

Structures of Trimethylammonium Tetrachlorometallates

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Abstract. $[\text{NH}(\text{CH}_3)_3]_2[\text{CuCl}_4]$, $M_r = 325.6$, monoclinic, $P2_1/c$, $a = 8.174(2)$, $b = 14.171(3)$, $c = 12.553(2)$ Å, $\beta = 96.25(1)^\circ$, $V = 1445.1(5)$ Å³, $Z = 4$, $D_x = 1.50$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 22.31$ cm⁻¹, $F(000) = 668$, $T = 180(5)$ K, $R = 0.0245$, $wR = 0.0261$ for 2505 data with $F \geq 6\sigma(F)$. $[\text{NH}(\text{CH}_3)_3]_2[\text{ZnCl}_4]$, $M_r = 327.4$, orthorhombic, $Pnma$, $a = 10.660(1)$, $b = 9.629(1)$, $c = 14.991(2)$ Å, $V = 1538.8(3)$ Å³, $Z = 4$, $D_x = 1.41$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 23.07$ cm⁻¹, $F(000) = 672$, $T = 295(1)$ K, $R = 0.041$, $wR = 0.063$ for 1195 data with $F \geq 6\sigma(F)$. Two new structures are reported for the $[\text{NH}(\text{CH}_3)_3]_2[M\text{Cl}_4]$ family of salts. The Zn complex has a regular tetrahedral ZnCl_4 ion [$\text{Zn}-\text{Cl} = 2.247\text{--}2.283(2)$ Å] whereas the CuCl_4 ion [$\text{Cu}-\text{Cl} = 2.236\text{--}2.259(1)$ Å] has a D_{2d} -type Jahn–Teller distortion with two angles of $132.9(1)$ and the rest between $97.0\text{--}101.6(1)^\circ$. The packing for the Zn complex bears a close resemblance to that of its tetramethylammonium analogue, with the ion centres lying in the mirror planes at $y = 0.25$ and 0.75 . Packing in the Cu complex is topologically related, but adoption of a different hydrogen-bond network leads to displacement of the ions and a lowering of symmetry.

Introduction. Alkylammonium chlorometallates have been the subject of considerable attention for their rich phase-transition behaviour. The most widely studied family are the tetramethylammonium tetrachlorometallates $[\text{N}(\text{CH}_3)_4]_2[M\text{Cl}_4]$ where M may be a variety of divalent metal ions, Mn, Fe, Co, Ni, Cu, Zn, Cd and Zn. The report of an anomalously high electro-optic effect for $[\text{N}(\text{CH}_3)_4]_2[\text{ZnCl}_4]$ (Saito, Kunishima, Kobayashi & Uesu, 1985) led us to consider the doping of trimethylammonium ions into this material. Structural studies of the corresponding pure trimethylammonium salts $[\text{NH}(\text{CH}_3)_3]_2[M\text{Cl}_4]$ appear to be limited to the Hg complex (Ben Salah, Bats, Fuess & Daoud, 1983). Herein we report the structures of two other members of this family, $[\text{NH}(\text{CH}_3)_3]_2[\text{CuCl}_4]$ and $[\text{NH}(\text{CH}_3)_3]_2[\text{ZnCl}_4]$.

Experimental. The compounds were prepared by reaction of the metal dihalide with trimethylammonium chloride in ethanol. Suitable orange-yellow crystals of $[\text{NH}(\text{CH}_3)_3]_2[\text{CuCl}_4]$ were grown by vapour diffusion of ethyl acetate into a methanolic solution of the compound at 295 K. A specimen $0.24 [100] \times 0.34 [010] \times 0.34 [01\bar{1}] \times 0.44$ mm $[011]$ was chosen. Accurate cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections with $20 < 2\theta < 30^\circ$. The cell constants at 295 K were $a = 8.330(1)$, $b = 14.459(3)$, $c = 12.466(2)$ Å, $\beta = 97.10(1)^\circ$, $V = 1489.6(5)$ Å³. A total of 1940 unique intensity data were collected on a Siemens $R3m/V$ four-circle diffractometer with graphite-monochromatized Mo radiation (0.71073 Å) at ambient temperature (295 K). The crystal was subsequently cooled and a collection made at low temperature (180 K). The cell constants had changed to $a = 8.174(2)$, $b = 14.171(3)$, $c = 12.553(2)$ Å, $\beta = 96.25(1)^\circ$, $V = 1445.1(5)$ Å³. The results of only the low-temperature refinement are reported here, since no significant difference in the molecular packing was observed between the two refined structures, nor was there evidence of disorder at room temperature. Data for the room-temperature structure are available as supplementary material.* The ω -scan method was employed in the range $3 < 2\theta < 54^\circ$, $0 \leq h \leq 10$, $0 \leq k \leq 18$, $-16 \leq l \leq 15$, with a width of 1.2° in ω and a variable scan speed of $2.9\text{--}29.3^\circ \text{ min}^{-1}$. Two standard reflections were monitored periodically with less than 2% fluctuation

