Table 2 (*cont.*)

O(1)—O(2)	1	2·730 (11)
O(1)—O(3)	2	2·765 (9)
O(2)—O(3)	2	2·610 (8)
O(3)—O(3)	1	2·613 (8)
Average values		
Ca(1)-O		2·351
Ca(2)-O		2·386
Ca—–O		2·369
Si—–O		1·645
(*b*) Angles		
Ca(1) octahedron		
O(1)-Ca(1)-O(2)	2	84·9 (2)
O(1)-Ca(1)-O(2)	2	95·0 (2)
O(1)-Ca(1)-O(3)	2	83·5 (2)
O(1)-Ca(1)-O(3)	2	96·5 (2)
O(2)-Ca(1)-O(3)	2	67·4 (2)
O(2)-Ca(1)-O(3)	2	112·5 (2)
Ca(2) octahedron		
O(1)-Ca(2)-O(3)	2	80·9 (2)
O(1)-Ca(2)-C(3)	2	91·4 (2)
O(2)-Ca(2)-O(3)	2	100·7 (2)
O(2)-Ca(2)-O(3)	2	87·6 (2)
O(3)-Ca(2)-O(3)	1	65·2 (2)
O(3)-Ca(2)-O(3)	2	86·8 (2)
O(3)-Ca(2)-O(3)	1	120·7 (2)

Table 2 (*cont.*)

Si(1) tetrahedron		
O(1)-Si(1) -O(2)	1	112·2 (4)
O(1)-Si(1) -O(3)	2	114·8 (3)
O(2)-Si(1) -O(3)	2	104·4 (3)
O(3)-Si(1) -O(3)	1	105·0 (3)

The results confirm the structure found by Smith, Majumdar & Ordway (1963), but show that the distortion of the SiO_4 tetrahedron found by these workers is not real.

The author wishes to thank Miss S. Melzer for her assistance. The work was supported by the Arbeitsgemeinschaft Industrieller Forschungsvereinigungen (AIF). Calculations were done on an IBM 7094 computer at the Deutsches Rechenzentrum Darmstadt, Germany.

References

Czaya, R. (1970). *Z. anorg. allgem. Chem.* In the press.

Smith, D. K., Majumdar, A. & Ordway, F. (1963). *Acta Cryst.* **18**, 787.

Yamaguchi, G., Ono, Y., Kawamura, S. & Soda, Y. (1963). *J. Ceram. Assoc. Japan*, **71**, 9, 21.

Yannaquis, N. (1955). *Rev. Matér. Constr.* **480**, 213.

Acta Cryst. (1971). B**27**, 849

Crystal data and structure of $[(NH_3CH_2CH_2)_2NH_2]Cl(CuCl_4)$ at 20 °C and 120 °C.

By Gary L. Ferguson and B. Zaslow, *Department of Chemistry, Arizona State University, Tempe, Arizona* 85281, *U.S.A.*

(*Received* 4 *February* 1970 *and in revised form* 19 *August* 1970)

Cell constants for $[(NH_3CH_2CH_2)_2NH_2]Cl(CuCl_4)$ are $a=7{\cdot}117\pm0{\cdot}004$, $b=23{\cdot}78\pm0{\cdot}01$ and $c=7{\cdot}342\pm0{\cdot}004$ Å at 20°C; the space group is *Pnma*. Atomic parameters have been determined from zero and higher level precession data. The compound exhibits a network of planar $CuCl_4^{2-}$ ions, and thermochromism is observed both above and below room temperature. X-ray data indicate that heavy atom positions at 120°C are essentially unchanged from their values at 20°C.

