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The Crystal and Molecular Structure of Dipotassium *trans*-Dicarbonatotetraaquocobalt(II), *trans*-$K_2[Co(CO_3)_2(H_2O)_4]$

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The crystal structure of the salt *trans*-$K_2[Co(CO_3)_2(H_2O)_4]$ has been determined by single-crystal, X-ray diffraction methods. The crystals are monoclinic, space group $P2_1/n$, with $a = 11·450$ (1), $b = 6·184$ (1), $c = 6·817$ (1) Å, $\beta = 99·46$ (1)°, $Z = 2$, at 23°C. At −40°C, the temperature at which the intensities were collected, the unit-cell parameters were: $a = 11·424$ (1), $b = 6·173$ (1), $c = 6·809$ (1) Å, $\beta = 99·40$ (1)°. Full-matrix least-squares refinement of 2219 intensities $[I > 2\sigma(I)]$ collected by θ–2θ scans on a Syntex $P2_1$ diffractometer (Mo $K\alpha$ radiation) converged at a conventional R of 0·024. All non-hydrogen atoms were refined with anisotropic thermal parameters, H atoms with isotropic parameters. The Co atom (located on a crystallographic inversion center) is octahedrally coordinated with two monodentate carbonate groups to form a *trans*-$[Co(CO_3)_2(H_2O)_4]^{2-}$ complex anion, in agreement with predictions made on the basis of infrared and electronic spectra. The Co–O bond lengths are: Co–O (carbonate) = 2·068 (1); Co–O(water) = 2·121 (1) and 2·130 (1) Å. The carbonate group, with C–O distances of 1·291 (1), 1·291 (1) and 1·284 (1) Å, shows almost no distortion from D_{3h} symmetry. The complex ions are interconnected by a network of hydrogen bonds from the H atoms of the water molecules to the O atoms of the carbonate groups.

Introduction

The infrared spectrum of a carbonatometallate complex may often be used to discern the presence of a bidentate and/or monodentate carbonate ligand. From an analysis of the infrared spectrum, Scott (1967) and Blumentritt (1967) concluded that the title compound contained monodentate carbonate ions. From the electronic spectrum, they additionally deduced that the cobalt atom was octahedrally coordinated, forming a $[Co(CO_3)_2(H_2O)_4]^{2-}$ species. The crystal structure was undertaken to verify these predictions, to assist in further correlations between the infrared spectrum and the bonding of the carbonate ion, and to continue our investigation into the distortion (from D_{3h} symmetry) of the carbonate ion when coordinated to transition metal ions.

Experimental

Crystals of the title compound were prepared according to the method of Reynolds (1898). Preliminary unit-cell parameters and space-group information were obtained from Weissenberg photographs. The lattice parameters at 23 °C were refined by the least-squares method from the Bragg angles of 23 reflections ($135 < 2\theta < 147$°, Cu $K\alpha_1$, $\lambda = 1·54050$ Å) measured on a G.E. XRD-5 diffractometer. The lattice parameters at −40 °C were refined with 60 low-angle reflections ($24 < 2\theta < 30$°, Mo $K\alpha$, $\lambda = 0·71069$ Å) measured on a Syntex $P2_1$ diffractometer using the Syntex centering routine. Table 1 summarizes the crystal data.

A crystal with dimensions of 0·13 × 0·15 × 0·35 × 0·39 mm perpendicular to (100), $(10\bar{1})$, $(1\bar{1}0)$ and (110),

Table 1. *Crystal data*

trans-$K_2[Co(CO_3)_2(H_2O)]_4$, F.W. 329·2
Monoclinic, $P2_1/n$, $Z = 2$

	at 23 °C	at −40 °C
a	11·450 (1) Å	11·424 (1) Å
b	6·184 (1)	6·173 (1)
c	6·817 (1)	6·809 (1)
β	99·46 (1)	99·40 (1)°
V	476·1 Å^3	473·7 Å^3
D_m	2·293 g cm^{-3}	
D_x	2·296	

respectively, was mounted on the Syntex diffractometer (Mo $K\alpha$ radiation monochromatized by a graphite crystal). The θ–2θ scan technique was employed to collect intensity data for 2514 independent reflections in the range $4 < 2\theta < 75°$. The reflections were scanned 1·2° in 2θ below and beyond the $K\alpha_1$ and $K\alpha_2$ peaks respectively; P counts were accumulated. The scan rate, S, varied from 1·5 to 5·0° min^{-1} dependent on the number of counts measured in a rapid preliminary scan of each reflection. Background counts, B_1 and B_2, were taken at both ends of the scan range, each for a time equal to half the scan time. The intensities of four standard reflections were monitored after every 96 reflections; only statistical variations were noted.

