pared with $P2_1/n$, because of the long *c* axis and only to become stable if the entropy contribution at high temperature can reverse the sign of the free energy difference.

In Figure 3 the packing of adjacent anions around the center of symmetry is shown. These anions form the columns referred to above. The packing at the *cis* end of the centrosymmetrically related molecules is determined by steric interaction of the oxygen atoms since the pair O(6)–O(7) distances are 2.86 and 3.08 Å apart. The nearest *trans*-oxygen atom separations between anions lying at the *c*-axis length apart are 2.88 Å for the O(3)–O(5) pair and 2.92 Å for the O(2)–O(4) pair. Therefore the *c* axis cannot be substantially contracted, as would be required in the orthorhombic form of this phase with normal Ca(1)–O($\bar{6}'$) and Ca(2)–O(7′) bonds, without a substantial loss in energy from the compression of the oxygen atoms.

The nonreversible transformation between the β and α phases of $Ca_2P_2O_7$ reported by Parodi, Hickok, Segelken, and Cooper[15] is consistent with their large structural difference. In β-$Ca_2P_2O_7$ the P–P vectors of the angle make angles of 55 and 56° with the *ab* plane and adjacent anions pack by fitting at the terminal ends rather than *cis* to *cis* across the center of symmetry. In addition, considerable cation–anion rearrangement would be necessary in order to carry through this proposed transformation.

The anions themselves differ slightly. In β-$Ca_2P_2O_7$ the anions deviate by 6 and 11° from the eclipsed configuration whereas this angle is 13° in α-$Ca_2P_2O_7$. Since the larger of these angles in β-$Ca_2P_2O_7$ occurs on the anion showing a P–O–P bond angle farthest removed from that in α-$Ca_2P_2O_7$, there does not appear to be a simple relationship between this bond angle and the deviation from the eclipsed configuration. As is summarized in Table V, those pyrophosphates with cations having small radii show a large dispersion in their P–O–P angles while the deviation from a staggered configuration is minimal. Those pyrophosphates where the cations have larger radii, including Na^+, all show P–O–P bond angles near 130° but with variable deviations from the eclipsed configuration. All of the nearly eclipsed structures, however, show on the average positive deviations from the ideal tetrahedral angle at the terminal oxygen atoms and negative deviations for those O–P–O angles involving the central oxygen atom. Furthermore, these structures show a correlation between the oxygen atom coordination number and the P–O bond length, implying a greater bond strength (shorter P–O distance) as the coordination number decreases.

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[15] J. A. Parodi, R. L. Hickok, W. G. Segelken, and J. R. Cooper, *J. Electrochem. Soc.*, **112**, 688 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, SOUTH CAROLINA 29208

Electron-Deficient Bonding with Sulfur Atoms. III. Crystal and Molecular Structure of Bis(thiourea)silver(I) Chloride

BY E. A. VIZZINI, I. F. TAYLOR, AND E. L. AMMA

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The crystal structure of bis(thiourea)silver(I) chloride, $Ag[SC(NH_2)_2]_2Cl$, was determined from 1679 intensities measured by counter methods at room temperature. The crystals are monoclinic $P2_1/a$ with cell constants $a = 36.70$ (4), $b = 8.24$ (1), $c = 5.87$ (1) Å, and $\beta = 92° 50' \pm 15'$. With eight molecules (two crystallographically independent formula units) per cell the calculated and observed densities are 2.22 and 2.18 g cm^{-3}, respectively. Refinement by full-matrix least-squares including anisotropic temperature factors converged to a conventional *R* of 0.062. The structure is composed of almost trigonal-planar $Ag(S)_3$ units bonded together by sulfur bridges to form a spiraling linear polymer. The fourth coordination position of each Ag is completed by long axial Ag–Cl distances of 2.854 (5) and 3.035 (5) Å, respectively. The Ag–Ag distances alternate between a long 4.709 (2) Å and a short 3.132 (2) Å with accompanying Ag–S–Ag bridge angles of 133.4 (2) and 77.3 (2)°, respectively. The sharp bridge bond can be interpreted as an Ag–S–Ag three-center, two-electron, electron-deficient bridge bond. However, the broad-angle bridge is readily understandable in terms of two electron-pair donor–acceptor linkages. The Ag–S distances fall into the range of 2.49–2.59 Å with individual standard deviations of ±0.004 Å.

Introduction

Thiourea (hereafter, tu) is a chemically interesting ligand in that it has several different possible modes of binding to a metal ion. It may coordinate through the mostly nonbonding electron pairs of the nitrogen[1] (this has not been conclusively established by single-crystal structure studies, but only inferred from the infrared spectra) or *via* the sulfur atom. The sulfur itself may donate electrons by two different means: (a) electrons from the nonbonding sp^2 lobes or (b)

[1] T. J. Lane, D. N. Sen, and J. V. Quagliano, *J. Chem. Phys.*, **22**, 1855 (1954).

electrons from the S–C π molecular orbitals. The C–O and C–N bond lengths of 1.26 (1) and 1.33 (1) Å[2,3] in urea, as well as the complete planarity of this molecule, including hydrogen, indicate a delocalized π molecular orbital involving all of the nonhydrogen atoms. For reference the C–N bond in *s*-triazine[4] was found to be 1.338 (1) Å and a normal C–N single bond would be 1.47 Å.[5] Thiourea[6] has C–S and C–N bond lengths of 1.720 (9) and 1.340 (6) Å, respectively. The paucity of data on C–S multiple bonds does not allow a quantitative assessment of multiple bonding in thiourea, but 1.720 Å is considerably shorter than the 1.81 Å expected from single-bond radii.[5] The 1.33-Å C–N distances in both urea and thiourea compared to *s*-triazine indicate significant multiple C–N bonding in both of these molecules. Further evidence for planarity and conjugation is from nuclear magnetic resonance experiments[7] on thiourea indicating restricted rotation about the C–N bond. These facts indicate that thiourea is planar with a veritable storehouse of π electrons for complex formation.