Although originally characterized as a $CuCl_5^{3-}$ salt (Jonassen, Crumpler & O'Brien, 1945), it has been established that bis-(2-ammonioethyl)ammonium monochloride tetrachlorocuprate(II), $[(NH_3CH_2CH_2)_2NH_2]Cl(CuCl_4)$, is a double salt having both Cl^- and $CuCl_4^{2-}$ ions (Zaslow & Ferguson, 1967). Inasmuch as the $CuCl_4^{2-}$ ion can demonstrate both a tetrahedral geometry (*e.g.* Morosin & Lingafelter, 1961) and a square-planar geometry (Willett, 1964), and high-temperature crystal data have not previously been recorded for thermochromic $CuCl_4^{2-}$ salts, the following details of the structure of $[(NH_3CH_2CH_2)_2NH_2]Cl(CuCl_4)$ are of interest.

The method of Jonassen, Crumpler & O'Brien (1945) was used to prepare $[(NH_3CH_2CH_2)_2NH_2]Cl(CuCl_4)$. Crystals are yellow plates at room temperature, become pale green below room temperature, and convert to orange-brown upon heating to 120°C. Specimens suitable for X-ray analysis were obtained by slow evaporation of water from an aqueous solution of the compound; their diffraction symmetry is orthorhombic, *mmm*. Cell constants were obtained from measurements of a Guinier powder diagram, and are $a=7{\cdot}117\pm0{\cdot}004$, $b=23{\cdot}78\pm0{\cdot}01$ and $c=7{\cdot}342\pm0{\cdot}004$ Å at 20°C. Conditions for reflection are none for *hkl*, $k+l=2n$ for 0*kl*, and $h=2n$ for *hk*0. Possible space groups are *Pnma* or $Pn2_1a$; subsequently, application of the $N(z)$ test (Howells, Phillips & Rogers, 1950) fixed the space group as *Pnma*. The calculated density, assuming $Z=4$, and the observed density determined by flotation in acetone and bromoform are 1·85 and 1·87 g.cm^{-1}, respectively.

All intensity data were obtained from a crystal having dimensions $0{\cdot}15\times0{\cdot}02\times0{\cdot}2$ mm. Precession photographs taken with Zr-filtered Mo $K\alpha$ radiation at 20°C yielded 286 independent data. Timed exposures were rated visually and intensities were obtained for the levels, *h*0*l*, *h*2*l*, *h*3*l*, *h*4*l*, *h*6*l* and *hk*0. Intensities were not evaluated from photographs of the levels *h*1*l* and *h*5*l*; only a small number of extremely weak reflections were detected at these levels, except for 210, 250, 450 and 650 which were processed with *hk*0 data. Data reduction and other calculations utilized a modified version of the *X-ray* 63 program (*Crystal Structure Calculations System, X-ray* 63, 1964). Absorption corrections were not applied and hydrogen atoms were neglected.

Scattering curves for the structure factor calculations were obtained from the *International Tables for X-ray Crystallography* (1962).

At 120 °C, the crystals of $[(NH_3CH_2CH_2)_2NH_2]Cl(CuCl_4)$ become orange-brown. Lattice constants at this temperature are $a=7{\cdot}15\pm0{\cdot}03$, $b=23{\cdot}70\pm0{\cdot}08$ and $c=7{\cdot}36\pm0{\cdot}03$ Å; these were measured from precession *h*0*l* and *hk*0 nets, which showed *mm* symmetry. Temperature control was achieved using a heating element supported mechanically by the beam collimator so that the crystal could be aligned with the heater in place. Reference films of the *h*0*l* and *hk*0 nets were also photographed at 20 °C, when the heater was inactive, for the same camera settings and exposure times that were employed at 120 °C; the sets of photographs were developed simultaneously. Exposure times at 120 °C were shorter than the maximum times used in the intensity study made at 20 °C. A comparison of intensities of 51 independent reflections at the two temperatures revealed 48 to be the same, although the diffraction maxima on the high-temperature photographs were more diffuse. Three reflections that were barely visible at 20 °C were unobserved at 120 °C.

