

Structure of $[(\text{CH}_3)_2\text{NH}_2]_2\text{CoCl}_4$ at elevated temperatures

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Abstract

The crystal structure of the title compound, dimethylammonium tetrachlorocobaltate(II), has been determined at four temperatures between 297 and 366 K, in order to investigate possible phase transitions at 313 and 353 K [Kapustianik, Polovinko & Kaluza *et al.* (1996). *Phys. Status Solidi A*, **153**, 117–122]. We found that there is no significant change either in the hydrogen-bonding network or in the cell parameters, apart from a linear dilatation with temperature. This study reveals that the anomalous variation in electric conductivity and some of the other physical properties of the compound cannot be explained by structural changes.

1. Introduction

The crystals of alkylammonium tetrahalometallates with the general formula A_2MX_4 , where M corresponds to a divalent metal ion and X is a halogen, have been widely investigated owing to their interesting physical properties connected to the different phase transitions. Some of these compounds, with high enthalpy and reversible phase transitions in the temperature range 273–393 K, are of interest in thermal energy storage systems (Ruan *et al.*, 1995). The nature of the complicated phase transitions in these mixed organic–inorganic salts could be related either to a temperature annealing of the crystal structure with intrinsic disorder of alkylammonium and MX_4^- groups (Stucky *et al.*, 1967; Williams *et al.*, 1992a; Mahoui *et al.*, 1996a,b) or a reorientation of the organic cation and thus changing the hydrogen-bond network (Williams *et al.*, 1992b). Recently, crystals of dimethylammonium tetrachlorocobaltate(II) (DMA-CoCl₄) have been the subject of several studies, including optical and spectroscopic measurements (Torgashev *et al.*, 1991; Vlokh *et al.*, 1992; Kapustianik *et al.*, 1992), and dielectric and dilatometric investigations (Kapustianik *et al.*, 1995; Kapustianik, Kabelka *et al.*, 1996; Kapustianik, Polovinko & Kaluza, 1996; Kapustianik, 1998). It has been suggested that crystals of DMA-CoCl₄ possess different phase transitions, including ferroelectric, ferroelastic and incommensurate ones at 235, 313, 353, 380 and 419 K. The ferroelectric phase transition at 235 K has been structurally characterized by an

X-ray diffraction study (Williams *et al.*, 1992b). Structure determinations at 220 and 295 K show that the hydrogen-bond network, namely N–H...Cl, undergoes a considerable change in the course of this transition by a 60° rotation of one of the dimethylammonium cations about the b axis. Consequently, the other possible phase transitions at 313, 353, 380 and 419 K have been attributed to the further rearrangements of the organic sub-lattice and therefore to the modification of the hydrogen-bond network (Kapustianik *et al.*, 1995; Kapustianik, Kabelka *et al.*, 1996; Kapustianik, Polovinko & Kaluza, 1996; Kapustianik, 1998). Moreover, the above theorem has been extended to other compounds of the A_2MX_4 family as well (Kapustianik, 1998). This has promoted us to investigate the structure of DMA-CoCl₄ at elevated temperatures and clarify the possible changes in crystal structure during the claimed phase transitions at 313 and 353 K.

2. Experimental

Dark-blue crystals of dimethylammonium tetrachlorocobaltate(II) were grown from its solution in ethanol by slow evaporation at room temperature. Data were collected on the same crystal at 297, 320, 343 and 366 K, respectively, using a Siemens SMART CCD diffractometer equipped with a hot-gas (air) blowing device in consecutive heating runs. The crystal was allowed to relax for at least 1 h at the desired temperature before collecting the data. Temperatures were monitored with a thermocouple positioned in the hot-gas stream in the nozzle above the crystal. Calibration using a second thermocouple placed at the crystal site under the same conditions (pressure and flow of the air) was made. Thus, the stability and reproducibility were estimated to be within ± 2 K at the crystal position.

