Determination of the Solvothermal Synthesis Mechanism of Metal Imidazolates by X-ray Single-Crystal Studies of a Photoluminescent Cadmium(II) Imidazolate and Its Intermediate Involving Piperazine

Yun-Qi Tian,*[a,b] Li Xu,[a] Chen-Xin Cai,[a] Ji-Chong Wei,[a] Yi-Zhi Li,[a] and Xiao-Zeng You*[a]

Keywords: Cadmium / Crystal engineering / Fluorescence / Nitrogen heterocycles / Zeolite analogues

Cadmium(II) imidazolate (**3**), with a twofold interpenetrating diamondoid net, was obtained in a manner similar to cobalt(II) imidazolate. In the process, a crystallized intermediate involving piperazine (**2**), which was suitable for X-ray single crystal study, was isolated. Based on the composition of **2**, a mechanism for the solvothermal synthesis of metal imidazolates was proposed. **3**: a = 9.931(2), b = 10.739(2), c = 14.622(3) Å, $\alpha = \beta = \gamma = 90°$, orthorhombic, *Pcab*; **2**: a = 8.243(2), b = 9.883(2), c = 12.471(3) Å, α = 107.89(3)°, β = 92.56(3)°, γ = 100.87(3)°, triclinic, $P\bar{1}$. Both compounds are photoluminescent with λ_{max} = 459 nm for **3** and 444 nm for **2**; they also display quenching of the fluorescence with $\tau \approx 5$ ns.

Introduction

The search for crystalline solids with unusual electrochemical, magnetic, photophysical and porous properties[1] has attracted an increasing amount of attention from materials scientists and has made the subjects of molecular design and crystal engineering grow almost exponentially in recent years.[2] Because of this, polymorphism, or supramolecular isomerism, has been found to be more general than was previously expected according to the Cambridge Structural Database (CSD).[3] Nevertheless, the phenomenon of extended polymorphism[4] is still rare, although it has been demonstrated that the frequency of occurrence of polymorphic modifications is not necessarily uniform in all categories of substances and it is probably more common in molecules that have conformational flexibility and/or multiple groups capable of hydrogen bonding or coordination.[2]

More recently, in our investigations of metal-organic frameworks with zeolitic topologies, we have found that extended polymorphism also exists in cobalt(II) imidazolate frameworks that show zeolite-like flexibility with variable T−T−T angles.[5] Unlike the flexibility mentioned above, the flexibility of the T−T−T angles can allow extended polymorphism in many zeolite varieties. Because of this we believe that there should be even more supramolecular isomers (or framework polymorphs) of cobalt(II) imidazolate than we have so far obtained. Although cobalt(II) imidazolate isomers have been prepared by a solvothermal method, an apparently successful synthetic strategy,[5] to create more isomers other synthetic strategies have to be developed. In order to do this, however, more details of the mechanism of the formation of cobalt(II) imidazolates are needed. In the synthesis of cobalt(II) imidazolate we noticed that piperazine plays a more important role than other organic bases, such as trialkylamines.[5b] Therefore, it is essential to understand the effect of the piperazine in the solvothermal synthesis in order to determine the synthetic mechanism.

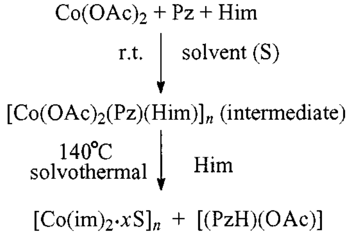
According to the IR spectrum and the element analysis of the intermediate of cobalt(II) imidazolate involving piperazine, which separated as a powder after 12 h reaction at room temperature, and X-ray single crystal studies on the final solvothermal product of cobalt(II) imidazolates, a mechanism for the solvothermal synthesis of cobalt(II) imidazolates was proposed (Scheme 1), in which the piperazine serves not only as a base to deprotonate the imidazole, but also as a ligand that can coordinate to the metal center in cooperation with the imidazolate. Nevertheless, this is only a proposal since the intermediate is formed at room temperature while the nature of the relevant species under solvothermal conditions are still unknown.