Thiourea complexes of the transition metals show some interesting and unusual properties; *e.g.*, *trans*-$Ni(tu)_4Cl_2$[8,9] shows two distinctly different Ni–Cl distances at 2.40 (2) and 2.52 (2) Å. This compound also has some unusual spectroscopic and magnetic properties as well.[10] On the other hand the bromine analog of this compound is unknown, but $Ni(tu)_6Br_2$ is known.[11] Further, thiourea as a ligand gives rise to a substantial reduction of the electron-repulsion parameters as determined from the visible absorption spectra of transition metal–thiourea complexes.[12]

Bis(thiourea)silver(I) chloride ($Ag(tu)_2Cl$) was first reported by Nardelli.[13] Although superficially the cation in this compound might be considered analogous to the ammoniated silver ion, particularly since a thiourea solution can be used to dissolve silver chloride, it was thought to be of interest to know the details of the silver to ligand binding. The complex also seems to be unusually insoluble in cold and hot water, once it is formed. A preliminary communication has been published on this structure and we wish to present the details of the analysis and the structure.[14]

Experimental Section

Bis(thiourea)silver(I) chloride, $Ag[SC(NH_2)_2]_2Cl$ or $Ag(tu)_2Cl$, was prepared by the method described by Nardelli,[13] and single crystals were grown by slow evaporation of the reaction mixture. From Weissenberg and precession photographs the crystals were found to be monoclinic with the systematic extinctions: for $h0l$, $h = 2n + 1$; and for $0k0$, $k = 2n + 1$. The space group is thus $P2_1/a$. The cell constants were measured from calibrated precession photographs with Mo Kα radiation (λ 0.7107 Å) and are: $a = 36.70$ (4), $b = 8.24$ (1), $c = 5.87$ (1) Å, and $\beta = 92°\ 50' \pm 15'$. The calculated density with eight formula entities per unit cell is 2.22 g cm^{-3}, compared to 2.18 ± 0.02 g cm^{-3} measured by flotation in a carbon tetrachloride–bromoform mixture.

A single crystal $0.02 \times 0.04 \times 0.1$ mm was mounted about the needle axis on a GE single-crystal orienter on a Picker diffractometer. The crystal was aligned on this apparatus by well-known methods.[15] With Ni-filtered Cu Kα radiation (λ 1.542 Å), backgrounds were estimated by stationary counting for 40 sec at $\pm 1.67°$ 2θ of 2θ peak maximum. The peaks were then scanned for 100 sec by the usual θ–2θ scanning technique at room temperature. Integrated intensities were calculated, assuming a linear variation in background from the function $I_{\text{net}} = I_{\text{scan}} - 1.25(B_1 + B_2)$, where B_1 and B_2 are the background counts. A standard reflection was measured every hour to ensure stability of operation. The take-off angle and crystal to counter and source to crystal values were 3.0°, 21 cm, and 18 cm, respectively. The mosaic spread of a reflection was satisfyingly low and the counting rate never exceeded 5000 counts/sec. The receiving aperature at the counter was 6 mm wide × 8 mm high.

Fifty equivalent reflections were measured and found to be in satisfactory agreement, otherwise only nonequivalent reflections were measured. Reflections were considered absent if the integrated intensity was less than $1.25(B_1 + B_2)$. In all, 1679 independent nonzero hkl intensities were measured. The linear absorption coefficient (μ) was calculated to be 32 cm^{-1}. No corrections were made for absorption, but anomalous dispersion effects were included in the refinement (see below). An upper limit to the effect of absorption on intensities would be 15%. Lorentz and polarization corrections were made and intensities reduced to structure factors.

Solution of Structure

With eight $Ag(tu)_2Cl$ molecules per cell it is most likely that all atoms are in the general positions of $P2_1/a$, $\pm(x, y, z;\ ^1/_2 + x,\ ^1/_2 - y, z)$. This gives two crystallographically independent $Ag(tu)_2Cl$ entities. The Ag, S, and Cl positions were readily found from an unsharpened three-dimensional Patterson function.[16] Using the phases from the Ag, S, and Cl atoms, a three-dimensional electron density function was computed and all of the nonhydrogen light atoms were easily located. The structure was refined by complete-matrix least squares[17] including anisotropic temperature factors with scattering factors for Ag^+ and Cl^-, and neutral S, N, and C from a standard source[18] and real and imaginary dispersion corrections[19,20] for Ag(I), S, and Cl^-. The function minimized was $\Sigma w(F_o - F_c)^2$ with weights based on counting statistics and a 4% intensity factor.[21] On the last cycle of refinement the

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[2] J. E. Worsham, H. A. Levy, and S. W. Peterson, *Acta Cryst.*, **10**, 319 (1957).

[3] P. Vaughan and J. Donohue, *ibid.*, **5**, 530 (1952).

[4] J. E. Lancaster and B. P. Stoicheff, *Can. J. Phys.*, **34**, 1016 (1956).

[5] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

[6] N. R. Kunchur and M. R. Truter, *J. Chem. Soc.*, 2551 (1958); M. R. Truter, *Acta Cryst.*, **22**, 556 (1967).

[7] J. W. Emsley and J. A. S. Smith, *Proc. Chem. Soc.*, 53 (1958).

[8] M. Nardelli, L. Cavalca, and A. Braibanti, *Gazz. Chim. Ital.*, **86**, 942 (1956).

[9] A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, 1309 (1963).

[10] C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 788 (1964).

[11] K. K. Chatterjee, M. Weininger, and E. L. Amma, to be submitted for publication.

[12] F. A. Cotton, O. D. Faut, and J. T. Mague, *Inorg. Chem.*, **3**, 17 (1964).

[13] M. Nardelli and A. Braibanti, *Gazz. Chim. Ital.*, **87**, 907 (1957).

[14] E. A. Vizzini and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 2872 (1966).

[15] T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

[16] Patterson and electron density calculations were made with the Sly–Shoemaker–Van den Hende ERF-2 program on the IBM 7090.

[17] Least squares performed with the ORFLS program of W. R. Busing, K. O. Martin, and H. A. Levy with local modifications for anomalous dispersion on the IBM 7040.

[18] Compilation of J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1961, pp 202, 212.

[19] D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

[20] Anomalous dispersion corrections made to F as suggested by J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

[21] S. W. Peterson and H. A. Levy, *ibid.*, **10**, 70 (1957).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

