584. *The Crystal Structure of Carbonatopenta-amminecobalt*(III) *Bromide Hydrate*

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The compound, carbonatopenta-amminecobalt(III) bromide hydrate, $[Co^{III}(NH_3)_5CO_3]Br,H_2O$, forms red, orthorhombic crystals with space group $Pna2_1$ and $a = 12{\cdot}37_0$, $b = 12{\cdot}14_4$, and $c = 6{\cdot}43_3$ Å. The co-ordination of the cobalt atom is octahedral, the carbonate ion acting as a monodentate ligand. The length of the Co–O bond is 1·99 Å. The five Co–N bond-lengths vary between 1·94 and 1·93 Å. The bromide ion appears to form six hydrogen-bonded contacts with five ammine groups and the water molecule. The presence of the two heavy atoms, coupled with the limited number of measurable intensities diffracted from the tiny specimens used, reduces the precision of this three-dimensional refinement.

This structure was solved under the mistaken impression that the crystals were those of a different (and, to us, more interesting) compound. As part of a programme of crystal-structure analyses of metal–peptide complexes,[1] we hoped to investigate the cobalt(II) complex of *dl*-alanylglycylglycine. According to Manyak *et al.*,[2] this complex may be isolated from an alkaline solution of the tripeptide and aquopentamminecobalt(III) bromide. After many attempts to crystallise the complex from aqueous alcoholic solutions over a wide range of compositions, a few tiny crystals were isolated from a viscous concentrate obtained by evaporation. There was insufficient material for chemical analysis. The preliminary *X*-ray data and density indicated a formula weight of 300 (calc. for $Co(NH_3)_2$ala·gly·gly,H_2O: 298). In view of the importance of structural information on any cobalt(II)–peptide complex, it was decided to proceed with the analysis despite the unfavourably small size of the crystals and the resulting paucity of the available data. It became apparent, only when the structure had been solved, that the complex contained no peptide at all, and that the composition was $[Co(NH_3)_5CO_3]Br,H_2O$.

Experimental

The complex was isolated as small, carmine-red, tabular crystals whose maximum dimension was 0·05 mm. The crystal data were as follows:

$CoBrCH_{17}N_5O_4$, $[Co(NH_3)_5CO_3]Br,H_2O$, $M = 302{\cdot}04$.
Orthorhombic, $a = 12{\cdot}370 \pm 0{\cdot}003$, $b = 12{\cdot}144 \pm 0{\cdot}003$, $c = 6{\cdot}433 \pm 0{\cdot}006$ Å, $U = 966{\cdot}4$ Å^3, $D_m = 2{\cdot}08$ g. cm.$^{-3}$, $Z = 4$, $D_x = 2{\cdot}075$ g. cm.$^{-3}$.
Space group: $Pna2_1$ or $Pnam$ from systematic absences, $Pna2_1$ confirmed by structure analysis.

The values of the unit-cell parameters were refined by a least-squares method similar to that of Cohen.[3] Spacings were measured on $0kl$ and hkL Weissenberg photographs taken with

[1] H. C. Freeman, G. Robinson, and J. C. Schoone, *Acta Cryst.*, 1964, **17**, 719; H. C. Freeman, J. C. Schoone, and J. G. Sime, *Ibid.*, 1965, **18**, 381; H. C. Freeman and M. R. Taylor, *Ibid.*, 1965, in the press.
[2] A. R. Manyak, C. B. Murphy, and A. E. Martell, *Arch. Biochem. Biophys.*, 1955, **59**, 373.
[3] M. U. Cohen, *Rev. Sci. Instr.*, 1935, **6**, 68; *ibid.*, 1936, **7**, 155; *Z. Krist.*, 1936, **94**, 288.

Cu K_α radiation and calibrated with Pt powder traces. Estimated standard deviations of the unit-cell parameters were obtained from the diagonal elements of the inverse matrix. The limits quoted are three times the standard deviations. Three-dimensional integrated intensity data were collected to a limit slightly outside the Cu K_α sphere, using Mo K_α radiation (*hkL* for $0 \leqslant L \leqslant 6$, *hKl* for $0 \leqslant K \leqslant 4$ and *0kl*). A total of **956** reflexions was measured photometrically. Owing to the small size of the crystals, **308** of these reflexions were too weak to be measured, even on Weissenberg films exposed for **100** hr. for **100°** oscillations.

Solution and Refinement.—Solution of the structure by conventional three-dimensional Patterson and Fourier methods was attempted as soon as it was realised that there were two heavy atoms in the asymmetric unit. The $F_{obs.}$ Fourier syntheses contained several spurious peaks, presumably due to the high proportion of unobservably weak reflexions. Difference syntheses contained no corresponding peaks, and confirmed the structure. The structure was refined by difference syntheses followed by full-matrix least-squares. The scattering curves used

TABLE 1

Atomic parameters in carbonatopenta-amminecobalt(III) bromide hydrate

Atom	x/a (σ_x, in Å)	y/b (σ_y, in Å)	z/c (σ_z, in Å)	B (σ_B)
Br	0·4686(0·004)	0·7607(0·004)	0·7500(—)	1·80(0·07)
Co	0·1981(0·004)	0·9166(0·004)	0·3305(0·006)	0·49(0·06)
N(1)	0·3243(0·024)	0·8396(0·027)	0·2182(0·034)	0·79(0·48)
N(2)	0·1056(0·028)	0·7955(0·027)	0·2221(0·039)	1·57(0·56)
N(3)	0·0725(0·028)	0·9983(0·029)	0·4230(0·032)	0·76(0·47)
N(4)	0·2890(0·029)	1·0398(0·027)	0·4119(0·029)	0·75(0·45)
N(5)	0·2127(0·029)	0·8464(0·028)	0·6072(0·027)	0·72(0·46)
O(1)	0·1689(0·026)	0·9795(0·029)	0·0607(0·031)	1·72(0·50)
O(2)	0·2951(0·030)	1·1067(0·029)	0·0061(0·032)	2·37(0·53)
O(3)	0·1568(0·026)	1·1030(0·031)	−0·1902(0·036)	2·84(0·60)
O(4_w)	0·4685(0·032)	1·0313(0·031)	0·7844(0·039)	3·70(0·70)
C	0·2086(0·036)	1·0580(0·031)	−0·0563(0·033)	0·93(0·56)

