Structure of Penta(dimethylammonium) Undecachlorotricadmate(II)

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Abstract. $5C_2H_8N^+.Cd_3Cl_{11}^{5-}$, $M_r = 957.6$, orthorhombic, *Cmcm*, $a = 18.108$ (15), $b = 11.413$ (8), $c = 15.789$ (10) Å, $V = 3263$ (5) Å³, $Z = 4$, D_m(flotation) $= 1.94$ (2), $D_x = 1.949$ (2) g cm⁻³, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 2.82$ mm⁻¹, $F(000) = 1864$, $T = 297$ (2) K, final $R = 0.0465$ for 2083 unique reflections. The structure is formed by two alternating layers parallel to [001]. One of these consists of the dimethylammonium cations and the other consists of the complex anions. Hydrogen bonds of the type N—H···Cl link the two layers. In the $[Cd_3Cl_{11}]^{5-}$ anion each Cd atom is octahedrally coordinated with the Cd—Cl distance ranging from 2.503 (3) to 2.784 (3) Å. Among the chloride ions there are six terminal and five bridging Cl atoms, two of which are bonded to three Cd atoms. One $=NH_2^+$ group exhibits site occupation disorder.

Introduction. Numerous crystals containing methylammonium cations exhibit phase transitions related to the dynamics of the organic cations and inorganic anions. A new crystalline compound with composition $[(CH_3)_2NH_2]_5Cd_3Cl_{11}$ has recently been reported (Czapla, Dacko, Krzewska & Waśkowska, 1989). The crystals undergo phase transitions at $T_1 = 260$, $T_2 = 180$ and $T_3 = 127$ K. The present study describes the X-ray crystal structure at room temperature which may facilitate an understanding of the molecular mechanism of the phase transitions.

Experimental. The compound was obtained from water solutions containing stoichiometric quantities of $CdCl_2.4H_2O$ and $[(CH_3)_2NH]_2Cl$ with a small excess of HCl. Transparent prismatic crystals were grown by slow evaporation at 304 K. The sample crystal was ground into a sphere of diameter 0.5 mm. Weissenberg photographs indicated that two space groups *Cmcm* or *Cmc*2₁ were possible. The X-ray

measurements were performed on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator, lattice parameters were refined from 2θ values of 15 reflections in the range $20 \le 2\theta \le 24°$. A total of 3547 reflections with $4 \le 2\theta \le 70°$ were collected using the $\theta/2\theta$ scan technique. 2083 independent reflections with $I > 3\sigma(I)$ were used for the structure determination. The *hkl* range was $h: 0 \rightarrow 28$, $k: 0 \rightarrow 17$, $l: 0 \rightarrow 24$. Two control reflections were measured after every 50 reflections; their intensity varied $\le 5\%$. The intensity data were corrected for Lorentz, polarization and absorption effects ($\mu R = 0.705$). The structure was solved by the Patterson method (*SHELXS*86; Sheldrick, 1986) and subsequent calculations of the electron density difference, $\Delta\rho$. The structure was least-squares refined (on F) with *SHELX*76 (Sheldrick, 1976). All non-H atoms were refined with anisotropic thermal parameters. The H atoms in the CH_3 groups were found in $\Delta\rho$ maps and refined at the constrained distance 1.08 Å. The positions of the H atoms belonging to the NH_2^+ groups were calculated and fixed at the constrained distance 1.00 Å. A constant $U_{iso} = 0.15$ Å² was assigned to all H atoms. An empirical correction for extinction, $F_{corr} = F(1 - xF^2\sin\theta)$, was applied (Larson, 1970). The parameter x converged to 0.00103 (1). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, with σ based on counting statistics. The final error indicators were $R = 0.0465$, $wR = 0.0462$ for 102 refined parameters, $(\Delta/\sigma)_{max} = 0.011$. Min. and max. residual electron density was -1.2 and 1.3 e Å⁻³. Scattering factors and corrections for anomalous dispersion for neutral atoms C, H, N and Cl were in *SHELX*76 (Sheldrick, 1976) and for Cd in *International Tables for X-ray Crystallography* (1974).

