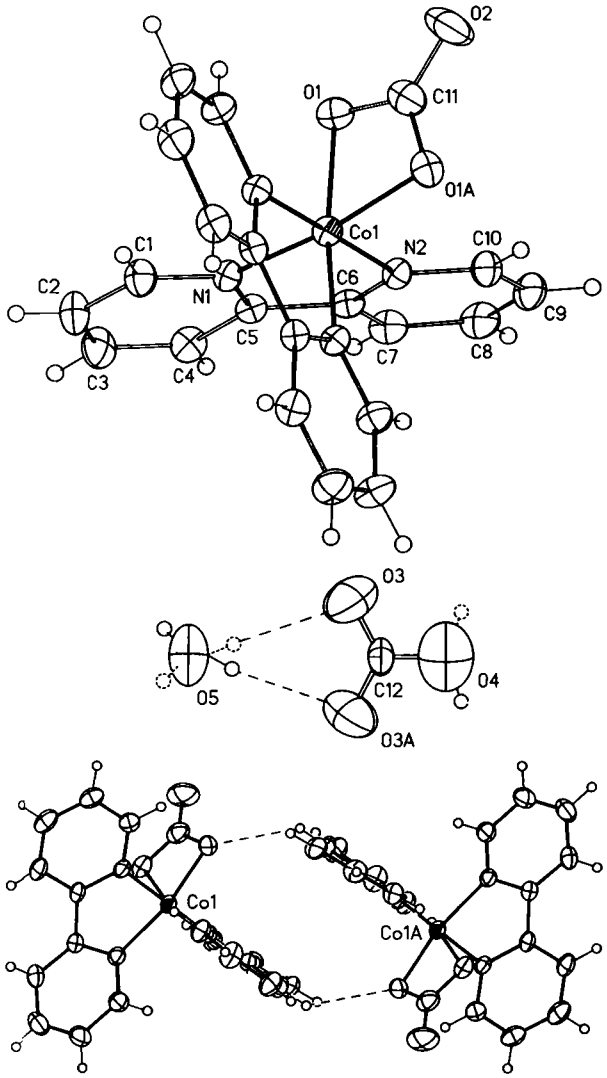
Crystal structure of bis(2,2′-bipyridine-*N*,*N*′)carbonatocobalt(III) hydrogencarbonate pentahydrate, $[Co(C_{10}H_8N_2)_2(CO_3)][HCO_3] \cdot 5H_2O$

H.-M. Guo and B.-S. Zhang*

Jinhua University, Normal College, Jinhua, Zhejiang 321017, P. R. China

Received September 15, 2006, accepted and available on-line December 17, 2006; CCDC no. 1267/1894



Abstract

$C_{22}H_{27}CoN_4O_{11}$, monoclinic, *C*12/*c*1 (no. 15), $a = 10.9420(7)$ Å, $b = 16.008(1)$ Å, $c = 14.458(1)$ Å, $\beta = 101.861(4)°$, $V = 2478.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.038$, $wR_{ref}(F^2) = 0.095$, $T = 273$ K.

Source of material

Freshly prepared $CoCO_3$ (0.12 g, 1.01 mmol), 2,2′-bipyridine (0.07 g, 0.45 mmol), 2-iodobenzoic acid (0.20 g, 0.81 mmol), 12 mL CH_3OH/H_2O (1:2, *v*/*v*) were mixed and stirred for ca. 3 h. Subsequently, the resulting suspension was heated in a 23 ml Teflon-lined stainless steel autoclave to 373 K and kept at this temperature for 7 days. After the autoclave was cooled to room temperature, the solid was filtered off. The resulting orange filtrate was allowed to stand at room temperature and slow evaporation for a month afforded orange block-shaped crystals.

* Correspondence author (e-mail: zbs_jy@163.com)

Experimental details

H atoms bound to C atoms were placed on calculated positions with d(C—H) = 0.93 Å and refined using the riding rigid-body approximation and $U_{iso} = 1.2U_{eq}$(C). H atoms at O atoms were located in Fourier difference maps and refined with an O—H distance restraint of 0.85 Å and U_{iso}(H) = $1.5U_{eq}$(O).

