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

In summary $[NH(CH_3)_3]_2[ZnCl_4]$ adopts a structure similar to its tetramethylammonium analogue. The rich series of phase transitions found in $[N(CH_3)_4]_2[ZnCl_4]$ 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 $[NH(CH_3)_3]_2[CuCl_4]$ 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 $[CuCl_4]^{2-}$ ion and the Cl—Cu—Cl angles from tetrahedral symmetry, thereby altering the geminal Cl$\cdots$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. $[NH_2(CH_3)_2]_2[CoCl_4]$, $M_r = 292.9$, $T = 295\,(1)$ K, monoclinic, $P2_1/n$, $a = 8.541\,(1)$, $b = 11.440\,(2)$, $c = 13.311\,(2)$ Å, $\beta = 90.02\,(1)°$, $V = 1300.7\,(4)$ Å^3, $Z = 4$, $D_x = 1.50$ 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, $\beta = 96.11\,(2)°$, $V = 1271.6\,(5)$ Å^3, $D_x = 1.53$ g cm^{-3}, $\mu = 21.53$ cm^{-1}, $R = 0.0203$ for 2523 observed reflections. The first-order phase transition which occurs in $[NH_2(CH_3)_2]_2[CoCl_4]$ 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 $[NH_2(CH_3)_2]_2$-$[MCl_4]$ 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

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s for* $[\text{NH}_2(\text{CH}_3)_2]_2[\text{CoCl}_4]$ *at* 295 (1) K

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

	x	y	z	U_{eq}
Co(1)	0.16965 (3)	0.29931 (2)	0.41877 (2)	0.0401 (1)
Cl(1)	0.18100 (7)	0.49671 (5)	0.40991 (5)	0.0564 (2)
Cl(2)	0.19215 (8)	0.23570 (5)	0.58033 (4)	0.0556 (2)
Cl(3)	−0.07356 (7)	0.23748 (5)	0.36886 (5)	0.0549 (2)
Cl(4)	0.36014 (8)	0.22076 (6)	0.32265 (5)	0.0658 (2)
N(1)	−0.2073 (3)	0.1903 (2)	0.5967 (2)	0.0599 (8)
C(1)	−0.3729 (4)	0.2199 (4)	0.5814 (4)	0.086 (2)
C(2)	−0.1741 (5)	0.0648 (3)	0.6069 (3)	0.086 (1)
H(11)	−0.148 (4)	0.224 (3)	0.549 (2)	0.075 (9)
H(12)	−0.165 (5)	0.227 (3)	0.646 (3)	0.104 (14)
N(2)	−0.2108 (2)	0.5023 (2)	0.3351 (2)	0.0550 (7)
C(3)	−0.1531 (4)	0.5107 (3)	0.2314 (2)	0.063 (1)
C(4)	−0.3794 (4)	0.4795 (4)	0.3425 (3)	0.082 (1)
H(21)	−0.152 (3)	0.440 (3)	0.367 (2)	0.080 (9)
H(22)	−0.181 (5)	0.562 (4)	0.366 (3)	0.126 (15)

Table 2. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s for* $[\text{NH}_2(\text{CH}_3)_2]_2[\text{CoCl}_4]$ *at* 220 (5) K

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

	x	y	z	U_{eq}
Co(1)	0.20846 (3)	0.29455 (2)	0.45369 (1)	0.0268 (1)
Cl(1)	0.21360 (5)	0.49525 (4)	0.44448 (3)	0.0368 (1)
Cl(2)	0.17795 (5)	0.23773 (4)	0.60276 (3)	0.0352 (1)
Cl(3)	−0.03172 (5)	0.22536 (4)	0.36683 (3)	0.0379 (1)
Cl(4)	0.45081 (6)	0.21356 (4)	0.40832 (3)	0.0409 (1)
N(1)	−0.2358 (2)	0.1928 (2)	0.5681 (1)	0.0393 (5)
C(1)	−0.2986 (4)	0.2275 (2)	0.6565 (2)	0.0541 (8)
C(2)	−0.2227 (4)	0.0638 (2)	0.5546 (2)	0.0584 (9)
H(11)	−0.305 (4)	0.220 (2)	0.519 (2)	0.076 (9)
H(12)	−0.145 (4)	0.225 (2)	0.570 (2)	0.062 (8)
N(2)	−0.1947 (2)	0.4849 (2)	0.3270 (1)	0.0348 (5)
C(3)	−0.1139 (3)	0.5197 (2)	0.2438 (1)	0.0418 (6)
C(4)	−0.3847 (3)	0.4801 (2)	0.3120 (2)	0.0469 (7)
H(21)	−0.154 (3)	0.414 (2)	0.342 (2)	0.062 (7)
H(22)	−0.171 (3)	0.523 (2)	0.371 (2)	0.058 (7)

235 (5) K. This has prompted us to carry out structural studies above and below the transition temperature for this material.