Discussion. Positional and thermal parameters are listed in Table 1, bond distances and angles in Table

Table 1. *Atomic positional parameters and equivalent isotropic thermal parameters*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

$U_{iso} = 0.15$ Å^2 for all H atoms.

	x	y	z	U_{eq}(Å^2)
Cd(1)	0	0·0250 (1)	0·25	0·0387 (3)
Cd(2)	−0·1105 (0)	0·3010 (1)	0·25	0·0430 (2)
Cl(1)	−0·1481 (1)	0·0780 (2)	0·25	0·0497 (6)
Cl(2)	0	0·4842 (3)	0·25	0·0437 (8)
Cl(3)	0	0·2080 (2)	0·3593 (1)	0·0377 (4)
Cl(4)	0	−0·1144 (2)	0·1276 (2)	0·0640 (7)
Cl(5)	−0·1708 (1)	0·3903 (2)	0·1286 (2)	0·0730 (7)
N(1)	−0·3267 (7)	0·1344 (11)	0·25	0·0940 (5)
N(2)	0·1241 (10)	0	0	0·165 (9)
N(3)	0	0·4704 (17)	0·0422 (13)	0·069 (6)
C(1)	−0·3335 (9)	0·2017 (11)	0·1738 (9)	0·118 (5)
C(2)	0·1649 (7)	−0·1048 (9)	−0·0153 (8)	0·089 (3)
C(3)	0	0·4045 (12)	−0·0351 (9)	0·097 (6)
H(1)	−0·336	0·073	0·25	
H(11)	−0·277	0·100	0·25	
H(2)	0·092	−0·015	0·051	
H(3)	0·045	0·448	0·075	
H(12)	−0·298 (4)	0·278 (5)	0·169 (7)	
H(13)	−0·390 (2)	0·228 (7)	0·180 (7)	
H(14)	−0·327 (5)	0·147 (8)	0·118 (4)	
H(21)	0·120 (4)	−0·170 (5)	−0·010 (6)	
H(22)	0·207 (4)	−0·122 (9)	0·032 (4)	
H(23)	0·189 (5)	−0·108 (9)	−0·078 (3)	

Table 2. *Bond distances* (Å) *and angles* (°)

Cd(1)—Cl(1)	2·749 (3)	Cd(2)—Cl(3)	2·735 (3)
Cd(1)—Cl(3)	2·709 (2)	Cd(2)—Cl(5)	2·508 (3)
Cd(1)—Cl(4)	2·503 (3)	N(1)—C(1)	1·433 (13)
Cd(2)—Cl(1)	2·682 (3)	N(2)—C(2)	1·427 (13)
Cd(2)—Cl(2)	2·784 (3)	N(3)—C(3)	1·433 (13)

C(1)—N(1)—C(1)^{ii}	114. (1·6)	Cl(3)—Cd(2)—Cl(1)	81·0 (1)
C(2)—N(2)—C(2)^{v}	117·6 (1·7)	Cl(3)—Cd(2)—Cl(2)	81·2 (1)
C(3)—N(3)—C(3)^{iv}	117·1 (2·8)	Cl(5)—Cd(2)—Cl(1)	103·2 (1)
Cl(3)—Cd(1)—Cl(1)	80·2 (1)	Cl(5)—Cd(2)—Cl(2)	91·4 (1)
Cl(3)—Cd(1)—Cl(3)^{iii}	79·0 (1)	Cl(5)—Cd(2)—Cl(3)	167·5 (1)
Cl(4)—Cd(1)—Cl(1)	98·0 (0)	Cd(1)—Cl(1)—Cd(2)	84·4 (1)
Cl(1)—Cd(1)—Cl(1)^{i}	154·6 (1)	Cd(2)—Cl(2)—Cd(2)^{i}	82·6 (1)
Cl(4)—Cd(1)—Cl(3)	169·0 (1)	Cd(2)—Cl(3)—Cd(1)	84·1 (1)
Cl(2)—Cd(2)—Cl(1)	157·0 (1)		

Symmetry code: None: x, y, z; (i) −x, y, −z; (ii) x, y, ½−z; (iii) −x, y, ½−z; (iv) x, 1 − y, z; (v) x, −y, −z.

