

The Crystal Structures of Tri- μ -hydroxo-bis[triammine cobalt(III)] Bromide and Iodide

PETER ANDERSEN

Chemistry Department I, Inorganic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark

The crystal structures of tri- μ -hydroxo-bis[triammine cobalt(III)] bromide and iodide have been determined from single crystal data.

The space group of the bromide is monoclinic, $P2_1$, the unit cell dimensions, as determined by powder photograph techniques, are

$$a = 7.30_6 \text{ \AA}, b = 10.34_8 \text{ \AA}, c = 9.19_6 \text{ \AA}; \beta = 91.2_5^\circ.$$

The space group of the iodide is orthorhombic, $Pm2_1n$, and the unit cell dimensions are $a = 7.66_8 \text{ \AA}, b = 10.84_8 \text{ \AA}, c = 9.50_7 \text{ \AA}$.

The two compounds are very closely related in structure. They contain two formula units, $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]^{3+}$, in the unit cell, and it was found from projections that the molecule is dinuclear with a Co—Co distance of 2.55 Å, the ligands being almost regularly octahedrally arranged around the cobalt atoms.

This work, on the structure of tri- μ -hydroxo-bis[triammine cobalt(III)], $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]^{3+}$, here called cobalt-triol, was started in connection with the investigation of some equilibrium mixtures of chromium(III)-amines which gave evidence for a high concentration of chromium-triol in solutions of the composition: $C_{\text{Cr}} = 0.3 \text{ M}, C_{\text{NH}_3\text{Cl}} = 4.5 \text{ M}$, and $C_{\text{NH}_3} = 3-4 \text{ M}$.¹ This analogous chromium compound has, however, not yet been isolated.

In the cobalt-triol one would expect the ligands to be octahedrally arranged around the metal atom. All halogen atoms in cobalt-triol halides are bound as ions, the triol has no acid-base properties in aqueous solution, and treatment with hydrochloric acid quantitatively yields dichloride, $[\text{Co}(\text{NH}_3)_3\text{Cl}_2\text{H}_2\text{O}]\text{Cl}$. As pointed out by Werner,² these properties, combined with analyses, show that the triol molecule can be dinuclear with three OH-bridges between the two cobalt atoms.

EXPERIMENTAL WORK AND CRYSTAL DATA

The cobalt-triol was first prepared by Werner,² 1907, by reaction of base with triammine cobalt(III) compounds. For the present work cobalt-triol chloride was pre-

pared from dichrochloride, by treatment with the equivalent amount of potassium hydroxide.³ Dichrochloride was synthesised from cobalt(II) acetate, which after treatment with sodium nitrite, ammonia, hydrogen peroxide, and charcoal gave $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$,⁴ which again by reaction with concentrated hydrochloric acid was converted to dichrochloride.⁵

The corresponding bromide and iodide were prepared from the chloride, by repeated precipitations with sodium bromide and potassium iodide solutions, respectively. The red, plate-like crystals of triol bromide and iodide looked very similar, and both showed parallel extinction under the polarizing microscope. X-Ray powder photographs indicated isomorphism, whereas the powder photograph of the triol chloride revealed no relationship to the two others. As the chloride, unlike the bromide, contains water of crystallization,² it was decided to investigate the bromide together with the related iodide.

The molecular weight of cobalt-triol bromide, $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]\text{Br}_3$, is 510.8. (Found: Co 23.0%; N 16.4%. Calc.: Co 23.09%; N 16.46%).

The powder photographs were taken with $\text{CuK}\alpha$ radiation using a focussing camera of the Guinier type, calibrated with sodium chloride.

The dimensions of the crystals used for single crystal work were approximately $0.1 \times 0.05 \times 0.005$ mm in the a -, b -, and c -direction, respectively. Oscillation and equiinclination Weissenberg photographs were obtained with $\text{CoK}\alpha$ radiation.

Cobalt-triol bromide. From the powder photographs (see Table 1) the following unit cell dimensions of the bromide were obtained:

$$a = 7.30, \text{ \AA}, b = 10.34, \text{ \AA}, c = 9.19, \text{ \AA}; \beta = 91.2^\circ, \alpha = \gamma = 90.0^\circ.$$

The specific density, as measured by flotation in mixtures of tribromomethane and 1,2-dibromopropane, was 2.41₅ g/ml corresponding to 1.98 molecules in the unit cell.

Absent reflections ($k = 2n + 1$ for $0k0$, from Weissenberg photographs), the shape of the unit cell, and lack of centre of symmetry (see later) determined the space group to be monoclinic, $P2_1$ (No. 4, *Intern. Tables*), the twofold screw axis being parallel to the b -axis.

Weissenberg photographs of the different levels, with the a - and b -axis as axes of rotation, showed that the crystals of the bromide were twins, which it was not possible to detect by optical methods. Several crystals grown under different conditions were investigated, and twinning found in all cases. The two reciprocal lattices in question have common b^* -axis as well as common c^* -axis, whereas the two a^* -axes intersect at an angle very close to 2° . The two a^* -axes and the c^* -axis apparently lie in the same plane, perpendicular to the b^* -axis. This is in good agreement with the fact that the crystals are monoclinic with $\beta = 91.2^\circ$.

