

50개의 원자로 이루어진 직사각형 망상에 근거한 2차원 그물 망:
Co-OBC-bipyen 배위 고분자, [Co(OBC)(bipyen)] · H₂O
(OBC = 4,4'-oxybis(benzoate); bipyen =
trans-1,2-bis(4-pyridyl)ethylene))

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2-Dimensional Network Based on 50-Membered Rectangular Grids:
Co-OBC-bipyen Coordination Polymer, [Co(OBC)(bipyen)] · H₂O
(OBC = 4,4'-oxybis(benzoate); bipyen =
trans-1,2-bis(4-pyridyl)ethylene))

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요 약

Co(NO₃)₂·6H₂O, *trans*-1,2-bis(4-pyridyl)ethylene(bipyen), 굵은 디카르복실산 4,4'-oxybis(benzoic acid)(OBCH₂)의 수열 반응으로 2차원 배위 고분자 [Co(OBC)(bipyen)] · H₂O (1)이 얻어졌다. 고분자 1은 13.74×13.20 Å 크기를 갖는 50개의 원자로 이루어진 직사각형들의 2차원 그물망 구조를 갖고 있다는 것을 X-ray 구조 결정이 밝혀내었다.

Abstract

The hydrothermal reaction of Co(NO₃)₂·6H₂O, *trans*-1,2-bis(4-pyridyl)ethylene (bipyen), and a bent 4,4'-oxybis(benzoic acid) (OBCH₂) gave a 2-D coordination polymer [Co(OBC)(bipyen)] · H₂O (1). X-ray structure determination revealed that polymer 1 has a 2-D network based on 50-membered rectangular grids, each of which has the dimension of 13.74 × 13.20 Å.

1. Introduction

Various zeolites with open frameworks have been continuously attracted due to their useful properties.¹⁾ Coordination polymers as organic zeolite-like solids, based on transition metals and multifunctional organic ligands, have recently received considerable attention,²⁾ presumably due to their useful applications in physical gas adsorption, chemical adsorption, selective catalysis, and exchange.^{1a,3)} The

structural outcome of coordination polymers is usually controlled and modified by the coordination geometry of a central metal and the coordination modes of organic ligands.^{3a,4)} In this context, stereochemically rigid, multifunctional ligands and various bridging-ligand systems are now employed in preparing a wide variety of coordination polymers.⁵⁾

Metal-dicarboxylate coordination polymers tend to form rigid frameworks due to the potential chelate

coordination of carboxylate groups. In particular, several research groups demonstrated the construction of highly porous polymers by employing linear dicarboxylates.^{3a,6)} On the contrary, metal-bipyridyl counterparts have rather flexible frameworks due to the monodentate coordination of pyridyl groups.⁷⁾ Recently, several synthetic strategies employed mixed-ligand systems containing both carboxylates and pyridyls in preparing novel coordination polymers.^{4a,8)} We have been continually interested in coordination polymers possessing dicarboxylate, bipyridyl, or mixed-ligands by hydrothermal reactions.⁹⁾ As a continuation of our research, we set out to prepare cobalt coordination polymers from cobalt(II) nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), bipyen, and dicarboxylate (OBCH_2) by hydrothermal reactions. Herein, we report the preparation and crystal structure of a cobalt coordination polymer $[\text{Co}(\text{OBC})(\text{bipyen})] \cdot \text{H}_2\text{O}$ (**1**).

2. Experimental Section

Cobalt(II) nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), *trans*-1,2-bis(4-pyridyl)ethylene (bipyen), and 4,4'-oxybis(benzoic acid) (OBCH_2) were purchased from Aldrich company. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer.