1000–1200 data frames were collected by 0.3° steps in ω -scans with a crystal-to-detector distance of 3.97 cm. Preliminary orientation matrices were obtained from the first 100 frames using SMART (Siemens, 1995). The β angle is very close to 90°, suggesting the orthorhombic crystal system. This has been excluded as R_{int} would be 0.419 and the monoclinic unit cell (with $R_{\text{int}} = 0.036$) was

Table 1. *Experimental details*

	297 K	320 K	343 K	366 K
Crystal data				
Chemical formula	2(C ₂ H ₈ N).CoCl ₄	2(C ₂ H ₈ N).CoCl ₄	2(C ₂ H ₈ N).CoCl ₄	2(C ₂ H ₈ N).CoCl ₄
Chemical formula weight	292.92	292.92	292.92	292.92
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	8.5313 (2)	8.5513 (5)	8.5640 (2)	8.5775 (5)
<i>b</i> (Å)	11.4382 (2)	11.4527 (7)	11.4573 (3)	11.4679 (6)
<i>c</i> (Å)	13.3070 (1)	13.3364 (8)	13.3590 (3)	13.3855 (6)
β (°)	90.038 (1)	90.010 (1)	90.037 (1)	90.021 (1)
<i>V</i> (Å ³)	1298.53 (4)	1306.11 (14)	1310.79 (5)	1316.68 (12)
<i>Z</i>	4	4	4	4
<i>D_x</i> (Mg m ⁻³)	1.498	1.490	1.484	1.478
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	3419	2719	2563	2910
θ range (°)	1–25	1–25	1–25	1–25
μ (mm ⁻¹)	2.100	2.088	2.080	2.071
Temperature (K)	297 (2)	320 (2)	343 (2)	366 (2)
Crystal form	Plate	Plate	Plate	Plate
Crystal size (mm)	0.50 × 0.35 × 0.06	0.50 × 0.35 × 0.06	0.50 × 0.35 × 0.06	0.50 × 0.35 × 0.06
Crystal color	Dark-blue	Dark-blue	Dark-blue	Dark-blue
Data collection				
Diffractionmeter	Siemens SMART CCD	Siemens SMART CCD	Siemens SMART CCD	Siemens SMART CCD
Data collection method	ω scans	ω scans	ω scans	ω scans
Absorption correction	Multi-scan (Blessing, 1995; Sheldrick, 1996)	Multi-scan (Blessing, 1995; Sheldrick, 1996)	Multi-scan (Blessing, 1995; Sheldrick, 1996)	Multi-scan (Blessing, 1995; Sheldrick, 1996)
<i>T</i> _{min}	0.4199	0.4216	0.4227	0.4241
<i>T</i> _{max}	0.8844	0.8850	0.8853	0.8858
No. of measured reflections	6987	6082	6097	7139
No. of independent reflections	2372	2397	2399	2412
No. of observed reflections	1794	1688	1639	1666
Criterion for observed reflections	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)
<i>R</i> _{int}	0.0355	0.0363	0.0391	0.0375
θ _{max} (°)	25.36	25.36	25.34	25.35
Range of <i>h</i> , <i>k</i> , <i>l</i>	–9 → <i>h</i> → 10 –13 → <i>k</i> → 13 –16 → <i>l</i> → 15	–9 → <i>h</i> → 10 –13 → <i>k</i> → 13 –16 → <i>l</i> → 10	–10 → <i>h</i> → 9 –13 → <i>k</i> → 13 –10 → <i>l</i> → 16	–9 → <i>h</i> → 10 –13 → <i>k</i> → 13 –16 → <i>l</i> → 15
Intensity decay (%)	None	None	None	None
Refinement				
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0336	0.0341	0.0357	0.0371
<i>wR</i> (<i>F</i> ²)	0.0816	0.0841	0.0846	0.0922
<i>S</i>	1.003	0.989	0.998	1.006
No. of reflections used in refinement	2372	2397	2399	2412
No. of parameters used	121	121	121	121
H-atom treatment	See experimental $w = 1/[\sigma^2(F_o^2) + (0.0419P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	See experimental $w = 1/[\sigma^2(F_o^2) + (0.0398P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	See experimental $w = 1/[\sigma^2(F_o^2) + (0.0365P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	See experimental $w = 1/[\sigma^2(F_o^2) + (0.0457P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
Weighting scheme	(Δ/σ) _{max}	0.001	0.001	0.001
$\Delta\rho$ _{max} (e Å ⁻³)	0.304	0.284	0.309	0.331
$\Delta\rho$ _{min} (e Å ⁻³)	–0.563	–0.343	–0.326	–0.314
Extinction method	<i>SHELXTL</i> (Bruker AXS, 1997)	<i>SHELXTL</i> (Bruker AXS, 1997)	<i>SHELXTL</i> (Bruker AXS, 1997)	<i>SHELXTL</i> (Bruker AXS, 1997)
Extinction coefficient	0.0066 (8)	0.0072 (8)	0.0119 (9)	0.0153 (11)
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C)	<i>International Tables for Crystallography</i> (1992, Vol. C)	<i>International Tables for Crystallography</i> (1992, Vol. C)	<i>International Tables for Crystallography</i> (1992, Vol. C)

