

Structure of Pentaammineaquacobalt(III) Hexacyanochromate(III), $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{Cr}(\text{CN})_6]$, by Time-of-Flight Neutron Diffraction at 11.5 K

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(Received 15 September 1984; accepted 26 November 1984)

Abstract. $M_r = 370.2$, rhombohedral, $R\bar{3}$, $a = 7.318(8) \text{ \AA}$, $\alpha = 97.5(1)^\circ$, $V = 381(1) \text{ \AA}^3$, $Z = 1$, $D_m(295 \text{ K}) = 1.593(5)$, $D_x = 1.613 \text{ g cm}^{-3}$, $\lambda = 0.7\text{--}5.3 \text{ \AA}$, $\mu(\lambda) = 1.82 + 0.0826\lambda$ (μ in cm^{-1}), $T = 11.5 \text{ K}$, $R = 0.071$ for 888 observed data. The highly regular nature of the cation and anion octahedra shown by a 120 K X-ray diffraction study was confirmed. The water molecule is disordered over the six 'ammine' sites of the cation, with its hydrogen atoms approximately occupying two of three particular sites of the ammine protons. The N–H bonds average $1.01(1) \text{ \AA}$. The strong hydrogen bonding involves only one of the three ammine hydrogen atoms, in a nearly linear system, with the cyanide ion of the anion [$\text{CN}\cdots\text{H} = 1.933(5) \text{ \AA}$].

Introduction. A charge-density study of pentaammineaquacobalt(III) hexacyanochromate(III) (Figgis & Reynolds, 1984) showed clear features of the metal–ligand bonding and suggested that there was substantial alteration of the ionic charges due to hydrogen-bonding interactions. The compound seems to be very suitable for the study of spin-density distribution by polarized neutron diffraction, and we present here the determination of the structure at very low temperature (11.5 K) as a prerequisite to that. This neutron diffraction study also serves to clarify some aspects of the ordering of the water molecule left uncertain by the X-ray structure determination.

The compound crystallizes in the space group $R\bar{3}$ with both metal atoms at sites of $\bar{3}$ symmetry, so that the water molecule must be disordered over the six ammine positions of the isostructural hexaamminecobalt(III) salt. The X-ray study shows that the water disorder is well modeled by the appropriate participation of oxygen at ammine sites, and by the two hydrogen atoms at two particular sites of the three for the ammine ligand.

Experimental. Large single crystals of pentaammineaquacobalt(III) hexacyanochromate(III) were grown by repeated seeding of freshly filtered 0.1 M aqueous

solutions of pentaammineaquacobalt(III) perchlorate and potassium hexacyanochromate(II) held at 278 K (Jepson & House, 1981).

A crystal of approximate hexagonal prismatic habit was mounted close to its unique axis on the single-crystal diffractometer on the Intense Pulsed Neutron Source (IPNS) at the Argonne National Laboratory (Schultz, Srinivasan, Teller, Williams & Lukehart, 1984). The crystal was surrounded by a cylindrical aluminum radiation shield *ca* 0.1 mm thick, and both were attached to the cold stage of a Displex® closed-cycle helium refrigerator (Air Products and Chemicals, Inc., Model CS-202) with the temperature controlled at 11.5 (5) K during the week of the experiment.

The scattered neutrons were incident on a $30 \times 30 \text{ cm}$ position-sensitive ^6Li -glass detector at a distance of 29 cm from the crystal and centered about the 90° scattering angle. The 100 time-of-flight histogram channels were arranged with $\Delta t/t = 0.015$ approximately constant, and corresponding to wavelengths of 0.7 to 5.3 \AA . The experimental detector responses and the incident neutron wavelength spectrum were calibrated with reference to Bragg reflections from a sodium chloride crystal (Schultz, Teller, Williams, Strauss & Brenner, 1982) and incoherent scattering by a vanadium alloy with zero coherent scattering (Schultz *et al.*, 1984). Neutron scattering lengths from a standard compilation (Koester, 1977).

Eleven crystal orientations were arranged so that nearly one third of the reflecting sphere was covered. The reflections were indexed in the hexagonal system and intensities were obtained from the detector element counts using computer programs from the IPNS library. The intensities recorded for a given reflection at different crystal orientations showed an average disagreement less than the sum of their standard deviations.

