Some Structural Aspects of $Co(NH_3)_6Cl_3$

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Powder X-ray spectra obtained from samples of $Co(NH_3)_6Cl_3$ supplied by different manufacturers are reported and compared with the calculated spectrum for the known crystal structure. These results and the information obtained from single-crystal X-ray studies reveal the existence of polymorphism in $Co(NH_3)_6Cl_3$.

Introduction

Nuclear magnetic resonance results obtained in studies of single crystals and powders of $Co(NH_3)_6Cl_3$ cannot be explained satisfactorily in terms of a unique crystal structure. Murray and Waugh (*1*) interpreted the unusually broad proton linewidth transition in a powdered sample in terms of a monoclinic unit cell which contains three cobalt atoms in two different crystallographic positions. The observations of a deuteron quadrupole investigation of a single crystal of $Co(ND_3)_6Cl_3$ by Ito and Chiba (*2*) are in some respects in agreement with the crystallographic results of Gimenez Huguet (*3*). The space group is $P2_1/m$ and the unit cell contains 12 molecules with cobalt atoms at four- and twofold positions of relative abundance $2:1$. The orientations of the $Co(NH_3)_6^{3+}$ octahedra relative to the crystal axes are, however, in disagreement with the results of Ito and Chiba (*2*). In a more recent single-crystal X-ray investigation by Kruger and Reynhardt (*4*) a similar unit cell was identified with space group $C2/m$, $a = 12.46$, $b = 21.3$, $c = 12.74$ Å, and $\beta =$ 122.96°. The cobalt positions are in agreement with those reported by Gimenez Huguet (*3*), but the orientations of the octahedra differ completely. This structure is in complete agreement with the results of ^2H and ^{59}Co single-crystal investigations (*2, 5*). A recent proton second moment study (*6*) of powdered $Co(NH_3)_6Cl_3$ revealed differences of up to 20% between the measured ^1H second moments and those reported by Murray and Waugh (*1*) at certain temperatures. These discrepancies could only be explained satisfactorily if it was assumed that the sample consisted of a mixture of different polytypes of $Co(NH_3)_6Cl_3$.

In this paper X-ray powder diffraction patterns for various samples of $Co(NH_3)_6Cl_3$ are reported. The calculated powder spectrum for the structure reported by Kruger and Reynhardt (*4*) is compared with the observed spectra.

Experimental

Powdered $Co(NH_3)_6Cl_3$ was supplied by Alfa Inorganics (sample 1). From this powder a saturated aqueous solution was pre-

pared and allowed to crystallize at room temperature. Cylindrical and disk-shaped crystals were obtained from the solution. Part of a big disk-shaped crystal, used in previous studies (5), was ground to a fine powder (sample 2). Sample 3 was supplied in powder form by BDH.

Diffraction patterns were obtained at 295 K with $CuK\alpha$ radiation. A Seifert MZIV diffractometer with scintillation counter and automatic registration of the diffraction patterns was used. 2θ was varied at a rate of 0.8°/min and the recorder speed was 3 cm/min. The parameters of the primary beam were 35 mA and 40 kV. Slits of 0.02 mm were used. All diffraction patterns were obtained under identical experimental conditions.

Results and Discussion

The observed diffraction peaks for the range $7° \leq 2\theta \leq 36°$ are listed in Table I. The calculated peaks for the structure reported by Kruger and Reynhardt (4) are also included in the same table. A striking feature of the powder spectra is the absence of the strong 020 peak observed in the single-crystal study. Closer investigation of the spectra reveals that some medium-intensity peaks, such as $\bar{1}11$, 040, and $\bar{3}13$, are also absent. In fact, with the exception of one reflection, only reflections with $k = 3n$, $n = 0, 1, 2, \ldots$, are observable above the background on the spectra for samples 1 to 3. It seems, therefore, likely that the powdered samples contain a polytype of the unit cell reported by Kruger and Reynhardt (4) with the b cell dimension $\frac{1}{3}$ the length, i.e., 7.1 Å.

Polytypism (7) has been observed and studied extensively in another octahedral cobalt complex, viz., $K_3Co(CN)_6$ (8). The 3M and 7M polytypes are formed by rotating the 1M cell about c and stacking the cells along [100]. The 40r polytype (9) is formed by stacking 1M cells along [100] and

shifting the center cells by $c/2$ along the [001] direction.

