

The Crystal Structure of Bis-trimethylbenzylammoniumtetrachlorocuprate (II)

M. BONAMICO and G. DESSY

Centro di Chimica dei Composti di Coordinazione ed Elemento-organici (CNR), Istituto di Chimica Generale e Inorganica della Università degli Studi, Roma, Italia

A. VACIAGO

Centro di Studio per la Strutturistica Chimica (CNR), Istituto di Chimica Farmaceutica e Tossicologica della Università degli Studi, Roma, Italia

Received December 19, 1966

The crystal structure of bis-trimethylbenzylammonium tetrachlorocuprate (II) was determined. The structure for the $[\text{CuCl}_4]^{2-}$ ion proposed in the spectroscopic work, i.e. a flattened tetrahedron of D_{2d} symmetry, was confirmed. It was shown, further, that the four S_4 axes of the four $[\text{CuCl}_4]^{2-}$ ions in the unit cell are practically parallel, because they lie almost parallel to the glide planes of symmetry. This fact proved to be of great importance for further collection and elaboration of spectral data. The unit cell has dimensions $a = 9.584$, $b = 9.104$, $c = 28.434$ Å, $\beta = 92^\circ 50'$, space group $P2_1/n$, and contains 4 molecules. $R = 0.077$ (computed on the 2861 observed independent reflections only).

La structure cristalline du tetrachlorocuprate (II) de bis-triméthylbenzylammonium a été déterminée. La structure de l'ion $[\text{CuCl}_4]^{2-}$ proposée dans l'étude spectroscopique, c.a. d'un tétraèdre plat de symétrie D_{2d} , a été confirmée. On a montré, de plus, que les quatre axes S_4 des quatre ions $[\text{CuCl}_4]^{2-}$ dans la maille élémentaire sont pratiquement parallèles, car ils sont presque parallèles aux plans de symétrie de glissement, fait qui s'avère de grande importance pour l'accumulation et la mise au point des données spectrales. La maille élémentaire a pour dimensions $a = 9.584$, $b = 9.104$, $c = 28.434$ Å, $\beta = 92^\circ 50'$, groupe d'espace $P2_1/n$, et contient quatre molécules. $R = 0.077$ (calculé à l'aide seulement de 2861 réflexions indépendantes observées).

Die Kristallstruktur von $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_3]_2\text{CuCl}_4$ wird bestimmt, wobei die aus spektroskopischen Studien vorgeschlagene Struktur des Ions $[\text{CuCl}_4]^{2-}$ bestätigt wird (gestauchtes Tetraeder der Symmetrie D_{2d}). Ferner wird gezeigt, daß die S_4 Achsen der vier $[\text{CuCl}_4]^{2-}$ -Ionen in der Einheitszelle praktisch parallel sind; diese Tatsache erwies sich als sehr wichtig bei der Messung und Auswertung des Spektrums. Die Einheitszelle hat die Dimensionen $a = 9.584$, $b = 9.104$, $c = 28.434$ Å, $\beta = 92^\circ 50'$, Raumgruppe $P2_1/n$, und enthält vier Moleküle. $R = 0.077$ (nur mit Hilfe der 2861 unabhängigen Reflexionen berechnet).

The properties and electronic structure of some tetrahalogenocuprate (II) complexes with "onium" cations, including bis-trimethylbenzylammonium tetrachlorocuprate (II), have been described by FURLANI and MORPURGO [6], who measured and interpreted the absorption spectra of several of these complexes in solution. They also measured the spectra in the solid state (as reflection spectra of the powdered crystals, and in some cases also in nujol or hexachlorobutadiene mulls). FURLANI and MORPURGO proposed for the $[\text{CuX}_4]^{2-}$ ion ($X = \text{Cl}, \text{Br}$) a

distorted tetrahedral structure, namely, a flattened tetrahedron of symmetry D_{2d} . Such a distorted tetrahedron would retain one of the three S_4 symmetry axes of the regular tetrahedron. FURLANI and MORPURGO also showed that their spectroscopic results could be interpreted, in the case of the $[\text{CuCl}_4]^{2-}$ ion, on the basis of a point charge model, assuming a Cl-Cu-Cl angle (smaller value) of about $101^\circ 30'$.

