

X-Ray Crystallographic Study and Thermogravimetric Analysis of Tetrammine-Carbonatocobalt(III) Nitrate Hemihydrate, $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$

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The crystal structure of tetrammine-carbonatocobalt(III) nitrate hemihydrate, $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$, was solved by direct methods from single crystal X-ray diffraction data. The size of the single crystal used was $0.075 \times 0.075 \times 0.007 \text{ mm}^3$. The structure is monoclinic, space group $P2_1/n$ (No. 14), with the lattice parameters $a = 7.4519(4)$, $b = 22.647(1)$, $c = 10.4103(5) \text{ \AA}$, $\beta = 92.052(1)^\circ$ and $Z = 8$. The structure has two independent $\text{Co}(\text{NH}_3)_4\text{CO}_3$ coordination octahedra. The Co–N bonds are in the range $1.944(6)$ – $1.976(5) \text{ \AA}$ and the Co–O bonds in the range $1.903(4)$ – $1.918(5) \text{ \AA}$. Indexing of the X-ray powder pattern gave the lattice parameters $a = 7.482(4)$, $b = 22.667(6)$, $c = 10.540(4) \text{ \AA}$, $\beta = 91.37(4)^\circ$, using $\lambda = 1.5406 \text{ \AA}$. Thermogravimetric analysis of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$ show a complete decomposition to Co_3O_4 at 430°C .

In 1892 the synthesis of a series of tetrammine-carbonatocobalt(III) salts was reported by Jørgensen.¹ The crystal morphology of some of the salts was later described,² and single crystal X-ray analyses have been made on $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Br}$,^{3,4} $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{I} \cdot \text{H}_2\text{O}$ ⁵ and on $[\text{Co}(\text{NH}_3)_4\text{CO}_3]_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$.⁶ The carbonate ion is a monodentate ligand in the iodine salt⁵ but a bidentate ligand in the two other salts.^{3,4,6} The present investigation was made to clarify the coordination of the cation in tetrammine-carbonatocobalt(III) nitrate hemihydrate.

Experimental

The tetrammine-carbonatocobalt(III) nitrate hemihydrate was prepared as described by Jørgensen¹ with the chemicals CoCO_3 (Baker), HNO_3 (Merck) and NH_3 (Merck). Jørgensen¹ reported a composition corresponding to the formula $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$. The single crystal X-ray analysis confirms this composition.

Results of a thermogravimetric analysis are displayed in Fig. 1. A Stanton Redcroft TG-DTA simultaneous thermal analyzer STA 1000/1500 was used with a heating rate of 5°C min^{-1} and Ar gas flow on the sample. The weight loss of 3.3% at 125°C corresponds to the loss of a half water molecule per formula unit, calculated loss 3.5%. The final weight loss of 68.3% at 430°C corre-

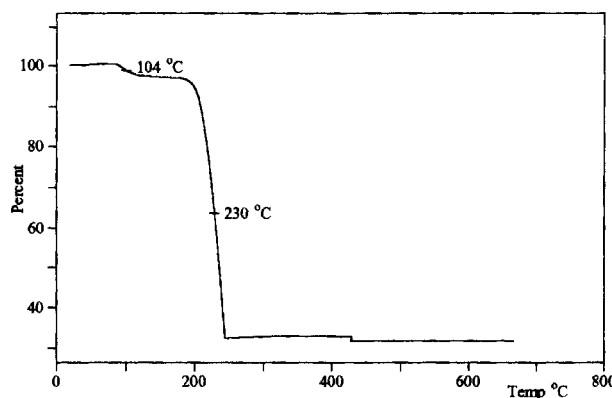


Fig. 1. Thermogravimetric diagram of the decompositions in the temperature range 25 – 670°C of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$ to Co_3O_4 .

