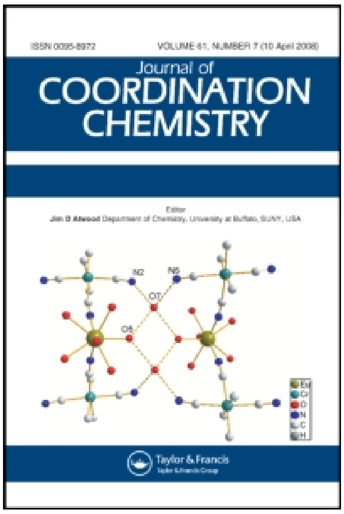

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 53. THE CRYSTALLIZATION BEHAVIOR OF TWO COBALT(III) CARBONATO AMINE COMPOUNDS

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 53. THE CRYSTALLIZATION BEHAVIOR OF TWO COBALT(III) CARBONATO AMINE COMPOUNDS

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Two new cobalt(III) carbonato amine compounds were synthesized, and their crystal structures were determined.

Compound (I), $Na_2[Co(tren)(CO_3)]_2(ClO_4)_4 \cdot 3H_2O$, $Co_2C_{14}Cl_4H_{42}N_8Na_2O_{25}$, crystallized as a racemate in the orthorhombic system, space group Pcab (No. 61). The cell dimensions, obtained from the centering of 25 reflections, are $a = 10.684(5)$ Å, $b = 18.559(8)$ Å, $c = 37.528(10)$ Å, $V = 7441(5)$ Å^3. FW = 1028.18, $Z = 8$, $F(000) = 4203.87$, dc = 1.836 Mg · m^{-3}, $\mu = 1.30$ mm^{-1}, $\lambda = 0.70930$ Å. A total of 3457 data were collected over the range of $4° \leq 2\Theta \leq 40°$; of these, 2377 (independent and $I \geq 2.5\sigma(I)$) were used in the structural analysis. The final RF and Rw residuals were 0.055 and 0.064.

Compound (II), [*cis*-β-Co(trien)(CO_3)](HCO_3) · H_2O, $CoC_8H_{21}N_4O_7$, crystallized as a conglomerate in the orthorhombic system, space group $P2_12_12_1$ (No. 19). The cell dimensions, obtained from the centering of 25 reflections, are $a = 8.869(4)$ Å, $b = 12.032(8)$ Å, $c = 12.522(7)$ Å, $V = 1336(1)$ Å^3. FW = 344.20, $Z = 4$, $F(000) = 713.62$, dc = 1.701 Mg · m^{-3}, $\mu = 1.32$ mm^{-1}, $\lambda = 0.70930$ Å. A total of 3504 data were collected over the range of $4° \leq 2\Theta \leq 40°$; of these, 2497 (independent and $I \geq 2.5\sigma(I)$) were used in the structural analysis. The final RF and Rw residuals were 0.049 and 0.059.

Keywords: Conglomerate crystallization; carbonate; cobalt; amine; crystal structure

INTRODUCTION

Conglomerate crystallization is the phenomenon whereby a solution of a racemate deposits a mechanical mixture of crystals each of which is made

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* Corresponding author.

up of pure homochiral molecules. Although conglomerate crystallization occurs less often than racemic crystallization, many examples of conglomerate crystallization of cobalt(III) amine nitrite and cobalt amine oxalato complexes have been reported,[1,2] and conglomerate crystallization mechanisms were proposed for some selected series.[1,3]

It also has been known for some time that the cobalt amine carbonato compounds of composition [Co(meso-2,3-butanediamine)$_2$(CO$_3$)]I · H_2O[4] and [*cis*-β-Co(2,3,2-tet)(CO$_3$)]ClO$_4$ · H_2O[5] crystallize as conglomerates. Moreover, in spite of the lack of structural data, one of the three crystalline phase of [Co(en)$_2$(CO$_3$)]Br · H_2O is a conglomerate.[6] None of the three phases produce crystals stable enough for single crystal, X-ray diffraction studies, and Yamanari characterizes the phase diagram for this system as being very difficult,[6,7] some results with single crystals have been reported by Bernal *et al.*[7] Recently it was found that the compound [*cis*-(-Co(trien)-(CO$_3$)]ClO$_4$ · H_2O also crystallizes as a conglomerate.[8,9]

Given the above, it seemed that further efforts were needed to probe the reasons for the crystallization behavior of the metal amine carbonato compounds. The results of our crystallization experiments and structural determinations are described below.

EXPERIMENTAL

Preparation of Compound (I)

$Co(ClO_4)_2 \cdot 6HO_2$ (1.13 g) (0.0031 mmol) was dissolved in 15 mL H_2O and 1 mL 30% H_2O_2 was added, drop by drop. Tren (0.45 g) (0.0031 mmol; tren = tris (2-aminoethyl)amine) were dissolved in another 15 mL H_2O. The two solutions were mixed and treated with 0.26 g $NaHCO_3$ (0.0031 mmol). The resulting solution was heated to 60°C for 3 h and then cooled to room temperature. After slow evaporation for several days, reddish crystals formed and were filtered. Single crystals suitable for X-ray determination were obtained upon recrystallization.

Preparation of Compound (II)

$Na_2[Co(CO_3)_3] \cdot 3H_2O$ was prepared utilizing the previously published procedure.[10] To the solution of $Na_2[Co(CO_3)_3] \cdot 3H_2O$ triethylenetetramine hydrate (trien · H_2O) was added in a 1:1 ratio, with continuous stirring. The mixture was warmed on a steam bath for 30 min and allowed to crystallize.

Reddish crystals were obtained, and single crystals suitable for X-ray structure determination were obtained upon recrystallization.

Elemental Analysis

Elemental analysis were carried out by Galbraith.[11] Compound (I): Theory for $Co_2C_{14}Cl_4H_{42}N_8Na_2O_{25}$: C = 16.20%, N = 10.7%, H = 4.08%. Observed C = 16.35%, N = 10.9%, H = 4.12%. Compound (II): Theory for CoC_8-$CH_{21}N_4O_7$: C = 27.85%, N = 16.19%, H = 6.20%. Observed C = 27.92%, N = 16.28%, H = 6.15%.

X-ray Crystallography

Data for both compounds (I and II) were collected with an Enraf-Nonius CAD-4 diffractometer (Table I). The procedure used for crystal alignment, cell constant determination, space group determination, and data collection were uniform for both crystals. A crystal of compound (I) was centered in the $4° \leq 2\Theta \leq 40°$ range. Cell dimensions were obtained from 25 reflections, in both cases. A crystal of compound (II) was centered in the $4° \leq 2\Theta \leq 50°$ range. Data were corrected for absorption using empirical curves derived from Psi scans of suitable reflections. The scattering curves were taken from Cromer and Waber's compilation[12] (Tables II and III).

Processing of the data was carried out with the PC version of the NRCVAX package.[13] The positions of the Co atoms were determined using direct methods. After refinement of the scale factor and the positional parameters of the Co atoms, a difference Fourier map found many of the non-hydrogen atoms. The remaining atoms were found in subsequent difference maps. The positions and anisotropic thermal parameters of heavy atoms, including the oxygen of the water of crystallization were refined. The hydrogens of the cations were added to the ideal positions and used for least squares calculation. Those of the waters were found, experimentally, at reasonable positions, using O–H bond lengths and H–O–H angles as the criteria. The details of data collection for compounds (I) and (II) are summarized in Table I.