TABLE 2

Comparison of observed and calculated structure factors for carbonatopenta-amminecobalt(III) bromide hydrate. The data are arranged in groups of common *h*, *l*. Each line contains *k*, $|F_{obs.}|$, $|F_{calc.}|$. Unobserved reflexions are marked ×; seven observed reflexions omitted from the refinement are marked *.

h	*l*	*k*	$\lvert F_{obs}\rvert$	$\lvert F_{calc}\rvert$
0	0	2	19·1	12·1
		4	66·1	72·3
		6	110·9	127·3
		8	40·4	41·0
		10	19·8 ×	17·5
		12	64·6	77·3
1	0	1	51·1	38·9 *
		2	66·5	67·5 *
		3	23·9	23·2
		4	27·2	14·3
		5	33·8	39·0
		6	15·7 ×	11·9
		7	15·7 ×	17·9
		8	19·8 ×	32·5
		9	19·8 ×	18·5
		10	19·8 ×	41·5
		11	53·6	60·4
		12	26·5 ×	13·1
		13	31·3 ×	13·9
		14	51·4	53·1
2	0	0	59·9	41·1 *
		2	141·0	160·4
		3	80·1	91·2
		4	159·8	180·5
		5	12·7 ×	13·4
		6	15·7 ×	9·5
		7	29·4	28·8
		8	72·0	88·5
		9	19·8 ×	45·3
		10	47·7	48·0
3	0	1	114·9	120·0
		2	27·5	21·9
		3	12·7 ×	9·8
		4	40·4	41·2
3	0	5	23·5	19·0
		6	15·7 ×	39·4
		7	70·5	81·9
		8	19·8 ×	6·1
		9	19·8 ×	36·6
		10	37·5	50·1
4	0	0	107·2	105·3
		1	108·7	112·6
		2	40·4	39·3
		3	30·5	18·4
		4	44·4	50·9
		5	87·0	96·0
		6	62·8	73·6
		7	73·4	81·2
		8	19·8 ×	28·6
		9	19·8 ×	3·8
		10	40·8	44·2
5	0	1	39·3	40·3
		2	12·7 ×	0·9
		3	15·7 ×	11·3
		4	32·7	32·7 *
		5	85·6	91·0
		6	19·8 ×	3·8
		7	19·8 ×	33·0
		8	19·8 ×	48·0
		9	29·7	32·2
		10	26·5 ×	23·3
		11	47·0	51·9
6	0	0	94·0	92·7
		1	36·4	34·9
		2	15·7 ×	5·2
		3	174·1	182·2
		4	15·7 ×	0·9
		5	37·1	37·0 *
6	0	6	51·4	49·4
		7	19·8 ×	27·6
		8	19·8 ×	11·8
		9	64·6	71·6
7	0	1	44·1	43·0
		2	43·3	40·2
		3	15·7 ×	4·1
		4	19·8 ×	7·3
		5	19·8 ×	14·8
		6	19·8 ×	18·0
		7	34·2	30·1
8	0	0	92·2	98·7
		1	112·7	123·5
		2	46·3	51·8
		3	29·7	32·0
		4	41·9	24·3
		5	49·2	52·9
		6	39·3	33·7
		7	68·7	73·7
9	0	1	19·8 ×	4·2
		2	41·9	45·8
		3	34·2	35·0
		4	47·7	51·1
10	0	0	56·9	49·8
		1	46·6	41·8
		2	45·2	45·7
		3	47·7	52·4
		4	49·2	51·6
		5	54·7	61·7
		6	26·5 ×	29·7
		7	47·0	46·2
11	0	1	26·5 ×	27·0
		2	39·7	40·2
		3	26·5 ×	12·2
		4	26·5 ×	3·6
		5	26·5 ×	0·6
		6	31·3 ×	1·7
		7	31·3 ×	30·8
		8	53·3	60·0
12	0	0	67·6	75·9
		1	26·5 ×	14·5
		2	26·5 ×	16·2
		3	56·9	63·5
		4	31·3 ×	9·0
		5	31·3 ×	6·6
		6	62·4	65·2
0	1	1	48·5	65·9
		3	188·0	230·5
		5	37·1	46·5
		7	65·7	68·5
		9	103·2	116·8
		11	41·5	35·6
		13	19·6 ×	7·0
		15	48·5	51·6
1	1	1	73·8	76·1 *
		2	36·0	47·7
		3	19·8 ×	9·2
		4	19·8 ×	16·9
		5	28·3	29·6
		6	29·7	34·1
		7	38·2	42·7
		8	66·5	74·6
		9	16·8 ×	16·5
		10	26·4	27·8
		11	39·7	44·0
1	1	12	32·3	29·2
		13	33·4	31·2
		14	34·5	32·3
2	1	0	110·5	94·7
		1	152·4	151·5
		2	29·7	16·9
		3	63·9	66·7
		4	74·2	71·7
		5	91·4	95·8
		6	55·5	62·7
		7	101·0	109·7
		8	16·8 ×	6·8
		9	29·7	33·2
		10	17·6 ×	16·2
		11	56·9	60·2
		12	34·2	36·3
		13	40·4	40·0
		1	53·3	45·7
		2	74·9	73·4
		3	29·7	19·9
		4	20·5	18·9
		5	37·8	33·1
		6	13·7	8·1
		7	42·2	49·0
		8	25·3	22·5
		9	17 6	20·4
		10	51·1	54·4
		11	18·6 ×	3·0
		12	37·5	41·6
4	1	0	97·7	84·3
		1	112·0	100·2
		2	114·2	105·6
		3	90·7	88·7
		4	120·5	113·3

