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Synthesis and characterization of the mixed ligand coordination polymer CPO-5

Kjell Ove Kongshaug and Helmer Fjellvåg*

Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

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Abstract

The synthesis and crystal structures of a novel coordination polymer and its high-temperature variant are described. The as-synthesized material (CPO-5-as), of composition $\text{Zn}(4,4'\text{-bipyridine})(4,4'\text{-biphenyldicarboxylate}) \cdot 3\text{H}_2\text{O}$, crystallizes in the triclinic space group *P*-1 (No. 2) with $a = 11.0197(2)$, $b = 14.2975(3)$, $c = 7.6586(1)$ Å, $\alpha = 95.9760(9)^\circ$, $\beta = 108.026(1)^\circ$, $\gamma = 91.373(1)^\circ$ and $V = 1139.16(4)$ Å³. CPO-5-as is composed of tetrahedral zinc centers that are connected by the organic linkers to give five independent, interpenetrating diamond networks. In the structure, there is additional space for channels that are filled with three water molecules. These water molecules can be removed, leading to an anhydrous variant at 130°C. CPO-5-130, of composition $\text{Zn}(4,4'\text{-bipyridine})(4,4'\text{-biphenyldicarboxylate})$, crystallizes in the triclinic space group *P*-1 (No. 2) with $a = 11.1844(6)$, $b = 14.0497(7)$, $c = 7.7198(3)$ Å, $\alpha = 96.917(2)^\circ$, $\beta = 109.527(2)^\circ$, $\gamma = 89.115(3)^\circ$ and $V = 1134.6(1)$ Å³. The structure of the five interpenetrating networks is virtually unchanged after the dehydration resulting in CPO-5-130 being a porous structure with an estimated free volume of 19.8%.

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1. Introduction

The construction of infinite frameworks by use of multifunctional ligands and metal centers has become an important research area in recent years. Many of these crystalline coordination polymers have perspectives for potential applications, such as selective guest absorption [1], gas storage [2], ion exchange [3] and heterogeneous catalysis [4].

Organic molecules such as 4,4'-bipyridine (bpy) and 4,4'-biphenyldicarboxylic acid (bpdc) are both known rigid ligands in the design of coordination polymers. Bpy is an excellent bridging ligand, and a large number of one-, two-, and three-dimensional metal–bpy frameworks have been generated [5–7]. The bpdc ligand is so far less explored; however, by exhibiting a variety of bridging abilities, it is a versatile building unit for construction of coordination frameworks [8,9]. Until now, most coordination polymers have been built by just one type of organic ligand. In spite of several interesting examples of these more complex compounds [10–13], synthetic systems containing two or more

bridging ligands have remained much less well explored. In pursuing synthetic efforts towards construction of open, porous frameworks, the use of mixed ligand systems opens for new flexibility. Presently, we report on novel compounds obtained by reactions in the mixed ligand system Zn, bpdc and bpy.

2. Experimental

CPO-5 was synthesized by hydrothermal methods under autogenous pressure. A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98%, Fluka), bpdc (85%, Merck), bpy (99%, Fluka), NaOH and deionized water, with a molar composition of 2:1:1:2:350, was heated at 120°C in a Teflon-lined steel autoclave for 1 day. The polycrystalline product was filtered off, washed with water and dried in air at 60°C. The yield based on Zn was 52% (Found: C, 55.60; H, 3.73; N, 5.34. Calc for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_7\text{Zn}$: C, 55.88; H, 4.30; N, 5.43%). The high-temperature variant CPO-5-130 was obtained by calcination at 130°C in air for 8 h.

Thermogravimetric analysis (TGA) was performed with a Rheometric Scientific STA 1500. The sample

*Corresponding author. Fax: +47-22855565.

E-mail address: helmer.fjellvag@kjemi.uio.no (H. Fjellvåg).

(ca. 20 mg) was heated in flowing oxygen at a rate of 5 K min^{-1} . High-temperature powder X-ray diffraction data were collected using a Bühler furnace on a Siemens D500 instrument in Bragg–Brentano geometry with $\text{CuK}\alpha$ radiation. The sample was smeared on a platinum filament and data were collected at 25°C and between 100°C and 400°C in steps of $\Delta T = 25^\circ\text{C}$.

