

단 신

[Co(phen)₂(CO₃)]·(HCO₃)·4H₂O의 수열합성과 결정구조 (phen=1,10-phenanthroline)

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Hydrothermal Synthesis and Crystal Structure of [Co(phen)₂(CO₃)]·(HCO₃)·4H₂O (phen=1,10-phenanthroline)

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The self-assembly of highly organized metal-organic frameworks comprised of metal ions as nodes and bridged ligands as spacers has achieved considerable progress in supramolecular chemistry and material chemistry.¹⁻⁴ The increasing interest in this field is not only because of their intriguing variety of architectures and topologies, but also because of their potential applications as functional materials.⁵⁻⁹ By selecting appropriate metal ions and bridged ligands, coordination polymers with fantastic structures and desirable properties can be obtained. The dicarboxylate ligand and d-block metal ions have been extensively used in much of this work.¹⁰ The coordination polymers bearing dicarboxylate anion ligands have been shown to form a wide range of interesting network topologies, for examples, 1D chains, 2D open layers, and 3D diamondoid networks.¹¹ In our ongoing investigation on the coordination chemistry of d-block metal(II) complexes containing diamine and/or dicarboxylate

anion, the monomeric title compound **1** was obtained by the reaction of phen and malonic acid with the CoCO₃·xH₂O. The crystal structures of some cobalt(III) complexes with phen and other ligands have been studied, such as [Co(phen)₂Cl₂]-Cl·3H₂O, [Co(phen)₂CO₃]-X (X=Cl, Br, NO₃, and ClO₄).¹² However, to our knowledge, trivalent cobalt complex with bicarbonate as counter ion in the formula is not known up to now. Thereby, we report here the preparation and structure of **1**.

EXPERIMENTAL

Synthesis. All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H, N) were performed on a Carlo Erba EA-1106 Elemental Analyzer. IR spectrum was recorded in the range 400-4000 cm⁻¹ on a Mattson Polaris FT-IR Spectrophotometer using KBr pellets. The initial and final pH of the

reaction was measured using Sentron 1001 pH meter.

A mixture of $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ (0.059 g, 0.5 mmol), $\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$ (0.052 g, 0.5 mmol), 1,10-phen (0.180 g, 1.0 mmol), and water (9 ml, 500 mmol) in the mole ratio 1:1:2:1000 was placed in a 23 ml Teflon-lined Parr acid digestion bomb and heated for 2 d at 150 °C under autogenous pressure. After the mixture was removed from the oven and allowed to cool under ambient conditions for 3 d, the red needles of **1** suitable for X-ray diffraction were isolated in 20% (0.06 g) yield based on cobalt. Initial pH, 4; final pH, 5. Anal. Calcd. for $\text{C}_{26}\text{H}_{25}\text{CoN}_4\text{O}_{10}$: C, 50.99; H, 4.11; N, 9.15. Found: C, 50.92; H, 4.15; N, 9.18. IR (KBr pellet, cm^{-1}): 3409(s), 1628(m), 1565(s), 1517(m), 1422(s), 1385(m), 849(m), 724(m), 646(m).

X-ray crystallography. X-ray diffraction data of the single crystal was collected at 293(2) K on an ADSC Quantum 210 detector at Beam-line 4A MXW of Pohang Light Source. The crystal evaluation and data collection were done using 0.77001 Å-wavelength radiation with a detector-to-crystal distance of 6.0 cm. Preliminary cell constants and an orientation matrix were determined from 36 sets of frames collected at scan intervals of 5° with an exposure time of 1 s per frame. The basic scale file was obtained from program HKL2000.¹³ The reflections were successfully indexed by the automated indexing routine of the DENZO program. A total of 29,499 reflections were harvested by collecting 72 sets of frames with 5° scans with an exposure time of 1 second per frame. This highly redundant data set was corrected for Lorentz and polarization effects, and a (negligible) correction for crystal decay was also applied. The space group P-1 was determined by the program XPREP (ver. 6.12, Bruker-AXS). The structure was solved by direct method¹⁴ and refined on F^2 by full-matrix least-squares procedures.¹⁵ All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation

Table 1. Crystal data and structure refinement for **1**

Empirical formula	$\text{C}_{26}\text{H}_{25}\text{CoN}_4\text{O}_{10}$
Formula weight	612.44
T (K)	293(2)
λ (Å)	0.77001
Crystal system	Triclinic
Space group	P-1
a (Å)	7.9750(16)
b (Å)	10.415(2)
c (Å)	16.578(3)
α (°)	106.27(3)
β (°)	103.41(3)
γ (°)	90.23(3)
V (Å ³)	1282.3(4)
Z	2
μ (mm ⁻¹)	0.737
$F(000)$	618
θ (°)	1.43 to 30.40
Limiting indices	$0 \leq h \leq 10$, $-13 \leq k \leq 13$, $-20 \leq l \leq 20$
Reflections collected/unique	5516/5516 [R(int)=0.0000]
Absorption correction	None
Goodness-of-fit on F^2	1.039
R_1 [$I \geq 2\sigma(I)$]	0.0524
wR_2 [$I \geq 2\sigma(I)$]	0.1551
Largest peak and hole (e Å ⁻³)	0.603 and -0.746

at idealized positions by using riding model, but not refined. A summary of the experimental and crystallographic data for compound **1** is presented in Table 1.

RESULTS AND DISCUSSION

The hydrothermal reaction of $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$, $\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$, 1,10-phen, and water in the mole ratio 1:1:1:1000 at 150 for 2 d yielded the title compound in 20% yield as red needles. The malonic acid present in the initial reaction mixture was not found in the crystalline product. It is not uncommon for necessary reactants in hydrothermal processes to be absent from the product, while their specific role in complexation remains elusive.¹⁶ It may be that malonic acid acts to form the bicarbonate ion (HCO_3^-).¹⁷ The formal valence of cobalt atom on

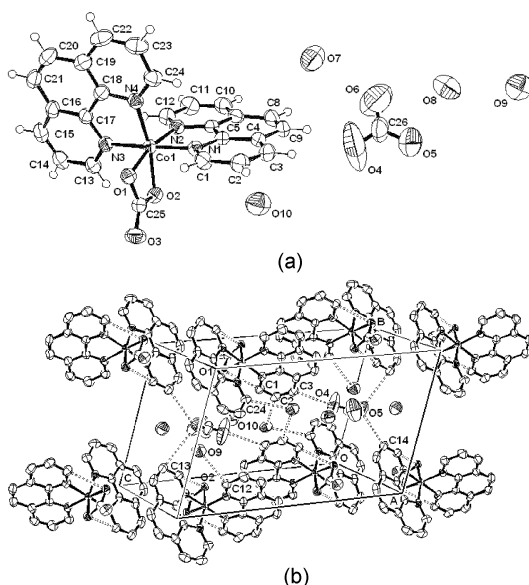


Fig. 1. (a) ORTEP representation of the complex, [Co(phen)₂(CO₃)]·H₂CO₃·4H₂O at 30% probability and (b) packing diagram showing the hydrogen bonds in the unit cell (hydrogen atoms were omitted for clarity).

the basis of overall charge consideration in the formula is Co(III). The oxidation state is conformed from bond valence calculations.¹⁸

As shown in Fig. 1(a), the structure of **1** contains a six-coordinated cobalt atom chelated by two phen ligands and one carbonate anion. The cobalt

center has a distorted octahedral geometry and is surrounded by four nitrogen atoms of two phen (N(1)-N(4)) and the two oxygen atoms of carbonato ligand, O(1) and O(2). The bite angles of phen and carbonato chelate rings to the cobalt atom are ca. 83.79(9)° and 69.63(8)°, respectively, which are almost the same with other complexes.¹² The small bite of the CO₃²⁻ ligand produces a significant distortion from a regular octahedron, with other angles also deviating from 90 or 180° (Table 2). Cobalt-nitrogen bond distances (Co-N1 1.938(2), Co-N2 1.962(2) Å) are in agreement with 1.936(15) Å found in [Co(NH₃)₆]³⁺.¹⁹ It is also known that a Co-N bond distance of approximately 1.9 Å is characteristic of Co(III) and is about 0.18 Å shorter than the corresponding distance in Co(II) complexes.²⁰ The bond distances of Co-N2 and Co-N4 which are *trans* to the carbonato ligand are slightly longer than those of Co-N1 and Co-N3 which are *cis* to the carbonato ligand. This can be interpreted on the basis of the *trans* effect to oxygen atoms of carbonato ligand. The Co-O bond distances (ca. 1.89 Å) of carbonato ligand are consistent with bidentate coordination found in the other [Co(phen)₂(CO₃)]⁺ structures.¹² The C-O bond distances of carbonato ligand reveal two longer C-O_{coord.} bonds