Cobalt-triol iodide. The powder photographs (see Table 1) gave the following unit cell dimensions for the iodide:

$$a = 7.66, \text{ \AA}, b = 10.84, \text{ \AA}, c = 9.50, \text{ \AA}; \alpha = \beta = \gamma = 90.0^\circ.$$

Absent reflections ($h + k = 2n + 1$ for $hk0$, from Weissenberg photographs), the shape of the unit cell, and lack of centre of symmetry (see later) determined the space group to be orthorhombic, $Pm2_1n$ (No. 31, *Intern. Tables*), the twofold screw axis being parallel to the b -axis, and the mirror plane being perpendicular to the a -axis.

DETERMINATION OF THE ATOMIC POSITIONS

Intensities $I(hkl)$ were visually estimated and corrected for Lorentz-polarization factor using program 1 (the programs used for computer calculations are listed in Table 6). Because of the small size of the crystals, no corrections were made for absorption.

The Patterson projections, on (100) of the bromide, and on (100) and (010) of the iodide were calculated by means of programs 2 and 4. The projections on (100) show that the bromide and the iodide are very closely related in structure.

Table 1. X-ray powder data, CuK α radiation.

Cobalt-triol bromide				Cobalt-triol iodide						
<i>h k l</i>	$10^4 \cdot \sin^2 \theta$ obs	$10^4 \cdot \sin^2 \theta$ calc	I_{obs}	<i>h k l</i>	$10^4 \cdot \sin^2 \theta$ obs	$10^4 \cdot \sin^2 \theta$ calc	I_{obs}			
0 1 1	125	126	w	0 1 1	115	116	w			
1 1 0	166	167	w	1 1 0	151	152	vw			
0 2 0	221	222	w	0 2 0	201	202	vw			
0 0 2	280	281	vw	0 0 2	263	263	w			
0 2 1	292	292	w	0 2 1	267	268	mw			
0 1 2	336	337	mw	0 1 2	314	314	mw			
$\bar{1}$ 0 2	385	386	vw	1 0 2	363	364	mw			
1 0 2	399	399	ms	1 2 1	368	369	vs			
$\bar{1}$ 2 1	400	400								
1 2 1	406	407	ms	2 0 0	404	404	s			
2 0 0	445	445	ms	1 1 2	414	415	vw			
0 3 1	570	570	vw	0 3 1	519	520	mw			
1 2 2	621	621	vw	2 1 1		520				
$\bar{1}$ 3 1	676	678	vw	1 2 2	567	566	w			
1 3 1	685	684	vw	1 3 1	622	621	w			
$\bar{2}$ 0 2	712	712	vw	2 0 2	667	667	mw			
$\bar{2}$ 2 1	730	730	vw	2 2 1	673	672	mw			
$\bar{2}$ 1 2	769	768	vw	2 1 2	716	718	w			
2 1 2	797	795	vw	0 3 2		717				
0 2 3	855	855	w	0 2 3	794	794	mw			
0 4 0	888	888	w	0 4 0	808	808	mw			
$\bar{2}$ 3 1	1007	1008	vw	2 3 1	924	924	mw			
2 3 1	1022	1021	vw	0 4 2	1070	1071	vw			
$\bar{3}$ 2 1	1284	1283	vw	1 3 3	1149	1147	vw			
3 2 1	1306	1304	vw	1 0 4		1153				
$\bar{2}$ 4 2	1597	1600	vw	3 2 1	1175	1177	mw			
2 3 3				1598	2 2 3	1195	1198	vw		
4 0 0				1780	1780	vw	2 4 0	1212	1212	vw
							1 2 4	1353	1355	vw
				2 4 2	1475	1475	w			
				2 1 4	1508	1507	vw			
				0 3 4		1507				
				0 5 2	1524	1525	vw			
				4 0 0	1617	1617	vw			
				4 0 2	1880	1880	vw			
				2 5 2	1929	1930	w			
				4 1 2		1930				
				1 5 3	1957	1955	vw			
				3 3 3		1956				
				3 4 2		1981		vw		
				1 6 1	1982	1985				

Table 2. Atomic parameters for cobalt-tri-iodide bromide and iodide.

Cobalt-tri-iodide bromide				Cobalt-tri-iodide					
89 $h0l$ -reflections with $R = 0.099$		78 $0kl$ -reflections with $R = 0.064$		51 $h0l$ -reflections with $R = 0.136$		98 $0kl$ -reflections with $R = 0.112$			
atom	x	z	B (\AA^2)	y	z	B (\AA^2)	y	z	B (\AA^2)
2 Br	0.243	0.163	4.0	0.028	0.157	3.9	0.022	0.159	1.4
2 Br	0.224	0.193	4.0	0.468	0.201	3.9	0.470	0.197	1.4
2 Br	0.250	0.669	4.0	0.270	0.661	3.9	0.259	0.667	1.4
2 Co(1) ^a	0.271	0.827	3.6	0.743	0.826	3.9	0.737	0.822	0.7
2 Co(2)	0.257	0.580	3.6	0.861	0.585	3.9	0.846	0.582	0.7
2 O (1)	0.259	0.767	1.4	0.929	0.783	1.1	0.917	0.794	-1.8
2 N (1)	0.225	0.828	1.4	0.557	0.831	1.1	0.562	0.835	-1.8
2 N (2)	0.080	0.983	1.4	0.756	0.985	1.1	0.747	0.961	-0.5
2 N (3)	0.469	0.969	1.4	0.752	0.964	1.1			
2 O (2)	0.090	0.660	1.4	0.725	0.674	1.1	0.721	0.662	-0.5
2 O (3)	0.432	0.658	1.4	0.741	0.655	1.1			
2 N (4)	0.058	0.528	1.4	0.985	0.542	1.1	0.947	0.529	-0.5
2 N (5)	0.453	0.525	1.4	0.004	0.490	1.1			
2 N (6)	0.268	0.387	1.4	0.779	0.404	1.1	0.766	0.406	-1.8

^a The numbers in brackets refer to the numbering in Fig. 3.