Experimental. $[\text{NH}_2(\text{CH}_3)_2]_2[\text{CoCl}_4]$ was prepared from reaction of $\text{CoCl}_2.6\text{H}_2\text{O}$ with dimethylammonium chloride. Deep-blue prisms were grown by vapour diffusion of ethyl acetate into a methanolic solution of the compound at 295 K. A specimen 0.43 × 0.38 × 0.38 mm was chosen. Accurate cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections with $20 < 2\theta < 30°$. Intensity data were collected on a Siemens $R3m/V$ four-circle diffractometer with graphite-monochromatized Mo radiation (0.71073 Å) at both ambient (295 K) and low (220 K) temperature. The ω-scan method was employed in the range $3.5 < 2\theta < 55°$, $0 \le h \le 11$, $0 \le k \le 14$, $-17 \le l \le 17$, with a width of 1.2° in ω and a variable scan speed 2.9–29.3° min^{-1}. Two standard reflections were monitored periodically with less than 2% fluctuation

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 factors and anomalous dispersion for Cl and Co were used (Cromer & Waber, 1974; Stewart, Davidson & Simpson, 1965). A semi-empirical absorption correction based on ψ-scan data was applied. Transmission factors varied between 0.27 and 0.31. At 295 K a total of 2983 data were collected (all unique) of which 2406 with $F \ge 6\sigma(F)$ 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 the difference Fourier technique and refined positionally with individual isotropic thermal parameters. All non-H atoms were refined anisotropically. A weighting scheme $w = [\sigma^2(F) + gF^2]^{-1}$ was applied with $g = 0.0003$. An empirical parameter $\chi = 0.00099$ (13) was used to correct for extinction, where $F_{cor} = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$. Maximum residual electron density was $+0.47$ and difference hole -0.25 e Å^{-3}. Largest and mean Δ/σ in the final cycle were 0.776 and 0.051 respectively. Convergence was reached for a conventional $R = 0.026$, $wR = 0.036$, $S = 1.27$ for 165 refined parameters (14.6:1 data:parameter ratio) and $R = 0.035$, $wR = 0.038$ for
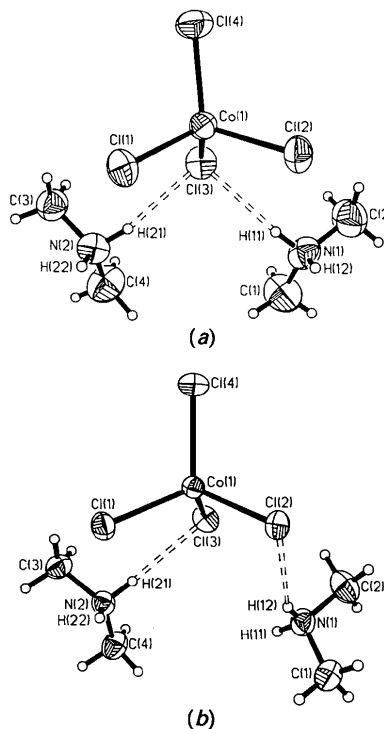

Fig. 1. Molecular structure of $[\text{NH}_2(\text{CH}_3)_2]_2[\text{CoCl}_4]$ (*a*) at 295 K and (*b*) at 220 K.

Table 3. *Bond lengths* (Å), *angles* (°) *and hydrogen-bond contacts* (Å) *for* [NH₂(CH₃)₂]₂[CoCl₄] *with e.s.d.'s in parentheses*