Preparation of $[\text{Co}(\text{OBC})(\text{bipyen})] \cdot \text{H}_2\text{O}$ (1**).** A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.090 g, 0.310 mmol), OBCH_2 (0.080 g, 0.310 mmol), bipyen (0.056 g, 0.310 mmol), and H_2O (6 mL) was heated in a 23-mL capacity Teflon-lined reaction vessel at 150°C for 2 days and then cooled to room temperature by air-cooling. The purple-red crystalline product was collected by filtration, washed with H_2O (2×5 mL), ethanol (3×5 mL), and acetone (2×5 mL), and then air-dried to give $[\text{Co}(\text{OBC})(\text{bipyen})] \cdot \text{H}_2\text{O}$ (0.071 g, 0.137 mmol, 44.2%). IR (KBr): 3422 (br), 3069,

Table 1. X-ray data collection and structure refinement for **1**

empirical formula	$\text{C}_{26}\text{H}_{20}\text{CoN}_2\text{O}_6$
fw	515.37
temperature, K	293(2)
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> , Å	9.109(2)
<i>b</i> , Å	11.355(2)
<i>c</i> , Å	12.557(3)
α , deg	69.92(1)
β , deg	80.72(2)
γ , deg	88.98(2)
<i>V</i> , Å ³	1202.8(5)
<i>Z</i>	2
<i>d</i> _{calc} , g cm ⁻³	1.423
μ , mm ⁻¹	0.757
<i>T</i> _{min}	0.1531
<i>T</i> _{max}	0.6256
<i>F</i> (000)	530
2 θ range (°)	3.5-50
scan type	ω
scan speed	variable
No. of reflns measured	4322
No. of reflns unique	4044
No. of reflns with <i>I</i> > 2 σ (<i>I</i>)	2942
No. of params refined	322
Max., in $\Delta\rho$ (e Å ⁻³)	0.392
Min., in $\Delta\rho$ (e Å ⁻³)	-0.489
<i>GOF</i> on <i>F</i> ²	1.035
<i>R</i>	0.0588
<i>wR</i> ₂ ^a	0.1363

$$^a wR_2 = \Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)]^{1/2}$$

1606, 1532, 1421, 1397, 1300, 1230, 1166, 1100, 1020, 877, 838, 778, 657, 556 cm⁻¹.

Structure determination. All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. Intensity data were empirically corrected for absorption with Ψ -scan data. All calculations were carried out with the use of the

Table 2. Selected bond distances (Å) and bond angles (°) in **1**

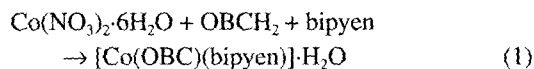
Co1-O1	1.991(3)	Co1-N2	2.078(4)	Co1N1	2.083(4)
Co1-O3	2.100(4)	Co1-O4	2.231(4)		
O1-Co1-N2	97.67(14)	O1-Co1-N1	113.16(16)	N2-Co1-N1	99.64(15)
O1-Co1-O3	98.46(15)	N2-Co1-O3	100.04(15)	N1-Co1-O3	139.80(15)
O1-Co1-O4	156.97(16)	N2-Co1-O4	92.98(15)	N1-Co1-O4	84.86(15)
O3-Co1-O4	59.44(15)				

SHELXTL programs.¹⁰⁾ The structure was solved by direct methods. This crystal belongs to the triclinic system, and structure analyses converged only in the centrosymmetric space group *P*-1. All non-hydrogen atoms were refined anisotropically.

A purple-red crystal of **1**, shaped as a plate of approximate dimensions of 0.20 × 0.16 × 0.06 mm, was used for crystal- and intensity-data collection. The hydrogen atoms in the aqua ligand could not be located. The remaining hydrogen atoms were generated in ideal positions and refined in a riding mode. Details on crystal data and refinement details are given in Table 1. Selected bond lengths and bond angles are given in Table 2.

3. Results and Discussion

Preparation. The title compound has been prepared by hydrothermal reactions. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ reacts with a bent dicarboxylic acid OBCH_2 (coordination angle = 115°) at 150°C for 2 days in the presence of bipyen to give a 2-D cobalt coordination polymer with an empirical formula of $[\text{Co}(\text{OBC})(\text{bipyen})] \cdot \text{H}_2\text{O}$ (**1**) (eq. 1).