H	F(O)	F(C)
* H	0	0 *
4	324	-363
10	21	-20
12	211	214
14	47	-50
16	315	-313
18	29	30
20	58	57
22	22	-21
24	71	68
28	156	-153
30	38	-35
32	224	214
40	78	-71
42	52	50
44	109	102
* H	1	0 *
1	57	65
4	58	62
5	93	-94
6	123	121
7	34	-44
8	81	69
9	23	-13
10	44	48
12	71	-70
13	175	165
14	378	-393
15	89	79
17	71	-76
18	235	233
19	27	31
20	36	-33
21	27	28
22	30	31
23	44	49
24	62	49
26	152	-140
27	80	-81
28	50	52
29	109	97
30	229	219
32	42	42
34	95	-92
35	33	-40
36	59	64
37	53	-50
* H	2	0 *
0	155	-174
1	119	-122
3	101	95
4	95	96
5	49	-44
6	185	-168
7	349	361
8	92	-80
9	184	185
10	81	83
11	71	-70
12	317	-309
14	61	-52
15	93	-86
16	395	402
17	42	44
19	117	114
20	142	-130
21	70	67
22	74	74
23	83	-78
24	94	-92
25	171	-159
26	25	27
28	158	155
29	32	36
30	56	-63
31	51	52
32	105	-97
33	46	-41
34	44	45
35	47	-42
38	47	-43
* H	3	0 *
1	271	-284
2	230	242
3	209	215
5	171	178
6	56	50
7	180	184
8	160	163
9	195	-187
10	253	-255
11	156	-152
12	130	-128
14	288	287
15	79	75
16	25	-21
17	40	38
18	214	-209
20	70	62
21	205	-195
22	46	42
23	173	-167
24	66	-61
25	32	32
26	37	35
27	27	27
29	52	58
30	122	-115
31	21	26
32	66	66
33	90	-83
34	54	50
35	27	30
36	28	-29
37	51	46
39	58	53
* H	4	0 *
0	128	127
1	100	102
2	27	-31
3	199	201
4	168	-169
5	96	94
6	129	126
7	214	-213
8	111	-101
9	244	-237
10	35	-35
12	210	204
13	70	68
14	37	-31
16	79	-74
17	40	-34
18	89	82
19	96	-94
20	80	77
22	62	-57
23	87	79
25	34	35
26	116	104
28	108	-98
30	42	-41
31	56	-56
32	72	65
34	31	-29
35	107	95
37	50	43
38	40	39
39	46	-43
* H	5	0 *
1	41	-39
2	89	-87
3	79	74
4	159	154
5	149	-147
6	136	129
7	95	-89
8	197	-187
9	124	119
10	66	66
11	134	126
12	32	31
13	95	90
14	24	-23
15	52	-48
16	96	90
17	115	-107
18	56	47
19	47	42
20	88	-83
21	125	112
23	61	54
24	121	112
25	55	-49
26	92	-86
27	50	-46
28	112	-102
30	29	27
33	27	24
35	41	37
36	31	28
37	57	-52
* H	6	0 *
0	44	39
1	54	54
2	69	64
3	55	-55
4	64	60
5	73	-71
6	132	-125
7	56	51
9	98	93
10	187	175
13	100	-94
14	101	-92
15	73	-65
17	57	51
18	105	-97
19	149	136
21	69	62
22	151	139
23	101	-89
24	50	-44
25	50	-44
26	97	-93
28	25	26
30	28	-26
34	61	52
* H	7	0 *
1	75	-71
3	40	-30
4	136	-125
5	74	71
7	67	58
8	146	133
11	87	-80
12	166	-152
14	31	-28
15	26	-25
17	23	25
19	73	65
20	93	87
21	77	-71
24	66	-62
25	48	45
26	35	32
29	23	19
32	49	54
* H	8	0 *
2	97	-83
3	59	53
6	147	134
7	38	-36
10	107	-95
11	64	57
15	45	-39
16	21	19
17	55	52
18	44	38
* H	9	0 *
3	37	32
4	93	84
7	36	34
8	81	-77
9	61	52
11	54	-50
12	58	54
13	51	-46
14	22	21
* H	0	1 *
-4	265	265
6	155	-176
-6	40	-35
8	229	222
-8	345	-336
10	191	-192
-10	81	73
12	48	-50
-12	390	397
14	75	76
-14	235	228
16	331	-324
-16	71	-70
18	350	335
-18	166	148
20	213	207
22	193	-189
-22	224	-222
24	39	-47
-24	247	238
26	122	120
-28	138	-126
-30	36	-30
32	101	126
36	104	-105
-36	103	93
-40	142	-128
* H	1	1 *
0	58	-79
1	46	-54
-1	33	39
2	333	-398
-2	88	89
3	95	-86
-3	181	185
4	233	242
-4	125	-136
5	49	55
-5	203	216
6	348	355
-6	191	189
7	171	-186
-7	174	-172
8	21	-30
-8	169	149
9	99	102
-9	268	-270
10	186	-188
-10	441	-439
11	217	206
-11	185	157
12	73	74
-12	133	-127
-13	84	82
14	93	-98
-14	287	261
15	43	-49
-15	94	85
16	211	202
-16	96	88
-17	107	-101
18	360	355
-18	95	-88
19	59	71
-19	161	-149
20	97	-95
-20	120	111
21	39	40
22	136	-143
-22	125	-121
23	106	-119
25	168	-165
26	55	55
-26	248	232
28	39	-34
-28	70	64
-29	52	48
30	78	76
-30	49	-47
31	41	43
32	41	-39
-33	94	84
34	145	-141
-34	42	-38
35	79	-77
36	42	42
-38	88	79
40	30	-32
-42	104	-99
* H	2	1 *
0	157	-171
1	47	-55
-1	46	49
2	251	274
-2	45	55
3	213	229
-3	48	43
4	363	381
-4	94	-93
-5	190	197
6	226	-230
-6	268	-291
7	81	83
-7	211	212
8	155	-162
-8	273	286
10	33	35
-10	45	48
11	258	-253
-11	135	-139
-12	388	-384
12	33	-23
13	132	-132
-13	54	-54
14	75	76
16	244	243
-16	64	77
17	180	175
18	50	-52
-19	195	-193
20	288	-284
-20	99	90
21	41	-42
-21	82	-77
23	139	-133
-23	36	-44
24	139	144
-24	216	-205
-25	78	67
26	46	-43
27	110	110
-28	140	123
-29	58	59
-31	73	-63
32	153	-148
-33	47	-49
34	78	88
-34	62	60
36	100	97
-38	57	-59
* H	3	1 *
-1	109	-114
2	254	276
-2	101	-98
3	39	47
-3	233	-237
4	60	-53
-4	104	100
-5	68	68
6	241	-249
-6	162	-161
7	114	-113
-7	204	199
8	124	124
-8	116	-115
9	285	-294
11	49	49
12	167	-165
13	51	54
-13	47	-45
14	71	78
-14	157	-153
15	154	154
-15	46	-54
-17	180	177
18	131	-133
-18	84	-79
19	135	-131
-19	38	43
20	41	40
-20	99	-95
-21	50	55
22	118	118
-22	136	129
-23	72	-67
25	81	80
-25	105	-103
30	98	-98
-30	129	119
32	78	84
-32	71	-69
-33	70	-64
34	90	92
-35	103	-98
36	59	-63
-36	48	45
37	39	44
38	50	-50
40	52	54
-42	77	43
* H	4	1 *
0	165	165
1	176	175
-1	78	80
2	131	131
3	60	56
-3	254	-254
4	178	-184
-4	115	-117
5	164	-161
-5	259	-261
6	160	160
7	194	-197
9	159	155
-9	73	80
10	215	-215
-10	142	-135
11	209	207
-11	81	81
-12	60	64
14	87	88
15	103	-100
-15	95	-88
16	89	-84
-16	35	-32
-17	105	-104
-18	170	170
20	67	63
21	54	50
-21	69	66
22	100	-90
-22	96	-94
23	68	67
-23	99	95
-24	88	80
26	64	67
-26	73	69
27	115	-114
28	90	-94
-28	133	-126
-31	88	85
-33	52	51
-36	59	56
-37	63	-59
39	73	-79
* H	5	1 *
0	119	120
1	73	-77
-1	194	190
2	86	-84
-2	78	74
3	170	-165
-3	127	128
-4	109	-106
6	166	162
-6	59	-57
7	126	121
-7	101	-104
8	186	-186
-8	94	93
9	166	162
-9	79	-78
12	76	72
-12	91	87
13	167	-167
-13	63	55
14	74	-74
-14	100	94
15	56	-57
-15	69	66
16	78	-74
-16	161	-152
-17	60	-55
18	70	70
-19	156	-144
-20	68	61
21	103	96
-23	107	106
24	115	110
-24	110	-106
25	155	-155
26	85	-87
28	88	-84
-29	86	-79
30	69	65
31	57	59
32	56	59
-33	71	69
35	39	-44
* H	6	1 *
0	95	-90
-1	110	-108
2	75	-71
-2	159	152
5	91	89
-5	76	72
6	60	-59
-6	160	-154
7	59	60
8	45	46
-8	73	71
10	57	56
-10	78	74
11	89	-87
12	96	-97
13	54	-53
14	92	-90
-14	112	105
15	54	55
-15	96	89
-17	107	99
18	53	53
-18	90	-86
19	74	73
-21	136	-132
22	80	73
-22	79	74
23	109	-111
26	70	-68
27	59	62
28	41	40
29	40	39
30	60	58
-30	70	-69
-31	51	-44
-34	52	52
* H	7	1 *
0	163	-151
-3	110	-106
-4	143	133
5	54	54
-5	61	57
6	119	112
-6	36	-34
-7	52	43
-8	127	-119
10	104	-95
-11	39	37
12	99	-94
13	40	40
-13	91	-87
14	110	104
-15	73	-63
16	99	94
-16	101	100
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19	97	91
20	53	-52
-24	89	-80
25	26	-29
-25	33	30
26	33	-30
27	29	36
28	39	39
29	72	76
-29	49	-43
31	34	-34
* H	4	4 *
-1	85	-78
-2	53	-51
3	69	63
-3	105	-100
-4	83	71
5	63	58
6	75	-66
8	69	63
9	56	-53
10	71	61
-10	38	31
11	59	-56
12	111	-103
-14	56	-49
15	104	95
16	89	83
17	100	88
-17	83	74
18	97	-98
-20	84	-79
21	64	-65
-21	58	-55
23	34	-37
25	36	35
-26	62	-58
27	44	48
-27	65	63
29	36	-38
-29	55	52
30	45	-42
31	40	-40
* H	5	4 *
0	44	41
1	141	113
-1	15	-15
2	35	27
-2	69	-58
3	62	56
-3	107	-87

