

Orientalional Disordering in CsCo(ND₃)₆(ClO₄)₂Cl₂ Crystals Studied by Single Crystal Neutron Diffraction between 20 and 290 K

Philip A. Reynolds,^{*,1} Robert W. Henning,[†] and Arthur J. Schultz[†]

^{*}Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia, and [†]IPNS, Argonne National Laboratory, Argonne, Illinois 60439

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A member of the series $M(\text{I})M(\text{III})(\text{ND}_3)_6(\text{ClO}_4)_2X_2$, CsCo(ND₃)₆(ClO₄)₂Cl₂, has been examined by single crystal time-of-flight neutron diffraction at 20, T_c-10 , T_c+10 , and 290 K, adding to previous X-ray diffraction studies of some compounds in this series. T_c is the phase transition temperature of 250(1) K observed by DSC between closely related simple trigonal structures—twinned ordered $R\bar{3}$ and disordered $R\bar{3}m$, both with $Z=3$ and the former with $a=7.210(2)$ Å, $c=26.819$ Å at 20 K. The twin populations, orientational order parameter, and deuterium disordering are much more clearly observed by neutron than by X-ray diffraction. A simple model involving both twinning and order–disorder with differing ranges of ionic orientational correlations is appropriate for this crystal at all temperatures. This type of subtle transition, sometimes involving anharmonicity, floppy modes, and substantial disorder below the transition temperature, is easily missed by diffraction studies and yet the thermal and electrical consequences of such disorder may be severe. © 2000 Academic Press

Key Words: phase transition; orientational disordering; low-temperature neutron diffraction.

INTRODUCTION

Simple double salts such as alums, elpasolites, and tutton salts have played a significant role in materials chemistry. They are excellent model systems both for metal ions in various site symmetries, and for the often subtle structural changes observed in many more complex materials, e.g., (1, 2). $M(\text{I})M(\text{III})(\text{ND}_3)_6(\text{ClO}_4)_2X_2$ salts are of simple trigonal structure with a trigonal transition metal site. In this paper we present a detailed structural study of changes with temperature of ionic orientations and motions in the salts which we believe has lessons for those interested in more complex situations such as the floppy modes and “boson peaks” in silicates and other glasses (3).

¹To whom correspondence should be addressed. E-mail: phil@rsc.anu.edu.au.

These double salts have been known since the initial studies in 1978–1980 of the spectra, magnetism, and structure of Cr(III) and Co(III) crystals (4–7). Study has now resumed—the spectra of two Os(III) and Cr(III) (8, 9) members and X-ray diffraction studies of 10 salts at temperatures of 10, 92, and 293 K are recently completed (10, 11).

At 293 K all are isomorphous, trigonal $R\bar{3}m$, $Z=3$, of extremely simple and symmetrical but disordered structure. The hexaammine- $M(\text{III})$ and perchlorate ions are rotated from 3 to 11° about the threefold axis away from the $R\bar{3}m$ mirror plane, with equal populations in both senses. This local disordering results in the Bragg diffraction giving a disordered $R\bar{3}m$ structure. At lower temperatures most crystals undergo a reversible change to an equally simple twinned, but locally atomically ordered, $R\bar{3}$ phase. This arises from the establishment of long-range correlation, and concomitant strong local correlation, in the rotations. All the ions in one region of the crystal adopt the same sense of rotation and give Bragg diffraction as from a single twin of an ordered $R\bar{3}$ phase. However, further away there is a region in which all ions are rotated in the opposite sense and which gives Bragg scattering appropriate to the other $R\bar{3}$ twin. Thermal parameters, unit cells, and structures vary systematically with $M(\text{I})$ ionic radii and $M(\text{III})-N$ distances. The K^+ members appear to remain $R\bar{3}m$, while the larger $M(\text{I})$ and longer $M(\text{III})-N$ members undergo the greatest rotations and larger amplitudes of displacement around the threefold axis at room temperature.

The X-ray data answer only some questions, since the electron-rich metal sites dominate them and the electron-poor hydrogen atoms are scarcely visible. The consequence is that the small changes in nitrogen and oxygen atoms are hard to define, and even more so for the hydrogen atoms. Neutron diffraction does not suffer this. Since all the scattering lengths are in the same size range, changes in the ammine and perchlorate sites affect the data much more. In this paper we will define the changes in proton position and motion and explore the amount of both twinning and

disorder as we pass through the supposed phase transition in a typical salt—CsCo(ND₃)₆(ClO₄)₂Cl₂.