The net intensity, I (relative to a 1·0° min^{-1} scan rate), and its estimated standard deviation, $\sigma(I)$, were calculated as follows: $I = S(P - B_1 - B_2)$; $\sigma^2(I) = S^2(P + B_1 + B_2) + pI^2$, where p was assigned a judicious value of 0·03. Absorption corrections based on crystal shape were applied to the data (transmission coefficients ranged from 0·62 to 0·75; $\mu(\text{Mo } K\alpha) = 27{\cdot}8\ \text{cm}^{-1}$). Conversion to structure amplitudes was completed with the application of Lorentz and polarization factors. Values of $\sigma(F_o)$ were derived directly from $\sigma(I)$ taking into account the various corrections that were made.

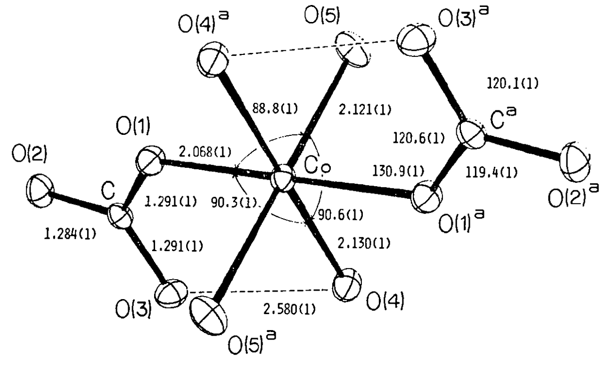

Fig. 1. Bond distances and angles for the *trans*-$[\text{Co(CO}_3)_2(\text{H}_2\text{O})_4]^{2-}$ complex.

Structure solution and refinement

The structure amplitudes were initially phased by placing the Co atom on the inversion center at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ $(Z = 2)$; a Fourier map readily revealed the position of the K$^+$ ion. The remaining non-hydrogen atoms were then located in a subsequent electron-density map. Refinement of the structure by the full-matrix least-squares method was carried out using only those 2219 reflections for which $I > 2\sigma(I)$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and w is the weight calculated as $1/\sigma^2(F_o)$. A difference map was used to locate the H atoms. During the refinement, H(4*A*) moved unreasonably close (0·74 Å) to O(4) and it was then fixed at the position found in the difference map. Refinement of all other positional and all thermal (anisotropic for the non-hydrogen atoms and isotropic for the H atoms) parameters, a total of 83 variables, converged at a conventional $R = (\sum||F_o| - |F_c||/\sum|F_o|)$ of 0·024 and a weighted $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ of 0·032. Because extinction effects were not evident, an extinction parameter was not refined.

In the final cycle of refinement, the largest shift in any parameter was 0·09σ. The largest peak in the final difference Fourier was located near the Co atom and had a height of 0·5 e Å^{-3}. The standard deviation of an observation of unit weight was 1·47. The positional and thermal parameters are given in Table 2.*

The atomic scattering factors for Co, K$^+$, O and C were those of Cromer & Waber (1965); for H, those of Stewart, Davidson and Simpson (1965) were used. The Co and K$^+$ scattering factors were corrected for anomalous dispersion (Cromer, 1965). Four electrons per unit cell, electrons associated with the π-density of the carbonate ions, have not been accounted for.

Table 2. *Final positional and thermal parameters for trans*-$\text{K}_2[\text{Co(CO}_3)_2(\text{H}_2\text{O})_4]$

The anisotropic thermal parameters are $\times 10^5$ for the Co and K atoms, $\times 10^4$ for the C and O atoms, and are in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + klb^*c^*U_{23})]$.

