The bonding of the complex cation is different from the corresponding copper(I) complex. The orientation of the thiourea molecules suggests use of electron pairs of pπ sulphur-carbon MO's in the terminal as well as (together with sulphur sp^2 orbitals) in the bridge Ag-S bonds.

Introduction

Crystal structure studies on a number of metal-thiourea complexes have shown that the thiourea (tu) ligands are normally coordinated through the sulphur atoms; coordination via the nonbonding electrons of the nitrogen atoms has in no case been conclusively established. Structure analyses on the free thiourea molecule indicate the S-C and C-N bonds being intermediate between single and double bonds; the S-C and C-N bond lengths of 1.720 and 1.340 Å obtained from X-ray data[3] and the neutron diffraction values of 1.746 and 1.350 Å[4] are considerably shorter than the accepted single bond covalent radii of 1.82 and 1.48 Å, respectively.[5] The completely planar molecule may be described as a conjugated system with delocalized π molecular orbitals formed from p orbitals of the S, C and N atoms[6] with the σ-bonds made up essentially from sp^2 orbitals. In terms of this bond description the sulphur atoms can coordinate to the central metal through (1): electrons from the nonbonding sp^2 orbitals or (2): electrons from a π molecular orbital. The second kind of bonding has been observed in a number of thiourea complexes such as $Ag(tu)_2Cl$,[7] $Cu_4(tu)_9(NO_3)_4$,[8] $Cu_2(tu)_6(BF_4)_2$,[9] $Cu(tu)_3ClO_4$,[10] $Co(tu)_4(NO_3)_2$ and $Co(tu)_4(NO_3)_2\,NO_3{\cdot}H_2O$[11] and $Cu(tu)_2Cl$.[6] In some of the examples[6,7,10] these π-electrons are involved in a very interesting three-center sulphur bridge bond.

In order to obtain more information on the bonding in systems of this kind the complete structure of $Ag(tu)_3ClO_4$ was investigated.

Experimental Section

Tris(thiourea)silver(I) perchlorate, $Ag[SC(NH_2)_2]_3ClO_4$ or $Ag(tu)_3ClO_4$, was prepared by adding a little more (10%) than the molar quantity of thiourea to a solution of silver oxide in the equivalent quantity of aqueous perchloric acid. Single crystals were obtained by slow evaporation of the reaction mixture. The composition was checked by chemical analysis: calcd: Ag 24.76, C 8.27, H 2.78, N 19.29, S 22.08, Cl 8.14; found: Ag 24.7, C 8.36, H 2.82, N 19.35, S 22.2, Cl 8.02%.

Weissenberg and Precession photographs showed the crystals to be monoclinic with the following unit cell dimensions (at 20°C, obtained by least-squares refinement of diffractometer settings for 18 reflections; errors given are 2σ):

$$a = 19.537(8),\ b = 13.436(6),\ c = 10.791(5)\text{Å},$$
$$\beta = 103.57(5)°,\ V = 2754\ \text{Å}^3.$$

The systematic absences on hk0, hk1, and hk2 Weis-

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senberg (CuKα) and h0l, h1l, and h2l Precession photographs (MoKα) were found to be hkl with $h+k = 2n+1$ and h0l with $l = 2n+1$ which is consistent with the space groups C2/c-C_{2h}^6 and Cc-C_s^4. The statistical distribution of the normalized structure factors suggested C2/c being the correct choice; this was confirmed later in the course of the structure determination. The X-ray density is $d_c = 2.102$ g.cm^{-3} for Z = 8 Ag(tu)$_3$ClO$_4$ units which agrees well with the experimental value $d_m = 2.09(1)$ g.cm^{-3}, obtained pycnometrically (benzene).

Using a prismatic crystal with the dimensions $0.12 \times 0.16 \times 0.22$ mm (these dimensions being approximately along a, b, and c) mounted along c*, the intensity data were collected on a computer-controlled Hilger-Watts four-circle diffractometer (MoKα radiation, $\lambda(K\alpha_1)$ 0.70926 Å, Zr filter, ω-2θ scan method, scintillation counter, pulse height discrimination). The receiving aperture was 3.5 mm in diameter. The ω and 2θ circles were scanned for 240 sec. in steps of 0.02° over 0.96° in θ, with a take-off angle of 4.0°.

Individual background counts (48 sec.) were taken at each end of the scan. A standard reflection was measured every 30 reflections. The source to crystal and crystal to counter distances were 21 cm and 30 cm, respectively. The mosaic spread was within normal limits, as indicated by a narrow-source open-counter peak width of $\theta = 0.07$-$0.09°$ for an average reflection.