High-resolution synchrotron powder X-ray diffraction data for CPO-5-as were collected at the Swiss–Norwegian Beam Line (BM01) at ESRF, Grenoble. The sample was loaded in a 1.0 mm diameter borosilicate capillary, and diffraction data were collected over the range $1\text{--}26^\circ$ in 2θ using a wavelength of $\lambda = 0.50012 \text{ \AA}$ (calibrated by means of an Si-standard). Powder X-ray diffraction data for CPO-5-130 were collected in transmission mode with a Siemens D5000 diffractometer using $\text{CuK}\alpha_1$ ($\lambda = 1.540598 \text{ \AA}$) radiation selected with an incident beam germanium monochromator. The detector was a Braun PSD. The powder sample was kept in a 0.5 mm diameter sealed borosilicate capillary. The diffraction pattern was collected during 24 h for the 2θ range $8\text{--}90^\circ$.

3. Characterization and structure determination

3.1. Structure determination of CPO-5-as

The synchrotron powder diffraction pattern of the as-synthesized CPO-5-as was autoindexed with the program ITO [14] on the basis of the 20 first observed Bragg reflections. The best solution ($M_{20} = 30$) indicated a triclinic unit cell with dimensions $a = 11.033$, $b = 14.326$, $c = 7.672 \text{ \AA}$, $\alpha = 95.97^\circ$, $\beta = 108.01^\circ$ and $\gamma = 91.41^\circ$. The crystal structure of CPO-5-as was determined in space group $P-1$ using the EXPO program [15], which integrates the program EXTRA [16] for extracting intensities and SIRPOW.92 [17] for direct methods structure solution. The Zn atom and all C and N atoms of bpy could be located in the E-map with the highest FOM. This structural information made it possible to find the probable positions for the C and O atoms of bpdC. These atomic positions were used as a starting model for Rietveld refinements using the GSAS program [18]. Initially, scale, background, zero point and lattice parameters were refined. The profile parameters were optimized by first fitting the pattern using the LeBail method. The atomic coordinates were refined with soft constraints being introduced: $d(\text{C}-\text{C}) = 1.39(2)$, $d(\text{C}-\text{N}) = 1.35(2)$ and $d(\text{C}-\text{O}) = 1.26(2) \text{ \AA}$. In addition, $d(\text{C}-\text{C}) = 2.41(3)$ and $d(\text{C}-\text{N}) = 2.39(3) \text{ \AA}$ were constrained to keep the angles near 120° . Common isotropic displacement parameters were adopted for C, O, N and the water oxygen atoms, respectively. The contribution of the hydrogen atoms to the scattered

Table 1

Crystal data and structure refinement data for CPO-5-as and CPO-5-130

Identification code	CPO-5-as	CPO-5-130
Empirical formula	$\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_7\text{Zn}$	$\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_4\text{Zn}$
Formula weight	515.82	461.77
Pattern range 2θ (deg)	1–26	7–90
Step size $\Delta 2\theta$ (deg)	0.0025	0.0154558 ^a
Wavelength (Å)	0.50012	1.540598
Crystal system	Triclinic	Triclinic
Space group	$P-1$ (No. 2)	$P-1$ (No. 2)
a (Å)	11.0197(2)	11.1844(6)
b (Å)	14.2975(3)	14.0497(7)
c (Å)	7.6586(1)	7.7198(3)
α (deg)	95.9760(9)	96.917(2)
β (deg)	108.026(1)	109.527(2)
γ (deg)	91.373(1)	89.115(3)
V (Å ³)	1139.16(4)	1134.6(1)
Z	2	2
No. of observations	10 000	5356
No. of reflections	1801	2058
No. of refined params.	139	129
R_{wp}	0.057	0.045
R_{F}^2	0.085	0.050

^a Defined by the PSD setting.

intensity was neglected. The weight on the soft constraints could not be relaxed without unrealistic bond distances occurring in the structure. The refinement involved 139 parameters and converged to satisfactory residual factors $R_{\text{F}}^2 = 0.0852$ and $R_{\text{wp}} = 0.0568$. Experimental conditions of the Rietveld refinement are reported in Table 1. Atomic coordinates and isotropic displacement parameters are given in Table 2 and selected bond distances and angles are presented in Table 3. Fig. 1 shows the observed, calculated and difference diffraction profiles from the Rietveld analysis.