	x	y	z	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0·5	0·5	0·5	984 (8)	1065 (8)	1195 (8)	−29 (6)	185 (5)	134 (6)
K	0·31494 (2)	0·14754 (4)	0·08588 (4)	1825 (10)	1521 (10)	1648 (10)	−18 (7)	445 (7)	−58 (7)
C	0·32086 (9)	0·15262 (16)	0·57845 (14)	127 (4)	106 (4)	121 (4)	−2 (3)	39 (3)	−12 (3)
O(1)	0·34941 (7)	0·30923 (13)	0·47004 (12)	137 (3)	152 (3)	154 (3)	−30 (3)	12 (2)	39 (3)
O(2)	0·21909 (7)	0·06173 (15)	0·53204 (13)	138 (3)	172 (3)	209 (4)	−46 (3)	43 (3)	−13 (3)
O(3)	0·39374 (7)	0·08714 (15)	0·73204 (12)	192 (4)	166 (4)	144 (3)	−17 (3)	4 (3)	34 (3)
O(4)	0·59270 (7)	0·27205 (15)	0·70310 (13)	137 (3)	176 (4)	183 (3)	−1 (3)	11 (3)	28 (3)
O(5)	0·55212 (9)	0·33189 (15)	0·25671 (14)	232 (4)	150 (4)	216 (4)	17 (3)	108 (3)	5 (3)
H(4*A*)*	0·633	0·325	0·821	0·059 (8)					
H(4*B*)	0·524 (2)	0·216 (4)	0·719 (4)	0·047 (7)					
H(5*A*)	0·606 (1)	0·386 (3)	0·196 (3)	0·014 (4)					
H(5*B*)	0·576 (2)	0·207 (4)	0·267 (4)	0·041 (6)					

* Position determined from difference map and not refined by least-squares calculations.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31223 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Computer programs include the following: *SYSABS*, a local version of *ORABS* by W. R. Busing and H. A. Levy as modified by J. M. Williams, for absorption correction; *RFOUR*, Fourier synthesis, by S. T. Rao, modified by R. E. Davis; *NUCLS*, full-matrix least-squares refinement, *ORFLS* as modified by J. A. Ibers; *DAESD*, distance, angles and their estimated standard deviations, by D. R. Harris, modified by R. E. Davis; and *ORTEP*, by C. K. Johnson.

Table 3. *Bond angles* (°) *to accompany the bond distances given in Fig.* 2

(*a*) K^{+} environment

O(1)–K–O(5)	61·0 (1)	O(3)^{b}–K–O(4)^{c}	99·2 (1)
O(1)–K–O(3)^{b}	150·0 (1)	O(3)^{b}–K–O(4)^{d}	135·5 (1)
O(1)–K–O(4)^{c}	82·9 (1)	O(3)^{b}–K–O(1)^{e}	95·1 (1)
O(1)–K–O(4)^{d}	70·5 (1)	O(3)^{b}–K–O(2)^{f}	85·3 (1)
O(1)–K–O(1)^{e}	112·8 (1)	O(4)^{c}–K–O(4)^{d}	105·8 (1)
O(1)–K–O(2)^{f}	86·0 (1)	O(4)^{c}–K–O(1)^{e}	66·7 (1)
O(5)–K–O(3)^{b}	89·2 (1)	O(4)^{c}–K–O(2)^{f}	164·9 (1)
O(5)–K–O(4)^{c}	85·3 (1)	O(4)^{d}–K–O(1)^{e}	63·6 (1)
O(5)–K–O(4)^{d}	128·4 (1)	O(4)^{d}–K–O(2)^{f}	79·9 (1)
O(5)–K–O(1)^{e}	152·0 (1)	O(1)^{e}–K–O(2)^{f}	127·5 (1)
O(5)–K–O(2)^{f}	80·3 (1)		

(*b*) CO_3^{2-} environment

C–O(1)–Co	130·9 (1)	Co——O(1)–K	106·6 (1)
C–O(1)–K	105·1 (1)	Co——O(1)–K^{f}	96·8 (1)
C–O(1)–K^{f}	114·3 (1)	K——O(1)–K^{f}	98·8 (1)
C–O(2)–K^{h}	124·8 (1)	K^{h}——O(2)–H(4*A*)^{d}	96
C–O(2)–H(4*A*)^{d}	113	K^{h}——O(2)–H(5*A*)^{i}	105 (1)
C–O(2)–H(5*A*)^{i}	118 (1)	H(4*A*)^{d}–O(2)–H(5*A*)^{i}	94
C–O(3)–K^{g}	114·2 (1)	K^{g}——O(3)–H(4*B*)	114 (1)
C–O(3)–H(4*B*)	105 (1)	K^{g}——O(3)–H(5*B*)^{c}	103 (1)
C–O(3)–H(5*B*)^{c}	114 (1)	H(4*B*)–O(3)–H(5*B*)^{c}	107 (1)