RESULTS AND DISCUSSION

Compound (I), $Na_2[Co(tren)(CO_3)]_2(ClO_4)_4 \cdot 3H_2O$ crystallized as a racemate in the orthorhombic system. Examination of the cell constants,

TABLE I Summary of data collection and processing parameter for $Na_2[Co(tren)(CO_3)]_2 \cdot 4ClO_4 \cdot 3H_2O$ compound (I) and $[cis\text{-}\beta\text{-}Co(trien)(CO_3)] \cdot HCO_3 \cdot H_2O$ compound (II)

	$Na_2[Co(tren)(CO_3)]_2 \cdot 4ClO_4 \cdot 3H_2O$	$[cis\text{-}\beta\text{-}Co(trien)(CO_3)] \cdot HCO_3 \cdot H_2O$
Space group	Pcab	$P2_12_12_1$
Cell constants	$a = 10.684(5)$ Å	$a = 8.869(4)$ Å
	$b = 18.559(8)$ Å	$b = 12.032(8)$ Å
	$c = 37.528(10)$ Å	$c = 12.522(7)$ Å
Cell volume (Å^3)	7441(5)	1336(1)
Molecular formula	$Co_2C_{14}Cl_4H_{42}N_8Na_2O_{25}$	$CoC_8H_{21}N_4O_7$
Molecular weight	1028.18	344.20
$F(000)$	4203.87	713.62
Z	8	4
Density ($Mg \cdot m^{-3}$)	1.836	1.701
Temperature (K)	298 K	298 K
Radiation employed	MoKα (0.70930 Å)	MoKα (0.70930 Å)
μ	1.30 mm^{-1}	1.32 mm^{-1}
h (min, max)	0, 10	0, 11
k (min, max)	0, 17	0, 15
l (min, max)	0, 36	0, 16
Absorption coefficient	Yes	Yes
Relative transmission coefficients	0.6780, 0.7422	0.6307, 0.7423
Data collection range	4–40	4–55
Scan width	$0.60 + 0.35 \tan\theta$	$1.00 + 0.35 \tan\theta$
Total data collected	3457	3405
Total unique data collected	3457	3078
Data used in refinement	2377 ($I > 2.5\sigma(I)$)	2497 ($I > 3\sigma(I)$)
Merging R-value	0.000	0.028
RF, Rw for significant reflections	0.055, 0.064	0.049, 0.059
RF, Rw for all reflections	0.055, 0.064	0.049, 0.059
GoF	0.59	0.55
Max shift/sigma ratio	0.000	0.000
Deepest hole (e/Å^3)	−0.48	−0.85
Highest peak (e/Å^3)	0.95	0.90
Weights used	$w = \sigma[(F_o)]^{-2}$	$w = \sigma[(F_o)]^{-2}$

$RF = \sum(F_o - F_c)/\sum(F_o)$, $Rw = [\sum(w(F_o - F_c)**2)/\sum(wF_o)**2)]^{1/2}$, $GoF = [\sum(w(F_o - F_c)**2)/($No. o reflns − No. of params.$)]^{1/2}$.

TABLE II Atomic parameters x, y, z and Biso for compound (I), $Na_2[Co(tren)(CO_3)]_2 \cdot 4ClO_4 \cdot 3H_2O$ ESDs refer to the last digit printed

	x	y	z	*Biso*
Co	0.76220(15)	0.33764(9)	0.05338(5)	2.06(8)
Co2	0.99985(15)	0.16838(9)	0.29655(5)	1.90(8)
Cl	0.9546(3)	0.42342(19)	0.26588(10)	3.07(18)
Cl2	0.7200(3)	0.39999(20)	0.16966(11)	3.49(18)
Cl3	0.7069(3)	0.07382(21)	0.07406(11)	3.39(20)
Cl4	0.6156(5)	0.6217(3)	0.07349(13)	5.35(25)
Na	0.8755(5)	0.2550(3)	0.21016(14)	3.5(3)
Na2	0.6629(4)	0.2242(3)	0.13516(14)	3.1(3)
N1	0.7591(10)	0.3831(6)	0.0074(3)	3.2(6)
N2	0.6017(9)	0.3829(5)	0.0630(3)	2.5(5)
N3	0.6861(10)	0.2549(6)	0.0300(3)	3.1(5)
N4	0.8509(10)	0.4221(6)	0.0705(3)	3.4(6)

TABLE II (*Continued*)

	x	y	z	*Biso*
N5	1.0052(10)	0.1322(5)	0.3446(3)	2.4(5)
N6	1.0991(10)	0.0851(6)	0.2828(3)	3.1(6)
N7	0.8431(10)	0.1162(5)	0.2906(3)	2.8(5)
N8	0.9141(9)	0.2521(6)	0.3166(3)	2.4(5)
C1	0.9058(14)	0.2667(7)	0.0848(4)	2.3(7)
C2	0.6400(13)	0.4275(8)	0.0031(4)	3.7(7)
C3	0.5416(13)	0.4013(8)	0.0286(4)	4.4(8)
C4	0.7689(14)	0.3240(10)	−0.0186(4)	4.2(8)
C5	0.6778(15)	0.2666(9)	−0.0089(5)	4.9(9)
C6	0.8702(13)	0.4332(9)	0.0073(5)	4.4(8)
C7	0.8682(14)	0.4748(8)	0.0418(5)	4.2(8)
C8	1.1289(14)	0.2420(7)	0.2621(4)	2.5(7)
C9	1.1205(12)	0.0858(8)	0.3464(4)	3.2(7)
C10	1.1193(14)	0.0375(8)	0.3147(5)	4.2(8)
C11	0.8893(13)	0.0873(8)	0.3524(4)	3.4(7)
C12	0.7862(13)	0.1063(7)	0.3266(4)	3.4(7)
C13	1.0136(13)	0.1967(7)	0.3679(4)	3.0(7)
C14	0.9128(13)	0.2490(8)	0.3559(4)	3.3(7)
O1	0.7955(8)	0.2868(4)	0.09695(24)	2.4(4)
O2	0.9212(7)	0.2873(4)	0.05153(24)	2.3(4)
O3	0.4866(8)	0.2657(5)	0.10215(23)	2.8(4)
O4	1.0238(7)	0.2137(4)	0.25079(24)	2.6(4)
O5	1.1510(7)	0.2245(4)	0.29596(23)	2.0(4)
O6	0.7022(8)	0.2198(5)	0.24458(23)	2.4(4)
O11	0.9871(11)	0.4077(5)	0.3015(3)	5.9(6)
O12	0.8925(9)	0.4915(5)	0.2646(3)	4.3(5)
O13	1.0633(10)	0.4268(6)	0.2431(3)	6.6(7)
O14	0.8717(9)	0.3666(5)	0.2532(3)	3.8(5)
O21	0.6582(11)	0.4148(7)	0.1371(3)	6.5(7)
O22	0.7167(9)	0.3249(5)	0.1776(3)	4.3(5)
O23	0.6657(12)	0.4406(6)	0.1978(3)	5.9(6)
O24	0.8487(10)	0.4222(6)	0.1665(5)	8.7(9)
O31	0.7161(19)	0.0010(6)	0.0771(3)	10.4(12)
O32	0.6649(13)	0.0894(7)	0.0382(3)	7.2(7)
O33	0.6215(10)	0.1007(8)	0.1002(4)	8.6(8)
O34	0.8125(13)	0.1116(10)	0.0802(4)	11.6(11)
O41	0.6796(19)	0.6679(10)	0.0928(5)	14.6(14)
O42	0.6299(18)	0.5505(8)	0.0849(6)	13.3(13)
O43	0.6353(15)	0.6182(11)	0.0373(4)	12.1(13)
O44	0.5003(24)	0.6501(15)	0.0728(7)	23.5(22)
O1W	0.5460(8)	0.1806(5)	0.18268(24)	3.4(5)
O2W	0.8534(9)	0.1760(5)	0.1618(3)	4.1(5)
O3W	0.3868(12)	0.4753(7)	0.1508(4)	8.0(8)
H1	0.608	0.424	−0.023	4.1
H2	0.660	0.481	0.007	4.1
H3	0.500	0.357	0.019	4.4
H4	0.477	0.440	0.033	4.4
H5	0.616	0.426	0.077	2.8
H6	0.551	0.351	0.077	2.8
H7	0.750	0.342	−0.044	4.5
H8	0.855	0.302	−0.019	4.5
H9	0.589	0.280	−0.017	5.0
H10	0.697	0.219	−0.023	5.0