This interpretation of the spectra was consistent with the geometry of the $[\text{CuX}_4]^{2-}$ ion which had resulted from the X-ray analysis of the structure of Cs_2CuCl_4 [8, 11] and Cs_2CuBr_4 [10], and which, in the case of Cs_2CuCl_4 , had also been explained theoretically [3]. Further support for this has come more recently from the spectroscopic evidence that the structure of the $[\text{CuCl}_4]^{2-}$ ion in solution is close to that found in the crystal of Cs_2CuCl_4 [4].

However, the crystal structure of bis-trimethylbenzylammonium tetrachlorocuprate (II), $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_3]_2\text{CuCl}_4$, was investigated and is described in this paper because: (1) direct proof was lacking that the structure of the $[\text{CuCl}_4]^{2-}$ ion in the salts R_2CuX_4 (R = an "onium" cation) is the same as that found in Cs_2CuCl_4 (except for the preliminary evidence given for $[(\text{CH}_3)_4\text{N}]_2\text{CuCl}_4$ [11]); (2) planar, almost square $[\text{CuCl}_4]^{2-}$ ions had been found by WILLETT [15] in the very similar "light yellow" compounds $(\text{NH}_4)_2\text{CuCl}_4$, $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ and $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$; (3) it seemed expedient to provide the structural information that would make it possible to measure and interpret the crystal spectrum of one of the compounds of FURLANI and MORPURGO under polarized light; and (4) an accurate, three-dimensional analysis of the structure of at least one tetrahalogenocuprate (II) complex was still lacking.

Results

There is a monoclinic and an orthorhombic modification of bis-trimethylbenzylammonium tetrachlorocuprate (II) $[(\text{TMBA})_2\text{CuCl}_4$ henceforth]. In both cases the small crystals suitable for X-ray analysis are yellow. They grow from acetonitrile, in the first case, and from absolute ethanol, in the second. The α (monoclinic) form was examined in this work*. Detailed morphological and optical data can be found in the work of FURLANI et al. on the crystal spectrum of $(\text{TMBA})_2\text{CuCl}_4$ [5]. The goniometric values of the axial ratios, $(a:b:c)_{\text{gon}} = 1.05319:1:3.12459$, and of the β angle, $92^\circ 40'$, are in very good agreement with the values found from the X-ray analysis and reported below. Crystals as large as those used for the optical studies are obviously of a deeper colour, even to the extent of being orange-red.

Crystal data. $\text{C}_{20}\text{H}_{32}\text{N}_2\text{CuCl}_4$. $M = 505.86$. Monoclinic prismatic. $a = 9.584 \pm 0.010$, $b = 9.104 \pm 0.005$, $c = 28.434 \pm 0.010$ Å; $(a:b:c) = 1.053:1:3.124$; $\beta = 92^\circ 50'$; $U = 2477.9$ Å³; $D_m = 1.4$ (by flotation); $Z = 4$; $D_c = 1.356$ g cm⁻³; $F(000) = 1052$; $\mu = 53$ cm⁻¹. Space group $P2_1/n$ (C_{2h}^5 , No. 14) from systematic absences. Cu-K α radiation (λ taken as 1.5418 Å), unit cell dimensions determined by a modified, improved version of Christ's method [9] from zero-layer Weissenberg photographs about the a and b axes.

* The main crystal data for the orthorhombic modification are: $a = 9.54$, $b = 9.18$, $c = 28.52$ Å; space group $P2_12_12_1$ (D_2^7 , No. 19) from systematic absences.