(*c*) Environment of the O(4) water molecule

Co–O(4)–K^{c}	163·6 (1)	K^{j}——O(4)——O(2)^{j}	77·4 (1)
Co–O(4)–K^{j}	94·3 (1)	K^{j}——O(4)——O(3)	160·5 (1)
Co–O(4)–O(2)^{j}	115·8 (1)	K^{j}——O(4)——H(4*A*)	81
Co–O(4)–O(3)	89·5 (1)	K^{j}——O(4)——H(4*B*)	165 (2)
Co–O(4)–H(4*A*)	117	O(2)^{j}—O(4)——O(3)	118·0 (1)
Co–O(4)–H(4*B*)	89 (2)	O(2)^{j}—O(4)——H(4*B*)	115 (2)
K^{c}–O(4)–K^{j}	91·4 (1)	O(3)——O(4)——H(4*A*)	115
K^{c}–O(4)–O(2)^{j}	80·4 (1)	H(4*A*)-O(4)——H(4*B*)	111
K^{c}–O(4)–O(3)	80·2 (1)	O(4)——H(4*A*)-O(2)^{j}	174
K^{c}–O(4)–H(4*A*)	79	O(4)——H(4*B*)-O(3)	174 (3)
K^{c}–O(4)–H(4*B*)	82 (2)		

(*d*) Environment of the O(5) water molecule

Co–O(5)–K	97·9 (1)	K——O(5)——H(5*B*)	87 (2)
Co–O(5)–O(2)^{k}	129·4 (1)	O(2)^{k}—O(5)——O(3)^{c}	94·0 (1)
Co–O(5)–O(3)^{c}	123·2 (1)	O(2)^{k}—O(5)——H(5*B*)	91 (2)
Co–O(5)–H(5*A*)	120 (1)	O(3)^{c}—O(5)——H(5*A*)	102 (1)
Co–O(5)–H(5*B*)	122 (2)	H(5*A*)–O(5)——H(5*B*)	99 (2)
K—O(5)–O(2)^{k}	123·2 (1)	O(5)——H(5*A*)–O(2)^{k}	166 (2)
K—O(5)–O(3)^{c}	80·4 (1)	O(5)——H(5*B*)-O(3)^{c}	171 (3)
K—O(5)–H(5*A*)	129 (1)		

Symmetry operations used in Figs. 1 and 2 and Table 3:

(*a*)	$1-x$,	$1-y$,	$1-z$	(*g*)	x,	y,	$1+z$
(*b*)	x,	y,	$-1+z$	(*h*)	x,	$-1+y$,	z
(*c*)	$1-x$,	$-y$,	$1-z$	(*i*)	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
(*d*)	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$	(*j*)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
(*e*)	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$	(*k*)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$
(*f*)	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$				