TABLE II (*Continued*)

	x	*y*	*z*	*Biso*
H11	0.603	0.246	0.039	3.4
H12	0.735	0.212	0.034	3.4
H13	0.865	0.466	−0.013	4.9
H14	0.949	0.404	0.006	4.9
H15	0.952	0.501	0.043	4.6
H16	0.801	0.511	0.040	4.6
H17	0.933	0.408	0.080	4.3
H18	0.806	0.445	0.090	4.3
H19	1.119	0.057	0.369	4.2
H20	1.197	0.116	0.346	4.2
H21	1.201	0.010	0.313	4.4
H22	1.050	0.001	0.317	4.4
H23	1.178	0.101	0.273	3.1
H24	1.056	0.059	0.264	3.1
H25	0.859	0.096	0.378	4.4
H26	0.908	0.034	0.350	4.4
H27	0.745	0.153	0.335	4.2
H28	0.721	0.068	0.326	4.2
H29	0.860	0.070	0.280	3.4
H30	0.789	0.142	0.275	3.4
H31	1.008	0.183	0.394	3.5
H32	1.102	0.220	0.365	3.5
H33	0.926	0.300	0.367	3.7
H34	0.826	0.234	0.365	3.7
H35	0.828	0.254	0.307	2.9
H36	0.954	0.296	0.308	2.9
H37	0.512	0.135	0.175	4.2
H38	0.605	0.171	0.201	4.2
H39	0.924	0.178	0.146	4.9
H40	0.844	0.126	0.169	4.9

Biso is the mean of the principle axes of the thermal ellipsoid.

TABLE III Atomic parameters x, y, z and Biso for compound (**II**), [*cis*-β-Co(trien)(CO_3)] · $HCO_3 \cdot H_2O$ ESDs refer to the last digit printed

	x	*y*	*z*	*Biso*
Co	0.23796(14)	0.06516(10)	0.04216(10)	1.87(4)
O1	0.2034(7)	0.1988(5)	−0.0366(5)	2.65(24)
O2	0.2475(8)	0.0385(4)	−0.1080(4)	2.23(24)
O3	0.2200(9)	0.1858(6)	−0.2164(5)	3.4(3)
N1	0.4588(8)	0.0843(8)	0.0458(9)	3.4(4)
N2	0.2728(9)	−0.0855(6)	0.0861(6)	2.5(3)
N3	0.0229(8)	0.0264(7)	0.0451(8)	2.7(3)
N4	0.2097(9)	0.1265(7)	0.1839(6)	2.6(3)
C1	0.5251(12)	−0.0196(11)	0.0859(10)	3.8(5)
C2	0.4281(12)	−0.1151(10)	0.0483(11)	3.4(5)
C3	0.1547(13)	−0.1518(9)	0.0394(11)	3.8(5)
C4	0.0076(12)	−0.0933(10)	0.0720(9)	3.0(4)
C5	−0.0472(11)	0.1022(9)	0.1246(9)	3.3(5)
C6	0.0503(12)	0.1085(10)	0.2217(8)	3.3(5)
C7	0.2228(11)	0.1441(8)	−0.1262(7)	2.3(4)

TABLE III (*Continued*)

	x	*y*	*z*	*Biso*
H1	0.486	0.145	0.093	4.3
H2	0.498	0.101	−0.023	4.3
H3	0.522	−0.021	0.166	4.7
H4	0.629	−0.031	0.060	4.7
H5	0.433	−0.120	−0.033	4.1
H6	0.465	−0.188	0.077	4.1
H7	0.268	−0.086	0.163	3.3
H8	0.164	−0.154	−0.040	4.4
H9	0.156	−0.230	0.068	4.4
H10	−0.013	−0.103	0.150	4.0
H11	−0.081	−0.126	0.031	4.0
H12	−0.015	0.042	−0.025	3.5
H13	−0.055	0.179	0.092	4.1
H14	−0.150	0.075	0.143	4.1
H15	0.015	0.172	0.270	4.2
H16	0.040	0.037	0.265	4.2
H17	0.232	0.204	0.184	3.5
H18	0.278	0.091	0.233	3.5
O4	0.6263(9)	0.1294(8)	0.8300(9)	4.7(5)
O5	0.8658(10)	0.1318(10)	0.8426(10)	5.9(6)
O6	0.7460(12)	−0.0158(8)	0.8795(7)	5.4(4)
C8	0.7464(12)	0.0815(7)	0.8502(6)	2.4(3)
O7	0.5208(10)	0.1511(8)	0.2895(7)	4.6(4)
H19	0.574(12)	0.200(9)	0.265(8)	2.5(25)

Biso is the mean of the principle axes of the thermal ellipsoid.

absences and Niggli matrix[14] showed the space group is Pcab (No. 61). An ORTEP view of the molecular structure of compound (I) is shown in Figure 1. Selected bond distances, bond angles and torsion angles are shown in Table IV. In the asymmetric unit there are two [Co(tren)(CO$_3$)]$^+$ cations, two Na$^+$ cations and four ClO$_4^-$ anions as well as three water molecules of crystallization. The cobalt cations are in disordered octahedral environments. Each cobalt atom is coordinated by four nitrogens of the amine ligand and two oxygens of carbonato ligand. The average bond length of Co–O is 1.928(8) Å, in the range of Co–N(amine) (average 1.941(11) Å). For the carbonato ligand, the angles of O–C–O involving two coordinated oxygens are 110.9(12)° and 111.3(13)°. The Na$^+$ cations are in disordered octahedral environments; that is, each Na$^+$ cation is coordinated by six oxygens from waters of crystallization, perchlorate anion oxygens or non-coordinated carbonato oxygen (see the relevant bond lengths and bond angles in Table II for details).