Discussion

The title compound has a crystal structure which is isotypic or strong related to the structures of $[Co(C_{10}H_8N_2)_2(CO_3)]NO_3 \cdot 5H_2O$ [1], $[Co(C_{10}H_8N_2)_2(NO_3)](NO_3)(OH) \cdot 4H_2O$ [2], and $[Co(2,2'\text{-bpy})_2(NO_3)]NO_3 \cdot 5H_2O$ [3].

The title compound consists of the monovalent $[Co(2,2'\text{-bpy})_2(CO_3)]^+$ complex cations, hydrogencarbonate anions and crystal water molecules (figure, top and middle). Within the $[Co(2,2'\text{-bpy})_2(CO_3)]^+$ ion, the Co atoms are each coordinated by four N atoms from two bidentate chelating 2,2′-bipyridine ligands and two O atoms from one bidentate chelating carbonate anion, to complete significantly distorted CoN_4O_2 octahedral environment with d(Co—N) = 1.922(2) Å (2×), 1.934(2) Å (2×) and d(Co—O) = 1.892(2) Å (2×). Two $[Co(2,2'\text{-bpy})_2(CO_3)]^+$ complex cations are interlinked by hydrogen bonds and π-π stacking interactions into 1D supramolecular chains along the [100] direction, but the interplanar distance of 3.639 Å indicates that the intercationic π-π stacking interactions between the neighboring 2,2′-bpy planes are very weak (figure, bottom). Moreover, there are hydrogen bonds and weak C–H···O interactions between the coordinating carbonato and non-coordinating hydrogencarbonato groups, crystal water molecules and 2,2′-bipyridyl H atoms with d(O–H···O) = 2.668 Å – 3.173 Å, ∠O–H···O = 125.1° – 170.5°, d(C4–H4···O1^i) = 3.264 Å, ∠C4–H4···O1^i = 135.4° (i:–*x*,2–*y*,–*z*), d(C7–H7···O6^{ii}) = 3.465 Å, ∠C7–H7···O6^{ii} = 81.5° (ii:–*x*,2-*y*,-*z*). Through these hydrogen bonds and intercationic π-π stacking interactions the compound is interlinked to form the 3D network.

Table 1. Data collection and handling.

Crystal:	orange block, size 0.09 × 0.12 × 0.23 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.61 cm^{-1}
Diffractometer, scan mode:	Bruker APEX CCD II, φ/ω
$2\theta_{max}$:	61.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10023, 3244
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1524
$N(param)_{refined}$:	196
Programs:	SHELXS-97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	8f		0.2221	0.8911	0.2548	0.059
H(2)	8f		0.2769	0.7923	0.1556	0.074
H(3)	8f		0.1445	0.7645	0.0130	0.075
H(4)	8f		−0.0389	0.8407	−0.0302	0.059
H(7)	8f		−0.2066	0.9262	−0.0621	0.059
H(8)	8f		−0.3827	1.0088	−0.0729	0.072
H(9)	8f		−0.4072	1.0875	0.0561	0.068
H(10)	8f		−0.2562	1.0831	0.1930	0.059
H(4A)	8f	0.5	0.553(8)	0.2510(3)	0.295(5)	0.315
H(5A)	8f	0.5	0.467(5)	1.002(2)	0.234(6)	0.193
H(5B)	8f	0.5	0.530(8)	0.937(5)	0.207(4)	0.193
H(6A)	8f		0.788(5)	0.733(3)	0.135(2)	0.196
H(6B)	8f		0.764(8)	0.747(4)	0.041(2)	0.196
H(7A)	8f		0.619(2)	0.829(3)	0.116(3)	0.178
H(7B)	8f		0.525(4)	0.808(2)	0.158(3)	0.178