* Lists of anisotropic displacement parameters and H-atom parameters for $[\text{NH}(\text{CH}_3)_3]_2[\text{CuCl}_4]$ at 180 K, fractional coordinates, bond lengths and angles, anisotropic displacement parameters and H-atom parameters for $[\text{NH}(\text{CH}_3)_3]_2[\text{CuCl}_4]$ at 295 K, anisotropic displacement parameters and H-atom parameters for $[\text{NH}(\text{CH}_3)_3]_2[\text{ZnCl}_4]$, structure factors for $[\text{NH}(\text{CH}_3)_3]_2[\text{CuCl}_4]$ at 180 and 295 K and for $[\text{NH}(\text{CH}_3)_3]_2[\text{ZnCl}_4]$ have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54514 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0513]

through the course of data collection. Data reduction, structure solution and refinement were carried out using the Siemens *SHELXTL-Plus* program package (Sheldrick, 1990). Neutral-atom scattering and anomalous-dispersion factors were used (Cromer & Waber, 1974; Stewart, Davidson & Simpson, 1965). Data were corrected numerically for absorption following indexing and measurement of the crystal faces. Transmission factors varied between 0.53 and 0.61. At 180 K, 3153 unique data were collected of which 2505 with $F \geq 6\sigma(F)$ were used in refinement. The structure was solved by analysis of the Patterson function and refined by full-matrix least squares, with minimization of the function $\sum w(F_o - F_c)^2$. All H atoms were located by difference Fourier and included in final refinement cycles, with individual positional and isotropic thermal parameters. All non-H atoms were refined anisotropically. Convergence was reached for a conventional $R = 0.025$, $wR = 0.026$, $S = 1.21$ for 198 parameters. A weighting scheme $w = [\sigma^2(F) + gF^2]^{-1}$ was applied with $g = 0.00025$. Maximum residual electron density was 0.34 near Cl(4) and difference hole $-0.30 \text{ e} \cdot \text{\AA}^{-3}$. The largest Δ/σ in the final cycle was 0.03 and the mean less than 0.001. Final positional and thermal parameters are given in Table 1.

Colourless crystals of $[\text{NH}(\text{CH}_3)_3]_2[\text{ZnCl}_4]$ were obtained by layer diffusion of ethyl acetate into a methanolic solution at 295 K. A prism $0.56 [1\bar{1}0] \times 0.56 [110] \times 0.40 \text{ mm} [001]$ was used. Experimental details and protocols were as for the Cu complex except where noted below. Difficulties with crystal cracking were encountered upon cooling the compound and data collection had to be carried out at ambient temperature. In all, 3948 reflections (hkl and $h\bar{k}l$ pairs) were measured with 1974 unique ($R_{\text{int}} = 0.0419$) in the range $4 < 2\theta < 56^\circ$ with index ranges $0 \leq h \leq 14$, $0 \leq k \leq 12$ and $0 \leq l \leq 19$. A numerical absorption correction was applied with minimum/maximum transmission of 0.19/0.24 and extinction was corrected for by the formula $F_{\text{cor}} = F(1 + 0.002\chi F^2/\sin 2\theta)^{-1/4}$ where the empirical parameter $\chi = 0.0026$ (5). A total of 1194 intensity data with $F \geq 6\sigma(F)$ were used in refinement (99 parameters) to give $R = 0.041$, $wR = 0.063$, $S = 1.12$ for $g = 0.0021$. High thermal parameters were found for the methyl C atoms, a feature previously observed in the commensurate $Pnma$ phase of $[\text{N}(\text{CH}_3)_4]_2[\text{ZnCl}_4]$. The effect was particularly marked in the trimethylammonium ion associated with N(2) and led to it being modelled as a disordered group, since refinement of an ordered structure in noncentrosymmetric $Pn2_1a$ led to no significant improvement. The basis for the disordered model came from a Fourier map which showed a split peak for the off-mirror atom C(4) with an electron density minimum at the centre. This was subsequently refined as