Structure analysis. The crystal data require the asymmetric unit to comprise one molecule. From a three-dimensional Patterson function, computed by using the full set of 2861 independent terms observed with intensity above film background, approximate co-ordinates for the copper and chlorine atoms were found. A Fourier synthesis phased on the contribution of the five atoms located from the Patterson gave the positions of all other atoms, except for the hydrogens. At this stage the reliability index R was 0.32, where

$$R = \frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|},$$

the summations being over all the observed independent reflections.

Table 1

	x/a	y/b	z/c		x/a	y/b	z/c
<i>a) Atomic co-ordinates ($\cdot 10^4$) with standard deviations for the heavy atoms</i>				<i>b) Atomic co-ordinates ($\cdot 10^3$) for the hydrogen atoms</i>			
Cu	2278 (1)	1697 (1)	3882 (< 1)	H(1)	41	197	278
Cl(1)	1663 (3)	3259 (2)	4437 (1)	H(2)	965	263	201
Cl(2)	2857 (2)	3298 (2)	3317 (1)	H(3)	743	310	170
Cl(3)	4112 (2)	144 (2)	3844 (1)	H(5)	606	257	319
Cl(4)	522 (2)	41 (2)	3924 (1)	H(6)	867	194	335
N(1)	4279 (6)	1868 (6)	2091 (2)	H(7) <i>a</i>	520	403	189
N(2)	7348 (6)	1967 (6)	4829 (2)	H(7) <i>b</i>	446	362	258
C(1)	9839 (8)	2117 (9)	2702 (3)	H(8) <i>a</i>	431	54	153
C(2)	8990 (8)	2472 (12)	2237 (3)	H(8) <i>b</i>	494	206	140
C(3)	7630 (8)	2851 (10)	2100 (3)	H(8) <i>c</i>	608	97	170
C(4)	6596 (7)	2857 (8)	2417 (2)	H(9) <i>a</i>	228	123	179
C(5)	6951 (8)	2548 (10)	2890 (3)	H(9) <i>b</i>	229	288	229
C(6)	8337 (9)	2197 (11)	3026 (3)	H(9) <i>c</i>	293	320	167
C(7)	5141 (8)	3227 (7)	2263 (3)	H(10) <i>a</i>	341	-5	233
C(8)	4869 (8)	1236 (9)	1656 (3)	H(10) <i>b</i>	526	32	255
C(9)	2817 (7)	2382 (9)	1977 (3)	H(10) <i>c</i>	385	107	274
C(10)	4243 (9)	715 (8)	2473 (3)	H(11)	626	807	399
C(11)	6433 (9)	7036 (9)	4083 (3)	H(12)	421	611	388
C(12)	5416 (8)	5938 (11)	4008 (3)	H(13)	536	361	400
C(13)	5776 (8)	4492 (9)	4091 (3)	H(15)	914	486	439
C(14)	7142 (7)	4111 (7)	4250 (2)	H(16)	849	760	428
C(15)	8124 (7)	5199 (8)	4318 (3)	H(17) <i>a</i>	840	239	424
C(16)	7772 (8)	6665 (8)	4237 (3)	H(17) <i>b</i>	700	168	407
C(17)	7491 (8)	2492 (8)	4327 (2)	H(18) <i>a</i>	522	165	467
C(18)	5873 (10)	2158 (12)	4970 (3)	H(18) <i>b</i>	570	302	496
C(19)	7706 (10)	376 (8)	4836 (3)	H(18) <i>c</i>	597	176	541
C(20)	8328 (11)	2792 (10)	5169 (3)	H(19) <i>a</i>	690	-14	458
				H(19) <i>b</i>	861	34	466
				H(19) <i>c</i>	770	-10	515
				H(20) <i>a</i>	811	243	547
				H(20) <i>b</i>	929	288	507
				H(20) <i>c</i>	811	369	521