sponds to the formation of Co_3O_4 , calculated loss 68.8%. The formation of Co_3O_4 was confirmed by an X-ray powder pattern taken of the sample used in the TG-DTA investigation. A Stoe Stadi diffractometer using $\text{Cu K}\alpha_1$ radiation and a position-sensitive detector was used to record the powder pattern of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$. A Ni foil was placed in front of the detector to reduce the fluorescence from the sample. A Philips reflection diffractometer using $\text{Cu K}\alpha_1$ radiation and an analyzer crystal was also used to record the X-ray powder pattern. An external standard of silicon ($a_{\text{Si}} = 5.43050 \text{ \AA}$)

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Table 1. X-Ray powder pattern measured on a Philips reflection diffractometer of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$: $a = 7.482(4)$, $b = 22.667(6)$, $c = 10.540(4)$ Å, $\beta = 91.37(4)^\circ$.

$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	d_{obs}	d_{calc}	I_{obs}	h	k	l
7.78	7.79	11.35	11.33	10	0	2	0 ^a
14.20	14.18	6.232	6.243	18	1	2	0
14.87	14.87	5.953	5.953	4	-1	1	1
15.21	15.19	5.820	5.829	12	1	1	1
15.64	15.63	5.661	5.667	3	0	4	0
16.34	16.35	5.420	5.419	2	-1	2	1
16.85	16.82	5.257	5.268	19	0	0	2
18.58	18.55	4.772	4.779	100	-1	3	1
18.82	18.81	4.711	4.714	9	1	3	1
19.66	19.64	4.512	4.517	38	1	4	0
20.76	20.75	4.275	4.278	3	-1	1	2
21.25	21.27	4.178	4.173	8	1	1	2
21.85	21.84	4.064	4.067	22	-1	2	2
22.27	22.28	3.989	3.987	9	1	2	2
23.04	23.03	3.857	3.858	36	0	4	2
23.53	23.53	3.778	3.778	67	0	6	0
25.03	25.05	3.555	3.551	5	2	2	0
25.32	25.37	3.515	3.509	24	-2	1	1
25.73	25.75	3.460	3.457	27	2	1	1
26.43	26.41	3.370	3.372	5	1	6	0
27.72	27.73	3.216	3.214	6	-2	3	1
28.08	28.06	3.175	3.177	8	-1	1	3
28.61	28.58	3.118	3.120	30	1	1	3
28.95	28.92	3.082	3.085	17	-2	0	2
29.42	29.40	3.034	3.035	10	1	2	3
29.87	29.87	2.989	2.989	6	2	1	2
30.63	30.65	2.916	2.914	5	2	2	2
31.30	31.33	2.856	2.853	7	1	7	1
31.54	31.55	2.834	2.833	5	0	8	0
31.91	31.93	2.802	2.801	10	2	3	2
32.49	32.49	2.754	2.753	4	1	4	3
33.03	33.04	2.710	2.709	2	-2	4	2
33.80	33.80	2.650	2.650	10	1	8	0
33.99	34.01	2.635	2.634	10	0	0	4
34.82	34.82	2.574	2.575	6	-2	1	3
36.06	36.07	2.489	2.488	6	-1	1	4
36.76	36.74	2.443	2.445	22	1	1	4
37.17	37.23	2.417	2.413	7	3	0	1
37.63	37.63	2.388	2.389	7	0	4	4
38.58	38.58	2.332	2.332	8	-1	9	1
39.71	39.73	2.268	2.267	64	0	10	0

^aThe observed data for the 020 reflection is from the pattern measured on the Stoe Stadi diffractometer.

was used to calibrate the diffractometers. The Philips pattern is listed in Table 1.

Using a polarising microscope a single crystal of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$ was selected and mounted on a glass fiber. The single crystal diffraction data were measured on a Siemens SMART diffractometer with an area detector, using $\text{Mo K}\alpha$ radiation ($\lambda = 0.7107$ Å). The crystallographic data are listed in Table 2. The model of the structure was solved with the program SIR⁷ and refined with the least-squares program LINUS⁸ with scattering contributions from neutral atoms⁹ and corrections for anomalous scattering contributions for the cobalt atom.¹⁰ No absorption corrections were made.