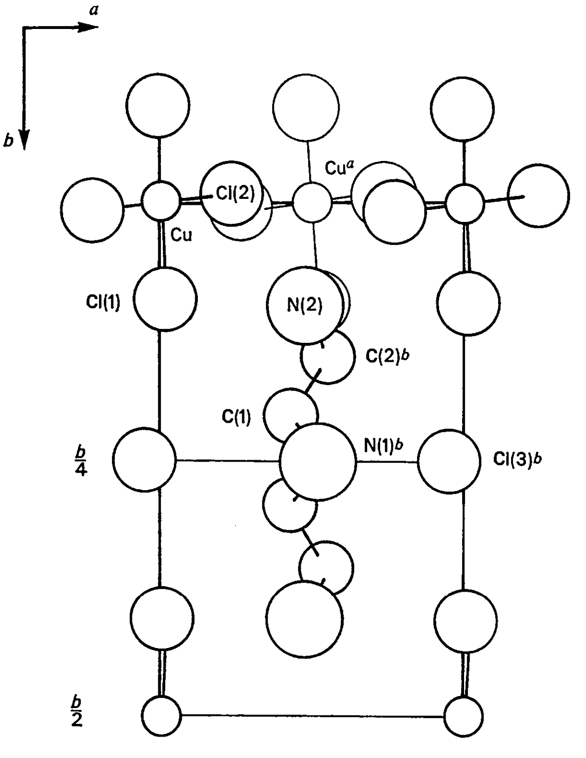

Fig. 1. A portion of the unit cell of $[(NH_3CH_2CH_2)_2NH_2]Cl(CuCl_4)$ as viewed in the *c* axis direction. The diagram shows three of the four $CuCl_4^{2-}$ that are adjacent to the terminal $-NH_3^+$ of the cation.

The structure determination was made at 20 °C using the observed data after correcting for the Lorentz and polarization factors. Corrected, observed structure factors, F_o, are listed in Table 1; *U* denotes unobserved reflections. The copper atoms are located in special positions on centers of symmetry while trial parameters for Cl(1) and Cl(2) were obtained by reference to $(NH_4)_2CuCl_4$ (Willett, 1964). A three-dimensional Fourier map, with signs of the structure factors based on a trial model for $CuCl_4^{2-}$, located Cl(3); an additional cycle of calculations determined positions for N(1), N(2), C(1) and C(2). Refinement was obtained by three cycles of full-matrix least-squares calculations using isotropic temperature factors, followed by three cycles employing anisotropic temperature factors having the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$. Unitary weights were applied to the observed reflections in all calculations. The value for $R=\sum||F_o|-|F_c||/\sum|F_o|$, omitting unobserved reflections, minimized at 0·10. A difference synthesis based on the refined atom parameters showed no spurious peaks. Final atomic coordinates and thermal parameters are listed in Table 2, with standard deviations specified in parentheses for the least-significant figures.

Table 1. *Observed and calculated structure factors for* $[(NH_3CH_2CH_2)_2NH_2]Cl(CuCl_4)$ *at* 20 °C