Table 1 (cont.)

	297 K	320 K	343 K	366 K
Computer programs				
Data collection	<i>SMART</i> (Siemens, 1995)	<i>SMART</i> (Siemens, 1995)	<i>SMART</i> (Siemens, 1995)	<i>SMART</i> (Siemens, 1995)
Cell refinement	<i>SAINT</i> (Siemens, 1995)	<i>SAINT</i> (Siemens, 1995)	<i>SAINT</i> (Siemens, 1995)	<i>SAINT</i> (Siemens, 1995)
Data reduction	<i>SAINT</i> and <i>SADABS</i> (Siemens, 1995; Shel- drick, 1996)	<i>SAINT</i> and <i>SADABS</i> (Siemens, 1995; Shel- drick, 1996)	<i>SAINT</i> and <i>SADABS</i> (Siemens, 1995; Shel- drick, 1996)	<i>SAINT</i> and <i>SADABS</i> (Siemens, 1995; Shel- drick, 1996)
Structure solution	<i>SHELXTL</i> (Bruker AXS, 1997)	<i>SHELXTL</i> (Bruker AXS, 1997)	<i>SHELXTL</i> (Bruker AXS, 1997)	<i>SHELXTL</i> (Bruker AXS, 1997)
Structure refinement	<i>SHELXTL</i> (Bruker AXS, 1997)	<i>SHELXTL</i> (Bruker AXS, 1997)	<i>SHELXTL</i> (Bruker AXS, 1997)	<i>SHELXTL</i> (Bruker AXS, 1997)

Table 2. Selected bond lengths and angles for DMA-CoCl₄ (Å, °)

	297 (2) K	320 (2) K	343 (2) K	366 (2) K
Co1—Cl4	2.2529 (9)	2.2533 (10)	2.2525 (10)	2.2520 (10)
Co1—Cl3	2.2631 (9)	2.2628 (9)	2.2611 (10)	2.2602 (10)
Co1—Cl2	2.2770 (9)	2.2763 (10)	2.2738 (10)	2.2752 (10)
Co1—Cl1	2.2911 (9)	2.2910 (10)	2.2887 (10)	2.2897 (10)
N1—C11	1.464 (4)	1.463 (4)	1.471 (5)	1.463 (5)
N1—C12	1.476 (4)	1.466 (5)	1.469 (5)	1.469 (5)
N2—C21	1.464 (5)	1.465 (5)	1.466 (5)	1.455 (6)
N2—C22	1.472 (5)	1.469 (5)	1.467 (6)	1.466 (6)
Cl4—Co1—Cl3	109.68 (4)	109.65 (4)	109.54 (4)	109.52 (4)
Cl4—Co1—Cl2	110.39 (4)	110.48 (4)	110.53 (4)	110.54 (5)
Cl3—Co1—Cl2	111.37 (3)	111.30 (4)	111.28 (4)	111.36 (4)
Cl4—Co1—Cl1	111.45 (4)	111.42 (4)	111.51 (4)	111.59 (5)
Cl3—Co1—Cl1	109.34 (3)	109.31 (4)	109.26 (4)	109.17 (4)
Cl2—Co1—Cl1	104.53 (3)	104.60 (4)	104.65 (4)	104.57 (4)
C11—N1—C12	113.3 (3)	113.3 (3)	113.1 (4)	113.2 (4)
C21—N2—C22	114.4 (3)	114.4 (4)	114.2 (4)	115.0 (4)