Crystal-data information is given in Table 1. Unit-cell parameters obtained from a least-squares fit of the positions (on the detector) and wavelengths of 738 Bragg peaks. Integrated intensity data corrected for Lorentz and absorption factors by standard procedures (Schultz *et al.*, 1984). The linear absorption coefficients for reflections with wavelengths between $\lambda = 0.7 \text{ \AA}$

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Table 1. *Crystal data for pentaammineaquacobalt(III) hexacyanochromate(III)*

	Neutron, 11.5 K	X-ray, 120 K
M_r	370.2	370.2
Space group	$R\bar{3}$	$R\bar{3}$
$a = b$ (Å)	Hexagonal 11.00 (1)	10.986 (4)
c (Å)	setting, $Z = 3$ 10.91 (1)	10.817 (4)
$a = b = c$ (Å)	Rhombohedral 7.318 (8)	7.296 (3)
α (°)	setting, 97.5 (1)	97.68 (3)
V (Å ³)	$Z = 1$ 381 (1)	376.9 (3)
D_m (295 K) (g cm ⁻³)		1.593
D_x (g cm ⁻³)	1.613	1.631
Dimensions (mm)	(120) to (120) (210) to (210) (001) to (001)	0.95 (2) 1.13 (2) 2.58 (2)
Transmission factors	0.74 to 0.86	

($\mu = 1.82 \text{ cm}^{-1}$) and $\lambda = 5.3 \text{ \AA}$ ($\mu = 2.20 \text{ cm}^{-1}$) were determined by a simple linear interpolation, which is appropriate in the absence of nuclear resonances for any of the elements in the crystal. These reflections were further corrected for the incident neutron spectrum and wavelength-dependent detector efficiencies (Schultz *et al.*, 1984). 1689 data ($h -18 \rightarrow 20$, $k -21 \rightarrow 23$, $l -18 \rightarrow 0$), of which 888 had $F_{\text{obs}}^2/\sigma(F_{\text{obs}}) > 3.0$. The agreement between equivalent reflections, which were not averaged because they appear at different wavelengths, was $R = \sum(F_{\text{obs}}^2 - \langle F_{\text{obs}}^2 \rangle) / \sum F_{\text{obs}}^2 = 0.040$. Reflection data analyzed using a locally modified least-squares program for variable-wavelength data (Schultz *et al.*, 1984). Function $\sum w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2$ minimized where $w = 1/\sigma(F_{\text{obs}}^2)$ and $\sigma(F_{\text{obs}}^2) = [\sigma_{\text{counting}}^2 \times (F_{\text{obs}}^2) + (0.02F_{\text{obs}}^2)^2]^{1/2}$. Starting parameters from 120 K X-ray structure results (Figgis & Reynolds, 1984). Data with $F_{\text{obs}}^2/\sigma(F_{\text{obs}}) > 3.0$ employed. Refinement of all positional and anisotropic thermal parameters and of isotropic extinction, with individual scale factors for each crystal orientation, proceeded in the normal manner.

The disorder of the water molecule was examined by refining the ammine hydrogen-atom populations. This cannot provide an exact account of the water-proton positions, as the bond lengths and angles differ from those of ammonia. However, the differences probably could not be resolved by our data. As suggested by the X-ray results, the populations of H(1) and H(3) were found to be unity within the errors (0.04), and they were then fixed at that value. The population, p , of H(2) was allowed to refine and its value was coupled to the scattering length, b , for 'N'(2) by the relationship $b[\text{'N'(2)}] = b(\text{N}) \times p + b(\text{O}) \times (1 - p)$.

Refinement proceeded until all shift/error ratios < 0.1 , with $R(F) = 0.071$, $wR(F^2) = 0.098$, $S = 1.64$. Isotropic extinction parameter, g , was $0.59(7) \times 10^{-4}$ and corresponded to a maximum correction factor of 1.4. No element of the correlation matrix exceeded 0.7. Difference Fourier map on final least-squares refinement showed no value $> 0.8 \text{ fm}$ and was essentially featureless. A refinement employing all 1689 data

caused no significant shift in parameter values nor decrease in standard errors.