3.2. Thermal behavior of CPO-5

Fig. 2 shows a three-dimensional representation of the progressive change in the powder diffraction patterns that occurs over the temperature range $25\text{--}400^\circ\text{C}$. The patterns show that the decomposition of CPO-5 proceeds through two stages. The same two stages are also evident in the TGA curve (Fig. 3) that shows two distinct weight losses. The first weight loss of 9.95% corresponds to loss of the three water molecules of the as-synthesized $[\text{Zn}(\text{bpy})(\text{bpdC}) \cdot 3\text{H}_2\text{O}]$ material (calculated 10.47%). The dehydration process is evident also from Fig. 2 where the anhydrous phase emerges at around 125°C and has a diffraction pattern distinctly different from that of the as-synthesized variant. On further heating, CPO-5-130 transforms into an amorphous phase during the decomposition of the organic ligands at around 350°C .

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for CPO-5-as

Atom	x	y	z	U (eq)
Zn	1.10367(34)	-0.25027(22)	0.5385(4)	0.0254(12)
O1	1.1883(13)	-0.3335(9)	0.4080(18)	0.0261(29)
O2	1.1947(12)	-0.2160(8)	0.2078(17)	0.0261(29)
O3	0.9523(12)	-0.1696(8)	0.4974(18)	0.0261(29)
O4	0.8316(11)	-0.2863(8)	0.2883(17)	0.0261(29)
N1	0.7465(15)	0.1620(10)	0.2854(21)	0.021(5)
N2	0.9501(17)	-0.6521(11)	0.3061(21)	0.021(5)
C1	1.3139(17)	-0.3520(12)	0.2103(27)	0.013(2)
C2	1.3557(19)	-0.3196(9)	0.0717(27)	0.013(2)
C3	1.4287(18)	-0.3756(13)	-0.0103(22)	0.013(2)
C4	0.4629(20)	-0.4650(12)	0.0472(29)	0.013(2)
C5	1.4095(18)	-0.4986(8)	0.1769(28)	0.013(2)
C6	1.3475(19)	-0.4386(14)	0.2708(20)	0.013(2)
C7	1.2229(18)	-0.2907(11)	0.2893(24)	0.013(2)
C8	0.7645(15)	-0.1405(12)	0.4607(26)	0.013(2)
C9	0.6362(18)	-0.1650(10)	0.3437(22)	0.013(2)
C10	0.5350(11)	-0.1092(14)	0.3636(24)	0.013(2)
C11	0.5587(13)	-0.0258(14)	0.4872(33)	0.013(2)
C12	1.3122(18)	-0.0003(10)	0.4087(21)	0.013(2)
C13	1.2126(10)	0.0491(13)	0.4409(25)	0.013(2)
C14	0.8504(13)	-0.2118(11)	0.3966(28)	0.013(2)
C15	0.6244(19)	0.1778(10)	0.2791(24)	0.013(2)
C16	0.5272(11)	0.1165(14)	0.1621(28)	0.013(2)
C17	0.5542(15)	0.0379(11)	0.0559(26)	0.013(2)
C18	0.6846(19)	0.0259(10)	0.0668(23)	0.013(2)
C19	0.7809(10)	0.0835(14)	0.1999(27)	0.013(2)
C20	1.0101(20)	-0.6863(8)	0.1897(29)	0.013(2)
C21	1.0349(17)	-0.6231(14)	0.0744(24)	0.013(2)
C22	1.0149(20)	-0.4660(12)	-0.0636(24)	0.013(2)
C23	0.9207(18)	-0.5024(8)	0.1902(27)	0.013(2)
C24	0.9066(18)	-0.5631(13)	0.3137(22)	0.013(2)
OW1	0.0154(17)	0.0911(10)	0.9438(22)	0.179(5)
OW2	0.2254(15)	0.1983(11)	0.0293(21)	0.179(5)
OW3	0.3918(16)	0.3269(11)	0.3721(23)	0.179(5)

Space group *P*-1. Calculated standard deviations in parentheses.