Table 3. Observed and calculated structure factors for cobalt-triol bromide and iodide.

Bromide.

$h k l$	F_o	F_c	$h k l$	F_o	F_c
0 0 0	—	432.5	3 0 $\bar{1}$	12.6	— 12.2
0 0 1	11.7	— 11.3	3 0 0	23.2	— 19.5
0 0 2	74.1	— 87.4	3 0 1	8.9	— 17.0
0 0 3	70.2	— 75.5	3 0 2	78.0	— 73.7
0 0 4	63.3	— 52.9	3 0 3	18.2	— 7.3
0 0 5	92.3	79.7	3 0 4	25.8	— 28.9
0 0 6	91.4	89.1	3 0 5	—	— 11.5
0 0 7	—	4.5	3 0 6	—	— 4.2
0 0 8	47.3	— 45.5	3 0 7	25.2	— 18.6
0 0 9	15.0	— 5.9	3 0 8	—	— 5.7
			3 0 9	13.0	— 13.4
1 0 $\bar{6}$	17.4	21.8			
1 0 $\bar{5}$	—	— 4.9	4 0 $\bar{8}$	26.5	— 31.8
1 0 $\bar{4}$	44.2	— 43.5	4 0 7	—	— 5.2
1 0 $\bar{3}$	38.8	— 46.5	4 0 $\bar{6}$	25.8	— 30.8
1 0 $\bar{2}$	114.9	118.3	4 0 $\bar{5}$	41.3	— 51.2
1 0 $\bar{1}$	35.7	— 28.8	4 0 $\bar{4}$	—	— 3.8
1 0 0	—	2.4	4 0 $\bar{3}$	47.7	— 41.6
1 0 1	41.2	40.0	4 0 $\bar{2}$	81.5	— 75.2
1 0 2	129.0	— 132.3	4 0 $\bar{1}$	36.2	— 36.5
1 0 3	31.9	34.4	4 0 0	165.3	— 164.0
1 0 4	44.3	48.8	4 0 1	37.9	— 31.2
1 0 5	—	12.5	4 0 2	27.8	— 24.9
1 0 6	12.4	— 14.1	4 0 3	63.8	— 57.2
			4 0 4	65.0	— 63.6
2 0 $\bar{9}$	13.5	7.0	4 0 5	29.3	— 36.0
2 0 $\bar{8}$	45.5	46.4	4 0 6	40.5	— 44.3
2 0 $\bar{7}$	—	— 5.0	4 0 7	19.9	— 20.0
2 0 $\bar{6}$	44.0	— 41.0	4 0 8	21.5	— 25.8
2 0 $\bar{5}$	81.8	— 79.1			
2 0 $\bar{4}$	43.4	47.5	5 0 $\bar{4}$	18.6	— 19.9
2 0 $\bar{3}$	84.8	78.5	5 0 $\bar{3}$	31.9	— 38.1
2 0 $\bar{2}$	146.8	143.3	5 0 $\bar{2}$	40.5	— 35.7
2 0 $\bar{1}$	22.3	19.3	5 0 $\bar{1}$	12.6	— 13.9
2 0 0	236.1	— 235.6	5 0 0	—	— 3.7
2 0 1	40.3	— 34.0	5 0 1	25.3	— 27.6
2 0 2	109.9	99.5	5 0 2	70.3	— 71.4
2 0 3	97.4	92.6	5 0 3	—	— 3.6
2 0 4	82.7	91.6	5 0 4	18.6	— 19.4
2 0 5	64.0	— 65.0			
2 0 6	49.4	— 52.7	6 0 $\bar{6}$	12.3	— 19.1
2 0 7	18.6	— 19.6	6 0 $\bar{5}$	15.0	— 27.2
2 0 8	44.9	42.3	6 0 $\bar{4}$	—	— 1.8
2 0 9	16.1	18.7	6 0 $\bar{3}$	17.8	— 9.0
			6 0 $\bar{2}$	40.8	— 43.1
3 0 $\bar{9}$	11.5	— 14.9	6 0 $\bar{1}$	37.0	— 39.2
3 0 $\bar{8}$	11.1	3.7	6 0 0	86.7	— 93.7
3 0 $\bar{7}$	12.8	— 6.3	6 0 1	26.0	— 21.5
3 0 $\bar{6}$	22.7	— 25.0	6 0 2	—	— 7.3
3 0 $\bar{5}$	—	0.0	6 0 3	21.5	— 17.4
3 0 $\bar{4}$	11.3	15.5	6 0 4	34.9	— 40.7
3 0 $\bar{3}$	32.9	19.5	6 0 5	10.2	— 14.3
3 0 $\bar{2}$	57.0	— 59.6	6 0 6	32.1	— 36.5

<i>h k l</i>	F_o	F_c	<i>h k l</i>	F_o	F_c
7 0 $\bar{3}$	9.8	10.0	7 0 1	21.9	— 19.6
7 0 $\bar{2}$	18.4	— 22.2	7 0 2	29.5	29.7
7 0 $\bar{1}$	—	— 1.9	7 0 3	—	5.1
7 0 0	11.1	— 7.7			

Bromide.