Discussion. The atomic positional and equivalent isotropic thermal parameters are given in Table 2, together with the water-molecule site-occupation information.* Important bond lengths and angles are given in Table 3, no correction for thermal motion having been made. In Tables 1–3 the information from the 120 K X-ray structure determination, where relevant, is given for comparison. A stereoscopic view of the unit-cell contents, displaying the cation and the anion and the hydrogen bonding between them, is provided in Fig. 1.

The neutron diffraction structure, with its good definition of the hydrogen-atom positions and populations, and lower thermal motion, provides a markedly improved description of pentaammineaquacobalt(III) hexacyanochromate(III) relative to the X-ray study. All the major features of the earlier structure are reproduced in the present study.

In particular, the model for the disorder of the water molecule is seen to be very satisfactory. When the hydrogen-atom populations are allowed to vary, the occupation of sites H(1) and H(3) does not change from the value of unity, while that for H(2) does. With the H(1) and H(3) populations fixed at unity the H(2) population reduces to 0.88 (3), which is to be compared with the value of 0.833 expected for complete ordering of the water-molecule protons into the H(1) and H(3) 'amine' sites. The scattering length of the 'N'(2) atom, coupled in the refinement to the H(2) occupancy, likewise reduces from 9.30 fm for a 'pure' nitrogen atom to 8.88 (6) fm, which is to be compared with 8.72 fm, the mean scattering length for five nitrogen and one oxygen atoms. The model of the disordered water molecule seems to be reasonable as the isotropic thermal parameters for all three hydrogen atoms are very similar, with the value for H(2) between those for H(1) and H(3), and the anisotropy in the principal values of the thermal tensor is also quite similar, *viz* $U_{ii}(\text{max.}) - U_{ii}(\text{min.})$ being 0.027, 0.010 and 0.012 Å² for H(1), H(2) and H(3), respectively.

The CoN_6 and CrC_6 octahedra are, as found previously, highly regular, the latter scarcely departing from the ideal geometry at the level of significance. For the CoN_6 case there appears to be a small but significant difference between the neutron and the X-ray studies [$\text{'N'(2)} - \text{Co} - \text{'N'(2)} = 88.7(1)$ versus $89.45(5)^\circ$]. There is no difference between the X-ray result at 120 K and that for the hexaamminecobalt(III) salt at 80 K (Iwata, 1977).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39937 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors for pentaammineaquacobalt(III) hexacyanochromate(III) at 11.5 K

	x	y	z	$U_{eq}^*(\text{\AA}^2)$
Co	0	0	5000	0.004 (1)
'N'(2) ^a	1279 (1)	1574 (1)	6070 (2)	0.0085 (4)
H(1)	928 (6)	2211 (6)	6303 (8)	0.039 (3)
H(2) ^b	1461 (8)	1269 (7)	6896 (9)	0.037 (3)
H(3)	2252 (4)	2194 (5)	5711 (6)	0.027 (2)
Cr	0	0	0	0.007 (2)
C(1)	1453 (2)	1615 (2)	1096 (3)	0.0120 (6)
N(1)	2231 (2)	2527 (2)	1736 (2)	0.0189 (6)

(a) $b[{}'N'(2)] = 8.88$ (6) fm. (b) $p[H(2)] = 0.88$ (3). Value from the 120 K X-ray study (Figgis & Reynolds, 1984) scaled to 17 protons in the cation is 0.86.

$$* U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 3. Principal bond lengths and angles and hydrogen bonds in pentaammineaquacobalt(III) hexacyanochromate(III) at 11.5 K (neutron) and 120 K (X-ray)

Bond lengths are in Å and bond angles are in degrees. The quotation marks around the ammonia nitrogen atom, viz 'N'(2), emphasize that it is an average of five nitrogen and one oxygen atoms.