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for $[\text{NH}(\text{CH}_3)_3]_2[\text{CuCl}_4]$ at 180 (5) K with e.s.d.'s in parentheses*

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cu(1)	0.22044 (3)	0.10566 (2)	0.26554 (2)	0.0237 (1)
Cl(1)	-0.03713 (7)	0.15315 (4)	0.20864 (5)	0.0327 (2)
Cl(2)	0.21615 (7)	0.10580 (4)	0.44467 (4)	0.0323 (2)
Cl(3)	0.24015 (7)	-0.01068 (4)	0.14454 (5)	0.0345 (2)
Cl(4)	0.46685 (8)	0.17375 (5)	0.26355 (5)	0.0421 (2)
N(1)	-0.1523 (2)	-0.0662 (1)	0.1660 (2)	0.0265 (6)
C(1)	-0.3258 (3)	-0.0332 (2)	0.1441 (3)	0.0431 (9)
C(2)	-0.1199 (4)	-0.1467 (2)	0.0948 (3)	0.0422 (9)
C(3)	-0.1112 (4)	-0.0910 (2)	0.2806 (2)	0.0434 (9)
H(11)	-0.088 (3)	-0.023 (2)	0.158 (2)	0.035 (7)
N(2)	0.6294 (2)	0.1808 (1)	0.5052 (2)	0.0276 (6)
C(4)	0.5998 (4)	0.1370 (2)	0.6085 (2)	0.0382 (9)
C(5)	0.6058 (4)	0.2849 (2)	0.5067 (2)	0.0376 (8)
C(6)	0.7951 (4)	0.1560 (2)	0.4745 (3)	0.0437 (9)
H(21)	0.556 (3)	0.162 (2)	0.460 (2)	0.038 (8)

Table 2. *Final fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for $[\text{NH}(\text{CH}_3)_3]_2[\text{ZnCl}_4]$ at 295 K with e.s.d.'s in parentheses*

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Zn(1)	0.24751 (5)	0.25000	0.06388 (4)	0.0584 (2)
Cl(1)	0.0381 (2)	0.25000	0.0811 (2)	0.0999 (8)
Cl(2)	0.2918 (2)	0.25000	-0.0851 (1)	0.0958 (7)
Cl(3)	0.3415 (1)	0.0647 (1)	0.1278 (1)	0.0936 (5)
N(1)	0.0152 (4)	0.25000	-0.1613 (3)	0.058 (1)
C(1)	0.0588 (12)	0.25000	-0.2568 (6)	0.139 (5)
C(2)	-0.0515 (9)	0.1231 (9)	-0.1435 (7)	0.178 (5)
H(1)	0.0842	0.25000	-0.1268	0.074 (18)
N(2)	0.6145 (5)	0.25000	0.1153 (3)	0.065 (2)
C(3)*	0.6255 (15)	0.2897 (31)	0.0247 (8)	0.157 (15)
C(4)*	0.6795 (16)	0.1113 (16)	0.1286 (14)	0.122 (7)
C(44)*	0.6631 (22)	0.3400 (24)	0.1827 (12)	0.152 (8)
H(2)*	0.5334	0.2362	0.1295	0.096 (25)

* Disordered atoms with site occupancy set at 0.5.

two atoms C(4) and C(44), each with 0.5 occupancy factors. In addition the methyl C atom in the mirror plane C(3) had a physically unreasonable vibration amplitude U_{22} perpendicular to the mirror. In the disordered model this atom was allowed to refine off the mirror keeping a site occupancy of 0.5. The sets C(3), C(4), C(44) and C(3'), C(4'), C(44') thus describe two rotational orientations for the ion. H atoms were located in difference Fourier maps, except for those in the disordered trimethylammonium group, and were given idealized geometries with riding constraints $d_{\text{C-H,N-H}} = 0.96 \text{ \AA}$ and individual isotropic thermal parameters. Discrepancy indices for all data were $R = 0.066$ and $wR = 0.082$. The largest residual electron density was $+0.43$ and difference hole $-0.48 \text{ e} \cdot \text{\AA}^{-3}$. The largest Δ/σ in the final cycle was 0.486 and the mean 0.070. Final fractional coordinates and thermal parameters are given in Table 2.