Table 3
Selected bond distances (\AA) and angles (deg) for CPO-5-as and CPO-5-130

CPO-5-as			
Zn–O1	1.915(13)	O1–Zn–O3	141.8(5)
Zn–O3	2.013(12)	O1–Zn–N1	102.7(7)
Zn–N1	2.075(9)	O1–Zn–N2	98.4(6)
Zn–N2	2.111(9)	O3–Zn–N1	103.6(6)
		O3–Zn–N2	99.0(7)
		N1–Zn–N2	108.4(7)
CPO-5-130			
Zn–O1	2.011(17)	O1–Zn–O3	152.4(8)
Zn–O3	1.957(17)	O1–Zn–N1	102.6(10)
Zn–N1	2.107(11)	O1–Zn–N2	87.1(8)
Zn–N2	2.159(11)	O3–Zn–N1	100.7(9)
		O3–Zn–N2	101.7(9)
		N1–Zn–N2	103.1(10)

Calculated standard deviations in parentheses.

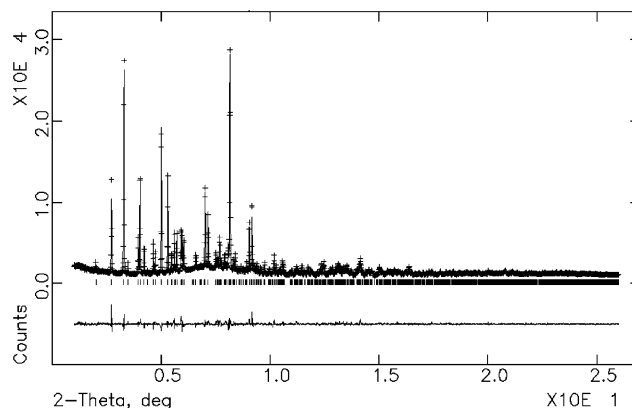


Fig. 1. Observed, calculated and difference powder X-ray diffraction profiles for CPO-5-as, $\lambda = 0.50012 \text{\AA}$.

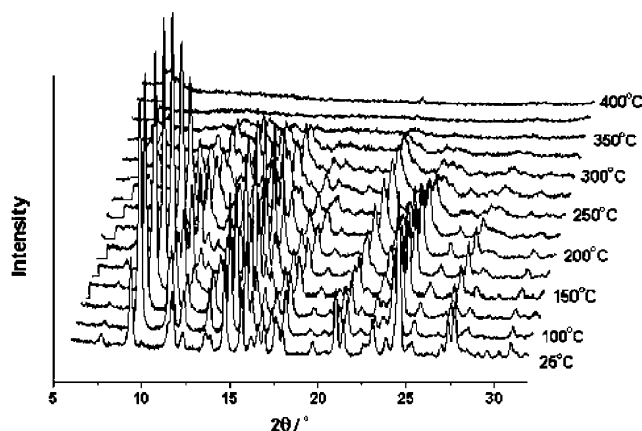


Fig. 2. Three-dimensional representation of high-temperature powder X-ray data for UiO-28 between 25°C and 600°C.

3.3. Structure determination of CPO-5-130

The diffraction pattern of CPO-5-130 was indexed from the first 20 Bragg reflections with the program TREOR-90 [19] leading to a triclinic unit cell: $a = 11.261$, $b = 14.022$, $c = 7.715 \text{\AA}$, $\alpha = 97.14^\circ$, $\beta = 109.78^\circ$ and $\gamma = 88.92^\circ$ ($M_{20} = 17$). The unit-cell dimensions are quite similar to those of CPO-5-as, and hence a starting model for the structure of CPO-5-130 could be built. By means of the Accelrys software, the water molecules were removed from the structure of CPO-5-as, and the unit-cell dimensions were modified to fit the indexation of CPO-5-130. This starting model was transferred into the GSAS program [18] for Rietveld analysis. Refinements of scale, background, zero point and unit-cell dimensions were followed by refinements of the atomic coordinates. Soft constraints were introduced as described for CPO-5-as above. Isotropic displacement parameters were refined and common parameters were adopted for C, N and O. The contribution of the hydrogen atoms to the scattered intensity was neglected. The weight on the soft constraints could not be