A complete set of unique data within the limits $\sin \theta/\lambda < 0.58$ Å^{-1} was recorded, yielding a total of 2202 nonequivalent reflection intensities. The linear absorption coefficient for MoKα radiation is $\mu = 20.7$ cm^{-1}; the minimum and maximum μR values for the crystal used are 0.13 and 0.28. Regarding these data, no absorption correction was applied. The data were reduced to F_o values in the usual way by Lorentz and polarization corrections and subsequent treatment by the Wilson method.

Determination and Refinement of the Structure. The structure was solved by interpretation of the three-dimensional Patterson function. The Ag and S positions could be located from the Patterson map, the C, N, Cl, and O positions from subsequent difference Fourier syntheses. The atomic coordinates were refined together with isotropic temperature factors and with one scale factor by full matrix least-squares to an R_2 value of 0.068. Approximate coordinates for all H atoms could be obtained from a difference Fourier map which was computed after convergence of the isotropic refinement. The refinement was continued with inclusion of the H atoms with anisotropic temperature factors for all atoms except H; for the H atoms x, y and z were varied, the (isotropic) temperature factors for these atoms were kept constant at B = 5 Å^2.

The atomic scattering factors of Ag, Cl, S, O, N, and C were used as tabulated by Ibers,[12] the scattering curve for H was taken from Stewart *et al.*[13] The effects of anomalous dispersion and extinction were neglected. The expression minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme was based on the statistical deviations σ of the reduced counting rates I with an additional term, being proportional to the

Table I. Final atomic coordinates *.

Ag	0.07475(3)	0.08587(4)	0.29017(5)
S1	0.00849(9)	0.11849(12)	0.04836(14)
S2	0.12744(9)	—0.08610(12)	0.32905(15)
S3	0.16156(9)	0.23155(14)	0.34845(15)
N1	—0.0367(3)	0.2735(5)	—0.0999(5)
N2	0.0249(3)	0.3117(4)	0.1081(5)
N3	0.2566(3)	—0.0679(5)	0.2945(6)
N4	0.1687(3)	—0.0683(4)	0.1136(5)
N5	0.2075(3)	0.1770(5)	0.1445(5)
N6	0.2913(3)	0.1902(5)	0.3320(5)
C1	—0.0014(3)	0.2447(5)	0.0190(6)
C2	0.1883(3)	—0.0722(4)	0.2364(6)
C3	0.2237(3)	0.1960(5)	0.2692(6)
Cl	0.38459(8)	0.04076(12)	0.12015(15)
O1	0.4349(3)	0.0136(4)	0.0529(5)
O2	0.3785(5)	0.1456(5)	0.1178(9)
O3	0.4025(3)	0.0084(6)	0.2484(6)
O4	0.3170(3)	0.0024(6)	0.0639(5)

* Estimated standard deviations here and in succeeding tables are given in parentheses in units of the least significant digits.

Table II. Anisotropic thermal parameters *.
Ag, S, Cl : × 10^5 N, C, O : × 10^4

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag	179(2)	537(4)	977(7)	22(2)	85(2)	2(3)
S1	165(5)	359(9)	458(14)	13(5)	65(6)	2(9)
S2	201(5)	443(10)	504(15)	38(6)	119(7)	92(9)
S3	167(5)	584(11)	551(16)	—67(6)	65(7)	—141(11)
N1	22(2)	70(5)	70(6)	—3(2)	—5(3)	33(4)
N2	27(2)	39(3)	85(6)	—4(2)	10(3)	1(4)
N3	21(2)	63(4)	89(7)	—1(2)	8(3)	6(4)
N4	29(2)	62(4)	42(5)	—1(2)	7(3)	—3(4)
N5	33(2)	66(4)	50(5)	—3(2)	3(3)	—19(4)
N6	19(2)	69(4)	95(7)	1(2)	1(3)	—24(4)
C1	11(2)	53(4)	68(6)	2(2)	9(3)	13(4)
C2	20(2)	28(3)	60(6)	1(2)	10(3)	—6(4)
C3	17(2)	33(4)	87(7)	—6(2)	11(3)	—5(4)
Cl	164(5)	489(10)	619(15)	—19(6)	105(7)	—13(10)
O1	38(2)	82(4)	132(7)	20(3)	48(3)	19(4)
O2	105(5)	60(5)	358(15)	1(4)	145(8)	—14(7)
O3	30(2)	222(10)	100(7)	—1(4)	5(3)	53(7)
O4	32(2)	170(8)	90(6)	—41(3)	—3(3)	21(6)

* The anisotropic temperature factors are expressed in the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Table III. Coordinates of the hydrogen atoms.

	x	y	z
H1	—0.029(4)	0.344(5)	—0.122(7)
H2	—0.048	0.217	—0.156
H3	0.020	0.376	0.089
H4	0.051	0.283	0.180
H5	0.283	—0.065	0.241
H6	0.277	—0.076	0.392
H7	0.201	—0.063	0.047
H8	0.121	—0.075	0.069
H9	0.162	0.178	0.086
H10	0.238	0.159	0.078
H11	0.314	0.204	0.432
H12	0.315	0.190	0.258

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Table IV. Observed and calculated structure factors.

