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Bis(diethylammonium) Tetrachlorocobaltate(II) Monohydrate

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Abstract. $2C_4H_{12}N^+.[CoCl_4]^{2-}.H_2O$, $M_r = 367\cdot0$, monoclinic, Pn, $a = 7\cdot414\,(2)$, $b = 11\cdot534\,(4)$, $c = 10\cdot670\,(3)$ Å, $\beta = 91\cdot01\,(3)°$, $V = 912\cdot3\,(5)$ Å^3, $Z = 2$, $D_x = 1\cdot34$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1\cdot52$ mm^{-1}, $F(000) = 378$, $T = 295$ K, $R = 0\cdot114$ for 1240 unique observed $[F \geq 3\sigma(F)]$ reflections and 156 parameters. The structure contains discrete tetrahedral $CoCl_4^{2-}$ anions (Co—Cl = 2·266 Å, average), $(C_2H_5)_2NH_2^+$ cations and a water molecule. The structure is isomorphous with the room-temperature phase of $[(C_2H_5)_2NH_2]_2[ZnCl_4].H_2O$ [Bloomquist & Willett (1981). *Acta Cryst.* B**37**, 1353–1356].

Experimental. As part of our continued interest in the crystal chemistry of the diethylammonium salts of halometallates, $[(C_2H_5)_2NH_2]_2CoCl_4.H_2O$ was prepared. Deliquescent crystals were obtained by slow evaporation of a stoichiometric mixture of $(C_2H_5)_2NH_2Cl$ and $CoCl_2$ in absolute ethanol. A small irregularly shaped crystal with a maximum dimension of 0·4 mm was selected for data collection on a Syntex $P2_1$ diffractometer, with graphite monochromator, upgraded to Nicolet $P3F$ specifications. Lattice constants from 25 reflections in the range $24 < 2\theta < 27°$. Data were collected with ω scans (1·2°); two check reflections (013 and 121) monitored every 96 reflections showed no systematic deviations; 1775 reflections to $2\theta = 45°$, 1686 unique; hkl ranges, $0 \leq h \leq 8$, $0 \leq k \leq 13$, $-12 \leq l \leq 12$ (Campana, Shepard & Litchman, 1981). No absorption correction applied. Intensity statistics were consistent with the choice of noncentrosymmetric space group, Pn.

Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å$^2 \times 10^3$) *for* $[(C_2H_5)_2NH_2]_2CoCl_4.H_2O$

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

	x	y	z	U_{eq}
Co	0	2505 (2)	0	90 (1)
Cl(1)	2099 (5)	2551 (5)	180 (14)	132 (3)
Cl(2)	−845 (5)	4314 (4)	−427 (11)	115 (2)
Cl(3)	−697 (7)	1430 (5)	−2405 (9)	125 (2)
Cl(4)	−824 (5)	1702 (6)	2464 (9)	114 (2)
N(1)	2003 (18)	9954 (17)	5447 (37)	128 (8)
C(2)	954 (29)	9200 (23)	4842 (64)	145 (12)
C(3)	682 (31)	8273 (26)	5502 (64)	160 (15)
C(4)	2386 (26)	10999 (20)	4809 (62)	153 (14)
C(5)	3458 (31)	11528 (29)	5297 (65)	158 (14)
N(11)	3740 (16)	6114 (13)	106 (29)	106 (6)
C(12)	2395 (24)	5758 (21)	−166 (49)	132 (11)
C(13)	1575 (24)	6772 (28)	505 (77)	179 (19)
C(14)	4686 (25)	5246 (24)	−386 (35)	126 (10)
C(15)	5918 (24)	5621 (25)	−37 (58)	146 (12)
O	2096 (31)	9896 (22)	9461 (87)	285 (22)

Table 2. *Bond lengths* (Å) *and angles* (°) *for* $[(C_2H_5)_2NH_2]_2CoCl_4.H_2O$

Co—Cl(1)	2·242 (6)	N(11)—C(12)	1·504 (31)
Co—Cl(2)	2·293 (5)	N(11)—C(13)	1·472 (32)
Co—Cl(3)	2·285 (7)	C(12)—C(13)	1·548 (43)
Co—Cl(4)	2·242 (6)	C(14)—C(15)	1·404 (38)
N(1)—C(2)	1·480 (37)	O—Cl(1)	3·11 (1)
N(1)—C(4)	1·361 (34)	O—N(1)	2·98 (4)
C(2)—C(3)	1·214 (46)	O—Cl(4)	3·26 (1)
C(4)—C(5)	1·340 (44)		
Cl(1)—Co—Cl(2)	112·1 (2)	C(2)—N(1)—C(4)	130·2 (28)
Cl(1)—Co—Cl(3)	111·7 (3)	N(1)—C(2)—C(3)	125·5 (38)
Cl(2)—Co—Cl(3)	105·3 (2)	N(1)—C(4)—C(5)	124·7 (33)
Cl(1)—Co—Cl(4)	111·5 (3)	C(12)—N(11)—C(14)	116·0 (18)
Cl(2)—Co—Cl(4)	109·3 (2)	N(11)—C(12)—C(13)	107·1 (20)
Cl(3)—Co—Cl(4)	106·5 (2)	N(11)—C(14)—C(15)	112·9 (23)

