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Bis(*n*-dodecylammonium) Tetrachlorozincate

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Abstract. $(n\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$, monoclinic, $P2_1/c$, $a = 7{\cdot}409\ (3)$, $b = 10{\cdot}379\ (5)$, $c = 44{\cdot}399\ (10)$ Å, $\beta = 105{\cdot}56°$ (5) at room temperature; $D_x = 1{\cdot}159$ g cm^{-3}, $Z = 4$. The structure is characterized by ionic layers sandwiched between layers of paraffinic chains.

Introduction. Weissenberg photographs showed systematic absences uniquely consistent with the monoclinic space group $P2_1/c$ ($0k0$ with k odd, $h0l$ with l odd). A white crystal, in the shape of a thin platelet, $0{\cdot}04 \times 0{\cdot}007 \times 0{\cdot}04$ cm, was used for the intensity data collection. Intensities were collected (Ni filter, Cu $K\alpha$ radiation) by a Siemens automatic single-crystal diffractometer. 1712 non-zero independent reflexions were collected and corrected for absorption ($\mu = 47{\cdot}0$ cm^{-1}, the absorption factor ranged between 0·89 and 0·39) and Lorentz–polarization effects.

The structure was solved by the Patterson method. The Fourier map, calculated by phasing the reflexions with the Zn and four Cl atoms revealed all the remaining atoms except the H.

The refinement of the coordinates and anisotropic thermal parameters (the coordinates of the H atoms were calculated from stereochemical considerations;