<i>h k l</i>	F_o	$ F_c $	phase	<i>h k l</i>	F_o	$ F_c $	phase
0 0 0	—	432.5	0.0	0 4 5	12.7	16.4	— 42.9
0 0 1	14.8	13.2	180.0	0 4 6	87.4	85.5	7.8
0 0 2	71.5	83.1	180.0	0 4 7	32.4	31.1	127.6
0 0 3	67.5	72.2	180.0	0 4 8	20.1	15.6	152.6
0 0 4	57.3	59.5	180.0				
0 0 5	86.3	85.2	0.0	0 5 0	—	0.0	
0 0 6	83.0	78.9	0.0	0 5 1	78.6	76.2	146.6
0 0 7	—	2.9	180.0	0 5 2	122.0	120.8	189.9
0 0 8	40.3	35.2	180.0	0 5 3	42.7	47.2	28.1
0 0 9	—	0.1	180.0	0 5 4	53.9	53.5	6.3
				0 5 5	41.1	38.4	— 57.6
0 1 0	—	0.0		0 5 6	19.1	18.4	200.3
0 1 1	60.0	58.6	193.6	0 5 7	39.0	39.0	171.5
0 1 2	80.8	90.0	149.9	0 5 8	12.8	11.2	139.5
0 1 3	20.4	21.3	125.1				
0 1 4	78.7	84.1	23.6	0 6 0	34.8	29.9	171.2
0 1 5	64.7	61.2	257.7	0 6 1	—	16.6	161.4
0 1 6	37.0	38.2	250.6	0 6 2	28.4	29.4	40.8
0 1 7	19.2	19.9	145.6	0 6 3	45.0	46.4	212.4
0 1 8	36.8	39.2	139.6	0 6 4	33.9	27.7	— 69.6
0 1 9	24.1	26.1	70.5	0 6 5	—	3.4	224.8
				0 6 6	26.0	25.8	179.6
0 2 0	66.2	65.7	254.6	0 6 7	36.4	35.5	72.3
0 2 1	68.1	71.5	50.8				
0 2 2	23.0	23.5	199.8	0 7 0	—	0.0	
0 2 3	151.6	149.9	186.2	0 7 1	57.2	52.1	224.7
0 2 4	36.9	36.6	1.0	0 7 2	44.7	45.2	105.0
0 2 5	38.3	37.8	— 66.1	0 7 3	23.3	25.0	— 66.2
0 2 6	31.6	32.3	115.9	0 7 4	19.2	20.7	9.6
0 2 7	—	7.2	55.7	0 7 5	18.6	20.6	30.8
0 2 8	—	8.4	80.1	0 7 6	—	4.4	257.7
0 2 9	10.3	18.0	219.5	0 7 7	9.8	9.7	222.9
0 2 10	7.2	13.7	— 54.8				
				0 8 0	55.0	55.2	2.6
0 3 0	—	0.0		0 8 1	9.6	14.0	155.3
0 3 1	76.4	72.7	192.1	0 8 2	—	9.1	10.3
0 3 2	35.8	40.9	21.6	0 8 3	13.4	14.4	66.1
0 3 3	46.3	50.7	99.7	0 8 4	24.0	21.7	241.9
0 3 4	34.0	33.0	— 39.8	0 8 5	16.7	17.3	— 67.5
0 3 5	—	17.1	— 25.6	0 8 6	22.3	22.8	45.2
0 3 6	29.6	27.8	256.6	0 8 7	4.8	8.5	69.2
0 3 7	16.6	13.9	— 72.9				
0 3 8	39.1	40.4	71.2	0 9 0	—	0.0	
				0 9 1	47.0	50.2	148.5
0 4 0	177.1	170.1	7.9	0 9 2	31.2	30.1	213.9
0 4 1	38.3	42.3	— 18.9	0 9 3	—	10.4	186.5
0 4 2	71.1	64.6	159.8	0 9 4	37.7	38.5	10.0
0 4 3	36.3	35.7	153.4	0 9 5	15.0	14.9	— 66.7
0 4 4	47.2	44.5	250.1				

STRUCTURE OF COBALT-TRIOL

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<i>h k l</i>	F_o	$ F_c $	phase	<i>h k l</i>	F_o	$ F_c $	phase
0 10 0	35.7	38.4	201.3	0 10 4	8.1	8.7	- 13.4
0 10 1	23.7	20.4	118.7	0 11 0	—	0.0	
0 10 2	7.6	11.4	- 16.5	0 11 1	13.5	13.5	248.6
0 10 3	18.2	15.3	- 82.4				

Iodide.