Table III. (continued)

H	K	L	FOB	FCA	H	K	L	FOB	FCA	H	K	L	FOB	FCA	H	K	L	FOB	FCA	H	K	L	FOB	FCA
14	0	-10	10	-11	15	1	-8	34	40	16	2	-8	10	-1	17	3	3	79	-81	19	1	-4	44	49
14	0	-8	85	-85	15	1	-7	0	-9	16	2	-7	99	-100	17	3	4	27	24	19	1	-3	21	19
14	0	-6	22	17	15	1	-6	14	8	16	2	-6	40	-44	17	3	5	30	27	19	1	-2	122	123
14	0	-4	228	231	15	1	-5	138	141	16	2	-5	147	148	17	5	-8	28	-23	19	1	-1	24	-28
14	0	-2	57	-56	15	1	-4	112	111	16	2	-4	28	28	17	5	-7	38	-44	19	1	0	88	-89
14	0	0	143	142	15	1	-3	111	-107	16	2	-3	24	-23	17	5	-6	60	63	19	1	1	0	0
14	0	2	115	-119	15	1	-2	184	-185	16	2	-2	82	-77	17	5	-5	39	40	19	1	2	70	70
14	0	4	39	37	15	1	-1	25	22	16	2	-1	28	-23	17	5	-4	108	-111	19	1	3	62	-62
14	0	6	35	39	15	1	0	152	151	16	2	0	122	124	17	5	-3	17	-11	19	3	-8	27	-25
14	2	-11	65	64	15	1	1	7	6	16	2	1	25	-25	17	5	-2	49	46	19	3	-7	39	-40
14	2	-10	12	10	15	1	2	24	-24	16	2	2	10	-7	17	5	-1	27	-24	19	3	-6	21	-21
14	2	-9	35	-33	15	1	3	66	-65	16	2	3	60	-61	17	5	0	14	-14	19	3	-5	37	33
14	2	-8	6	0	15	1	4	8	2	16	2	4	100	-106	17	5	1	26	28	19	3	-4	8	2
14	2	-7	49	48	15	1	5	18	-13	16	2	5	26	25	17	5	2	90	-94	19	3	-3	40	37
14	2	-6	49	-46	15	1	6	8	8	16	2	6	42	47	17	5	3	36	34	19	3	-2	13	16
14	2	-5	152	151	15	3	-10	5	-7	16	4	-9	23	21	17	5	4	98	101	19	3	-1	112	-113
14	2	-4	11	10	15	3	-9	55	57	16	4	-8	26	-22	17	7	-7	72	72	19	3	0	20	-21
14	2	-3	195	-193	15	3	-8	20	14	16	4	-7	83	-84	17	7	-6	70	72	19	3	1	55	55
14	2	-2	53	53	15	3	-7	51	-51	16	4	-6	13	-14	17	7	-5	48	-49	19	3	2	30	-27
14	2	-1	160	152	15	3	-6	16	14	16	4	-5	116	119	17	7	-4	35	-32	19	3	3	53	-52
14	2	0	11	13	15	3	-5	88	87	16	4	-4	84	-85	17	7	-3	40	-43	19	5	-7	18	-14
14	2	1	141	-142	15	3	-4	46	-43	16	4	-3	46	-47	17	7	-2	44	44	19	5	-6	37	34
14	2	2	123	-126	15	3	-3	152	-154	16	4	-2	97	97	17	7	-1	18	16	19	5	-5	0	5
14	2	3	4	-14	15	3	-2	79	-78	16	4	-1	35	35	17	7	0	0	-8	19	5	-4	25	-27
14	2	4	42	45	15	3	-1	129	131	16	4	0	72	-73	17	7	1	21	22	19	5	-3	22	21
14	2	5	14	-13	15	3	0	4	-6	16	4	1	35	-32	17	7	2	33	-36	19	5	-2	61	-63
14	2	6	34	32	15	3	1	72	-72	16	4	2	6	0	17	7	3	56	56	19	5	-1	0	-6
14	2	7	26	-24	15	3	2	0	-7	16	4	3	51	-55	17	9	-5	35	-38	19	5	0	87	91
14	4	-10	18	17	15	3	3	45	-46	16	4	4	68	70	17	9	-4	0	7	19	5	1	19	15
14	4	-9	66	-64	15	3	4	33	34	16	4	5	69	71	17	9	-3	19	17	19	5	2	77	-78
14	4	-8	39	-39	15	3	5	26	26	16	6	-9	46	-46	17	9	-2	46	48	19	7	-5	26	30
14	4	-7	0	0	15	3	6	5	1	16	6	-8	41	-46	17	9	-1	6	-13	19	7	-4	6	8
14	4	-6	23	26	15	5	-9	19	-14	16	6	-7	52	-51	17	9	0	32	29	19	7	-3	23	-22
14	4	-5	140	133	15	5	-8	6	0	16	6	-6	54	55	17	9	1	17	-20	19	7	-2	23	-20
14	4	-4	3	-5	15	5	-7	46	-42	16	6	-5	10	-13	18	0	-8	104	99	19	7	-1	7	0
14	4	-3	123	-119	15	5	-6	8	6	16	6	-4	135	-137	18	0	-6	34	-34	19	7	0	61	60
14	4	-2	8	4	15	5	-5	39	37	16	6	-3	70	74	18	0	-4	37	39	20	0	-8	40	37
14	4	-1	67	67	15	5	-4	104	-107	16	6	-2	120	124	18	0	-2	5	5	20	0	-6	46	47
14	4	0	128	-130	15	5	-3	89	-90	16	6	-1	26	-23	18	0	0	11	8	20	0	-4	18	18
14	4	1	104	-108	15	5	-2	58	60	16	6	0	65	-67	18	0	2	129	133	20	0	-2	76	72
14	4	2	78	83	15	5	-1	78	76	16	6	1	6	9	18	0	4	124	-125	20	0	0	100	-106
14	4	3	66	64	15	5	0	142	-143	16	6	2	10	-12	18	2	-9	119	122	20	0	2	111	116
14	4	4	16	-10	15	5	1	59	55	16	6	3	43	49	18	2	-8	31	23	20	2	-7	47	49
14	4	5	11	-5	15	5	2	88	87	16	6	4	30	32	18	2	-7	51	-52	20	2	-6	21	-26