The preparation of compound (I) was affected by synthetic problems. The compound we wished to prepare is not the double salt reported here but the salt of composition [Co(tren)(CO$_3$)]ClO$_4$. The compelling reason for

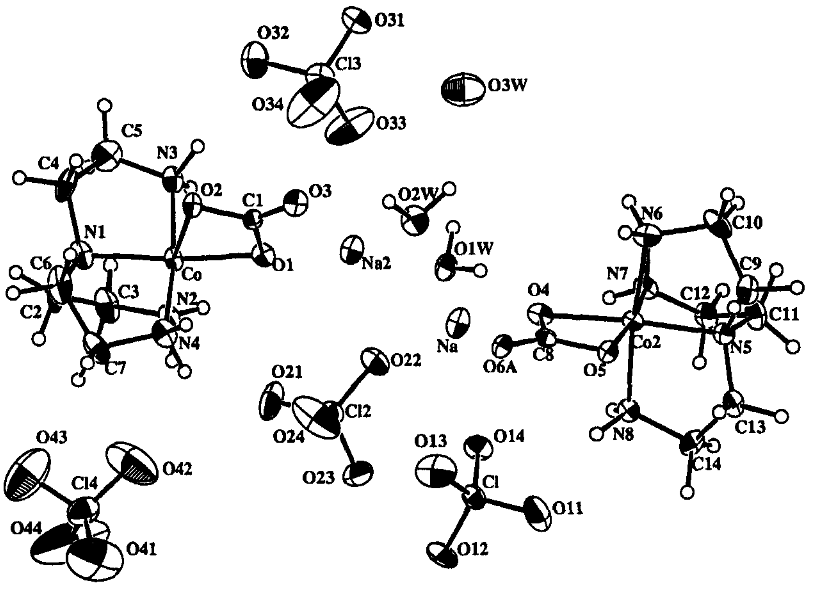

FIGURE 1 Ortep view of the molecular structure of compound (I), $Na_2[Co(tren)(CO_3)]_2 \cdot 4ClO_4 \cdot 3H_2O$. Thermal ellipsoids are drawn at 30% probability level.

TABLE IV Selected bond distances, bond angles and torsion angles for compound (I) $Na_2[Co(tren)(CO_3)]_2 \cdot 4ClO_4 \cdot 3H_2O$

Co–N1	1.921(11)	Na–O2W	2.344(11)
Co–N2	1.943(10)	Na2–O1	2.327(10)
Co–N3	1.947(12)	Na2–O3	2.382(10)
Co–N4	1.941(11)	Na2–O22	2.523(11)
Co–O1	1.921(9)	Na2–O33	2.677(15)
Co–O2	1.940(8)	Na2–O1W	2.322(10)
Co2–N5	1.927(11)	Na2–O2W	2.438(11)
Co2–N6	1.944(11)	N1–C2	1.525(17)
Co2–N7	1.946(10)	N1–C4	1.473(21)
Co2–N8	1.955(11)	N1–C6	1.508(19)
Co2–O4	1.929(9)	N2–C3	1.483(19)
Co2–O5	1.922(8)	N3–C5	1.480(20)
Cl–O11	1.413(12)	N4–C7	1.467(19)
Cl–O12	1.428(10)	N5–C9	1.504(17)
Cl–O13	1.442(11)	N5–C11	1.520(17)
Cl–O14	1.457(9)	N5–C13	1.485(17)
Cl2–O21	1.416(11)	N6–C10	1.505(20)
Cl2–O22	1.425(10)	N7–C12	1.493(19)
Cl2–O23	1.420(11)	N8–C14	1.476(17)
Cl2–O24	1.440(11)	C1–O1	1.318(18)
Cl3–O31	1.360(12)	C1–O2	1.317(17)
Cl3–O32	1.447(12)	C1–O3a	1.236(18)
Cl3–O33	1.429(12)	C2–C3	1.502(20)
Cl3–O34	1.348(13)	C4–C5	1.488(24)
Cl4–O41	1.315(16)	C6–C7	1.51(3)

TABLE IV (*Continued*)

C14-O42	1.398(17)	C8-O4	1.310(18)
C14-O43	1.375(18)	C8-O5	1.334(17)
C14-O44	1.339(22)	C8-O6a	1.244(19)
Na-Na2	3.662(7)	C9-C10	1.487(23)
Na-O4	2.329(10)	C11-C12	1.509(20)
Na-O6	2.351(10)	C13-C14	1.517(19)
Na-O14	2.627(11)	O3-C1b	1.236(18)
Na-O22	2.461(11)	O6-C8b	1.244(19)
Na-O1Wa	2.410(10)	O1W-Nab	2.410(10)
N1-Co-N2	87.8(5)	N4-Co-O1	91.4(4)
N1-Co-N3	86.2(5)	N4-Co-O2	88.5(4)
N1-Co-N4	87.2(5)	O1-Co-O2	68.4(4)
N1-Co-O1	169.6(4)	N5-Co2-N6	87.4(5)
N1-Co-O2	101.2(4)	N5-Co2-N7	87.6(5)
N2-Co-N3	93.2(4)	N5-Co2-N8	86.0(4)
N2-Co-N4	91.1(5)	N5-Co2-O4	169.1(4)
N2-Co-O1	102.5(4)	N5-Co2-O5	100.1(4)
N2-Co-O2	170.9(4)	N6-Co2-N7	92.5(4)
N3-Co-N4	172.0(5)	N6-Co2-N8	171.8(5)
N3-Co-O1	94.2(4)	N6-Co2-O4	92.2(4)
N3-Co-O2	88.3(4)	N6-Co2-O5	88.3(4)
N7-Co2-N8	92.1(4)	O3-Na2-O22	105.6(4)
N7-Co2-O4	103.2(4)	O3-Na2-O33	83.7(4)
N7-Co2-O5	172.3(4)	O3-Na2-O1W	95.0(3)
N8-Co2-O4	93.4(4)	O3-Na2-O2W	172.8(4)
N8-Co2-O5	88.1(4)	O22-Na2-O33	169.0(5)
O4-Co2-O5	69.0(4)	O22-Na2-O1W	84.0(4)
O11-C1-O12	109.2(7)	O22-Na2-O2W	79.8(4)
O11-C1-O13	111.8(8)	O33-Na2-O1W	89.4(4)
O11-C1-O14	107.9(6)	O33-Na2-O2W	91.4(4)
O12-C1-O13	108.4(7)	O1W-Na2-O2W	90.3(4)
O12-C1-O14	110.3(6)	Co-N1-C2	110.3(8)
O13-C1-O14	109.2(7)	Co-N1-C4	105.5(8)
O21-C12-O22	111.0(7)	Co-N1-C6	105.1(9)
O21-C12-O23	110.3(7)	C2-N1-C4	113.1(11)
O21-C12-O24	108.6(9)	C2-N1-C6	108.9(11)
O22-C12-O23	110.7(7)	C4-N1-C6	113.6(12)
O22-C12-O24	108.7(7)	Co-N2-C3	108.6(8)
O23-C12-O24	107.4(8)	Co-N3-C5	110.7(9)
O31-C13-O32	107.3(8)	Co-N4-C7	110.9(9)
O31-C13-O33	109.7(10)	Co2-N5-C9	105.3(8)
O31-C13-O34	116.3(12)	Co2-N5-C11	110.3(8)
O32-C13-O33	111.7(8)	Co2-N5-C13	105.7(7)
O32-C13-O34	108.4(10)	C9-N5-C11	110.2(10)
O33-C13-O34	103.6(9)	C9-N5-C13	112.8(10)
O41-C14-O42	113.0(13)	C11-N5-C13	112.2(10)
O41-C14-O43	119.7(14)	Co2-N6-C10	109.5(8)
O41-C14-O44	103.5(13)	Co2-N7-C12	108.0(8)
O42-C14-O43	103.9(12)	Co2-N8-C14	111.0(8)
O42-C14-O44	118.6(17)	O1-C1-O2	110.9(12)
O43-C14-O44	98.1(13)	O1-C1-O3a	125.5(13)
Na2-Na-O4	150.9(3)	O2-C1-O3a	123.6(13)
Na2-Na-O6	83.7(3)	N1-C2-C3	109.9(11)
O4-Na-O6	94.8(3)	N2-C3-C2	109.1(11)
O4-Na-O14	82.4(3)	N1-C4-C5	108.9(12)