Table 1. *Final fractional coordinates and thermal parameters*

Temperature factor is in the form: $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}klb^*c^*)]$. E.s.d.'s refer to the last significant figure.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	0·2239 (2)	0·2696 (8)	−0·0164 (1)	5·2 (0·1)	6·5 (0·1)	4·6 (0·1)	0·4 (0·2)	2·2 (0·1)	−0·4 (0·2)
Cl(1)	0·2121 (7)	0·4817 (4)	−0·0300 (1)	11·3 (0·3)	6·2 (0·2)	4·6 (0·2)	0·1 (0·4)	3·9 (0·4)	0·1 (0·3)
Cl(2)	−0·0513 (5)	0·1697 (4)	−0·0408 (1)	4·6 (0·1)	7·6 (0·2)	5·2 (0·2)	−1·1 (0·3)	0·9 (0·3)	−1·8 (0·4)
Cl(3)	0·4591 (5)	0·1658 (4)	−0·0296 (1)	4·7 (0·2)	8·3 (0·2)	4·8 (0·2)	0·9 (0·3)	3·4 (0·3)	0·4 (0·3)
Cl(4)	0·2486 (5)	0·2495 (4)	0·0360 (1)	5·8 (0·2)	8·3 (0·3)	3·7 (0·1)	−1·0 (0·3)	2·7 (0·2)	0·1 (0·3)
N(1)	0·8274 (14)	0·1125 (10)	0·0284 (2)	7·0 (0·6)	3·8 (0·5)	3·9 (0·5)	−3·0 (0·9)	4·9 (0·9)	−0·1 (0·8)
C(1)	0·7659 (20)	0·1748 (14)	0·0522 (3)	6·5 (0·8)	6·6 (0·9)	4·5 (0·6)	2·6 (1·3)	1·3 (1·1)	−0·3 (1·3)
C(2)	0·8936 (20)	0·1650 (11)	0·0851 (3)	6·3 (0·7)	7·8 (1.)	4·1 (0·6)	4·0 (1·4)	1·7 (1·1)	0·9 (1·3)
C(3)	0·8340 (22)	0·2450 (15)	0·1094 (3)	9·1 (0·9)	5·7 (0·8)	4·9 (0·6)	0·6 (1·4)	4·2 (1·3)	0·2 (1·3)
C(4)	0·9394 (22)	0·2069 (19)	0·1426 (3)	7·9 (0·9)	11·0 (1·3)	4·6 (0·7)	2·9 (1·8)	3·3 (1·3)	3·0 (1·6)
C(5)	0·8789 (22)	0·2808 (17)	0·1689 (3)	7·5 (0·8)	8·7 (1·0)	6·0 (0·8)	1·9 (1·6)	4·4 (1·3)	−3·8 (1·5)
C(6)	0·9783 (22)	0·2230 (17)	0·2013 (3)	8·9 (0·9)	8·9 (1.)	4·0 (0·6)	1·4 (1·7)	2·8 (1·3)	0·5 (1·5)
C(7)	0·9189 (23)	0·2856 (16)	0·2278 (3)	8·8 (0·9)	7·5 (1.)	5·1 (0·7)	0·7 (1·7)	4·0 (1·3)	1·3 (1·4)
C(8)	1·0175 (21)	0·2280 (17)	0·2599 (3)	7·3 (0·8)	8·5 (1.)	5·4 (0·7)	2·4 (1·6)	3·1 (1·3)	−0·8 (1·5)
C(9)	0·9566 (21)	0·2892 (18)	0·2871 (3)	6·9 (0·8)	9·9 (1·1)	5·0 (0·7)	−0·2 (1·6)	3·5 (1·2)	−0·1 (1·6)
C(10)	1·0499 (21)	0·2313 (18)	0·3187 (3)	6·7 (0·8)	10·7 (1·2)	5·0 (0·7)	0·7 (1·6)	3·5 (1·2)	−2·9 (1·6)
C(11)	0·9902 (23)	0·2857 (18)	0·3456 (3)	8·5 (0·9)	9·2 (1.)	5·7 (0·7)	−3·2 (1·7)	5·3 (1·4)	−3·2 (1·6)
C(12)	1·0868 (25)	0·2321 (20)	0·3784 (4)	9·6 (1·1)	12·4 (1·4)	5·3 (0·7)	−0·9 (2·0)	2·5 (1·5)	5·0 (1·8)
N(2)	0·6937 (17)	0·0614 (14)	0·4557 (2)	9·8 (0·8)	6·0 (0·7)	2·9 (0·5)	−2·3 (1·2)	0·1 (1.)	−1·3 (0·9)
C(13)	0·5760 (22)	0·0719 (18)	0·4229 (3)	9·5 (1·0)	11·1 (1·2)	1·7 (0·5)	5·0 (1·7)	1·2 (1·2)	−0·6 (1·3)
C(14)	0·6682 (19)	0·0150 (15)	0·3997 (3)	7·0 (0·8)	8·3 (1·0)	2·9 (0·5)	2·4 (1·4)	2·7 (1·0)	1·5 (1·3)
C(15)	0·5549 (22)	0·0436 (19)	0·3661 (3)	7·5 (0·9)	11·4 (1·3)	4·1 (0·6)	−1·4 (1·8)	2·4 (1·3)	0·1 (1·6)
C(16)	0·6264 (21)	−0·0093 (17)	0·3404 (3)	7·6 (0·9)	9·3 (1·0)	3·8 (0·6)	−2·8 (0·6)	3·1 (1·2)	−2·6 (1·4)
C(17)	0·5202 (20)	0·0334 (16)	0·3078 (3)	7·6 (0·8)	8·6 (1·0)	2·5 (0·5)	1·4 (1·5)	2·1 (1·1)	−1·4 (1·2)
C(18)	0·5925 (20)	−0·0214 (16)	0·2813 (3)	7·2 (0·8)	7·8 (0·9)	3·6 (0·6)	1·2 (1·5)	1·7 (1·1)	−0·4 (1·3)
C(19)	0·4888 (22)	0·0382 (17)	0·2499 (3)	7·3 (0·8)	9·7 (1·0)	3·5 (0·5)	3·2 (1·6)	2·8 (1·1)	−0·1 (1·4)
C(20)	0·5516 (19)	−0·0182 (16)	0·2224 (3)	6·4 (0·8)	8·3 (1.)	3·5 (0·6)	−0·6 (1·4)	3·4 (1·1)	1·7 (1·2)
C(21)	0·4525 (19)	0·0361 (17)	0·1906 (3)	5·9 (0·8)	10·5 (1·1)	4·3 (0·6)	−1·4 (1·5)	1·7 (1·2)	−0·3 (1·4)
C(22)	0·5084 (20)	−0·0195 (17)	0·1632 (3)	6·3 (0·8)	9·1 (1·1)	3·9 (0·6)	3·4 (1·5)	2·5 (1·1)	−0·9 (1·4)
C(23)	0·4005 (20)	0·0312 (19)	0·1315 (3)	6·7 (0·8)	12·7 (1·3)	3·2 (0·6)	−4·1 (1·7)	1·8 (1·1)	0·3 (1·5)
C(24)	0·4507 (22)	−0·0258 (19)	0·1037 (3)	8·1 (0·9)	11·5 (1·3)	4·7 (0·7)	−5·5 (1·8)	2·2 (1·4)	−2·9 (1·7)

