Contribution from the Institute of Inorganic Chemistry of the Slovak Academy of Sciences, Bratislava, and Department of Inorganic Chemistry of the Slovak Technical University, Bratislava, Czechoslovakia

The Crystal Structure of Tris(thiourea)copper(I) Perchlorate $Cu(SCN_2H_4)_3ClO_4$

F. Hanic and E. Ďurčanská

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Tris(thiourea)copper(I) perchlorate crystallizes in the monoclinic system with a = 13.56, b = 11.57, c = 9.09 Å, β = 94.9°; the space group is $P2_1/c$. The crystal structure was determined by means of the heavy atom method from three-dimensional x-ray data. Positional and anisotropic thermal parameters were refined by the least-square method. The ionic structure consists of binuclear complex ions $[Cu_2(SCN_2H_4)_6]^{2+}$ and perchlorate anions ClO_4^-. The Cu-Cu distance is 2.826 Å. Thiourea ligands are coordinate to the monovalent copper atoms by sulphur atoms. The tetrahedral coordination around each Cu^I is slightly distorted with S - Cu - S angles ranging from 98.3° to 125.9°. Two of the six sulphur atoms of the binuclear complex cations are shared by the two copper atoms. The bridging bond lengths Cu - S: 2.395 and 2.460 Å are significantly longer than the remaining four Cu - S distances: 2.321 (2x) and 2.326 Å (2x), respectively. The complex cation $[Cu_2(SCN_2H_4)_6]^{2+}$ is centrosymmetric. The bond angle Cu - S - Cu: 72.2° is most easily understood in terms of a bridging poly-center delocalized system involving a $p\pi$ sulphur-carbon MO and its electron pair and σ (e.g. sp^3 hybrids) orbitals from each copper. Another poly-center bonding MO can be constructed from the sulphur 3 d_{xz} orbitals which overlaps with the appropriately oriented metal d orbitals.

Introduction

In the crystal structure of $Cu(thiourea)_3Cl$, the monovalent copper atom was found to exhibit tetrahedral coordination by sharing one of the three sulphur atoms of the thiourea ligands by two copper atoms. The tetrahedra are linked into infinite spiral chains [1.2]. The crystal structure of tris(thiourea)copper(I) perchlorate has been examined by x-rays in order to show the influence of anionic substitution of Cl^- for ClO_4^-.

Crystalographic data. Crystals of $Cu(thiourea)_3ClO_4$ were kindly supplied by prof. F. Hein. The material is colorless. Tris(thiourea)copper(I) perchlorate crystallizes in the monoclinic system with the cell dimensions a = 13.56±0.01, b = 11.57±0.01, c = 9.09±0.02 Å, β = 94.9±0.1°. From the observed density of 1.89 gcm^{-3}, the number of chemical units $Cu(SCN_2H_4)_3ClO_4$ in the above cell was found to be four. The calculated density is 1.85 gcm^{-3}. The space group symmetry $P2_1/c$ was determined from the observed systematic absences.

The three-dimensional x-ray data were obtained from equi-inclination Weisenberg photographs around the b axis using a crystal with the cross-section of 0.1×0.3 mm alongated in the direction of rotation. $CuK\alpha$ radiation was used. The linear absorption coefficient μ is 60. Transmission at 90° is about 30% larger than transmission at 0° in the direction of maximal absorption. The transmission difference in the direction of minimal absorption is less than 5%. Errors from absorption effects were not corrected. In all, 1576 nonequivalent reflections were observed. The observed intensity data, after being corrected for Lorentz and polarization factors, were used to compute a three-dimensional Patterson function. The different layers of b-axis data were brought to an approximately common scale by comparison with hkO spectra. The scale factor and overall temperature factor were latter refined. First, the position of the copper atom was located. The coordinates of the copper atom were used to determine probable signs of the structure factors. The first approximate three-dimensional electron-density function was computed with signs from the heavy atom contribution and with observed structure factors modified by the Sim's weigting scheme [5]. The electron density function showed in addition the position of the three sulphur

Table I. Final atomic coordinates, with standard deviations in parentheses

Atom	x	y	z
Cu	0.0914(2)	0.0486(2)	0.0617(3)
S(1)	–0.0769(2)	0.1102(3)	0.1079(3)
S(2)	0.1472(3)	0.2225(4)	–0.0292(5)
S(3)	0.1512(3)	–0.0401(4)	0.2804(4)
N(1)	–0.0940(11)	0.1590(15)	0.3861(15)
N(2)	0.3117(19)	0.3174(30)	–0.1930(62)
N(3)	0.3230(12)	–0.1324(19)	0.3796(18)
N(4)	–0.1028(11)	–0.0364(13)	0.3293(14)
N(5)	0.3360(17)	0.1337(24)	–0.0091(46)
N(6)	0.2939(10)	–0.1289(17)	0.1254(17)
C(1)	–0.0930(9)	0.0717(13)	0.2909(14)
C(2)	0.2752(12)	0.2225(17)	–0.0388(19)
C(3)	0.2658(10)	–0.1032(15)	0.2577(20)
Cl	0.5628(3)	0.0924(4)	0.2494(5)
O(1)	0.5115(23)	–0.0107(23)	0.2589(32)
O(2)	0.6665(11)	0.0696(18)	0.2839(26)
O(3)	0.5499(15)	0.1381(23)	0.0995(19)
O(4)	0.5309(12)	0.1814(20)	0.3494(23)

Table II.