TABLE IV (*Continued*)

O4–Na–O22	165.5(4)	N3–C5–C4	108.0(12)
O4–Na–O1Wa	86.0(3)	N1–C6–C7	107.5(11)
O4–Na–O2W	111.6(4)	N4–C7–C6	106.9(12)
O6–Na–O14	82.5(3)	O4–C8–O5	111.3(13)
O6–Na–O22	82.9(3)	O4–C8–O6a	126.7(13)
O6–Na–O1Wa	165.6(4)	O5–C8–O6a	122.0(13)
O6–Na–O2W	99.9(4)	N5–C9–C10	107.7(10)
O14–Na–O22	83.1(4)	N6–C10–C9	106.4(11)
O14–Na–O1Wa	83.4(3)	N5–C11–C12	110.1(11)
O14–Na–O2W	165.4(4)	N5–C11–H25	110.3(12)
O22–Na–O1Wa	92.7(4)	N7–C12–C11	108.2(11)
O22–Na–O2W	82.9(4)	N5–C13–C14	107.4(10)
O1Wa–Na–O2W	93.2(4)	N8–C14–C13	108.3(11)
O1–Na2–O3	90.0(3)	Co–O1–C1	90.6(8)
O1–Na2–O22	83.1(4)	Co–O2–C1	89.8(8)
O1–Na2–O33	103.0(4)	Co2–O4–C8	90.0(8)
O1–Na2–O1W	167.1(4)	Co2–O5–C8	89.6(8)
O1–Na2–O2W	85.9(3)		

N2	Co	N1	C2	−0.1(6)	N2	Co	N1	C4	−122.6(10)
N2	Co	N1	C6	117.1(9)	N3	Co	N1	C2	93.3(8)
N3	Co	N1	C4	−29.2(7)	N3	Co	N1	C6	−149.5(10)
N4	Co	N1	C2	−91.4(8)	N4	Co	N1	C4	146.2(10)
N4	Co	N1	C6	25.8(7)	O1	Co	N1	C2	−173.8(10)
O1	Co	N1	C4	63.7(8)	O1	Co	N1	C6	−56.6(8)
O2	Co	N1	C2	−179.3(10)	O2	Co	N1	C4	58.3(8)
O2	Co	N1	C6	−62.0(8)	N1	Co	N2	C3	21.8(7)
N3	Co	N2	C3	−64.3(8)	N4	Co	N2	C3	108.9(9)
O1	Co	N2	C3	−159.4(9)	O2	Co	N2	C3	−163.6(9)
N1	Co	N3	C5	5.3(7)	N2	Co	N3	C5	93.0(9)
N4	Co	N3	C5	−30.0(8)	O1	Co	N3	C5	−164.2(10)
O2	Co	N3	C5	−96.0(9)	N1	Co	N4	C7	0.7(7)
N2	Co	N4	C7	−87.1(9)	N3	Co	N4	C7	36.0(7)
O1	Co	N4	C7	170.3(10)	O2	Co	N4	C7	102.0(9)
N1	Co	O1	C1	−2.5(7)	N2	Co	O1	C1	−176.1(9)
N3	Co	O1	C1	89.7(8)	N4	Co	O1	C1	−84.6(8)
O2	Co	O1	C1	3.2(7)	N1	Co	O2	C1	175.7(9)
N2	Co	O2	C1	1.2(7)	N3	Co	O2	C1	−98.4(8)
N4	Co	O2	C1	88.9(8)	O1	Co	O2	C1	−3.2(7)
N6	Co2	N5	C9	24.3(6)	N6	Co2	N5	C11	−94.6(8)
N6	Co2	N5	C13	143.8(9)	N7	Co2	N5	C9	116.9(9)
N7	Co2	N5	C11	−2.0(6)	N7	Co2	N5	C13	−123.6(9)
N8	Co2	N5	C9	−150.9(9)	N8	Co2	N5	C11	90.3(8)
N8	Co2	N5	C13	−31.3(6)	O4	Co2	N5	C9	−63.9(7)
O4	Co2	N5	C11	177.2(9)	O4	Co2	N5	C13	55.7(7)
O5	Co2	N5	C9	−63.5(7)	O5	Co2	N5	C11	177.6(9)
O5	Co2	N5	C13	56.1(7)	N5	Co2	N6	C10	3.1(7)
N7	Co2	N6	C10	−84.4(8)	N8	Co2	N6	C10	39.5(7)
O4	Co2	N6	C10	172.2(10)	O5	Co2	N6	C10	103.3(9)
N5	Co2	N7	C12	24.3(6)	N6	Co2	N7	C12	111.6(9)
N8	Co2	N7	C12	−61.6(7)	O4	Co2	N7	C12	−155.6(9)
O5	Co2	N7	C12	−152.9(9)	N5	Co2	N8	C14	7.0(6)
N6	Co2	N8	C14	−29.4(7)	N7	Co2	N8	C14	94.5(8)
O4	Co2	N8	C14	−162.1(9)	O5	Co2	N8	C14	−93.2(8)
N5	Co2	O4	C8	1.3(7)	N6	Co2	O4	C8	−86.4(8)
N7	Co2	O4	C8	−179.5(9)	N8	Co2	O4	C8	87.6(8)

TABLE IV (*Continued*)