Table 2. Selected bond lengths (Å) and angles (°) for **1**

Co(1)-O(1)	1.887(2)	Co(1)-O(2)	1.896(2)
Co(1)-N(3)	1.935(2)	Co(1)-N(1)	1.938(2)
Co(1)-N(4)	1.951(2)	Co(1)-N(2)	1.962(2)
C(25)-O(3)	1.223(3)	C(25)-O(1)	1.321(3)
C(25)-O(2)	1.323(3)	C(26)-O(4)	1.153(6)
C(26)-O(5)	1.193(5)	C(26)-O(6)	1.209(6)
O(1)-Co(1)-O(2)	69.63(8)	O(1)-Co(1)-N(3)	90.50(9)
O(2)-Co(1)-N(3)	92.13(9)	O(1)-Co(1)-N(1)	91.07(9)
O(2)-Co(1)-N(1)	89.31(9)	N(3)-Co(1)-N(1)	178.16(8)
O(1)-Co(1)-N(4)	96.75(8)	O(2)-Co(1)-N(4)	165.86(9)
N(3)-Co(1)-N(4)	84.00(9)	N(1)-Co(1)-N(4)	94.87(9)
O(1)-Co(1)-N(2)	167.33(8)	O(2)-Co(1)-N(2)	98.74(8)
N(3)-Co(1)-N(2)	95.08(9)	N(1)-Co(1)-N(2)	83.57(9)
N(4)-Co(1)-N(2)	95.15(9)	O(3)-C(25)-O(1)	124.9(3)
O(3)-C(25)-O(2)	125.6(3)	O(1)-C(25)-O(2)	109.5(2)
O(4)-C(26)-O(5)	120.7(6)	O(4)-C(26)-O(6)	120.8(5)
O(5)-C(26)-O(6)	118.4(5)		

(ca. 1.322(3)Å) and the shorter C-O_{uncoord.} bond (1.223(3)Å). The two coordinated oxygens have more single bond character than the unbound oxygen. Thus, this result is not at all surprising. However, the shorter bond distances of C-O (1.153(6)-1.209(6)Å) in the bicarbonate acting as a counter ion are distinguished from those of carbonate ligand. The bond distance of C26-O6 (1.209(6)Å) is longer than those of C26-O4 (1.153(6)Å) and C26-O5 (1.193(5)Å), indicating that the oxygen atom, O6 is protonated. The rest of the C-N and C-C bond distances of the phen ligand are all considered normal and agree well with those found in other complexes.^{10c} The mononuclear structure of **1** is further expended through weak hydrogen bonds between carbon atoms of 1,10-phen ring and oxygen atoms of uncoordinated water (C2-H2...O10 d(D...A)=3.512(4)Å ∠(D-H...A)=175°, C12-H12...O9 d(D...A)=3.264(4)Å ∠(D-H...A)=141°, and C24-H24...O10 (1-x, 1-y, 1-z) d(D...A)=3.270(4)Å ∠(D-H...A)=134°) or bicarbonate ions (C3-H3...O4 d(D...A)=3.214(6)Å ∠(D-H...A)=164°, C14-H14...O5 d(D...A)=3.316(6)Å ∠(D-H...A)=137°), respectively. In addition, there is two types of intramolecular hydrogen bonds between carbon atoms of 1,10-phen ring and oxygen atoms of carbonate ion (C1-H1...O1 d(D...A)=2.928(3)Å ∠(D-H...A)=110° and C13-H13...O2 d(D...A)=3.002(3)Å ∠(D-H...A)=109°). The packing diagram showing hydrogen bonds is shown in Fig. 1(b).

The IR spectrum of the title compound show characteristic band at 1628 cm⁻¹ for the C=O stretching vibration. The absence of the carbonyl peak near 1700 cm⁻¹ for the carbonic acid indicates the presence of carbonate and/or bicarbonate ion in the formula.²¹ The strong absorption band at 3409 cm⁻¹ is assigned to the ν(OH) of uncoordinated water molecules.

