metal-organic compounds

Potassium bis(carbonato-*O*,*O*′)-(ethylenediamine-*N*,*N*′)cobaltate(III) monohydrate at 173 K

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The title salt, K[Co(C$_2$H$_8$N$_2$)(CO$_3$)$_2$]·H$_2$O, consists of a distorted octahedral cobalt complex anion and a seven-coordinate potassium cation. Both metal atoms have crystallographic twofold symmetry, one C_2 axis passing through the Co atom and C—C bond, and another along a short K—O (water) bond of 2.600 Å (corrected for libration). The carbonate is bidentate to both cobalt and potassium and the water forms a hydrogen bond to a carbonate O atom.

Comment

Carbonate complexes of cobalt(III) are important intermediates, allowing access to a wide range of cobalt complexes (Kitamura & Shibata, 1993; Shibata, 1983). There have been several reports of the structure of [CoCO$_3$(en)$_2$]$^+$ (en is ethylenediamine) with various anions (Bigoli *et al.*, 1980; Healy *et al.*, 1981; Bernal *et al.*, 1993; Garcia-Granda *et al.*, 1993; Hu *et al.*, 1997). Structures of other mono-carbonatocobalt(III) complexes have also been reported. To our knowledge, the only previous structure report of a cobalt(III) complex containing two coordinated carbonates on a single Co atom is the binuclear complex (NH$_3$)$_4$Co(μ-NH$_2$)(μ-OH)Co(CO$_3$)$_2$ (Churchill *et al.*, 1979).

(I)
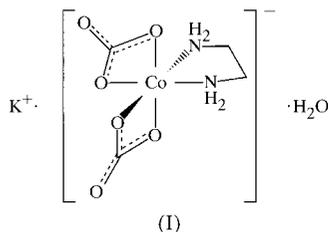
The title salt, K[Co(CO$_3$)$_2$(NH$_2$CH$_2$CH$_2$NH$_2$)]·H$_2$O, (I), contains a distorted octahedral cobalt(III) anion (Fig. 1) with a crystallographic twofold axis passing through the Co atom and the C—C bond of the en ligand. The main distortions from octahedral geometry arise from the narrow 'bite' of the carbonate ligand, with an O1—Co—O2 angle of 69.12 (4)°.

The C1⋯O3 bond is slightly shorter (by about 0.07 Å) than C1⋯O1 and C1⋯O2, suggesting partial localization of the charge on the coordinated carbonate. Other distances and angles of the anion are as expected.

The potassium cation is seven-coordinate (Fig. 2). The carbonate is bidentate to Co through O1 and O2, and also bidentate to K through O2 and O3. The water O4 atom is bound to K along a crystallographic twofold axis, and carbonates from two neighboring anions bind in a monodentate fashion through O1. The two carbonate O1 atoms and the O4 water oxygen form a trigonal plane with the K atom, having O—K—O angles of 124.28 (2), 124.28 (2) and 111.43 (5)°. The remaining O atoms from the bidentate carbonates form another approximate plane nearly perpendicular to the trigonal plane. Thus, the K coordination might be described as a type of trigonal bipyramidal geometry where each axial ligand is split in two. This arrangement, which is facilitated by the small bite angle of carbonate [the O2—K—O3 angle is 46.68 (3)°], allows the O4 water oxygen to have less steric interaction with the other O atoms around the K atom. This partially accounts for the short O4—K distance of 2.583 (2) Å.

In addition, the displacement ellipsoid of O4 is elongated along an axis perpendicular to the K—O bond, indicating a librational shortening of the bond length. A libration calcu-
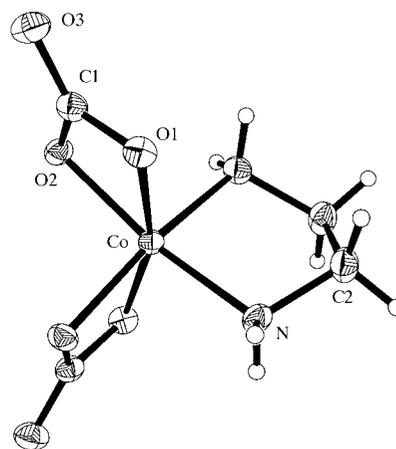

Figure 1
A view of the title anion. Displacement ellipsoids are drawn at the 50% probability level.
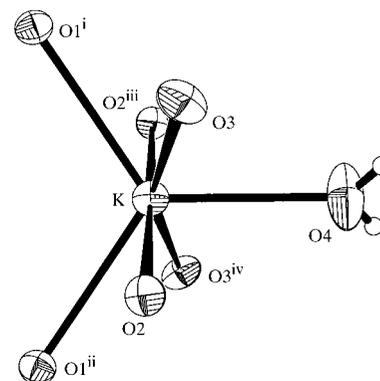

Figure 2
A view of the potassium coordination sphere. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $\frac{1}{2}+x$, $1-y$, $\frac{1}{2}+z$; (ii) $-x$, $1-y$, $1-z$; (iii) $\frac{1}{2}-x$, y, $\frac{3}{2}-z$; (iv) $\frac{1}{2}-x$, y, $\frac{3}{2}-z$.]

lation using the full Schomaker–Trueblood tensor analysis (Schomaker & Trueblood, 1968) yielded a corrected K—O4 bond length of 2.598 Å, while the 'riding model' correction (Johnson, 1970) was similar, giving a corrected length of 2.600 Å, with an upper limit of 2.638 Å. Use of the riding model was justified based on parallel and perpendicular r.m.s. amplitudes of K and O4.