O5	Co2	O4	C8	0.9(7)	N5	Co2	O5	C8	179.2(9)
N6	Co2	O5	C8	92.1(8)	N7	Co2	O5	C8	−3.7(7)
N8	Co2	O5	C8	−95.3(8)	O4	Co2	O5	C8	−0.9(7)
Co	N1	C2	C3	−21.5(7)	C4	N1	C2	C3	96.4(13)
C6	N1	C2	C3	−136.3(15)	Co	N1	C4	C5	48.0(8)
C2	N1	C4	C5	−72.7(12)	C6	N1	C4	C5	162.6(17)
Co	N1	C6	C7	−47.3(8)	C2	N1	C6	C7	70.8(12)
C4	N1	C6	C7	−162.2(17)	Co	N2	C3	C2	−38.6(7)
Co	N3	C5	C4	19.9(7)	Co	N4	C7	C6	−27.2(7)
Co2	N5	C9	C10	−47.8(8)	C11	N5	C9	C10	71.2(11)
C13	N5	C9	C10	−162.5(15)	Co2	N5	C11	C12	−20.8(6)
C9	N5	C11	C12	−136.6(14)	C13	N5	C11	C12	96.8(12)
Co2	N5	C13	C14	49.1(7)	C9	N5	C13	C14	163.6(15)
C11	N5	C13	C14	−71.2(11)	Co2	N6	C10	C9	−30.3(7)
Co2	N7	C12	C11	−41.0(7)	Co2	N8	C14	C13	18.8(6)
O2	C1	O1	Co	−4.7(4)	O1	C1	O2	Co	4.6(4)
N1	C2	C3	N2	39.1(8)	N1	C4	C5	N3	−44.5(9)
N1	C6	C7	N4	48.9(9)	O5	C8	O4	Co2	−1.3(4)
O4	C8	O5	Co2	1.4(4)	N5	C9	C10	N6	51.1(9)
N5	C11	C12	N7	40.2(8)	N5	C13	C14	N8	−44.3(8)

wanting to determine the crystallization behavior of the single salt is due to the report that [*cis*-β-Co(trien)(CO_3)]$ClO_4 \cdot H_2O$,[8,9] [Co(meso-2,3-butanediamine)$_2$(CO_3)]H_2O[4] and [*cis*-β-Co(2,3,2-tet)(CO_3)]$ClO_4 \cdot H_2O$[5] crystallize as conglomerates. Since the compound we obtained here is a double salt, we were not able to compare and rationalize the conglomerate crystallization behavior of the above carbonato amine cobalt(III) conglomerate with our racemate.

Compound (II), crystallized as a conglomerate in the primitive, orthorhombic space group $P2_12_12_1$ (No. 19). Examination of the cell constants, Niggli matrix[14] and systematic absences showed no higher symmetry than that. An ORTEP view of the molecular structure of compound (II) is shown in Figure 2. Selected bond distances, bond angles and torsion angles are shown in Table V. In the asymmetric unit there is one [*cis*-β-Co(trien)(CO_3)]$^+$ cation, one water of crystallization and one bicarbonate counter anion. The cobalt cations are in disordered octahedral environments. Each cobalt is coordinated by four nitrogens of amine ligand, and two oxygens of the carbonato ligand. The average bond length for Co–O is 1.910(6) Å, a little shorter than bond lengths of the Co–N(amine) (average 1.948(7) Å). And, for the carbonato ligand, the angle of O–C–O involving two coordinated oxygens is 111.0(7)°, the chelating angle of O–Co–O is 68.9(3)°, while the O–C–O angles for the bicarbonate anion is near 120°.

Earlier, we reported that compounds [*cis*-β-Co(trien)(NO_2)$_2$]$\cdot X \cdot H_2O$, $X = Cl^-$, I^-, crystallized as conglomerates and share the same mechanism

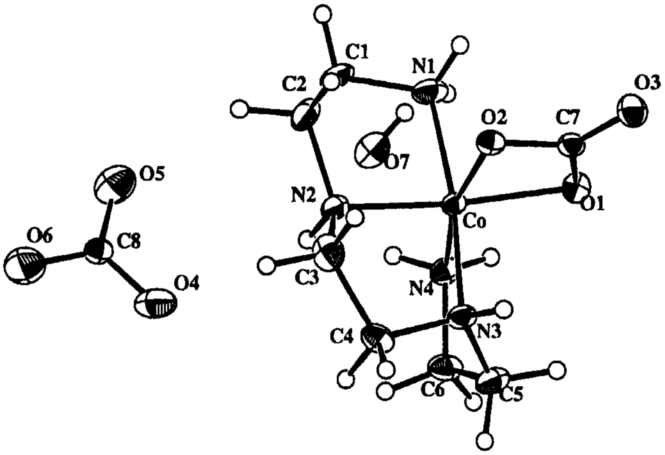

FIGURE 2 Ortep view of the molecular structure of compound (II), [*cis*-β-[Co(trien)(CO_3)] · HCO_3 · H_2O. Thermal ellipsoids are drawn at 30% probability level.

TABLE V Selected bond distances, bond angles and torsion angles for compound (II) [*cis*-β-Co(trien)(CO_3)] · HCO_3 · H_2O

Co–O1	1.911(6)	C1–C2	1.511(18)
Co–O2	1.909(6)	C1–H3	1.007(12)
Co–N1	1.973(7)	C1–H4	0.985(10)
Co–N2	1.919(8)	C2–H5	1.022(13)
Co–N3	1.964(7)	C2–H6	1.009(11)
Co–N4	1.938(8)	C3–C4	1.537(16)
O1–C7	1.312(11)	C3–H8	0.999(14)
O2–C7	1.309(11)	C3–H9	1.005(11)
O3–C7	1.237(11)	C4–H10	0.997(11)
N1–C1	1.470(16)	C4–H11	1.024(10)
N1–H1	0.969(10)	C5–C6	1.494(16)
N1–H2	0.957(10)	C5–H13	1.010(11)
N2–C2	1.499(13)	C5–H14	0.994(10)
N2–C3	1.442(14)	C6–H15	1.018(11)
N2–H7	0.962(7)	C6–H16	1.015(12)
N3–C4	1.485(15)	H1–H2	1.5513(7)
N3–C5	1.486(14)	H17–H18	1.5513(8)
N3–H12	0.963(10)	O4–C8	1.237(14)
N4–C6	1.507(14)	O5–C8	1.223(14)
N4–H17	0.951(8)	O6–C8	1.228(12)
N4–H18	0.967(8)	O7–H19	0.81(11)
O1–Co–O2	68.9(3)	Co–N2–C3	106.8(6)
O1–Co–N1	94.2(3)	C2–N2–C3	114.1(8)
O1–Co–N2	165.5(3)	Co–N3–C4	108.8(6)
O1–Co–N3	93.1(3)	Co–N3–C5	105.8(6)
O1–Co–N4	97.6(3)	C4–N3–C5	114.0(9)
O2–Co–N1	89.9(4)	Co–N4–C6	110.8(6)
O2–Co–N2	96.7(3)	N1–C1–C2	108.2(9)
O2–Co–N3	91.3(4)	N2–C2–C1	104.1(9)
O2–Co–N4	166.2(3)	N2–C3–C4	104.8(8)
N1–Co–N2	86.8(4)	N3–C4–C3	107.9(8)

TABLE V (*Continued*)

