

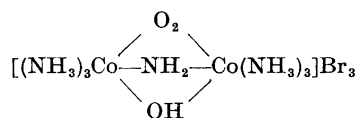
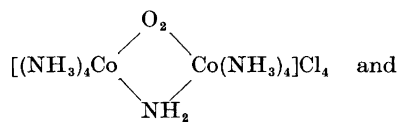
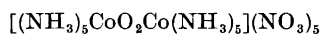
The Crystal Structure of $[(\text{NH}_3)_5\text{CoNH}_2\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$

NILS-GÖSTA VANNERBERG

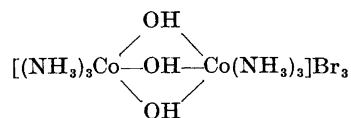
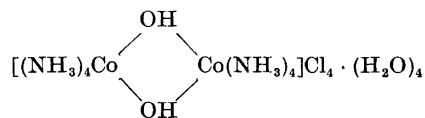
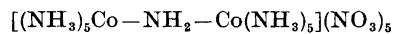
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The crystal structure of $[(\text{NH}_3)_5\text{CoNH}_2\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$ has been determined with X-ray methods. It is nearly isomorphous with $[(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$. The space group is $P4_2nm$ (No. 102) $a = b = 11.68 \text{ \AA}$, $c = 8.28 \text{ \AA}$.

Cobalt forms two series, where, in each, dinuclear complexes are joined by one, two, or three bridging atoms. The first series contains dark green paramagnetic compounds, for instance



The second series consists of red diamagnetic compounds, for instance

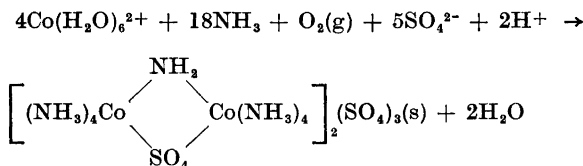


The crystal structure of the first of the paramagnetic compounds has been determined at this institute some time ago. The present investigation was started to determine the crystal structure of the first of the diamagnetic compounds above.

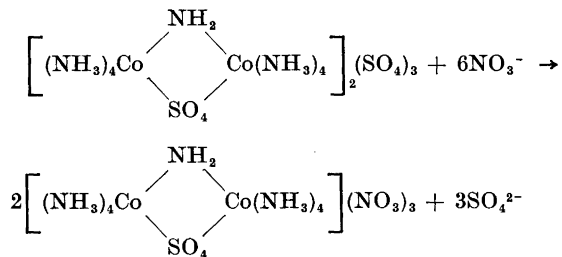
Decammine- μ -amido dicobalt(III) pentanitrate $[(\text{NH}_3)_5\text{CoNH}_2\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$ has been prepared by Werner¹ in 1907. He described the compound as consisting of violet needle-like crystals, which were fairly soluble in neutral water solution. Werner's preparation method was used in this investigation¹⁻⁵.

EXPERIMENTAL

Commercial $[\text{Co}(\text{H}_2\text{O}_6)](\text{NO}_3)_2$ was recrystallized and dissolved in concentrated ammonia. A stream of air was blown through the solution for 8 h at 32°C. The product formed was allowed to stand for a day at this temperature. The reaction mixture was then neutralized with 3 M sulphuric acid under cooling. The temperature was not allowed to exceed 10°C. At the end of the neutralization oxygen was evolved and the colour changed from green to red. From the neutral solution reddish-brown crystals separated.

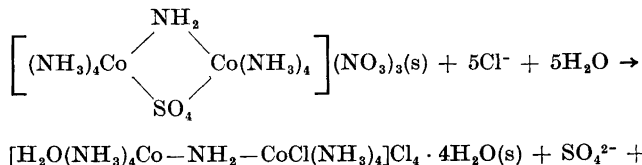


The sulphate, called Vortmann's sulphate, was treated with concentrated nitric acid until the octa-ammonia- μ -amido sulphate dicobalt(III) trinitrate was formed.



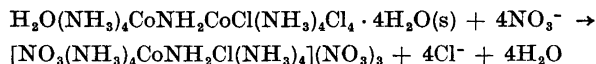
This salt was then converted into

6-monoaqua-2,3,4,5-tetrammine-2',3',4',5'-tetrammine-6'-monochloro- μ -amido cobalt(III) tetrachloride tetrahydrate, by treating first with concentrated nitric acid, then with water and finally with ice cold hydrogen chloride.

