111. *The Crystal Structure of Carbonatotetra-amminecobalt*(III) *Bromide.*

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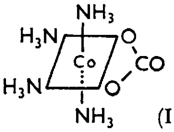
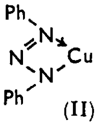
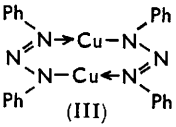
The structure of carbonatotetra-amminecobalt(III) bromide has been determined by Fourier syntheses, three dimensional *X*-ray diffraction spectra being used. There are four molecules in the orthorhombic unit cell (space-group *Pcmn*) with dimensions $a = 6·760 \pm 0·005$, $b = 7·629 \pm 0·005$, $c = 16·886 \pm 0·010$ Å. The structure consists of layers of carbonatotetra-amminecobalt(III) ions interleaved with bromide ions. Within these layers, the complex ions are held together by N–H · · · O hydrogen bonds. The carbonate group acts as a chelate group to form a four-membered ring. The cobalt atom is surrounded by four nitrogen and two oxygen atoms at the corners of a somewhat distorted octahedron.

The carbonate group in the carbonatotetra-amminecobalt(III) ion (I) is generally thought to form a four-membered chelate ring. Although transition-metal complexes of 1,3-diphenyltriazen were first postulated to contain a four-membered ring (II),[1] the copper(I) compound has been shown to possess the dimeric structure (III);[2] the steric strain inherent in the chelate ring is not present in the dimer. Further, on the basis of its magnetic susceptibility and molecular weight a binuclear structure has been suggested for the bivalent copper derivative.[3]


(I)


(II)


(III)

Because of the doubt about the existence of four-membered chelate ring systems, and since it has been suggested that the carbonatotetra-amminecobalt(III) ion exists in aqueous solution as a hydrogen carbonato-complex,[4] the crystal structure of carbonatotetra-amminecobalt(III) bromide has been determined.

Experimental

Carbonatotetra-amminecobalt(III) bromide was prepared by the method quoted by Gmelin.[5] Crystals for the *X*-ray study were obtained by slow evaporation of an aqueous solution of the complex containing a small quantity of ammonium carbonate (Found: C, 4·7; H, 4·5; N, 20·5; Co, 22·3. Calc. for $CH_{12}BrCoN_4O_3$: C, 4·5; H, 4·6; N, 21·0; Co, 22·1%).

Table 1.

Atomic parameters.

Atom	ρ (obs)	ρ (calc.)	x/a	y/b	z/c	σ (r.m.s.)(Å)
Br	54·9	56·6	0·5426	0·2500	0·2758	0·002
Co	40·4	42·0	0·1173	0·2500	0·0903	0·003
N(1)	7·9	8·7	0·0273	0·2500	0·2003	0·014
N(2)	7·6	7·0	0·3032	0·2500	0·4805	0·017
N(3)	6·9	6·7	0·3145	0·0548	0·1118	0·021
C	6·5	7·1	−0·2053	0·2500	0·0446	0·015
O(1)	8·7	9·3	−0·3745	0·2500	0·0166	0·013
O(2)	10·5	10·1	−0·1032	0·1061	0·0637	0·010

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[1] Dwyer, *J. Amer. Chem. Soc.*, 1941, **63**, 78; Dwyer and Mellor, *ibid.*, p. 81.

[2] Brown and Dunitz, Internat. Conference Co-ordination Chem., London, April, 1959.

[3] Harris, Hoskins, and Martin, *J.*, 1959, 3728.

[4] Harris and Stranks, *Trans. Faraday Soc.*, 1952, **48**, 137.

[5] Gmelin, " Handbuch der anorganischen Chemie," Verlag Chemie, Berlin, 1930, Vol. 58, *B*, p. 199.

The systematic absences ($0kl$ with $l = 2n + 1$; $hk0$ with $h + k = 2n + 1$) do not distinguish between the space groups *Pcmn* and $Pc2_1n$; a satisfactory solution was found in the centrosymmetric space group, *Pcmn*.