Fortunately, during the synthesis of cadmium(II) imidazolate, besides the intermediate involving piperazine (Pz), $[Cd(OAc)_2(Pz)(im\text{-}H)]_n$ (**1**), which is similar to the cobalt(II) imidazolate intermediate that separated at room tempera-

---

[a] State Key Laboratory of Coordination Chemistry, Institute of Coordination Chemistry, Nanjing University,
210093 Nanjing, China
Fax: (internat.) +86-25-359-3522
E-mail: xyz@nju.edu.cn
[b] Department of Chemistry, Liaoning University,
210036 Shenyang, China
Fax: (internat.) +86-24-6220-2053
E-mail: ytian588@sina.com.cn

DOI: 10.1002/ejic.200300560



Scheme 1. Proposed reaction scheme for the solvothermal formation of cobalt imidazolate polymers

ture, we also obtained another compound with piperazine, $[Cd_2(OAc)_3(Pz)(im)]_n$ (**2**), which was obtained as single crystals under solvothermal conditions. To prepare the piperazine-free polymer, $[Cd(im)_2]_\infty$ (**3**), an even higher solvothermal temperature has to be used. Therefore, the solvothermal synthesis of the cadmium(II) imidazolate could be suitable for demonstrating the effect of the piperazine, and also for determining the solvothermal synthetic mechanism of metal imidazolates. In this paper, we present the crystal structures and photoluminescent properties of the cadmium imidazolate (**3**) and its intermediate(**2**), which are used to support the supposed solvothermal synthetic mechanism of cadmium(II) imidazolate and its cobalt analogues.

Results and Discussion

X-ray Crystal Structures

X-ray single crystal studies showed that **2** is a 2D quaternary coordination polymer (i.e., one with four different chemical components). In the asymmetric unit (Figure 1, top) of **2**, there are two Cd^{II} atoms, three acetates, two halves of different piperazine molecules and one imidazolate; the Cd1···Cd2 distance is 4.39 Å. In order to understand this complicated crystal structure easily, we can view the 2D coordination polymer as an assembly of cadmium(II) acetate chains (Figure 1, bottom) with piperazine and imidazolates. The chains are composed of two different cadmium-acetate links: (i) [(OAc)Cd1(μ-OAc)$_2$Cd1′(OAc)] (simplified as link A−A′, in which each cadmium is chelated by two acetates; Cd1 and Cd1′, separated by 3.74 Å, are doubly bridged by two oxygen atoms of the two inner acetates), and (ii) [Cd2(μ-OAc)$_2$Cd2′] (simplified as link B−B′, in which each cadmium is chelated by one acetate; the two cadmiums Cd2 and Cd2′ are separated by a distance of 3.87 Å and doubly bridged by two oxygen atoms of the carboxylic groups). Subsequently, the two kinds of links, A−A′ and B−B′, are alternately connected to each other by the single oxygen bridges of the outside carboxylic groups of the A−A′ links in the [1 0 −1] direction. In the chains, the carboxylic oxygen atoms are all coordinated to the equatorial positions of the cadmium ions, while the axial positions of the metals are occupied alternately by imidazolate and piperazine within the chains along the [1 0 −1] axis and between the chains along the [3 0 1] axis, forming a 2D sheet that parallels the (0 1 0) plane (Figure 2, top).

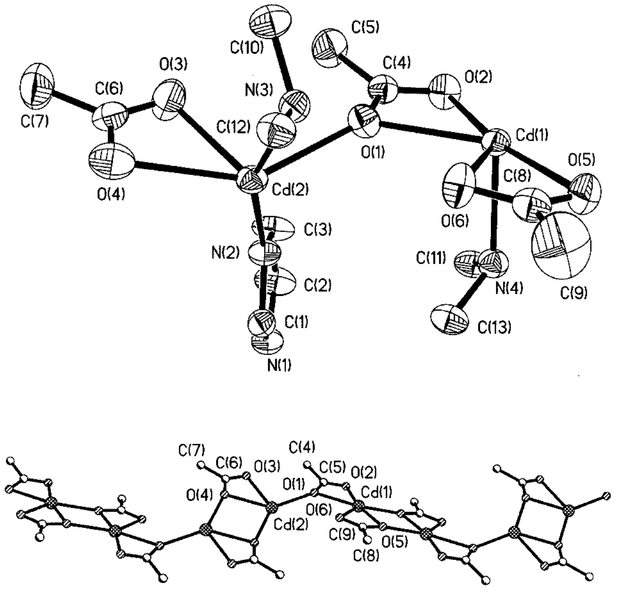
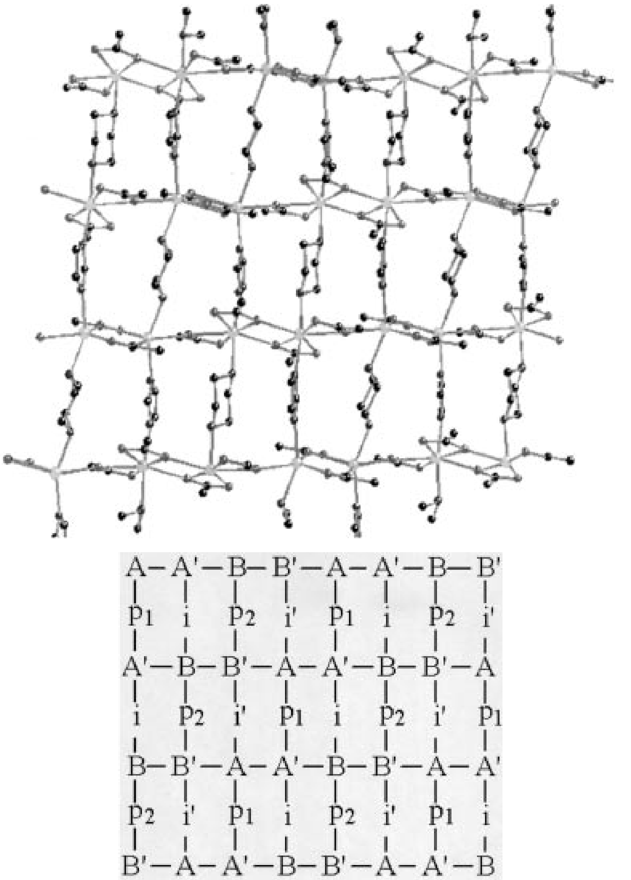