Table 2. *Anisotropic thermal parameters of the heavy atoms (with e.s.d.s)**

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Cu	113 (1)	42 (2)	-5.7 (0.6)	106 (1)	0.3 (0.6)	11.9 (0.1)
Cl(1)	204 (3)	-2 (6)	28 (2)	187 (3)	-47 (1)	20.6 (0.3)
Cl(2)	135 (2)	32 (4)	-3 (1)	154 (2)	21 (1)	14.8 (0.2)
Cl(3)	132 (2)	118 (4)	-11 (1)	150 (2)	1 (1)	23.4 (0.3)
Cl(4)	136 (2)	-17 (4)	-8 (1)	140 (2)	1 (1)	16.3 (0.2)
N(1)	121 (6)	3 (13)	-1 (4)	117 (7)	2 (4)	13.7 (0.6)
N(2)	133 (7)	7 (14)	1 (4)	130 (7)	-4 (4)	12.0 (0.6)
C(1)	129 (8)	-86 (19)	-26 (6)	150 (10)	-9 (6)	24.3 (1.3)
C(2)	107 (8)	-56 (22)	-1 (6)	279 (16)	-25 (8)	22.0 (1.3)
C(3)	121 (8)	-91 (19)	-1 (5)	228 (13)	-5 (6)	14.4 (0.9)
C(4)	108 (7)	-15 (15)	2 (4)	128 (8)	-2 (4)	12.0 (0.7)
C(5)	133 (8)	16 (20)	-15 (5)	197 (12)	-1 (6)	14.9 (0.9)
C(6)	164 (10)	25 (24)	-22 (5)	232 (15)	11 (7)	16.7 (1.0)
C(7)	139 (8)	4 (16)	-13 (5)	122 (8)	2 (5)	15.4 (0.9)
C(8)	120 (7)	-23 (18)	10 (5)	171 (10)	-31 (5)	15.1 (0.9)
C(9)	90 (7)	2 (17)	-8 (5)	163 (11)	-5 (6)	22.9 (1.2)
C(10)	177 (9)	-31 (20)	-4 (5)	128 (9)	15 (5)	15.6 (0.9)
C(11)	193 (11)	110 (21)	-7 (6)	164 (10)	6 (5)	14.5 (0.9)
C(12)	143 (8)	132 (20)	-18 (5)	240 (15)	22 (6)	16.4 (0.9)
C(13)	133 (8)	24 (20)	-22 (5)	183 (11)	2 (6)	15.7 (0.9)
C(14)	133 (7)	73 (16)	8 (4)	143 (8)	10 (4)	9.6 (0.6)
C(15)	113 (7)	-1 (16)	6 (4)	140 (9)	7 (5)	16.3 (0.9)
C(16)	149 (9)	69 (18)	5 (5)	139 (9)	21 (5)	16.9 (1.0)
C(17)	153 (9)	37 (17)	13 (5)	127 (8)	8 (4)	13.5 (0.8)
C(18)	194 (12)	61 (25)	50 (6)	242 (16)	10 (8)	19.0 (1.2)
C(19)	227 (12)	60 (22)	7 (7)	112 (8)	8 (5)	18.6 (1.1)
C(20)	289 (16)	-71 (25)	-36 (7)	136 (10)	4 (6)	16.0 (1.0)

* The b_{ij} coefficients as given here are defined by: $T = \exp \{-10^{-4}(b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2)\}$, T being the function by which the atomic scattering factors must be multiplied in order to take the anisotropic thermal motion of the heavy atoms into account in the calculation of the structure factors. For the hydrogen atoms the isotropic temperature factor $B = 6 \text{ \AA}^2$ was used. Hence the general SF formula used is: $F(hkl) = \sum_n^N f_n T_n \exp \{2\pi i(hx_n + ky_n + lz_n)\} + f_H \exp \left(-B \frac{\sin^2 \theta}{\lambda^2} \right) \sum_m^M \exp \{2\pi i(hx_m + ky_m + lz_m)\}$, where the first summation is over all the heavy atoms in the unit cell and the second summation over all the hydrogen atoms.

