

Evidence for the Isomorphism of the Low-Temperature Form of Hexaammincobalt(III) Iodide with the Room-Temperature Structure of Hexaammincobalt(III) Chloride

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Abstract. Crystals of $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ which are cubic at room temperature become polydomained on cooling below 280 K. We show that oscillation photographs taken below the transition may be indexed on the assumption that 12 twinned orientations of a monoclinic cell are present in the crystal. With the adoption of this new cell, the powder data of Borzęcka, Hodorowicz & Ciechanowicz-Rutkowska [*Acta Phys. Pol. A* (1980), **57**, 813–817] have been reinterpreted to yield: $a = 13.44$ (2), $b = 23.02$ (3), $c = 13.37$ (2) Å, $\beta = 110.69$ (7)°.

The halides of transition-metal complexes of the form $[\text{M}(\text{NH}_3)_6]\text{X}_{2,3}$ have been the centre of recent attention owing to the existence of temperature-dependent large-amplitude motions of the complex cation and the coordinating ammonia molecules, as revealed for example by NMR experiments. The triiodide salt of $\text{Co}(\text{NH}_3)_6^{3+}$, which was reported (Kime & Ibers, 1969) to be cubic $Fm\bar{3}m$ with $a = 10.82$ Å at room temperature, seemed to be a suitably simple system for study although it was known to undergo a phase transition at about 280 K (Ziegler, 1941; Le Postollec, 1975; Pislowski, Stankowski & Latanowicz, 1976; Goettel, Janik, Janik & Rachwalska, 1976). The interpretation of the results of previous investigations (Murray & Waugh, 1958; Kim, 1960; Le Postollec, 1975; Pislowski *et al.*, 1976; Goettel *et al.*, 1976) has been hampered by the lack of knowledge of the low-temperature structure. Borzęcka, Hodorowicz & Ciechanowicz-Rutkowska (1980) reported the low-temperature phase to be monoclinic with $a = 10.836$, $b = 11.024$, $c = 10.748$ Å, and $\beta = 90.56^\circ$, on the basis of X-ray powder diffraction. No structural details were reported, however, since attempts at single-crystal experiments revealed the sample to become polycrystalline on transformation.

The related trichloride compound $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is known to be monoclinic at room temperature (Kruger & Reynhardt, 1978) and we have also found in our present studies that the tribromide can be assigned an analogous monoclinic cell (see Table 1). Although superficially these monoclinic cells do not appear to be simply derived from a cubic cell, a close examination of the chloride structure reveals that the atomic packing is

similar to that in the cubic iodide when the monoclinic b axis is aligned with the $[101]$ direction of the cubic cell. Fig. 1 illustrates the relationship between the cells.

It seemed possible to us that the low-temperature phase of the iodide could have the same monoclinic structure as the chloride, if we assumed that the cell dimensions given by Borzęcka *et al.* represented the distortion of the original cube and not the true unit cell. This seemed feasible since the measurements were based on a relatively few strong powder lines. For this reason we undertook further single-crystal investigations.

A sample of $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ obtained by slow evaporation of an aqueous solution was mounted with $[101]$ as oscillation axis and a series of 20° oscillation photographs were taken at temperatures above (295 K) and below (190 K) the phase transition. In accordance with the findings of Borzęcka *et al.* (1980) we found the sample to become polycrystalline below the transition

Table 1. Unit-cell parameters of $[\text{Co}(\text{NH}_3)_6]\text{X}_3$ ($X = \text{Cl, Br, I}$)

Compound	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	$[\text{Co}(\text{NH}_3)_6]\text{Br}_3$	$[\text{Co}(\text{NH}_3)_6]\text{I}_3$	
Temperature	Room temperature	Room temperature	Low temperature (< 280 K)	
Reference	Kruger & Reynhardt (1978)	Present work	Present work; idealized cell	Adapted from Borzęcka <i>et al.</i> (1980)
Space group	$C2/m$	$C2/m$?	?
a	12.46 (1) Å	12.83 (1) Å	13.25 Å	13.44 (2) Å
b	21.30 (2)	21.86 (1)	22.95	23.02 (3)
c	12.74 (1)	13.00 (1)	13.25	13.37 (2)
β	112.96 (8)°	112.77 (2)°	109.47°	110.69 (7)°

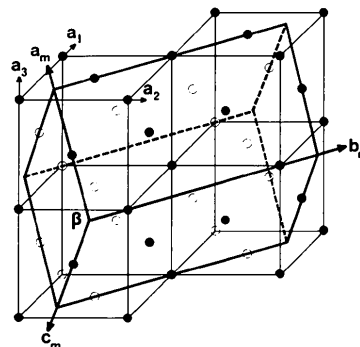


Fig. 1. Relationship between the cubic and monoclinic cells.

