X-RAY STUDIES OF PHASE TRANSITION IN $[Co(NH_3)_6]I_3$ POLYCRYSTALS

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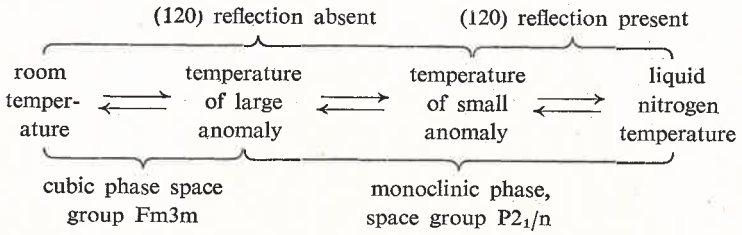
$[Co(NH_3)_6]I_3$ was studied using X-ray powder diffraction methods in the temperature range of 293 — 80 K. It was found that this compound undergoes enantiotropic transition at about 273 K: the cubic form ($a = 10.88$ Å) changes to the monoclinic ($a = 10.836$, $b = 11.024$, $c = 10.748$ Å, $\beta = 90.56°$).

1. Introduction

Complexes of the general formula $[Me(NH_3)_6]X_{2,3}$, where Me can be Ni, Co or Mg, and X for Cl, J, Br, BF_4 or ClO_4, were extensively studied for their phase transitions in the last few years. The most comprehensive data were obtained for three compounds, namely $[Ni(NH_3)_6](ClO_4)_2$, $[Ni(NH_3)_6](BF_4)_2$ and $[Mg(NH_3)_6](ClO_4)_2$. The curves for the specific heat of these compounds plotted vs. temperature show two anomalies different in intensity within the temperature range of 173–115 K [1–3]. X-ray studies [3–5] showed that these anomalies are connected with changes in the lattice symmetry which can be illustrated by the following diagram:



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Data concerning trivalent metal complexes are not so extensive. The calorimetric studies [6, 7] carried out for $[Co(NH_3)_6]I_3$s howed, similarly as for bivalent metal complexes, the presence of two anomalies at 281.9 and 276.2 K.

The aim of this work was to determine whether these anomalies are also connected with changes in the lattice symmetry of the $[Co(NH_3)_6]I_3$ complex, and, if so, to evaluate the lattice parameters of the low temperature modification. At room temperature the complex is known to crystallize in a cubic system [8, 9].

2. *Experimental*

The photographs of the reciprocal lattice of the investigated crystals were taken using CuK_α radiation with an ENRAF-NONIUS precession camera equipped with a low--temperature attachment produced by the same company. The dimensions of the crystals were about 0.1 mm.

Lattice constants having the cubic form of $[Co[NH_3)_6]I_3$ were obtained on a CAD-4 (ENRAF-NONIUS) single crystal diffractometer. The θ angles were about 12–40° and were derived from measurements on both sides of the primary beam.

X-ray powder diffraction data were collected with filtered CuK_α radiation on a DRON-1 (Burevestnik) diffractometer using previously described [4] low temperature attachment. The temperatures, in the investigated range of 293–80 K, were controlled within an accuracy of 0.1°.

The measured samples were kept at a given tempe rature for about 15 minutes before recording the diffraction pattern.

3. *Results and discussion*

The X-ray powder diffraction pattern obtained at ca 25°C was successfully indexed in a cubic system with $a = 10.87 \mp 0.01$ Å; this remains in agreement with previous data [8]. All the diffraction maxima quoted in ASTM [10], including reflection (3 2 0) identified earlier by Natta [10] are present in the pattern. Since the presence of a (3 2 0) maximum puts into question the Kime and Ibers space group determination (Fm3m), additional measurements were done on the single crystals and on the recrystallized powder sample (single crystals were obtained by recrystallization from water initially using polycrystalline material). Neither showed the presence of a (3 2 0) reflection.

The lattice parameter a calculated using the LSQ method for 12 reflections measured on a single crystal CAD-4 diffractometer is 10.875(1) Å, i.e., ca 0.06 Å longer than that found by Kime and Ibers [9].