	F_o	F_c
h 0 0		
1	67.2	71.2
2	65.2	68.1
3	86.5	-86.4
4	120.7	-152.9
5	223.6	-299.7
6	58.6	-68.4
7	22.1	17.1
8	81.7	-49.5
9	53.8	46.2
10	2.6	-4.1
11	58.6	58.1
12	51.3	73.1
13	65.3	53.1
14	41.3	38.9
15	19.6	-17.4
16	49.0	-32.5
17	52.8	-45.8
h 0 2		
0	26.9	-23.6
1	121.0	129.1
2	101.8	-77.9
3	2.6	-3.5
4	58.9	-54.0
5	75.9	-76.0
6	2.6	-10.1
7	2.6	3.7
8	76.8	73.5
9	16.3	15.3
10	56.7	52.5
11	35.5	-30.0
12	32.7	-31.0
-1	113.3	120.0
-2	14.4	17.2
-3	82.6	90.2
-4	2.6	-7.8
-5	31.7	-31.6
-6	53.8	-49.9
-7	101.8	-111.9
-8	56.7	-45.6
-9	51.9	-42.0
-10	23.0	32.8
-11	58.6	57.8
-12	58.6	55.8
-13	63.4	56.3
-14	6.5	6.0
-15	6.5	9.5
-16	52.8	-47.6
-17	8.6	-15.6
h 0 4		
0	55.5	-50.6
1	2.6	-4.0
2	51.8	-48.6
3	52.8	-42.6
4	57.6	-46.5
5	9.6	-13.9
6	47.0	33.7
7	42.3	31.6
8	59.9	113.5
9	62.4	45.2
10	6.5	14.8
11	32.7	-28.9
12	6.5	-10.7
13	39.5	-35.8
-1	26.9	30.5
-2	39.5	38.5
-3	55.8	-27.5
-4	2.6	4.3
-5	68.3	49.7
-6	55.5	48.4
-7	55.7	43.5
-8	2.6	2.4
-9	29.8	-29.2
-10	91.2	-72.4
-11	19.6	-19.0
-12	2.6	17.3
-13	2.6	5.0
-14	58.6	36.9
h 0 6		
0	55.5	-50.6
1	2.6	-6.6
2	51.8	-48.6
3	52.8	-42.6
4	57.6	-48.5
5	9.6	-13.9
6	47.0	33.7
7	42.3	31.6
8	59.9	113.5
9	62.4	45.2
10	6.5	14.8
11	32.7	-28.9
12	55.7	-44.3
13	46.1	-40.7
14	27.9	-27.7
-1	24.9	-20.9
-2	37.5	-32.7
-3	84.5	70.6
-4	55.1	64.6
-5	88.5	83.7
-6	88.4	85.8
-7	13.4	-20.6
-8	55.4	-46.5
-9	92.2	-80.3
-10	6.5	-18.3
-11	31.7	-29.3
-12	6.5	1.1
-13	12.4	19.1
h 0 8		
0	9.6	11.2
1	70.1	-52.0
2	24.0	-20.1
3	22.1	-16.6
4	22.1	20.9
8	21.1	-25.0
-1	24.0	-15.5
-2	23.0	20.8
-3	27.9	27.2
-4	9.6	17.5
-5	24.0	22.0
-7	30.7	26.2
-8	29.8	-29.0
-10	46.1	-35.2
-11	25.9	-19.3
h 0 10		
1	63.4	34.4
2	41.5	35.0
3	39.5	25.1
-2	47.0	-36.6
h 1 0		
1	6.5	3.2
2	41.3	-41.1
3	55.7	64.5
4	12.5	-16.4
5	89.3	100.6
6	16.3	-15.6
7	26.9	24.5
8	53.8	-37.4
9	29.7	-25.0
10	19.6	-10.7
11	19.6	-10.5
12	16.2	15.4
h 1 1		
0	68.2	116.1
1	96.0	68.4
2	11.2	-18.5
3	91.2	95.8
4	52.8	-60.0
5	20.2	2.5
6	91.2	99.8
7	31.7	-31.1
8	59.5	-75.1
9	22.1	-14.8
10	56.7	48.6
11	37.5	32.3
12	66.2	59.6
13	13.1	9.5
14	6.5	13.0
15	22.1	-19.6
16	18.4	-14.2
-1	104.7	-49.3
-2	104.6	115.7
-3	124.2	-103.7
-4	19.6	-27.9
-5	150.9	-150.5
-6	117.7	-82.3
-7	104.6	-40.8
-8	78.4	34.6
-9	65.4	34.8
-10	19.6	12.3
-11	65.0	54.8
-12	7.8	1.7
-13	40.5	31.7
h 1 2		
0	4.8	3.4
1	120.9	-146.7
2	68.2	-58.6
3	50.9	-43.8
4	41.3	37.3
5	26.9	23.7
6	89.8	90.3
7	23.0	27.5
8	3.9	9.0
9	26.9	-23.9
10	17.3	-13.0
11	18.2	19.0
12	25.5	-26.5
13	7.8	-3.3
14	19.6	-13.8
15	20.2	-17.9
16	19.2	-20.4
-1	82.6	86.1
-2	25.9	-18.2
-3	35.5	25.4
-4	3.9	6.5
-5	33.6	-29.2
-6	20.2	-20.1
-7	57.6	46.0
-8	38.0	39.5
-9	13.1	9.0
-10	13.0	6.9
-11	58.6	-45.4
-12	25.5	-21.6
-13	19.6	-16.8
-14	13.0	8.2
-15	19.2	11.9
h 1 3		
0	111.4	107.4
1	24.0	18.6
2	52.8	32.9
3	113.3	-90.5
4	123.9	-101.7
5	86.4	-82.1
6	30.7	31.1
7	15.4	16.0
8	76.8	77.4
9	76.8	78.6
10	22.1	-15.7
11	6.5	-4.1
12	30.7	-27.6
13	13.1	-14.3
14	31.7	-30.4
-1	130.7	66.6
-2	48.0	-27.5
-3	24.0	25.6
-4	17.3	-18.4
-5	12.5	-14.5
-6	24.0	-23.5
-7	25.0	-25.4
-8	52.8	-48.2
-9	47.1	-40.3
-10	31.7	26.5
-11	20.2	24.2
-12	74.5	66.3
-13	22.1	18.1
-14	16.3	14.0
-15	19.6	-20.2
-16	34.6	-35.9
h 1 4		
0	13.4	-11.4
1	42.3	-39.0
2	92.2	-71.6
3	49.0	-31.2
4	40.3	-38.6
5	37.5	28.9
6	39.4	44.8
7	33.6	30.9
8	31.7	29.7
9	26.1	-11.8
10	6.5	-1.2
11	20.2	-22.2
-1	50.9	48.7
-2	2.6	-7.8
-3	12.5	11.3
-4	28.8	28.2
-5	13.4	13.8
-6	20.2	16.5
-7	55.7	50.0
-8	13.1	14.0
-9	18.2	-20.5
-10	56.7	-50.2
-11	26.9	-25.2
-12	40.3	-36.2
-13	3.9	1.7
-14	17.3	16.5
-15	27.9	27.2
h 1 5		
0	121.0	-93.2
1	106.6	-85.6
2	154.6	-124.7
3	24.0	-20.6
4	19.6	-13.6
5	53.8	50.9
6	55.6	33.5
7	59.7	59.4
8	37.5	40.4
9	18.2	22.1
10	44.2	35.7
11	29.8	-27.4
12	20.2	-20.1
13	59.6	-54.5
14	26.9	-27.8
-1	19.2	-15.9
-2	98.9	83.7
-3	79.7	75.2
-4	59.9	53.2
-5	42.3	35.3
-6	22.1	20.3
-7	34.6	-37.3
-8	17.3	-20.3
-9	2.6	-10.0
-10	41.3	-37.5
-11	18.3	-12.6
-12	29.8	-27.9
-13	13.1	7.7
-14	6.5	-3.8
-15	24.0	21.1
h 1 6		
0	19.4	16.1
1	21.1	-20.5
2	3.9	-4.5
3	16.3	-15.2
4	6.5	7.2
5	10.5	-10.1
6	19.6	19.0
7	3.9	-7.3
8	19.6	17.2
-1	37.5	26.3
-2	3.9	-1.8
-3	19.6	17.2
-4	23.0	-17.8
-5	13.1	7.4
-6	3.9	-6.5
-7	13.1	12.1
-8	10.5	6.6
-9	10.7	-10.7
-10	2.7	-17.1
-11	29.8	-31.2
-12	6.5	6.1
-13	6.5	-1.1
-14	26.9	22.9
h 1 7		
1	22.1	-20.9
2	44.2	-35.6
3	74.8	-65.6
4	3.9	-0.9
5	13.1	-12.9
6	44.2	44.2
7	25.0	39.5
8	30.7	34.4
9	3.9	6.8
10	18.2	-18.6
11	3.9	-3.5
12	19.2	-17.2
-1	3.9	-5.5
-2	17.3	-16.2
-3	49.9	40.0
-4	13.1	10.3
-5	74.2	66.3
-6	48.0	42.6
-7	28.8	28.6
-8	25.9	-24.5
-9	56.7	-54.2
-10	39.4	-39.4
-11	42.3	-42.8
-13	6.5	5.9
-14	27.5	27.0
h 1 8		
0	36.5	32.5
1	40.3	32.0
2	10.4	8.3
3	10.9	12.2
4	3.9	8.1
5	3.9	10.0
6	6.5	-11.8
7	6.5	5.2
8	6.5	-15.7
9	24.8	-27.2
10	21.1	-15.6
-1	16.3	-14.9
-2	13.1	-9.1
-3	50.9	-41.0
-4	25.9	-24.0
-5	26.8	-27.7
-6	20.2	17.7
-7	20.2	21.2
h 1 9		
0	33.6	-27.5
1	17.3	-13.9
2	3.9	2.9
3	30.7	32.9
4	11.5	10.1
-1	25.0	-22.9
h 1 10		
0	3.9	5.1
1	6.7	13.5
2	22.1	17.0
3	13.1	9.7
4	13.4	15.2
-1	3.9	-4.9
-2	23.1	-22.0
-3	18.3	-16.7
-4	23.1	-21.6
-5	6.5	-8.2
-6	6.5	-0.3
-7	14.4	14.0
-8	13.5	13.8
-9	9.6	9.5
h 1 11		
0	7.8	9.8
1	2.9	7.3
2	2.9	17.4
3	18.3	7.3
-1	3.9	-0.7
-2	29.8	-22.8
-3	31.7	-26.4
-4	37.5	-32.9
h 2 0		
1	46.1	72.9
2	64.4	85.8
3	43.2	-34.6
4	64.4	-73.9
5	86.5	-68.4
6	50.3	-75.4
7	69.2	-58.8
8	21.1	-18.5
9	35.5	36.5
10	44.2	34.5
11	49.0	45.3
12	51.9	47.2
15	24.0	-27.3
h 2 1		
0	82.6	-101.6
1	22.1	-24.6
2	128.7	-164.6
5	66.3	70.9
6	114.3	92.0
7	60.5	55.3
8	96.1	87.8
9	62.4	-57.4
10	18.3	-16.1
11	48.0	-38.0
12	27.9	-34.5
13	32.7	-31.1
-1	79.7	72.2
-2	92.2	-88.9
-3	46.1	50.2
-4	35.5	43.5
-5	24.0	-21.5
-6	58.6	-56.7
-7	30.7	18.2
-8	47.1	31.7
-9	51.9	40.5
-11	40.3	36.1
-12	2.8	-5.3
-13	18.3	18.4
-14	7.8	-7.1
-15	19.2	23.5
h 2 2		
0	109.5	-116.1
1	26.9	-20.0
2	12.5	-7.4
3	25.9	21.5
4	29.8	-37.3
5	17.3	-15.1
6	54.8	-52.8
7	41.3	-43.7
8	17.3	20.0
9	52.8	53.4
10	68.2	60.7
11	52.7	28.5
12	18.2	-14.6
13	20.2	-22.3
14	47.1	-38.3
-1	97.0	80.9
-2	85.5	80.3
-3	107.6	108.9
-4	73.9	76.1
-5	16.3	-18.5
-6	106.6	-100.5
-7	123.9	-114.0
-8	46.1	42.4
-9	20.9	-4.9
-10	67.2	64.6
-11	46.1	42.1
h 2 3		
0	67.2	-65.5
1	123.9	-128.3
2	66.4	-67.7
3	20.2	16.3
4	2.6	3.0
5	46.1	46.7
6	62.4	58.5
7	72.0	74.5
8	15.4	-10.8
9	53.8	67.5
10	2.6	-7.8
11	27.5	-26.2
12	30.7	-29.0
13	33.6	-24.7
14	2.6	-11.1
15	14.0	-25.9
-1	101.8	-88.1
-2	17.3	-16.6
-3	64.4	55.6
-4	51.9	58.6
-5	74.9	62.7
-6	50.9	53.6
-7	43.2	45.4
-8	9.2	-11.8
-9	2.6	1.4
-10	36.5	-38.9
-11	41.3	-38.3
-12	29.8	-29.3
-13	39.4	-39.5
-14	2.6	9.3
-15	2.4	-7.4
-16	24.0	23.5
h 2 4		
0	41.3	37.3
1	99.1	-92.7
2	61.5	-51.7
3	58.6	-65.0
4	2.6	3.2
5	2.6	5.5
6	35.5	35.2
7	29.8	24.9
8	13.1	-9.7
9	3.9	10.5
10	8.6	14.0
11	2.6	14.0
12	2.6	10.0
13	2.6	-8.3
14	18.3	-20.2
15	32.7	-30.8
-1	27.9	26.7
-2	105.7	97.2
-3	31.7	29.3
-5	17.3	-15.7
-6	34.6	-37.4
-7	2.6	-6.6
-8	2.6	-7.4
-9	2.6	13.6
-10	24.9	-20.9
-11	11.8	-7.8
-12	2.6	-7.6
-13	2.6	0.4
-14	2.6	16.3
-15	2.6	13.9
-16	17.3	15.8
h 2 5		
0	32.7	-35.7
1	24.0	-18.9
2	40.3	-38.4
3	38.5	-32.6
4	16.3	14.9
5	2.6	8.4
6	38.4	35.2
7	20.2	-5.7
8	25.9	26.7
9	33.6	-38.5
10	3.9	1.5
11	2.6	5.0
12	2.6	5.6
13	21.1	16.3
-1	45.1	38.3
-2	2.6	-10.2
-3	2.6	5.3
-4	28.8	21.6
-5	22.1	22.6
-6	28.8	27.5
-7	16.3	14.9
-8	40.3	41.6
-9	46.1	-41.1
-10	40.3	-37.7
-11	42.3	-41.3
-12	17.3	-24.0
-13	2.6	-3.7
-14	2.6	9.8
-15	42.3	43.9
h 2 6		
0	67.2	-60.2
1	40.3	-39.2
2	47.1	-44.7
3	13.4	-12.2
4	18.2	-19.4
5	2.6	1.4
6	23.1	23.1
7	23.1	25.3
8	37.5	42.4
9	26.9	23.6
10	2.6	16.0
11	2.6	-15.8
12	37.5	-32.4
13	23.1	-23.1
-2	22.1	16.1
-3	68.2	62.5
-4	58.6	57.5
-5	34.6	35.7
-6	9.2	-4.5
-7	35.4	-36.9
-8	19.2	-20.9
-9	24.9	-18.8
h 2 7		
0	42.3	38.3
1	29.8	27.6
2	73.0	70.2
3	2.6	6.8
4	2.6	9.1
5	2.6	-4.4
6	39.4	-42.5
7	22.0	-22.0
8	25.9	-31.3
9	2.6	-3.2
10	16.3	-23.1
-1	20.2	-20.9
-2	3.8	2.5
-3	32.7	-34.4
-4	34.6	-32.2
-5	2.6	-1.2
-6	26.9	-20.8
-7	2.6	10.5
-8	19.2	-22.8
-9	19.2	20.5
h 2 8		
0	22.1	-22.9
1	64.4	-60.4
2	59.6	-40.0
3	2.6	-6.6
4	28.8	30.3
5	45.1	48.7
6	27.9	31.8
7	10.6	16.1
8	20.2	-23.3
9	21.1	-19.4
10	18.3	-15.6
-1	2.6	-2.5
-2	26.9	28.3
-3	3.9	15.9
-4	2.6	12.8
-5	2.6	1.1
-6	2.6	-0.9
-7	3.9	17.2
-8	15.2	19.3
-9	18.3	8.1
-10	3.9	-22.0