h	k	l	F_o	F_c
0	0	2	287	264
0	0	4	201	199
0	0	6	59	56
0	0	8	U	-14
1	0	1	113	143
1	0	2	91	-81
1	0	3	108	102
1	0	4	25	32
1	0	5	68	73
1	0	6	59	-65
1	0	7	26	30
1	0	8	21	17
2	0	0	209	249
2	0	1	U	-21
2	0	2	325	350
2	0	3	U	12
2	0	4	104	107
2	0	5	U	-9
2	0	6	42	48
2	0	7	U	-5
2	0	6	22	21
3	0	1	101	117
3	0	2	U	-9
3	0	3	120	108
3	0	4	108	-102
3	0	5	41	47
3	0	6	U	-2
3	0	7	44	43
3	0	8	43	-46
4	0	0	226	241
4	0	1	U	25
4	0	2	86	97
4	0	3	U	-23
4	0	4	113	110
4	0	5	U	-1
4	0	6	38	41
5	0	1	74	90
5	0	2	67	-62
5	0	3	49	52
5	0	4	U	-15
5	0	5	76	62
5	0	6	77	-71
6	0	0	57	44
6	0	1	24	-30
6	0	2	102	106
6	0	3	U	12
6	0	4	38	39
6	0	5	22	-18
6	0	6	38	27
7	0	1	53	43
7	0	2	U	-7
7	0	3	55	55
7	0	4	63	-57
8	0	0	63	63
8	0	1	22	23
8	0	2	U	18
8	0	3	22	-22
8	0	4	37	37
9	0	1	30	33
9	0	2	29	-22
9	0	3	U	9
2	1	0	23	26
4	1	0	U	6
6	1	0	U	-4
8	1	0	U	-13
0	2	2	46	-47
0	2	4	105	95
0	2	6	56	55
0	2	8	21	24
1	2	1	152	136
1	2	2	37	-40
1	2	3	91	88
1	2	4	75	71
1	2	5	65	63
1	2	6	41	-36
1	2	7	24	30
1	2	8	34	32
2	2	0	43	-45
2	2	1	16	-21
2	2	2	136	143
2	2	3	U	14
2	2	4	32	35
2	2	5	U	-1
2	2	6	46	50
2	2	7	U	5
2	2	8	52	54
3	2	1	93	94
3	2	2	52	59
3	2	3	77	88
3	2	4	20	-21
3	2	5	40	35
3	2	6	65	60
3	2	7	42	40
4	2	0	124	144
4	2	1	22	27
4	2	2	16	27
4	2	3	U	-14
4	2	4	78	82
4	2	5	U	14
4	2	6	43	46
5	2	1	71	81
5	2	2	U	-9
5	2	3	42	44
5	2	4	61	56
5	2	5	59	57
5	2	6	U	-12
5	2	7	U	8
5	2	8	29	27
6	2	0	21	29
6	2	1	19	-26
6	2	2	86	94
6	2	3	U	21
6	2	4	32	34
6	2	5	U	-5
6	2	6	36	27
6	2	7	U	5
6	2	8	31	30
7	2	1	46	49
7	2	2	25	24
7	2	3	60	61
7	2	4	U	-13
7	2	5	U	12
7	2	6	34	29
7	2	7	32	34
8	2	0	76	72
8	2	1	22	23
8	2	2	32	25
8	2	3	U	-20
8	2	4	45	39
8	2	5	U	7
8	2	6	30	24
9	2	1	46	41
0	3	3	122	-115
0	3	5	86	-86
0	3	7	61	-60
0	3	9	37	-37
1	3	2	62	-64
1	3	3	U	-23
1	3	4	76	-72
1	3	5	U	9
1	3	6	57	-55
1	3	7	U	-5
1	3	8	33	-33
2	3	0	53	-58
2	3	1	58	-62
2	3	2	40	-49
2	3	3	68	-72
2	3	4	U	-18
2	3	5	82	-80
2	3	6	U	-4
2	3	7	61	-57
3	3	1	51	-52
3	3	2	33	-37
3	3	3	U	-17
3	3	4	43	-42
3	3	5	22	-16
3	3	6	36	-40
4	3	0	59	-62
4	3	1	U	-9
4	3	2	37	-40
4	3	3	56	-57
4	3	4	U	-25
4	3	5	46	-50
4	3	6	U	-2
4	3	7	32	-37
5	3	1	39	-45
5	3	2	U	-12
5	3	3	37	-57
6	3	0	43	-31
6	3	1	U	-18
6	3	2	34	-36
7	3	1	33	-37
8	3	0	30	-25
0	4	0	164	163
0	4	2	30	-37
0	4	4	96	90
0	4	6	53	52
1	4	2	44	-49
1	4	3	79	82
1	4	4	60	54
1	4	5	78	68
1	4	6	45	-45
1	4	7	36	38
1	4	8	22	25
2	4	0	54	-63
2	4	1	U	-25
2	4	2	111	115
2	4	3	U	0
2	4	4	23	23
2	4	5	U	-15
2	4	6	44	45
2	4	7	U	-7
2	4	8	50	52
3	4	1	54	64
3	4	2	32	35
3	4	3	67	76
3	4	4	41	-45
3	4	5	57	40
