Monomethylammonium Tetrachlorozincate(II)*

By B. Morosin

Sandia Laboratories, Albuquerque, New Mexico 87115

AND K. Emerson

Montana State University Bozeman, Montana 59715

Abstract. $(CH_3NH_3)_2ZnCl_4$, $P2_1/a$, $a = 10.873$ (3), $b = 12.655$ (2), $c = 7.648$ (1) Å, $\beta = 96.71$ (2)°, $Z = 4$. The crystal structure is similar to the orthorhombic K_2SO_4 type containing tetrahedral MX_4^{2-} ions. The average Zn–Cl bond length is 2.267 (2) Å with a slight departure from tetrahedral arrangement.

Introduction. Substituted ammonium compounds of the general formula $(RR'R''R'''N)_2MX_4$ prove to exhibit various interesting structure types, including discrete MX_4^{2-} ions, $(MX_2)_n^{2n-}$ ribbons as well as metal halide layers. While studying the temperature dependence of the structure of several layered materials, the title compound was characterized and found to be structurally similar to some previously studied (orthorhombic) tetramethyl substituted (TM) compounds (Morosin & Lingafelter, 1959; Wiesner, Srivastava, Kennard, DiVaira & Lingafelter, 1967; Lauher & Ibers, 1975). These TM compounds appeared to show a slight disordering of the ions in most of the compounds studied, which might have obscured the small distortion of the MX_4^{2-} tetrahedra observed. In the present material, no disorder appears present, yet the $ZnCl_4^{2-}$ tetrahedron is slightly distorted.

The refractive indices were measured by the immersion method to be nearly identical within experimental error ($1.568 - 1.572 \pm 0.004$). From the average refractive index value of 1.57, the molar refractivity, M.R., can be found to be 51.1 employing the relation

$$M.R. = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\varrho}$$

where n is the refractive index, M is the molecular weight and ϱ is the density. This function has been observed to be additive with respect to chemical groups in many organic compounds (Vogel, 1948); small anomalies in this additivity have been observed for some members of the substituted ammonium metal halide compounds (Tripathi, 1972). Our particular compound behaves in a normal way and one obtains a value of 29.1 for the molar refractivity contribution of the $ZnCl_4^{2-}$ ion.

Lattice parameters given in the abstract were determined on a Picker diffractometer with Mo $K\alpha$ radiation. The $\theta-2\theta$ scan technique and a scintillation detector employing pulse-height discrimination were used to measure Mo $K\alpha$ intensity data to 55° 2θ on a complete hemisphere of data. For the averages of 1842 unique intensities, 1248 were greater than 3σ where $\sigma = (N_{sc} + K^2 N_B)^{1/2}$ and N_{sc}, N_B and K are the total scan count, background counts and the time ratio of the scan to background, respectively. Scattering factors were taken from Table 3.31A of *International Tables for X-ray Crystallography* (1962) and (for hydrogen) from Stewart, Davidson & Simpson (1965). Initial parameters were determined from a Patterson Fourier synthesis and succeeding difference syntheses. Intensity data were subjected to least-squares refinement using isotropic thermal parameters. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/\sigma^2$. The difference Fourier synthesis clearly showed the positions of the H atoms about the C and N atoms. The positional parameters for the H atoms were included, with fixed isotropic thermal parameters, in subsequent refinement cycles in which anisotropic thermal parameters for the remaining atoms were used. The final residual value,

Table 1. *Positional and thermal parameters for* $(CH_3NH_3)_2ZnCl_4$

Positional parameters except for H are $\times 10^4$.
Thermal parameters are of the form $\exp(-2\pi^2 \sum\sum U_{ij} h_i h_j a_i^* a_j^*)$ in units 10^{-2} Å^2.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	2276·7 (7)	634·4 (6)	2670 (1)	2·73 (4)	2·75 (4)	2·81 (4)	0·01 (4)	0·34 (3)	−0·16 (4)
Cl(1)	4228 (2)	1291 (2)	3026 (3)	2·97 (9)	5·98 (12)	4·26 (11)	−0·93 (9)	0·31 (8)	−0·75 (9)
Cl(2)	2254 (2)	−1156 (1)	2431 (3)	4·54 (10)	2·65 (9)	7·42 (15)	0·10 (8)	0·38 (9)	−0·26 (9)
Cl(3)	1292 (2)	1122 (2)	4991 (3)	5·47 (12)	5·29 (12)	3·58 (10)	1·09 (10)	1·60 (9)	−0·52 (9)
Cl(4)	1245 (2)	1249 (2)	126 (2)	4·31 (10)	5·03 (11)	3·18 (9)	0·47 (9)	−0·23 (8)	0·69 (9)
N(1)	84 (7)	7098 (7)	2966 (12)	4·8 (5)	4·6 (4)	4·1 (4)	0·2 (4)	1·1 (4)	−0·7 (3)
N(2)	3733 (6)	4026 (7)	2213 (11)	3·6 (4)	6·4 (5)	7·1 (5)	0·3 (4)	0·8 (3)	0·9 (4)
C(1)	587 (9)	6379 (9)	1730 (14)	5·7 (6)	6·2 (6)	7·1 (7)	1·4 (5)	2·5 (5)	−1·9 (5)
C(2)	2423 (8)	3797 (8)	2405 (15)	4·6 (5)	5·9 (6)	9·8 (8)	−0·9 (5)	2·1 (5)	−0·1 (6)

Table 1 (cont.)