[a] Left to right: first column H, then F_o, followed by F_c. F_o(absolute) $= F_o/(10 \times \text{scale factor})$; scale factor $= 0.1512 \pm 0.0004$.

parameter shifts were all less than 0.1 standard deviation. The final R, weighted R, and standard error of an observation of unit weight[22] were 0.064, 0.089, and 0.5, respectively. A difference electron density map calculated after the last refinement cycle was qualitatively featureless. The final tabulation of observed and calculated structure factors is listed in Table I. Final parameters are seen in Table II. With the parameters and variance–covariance matrix from the last cycle of least-squares, distances, angles, errors, root-mean-square displacements, and dihedral angles between normals to planes were computed[23] and are found in Table III.

Description of Structure

The structure may be described as made up of very much flattened tetrahedra (silver atom in the center and Cl or S at the apices) sharing two sulfur apices with different neighboring tetrahedra to form an infinite

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[22] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; weighted $R = \Sigma w(F_o - F_c)^2/\Sigma wF_o^2$; standard error $= [\Sigma w(F_o - F_c)^2/(NO - NV)]^{1/2}$, where $NO = 1679$ and $NV = 181$.

[23] These calculations performed with ORFFE program of W. R. Busing, K. O. Martin, and H. A. Levy on the IBM 7040.

Table II

Positional Parameters and Esd's (Esd's in Parentheses)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag_1	0.09234 (4)	0.1905 (1)	0.2095 (3)	N_5	0.33053 (51)	0.3623 (19)	0.2812 (37)
Ag_2	0.15888 (3)	0.2592 (2)	0.9095 (3)	N_7	0.45467 (45)	0.3872 (19)	0.5507 (36)
S_3	0.12762 (13)	0.1032 (5)	0.5822 (10)	N_8	0.49268 (37)	0.2978 (21)	0.8369 (36)
S_4	0.43365 (12)	0.4402 (5)	0.9708 (9)	N_4	0.09593 (36)	0.5095 (18)	0.6375 (34)
S_1	0.21370 (12)	0.1407 (7)	0.0904 (10)	N_3	0.04999 (33)	0.5031 (18)	0.8805 (30)
S_2	0.11636 (10)	0.4587 (4)	0.0692 (8)	N_1	0.23722 (49)	0.1564 (25)	0.6670 (42)
Cl_1	0.02565 (10)	0.3285 (5)	0.3484 (8)	C_2	0.08455 (38)	0.4946 (16)	0.8481 (32)
Cl_2	0.18463 (10)	0.4914 (5)	0.5498 (9)	C_4	0.46173 (38)	0.3745 (17)	0.7642 (42)
N_2	0.27778 (46)	0.0616 (23)	0.9400 (38)	C_1	0.24401 (44)	0.1200 (22)	0.8802 (46)
N_6	0.36000 (42)	0.3284 (17)	0.6311 (32)	C_3	0.35298 (47)	0.4199 (18)	0.4415 (38)