3	4	6	34	37
3	4	7	52	50
4	4	0	69	88
4	4	1	U	20
4	4	2	U	-14
4	4	3	U	-28
4	4	4	56	57
4	4	5	U	-4
4	4	6	35	38
5	4	1	35	39
5	4	2	U	-20
5	4	3	18	21
5	4	4	32	37
5	4	5	47	54
5	4	6	21	-27
5	4	7	22	20
5	4	8	25	17
6	4	0	20	-20
6	4	1	U	-27
6	4	2	44	50
6	4	3	U	15
6	4	4	U	11
6	4	5	U	-12
6	4	6	U	22
6	4	7	U	-3
6	4	8	35	34
7	4	2	23	20
7	4	3	30	31
7	4	4	U	-16
7	4	5	U	6
7	4	6	26	25
7	4	7	37	41
8	4	0	28	35
8	4	1	U	25
8	4	2	U	-4
8	4	3	U	-12
8	4	4	22	23
8	4	5	U	12
8	4	6	25	21
2	5	0	48	47
4	5	0	17	27
6	5	0	33	30
0	6	0	U	21
0	6	4	34	37
0	6	6	36	36
0	6	8	24	26
0	6	10	41	51
1	6	3	18	18
1	6	4	66	60
1	6	5	61	55
1	6	6	31	-32
1	6	7	56	54
1	6	8	29	30
1	6	9	43	52
2	6	0	177	-141
2	6	2	31	35
2	6	3	33	39
2	6	4	U	-13
2	6	5	24	24
2	6	6	32	31
2	6	7	16	19
2	6	8	59	53
3	6	1	13	15
3	6	2	42	50
3	6	3	37	47
3	6	4	U	-16
3	6	5	38	35
3	6	6	57	58
3	6	7	54	58
3	6	8	U	-5
3	6	9	30	33
4	6	0	35	43
4	6	1	30	37
4	6	2	36	-44
4	6	3	23	19
4	6	4	38	35
4	6	5	47	43
4	6	6	33	31
4	6	7	28	27
4	6	8	18	18
4	6	9	U	8
4	6	10	38	40
5	6	1	38	44
5	6	2	U	-2
5	6	3	26	26
5	6	4	58	60
5	6	5	49	55
5	6	6	U	0
5	6	7	21	20
5	6	8	34	34
5	6	9	36	33
6	6	0	19	-26
6	6	1	U	-13
6	6	2	39	40
6	6	3	41	43
6	6	4	U	7
6	6	5	23	21
6	6	6	21	20
6	6	7	21	20
6	6	8	36	34
7	6	1	35	33
7	6	2	22	30
7	6	3	44	49
7	6	4	U	2
7	6	5	21	13
7	6	6	41	40
7	6	7	37	56
8	6	0	37	35
8	6	1	22	28
8	6	2	U	-1
8	6	3	U	-2
8	6	4	24	23
8	6	5	25	22
8	6	6	22	21
8	6	7	18	12
9	6	1	40	35
9	6	2	U	1
9	6	3	22	14
9	6	4	26	28
9	6	5	36	35
2	7	0	U	9
4	7	0	U	-14
6	7	0	23	16
8	7	0	U	-2
0	8	0	287	255
2	8	0	84	74
4	8	0	155	144
6	8	0	23	19
8	8	0	63	43
2	9	0	U	12
4	9	0	U	0
6	9	0	30	33
8	9	0	U	-4
0	10	0	245	219
2	10	0	94	73
4	10	0	151	144
6	10	0	57	55
8	10	0	89	76
2	11	0	U	10
4	11	0	27	-25
6	11	0	U	7
8	11	0	29	-20
0	12	0	280	251
2	12	0	140	129
4	12	0	151	153
6	12	0	56	44
8	12	0	61	47
2	13	0	U	12
4	13	0	U	-13
6	13	0	U	16
8	13	0	28	-29
0	14	0	U	36
2	14	0	25	-31
4	14	0	30	38
6	14	0	U	1
8	14	0	36	29
2	15	0	19	-17
4	15	0	51	-54
6	15	0	U	-7
8	15	0	35	-30
0	16	0	55	51
2	16	0	U	-5
4	16	0	U	28
6	16	0	U	-10
2	17	0	41	41
4	17	0	24	19
6	17	0	44	46
0	18	0	U	6
2	18	0	U	-11
4	18	0	22	38
6	18	0	34	26
2	19	0	U	3
4	19	0	U	-17
6	19	0	U	32
0	20	0	215	202
2	20	0	166	158
4	20	0	93	114
6	20	0	59	56
2	21	0	U	23
4	21	0	U	-7
6	21	0	U	20
0	22	0	68	70
2	22	0	82	73
4	22	0	60	74
6	22	0	57	60
2	23	0	U	-17
4	23	0	43	-48
0	24	0	U	54
2	24	0	46	58
4	24	0	U	32
2	25	0	U	18
4	25	0	U	-3
0	26	0	43	-43
2	26	0	U	-17
4	26	0	20	-25
2	27	0	U	8
0	28	0	U	24
2	28	0	41	52
0	30	0	27	32