The space and thermal parameters of all the 27 heavy atoms were then refined by Fourier and least-squares methods, assuming first isotropic and then anisotropic thermal motion, to a set of values corresponding to $R = 0.095$. The introduction of approximate positions and of an average isotropic temperature factor $B = 6 \text{ \AA}^2$, for the 32 hydrogen atoms in the asymmetric unit, deduced without ambiguity from a three-dimensional difference synthesis computed at this stage, when the value of $\sigma(\rho_0)$ was 0.2 e\AA^{-3} , and from the geometry of the molecule, brought the R index to 0.084. The space co-ordinates of all the 59 atoms of the molecule and the anisotropic temperature parameters of the 27 heavy atoms were further refined by least-squares to the final values given in Tabs. 1 and 2*. They

* For a key to the numbering of atoms see Fig. 1. Hydrogen atoms are numbered by reference to their respective carbon atoms.

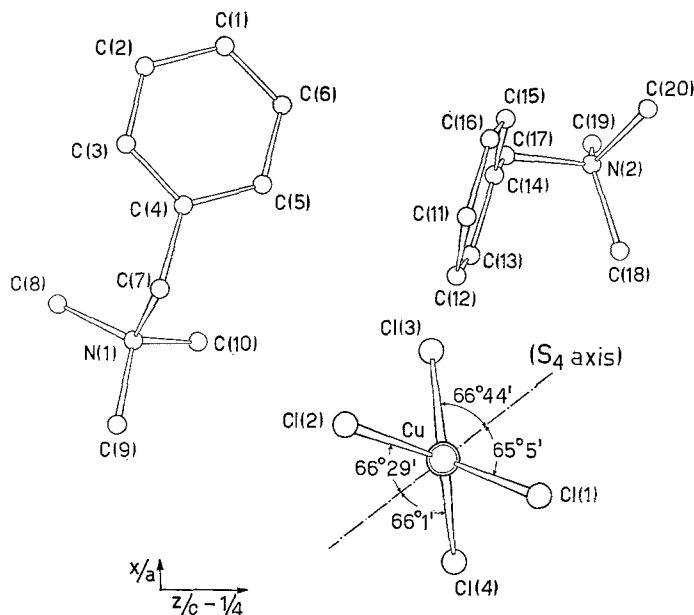


Fig. 1. Projection of one unit of $(\text{TMBA})_2\text{CuCl}_4$, as seen down the b axis

correspond to $R = 0.077$ (calculated on the 2861 observed independent reflections only) and represent the final stage of refinement consistent with the quality of experimental data, the residual shifts being, on average, smaller than the corresponding e.s.d.s. A final difference Fourier synthesis ($\sigma(\rho_0) = 0.2 \text{ e}\text{\AA}^{-3}$) gave a very smooth residual electron density, oscillating around a null value with maxima and minima of absolute value $0.2\text{--}0.3 \text{ e}\text{\AA}^{-3}$ in the general field (rising to $0.4\text{--}0.5 \text{ e}\text{\AA}^{-3}$ in the region of the $[\text{CuCl}_4]^{2-}$ ion only)*.

Discussion

A projection of one unit of $(\text{TMBA})_2\text{CuCl}_4$, as seen down the b axis, is represented in Fig. 1. The crystallographic numbering of atoms is included in Fig. 1, except for the hydrogen atoms, which are not represented in Fig. 1 and are numbered by reference to their respective carbon atoms. Bond lengths and angles (not including hydrogen atoms**) with their e.s.d.s [2], are listed in Tab. 3. There are no relevant interaction and contact distances either between the three ions represented in Fig. 1 or between any one of them and the other units of $(\text{TMBA})_2$

* A table containing the calculated structure factors based on the parameters in Tabs. 1 and 2, and the observed structure amplitudes for the 2861 observed independent reflections has been deposited as Document No. 9415 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D.C. 20540, U.S.A. A copy may be secured by citing the Document number and by remitting \$ 1.25 for photoprints, or \$ 1.25 for 35 mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

** The partial refinement of the hydrogen atoms (space co-ordinates only) led to carbon-hydrogen bond lengths between 0.80 and 1.30 \AA (average value 1.07 \AA), $\sigma = 0.10 \text{ \AA}$.