Accurate cell dimensions were determined by the Straumanis method with single crystals. Intensities were estimated visually, by the multiple film technique, from equi-inclination

TABLE 2.

Observed structure amplitudes and calculated structure factors.

l	$\lvert F_o \rvert$	F_c
	0,0,l	
2	26	16
4	58	54
6	116	−146
10	55	59
14	28	26
16	44	−46
18	17	19
	0,1,l	
2	99	−109
4	124	−165
6	69	64
8	9	−13
10	85	103
12	61	−72
14	21	15
16	24	−27
18	19	20
	0,2,l	
0	177	−241
2	60	43
4	113	−108
6	74	71
8	8	−5
10	49	−48
12	8	−12
14	29	−28
16	53	58
18	7	−3
	0,3,l	
2	15	−2
4	63	62
6	64	−61
8	33	28
10	84	−75
12	69	71
16	25	30
	0,4,l	
0	146	167
2	47	−43
4	56	48
6	56	−54
8	31	28
10	55	51
14	12	11
16	38	−49
	0,5,l	
2	51	−45
4	73	−70
6	64	57
10	53	49
12	54	56
	0,6,l	
0	125	−129
2	13	11
4	22	−25
6	64	54
10	28	−25
	0,7,l	
2	28	20
4	57	50
6	20	−17
	0,8,l	
0	61	63
4	16	23
	1,0,l	
1	82	107
2	73	−67
	1,0,l	
3	67	−64
4	37	27
5	39	28
6	73	64
7	153	−164
8	96	104
9	61	58
10	4	−3
11	37	−32
12	11	−11
13	53	58
14	25	−25
15	21	−25
16	9	10
18	9	14
	1,1,l	
0	26	−8
1	55	55
2	33	−27
3	145	−162
4	63	74
5	41	37
6	25	24
7	10	−8
8	12	−8
9	71	72
10	50	−44
11	32	27
12	29	−29
13	30	−30
14	14	14
15	20	19
16	14	11
17	21	−24
18	14	18
	1,2,l	
1	67	−69
2	15	21
3	83	84
4	17	−8
5	25	−18
6	12	4
7	108	112
8	71	−71
9	79	−89
10	28	−28
11	28	22
12	19	−19
13	38	−39
14	23	24
15	33	35
17	11	7
	1,3,l	
0	16	11
1	48	−52
2	46	42
3	92	98
4	27	−30
5	66	−69
6	29	−28
7	18	−14
8	37	−32
9	56	−46
10	20	13
12	34	32
13	39	41
14	5	4
15	18	−16
17	11	15
	1,4,l	
1	29	27
2	45	−48
3	62	−58
	1,4,l	
4	27	−15
5	28	25
7	67	−74
8	59	60
9	66	70
10	23	17
11	18	−16
12	14	12
13	32	32
14	17	−14
15	28	−31
	2,0,l	
0	63	78
1	59	−67
2	123	−122
3	56	40
4	75	74
5	29	−27
6	50	−50
7	58	54
8	16	−11
9	31	35
10	7	5
11	19	−17
12	13	−9
13	32	−32
14	36	36
15	42	−49
16	25	−23
17	14	15
	2,1,l	
1	56	54
2	25	18
3	36	−30
4	45	−41
5	52	56
6	45	43
7	29	−27
8	61	−54
9	9	−7
10	55	57
11	75	−81
12	47	−47
13	8	4
14	20	23
15	7	7
16	25	−26
17	33	34
	2,2,l	
0	91	−97
1	94	107
2	99	107
3	48	44
4	31	−33
5	55	48
6	52	51
7	67	−65
8	21	−17
9	39	−43
10	26	−22
11	12	13
12	24	17
13	22	19
14	22	−21
15	30	33
16	22	22
17	12	−14
	2,3,l	
1	100	105
2	6	−3
3	27	28
4	35	29
5	75	−82
6	62	−58
	2,3,l	
7	16	−8
8	43	37
9	5	−7
10	37	−36
11	55	63
12	48	52
14	19	−19
16	15	17
	2,4,l	
0	44	52
1	65	−73
2	70	−79
