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Structure of Hexaaquacobalt(II) Dichloride Bis(hexamethylenetetramine)* Tetrahydrate

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Abstract. $[Co(H_2O)_6]Cl_2.2C_6H_{12}N_4.4H_2O$, M_r = 590·03, triclinic, $P\bar{1}$, a = 9·508 (1), b = 9·428 (1), c = 9·309 (1) Å, α = 78·86 (1), β = 105·08 (1), γ = 120·13 (1)°, V = 694·9 (1) Å^3, Z = 1, D_x = 1·41, D_m = 1·40 Mg m^{-3}, T = 296 K, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·804 mm^{-1}, F(000) = 347. The crystal structure was solved by the heavy-atom method and refined to R = 0·042 and wR = 0·047 for 3409 unique observed reflections. The packing is stabilized by an extensive hydrogen-bonding network. Each hexamethylenetetramine molecule is linked to three different $Co(H_2O)_6^{2+}$ octahedra and each $Co(H_2O)_6^{2+}$ octahedron is linked to six different hexamethylenetetramine molecules through hydrogen bonds.

Introduction. The cobalt(II)–water–chloride–hexamethylenetramine system affords an interesting variety of transformations in the compositions of the complexes and the stereochemistry of cobalt with respect to the variations in the concentration of ligands and temperature. As part of a study of the various phases in this system, the crystal structure of the title compound was determined.

Experimental. Crystals of the title compound were obtained by controlled evaporation of an aqueous solution containing cobalt chloride, hexamethylenetetramine and hexamethylenetetramine monohydrochloride in the molar ratio 1:10:2.

Pale-red crystals of dimensions 0·425 × 0·425 × 0·5 mm, density measured by flotation, data collection by Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from least-squares analysis of 23 reflections in the range $35 < 2\theta < 45°$, $\omega/2\theta$ scan technique, $2\theta_{max}$ = 66°, index range $-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $0 \leq l \leq 13$; two standard reflections monitored every hour showed no significant variation; 4056 reflections measured, 3409 considered observed with $I \geq 3\sigma(I)$; Lorentz and polarization corrections applied; structure solved by heavy-atom method (Sheldrick, 1976); the single Co atom in the unit cell was placed at the centre of inversion $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ in space group $P\bar{1}$ which correctly gave the positions of the other atoms in the structure. All H-atom positions were located from difference Fourier maps; anisotropic refinement of all non-H atoms and isotropic refinement of H atoms; six H-atom positions were kept fixed and the isotropic thermal parameters of nine H atoms were kept fixed at 0·05 Å^2 during refinement, since they showed considerable movement; no absorption correction applied; the refinement converged to a final R = 0·042 and wR = 0·047; the weighting scheme used was $w = 1{\cdot}0/[\sigma^2(F_o) + 0{\cdot}0007|F_o|^2]$; $\sum w(F_o - F_c)^2$ minimized; (shift/e.s.d)$_{max}$ = 0·018 in the final cycle of refinement of non-H atoms; reflection/parameter ratio was about 13, the maximum height in the final difference Fourier map was 0·69 e Å^{-3}. Atomic scattering factors from Cromer & Mann (1968) for non-H atoms and from Stewart, Davidson & Simpson (1965) for H atoms; anomalous-dispersion correction factors from Cromer & Liberman (1970).

Discussion. The crystal structure consists of a $Co(H_2O)_6^{2+}$ octahedron, two hexamethylenetetramine (HMT) molecules, four independent water molecules which are not coordinated to the cobalt ion and two Cl^-. The stereochemistry around the cobalt is a slightly distorted octahedron with the six vertices

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* Hexamethylenetetramine is 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane.

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taken up by the water O atoms. The HMT and the Cl^- ions are not bonded to cobalt.

Fig. 1 shows the packing of the molecule (Motherwell & Clegg, 1978) in the unit cell with the atom-numbering scheme. Table 1 lists the positions of the non-H atoms with equivalent isotropic thermal parameters. Table 2* lists the bond lengths and bond angles involving non-H atoms.