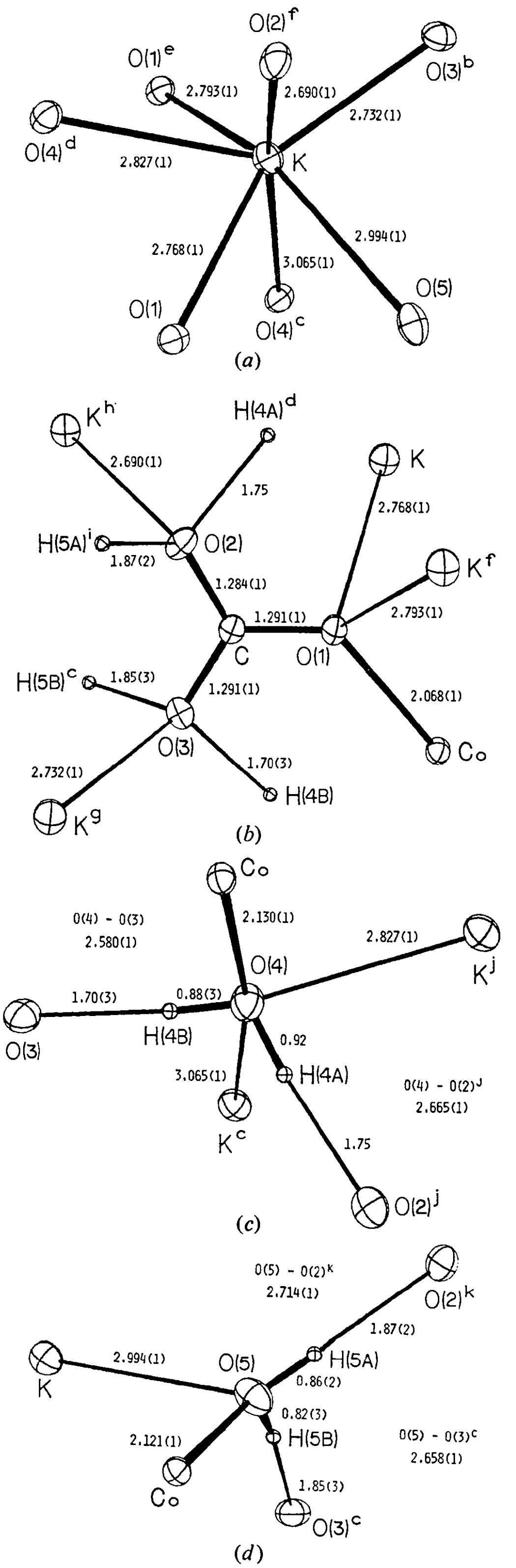

Fig. 2. Environments of the various chemical species (bond angles are given in Table 3); (*a*) the potassium ion, (*b*) the carbonate ion, (*c*) the O(4) water molecule, (*d*) the O(5) water molecule.

Discussion

The structure of the cobalt complex is precisely that predicted by Scott (1967) and Blumentritt (1967) and consists of *trans*-$[Co(CO_3)_2(H_2O)_4]^{2-}$ units in which the Co atom is octahedrally coordinated to four water molecules and two monodentate carbonate ions (Fig. 1). Strong intramolecular hydrogen bonds exist between two of the water molecules and the carbonate groups. Hydrogen bonds between neighboring complex units are the main feature of the crystal structure. The K^+ ions are located within an irregular polyhedron of seven O atoms. Figs. 2 and 3 and Table 3 give the details of these interactions.

The Co complex shows only small distortions from true octahedral symmetry. The largest deviation (from 90°) of any O–Co–O angle is 1·2°. The Co–O bond lengths vary from 2·068(1) Å for the carbonate group to 2·121(1) and 2·130(1) Å for the water molecules containing O(5) and O(4), respectively. The shorter Co–O distance for the carbonate group reflects the better donor capabilities of a charged species. It was pointed out by the referee that Fig. 1 gives the impression that O(3) of the carbonate group is partially bonded to the Co atom. With a Co–O(3) distance of 3·331(1) Å and a C–O(3)–Co angle of 67·2 (1)°, there is clearly no bond between the two. The difference in the two Co–O(water) distances, admittedly small, is consistent with the observation that O(5) only interacts with one neighboring K^+ while O(4) interacts with two; hence, O(4) forms a weaker bond with the Co atom. The Co–O(water) distances are somewhat longer than those found for the $[Co(H_2O)_6]^{2+}$ ion [2·08 ± 0·03 Å: Lynton & Siew (1973); Ottersen, Warner & Seff (1974); Prelesnik, Gabela, Ribár & Krstanović (1973)], but is in reasonable accord with Co(II) complexes containing both water and anionic ligands [as in $Co(IO_3)_2(H_2O)_2$, 2·090 and 2·134 Å, Elemans & Verschoor (1973)].

Previous studies of carbonate complexes of transition metal ions have shown that the carbonate group can function as a monodentate, a bidentate, or as a bridging group of the type M–O–(CO)–O–M′. It is generally found that the carbonate ion distorts from D_{3h} symmetry with an increase in the C–O bond length(s) for the coordinated O atom(s) and a decrease in the C···O distance(s) for the non-coordinated O atom(s) (Harlow & Simonsen, 1975; Healy & White, 1972; Meyer, Singh, Hatfield & Hodgson, 1972; Geue & Snow, 1971; Kaas & Sorensen, 1973; Freeman & Robinson, 1965; and references therein). In addition, the metal atom is usually coplanar with a bidentate carbonate ion, but deviates significantly from the plane of a unidentate or bridging carbonate group. The carbonate ion in the present structure, however, is unusual in two respects: (i) There is virtually no distortion from D_{3h} symmetry. (Although two of the C–O bond lengths differ significantly on the basis of the estimated standard deviations, the maximum difference, 0·007 Å, is a very small number in an absolute sense. Furthermore, since there is no ready explanation for the difference between C–O(2) and C–O(3), where the O atoms have very similar environments, one is led to suspect that the error in the bond lengths is greater than the e.s.d.'s would indicate. The use of spherical-atom scattering factors for light atoms with lone-pairs and π-bonds almost guarantees that such errors will occur.) (ii) The Co atom is nearly in the plane of the carbonate group, deviating by only 0·060 Å. There is a possibility that these two features are interrelated; Healy & White (1972) have suggested that there is a direct relationship between the carbonate distortion and the distance of the metal atom from the unidentate carbonate plane. The Co–O(1)–C angle of 130·9(1)°, although rather large [evidently to accommodate the intramolecular hydrogen bond between carbonate O(3) and the water O(4)], does not seem unusual. A value of 129·9° has been reported for a bridging carbonate ion (Harlow & Simonsen, 1975), and a value of 137° was noted for the $[Co(NH_3)_5CO_3]^+$ complex, where an intramolecular hydrogen bond – between an NH_3 group and the CO_3^{2-} ion – similar to the one in the title compound was found (Freeman & Robinson, 1965).