Figure 1. Top: ORTEP drawing of the asymmetric unit of **2** with thermal ellipsoids at 50% probability; bottom: ball and stick diagram of **2** showing the cadmium acetate chain of alternate connected links A−A′ ([(OAc)Cd1(μ-OAc)$_2$Cd1′O(OAc)]) and B−B′ ([Cd2(μ-OAc)$_2$ Cd2′])



```
A− A'−B− B'−A− A'−B− B'
|   |   |   |   |   |   |   |
P1  i   P2  i'  P1  i   P2  i'
|   |   |   |   |   |   |   |
A'−B− B'−A− A'−B− B'−A
|   |   |   |   |   |   |   |
i   P2  i'  P1  i   P2  i'  P1
|   |   |   |   |   |   |   |
B− B'−A− A'−B− B'−A− A'
|   |   |   |   |   |   |   |
P2  i'  P1  i   P2  i'  P1  i
|   |   |   |   |   |   |   |
B'−A− A'−B− B'−A− A'−B
```

Figure 2. Top: View of the 2D structural layer of compound **2** along the [0 1 0] axis; top: ball and stick diagram of **2** (the hydrogen atoms are omitted for clarity); bottom: symbolized representation of the supramolecular 2D assembly of the quaternary coordination polymer (p = piperazine, i = imidazolate, A to A′, B to B′ and i to i′ are symmetry-related)

Thus, the Cd^{II} ions in A−A′ are seven coordinate while the Cd^{II} ions in links B−B′ are six coordinate. For a distinct view of the supramolecular assembly of compound **2**, a 2D structure of symbolized components is illustrated as Figure 2, bottom. In the crystal of **2** such sheets are stacked parallel to the (010) plane with an interlayer distance of 9.883 Å, equal to the value of the crystal unit-cell parameter *b*.