Discussion. The molecular structures of $[\text{NH}(\text{CH}_3)_3]_2\text{[CuCl}_4\text{]}$ and $[\text{NH}(\text{CH}_3)_3]_2\text{[ZnCl}_4\text{]}$ are shown in Figs. 1 and 2 respectively. In each case discrete trimethylammonium cations and $[\text{MCl}_4]$ dianions are found with $\text{N}\cdots\text{H}\cdots\text{Cl}$ hydrogen bonding between the ions. Bond lengths and angles for the two compounds are given in Table 3. The tetrachlorocuprate(II) ion is found to have a flattened tetrahedral geometry. Two opposite $\text{Cl}\text{—Cu}\text{—Cl}$ angles are opened up to $132.9(1)^\circ$ while the others range between $97.0\text{--}101.6(1)^\circ$. The $\text{Cu}\text{—Cl}$ distances vary between $2.236\text{--}2.259(1)\text{ \AA}$. This D_{2d} distortion has been observed previously in $[\text{N}(\text{CH}_3)_4]_2\text{[CuCl}_4\text{]}$ (Clay, Murray-Rust & Murray-Rust, 1975) and other $[\text{CuCl}_4]^{2-}$ salts (Lamotte-Brasseur, Dupont & Dideberg, 1973) and may be traced to the d^9 configuration of the Cu atom. In contrast, a less distorted tetrahedral geometry is found for the $[\text{ZnCl}_4]^{2-}$ ion, with $\text{Zn}\text{—Cl}$ distances between $2.247\text{--}2.283(2)\text{ \AA}$ and $\text{Cl}\text{—Zn}\text{—Cl}$ angles ranging from $104.3\text{--}113.1(1)^\circ$.

Both crystal structures display new packing arrangements in this family of compounds. The Hg analogue possesses two simple hydrogen bonds from the $\text{N}\text{—H}$ groups of the two independent $[\text{NH}(\text{CH}_3)_3]$ cations to a single Cl of the $[\text{HgCl}_4]^{2-}$ ion (Ben Salah, Bats, Fuess & Daoud, 1983). In $[\text{NH}(\text{CH}_3)_3]_2\text{[CuCl}_4\text{]}$ two asymmetric bifurcated hydrogen bonds are formed involving both amine H atoms and all four Cl atoms of the asymmetric unit. Two short contacts $\text{H}(11)\cdots\text{Cl}(1) = 2.50(3)$ and $\text{H}(21)\cdots\text{Cl}(4) = 2.60(3)\text{ \AA}$ are augmented by two additional incipient contacts $\text{H}(11)\cdots\text{Cl}(3) = 2.87(3)$ and $\text{H}(21)\cdots\text{Cl}(2) = 2.88(3)\text{ \AA}$. The bifurcating H atoms are associated with the Cl pairs with the

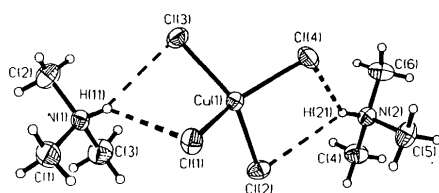


Fig. 1. Molecular structure of $[\text{NH}(\text{CH}_3)_3]_2\text{[CuCl}_4\text{]}$ showing hydrogen bonds.

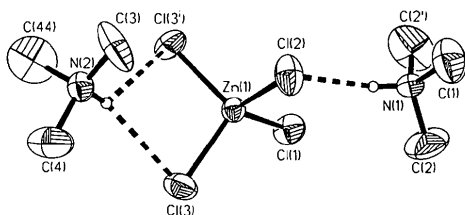


Fig. 2. Molecular structure of $[\text{NH}(\text{CH}_3)_3]_2\text{[ZnCl}_4\text{]}$ showing hydrogen bonds. One orientation of the disordered cation is shown for clarity.

