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A Redetermination of the Structure of Tetramethylammonium Tetrachlorocuprate(II)

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Abstract. $C_8H_{24}CuCl_4N_2$, $M = 353{\cdot}63$, orthorhombic, *Pnma*, $a = 12{\cdot}30$ (2), $b = 9{\cdot}03$ (1), $c = 15{\cdot}59$ (2) Å, from precession photographs, refined by diffractometer. $Z = 4$, $\mu = 18$ cm^{-1} for Mo $K\alpha$ radiation, approximate crystal dimensions $0{\cdot}4 \times 0{\cdot}4 \times 0{\cdot}4$ mm. The crystals were prepared by evaporation of an aqueous solution containing stoichiometric proportions of $CuCl_2$ and Me_4NCl.

Introduction. With the exceptions of the few weak reflexions of the superlattice (see Discussion), systematic absences $hk0$, h odd, and $0kl$, $(k+l)$ odd, indicated space groups *Pnma* or $Pn2_1a$. *Pnma* was assumed initially (*cf.* Morosin & Lingafelter, 1961), and a later unsuccessful attempt to refine the structure in $Pn2_1a$ confirmed the centrosymmetric space group. Data were collected for layers 0–$6kl$ and $h0$–$3l$ (based on the above cell) on a Hilger–Watts linear diffractometer with Mo $K\alpha$ radiation. Lorentz and polarization corrections were applied, and after layer scaling a merged data set containing 670 independent reflexions was obtained with $I \geq 3\sigma(I)$, and placed on an absolute scale by the Wilson-plot method. No absorption correction was applied. The positional parameters obtained for the isomorphous $(Me_4N)_2CoCl_4$ by Wiesner, Srivastava, Kennard, DiVaira & Lingafelter (1967) were used as the starting point for refinement, with estimated isotropic temperature factors. Refinement was by full-matrix least-squares calculations with our adaptation of the *PORFLS* program in the CRYSTAL 69 system of Powell & Griffiths (1969). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968). Four cycles of refinement of positional and isotropic thermal parameters with unit weights gave $R = 0{\cdot}173$ $(R = \sum|F_o - |F_c||/\sum F_o)$ and a further seven cycles of positional and anisotropic thermal parameters with the weighting scheme $w = 1/[F - \{(F - F^*)/G^*\}^2]$ for $F \geq F^*$, $w = 1$ for $F < F^*$ and the values $F^* = 25$, $G^* = 50$ converged at $R = 0{\cdot}075$.† In view of the large thermal parameters of the C and N atoms, which are probably a result of disorder in the Me_4N^+ groups, no attempt was made to locate the hydrogen atoms. Atomic parameters are given in Table 1.

Discussion. The present work confirms the structure found by Morosin & Lingafelter, who solved projections with $R(hk0) = 0{\cdot}18$, $R(h0l) = 0{\cdot}12$, but gives improved standard deviations for the bond lengths and angles. The main interest in redetermining the structure was to obtain more accurate dimensions of the $CuCl_4^{2-}$ ion for comparison with the structures of $(Me_4N)_2CoCl_4$ and $(Me_4N)_2(Cu,Co)Cl_4$ (Cu:Co = 1:1) (Murray-Rust, 1971).

A tripling of a to give an axis of about 36 Å was observed by Morosin & Lingafelter and confirmed by us; the faint rather diffuse reflexions corresponding to the larger cell were found on $hk0$ but not $h0l$, and the strongest of them were (all with $l = 0$) $(0\frac{2}{3},2)$, $(1\frac{1}{3},2)$, $(0\frac{2}{3},3)$, $(0\frac{2}{3},4)$, $(1\frac{1}{3},4)$, $(2\frac{2}{3},4)$, $(3\frac{1}{3},4)$, $(4\frac{2}{3},4)$, $(2\frac{1}{3},5)$, $(0\frac{2}{3},6)$. Morosin & Lingafelter concluded that the true structure consisted of three subcells which

Table 1. *Atomic positions* (× 10⁴) *and anisotropic temperature factors* (× 10⁴)

E.s.d.'s are given in parentheses. β_{11} *etc.* are the coefficients in the expression for the anisotropic temperature factor:

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

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	2258 (2)	2500	4032 (1)	78 (2)	210 (4)	50 (1)	*	0 (1)	*
Cl(1)	467 (4)	2500	3689 (4)	76 (4)	412 (16)	83 (3)	*	−6 (3)	*
Cl(2)	2736 (4)	315 (5)	3503 (4)	174 (5)	201 (8)	178 (4)	31 (6)	−48 (4)	−30 (5)
Cl(3)	3127 (5)	2500	5315 (3)	125 (6)	612 (23)	53 (3)	*	−18 (3)	*
N(1)	1305 (11)	2500	920 (9)	74 (12)	270 (32)	51 (7)	*	2 (8)	*
N(2)	5112 (11)	2500	8301 (8)	89 (14)	232 (29)	36 (7)	*	3 (7)	*
C(1)	2535 (15)	2500	1106 (21)	51 (22)	481 (80)	192 (28)	*	−28 (18)	*
C(2)	1130 (23)	2500	−56 (12)	211 (32)	564 (78)	34 (9)	*	−20 (14)	*
C(3)	814 (19)	3850 (21)	1322 (12)	246 (30)	279 (38)	150 (16)	118 (29)	46 (17)	−80 (22)
C(4)	4331 (22)	2500	7503 (17)	144 (29)	508 (76)	109 (16)	*	−61 (19)	*
C(5)	4465 (28)	2500	9085 (24)	184 (38)	778 (139)	155 (26)	*	76 (28)	*
C(6)	5744 (21)	3859 (25)	8376 (14)	314 (37)	369 (46)	151 (16)	−193 (35)	−86 (21)	83 (24)

* β_{12} and β_{23} are required by symmetry to be zero.