14	4	6	25	21	15	5	3	19	-23	16	8	-7	49	48	18	2	-6	55	-60	20	2	-5	46	-46
14	4	7	31	-35	15	5	4	16	18	16	8	-6	31	32	18	2	-5	33	37	20	2	-4	17	-12
14	6	-9	38	-41	15	5	5	20	-13	16	8	-5	89	-86	18	2	-4	7	-8	20	2	-3	47	47
14	6	-8	15	10	15	5	6	47	-51	16	8	-4	14	5	18	2	-3	0	-8	20	2	-2	27	29
14	6	-7	12	6	15	7	-9	0	11	16	8	-3	64	62	18	2	-2	10	-7	20	2	-1	70	-69
14	6	-6	9	4	15	7	-8	10	3	16	8	-2	73	75	18	2	-1	14	-16	20	2	0	62	-65
14	6	-5	0	-2	15	7	-7	10	10	16	8	-1	0	8	18	2	0	39	-40	20	2	1	50	49
14	6	-4	74	-69	15	7	-6	41	43	16	8	0	0	-13	18	2	1	12	12	20	2	2	16	14
14	6	-3	39	-39	15	7	-5	137	-138	16	8	1	41	-41	18	2	2	80	84	20	4	-7	20	29
14	6	-2	92	95	15	7	-4	70	-71	16	8	2	28	31	18	2	3	94	-96	20	4	-6	27	23
14	6	-1	0	-2	15	7	-3	64	52	16	8	3	22	20	18	2	4	64	-64	20	4	-5	32	-34
14	6	0	118	-121	15	7	-2	99	97	16	10	-5	21	-15	18	4	-8	0	0	20	4	-4	10	12
14	6	1	38	-41	15	7	-1	4	-11	16	10	-4	40	38	18	4	-7	69	-65	20	4	-3	25	24
14	6	2	62	63	15	7	0	61	-61	16	10	-3	43	45	18	4	-6	28	30	20	4	-2	113	-117
14	6	3	45	42	15	7	1	49	47	16	10	-2	38	-37	18	4	-5	28	30	20	4	-1	50	-47
14	6	4	46	-48	15	7	2	23	20	16	10	-1	31	-33	18	4	-4	106	-109	20	4	0	51	51
14	6	5	12	13	15	7	3	34	31	16	10	0	0	14	18	4	-3	11	5	20	4	1	64	64
14	6	6	0	-5	15	7	4	11	-3	16	10	1	26	-28	18	4	-2	30	-32	20	6	-5	23	-27
14	8	-8	0	0	15	7	5	13	7	17	1	-10	40	-33	18	4	-1	28	-27	20	6	-4	2	1
14	8	-7	0	-4	15	9	-7	64	64	17	1	-9	67	66	18	4	0	61	64	20	6	-3	24	-21
14	8	-6	35	38	15	9	-6	30	-28	17	1	-8	35	33	18	4	1	41	40	20	6	-2	67	-70
14	8	-5	48	-50	15	9	-5	96	-99	17	1	-7	38	-35	18	4	2	59	-57	20	6	-1	38	42
14	8	-4	21	19	15	9	-4	50	52	17	1	-6	39	-37	18	4	3	56	-57	20	6	0	74	73
14	8	-3	140	141	15	9	-3	67	66	17	1	-5	82	82	18	4	4	67	66	21	1	-6	16	19
14	8	-2	45	45	15	9	-2	40	38	17	1	-4	169	169	18	6	-7	39	-38	21	1	-5	7	1
14	8	-1	155	-156	15	9	-1	37	-35	17	1	-3	14	11	18	6	-6	43	40	21	1	-4	67	-68
14	8	0	9	-1	15	9	0	6	7	17	1	-2	59	-64	18	6	-5	46	-43	21	1	-3	21	18
14	8	1	46	47	15	9	1	27	26	17	1	-1	54	-65	18	6	-4	39	-40	21	1	-2	124	128
14	8	2	77	78	15	9	2	0	2	17	1	0	14	-18	18	6	-3	7	0	21	1	-1	59	-57
14	8	3	20	22	15	9	3	8	-8	17	1	1	20	-26	18	6	-2	29	-34	21	1	0	51	-50
14	8	4	27	-29	15	11	-4	11	14	17	1	2	61	61	18	6	-1	80	82	21	1	1	26	29
14	8	5	11	7	15	11	-3	18	15	17	1	3	8	-3	18	6	0	34	35	21	3	-6	16	-22
14	10	-7	51	50	15	11	-2	50	-51	17	1	4	75	-77	18	6	1	9	-5	21	3	-5	74	-75
14	10	-6	7	0	15	11	-1	28	-24	17	1	5	0	8	18	6	2	78	-80	21	3	-4	25	-30
14	10	-5	0	1	15	11	0	69	61	17	3	-9	68	72	18	6	3	0	7	21	3	-3	92	93
14	10	-4	8	13	16	0	-10	0	5	17	3	-8	18	-8	18	8	-5	36	-35	21	3	-2	8	-9
14	10	-3	59	59	16	0	-8	46	43	17	3	-7	40	-39	18	8	-4	13	-6	21	3	-1	67	-67
14	10	-2	48	-49	16	0	-6	123	-122	17	3	-6	10	14	18	8	-3	10	-7	21	3	0	17	11
14	10	-1	109	-113	16	0	-4	168	171	17	3	-5	112	112	18	8	-2	41	40	21	5	-4	45	44
14	10	0	79	73	16	0	-2	7	7	17	3	-4	20	25	18	8	-1	44	43	21	5	-3	38	40
14	10	1	91	90	16	0	0	96	98	17	3	-3	103	-105	18	8	0	33	37	21	5	-2	89	-90
14	10	2	44	-41	16	0	2	5	-6	17	3	-2	51	-47	18	8	1	22	-18	22	0	-4	25	-22
14	10	3	27	-31	16	0	4	53	-52	17	3	-1	34	-31	19	1	-8	38	34	22	0	-2	116	118
14	12	-2	65	-65	16	0	6	70	73	17	3	0	59	-59	19	1	-7	14	18	22	2	-4	45	-48
15	1	-10	41	-44	16	2	-10	15	-15	17	3	1	57	57	19	1	-6	60	-58	22	2	-3	34	34
15	1	-9	10	3	16	2	-9	56	58	17	3	2	10	1	19	1	-5	3	5	22	2	-2	29	28