3	42	−33
4	39	38
5	57	−52
6	36	−30
7	40	−35
8	8	9
9	38	37
10	16	13
12	14	−10
13	10	−8
14	23	20
15	23	−29
	3,0,l	
1	24	−19
2	36	−43
3	57	−54
4	34	32
5	74	68
6	37	−31
7	17	−14
8	72	80
9	57	59
10	30	−30
11	43	−47
12	8	8
13	7	6
14	43	−44
16	6	5
	3,1,l	
0	42	39
1	71	67
2	46	−49
3	12	−9
4	90	86
5	53	52
6	10	11
7	48	−46
8	29	22
9	33	−24
10	32	−25
11	17	−15
12	26	−28
13	14	−8
14	20	24
15	24	22
	3,2,l	
1	39	35
2	73	79
3	27	23
4	12	9
5	76	−88
6	37	36
7	29	28
8	76	−80
9	31	−24
10	21	18
11	44	47
12	16	−17
13	19	−22
14	34	32
15	4	−2
16	7	−8
	3,3,l	
0	25	15
1	66	−65
2	68	68
3	7	2
4	71	−78
5	27	−25
6	39	−33
7	53	57
8	41	−37
9	22	16
10	18	12
11	10	−5
12	22	23
14	11	−14
15	15	−14
	3,4,l	
1	13	−10
2	57	−61
3	24	−22
4	24	−15
5	25	51
6	41	−38
7	28	−22
8	50	59
9	24	25
10	8	−7
11	34	−37
12	24	21
13	14	13
14	23	−24
	4,0,l	
0	44	−41
1	79	−84
2	86	−82
3	39	34
4	50	53
5	41	−36
6	41	34
7	33	32
8	19	17
9	11	−6
10	15	−20
11	30	−31
12	39	−37
14	7	6
15	12	−18
	4,1,l	
1	5	5
2	71	63
3	9	−12
4	40	39
5	52	51
6	27	17
7	35	−35
8	60	−54
9	39	37
11	38	−39
13	33	32
14	34	39
15	14	−12
	4,2,l	
0	20	11
1	60	62
2	60	57
3	50	−44
4	50	−47
5	51	53
6	24	−17
7	5	−3
8	5	−1
9	4	1
10	24	26
12	34	34
	4,2,l	
13	13	−12
14	15	−11
15	15	25
	4,3,l	
2	4	−34
3	27	24
5	31	−34
7	14	17
8	49	44
9	48	−51
10	20	−14
11	25	30
12	13	−8
13	17	−17
14	27	−39
	4,4,l	
1	53	−57
2	38	−38
3	24	19
4	38	36
5	42	−41
6	14	8
7	10	11
8	9	−6
10	27	−24
11	4	−9
12	26	−26
	5,0,l	
1	37	−33
3	10	11
4	45	48
5	72	69
6	54	−55
7	23	23
8	19	20
10	44	−44
11	30	−27
12	33	33
	5,1,l	
0	66	65
1	40	32
2	44	−41
3	37	34
4	23	19
5	21	20
6	47	−48
7	29	−30
8	12	10
9	30	−23
10	7	9
13	8	12
	5,2,l	
4	43	−43
5	39	−40
6	42	42
7	8	−10
8	20	−23
9	5	−5
10	41	45
11	29	27
12	24	−25
13	8	9
	5,3,l	
0	51	−52
1	15	−11
2	38	35
4	20	−22
6	43	39
7	19	22
8	4	−4
9	16	14
	5,3,l	
10	4	−4
11	9	−1
	5,4,l	
1	5	2
3	14	11
4	39	36
5	37	35
6	36	−36
7	4	1
8	16	17
9	9	−6
10	26	−35
	6,0,l	
0	7	−7
1	24	−26
2	4	−7
3	72	69
5	18	−18
6	17	12
7	7	−3
8	8	10
9	9	−10
10	8	4
	6,1,l	
1	37	32
2	13	7
3	20	−17
4	11	14
6	5	1
7	42	−40
9	40	40
10	1	−7
	6,2,l	
1	28	27
3	59	−64
6	12	−10
7	10	−7
8	6	4
9	12	12
	6,3,l	
1	36	−32
2	4	−5
3	4	9
4	4	−4
5	6	−2
7	47	43
	6,4,l	
1	17	−17
2	3	3
3	54	58
	7,0,l	
3	11	−6
4	25	25
5	24	−19
6	21	−27
	7,1,l	
0	31	34
1	17	−14
2	26	−24
3	5	2
4	5	7
5	4	−5
	7,2,l	
2	13	−13
3	7	4
4	27	−35