Polytypism is indeed a likely explanation for the observations reported in this paper. Cobalt and chlorine atoms form layers in planes perpendicular to the [010] direction, approximately 3.6 Å $(=b/6)$ apart (4). Each layer has two cobalt atoms at either $\frac{1}{2},0,0$ and $0,0,\frac{1}{2}$ or $0,0,0$ and $\frac{1}{2},0,\frac{1}{2}$. The most prominent differences among the six layers are observed in the orientations of the $Co(NH_3)_6^{3+}$ octahedra relative to the crystal axes. In the cell described by Kruger and Reynhardt (4) the only slightly distorted $Co(NH_3)_6^{3+}$ octahedra are chemically similar and, if small differences are ignored, there are three different orientations of the octahedra relative to the crystal axes. In orientation A four nitrogen atoms are in a plane parallel to (001) and two nitrogen atoms are above and below this plane such that two Co–N bonds are perpendicular to the (001) plane. Orientation B has four nitrogen atoms in a plane parallel to (010) and two Co–N bonds perpendicular to this plane. In orientation C four nitrogen atoms are in a plane parallel to (101) with two Co–N bonds perpendicular to this plane. C octahedra are surrounded by regular polyhedra of 14 chlorine atoms. Each Co–N bond points at a vertex of the polyhedron, i.e., directly at a chlorine atom. A and B octahedra are also surrounded by a cage of 14 chlorines, but in contrast to the regular polyhedron surrounding a C octahedron these polyhedra are severely distorted. These $Co(NH_3)_6^{3+}$ octahedra are oriented in such a way that two Co–N bonds point directly at vertices while four Co–N bonds point at the faces of the polyhedron. The distribution of these orientations among the six layers is shown in Table II. The octahedra in the two top layers (layers 5 and 6) are identically oriented (orientation C). Layer 4 contains one type A and one type B octahedra. The contents of layers 2 and 3 are the same as that of layers 3, 5, and 6, while

TABLE I

OBSERVED INTENSITIES (ARBITRARY UNITS) AND 2θ ANGLES (DEGREES) FOR THE DIFFERENT $Co(NH_3)_6Cl_3$ SAMPLES. THE CALCULATED SPECTRUM IS ALSO LISTED[a]

Calculated powder pattern					Sample 1		Sample 2		Sample 3	
2θ	h	k	l	I	$2\theta_{obs}$	I	$2\theta_{obs}$	I	$2\theta_{obs}$	I
8.29	0	2	0	50						
9.38	$\bar{1}$	1	1	12						
13.38	1	1	1	4						
14.66	$\bar{1}$	3	0	3						
15.09	0	0	2	100	15.10	66	15.12	100	15.10	100
15.43	2	0	0	38	15.47	11	15.42	41	15.45	7
16.63	0	4	0	13						
16.87	$\bar{2}$	0	2	23	16.86	10	16.86	10	16.90	8
17.24	0	2	2	5						
17.55	$\bar{2}$	2	0	5						
17.83	1	3	1	41	17.86	7	17.84	22	17.86	11
21.39	2	2	1	3						
21.83	$\bar{3}$	1	1	3						
21.94	$\bar{2}$	0	3							
22.53	0	4	2	4						
22.63	$\bar{3}$	1	2							
22.77	$\bar{2}$	4	0	4						
24.43	$\bar{1}$	3	3	51						
24.48	1	5	1		24.46	31	24.45	49	24.48	41
24.86	3	3	1	59	24.86	36	24.89	51	24.90	40
25.06	0	6	0	38	25.08	100	25.08	30	25.10	58
25.59	2	0	2	31	25.57	13	25.52	36	25.62	34
25.77	$\bar{3}$	1	3	11						
26.94	2	2	2	3						
28.29	0	4	3	7						
28.40	$\bar{3}$	3	3	15	28.37	3	28.40	2		
					28.61	17				
28.80	$\bar{4}$	0	2	5						
29.48	$\bar{2}$	2	4	9						
29.63	1	3	3	12						
30.02	$\bar{4}$	2	2	7						
30.06	$\bar{3}$	5	1							
30.60	$\bar{4}$	0	3	4	30.56	5			30.62	6
33.09	$\bar{3}$	5	3	3						
33.63	0	8	0	3						
34.12	$\bar{4}$	0	4	12	34.16	16	34.16	10	34.13	13
34.17	1	5	3							
36.18	2	6	2	24	36.21	12	36.29	17	36.20	19

[a] Data drawn from Ref. (4).

layer 1 is similar to layer 4. It is clear that the cell with $b = 21.3$ Å can be constructed as illustrated in Fig. 1. It consists of four CC subcells (two octahedra with C orientations in each subcell) and two AB subcells. Subcells 3 (CC), 4 (AB), and 5 (CC) are shifted by $a/2$ with respect to subcells 1 (AB), 2(CC), and 6(CC).

Several of the cylindrical and disk-shaped crystals were investigated by means

TABLE II

COBALT FRACTIONAL COORDINATES AND
ORIENTATIONS OF OCTAHEDRA SURROUNDING
COBALT ATOMS IN THE SIX LAYERS OF THE CELL
WITH $b = 21.3 \text{ Å}$ (4)

Layer	Cobalt coordinates[a]			Orientation of octahedron
1	0.5	0	0	A
	0	0	0.5	B
2	0	0	0	C
	0.5	0	0.5	C
3	0.5	0	0	C
	0	0	0.5	C
4	0	0	0	A
	0.5	0	0.5	B
5	0.5	0	0	C
	0	0	0.5	C
6	0	0	0	C
	0.5	0	0.5	C

[a] $b = 3.6 \text{ Å}$.