In the title compound, the Co—O bond lengths are 2·051 (2), 2·086 (2) and 2·086 (2) Å as compared to the sum of the corresponding ionic radii, 2·04 Å. Similar variations in Co—O bond lengths are observed in $[Co(H_2O)_6](NO_3)_2.2C_6H_{12}N_4.4H_2O$ (Viossat, Khodadad & Rodier, 1981) and $[Co(H_2O)_6][Co(C_9H_7NO_3)_2]_2.2H_2O$ (Nassimbeni, Percy & Rodgers, 1976). Dahan (1974) and Whitaker & Jeffery (1970) observed that these variations in metal—water oxygen distances are presumably due to the different environment of the water O atoms and not due to hydrogen-bonding interactions. Since in the present compound the three water O atoms bonded to Co take part in similar hydrogen-bonding interactions, it is likely that the variations in Co—O distances are due to the different environment around them. The O—Co—O angles are in the range 85·8 (1) to 91·6 (1)°. The geometry exhibited by the six O atoms around Co is nearly octahedral. The deviations of the $Co(H_2O)_6^{2+}$ octahedral angles from cubic symmetry are significant but this is usually observed in such hydrogen-bonded structures (Mazzarella, Kovacs, Santis & Liquori, 1967; Viossat *et al.*, 1981). The O atoms surrounding the Co^{2+} ion are hydrogen bonded to the N atoms of six different HMT molecules, O atoms of the independent water molecules and chloride ions. Thus each oxygen

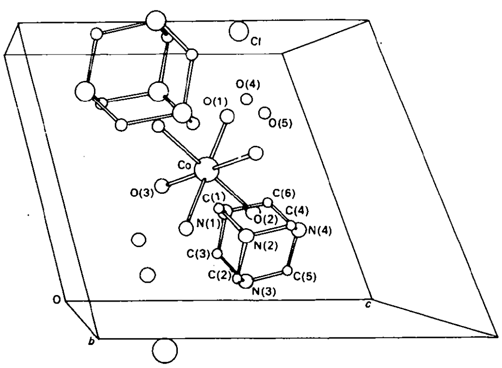

Fig. 1. Packing of the molecule with the atom-numbering scheme.

Table 1. *Fractional atomic coordinates of non-*H *atoms and their equivalent isotropic thermal parameters* (Å^2 × 10^3)

$U_{eq} = (1/3\sin\alpha\sin\beta\sin\gamma)[(U_{11}\sin\alpha/\sin\beta\sin\gamma) + (U_{22}\sin\beta/\sin\alpha\sin\gamma) + (U_{33}\sin\gamma/\sin\alpha\sin\beta) + (U_{23}\sin2\alpha/\sin^2\alpha) + (U_{13}\sin2\beta/\sin^2\beta) + (U_{12}\sin2\gamma/\sin^2\gamma)]$.

	x	y	z	U_{eq}
Co	0·5000	0·5000	0·5000	26 (< 1)
Cl	0·9358 (1)	0·7596 (1)	0·1876 (1)	62 (< 1)
O(1)	0·6988 (2)	0·4709 (2)	0·6207 (2)	49 (1)
O(2)	0·3445 (2)	0·3212 (2)	0·6390 (2)	51 (1)
O(3)	0·4428 (2)	0·3049 (2)	0·3821 (2)	43 (1)
O(4)	0·1986 (4)	0·1455 (4)	0·1494 (3)	86 (2)
O(5)	0·7198 (2)	0·2196 (2)	0·8033 (2)	49 (1)
N(1)	0·6746 (2)	0·2215 (2)	0·3407 (2)	36 (1)
C(1)	0·6502 (3)	0·0534 (3)	0·3932 (3)	38 (1)
N(2)	0·7573 (2)	0·0166 (2)	0·3337 (2)	37 (1)
C(2)	0·9307 (3)	0·1371 (3)	0·3855 (3)	39 (1)
N(3)	0·9612 (2)	0·3069 (2)	0·3340 (2)	37 (1)
C(3)	0·8495 (3)	0·3377 (3)	0·3927 (3)	39 (1)
N(4)	0·7453 (2)	0·2020 (2)	0·1136 (2)	37 (1)
C(4)	0·7192 (3)	0·0357 (3)	0·1699 (3)	41 (1)
C(5)	0·9194 (3)	0·3197 (3)	0·1705 (3)	41 (1)
C(6)	0·6389 (3)	0·2363 (3)	0·1767 (3)	42 (1)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *involving non-*H *atoms with e.s.d.'s in parentheses*