<i>h k l</i>	F_o	F_c	<i>h k l</i>	F_o	F_c
0 0 0	—	539	3 0 7	43	35
0 0 1	—	3	3 0 8	—	15
0 0 2	105	-146	3 0 9	—	36
0 0 3	112	-122			
0 0 4	95	- 74	4 0 0	258	249
0 0 5	153	121	4 0 1	—	- 4
0 0 6	188	160	4 0 2	137	-124
0 0 7	—	4	4 0 3	98	-100
0 0 8	141	-114	4 0 4	50	- 66
0 0 9	26	- 21	4 0 5	60	73
0 0 10	—	- 1	4 0 6	80	90
			4 0 7	—	8
1 0 0	—	0	4 0 8	87	- 91
1 0 1	29	6	4 0 9	28	- 21
1 0 2	171	-199			
1 0 3	36	53	5 0 0	—	0
1 0 4	127	127	5 0 1	—	10
1 0 5	25	31	5 0 2	120	-116
1 0 6	40	- 33	5 0 3	30	30
1 0 7	—	- 1	5 0 4	61	60
1 0 8	30	- 32	5 0 5	—	8
1 0 9	—	9	5 0 6	—	- 30
1 0 10	49	57	5 0 7	—	0
2 0 0	353	-354	6 0 0	187	-188
2 0 1	32	- 38	6 0 1	—	3
2 0 2	189	172	6 0 2	61	58
2 0 3	117	129	6 0 3	42	52
2 0 4	73	76	6 0 4	29	33
2 0 5	111	-111	6 0 5	27	- 53
2 0 6	123	-113	6 0 6	65	- 77
2 0 7	—	- 23			
2 0 8	117	115	7 0 0	—	0
2 0 9	24	32	7 0 1	—	2
2 0 10	22	- 27	7 0 2	60	51
			7 0 3	—	- 16
3 0 0	—	0	7 0 4	23	- 46
3 0 1	45	24			
3 0 2	161	131	8 0 0	63	83
3 0 3	—	- 11	8 0 1	—	30
3 0 4	78	- 89	8 0 2	26	- 38
3 0 5	—	- 13	8 0 3	15	- 27
3 0 6	—	39			

Iodide.

h	k	l	F_o	$ F_c $	phase	h	k	l	F_o	$ F_c $	phase
0	0	0	—	539	0.0	0	5	0	—	0	—
0	0	1	—	1	0.0	0	5	1	100	89	142.1
0	0	2	123	147	180.0	0	5	2	196	202	177.5
0	0	3	107	115	180.0	0	5	3	61	60	22.5
0	0	4	85	95	180.0	0	5	4	127	126	3.7
0	0	5	136	121	0.0	0	5	5	70	66	— 74.7
0	0	6	173	162	0.0	0	5	6	58	50	211.0
0	0	7	—	10	180.0	0	5	7	90	78	156.3
0	0	8	129	120	180.0	0	5	8	40	37	138.8
0	0	9	24	7	180.0	0	5	9	33	29	107.4
0	0	10	18	9	180.0	0	6	0	51	36	177.9
0	1	0	—	0	—	0	6	1	39	33	50.9
0	1	1	49	42	200.8	0	6	2	33	22	42.1
0	1	2	102	128	153.6	0	6	3	111	96	190.2
0	1	3	44	40	129.4	0	6	4	59	53	267.2
0	1	4	133	141	20.7	0	6	5	55	47	— 7.3
0	1	5	115	105	246.2	0	6	6	42	56	168.1
0	1	6	96	72	243.5	0	6	7	87	84	52.2
0	1	7	27	14	161.3	0	6	8	21	22	44.5
0	1	8	103	95	129.8	0	6	9	45	54	231.0
0	1	9	78	68	73.6	0	7	0	—	0	—
0	1	10	30	40	— 28.8	0	7	1	139	132	199.8
0	2	0	80	68	268.3	0	7	2	62	59	80.5
0	2	1	118	125	31.1	0	7	3	—	16	— 88.3
0	2	2	45	48	200.9	0	7	4	49	48	— 4.2
0	2	3	226	246	178.8	0	7	5	58	64	5.4
0	2	4	41	40	— 25.2	0	7	6	25	26	263.8
0	2	5	83	79	— 30.6	0	7	7	57	53	190.4
0	2	6	54	40	82.1	0	8	0	108	103	— 19.0
0	2	7	27	24	29.2	0	8	1	27	22	67.4
0	2	8	26	26	72.0	0	8	2	43	40	176.8
0	2	9	55	62	204.1	0	8	3	27	36	43.7
0	2	10	33	41	— 60.7	0	8	4	51	54	218.1
0	3	0	—	0	—	0	8	5	47	58	— 80.0
0	3	1	148	127	186.5	0	8	6	58	64	28.8
0	3	2	46	52	16.3	0	8	7	34	32	91.6
0	3	3	81	78	87.2	0	9	0	—	0	—
0	3	4	39	35	— 48.7	0	9	1	85	95	131.6
0	3	5	56	58	— 22.6	0	9	2	96	111	193.6
0	3	6	72	60	— 85.4	0	9	3	26	24	92.1
0	3	7	52	51	216.7	0	9	4	108	119	— 10.7
0	3	8	108	99	66.3	0	9	5	27	24	— 83.8
0	3	9	44	34	55.5	0	9	6	28	29	174.3
0	3	10	15	23	176.2	0	10	0	89	99	175.3
0	4	0	269	264	— 1.9	0	10	1	29	37	36.3
0	4	1	54	60	— 10.3	0	10	2	23	14	71.9
0	4	2	130	131	167.0	0	10	3	25	38	251.2
0	4	3	57	53	144.6	0	10	4	20	28	— 59.3
0	4	4	94	85	228.8	0	10	5	16	20	196.1
0	4	5	35	38	— 29.9	0	11	0	—	0	—
0	4	6	167	163	— 4.0	0	11	1	69	71	202.3
0	4	7	82	78	116.2	0	11	2	18	27	136.8
0	4	8	82	70	165.1	0	11	3	16	30	0.7
0	4	9	32	25	251.9	0	11	4	14	29	— 87.2

Cobalt-triol iodide. Only two space groups are in accordance with the systematic absences for the iodide: $Pm\bar{m}n$ (No. 59, *Intern. Tables*) with a centre of symmetry and $Pm2_1n$ without. The positions of the 6 heavy iodine atoms were found from the Patterson projections, but gave no further information on this point. However, these space groups have the same symmetry elements (including a centre of symmetry) in the projections on (010). The heavy atom method was used for the projection on (010) of the iodide (programs 2, 4, and 5), and in this way it was possible to deduce the signs of all the observed $h0l$ -reflections, required for an electron density projection on (010) of the iodide. The positions of the cobalt and nitrogen/oxygen atoms were now revealed and they showed that the space group is $Pm2_1n$.