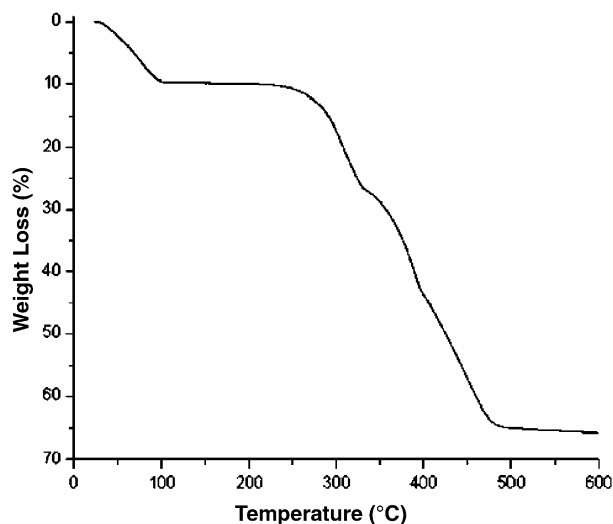


Fig. 3. TG curve for CPO-5 heated in N_2 at a rate of 5 K/min.

Table 4

Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for CPO-5-130

Atom	x	y	z	U (eq)
Zn	1.1070(5)	-0.2553(4)	0.5404(7)	0.0585(22)
O1	1.1992(18)	-0.3586(12)	0.4361(26)	0.053(4)
O2	1.1936(16)	-0.2264(10)	0.2685(23)	0.053(4)
O3	0.9628(18)	-0.1716(11)	0.5209(21)	0.053(4)
O4	0.8436(16)	-0.2808(11)	0.3259(22)	0.053(4)
N1	0.7433(20)	0.1662(16)	0.2752(32)	0.018(6)
N2	0.9216(23)	-0.6426(15)	0.2883(28)	0.018(6)
C1	1.3061(24)	-0.3616(20)	0.218(4)	0.0349(23)
C2	1.3306(24)	-0.3315(12)	0.065(4)	0.0349(23)
C3	1.4298(25)	-0.3731(20)	0.0158(29)	0.0349(23)
C4	0.4677(25)	-0.4663(19)	0.057(4)	0.0349(23)
C5	1.4263(30)	-0.5046(12)	0.191(4)	0.0349(23)
C6	1.3396(26)	-0.4544(22)	0.2593(32)	0.0349(23)
C7	1.2217(29)	-0.3100(14)	0.321(4)	0.0349(23)
C8	0.7545(21)	-0.1304(20)	0.442(4)	0.0349(23)
C9	0.6342(30)	-0.1746(10)	0.3705(32)	0.0349(23)
C10	0.5306(16)	-0.1248(20)	0.3904(35)	0.0349(23)
C11	0.5512(20)	-0.0317(20)	0.483(4)	0.0349(23)
C12	1.3273(30)	-0.0070(13)	0.4215(33)	0.0349(23)
C13	1.2234(14)	0.0476(21)	0.430(4)	0.0349(23)
C14	0.8559(16)	-0.1937(13)	0.3982(29)	0.0349(23)
C15	0.6224(27)	0.1835(15)	0.2717(35)	0.0349(23)
C16	0.5237(13)	0.1221(20)	0.155(4)	0.0349(23)
C17	0.5511(23)	0.0382(19)	0.058(4)	0.0349(23)
C18	0.6791(29)	0.0207(13)	0.0781(35)	0.0349(23)
C19	0.7760(13)	0.0819(22)	0.199(4)	0.0349(23)
C20	0.9996(26)	-0.6836(10)	0.198(4)	0.0349(23)
C21	1.0247(22)	-0.6345(16)	0.0665(33)	0.0349(23)
C22	1.0031(27)	-0.4622(16)	0.062(4)	0.0349(23)
C23	0.9193(25)	-0.4968(10)	0.1580(34)	0.0349(23)
C24	0.8991(22)	-0.5464(16)	0.2944(27)	0.0349(23)