	Bond lengths			Bond angles	
	Neutron	X-ray		Neutron	X-ray
Co-'N'(2)	1.975 (2)	1.957 (1)	'N'(2)-Co-'N'(2)	88.7 (1)	89.5 (1)
'N'(2)-H(1)	0.989 (5)	0.85 (2)	Co-'N'(2)-H(1)	114.5 (4)	114 (1)
'N'(2)-H(2)	1.016 (8)	0.85 (2)	Co-'N'(2)-H(2)	114.0 (4)	114 (1)
'N'(2)-H(3)	1.017 (4)	0.79 (2)	Co-'N'(2)-H(3)	114.2 (4)	114 (1)
			H(1)-'N'(2)-H(2)	102.5 (8)	100 (2)
			H(1)-'N'(2)-H(3)	106.1 (5)	105 (2)
			H(2)-'N'(2)-H(3)	104.3 (6)	109 (2)
Cr-C(1)	2.074 (3)	2.068 (1)	C(1)-Cr-C(1)	90.1 (1)	90.3 (1)
C(1)-N(1)	1.170 (3)	1.147 (1)	Cr-C(1)-N(1)	177.5 (2)	177.5 (2)
Hydrogen bonds					
N(1)...H(3)	1.933 (5)	2.16 (2)	'N'(2)-H(3)...N(1)	168.3 (5)	165 (2)
N(1)...'N'(2)	2.936 (2)	2.930 (2)	'N'(2)-H(1)...N(1)	123.4 (7)	
N(1)...H(1)	2.54 (1)		'N'(2)-H(1)...N(1)	128.4 (7)	
N(1)...H(1)	2.53 (1)		'N'(2)-H(2)...N(1)	154.3 (8)	
N(1)...H(2)	2.45 (1)				

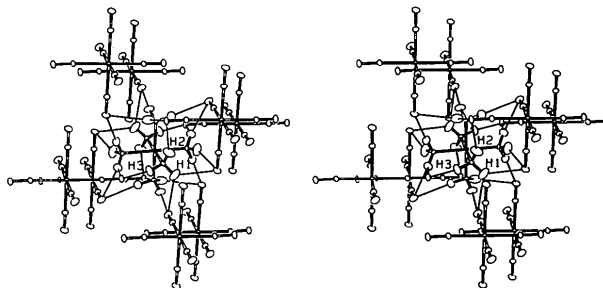


Fig. 1. A stereoscopic view of the environment around the $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ cation. Hydrogen bonds $[\text{N}(1)\cdots\text{H} < 2.55 \text{ \AA}]$ are shown as narrow solid lines. The thermal ellipsoids are drawn at the 50% probability level.

The Co-'N'(2) and C(1)-N(1) bond lengths reported are distinctly longer than in the X-ray study, and this reflects the larger unit-cell volume found at the lower temperature. The shorter bond length in the 120 K X-ray case could be due to the effects of thermal motion or non-spherical electron distributions. However, the apparent difference in unit-cell volumes is unlikely to be correct, and may reflect overestimation of the precision of the cell parameters and atom coordinates in the two techniques. The underestimation of bond-length errors by the least-squares values is perhaps emphasized by the fact that the Cr-C(1) bond lengths agree quite well, while the C(1)-N(1) length reported is closer to that given for the hexaammine salt at 80 K (Iwata, 1977).

The 'N'(2)-H bond lengths found in the present study are in the usual range for N-H bonds, the lengthening by *ca* 0.01 Å due to 20% oxygen occupation of nitrogen sites being barely significant. They are, of course, systematically larger than the X-ray values, on average 1.01 (1) versus 0.84 (4) Å. The good agreement between the Co-'N'(2)-H and H-'N'(2)-H angles for the two techniques supports the suggestion made in the X-ray study that the shift of electron density responsible for the short effective N-H bonds is essentially along the internuclear axes (Figgis & Reynolds, 1984).

The hydrogen bonding principally concerns H(3) with a strong, almost linear, 'N'(2)-H(3)...N(1) system between the ammine and cyanide ligands of the cation and the anion. However, it appears that there may be very weak interactions involving H(1) and H(2), with N(1)...H distances of *ca* 2.5 Å. The interaction involving H(1) is of some interest as it is a strictly planar, trigonal, bifurcated system involving the ammine 'N'(2) and two cyanide N(1) atoms, the latter both at about the same distance.

Thermal motion of the non-hydrogen atoms at 11.5 K, measured as U_{iso} , averages about 0.47 times that observed in the 120 K X-ray study. The ratio is lower for the metal atoms (Co 0.22, Cr 0.39) and quite uniform for the lighter atoms (0.47 to 0.54). The ratios emphasize the non-linearity with temperature observed in the X-ray experiment when 120 and 295 K results were compared, and predict the ratio of 0.35 on extrapolation.

We thank E. S. Kucharski for assistance with the growth of the single crystals. BNF is grateful to the University of Western Australia for support on a field-work program and to the Argonne Division of Educational Programs for sponsoring a resident-associate appointment. Work at Argonne was performed under the auspices of the office of Basic Energy Science, Division of Materials Science, of the US Department of Energy under contract W-31-109-ENG-38.