The projection on (100) of the iodide was calculated in the same way. This projection has no centre of symmetry, but because of the almost centrosymmetrical positions of the iodine atoms, space group $Pm\bar{m}n$ was used in a first approximation. An electron density projection, calculated with signs obtained using this assumption, revealed the positions of the cobalt atoms and some of the lighter atoms. Those atoms which are not centrosymmetrically related appeared as two atoms of half weight in correspondence with the symmetry plane perpendicular to the b -axis, which is present in $Pm\bar{m}n$, but absent in $Pm2_1n$. In this way the y -parameters of the atoms were determined, and the final result was obtained by refinement with program 6, used in the space group $Pm2_1n$ (not including unobserved reflections).

Cobalt-triol bromide. The parameters from the iodide were used for the bromide and were refined using program 6 in the space group $P2_1$ (not including

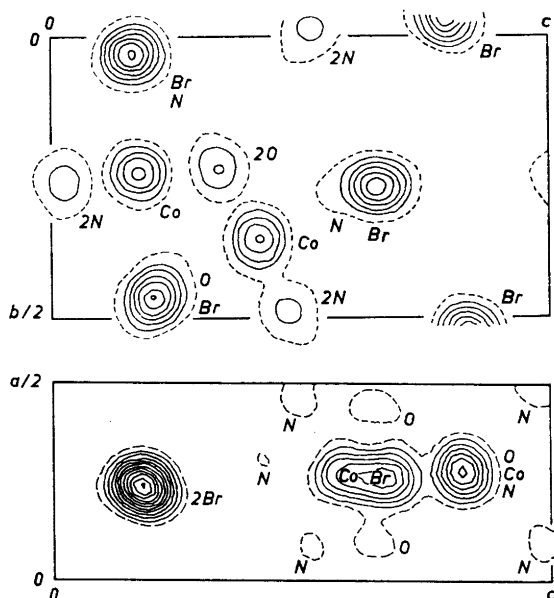


Fig. 1. Electron density projection of cobalt-triol bromide on (100) and (010). The zero contour lines are dashed.

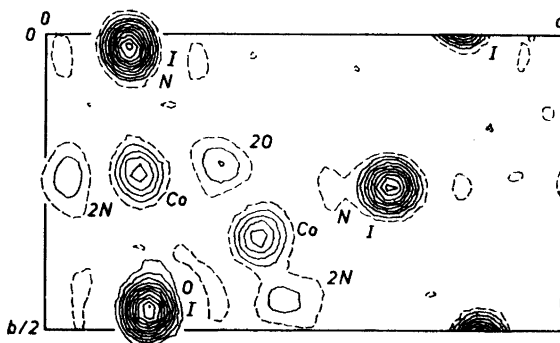


Fig. 2. Electron density projection of cobalt-triiodide on (100). The zero contour lines are dashed.

unobserved reflections). Since bromine is considerably lighter than iodine, it was expected that a better image of the triol molecule could be obtained in this way.

Weissenberg photographs with the b -axis as axis of rotation gave two sets of identical twin-reflections at the zero level, whereas it was difficult to resolve all the twin-reflections at the upper levels. Weissenberg photographs with the a -axis as axis of rotation exhibited no twinning at the zero level, but the upper levels had twin-reflections, some of which were difficult to resolve. The fact that for the space group $P2_1$, $|F0kl| = |F(0k\bar{l})|$ made it possible to calculate an electron density projection on (100), although the two twin reciprocal lattices here coincide. The difficulties in separating the reflections at the upper levels made three-dimensional work look less promising.

The final x -, y -, and z -parameters together with the temperature factor, B , are given in Table 2. A list of calculated and observed structure factors and calculated phase angles are given in Table 3. Finally the electron density projections on (100) and (010) of the bromide and the projection on (100) on the iodide, are given in Figs. 1 and 2. These projections are based on the observed structure factors and the calculated phase angles.

DISCUSSION OF THE RESULTS

For each atom the B -parameters as well as the x -, y -, and z -parameters were chosen as those which gave a minimum value of $R' = \sum(|F_o| - k|F_c|)^2 / \sum|F_o|^2$, using program 6. The same B -parameter was not found for the same type of atom, the differences being small for the iodine, bromine, and cobalt, but rather large for the lighter atoms. The final x -, y -, and z -parameters were found using a fixed B -value, namely the averages for the same type of atom (I, Br, and N/O) within the same projection. These average B -values are given in Table 2 together with the final x -, y -, and z -parameters.

As no correction has been made for absorption, some absorption should be expected to be included in the temperature factor, especially in the case of

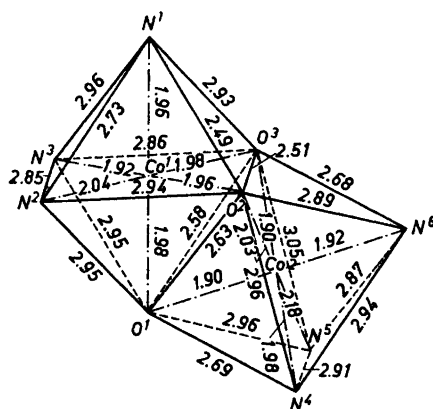


Fig. 3. Interatomic distances (Å) in the triol molecule (bromide).

the iodide. It should also be noted that the rather large number of hydrogen atoms is not included in the calculations.