Table 3. Bond lengths (Å) and bond angles (degrees) within the formula unit, with standard deviations

Cu-Cl(1)	2.229	(0.003)	Cl(3)-Cu-Cl(4)	99.7	(0.1)
Cu-Cl(2)	2.263	(0.003)	C(1)-C(2)-C(3)	119.9	(0.8)
Cu-Cl(3)	2.263	(0.002)	C(2)-C(3)-C(4)	121.3	(0.8)
Cu-Cl(4)	2.268	(0.002)	C(3)-C(4)-C(5)	119.0	(0.7)
C(1)-C(2)	1.38	(0.01)	C(4)-C(5)-C(6)	119.0	(0.7)
C(2)-C(3)	1.38	(0.01)	C(5)-C(6)-C(1)	121.2	(0.8)
C(3)-C(4)	1.38	(0.01)	C(6)-C(1)-C(2)	119.4	(0.7)
C(4)-C(5)	1.40	(0.01)	C(3)-C(4)-C(7)	120.7	(0.6)
C(5)-C(6)	1.40	(0.01)	C(5)-C(4)-C(7)	120.2	(0.6)
C(6)-C(1)	1.37	(0.01)	C(4)-C(7)-N(1)	112.8	(0.5)
C(4)-C(7)	1.48	(0.01)	C(7)-N(1)-C(8)	110.2	(0.6)
N(1)-C(7)	1.55	(0.01)	C(7)-N(1)-C(9)	107.1	(0.5)
N(1)-C(8)	1.51	(0.01)	C(7)-N(1)-C(10)	111.2	(0.5)
N(1)-C(9)	1.49	(0.01)	C(8)-N(1)-C(9)	109.6	(0.6)
N(1)-C(10)	1.51	(0.01)	C(8)-N(1)-C(10)	110.5	(0.6)
C(11)-C(12)	1.40	(0.01)	C(9)-N(1)-C(10)	108.2	(0.6)
C(12)-C(13)	1.38	(0.01)	C(11)-C(12)-C(13)	119.3	(0.7)
C(13)-C(14)	1.40	(0.01)	C(12)-C(13)-C(14)	120.7	(0.7)
C(14)-C(15)	1.37	(0.01)	C(13)-C(14)-C(15)	119.1	(0.6)
C(15)-C(16)	1.39	(0.01)	C(14)-C(15)-C(16)	120.7	(0.6)
C(16)-C(11)	1.37	(0.01)	C(15)-C(16)-C(11)	120.1	(0.7)
C(14)-C(17)	1.52	(0.01)	C(16)-C(11)-C(12)	120.0	(0.8)
N(2)-C(17)	1.52	(0.01)	C(13)-C(14)-C(17)	118.6	(0.6)
N(2)-C(18)	1.50	(0.01)	C(15)-C(14)-C(17)	122.3	(0.6)
N(2)-C(19)	1.49	(0.01)	C(14)-C(17)-N(2)	114.1	(0.5)
N(2)-C(20)	1.51	(0.01)	C(17)-N(2)-C(18)	110.7	(0.6)
			C(17)-N(2)-C(19)	106.6	(0.6)
Cl(1)-Cu-Cl(2)	100.3	(0.1)	C(17)-N(2)-C(20)	111.0	(0.6)
Cl(1)-Cu-Cl(3)	132.1	(0.1)	C(18)-N(2)-C(19)	109.2	(0.7)
Cl(1)-Cu-Cl(4)	99.1	(0.1)	C(18)-N(2)-C(20)	109.4	(0.6)
Cl(2)-Cu-Cl(3)	98.3	(0.1)	C(19)-N(2)-C(20)	110.0	(0.6)
Cl(2)-Cu-Cl(4)	132.8	(0.1)			