Weissenberg photographs of the layers $0kl$ and $h0l \longrightarrow h4l$. Lorentz and polarisation corrections were applied by using a Cochran chart.[6] The crystals used for intensity photographs were 0·06 × 0·08 and 0·07 × 0·08 mm. in cross section for the *a* and the *b* axis, respectively. The structure amplitudes were placed on the same arbitrary scale by correlation of the layers $h0l \longrightarrow h4l$ with the $0kl$ layer. The 459 independent terms were finally placed on an absolute scale by making $\sum|F_o| = \sum|F_c|$. No allowance was made for absorption or extinction.

Scattering factors for carbon, nitrogen, and oxygen were those given by Berghuis *et al.*,[7] and for cobalt and bromine those of Thomas and Umeda.[8] An overall Debye–Waller temperature factor with $B = 3{\cdot}0$ Å^2, determined in the usual way, was applied.

Three-dimensional Fourier series and structure factors were calculated on UTECOM (a DEUCE digital electronic computer) by means of programmes written by Dr. J. S. Rollett. Peak maxima in the three-dimensional Fourier syntheses were estimated by the method of Shoemaker *et al.*[9] The estimates of the standard deviation of the atomic co-ordinates were calculated by Cruickshank's method.[10] The root mean squares of the e.s.d.'s are given in Table 1.

Crystal Data.—Carbonatotetra-amminecobalt(III) bromide, $CH_{12}BrCoN_4O_3$, $M = 267{\cdot}0$, orthorhombic, $a = 6{\cdot}760 \pm 0{\cdot}005$, $b = 7{\cdot}629 \pm 0{\cdot}005$, $c = 16{\cdot}886 \pm 0{\cdot}010$ Å, $U = 870{\cdot}8$ Å^3, $D_m = 2{\cdot}028$ g. cm.$^{-3}$ (by flotation), $Z = 4$, $D_c = 2{\cdot}036$ g. cm.$^{-3}$, $F(000) = 520$. Space group, *Pcmn* (D_{2h}^{16}, No. 62). Co-K_α radiation, single-crystal oscillation and Weissenberg photographs. Absorption coefficient, $\mu = 127$ cm.$^{-1}$.

STRUCTURE DETERMINATION

Neither the systematically absent spectra nor the statistical test of Howells *et al.*[11] of the intensity data distinguished between the space groups *Pcmn* and $Pc2_1n$. The centrosymmetric space group has the eight general equivalent positions $\pm(x, y, z;\ \tfrac{1}{2} - x, \tfrac{1}{2} - y, \tfrac{1}{2} + z;\ \bar{x}, \tfrac{1}{2} + y, \bar{z};\ \tfrac{1}{2} + x, \bar{y}, \tfrac{1}{2} - z)$. If this is the correct space group, the cobalt, bromine, carbon, and either one or all of the three oxygen atoms in the molecule must occupy special positions. The cobalt–cobalt, cobalt–bromine, and bromine–bromine vectors appeared only on the sections at $y = 0$ and $y = \tfrac{1}{2}$ of the three-dimensional Patterson function; this suggests that the cobalt and bromine atoms occupy special positions of the type $\pm(x, \tfrac{1}{4}, z;\ \tfrac{1}{2} - x, \tfrac{1}{4}, \tfrac{1}{2} + z)$ in the space group *Pcmn*.