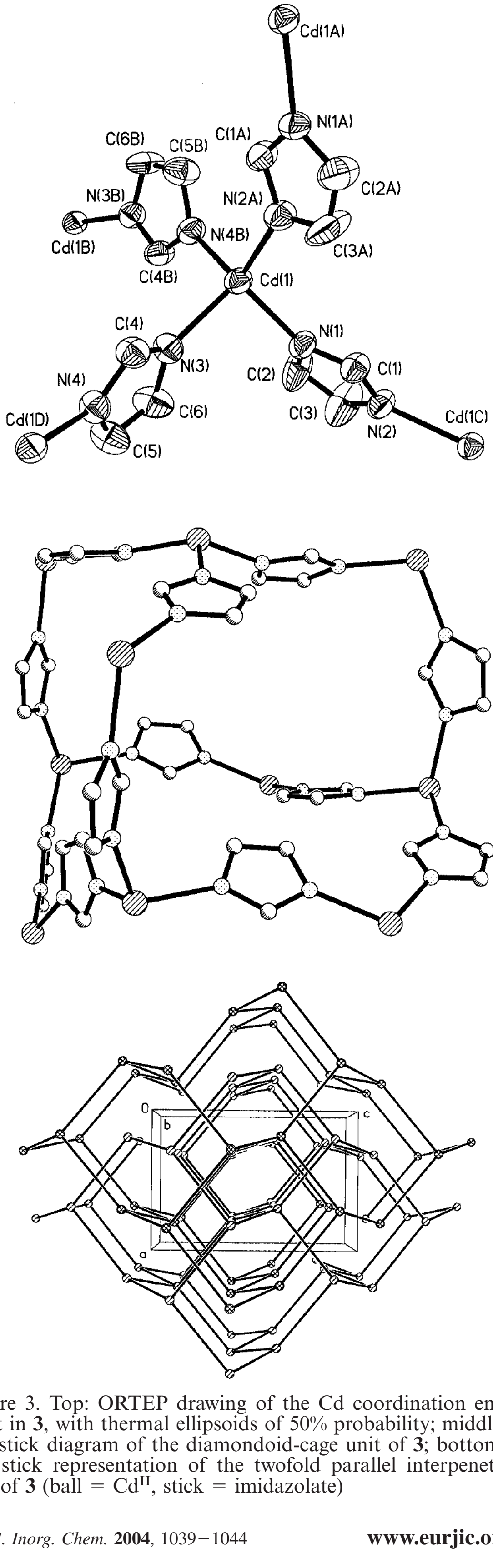


Figure 3. Top: ORTEP drawing of the Cd coordination environment in **3**, with thermal ellipsoids of 50% probability; middle: ball and stick diagram of the diamondoid-cage unit of **3**; bottom: ball and stick representation of the twofold parallel interpenetrating nets of **3** (ball = Cd^{II}, stick = imidazolate)

X-ray single-crystal studies on compound **3** show that this compound contains one Cd^{II} atom and two imidazolates in its asymmetric unit. In the structure, the Cd^{II} is four coordinate (Figure 3, top) like Co^{II} in all of the cobalt imidazolate isomers.[5b] The MN_4 tetrahedra exhibit almost the same deviations from a regular tetrahedron as those in $[Co_5(im)_{10}{\cdot}2MB]_\infty$.[5a] However, the deviation of the T−T−T angles from a regular tetrahedron are much smaller than those in any of the cobalt(II) imidazolate isomers prepared so far (Table 1). It is known that a 3D net with regular tetrahedral nodes is likely to have a diamondoid structure,[6] and $[Cd(im)_2]_\infty$ indeed forms such a net with a cristobalite-like structure (Figure 3, middle). As an expanded diamondoid framework, compound **3** exhibits a "normal" mode[7] of twofold interpenetrating nets (Figure 3, bottom), in each of which the shortest Cd···Cd distance is ca. 6.4 Å. Compound **3** is, to the best of our knowledge, the first structurally characterized cadmium imidazolate homopolymer and is also the only metal imidazolate with a diamondoid topology that responds to the problem raised by Masciocchi et al.[4] The preparation of other structures of cadmium imidazolate has not yet been successful. The absence of polymorphism for this substance might be due to the limited flexibility of the Cd···Cd···Cd angles, which suffer from restrained Cd−N bond rotation.

Photoluminescent Properties

The diffuse-reflectance absorption and photoluminescence spectra of pure compounds **2** and **3** in the solid state at room temperature are shown in Figure 4. Compound **2** displays an intense photoluminescence emission at 444 nm (22523 cm^{-1}) that is red-shifted by about 1630 cm^{-1} from the 0−0 transition band (414 nm, 24155 cm^{-1}), while that of **3** is found at 459 nm (21786 cm^{-1}) and is red-shifted by about 1800 cm^{-1} from the 0−0 transition band (424 nm, 23585 cm^{-1}). It is well-known that the lowest excited state of imidazole is an $n{\rightarrow}\pi^*$ transition that displays no photoluminescence;[8] therefore the increase in the rigidity of the imidazolate ligand upon forming the polymeric complexes should not cause the fluorescent emission of these compounds, especially considering that $[Zn(im)_2]_n$ displays almost no photoluminescence. It has also been shown that $[Cd(Him)_6](NO_3)_2$ and the intermediate $[Cd(OAc)_2(Pz)(im\text{-}H)]$ (**1**) are also not photoluminescent. All this evidence suggests that the fluorescence must be due to the deprotonated imidazoles and/or the cadmium(II) centers. Therefore the fluorescent emissions in the two compounds are proposed to be ligand-to-metal charge-transfer (LMCT) in

Table 1. Deviations of bond and angle parameters in the cobalt(II) and cadmium(II) imidazolates