therefore chosen. The collected frames were integrated using the respective preliminary orientation matrix, which was updated every 100 frames. Final cell parameters were obtained by refinement on the position of reflections with $I > 10\sigma(I)$, after integration of all the frames using *SAINT* (Siemens, 1995). The data were empirically corrected for absorption and other effects (absorption by air, glue material and glass capillary) using *SADABS* (Sheldrick, 1996) and refined by full-matrix least-squares on all F^2 data using *SHELXTL* (Bruker AXS, 1997). The non-H atoms were refined anisotropically, whereas H atoms were treated isotropically using appropriate riding models.†

3. Result

The crystal structure of DMA-CoCl₄ at 297 K is shown in Fig. 1. Crystal data and structure refinements at 297, 320, 343 and 366 K are summarized in Table 1.

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS0024). Services for accessing these data are described at the back of the journal.

Obviously there is no abrupt change in symmetry and cell parameters up to 366 K. The net behaviour is a linear temperature dependence of the lattice parameters of DMA-CoCl₄, which is illustrated in Fig. 2. Selected bond distances and angles at different temperatures are given in Table 2. The changes can be well described by the increase in amplitude of the thermal motions of atoms. This means that the geometry around the cobalt site remains unchanged with increasing temperature.

The hydrogen-bonding scheme for the [CoCl₄]²⁻ anion is shown in Fig. 3. All Cl atoms take part in the hydrogen bonding with dimethylammonium groups, which stabilizes the packing in the crystal. The Cl1 atom participates in two medium-strong hydrogen bonds (Gilli, 1995) of the N—H...Cl type with N2 ($x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$) and N1 ($2 - x, 2 - y, 1 - z$) and a weak C—H...Cl hydrogen bond with C11 ($x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$). The Cl2 and Cl4 atoms are taking part in symmetrical N—H...Cl hydrogen bonding with N1 and N2, respectively, and C—H...Cl hydrogen bonding with C11 at ($\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$) and ($\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$), respectively. The Cl3 atom behaves differently and takes part only in a C—H...Cl hydrogen bond with C22 ($\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$). The geometry of the hydrogen bonds at four temperatures are given in Table 3. The hydrogen-bonding network

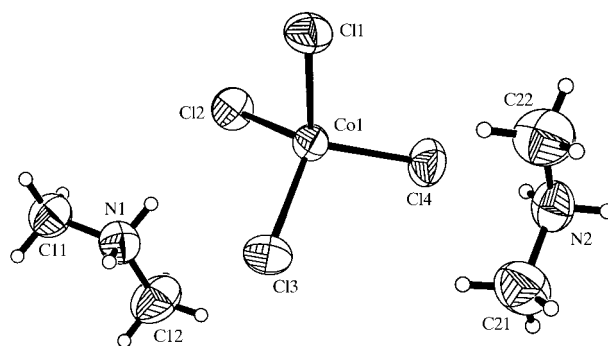


Fig. 1. The molecular structure of DMA-CoCl₄ at 297 K, showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

does not show any changes at elevated temperatures from 297 K up to 366 K.

