Inorg. Chem. **2004**, *43*, 4631–4635

Inorganic Chemistry
Article

Two Polymorphs of Cobalt(II) Imidazolate Polymers Synthesized Solvothermally by Using One Organic Template *N*,*N*-Dimethylacetamide

Yun-Qi Tian,*,†,‡ Zhen-Xia Chen,† Lin-Hong Weng,† Hui-Bin Guo,† Song Gao,*,§ and Dong Yuan Zhao*,†

Department of Chemistry, Fudan University, Shanghai 200433, Department of Chemistry, Liaoning University, Shenyang 110036, and State Key Laboratory of Rare Earth Material Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

Received March 5, 2004

Two structurally different polymorphs of cobalt(II) imidazolate frameworks are solvothermally synthesized by using *N*,*N*-dimethylacetamide as a template: The polymorph **6** (a = 9.797 (4) Å, b = 15.301(6) Å, c =14.902(6) Å, β = 98.904(6)°, monoclinic, $P2_1/n$) shows structures of silicate $CaAl_2Si_2O_8$ with CrB_4 topology, while polymorph **7** (a = 15.173(4) Å, b = 15.173(4) Å, c = 19.089(5) Å, *Pbca*) shows $CaGa_2O_4$-related topological structures. In addition, the **7′** (a = 15.9712(18) Å, b = 15.9253(19) Å, c = 18.475(2) Å, *Pbca*), a compound isostructural with **7**, is synthesized by using cyclohexanol as a template. Thus, these cobalt(II) imidazolate polymers are reminiscent of the zeolite syntheses in that not only the same topological structure can be synthesized by using the different organic templates, but also different topological structures can be synthesized by using the same organic template.

Introduction

Coordination polymers are currently the most attractive topics[1] in the investigation of properties and applications in catalysis, chirality, conductivity, luminescence, magnetism, sensors, nonlinear optics, and porosity. Especially the porosity of substances has attracted the increasing attention of scientists so that considerable efforts have been devoted to the rational design and synthesis of the new materials.[2,3] Yaghi et al. have developed a strategy for the synthesis of the MOFs (metal organic frameworks) by expanding and decorating the inorganic mineral topologies. With the strategy they have successfully obtained a large number of MOFs, some of which have exhibited relatively good stability,[4] unprecedented porosity,[5] and unusual adsorption properties.[5,6] To create such new materials, we are also undertaking a strategy of imitating the zeolitic structures,[7] namely, the natural choices for the porous materials. By employing cobalt(II) imidazolate polymer as an organic silica analogue, we have obtained a porous zeolite-like structure[7a] and some silica-like extended frameworks with structural features of zeolites.[7b] More interesting is that the cobalt(II) imidazolate synthesis is also reminiscent of the zeolite synthetic feature although its reaction mechanism[11] is quite different from that of the zeolite synthesis;[12] however, the same topological structures of cobalt(II) imidazolate can be generated by using different templates[7b] just similar to the zeolite synthesis. Can different structures of cobalt(II) imidazolate also be generated by using the same template as in the zeolitic synthesis that will imply the existence of further extended polymorphism

---

* Authors to whom correspondence should be addressed. E-mail: ytian588@sina.com.cn (Y.-Q.T.); dyzhao@fudan.edu.cn (D.Y.Z.); gaosong@pku.edu.cn (S.G.).

† Fudan University.

‡ Liaoning University.

§ Peking University.

(1) Janiak, C.; *J. Chem. Soc., Dalton Trans.* **2003**, 2781−2804.

(2) (a) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (b) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148−1150. (c) Kitagawa, S.; Condo, M. *Bull. Chem. Jpn.* **1998**, *71*, 1739. (d) Abraham, B. F.; Hoskins, B. F.; Robson, R. *Nature* **1994**, *369*, 727−729.

(3) Yaghi, O. M.; O'Keeffe, M.; Ockwig, O. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705−714.

(4) (a) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276−279. (b) Chen, B.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021−1023.

(5) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469−472.

(6) (a) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127−1129.

(7) (a) Tian, Y.-Q.; Cai, C.-X..; Ji, Y.; You, X.-Z.; Peng, S.-M.; Lee, G.-S. *Angew. Chem., Int. Ed.* **2002**, *41*, 1384−1386. (b) Tian, Y.-Q.; Cai, C.-X.; Ren, X.-M.; Duan, C.-Y.; Xu, Y.; Gao, S.; You, X.-Z. *Chem.—Eur. J.* **2003**, *9*, 5673−5685.