TABLE 2 (*Continued*)

h	l	k	$\|F_{obs}\|$	$\|F_{calc}\|$
4	1	5	38·2	37·0
		6	44·1	48·1
		7	43·0	40·6
		8	58·4	64·7
		9	38·2	42·5
		10	51·1	58·0
		11	13·6×	17·1
		12	19·6×	25·4
		13	20·8×	12·8
		14	31·2	28·7
5	1	1	41·5	34·5
		2	70·9	64·2
		3	20·6	21·7
		4	83·0	79·2
		5	45·5	43·2
		6	16·8×	20·3
		7	16·8×	28·1
		8	62·1	66·3
		9	17·6×	15·3
		10	38·2	32·2
		11	27·9	30·2
		12	19·6×	19·8
		13	20·8×	28·0
		14	33·8	36·9
6	1	0	149·5	141·1
		1	13·7×	10·5
		2	33·1	30·7
		3	81·2	79·2
		4	62·1	63·2
		5	31·6	22·6
		6	112·0	117·2
		7	26·1	22·5
		8	34·9	35·8
		9	32·0	30·9
		10	18·6×	24·2
		11	19·6×	5·3
		12	58·4	65·6
7	1	1	22·4	20·5
		2	41·9	39·8
		3	16·8×	13·9
		4	49·9	54·4
		5	59·9	58·0
		6	16·8×	22·9
		7	17·6×	24·6
		8	17·6×	21·0
		9	28·3	38·5
		10	29·4	32·3
		11	46·3	49·5
8	1	0	58·8	56·3
		1	26·1	31·3
		2	67·9	66·8
		3	59·5	60·3
		4	91·4	91·7
		5	17·6×	18·0
		6	33·1	26·2
		7	26·8	24·9
		8	54·0	54·9
		9	36·4	38·7
		10	55·5	59·1
9	1	1	70·1	71·8
		2	16·8×	14·8
		3	17·6×	10·4
		4	17·6×	14·0
		5	17·6×	16·4
		6	17·6×	16·8
		7	55·8	56·6
10	1	0	55·8	54·4
		1	55·5	50·3
		2	62·8	65·4
		3	37·5	34·9
		4	52·9	45·2
		5	45·2	42·6
		6	36·4	37·4
		7	37·1	36·9
		8	38·6	32·3
		9	31·2	35·2
		10	20·8×	28·4
		11	34·5	26·8
11	1	1	33·8	30·7
		2	18·6×	10·5
		3	18·6×	4·1
		4	18·6×	24·1
		5	50·3	51·3
		6	19·6×	7·4
		7	19·6×	27·1
11	1	8	20·8×	13·3
		9	20·8×	12·9
		10	20·8×	20·6
		11	46·3	38·9
12	1	0	52·5	69·7
		1	37·1	33·2
		2	18·6×	20·7
		3	58·0	59·3
		4	19·6×	22·0
		5	19·6×	8·9
		6	50·3	58·1
		7	20·8×	9·8
		8	20·8×	11·4
		9	49·6	46·8
13	1	1	19·6×	20·7
		2	30·1	32·0
14	1	0	32·0	28·9
		1	31·2	26·7
		2	31·2	28·5
		3	31·6	28·5
		4	33·1	34·6
		5	20·8×	34·8
		6	20·8×	26·4
		7	40·8	35·3
15	1	1	20·8×	9·3
		2	20·8×	27·6
		3	20·8×	11·4
		4	43·0	40·2
16	1	0	39·7	28·6
		1	41·5	35·3
0	2	0	222·9	186·5
		2	190·6	159·7
		4	59·9	63·1
		6	123·8	134·4
		8	43·7	40·2
		10	40·8	41·6
1	2	1	42·6	31·3
		2	75·3	71·9
		3	24·6	16·5
		4	47·0	48·1
		5	59·5	65·9
		6	13·2×	17·0
		7	13·2×	11·3
		8	62·8	72·9
		9	17·1×	27·7
		10	44·1	45·6
		11	44·8	44·6
		12	17·1×	12·3
		13	33·8	33·9
2	2	0	138·8	119·6
		1	51·1	40·7
		2	96·2	86·9
		3	40·4	44·8
		4	110·9	112·8
		5	23·1	21·0
		6	83·0	87·7
		7	13·2×	25·0
		8	67·6	70·7
		9	55·1	53·4
		10	55·8	55·2
		11	17·1×	17·1
		12	17·1×	16·3
		13	17·8×	18·9
		14	40·8	31·1
3	2	1	80·8	68·9
		2	43·0	36·9
		3	26·1	19·4
		4	77·1	69·2
		5	69·4	70·3
		6	19·8	20·4
		7	74·2	79·7
		8	38·2	41·0
		9	47·7	46·9
		10	25·7	34·8
		11	36·4	32·0
		12	28·6	20·0
		13	30·1	35·0
4	2	0	65·7	59·8
		1	59·1	54·4
		2	59·9	46·0
		3	71·2	67·0
		4	81·9	75·0
		5	77·1	81·5
4	2	6	44·8	48·9
		7	71·2	68·7
		8	47·0	43·2
		9	44·8	47·1
		10	36·4	28·5
		11	47·4	48·9
		12	17·1×	29·2
		13	27·2	20·1
5	2	1	43·7	40·5
		2	13·2×	11·2
		3	28·3	23·4
		4	13·2×	5·2
		5	96·2	92·9
		6	13·2×	19·4
		7	55·1	60·6
		8	32·3	33·7
		9	17·1×	2·8
		10	17·1×	31·3
		11	49·6	53·7
6	2	0	67·6	59·3
		1	85·9	79·7
		2	29·0	20·0
		3	129·3	120·4
		4	32·3	30·0
		5	56·9	51·3
		6	47·7	47·0
		7	44·1	45·8
		8	17·1×	22·5
		9	69·4	70·5
		10	17·1×	14·5
		11	17·1×	13·3
		12	26·8	27·1
7	2	1	47·7	42·5
		2	36·4	35·1
		3	13·2×	20·4
		4	13·2×	21·0
		5	35·3	29·5
		6	17·1×	7·7