Space group $P-1$. Calculated standard deviations in parentheses.

completely relaxed. For details of the refinements, see Table 1. Final atomic coordinates and displacement parameters are presented in Table 4, with selected bond distances and angles in Table 3. The observed,

calculated and difference diffraction profiles from the refinement are shown in Fig. 4.

4. Crystal structures

CPO-5-as $[\text{Zn}(\text{bpy})(\text{bpdc}) \cdot 3\text{H}_2\text{O}]$ is a three-dimensional coordination polymer whose crystal structure is constructed from tetrahedral zinc centers. The centers are linked together by two bpy and two bpdc units. The bpdc linkers bind to Zn in a monodentate fashion (Fig. 5). The inorganic tetrahedral building units are connected by the organic linkers to give five independent, interpenetrating diamond networks. The five interwoven frameworks do not occupy all the available space because channels appear in the crystal structure of CPO-5 that are filled with three water molecules per formula unit (Fig. 6). The CPO-5 structure adds to the few known examples of coordination polymer systems with five interpenetrating arrays [20–26].

The four Zn-(O/N) distances (Table 3) are quite similar to those found in literature for other coordination polymers with the same coordination environment. In addition, bond-valence calculations [27] confirms the divalent nature of Zn. The Zn–Zn separations are 11.2 and 15.2 \AA along the bpy and bpdc linkers, respectively. The three water molecules that occupy the extra space within the interpenetrated diamondoid networks are involved in hydrogen bonding interactions ($d(\text{OW1} \cdots \text{OW1}) = 2.87$, $d(\text{OW1} \cdots \text{OW2}) = 2.61$, $d(\text{OW2} \cdots \text{O4}) = 2.76$ and $d(\text{OW3} \cdots \text{OW2}) = 3.08 \text{\AA}$).

The structure of CPO-5-as is topologically related to other bpy-based coordination polymers like $[\text{Ag}(\text{bpy})_2\text{CF}_3\text{SO}_3]$ [28] and $[\text{Cu}(\text{bpy})_2\text{PF}_6]$ [29] in which four interpenetrating diamond networks are formed. In CPO-5-as, the replacement of two bpy linkers by two longer bpdc linker creates larger cavities in the structure. This space is filled by the inclusion of one extra Zn(bpy)(bpdc) lattice. The five diamondoid networks show the ‘normal’ mode of interpenetration as defined by Batten [30].

The structure of the five interpenetrating networks is virtually unchanged after the dehydration resulting in a porous structure, CPO-5-130. Therefore, this network is classified type III according to Kondo et al. [31]. The free volume was estimated by the program PLATON [32] to be about 19.8% of the unit-cell volume. The cavities form infinite one-dimensional channels extending in the [001] direction (Fig. 6). CPO-5-130 represents a structure that despite interpenetration have open available space in the structure. In the literature, a few such structures have been reported earlier [24,31,33–36], but in all cases no structural data have been given for the dehydrated, porous variants. A very prominent example of such an interpenetrated, porous structure is MOF-14 [37] that has an estimated free volume of 67%.

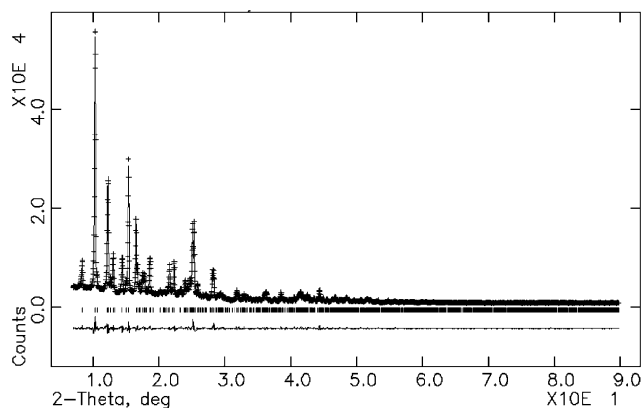


Fig. 4. Observed, calculated and difference powder X-ray diffraction profiles for CPO-5-130, $\lambda = 1.540598 \text{ \AA}$.