EXPERIMENTAL

A 1:2 molar mixture of Co(NH₃)₆Cl₃ and CsClO₄ was dissolved in D₂O at 60°C until it was almost saturated. Large single crystals of the sparingly soluble CsCo(ND₃)₆(ClO₄)₂Cl₂ were obtained by slow cooling of the solution to 20°C while encased in a large thermal mass inside a Dewar. The compound crystallizes as orange-brown hexagonal plates.

Differential scanning calorimetry was performed on this and related compounds using a TA Model 2920 in modulated mode. The reversible heat flow showed a phase transition at 250(1) K for CsCo(ND₃)₆(ClO₄)₂Cl₂, 248(1) K for CsCo(NH₃)₆(ClO₄)₂Cl₂, and 296(1) K for CsRu(NH₃)₆(ClO₄)₂Cl₂. These transitions were clearly visible only in modulated mode—conventional DSC (11), even on repeated cycling, showed ambiguous and thus weak evidence for a transition in CsRu(NH₃)₆(ClO₄)₂Cl₂. NH₄Ru(NH₃)₆(ClO₄)₂Cl₂ showed a transition at 288(2) K, while KCo(NH₃)₆(ClO₄)₂Cl₂ showed no transition above 165 K. The first three transitions were very asymmetric, showing a very long tail on the low temperature side extending at least 25 K—irrespective of whether the scan was of increasing or decreasing temperature. The enthalpy change is greater than ca. 0.8 kJ mol⁻¹, the long tail precluding more accurate estimate. This corresponds to more than ca. 0.5Rln2 entropy change. The transition in the ammonium salt was of different character—symmetric and sharp with an enthalpy change of 1.0 kJ mol⁻¹. This is probably associated with the ammonium disordering observed at 293 K in this compound (8), rather than the $R\bar{3}m \rightarrow R\bar{3}$ transition.

Four data sets were collected at 20, 240, 260, and 290 K using a 36-mg single crystal mounted in an Air Products Displex refrigerator on the single crystal time of flight neutron diffractometer SCD at the Intense Pulsed Neutron Source of the Argonne National Laboratory. Experimental details are collected in Table 1a and are described in more detail elsewhere (12); however, we note that the 20 K set was collected for three to four times longer per frame and the statistics are accordingly better. The 15-frame coverage used collected just over a unique set which was then corrected for absorption by use of an analytical spherical correction. Data were processed and the structure was refined using local IPNS software (12). Hydrogenous hexaamminecobalt(III) was used in the preparation so as to keep a small (ca. 10%) percentage of protons, which often seems to reduce extinction, a potential problem in these very large crystals. In this case refinement of extinction for each frame gave positive but not large values—a satisfactory result. The number of reflections collected increased as the temperature decreased, reflecting the increase in intensity due to lower

TABLE 1a
Crystal Data and Data Collection for CsCo(ND₃)₆(ClO₄)₂Cl₂, Where Appropriate Different Values for the Four Data Sets Are Listed in Order of Ascending Temperature

Radiation (λ , Å)	neutron, t-o-f, 0.7–4.2
Temperature (K)	20(1), 240(1), 260(1), 290(1)
Crystal size (mm)	4.5 × 4.5 × 1.0
Empirical formula	D ₁₈ Cl ₄ CoCsN ₆ O ₈
Formula weight	518.7
Crystal system	Trigonal
Space group	$R\bar{3}/R\bar{3}m$
Z	3
D_c (Mg m ⁻³)	2.366(1) at 290 K
μ (mm ⁻¹)	0.078 + 0.052 λ
a (Å)	7.210(2)
	7.220(2)
	7.224(2)
	7.228(2)
c (Å)	26.819(6)
	27.023(6)
	27.033(7)
	27.069(7)
Volume (Å ³)	1207.3(5)
	1219.9(5)
	1221.7(5)
	1224.9(5)
max $\sin\theta/\lambda$ (Å ⁻¹)	1.15, all to 0.85
k max	15
	12
	13
	13
l max	59
	49
	47
	46
Reflections collected	2257, 992, 859, 789
R (int)	No averaging
Transmission (max)	0.84
Transmission (min)	0.72

thermal motion. The large increase in observed reflections at 20 K reflects the increased counting time and indicates that the higher temperature data have been slightly compromised due to time constraints.