Table 2. *Final molecular parameters (e.s.d.'s refer to the last significant figure)*

Bond lengths (Å)		Bond angles (°)	
Zn–Cl(1)	2·278 (5)	Cl(1)–Zn–Cl(2)	110·51 (9)
Zn–Cl(2)	2·280 (4)	Cl(1)–Zn–Cl(3)	111·49 (9)
Zn–Cl(3)	2·262 (4)	Cl(1)–Zn–Cl(4)	110·15 (8)
Zn–Cl(4)	2·297 (4)	Cl(2)–Zn–Cl(3)	108·24 (8)
N(1)–C(1)	1·42 (2)	Cl(2)–Zn–Cl(4)	115·14 (7)
C(1)–C(2)	1·52 (2)	Cl(3)–Zn–Cl(4)	111·11 (7)
C(2)–C(3)	1·52 (2)	N(1)–C(1)–C(2)	116·6 (5)
C(3)–C(4)	1·52 (3)	C(1)–C(2)–C(3)	115·0 (6)
C(4)–C(5)	1·56 (2)	C(2)–C(3)–C(4)	111·9 (6)
C(5)–C(6)	1·55 (3)	C(3)–C(4)–C(5)	114·8 (6)
C(6)–C(7)	1·51 (2)	C(4)–C(5)–C(6)	110·1 (6)
C(7)–C(8)	1·54 (3)	C(5)–C(6)–C(7)	113·1 (7)
C(8)–C(9)	1·54 (2)	C(6)–C(7)–C(8)	112·9 (6)
C(9)–C(10)	1·51 (3)	C(7)–C(8)–C(9)	113·7 (6)
C(10)–C(11)	1·49 (2)	C(8)–C(9)–C(10)	114·1 (6)
C(11)–C(12)	1·54 (3)	C(9)–C(10)–C(11)	115·7 (8)
N(2)–C(13)	1·49 (2)	C(10)–C(11)–C(12)	117·1 (7)
C(13)–C(14)	1·50 (2)	N(2)–C(13)–C(14)	112·8 (6)
C(14)–C(15)	1·53 (2)	C(13)–C(14)–C(15)	111·2 (6)
C(15)–C(16)	1·49 (2)	C(14)–C(15)–C(16)	117·5 (7)
C(16)–C(17)	1·52 (2)	C(15)–C(16)–C(17)	115·1 (6)
C(17)–C(18)	1·53 (2)	C(16)–C(17)–C(18)	115·3 (6)
C(18)–C(19)	1·53 (3)	C(17)–C(18)–C(19)	111·0 (6)
C(19)–C(20)	1·54 (2)	C(18)–C(19)–C(20)	112·8 (6)
C(20)–C(21)	1·51 (2)	C(19)–C(20)–C(21)	115·1 (6)
C(21)–C(22)	1·50 (2)	C(20)–C(21)–C(22)	116·2 (6)
C(22)–C(23)	1·52 (3)	C(21)–C(22)–C(23)	115·4 (6)
C(23)–C(24)	1·50 (2)	C(22)–C(23)–C(24)	116·3 (7)

Internal rotation angles (°) [following the convention of Klyne & Prelog (1960)]