4. Discussion

Although the ferroelectric phase transition of dimethylammonium tetrachlorocobaltate(II) at 235 K has been characterized by X-ray structure analysis (Williams *et al.*, 1992b), there is no evidence for a similar change of the structure from room temperature up to 366 K and indeed, the hydrogen-bonding system remains unchanged. Thus, the anomalous variation in electric conductivity and other physical properties of DMA-CoCl₄ at 313 and 353 K (Vlokh *et al.*, 1992; Kapustianik *et al.*, 1992, 1995; Kapustianik, Kabelka *et al.*, 1996; Kapustianik, Polovinko & Kaluza, 1996; Kapustianik, 1998) cannot be explained by movement of the DMA groups or any structural changes. It is obvious that the results from the investigations on the optical and dielectric properties of DMA-CoCl₄ were suffering from the poor quality of the crystals used. We would like to

recall that the results of the measurements by Kapustianik *et al.* (1995) and Kapustianik, Polovinko & Kaluza (1996) were highly dependent on the history of the samples and presence of extrinsic water. It should be noted that the crystals of DMA-CoCl₄ are hygroscopic and the crystals subject to the measurements (Torgashev *et al.*, 1991; Kapustianik *et al.*, 1995; Kapustianik, Kabelka *et al.*, 1996; Kapustianik, Polovinko & Kaluza, 1996) were obtained from aqueous solutions of the compound. Therefore, the dielectric measurements suffered from the presence of extrinsic water which might be involved in the charge transfer mechanism reported by Kapustianik *et al.* (1995) and Kapustianik, Polovinko & Kaluza (1996). The present study reveals that the anomalous variation in electric conductivity of DMA-CoCl₄ at 313 and 353 K cannot be related to a first-order phase transition in the form of structural changes.

We have also found that only three Cl atoms of the [CoCl₄]²⁻ anion take part in the N-H...Cl hydrogen bonding. This is not consistent with the report on the