10.1021/ic049713z CCC: $27.50

of the substance? In this Article, we present two cobalt(II) imidazolate polymers, the $CaAl_2Si_2O_8$-related polymorph **6** and the $CaGa_2O_4$-related polymorph **7**, both of which are solvothermally synthesized by using *N*,*N*-dimethylacetamide (DMA) as a template. Also, cobalt(II) imidazolate **7′**, a species isostructural with **7**, is produced by using cyclohexanol (Ch) as a template, from which the polymorph **2′** [7b] was previously produced (the numeral symbols follow the serial numbers of the cobalt(II) imidazolates denoted in our former paper[7b]).

Results and Discussion

Synthesis of the Cobalt(II) Imidazolates. The cobalt(II) imidazolates **6** and **7** are prepared solvothermally by using DMA as the template and the piperazine as coordination buffering ligand, while **7′** is prepared by using Ch as the template. For the synthesis of **6**, the reaction mixture of cobalt(II) acetate tetrahydrate, imidazole, and piperazine is in a ratio of 1:2:1 (molar ratio) with a reaction time of 24 h at 130 °C. But for the preparation of the polymorphs **7** and **7′**, the reaction mixtures have to be modulated to a ratio of 1:2:1.6, the solvothermal temperature must be raised to 150 °C with addition of zeolite (4A) to the reaction mixture, and the solvothermal time should be prolonged to 3 days. It should be noticed that the formation of compound **7** is always accompanied by the crystallization of polymorph **6**, and if the zeolite were not added, the reaction product would be the cobalt(II) imidazolate **4**[7b] with a relatively larger framework density. The use of extra piperazine for preparing polymorph **7** (or **7′**) implies that the free Co^{2+} in the reaction mixture can be reduced; further, the polymerization of cobalt imidazolate will be slowed, which favors the formation of a thermodynamically controlled polymorph. Raising the solvothermal temperature and prolonging the solvothermal reaction time are also strategies for obtaining a thermodynamically controlled polymorph. However, the added zeolite in the reaction system is only to reduce free water in the reaction mixture since the free water not only competes with imidazolate in the cobalt imidazolate polymerization, but also automatically generates a high pressure in the autoclave, which favors the formation of an even more thermodynamically stable species, such as the cobalt imidazolate **4**. Thereby, we regard the polymorph **6** as a dynamically controlled polymorph and the polymorph **7** as the thermodynamically controlled one. To prepare a dynamically controlled cobalt imidazolate polymorph with a lower framework density (or even larger pores), a strategy is needed for decreasing the reaction temperature and finding new organic bases, or buffering ligands and work in this direction is in progress.

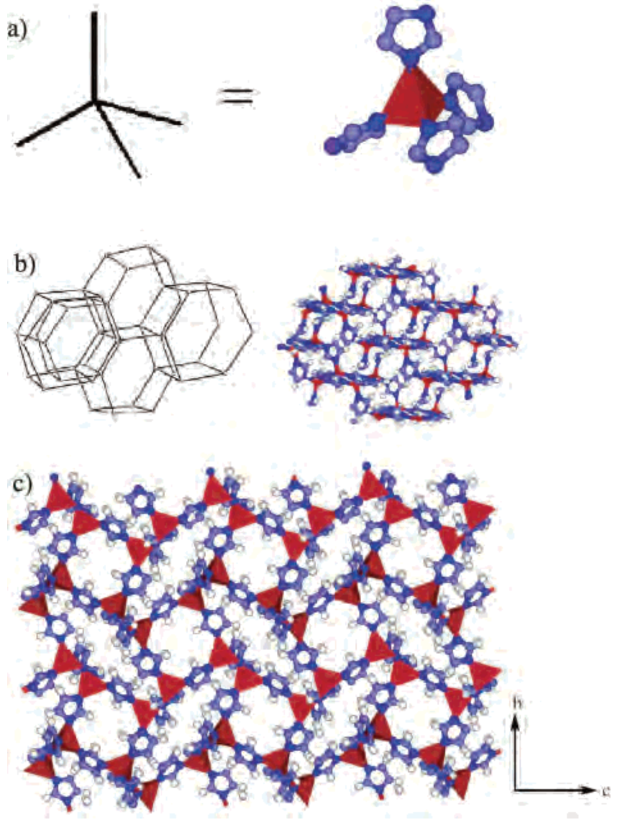

Figure 1. (a) $[Co(im)_4]$ tetrahedral building unit in cobalt(II) imidazolate polymers. (b) Polymorph **6** of $[Co(im)_4{\cdot}DMA]_\infty$ showing a boron framework of CrB_4. (c) Polyhedral view of the framework of polymorph **6** along the [100] direction. Key: Co, red tetrahedron; N, blue; C, gray; H, white.