2.* The structure of the [Cd$_3$Cl$_{11}$]$^{5-}$ anion is shown in Fig. 1 and a stereoview of the unit-cell contents is shown in Fig. 2.

The trinuclear unit [Cd$_3$Cl$_{11}$]$^{5-}$ has local symmetry *mm*. This anion consists of octahedrally coordinated Cd atoms with Cl atoms at the corners of the coordination polyhedron. Each of three distorted octahedra is connected to the others by sharing

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52802 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

faces in such a way that the edge Cl(3)—Cl(3)^{iii} is common to all three polyhedra, while the corners Cl(1), Cl(1)^{i} and Cl(2) are each shared by two. Each octahedron has thus two unshared corners, with two terminal Cl atoms. The three Cd atoms and the three doubly bonded Cl atoms lie in one plane forming an irregular six-membered ring with the corners occupied alternately by the Cd and Cl atoms. Above and below the equatorial plane there are two triply bonded Cl atoms.

The crystal structure is formed by two alternating layers parallel to the (001) plane. One of these consists of dimethylammonium cations with van der Waals interactions between them – as far as we can infer from those H atoms which are revealed in the $\Delta\rho$ maps (Table 3 gives the donor–acceptor distances shorter than 3·6 Å for N—H···Cl hydrogen bonds). The other layer comprises the chlorocadmate complexes linked in a chain by one of the cations, [N(1)H$_2$C(1)H$_2$]. The ammonium group of this cation connects two separate [Cd$_3$Cl$_{11}$]$^{5-}$ anions by forming hydrogen bonds with the equatorial, doubly bonded Cl(1) and Cl(2) atoms. The methyl group [C(1)H$_3$] points towards the terminal Cl(5) atom and the interaction is of a predominantly electrostatic
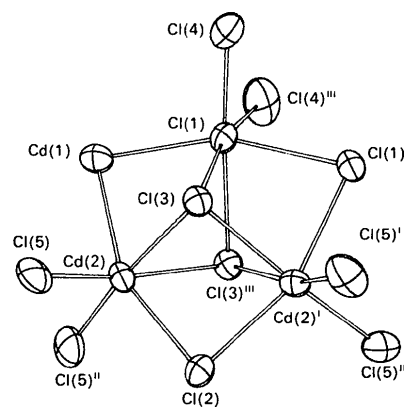

Fig. 1. *ORTEP* (Johnson, 1970) drawing of the [Cd$_3$Cl$_{11}$]$^{5-}$ anion. Symmetry code: none: x, y, z; (i) −x, y, z; (ii) x, y, ½ − z; (iii) −x, y, ½ − z.
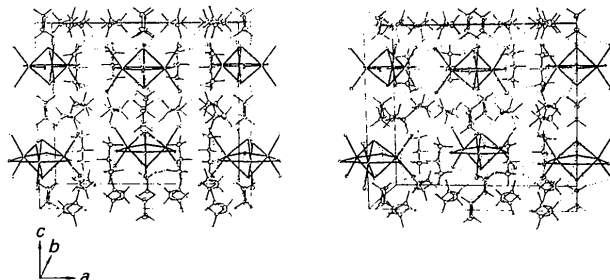

Fig. 2. Stereoscopic view of the molecular packing in the unit cell.