		7	39·3	37·5
		8	52·2	50·9
8	2	0	55·5	49·7
		1	90·0	86·1
		2	39·3	30·1
		3	62·4	62·0
		4	39·3	24·7
		5	72·0	67·2
		6	50·3	45·4
		7	54·4	52·7
		8	17·1×	21·5
		9	17·1×	25·1
		10	17·8×	19·5
		11	36·4	33·7
9	2	1	17·1×	20·7
		2	51·8	48·8
		3	17·1×	12·0
		4	63·2	61·2
		5	17·1×	18·4
		6	17·1×	17·1
		7	17·1×	13·3
		8	37·8	39·1
		9	17·1×	8·6
		10	47·4	46·3
10	2	0	51·1	41·4
		1	49·9	45·7
		2	42·6	39·5
		3	49·9	49·9
		4	32·0	24·6
		5	43·0	44·1
		6	43·7	41·0
		7	52·5	47·1
		8	36·7	33·9
11	2	1	17·1×	20·4
		2	50·3	44·8
		3	17·1×	6·2
		4	29·7	33·1
		5	17·1×	12·3
		6	17·1×	20·4
		7	17·8×	26·7
		8	58·0	51·3
12	2	0	56·9	49·2
		1	17·1×	25·4
		2	33·1	30·0
		3	52·5	52·3
12	2	4	38·2	35·9
		5	17·8×	15·7
		6	17·8×	43·1
		7	17·8×	19·7
		8	17·8×	26·3
		9	41·1	37·6
13	2	1	17·8×	26·3
		2	17·8×	10·6
		3	17·8×	8·1
		4	36·7	31·5
		5	37·1	33·4
14	2	0	53·3	51·6
		1	30·9	27·9
		2	39·3	34·0
		3	34·2	32·7
		4	46·6	31·6
15	2	1	44·4	35·2
0	3	1	73·8	59·2
		3	123·0	125·7
		5	93·3	97·1
		7	64·3	74·7
		9	68·7	62·0
		11	38·2	35·7
		13	29·7	31·9
		15	40·0	40·6
1	3	1	90·3	77·6
		2	36·0	33·2
		3	49·2	47·3
		4	43·0	45·4
		5	59·5	62·3
		6	20·6×	23·3
		7	45·9	46·5
		8	55·1	52·6
		9	18·1×	23·7
		10	17·4×	29·5
		11	26·1	32·9
		12	32·0	30·6
		13	31·2	30·1
2	3	0	63·5	49·5
		1	112·0	101·2
		2	65·7	59·0
		3	84·8	85·1
		4	31·6	26·3
		5	53·6	50·6
		6	44·1	46·5
		7	61·7	60·8
		8	18·1×	20·6
		9	56·6	60·6
		10	17·4×	22·5
		11	39·7	42·2
		12	17·1×	28·5
		13	17·1×	28·2
		14	17·1×	14·8
		15	32·3	30·4
3	3	1	73·8	65·2
		2	93·3	87·6
		3	20·6×	4·3
		4	63·9	58·4
		5	41·9	36·1
		6	20·6×	36·0
		7	32·3	29·7
		8	41·5	36·0
		9	17·4×	16·4
		10	45·9	39·3
		11	31·2	22·3
		12	25·7	24·3
		13	26·8	33·4
		14	35·6	38·2
4	3	0	96·2	85·5
		1	70·5	64·4
		2	84·5	76·7
		3	71·6	65·9
		4	62·4	54·2
		5	46·6	42·1
		6	55·5	54·9
		7	48·5	48·1
		8	45·2	48·2
		9	17·4×	18·5
		10	17·4×	23·9
		11	17·1×	23·8
		12	39·7	44·5
5	3	1	20·6×	10·3
		2	81·5	80·2
		3	20·6×	20·6
5	3	4	56·2	50·5
		5	36·0	31·5
		6	18·1×	15·9
		7	18·1×	18·5
		8	43·3	52·2
		9	17·4×	22·7
		10	32·0	35·7
6	3	0	127·4	118·1
		1	30·9	29·3
		2	61·0	53·9
		3	53·6	43·5
		4	57·3	58·9
		5	38·6	37·2
		6	78·2	70·3
		7	18·1×	18·2
		8	45·9	44·0
		9	29·7	24·4
		10	48·5	49·0
		11	17·1×	2·4
		12	38·2	37·7
7	3	1	43·7	36·0
		2	44·1	41·8
		3	20·6×	2·2
		4	37·5	34·9
		5	45·5	41·4
		6	18·1×	15·7
		7	43·3	41·3
		8	27·9	29·2
		9	33·8	34·9
8	3	0	42·6	36·8
		1	18·1×	20·4
		2	64·6	63·1
		3	43·0	40·3
		4	70·1	65·1
		5	32·0	26·3
		6	60·6	58·0
		7	17·4×	17·2
		8	49·9	48·4
		9	32·0	34·9
9	3	1	62·8	56·6
		2	18·1×	7·6
		3	30·1	23·8
		4	17·4×	17·3
		5	53·3	48·7
		6	17·4×	7·1
		7	49·6	45·4
10	3	0	84·5	84·6
		1	34·9	32·8
		2	27·2	30·3
		3	35·6	41·4
		4	55·1	50·9
		5	17·1×	23·0
		6	17·1×	18·9
		7	17·1×	18·0
		8	27·2	32·3
		9	28·3	35·2
11	3	1	51·4	44·2
		2	17·1×	19·0
		3	17·1×	9·7
		4	28·3	21·7
		5	46·3	43·1
12	3	0	49·6	46·7
		1	17·1×	30·0
		2	17·1×	30·4
		3	44·8	38·3
		4	36·4	35·5
		5	17·1×	21·4
		6	26·8	34·0
13	3	1	17·1×	22·8
		2	17·1×	27·0
		3	17·1×	7·9
		4	32·7	28·1
14	3	0	29·0	33·8
0	4	0	29·0	87·7
		2	97·3	102·6
		4	86·7	84·9
		6	66·1	69·9
		8	52·9	55·5
		10	39·3	42·8
		12	42·2	34·2
1	4	1	28·3	27·8
		2	53·6	55·7