-11	20.2	-29.6
-12	29.8	-24.0
-13	17.3	-10.5
h 2 9		
0	5.2	7.9
1	20.2	21.7
3	29.8	28.3
-1	5.2	12.2
-2	18.2	-17.7
-3	14.4	-16.6
-4	29.8	-26.1
-5	39.4	-41.5
h 2 10		
0	6.7	-5.1
-1	8.6	-13.1
-2	35.5	-31.0
-3	16.3	-17.6
-4	2.6	-2.3
-5	2.6	9.8
-6	24.5	18.0
h 2 11		
0	2.6	-0.1
1	2.6	-2.1
-1	31.7	-26.0
-2	24.0	-19.6
-3	21.1	-18.6
h 3 0		
1	72.0	134.8
2	35.5	-26.9
3	13.4	9.5
4	42.3	-45.3
5	17.3	-12.7
6	69.2	-56.5
7	76.8	59.9
8	51.3	73.6
9	25.0	25.0
10	20.2	18.6
11	80.7	-65.5
12	25.9	-24.2
13	58.7	-45.7
14	1.9	9.5
15	3.9	17.2
16	29.6	30.4
h 3 1		
0	6.7	-2.8
1	8.6	0.7
2	38.4	-41.3
3	53.8	-62.4
4	28.8	31.1
5	43.2	-45.8
6	16.2	-21.5
7	56.7	-38.8
8	2.0	2.1
9	26.9	20.5
10	69.3	61.9
11	52.8	43.5
12	13.1	17.8
13	2.0	-1.9
14	49.0	-42.3
15	31.7	30.2
16	16.3	-12.7
-1	44.2	41.7
-2	106.6	98.9
-3	90.3	88.0
-4	54.8	-50.8
-5	28.8	-30.7
-6	67.2	-51.9
-7	41.3	-37.3
-8	2.0	-13.5
-9	41.3	35.5
-10	27.9	23.7
h 3 2		
0	134.5	-129.2
1	133.5	-139.9
2	32.6	-33.4
3	34.6	-36.5
4	42.3	35.3
5	34.6	36.8
6	72.0	78.9
7	37.5	41.4
8	52.8	54.5
9	52.8	34.0
10	21.1	-18.6
11	2.0	1.1
12	83.6	-71.4
13	41.4	-36.3
14	43.2	-36.4
-1	35.5	-23.4
-2	62.4	-53.4
-3	114.3	102.1
-4	75.9	75.9
-5	93.2	93.2
-6	35.5	31.2
-7	1.9	12.3
-8	24.9	-25.2
-9	48.9	-42.3
-10	2.0	8.4
-11	53.8	-48.7
-12	2.0	9.5
-13	20.2	-18.3
h 3 3		
0	28.8	22.2
1	19.2	15.1
2	48.0	-45.7
3	82.6	-84.5
4	70.1	-62.5
5	66.3	-64.1
6	21.1	-22.2
7	29.8	32.8
8	43.2	50.9
9	28.8	25.9
10	33.6	42.4
11	20.2	14.9
12	2.0	-5.3
13	2.0	-11.9
14	2.0	0.7
15	23.0	-22.9
-1	65.3	61.6
-2	81.6	71.0
-3	75.9	76.0
-4	24.0	21.3
-5	29.8	32.0
-6	36.5	-37.2
-7	60.5	-56.6
-8	66.3	-67.6
-9	24.9	-25.5
-10	3.8	-15.8
-11	2.0	14.2
-12	25.9	25.7
-13	20.2	22.8
h 3 4		
0	88.4	-81.0
1	21.1	-23.5
2	23.1	-22.6
3	2.0	5.4
4	33.6	-26.8
5	44.2	44.7
6	7.7	13.2
7	34.6	38.8
8	45.1	52.0
9	12.5	16.1
10	2.0	-2.0
11	51.5	-51.5
12	2.0	-9.5
13	36.5	-30.1
-1	107.6	-88.8
-2	35.5	-26.6
-3	2.0	-7.5
-4	113.3	108.1
-5	76.8	76.0
-6	89.3	92.6
-7	31.7	27.5
-8	32.6	-28.9
-9	45.1	-48.3
-10	45.9	-45.6
-11	2.0	-5.7
-12	40.3	-40.6
-13	2.0	4.5
-14	2.0	-11.9
-15	1.9	1.9
-16	11.5	11.8
h 3 5		
0	42.3	-38.5
1	76.8	-66.6
2	26.8	-30.5
3	6.5	-5.9
4	16.2	16.1
5	26.9	29.5
6	2.0	3.4
7	2.0	0.9
8	2.0	-7.5
9	2.0	7.8
10	2.0	4.0
11	2.0	15.2
12	2.0	14.5
13	2.0	-9.5
14	15.4	-12.5
-1	23.1	19.8
-2	65.3	56.3
-3	57.6	52.6
-4	49.0	52.3
-5	2.0	-4.0
-6	29.8	-29.3
-7	25.8	-29.3
-8	2.0	-5.2
-9	2.0	-13.4
-10	2.0	2.5
-11	2.0	-2.1
-12	2.0	-7.2
-13	2.0	-5.5
-14	25.0	21.2
-15	23.1	23.1
h 3 6		
0	35.5	-35.5
1	41.3	-35.0
2	41.3	41.1
3	22.1	20.5
4	45.1	44.0
5	2.0	-13.5
6	2.0	3.6
7	45.1	-51.4
8	24.0	-29.5
9	2.0	9.8
10	2.0	-3.0
11	32.7	26.7
-1	2.0	-11.5
-2	2.0	-5.0
-3	65.3	48.6
-4	2.0	1.2
-5	35.4	38.7
-6	24.5	-25.6
-7	25.9	-25.4
-8	16.3	-17.9
-9	2.0	6.4
-10	2.0	16.8
-11	2.0	-12.3
-12	7.8	15.1
-13	20.9	-22.9
-14	2.9	-6.3
h 3 7		
0	2.0	0.2
1	22.1	-18.4
2	2.0	1.2
3	2.9	4.5
4	2.0	1.1
5	29.8	28.3
6	29.8	34.6
7	21.1	19.4
8	2.0	-7.4
9	2.0	-14.4
10	30.7	-26.5
11	24.0	-22.6
-1	2.0	-12.7
-2	12.5	-13.4
-3	35.5	-36.1
-4	2.0	-2.8
-5	2.0	4.8
-6	21.1	22.7
-7	9.6	18.6
-8	18.1	17.7
h 3 8		
0	14.1	10.2
1	47.1	41.6
2	29.8	27.4
3	46.1	41.9
4	2.0	10.8
5	24.0	22.3
6	9.6	-19.8
7	2.0	-12.4
8	36.5	-29.5
9	44.2	-33.9
-1	28.8	-23.7
-2	2.0	-14.0
-3	48.0	-49.0
-4	16.3	-20.1
-5	21.1	-24.0
-6	2.0	11.5
-7	2.0	1.6
-8	2.0	20.4
-10	2.0	4.0
-11	20.2	17.7
h 3 9		
0	12.5	-30.7
1	2.0	-15.7
2	2.0	-7.3
3	24.0	15.9
-1	23.0	-20.4
-2	20.2	-4.8
-3	9.6	13.2
h 3 10		
0	2.0	-9.3
1	2.0	6.9
2	34.6	38.6
3	34.6	29.6
4	36.5	30.5
-1	2.0	-14.0
-2	2.0	-11.3
-4	26.9	-21.6
-5	2.0	-7.5
-6	19.2	-18.8
-7	2.0	-2.8
-8	21.1	16.6
-9	32.7	30.2
h 4 0		
1	51.9	64.5
2	15.4	-17.2
3	106.6	-99.1
4	31.7	-35.3
5	23.0	13.8
6	73.9	52.4
7	28.8	23.9
8	88.4	68.4
9	47.1	-32.5
10	5.2	-3.1
11	23.0	-20.4
12	5.0	-3.9
13	5.2	7.1
14	5.2	-6.0
15	5.2	-4.7
16	27.8	-29.1
h 4 1		
0	17.3	-22.1
1	5.2	-17.7
2	40.3	-52.1
3	84.5	-82.3
4	26.9	-32.0
5	11.5	-5.6
6	54.8	56.6
7	61.9	58.0
8	100.9	86.8
9	5.2	7.3
10	5.2	-8.4
11	32.7	-32.9
12	46.1	-46.2
13	11.8	-14.4
14	20.2	-22.5
-1	14.4	12.1
-2	16.3	-4.4
-3	6.5	2.9
-4	80.7	67.8
-5	25.0	27.1
-6	74.0	58.3
-7	5.2	-6.5
-8	10.9	-11.2
-9	50.1	-77.1
-10	30.7	-25.5
-11	23.1	-17.7
-12	5.2	5.0
-13	35.5	35.4
-14	5.2	8.1
-15	15.4	17.5
h 4 2		
0	33.6	31.0
1	3.8	-1.0
2	25.9	-20.1
3	70.8	-70.5
4	50.0	-51.9
5	30.7	-35.1
6	47.1	-51.4
7	44.2	46.0
8	47.1	46.6
9	53.8	48.4
10	5.2	5.2
11	32.7	31.8
12	5.2	-5.5
13	18.3	-20.6
-1	23.1	24.3
-2	10.5	9.3
-3	64.4	52.2
-4	34.6	25.1
-5	41.3	37.3
-6	25.5	-24.6
-7	25.8	24.8
-8	66.3	-50.6
-9	24.5	-22.6
-10	30.5	-28.9
-11	5.2	-6.3
-12	5.2	1.2
-13	5.2	2.3
-14	16.3	17.0
-15	5.2	-2.5
-16	15.4	18.5
h 4 3		
0	75.9	-67.7
1	104.7	-91.0
2	5.2	-4.0
3	5.2	1.2
4	13.5	19.7
5	12.5	16.3
6	15.4	23.6
7	37.5	37.8
8	20.2	22.9
9	60.5	60.0
10	5.2	-3.4
11	34.6	-34.7
12	36.5	-34.7
13	49.0	-44.2
14	19.2	-13.6
-1	129.7	-129.1
-2	14.4	17.9
-3	93.2	76.5
-4	92.2	78.1
-5	119.1	101.2
-6	27.9	32.7
-7	5.2	-7.7
-8	89.3	-79.2
-9	5.2	-3.9
-10	25.0	-25.2
-11	5.2	2.1
-12	5.2	-3.6
-13	5.2	-5.0
-14	5.2	-7.5
-15	16.3	-18.6
-16	19.2	20.3
h 4 4		
0	75.9	65.2
1	34.6	32.1
2	15.4	-15.6
3	50.9	-48.7
4	42.3	-35.5
5	48.0	-51.2
6	5.2	7.7
7	15.4	-11.2
8	10.6	14.7
9	5.2	-7.6
10	20.2	15.0
11	5.2	4.7
12	15.4	16.4
13	24.0	23.5
-1	56.7	54.5
-2	23.1	23.5
-3	5.2	10.0
-4	5.2	-0.9
-5	31.7	-31.0
-6	23.1	16.6
-7	5.2	-15.8
-8	28.8	-25.0
-9	66.3	-61.0
-10	5.2	-12.2
-11	5.2	-9.7
-12	17.3	-16.5
-13	44.2	51.4
-14	34.6	34.3
-15	12.5	13.5
h 4 5		
0	80.7	-79.4
1	34.6	-34.6
2	48.0	-45.0
3	10.6	14.6
4	26.6	30.4
5	50.9	52.8
6	50.9	52.9
7	5.2	5.5
8	10.6	6.0
9	32.7	-34.3
10	18.3	-18.7
11	11.5	-16.6
-1	5.2	-13.6
-2	38.4	-34.0
-3	22.1	19.7
-4	40.3	36.3
-5	37.5	35.4
-6	57.6	53.2
-7	5.2	17.0
-8	22.1	19.1
-9	31.7	-33.1
-10	19.2	-20.1
-11	40.3	-39.9
-12	20.2	-22.6
-13	5.2	-1.7
-14	5.2	2.8
-15	20.2	23.8
h 4 6		
0	41.3	36.4
1	27.9	19.0
2	37.9	34.8
3	5.2	8.9
4	5.2	-4.2
5	19.2	-19.4
6	26.9	-23.7
7	16.3	22.2
8	5.2	-4.1
9	5.2	11.4
10	16.3	-18.8
11	15.4	-16.3
12	20.2	-16.7
-1	28.8	-20.4
-2	15.4	-12.4
-3	16.3	-17.0
-4	5.2	2.6
-5	5.2	9.7
-6	29.9	-20.4
-7	5.2	-2.1
-8	34.8	-34.8
-9	5.2	-4.4
-10	5.2	-3.1
-11	34.6	38.9
-12	[illegible]	[illegible]
-13	11.5	[illegible]
h 4 7		
0	11.5	-11.2
1	5.2	27.3
2	69.2	64.2
3	50.7	54.6
4	26.3	26.5
5	5.2	3.4
6	30.7	-31.2
7	7.7	-25.2
8	38.4	-35.6
-1	77.8	-61.8
-2	41.3	-30.2
-3	36.4	-30.2
-4	5.2	-1.5
-5	26.5	23.2
-6	5.2	[illegible]
-7	5.2	9.9
-8	5.2	-3.0
-9	17.3	18.9
h 4 8		
0	56.7	-65.2
1	5.2	-4.3
2	13.1	-13.2
3	5.2	5.9
4	20.2	20.8
5	37.9	35.5
6	35.4	29.3
-1	39.2	-16.0
-2	11.5	-13.6
-3	10.6	-10.6
-4	5.2	-1.1
-5	5.2	6.5
-6	31.7	25.1
-7	5.2	6.2
-8	23.1	20.4
h 4 9		
0	5.2	-2.9
1	15.4	10.2
2	23.1	5.9
3	24.0	23.4
4	23.1	24.3
5	5.2	6.5
6	5.2	[illegible]
7	40.3	-32.5
8	26.9	-27.6
-1	19.6	14.4
-2	19.6	-4.8
-3	5.2	-10.5
-4	26.8	-27.4
-5	41.3	-30.5
-6	13.5	-16.5
-7	5.2	-6.9
-8	34.6	28.8
-9	29.6	27.5
-10	25.9	24.2
h 4 10		
0	20.2	-16.0
1	14.4	-10.5
-1	38.4	-32.4
-2	25.9	-20.2
-3	5.2	-3.7
-4	23.1	17.1
-5	41.3	34.8
-6	31.7	30.2
-7	20.2	19.6
h 4 11		
1	14.4	12.6
-1	6.5	-10.7
-2	13.5	-12.2
-3	17.3	-18.0
h 5 0		
1	39.4	-57.4
2	79.7	-55.3
3	98.0	-92.3
4	70.1	-67.6
5	56.7	-59.2
6	43.2	42.2
7	53.8	54.6
8	61.5	64.3
9	52.8	46.5
10	55.7	44.0
11	17.3	-20.1
12	6.7	-14.1
13	23.1	-20.9
14	26.8	-20.5
15	15.4	-13.5
h 5 1		
0	20.9	-17.4
1	13.5	-16.8
2	30.7	-31.6
3	102.8	-85.5
4	2.0	2.0
5	2.0	1.2
6	36.5	29.3
7	28.8	25.5
8	52.8	42.1
9	32.7	29.2
10	31.7	-22.9
11	22.1	21.3
12	19.2	-20.5
13	3.9	-0.9
14	31.7	-26.7
-1	32.7	23.2
-2	26.9	-31.7
-3	34.8	33.0
-4	20.2	-15.1
-5	44.5	40.5
-6	30.5	27.9
-7	54.6	54.4
-8	18.3	20.5
-9	50.9	-41.5
-10	9.6	-14.7
-11	67.2	-53.5
-12	2.0	1.0
-13	18.3	-19.2
-14	32.7	27.5
h 5 2		
0	49.0	[illegible]
1	107.6	-133.7
2	113.3	[illegible]
3	45.2	-50.3
4	23.1	23.2
5	63.4	66.7
6	65.2	78.3
7	40.3	35.5
8	9.6	-11.1
9	2.0	3.2
10	18.3	-17.4
11	2.0	0.2
12	2.0	-4.1
13	2.0	-8.4
14	30.7	-25.6
15	14.4	-14.0
-1	24.0	20.5
-2	83.6	74.0
-3	91.3	97.5
-4	40.3	40.9
-5	20.9	29.3
-6	2.0	0.5
-7	2.9	-10.0
-8	2.0	-9.3
-9	22.1	-20.3
-10	51.9	-47.3
-11	66.3	-50.4
-12	6.7	-11.9
-13	2.0	1.5
-14	40.3	34.2
-15	55.7	54.9
-16	27.5	32.6
h 5 3		
0	54.6	55.2
1	49.0	40.6
2	16.3	-16.6
3	24.0	-27.5