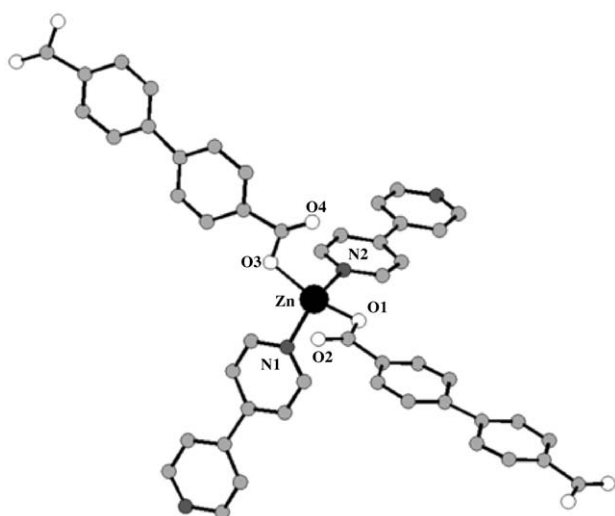


Fig. 5. The coordination environment of Zn in CPO-5-as.

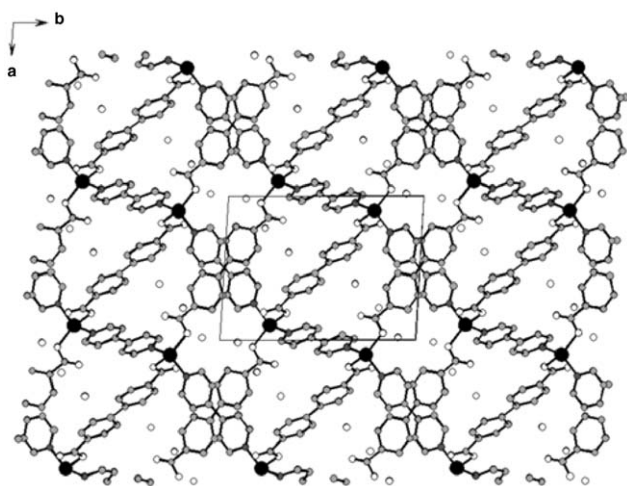


Fig. 6. The crystal structure of CPO-5-as seen along [001].

This indicates that materials composed of interpenetrating networks potentially can have future interest as advanced materials.