TABLE 2 (*Continued*)

h	l	k	$\|F_{obs}\|$	$\|F_{calc}\|$
1	4	3	13·9×	15·2
		4	61·7	70·5
		5	27·2	31·4
		6	28·6	27·4
		7	20·9	24·9
		8	26·8	26·2
		9	25·7	26·7
		10	34·5	33·9
2	4	0	113·8	108·2
		1	49·9	40·1
		2	64·3	57·9
		3	33·4	38·3
		4	66·5	64·4
		5	29·0	29·2
		6	64·6	72·1
		7	13·9×	19·8
		8	32·7	28·3
		9	13·9×	18·1
		10	43·3	45·5
		11	34·5	32·6
		12	38·6	45·7
3	4	1	81·5	76·0
		2	55·8	52·5
		3	13·9×	12·3
		4	38·9	34·5
		5	47·7	53·5
		6	13·9×	15·9
		7	19·1	22·3
		8	32·0	35·1
		9	13·9×	24·5
		10	17·1×	15·7
		11	41·5	45·9
4	4	0	43·0	37·2
		1	44·1	44·2
		2	41·9	42·0
		3	90·3	86·8
		4	51·1	48·4
		5	38·9	37·1
		6	39·3	38·1
		7	43·0	43·5
		8	41·9	37·6
		9	52·2	51·4
		10	17·1×	22·3
		11	18·3×	23·1
		12	19·3×	17·0
		13	19·3×	16·4
		14	19·3×	16·8
		15	30·9	39·4
5	4	1	67·2	70·5
		2	13·9×	9·4
		3	33·4	30·9
		4	13·9×	10·8
		5	31·2	27·5
		6	13·9×	20·5
		7	38·9	37·6
		8	29·7	27·2
		9	17·1×	15·2
		10	18·3×	21·0
		11	32·0	31·9
		12	19·3×	18·1
		13	34·5	39·2
6	4	0	55·1	49·6
		1	88·9	85·4
		2	44·8	36·9
		3	70·5	64·3
		4	23·9	23·6
		5	61·0	58·2
		6	13·9×	13·7
		7	45·9	40·5
		8	17·1×	22·5
		9	38·2	41·1
		10	18·3×	26·9
		11	37·1	40·9

h	l	k	$\|F_{obs}\|$	$\|F_{calc}\|$
7	4	1	27·9	27·3
		2	29·4	23·5
		3	13·9×	11·3
		4	40·8	39·5
		5	30·5	35·8
		6	13·9×	17·0
		7	27·5	26·8
8	4	0	45·9	36·8
		1	56·6	52·3
		2	13·9×	17·2
		3	70·1	71·4
		4	30·1	19·9
		5	36·0	36·4
		6	39·3	40·5
		7	49·2	48·0
		8	18·3×	17·5
		9	40·4	37·6
9	4	1	13·9×	0·2
		2	50·3	48·9
		3	13·9×	5·6
		4	44·8	44·7
		5	17·1×	16·4
		6	17·1×	9·8
		7	18·3×	5·0
		8	46·3	43·5
10	4	0	45·9	42·6
		1	36·4	38·1
		2	17·1×	12·4
		3	41·1	40·4
		4	17·1×	23·9
		5	38·9	34·7
		6	40·4	39·5
11	4	1	17·1×	17·4
		2	45·9	40·6
		3	18·3×	5·8
		4	40·4	39·2
12	4	0	29·7	21·5
		1	32·7	30·3
		2	32·3	28·0
		3	33·4	31·1
		4	36·0	35·2
13	4	1	19·3×	26·8
		2	29·0	28·9
14	4	0	41·1	41·5
		1	19·3×	16·4
		2	19·3×	29·4
		3	34·9	37·8
16	4	0	32·3	26·2
0	5	1	76·4	76·5
		3	51·8	57·3
		5	76·0	77·5
		7	73·4	80·9
		9	29·4	21·3
		11	35·3	38·4
		13	32·0	34·3
1	5	1	15·2×	25·6
		2	15·2×	6·9
		3	15·2×	15·5
		4	22·8	28·3
		5	44·4	47·0
		6	29·0	28·0
		7	47·0	54·3
		8	15·4×	16·1
		9	15·4×	2·1
		10	28·3	35·7
		11	28·6	24·2