Table 1. Crystal Data Collection and Structure Refinement

	6	**7**	**7′**
empirical formula	$C_{16}H_{21}N_9OCo_2$	$C_{16}H_{21}N_9OCo_2$	$C_{18}H_{23}N_8OCo_2$
fw	473.28	473.28	485.30
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	Pbca	Pbca
cryst dimensions	0.35 × 0.15 × 0.15	0.20 × 0.10 × 0.10	0.3 × 0.10 × 0.10
a (Å)	9.797(4)	15.173(4)	15.9712(18)
b (Å)	15.301(6)	15.173(4)	15.9253(19)
c (Å)	14.902(6)	19.089(5)	18.475(2)
α (deg)	90	90	90
β (deg)	98.904(6)	90	90
γ (deg)	90	90	90
V (Å^3)	2206.8(15)	4394.8(19)	4699.0(10)
Z	4	8	8
F(000)	968	1936	1992
ρ_{calcd} (g cm^{-3})	1.424	1.431	1.372
μ (mm^{-1})	1.527	1.534	1.435
R1 [$I > 2\sigma(I)$]	0.0672	0.0562	0.0473
wR2 [$I > 2\sigma(I)$]	0.0857	0.1435	0.0594
R1 (all data)	0.1220	0.1189	0.0976
wR2 (all data)	0.0958	0.1575	0.0682
GOF	1.001	1.015	1.003

Crystal Structures of the Cobalt(II) Imidazolate Compounds. Compounds **6** and **7** are polymorphs formulated as $[Co(Im)_2{\cdot}0.5DMA]_\infty$, while compound **7′** is formulated as $[Co(Im)_2{\cdot}0.5Ch]_\infty$. Their structures were determined by single-crystal X-ray diffraction measurements (Table 1). Like those of the other cobalt(II) imidazolate polymers,[7b] the cobalt(II) ions in the two polymorphs are also exclusively 4-coordinated (Figure 1a) and bridged by imidazolates, forming three-dimensional (3D) infinite frameworks. The polymorph **6** crystallizes centrosymmetrically in space group $P2_1/n$, and its secondary building units (SBUs) are 4- and 6-rings, from which the subunits of 4^26^4-cages (Figure 1b) are built up.

Further, from the cage units, the framework related to the silicate $CaAl_2Si_2O_8$ of CrB_4 topology[8] is constructed (Figure

---

(8) O'Keeffe, M.; Li, H.; Eddaoudi, M.; Reineke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3−20.

1b). $CaAl_2Si_2O_8$ is a natural calcium aluminosilicate, in which 4-, 6-, and 8-rings are present. However, these 8-rings are tilted ellipses forming rather small effective channels that are filled with calcium ions. Therefore, the $CaAl_2Si_2O_8$ is actually nonporous. However, as the expanded structure of $CaAl_2Si_2O_8$, compound **6** accommodates guest molecules: two DMA molecules are encapsulated in each of the 4^26^4-cages. Even so, the largest opening of the cages is only ca. 2.5 Å, while the 8-rings generated by the 4^26^4-cages also do not result in the expected channels since the imidazolato rings are all oriented toward the channels, and they are, therefore, stuffed (Figure 1c). Thus, compound **6** is also a nonporous material with framework atoms accounting for ca. 72.9% of the total unit cell volume.

The $CaAl_2Si_2O_8$-related structure with a boron framework of CrB_4 has been once reported in indium sulfide.[9] Here, the polymorph **6** is the first example of a coordination polymer related to the structure of feldspars. In 1997, Keller reported an interesting feldspar-like coordination polymer,[10] the structure of which is in an unprecedented topology and is confessedly different from any topological structure of the feldspars.