net intensity: $w = 4F_o^2/[\sigma(F_o^2)]^2$ with $\sigma(F_o^2) = ([\sigma(I)]^2 + (0.031I)^2)^{1/2}$ (1/Lp). An analysis of the residuals showed this scheme to be adequate. Reflections with $I < 2\sigma(I)$ were treated as unobserved and given zero weight. The final R values after convergence of the anisotropic refinement, were (including zero reflections): $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o| = 0.048$, $R_2 = (\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.050$. Acording to Hamilton's statistical test[14] on R_2 this improvement from the value after the isotropic refinement highly justifies the significance of the anisotropic vibration data.

A final difference Fourier synthesis did not show any significant peaks higher than 0.3 e/Å^3. The standard error of an observation of unit weight is 1.58.[15]

The final positional and thermal parameters, including the standard deviations obtained from the inverse matrix, are summarized in Tables I, II and III. Table IV gives the comparison of the observed and calculated structure factors.

Results and Discussion

The structure is ionic and consists of binuclear complexes $(Ag_2[SC(NH_2)_2]_6)^{2+}$ with crystallographic C_2 symmetry and of perchlorate ions. Interatomic distances and bond angles within the cations and anions are given in Table V together with the standard deviations. Figure 1 and Figure 2 show the configuration of the binuclear complex ion with the numbering of the atoms. A projection of the unit cell which shows the packing of the ions is given in Figure 3.

