X-Ray Crystallographic Study of Tetrammine–Carbonatocobalt(III) Sulfate Trihydrate, [Co(NH₃)₄CO₃]₂SO₄·3H₂O

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The crystal structure of tetrammine–carbonatocobalt(III) sulfate trihydrate, [Co(NH₃)₄CO₃]₂SO₄·3H₂O, was solved by direct methods from single-crystal X-ray diffraction data. The structure is monoclinic, space group $P2_1/c$ (No. 14) with the lattice parameters $a = 7.455(1)$, $b = 10.609(1)$, $c = 23.627(2)$ Å, $\beta = 98.346(7)°$ and $Z = 4$. The structure has two independent Co(NH₃)₄CO₃ co-ordination octahedra with Co–N bonds in the range 1.941–1.959 Å, and Co–O bonds in the range 1.896–1.919 Å.

A number of complex salts containing the tetrammine–carbonatocobalt(III) ion were synthesised by Jørgensen,[1] and the crystal morphology of a selection of these salts were later studied by Jaeger.[2] The shape of the crystals of tetrammine–carbonato cobalt(III) sulfate trihydrate, [Co(NH₃)₄CO₃]₂SO₄·3H₂O, was thus described as rhombic bipyramidal. Little has been reported concerning the crystal structure of tetrammine–carbonatocobalt(III) salts. The structure of tetrammine–carbonatocobalt(III) bromide, [Co(NH₃)₄CO₃]Br, was reported by Barclay and Hoskins,[3] based on visual estimation of multiple-film equi-inclination Weissenberg photographs, and by Haagensen and Rasmussen,[4] based on X-ray intensities, measured visually from precession photographs, and on intensities measured photometrically from integrated Weissenberg films. In the structure the carbonate ion is a bidentate ligand. Later the structure of pent-ammine–carbonatocobalt(III) iodide monohydrate, [Co(NH₃)₅CO₃]I·H₂O, in which the carbonate ion is a monodentate ligand, was reported by Nakai et al.[5] This investigation was also based on Weissenberg film data.

As the two structure investigations of [Co(NH₃)₄CO₃]Br were based on X-ray film techniques it was decided to investigate the structure of a tetrammine–carbonatocobalt(III) salt using X-ray diffractometer techniques to obtain a higher precision of the inter-atomic bonds in the tetrammine–carbonatocobalt(III) ion than obtained in the Refs. 3 and 4. For this investigation

the tetrammine–carbonatocobalt(III) sulfate trihydrate, [Co(NH₃)₄CO₃]₂SO₄·3H₂O, was chosen.

Experimental

The compound [Co(NH₃)₄CO₃]₂SO₄·3H₂O was prepared as described by Jørgensen.[1] The chemicals used were CoCO₃ (Baker), H₂SO₄ (Merck) and NH₃ (Merck). The dark-red crystals were washed with water and dried in air.

A thermogravimetric analysis was made of the compound and the result of this is displayed in Fig. 1. The Stanton Redcroft TG–DTA simultaneous thermal analyser STA 1000/1500 was used in the investigation, with
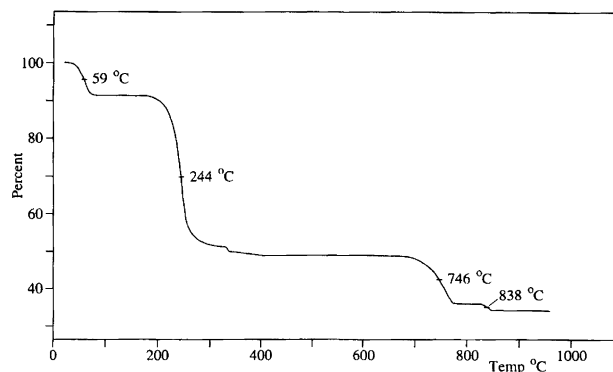

Fig. 1. Thermogravimetric /diagram of the decomposition of [Co(NH₃)₄CO₃]₂SO₄·3H₂O to Co₃O₄ in the temperature range 25–960 °C.

Table 1. Experimental data and unit cell parameters for the [Co(NH₃)₄CO₃]₂SO₄ · 3H₂O single crystal.