h	l	k	$\|F_{obs}\|$	$\|F_{calc}\|$
1	5	12	16·0×	20·1
		13	32·0	27·9
2	5	0	24·6	19·4
		1	49·6	43·4
		2	32·7	34·3
		3	89·6	92·2
		4	47·7	47·4
		5	36·0	38·3
		6	15·2×	20·9
		7	25·3	27·4
		8	29·7	34·5
		9	57·3	63·0
3	5	1	28·3	28·3
		2	41·9	41·2
		3	15·2×	13·8
		4	28·6	22·5
		5	15·2×	23·8
		6	15·2×	3·5
		7	15·2×	17·9
		8	45·5	51·2
		9	15·4×	13·0
		10	15·4×	19·6
		11	32·3	33·6
4	5	0	111·6	107·4
		1	57·3	50·3
		2	28·3	28·6
		3	31·6	33·0
		4	15·2×	19·8
		5	44·4	40·5
		6	69·0	69·9
		7	23·9	30·4
		8	15·4×	11·4
		9	15·4×	15·3
		10	15·4×	15·8
		11	16·9×	15·2
		12	38·6	43·9
5	5	1	15·2×	12·6
		2	37·5	32·9
		3	15·2×	16·9
		4	27·9	30·7
		5	15·2×	18·6
		6	15·4×	13·9
		7	15·4×	15·9
		8	37·5	35·2
		9	15·4×	14·7
		10	50·7	43·2
6	5	0	47·0	43·1
		1	29·0	28·4
		2	70·5	70·0
		3	26·1	16·2
		4	66·5	63·1
		5	28·3	24·6
		6	34·2	30·9
		7	24·2	27·9
		8	54·0	55·1
		9	15·4×	12·3
		10	29·7	34·9
7	5	1	15·2×	21·5
		2	15·2×	17·6
		3	15·2×	11·3
		4	15·4×	19·3
		5	15·4×	10·0
		6	15·4×	1·1
		7	49·2	47·0
		8	25·7	32·5
8	5	0	74·9	71·5
		1	15·4×	17·5
		2	26·8	25·9

h	l	k	$\|F_{obs}\|$	$\|F\|_{calc}$
8	5	3	30·9	34·7
		4	37·8	37·2
		5	15·4×	22·3
		6	61·0	62·6
		7	15·4×	21·7
		8	16·9×	19·6
		9	26·8	33·4
9	5	1	23·1	24·6
		2	15·4×	14·5
		3	15·4×	7·5
		4	15·4×	8·4
		5	47·7	50·6
		6	15·4×	2·0
		7	16·9×	28·4
		8	16·9×	12·8
		9	16·9×	19·1
		10	16·9×	5·1
		11	30·1	35·5
10	5	0	38·9	32·8
		1	15·4×	6·6
		2	44·8	46·0
		3	51·1	51·1
		4	15·4×	23·1
		5	16·9×	15·2
		6	25·3	31·0
		7	16·9×	11·6
		8	16·9×	17·5
		9	16·9×	33·6
		10	32·0	19·5
11	5	1	37·8	36·3
12	5	0	16·9×	20·8
		1	36·4	32·8
		2	34·2	34·6
14	5	0	33·8	43·4
0	6	0	15·5×	27·8
		2	64·8	61·7
		4	74·5	86·6
		6	52·8	23·7
		8	50·9	48·5
		10	47·6	48·9
1	6	1	15·5×	10·0
		2	15·5×	26·8
		3	14·7×	15·2
		4	43·8	47·6
		5	14·7×	9·8
		6	14·7×	11·2
		7	27·7	33·3
		8	14·7×	24·7
		9	14·7×	12·8
		10	31·8	32·3
2	6	0	71·9	80·3
		1	26·6	30·3
		3	14·7×	8·4
		4	28·1	23·6
		5	23·2	26·3
		6	71·2	72·7
		7	23·2	30·9
		8	14·7×	22·7
		9	14·7×	14·7
		10	16·7×	6·2
		11	30·0	25·3
		12	31·5	43·3
3	6	1	33·0	31·1
		2	25·5	25·6
		3	14·7×	12·7
		4	14·7×	19·3

h	l	k	$\|F_{obs}\|$	$\|F_{calc}\|$
3	6	5	46·1	43·5
		6	28·5	20·0
		7	14·7×	14·0
		8	28·5	27·0
		9	27·0	19·5
		10	16·7×	4·1
		11	34·5	37·5
4	6	0	14·7×	26·8
		1	14·7×	13·1
		2	37·5	35·3
		3	73·4	72·5
		4	35·6	32·9
		5	14·7×	18·3
		6	14·7×	17·7
		7	14·7×	1·4
		8	14·7×	22·7
		9	57·3	58·6
5	6	1	44·6	42·6
		2	14·7×	8·6
		3	14·7×	14·4
		4	14·7×	12·5
		5	22·1	17·4
		6	14·7×	8·7
		7	45·3	41·4
6	6	0	14·7×	5·8
		1	64·0	61·6
		2	27·3	26·0
		3	14·7×	1·2
		4	30·3	20·5
		5	52·4	50·0
		6	26·6	11·4
		7	56·9	52·9
7	6	1	22·8	21·6
		2	14·7×	14·5
		3	14·7×	6·5
		4	26·6	30·4
		5	14·7×	24·5
		6	14·7×	8·9
		7	25·1	25·8
8	6	0	29·6	24·1
		1	35·6	29·8
		2	14·7×	8·3
		3	62·9	58·1
		4	25·1	23·0
		5	14·7×	20·4
		6	33·3	38·3
		7	16·7×	11·3
		8	27·3	16·6
		9	38·9	39·8
9	6	1	14·7×	9·5
		2	31·1	32·8
		3	14·7×	17·6
		4	16·7×	26·5
		5	16·7×	2·2
		6	16·7×	16·0
		7	16·7×	1·2
		8	41·6	37·8
10	6	0	37·1	40·4
		1	16·7×	23·6
		2	16·7×	6·6
		3	34·5	30·4
		4	16·7×	6·8
		5	16·7×	25·0
		6	42·7	41·3
11	6	1	16·7×	8·1
		2	16·7×	23·5
		3	16·7×	3·8
		4	44·9	38·8

were those of Berghuis *et al.*[4] for carbon, oxygen, and nitrogen, and those of Watson and Freeman[4] for cobalt(0) and bromide. The real part of the dispersion correction [5] was applied to the cobalt(0) curve. For the least-squares refinement, individual weights for the observed reflexions were read from a plot of $|F_{obs.} - F_{calc.}|$ against $|F_{obs.}|$, calculated at the end of the difference-synthesis refinement. The unobservably weak reflexions were given zero weights, as were seven inner reflexions whose intensities had been measured on photographs taken with Cu K_{α} instead of

[4] "International Tables for *X*-ray Crystallography," 1962, vol. III, p. 201.
[5] C. H. Dauben and D. H. Templeton, *Acta Cryst.*, 1955, **8**, 841.