Table 2. *Final fractional coordinates and thermal parameters at* 20°C

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0	0	0	0·0071 (4)	0·0000 (1)	0·0072 (5)	0·0000 (3)	−0·0013 (5)	0·0023 (14)
Cl(1)	0·0162 (9)	0·0947 (4)	0·0411 (8)	0·0124 (9)	0·0000 (1)	0·0116 (17)	−0·0001 (4)	−0·0001 (11)	0·0009 (9)
Cl(2)	0·2336 (6)	−0·0013 (3)	0·2078 (6)	0·0070 (7)	0·0005 (2)	0·0085 (7)	0·0000 (4)	−0·0022 (6)	−0·0002 (9)
Cl(3)	0·4493 (11)	0·25	0·5400 (12)	0·0127 (15)	0·0004 (3)	0·0094 (22)	0	−0·0001 (12)	0
N(1)	0·020 (4)	0·25	0·546 (7)	0·0054 (46)	−0·0006 (6)	0·0092 (83)	0	0·0039 (63)	0
N(2)	0·493 (4)	0·098 (1)	0·024 (5)	0·0188 (37)	0·0002 (5)	0·0098 (54)	0·0026 (18)	−0·0056 (50)	0·0003 (58)
C(1)	0·426 (5)	0·198 (1)	0·036 (11)	0·0410 (94)	0·0001 (6)	0·0204 (134)	−0·0015 (20)	0·0136 (120)	−0·0031 (44)
C(2)	0·048 (3)	0·149 (1)	0·555 (8)	0·0088 (36)	0·0001 (1)	0·0046 (56)	−0·0001 (10)	−0·0026 (43)	0·0000 (0)

The structure analysis shows

$[(NH_3CH_2CH_2)_2NH_2]Cl(CuCl_4)$

to be a double salt with both square-planar tetrachlorocuprate(II) ions and chloride ions, Cl(3). Sheet-like networks of $CuCl_4^{2-}$ ions are located at the levels $b=0$ and $\frac{1}{2}$; Cu and Cl(2) atoms are nearly coplanar while Cl(1) atoms extend above and below the plane. The $CuCl_4^{2-}$ ions pack so that four Cl(1) atoms and four Cl(2) atoms form a pocket into which fit terminal $-NH_3^+$ groups from the linearly extended cations; nitrogen atoms in these groups are denoted as N(2). Cations and Cl(3) are found between the layers of $CuCl_4^{2-}$. Both Cl(3) and N(1), the central nitrogen atom of the cation, are found on the mirror plane at $y=\frac{1}{4}$. Some of these packing features are illustrated in Fig. 1. Interatomic distances and bond angles are listed in Table 3, wherein standard deviations are given in parentheses and refer to the last significant figure. Atoms with superscripts in Table 3 are related to the atom positions listed in Table 2: $a=\frac{1}{2}, 0, \frac{1}{2}$; $b=\frac{1}{2}+x, y, \frac{1}{2}-z$; $c=\frac{1}{2}-x, -y, \frac{1}{2}+z$; $d=-x, -y, -z$; $e=x, \frac{1}{2}-y, z$. Superscripts f and g refer to the following translations: $f=(+1, 0, 0)$; $g=(0, 0, -1)$.