$a/Å$	7.455(1)
$b/Å$	10.609(1)
$c/Å$	23.627(2)
$\beta/°$	98.346(7)
Cell volume/$Å^3$	1849
Space group	$P2_1/c$
Z	4
Density (calc)/g cm^{-3}	1.884
Size of crystal/mm	0.5×0.2×0.1
Linear absorption coefficient μ/cm^{-1}	19.7
No. of measured reflections (including two standard reflections for every 50 reflections)	3529
R (intern) of reflections (%)	2.2
No. of independent reflections	3260
No. of reflections with $I>3\sigma(I)$	2556
Scan method	ω–2θ
Scan range in $\theta/°$	1+0.346 tan θ
$\theta_{max}/°$	25
T/K	298

the heating rate of 5°C min^{-1} under Ar gas flow. The weight loss of 9% corresponds to the loss of three water molecules per formula unit, and the loss to 34% corresponds to the formation of Co₃O₄. This composition was confirmed by an X-ray powder pattern taken of a sample heated to 950°C.

The X-ray powder diffraction pattern of [Co(NH₃)₄CO₃]₂ SO₄·3H₂O was measured on a Philips reflection diffractometer using CuKα₁ radiation. The diffractometer was calibrated with an external standard of silicon (a_{si} = 5.430 50 Å). The JCPDS data base has two cards for the powder pattern of [Co(NH₃)₄CO₃]₂SO₄·3H₂O, nos. 22–584 and 24–320. The two reported powder patterns are unindexed. The measured powder pattern was in acceptable agreement with the reported patterns.

Single crystals of [Co(NH₃)₄CO₃]₂SO₄·3H₂O were selected using the polarising microscope, and precession and Weissenberg photographs were taken; the compound was monoclinic, and the space group was $P2_1/c$. The X-ray films showed a tendency to a disordered structure, as the films had diffuse diffraction spots. However, one crystal gave X-ray films without these diffuse spots, and this crystal was used in the X-ray diffraction data collection on a Huber four-circle diffractometer. The unit-cell parameters were calculated in a least-squares refinement using diffraction data from 52 reflections, and these unit-cell parameters and other experimental data are listed in Table 1.

Structure determination

The structure determination was made with 3260 reflections and the structure refinement was made with 2556 reflections with $I>3\sigma(I)$. The structure was solved by direct methods using the SHELX86 program.[6] This gave

the positions of all the atoms except the hydrogen atoms. However, the positions of the hydrogen atoms were calculated assuming the well established geometries of the ammonia and water molecules and hydrogen-bond considerations and confirmed by difference maps. A differ-

Table 2. Atomic coordinates and equivalent temperature factor parameters for [Co(NH₃)₄CO₃]₂SO₄·3H₂O.