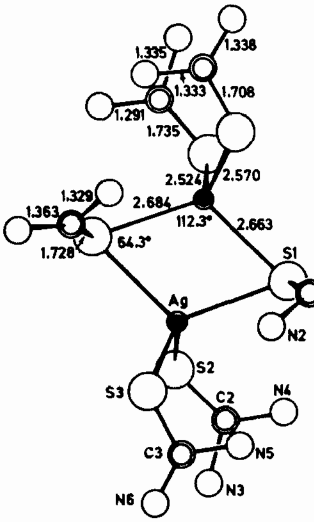

Figure 1. Configuration of the binuclear complex ion $(Ag_2[SC(NH_2)_2]_6)^{2+}$. The two halves of the complex are related by a twofold axis. H atoms are omitted.

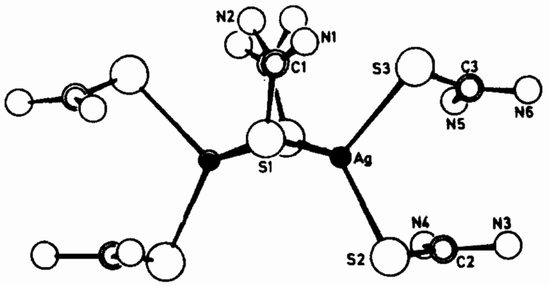

Figure 2. Different view of the complex. Twofold axis is vertical.

In the binuclear cation each silver atom is coordinated by the S atoms of four thiourea molecules; the S-atoms form a slightly distorted tetrahedron which shares one edge with the second AgS_4 tetrahedron in the complex. Two thiourea groups (S1) act as bridging ligands to both Ag atoms, four are terminal (S2 and S3). All four Ag-S bonds around one Ag atom are of different length, the bridging Ag-S distances (mean value 2.674 Å) being significantly longer than the terminal ones (2.547 Å). Ag-S distances found in other compounds are 2.428 Å in AgSCN,[16] 2.48...2.66 Å in $Ag[SC(NH_2)NHNH_2]Cl$,[17] 2.83 Å in $AgSCNP(C_3H_7)_3$,[18] and 2.433...2.588 Å in $Ag[SC(NH_2)_2]_2Cl$.[7] Comparing with the sum of the expected tetrahedral single bond covalent radii of 2.56 Å[5] it is quite clear

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[14] W.C. Hamilton, *Acta Cryst.*, *18*, 502 (1965).

[15] All computations were done on a Univac 1108, using besides own programs, modified versions of programs from the Brookhaven National Laboratory system; among them are the BNL version of the FORDAP Fourier program written by A. Zalkin, the Ibers-Hamilton version of the Busing-Martin-Levy program ORFLS, and the Busing-Martin-Levy program ORFFE.

[16] I. Lindqvist, *Acta Cryst.*, *10*, 29 (1957).

Table V. Bond lengths and bond angles in the binuclear complex cation and in the ClO_4^- anions.

Ag-S1	2.663(2) Å	S1-Ag-S1′	112,3(1)°
Ag-S1	2.684(2)	S1-Ag-S2	113.5(1)
Ag-S2	2.524(2)	S1′-Ag-S2	109,1(1)
Ag-S3	2.570(2)	S1-Ag-S3	104,8(1)
Ag-Ag′	2.845(1)	S1′-Ag-S3	100.5(1)
S-S′	3.343(3)	S2-Ag-S3	115.9(1)
		Ag-S1-Ag′	64.3(1)

S1-C1	1.728(6) Å	S2-C2	1.735(6) Å	S3-C3	1.708(6) Å
C1-N1	1.363(8)	C2-N3	1.335(8)	C3-N5	1.333(8)
C1-N2	1.329(8)	C2-N4	1.291(8)	C3-N6	1.338(8)
S1-C1-N1	117.5(4)°	S2-C2-N3	118.6(4)°	S3-C3-N5	122.1(4)°
S1-C1-N2	121.7(4)	S2-C2-N4	121.1(4)	S3-C3-N6	119.7(4)
N1-C1-N2	120.9(6)	N3-C2-N4	120.3(6)	N5-C3-N6	118.2(6)
Ag-S1-C1	110.4(3)	Ag-S2-C2	96.5(3)	Ag-S3-C3	99.8(3)
Ag′-S1-C1	102.7(3)				

		corrected		
Cl-O1	1.400(6) Å	1.422 Å	O1-Cl-O2	108.5(4)°
Cl-O2	1.413(6)	1.436	O1-Cl-O3	112.6(4)
Cl-O3	1.415(6)	1.440	O1-Cl-O4	112.4(4)
Cl-O4	1.415(6)	1.438	O2-Cl-O3	109.0(4)
			O2-Cl-O4	106.8(4)
			O3-Cl-O4	107.4(4)

that the Ag-S bonds in $Ag(tu)_3ClO_4$ are fairly strong covalent. The Ag-Ag distance in the complex ion is 2.845 Å. The central Ag-S-Ag-S four-membered ring is only approximately planar: the two Ag-S-Ag planes form an angle of 151° with each other.