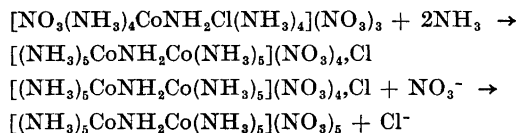


The last mentioned salt was treated with diluted nitric acid and

6-mono nitrate-2,3,4,5-tetrammine-2',3',4',5'-tetrammine-6-monochloro- μ -amido dicobalt(III) trinitrate was obtained.



This salt was finally dissolved in liquid ammonia which was then evaporated to dryness. The reaction product was then treated with boiling water until most of it was dissolved. The rest was filtered off and crystallized from boiling diluted acetic acid solution. The rest of the chloride ions in the salt was removed by repeated crystallizations from diluted nitric acid solutions.



The final product consisted of very thin blueish-red needleshaped crystals.

THE DETERMINATION OF THE CRYSTAL STRUCTURE

Some crystals were mounted in a Weissenberg camera with the needle axis parallel to the rotation axis. The elementary cell dimensions were determined from the rotation and Weissenberg photographs. All zones detectable with $\text{FeK}\alpha$ radiation were registered. As the crystals were very thin, the Weissenberg exposure had to be extended over a week. Even then only reflexions with $\xi < 1.2$ were registered. There are enough reflexions to determine the structure completely but the calculated atomic parameters could be more accurate.

The elementary cell had tetragonal symmetry

$$\begin{aligned} a &= 11.68 \pm 0.03 \text{ \AA} \\ c &= 8.28 \pm 0.02 \text{ \AA} \end{aligned}$$

There are two formula units in the elementary cell. Only reflexions of type $0kl$, where $k + l = 2n$, are present. Thus possible space groups are $P4_2mn$, $C4mn$ and $P4/mmn$. The first one was finally proved to be the correct one.

The Patterson projection of the structure of $[(\text{NH}_3)_5\text{CoNH}_2\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$ on (001) was almost identical with the corresponding projection for $[(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$. In fact these two structures were solved at the same time and the mentioned circumstance facilitated the work considerably.

The cobalt atom x, y -parameters, as well as those of all the ammonia molecules and of course also of the amide group could be found from the Patterson synthesis. This was enough to calculate the signs of most structure factors of type $hk0$. A Fourier projection then revealed the positions of most atoms. As in the peroxide structure, four of the ten nitrate groups were found to rotate about the positions $0 \frac{1}{2} 0$. When all the x - and y -parameters were known, the relative positions in space of all atoms could be approximately calculated, as most of the bond lengths and packing distances are known. The z -parameter of the cobalt atoms was arbitrarily chosen to be zero. Then a

Table 1. Observed and calculated structure factors for $[(\text{NH}_3)_5\text{CoNH}_2\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$.

hkl	F_o	$ F_c $	α	hkl	F_o	$ F_c $	α
020	—	1	180	351	—	4	57
040	14	13	0	441	—	6	6
060	—	5	0	451	11	12	341
110	14	13	0				
120	19	18	180	022	7	10	270
130	15	23	180	042	9	9	162
140	5	5	180	112	—	7	290
150	—	1	0	122	12	16	201
160	8	10	0	132	—	11	180
220	25	30	0	142	12	8	349
230	11	8	180	222	26	26	3
240	8	3	0	232	11	9	176
250	6	12	0	242	—	3	50
260	—	5	0	332	21	16	23
330	11	14	0	342	—	3	229
340	17	12	0	442	20	19	5
350	—	4	180				
360	14	10	0	013	—	3	118
440	26	26	0	033	—	4	227
450	7	1	0	053	23	22	182
460	—	3	0	073	16	16	337
550	16	16	0	113	5	4	222
560	8	8	180	123	10	8	359
011	17	18	353	133	—	8	142
031	24	23	188	143	15	14	187
051	—	8	255	153	11	13	360
111	6	7	274	163	—	4	248
121	9	12	203	223	9	14	174
131	22	22	176	233	—	1	39
141	10	10	182	243	—	3	72
151	—	6	328	253	—	6	315
221	17	19	177	263	15	12	39
231	9	5	134	333	15	10	173
241	12	8	161	343	10	13	347
251	9	5	219	353	—	6	41
331	9	7	109	443	10	3	145
341	—	5	5				

set of z -parameters and the phase angles of all reflexions were calculated. The final atomic parameters were determined from a three-dimensional Fourier synthesis; see Table 2. A comparison between observed and calculated structure factors can be found in Table 1. The unreliability index, $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, was calculated to be 0.19.