FIGURE 1

of Weissenberg and precession methods. The structure described by Kruger and Reynhardt (4) or a polytype related to that structure was not revealed by any of the photographs. All cylindrical crystals have an orthorhombic structure with the cell dimensions listed in Table III. All disk-shaped crystals are monoclinic but the cell dimensions of this monoclinic cell (see Table III) are not the same as the cell dimensions of the monoclinc unit cell reported by Kruger and Reynhardt (4). Since the volumes of these unit cells are about the same (3088 ± 25 Å³), each cell contains 12 formula units. It is therefore concluded that Co(NH₃)₆Cl₃ exhibits polymorphism.
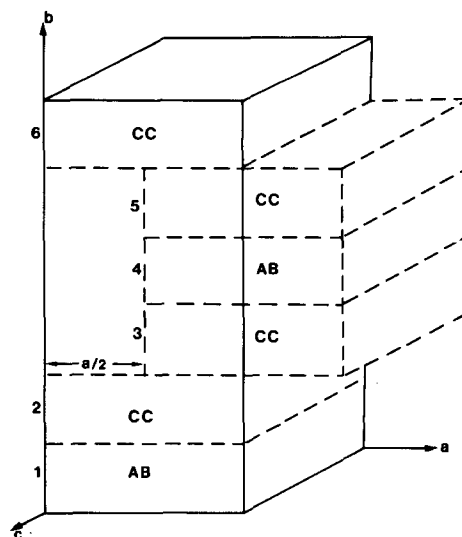
The fact that the intensities of peaks at the same 2θ values on the powder spectra differ by as much as factor of 3 (see Table I) shows that samples 1, 2, and 3 are not structurally identical. Sample 2, grown from a disk-shaped seed crystal, has a monoclinic ($\beta = 93°$) structure. Samples 1 and 3, supplied in powder form by Alfa Inorganics and BDH, respectively, most probably consist of mixtures of the polymorphic structures.

The fact that the powder spectrum of the monoclinic ($\beta = 93°$) single crystal (sample 2) is similar to the powder spectra of the samples in which more than one structure are present suggests that the powder spectra of the different polymorphic structures are very similar. An attempt was made to

TABLE III

CELL PARAMETERS OF THE DIFFERENT UNIT CELLS OF Co(NH₃)₆Cl₃ CRYSTALS

Crystal class	Shape	a (Å)	b (Å)	c (Å)	γ (°)	Volume (Å³)
Monoclinic	Cylinder	12.46	21.3	12.74	112.96	3113
Monoclinic	Disk	23.4	12.4	10.6	93	3071
Orthorhombic	Cylinder	21.1	10.5	13.9	90	3080

TABLE IV

Observed 2θ Values and Calculated 2θ Values
for the Monoclinic and Orthorhombic
Structures (All Angles Are in Degrees)

	Monoclinic ($\beta = 98°$)		Orthorhombic	
$2\theta_{obs}$	$2\theta_{calc}$	hkl	$2\theta_{calc}$	hkl
15.10	15.13	400	15.16	310
15.47	15.46	$\bar{3}11$		
16.86	16.89	$\bar{4}01$	16.81	400
17.86	17.93	$\bar{2}02$	17.91	302
24.46	24.40	$\bar{5}02$	24.47	313
24.86	24.90	$\bar{5}21$	24.77	421
25.08	25.09	003		
25.57	25.57	103	25.54	403
28.37	28.37	701	28.42	602
28.61	28.63	621	28.59	304
30.60	30.54	800	30.60	620
34.16	34.17	$\bar{3}04$	34.17	040
36.21	36.21	304	36.21	630

index the experimentally observed 2θ values in terms of the orthorhombic and monoclinic ($\beta = 93°$) structures. The results are shown in Table IV. All the observed 2θ values could be indexed successfully in terms of the monoclinic unit cell. Two 2θ values are not in agreement with the calculated 2θ values of the orthorhombic unit cell. Since our samples were either mixtures of both structures (samples 1 and 3) or only of the monoclinic structure (sample 2) this result is not necessarily in contradiction with the single-crystal results which revealed the orthorhombic structure. The differences in observed intensities indicate that the samples contain different ratios of the polymorphic structures. The structure described by Kruger and Reynhardt (4) is either not present in the commercially supplied samples or the fraction of crystals with that structure is too small to be detected.

A continuation of this investigation is being undertaken in which the complex is recrystallized under various conditions. The complete crystal and molecular structures of the polymorphic forms will also be investigated. The influence of polymorphism on the NMR results will be published soon in a separate paper.

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