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Lanthanum Thallium Bis(sulphate) Dihydrate, $\text{TlLa}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$

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(Received 30 October 1984; accepted 20 December 1984)

Abstract. $M_r = 571.44$, monoclinic, $P2_1/n$, $a = 7.216$ (1), $b = 11.853$ (1), $c = 10.486$ (1) Å, $\beta = 92.05$ (1)°, $V = 896.31$ Å³, $Z = 4$, $D_x = 4.233$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 233.5$ cm⁻¹, $F(000) = 1016$, $T = 293$ K, final $R = 0.035$ for 1791 observed reflections. The La and Tl atoms are nine-coordinated by O atoms, La atoms in the form of a distorted monocapped square antiprism [La–O distances 2.404 (7)–2.637 (6) Å] and Tl atoms in the form of an irregular polyhedron [Tl–O distances 2.740 (6)–3.465 (8) Å]. The sulphate groups join La and Tl polyhedra into a three-dimensional framework.

Introduction. The crystal structure of the title compound was determined as a continuation of our research programme concerning double salts of the rare earths of the general formula $M^{\text{I}}\text{Ln}^{\text{III}}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$ (Bukovec & Golič, 1975; Bukovec, Bukovec, Golič & Šiftar, 1977; Bukovec, Golič, Bukovec & Šiftar, 1978; Bukovec, Kaučič & Golič, 1980).

Experimental. Single crystals prepared by isothermal evaporation of aqueous solutions containing equivalent quantities of thallium and lanthanum sulphate.

D_m not determined. Single crystal $ca\ 0.06 \times 0.08 \times 0.34$ mm. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Unit-cell parameters by least-squares refinement of setting angles of 60 centred reflections with $2\theta > 20^\circ$. Intensities of reflections (h : 0→10; k : 0→16; l : -14→14) with $0.03 < \sin\theta/\lambda < 0.70$ Å⁻¹ measured at room temperature. ω - 2θ scan mode, scan angle $\Delta\omega = (0.60 + 0.20 \tan\theta)^\circ$. Three reflections ($\bar{3}22$, 314, 114) monitored after every 240 intensities measured; no significant variation in intensity. Of 2583 independent reflections measured, 1791 with $I_o > 3\sigma(I_o)$ considered as observed, 792 unobserved. Empirical absorption corrections applied (transmission factors from 0.163 to

0.301). Structure solved with direct methods, using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) to locate La and Tl atoms. Subsequent Fourier map revealed positions of the other non-H atoms. Refinement by full-matrix least squares on F of positional and anisotropic thermal parameters of all non-H atoms and an isotropic-extinction parameter (final value 0.53×10^{-3}) converged to final $R = 0.035$ and $wR = 0.036$. $(\Delta/\sigma)_{\text{max}} = 0.2$. 128 parameters. Weighting function $w = W_F W_S$ determined empirically from $W_F(|F_o| < 60) = (|F_o|/60)^2$, $W_F(|F_o| > 110) = (110/|F_o|)^2$, and $W_F(60 < |F_o| < 110) = 1.0$, and $W_S(\sin\theta < 0.30) = (\sin\theta/0.30)^2$, $W_S(\sin\theta > 0.38) = (0.38/\sin\theta)^2$, and $W_S(0.30 < \sin\theta < 0.38) = 1.0$.

Final difference Fourier map shows max. height of $1.08 \text{ e } \text{Å}^{-3}$ close to La atom. We could locate two of the four H atoms in the map: $0.44 \text{ e } \text{Å}^{-3}$ high maximum 1.06 Å from the water atom O(10) and $0.39 \text{ e } \text{Å}^{-3}$ high maximum 0.76 Å from the water atom O(9). These atoms were not included in the refinement.

All calculations, except direct methods, carried out using *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Atomic scattering factors for non-H atoms from Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965). Anomalous-dispersion-correction factors for non-H atoms from Cromer & Liberman (1970).

Discussion. The final atomic coordinates, bond lengths and bond angles are given in Tables 1 and 2.* The atom-numbering scheme is shown in Fig. 1.

* Lists of anisotropic thermal parameters and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39990 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.