Table 3. *Interatomic distances and bond angles at* 20°C

Cu —Cl(1)	2·276 (9) Å
Cu —Cl(2)	2·272 (4)
Cu^a —Cl(2)	2·876 (4)
$Cl(1)^b$–Cl(3)	3·770 (9)
C(1)—$C(2)^b$	1·60 (4)
$N(1)^b$–C(1)	1·53 (4)
N(2)—$C(2)^b$	1·40 (4)
$N(1)^b$–$Cl(3)^b$	3·06 (3)
N(2)—Cl(1)	3·40 (3)
N(2)—Cl(2)	3·46 (3)
N(2)—$Cl(1)^{+f}$	3·73 (3)
N(2)—$Cl(2)^{d+f}$	3·31 (3)
N(2)—$Cl(1)^b$	3·20 (4)
N(2)—$Cl(2)^b$	3·68 (3)
N(2)—$Cl(1)^{b+g}$	4·16 (4)
N(2)—$Cl(2)^{c+g}$	3·50 (3)
$Cl(1)^b$–Cu^a —$Cl(2)^c$	90·5 (2)°
Cl(2) -Cu^a —$Cl(2)^b$	88·3 (1)
N(2)—$C(2)^b$ -C(1)	108·0 (2·3)
$C(2)^b$ -C(1)—$N(1)^b$	100·6 (2·2)
C(1)—$N(1)^b$-$C(1)^e$	107·5 (3·2)

Willett (1964) reported that salts having planar $CuCl_4^{2-}$ ions exhibit thermochromism below room temperature; the low temperature color change to pale green was subsequently accounted for (Willett, Liles & Michelson, 1967) in terms of structural adjustment, *i.e.* a difference in coordination geometry about some of the Cu atoms. However, because of the constancy in lattice parameters and X-ray intensities at 20 and 120°C, major shifts in positions of the copper and chlorine atoms cannot explain the color change from yellow to orange-brown observed for

$[(NH_3CH_2CH_2)_2NH_2]Cl(CuCl_4)$

at these two temperatures. Thermochromism above room temperature may be a consequence of spectral band broadening with no shift in position of band maxima. Alternatively, the high temperature thermochromism may arise from a shift in location of hydrogen atoms involved in N-H···Cl interactions, which would lead to a shift in the position of the charge transfer band to longer wavelengths as temperature is increased. The effect of small displacements of hydrogen atoms on the X-ray intensities would be negligible.

The assistance of Dr James Sawyer who prepared the Guinier photograph, and of Dr B. Morosin who made the crystallographic program available, is gratefully acknowledged. All calculations were performed at the Arizona State University Computer Center on a CDC 3400 computer.

References

Crystal Structure Calculations System, X-ray 63 (1964). Technical Report TR-64-6 NsG-398, Computer Science Center, University of Maryland, College Park, Maryland, U.S.A.

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Jonassen, H., Crumpler, T. & O'Brien. T. D. (1945). *J. Amer. Chem. Soc.* **67**, 1709.

Morosin, B. & Lingafelter, E. C. (1961). *J. Phys. Chem.* **65**, 50.

Willett, R. D. (1964). *J. Chem. Phys.* **41**, 2243.

Willett, R. D., Liles, O. L. Jr & Michelson, C. (1967). *Inorg. Chem.* **6**, 1885.

Zaslow, B. & Ferguson, G. L. (1967). *Chem. Commun.* p. 822.