N(1)–C(1)–C(2)–C(3)	174
C(1)–C(2)–C(3)–C(4)	166
C(2)–C(3)–C(4)–C(5)	−177
C(3)–C(4)–C(5)–C(6)	173
C(4)–C(5)–C(6)–C(7)	−177
C(5)–C(6)–C(7)–C(8)	180
C(6)–C(7)–C(8)–C(9)	−179
C(7)–C(8)–C(9)–C(10)	179
C(8)–C(9)–C(10)–C(11)	−178
C(9)–C(10)–C(11)–C(12)	−178
N(2)–C(13)–C(14)–C(15)	−172
C(13)–C(14)–C(15)–C(16)	−179
C(14)–C(15)–C(16)–C(17)	−174
C(15)–C(16)–C(17)–C(18)	180
C(16)–C(17)–C(18)–C(19)	−174
C(17)–C(18)–C(19)–C(20)	−178
C(18)–C(19)–C(20)–C(21)	179
C(19)–C(20)–C(21)–C(22)	−179
C(20)–C(21)–C(22)–C(23)	177
C(21)–C(22)–C(23)–C(24)	−178

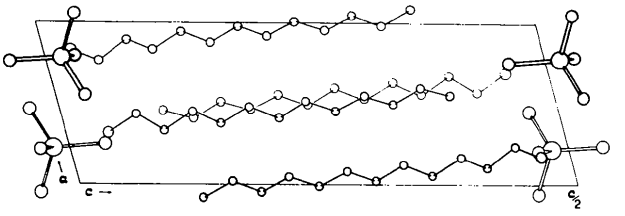

Fig. 1. Molecular model of $(n\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$: projection along the *b* axis.

their isotropic *B* factors were taken as equal to those of the bonded atoms) was performed by block-diagonal least squares to $R = 0{\cdot}075$.

The weighting scheme suggested by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) was adopted and the atomic scattering factors were calculated from the analytical constants of Moore (1963).

Table 1 shows the final positional and thermal parameters with their estimated standard deviations.* Molecular parameters are in Table 2. Fig. 1 shows the molecular packing along **b**.

Discussion. A series of compounds of general formula $(n\text{-}C_iH_{2i+1}NH_3)_2MCl_4$ with $i = 9,10\ldots17$ and M = Cu, Mn, Co, Fe, Zn have been recently synthetized in our laboratories. All these compounds show interesting order–disorder transitions which have been attributed to the gain in conformational freedom of the alkyl chains, while the three-dimensional ordering of the ions is retained (Landi & Vacatello, 1975). The structures of the compounds with M = Mn, Cu, Fe are characterized by the presence of $(MCl_4^{2-})_n$ extending periodically in two dimensions, as has been found in $(n\text{-}C_{10}H_{21}NH_3)_2MnCl_4$ (Ciajolo, Corradini & Pavone, 1976) where the metal atom has octahedral coordination. The calorimetric data and X-ray powder studies point to a different kind of structure for the Co and Zn compounds (Landi & Vacatello, 1975).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32178 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

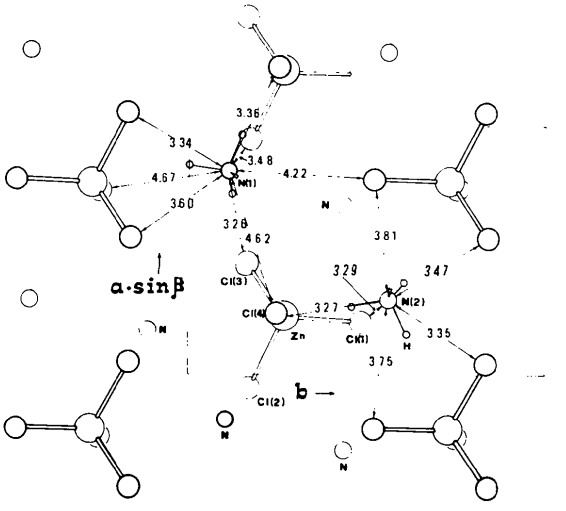

Fig. 2. Projection along the *c* axis of the ionic layer. All the N–Cl distances shorter than 5 Å are reported.