Compounds **7** and **7′** are isostructural; they crystallize centrosymmetrically in the space group *Pbca*. The SBUs of their frameworks are 4-and 6-rings, from which the subunits of 4^26^8-cages are constructed (Figure 2a). Similar to the sodalite net that is space-filled by β-cages (the 4^66^8-cages), the polymorph **7** (or **7′**) shows a net with the expanded Ga framework of $CaGa_2O_4$ that is space-filled by the 4^26^8-cages. Kim and co-workers first reported an MOF[15] with decorated $CaGa_2O_4$ topology. However, the polymorph **7** (or **7′**) is an MOF with expanded $CaGa_2O_4$ topology. Also, the $CaGa_2O_4$ topology can be described as a 3D net with 6-ring SBUs, from which the subunits of corrugated sheets (Figure 2b,c) are formed. These sheets of three-connected nodes are linked to each other in the *c*-direction, giving rise to a 3D framework by completing the 4-coordination of the nodes (Figure 2d,e). Like compound **6**, two DMA molecules are also encapsulated in each of the 4^26^8-cages of the polymorph **7**, with framework atoms accounting for ca. 73.2% of the total unit cell volume.

Although the polymorphs **6** and **7** show great differences in structure, they can be prepared by using the same organic template (solvent) of DMA. This synthetic feature that different zeolites can be prepared by using the same organic template and vice versa only exists in the zeolite syntheses.[13] Besides the structural features of zeolites,[7] the cobalt(II) imidazolate polymers are also reminiscent of the above-mentioned synthetic features of zeolites. For coordination polymers, the cases of one structure directed by different templates are quite common. However, the cases of different structures with identical chemical composition directed by one template are very rare. The case for inorganic zeolites (SiO_2) is due to the structural richness of the substances that benefit from the inherent flexibility of Si−Si−Si angles. As a compound related to SiO_2, $Co(im)_2$ should also exhibit the flexibility of Co−Co−Co angles that will give rise to the structural richness of the MOFs. Thereby, preparing more than one structure of cobalt(II) imidazolate frameworks by using one template is our purpose to prove $Co(im)_2$ is the analogue of SiO_2. It is this experimental result that let us see the great possibilities for realizing a real zeolitic structure from the cobalt(II) (or zinc(II)) imidazolate frameworks.

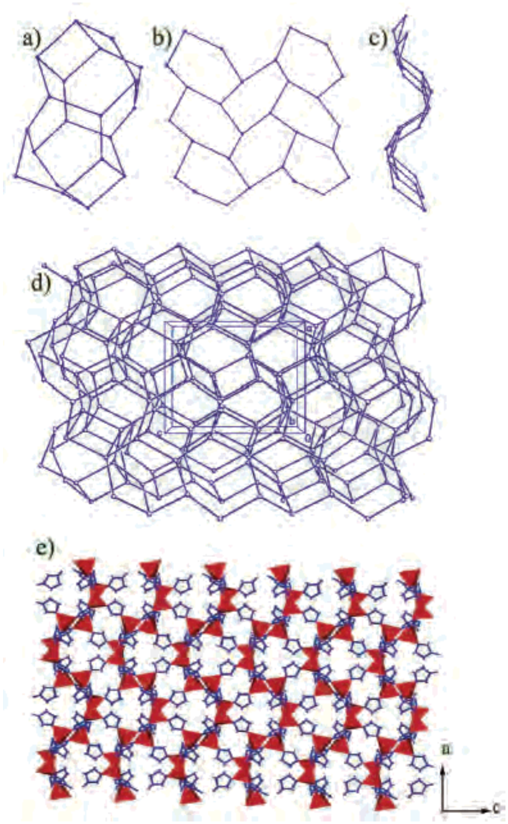

Figure 2. (a) View of the cobalt 4^26^8-cage in the polymorph **7**. (b) View along the [001] direction of the corrugated cobalt sheet in the polymorph **7**. (c) View along the [010] direction of the corrugated cobalt sheet in the polymorph **7**. (d) View of the cobalt network along the [010] direction in polymorph **7**. (e) Polyhedron diagram of the polymorph **7** viewed down the [010] direction. Key: Co, red tetrahedron; N, blue; C, gray; H, white.

Thermal Stabilities and Magnetic Properties of the Novel Cobalt(II) Imidazolate Compounds. Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) under a nitrogen stream show ca. 11.5% weight loss for the polymorph **6** from 100 to 240 °C and ca. 15.6% weight loss for the polymorph **7** from 50 to 200 °C, which are assigned to the loss of the all DMA molecules. There is almost no weight loss for polymorph **6** until 320 °C and for polymorph **7** until 345 °C. Then, the two polymorphs begin to decompose. The DTA and TGA measurements for compound **7′** were not conducted due to the impurity of the product.