	$Co(im)_2$ (1)	$Co(im)_2$ (2)	$Co(im)_2$ (3)	$Co(im)_2$ (4)	$Co(im)_2$ (5)	**3**
$(M-N)_{max} - (M-N)_{min}$ (Å)	0.045	0.020	0.059	0.116	0.042	0.031
$(M\cdots M)_{max} - (M\cdots M)_{min}$ (Å)	0.172	0.172	0.258	0.098	0.233	0.052
$(N-M-N)_{max} - (N-M-N)_{min}$ (°)	10.1	7.7	12.4	13.9	14.8	14.5
$(M\cdot\cdot M\cdot\cdot M)_{max} - (M\cdot\cdot M\cdot\cdot M)_{min}$ (°)	67.5	57.8	94.0	57.3	88.4	25.9

nature. It is also noticeable that compounds **2** and **3** display quenching of the fluorescence with $\tau = 4.8$ ns and 4.5 ns, respectively, which may mean that the substances are excellent candidates for potential photoactive materials.

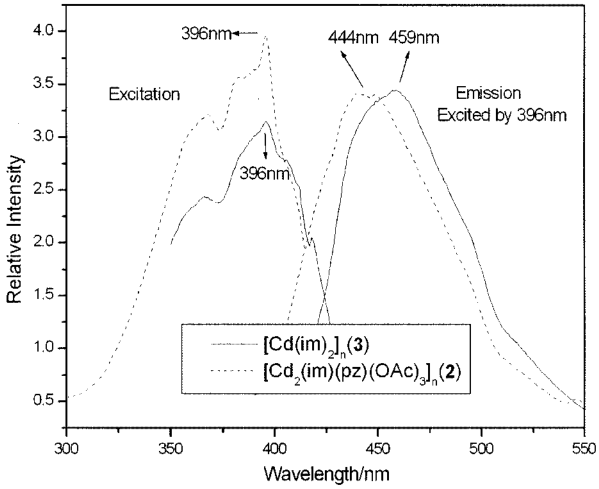
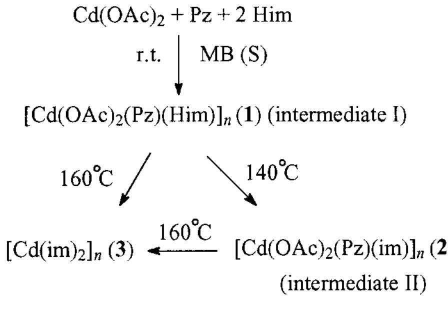


Figure 4. Solid-state excitation and emission spectra of $[Cd(im)_2]_n$ (**3**) and $[Cd_2(pz)(im)(OAc)_3]_n$ (**2**) at room temperature

The Coordination Buffering Effect of Piperazine

In the hydrothermal synthesis of inorganic zeolites, the organic amines play very important roles[9] in (i) structure-direction or templation, (ii) gel modification, and (iii) gel-PH alteration or buffering. Although organic amines are also necessary for the solvothermal synthesis of metal imidazolates, they are seemingly restricted to amines that are able to coordinate to metals. Nevertheless, the coordinating ability of the amines to metals should not be so strong that they cannot be replaced by imidazolates, and their basicity should not be so low that they are unable to deprotonate the imidazoles under solvothermal conditions. Our experiments show that piperazine is an ideal amine to act as both the ligand and the base (Scheme 1). Although we had managed to isolate a single crystal of the intermediate, a cobalt imidazolate involving piperazine formed at a lower solvothermal temperature, to support this proposed mechanism, all our attempts to isolate such an intermediate under the experimental conditions were in vain. However, in the cadmium imidazolate (**3**) synthesis, such a mass crystalline intermediate $[Cd_2(OAc)_3(Pz)(im)]_\infty$ (**2**), the intermediate II in Scheme 2, was separated and showed a different composition from $[Cd(OAc)_2(Pz)(im\text{-}H)]_n$ (**1**), the intermediate I, separated after 24 hours reaction at room temperature (the composition of **1** was determined according to the IR and elemental analyses as well as the charge balance principle. Although the mass spectrum was measured, no significant mass signals were observed due to the insolubility of the polymeric substances).