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30687 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Standard deviations are given in parentheses.

Cu—Cl(1)	2·25 (1)	N(1)–C(1)	1·54 (3)	N(2)–C(4)	1·55 (2)
Cu—Cl(2)	2·21 (1)	N(1)–C(2)	1·50 (1)	N(2)–C(5)	1·43 (2)
Cu—Cl(3)	2·23 (1)	N(1)–C(3)	1·49 (4)	N(2)–C(6)	1·46 (2)
Cl(1)-Cu-Cl(2)	101·1 (0·3)	C(1)–N(1)–C(2)	108·8 (1·4)	C(4)–N(2)–C(5)	107·9 (1·8)
Cl(1)-Cu-Cl(3)	132·1 (0·2)	C(1)–N(1)–C(3)	108·8 (1·4)	C(4)–N(2)–C(6)	113·1 (0·9)
Cl(2)-Cu-Cl(2′)	126·4 (0·3)	C(2)–N(1)–C(3)	110·3 (1·7)	C(5)–N(2)–C(6)	103·4 (1·1)
Cl(2)-Cu-Cl(3)	100·8 (0·2)	C(3)–N(1)–C(3′)	109·7 (1·5)	C(6)–N(2)–C(6′)	114·7 (1·3)

differed mainly in the *y* coordinates of the nitrogen and carbon atoms, and the large thermal parameters of these atoms could certainly be a result of a disordered structure. This tripling is clearly of some importance in the interpretation of spectral and magnetic properties of the solid, but as the superlattice reflexions were very few and weak our average parameters were felt to be a satisfactory approximation to the true structure, at least for the $CuCl_4^{2-}$ tetrahedron.

Bond distances and angles are given in Table 2. The $CuCl_4^{2-}$ tetrahedron is strongly distorted towards D_{2d} symmetry, as in Cs_2CuCl_4, $(Et_3NH)_2CuCl_4$ and other 'tetrahedral' $CuCl_4^{2-}$ ions (see references in Lamotte-Brasseur, Dupont & Dideberg, 1973).

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Europium Dichloride Dihydrate

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Abstract. $EuCl_2$ $2H_2O$, monoclinic, $C2/c$, $a=11{\cdot}661$ (5), $b=6{\cdot}404$ (3), $c=6{\cdot}694$ (3) Å, $\beta=105{\cdot}37$ (5)°, $V=482{\cdot}2$ Å^3, $Z=4$, $D_c=3{\cdot}56$, $D_m=3{\cdot}58$ g cm^{-3}. Final R 0·038 for 504 reflexions. $EuCl_2.2H_2O$ is isomorphous with $SrCl_2.2H_2O$.

Introduction. Analogous salts of Eu^{2+} on the one hand and Ba^{2+} or Sr^{2+} on the other are generally supposed to be isomorphous. This has been shown in several cases (*e.g.* McCoy & Pauling, 1937). In this respect we have investigated the dichloride dihydrates of the two elements europium and barium. We report here a structure determination of $EuCl_2.2H_2O$. This compound was prepared as indicated in Brauer (1962): a solution of Eu_2O_3 (99·97%, supplied by Th. Goldschmidt, Essen) in 6N hydrochloric acid was reduced by amalgamated zinc in an atmosphere of pure nitrogen; $EuCl_2.2H_2O$ was precipitated by concentrated hydrochloric acid.

Chemical analysis gave: Cl, 27·41 (27·39); Eu, 58·34 (58·68)%, where figures in parentheses are calculated values. The density was determined pycnometrically as 3·58 g cm^{-3} with tetraline under N_2.

A plate-like single crystal of $EuCl_2.2H_2O$ with dimensions 0·14 × 0·05 × 0·10 mm was mounted in a thin-walled capillary filled with N_2. An X-ray investigation by photographic methods showed it could belong to either the triclinic or the monoclinic crystal system. A decision between these could not be made because of strong absorption effects. A Nonius CAD-4 four-circle automatic diffractometer and graphite-monochromated Mo $K\alpha$ radiation were then used in conjunction with a scintillation detector and pulse-height discrimination. The crystal setting and the triclinic unit cell ($P\bar{1}$, $a=6{\cdot}410$, $b=6{\cdot}650$, $c=6{\cdot}699$ Å, $\alpha=103{\cdot}46$°, $\beta=90{\cdot}09$°, $\gamma=118{\cdot}72$°, $Z=2$) were found by using the program *SEARCH*. 1752 reflexions were collected in the range $2° \leq \theta \leq 35°$. Three reflexions were monitored periodically during the data-collection process. Subsequent analysis of these reflexions indicated no crystal decomposition.

Only the 908 reflexions with $I > 2\sigma(I)$ were used in