	x	y	z
H(11)	−0·03 (1)	0·72 (1)	0·31 (2)
H(12)	0·03 (1)	0·71 (1)	0·44 (2)
H(13)	0·07 (1)	0·77 (1)	0·34 (2)
H(14)	0·12 (1)	0·60 (1)	0·18 (2)
H(15)	0·03 (1)	0·71 (1)	0·06 (2)
H(16)	−0·02 (1)	0·53 (1)	0·12 (1)
H(21)	0·37 (1)	0·33 (1)	0·16 (2)
H(22)	0·43 (1)	0·49 (1)	0·35 (1)
H(23)	0·39 (1)	0·47 (1)	0·14 (2)
H(24)	0·18 (1)	0·47 (1)	0·18 (1)
H(25)	0·19 (1)	0·31 (1)	0·32 (1)
H(26)	0·24 (1)	0·27 (1)	0·07 (1)

$R = \{\sum |F_o| - |F_c| / \sum |F_o|\}$ was 0·035.* The positional and thermal parameters are given in Table 1 and the bond lengths and angles in Table 2. Values involving H atoms are not given because of their large standard deviations of about 0·1 Å or more for bond lengths, and as large as 20° for bond angles. One short (0·5 Å), four normal (1·0–1·1 Å) and one long (1·5 Å) N–H, and one normal (0·8 Å) and five long (1·3–1·9 Å) C–H bond lengths were obtained. The computations were performed with the X-RAY 72 System (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Table 2. Bond lengths and angles

Zn—Cl(1)	2·265 (2) Å	Cl(1)–Zn–C(2)	112·12 (8)°		
Zn—Cl(2)	2·273 (2)	Cl(1)–Zn–Cl(3)	109·13 (8)		
Zn—Cl(3)	2·263 (2)	Cl(1)–Zn–Cl(4)	109·90 (8)		
Zn—Cl(4)	2·267 (2)	Cl(2)–Zn–Cl(3)	109·46 (9)		
N(1)–C(1)	1·46 (1)	Cl(2)–Zn–Cl(4)	105·86 (8)		
N(2)–C(2)	1·48 (1)	Cl(3)–Zn–Cl(4)	110·33 (8)		
N(1)–Cl(3a)	3·210 (8)				
N(1)–Cl(1b)	3·234 (9)				
N(1)–Cl(2c)	3·281 (8)				
N(1)–Cl(2d)	3·293 (9)	(a)	$-x, 1-y, 1-z$		
N(2)–Cl(3e)	3·303 (7)	(b)	$\frac{1}{2}-x, \frac{1}{2}+y, 1-z$		
N(2)–Cl(4f)	3·335 (9)	(c)	$-\frac{1}{2}+x, \frac{1}{2}-y,$	z	
N(2)–Cl(4e)	3·338 (8)	(d)	$x, 1+y,$	z	
N(1)–Cl(4g)	3·356 (9)	(e)	$\frac{1}{2}+x, \frac{1}{2}-y,$	z	
N(2)–Cl(3b)	3·410 (9)	(f)	$\frac{1}{2}-x, \frac{1}{2}+y, 1-z$		
N(2)–Cl(1)	3·546 (9)	(g)	$-x, 1-y, 1-z$		

Discussion. The structure of this compound consists of discrete $CH_3NH_3^+$ and $ZnCl_4^{2-}$ ions packed in an arrangement similar to the orthrohombic K_2SO_4-like

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31388 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, Engalnd.

members. (The space group is Pnam when relabeled axes are used for direct comparison with the present cell). The smaller sized $CH_3NH_3^+$ ion results in cell dimensions more similar to the cesium compounds than the TM compounds. A comparison of the 001 projection shows this similarity; a z coordinate of 0·25 for the heavy atoms, except Cl (3) and (4), would be required in order to shift the monomethylammonium compound into registry with the TM compounds.

The values for the anisotropic thermal parameters for the $ZnCl_4^{2-}$ ion are much closer to expected values than those observed in TM compounds suggesting that the ions in this case are not disordered. The $ZnCl_4^{2-}$ ion is not perfectly tetrahedral and appears to repeat the results of the corresponding TM compound. Whether this apparent distortion results from the hydrogen bonding (Table 2) or some other packing artifact, is unknown. The shorter N–Cl contacts themselves do not clearly define the entire probable hydrogen-bonding network and undoubtedly bifurcated bonds are present; however, using the hydrogen positions and angles, H(11) appears bonded to Cl(3a) and Cl(2c) (see Table 2 for symmetry operations), H(12) to Cl(1b), H(13) to Cl(2d) and perhaps Cl(3a), H(21) to Cl(1) [though quite a long N(2)–Cl distance is involved and N(2) is closer to Cl(4e) with respect to this hydrogen], H(22) to Cl(3e) [again N(2) is also close to Cl(3b) with an acceptable N(2)–H (22)–Cl(3b) angle], and H(23) to Cl(4f).

References

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

LAUHER, J. W. & IBERS, J. A. (1975). *Inorg. Chem.* **14**, 348–352.

MOROSIN, B. & LINGAFELTER, E. C. (1959). *Acta Cryst.* **12**, 611–612.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). X-RAY 72: A System of Computer Codes for Crystallography, Technical Report TR-192, Univ. of Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TRIPATHI, U. P. (1972). Ph.D. Thesis, Montana State Univ.

VOGEL, A. I. (1948). *J. Chem. Soc.* p. 607. The six articles following this reference give data supporting the additivity rule.

WIESNER, J. R., SRIVASTAVA, R. C., KENNARD, C. H. L., DIVAIRA, M. & LINGAFELTER, E. C. (1967). *Acta Cryst.* **23**, 565–574.