CuCl₄ in the crystal structure. An outline of the environment of the ion [CuCl₄]²⁻ is given in Tab. 4. The two crystallographically independent trimethylbenzylammonium ions both have a very regular geometry. The atoms of the C(1) to C(6) aromatic ring and atom C(7) lie in a plane (calculated according to SCHOMAKER, WASER, MARSH, and BERGMAN [14], with all weights equal to 1, and determined by the equation: $0.188x + 0.966y + 0.167z = 4.849$) with a maximum deviation of 0.03 Å for C(1) and a mean deviation of 0.01₅ Å. The hydrogen atoms H(1) to H(6), not used in defining the plane given above, lie practically on it, with a maximum deviation of 0.15 Å for H(2) and a mean deviation of 0.05 Å. Similarly, the atoms of the C(11) to C(16) aromatic ring and atom C(17) lie in the plane $-0.303x + 0.089y + 0.965z = 9.907$ with maximum and mean deviations of 0.01 [for C(14)] and 0.005 Å, respectively. The maximum and mean deviations of the hydrogen atoms H(11) to H(16), not used in defining the plane, are 0.20 [for H(13)] and 0.10 Å, respectively. The structure of the [CuCl₄]²⁻ ion is indeed that of a squashed tetrahedron with S₄ symmetry retention in one direction. In fact, the plane through Cl(1), Cu, Cl(3) is at an angle of 89°31' with the plane through Cl(2), Cu, Cl(4). Bearing in mind that this angle is computed from the crystallographically

Table 4. *Environment of the $[\text{CuCl}_4]^{2-}$ ion (distances are in Å units)**

Cu	H(13)	3.43	Cl(3)	H(5)	3.49
Cu	H(18) <i>a</i>	3.49	Cl(3)	H(13)	3.39
Cu	H(19 ^{iv}) <i>c</i>	3.11	Cl(3)	H(17) <i>b</i>	3.13
Cl(1)	H(15 ⁱⁱⁱ)	2.82	Cl(3)	H(9 ⁱⁱⁱ) <i>c</i>	2.96
Cl(1)	H(17 ⁱⁱⁱ) <i>a</i>	3.24	Cl(3)	H(10) <i>c</i>	3.25
Cl(1)	H(19 ^{iv}) <i>c</i>	3.15	Cl(3)	H(18) <i>a</i>	2.86
Cl(1)	H(20 ⁱⁱⁱ) <i>a</i>	3.01	Cl(3)	H(18 ^{iv}) <i>c</i>	2.74
Cl(1)	H(20 ^v) <i>b</i>	2.96	Cl(3)	H(19) <i>a</i>	3.31
Cl(2)	H(1 ⁱⁱⁱ)	2.98	Cl(3)	H(19 ^{iv}) <i>c</i>	3.44
Cl(2)	H(5)	3.18	Cl(4)	H(6 ⁱⁱⁱ)	2.91
Cl(2)	H(12)	3.25	Cl(4)	H(7 ⁱⁱⁱ) <i>a</i>	2.54
Cl(2)	H(13)	3.01	Cl(4)	H(17 ⁱⁱⁱ) <i>a</i>	3.12
Cl(2)	H(7) <i>b</i>	2.70	Cl(4)	H(8 ⁱⁱⁱ) <i>b</i>	2.89
Cl(2)	H(8 ^v) <i>a</i>	2.96	Cl(4)	H(9 ⁱⁱⁱ) <i>c</i>	2.86
Cl(2)	H(9 ^v) <i>a</i>	2.69	Cl(4)	H(19 ⁱⁱⁱ) <i>b</i>	2.88
Cl(2)	H(9) <i>b</i>	2.96	Cl(4)	H(19 ^{iv}) <i>c</i>	3.05
Cl(2)	H(10 ^v) <i>a</i>	2.62	Cl(4)	H(20 ^{iv}) <i>a</i>	3.08
Cl(2)	H(10) <i>c</i>	2.81			