The phases determined by the co-ordinates of the cobalt and the bromine atoms ($x = 0{\cdot}543$ and $0{\cdot}116$ and $z = 0{\cdot}276$ and $0{\cdot}090$, respectively) were used in the calculation of a three-dimensional electron-density distribution from which all the remaining atoms were located. The bromine atom and all atoms of the complex ion except two nitrogen and two oxygen atoms were situated on the mirror plane at $y = \tfrac{1}{4}$. The structure was refined by successive three-dimensional Fourier sections until there were no further changes in the phases of the structure factors. The back-shift method was used to correct for termination-of-series errors.

The satisfactory refinement of the structure is partial justification for taking the centrosymmetric space group. Additional evidence that *Pcmn* is correct comes from the absence of spurious peaks in the electron-density maps and from a comparison of the electron densities at the atomic positions in the observed and the calculated syntheses (see Table 1).

The final atomic parameters are listed in Table 1; they gave an R value (based on the 459 observed reflections) of 0·12. The observed structure amplitudes and the calculated structure factors are given in Table 2.

Description of the Structure.—The structure as a whole consists of layers of carbonatotetra-amminecobalt(III) ions interleaved by bromide ions. A general view of the atomic arrangement is shown in Fig. 1(a). Each bromide ion has eight points of contact with the nitrogen atoms of four different complex ions [see Figs. 1(b) and (c)]. The bromine–nitrogen distances, which vary from 3·50 to 3·84 Å, suggest that there may be some hydrogen bonding present

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[6] Cochran, *J. Sci. Instr.*, 1948, **25**, 397.

[7] Berghuis, Haanappel, Potters, Loopstra, McGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[8] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

[9] Shoemaker, Donohue, Schomaker, and Corey, *J. Amer. Chem. Soc.*, 1950, **72**, 2328.

[10] Cruickshank, *Acta Cryst.*, 1949, **2**, 65; Cruickshank and Rollett, *ibid.*, 1953, **6**, 705.

[11] Howells, Phillips, and Rogers, *Acta Cryst.*, 1950, **3**, 210.

since the ammonia–bromine non-bonding distance would be about 4·0 Å. The N · · · Br distances and the Co–N · · · Br angles are listed in Table 3. The next greater distance is a bromine–carbon separation of 4·25 Å.