The average S-C (1.724 Å) and C-N (1.332 Å) distances are comparable with those of the free thiourea molecule; the S-C bond in the complex is not significantly elongated. The S-C-N and N-C-N bond angles range from 117.5 to 122.1°. The thiourea groups are strictly planar (within the limits of error including the hydrogen atoms, see below).

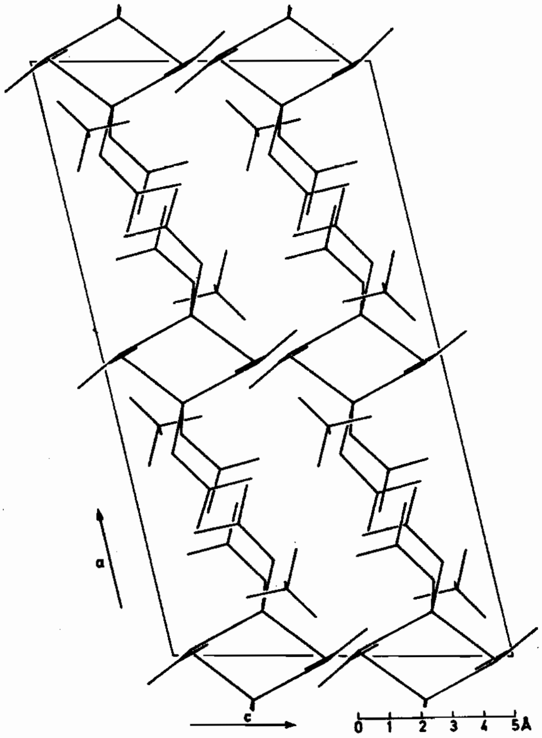

Figure 3. Projection of the unit cell parallel to b.

The bridge bonding is of special interest. The sharp bridge angle Ag-S-Ag (64.3°) and the very short Ag...Ag distance across the ring comparable with the bond angles Cu-S-Cu (69°) in $Cu_4(tu)_9(NO_3)_4$,[8] Ag-S-Ag (77.4°) in $Ag(tu)_2Cl$,[7] Cu-S-Cu (72.2°) in $Cu(tu)_3ClO_4$[10] or (82.5°) in $Cu(tu)_2Cl$[6] and to the corresponding metal...metal distances of 2.707, 3.132, 2.862, and 2.981 Å, respectively. These distances are in the order of the sum of the covalent bond radii and are similarly short as in the electron-deficient methyl-bridged bonds of alkyl beryllium, magnesium and aluminum compounds (literature see ref. 6).

The orientation of the bridge thiourea molecules shows that the bridge bonds in $Ag(tu)_3ClO_4$ are *not* of the type found in three of the four cited complexes with electron-deficient three-center bonding between a pπ sulphur-carbon molecular orbital and its electron pair and σ (most probably sp^3 hybrids) orbitals from two metals. As Figures 1 and 3 show, the line connecting N1 and N2 in the bridging thiourea molecules is parallel to one of the Ag-S1 bonds and almost perpendicular to the other. The dihedral angle between the normals of the Ag-S1-C1 and the S1 thiourea planes is 3°, the corresponding dihedral angle Ag′-S1-C1/S1 thiourea plane is 74°. Together with the values of the two Ag(Ag′)-S1-C1 angles (110.4 and 102.7°), this suggests the following alternatives for the description of the bonding situation, assuming that the sulphur atoms are sp^2 hybridized with a C-S σ and π bond and the nonbonding sp^2 electron pairs in the molecular plane:

(1) The four-membered Ag-S-Ag-S ring is considered as two sets of three-center electron-deficient bonds, each Ag contributing a σ (sp^3) orbital and each S one nonbonding sp^2 orbital with its electron pair: $\psi_{ED} = \sigma(Ag) + \sigma(Ag') + sp^2(S)$. This is equivalent to a

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(17) M. Nardelli, G.F. Gasparri, G.G. Battistini, and A. Musatti, *Chem. Comm.*, 187 (1965).
(18) C. Panattoni and E. Frasson, *Acta Cryst.*, *16*, 1258 (1963).

Table VI. NH...O and NH...S hydrogen bonds in the structure of $Ag(tu)_3ClO_4$.