Red crystalline polymer **1** is stable in air and

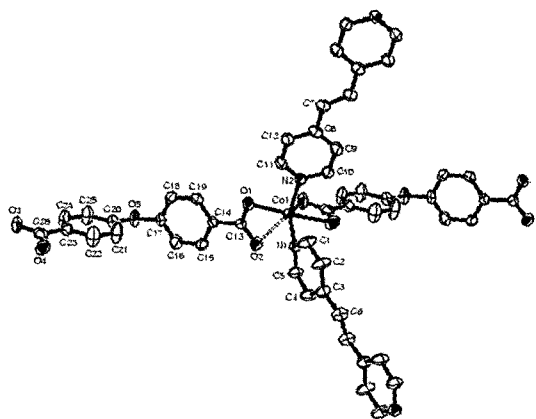


Fig. 1. ORTEP drawing of the local coordination environment of Co of polymer **1**, showing the atom-labeling scheme and 50% probability thermal ellipsoids. Unlabeled atoms are related to labeled atoms by the crystallographic inversion center.

insoluble in common organic solvents. The IR spectra display absorption bands characteristic of carboxylate groups at 1606~1397 cm^{-1} .

Structure. The structure of this polymer turned out to be isostructural with that of the nickel analogue, which has been very recently reported by our research group.⁹⁾ A monomer unit of polymer **1** is shown in Fig. 1. The coordination sphere of cobalt can be described as a distorted octahedron, which consists of four equatorial carboxylate oxygens and two axial bipyen nitrogens (N1 and N2). The Co-N and Co-O bond lengths are 2.078(4)-2.083(4) and 1.991(3)-2.231(4) Å, respectively.

The *a*-axis projection of polymer **1** is shown in Fig. 2, which illustrates a two-dimensional network. The bipyen and OBC ligands separately link Co metals to form one-dimensional layers, ultimately forming an undulated 2-D network based on 50-membered rectangular grids, each of which is com-

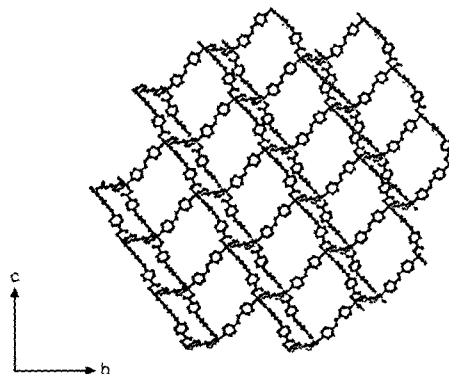


Fig. 2. An undulated 2-D structure of polymer **1** along the *a*-axis.

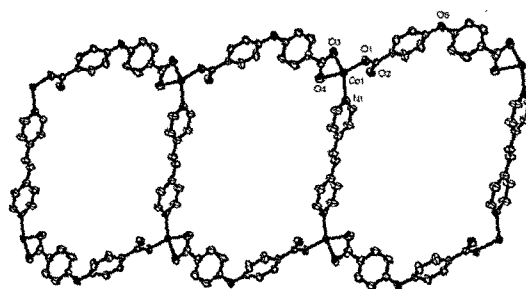


Fig. 3. A 50-membered rectangular repeating unit.

posed of four Co metals as the corners and two OBC ligands as the edges (Fig. 3). On the basis of Co...Co separations, the dimension of the rectangular unit can be calculated to be $13.74 \times 13.20 \text{ \AA}$.