As can be seen from Table 2, the agreement of the common z -parameters is better for the bromide than for the iodide. Also the discrepancy factor, $R = \sum |F_o - F_c| / \sum |F_o|$, is smaller for the bromide projections. Hence, because of the rather large uncertainty in the parameters of the iodide, only the distances in the bromide are used in the following discussion of the positions of the atoms.

The results of the present investigation fully confirm that the triol molecule is dinuclear as suggested by Werner.² The distances in the $\{(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3\}^{3+}$ -ion are given in Fig. 3, based on the x -, y -, and average z -parameters of the bromide. Some of the angles are given in Table 4. The Co—Co distance is 2.55 Å (the corresponding distance in the iodide is 2.57 Å). For comparison, it is of interest to look at the theoretical case where two mononuclear cobalt complexes with a regular octahedral shape and with a cobalt-ligand distance of 1.97 Å are put together with a common face. In this case the Co—Co distance is 2.28 Å.

From this it appears that the deviation from a regular shape mainly shows up in a longer Co—Co distance and shorter O—O distances, while the metal-ligand distances approach the usual ones found for cobalt complexes.

Table 4. Some angles ($^\circ$) in the triol molecule (bromide). The numbering of the atoms corresponds to that of Fig. 3.

$\text{N}^2\text{Co}^1\text{N}^3$	92	$\text{N}^3\text{Co}^1\text{N}^1$	99	$\text{N}^2\text{Co}^1\text{N}^1$	86
$\text{N}^3\text{Co}^1\text{O}^3$	94	$\text{N}^1\text{Co}^1\text{O}^2$	79	$\text{N}^1\text{Co}^1\text{O}^3$	96
$\text{O}^3\text{Co}^1\text{O}^2$	79	$\text{O}^2\text{Co}^1\text{O}^1$	84	$\text{O}^3\text{Co}^1\text{O}^1$	81
$\text{O}^2\text{Co}^1\text{N}^2$	95	$\text{O}^1\text{Co}^1\text{N}^3$	98	$\text{O}^1\text{Co}^1\text{N}^2$	94
$\text{N}^4\text{Co}^2\text{N}^5$	89	$\text{N}^5\text{Co}^2\text{N}^6$	89	$\text{N}^4\text{Co}^2\text{N}^6$	98
$\text{N}^5\text{Co}^2\text{O}^3$	97	$\text{N}^6\text{Co}^2\text{O}^2$	94	$\text{N}^6\text{Co}^2\text{O}^3$	89
$\text{O}^3\text{Co}^2\text{O}^2$	79	$\text{O}^2\text{Co}^2\text{O}^1$	84	$\text{O}^3\text{Co}^2\text{O}^1$	86
$\text{O}^2\text{Co}^2\text{N}^4$	95	$\text{O}^1\text{Co}^2\text{N}^5$	93	$\text{O}^1\text{Co}^2\text{N}^4$	88

The Co—Co distance is only slightly longer than in compounds with supposed Co—Co bonds, *e.g.* in $(\text{CO})_3\text{CoC}_6\text{F}_6(\text{CO})_3$: 2.47 Å,⁶ $\text{Co}_2(\text{CO})_8$: 2.52 Å,⁷ $\text{Co}_4(\text{CO})_{12}$: 2.50 Å,^{8,12} $\text{Co}_2(\text{CO})_6\text{C}_2(\text{C}_6\text{H}_5)_2$: 2.47 Å,⁹ $\text{Co}_2(\text{CO})_9\text{C}_2\text{H}_2$: 2.5 Å.¹⁰

The position of the triol molecule among the bromide ions is depicted in Fig. 4. The triol molecule lies in a hole in the bromide packing, surrounded by

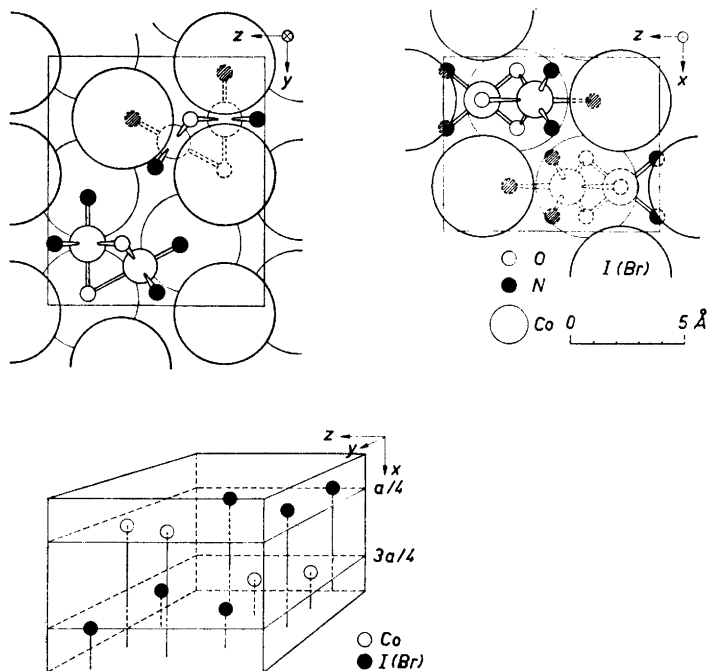


Fig. 4. The arrangement of the atoms in the unit cell of cobalt-triol iodide (bromide).