The structure solution was obtained *via* the *SOLV* routine in the *SHELXTL* crystallographic program package (Sheldrick, 1985). Refinement also used *SHELXTL*. A difference synthesis based on the Co- and Cl-atom positions obtained from *SOLV* yielded the C-, N- and O-atom positions. H atoms for the cations were constrained to ideal positions (C—H and N—H = 0·96 Å) and assigned isotropic thermal parameters of 0·12 Å^2. The larger thermal ellipsoid associated with the O atom implies disorder and/or partial occupancy of that atomic site. No residual electron density could be correlated with H-atom positions for the water molecule. Hence, these H atoms were omitted from the refinement. The final refinement resulted in $R = 0\cdot114$ $[F \geq 3\sigma(F)]$ and 0·130 (all data), $wR = 0\cdot155$ $[F \geq 3\sigma(F)]$ and 0·168 (all data) and $w = 1/[\sigma^2(F) + g(F)^2]$, with $g = 0\cdot0162$. The anisotropic thermal parameters of the Cl atoms gave evidence of considerable librational motion and the thermal ellipsoids for the atoms in the cations were very large. The inability of the anisotropic thermal parameters to model the apparent motion probably contributes significantly to the large R values. The goodness of fit was 1·097, $|\Delta/\sigma|$(max.) = 0·214 for one of the CH_3 rotation parameters. The

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largest peak on the final difference map was 1·5 e Å^{-3} near Co, while the most negative excursion was −0·5 e Å^{-3}. Extinction corrections were made. Atomic scattering factors from the *SHELXTL* program package. Atomic coordinates are listed in Table 1 and bond distances and angles are given in Table 2. A view of the structure is shown in Fig. 1.*

Related literature. This structure is isomorphous with the room-temperature phase of $[(C_2H_5)_2NH_2]_2ZnCl_4.H_2O$ (Bloomquist & Willett, 1981). The latter undergoes a phase transition to a *P*2$_1$*nm* phase at 330 K and melts at 362 K. Differential scanning calorimetry (DSC) measurements on the cobalt analog reported here also indicate a phase transition at 330 K, with melting at 360 K (Van Oort, Neshvad & White, 1987).

The $[(C_2H_5)_2NH_2]_2CuCl_4$ system shows interesting behavior (Willett, Haugen, Lebsach & Morrey, 1974; Harlow & Simonsen, 1977; Bloomquist, Pressprich & Willett, 1988). At room temperature, a superstructure is apparent with a tripling of the length of one unit-cell axis. At 323 K, the structure undergoes a phase transition to a new phase with two crystallographically independent $CuCl_4^{2-}$ anions.

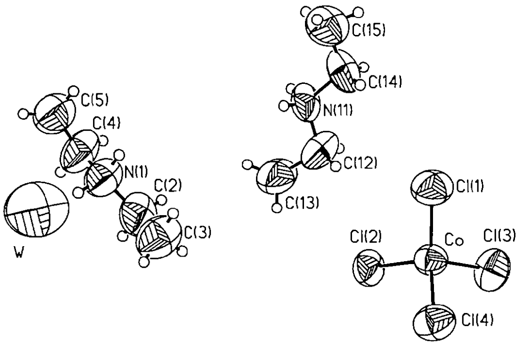

Fig. 1. Illustration of the structure of $[(C_2H_5)_2NH_2]_2CoCl_4.H_2O$.

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* Tables of data collection parameters, anisotropic thermal parameters, H-atom parameters and structure factors as well as a stereoview of the unit cell have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53727 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,4-Dimethyl-1,4-diazoniabicyclo[2.2.2]octane Octachlorotricuprate(II)

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Abstract. $C_8H_{18}N_2^{2+}.[Cu_3Cl_8]^{2-}$, $M_r = 616·5$, monoclinic, $P2_1/n$, $a = 7·335\ (2)$, $b = 19·499\ (8)$, $c = 13·532\ (6)$ Å, $\beta = 100·79\ (3)°$, $V = 1901\ (1)$ Å^3, $Z = 4$, $D_x = 2·15$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 4·45$ mm^{-1}, $F(000) = 1212$, $T = 295$ K, $R = 0·0569$ for 1436 unique observed $[F \geq 3\sigma(F)]$ reflections and 196 parameters. The structure consists of discrete organic cations and stacks of quasiplanar symmetrically bibridged $Cu_3Cl_8^{2-}$ dimers. A pronounced alternation of Cu—Cl distances occurs within the trimeric units: 2·243 (4) Å for terminal Cu—Cl, 2·369 (4) Å for first Cu—Cl bridge and 2·269 (4) Å for inner Cu—Cl bridge distances. The primary coordination geometry is nearly planar for the central Cu(2) atom, while a pronounced folding is exhibited for terminal Cu atoms. Formation of semicoordinate bonds between oligomeric units leads to the formation of stacks of trimers parallel to the *a* axis and yields a very elongated octahedral coordination sphere for each Cu$^{\rm II}$ ion. When each trimer is

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