A 'coordination' number of seven for the K^+ ion is quite common (*e.g.* Butler & Snow, 1975; Gartland, Gatehouse & Craven, 1975). The four shortest K–O contacts, 2·690–2·793 Å, involve the O atoms of the

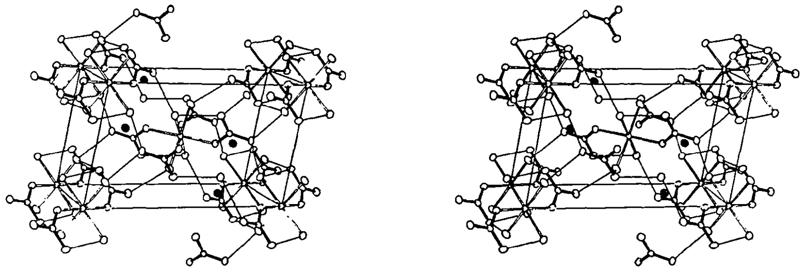

Fig. 3. Packing diagram for $K_2[Co(CO_3)_2(H_2O)_4]$. The view is nearly parallel to the *b* axis; the *a* axis is horizontal. The K ions and the carbonate C–O bonds have been blackened. The hydrogen bonds, as well as the unit-cell boundaries, are indicated by thin lines. The H atoms are not shown.

carbonate ion. The three remaining K–O(water) distances range from 2·827 to 3·065 Å. The variation in the K–O distances is typical.

The network of hydrogen bonds can be seen in Fig. 3. Each of the H atoms associated with the water molecules forms a single, strong hydrogen bond with an O atom of a neighboring carbonate group. The four unique O···O distances vary from 2·580 to 2·714 Å. The O–H···O angles are nearly linear: 166–174°.

A comparison of the powder-diffraction patterns indicates that the Ni salt, $K_2Ni(CO_3)_2(H_2O)_4$, is isomorphous with the Co salt presented here. This fact, coupled with the similarity of the infrared spectra, suggests that the two salts are isostructural.

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Conformational Studies on Oligomethylene Glycol Derivatives and Related Compounds. I. The Crystal and Molecular Structure of Ethylene Glycol Dibenzoate, $C_{16}H_{14}O_4$

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The crystal structure of ethylene glycol dibenzoate, $C_{16}H_{14}O_4$, has been solved by direct methods from 1590 reflexions collected on a Picker diffractometer. The final *R* value is 0·040. The crystals, which have an orthorhombic unit cell of dimensions $a=7{\cdot}558$ (5), $b=21{\cdot}834$ (7) and $c=16{\cdot}210$ (7) Å, belong to the space group *Pbca*. The molecule is in a quasi-*trans* conformation, only 0·15 Å short of the all-*trans* conformation. An interesting feature is the significant shortening of the ethylene part of the molecule where the CH_2–CH_2 distance is only 1·499 (2) Å. The implication of this observation may have important consequences for the structures of aliphatic and aromatic polyesters. The molecules are held in the crystal by van der Waals forces only.

Introduction

X-ray studies of various kinds of aliphatic polymers of the type $[O\text{–}(CH_2)_x\text{–}O\text{–}CO\text{–}(CH_2)_y\text{–}CO]_n$, especially of polyesters made of ethylene glycol ($x=2$), trimethylene glycol ($x=3$) and decamethylene glycol ($x=10$) were first investigated by Fuller & Erickson (1937), Fuller & Frosch (1939*a*, *b*), Fuller, Frosch & Pape (1942). For all the polyesters with $x=2$ and $y>4$, it was found that the length of the chemical repeat unit was always shorter, by about 0·5 Å, than the fully extended zigzag conformation.

Turner-Jones & Bunn (1962) determined the crystal structures of polyethylene adipate ($x=2$, $y=4$) and of polyethylene sebacate ($x=2$, $y=6$), and found a considerable deviation from the planar conformation in the glycol part of the chain.

Daubeny, Bunn & Brown (1954) were first to deter-