Thermal Parameters and Esd's; Anisotropic Temperature Factors of the Form

$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}kh + 2\beta_{13}hl + 2\beta_{23}kl)]$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag_1	0.00072 (1)	0.0097 (2)	0.0349 (7)	−0.0003 (0)	−0.0005 (1)	0.0020 (2)
Ag_2	0.00053 (1)	0.0141 (2)	0.0395 (7)	0.0008 (0)	0.0007 (1)	−0.0030 (3)
S_3	0.00095 (4)	0.0094 (6)	0.0337 (26)	0.0007 (1)	−0.0023 (2)	−0.0023 (8)
S_4	0.00071 (3)	0.0130 (6)	0.0216 (22)	0.0008 (1)	0.0001 (2)	0.0024 (8)
S_1	0.00069 (3)	0.0231 (9)	0.0235 (23)	0.0017 (1)	−0.0003 (2)	0.0001 (11)
S_2	0.00041 (2)	0.0096 (5)	0.0252 (20)	−0.0000 (1)	−0.0003 (1)	−0.0018 (7)
Cl_1	0.00050 (3)	0.0151 (6)	0.0260 (21)	−0.0000 (1)	−0.0001 (2)	0.0005 (8)
Cl_2	0.00052 (3)	0.0113 (5)	0.0316 (22)	0.0001 (1)	−0.0000 (2)	−0.0016 (8)
C_2	0.00049 (11)	0.0077 (19)	0.0110 (79)	−0.0001 (3)	−0.0006 (6)	0.0029 (26)
C_4	0.00044 (11)	0.0079 (20)	0.0277 (108)	0.0006 (4)	0.0002 (7)	−0.0026 (32)
C_1	0.00051 (12)	0.0142 (27)	0.0357 (120)	0.0016 (5)	−0.0000 (8)	−0.0051 (40)
C_3	0.00071 (14)	0.0080 (21)	0.0349 (97)	0.0007 (4)	0.0001 (8)	−0.0005 (36)
N_2	0.00077 (14)	0.0221 (32)	0.0417 (93)	0.0020 (5)	−0.0000 (8)	−0.0035 (41)
N_6	0.00087 (13)	0.0108 (21)	0.0318 (79)	−0.0003 (4)	−0.0008 (7)	0.0057 (33)
N_5	0.00111 (16)	0.0126 (24)	0.0459 (96)	−0.0011 (5)	−0.0036 (10)	0.0011 (37)
N_7	0.00103 (15)	0.0177 (27)	0.0043 (77)	0.0016 (5)	−0.0002 (8)	0.0018 (32)
N_8	0.00049 (11)	0.0195 (28)	0.0439 (87)	0.0008 (4)	0.0000 (7)	0.0030 (38)
N_4	0.00043 (10)	0.0161 (24)	0.0288 (82)	−0.0000 (4)	0.0005 (6)	−0.0022 (32)
N_3	0.00034 (10)	0.0161 (23)	0.0337 (77)	−0.0002 (4)	−0.0013 (6)	0.0019 (31)
N_1	0.00092 (15)	0.0246 (36)	0.0280 (95)	0.0018 (6)	−0.0008 (9)	0.0008 (47)

spiraling chain in the *c* direction (Figures 1, 2). These chains are then separated by normal van der Waals distances, Table III. However, the Ag–Ag distances are not uniformly repeating along the chain but alternate between a "long" (Table III) 4.71 Å and a "short" 3.13 Å. Concomitant with the "short" Ag–Ag distance is a "sharp" Ag_2–S_2–Ag_1 bridge angle of 77.3° whereas the "long" Ag–Ag distance is accompanied by a broad Ag_1–S_3–Ag_2 angle of 133.4°. It is informative to compare this "short" metal–metal distance of approximately twice the normal single-bond radii with its accompanying sharp bridge angle to similar distances and M–C–M angles of 66 and 74.3° found in methyl-bridged polymeric dimethylberyllium[24] and dimeric trimethylaluminum.[25,26] The orientation of the thiourea groups is particularly interesting. From Figure 3 and Table III it is seen that the N_3–N_4 line is almost parallel to the Ag_1–Ag_2 line. Further, the angle between the lines defined by S_2-bisector (Ag_1–Ag_2) and by S_2–C_2 is 104°. Hence the geometry of the Ag_1–$S_2C_2N_3N_4$–Ag_2 bridge may be viewed as two perpendicular triangles (Ag_1–S_2–Ag_2 and S_2–N_3–N_4) intersecting at a common point with the edges not containing a commom atom parallel. On the other hand, the broad-angled bridge is quite different (Figure 4). Although the N_5–N_6 line is also approximately parallel to the Ag_2–Ag_1 line, the angle between the lines defined by S_3–bisector (Ag_2–Ag_1) and S_3–C_3 is now 154° compared to the 104° of the sharp-angled bridge. Therefore, the geometry of the broad bridge may be described as two triangles ($Ag_2S_3Ag_1$, $S_3C_3N_5N_6$) joined at a common point (S_3) lying almost in the same plane (26° displacement), and the triangle edges without a common point are parallel.

The orientation of the terminal thiourea groups can be seen in Figure 5 and Table III. The Ag_2 atom lies essentially in the plane of the S_1 thiourea group with a Ag_2–S_1–C_1 angle of 106°. The Ag_1 lies somewhat out of the S_4 thiourea plane (36° between normals to Ag_1-S_4C_4 and $S_4N_7N_8$) with an Ag_1–S_4–C_4 angle of 101°.

The Ag–S distances fall into the range 2.48–2.59 Å and can be compared to 2.56 Å from the sum of the single-bond covalent radii.[5] This indicates a fairly strong covalent interaction. Silver to sulfur distances of 2.48–2.66 Å were found in thiosemicarbazidesilver(I) chloride,[27] 2.428 ± 0.011 Å in silver thiocyanate,[28] and 2.83 ± 0.02 Å in $AgSCNP(C_3N_7)_3$.[29] The Ag–Cl distances of 2.85 and 3.03 Å are relatively long compared to 2.51 Å expected from the sum of the covalent radii.[5] It is to be noted (Table III) that if S_2, S_3, and S_4 are used

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(24) A. I. Snow and R. E. Rundle, *Acta Cryst.*, **4**, 348 (1951).

(25) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

(26) R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc.*, **89**, 3121 (1967).

(27) M. Nardelli, G. F. Gasparri, G. G. Battistini, and A. Musatti, *Chem. Commun.*, 187 (1965).

(28) I. Lindquist, *Acta Cryst.*, **10**, 29 (1957).

(29) C. Panattoni and E. Frasson, *ibid.*, **16**, 1258 (1963).

TABLE III[a]

Interatomic Distances, Å

Bonded		Nonbonded	
Ag_1-Cl_1	2.854 (4)	Ag_2-Ag_1	3.132 (2)
Ag_2-Cl_2	3.035 (5)	Ag_1-Ag_2	4.709 (2)
Ag_1-S_4	2.487 (4)		
Ag_2-S_1	2.433 (5)	Cl_1-S_2	3.931 (6)
Ag_1-S_2	2.532 (4)	Cl_1-C_2	3.812 (17)
Ag_2-S_2	2.482 (4)	Cl_1-N_4	3.365 (16)
Ag_1-S_3	2.588 (5)	Cl_1-N_3	3.514 (18)
Ag_2-S_3	2.538 (5)		
S_1-C_1	1.710 (22)	Cl_1-C_4	3.832 (16)
S_4-C_4	1.718 (19)	Cl_1-N_7	3.415 (15)
S_2-C_2	1.728 (17)	Cl_1-N_8	3.334 (20)
S_3-C_3	1.679 (17)		
		Cl_2-S_2	3.698 (6)
C_1-N_2	1.359 (24)	Cl_2-C_2	
C_1-N_1	1.299 (30)	Cl_2-N_4	3.324 (14)
C_4-N_7	1.272 (25)	Cl_2-N_3	
C_4-N_8	1.350 (22)	Cl_2-S_3	3.832 (6)
C_2-N_4	1.330 (24)		
C_2-N_3	1.294 (20)	Cl_2-N_1	3.418 (19)
C_3-N_6	1.358 (26)		
C_3-N_5	1.309 (26)	N_1-N_2	2.270 (29)
		N_3-N_4	2.262 (23)
		N_5-N_6	2.290 (25)
		N_7-N_8	2.254 (26)