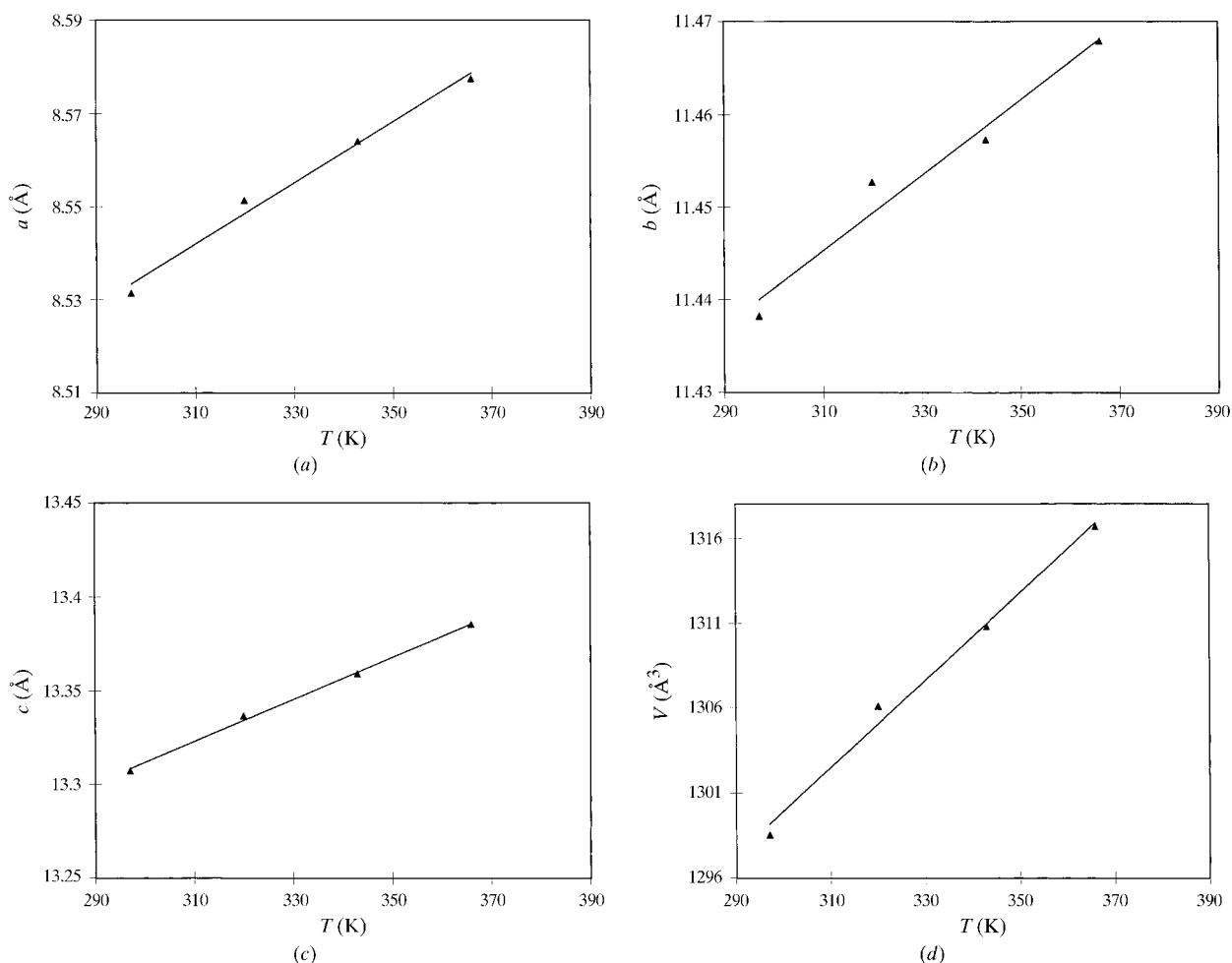


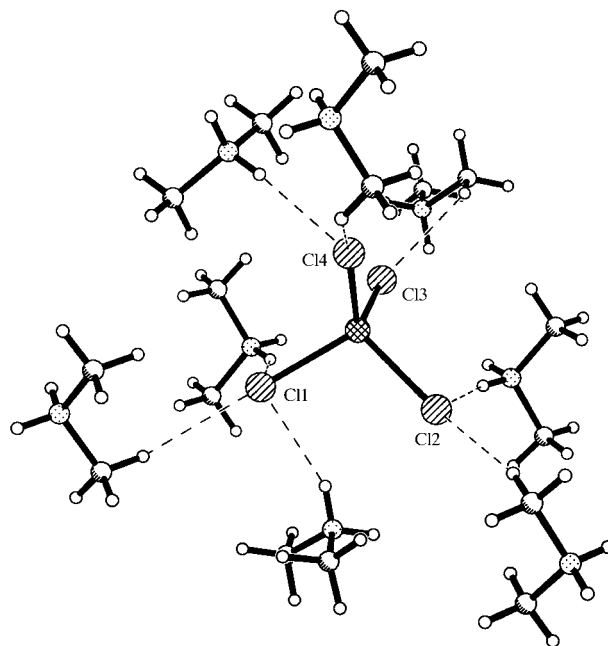
Fig. 2. Temperature dependence of the crystal parameters of DMA-CoCl₄.