Table 3. Bond lengths (\AA), angles ($^\circ$) and hydrogen-bond contacts for $[\text{NH}(\text{CH}_3)_3]_2\text{[MCl}_4\text{]}$ with e.s.d.'s in parentheses

$[\text{NH}(\text{CH}_3)_3]_2\text{[CuCl}_4\text{]}$		$[\text{NH}(\text{CH}_3)_3]_2\text{[ZnCl}_4\text{]}$	
$\text{Cu}(1)\text{—Cl}(1)$	2.251 (1)	$\text{Zn}(1)\text{—Cl}(1)$	2.247 (2)
$\text{Cu}(1)\text{—Cl}(2)$	2.253 (1)	$\text{Zn}(1)\text{—Cl}(2)$	2.283 (2)
$\text{Cu}(1)\text{—Cl}(3)$	2.259 (1)	$\text{Zn}(1)\text{—Cl}(3)$	2.259 (1)
$\text{Cu}(1)\text{—Cl}(4)$	2.236 (1)		
$\text{N}(1)\text{—C}(1)$	1.490 (3)	$\text{N}(1)\text{—C}(1)$	1.504 (11)
$\text{N}(1)\text{—C}(2)$	1.492 (4)	$\text{N}(1)\text{—C}(2)$	1.439 (10)
$\text{N}(1)\text{—C}(3)$	1.483 (3)	$\text{N}(2)\text{—C}(3)$	1.416 (15)
$\text{N}(2)\text{—C}(4)$	1.481 (3)	$\text{N}(2)\text{—C}(4)$	1.518 (16)
$\text{N}(2)\text{—C}(5)$	1.488 (3)	$\text{N}(2)\text{—C}(44)$	1.428 (21)
$\text{N}(2)\text{—C}(6)$	1.491 (4)		
$\text{Cl}(1)\text{—Cu}(1)\text{—Cl}(2)$	101.6 (1)	$\text{Cl}(1)\text{—Zn}(1)\text{—Cl}(2)$	108.5 (1)
$\text{Cl}(1)\text{—Cu}(1)\text{—Cl}(3)$	97.9 (1)	$\text{Cl}(1)\text{—Zn}(1)\text{—Cl}(3)$	113.1 (1)
$\text{Cl}(1)\text{—Cu}(1)\text{—Cl}(4)$	132.8 (1)	$\text{Cl}(2)\text{—Zn}(1)\text{—Cl}(3)$	108.9 (1)
$\text{Cl}(2)\text{—Cu}(1)\text{—Cl}(3)$	133.0 (1)	$\text{Cl}(3)\text{—Zn}(1)\text{—Cl}(3)$	104.3 (1)
$\text{Cl}(2)\text{—Cu}(1)\text{—Cl}(4)$	97.0 (1)		
$\text{Cl}(3)\text{—Cu}(1)\text{—Cl}(4)$	100.2 (1)	$\text{C}(1)\text{—N}(1)\text{—C}(2)$	109.2 (5)
$\text{C}(1)\text{—N}(1)\text{—C}(2)$	110.9 (2)	$\text{C}(2)\text{—N}(1)\text{—C}(2)$	116.3 (8)
$\text{C}(1)\text{—N}(1)\text{—C}(3)$	111.4 (2)	$\text{C}(3)\text{—N}(2)\text{—C}(4)$	109.0 (14)
$\text{C}(2)\text{—N}(1)\text{—C}(3)$	111.3 (2)	$\text{C}(3)\text{—N}(2)\text{—C}(44)$	118.9 (14)
$\text{C}(4)\text{—N}(2)\text{—C}(5)$	111.8 (2)	$\text{C}(4)\text{—N}(2)\text{—C}(44)$	106.0 (12)
$\text{C}(4)\text{—N}(2)\text{—C}(6)$	111.5 (2)		
$\text{C}(5)\text{—N}(2)\text{—C}(6)$	111.1 (2)		
Hydrogen-bond contacts			
$\text{H}(11)\cdots\text{Cl}(1)$	2.60 (3)	$\text{H}(1)\cdots\text{Cl}(2)$	2.30 (4)
$\text{H}(11)\cdots\text{Cl}(3)$	2.87 (3)	$\text{H}(1)\cdots\text{Cl}(1)$	3.16 (5)
$\text{H}(21)\cdots\text{Cl}(4)$	2.50 (3)	$\text{H}(2)\cdots\text{Cl}(3)$	2.63 (5)
$\text{H}(21)\cdots\text{Cl}(2)$	2.88 (3)	$\text{H}(2)\cdots\text{Cl}(3')$	2.63 (5)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