The phase transition was studied on the polycrystalline sample. The attempt to study it on a single crystal using the precession method showed that after phase transition the sample becomes polycrystalline. When the sample is cooled down the diffraction pattern does not undergo any essential changes down to temperatures corresponding to the occurrence of anomalies in the specific heat vs. temperature curve. At this point some reflections become split and new diffraction peaks form. New maxima increase in intensity on further

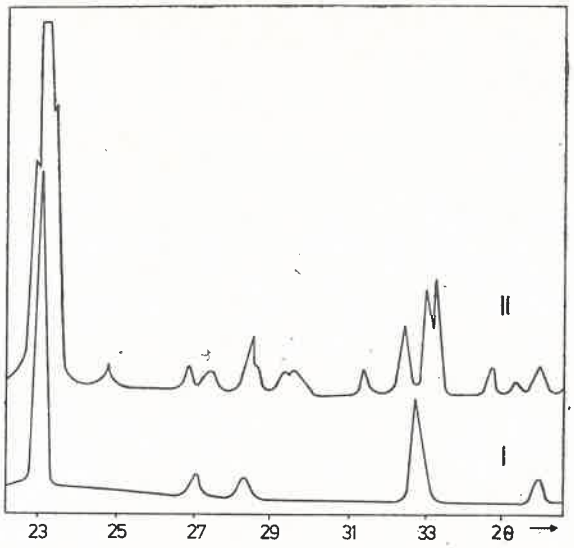

Fig. 1. The X-ray diffraction pattern of $[Co(NH_3)_6]I_3$: I — high-temperature phase, II — low-temperature phase (below 273 K)

cooling while the others gradually disappear. At about 273 K the new diffraction pattern was fully established and remained unchanged on cooling down to 80 K.

When the sample was heated to room temperature reverse changes in the diffraction pattern occured. They were carefully examined by recording the changes in the intensity of a chosen reflection and they showed marked temperature hysteresis of about 4 K.

TABLE I

X-ray powder data for low-temperature phase of $[Co(NH_3)_6]I_3$

d_{exp} [Å]	d_{cal} [Å]	I/I_0	h	k	l
3.87	3.864	55	2	2	0
3.83	3.834	100	2	0	$\bar{2}$
3.80	3.797	65	2	0	2
3.590	3.590	5	2	1	2
3.307	3.307	5	1	3	1
3.250	3.242; 3.258	8	1 1 3 ; 1	1	$\bar{3}$
3.147	3.147	5	2	2	$\bar{2}$
3.127	3.127	11	2	2	2
3.033	3.033	6	0	3	2
3.003	3.003	6	0	2	3
2.868	2.872	5	2	1	3
2.756	2.756	16	0	4	0
2.709	2.709	23	4	0	0
2.687	2.687	25	0	0	4
2.575	2.575	4	3	3	0
2.531	2.531	2	3	0	3
2.492	2.492	9	1	3	3

In Fig. 1 the X-ray diffraction pattern of the new phase of $[Co(NH_3)_6]I_3$ is shown. This was interpreted on the basis of the character of the splits [11] and Chojnacki's [12] method for deducing the $h\,k\,l$ indices. As a result, it was found that the phase below about 273 K crystallizes in the monoclinic lattice with the parameters: $a = 10.83(6)$ Å, $b = 11.02(4)$ Å, $c = 10.74(8)$ Å, $\beta = 90.5(6)°$. These parameters were calculated by the LSQ method using 17 reflections which are listed in Table I.

4. Conclusions

Summing up it can be said that $[Co(NH_3)_6]I_3$, analogically to bivalent metal complexes, exists in two crystallographic modifications, that is, a cubic high-temperature phase and monoclinic low-temperature phase. The phase transition is reversible and shows temperature hysteresis.

Examination of the reflection indices suggests the space group $P2_1/n$ ($P2_1/c$ in a conventional system). The calorimetric studies [7] showed the presence of two anomalies in the specific heat vs. temperature curve. In our X-ray investigations only one polymorphic transition was observed. This suggests that one of the above anomalies is connected with the λ transition.

The intensive movements of the molecular groups of hexamino-complexes at room temperature are well known in the literature. The complex cation $[Co(NH_3)_6]^{3+}$ makes, on the whole, a tumbling movement [13], and NH_3 groups vibrate independently in a torsional mode [14] and rotate around a threefold axis [15]. In bivalent hexammino-complexes according to Bates [16], as the phase transition point changes only the mode of rotation of the NH_3 groups, at temperatures higher than transition, rotate independently and in lower temperatures in a correlated way. Another hypothesis put forward is that the change in the rotation mode of the NH_3 groups is connected with the preceding changes in the structure at the transition point [17]. It is not known if the hypothesis mentioned above could be applied to trivalent complexes. In order to clarify the dynamics of these compounds a study of the series of complexes having different molecular groups is necessary. This study is undertaken in order to verify our hypothesis drawn on the basis of crystallographic speculations. According to this the change in temperature imposes some restriction on the rotation of molecular groups and the anion quickly forms the hydrogen bonds leading to the deformation of the octahedral cation complex.

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