Acknowledgments

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References

- [1] O.M. Yaghi, C.E. Davis, G.M. Li, H.L. Li, *J. Am. Chem. Soc.* 119 (1997) 2861.
- [2] S. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 2082.
- [3] M.V. Bennett, M.P. Shores, L.G. Beauvais, J.R. Long, *J. Am. Chem. Soc.* 122 (2000) 6664.
- [4] J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim, *Nature* 404 (2000) 982.
- [5] S.R. Batten, R. Robson, *Angew. Chem. Int. Ed. Engl.* 37 (1998) 1460.
- [6] S. Kitagawa, M. Kondo, *Bull. Chem. Soc. Jpn.* 71 (1998) 1735.
- [7] A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M.A. Withersby, M. Schröder, *Coord. Chem. Rev.* 183 (1999) 117.
- [8] L. Pan, N. Ching, X. Huang, J. Li, *Inorg. Chem.* 39 (2000) 5333.
- [9] Y. Liang, M. Hong, R. Cao, J. Weng, W. Su, *Inorg. Chem. Commun.* 4 (2001) 599.
- [10] P. Lightfoot, A. Snedden, *J. Chem. Soc. Dalton Trans.* (1999) 3549.
- [11] J. Tao, M.L. Tong, X.M. Chen, *J. Chem. Soc. Dalton Trans.* (2000) 3669.
- [12] S. Dalai, P.S. Mukherjee, E. Zangrado, F. Lloret, N.R. Chaudhuri, *J. Chem. Soc. Dalton Trans.* (2002) 822.
- [13] H.S. Huh, D. Min, Y.K. Lee, S.W. Lee, *Bull. Korean Chem. Soc.* 23 (2002) 619.
- [14] J.W. Visser, *J. Appl. Crystallogr.* 2 (1969) 89.
- [15] A. Altomare, M.C. Burla, M. Camalli, B. Carrozzini, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Rizzi, *J. Appl. Crystallogr.* 32 (1999) 339.
- [16] A. Altomare, M.C. Burla, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, *J. Appl. Crystallogr.* 28 (1995) 842.
- [17] G. Cascarano, L. Favia, C. Giacovazzo, *J. Appl. Crystallogr.* 25 (1992) 267.
- [18] A.C. Larson, R.B. von Dreele, Los Alamos National Laboratory Report, LA-UR-86-784, 1987.
- [19] P.E. Werner, L. Eriksson, J. Westdahl, *J. Appl. Crystallogr.* 18 (1985) 367.
- [20] R. Robson, B.F. Abrahams, S.R. Batten, R.W. Gable, B.F. Hoskins, J. Liu, in: T. Bein (Ed.), *Supramolecular Architecture*, ACS Symposium Series 499, Am. Chem. Soc., Washington, DC, 1992, p. 256.
- [21] S.R. Batten, J.C. Jeffery, M.D. Ward, *Inorg. Chim. Acta* 292 (1999) 231.
- [22] M.A. Withersby, A.J. Blake, N.R. Champness, P.A. Cooke, P. Hubberstey, A.L. Realf, S.J. Teat, M. Schroder, *J. Chem. Soc. Dalton Trans.* (2000) 3261.
- [23] S.R. Batten, A.R. Harris, P. Jensen, K.S. Murray, A. Ziebell, *J. Chem. Soc. Dalton Trans.* (2000) 3829.
- [24] O.R. Evans, R.G. Ziong, Z. Wang, G.K. Wong, W. Lin, *Angew. Chem. Int. Ed.* 38 (1999) 536.
- [25] Y.H. Liu, C.S. Lin, S.Y. Chen, H.L. Tsai, C.H. Ueng, K.L. Lu, *J. Solid State Chem.* 157 (2001) 166.
- [26] O.R. Evans, W. Lin, *Chem. Mater.* 13 (2001) 2705.
- [27] N.E. Brese, M. O'Keeffe, *Acta Crystallogr. B* 47 (1991) 192.
- [28] L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi, *J. Chem. Soc. Chem. Commun.* (1994) 2755.

- [29] L.R. MacGillivray, S. Subramanian, M.J. Zaworotko, *J. Chem. Soc. Chem. Commun.* (1994) 1325.
- [30] S.R. Batten, *Cryst. Eng. Commun.* 3 (18) (2001) 67.
- [31] M. Kondo, M. Shimamura, S. Noro, S. Minakoshi, A. Asami, K. Seki, S. Kitagawa, *Chem. Mater.* 12 (2000) 1288.
- [32] A.L. Spek, *Acta Crystallogr. A* 46 (1990) C34.
- [33] M.C. Laskoski, R.L. LaDuca, R.S. Rarig, J. Zubieta, *J. Chem. Soc. Dalton Trans.* (1999) 3467.
- [34] L. Carlucci, G. Ciani, D.M. Proserpio, S. Rizzato, *J. Chem. Soc. Dalton Trans.* (2000) 3821.
- [35] J. Zhang, W. Lin, Z.F. Chen, R.G. Xiong, B.F. Abrahams, H.K. Fun, *J. Chem. Soc. Dalton Trans.* (2001) 1806.
- [36] Y.H. Liu, Y.L. Lu, H.L. Tsai, J.C. Wang, K.L. Lu, *J. Solid State Chem.* 158 (2001) 315.
- [37] B.L. Chen, M. Eddaoudi, S.T. Hyde, M. O'Keeffe, O.M. Yaghi, *Science* 291 (2001) 1021.