Co—O(1)	2·051 (2)	Co—O(2)	2·086 (2)
Co—O(3)	2·086 (2)	N(1)—C(1)	1·481 (3)
N(1)—C(3)	1·469 (3)	N(1)—C(6)	1·470 (3)
N(2)—C(1)	1·479 (4)	N(2)—C(2)	1·469 (3)
N(2)—C(4)	1·470 (3)	N(3)—C(2)	1·479 (3)
N(3)—C(3)	1·478 (4)	N(3)—C(5)	1·467 (3)
N(4)—C(4)	1·467 (3)	N(4)—C(5)	1·476 (3)
N(4)—C(6)	1·478 (4)		

O(1)—Co—O(2)	91·6 (1)	O(2)—Co—O(3)	85·8 (1)
O(1)—Co—O(3)	86·4 (1)	C(1)—N(1)—C(3)	107·7 (2)
C(1)—N(1)—C(6)	109·1 (2)	C(3)—N(1)—C(6)	108·6 (2)
N(1)—C(1)—N(2)	111·0 (2)	C(1)—N(2)—C(2)	108·2 (2)
C(1)—N(2)—C(4)	108·6 (2)	C(2)—N(2)—C(4)	108·6 (2)
N(2)—C(2)—N(3)	111·3 (2)	C(2)—N(3)—C(3)	108·0 (2)
C(2)—C(3)—C(5)	108·7 (2)	C(3)—N(3)—C(5)	108·5 (2)
N(1)—C(3)—N(3)	111·6 (2)	C(4)—N(4)—C(5)	108·1 (2)
C(4)—N(4)—C(6)	108·1 (2)	C(5)—N(4)—C(6)	107·7 (2)
N(2)—C(4)—N(4)	112·5 (2)	N(3)—C(5)—N(4)	112·0 (2)
N(1)—C(6)—N(4)	112·0 (2)		

Table 3. *Hydrogen-bond parameters with e.s.d.'s in parentheses*

D—H···*A*	*D*···*A* (Å)	*D*—H (Å)	H···*A* (Å)	*D*—H···*A* (°)
O(1)—H(1)···N(3^{i})	2·802 (2)	0·60 (3)	2·22 (3)	166 (3)
O(1)—H(2)···O(5)	2·699 (3)	0·88 (3)	1·84 (3)	167 (2)
O(2)—H(3)···Cl^{ii}	3·164 (3)	1·19	2·00	164
O(2)—H(4)···N(2^{iii})	2·804 (3)	0·91	1·91	167
O(3)—H(5)···O(4)	2·734 (3)	0·80 (3)	1·97 (2)	160 (3)
O(3)—H(6)···N(1)	2·815 (3)	0·87	1·95	172
O(4)—H(7)··Cl^{iv}	3·202 (3)	0·91 (4)	2·36 (4)	154 (3)
O(4)—H(8)···Cl^{v}	3·232 (3)	1·01 (3)	2·22 (3)	179 (3)
O(5)—H(9)···Cl^{vi}	3·160 (3)	0·69	2·47	172
O(5)—H(10)···N(4)	2·814 (3)	0·90	1·92	176

Symmetry code: (i) $2 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 - x, -y, 1 - z$; (iv) $1 - x, 1 - y, -z$; (v) $x - 1, y - 1, z$; (vi) $2 - x, 1 - y, 1 - z$.