Table II. (continued)

h 5 3	F_o	F_c
4	62.4	-64.5
5	30.5	-39.0
6	36.5	-32.3
7	42.3	36.4
8	9.6	18.7
9	2.6	-4.2
10	31.7	27.0
11	2.0	-7.0
12	16.3	18.1
13	2.6	7.9
14	29.6	26.4
-1	2.0	5.8
-2	38.4	31.5
-3	44.2	-38.5
-4	37.9	39.1
-5	2.0	-8.1
-6	30.7	33.5
-7	3.5	-7.1
-9	38.4	-33.3
-10	44.2	-42.7
-11	3.5	6.4
-12	2.0	-9.6
-13	44.2	39.7
h 5 4		
0	25.5	-25.4
1	2.6	5.6
2	25.0	-24.0
3	2.6	8.1
4	30.6	31.0
5	46.1	46.2
6	41.2	41.0
7	59.6	61.0
8	2.0	2.4
9	49.0	-43.5
10	51.9	-52.7
11	56.6	-49.7
12	30.7	-26.0
13	2.0	6.5
14	25.0	23.9
-1	64.4	-63.0
-2	43.2	-37.0
-3	60.5	-55.5
-4	2.0	0.1
-5	47.1	38.1
-6	61.5	72.5
-7	52.8	47.6
-8	28.8	29.4
-9	2.5	-14.1
-10	50.0	-42.3
-11	28.8	-27.5
-12	20.2	-20.1
h 5 5		
0	52.8	37.8
1	29.8	30.7
2	38.4	37.6
3	24.0	21.2
4	2.0	4.5
5	44.8	-39.2
6	19.2	-20.0
7	27.5	-31.9
8	2.0	3.6
9	2.0	9.2
10	9.6	-11.4
11	13.5	18.4
12	7.7	-6.2
13	16.3	17.4
-1	43.2	32.0
-2	14.5	-17.0
-3	34.6	30.7
-4	34.6	-35.0
-5	2.9	-12.7
-6	47.1	-37.4
-7	2.0	1.1
-8	34.6	-33.9
-9	17.3	-21.8
-10	20.3	21.9
-11	2.0	6.4
-12	33.6	32.3
-13	16.3	19.1
-14	30.7	29.0
h 5 6		
0	32.7	-30.5
1	32.7	-30.2
2	2.6	5.4
3	33.6	35.1
4	54.8	59.3
5	35.5	39.3
6	9.6	15.8
7	2.6	-5.4
8	30.7	-26.7
9	21.1	-25.6
10	19.2	-17.0
-1	37.5	-35.5
-2	32.7	-24.6
-3	12.5	-11.6
-4	2.0	-5.0
-5	2.0	7.7
-6	2.0	7.6
-7	33.6	29.7
-8	48.0	40.7
-9	17.3	20.6
-10	2.0	12.2
-11	2.0	-10.4
-12	26.9	-25.3
-13	29.8	-25.0
h 5 7		
0	2.0	-0.6
1	22.1	19.4
2	4.8	12.5
3	31.7	29.8
4	2.0	-8.7
5	29.8	30.1
6	2.0	3.4
7	2.0	10.3
8	2.0	-6.1
9	25.5	-19.4
10	20.2	-17.5
11	31.[illegible]	-28.3
-1	28.8	-22.0
-2	17.3	-19.7
-3	62.4	-48.6
-4	2.0	2.3
-5	2.0	-5.2
-6	22.1	24.8
-7	2.0	3.2
-8	2.0	1.0