In conclusion, we have synthesized a new title compound [Co(phen)₂(CO₃)]·(HCO₃)·4H₂O from the reaction mixtures of CoCO₃·xH₂O, HO₂CCH₂CO₂H,

1,10-phen, and water by hydrothermal reaction. It is noteworthy that the complex is the first example of cobalt(III) complex with both carbonate and bicarbonate ion in the crystal structure.

Supplementary materials. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition NO. CCDC-647828). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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REFERENCES

1. Noro, S.; Kitagawa, S.; Kondo, M.; Seki, K. *Angew. Chem. Int. Ed.* **2000**, *39*, 2081.
2. Poulton, B.; Zaworotko, M. *Chem. Rev.* **2001**, *101*, 1629.
3. Eddaoudi, M.; Kim, K.; Rosi, N. L.; Vodak, D. T.; Wachter, J.; O'Keeffe M.; Yaghi, O. M. *Science* **2002**, *295*, 469.
4. Pan, L.; Sander, M. B.; Huang, X. Y.; Li, J.; Smith, M.; Bittner, E.; Bochrath, B.; Johnson, J. K. *J. Am. Chem. Soc.* **2004**, *126*, 1308.
5. Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151.
6. Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982.
7. Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369.
8. Janlak, C. *J. Chem. Soc., Dalton Trans.* **2003**, 2781.
9. Dybtsev, D. N.; Chun, H.; Yoon, S. H.; Kim, D.; Kim, K. *J. Am. Chem. Soc.* **2004**, *126*, 32.
10. (a) Padmanabhan, M.; Kumary, S. M.; Huang, X.; Li, J. *Inorg. Chim. Acta* **2005**, *358*, 3537. (b) Ghosh, S. K.; Fallah, M. S. E.; Ribas, J.; Bharadwaj, P. K. *Inorg. Chim. Acta* **2006**, *359*, 468. (c) Jheng, Y. Q.; Kong, Z. P. *Inorg. Chem. Commun.* **2003**, *6*, 478. (d) Ye, B. H.; Tong, M. L.; Chen, X. M. *Coord. Chem. Rev.* **2005**, *249*, 545.
11. (a) Lou, B. Y.; Yuan, D. Q.; Wu, B. L.; Han, L.; Jiang, F. L.; Hong, M. C. *Inorg. Chem. Commun.* **2005**, *8*, 539. (b) Ohata, N.; Masuda, H.; Yamauchi, O. *Angew. Chem. Int. Ed.* **2004**, *43*, 5036. (c) Lou, B. Y.; Wang, R. H.;

- Yuan, D. Q.; Wu, B. L.; Jiang, F. L.; Hong, M. C. *Inorg. Chem. Commun.* **2005**, 8, 971. (d) Mahata, P.; Natarajan, S. *Eur. J. Inorg. Chem.* **2005**, 2156.
12. (a) Ye, B. H.; Chen, X. M.; Zeng, T. X.; Ji, L. N. *Polyhedron*, **1994**, 13, 2185. (b) Niederhoffer, E. C.; Martell, A. E.; Rudolf, P.; Clearfield, A. *Inorg. Chem.* **1982**, 21, 3734. (c) Junk, P. C.; Steed, J. W. *Polyhedron*, **1999**, 18, 3593.
13. Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, 276, 307.
14. Sheldrick, G. M. *Acta Cryst.* **1990**, A46, 467.
15. Sheldrick, G. M. SHELXS97-2 and SHELXL97-2; University of Gottingen: Gottingen, Germany, 1997.
16. (a) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J. *Science* **1993**, 259, 1596. (b) Zapf, P. J.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1997**, 9, 2019.
17. Zheng, Y. Q.; Sun, J.; Lin, J. L. *Z. Anorg. Allg. Chem.* **2000**, 626, 613.
18. (a) Brown, I. D.; O'Keefe, M.; Navrotsky, A. (Eds.), *Structure and Bonding in Crystals*, Academic Press, New York, 1981, vol. II, pp. 1-30. (b) Brown, I. D.; Altermatt, D. *Acta Cryst.* **1985**, B41, 244. (c) Brown, I. D. Private communication.
19. Kime, N. E.; Ibers, J. A. *Acta Cryst.* **1969**, B25, 168.
20. Reimann, C. W.; Zocchi, M.; Mighell, A. D.; Santoro, A. *Acta Cryst.* **1971**, B27, 2211.
21. Hashim, A.; Hosney, A.; Grassian, V. H. *J. Am. Chem. Soc.* **2004**, 126, 8068.
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