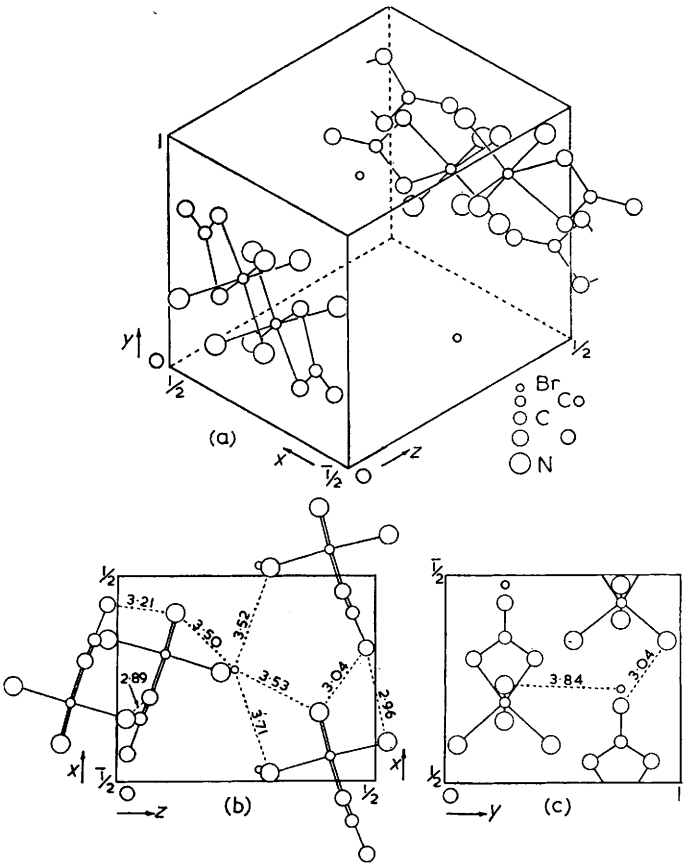

FIG. 1. Atomic arrangement and interatomic distances (Å) in carbonatotetra-amminecobalt(III) bromide.

Within the layers, the carbonatotetra-amminecobalt(III) ions are held together by N–H · · · O hydrogen bonds. There are three distinct distances (2·89 to 3·01 Å) between nitrogen and oxygen atoms of different ions (cf. Table 3). Each complex ion is involved in a total of 8 hydrogen bonds—two to each of two ions whose centres are separated by *b*/2 and two to each of two ions centred on the same mirror plane [Figs. 1(b) and (c)]. There is another short distance 3·21 Å between N(3) and O(1) of two ions *b*/2 apart.

TABLE 3.

Hydrogen bonding.

	Distance (Å)	∠Co–N · · · Br		Distance (Å)	∠Co–N · · · O
N(1)...Br	3·52	129°	N(3)...Br	3·53	104°
N(1)...Br	3·71	92	N(2)...O(2) ...	2·89	101
N(1)...Br	3·84	95	N(2)...O(1) ...	2·96	94
N(3)...Br	3·50	97	N(3)...O(1) ...	3·01	90

The cobalt atom is surrounded by four nitrogen and two oxygen atoms at the corners of a somewhat distorted octahedron. These two oxygen atoms are crystallographically equivalent and are bonded to the same carbon atom; thus the carbonate group is acting as a chelate group with the formation of a four-membered ring. The bond distances and angles are shown diagrammatically in Fig. 2 and are listed, together with their estimated standard deviations, in Table 4.

TABLE 4.

Bond distances and angles.

Bond	Length (Å)	σ (Å)	Angle	Value	σ
Co–N(1)	1·953	0·014	N(1)–Co–N(3)	92·8°	0·8°
Co–N(2)	1·931	0·018	N(2)–Co–N(3)	89·3	0·8
Co–N(3)	2·031	0·022	N(3)–Co–N(3′)	94·3	0·9
Co–O(2)	1·905	0·011	N(1)–Co–O(2)	88·9	0·5
C–O(1)	1·237	0·020	N(2)–Co–O(2)	89·5	0·6
C–O(2)	1·336	0·018	O(2)–Co–O(2′)	70·5	0·5
			O(2)–Co–N(3)	97·7	0·7
			O(2)–C–O(1)	124·8	1·4
			O(2)–C–O(2′)	110·4	1·3
			C–O(2)–Co	89·5	0·8

In general the bond distances are in good agreement with previous values.[12] The Co–N(3) bond appears to be significantly longer than the Co–N(1) and Co–N(2) bonds; in each case they differ by more than three times the estimated standard deviation of their difference. It is interesting that N(3) is *trans* to the highly polarisable carbonate group; this ammonia molecule would be expected to be more labile than if it were *trans* to another neutral molecule as N(1) and N(2) are. The carbon–oxygen bond which is not involved in the chelate ring is significantly shorter (1·24 Å) than the others (1·34 Å) and is shorter than the carbon–oxygen bonds of the carbonate ion (1·29 Å) in calcite.[13] These bond-lengths indicate localisation of the π-electron cloud in the chelated carbonate group as in carboxylic acids and esters (C–O distances 1·22 and 1·36 Å); Pauling [14] assigns bond numbers of 1·85 and 1·15 to the carbon–oxygen bonds in formic acid.