h 5 7	F_o	F_c
-9	2.0	1.6
-10	2.0	-4.2
-11	24.0	23.2
-12	2.0	9.8
-13	17.3	18.4
h 5 8		
0	2.5	10.5
1	20.2	18.4
2	2.5	5.7
8	2.5	-2.3
-1	2.0	2.4
-2	39.4	-30.2
-3	53.8	-42.3
-4	25.5	-21.6
-5	10.5	4.1
-6	37.5	28.6
-7	54.8	42.7
-8	33.6	26.2
-9	2.9	-4.4
-10	24.0	-20.9
-11	18.3	-14.1
h 5 9		
0	25.0	-22.5
1	2.0	-7.5
2	2.0	9.5
3	3.8	-1.3
4	2.0	18.3
5	2.0	-0.8
6	2.0	11.3
7	2.0	3.3
8	11.5	13.5
-1	36.5	-26.8
-2	31.7	-23.8
-3	2.0	5.1
-4	2.0	-3.0
-5	26.9	22.3
-6	11.5	14.3
-7	7.7	12.6
-8	5.8	9.0
-9	2.0	5.2
-10	10.6	10.2
h 5 10		
0	2.6	8.7
1	16.3	15.2
2	27.9	23.1
3	19.2	14.7
4	2.0	3.3
5	19.2	-19.8
-1	2.0	-1.3
-2	2.0	-4.5
-3	1.4	1.7
-4	2.0	-7.4
-5	19.2	-6.3
h 6 0		
0	48.0	-48.4
1	31.7	-33.6
2	8.7	-9.8
3	6.7	3.5
4	46.1	43.3
5	24.0	10.5
6	68.2	48.7
7	1.5	-14.0
8	26.9	21.8
9	21.1	-17.8
10	24.8	17.9
11	18.3	-16.3
12	19.2	-21.1
13	3.3	-4.4
14	28.8	-26.9
h 6 1		
0	26.9	25.4
1	56.7	-52.6
2	95.1	-86.6
3	137.4	-136.2
4	56.7	-56.2
5	3.3	1.5
6	50.0	47.2
7	69.2	61.4
8	8.7	14.2
9	3.3	10.6
10	3.3	4.2
11	3.3	8.4
12	3.3	7.2
13	3.3	15.8
14	3.3	-7.4
15	27.5	-32.5
-1	102.8	92.7
-2	122.0	124.2
-3	24.0	31.1
-4	3.3	10.0
-5	37.5	35.2
-6	21.1	-27.7
-7	3.3	-7.7
-8	14.4	-16.0
-9	43.2	-41.1
-10	84.5	-73.4
-11	32.7	-30.6
-12	3.3	-6.5
-13	18.3	21.0
-14	60.4	50.3
-15	37.5	38.2
h 6 2		
0	12.5	6.9
1	50.0	-46.0
2	15.4	-12.5
3	13.5	9.7
4	3.3	3.1
5	3.3	2.8
6	18.3	-20.0
7	22.1	20.6
8	25.0	-19.9
9	36.5	28.8
-1	34.6	-32.1
-2	24.0	20.8
-3	43.2	42.1
-4	3.3	8.6
-5	25.0	21.3
-6	27.9	-22.5
-7	3.3	9.0
-8	28.8	-26.5
-9	43.2	39.7
-10	20.2	-20.2
-11	3.3	-3.1
-12	3.3	-7.1
-13	22.1	-25.4

h 6 3	F_o	F_c
0	43.2	-40.1
1	29.6	-30.7
2	34.6	-37.7
3	3.3	6.5
4	23.1	26.0
5	35.5	31.4
-1	3.3	-1.2
-2	38.4	25.4
-3	27.9	28.3
-4	68.0	42.5
-5	3.3	12.5
-6	11.3	-15.3
-7	32.7	-29.4
-8	3.3	0.7
-9	23.1	-24.9
-10	3.3	-10.7
-11	3.3	-0.5
-12	3.3	2.8
-13	3.3	2.8
-14	3.4	15.3
-15	25.5	26.6
h 6 4		
0	49.0	-40.7
1	13.5	13.9
2	3.3	-4.6
3	3.3	13.5
4	3.3	3.6
5	3.3	9.4
6	3.3	6.0
7	44.2	-45.6
8	3.3	-1.6
9	18.3	-19.2
10	15.4	16.8
-1	26.9	31.8
-2	3.3	7.3
-3	16.3	16.8
-4	3.3	0.8
-5	3.3	-10.4
-6	42.3	-37.9
-8	3.3	10.4
-9	3.3	-13.3
-10	12.5	11.6
h 6 5		
0	4.8	-5.4
1	51.9	-46.6
2	25.0	-18.8
3	16.3	8.2
4	53.8	57.4
5	80.7	80.4
6	72.0	70.1
7	28.8	29.9
8	29.8	-32.9
9	58.6	-52.8
10	70.1	-61.4
11	30.7	-26.1
-1	47.1	-36.3
-2	38.5	-33.1
-3	46.1	-44.9
-4	31.7	-31.0
-5	3.3	-9.8
-6	48.0	45.6
-7	76.8	61.6
-8	45.2	44.0
-9	20.2	22.7
-10	23.1	-21.9
-11	37.5	-41.2
-12	31.7	-36.3
-13	3.3	2.8
-14	15.4	15.1
h 6 6		
0	38.4	30.0
1	3.3	5.8
2	40.3	33.8
3	20.2	24.5
4	8.7	11.9
5	3.3	4.1
6	24.0	-23.0
7	3.3	-7.7
8	32.7	-35.6
9	3.3	-4.3
10	19.2	-18.4
-1	3.3	-10.1
-2	3.3	-1.2
-3	31.7	-24.6
-4	24.0	-24.9
-5	22.1	-22.4
-6	34.6	-32.1
-7	3.3	10.6
-8	3.3	9.2
-9	34.6	36.4
-10	3.3	15.3
-11	3.3	15.5
-12	3.3	-3.6
-13	18.3	-18.0
h 6 7		
0	34.6	-23.3
1	19.2	14.7
2	3.3	6.7
3	40.3	37.4
4	24.0	19.5
-1	55.7	-43.4
-2	74.0	-69.9
-3	34.6	-33.1
-4	3.3	-2.6
-5	25.0	21.2
-6	45.2	44.5
-7	41.3	44.6
-8	37.5	39.4
-9	3.3	1.6
-10	3.3	-0.5
-11	3.3	-5.5
-12	23.1	-19.1
h 6 8		
0	3.3	-6.7
1	3.3	4.1
2	3.3	-2.9
3	3.3	5.4
4	3.3	5.4
5	3.8	-2.5
-1	15.4	16.8
-3	3.3	-2.8
-4	3.3	-11.8
-5	18.3	-19.9
h 6 9		
0	3.3	7.6
-1	3.3	12.7