Initial refinement of the 20 K data used the initial coordinates and displacement parameters found by X-ray diffraction for CsRu(NH₃)₆(ClO₄)₂Cl₂ at 9.5 K (9). Neutron scattering lengths were taken from Sears (13). The model used invoked 10 unique nuclear sites and was refined in all cases in space group $R\bar{3}$, but it also incorporated the effects of twinning and disorder on the intensities. We write the structure factor for an ordered untwinned $R\bar{3}$ crystal as $F_0(hkl)$ and define a refinable twin parameter as t and a refinable order parameter as d . The sample is composed of two twins of population 100 t % and 100(1 - t)%, respectively. One twin has 100 d % and 100(1 - d)% of the sites related by a mirror plane in $R\bar{3}m$ occupied, while the other has the opposite viz. 100(1 - d)% and 100 d %. The

resultant observed apparent structure factor is written as $F_1(hkl)$ and we can write an equation for the square of this as

$$F_1(hkl)^2 = t^*[(1+d)/2*F_0(hkl) + (1-d)/2*F_0(-h-kl)]^2 \\ + (1-t)^*[(1-d)/2*F_0(hkl) \\ + (1+d)/2*F_0(-h-kl)]^2.$$

This equation expresses the fact that when there are twins we must add the square of the structure factors of each twin, but that where there is disorder then we must add the structure factors for each disordered component and then square the result. The difference arises because the disorder is local, but the twinning involves long-range separation of the two disorder arrangements. We remark that d and t are less correlated the greater the difference of $F_0(hkl)$ and $F_0(-h-kl)$ —which are different in the Laue group $R\bar{3}$. This difference is also accentuated for neutrons over X-rays since the former are more affected by the ammine and perchlorate orientations. We also note that for $d = 0$, complete disorder, both twin structures are identical and thus the twin parameter is meaningless. We would then expect that as d approaches zero then the error in t will diverge.

In addition to the 18 positional, 40 displacement, and order and twin parameters, we also refined an overall deuteration percentage and a scale factor and extinction for each of the 15 frames, giving a total of 91 parameters. We used a full matrix least-squares procedure minimizing the quantity $w(F_o^2 - F_c^2)^2$, with $w = [\sigma^2(F_o^2) + (0.04*F_o^2)^2]^{-1}$, until the maximum shift on error was less than 0.01. A rejection criterion $F_{obs}^2 > 2F_c^2 > 4F_{obs}^2$ caused rejection of 13 badly integrated reflections. Agreement factors ($R(F) = \|F_o\| - \|F_c\| / \|F_o\|$, $wR(F^2) = \{[w(F_o^2 - F_c^2)^2] / [w(F_o^2)^2]\}^{1/2}$ and $GOF = \{[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined) and other results are listed in Table 1b. Successful refinement of all observed peaks, including some which would be equivalent except for observation at different

TABLE 1b
**Data Refinement and Results for CsCo(ND₃)₆(ClO₄)₂Cl₂,
Where Appropriate Different Values for the Four Data Sets Are
Listed in Order of Ascending Temperature**

Reflections used in refinement	2244, 919, 797, 745
Parameter No.	91, 91, 91, 90
GOF (on F^2)	1.045, 1.013, 0.935, 0.973
$R(F)$ ($I > 3\sigma(I)$)	0.0351, 0.0635, 0.0564, 0.0556
$wR(F^2)$ (all data)	0.0566, 0.1020, 0.0910, 0.0893
$R(F^2)$ (all data)	0.0658, 0.0886, 0.0785, 0.0792
Order parameter, d	1.004(3), 0.603(9), 0.10(2), 0.04(5)
Twin population, t	0.478(1), 0.474(4), 0.50(2), 0.50
Deuteration (%)	89.0(1), 88.4(3), 88.4(5), 87.9(6)

TABLE 2a
**Atomic Coordinates and Equivalent Isotropic Displacement
Parameters ($\text{\AA}^2 \times 10^4$) for CsCo(ND₃)₆(ClO₄)₂Cl₂**

Atom	x	y	z	U(eq)
Co(1)	0	0	0	40(3)
				120(10)
				152(10)
				165(9)
N(1)	0.08294(6)	-0.16849(5)	-0.04232(1)	64(1)
				232(10)
				280(20)
				310(20)
Cl(1)	0	0	0.19156(1)	46(1)
				191(3)
				204(3)
				229(3)
O(1)	0	0	0.13766(3)	97(1)
				504(7)
				565(7)
				642(7)
O(2)	0.13901(9)	-0.075456(9)	0.20962(3)	86(2)
				340(10)
				410(50)
				470(40)
Cl(2)	0	0	0.36889(2)	63(1)
				249(3)
				276(3)
				310(3)
Cs(1)	0	0	1/2	46(1)
				225(6)
				271(6)
				298(6)
D(1)	0.1953(2)	-0.1943(2)	-0.02577(3)	211(3)
				700(20)
				660(40)
				730(40)
D(2)	0.1404(2)	-0.1037(2)	-0.07620(2)	207(3)
				810(30)
				800(50)
				820(50)
D(3)	-0.0432(1)	-0.3185(1)	-0.04907(8)	184(2)
				560(20)
				550(20)
				600(20)