TABLE 3

Bond-lengths and angles in carbonatopenta-amminecobalt(III) bromide hydrate

Bond	Length, l (Å)	$\sigma(l)$ (Å)	Angle	θ	$\sigma(\theta)$	Angle	θ	$\sigma(\theta)$
Co–N(1)	1·96	0·03	N(1)–Co–N(2)	88·6°	1·2°	N(3)–Co–N(4)	89·3°	1·2°
Co–N(2)	1·99	0·03	N(1)–Co–N(3)	175·9	1·2	N(3)–Co–N(5)	91·0	1·2
Co–N(3)	1·94	0·03	N(1)–Co–N(4)	90·3	1·2	N(3)–Co–O(1)	85·6	1·2
Co–N(4)	1·94	0·03	N(1)–Co–N(5)	93·0	1·2	N(4)–Co–N(5)	92·1	1·2
Co–N(5)	1·98	0·03	N(1)–Co–O(1)	90·4	1·2	N(4)–Co–O(1)	92·6	1·2
Co–O(1)	1·93	0·03	N(2)–Co–N(3)	91·4	1·2	N(5)–Co–O(1)	174·2	1·2
O(1)–C	1·31	0·05	N(2)–Co–N(4)	175·0	1·2	Co–O(1)–C	137·2	2·3
O(2)–C	1·29	0·05	N(2)–Co–N(5)	92·8	1·2	O(1)–C–O(2)	117·9	3·4
O(3)–C	1·20	0·05	N(2)–Co–O(1)	82·5	1·2	O(1)–C–O(3)	122·7	3·4
						O(2)–C–O(3)	117·2	3·4

TABLE 4

Hydrogen bonds and short contacts

(* indicates short contacts which are not hydrogen bonds)

Symmetry-related atoms are indicated by superscripts:

Superscript	Position	Superscript	Position
—	$x, \quad y, z$	ix	$\frac{1}{2} - x, y - \frac{1}{2}, z + \frac{1}{2}$
i	$x, \quad y, z - 1$	x	$\frac{1}{2} - x, y + \frac{1}{2}, z - \frac{1}{2}$
ii	$x, \quad y, z + 1$	xi	$x - \frac{1}{2}, 1\frac{1}{2} - y, z - 1$
iii	$\bar{x}, \quad \bar{y}, z - \frac{1}{2}$	xii	$x - \frac{1}{2}, 1\frac{1}{2} - y, z$
iv	$\bar{x}, \quad \bar{y}, z + \frac{1}{2}$	xiii	$x + \frac{1}{2}, 1\frac{1}{2} - y, z$
v	$\bar{x}, 2 - y, z - \frac{1}{2}$	xiv	$x + \frac{1}{2}, 1\frac{1}{2} - y, z + 1$
vi	$\bar{x}, 2 - y, z + \frac{1}{2}$		
vii	$1 - x, 2 - y, z - \frac{1}{2}$		
viii	$1 - x, 2 - y, z + \frac{1}{2}$		

Bond or contact	Length (Å)	Bond or contact	Length (Å)	Bond or contact	Length Å
Br ······· H–N(1^{ii})	3·63	N(3)–H ··· Br^{x}	3·41	O(2) ······ H–N(4)	2·73
Br ······· H–N(2^{xiv})	3·54	N(3)–H ··· O(3^{ii})	2·98	O(2) ······ H–N(5^{v})	2·98
Br ······· H–N(3^{ix})	3·41	N(3) ······ O(1^{vi})	3·13 *	O(2) ······ H–O(4_w^{i})	2·73
Br ······· H–N(5)	3·46	N(3) ······ O(3^{vi})	3·18 *	O(2) ······ N(2^{x})	3·18 *
Br ······· H–N(5^{xiii})	3·41				
Br ······· H–O(4_w)	3·29	N(4)–H ··· O(2)	2·73	O(3) ······ H–N(1^{x})	2·94
		N(4) ······ O(3^{ii})	3·13 *	O(3) ······ H–N(3^{i})	2·98
N(1)–H ··· Br^{i}	3·63			O(3) ······ N(3^{v})	3·18 *
N(1)–H ··· O(3^{ix})	2·94	N(5)–H ··· Br	3·46	O(3) ······ N(4^{i})	3·13 *
N(1)–H ··· O(4_w^{vii})	3·03	N(5)–H ··· Br^{xii}	3·41		
		N(5)–H ··· O(2^{ix})	2·98	O(4_w)–H ··· Br	3·29
N(2)–H ··· Br^{xi}	3·54			O(4_w) ····· H–N(1^{viii})	3·03
N(2) ····· O(2^{ix})	3·18 *	O(1) ····· N(3^{v})	3·13 *	O(4_w)–H ··· O(2^{ii})	2·73