All others >4

Angles, Deg

$Ag_1-S_2-Ag_2$	77.3 (1)	$S_2-C_2-N_4$	118.9 (1.1)
$Ag_1-S_3-Ag_2$	133.4 (2)	$S_2-C_2-N_3$	122.0 (1.5)
		$N_4-C_2-N_3$	119.1 (1.5)
$S_3-Ag_1-S_4$	107.1 (2)		
$S_4-Ag_1-S_2$	135.9 (2)	$S_3-C_3-N_6$	120.3 (1.5)
$Cl_1-Ag_1-S_4$	97.8 (1)	$S_3-C_3-N_5$	121.4 (1.6)
$Cl_1-Ag_1-S_2$	93.6 (1)	$N_5-C_3-N_6$	118.3 (1.6)
$S_3-Ag_1-S_2$	110.5 (1)		
$S_3-Ag_1-Cl_1$	105.6 (2)	$S_4-C_4-N_7$	124.7 (1.3)
		$S_4-C_4-N_8$	116.7 (1.8)
$S_1-Ag_2-S_3$	117.4 (2)	$N_7-C_4-N_8$	118.5 (1.7)
$S_2-Ag_2-S_3$	110.6 (1)		
$S_2-Ag_2-S_1$	128.5 (2)	$S_1-C_1-N_1$	124.8 (1.4)
$S_2-Ag_2-Cl_2$	93.9 (1)	$S_1-C_1-N_2$	117.8 (2.0)
$S_1-Ag_2-Cl_2$	106.1 (2)	$N_1-C_1-N_2$	117.3 (1.9)
$S_3-Ag_2-Cl_2$	86.4 (2)		
$Ag_1-S_2-C_2$	99.2 (5)	S_3-C_3–bisector (Ag_1-Ag_2)	154.4 (2)
$Ag_1-S_3-C_3$	112.1 (8)	S_2-C_2–bisector (Ag_2-Ag_1)	104.3 (2)
$Ag_1-S_4-C_4$	101.1 (7)		
$Ag_2-S_2-C_2$	104.1 (6)		
$Ag_2-S_3-C_3$	109.9 (7)		
$Ag_2-S_1-C_1$	106.2 (8)		

Dihedral Angles (Deg) between Normals to Planes Defined Here

$(S_2-Ag_2-C_2)(Ag_1-S_2-C_2)$	100.9 (2)
$(Ag_1-S_2-C_2)(S_2-C_2-N_4)$	120.3 (1.1)
$(Ag_1-S_2-C_2)(S_2-C_2-N_3)$	57.8 (1.3)
$(S_2-Ag_2-C_2)(S_2-C_2-N_4)$	138.9 (1.2)
$(S_2-Ag_2-C_2)(S_2-C_2-N_3)$	43.0 (1.2)
$(Ag_2-S_3-C_3)(Ag_1-S_3-C_3)$	159.5 (6)
$(Ag_1-S_3-C_3)(S_3-C_3-N_5)$	7.1 (1.6)
$(S_3-C_3-N_5)(Ag_1-S_3-C_3)$	172.1 (1.5)
$(Ag_2-S_3-C_3)(S_3-C_3-N_6)$	166.6 (1.2)
$(Ag_2-S_3-C_3)(S_3-C_3-N_5)$	12.6 (1.8)
$(S_4-C_4-Ag_1)(S_4-C_4-N_7)$	36.0 (1.5)
$(S_4-C_4-Ag_1)(S_4-C_4-N_8)$	147.0 (1.2)
$(S_1-C_1-N_2)(Ag_2-S_1-C_1)$	166.9 (6)

Best Least-Squares Planes. Equation of the Form $Ax + By + Cz - D = 0$, Where x, y, z Refer to an Internal Orthogonal Coordinate System.[b] Esd's of Atomic Coordinates Provided Weights for the Respective Atoms

Thiourea group	$S_1C_1N_1N_2$	$S_2C_2N_3N_4$	$S_3C_3N_5N_6$	$S_4C_4N_7N_8$
A	−0.3182	−0.0863	+0.7941	−0.4731
B	−0.9316	−0.9858	−0.4213	−0.8807
C	−0.1754	−0.1439	−0.4379	−0.0184
D	+4.5918	+4.9673	−7.5849	+10.6906
	Dev from best plane, Å			
S	−0.0000 (10)	0.0001 (11)	−0.0000 (10)	0.0003 (10)
C	0.0011 (35)	−0.0106 (40)	0.0047 (32)	−0.0157 (36)
N_i	−0.0005 (30)	0.0037 (35)	−0.0018 (31)	0.0078 (33)
N_{i+1}	−0.0004 (32)	0.0040 (30)	−0.0012 (34)	0.0062 (31)

Root-Mean-Square Displacements Along Principal Axes of Thermal Ellipsoid (Å)

Atom	Axis 1	Axis 2	Axis 3
Ag_1	0.178 (2)	0.214 (2)	0.258 (2)
Ag_2	0.169 (2)	0.221 (2)	0.277 (2)
S_2	0.160 (5)	0.180 (5)	0.217 (7)
S_3	0.171 (6)	0.190 (7)	0.305 (6)
S_4	0.175 (7)	0.203 (7)	0.243 (5)
S_1	0.175 (6)	0.208 (8)	0.307 (6)
Cl_1	0.184 (5)	0.214 (8)	0.229 (5)
Cl_2	0.186 (5)	0.196 (5)	0.238 (8)
C_2	0.115 (45)	0.166 (21)	0.196 (22)
C_3	0.153 (23)	0.228 (22)	0.248 (33)
C_4	0.136 (22)	0.191 (20)	0.224 (25)
C_1	0.127 (21)	0.230 (24)	0.278 (23)
N_4	0.168 (19)	0.217 (26)	0.243 (21)
N_3	0.134 (24)	0.230 (18)	0.261 (23)
N_6	0.171 (23)	0.223 (21)	0.273 (21)
N_5	0.170 (25)	0.222 (23)	0.353 (25)
N_7	0.081 (21)	0.203 (27)	0.302 (22)
N_8	0.170 (23)	0.259 (21)	0.284 (26)
N_2	0.178 (23)	0.264 (22)	0.317 (25)
N_1	0.189 (22)	0.238 (20)	0.325 (33)

[a] Esd of the last figure is in parentheses. [b] J. S. Rollett, "Computing Methods in Crystallography," Pergamon Press Inc., New York, N. Y., 1965, p 22.

to define a plane, then Ag_1 is 0.36 Å from this plane, and if S_1, S_2, and S_3 also define a plane, then Ag_2 is 0.26 Å from this plane. For an idealized tetrahedron with Ag–S distances of 2.5 Å this distance would be 0.83 Å. Hence, the $Ag_3(S)Cl$ tetrahedra are considerably flattened. The thiourea groups both bridged and terminal are planar (Table III) well within experimental error. The C–S and C–N distances of the thiourea groups (Table III) are probably not significantly different from the free thiourea values of 1.71 (1) and 1.33 (1) Å,[6] respectively.