smallest bite angles $\text{Cl}(1)\text{—Cu}(1)\text{—Cl}(3) = 97.9(1)^\circ$ and $\text{Cl}(2)\text{—Cu}(1)\text{—Cl}(4) = 97.0(1)^\circ$. In $[\text{NH}(\text{CH}_3)_3]_2\text{[ZnCl}_4\text{]}$ a different situation is found with one symmetric bifurcated hydrogen bond, $\text{H}(2)\cdots\text{Cl}(3)$, $\text{H}(2)\cdots\text{Cl}(3') = 2.63(5)\text{ \AA}$, again associated with the smallest bite angle of the tetrachlorometallate ion $\text{Cl}(3)\text{—Zn}\text{—Cl}(3') = 104.3(1)^\circ$, and a simple hydrogen bond $\text{H}(1)\cdots\text{Cl}(2) = 2.30(4)\text{ \AA}$. This has no bifurcating character, the contact $\text{H}(1)\cdots\text{Cl}(1) = 3.16(5)\text{ \AA}$ being greater than 3.0 \AA , the sum of the van der Waals radii for H and Cl.

The ionic packing in $[\text{NH}(\text{CH}_3)_3]_2\text{[ZnCl}_4\text{]}$ (Fig. 3) bears strong resemblance to that of $[\text{N}(\text{CH}_3)_4]_2\text{[ZnCl}_4\text{]}$ which is also found in space group $Pnma$ at 295 K with unit-cell dimensions of 12.276, 8.998 and 15.541 \AA (Wiesner, Srivastava, Kennard, DiVaira & Lingafelter, 1967) and belongs to the $\beta\text{-K}_2\text{SO}_4$ family of structures. The molecular-ion centres lie on the ac mirror planes at $y = 0.25$ and 0.75 , and their positions correlate well between the two compounds (Figs. 4a and 4b), once an origin shift of $(\frac{1}{2}, 0, 0)$ is applied. Correspondence is lost when the Cl and methyl group orientations are considered. Three close $\text{Zn}\cdots\text{N}$ interionic distances of 4.971, 4.978 and 5.201 \AA are found in the ac plane for $[\text{N}(\text{CH}_3)_4]_2\text{[ZnCl}_4\text{]}$, the nearest contacts between layers being two each of 5.508, 5.518 and 6.610 \AA . By comparison,

in $[\text{NH}(\text{CH}_3)_3]_2[\text{ZnCl}_4]$ the three in-plane $\text{Zn}\cdots\text{N}$ contacts are now 3.987, 4.187 and 5.014 Å. The hydrogen bonding takes place in the ac plane and the two highly shortened contacts are due to the hydrogen-bonded ion pairs. Longer interlayer $\text{Zn}\cdots\text{N}$ distances of 5.706, 5.758 and 6.823 Å are found and the contact polyhedron about the $[\text{ZnCl}_4]^{2-}$ ion is best described by seven rather than nine nearest ammonium neighbours. In the case of $[\text{NH}(\text{CH}_3)_3]_2[\text{CuCl}_4]$ the packing of the ion centres bears some resemblance to the other two (Fig. 4c), more readily

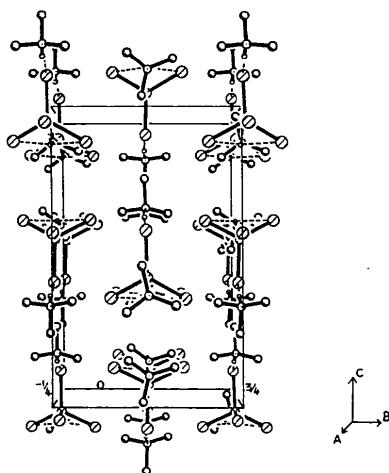


Fig. 3. Packing diagram for $[\text{NH}(\text{CH}_3)_3]_2[\text{ZnCl}_4]$ viewed up the a axis. One orientation of the disordered ions is shown for clarity.