h 6 9	F_o	F_c
-2	3.3	15.5
-3	3.3	0.5
-4	16.3	-11.8
-5	3.3	-7.5
-6	3.3	-0.7
-7	3.3	15.0
-8	5.6	13.7
-9	12.5	3.2
h 6 10		
0	3.3	1.9
1	16.3	-16.2
h 7 0		
1	25.0	-38.4
2	23.1	-23.8
3	87.4	-83.7
4	51.3	-76.4
5	90.0	-81.6
6	10.6	12.0
7	39.4	41.7
8	67.2	75.1
9	76.8	77.9
10	32.7	21.2
12	45.2	-35.6
13	16.3	-13.8
14	27.9	-20.8
h 7 1		
0	44.2	-55.0
1	48.0	-59.6
2	23.1	29.1
3	29.8	35.5
4	43.2	47.9
5	25.0	25.9
6	14.4	16.5
7	29.8	-25.7
8	21.1	-17.8
9	14.4	11.3
10	11.5	-12.1
12	35.5	-23.2
13	14.4	11.3
14	7.7	-11.7
-1	25.9	-34.3
-2	18.3	-27.4
-3	26.9	31.4
-4	20.2	22.3
-5	29.8	30.2
-6	2.0	-1.8
-7	2.0	1.8
-8	2.0	-5.1
-9	2.0	0.1
-10	2.0	11.2
-11	25.0	-11.8
-12	2.0	0.4
-13	19.2	-17.5
h 7 2		
0	8.7	-8.0
1	28.8	-31.6
2	38.4	-46.2
3	11.5	-10.3
4	17.3	-11.0
5	31.7	28.7
6	11.5	-14.9
7	2.0	-5.6
8	2.0	-2.4
9	2.0	6.6
10	2.0	9.7
11	2.0	1.4
12	28.8	24.4
13	12.5	15.2
-1	9.6	-5.1
-2	75.9	73.3
-3	39.4	45.4
-4	51.9	60.7
-5	16.3	-15.4
-6	2.0	1.8
-7	42.3	-36.3
-8	45.2	-38.4
-9	27.9	-28.5
-10	32.7	-29.9
-11	2.0	0.9
-12	2.9	-11.7
-13	32.7	28.5
-14	26.9	24.9
-15	25.9	37.6
h 7 3		
0	48.0	-46.9
1	14.4	-16.3
2	11.5	11.7
3	65.3	72.8
4	30.7	35.5
5	43.2	52.3
6	2.0	6.3
7	28.8	28.6
8	49.0	-48.6
9	40.3	-36.4
10	2.0	-0.4
11	2.0	-12.8
12	31.7	23.2
-1	34.6	-32.2
-2	2.0	-3.3
-3	31.7	-33.5
-4	5.2	7.3
-5	9.6	14.8
-6	2.0	1.3
-7	2.0	-8.2
-8	46.1	50.9
-9	50.5	45.6
-10	17.3	15.6
-11	2.0	10.6
-12	34.6	-27.1
-13	37.5	-33.4
-14	29.8	-30.6
h 7 4		
0	18.3	-18.1
1	15.4	16.0
2	37.5	36.7
3	2.9	8.8
4	33.6	35.1
5	2.0	-3.5
6	29.8	33.1
7	2.5	15.7
8	2.0	4.3
9	31.7	-24.1
10	46.1	-39.5
11	42.3	-33.0
12	44.2	-35.2
13	8.7	10.7

h 7 4	F_o	F_c
-1	30.7	-29.3
-2	61.5	-60.3
-3	22.1	-18.2
-4	25.5	-26.6
-5	47.1	45.3
-6	8.7	14.0
-7	18.3	14.4
-8	7.6	-10.4
-9	2.0	-3.3
-10	2.0	2.5
-11	2.0	-0.8
-12	20.2	31.3
h 7 5		
0	10.6	11.2
1	2.0	1.2
h 7 5		
2	15.2	18.4
3	6.7	11.1
4	14.4	15.4
5	11.5	-15.3
6	2.0	-7.6
7	30.7	-25.4
8	10.6	-20.2
9	2.0	7.7
10	2.0	4.5
11	17.3	20.2
-1	10.6	13.3
-2	2.0	-1.0
-3	6.5	5.8
-4	35.5	-35.2
-5	26.9	-23.7
-6	28.8	-24.8
-7	2.0	-4.1
-8	25.5	21.2
-9	30.5	32.6
-10	30.7	27.6
-11	5.2	-5.5
-12	2.0	0.9
-13	15.2	-16.6
h 7 6		
0	65.0	-66.3
1	35.5	-29.2
2	2.0	-7.2
3	50.5	54.7
4	45.0	53.6
5	54.8	66.2
6	6.5	8.0
7	2.9	5.8
8	8.7	-14.3
9	23.1	-16.8
-1	75.9	-71.3
-2	22.1	-21.5
-3	6.7	-5.5
-4	25.8	24.5
-5	2.0	1.5
-6	28.8	25.1
-7	19.2	17.5
-8	32.7	25.1
-9	30.7	28.0
-10	7.7	15.6
-11	2.0	1.2
-12	35.5	-32.1
h 7 7		
0	3.9	2.9
-1	11.5	15.9
-2	23.1	23.0
-3	3.5	7.1
-4	2.0	3.2
-5	2.0	-19.5
-6	18.3	-18.3
-7	2.0	-10.1
-8	2.0	3.1
-9	16.3	13.1
-10	14.4	3.4
h 7 8		
0	12.5	-11.2
1	2.0	-8.6
2	2.0	7.1
3	2.0	-7.9
4	14.4	8.2
5	2.0	4.4
6	2.0	23.8
7	6.7	5.4
-1	11.5	-12.9
-2	34.6	-32.4
-3	21.1	-17.1
-4	2.0	-6.9
-5	32.7	28.5
-6	37.5	32.6
-7	38.4	35.8
-8	25.0	19.7
h 7 9		
0	21.1	16.8
1	2.0	1.7
2	2.0	2.9
3	2.0	-9.3
4	2.0	-4.7
5	13.5	-13.0
-1	27.9	21.0
-2	2.0	9.2
-3	12.5	3.6
-4	11.5	-12.9
-5	25.0	-11.2
h 7 10		
0	2.0	6.6
1	14.4	13.1
2	3.5	13.1
3	17.3	10.4
-1	2.5	3.6
-2	14.4	15.9
h 8 0		
1	15.2	-27.6
2	11.5	-12.5
3	15.2	16.7
4	29.8	34.3
5	23.1	21.4
6	22.1	20.5
7	1.3	1.4
8	21.1	-13.6
9	33.6	-27.4
10	20.2	-18.6
11	1.3	-10.8
12	1.3	-5.4
13	1.3	4.5
14	10.6	11.1

h 8 1	F_o	F_c
0	32.7	35.2
1	3.5	-7.4
2	1.3	-1.3
3	66.3	-62.8
4	75.9	-62.6
5	22.1	-26.5
6	14.4	-14.4
7	45.2	38.5
8	30.7	26.5
9	58.6	53.6
-1	6.7	-6.2
-2	31.7	35.6
-3	22.1	21.0
-4	31.7	31.1
-5	40.3	40.0
-6	18.3	14.3
-7	2.0	-1.0
-8	55.1	-70.5
-9	38.4	-40.4
-10	38.4	36.2
-11	1.3	1.4
-12	28.8	20.5
-13	35.5	33.4
-14	26.9	28.5
h 8 2		
0	1.3	4.2
1	18.3	20.5
2	27.9	29.7
3	56.7	56.5
4	30.7	27.3
5	36.5	33.2
6	17.3	20.6
7	1.3	1.7
8	45.2	-42.6
9	45.2	-32.5
10	54.8	-40.8
11	43.2	-33.9
12	2.0	1.1
13	24.0	21.4
-1	30.7	-34.6
-2	49.0	-51.9
-3	59.6	-59.2
-4	43.2	-45.0
-5	2.0	-11.3
-6	23.1	20.7
-7	39.4	36.5
-8	46.1	41.1
-9	28.8	25.2
-10	1.3	5.6
-11	1.3	1.5
-12	1.3	-8.2
-13	10.6	-11.5
-14	11.5	1.5
h 8 3		
0	65.3	-65.1
1	16.3	15.8
2	1.3	4.9
3	45.2	38.7
4	21.1	17.6
5	17.3	-12.3
6	15.4	-12.5
7	13.5	-14.6
8	45.0	33.7
9	10.5	-2.1
10	6.5	10.5
11	26.9	-23.2
12	36.5	-30.7
13	15.4	-14.3
-1	26.9	-26.2
-2	32.7	-31.1
-3	47.1	43.3
-4	52.8	54.6
-5	36.5	37.5
-6	1.3	5.4
-7	50.0	-53.7
-8	31.7	-29.7
-9	37.5	-37.5
-10	16.3	16.1
-11	16.3	22.0
-12	21.1	25.3
-13	1.3	4.9
-14	10.6	-13.1
h 8 4		
0	6.7	-22.4
1	1.3	-0.3
2	27.9	29.7
3	39.9	27.2
4	40.3	38.3
5	14.4	17.1
6	13.1	7.4
7	1.3	-7.3
8	1.3	2.0
9	11.5	-13.8
10	6.5	-11.7
11	1.3	4.6
12	11.5	-13.9
-1	42.3	-41.2
-2	47.1	-46.6
-3	41.3	-35.4
-4	5.2	-5.3
-5	13.5	5.7
-6	21.1	24.2
-7	33.6	28.1
-8	26.9	27.7
-9	15.4	14.8
-10	1.3	6.9
-11	1.3	4.7
-12	1.3	-6.8
-13	14.4	-13.0
h 8 5		
0	25.5	-25.1
1	24.0	-25.1
2	34.6	34.0
3	25.5	26.1
4	43.2	44.3
5	46.0	50.6
6	7.8	11.1
7	1.3	-1.0
8	44.2	-38.3
9	15.4	-12.5
10	37.5	-30.5
11	15.4	-5.5
-1	67.2	-59.3
-2	15.4	-16.3
-3	32.7	-32.0
-4	2.6	-10.7
-5	22.1	20.8