N1–Co–N3				172.6(4)	N3–C5–C6				109.5(8)
N1–Co–N4				93.6(4)	N4–C6–C5				107.1(8)
N2–Co–N3				85.8(4)	O1–C7–O2				111.0(7)
N2–Co–N4				96.8(3)	O1–C7–O3				125.1(9)
N3–Co–N4				87.0(4)	O2–C7–O3				123.8(9)
Co–O1–C7				89.9(5)	O4–C8–O5				120.0(10)
Co–O2–C7				90.1(5)	O4–C8–O6				120.2(10)
Co–N1–C1				107.8(7)	O5–C8–O6				119.8(11)
Co–N2–C2				106.4(6)					
O2	Co	O1	C7	−1.3(5)	N1	Co	O1	C7	87.0(6)
N2	Co	O1	C7	−6.2(5)	N3	Co	O1	C7	−91.4(6)
N4	Co	O1	C7	−178.8(7)	O1	Co	O2	C7	1.3(5)
N1	Co	O2	C7	−93.2(6)	N2	Co	O2	C7	−180.0(7)
N3	Co	O2	C7	94.1(6)	N4	Co	O2	C7	11.7(5)
O1	Co	N1	C1	−169.5(8)	O2	Co	N1	C1	−100.7(7)
N2	Co	N1	C1	−4.0(5)	N3	Co	N1	C1	−1.7(5)
N4	Co	N1	C1	92.6(7)	O1	Co	N2	C2	68.2(6)
O1	Co	N2	C3	−54.0(6)	O2	Co	N2	C2	63.6(6)
O2	Co	N2	C3	−58.7(6)	N1	Co	N2	C2	−26.0(5)
N1	Co	N2	C3	−148.2(7)	N3	Co	N2	C2	154.3(7)
N3	Co	N2	C3	32.1(6)	N4	Co	N2	C2	−119.2(7)
N4	Co	N2	C3	118.5(7)	O1	Co	N3	C4	162.4(8)
O1	Co	N3	C5	−74.7(6)	O2	Co	N3	C4	93.5(6)
O2	Co	N3	C5	−143.7(7)	N1	Co	N3	C4	−5.5(5)
N1	Co	N3	C5	117.4(7)	N2	Co	N3	C4	−3.2(5)
N2	Co	N3	C5	119.7(7)	N4	Co	N3	C4	−100.2(7)
N4	Co	N3	C5	22.7(5)	O1	Co	N4	C6	95.3(6)
O2	Co	N4	C6	85.5(6)	N1	Co	N4	C6	−170.0(7)
N2	Co	N4	C6	−82.8(6)	N3	Co	N4	C6	2.6(5)
Co	O1	C7	O2	1.8(3)	Co	O1	C7	O3	−177.5(9)
Co	O2	C7	O1	−1.8(3)	Co	O2	C7	O3	177.5(9)
Co	N1	C1	C2	33.1(6)	Co	N2	C2	C1	49.3(6)
C3	N2	C2	C1	166.9(13)	Co	N2	C3	C4	−52.2(6)
C2	N2	C3	C4	−169.5(12)	Co	N3	C4	C3	−24.5(5)
C5	N3	C4	C3	−142.4(12)	Co	N3	C5	C6	−44.2(6)
C4	N3	C5	C6	75.3(9)	Co	N4	C6	C5	−27.3(5)
N1	C1	C2	N2	−54.2(8)	N2	C3	C4	N3	50.1(7)
N3	C5	C6	N4	47.1(7)					

for doing so.[15,16] We also reported that compounds [*cis*-$Co(en)_2(NO_2)_2$] · X, X = Cl^-, Br^-, I^-, all crystallized as conglomerates and also share the same mechanism of conglomerate crystallization.[15–17] In both series, strong intermolecular hydrogen bonds involving nitro oxygens of one cation and amine hydrogens of an adjacent one helped hold the cations together in an infinite helical array characteristic of this crystallization mode. The halides and/or waters of crystallization (where relevant) linked the pair of basal amine hydrogens, thus joining adjacent helical conglomerate chains. The charge compensating counter anion has been found to be very important in conglomerate crystallization.[15–17] When halide anions are replaced by powerful hydrogen bonding species, such as NO_3^- and NO_2^-, these species successfully compete for the amino hydrogens with the nitro (NO_2^-) oxygens and racemic crystals obtained since helix formation is hindered.[18,19]

For the carbonato compounds, we noted that [*cis*-β-Co(trien)(CO_3)]$ClO_4 \cdot H_2O$,[8,9] [Co(meso-2,3-butanediamine)$_2$(CO_3)]H_2O[4] and [*cis*-β-Co (2,3,2-tet)(CO_3)]$ClO_4 \cdot H_2O$[5] crystallize as conglomerates. But two differences exist between these carbonato amine cobalt(III) compounds, first, unlike the dinitro series discussed above, which crystallize in the same space groups, those of the carbonato series do not. Therefore the packing motifs differ widely, which makes it difficult to compare their intermolecular and intramolecular bonding modes.

For example, [*cis*-β-Co(trien)(CO_3)]$ClO_4 \cdot H_2O$,[8,9] crystallized in the monoclinic, enantiomorphic, space group $P2_1$ with two independent molecules in the asymmetric unit. The complex cations are linked to the adjacent water molecules through hydrogen bonds; that is, there are hydrogen bonds between the non-coordinated carbonato oxygens of one complex cation and a water hydrogen, and the water oxygen forms hydrogen bonds with a hydrogen of the amino nitrogen of another complex cation. The complex cations thus form an infinite chain along the *b*-axis, while the perchlorate anions link the infinite chains together by forming additional hydrogen bonds.

On the other hand, compound (II), [*cis*-β-Co(trien)(CO_3)](HCO_3)$\cdot H_2O$, crystallizes in the orthorhombic system, space group $P2_12_12_1$, and there is only one molecule in its asymmetric unit. The water molecule does not hydrogen bond to the non-coordinated oxygen, O3 and does not link to another cation through hydrogen bonds, as described in the case of [*cis*-β-Co(trien)(CO_3)]$ClO_4 \cdot H_2O$. Instead, the complex cations of (II) are linked together by hydrogen bonds between O3 and the secondary hydrogen H7 of N2, with an O3 $\cdots$ H7 bond of 1.932 Å. A similar hydrogen bond was described by Oliver *et al.*,[8] but not shown in the paper of Masuda *et al.*[9] The homochiral complex cation chains formed in compound (II) are along the *c*-axis (Figure 3). The HCO_3^- anion and water molecule help to hold these complex cation chiral chains by electrostatic interactions and/or hydrogen bonds (≤ 2.5 Å) such as O4–H2(N1) of 2.185 Å, O4–H17(N4) of 2.21 Å, O5–H12(N3) of 2.241 Å, O5–H17(N4) of 2.331 Å, O7–H18(N4) of 2.380 Å and O7–H1(N1) of 2.483 Å.