* Note. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor. There are four entries for each atom corresponding to the 20, 240, 260, 290 K results.

neutron wavelengths (which precludes averaging of equivalents) confirms the choice of space group. Positional and displacement parameters are listed in Tables 2a and 2b. Selected bond lengths and angles are given in Tables 3a and 3b. The data at 240, 260, and 290 K were treated the same as the 20 K data, with one exception. The 290 K data had the value of the twin parameter, t , fixed at 0.5 since the derived value of the order parameter d was so close to zero that the error in t was very large. Physically this means that the two twin structures are insignificantly different. The unit cell is

TABLE 2b
Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^4$)
for CsCo(ND₃)₆(ClO₄)₂Cl₂

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co(1)	44(5)	U11	33(6)	0.5*U11	0	0
	140(20)		80(20)			
	170(17)		110(20)			
	179(16)		140(20)			
N(1)	73(1)	67(1)	60(1)	40(1)	4(1)	-6(1)
	307(13)	260(10)	195(4)	190(10)	25(5)	-24(5)
	400(20)	350(20)	217(5)	270(20)	35(6)	-24(6)
	440(30)	390(30)	233(5)	290(30)	33(6)	-31(7)
Cl(1)	47(1)	U11	45(1)	0.5*U11	0	0
	218(5)		138(5)			
	220(5)		173(5)			
	246(5)		196(6)			
O(1)	118(2)	U11	54(2)	0.5*U11	0	0
	668(15)		177(9)			
	749(13)		198(9)			
	858(15)		210(9)			
O(2)	84(2)	95(2)	100(2)	61(2)	-14(1)	-5(1)
	280(20)	300(20)	469(9)	170(20)	-90(10)	-50(10)
	410(60)	420(70)	530(9)	290(60)	-140(40)	-100(40)
	430(50)	490(60)	600(10)	320(50)	-160(40)	-120(40)
Cl(2)	62(1)	U11	65(1)	0.5*U11	0	0
	260(5)		228(5)			
	278(5)		270(5)			
	316(5)		299(6)			
Cs(1)	44(2)	U11	50(3)	0.5*U11	0	0
	240(11)		200(10)			
	280(10)		250(10)			
	290(10)		310(10)			
D(1)	215(4)	286(4)	227(3)	196(3)	-76(3)	-73(3)
	750(30)	1120(40)	690(20)	810(20)	-340(20)	-470(30)
	610(30)	1030(70)	710(20)	690(50)	-280(30)	-410(40)
	660(40)	1150(70)	780(20)	760(50)	-350(30)	-510(40)
D(2)	316(4)	191(3)	121(2)	132(3)	101(2)	52(2)
	1580(60)	730(30)	390(10)	780(40)	600(20)	300(20)
	1470(80)	730(40)	400(10)	700(50)	560(30)	240(30)
	1440(90)	790(50)	430(10)	710(60)	550(30)	230(30)
D(3)	158(3)	117(3)	226(3)	31(2)	-1(2)	-53(2)
	770(30)	420(20)	600(20)	370(20)	-40(20)	-210(20)
	730(20)	440(20)	580(20)	370(20)	-50(20)	-230(20)
	800(20)	480(20)	660(20)	410(20)	-80(20)	-280(20)

Note. There are four entries for each atom corresponding to the 20, 240, 260, and 290 K results. The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

plotted in Fig. 1 and the temperature evolution of thermal motion for the hexaamminecobalt(III) ion is illustrated in Fig. 2.

Given that the order parameter at 290 K is, within the error, 0.0, the structure can be described as perfectly disordered $R\bar{3}m$. There are five half-occupied N(1), O(2), and D(1-3) positions modeled. Each hexaammine and perchlorate ion can occupy either of two positions defined by positive and negative rotations of the ions about the threefold axis away from the $R\bar{3}m$ mirror plane. For the X-ray refine-