Angles at hydrogen-bonded atoms

Angle		Angle		Angle	
N(1^{ii}) ···· Br ··· N(2^{xiv})	65°	Br^{i} ····· N(1) ··· O(3^{ix})	82°	C–O(2) ·········· N(4)	98°
··· N(3^{iv})	84	··· O(4_w^{vii})	81	··· N(5^{x})	119
··· N(5)	72	O(3^{ix}) ··· N(1) ··· O(4_w^{viii})	114	··· O(4_w^{i})	110
··· N(5^{xiii})	139			N(4) ······ O(2) ··· N(5^{x})	95
··· O(4_w)	71	Co–N(2) ········ Br^{xi}	136	··· O(4_w^{i})	115
N(2^{xiv}) ··· Br ··· N(3^{ix})	67			N(5^{x}) ······ O(2) ··· O(4_w^{i})	118
··· N(5)	136	Co–N(3) ········ Br^{x}	120		
··· N(5^{xiii})	75	··· O(3^{ii})	101	C–O(3) ··········· N(1^{x})	123
··· O(4_w)	98	Br^{x} ····· N(3) ··· O(3^{ii})	86	··· N(3^{i})	126
N(3^{ix}) ···· Br ··· N(5)	103			N(1^{x}) ····· O(3) ··· N(3^{i})	106
··· N(5^{xiii})	82	Co–N(4) ········ O(2)	89		
··· O(4_w)	155			Br ······· O(4_w) ··· N(1^{viii})	120
N(5) ····· Br ··· N(5^{xiii})	149	Co–N(5) ········ Br	117	··· O(2^{ii})	112
··· O(4_w)	74	··· Br^{xii}	110	N(1^{viii}) ··· O(4_w) ··· O(2^{ii})	124
N(5^{xiii}) ··· Br ··· O(4_w)	113	··· O(2^{ix})	103		
Co–N(1) ······· Br^{i}	146	Br ····· N(5) ··· Br^{xii}	129		
··· O(3^{ix})	117	··· O(2^{ix})	78		
··· O(4_w^{vii})	112	Br^{xii} ···· N(5) ··· O(2^{ix})	70		

Mo K_α radiation. The final reliability factor was $R = 0{\cdot}095$ for the observed data, and $R = 0{\cdot}138$ for the complete data. The poor agreement for $F_{\text{unobs.}}$ was to be expected from the large values of $F_{\text{min.}}$ and the consequently large uncertainties in the values of $F_{\text{unobs.}}$. It was noted that the thermal parameters were unusually low for this type of structure. The least-squares refinement was therefore repeated (i) with the observed reflexions alone, and with weights $w = 1/(1 + F_{\text{obs.}}^2/8F_{\text{min.}})$, and (ii) with the observed reflexions weighted as in the original refinement, and with the unobservably weak reflexions included as $0{\cdot}67F_{\text{min.}}$ with weights $18/F_{\text{min.}}^2$. The results and refinement criteria of these refinements were not significantly different from those obtained originally. The final atomic co-ordinates and isotropic thermal parameters from the first refinement are shown in Table 1, and the observed and calculated structure factors in Table 2.

Description of Structure.—The carbonate ion acts as a monodentate, rather than a bidentate ligand. The co-ordination about the cobalt atom is octahedral, the donor atoms being one oxygen of the carbonate ion and the nitrogens of five ammine groups. The carbonate ion is twisted out of the plane of CoN(2)N(5)N(4)O(1), the Co–O(1)–C angle being 137°. There is an internal hydrogen bond between ammine nitrogen N(4) and O(2) of the carbonate ion. The complex-ion is illustrated in Figure 1. The bond-lengths and angles in the complex are shown in Table 3. The six nearest-neighbours of the bromide ion (a water molecule and five ammine nitrogens) lie at distances of 3·3 to 3·6 Å from it. These values are close to the corresponding sums of the van der Waals radii, if the hydrogen atoms are ignored. Although the longer of these distances may merely reflect electrostatic interactions, their values and those of the inter-vector angles are consistent with the description of all six bromide–neighbour vectors as hydrogen bonds (Table 4). The details of the hydrogen-bond system are shown in Figure 2 and listed in Table 4. The assignment of all nitrogen–oxygen contacts shorter than 3·1 Å as hydrogen bonds leads to reasonable values of the relevant inter-bond angles. There are several other short nitrogen–oxygen contacts near the limiting van der Waals value (asterisked in Table 4). Inter-vector angles calculated for these short contacts show that they are not

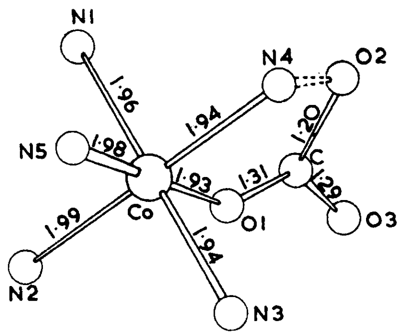

FIGURE 1

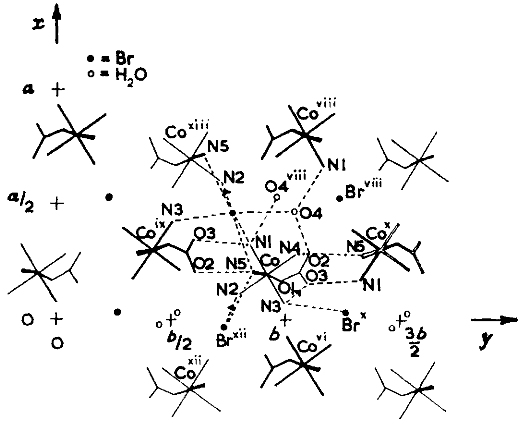

FIGURE 2

FIGURE 1. The carbonatopenta ammine cation

FIGURE 2. Projection of structure along z axis. The positive direction of z rises out of the paper. Only the cobalt atoms of symmetry-related complexes have been superscripted. Complexes drawn with light lines are at z, those with heavy lines at $z + \frac{1}{2}$, and that drawn with hollow lines at $z - \frac{1}{2}$. Broken lines represent hydrogen bonds. An arrow indicates that the corresponding hydrogen bond leads to an atom one unit-cell above the atom shown in the Figure

hydrogen bonds. The bond-lengths and angles are in general agreement with the values found in similar compounds (average Co^{III}–N = 1·96, Co^{III}–O = 1·93, average C–O = 1·26 Å). The large standard deviations prevent detailed comparisons with, for instance, carbonatotetra-amminecobalt(III) bromide [6] in which the bidentate carbonate ligand exhibits a "*trans*"-effect.

[6] G. A. Barclay and B. F. Hoskins, *J.*, 1962, 586.

The three carbon–oxygen bond-lengths are not significantly different, but their trend is consistent with the environments of their oxygen atoms (1·31 Å, O(1) bonded to Co; 1·29 Å, O(2), three H-bonds; 1·20 Å, O(3), two H-bonds).

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