---

(9) Li, H.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145−1147.

(10) Keller, S. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 247−248.

(11) Tian, Y.-Q.; Xu, L.; Cai, C.-X.; Wei, J.-C.;Li, Y.-Z.; You, X.-Z. *Eur. J. Inorg. Chem.* **2004**, 1039−1044.

(12) Szostak, R. *Molecular Sieves: Principles of Synthesis and Indentification*, 1st ed.; van Nostrand Reinhold: New York, 1998.

(13) Engelfriet, D. W.; Groeneveld, W. L.; Groenendijk, H. A.; Smit, J. J.; Nap, G. M. *Z. Naturforsch., A* **1980**, *35*, 115−128.

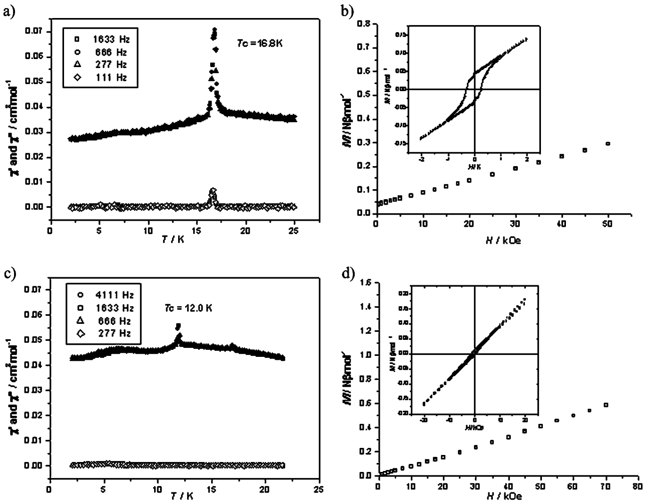

Figure 3. Temperature dependence of ac susceptibility χ' (top) and χ'' (bottom) obtained at 2 Oe field (a, for the polymorph **6**; c, for the polymorph **7**; the small peak at ca. 16.8 K is from the contaminant of the polymorph **6**) and magnetization versus applied magnetic field at 1.8 K. Inset: Hysteresis loops in the ±20 kOe range at 1.8 K (b, for the polymorph **6**; d, for the polymorph **7**).

dc and ac magnetic measurements for **6** and **7** at 2−300 K reveal a dominant antiferromagnetic coupling between thecobalt(II) ions, which is exclusively similar to the cases for the cobalt(II) imidazolate polymers **1**−**5**.[7b,14] Although polymorphs **6** and **7** crystallize in the centrosymmetric space groups, both of them show weak ferromagnetism from spin-canting at low temperature. The single-bridging imidazolate linkages producing a low-symmetry $Co^{II-}L-Co^{II}$ exchange pathway should be responsible for the antisymmetric interaction. The magnetic ordering temperatures are 16.6 and 12.6 K for **6** and **7**, respectively (Figure 3). However, for the polymorph **7**, the weak magnetism from canting seems also to be hidden,[13] which is similar to the case for the cobalt(II) imidazolate **5**.[7b]

Conclusion

Two polymorphs of cobalt(II) imidazolate polymers have been solvothermally synthesized by using DMA as a template. Both of the polymorphs show zeolite-like structures: polymorph **6** is related to the structure of the silicate $CaAl_2Si_2O_8$, and polymorph **7** shows a Ga network of $CaGa_2O_4$. Similar to the results of zeolite synthesis, our results reveal for the first time that not only the same framework of a coordination polymer can be prepared by using different templates,[7b] but also different frameworks of a coordination polymer can be prepared by using the same template, which implies the richness of cobalt(II) imidazolate structures similar to that of the silicates; thereby, this substance can serve as a metal−organic silica analogue, from which a real zeolitic structure may be eventually realized if a proper synthetic strategy is employed.