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	4e	0	1.00609(3)	¼	0.0366(3)	0.0405(3)	0.0275(3)	0	0.0018(2)	0
O(1)	8f	0.0564(2)	1.1031(1)	0.1968(1)	0.053(1)	0.052(1)	0.039(1)	−0.0062(8)	0.0036(9)	0.0073(8)
O(2)	4e	0	1.2264(2)	¼	0.122(3)	0.037(2)	0.126(3)	0	0.008(2)	0
N(1)	8f	0.0623(2)	0.9231(1)	0.1739(1)	0.035(1)	0.043(1)	0.032(1)	0.0016(9)	0.003(1)	0.0014(9)
N(2)	8f	−0.1422(2)	1.0054(1)	0.1468(1)	0.035(1)	0.044(1)	0.030(1)	0.0021(9)	0.0010(8)	0.0051(9)
C(1)	8f	0.1688(2)	0.8805(2)	0.1971(2)	0.044(2)	0.058(2)	0.043(2)	0.007(1)	0.002(1)	−0.005(1)
C(2)	8f	0.2020(3)	0.8212(2)	0.1380(2)	0.052(2)	0.071(2)	0.062(2)	0.018(1)	0.012(2)	−0.007(2)
C(3)	8f	0.1240(3)	0.8051(2)	0.0531(2)	0.066(2)	0.067(2)	0.056(2)	0.006(2)	0.017(2)	−0.020(2)
C(4)	8f	0.0146(2)	0.8499(2)	0.0278(2)	0.052(2)	0.061(2)	0.034(2)	−0.004(1)	0.006(1)	−0.009(1)
C(5)	8f	−0.0141(2)	0.9082(1)	0.0893(2)	0.039(1)	0.042(1)	0.031(2)	−0.004(1)	0.006(1)	−0.001(1)
C(6)	8f	−0.1290(2)	0.9579(1)	0.0720(2)	0.040(1)	0.042(1)	0.025(2)	−0.008(1)	0.000(1)	−0.001(1)
C(7)	8f	−0.2176(2)	0.9585(2)	−0.0109(2)	0.052(2)	0.057(2)	0.032(2)	−0.007(1)	−0.007(1)	0.000(1)
C(8)	8f	−0.3223(2)	1.0075(2)	−0.0173(2)	0.050(2)	0.068(2)	0.050(2)	−0.007(2)	−0.017(1)	0.009(2)
C(9)	8f	−0.3367(2)	1.0543(2)	0.0593(2)	0.037(2)	0.064(2)	0.063(2)	0.005(1)	−0.006(1)	0.010(2)
C(10)	8f	−0.2456(2)	1.0519(2)	0.1409(2)	0.045(2)	0.053(2)	0.048(2)	0.007(1)	0.006(1)	0.002(1)
C(11)	4e	0	1.1500(2)	¼	0.061(3)	0.049(3)	0.055(3)	0	−0.009(2)	0
O(3)	8f	0.4179(3)	0.1307(2)	0.1998(3)	0.172(3)	0.153(3)	0.154(4)	−0.054(2)	−0.025(2)	−0.016(2)
O(4)	4e	½	0.2341(4)	¼	0.239(7)	0.162(5)	0.238(8)	0	0.067(5)	0
C(12)	4e	½	0.1636(3)	¼	0.079(3)	0.034(2)	0.074(4)	0	0.015(3)	0
O(5)	4e	½	0.9566(3)	¼	0.187(5)	0.086(3)	0.097(4)	0	−0.006(3)	0
O(6)	8f	0.7569(3)	0.7652(2)	0.0932(3)	0.113(2)	0.138(3)	0.132(3)	−0.005(2)	0.003(2)	0.007(2)
O(7)	8f	0.5480(3)	0.8402(2)	0.1217(2)	0.130(2)	0.113(2)	0.116(3)	0.019(2)	0.028(2)	0.009(2)

Acknowledgment. The authors gratefully acknowledge the financial support of the Education office of Zhejiang province (grant no. 20051316).

References

1. Niederhoffer, E.-C.; Martell, A.-E.; Rudolf, P.; Clearfield, A.: Structure of (Carbonato)bis(2,2′-bipyridine)cobalt(III) and (Carbonato)bis(1,10-phenanthroline)cobalt(III) Complexes. Inorg. Chem. **21** (1982) 3734-3741.
2. Reimann, C.-W.; Zocchi, M.; Mighell, A.-D.; Santorro, A.: Crystal and Molecular Structure of Nitratobis(2,2′-dipyridyl)cobalt(III) Hydroxide Nitrate Tetrahydrate, $[Co(C_{10}H_8N_2)_2(NO_3)](NO_3)(OH) \cdot 4H_2O$. Acta Crystallogr. B**27** (1971) 2211-2218.
3. Zheng, Y.-Q.; Lin, J.-L.: Crystal Structure of bis(2,2′-bipyridine-*N,N′*)nitratocobalt(II) nitrate pentahydrate, $[Co(2,2'\text{-bpy})_2(NO_3)]NO_3 \cdot 5H_2O$. Z. Kristallogr. NCS **217** (2002) 331-332.
4. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. Acta Crystallogr. A**46** (1990) 467-473.
5. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.