Table 3. Hydrogen bonding geometry for DMA-CoCl₄ (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
T = 297 (2) K				
N1—H1B...Cl2	0.90	2.33	3.203 (3)	163.1
N1—H1A...Cl1 ⁱ	0.90	2.48	3.277 (3)	148.1
N2—H2B...Cl1 ⁱⁱ	0.90	2.44	3.281 (3)	156.4
N2—H2A...Cl4	0.90	2.36	3.266 (3)	161.2
C11—H11B...Cl2 ⁱⁱⁱ	0.96	2.76	3.705 (4)	167.4
C11—H11C...Cl1 ^{iv}	0.96	2.81	3.733 (4)	162.6
C11—H11A...Cl4 ^v	0.96	2.85	3.545 (4)	130.0
C22—H22A...Cl3 ^{vi}	0.96	2.89	3.643 (5)	136.1
T = 320 (2) K				
N1—H1B...Cl2	0.90	2.34	3.210 (3)	162.7
N1—H1A...Cl1 ⁱ	0.90	2.48	3.286 (3)	148.8
N2—H2B...Cl1 ⁱⁱ	0.90	2.44	3.287 (3)	156.4
N2—H2A...Cl4	0.90	2.37	3.233 (4)	161.1
C11—H11B...Cl2 ⁱⁱⁱ	0.96	2.77	3.715 (4)	168.6
C11—H11C...Cl1 ^{iv}	0.96	2.82	3.741 (4)	162.0
C11—H11A...Cl4 ^v	0.96	2.87	3.553 (4)	129.4
C22—H22A...Cl3 ^{vi}	0.96	2.90	3.649 (5)	136.2
T = 343 (2) K				
N1—H1B...Cl2	0.90	2.35	3.221 (8)	161.8
N1—H1A...Cl1 ⁱ	0.90	2.47	3.283 (4)	149.8
N2—H2B...Cl1 ⁱⁱ	0.90	2.46	3.299 (4)	155.4
N2—H2A...Cl4	0.90	2.36	3.231 (4)	162.0
C11—H11B...Cl2 ⁱⁱⁱ	0.96	2.77	3.718 (5)	169.6
C11—H11C...Cl1 ^{iv}	0.96	2.82	3.742 (5)	161.8
C11—H11A...Cl4 ^v	0.96	2.87	3.559 (5)	129.3
C22—H22A...Cl3 ^{vi}	0.96	2.91	3.658 (6)	135.7
T = 366 (2) K				
N1—H1B...Cl2	0.90	2.35	3.222 (4)	162.9
N1—H1A...Cl1 ⁱ	0.90	2.49	3.297 (4)	149.1
N2—H2B...Cl1 ⁱⁱ	0.90	2.47	3.306 (4)	155.0
N2—H2A...Cl4	0.90	2.37	3.243 (4)	162.6
C11—H11B...Cl2 ⁱⁱⁱ	0.96	2.78	3.735 (5)	170.6
C11—H11C...Cl1 ^{iv}	0.96	2.83	3.749 (5)	160.8
C11—H11A...Cl4 ^v	0.96	2.88	3.561 (5)	128.4
C22—H22A...Cl3 ^{vi}	0.96	2.90	3.661 (6)	136.6

Symmetry codes: (i) $2 - x, 2 - y, 1 - z$; (ii) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; (v) $\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$; (vi) $\frac{3}{2} - x, y - \frac{1}{2}, -z$.

room-temperature structure by Williams *et al.* (1992*b*). Obviously, the closest (N—)H...Cl contact for Cl3 with H1B on N1 (3.00 Å) is ~0.4 Å longer than the distance range for the (N—)H...Cl hydrogen bonding suggested by Steiner (1998). Since this distance is so much longer than the corresponding values for the other Cl atoms (2.33–2.48 Å), it cannot be regarded as a N—H...Cl hydrogen bond. We have performed a further check on the structure reported by Williams *et al.* (1992*b*) using the data (SINSUD01) deposited in the Cambridge Structural Database, October 1998 update with 190 307 entries (Allen & Kennard, 1993). The search for hydrogen bonds and other short contacts was performed using PLATON (Spek, 1998). No reasonable N—H...Cl contact is found for the respective Cl ion, which is in accordance with our results.

Fig. 3. The hydrogen-bonding scheme for a [CoCl₄]²⁻ anion.

On the other hand, the presence of C—H...Cl hydrogen bonding in the structure of DMA-CoCl₄ was not considered by Williams *et al.* (1992*b*). Crystallographic evidence for the existence of C—H...Cl hydrogen bonds has been reported by Taylor & Kennard (1982). The importance of this type of hydrogen bond has also been described by Hitchcock *et al.* (1993) in the structure of 1-ethyl-3-methylimidazolium tetrachlorocobaltate(II) in order to describe the nature of cation-anion interactions in ionic liquids. In this study we have found that each Cl atom contributes in one C—H...Cl hydrogen bond with the DMA groups.

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