	295 K	220 K
Co(1)—Cl(1)	2.264 (1)	2.269 (1)
Co(1)—Cl(2)	2.278 (1)	2.295 (1)
Co(1)—Cl(3)	2.293 (1)	2.283 (1)
Co(1)—Cl(4)	2.257 (1)	2.261 (1)
N(1)—C(1)	1.468 (4)	1.475 (3)
N(1)—C(2)	1.471 (4)	1.474 (3)
N(2)—C(3)	1.469 (4)	1.474 (3)
N(2)—C(4)	1.468 (4)	1.476 (3)
Cl(1)—Co(1)—Cl(2)	111.4 (1)	109.8 (1)
Cl(1)—Co(1)—Cl(3)	109.4 (1)	109.1 (1)
Cl(1)—Co(1)—Cl(4)	109.7 (1)	111.5 (1)
Cl(2)—Co(1)—Cl(3)	104.5 (1)	105.3 (1)
Cl(2)—Co(1)—Cl(4)	110.3 (1)	109.6 (1)
Cl(3)—Co(1)—Cl(4)	111.5 (1)	111.3 (1)
C(1)—N(1)—C(2)	115.0 (3)	114.3 (2)
C(3)—N(2)—C(4)	113.9 (2)	113.6 (2)

Hydrogen-bond contacts

295 K		220 K	
H(11)···Cl(3)	2.48 (3)	H(11)···Cl(4ⁱⁱⁱ)	2.36 (3)
H(12)···Cl(4ⁱ)	2.44 (4)	H(12)···Cl(2)	2.52 (3)
H(21)···Cl(3)	2.41 (4)	H(21)···Cl(3)	2.35 (3)
H(22)···Cl(1ⁱⁱ)	2.89 (4)	H(22)···Cl(1ⁱⁱ)	2.72 (4)
H(22)···Cl(2ⁱⁱ)	2.42 (4)	H(22)···Cl(2ⁱⁱ)	2.74 (4)

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

all data. Final positional and thermal parameters are given in Table 1.*

The specimen was slowly cooled to 220 K by controlling a cold-nitrogen gas flow from a Siemens cryosystem and after unit-cell refinement, 2911 unique data were collected of which 2523 were observed $F \geq 6\sigma(F)$, for the range $3.5 \leq 2\theta \leq 55.0°$ the index range was now $0 \leq h \leq 10$, $0 \leq k \leq 14$, $-18 \leq l \leq 18$. The scan width was increased to 1.3°. The low-temperature structure was solved independently and refinement carried out as above and resulted in final discrepancy indices $R = 0.020$, $wR = 0.029$, $S = 1.36$ for $g = 0.0002$ and 164 variables, no extinction correction being applied. For all data $R = 0.0253$, $wR = 0.0308$. The data:parameter ratio was 15.4:1, the largest difference peak was $+0.26$ and difference hole -0.18 e Å⁻³, and maximum and mean Δ/σ for the final cycle were 0.220 and 0.006 respectively. Final atomic parameters are given in Table 2.*

Discussion. The molecular structure of [NH₂(CH₃)₂]₂[CoCl₄] at 295 and 220 K is shown in Figs. 1(*a*) and 1(*b*) respectively. In each case one unit formula is contained per asymmetric unit and discrete dimethyl-ammonium cations and [*M*Cl₄] dianions are found. Bond lengths and angles for the two structures are given in Table 3, together with possible hydrogen-bonding contacts. The tetrachlorocobaltate(II) ion is found to have a fairly undistorted tetrahedral geometry. The Co—Cl distances vary between 2.257–2.293 (1) Å at 295 K and 2.261–2.295 (1) Å at 220 K. These are comparable with the ion found in [N(CH₃)₄]₂[CoCl₄] which has a slightly compressed tetrahedral geometry 2.229–2.266 (9) Å (Wiesner, Srivastava, Kennard, DiVaira & Lingafelter, 1967). A slight lengthening effect on the Co—Cl bonds due to the hydrogen bonding in [NH₂(CH₃)₂]₂[CoCl₄] appears to exist. Support for this comes from the observation that the Cl atom with two hydrogen-bond contacts forms the longest Co—Cl bond [Co—Cl(3) = 2.293 (1) Å at 295 K and Co—Cl(2) = 2.295 (1) Å at 220 K].
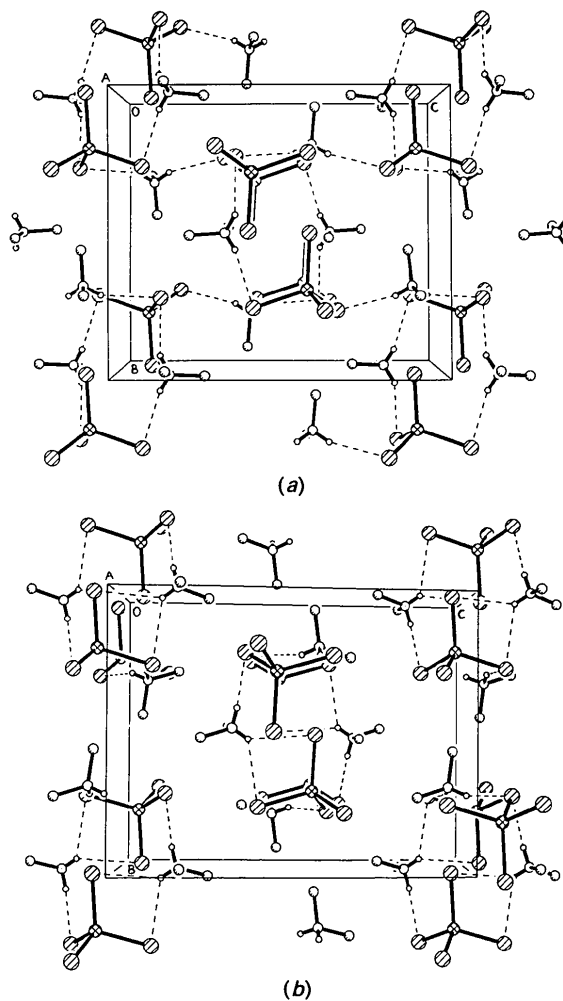
(*a*)