Discussion of Structure

There are several unusual features of this structure worthy of note. First of all, the Ag atoms deviate only 0.36 and 0.26 Å from being in the same plane with the sulfur atoms. Trigonal-planar Ag(I) has also been found in $AgC(CN)_3$.[30] The Ag–S distances are sufficiently short to be considered as a substantial Ag–S interaction and the fact that the Ag–Cl distances are long (2.85 and 3.03 Å) is consistent with the fact that

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(30) J. Konnert and D. Britton, *Inorg. Chem.*, **5**, 1193 (1966).

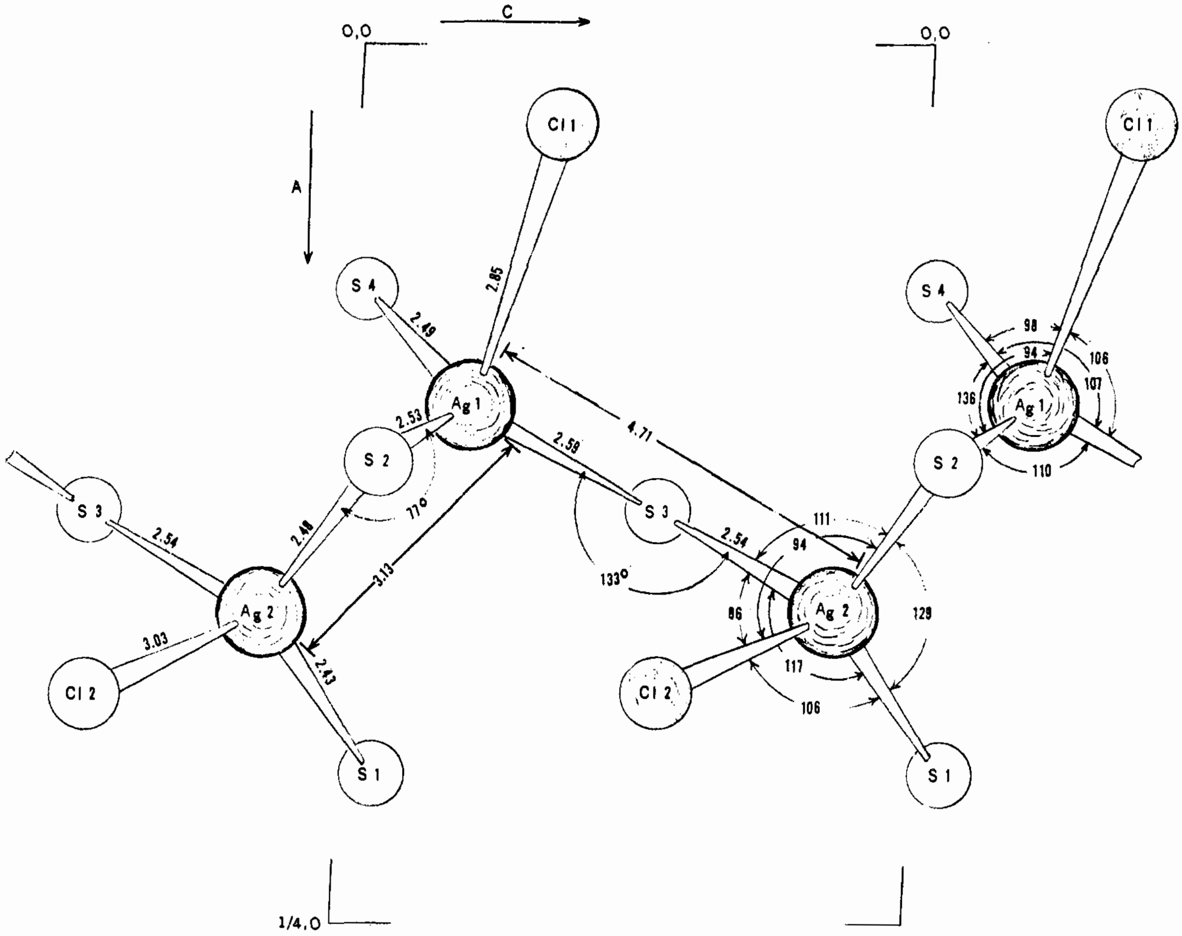

Figure 1.—Segment of the –Ag–S–Ag– chain looking down the *b* axis showing the principal distances and angles. The carbon and nitrogen atoms are not shown with their respective distances and angles for reasons of simplicity.

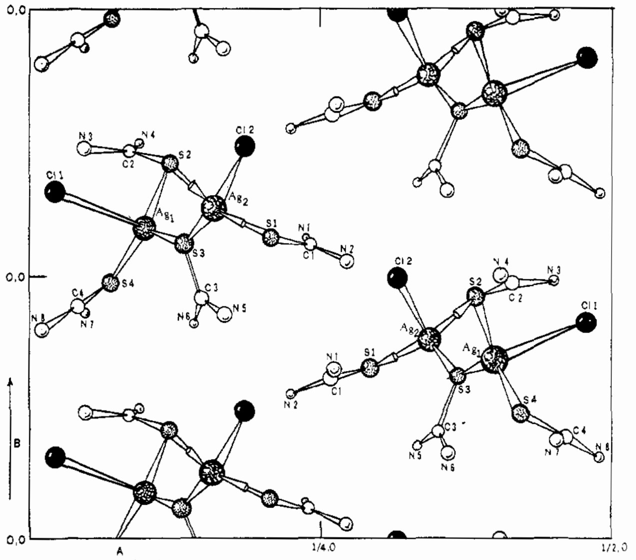

Figure 2.—View of the –Ag–S–Ag– chain down the *c* axis, the direction of the spiral. The differences in the orientation of the S_2 thiourea and the S_3 thiourea groups are to be noted. The cutoff cones denote, *e.g.*, Ag_2–S_1–S_2 bonds to S_1 and S_2 atoms above those shown.

these bonds are, at best, only bonds between the diffuse Ag 5p orbitals and halogen rather than the usual sp or sp^3 hybrid orbitals normally used by silver in complex formation. It might be argued that both of these chlorine atoms (Cl_1 and Cl_2) are essentially ionic chlorines and do not affect the Ag coordination geometry, but it is interesting to note that the smaller deviation from planarity (Ag_2, 0.26 Å) is associated with the longer Ag–Cl distance (3.03 Å).