Table 2. Experimental data and unit cell parameters for the single crystal of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$.

$a/\text{Å}$	7.4519(4)
$b/\text{Å}$	22.647(1)
$c/\text{Å}$	10.4103(5)
$\beta/^\circ$	92.052(1)
Cell volume/Å ³	1756
Space group	$P2_1/n$
Z	8
Density(calc)/g cm ⁻³	1.95
Size of crystal/mm	$0.075 \times 0.075 \times 0.007$
Linear absorption coefficient μ/cm^{-1}	20.5
No. of measured reflections	4935
No. of independent reflections with $I > 3\sigma(I)$	3213
$R(F)$ (%)	7.5
T/K	298

Results and discussion

The direct method program gave the positions of all the atoms except the hydrogen atoms, the positions of which were calculated from the known geometries of ammonia and water molecules and hydrogen bond considerations. The hydrogen atom positions were confirmed by Fourier maps. A final difference Fourier map did not show any additional electron density. The hydrogen atom positions were not refined and are for this reason omitted in the list of coordinates.

Atomic coordinates and thermal displacement parameters are listed in Table 3 and some interatomic dis-

Table 3. Atomic coordinates and equivalent thermal displacement parameters for $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$.

Atom	x/a	y/b	z/c	U_{eq}
Co1	0.41530(11)	0.09893(4)	0.74190(8)	0.0157(5)
N1	0.1597(6)	0.0976(3)	0.6865(5)	0.020(3)
N2	0.4085(8)	0.1853(3)	0.7488(6)	0.024(4)
N3	0.6677(6)	0.1005(3)	0.8048(5)	0.019(3)
N4	0.4906(6)	0.0983(3)	0.5640(5)	0.022(3)
O1	0.3437(5)	0.0828(2)	0.9120(4)	0.018(3)
O2	0.4092(6)	0.0156(2)	0.7726(4)	0.019(3)
O3	0.3013(6)	-0.0136(2)	0.9647(4)	0.026(3)
C1	0.3500(8)	0.0259(3)	0.8886(6)	0.018(4)
Co2	0.91312(10)	-0.09112(4)	0.76400(8)	0.0152(5)
N5	0.6575(7)	-0.0944(3)	0.8074(5)	0.019(3)
N6	0.9236(7)	-0.1769(2)	0.7593(5)	0.021(3)
N7	1.1646(7)	-0.0889(3)	0.7100(5)	0.020(3)
N8	0.9927(7)	-0.0902(3)	0.9445(5)	0.022(4)
O4	0.8982(6)	-0.0076(2)	0.7347(4)	0.018(3)
O5	0.8352(5)	-0.0745(2)	0.5909(4)	0.020(3)
O6	0.7984(6)	0.0220(2)	0.5364(5)	0.028(3)
C2	0.8409(8)	-0.0176(3)	0.6143(6)	0.021(4)
N9	0.3788(7)	0.2739(3)	1.0717(5)	0.026(4)
O7	0.5061(7)	0.3011(2)	1.0233(5)	0.036(4)
O8	0.2535(7)	0.3020(3)	1.1232(5)	0.040(4)
O9	0.3738(7)	0.2183(2)	1.0698(6)	0.041(4)
N10	0.0302(7)	0.2610(3)	0.8645(6)	0.029(4)
O10	0.1455(9)	0.2940(3)	0.8166(6)	0.053(5)
O11	-0.0991(7)	0.2846(3)	0.9192(6)	0.044(4)
O12	-0.0436(7)	0.2064(3)	0.8593(6)	0.045(5)
O13	-0.2614(7)	0.1844(2)	1.0342(5)	0.038(4)

tances are in Table 4. Figure 2 shows the two $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ coordination polyhedra with displacement ellipsoids of the atoms. Figure 3 is a projection of the structure along $[100]$ with the c -axis across the page.

Table 4. Bond length in the two coordination polyhedra and in the nitrate groups, calculated from the single crystal data.