TABLE 3a
Bond Lengths (\AA) for CsCo(ND₃)₆(ClO₄)₂Cl₂

	Neutron		
	20 K	290 K	293 K X-ray
Cl(1)-O(1)	1.4445(9)	1.416(2)	1.432(4)
Cl(1)-O(2)	1.4422(6)	1.431(3)	1.427(2)
Co(1)-N(1)	1.9611(5)	1.959(1)	1.946(3)
N(1)-D(1)	1.019(2)	1.015(8)	—
N(1)-D(2)	1.010(1)	0.989(4)	—
N(1)-D(3)	1.022(1)	0.995(4)	—

Note. There are three entries for each atom corresponding to the 20 and 290 K neutron results and the 293 K X-ray results for CsCo(NH₃)₆(ClO₄)₂Cl₂ (not shown for H-atom related values).

ment, we previously modeled the data in an alternative way with N(1), O(2) fully occupied and on the mirror plane so that $x = -y$, together with D(2) also on a mirror plane and equally disordered between N-Co-N-D(2) dihedral angles of 0 and 180°. D(2) and D(3) are now equivalent due to mirror plane symmetry. We also modeled our neutron data at 290 K in this manner, but some more flexibility produced significant improvement. Allowing the 0 and 180° dihedral populations of D(1) and D(2) to become different from 0.5 (but still summing to a population of 1) produced significant improvement. The parameter number is reduced from 90 to 84 from our present “twinned $R\bar{3}$ ” model to this improved “ $R\bar{3}m$ ” model but the agreement factors increase a noticeable amount— χ^2 0.97 \rightarrow 1.07, $R(F)$ 0.056 \rightarrow 0.060, $wR(F^2)$ 0.089 \rightarrow 0.093, $R(F^2)$ 0.079 \rightarrow 0.079. In addition, the number of outlying rejected, reflections increases from 44 to 61 and the site D(2) now has unphysical non-positive-definite site displacement parameters.

TABLE 3b
Selected Angles ($^\circ$) for CsCo(ND₃)₆(ClO₄)₂Cl₂

	Neutron		
	20 K	290 K	293 K X-ray
O(1)-Cl(1)-O(2)	109.61(2)	110.1(1)	110.1(1)
O(2)-Cl(1)-O(2')	109.34(5)	108.9(2)	108.9(1)
N(1)-Co(1)-N(1')	89.91(3)	89.89(4)	89.7(1)
Co(1)-N(1)-D(1)	112.17(7)	111.2(3)	—
Co(1)-N(1)-D(2)	114.47(9)	114.7(5)	—
Co(1)-N(1)-D(3)	111.81(6)	112.5(3)	—
D(1)-N(1)-D(2')	107.2(1)	106.4(5)	—
D(1)-N(1)-D(3')	104.6(1)	106.0(5)	—
D(2)-N(1)-D(3')	105.8(1)	105.4(3)	—

Note. There are three entries for each atom corresponding to the 20 and 290 K neutron results and the 293 K X-ray results. *Transformation* is $-y, x - y, z$.

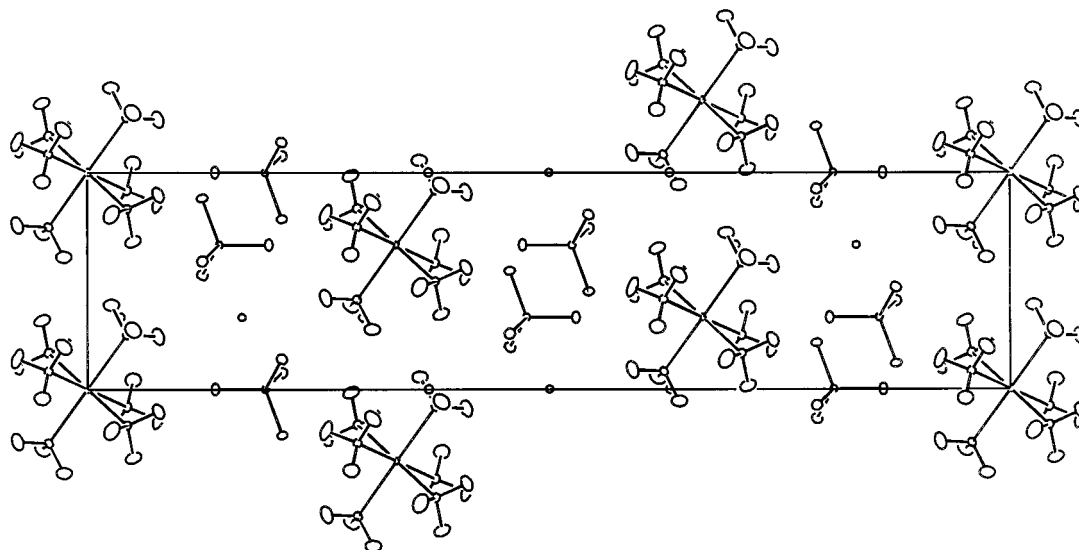


FIG. 1. $R\bar{3}$ unit cell at 20 K, c horizontal, $[110]$ projection, illustrating the layered nature of the crystal structure. The small tetrahedra are ClO_4^- with unbonded Cs^+ in the same layer. 50% thermal ellipsoids are shown.