seen by transposing the unit cell to the setting $P112_1/a$ (c unique) using the transformation $a' = c$, $b' = -a$, $c' = -b$. Although there are remnants of the layer-type structure found in the Zn compounds, the ion centres are no longer coplanar with $b' = 0.25$, 0.75 and, in addition to the loss of mirror symmetry, a considerable monoclinic angular distortion is introduced. The major cause of these distortions is that the hydrogen bonding now occurs between ions in different 'layers'. This is reflected in the two short $\text{Cu}\cdots\text{N}$ interlayer contacts, $\text{Cu}(1)\cdots\text{N}(1) = 3.993$ and $\text{Cu}(1)\cdots\text{N}(2) = 4.379$ Å, the other four being 5.786, 5.931, 6.057 and 6.311 Å. The $\text{Cu}\cdots\text{N}$ intralayer contacts (*i.e.* those most parallel to $a'c'$) are 4.772, 5.123 and 5.415 Å. It is also of note that many $[\text{N}(\text{CH}_3)_4]_2[\text{MX}_4]$ compounds with the prototypic $Pnma$ structure under ambient conditions have a commensurate low-temperature phase with space group $P2_1/c$ and $Z = 4$ (Gesi, 1986).

The choice of space group $Pnma$ in $[\text{NH}(\text{CH}_3)_3]_2[\text{ZnCl}_4]$ was supported by the inability of the material to generate second-harmonic radiation of laser light (Nd glass, $\lambda = 1.06 \mu\text{m}$) in index-matched fluids or piezoelectric signals from a Giebe-Schiebe piezoelectric analyser. This implies a lack of long-range ordering for the disordered trimethylammonium groups and no major deviation from a 50:50 disorder. The possibility of a low-temperature ferroelectric nature for $[\text{NH}(\text{CH}_3)_3]_2[\text{ZnCl}_4]$ exists; however, differential scanning calorimetry does not reveal any phase transition down to 200 K. Cooling of the crystals resulted in stress fracture, which we have commonly