h 8 5	F_o	F_c
-6	22.1	21.1
-7	29.9	27.3
-8	2.6	6.5
-9	24.0	20.8
h 8 6		
-1	18.3	5.2
-2	1.3	-5.1
-3	1.3	-6.0
-4	19.2	-15.1
-5	1.3	-3.8
-6	1.3	7.6
-7	10.5	15.5
-8	10.5	11.1
-9	13.5	15.1
-10	1.3	3.0
-11	10.6	-12.6
-12	10.6	-12.7
h 8 7		
0	41.3	-35.8
1	7.7	6.9
2	18.3	17.0
3	20.2	27.8
4	1.3	12.9
5	1.3	-3.2
6	1.3	4.1
7	1.3	-7.7
8	18.3	21.3
-1	37.5	-31.4
-2	40.3	-36.9
-3	1.3	-3.5
-4	18.3	18.9
-5	23.1	21.1
-6	14.4	18.4
-7	1.3	-7.8
-8	10.5	7.8
-9	1.3	4.1
-10	20.2	21.1
h 8 8		
0	35.5	30.1
1	21.1	19.8
2	2.6	6.2
3	1.3	-8.8
4	25.9	-23.8
5	45.2	-39.0
6	27.9	-27.2
7	17.3	-13.8
-1	26.9	22.1
-2	15.7	11.8
-3	13.5	13.2
-4	1.3	3.1
-5	10.5	-10.2
-6	16.3	-12.8
-7	24.0	-19.4
-8	22.1	-21.4
-9	12.5	-17.3
h 8 9		
0	1.3	-4.2
1	35.3	-25.8
-1	1.9	-0.4
-2	24.0	22.8
h 9 0		
1	5.8	-11.8
2	3.9	0.8
3	45.2	-40.1
4	9.6	-9.6
5	41.3	-29.0
6	11.5	14.4
7	23.1	15.1
8	52.8	35.9
9	29.8	20.0
10	3.9	-5.6
11	3.9	-0.6
12	28.8	-28.9
13	7.7	-6.7
h 9 1		
0	22.1	28.8
1	24.0	27.3
2	19.2	22.0
3	27.5	26.3
4	6.7	-4.9
5	12.5	7.9
6	15.4	12.1
7	21.1	21.6
8	3.9	-5.3
9	49.0	-33.2
10	54.8	-36.8
11	53.8	-38.1
12	13.5	-11.4
-1	10.6	-15.2
-2	51.9	-49.0
-3	64.4	-55.7
-4	10.6	-10.5
-5	8.7	-1.1
-6	33.6	36.7
-7	36.5	28.7
-8	7.8	-0.3
-9	26.9	-18.5
-10	31.7	-24.1
-11	3.9	-0.8
-12	11.5	10.6
-13	37.5	36.0
h 9 2		
0	20.2	-26.0
1	10.6	-17.0
2	36.5	-33.3
3	15.4	14.1
4	3.9	2.7
5	38.4	39.2
6	5.8	-6.0
7	3.9	1.7
8	11.5	-5.9
9	10.6	20.0
10	13.5	11.8
11	3.9	-0.5
12	9.6	9.1
13	12.5	-13.2
-1	3.9	-4.6
-2	22.1	24.1
-3	7.8	-1.3
-4	37.5	26.3
-5	13.5	-14.0
-6	9.6	9.6
-7	3.9	1.0
-8	10.6	11.0
-9	3.8	-2.5
-10	10.6	-14.1

h 9 2	F_o	F_c
-11	3.9	-2.5
-12	20.8	-23.7
h 9 3		
0	14.4	-17.5
1	13.5	20.3
2	20.8	31.5
3	32.7	33.8
4	73.1	64.8
5	47.1	43.1
6	50.0	33.6
7	3.9	-1.8
8	24.0	-15.7
9	65.3	-45.4
10	76.8	-55.6
11	35.5	-28.5
-1	54.8	-56.5
-2	85.6	-75.1
-3	50.0	-52.9
-4	43.2	-46.2
-5	7.8	7.1
-6	33.6	37.1
-7	65.3	64.1
-8	40.3	43.4
-9	18.3	21.7
-10	10.6	11.7
-11	7.8	-5.7
-12	12.5	-16.5
-13	21.1	-22.7
h 9 4		
0	8.7	6.0
1	5.6	-8.6
2	15.4	17.8
3	17.3	-18.6
4	8.7	-7.3
5	15.4	-14.6
6	30.7	22.6
7	3.9	6.0
8	3.9	8.1
9	10.6	7.0
10	21.1	-16.2
-1	8.7	9.7
-2	25.0	-24.9
-3	3.9	-2.6
-4	3.9	-2.3
-5	22.1	23.5
-6	3.9	0.1
-7	19.2	12.1
-8	3.9	-4.2
-9	23.1	-16.1
-10	3.9	1.4
-11	3.9	-2.8
-12	18.3	12.8
h 9 5		
0	9.6	7.7
1	32.7	33.5
2	15.2	18.5
3	17.3	15.4
4	12.5	-16.6
5	3.9	-6.5
6	3.9	-6.3
7	26.5	19.4
8	12.5	12.0
-1	35.5	-32.0
-2	44.2	-46.7
-3	53.9	-54.2
-4	13.5	-16.9
-5	18.3	19.7
-6	51.9	51.8
-7	31.7	34.9
-8	23.1	23.7
-9	7.8	3.2
-10	18.3	-18.1
h 9 6		
0	22.1	-24.2
1	14.4	-17.0
2	8.7	-9.5
3	23.1	21.7
4	15.4	12.8
5	26.9	23.3
6	3.9	0.8
7	9.6	-4.0
-1	19.2	-17.5
-2	3.9	8.4
-3	3.9	4.5
-4	18.3	18.7
h 9 7		
0	17.3	12.4
1	22.1	16.4
2	4.8	6.2
3	17.3	-16.7
4	13.5	-12.5
5	39.4	-31.5
6	30.7	-25.1
7	18.3	-17.2
-1	11.5	6.5
-2	5.8	9.1
-3	17.4	17.4
-4	5.8	6.3
-5	5.8	6.1
-6	5.8	-0.7
-7	14.4	-11.8
-8	20.2	-19.5
-9	15.4	-16.8
h 9 8		
1	3.9	3.1
2	5.8	6.5
3	3.9	-3.3
4	14.4	10.0
10	3.5	-12.2
-1	3.9	-1.1
-2	27.5	-28.3
-3	10.6	-5.8
-4	15.3	-17.4
-5	9.6	9.3
-6	13.5	10.3
-7	15.4	16.1
h 9 9		
0	38.4	36.5
1	31.7	31.6
-1	28.6	25.6
-2	15.4	15.7

atoms and of the chlorine atom. The location of the rest of atoms was possible from the next three-dimensional electron density synthesis where nitrogen, oxygen and carbon atoms were clearly discernible. The calculation were performed on a Saab D21 computer using a set of crystallographic programs of Abrahamsson and Larsson [4,5].

Refinement of the structure. The coordinates of the atoms so far obtained were subjected to least-square refinement using a program written by R. Hazell [6]. The computations were carried out on a GIER computer at Slovak Academy of Sciences in Bratislava. First, the coordinates and the individual isotropic temperature factors of 18 atoms together with the scale factor were refined. The least-square program employs a block-diagonal aproximation and weighting scheme proposed by Hughes [7]. The scale factor and overall temperature factor are refined by means of 2×2 matrix and all individual temperature factors are modified by the shift computed from the 2×2 matrix. The effects of anomalous dispersion were neglected. After six cycles an R-value of 17.2% was obtained. At this point the least-square refinement was extended to include 602 non-observed reflections and anisotropic thermal vibrations. The scattering curves were approximated by Bassi polynomials [8]. After 3 cycles, the final R-index was 13.3% for the observed reflections and 16.4% for all 2178 structure factors.
The final atomic parameters and their standard deviations are given in Table I, while Table II includes the observed and calculated structure factors. Figure 1 shows a survey of the structure.

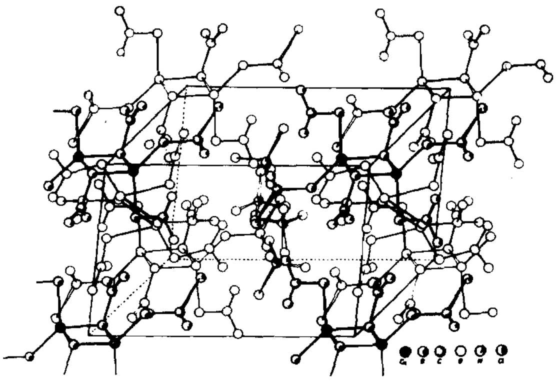


Figure 1. Atoms in the unit cell of $Cu(SCN_2H_4)_3ClO_4$.

Results and Discussion

Distances and angles are given in Table III together with the standard deviations (in parantheses). They were calculated using a program written by Danielsen and Nyborg [9]. The intramolecular distances and bond angles are shown in Figure 2. The structure consists of perchlorate anions and binuclear complex cations $[Cu_2(thiourea)_6]^{2+}$. The Cu - Cu distance in this complex is 2.862±0.003 Å. The thiourea ligands are coordinated to the monovalent copper atoms trough the sulphur atoms. The coordination around each Cu^I is a slightly distorted tetahedron. Two of the six sulphur atoms bonded to the binuclear complex cation are shared between the two copper atoms (bi-coordinated sulphur atoms).

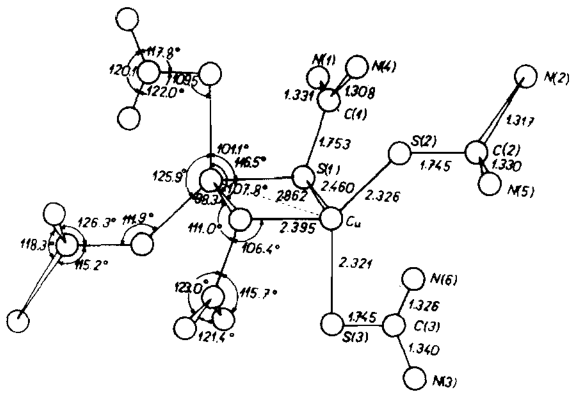


Figure 2. Arrangement of atoms in the complex ion $[Cu(SCN_2H_4)_3]^+$.

