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Crystal Structure of Hexaamminecobalt(III) Chloride Chromate Trihydrate

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Abstract

The preparation of the title compound $[Co(NH_3)_6](CrO_4)Cl,3H_2O$ is reported together with the determination of its crystal structure at 295(1) K. Crystals are orthorhombic, *Pcmn*, *a* 8·594(5), *b* 8·598(5), *c* 18·126(9) Å, *Z* 4.

During an attempted preparation of $[Co(NH_3)_6][Cr(CN)_6]$ from an aqueous mixture of $[Co(NH_3)_6]Cl_3$, and $K_3[Cr(CN)_6]$ solution, the latter formed through (presumably incomplete) reduction of K_2CrO_4 in ethanolic solution with subsequent treatment with KCN, a quantity of unexpected highly crystalline product was obtained. This was shown by chemical analysis and structure determination (reported below) to be $[Co(NH_3)_6](CrO_4)Cl,3H_2O$. The preparation has since been repeated by crystallization of stoichiometric quantities of $[Co(NH_3)_6]Cl_3$ and K_2CrO_4 from aqueous solution. [Analysis: $Co(NH_3)_6^{3+}$, 43·5; CrO_4^{2-}, 31·5; Cl^-, 9·9%; required $Co(NH_3)_6^{3+}$, 43·9; CrO_4^{2-}, 31·6; Cl^-, 9·7%.] Infrared absorption bands appear at 340 (O–H), 320 (N–H), 134 (not assigned), 89 (CrO_4), 84 (NH_3) and 52 mm^{-1} (Co–N).

Previous reports of the coexistence of CrO_4^{2-} and Cl^- as anions in crystalline solids are not well documented: for example, Carobbi has described a compound which may be formulated as $Pb_5(PO_4)(CrO_4)_3Cl$.[1]

The structure determination described in this paper (Fig. 1 and Tables 1–3) has verified the unusual stoichiometry of the compound.

Crystallography

Crystal data.—$ClCoCrH_{24}N_6O_7$, *M* 366·6, orthorhombic, space group *Pcmn* (variant of *Pnma*, D_{2h}^{16}, No. 62), *a* 8·594(5), *b* 8·598(5), *c* 18·126(9) Å, *U* 1339(2) Å^3, D_m 1·80(1) g cm^{-3}, D_c 1·82 g cm^{-3}, *Z* 4. *F*(000) 760. Monochromatic Mo Kα radiation, λ 0·71069 Å, μ 22·0 cm^{-1}. Specimen size: 0·26 by 0·22 by 0·44 mm. *T* 295(1) K.

Structure determination.—Data acquisition: Syntex P$\bar{1}$ four-circle diffractometer, $2\theta/\theta$ scan mode, unique data set to $2\theta_{max}$ 50° yielding 1271 independent reflections, 933 of these with $I > 3\sigma(I)$ considered 'observed' and used in the structure determination and refinement after absorption correction. Solution: heavy atom method. Refinement: block diagonal least squares, parameter blocking corresponding to (i) heavy atoms, (ii) ligands, (iii) chromate ion, (iv) water molecules. Thermal parameters: U_H isotropic (H_2O) constrained at $\langle U_{ii}(O)\rangle$, others refined; *U* (other atoms) refined anisotropically. Residuals: *R* 0·036, *R'* 0·047, *S* 1·34. Reflection weights: $[\sigma^2(F_o)^2]^{-1}$. Scattering

[1] Carobbi, G., *Atti III Congr. Naz. Chim. Pura Appl.*, 1929, S341.

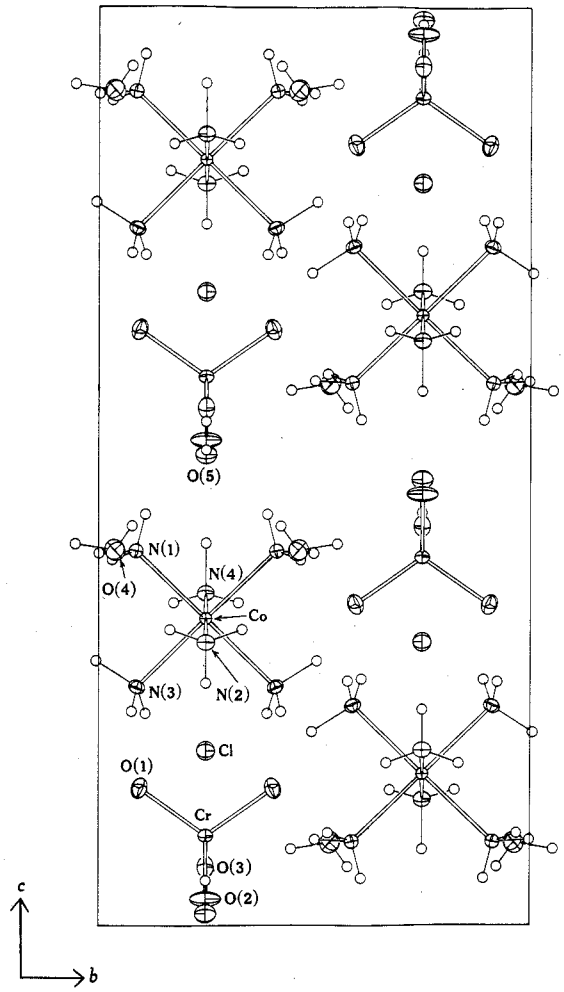


Fig. 1. Unit cell contents projected down *a*; non-hydrogen atom thermal ellipsoids are shown (20%), together with atom labelling. Hydrogen atoms are shown with an arbitrary radius of 0·1 Å.