Atom	x/a	y/b	z/c	U_{eq}[a]
Co(1)	0.05187(6)	0.25821(4)	0.41224(2)	0.0164(3)
N(1)	0.0082(5)	0.2510(4)	0.3287(1)	0.034(2)
N(2)	0.3029(5)	0.3109(3)	0.4098(1)	0.026(2)
N(3)	−0.1973(4)	0.2013(3)	0.4134(1)	0.025(2)
N(4)	−0.0239(5)	0.4326(3)	0.4178(2)	0.030(2)
O(1)	0.1084(4)	0.2235(2)	0.4923(1)	0.027(1)
O(2)	0.1367(4)	0.0906(2)	0.4248(1)	0.027(1)
O(3)	0.2191(4)	0.0291(3)	0.5161(1)	0.047(2)
C(1)	0.1586(5)	0.1084(3)	0.4808(2)	0.029(2)
Co(2)	0.62863(6)	0.25910(4)	0.09687(2)	0.0173(3)
N(5)	0.5446(6)	0.4322(3)	0.0979(2)	0.030(2)
N(6)	0.3804(5)	0.1984(3)	0.0972(1)	0.029(2)
N(7)	0.6783(6)	0.2500(4)	0.1808(1)	0.035(2)
N(8)	0.8780(5)	0.3142(3)	0.0945(2)	0.028(2)
O(4)	0.5984(4)	0.2311(2)	0.0157(1)	0.025(1)
O(5)	0.6991(3)	0.0923(2)	0.0798(1)	0.027(1)
O(6)	0.6908(4)	0.0414(2)	−0.0132(1)	0.037(2)
C(2)	0.6631(5)	0.1159(3)	0.0246(2)	0.025(2)
S	0.2148(1)	0.4348(1)	0.2225(0)	0.025(0)
O(7)	0.0172(4)	0.4368(3)	0.2131(1)	0.055(2)
O(8)	0.2841(6)	0.3112(3)	0.2073(2)	0.063(3)
O(9)	0.2837(5)	0.5320(4)	0.1881(2)	0.067(2)
O(10)	0.2766(5)	0.4566(3)	0.2837(1)	0.054(2)
Ow(1)	0.3938(6)	0.1544(4)	0.3066(2)	0.069(3)
Ow(2)	0.0790(6)	0.0914(4)	0.1918(2)	0.070(3)
Ow(3)	0.6438(8)	0.4124(6)	0.3224(3)	0.106(3)
Hw(1)	0.378(10)	0.194(8)	0.273(3)	0.11(3)
Hw(2)	0.469(12)	0.092(8)	0.301(4)	0.14(3)
Hw(3)	0.036(17)	0.035(12)	0.229(5)	0.32(5)
Hw(4)	0.130(21)	0.195(16)	0.192(6)	0.40(7)
Hw(5)	0.548(10)	0.438(7)	0.309(3)	0.08(2)
Hw(6)	0.698(10)	0.454(6)	0.296(3)	0.04(2)
H(11)	0.057(9)	0.174(6)	0.320(3)	0.08(2)
H(12)	0.872(15)	0.253(7)	0.316(4)	0.14(4)
H(13)	0.090(12)	0.294(8)	0.309(3)	0.13(3)
H(21)	0.349(7)	0.269(4)	0.387(2)	0.04(1)
H(22)	0.300(9)	0.400(7)	0.403(3)	0.10(2)
H(23)	0.378(7)	0.300(5)	0.445(2)	0.06(1)
H(31)	0.788(11)	0.128(8)	0.392(3)	0.12(3)
H(32)	0.712(10)	0.252(6)	0.407(3)	0.09(2)
H(33)	0.800(12)	0.176(8)	0.448(4)	0.14(3)
H(41)	0.843(10)	0.456(6)	0.445(3)	0.12(2)
H(42)	−0.036(9)	0.472(6)	0.386(3)	0.09(2)
H(43)	0.046(12)	0.460(7)	0.441(3)	0.11(3)
H(51)	0.480(7)	0.448(4)	0.072(2)	0.04(2)
H(52)	0.508(8)	0.453(5)	0.130(3)	0.06(2)
H(53)	0.613(10)	0.486(7)	0.089(3)	0.10(3)
H(61)	0.318(8)	0.231(4)	0.123(2)	0.05(2)
H(62)	0.356(9)	0.108(7)	0.095(3)	0.09(2)
H(63)	0.300(9)	0.212(5)	0.059(3)	0.08(2)
H(71)	0.577(8)	0.285(5)	0.196(2)	0.06(2)
H(72)	0.785(8)	0.301(5)	0.197(2)	0.06(1)
H(73)	0.720(11)	0.193(8)	0.191(3)	0.12(3)
H(81)	0.969(11)	0.267(6)	0.107(3)	0.09(2)
H(82)	0.931(11)	0.386(8)	0.116(3)	0.14(3)
H(83)	0.909(6)	0.313(4)	0.062(2)	0.08(1)

[a] $U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table 3. Comparison of bond lengths in octahedra with those reported previously.

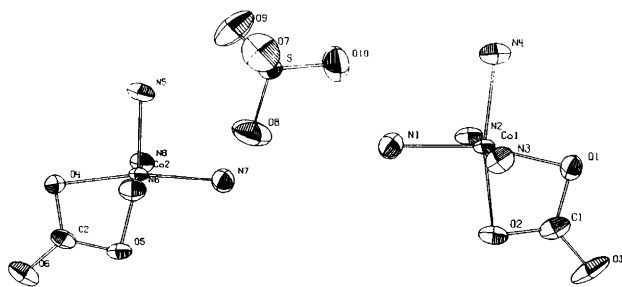|	This work	Ref. 3
Co1–O2	1.897(2)	1.905±1 (×2)
Co1–O1	1.915(2)	
Co1–N4	1.944(3)	
Co1–N1	1.955(3)	1.95±1
Co1–N3	1.957(3)	2.03±2 (×2)
Co1–N2	1.963(3)	1.93±2
Co2–O5	1.905(2)	
Co2–O4	1.919(2)	
Co2–N5	1.942(3)	
Co2–N8	1.957(4)	
Co2–N6	1.960(3)	
Co2–N7	1.967(4)	
O1–C1	1.315(5)	1.24±2
O2–C1	1.319(5)	1.34±2 (×2)
O3–C1	1.226(4)	
O4–C2	1.317(4)	
O5–C2	1.319(4)	
O6–C2	1.234(4)	

Fig. 2. The coordination polyhedra of the two $[Co(NH_3)_4CO_3]^+$ ions and the SO_4^{2-} ion with thermal ellipsoids.