Although many square-grid coordination polymers are now well known, their rectangular counterparts are relatively rare.¹¹ There are currently three general synthetic strategies to prepare non-interpenetrating rectangular-grid coordination polymers with large pores or channels: (1) the use of bipyridine-type ligands of different lengths,¹² (2) the use of a mixed-ligand system of dicarboxylate and bipyridyl,¹³ and (3) the modification of the ligand to affect the shape of the grid.¹⁴ Our synthetic strategy employed a mixed-ligand system of bipyen and OBC, and a non-interpenetrating rectangular-grid coordination polymer **1** could be prepared.

In summary, a 2-dimensional cobalt coordination polymer [Co(OBC)(bipyen)]·H₂O, has been prepared by hydrothermal reactions. Its X-ray structure shows that it has an undulated 2-D network based on 50-membered rectangular grids, each of which has the dimension of $13.74 \times 13.20 \text{ \AA}$.

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Supplementary Material

Crystallographic data for the structural analysis are available from the author Soon W. Lee.

References

- (a) Breck, D. W., *Zeolite Molecular Sieves*; John Wiley & Sons: New York, 1974. (b) Bhatia, S., *Zeolite Catalysts: Principles and Applications*; CRC Press, Inc.: Boca Raton, 1990.
- (a) Batten, S. R. and Robson, R., *Angew. Chem., Int. Ed.*, **37**, 1461 (1998). (b) Munakata, M., Wu, L. P. and Kuroda, S. T., *Adv. Inorg. Chem.*, **46**, 173 (1999). (c) Hagrman, P. J., Hagrman, D. and Zubieta, J., *Angew. Chem., Int. Ed.*, **38**, 2638 (1999). (d) O'Keeffe, M., Eddaoudi, M., Li, H. and Yaghi, O. M., *J. Solid State Chem.*, **152**, 3 (2000). (e) Eddaoudi, M., Moler, D. B., Li, H., Chen, B., Reineke, T. M., O'Keeffe, M. and Yaghi, O. M., *Acc. Chem. Res.*, **34**, 319 (2001). (f) Zaworotko, M. J. and Moulton, B., *Chem. Rev.*, **101**, 629 (2001).
- (a) Yaghi, O. M., Li, H., Davis, C., Richardson, D. and Groy, T. L., *Acc. Chem. Res.*, **31**, 474 (1998). (b) Mori, W. and Takamizawa, S., *J. Solid State Chem.*, **152**, 120 (2000). (c) Noro, S. I., Kitaura, R., Kondo, M., Kitagawa, S., Ishii, T., Matsuzaka, H. and Yamashita, M., *J. Am. Chem. Soc.*, **124**, 2568 (2002).
- (a) Kasai, K., Aoyagi, M. and Fujita, M., *J. Am. Chem. Soc.*, **122**, 2140 (2000). (b) Shi, Z., Zhang, L., Gao, S., Yang, G., Hua, J. and Feng, S., *Inorg. Chem.*, **39**, 1990 (2000).
- (a) Cui, Y., Ngo, H. L. and Lin, W., *Inorg. Chem.*, **41**, 1033 (2002). (b) Bourne, S. A., Lu, J., Moulton, B. and Zaworotko, M. J., *Chem. Commun.*, 861 (2001). (c) Ko, J. W., Min, K. S. and Pack Suh, M. H., *Inorg. Chem.*, **41**, 2151 (2002).
- (a) Li, H., Eddaoudi, M., Groy, T. L. and Yaghi, O. M., *J. Am. Chem. Soc.*, **120**, 8571 (1998). (b) Pan, L., Woodlock, E. B. and Wang, X., *Inorg. Chem.*, **39**, 4174 (2000). (c) Pan, L., Zheng, N., Wu, Y., Han, S., Yang, R., Huang, X. and Li, J., *Inorg. Chem.*, **40**, 828 (2001). (d) Seki, K. and Mori, W., *J. Phys. Chem. B*, **106**, 1380 (2002).
- (a) Lu, J. Y., Cabrera, B. R., Wang, R. J. and Li, J., *Inorg. Chem.*, **38**, 4608 (1999). (b) Lu, J., Yu, C., Niu, T., Paliwala, T., Crisci, G., Somosa, F. and Jacobson, A. J., *Inorg. Chem.*, **37**, 4637 (1998). (c) Fujita, M., Kwon, Y. T., Washizu, S. and Ogura, K., *J. Am. Chem. Soc.*, **116**, 1151 (1994). (d) Knaust, J. M. and Keller, S. W., *Inorg. Chem.*, **41**, 5650 (2002).
- (a) Wu, C. D., Lu, C. Z., Lu, S. F., Zhuang, H. H. and Huang, J. S., *Inorg. Chem. Commun.*, **5**, 171 (2002). (b) Tao, J., Zang, Y., Tong, M.-L., Chen, X.-M., Yuen, T., Lin, C. L., Huang, X. and Li, J., *Chem. Commun.*, 1342 (2002). (c) Shi, Z., Feng, S., Sun, Y. and Hau, J., *Inorg. Chem.*, **40**, 5312 (2001).
- (a) Min, D., Yoon, S. S., Lee, C. Y., Suh, M., Hwang, Y. J., Han, W. S. and Lee, S. W., *Bull. Korean Chem. Soc.*, **22**, 531 (2001). (b) Min, D.,