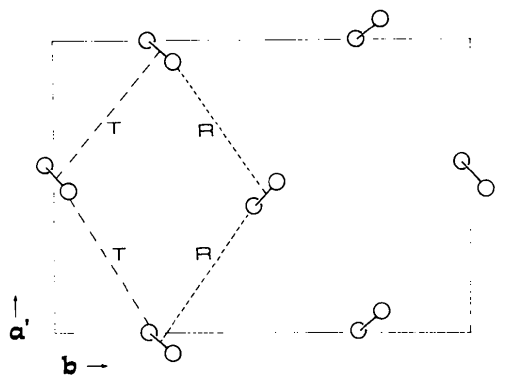

Fig. 3. Projection along the chain axis of the paraffinic part of $(n\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$, $a' = 7{\cdot}20$ Å. *T* and *R* refer to triclinic and orthorhombic contacts according to the nomenclature of Kitaigorodsky.

As shown in Fig. 1, the structure of $(n\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$ consists of ionic layers sandwiched between layers of paraffinic chains. Unlike $(n\text{-}C_{10}H_{21}NH_3)_2MnCl_4$, the ionic layers are comprised of single tetrahedral $ZnCl_4^{2-}$ anions in a nearly hexagonal planar array, each $ZnCl_4^{2-}$ anion being surrounded by six NH_3^+ groups. A model of this kind of array is shown in Fig. 2, where all the N—Cl distances shorter than 5 Å are reported.

The Zn—Cl distances are all equal within 0·02 Å and the distortions of the bond angles are less than 5° with respect to the tetrahedral value.

The paraffinic chains have a nearly planar zigzag conformation; the slight distortions of the internal rotation angles from 180° may be due to the need to achieve a closest packing arrangement of the chains in the spatial regions far from the ions. In these regions alternation of *T* and *R* [nomenclature of Kitaigorodsky (1961)] types of side-by-side packing of paraffinic chains is realized, as can be seen in Fig. 3, giving rise locally to a packing density very near that of polyethylene.

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Intermetallic Compounds: Antimony–Beryllium $SbBe_{13}$

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Abstract. $SbBe_{13}$, F.W. 238·88 space group *Fm3c*; $a = 10{\cdot}046\,(3)$ Å, $Z = 8$; $D_c = 3{\cdot}13$ g cm^{-3}; $U = 1013{\cdot}9$ Å^3; μ(Mo $K\alpha$) = 53·1 cm^{-1}; $F(000) = 688$. This structure was solved by the Patterson method and refined by least-squares analysis to an *R* of 0·043, including 105 reciprocal points. $SbBe_{13}$ has the $NaZn_{13}$-type structure.

Introduction. This work is part of a structural study of the intermetallic compounds formed by alkaline-earth metals with the Group V*a* elements.

It is well known that Mg reacts with the elements of the V*a* main group giving rise to salt-like structures of the type Mg_3X_2, where X = N, P, As, Sb, Bi (Stackelberg & Paulus, 1933; Zintl & Husemann, 1933; Martínez-Ripoll, Haase & Brauer, 1974), although von Schnering & Menge (1976) reported a compound with the formula MgP_4.

The heavy alkaline-earth metals form compounds which deviate from the above-mentioned salt-like stoichiometry [MX, $M_{11}X_{10}$, M_5X_3, M_2X, where M = Ca, Sr, Ba (Iandelli & Franceschi, 1973; Deller & Eisenmann, 1976; Eisenmann & Deller, 1975)], showing their similarity to the divalent lanthanide and actinide elements (Iandelli & Franceschi, 1973; Yoshihara, Taylor, Calvert & Despault, 1975).

The same salt-like formulae as for Mg have been found for several compounds between Be and the Group V*a* elements: Be_3N_2, Be_3P_2 (Stackelberg & Paulus, 1933) and Be_3As_2 (Weibke, 1930). Baird,