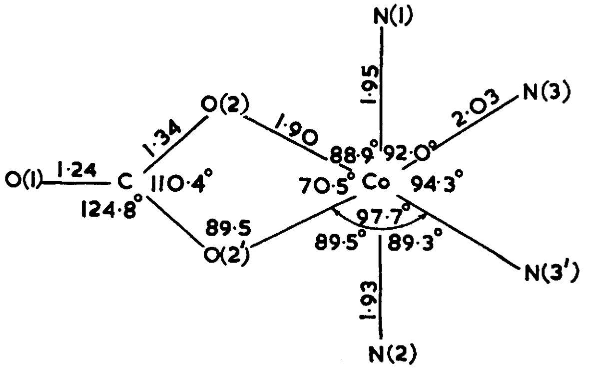

FIG. 2. Bond lengths and bond angles in the carbonatotetra-amminecobalt(III) ion.

The strain involved in the four-membered ring is evident from the O(2)–Co–O(2′) bond angle of 70° which differs greatly from the expected value of 90°. Further evidence of this strain comes from the C–O(2)–Co angle of 90° and the O(2)–C–O(2′) angle of 110°. Within experimental error, the atoms N(1)–Co–N(2) lie along a line which is normal to the plane containing the O(2), O(2′), Co, N(3), and N(3′) atoms. As a result of the formation of the four-membered ring the O(2)–Co–N(3) and the N(3)–Co–N(3′) angles are greater than 90°. Both the carbonate group and the O(2)–O(2′)–Co–N(3)–N(3′) group are planar; however,

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[13] Sass, Vidale, and Donohue, *Acta Cryst.*, 1957, **10**, 567.

[14] Pauling, " The Nature of the Chemical Bond and the Structure of Molecules and Crystals," Cornell Univ. Press, 3rd edn., 1960, p. 276.

these planes make a dihedral angle of 7° to one another. The equations for these planes (and the deviations of the atoms from them) are:

$$-0{\cdot}399x + 0{\cdot}917z - 1{\cdot}259 = 0$$

[C, 0·017; O(1), 0·007; O(2) and O(2′), 0·005 Å]

$$-0{\cdot}276x + 0{\cdot}961z - 1{\cdot}230 = 0$$

[N(3) and N(3′), 0·004; Co, 0·017; O(2) and O(2′), 0·004 Å]

DISCUSSION

Recent *X*-ray crystal studies of some metal alkanoates suggest that four-membered chelate rings of the type observed in carbonatotetra-amminecobalt(III) bromide are rare. Although Lowry and French [15] postulated four-membered ring structures for copper acetate, van Niekerk and Schoening [16] showed that copper acetate monohydrate adopts a binuclear structure in which the copper atoms are bridged in pairs by four acetate groups with two water molecules occupying the terminal positions; this eliminates the steric strain associated with the proposed four-membered ring. Monopyridinecopper(II) acetate [17] and chromous acetate monohydrate [18] have similar structures.

Anhydrous copper formate and copper formate tetrahydrate have also been examined [19] and in each of these compounds the copper atoms are bridged to each other by formate groups. Martin and Waterman [20] suggested that the bridging arrangements observed in copper acetate monohydrate and the two formates are a consequence of the sp^2-hybridisation of the oxygen atoms. This gives rise to three possible bridging modes of the carboxylate group, all of which have been observed. Copper and chromous acetate are examples of the *syn-syn*-arrangements while copper formate tetrahydrate and anhydrous copper formate exhibit the *anti-anti-* and *anti-syn*-configuration, respectively.

Because of the geometrical resemblance of the carbonate group to the carboxylate group, it seems unexpected that the carbonate ion in carbonatotetra-amminecobalt(III) bromide adopts a highly strained four-membered ring and does not parallel the general behaviour of the carboxylate group. Zinc acetate dihydrate [21] provides one further example of the highly strained four-membered ring of the type observed in carbonatotetra-amminecobalt(III) bromide.

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[19] Kariyama, Ibamato, and Matsuo, *Acta Cryst.*, 1954, **7**, 482; Barclay and Kennard, *J.*, 1961, 3289.
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