DESCRIPTION OF STRUCTURE

The Structure at 20 K

The 20 K data refine to give a well behaved ordered structure, mildly unusual only in that we have needed to invoke twinning. The twin population has a value of 0.478(1) at 20 K, while the order parameter refines to 1.004(3), reflecting a completely ordered local structure. One may expect the twin parameter to approach 0.5 for a perfect infinite sample. The observation of 0.478(1) is 22 standard deviations different from this and highly significant. We may infer from this either that the twin domain size is not very small compared with the sample size or, alternatively, that there are defects or strains favoring one twin over the other.

The structure has been described before (10, 11), and we will summarize it here. This compound forms three different kinds of coordination polyhedra: octahedra from $M(\text{III})(\text{NH}_3)_6^{3+}$ cations, tetrahedra from ClO_4^- anions, and distorted rhombohedra from the $M(\text{I})^+$ ion with Cl or Br atoms in axial positions directed along c and oxygen atoms from the perchlorate groups in equatorial sites. The $M(\text{III})(\text{NH}_3)_6^{3+}$ octahedra form layers perpendicular to c separated by layers of tetrahedrons and rhombohedra (Fig. 1).

The perchlorate ion has almost identical Cl–O bond lengths, 1.4445(9) and 1.4422(6) Å, and the ion is hardly distorted from tetrahedral, with the maximum difference from the ideal tetrahedral angle of 109.47° of only $0.14(2)^\circ$. The hexaammine $M(\text{III})$ ions are also relatively ideal. The $M(\text{III})\text{N}_6$ fragment is only $0.09(3)^\circ$ different from octahedral symmetry. The various N–D bond lengths and angles differ only slightly from free NH_3 whose bond length is 1.0124 Å

and H–N–H angle is 106.7° (14). Our observed D–N–D angles differ from this by up to $2.1(1)^\circ$.

The anisotropic displacement parameters have typical values for zero-point motion. The amplitudes for the nuclei change as approximately the inverse of the square root of the mass. This is appropriate for zero-point motions, which are dominated by higher frequency modes. The displacements of Co(1), N(1), Cl(1), Cl(2), and Cs(1) are all almost isotropic—as we expect from atoms that are either entirely nonbonded or with a relatively isotropic covalent bonding array. However, again as expected, the covalently bound terminal D and O sites show distinct anisotropy, with greater displacement perpendicular to the covalent bond than parallel to it. This reflects the lower force constant for bond bending than bond stretching. For the deuterium atoms there is also a slight elongation in displacement corresponding to ND_3 libration about the Co–N bond (Fig. 2a).

The derived structure is more precise than any of (10, 11). This reflects the low temperature, the high maximum $\sin\Theta/\lambda$ of 1.15 \AA^{-1} of this time-of-flight spallation source data, and the use of neutrons in which there is no falloff with $\sin\Theta/\lambda$ of “atomic” form factor and where all scattering lengths are about the same.

The Structure at 290 K

The high temperature phase can be successfully modeled in terms of the same model as for the 20 K structure. The structure is now completely disordered with a long-range order parameter of 0.04(5).

Due to the greater sensitivity of neutron scattering to the ammine coordinates we are now able to reject our previous