* The superscripts refer to the positions:

$$\text{I: } \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$$

$$\text{II: } -1 + x, y, z$$

$$\text{III: } \frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$$

$$\text{IV: } 1 - x, -y, 1 - z$$

$$\text{V: } 1 - x, 1 - y, 1 - z$$

independent general positions found for the five atoms involved, the intersection of the two planes defined above, namely, the line*:

$$x' = 0.7098z' - 6.1877; y' = 0.0336z' + 1.1751$$

can be said to be, within experimental error and computational approximation, an S_4 symmetry axis of the $[\text{CuCl}_4]^{2-}$ ion. This axis is at an angle of $88^\circ 26'$ with the y axis and therefore lies practically parallel to the xz plane. It is shown by a broken line in Fig. 1, at an angle of $54^\circ 39'$ with the x axis. The values of the four polar angles of the $[\text{CuCl}_4]^{2-}$ ion are also indicated in Fig. 1. There are four symmetry correlated $[\text{CuCl}_4]^{2-}$ ions in the unit cell, forming two centro-symmetrical pairs. Not only are the two S_4 axes of each pair parallel for symmetry reasons, but, as the S_4 axis of the asymmetric unit is practically parallel to the xz plane and therefore parallel to the glide plane of symmetry, all the four S_4 axes in the unit cell are practically parallel.

Thus, on the basis of these crystallographic results, it is possible to perform spectrophotometric measurements on single crystals of $(\text{TMBAl})_2\text{CuCl}_4$ using polarized light with the electric vector in selected orientations with respect to the direction of the S_4 axes of the $[\text{CuCl}_4]^{2-}$ ions. This has been done by FURLANI et al., and their results are reported in the following paper [5].

Experimental Part

The X-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken about the a (4 layers) and the b axis (6 layers) for approximately square crystals, 0.02 cm thick. 2861 reflections were collected (about 50% of the possible

* Equations given in absolute (Å), rectangular co-ordinates, with the x' and y' axes parallel to the x and y crystallographic axes, the origin being the same for both systems.

ones with Cu radiation). Intensities were corrected for spot-size (according to PHILLIPS [12]), Lorentz and polarization factors and placed on a common scale by the method of ROLLETT and SPARKS [13]. No absorption or extinction corrections were applied.

The calculations were carried out on the IBM 1620 and 7040 computers of the University of Rome. On the 1620 computer intensity corrections and structure factors were calculated using programmes of SCATTURIN and his co-workers. VAN DER HELM's general Fourier synthesis and GIGLIO's differential Fourier synthesis programmes were also used. The two least-squares planes were calculated by a programme written by CHU (equation of the plane referred to the crystallographic axes). On the 7040 computer the programmes written by DOMENICANO, and VACIAGO for the Fourier synthesis and the interatomic distances and angles with standard deviations, and by ALBANO, DOMENICANO, and VACIAGO for SFLS calculations, were used. The standard deviations for the space and temperature parameters are computed by the SFLS programme as described by CRUICKSHANK and his co-workers [1]. Weights were assigned to the reflections according to the function $w = \{a + bk|F_0| + c(kF_0)^2\}^{-1}$, with $a = 10.0$, $b = 1.0$ and $c = 0.01$. The atomic scattering factors used in the last stages of refinement were those given by HANSON, HERMAN, LEA, and SKILLMAN [7], those of the copper and chlorine atoms were corrected for anomalous dispersion.

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Prof. Dr. A. VACIAGO
 Centro di Studio per la Strutturistica Chimica (CNR)
 Istituto di Chimica Farmaceutica e Tossicologica
 Università degli Studi
 Roma, Italia