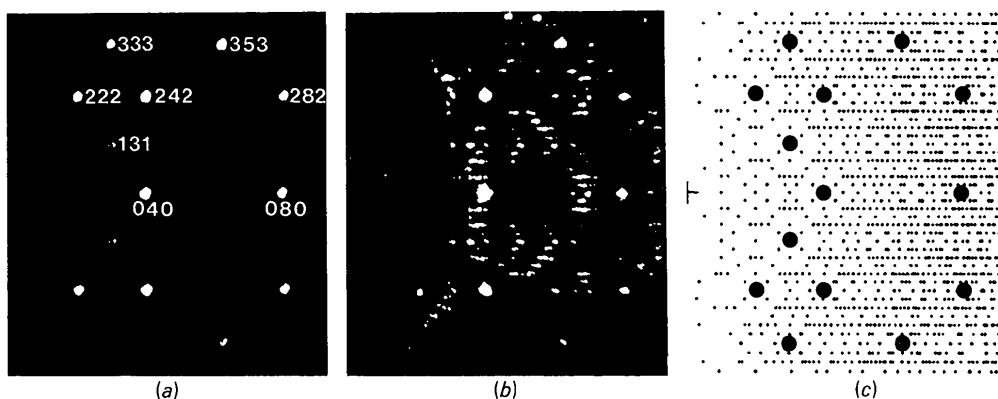


Fig. 2. Small region of a 20° oscillation photograph. (a) Room temperature. (b) Low temperature (190 K). (c) Pattern calculated with the assumed monoclinic cell and twinning scheme.

or, rather, to consist of many crystalline domains whose orientations were, however, closely correlated to the parent-crystal orientation. A section of one 20° oscillation photograph is shown in Fig. 2 for both the room- and low-temperature phases. The indices of the principle reflections of the cubic phase are marked on the photograph and these same reflections are still evident in the low-temperature photograph, although now many more superlattice reflections are evident. These are clearly seen to lie on layer-lines of a spacing of $\frac{1}{6}$ of the original spacing. In other oscillation ranges this layer-line pattern was not so clearly discernible and we attribute this to the fact that only in some directions do the old and new spacings coincide sufficiently precisely to reveal this superstructure. We have been able to interpret this low-temperature oscillation photograph in terms of the superposition of twelve different orientations of a monoclinic cell derived from the parent cubic cell in the way shown in Fig. 1.

We assume that each of the six cubic directions $\langle 110 \rangle$ may equally likely become the monoclinic b axis of the new phase and the monoclinic a and c axes are derived from original cubic directions of the form $\langle 112 \rangle$; e.g., a particular orientation might be

$$\begin{aligned} \mathbf{a}_m &= \mathbf{a}_1/2 - \mathbf{a}_2/2 + \mathbf{a}_3 \\ \mathbf{b}_m &= 3\mathbf{a}_1/2 + 3\mathbf{a}_2/2 \\ \mathbf{c}_m &= \mathbf{a}_1/2 - \mathbf{a}_2/2 - \mathbf{a}_3 \end{aligned} \quad (1)$$

where \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 are the unit cube vectors of the cubic cell. For a given choice of the \mathbf{b}_m direction, \mathbf{a}_m and \mathbf{c}_m may be chosen in two different ways (since we assume they may be distinguished by the C -centring of the monoclinic cell that occurs for the chloro derivative). There are therefore 12 possible twin orientations of the monoclinic cell which will contribute to the diffraction pattern. In Fig. 2(c) we show a plot of the calculated positions of reflections in the appropriate 20° oscillation range for all 12 orientations. Although this plot does not show relative intensities of reflections so that the appearance of Fig. 2(c) does not closely

resemble 2(b), superposition of this plot and the photograph of Fig. 2(b) reveals excellent agreement between the positions of reflections. Only a few reflections observed in 2(b) do not appear in 2(c) and these we presume are missing because of a slight change in the range of oscillation.

The cell transformation given by equation (1) gives the values for the monoclinic cell parameters given in Table 1, when the cube is maintained at its undistorted room-temperature size ($a = 10.82 \text{ \AA}$). The second set of cell dimensions given were obtained from the powder data of Borzęcka *et al.* after the powder lines were reindexed using the new cell defined here.

Our present findings give strong support to the conjecture that the low-temperature phase of $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ is isomorphous with the room-temperature structure of the chloride, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. However, we have no direct evidence for the structure and, in particular, cannot say whether the cell is C -centred since the systematic absences would be masked by the twinning scheme we propose. It seems possible that if crystals could be grown at temperatures below the phase transition they would consist of a single domain and thus enable further investigations to be made. We have not pursued this possibility.

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