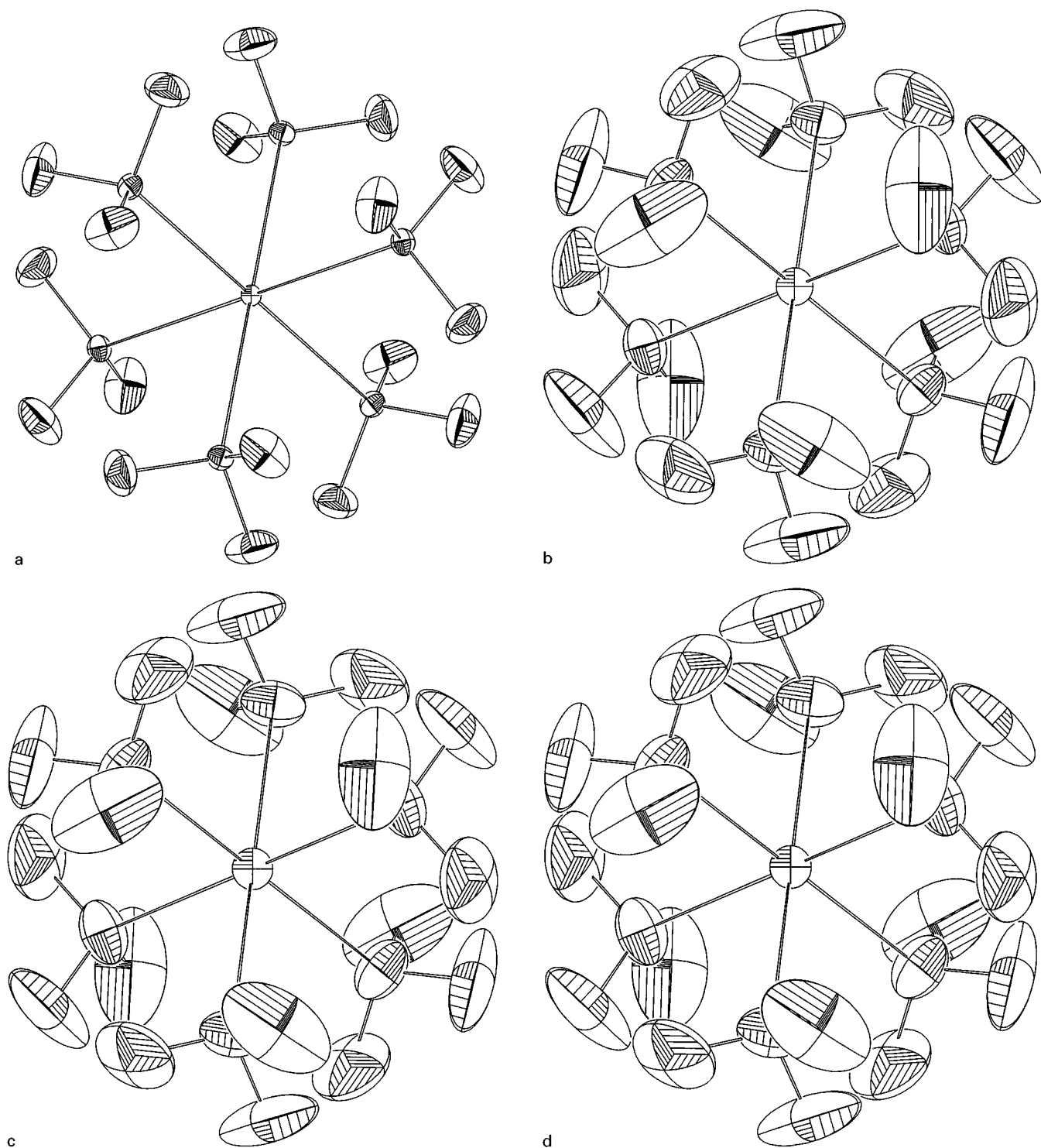


FIG. 2. Hexaamminecobalt (III) ion, projection on c , showing 50% thermal ellipsoids at (a) 20 K, (b) 240 K, (c) 260 K, (d) 290 K. Only one of the two disordered sites is shown for clarity; the other site (where present) is produced by application of a vertical mirror plane.

model derived from the X-ray data in which the ammine group performed harmonic displacements about coordinates in which N(1) and D(1) are ordered and on the $\bar{3}m$ mirror plane. We instead require a more flexible model in

which there are 12 ammine sites per hexaammine ion, each half-occupied and, on general positions, with harmonic displacements. An alternative model has six ordered N(1) and D(1) sites and distinctly anharmonic displacements, but

this is more complex and reduces to the same physical interpretation. That is that each hexaammine and perchlorate group can be modeled as performing harmonic motion about the threefold axis in either of two positions between which it jumps. Since, for the perchlorate ion, the two positions are separated by 19.4° , while the root mean square amplitude of libration can be up to 11.3° , this simple model of anharmonicity should not be taken literally.