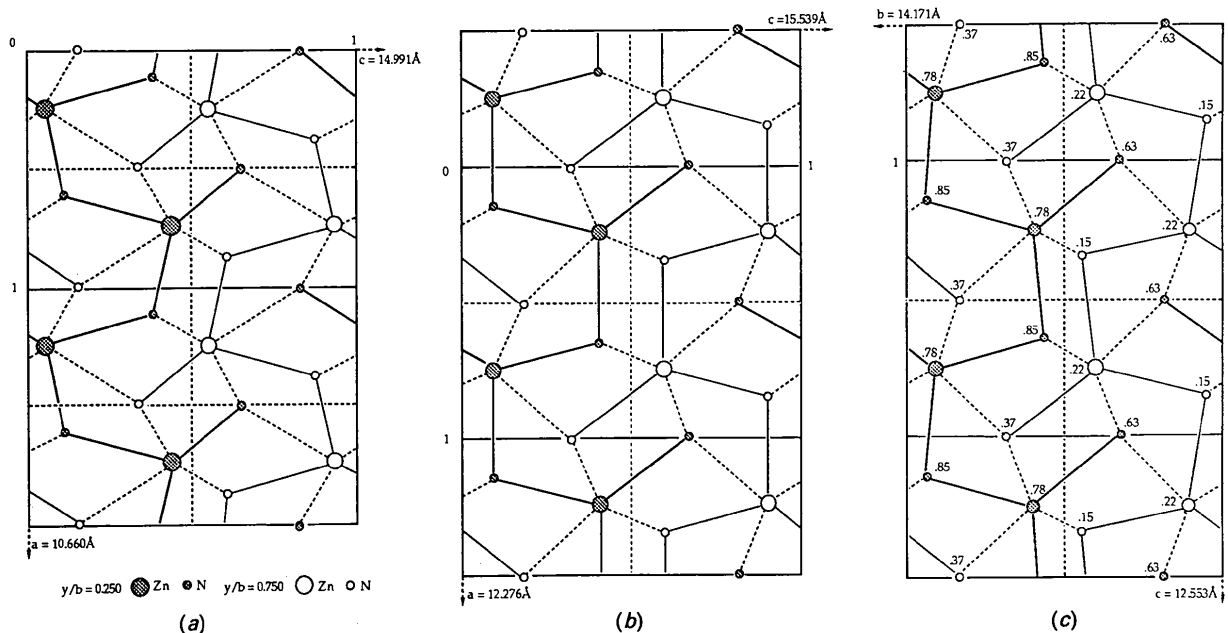


Fig. 4. Comparison of the packing of molecular ions in $[\text{NH}(\text{CH}_3)_3]_2[\text{MCl}_4]$: (a) $M = \text{Zn}$, (b) $[\text{N}(\text{CH}_3)_4]_2[\text{ZnCl}_4]$ and (c) $M = \text{Cu}$.

found in these materials, owing to negative thermal expansion vectors.

In summary $[\text{NH}(\text{CH}_3)_2]_2[\text{ZnCl}_4]$ adopts a structure similar to its tetramethylammonium analogue. The rich series of phase transitions found in $[\text{N}(\text{CH}_3)_4]_2[\text{ZnCl}_4]$ are not found in the trimethylammonium compound since hydrogen bonding apparently locks-in the commensurate *Pnma* phase. Study of possible solid solutions would provide further insight on this effect. In $[\text{NH}(\text{CH}_3)_2]_2[\text{CuCl}_4]$ an alternative hydrogen-bond arrangement is found which lowers the crystal symmetry to $P2_1/c$. The most probable cause of this is a distortion of the $[\text{CuCl}_4]^{2-}$ ion and the Cl—Cu—Cl angles from tetrahedral symmetry, thereby altering the geminal Cl...Cl distances and the energetics of hydrogen-bond bifurcation.

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235 K Structural Phase Transition in Dimethylammonium Tetrachlorocobaltate(II)

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Abstract. $[\text{NH}_2(\text{CH}_3)_2]_2[\text{CoCl}_4]$, $M_r = 292.9$, $T = 295$ (1) K, monoclinic, $P2_1/n$, $a = 8.541$ (1), $b = 11.440$ (2), $c = 13.311$ (2) Å, $\beta = 90.02$ (1)°, $V = 1300.7$ (4) Å³, $Z = 4$, $D_x = 1.50$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 21.05$ cm⁻¹, $F(000) = 596$, $R = 0.0260$ for 2406 observed reflections; $T = 220$ (5) K, monoclinic, $P2_1/n$, $a = 7.803$ (2), $b = 11.285$ (3), $c = 14.523$ (4) Å, $\beta = 96.11$ (2)°, $V = 1271.6$ (5) Å³, $D_x = 1.53$ g cm⁻³, $\mu = 21.53$ cm⁻¹, $R = 0.0203$ for 2523 observed reflections. The first-order phase transition which occurs in $[\text{NH}_2(\text{CH}_3)_2]_2[\text{CoCl}_4]$ at 235 K has been structurally characterized. The hydrogen-bond network in the material undergoes considerable change through the transition, effected primarily by a 60° rotation of one of the dimethylammonium ions about the *b* axis. The low-temperature form is isostructural with the mercury analogue. The Co—Cl

bond lengths of the tetrachlorocobaltate(II) ion range between 2.261–2.295 (1) Å at 220 K, the hydrogen bonds causing a slight lengthening effect.

Introduction. The mixed organic: inorganic salts, the organoammonium chlorometallates, have received wide attention owing to their rich structural diversity and phase-transition behaviour. Compared with their tetramethylammonium analogues, the dimethylammonium tetrachlorometallates $[\text{NH}_2(\text{CH}_3)_2]_2[M\text{Cl}_4]$ have been less studied, although the opportunity for a variety of interionic hydrogen-bond networks is high. The only previously reported structure in this family is for the mercury salt at ambient temperature (Ben Salah, Bats, Fuess & Daoud, 1982). Thermal analysis of the cobalt analogue indicated a phase transition occurring at