Co1-O1	1.903(4)	Co2-O5	1.911(4)
Co1-O2	1.914(5)	Co2-O4	1.918(5)
Co1-N4	1.955(5)	Co2-N6	1.944(6)
Co1-N2	1.958(6)	Co2-N8	1.950(5)
Co1-N3	1.969(5)	Co2-N5	1.975(5)
Co1-N1	1.970(5)	Co2-N7	1.976(5)
C1-O1	1.313(9)	C2-O4	1.329(8)
C1-O2	1.320(7)	C2-O5	1.312(9)
C1-O3	1.257(8)	C2-O6	1.243(8)
N10-O7	1.251(7)	N9-O10	1.255(8)
N10-O8	1.266(7)	N9-O11	1.256(8)
N10-O9	1.261(8)	N9-O12	1.243(8)

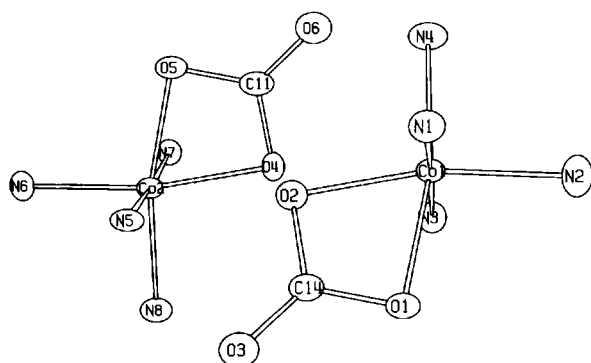


Fig. 2. Coordination arrangement with thermal ellipsoids of the two $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ ions.

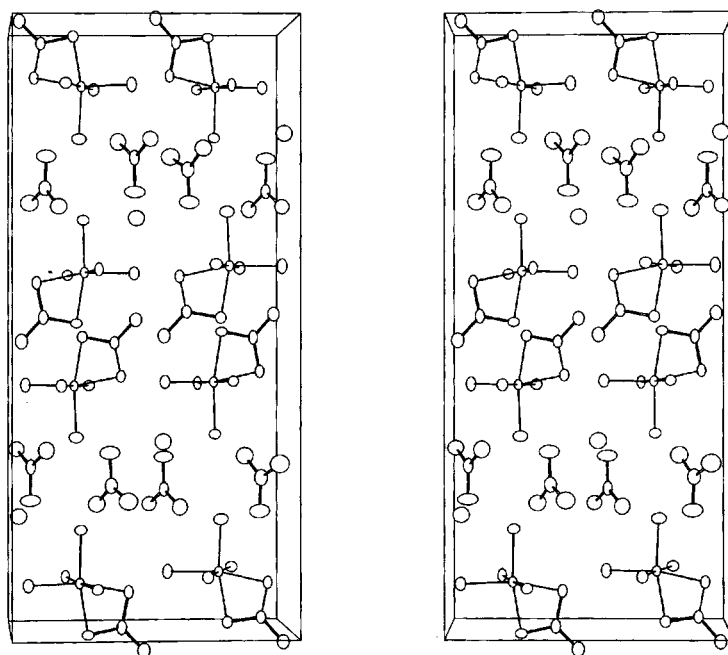


Fig. 3. Stereoscopic view of the structure of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$ along $[100]$. b is along the page.

The carbonate ions act as bidentate ligands in the two coordination polyhedra, and the carbonate ions are slightly deformed (Table 4). The packing of the ions in the structure of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$ is very close to the one of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ with layers of the cations and layers containing the anions and the water molecules. The Co-N distances have two short and two longer bonds but one short and three longer bonds were observed in the previous investigations.³⁻⁶ The standard deviations of the interatomic distances are comparable with the values found in the structure analysis of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$.⁶ The powder pattern of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$, Table 1, has observed intensities in acceptable agreement with calculated intensities from the use of the program LAZY PULVERIX.¹¹ The unit cell parameters and the calculated values $2\theta_{\text{calc}}$ and d_{calc} were derived from indexing of the powder pattern with the program DICVOL.¹²

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