Table III. Interatomic distances in Å and bond angles (standard deviations are given in parentheses)

Bond	Bond angle
Cu—Cu: 2.862(3)	S(1)—Cu—S(1)′: 107.8(0.1)°
Cu—S(1): 2.460(4)	S(1)—Cu—S(2): 98.3(0.2)°
Cu—S(1)′: 2.395(4)	S(1)′—Cu—S(2): 116.5(0.2)°
Cu—S(2): 2.326(5)	S(1)—Cu—S(3): 104.1(0.1)°
Cu—S(3): 2.321(4)	S(1)′—Cu—S(3): 102.4(0.2)°
S(1)—C(1): 1.75(1)	S(2)—Cu—S(3): 125.9(0.2)°
S(2)—C(2): 1.75(2)	Cu—S(1)—Cu: 72.2(0.1)°
S(3)—C(3): 1.75(2)	Cu—S(1)—C(1): 111.0(0.5)°
C(1)—N(1): 1.33(2)	Cu—S(1)′—C(1)′: 106.4(0.5)°
C(1)—N(4): 1.31(2)	Cu—S(2)—C(2): 111.9(0.7)°
C(2)—N(2): 1.32(4)	Cu—S(3)—C(3): 109.5(0.7)°
C(2)—N(5): 1.33(3)	S(1)—C(1)—N(1): 115.7(1.2)°
C(3)—N(3): 1.34(2)	S(1)—C(1)—N(4): 123.0(1.5)°
C(3)—N(6): 1.33(2)	S(2)—C(2)—N(2): 115.2(1.7)°
Cl—O(1): 1.39(3)	S(2)—C(2)—N(5): 126.3(1.8)°
Cl—O(2): 1.44(2)	S(3)—C(3)—N(3): 117.8(1.4)°
Cl—O(3): 1.46(2)	S(3)—C(3)—N(6): 122.0(1.3)°
Cl—O(4): 1.46(2)	N(1)—C(1)—N(4): 121.4(1.5)°
N(2) . . . O(4): 3.06(3)	N(2)—C(2)—N(5): 118.3(2.1)°
N(3) . . . O(1): 3.19(4)	N(3)—C(3)—N(6): 120.1(1.5)°
N(3) . . . O(2): 3.14(3)	O(1)—Cl—O(2): 108.3(1.5)°
N(3) . . . O(3): 3.16(3)	O(1)—Cl—O(3): 110.5(1.5)°
N(3) . . . O(4): 3.08(3)	O(1)—Cl—O(4): 113.0(1.5)°
N(5) . . . O(3): 2.98(3)	O(2)—Cl—O(3): 107.9(1.3)°
N(6) . . . O(3): 3.07(3)	O(2)—Cl—O(4): 109.2(1.1)°
N(6) . . . O(4): 3.23(3)	O(3)—Cl—O(4): 107.9(1.3)°

The bridging bond lengths Cu - S: 2.395 and 2.460± ±0.004 Å are significantly longer than the remaining four Cu - S distances: 2.321–2.326±0.004 Å, respectively (mono-coordinated sulphur atoms). The S - Cu - S bond angles range from 98.3 to 125.9±0.2°. Similar differences were observed in the crystal structure of $Cu(thiourea)_3Cl$. The thiourea ligands which form bridges between two copper atoms possesse two unequal Cu - S distances: 2.379 and 2.434 Å, respectively. The remaining two Cu - S distances in the coordination tetrahedron around the copper atom are 2.278 and 2.346 Å, respectively.[2]

The binuclear complex cation $[Cu_2(thiourea)_6]^{2+}$ is centrosymmetric. The interatomic distances in the

Table IV. The mean bond length (in Å) and bond angle data for the thiourea complex

Complex	C—N	C—S	<Me—S—Me	<Me—S—C	<N—C—N	<S—C—N	Literature
$Nitu_4Cl_2$	1.33	1.73		114°	121°	120°	/14/
$Nitu_2(NCS)_2$	1.315	1.758	96.4°	111°	122°	119°	/15/
$Cutu_3Cl$	1.326	1.722	134°	114°	122°	119°	/2/
$Cutu_3ClO_4$	1.325	1.747	72,2°	110°	120°	120°	This work
$Zntu_2Cl_2$	1.28	1.78		109°	123°	119°	/16/
$Agtu_2Cl$			77.3°, 133°				/17/
$Cdtu(HCO_2)_2$	1.295	1.76	92.4°	109°	120°	120°	/18/
$Cdtu_2Cl_2$	1.325	1.64		113°	115°	122°	/19/
$Pbtu_2Cl_2$	1.35	1.73	84.4°	110°			/20/
$Pbtuac_2$	1.37	1.68	94.6°, 105.8°	116°	121°	120°	/21/
$CS(NH_2)_2$	1.33	1.71			116°	122°	/10/

tu = thiourea

thiourea ligands are only slightly changed in comparison with a free thiourea molecule. The C - S distances in Cu(thiourea)ClO_4 range from 1.745 to 1.753 Å (table 3) whereas the C - S bond length in a free thiourea molecule is 1.71 Å.[10] The slight elongation of the C - S bond lengths in the thiourea transition-metal complexes is observed for the most crystal structures (Table IV). The C - S and C - N bond lengths in the free thiourea molecule are influenced (a) by a fractional positive charge on the N atom owing to the contribution from polar or delocalized bonding structure $^-S—C(={}^+NH_2)NH_2$, (b) by hybridization state of the nitrogen and carbon atoms. The nitrogen and carbon atoms in thiourea are trigonally hybridized (sp^2). For example, single bond radii of a carbon atom are 0.777 Å for sp^3–, 0.73 Å for sp^2– and 0.69 Å for sp-hybridization. (c) Influence of the intramolecular van der Waals-London attraction between the NH_2 and high polarizable CS group confers additional stability upon the molecule.[11,12] Owing to these factors, the experimental carbon-sulphur and carbon-nitrogen bond lengths are significantly shorter than the generaly accepted single bond values, 1.82 and 1.48 Å (Table IV). Close resemblance of the interatomic distances both in free and in coordinated thiourea molecules must be taken into account by explanation of the nature of the coordination bond.

Sulphur atoms form two or three coordinative bonds in the polynuclear thiourea compounds. The corresponding bond angles Me - S - Me range from 72.2 to 134° (Table IV). The bond angle Cu - S - Cu in the binuclear Cu(thiourea)$_3ClO_4$ complex is 72.2°. It is directly comparable with the bond angle Ag -S - Ag (77.3°) in Ag(thiourea)$_2$Cl.[17] The orbital interactions are most easily understood in terms of a bridging poly-center delocalized system involving a pπ suphur-carbon molecular orbital and its electron pair and σ (*e.g.* sp^3 hybrids) orbitals from each copper. Another poly-center bonding molecular orbital can be constructed from the sulphur 3 d_{xz} orbital which overlaps with the appropriately oriented metal d orbitals . These would led to bonding π poly-centre molecular orbital which would be able to return much of the charge withdrawn from the C - S pπ molecular orbital by the poly-centre σ - pπ - σ molecular orbital. The wide angle bridging Cu - S - Cu (134°) in the Cu(thiourea)$_3$Cl complex can be explained in terms of two filled sp^2 sulphur orbitals forming two electron-pair donor-acceptor bonds. These orbitals are non-bonding in thiourea itself and use of these orbitals would not elongate the C - S bond distance.[13] The orbital interaction are shown in Figure 3.

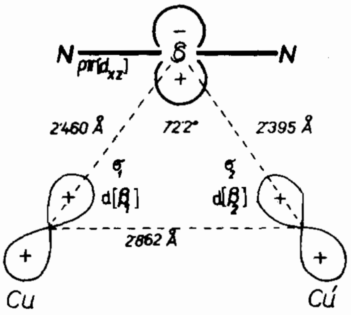
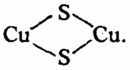


Figure 3. The orbital interactions in the bridging poly-center system 

The S - C - N bond angles in Cu(thiourea)$_3ClO_4$ range from 115.2 to 126.3° (Table III), while N - C - N angles deviate from 120° only in limits of standard deviations (118.3-121.4°). The mean C - N bond length: 1.33 Å is very close to the mean value of the C - N distance in the free thiourea molecule: 1.33 Å.[10]

The thiourea ligands are all planar within experimental errors. The maximal deviations of atoms

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from the mean planes transposed through the group of atoms SCN_2 are 0.003 Å in the case of the S(1) C(1) N(1) N(4) group, 0.07 Å for the S(2) C(2) N(2) N(5) group and 0.05 Å for the S(3) C(3) N(3) N(6) group of atoms.

The ClO_4 anion has the tetrahedral arrangement with the Cl - O distances 1.39-1.46 Å and with the O - Cl - O bond angles 108-113° (Table III). The negative charge of the ClO_4 anion is distributed over anion in the Cu(thiourea)$_3$Cl complex. The creation of the binuclear complex ion $Cu_2(thiourea)_6^{2+}$ instead of spiral chains by substitution ClO_4^- for Cl^- is most probably affected by the space effect of the negative ions. The perchlorate groups are large enough to create a sheet of negative ions completely neutralizing the partial positive charges localized at the NH_2 groups. Layers of ClO_4^- anions alternate with layers of $[Cu_2(thioura)_6]^{2+}$. They are perpendicularly oriented to the [100] direction. Only the non-bridging thiourea molecules take part on hydrogen bonds. While the N(2) and N(5) atoms are associated with only one short N - H... O contact, the other thiourea group containing N(3) and N(6) atoms is bonded by six hydrogen bonds.

Free rotation of the $C(NH_2)_2$ groups around the C - S bonds is hindered by short N - H... O contacts. Each of N(2) and N(5) atoms are associated with one hydrogen bond, N(2)... O(4) and N(5)... O(3) being 3.06 and 2.98 Å, respectively. The positions N(3) and N(6) atoms are fixed by four and two short N - H... O contacts (Table III), respectively. It seems to be reasonable to admit a limited oscillation of the N(5) - C(2) - N(2) group as it follows from the lower electron densities at the positions of these atoms (approximately 2/3 of the peak hight at the positions of the other nitrogen atoms), from the large value of the corresponding temperature factor components and from the substantialy smaller number of NH...O contacts of this group in comparison with those of the N(3) - C(3) - N(6) group.

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