Experimental Section

$[Co(im)_2·0.5DMA]_\infty$ (6). $Co(Ac)_2·4H_2O$ (1.245 g, 5.0 mmol), imidazole (0.68 g, 10 mmol), and piperazine (0.43 g, 5 mmol) were added to DMA (25 mL). The reaction mixture was stirred at room temperature for 12 h and then placed in a Teflon-lined autoclave. The autoclave was sealed and heated at 130 °C for 24 h. After cooling to room temperature, violet prism crystals were collected and washed with 3 × 10 mL of ethanol (0.6 g, yield ca. 50%). Anal. Calcd for $C_{16}H_{21}N_9OCo_2$ (fw 473.28): C, 40.60; H, 4.47; N, 26.64. Found: C, 39.54; H, 3.99; N, 25.78. FT-IR (KBr) shows the B type.[7b]

$[Co(im)_2·0.5DMA]_\infty$ (7). $Co(Ac)_2·4H_2O$ (1.245 g, 5.0 mmol), imidazole (0.68 g, 10 mmol), and piperazine (0.68 g, 8 mmol) were added to DMA (25 mL). The reaction mixture was stirred at room temperature for 12 h and then placed in a Teflon-lined autoclave with 5 g of newly activated 4A-zeolite. The autoclave was sealed and heated at 150 °C for 3 days. After cooling to room temperature, violet octahedral crystals were collected and washed with 3 × 15 mL of ethanol (0.6 g, yield ca. 50%). Anal. Calcd for $C_{16}H_{21}N_9OCo_2$ (fw 473.28): C, 40.60; H, 4.47; N, 26.64. Found: C, 40.11; H, 4.25; N, 27.10. FT-IR (KBr) shows the B type.[7b]

$[Co(im)_2·0.5Ch]_\infty$ (7′). $Co(Ac)_2·4H_2O$ (1.245 g, 5.0 mmol), imidazole (0.68 g, 10 mmol), and piperazine (0.68 g, 8 mmol) were added to cyclohexanol (25 mL). The reaction mixture was stirred at room temperature for 12 h and then placed in a Teflon-lined autoclave with 5 g of newly activated 4A-zeolite. The autoclave was sealed and heated at 150 °C for 3 days. After cooling to room temperature, violet octahedral crystals of **7′** mixed with compound **2**[7b] were collected and washed with 3 × 15 mL of ethanol (0.6 g, yield ca. 43%).

X-ray Structure Data. Crystallographic measurements were carried out using a Bruker SMART CCD diffractometer, ω scans, graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), SAINT for data integration, SADABS for absorption correction, and XPREP for correction of Lorenz and polarization effects, and the structures were solved by direct methods and refined by full-matrix least-squares on F^2 values using the SHELXS-97 (version 5.1) package of crystallographic software.[16] All non-hydrogen atoms (sometimes excluding those of solvent molecules) were refined anisotropically. Hydrogen atoms were generated and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. For the full-matrix least-squares refinements [$I > 2\sigma(I)$], the unweighted and weighted agreement factors of $R1 = \sum(F_o - F_c)/\sum F_o$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$ were used. The crystal data and details of the structure determinations are summarized in Table 1. The disordered atoms C5, C5′ and C6, C6′ in compound **7** were modeled in 50% SOF.

---

(14) The plots of the temperature dependence of χ_M for **6** and **7** measured at 10 kOe field and plots of field-cooled (FCM) and zero-field-cooled (ZFCM) magnetization for **6** and **7** measured at 200 Oe field are presented in the Supporting Information.

(15) Kim, J.; Chen, B.; Reineke, T. M.; Li, H.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 8239−8247.

(16) Sheldrick, G. M. *SHELXTL-Plus V5.1 software Reference Manual*; Bruker AXS Inc.: Madison, WI, 1997.

Physical Measurement. Fourier transform infrared (FT-IR) spectra were measured from KBr pellets using a Nicolet FT-IR 17SX. TGA was carried out by using TA-SDT 2960 with a heating rate of 5 °C/ min from 20 to 600 °C under a flux of nitrogen. The magnetic measurements for **6** and **7** were carried out on crystalline samples using a MagLab System 2000 magnetometer in a magnetic field up to 70 kOe. Diamagnetic corrections were estimated from Pascal's constants.

Acknowledgment. This work was supported by the National Postdoctoral Foundation, Postdoctoral Foundation of Shanghai City, NSF of China (Grants 20241004 and 29925309), State Key Basic Research Program of the People's Republic of China (Grant G200048001), and NSF of China for Distinguished Young Scholars (Grant 20125104). Special acknowledgment is made to one of the reviewers, who pointed out that the polymorph **7** has the topology of $CaGa_2O_4$.

Supporting Information Available: Crystallographic data in CIF format and additional structural and magnetic figures in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049713Z