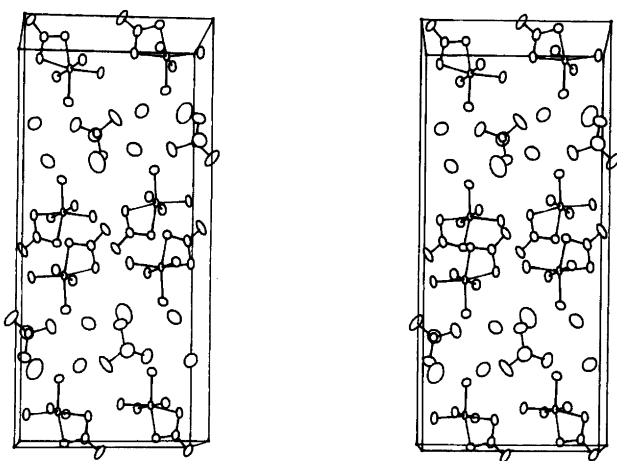*Fig. 3.* Stereoscopic view of the structure of $[Co(NH_3)_4CO_3]_2SO_4 \cdot 3H_2O$ along [100].

ence Fourier map did not show any additional electron density.

The model of the structure of $[Co(NH_3)_4CO_3]_2SO_4 \cdot 3H_2O$ was refined in a least-

squares procedure using the program LINUS,[7] and scattering contributions from neutral atoms.[8] Positions and isotropic displacement parameters for the hydrogen atoms were refined, and anisotropic displacement para-

Table 4. X-Ray powder pattern measured on a Phillips reflection diffractometer of $[Co(NH_3)_4CO_3]_2SO_4 \cdot 3H_2O$.

$2\theta_{obs}$	$2\theta_{calc}$	δ	$d/\text{Å}$	I_{obs}	h	k	l
7.56	7.56	0.00	11.688	35	0	0	2 [a]
11.92	11.97	−0.05	7.419	3	1	0	0
13.12	13.20	−0.08	6.743	7	−1	0	2
14.04	14.07	−0.03	6.303	5	0	1	3
14.54	14.63	−0.09	6.087	14	−1	1	1
15.00	15.07	−0.07	5.902	19	1	0	2
15.54	15.62	−0.08	5.698	21	−1	1	2
16.64	16.66	−0.02	5.323	44	0	2	0
17.12	17.23	−0.11	5.175	100	1	1	2
17.92	17.91	0.01	4.946	31	−1	0	4
18.24	18.31	−0.07	4.860	44	0	2	2
19.56	19.56	0.00	4.535	33	1	1	3
19.74	19.77	−0.03	4.494	42	−1	1	4
20.20	20.19	0.01	4.392	4	0	2	3
20.64	20.67	−0.03	4.300	63	1	0	4
21.28	21.31	−0.03	4.172	12	−1	2	2
22.30	22.31	−0.01	3.983	35	1	1	4
22.56	22.58	−0.02	3.938	97	0	2	4
22.80	22.78	0.02	3.897	15	0	0	6
24.24	24.17	0.07	3.669	4	−2	0	2
25.50	25.50	−0.00	3.490	50	2	1	0
26.56	26.58	−0.02	3.353	5	−2	0	4
26.80	26.87	−0.07	3.324	6	−1	2	5
27.28	27.33	−0.05	3.266	2	1	0	6
27.96	27.89	0.07	3.188	13	1	3	0
28.28	28.35	−0.07	3.153	14	0	2	6
28.38	28.46	−0.08	3.142	14	−1	3	2
29.32	29.28	0.04	3.044	41	1	2	5
30.36	30.40	−0.04	2.942	3	2	0	4
30.52	30.53	−0.01	2.927	4	0	0	8
30.94	31.01	−0.07	2.888	1	−1	3	4
31.58	31.58	−0.00	2.831	7	0	2	7
32.30	32.32	−0.02	2.769	5	−1	1	8
32.88	32.89	−0.01	2.722	6	2	2	3
33.68	33.68	−0.00	2.659	10	0	4	0
33.88	33.91	−0.03	2.644	5	0	4	1
34.58	34.57	0.01	2.592	10	0	4	2
35.18	35.14	0.04	2.549	25	−1	3	6
35.50	35.50	−0.00	2.527	20	0	1	9
35.72	35.58	0.14	2.512	20	1	1	8
35.88	35.88	−0.00	2.501	17	−1	4	1
36.26	36.27	−0.01	2.476	11	1	4	1
36.46	36.45	0.01	2.462	6	3	0	0
36.90	36.88	0.02	2.434	14	−2	3	4
37.14	37.09	0.05	2.419	30	−3	1	1
37.52	37.48	0.04	2.395	7	−3	0	4
38.44	38.43	0.01	2.340	22	0	0	10
39.42	39.33	0.04	2.284	6	0	1	10
40.00	39.99	0.01	2.252	3	−1	4	5
40.46	40.44	0.02	2.228	3	−1	3	8
41.30	41.27	0.03	2.148	3	−3	2	4
42.12	42.15	−0.03	2.144	14	0	2	10
43.00	42.99	0.01	2.102	5	−2	2	9
44.70	44.66	0.04	2.026	3	−1	5	2
45.34	45.31	0.03	1.999	15	1	5	2
46.48	46.43	0.05	1.952	10	−1	5	4