Figure 2d illustrates one of the half-occupied hexaammine ion sites. The other half-occupied site is related by applying a vertical mirror operation to the diagram or, alternatively, for the nitrogen position only (not the thermal motion or hydrogen data), by rotating the ion 14° anticlockwise. Fig. 2 also illustrates the change in thermal motion at 290 K from that at 20 K. As expected, the motions are greatly increased in amplitude—by a factor of about four. Again as expected, the heavier the atom the greater this factor of increase is. At high temperatures the amplitudes become more similar for all atoms since the amplitudes become dominated by external modes; while at low temperatures the differing nuclear masses strongly affect the high-frequency zero-point motions. In nitrogen we can also see an elongation around the threefold axis associated with rocking motion. The effect on the deuterium atoms is more subtle. There is clearly an increase in amplitude of ND_3 librations about the Co–N bonds. However, we also notice that the shortest principal axis of the ellipsoid of displacement has moved from collinear with the N–D bond to line up more closely with the Co–D vectors. This again is associated with an increased amplitude of libration of the whole $\text{Co}(\text{ND}_3)_6^{3+}$ ion about the threefold crystal axis. Thus, as at 20 K, the amplitudes of displacement can be interpreted in some detail in terms of vibrational motions.

The Phase Transition

In previous experiments (10, 11) we have assumed a phase transition—as opposed to a continuous evolution of structure with temperature—with no convincing direct experimental evidence on this point. One might argue that such a subtle change requires only a higher order transition not easily distinguishable from a continuous change.

However, our present DSC measurements do show a distinct anomaly associated with the $R\bar{3}m \leftrightarrow R\bar{3}$ transition for two of the cesium double salts, while an ammonium and a potassium salt showed no such transition. These four observations, two transition temperatures and the absence in two other cases above 165 K, agree with our previous observations on relative sizes of rotations about the threefold axes and other similar data. The observed transition temperatures do increase as both $M(\text{I})$ ionic radius and $M(\text{III})$ –N distances increase.

For a transition between complete order and complete disorder we expect an entropy change of $R\ln 2$. We observe

a minimum value of half of this. Part of the difference may well reside in residual local orientational correlation above the transition temperature; however, the major source is probably the difficulty of estimation of this quantity given the extremely long tail to lower temperatures that we observe. This indicates that the disordering process is substantial well below the transition temperature itself, ruling out a largely first-order transition.

This is confirmed and quantified by our diffraction measurements. The modeling behaves well in that the twin population, where meaningful, remains constant. However, the long-range orientational order parameter changes dramatically. At 20 K it is 1.004(3), at $T_c - 10$ it is 0.603(9), at $T_c + 10$ it is 0.10(2), and at 290 K it is 0.04(5). Thus, even as far as 10 K below the transition the order parameter is already as low as 0.603. At $T_c + 10$ there may still be residual long-range order, but this is gone at 290 K.

The changes in order parameter are accompanied by noticeable changes in the mean ionic orientations. The hexaammine average rotations away from the mirror plane are $11.1, 8.5, 7.4,$ and 7.0° as the temperature is raised, while for the perchlorate we observe $9.7, 7.3, 4.9, 4.6^\circ$.

The U_{11} parameters for N(1) and O(2) increase more rapidly between 240 and 260 K than from 260 to 290 K, but this is not a strong effect. This can be seen by examination of Fig. 2. The transition does not seem to be strongly driven by vibrational softening, even libration about the threefold axis. The cell size appears to also change without a large anomaly at T_c .

This appears to imply that to a crude approximation we have a simple spin $1/2$ Ising system, where the two orientations correspond to the spin states and a second-order transition at T_c . At 240 K, $T/T_c = 0.96$, a simple triangular two-dimensional $S = 1/2$ Ising model predicts an order parameter of 0.8, while a mean-field solution gives 0.4 (15). Our observed value of 0.6 falls between these. The mean field solution characteristically provides a rough lower bound on the order parameter for the most appropriate exact model. This may not be the coupling parameter arrangement assumed in the simple triangular model. In any case, the observed temperature dependence of the ions' angular deviation from the mirror plane is *a priori* evidence that the $S = 1/2$ Ising model is not an exact model for this system, as indeed is the 0.10(2) order observed at $T_c + 10$ K.

In a wider context it is encouraging that such a subtle change can still be interpreted, at least approximately, in a simple vibrationally harmonic order–disorder model. We appear to have no evidence for necessary anharmonicity as archetypally demonstrated for potassium dihydrogen phosphate, nor the substantial translational–librational coupling observed in, for example, the cubic hexaammines (16).

This experiment has quantified the long-range order parameter, but it is clear that a study of local correlations by

diffuse X-ray, or preferably neutron, scattering would also be valuable. More critical to the relevance of this system to glasses and similar systems would be a phonon density of states measurement to examine if here too we observe a peak in the density of states at between about 0 and 8 cm⁻¹. In glasses the detailed origin of the so-called “boson” peak is not clear. If it is present here then a simple two-site anharmonic model may be a sufficient model in glasses as well.

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