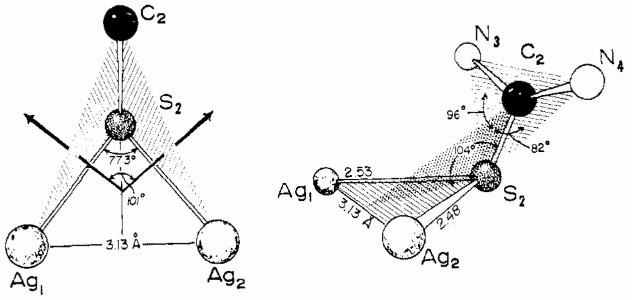

Figure 3.—Two views of the S_2 bridging thiourea group. These distances and angles completely specify the orientation of the planar $S_2C_2N_3N_4$ grouping relative to the Ag_1–S_2–Ag_2 plane.

The bridge bonding is of considerable interest. Since the S_3 thiourea group is only 26° out of the Ag_1–S_3–Ag_2 plane with an Ag_1–S_3–Ag_2 angle of 133°, this can easily be understood as sulfur supplying two nonbonding sp^2 orbitals and electron pairs to form two donor–acceptor Ag–S electron-pair bonds. On the other hand, the sharp bridge angle (77.3°) Ag_2–S_2–Ag_1 bridge must be completely different since the S_2 thiourea group is only 14° from being perpendicular to the Ag_2–S_2–Ag_1 plane.

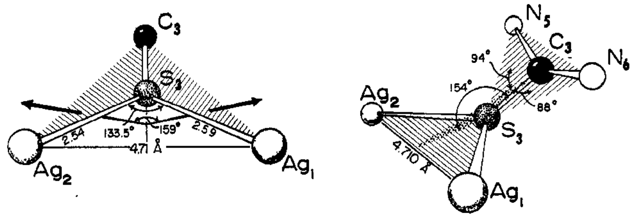

Figure 4.—Two views of the S_3 bridging thiourea group. These distances and angles completely specify the relative orientations of the Ag_2–S_3–Ag_1 and $S_3C_3N_5N_6$ planes.

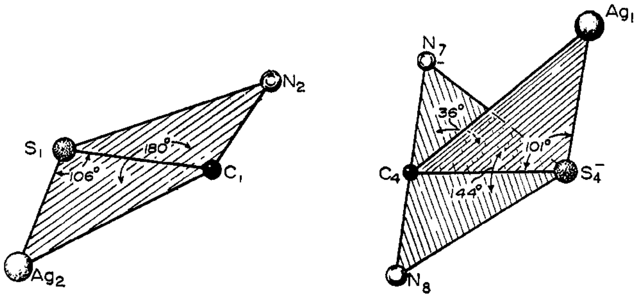

Figure 5.—Relevant angles between planes to specify the orientation of the S_1 and S_4 terminal thiourea groups.

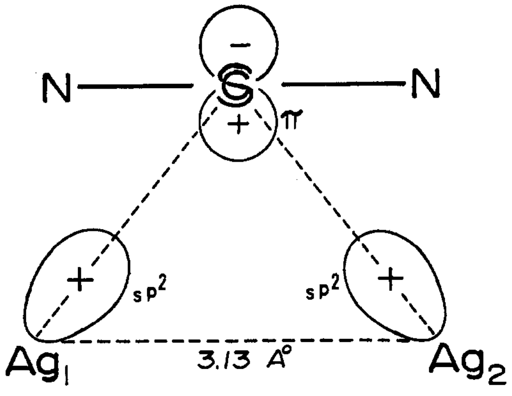

Figure 6.—View of the orbitals perpendicular to the Ag_1–S_2–Ag_2 plane used to specify the bonding in the three-center, two-electron bridge bond. Sulfur and carbon atoms are superposed in this idealized projection. The Ag orbitals are sp^2 hybrids as specified by the planarity of the $Ag(S)_3$, units and the upper orbital is the S–C pπ MO as specified by the S_2 thiourea group orientation. The three-center MO is then $sp^2(Ag_1) + sp^2(Ag_2) + $ S–C pπ.

Further, the short metal–metal distance (3.13 Å) and sharp bridge angle are reminiscent of methyl carbon electron-deficient bonding.[24–26] In fact, we believe the bonding to be very similar. With this geometry the only orbital that the thiourea molecule can contribute to the bridge bonding is the pπ S–C MO (some dπ–pπ S–C interactions would not affect the argument) with its electron pair. This orbital with two sp^2 hybrid orbitals of the Ag atom would lead to a three-center, two-electron, electron-deficient bridge bond (Figure 6): $\Psi_{ED} = \sigma_1 + \sigma_2 + p\pi$. This might be expected to elongate the S–C bond from that of free thiourea, but if it does, it is too small to be discernible from our data. Hence, one might wish to invoke a back-bonding mechanism[14] to explain the invariance of this S–C bond, but this is not necessary because it is reasonable to assume that the normal nonbonding nitrogen electrons of the thiourea group can be used to supply electrons to the S–C π bond. This is particularly true if the free thiourea molecule is planar as evidence indicates. We believe this is the first observed example of an electron-deficient bond involving sulfur atoms. However, we do not believe it is an isolated example and have found similar bonding in two other cases with thiourea in the compounds $Cu_4(tu)_9(NO_3)_4$[31] and $Cu(tu)_2Cl$.[32] Another possible description of bonding for the sharp-angle bridge is to consider it as more of an interaction with an ethylenic type π bond than the above description, *i.e.*, the Ag orbital pointing toward the center of the S–C π bond rather than toward the S itself. Although this description would make the Ag and its three neighbors even more coplanar by pushing the Ag ~0.1 Å closer to the plane, it distorts the S–Ag–S angles more from the idealized 120°. No doubt the maximum in the bonding electron density is displaced somewhat toward the C_2 atom from S_2 and the true bonding is somewhat between the two described.

It is clear from Figure 5 that the terminal Ag–S bonds (S_1S_4) are donor–acceptor bonds in which sulfur contributes a nonbonding sp^2 orbital and electron pair to Ag.

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[31] R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 4270 (1966).

[32] W. A. Spofford and E. L. Amma, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract O-073.