Table 3. *Possible hydrogen bonds* (Å,°)

X—H$\cdots Y$	H$\cdots Y$	$X\cdots Y$	X—H—Y
N(1)—H(1)$\cdots$Cl(2)^{viii,ix}	2·63 (1)	3·576 (13)	158 (6)
N(1)—H(11)$\cdots$Cl(1)^{0,viii}	2·35 (2)	3·298 (13)	161 (6)
N(2)—H(2)$\cdots$Cl(4)^{0,vi}	2·35 (2)	3·288 (13)	154 (6)
N(3)—H(2)$\cdots$Cl(5)^{vi}	2·52 (2)	3·502 (10)	168 (9)

Symmetry code: (0) x, y, z; (vi) $-x, y, z$; (vii) $x, y, \frac{1}{2}-z$; (viii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (ix) $x - \frac{1}{2}, y - \frac{1}{2}, z - \frac{1}{2}$.

nature. The shortest C$\cdots$Cl distances are about 3·7 (1) Å. Connection to the organic layer occurs *via* the hydrogen-bond system formed by the terminal Cl(4) and Cl(5) atoms and the ammonium and methyl groups. The distance 3·288 (13) Å for the N(2)—H(2)$\cdots$Cl(4) contact appears to be the shortest of this type in the structure. The third ammonium group [N(3)H$_2$] exhibits positional disorder relative to the mirror plane *m*. The N(3) atom was thus refined in two statistically equivalent positions, both with an occupancy factor of 0·5. The two statistically occupied positions correspond to two equivalent potential-energy minima in the room temperature

phase. Transition to the low temperature phase may cause a freezing of the [N(3)H$_2$] group in one preferred orientation.

Further studies on the dynamics of this cation group will give information on the character and phase-transition mechanism in [(CH$_3$)$_2$NH$_2$]$_5$Cd$_3$Cl$_{11}$ crystals.

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Structure of a Copper(II) Complex of the Deprotonated Anion of 3,10-Dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione Dioxime

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Abstract. Bis[μ-3,10-dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione dioximato(1$-$)-μ-O,N,N',N'',N''']-dicopper(II) diperchlorate [Cu(C$_{12}$H$_{21}$N$_4$O$_2$)]$_2^{2+}$.-2ClO$_4^-$, $M_r = 832·6$, monoclinic, $P2_1/n$, $a = 6·484$ (2), $b = 21·711$ (4), $c = 12·397$ (3) Å, $\beta = 96·59$ (2)°, $V = 1733·5$ (6) Å^3, $Z = 2$, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 14·51$ cm^{-1}, $D_x = 1·595$ g cm^{-3}, $T = 297$ K, $R = 0·0448$, $wR = 0·0452$ for 1897 independent reflections [$I > 3\sigma(I)$]. The crystal contains a binuclear complex with two oxime groups as bridging ligands. The copper coordination is a buckled square pyramid. The four donor N atoms of the diazadioxime form a very slightly distorted plane and an oxime O atom of the other diazadioxime occupies the axial position. An oxime proton is lost from the ligand in forming the complex and the remaining oxime proton forms a hydrogen bond between the two oxime O atoms of the same molecule.

Introduction. Copper(II)–diazadioxime complexes present considerable interest in bio-inorganic chemistry (Gagné, 1976; Gagné, Allison, Gall & Koval, 1977; Gagné, Allison & Ingle, 1979). They may serve as model compounds of copper enzymes with 'type 2' copper sites (Giordano & Bereman, 1974; Morpurgo, Giovagnoli & Rotilio; 1973; Richardson, Thomas, Rubin & Richardson, 1975). However, very little attention has been devoted to the crystal structures of this type of complex. The crystal structure of the copper(II) complex with the deprotonated anion of 3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioxime has been reported by Bertrand, Smith & VanDerveer (1977). We report here the crystal structure of the copper(II) complex with the deprotonated anion of 3,10-dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione dioxime (H$_{-1}L$ in formulae).

Experimental. Preparation of 3,10-dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione dioxime: 2,3-

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