Acta Cryst. (1971). **B27**, 852

Crystallographic polarity determination of γ-CuI.

By A. S. Bhalla and E. W. White, *Materials Research Laboratory, The Pennsylvania State University, University Park, Pa.* 16802, *U.S.A.*

(*Received* 14 *March* 1970 *and in revised form* 7 *July* 1970)

The polarity of single crystals of CuI having the sphalerite structure was determined from intensities measured on a double-crystal X-ray spectrometer, making use of anomalous scattering. If the direction from Cu to I is defined as [111], the results confirm that the (111) plane contains Cu^+ ions while the $(\bar{1}\bar{1}\bar{1})$ plane contains I^- ions, and that the natural faces of the tetrahedral crystals are of the type $(\bar{1}\bar{1}\bar{1})$.

Halides of Cu^+ have the sphalerite structure with space group $F\bar{4}3m$. The positive sense of the [111] direction is defined from Cu^+ to the halide ion, when Cu^+ is considered at position (0,0,0) and the halide at position $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. The opposite faces (111) and $(\bar{1}\bar{1}\bar{1})$ of this type of structure behave differently with regard to oxidation (Lavine, Rosenberg & Gatos, 1958) and etching (Maringer, 1958; Schell, 1957) and show differences in the integrated X-ray intensities (Coster, Knol & Prins, 1930) of reflection (Coster, Knol & Prins, 1930; Geib & Lark-Horowitz, 1932). The crystallographic polarity of CuCl and CuBr was established by Monier & Kern (1955). In this note results on γ-CuI are reported and correlated with the above definition of the [111] direction.

Crystals of γ-CuI (1 mm diameter) were used for experimental measurements on a double crystal X-ray spectrometer (Bhalla & White, 1970) having a finely collimated beam diameter smaller than the size of the crystal. Table 1 shows the calculated and measured intensity ratios from the two opposite faces, perpendicular to [111], for different orders of diffraction.

The observed ratios are very close to the calculated values. The X-ray conditions (counting time, current and voltage) were identical only while comparing a particular pair (*hkl*) and $(\bar{h}\bar{k}\bar{l})$.

Calculations were made considering Cu^+ at (0,0,0) and I^- at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and using the formula (Warekois & Metzger, 1959):

$$|F_n|^2=16[f_{Cu}+f_I e^{ix}]\,[f^*_{Cu}+f^*_I e^{-ix}]$$

where $f_{Cu}=f^0_{Cu}+\Delta f'_{Cu}+i\Delta f''_{Cu}$ *etc.* Asterisk symbols are the conjugate values of the complex quantities, and

$$x=2\pi\frac{3n}{4}\,,\ n=\pm 1,2,3\,.$$

Values of f°, $\Delta f'$ and $\Delta f''$ were taken from *International Tables for X-ray Crystallography* (1967) and calculated for the appropriate order of diffraction.

The peaks, scanned from (111) and $(\bar{1}\bar{1}\bar{1})$ faces, were found to have different full widths at half maximum. (Three sets of observations for first, second and third orders, in seconds of arc, are: 50 and 35, 31 and 33, and 38 and 54 respectively.) These differences could be explained qualitatively from the prediction of the Darwin theory that, for a small angle of reflection from a perfect, nonabsorbing crystal, the peak half width at half maximum ω, in radians, is related to the structure factor as given by (Compton & Allison, 1935).

$$\omega=2{\cdot}8\,\delta F Z^{-1}\csc 2\theta_0\,.$$

Table 1. *Calculated and measured ratios of integrated intensities from opposite faces of* γ-CuI *single crystal for* Cr *K*α *radiation*

	Total counts (above background)		$\frac{FF^*(hkl)}{FF^*(\bar{h}\bar{k}\bar{l})}$	
hkl	*hkl*	$\bar{h}\bar{k}\bar{l}$	measured	calculated
(111)	4332	2869	1·510	1·608
(222)	1995	2029	0·983	1·000
(333)	809	1723	0·470	0·507