- Yoon, S. S., Lee, J. H., Suh, M. and Lee, S. W., *Inorg. Chem. Commun.*, **4**, 297 (2001). (c) Min, D., Yoon, S. S., Lee, C. Y., Han, W. S. and Lee, S. W., *Bull. Korean Chem. Soc.*, **22**, 1041 (2001). (d) Min, D., Yoon, S. S., Jung, D.-Y., Lee, C. Y., Kim, Y., Han, W. S. and Lee, S. W., *Inorg. Chim. Acta*, **324**, 293 (2001). (e) Huh, H. S., Min, D. W., Lee, Y. K. and Lee, S. W., *Bull. Korean Chem. Soc.*, **23**, 619 (2002). (f) Min, D., Yoon, S. S. and Lee, S. W., *Inorg. Chem. Commun.*, **5**, 143 (2002). (g) Min, D. and Lee, S. W., *Inorg. Chem. Commun.*, **5**, 978 (2002). (h) Min, D. and Lee, S. W., *Bull. Korean Chem. Soc.*, **23**, 948 (2002). (i) Baeg, J. Y. and Lee, S. W., *Inorg. Chem. Commun.*, **6**, 313 (2003). (j) Lee, Y. K. and Lee, S. W., *Bull. Korean Chem. Soc.*, **24**, 906 (2003).
- 10) Bruker, SHELXTL, *Structure Determination Software Programs*, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA (1997).
- 11) (a) Pan, L., Thomas, F., Michelle, B. S., Huang, X. and Li, J., *Inorg. Chem.*, **40**, 1271 (2001). (b) Zaworotko, M. J., *Chem. Commun.*, (feature article) 1 (2001). (c) Knaust, J. M., Lopez, S. and Keller, S. W., *Inorg. Chim. Acta*, **324**, 81 (2001). (d) Bu, X.-H., Chen, W., Hou, W.-F., Du, M., Zhang, R.-H. and Brisse, F., *Inorg. Chem.*, **41**, 3437 (2002).
- 12) (a) Biradha, K. and Fujita, M., *Chem. Commun.*, 15 (2001) and references therein. (b) Stang, P. J. and Olenyuk, B., *Acc. Chem. Res.*, **30**, 502 (1997).
- 13) Suresh, E., Boopalan, K., Jasra, R. V. and Bhadbhade, M. M., *Inorg. Chem.*, **40**, 4078 (2001).
- 14) Pschirer, N. G., Ciurtin, D. M., Smith, M. D., Bunz, U. H. F. and zur Loye, H.-C., *Angew. Chem., Int. Ed.*, **41**, 583 (2002).