(*b*)

Fig. 2. Packing diagram for [NH₂(CH₃)₂]₂[CoCl₄] viewed along the *a* axis (*a*) at 295 K and (*b*) at 220 K.

The phase transition reflects a concerted change in the hydrogen-bond network between the ions. As shown in Fig. 2, no major structural readjustment occurs but each individual ion undergoes a rotational change, the most dramatic effect associated with the N(1) dimethylammonium ion which effectively rotates about the b axis by about 60°. As a consequence several modifications are made to the N—H···Cl contacts in the system. At room temperature three simple hydrogen bonds and one asymmetric bifurcated hydrogen bond are found. These involve all four amine H atoms of the two independent [NH$_2$(CH$_3$)$_2$] ions of the asymmetric unit as well as all four Cl atoms of the [CoCl$_4$]. As shown in Fig. 1, Cl(3) has contact with two H atoms H(11) and H(21) at distances of 2.48 (3) and 2.41 (4) Å respectively. In addition H(12) is bonded to Cl(4) of the ion at $(x - \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2})$ and H(22) is asymmetrically bifurcated to Cl(2) and Cl(1) of another [CoCl$_4$] ion at $(-x, 1 - y, 1 - z)$ with distances of 2.42 (4) and 2.89 (4) Å. Upon cooling below the transition temperature one of the dimethylammonium ions rotates substantially about the b axis, so that the two hydrogen bonds it formed previously are broken and replaced by the new contacts H(12)···Cl(2) and H(11)···Cl(4) $(x - 1, y, z)$. The crosslinking of the hydrogen-bond network in the bc plane is lost with the result that isolated stacks of ions are formed along the a axis. The bonding from the second ammonium ion is perturbed much less; the bond from H(21) to Cl(3) is retained, whereas H(22) takes up a more symmetrically bifurcated

position between Cl(2) and Cl(1) of the adjacent ion at $(-x, 1 - y, 1 - z)$ with distances of 2.74 (4) and 2.72 (4) Å respectively.

The low-temperature form of the cobalt compound is isostructural with the room-temperature form of the previously reported mercury analogue (Ben Salah, Bats, Fuess & Daoud, 1982). A unit cell for the cadmium analogue [NH$_2$(CH$_3$)$_2$][CdCl$_4$] of $Pnma$, $a = 18.05$, $b = 15.68$ and $c = 11.36$ Å has been reported (Daoud, 1976), implying that other hydrogen-bond networks may be possible in this family.

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Disorder in the Structure of (η^6-Benzo[b]thiophene)tricarbonylchromium(0)

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Abstract. [Cr(C$_8$H$_6$S)(CO)$_3$], $M_r = 270.23$, monoclinic, $P2_1/n$, $a = 6.619$ (3), $b = 11.708$ (4), $c = 13.995$ (5) Å, $\beta = 100.15$ (3)°, $V = 1067.58$ Å^3, $Z = 4$, $D_x = 1.681$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 12.181$ cm^{-1}, $F(000) = 544$, $T = 298$ K, $R = 0.041$ for 1725 reflections with $I > 2\sigma(I)$. The structure shows that the Cr(CO)$_3$ tripod is complexed to the benzene part of the benzothiophene moiety with

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