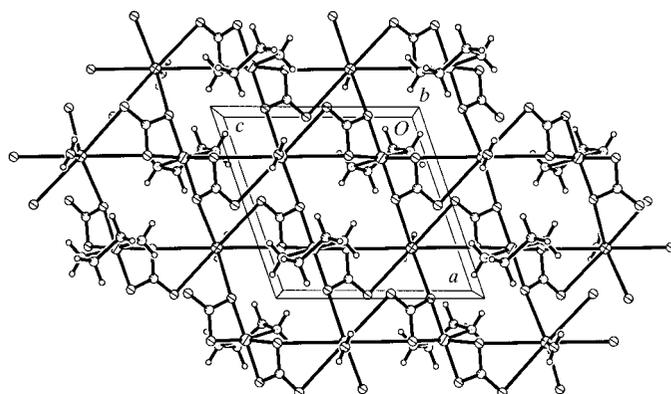A packing diagram of (I) is given in Fig. 3.

Figure 3
The unit-cell packing viewed down **b**.

Experimental

The title compound was synthesized according to literature methods (Kitamura & Shibata, 1993). Suitable crystals were obtained by evaporation of an aqueous solution of (I) containing excess $KHCO_3$.

Crystal data

$K[Co(C_2H_8N_2)(CO_3)_2] \cdot H_2O$	$D_x = 2.005$ Mg m^{-3}
$M_r = 296.17$	Mo $K\alpha$ radiation
Monoclinic, $P2/n$	Cell parameters from 4154
$a = 8.2527$ (13) Å	reflections
$b = 7.3864$ (12) Å	$\theta = 2.5–28.3°$
$c = 8.5085$ (14) Å	$\mu = 2.19$ mm^{-1}
$\beta = 108.947$ (2)°	$T = 173$ (2) K
$V = 490.56$ (14) Å^3	Block, purple
$Z = 2$	$0.24 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	1139 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.022$
Absorption correction: multi-scan (SADABS; Blessing, 1995)	$\theta_{max} = 28.3°$
$T_{min} = 0.538$, $T_{max} = 0.645$	$h = -10 \rightarrow 10$
5227 measured reflections	$k = -9 \rightarrow 9$
1193 independent reflections	$l = -11 \rightarrow 11$
	Intensity decay: <1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.021$	$+ 0.12P]$
$wR(F^2) = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
1193 reflections	$\Delta\rho_{max} = 0.44$ e Å^{-3}
91 parameters	$\Delta\rho_{min} = -0.52$ e Å^{-3}
All H-atom parameters refined	Extinction correction: SHELXL97
	Extinction coefficient: 0.030 (3)

H atoms were refined isotropically from observed positions; the C—H distances are 0.95 (2) and 0.924 (18) Å.

Table 1
Selected geometric parameters (Å, °).

Co—O1	1.9073 (11)	O2—C1	1.3109 (17)
Co—O2	1.9190 (10)	O2—K	2.8475 (10)
Co—N	1.9383 (12)	O3—C1	1.2409 (17)
N—C2	1.4846 (19)	O3—K	2.8473 (11)
O1—C1	1.3182 (18)	O4—K	2.583 (2)
O1—K^i	2.7138 (11)	C2—C2^{ii}	1.516 (3)
O1^{ii}—Co—O1	162.12 (7)	O4—K—O3	81.76 (3)
O1—Co—O2	69.12 (4)	O1^i—K—O3	72.67 (3)
O1—Co—O2^{ii}	98.35 (4)	O1^{iii}—K—O3	117.34 (3)
O2—Co—O2^{ii}	94.37 (6)	O3^{iv}—K—O3	163.52 (5)
O1^{ii}—Co—N	94.27 (5)	O4—K—O2	90.40 (2)
O1—Co—N	98.73 (5)	O1^i—K—O2	104.93 (3)
O2—Co—N	167.36 (5)	O1^{iii}—K—O2	74.61 (3)
O2^{ii}—Co—N	90.79 (5)	O3^{iv}—K—O2	133.48 (3)
N—Co—N^{ii}	86.56 (8)	O3—K—O2	46.68 (3)
O4—K—O1^i	124.28 (2)	O2^{iv}—K—O2	179.20 (4)
O1^i—K—O1^{iii}	111.43 (5)		
Co—N—C2—C2^{ii}	−38.67 (17)	N—C2—C2^{ii}—N^{ii}	50.1 (2)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $\frac{1}{2}-x, y, \frac{1}{2}-z$; (iii) $\frac{1}{2}+x, 1-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, y, \frac{3}{2}-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N—H0A⋯O1^i	0.87 (2)	2.30 (2)	3.0910 (17)	150.8 (17)
N—H0B⋯O3^{ii}	0.80 (2)	2.17 (2)	2.9678 (17)	173.3 (19)
O4—H4A⋯O3^{iii}	0.72 (2)	2.07 (2)	2.7866 (17)	171 (3)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $\frac{1}{2}+x, 1-y, z-\frac{1}{2}$; (iii) $-x, 2-y, 1-z$.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SHELXTL (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL.

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