Second, for the two dinitro series of conglomerate crystallization, derivatives with halide as counter anions form conglomerates. When halide anions are replaced by powerful hydrogen bonding species, racemic crystals were obtained. We found that these powerful hydrogen bonding anions, such as NO_3^-, NO_2^-, successfully compete for the amino hydrogens with the nitro

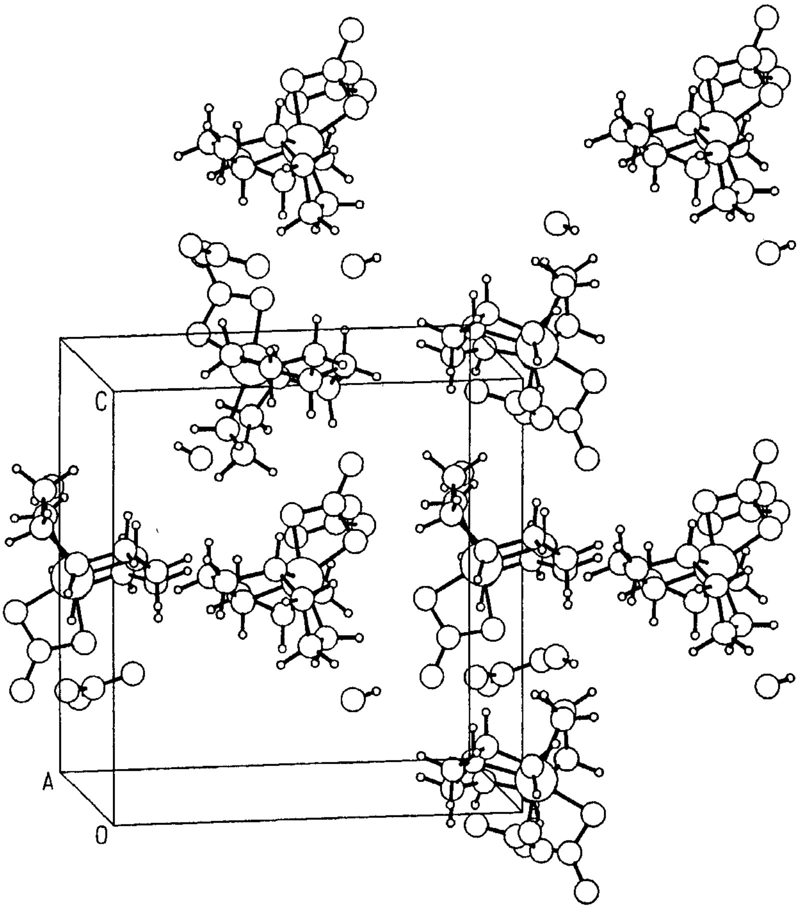

FIGURE 3 Packing diagram of compound (II) [*cis*-β-Co(trien)(CO_3)] · HCO_3 · H_2O.

(NO_2^-) oxygens, and the desired hydrogen bonding pattern essential for conglomerate crystallization is impeded; thus, racemate crystals were obtained. By contrast, in carbonato compounds such as [*cis*-β-Co(trien)(CO_3)](HCO_3) · H_2O (II) and [*cis*-β-Co(trien)(CO_3)]ClO_4 · H_2O, both anions are relatively strong hydrogen bonding moieties. Racemic crystals would be expected, if such a criterion were applied here. We think this apparent contradiction is caused by the differing composition and stereochemistry of the cations. In the preceding series of dinitro complex cations there are four nitro oxygens which have the potential to form hydrogen bonds, and the homochiral complex chain is formed by "a three-point recognition mechanism" (detailed in the above references). However, in these two carbonato complexes, there is only one non-coordinated carbonato oxygen that has the potential to form strong hydrogen bonds. Therefore, the HCO_3^-, and ClO_4^- anions do not have to compete for the amine hydrogen as was the case with the dinitro compounds. On the contrary, we think that these hydrogen bonding species, instead of destroying the opportunity for conglomerate crystallization, are important in both stabilizing the infinite complex cation chain and holding different infinite chains together.

Thus, from the above discussion, the crystallization behavior of compounds [*cis*-β-Co(trien)(CO_3)](HCO_3) · H_2O (**II**) and [*cis*-β-Co(trien)(CO_3)]-ClO_4 · H_2O provide more information about the ways these compounds can achieve conglomerate crystallization. In other words, all the possibilities of packing that may lead to conglomerates rather than racemates are not yet understood. Before we conclude this discussion, the composition of compound (**II**) must be examined. The positions of all hydrogens other than those of the water of crystallization were added at their ideal positions. Charge compensation and chemical composition made us choose between the formulae [*cis*-β-Co(trien)(CO_3)](HCO_3) · H_2O and [*cis*-β-Co(trien)-(HCO_3)](CO_3) · H_2O; the former was chosen because of the well-known fact that the carbonato anion is a better ligand than bicarbonate, having a higher Coulombic charge. However, if the latter is eventually found to be correct, it will not affect our conclusions on conglomerate crystallization of compound (**II**).

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References

[1] I. Bernal, X. Xia and F. Somoza, in *Fundamental Principles of Molecular Modeling* (Eds. W. Gans, A. Amman and J.C.A. Boeyenes) (New York: Plenum Press 1996) p. 223.
[2] I. Bernal, F. Somoza, Ya-Chen Chen and S.S. Massoud, *J. Coord. Chem.*, **42**, 1, 1997.
[3] R. Wen and I. Bernal, *J. Coord. Chem.*, 1999 (in press).
[4] M.F. Gargallo, J.D. Mather, E.N. Duesler and R.E. Tapscott, *Inorg. Chem.*, **22**, 2888 (1983).
[5] J.H. Loehlin and E.B. Fleisher, *Acta Cryst.*, **B32**, 3063 (1976).
[6] K. Yamanari, private communication to I. Bernal, December 3, 1987.
[7] I. Bernal, J. Myrczek and J. Cetrullo, *J. Coord. Chem.*, **29**, 319 (1993).
[8] P.J. Oliver, B.F. Hoskins and H.M. Grant, *Acta Cryst. Sect.*, **C47**, 2348 (1991).
[9] H. Masuda, C. Masuda, K. Jitsukawa and H. Einaga, *Bull. Chem. Soc. Jpn.*, **67**, 3000 (1994).
[10] H.F. Bauer and W.C. Drinkard, *J. Am. Chem. Soc.*, **72**, 5031 (1960).
[11] Galbraith Laboratories, Inc., P.O. Box 51610, Knoxville, TN, 37950-1610.

[12] D.T. Cromer and J.T. Waber, J.T., in *International Tables for X-Ray Crystallography*, The Kynoch Press, Birmingham, England, 1975; Vol. IV, Tables 2.2.8 and 2.3.1, respectively, for the scattering factor curves and the anomalous dispersion values.

[13] The NRCVAX Crystal Structure System, A.C. Larson, F.L. Lee, Y. Le Page, M. Webster, J.P. Charland and E.J. Gabe, as adapted for PC use by P.S. White, University of North Carolina, Chapel Hill, N. C., 27599-3290.

[14] R.B. Roof, in A theoretical extension of the reduced cell concept crystallography, Report LA-4038, Los Alamos Scientific Laboratory, 1969.

[15] I. Bernal, *Inorg. Chim. Acta*, **96**, 99 (1985).

[16] I. Bernal, J. Cetrullo, *Inorg. Chim. Acta*, **134**, 105 (1987).

[17] I. Bernal, J. Cetrullo, J. Myerzek, *Mater. Chem. Phys.*, **35**, 290 (1993).

[18] I. Bernal, J. Cetrullo, S. Berhane, *Struct. Chem.*, **1**, 361 (1990).

[19] I. Bernal, J. Cetrullo, *Inorg. Chim. Acta*, **142**, 235 (1988).