DISCUSSION OF THE STRUCTURE

The atomic parameters can be found in Table 2. The structure consists of a dinuclear complex cation $[(\text{NH}_3)_5\text{CoNH}_2\text{Co}(\text{NH}_3)_5]^{5+}$ and nitrate ions. The structure of the former ion can be seen in Fig. 1. The whole ion can be regarded as an ammonium ion, where two of the hydrogen atoms have been substituted by complex cobalt groups, $\text{Co}(\text{NH}_3)_5$. Thus the angle between the amide-cobalt

Table 2. Parameter values for $[(\text{NH}_3)_5\text{CoNH}_2\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$; space group $P4_2nm$, No. 102.

Atom	Position	Number	x	y	z
Co	c	4	0.127	0.127	0.000
NH ₃	d	8	0.241	0.064	0.167
NH ₃	d	8	0.185	0.008	0.833
NH ₃	c	4	0.217	0.217	0.900
NH ₂	a	2	0.500	0.500	0.583
N	a	2	0.500	0.500	0.988
N	b	4	0.500	0.000	0.000
N	c	4	0.265	0.265	0.500
O	a	2	0.500	0.500	0.138
O	c	4	0.438	0.438	0.913
O	c	4	0.192	0.192	0.500
O	c	4	0.297	0.297	0.364
O	c	4	0.297	0.297	0.636
O	b	4	rotating $r = 1.2 \text{ \AA}$		
O	b	4			
O	b	4			

bonds should be 109° , the tetrahedron angle. Actually it is much greater, 144° . This is caused by the repulsion between the large complex groups. The closest distance between the two cobalt complex groups can be expected when the ammonia molecules from the two groups are in contact with each other, *i.e.* when the distance between these molecules is about 3 \AA . This has actually happened. The distance between a pair of ammonia molecules in one cobalt complex group and the corresponding pair in the other group is 3.2 \AA . The contact between these ammonia molecules has caused distortion of the bond angles in the cobalt complex groups (Fig. 1).

The bond lengths and the bond angles in the nitrate groups have all values close to the expected ones. Four of the ten nitrate groups have been found to rotate freely about the positions $b \ 0 \ \frac{1}{2} \ 0$. This is required by the symmetry of the space group.

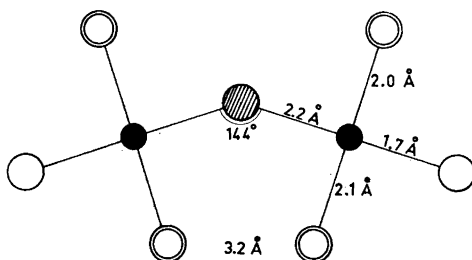


Fig. 1. Projection of the ion $[(\text{NH}_3)_5\text{CoNH}_2\text{Co}(\text{NH}_3)_5]^{5+}$ on the (100) plane. Shaded, NH₂; white, NH₃; black, Co;

Table 3. Bond distances in $[(\text{NH}_3)_6\text{CoNH}_2\text{Co}(\text{NH}_3)_5](\text{NO}_3)_6$.

	Å
Co —NH ₃	2.2
Co —NH ₃ '	2.0
Co —NH ₃ ''	2.1
Co —NH ₃ '''	1.7
N' —O'	1.2
N' —O''	1.2
N'' —O'''	1.2
N'' —O''''	1.2
N —O (rotating)	1.2
NH ₃ '' —NH ₃ ''' packing dist.	3.2

Table 4. Angles between bonds in $[(\text{NH}_3)_6\text{CoNH}_2\text{Co}(\text{NH}_3)_5](\text{NO}_3)_6$.

Co —NH ₃ —Co	144°
NH ₃ ' —Co —NH ₃ '	91°
NH ₃ '' —Co —NH ₃ ''	90°
NH ₃ ' —Co —NH ₃ ''	90°
NH ₃ ''' —Co —NH ₃ '	95°
NH ₃ ''' —Co —NH ₃ '	84°
NH ₃ —Co —NH ₃ '	89°
NH ₃ —Co —NH ₃ ''	89°

It is of some value to consider the overall coordination of anions around the large cation. Each cation is surrounded by twelve nitrate ions in the following way: In a plane perpendicular to the cobalt-cobalt axis, *i.e.* for instance the $(\bar{1}10)$ plane, there are four nitrate groups which approach the cation very closely. The distances between the gravity centers of the cation and the nitrate ion are 4.04, 3.88, 3.88, and 4.24. The four nitrate groups form a regular rhomb. In the (001) plane there are four rotating nitrate groups at a distance of 5.84 Å from the cation. Further, in the (110) plane there are four more nitrate groups at the distance of 6.0 Å.

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