6 bromide ions, which lie almost in a plane (the plane of $\text{N}^1\text{Co}^1\text{O}^1\text{Co}^2\text{N}^6$), 3 bromide ions in a parallel plane above, and 3 in a parallel plane under the molecule. The average Br—Br distance (nearest neighbours) is 5.03 Å (all distances are between 4.6 and 5.8 Å). The average Br—N distance (nearest neighbours) is 3.58 Å (3.3–4.1 Å). The average Br—O distance (nearest neighbours) is 3.70 Å (3.6–3.9 Å).

The standard deviations estimated for the x -, y -, z -, and B -parameters of the bromide (using program 6) are:

$$\begin{aligned} \text{Projection on (100):} \quad & \text{Br: } \sigma(y) = 0.0010, \sigma(z) = 0.0012, \sigma(B) = 0.3 \text{ \AA}^2 \\ & \text{Co: } \sigma(y) = 0.0014, \sigma(z) = 0.0016, \sigma(B) = 0.4 \text{ \AA}^2 \\ & \text{N/O: } \sigma(y) = 0.005, \sigma(z) = 0.006, \sigma(B) = 1.4 \text{ \AA}^2 \end{aligned}$$

$$\begin{aligned} \text{Projection on (010):} \quad & \text{Br: } \sigma(x) = 0.002, \sigma(z) = 0.002, \sigma(B) = 0.4 \text{ \AA}^2 \\ & \text{Co: } \sigma(x) = 0.003, \sigma(z) = 0.002, \sigma(B) = 0.5 \text{ \AA}^2 \\ & \text{N/O: } \sigma(x) = 0.011, \sigma(z) = 0.009, \sigma(B) = 2.2 \text{ \AA}^2 \end{aligned}$$

which give estimated standard deviations of 0.02 Å for the Co—Co and Br—Br distances, 0.07 Å for the Co—N/O and Br—N/O distances, 0.09 Å for the N/O—N/O distances, and 3° for the angles in Table 4.

Table 5. Observed and calculated structure factors for cobalt-triol bromide. F_o is obtained from 1. and 2. level Weissenberg photographs, with the a -axis as axis of rotation. F_c is calculated on the basis of the final parameters from Table 2.

h	k	l	F_o	$ F_c $	h	k	l	F_o	$ F_c $
1	0	$\bar{4}$	54	42	1	5	0	82	69
1	0	$\bar{3}$	51	46					
1	0	$\bar{2}$	111	116	1	7	0	90	77
1	0	$\bar{1}$	32	27					
1	0	1	33	41	2	0	$\bar{5}$	90	86
1	0	2	113	134	2	0	$\bar{4}$	58	54
1	0	3	41	39	2	0	$\bar{3}$	87	75
1	0	4	50	47	2	0	$\bar{2}$	105	142
					2	0	2	76	97
1	1	$\bar{5}$	52	53	2	0	3	82	92
1	1	$\bar{3}$	59	62	2	0	4	79	93
1	1	$\bar{2}$	60	49	2	0	5	69	68
1	1	0	57	49					
1	1	2	48	54	2	1	$\bar{4}$	103	110
1	1	3	46	53	2	1	$\bar{2}$	81	82
1	1	5	46	53	2	1	2	80	90
					2	1	4	80	92
1	2	$\bar{5}$	76	66					
1	2	$\bar{4}$	47	52	2	2	$\bar{3}$	53	53
1	2	$\bar{3}$	53	51	2	2	$\bar{1}$	97	98
1	2	$\bar{2}$	61	60	2	2	0	55	56
1	2	$\bar{1}$	145	180	2	2	1	117	102
1	2	1	131	167	2	2	3	54	66
1	2	2	62	74					
1	2	3	40	36	2	3	$\bar{1}$	108	89
1	2	4	47	35	2	3	1	95	79
1	2	5	66	87					
					2	4	$\bar{2}$	107	109
1	3	$\bar{3}$	85	87	2	4	$\bar{1}$	48	35
1	3	$\bar{1}$	73	69	2	4	0	105	73
1	3	0	29	32	2	4	1	63	67
1	3	1	79	86	2	4	2	79	72
1	3	3	77	82					
					2	5	$\bar{2}$	116	95
1	4	$\bar{4}$	77	64	2	5	2	130	127
1	4	$\bar{2}$	45	32					
1	4	2	39	36					
1	4	4	72	66					

Table 6. Programs used for computer calculation.

- Program 1: Lorentz-polarization corrections of the observed reflections. D 17.¹¹
 Program 2: Centrosymmetrical Fourier summation.
 Program 3: Non-centrosymmetrical Fourier summation. D 43.¹¹
 Program 4: Drawing of Fourier maps.
 Program 5: Structure factor calculations with exponential approximation of the scattering factors.¹³ D 45.¹¹
 Program 6: Refinement based on minimizing $R' = \sum(|F_o| - k|F_c|)^2 / \sum|F_o|^2$. D 45.¹¹

The positions of the unit cells in the twin crystals can be described either in the way that part of the crystal is turned 180° round an axis perpendicular to the *ab*-plane, or 180° round the *a*-axis. It is not possible to distinguish between the two ways of twinning because $|F(hkl)| = |F(h\bar{k}l)|$.

As a control, a few of the upper level reflections, which it was possible to distinguish as separate pairs, have been listed in Table 5, together with the corresponding calculated structure factors.

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