Table 1. Atomic fractional cell coordinates
Coordinates $\times 10^3$ for H; $\times 10^4$ for others

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
	Cation				Anions		
Co	1759·2(10)	2500(–)	3343·4(4)	Cr	3878(1)	2500(–)	0981·9(6)
N(1)	2100(6)	0872(5)	4083(3)	O(1)	4120(4)	0953(4)	1497(2)
H(11)	289(12)	032(11)	399(5)	O(2)	5114(6)	2500(–)	0292(3)
H(12)	151(10)	001(10)	406(5)	O(3)	2094(5)	2500(–)	0641(3)
H(13)	207(6)	108(6)	448(3)	Cl	8123(2)	2500(–)	1907(1)
N(2)	3980(8)	2500(–)	3082(4)				
H(21)	418(11)	250(–)	264(5)				
H(22)	440(6)	166(5)	322(3)		Water molecules		
N(3)	1365(6)	0896(6)	2600(3)	O(4)	5577(5)	0376(5)	4093(2)
H(31)	198(7)	077(3)	233(4)	H(4α)	588(7)	−054(7)	416(3)
H(32)	067(8)	109(8)	231(4)	H(4β)	592(7)	078(8)	436(3)
H(33)	138(8)	−006(9)	288(4)	O(5)	6744(7)	2500(–)	5133(3)
N(4)	−0441(7)	2500(–)	3621(4)	H(5α)	760(10)	250(–)	518(5)
H(41)	−062(9)	250(–)	417(5)	H(5β)	638(10)	250(–)	549(4)
H(42)	−095(6)	175(6)	352(3)				

factors: neutral atom (Cl^- excepted), Co, Cr, Cl corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[2-4] Computation: X-RAY 76 program system,[5] CYBER 73 computer. Material deposited: structure factor amplitudes, thermal parameters, hydrogen atom thermal parameters and geometries.*

Table 2. Non-hydrogen ionic geometries: distances (Å) and angles (degrees)

Transformations of the asymmetric unit: i (x, $\frac{1}{2}-y$, z)

Atoms	Distance	Atoms	Angle	Atoms	Angle
		Cation			
Co–N(1)	1·960(5)	N(1)–Co–N(2)	91·1(2)	N(2)–Co–N(1^i)	91·1(2)
Co–N(2)	1·966(7)	N(1)–Co–N(3)	89·6(2)	N(2)–Co–N(3^i)	90·1(2)
Co–N(3)	1·958(5)	N(1)–Co–N(4)	88·2(2)	N(3)–Co–N(4)	90·5(2)
Co–N(4)	1·957(7)	N(1)–Co–N(1^i)	91·1(2)	N(3)–Co–N(3^i)	89·6(2)
		N(1)–Co–N(3^i)	178·5(2)	N(4)–Co–N(1^i)	88·2(2)
		N(2)–Co–N(3)	90·1(2)	N(4)–Co–N(3^i)	90·5(2)
		N(2)–Co–N(4)	179·0(3)		
		Chromate anion			
Cr–O(1)	1·638(3)	O(1)–Cr–O(2)	110·6(2)	O(2)–Cr–O(3)	108·4(3)
Cr–O(2)	1·640(5)	O(1)–Cr–O(3)	109·3(2)	O(2)–Cr–O(1^i)	110·6(2)
Cr–O(3)	1·654(5)	O(1)–Cr–O(1^i)	108·6(2)	O(3)–Cr–O(1^i)	109·3(2)

Table 3. Chlorine–, oxygen–hydrogen contacts

Transformations of the asymmetric unit (x, y, z): i (x, $\frac{1}{2}-y$, z); ii ($1\frac{1}{2}-x$, y, $z-\frac{1}{2}$); iii ($\frac{1}{2}-x$, y, $z-\frac{1}{2}$); iv ($x-\frac{1}{2}$, y, $\frac{1}{2}-z$); v ($x-\frac{1}{2}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$); vi ($1+x$, y, z); vii ($1+x$, $\frac{1}{2}-y$, z); viii ($\frac{1}{2}+x$, $\bar{y}$, $\frac{1}{2}-z$); ix ($\frac{1}{2}+x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$)

Species	Atoms	Dist. (Å)	Species	Atoms	Dist. (Å)
Chromate	O(2)···H($5\alpha^{ii}$)	1·97(9)	Chloride	Cl···H($32^{vi,vii}$)	2·61(7)
	O(2)···H(41^{iii})	2·08(8)		Cl···H($5\beta^{ii}$)	2·60(8)
	O(3)···H($4\alpha^{iv,v}$)	2·02(6)		Cl···H($33^{viii,ix}$)	2·61(7)
Water	O(4)···H(21)	2·18(5)			
molecules	O(5)···H(4β,$4\beta^i$)	2·16(6)			

(In spite of the equivalence of a and b cell dimensions, the structure displays no other pseudo-tetragonal features.)

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* Copies are available on application to the Editor-in-Chief, Editorial and Publications Service, CSIRO, 314 Albert Street, East Melbourne, Vic. 3002.

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