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* Lists of observed and calculated structure factors, H-atom parameters, bond lengths and bond angles involving H atoms and anisotropic thermal parameters of non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52545 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

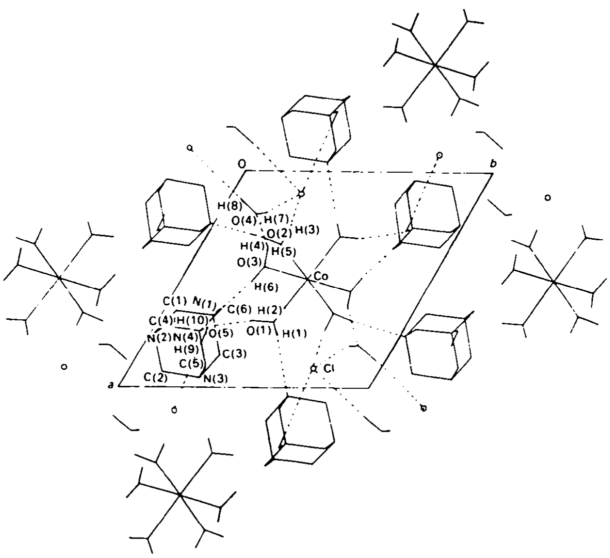

Fig. 2. Hydrogen-bonding network observed in the structure.

bonded to Co takes part in two hydrogen-bonding interactions. Table 3 lists the hydrogen bonds involved in the crystal structure. Fig. 2 shows the hydrogen-bonding network observed in the structure.

The bonding parameters in the HMT molecule are in good agreement with those found by Becka & Cruickshank (1963) for the HMT molecule. Each of the three N atoms in the HMT molecule is hydrogen bonded to O atoms of three different $Co(H_2O)_6^{2+}$ octahedra. The fourth nitrogen in the HMT molecule forms a hydrogen bond with the oxygen of an independent water molecule. The chloride ion has four short contacts to $O(2)(1-x,\ 1-y,\ 1-z)$, $O(4)(1+x,\ 1+y,\ z)$, $O(4)(1-x,\ 1-y,\ -z)$ and $O(5)(2-x,\ 1-y,\ 1-z)$ which is interesting and rare. The Cl···O contacts range from 3·160 (3) to 3·232 (3) Å. In $AlCl_3.6H_2O$ (Buchanan & Harris, 1968) the chloride ion participates in four hydrogen bonds with Cl···O distances ranging from 3·03 to 3·26 Å. Such an extended hydrogen-bonded network is also observed in $[Co(H_2O)_6](NO_3)_2.2C_6H_{12}N_4.4H_2O$ (Viossat *et al.*, 1981), $CaBr_2.2C_6H_{12}N_4.10H_2O$ (Mazzarella *et al.*, 1967), $MgCr_2O_7.2C_6H_{12}N_4.6H_2O$ (Dahan, 1974) and $CaCr_2O_7.2C_6H_{12}N_4.7H_2O$ (Dahan, 1975).

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Structures of the Meridional and Facial Isomers of Triamminechromium Pyrophosphate Dihydrate

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Abstract. The meridional and facial isomers of triamminechromium pyrophosphate were separated by chromatography on Dowex-50-H^+, and crystallized as isoionic species. The meridional isomer crystallized as a monomer $[Cr(HP_2O_7)(NH_3)_3(H_2O)].2H_2O$ but the facial isomer crystallized as a centrosymmetric dimer of $[Cr(HP_2O_7)(NH_3)_3].2H_2O$, in which the remaining water in the coordination sphere of each chromium is replaced by a phosphate oxygen from the other monomer unit. *Meridional isomer*: monoaquatriammine(pyrophosphato)chromium(III) dihydrate, $M_r = 332{\cdot}1$, monoclinic, $P2_1/c$,

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