[a] Below the two theta min. limit of the powder pattern. Calculated values are listed for this reflection.

meters were refined for the remaining atoms. The weights used in the refinements were $1/\sigma^2(F)$, $\sigma(F) = [\sigma_{count}(F^2) + 1.03F^2]^{1/2} - |F|$, and $\sigma_{count}(F^2)$ is (number of counts)$^{1/2}$. The final R-values were $R_F = 3.3\%$, $R_w = 4.5\%$. Atomic coordinates and displacement parameters are listed in Table 2, interatomic distances and angles are given in Table 3. Figure 2 displays the two coordination polyhedra and the sulfate ion with the displacement ellipsoids of the atoms, and Fig. 3 is a projection of the structure along [100] with the *b*-axis across the page.

Discussion

The two coordination polyhedra have a higher precision of the interatomic bonds than reported previously for the bonds in a tetrammine–carbonatocobalt(III) complex.[3,4] In this work the standard deviation of the interatomic distances are 0.002 to 0.004 Å. In the two investigations based on film data the r.m.s. errors were of the order of 0.01 Å on the heavy atoms and about 0.05–0.08 Å for the lighter atoms. Table 3 shows a comparison of the interatomic distances in the coordination polyhedra with the reported structure investigation.[3] The carbonate ion is slightly deformed with a short and two longer bonds. The Co–N distances have one short and three longer bonds in all three investigations. The Co–N distances are comparable with the metal–nitrogen bonds found in the structure of *trans*-dichlorotetrammine cobalt(III) bisulfate,[9] Co–N range 1.946(6)–1.973(6) Å, and in the pentammine-carbonatocobalt(III) iodide monohydrate,[5] Co–N range 1.90–1.98 Å. The water molecules form hydrogen bonds with the sulfate oxygen atoms with bond lengths in the range 2.73–2.95 Å.

The powder pattern of [Co(NH₃)₄CO₃]₂SO₄ · 3H₂O is listed in Table 4. The observed intensities are in accept-

able agreement with the calculated intensities obtained with the program LAZY PULVERIX.[10] The values for $2\theta_{obs}$ were derived in a profile fit with the least squares program ALLHKL.[11]

References

1. Jørgensen, S. M. *Z. Anorg. Chem. 2* (1982) 279.
2. Jaeger, F. M. *Z. Kristallogr. 39* (1904) 567.
3. Barclay, G. A. and Hoskins, B. F. *J. Chem. Soc.* (1962) 586.
4. Haagensen, C. O. and Rasmussen, S. E. *Acta Chem. Scand. 17* (1963) 1630.
5. Nakai, H., Kúshi, Y. and Kúroya, H. *J. Chem. Soc. Jpn., Pure Chem. Sect. 88* (1967) 1126.
6. Sheldrick, G. *SHELX86, Program for the Solution of Crystal Structures*, University of Göttingen, Germany 1986.
7. Busing, W. R., Martin, K. O. and Levy, H. A. *ORFLS, A Fortran Crystallographic Least Squares Program*, Report ORNL-TM 305. Oak Ridge National Laboratory, Oak Ridge, TN 1962. LINUS is a 1971 version of ORFLS.
8. Cromer, D. T. and Waber, J. T. Report LA-3056, Los Alamos Scientific Laboratory of the University of California, Los Alamos, NM 1964.
9. Alberto, J., Bonapace, P. and Mandel, S. *Acta Crystallogr., Sect. B31* (1975) 2540.
10. Yvon, K., Jeitschko, W. and Parthé, E. *J. Appl. Crystallogr. 10* (1977) 73.
11. Pawley, G. S. *J. Appl. Crystallogr. 13* (1980) 630.