H donor	H acceptor	N...O or N...S bridge distance, Å	H...O or H...S bridge distance, Å
N1 - H2	S2(a)*	3.680	2.76
N2 - H3	O1(b)	3.211	2.46
(bifurcated)	O1(c)	3.128	2.44
N2 - H4	S3	3.431	2.57
N3 - H5	O3	3.176	2.52
(bifurcated)	O4	3.139	2.35
N3 - H6	O4(d)	3.002	2.09
N4 - H7	O4	.557	2.39
N4 - H8	S1(a)	3.212	2.62
N5 - H9	S2(e)	3.609	2.96
N6 - H11	S3(f)	3.514	2.46
N6 - H12	O2	3.234	2.25

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

four-center, four-electron, electron-deficient model, and it corresponds to the type I bridge reported for $Cu_4(tu)_9(NO_3)_4$.[8] This bond description would not result in any lengthening of the S-C bond, because no bond electrons (e.g. S-C pπ electrons) are involved.

A weak point of this bond description is the unsymmetrical orientation of the bridge thiourea molecules. In order to obtain optimal overlap of the sp^2 (S) with the sp^3 (Ag) orbitals in the three-center bridges, the bridge thiourea molecular planes should be parallel to a plane defined by S1, S1', and the point midway between the two Ag atoms. The deviation from this ideal orientation may be caused by sterical reasons, especially by repulsion of the H4 and H4′ atoms (bonded to N2 and N2′) across the twofold axis of the binuclear complex.

(2) Alternatively, the bridge bonds could be essentially two center bonds, each sulphur atom using a nonbonding sp^2 orbital for one bond and the pπ S–C orbital, which is approximately in the correct orientation, for the other. In terms of a more general MO description of the thiourea molecule,[8] this π-orbital is the highest filled (delocalized) approximately nonbonding π-MO with symmetry designation a_1'. In this case, an additional back bonding mechanism from filled d orbitals of the silver atoms to appropriately oriented d orbitals of the S atoms may be invoked to explain the result that there is no lengthening of the S–C bond in the bridge compared to the free thiourea molecule. This second alternative for the description of the bridge bonding is very likely the correct one.

The orientation of the terminal thiourea groups in the complex is characterized by the Ag-S2-C2 (96.5°) and Ag-S3-C3 (99.8°) bond angles besides the dihedral angles between the planes defined by Ag-S2-C2 and S2-C2-N3 (70,2°) and between the corresponding planes Ag-S3-C3/S3-C3-N5 (54.5°). From these data it is evident that the Ag-thiourea interaction cannot be using the sulphur sp^2 orbitals.

In both cases much better overlap with the silver sp^3 orbitals is to be expected using delocalized π-molecular orbitals of the thiourea molecules (see above). This use of π-electrons instead of nonbonding sp^2 pairs in terminal thiourea ligands is quite unusual and has been observed only in a few cases, e.g. in $Co[SC(NH_2)_2]_4(NO_3)_2$;[11] the corresponding bond and dihedral angles are in this case 103.0° and 75.8, respectively. In $Ag(tu)_3ClO_4$ the significantly better overlap in the Ag-S2 bond compared to the Ag-S3 bond, as indicated by the different dihedral angles of 70.2° and 54.5', may explain the different Ag-S2 (2.524 Å) and Ag-S3 (2.570 Å) bond lengths.

The fact that both dihedral angles are significantly different (19,8 and 35,5°) from the angles of maximum overlap seems to be caused by intermolecular packing effects and especially by the N-H. . . X hydrogen bond system (see Table VI).

The tetrahedral symmetry of the ClO_4^- ions is close to ideal; the bond angles are only slightly (but significantly) distorted by crystal forces. The Cl-O bond lengths have been corrected according to Cruickshank's[19] method for the effect of rotational oscillations of the ClO_4^- ion in the rigid body approximation (for the corrected values see Table V). The ω tensor has been computed using the Schomaker and Trueblood[20] method. The bond lengths are well within reported literature values. Nonbonded O . . O distances in the range from 2.271 to 2.342 Å.

Due to the presence of heavy atoms like silver in the structure, the hydrogen parameters are to be considered only approximate. But they show definitely (1): that the thiourea molecules are planar including the hydrogen atoms, and (2): that there is a hydrogen bond system between the NH_2 groups and oxygen as well as sulphur atoms.

Experimental NH bond lengths with standard deviations range from 0.86(8) to 1.08(8) Å, H-N-H bond angles from 98(11) to 128(12) Å, H . . . H distances in the NH_2 groups from 1.53(12) to 1.89(12) Å. The hydrogen bridges are tabulated in Table VI. All bridge distances and all interatomic angles within the bridges are within normal limits.

Acknowledgements. We would like to thank Professor O. Glemser for substantial support of this work. Financial assistance by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

(19) D.W.J. Cruickshank, *Acta Cryst.*, *9*, 754, 757 (1956); *14*, 896 (1961).
(20) V. Schomaker and K.N. Trueblood, *Acta Cryst.*, *B24*, 63 (1968).