In order to confirm **2** as a real intermediate of **3**, we separated **2** and then allowed it to react with imidazole in a ratio of 1:3 under the same solvothermal conditions for another 24 hours. As expected, the product was as same as that of the one-pot reaction at 160 °C. Therefore, the solvothermal synthetic route of cadmium(II) imidazolate could be as depicted in Scheme 2, similar to that of the cobalt(II) imidazolate. However, in the latter case, the intermediate under solvothermal conditions is still unknown and it may not be the same as that of the cadmium imidazolate, although the fact that piperazine has taken part in the intermediate formation is undeniable. It is the buffering effect on the concentration of free metal ions by piperazine under solvothermal conditions that gives the template solvent enough time to direct the metal imidazolate to the default or the non-default structures[11] and allows the substance to crystallize with sufficient crystal size. So far, there have been six different topological structures[5,10] of cobalt imidazolates prepared by using piperazine as organic base and buffering ligand.



Scheme 2. Solvothermal synthetic route of cadmium(II) imidazolate

NB: During the writing of this paper the structure of **3** was published.[12] However, as the powdery product resulted from a different synthetic procedure, its structure had to be determined by an ab initio XRPD method.

Conclusion

The solvothermal synthesis of metal imidazolates is regarded as similar to the hydrothermal synthesis of inorganic zeolites or molecular sieves. However, depending on the effects of the organic bases in both of the above mentioned syntheses, the reaction mechanism of metal imidazolates should be different from that of zeolites or molecular sieves:[9] An amine with a certain coordinating ability can form coordination compounds with metals at room temperature and then release the metals steadily under the solvothermal conditions, thus facilitating the crystallization of porous structures of metal imidazolates. Therefore, it is understandable why the trialkylamines commonly used in the hydrothermal synthesis of zeolites are useless for the synthesis of metal imidazolates. As for an amine with strong coordinating ability, such as ethylenediamine, the use of such an organic base in the synthesis of metal imidazolates may lead to the need for a higher solvothermal temperature that will not facilitate a porous structure, or sometimes, due to the high stability of the metal-amine complexes, the metal imidazolate polymers may even not be realizable. Although the use of piperazine as the organic base was initially a random choice, it should now be seen as inevitable, although the search for other suitable organic amines, as synthetic variables is encouraged.

Experimental Section

General Remarks: Imidazole, cadmium acetate dihydrate and anhydrous piperazine were obtained from commercial sources and used without further purification. Elemental analyses for C, H and N were performed at the Materials Analysis Center of Nanjing University with a Perkin−Elmer 240 analyzer. Fourier Transform Infrared (FT-IR) Spectra were measured from KBr pellets by using a Nicolet FT-IR 17SX. The diffuse-reflection absorption UV/Vis spectra were performed on a Perkin−Elmer Lambda35 UV/Vis Spectrometer (No. 101N1102201). The fluorescence spectroscopic studies were conducted on an AMINCO Bowman Series 2 Luminescence Spectrometer, whilst the fluorescent quenching was measured on an SLM48000DSCF System.

[Cd(OAc)$_2$(Pz)(Him)] (1): Cd(OAc)$_2$·2H$_2$O (1.33 g, 5 mmol), anhydrous piperazine (0.43 g, 5 mmol) and imidazole (0.68 g, 10 mmol) were added to 30 mL of 3-methyl-1-butanol, and this heterogeneous mixture was then stirred at room temperature for 24 h. The resulting powder was separated by filtration, washed with ethanol and diethyl ether, and dried in vacuo to give 1.34 g of **1**; yield ca. 70%. $C_{11}H_{20}CdN_4O_4$ (384.4): calcd. C 34.34, H 5.20, N 14.57; found C 35.01, H 5.86, N 13.27. IR (KBr pellet): $\tilde{\nu}$ = 3117 (vs, sh), 3059 (m), 2952 (m), 2885 (m), 2849 (m), 1579 (vs), 1464 (s), 1417 (vs), 1338 (m), 1329 (m), 1076 (s), 1058 (s), 941 (m), 835 (m), 791 (s), 667−621 (s) cm^{-1}.

[Cd$_2$(OAc)$_3$(Pz)(im)]$_\infty$ (2): Cd(OAc)$_2$·2H$_2$O (1.33 g, 5 mmol), anhydrous piperazine (0.43 g, 5 mmol) and imidazole (0.68 g, 10 mmol) were added to 30 mL of 3-methyl-1-butanol, and after being stirred at room temperature for 12 h, this heterogeneous mixture was placed into a Teflon-lined autoclave (34 mL). The autoclave was then sealed and heated at 140 °C for 24 hours. After cooling to room temperature, colorless crystals were collected and washed with 3 × 15 mL of ethanol and dried in vacuo to give 0.83 g of **2**; yield ca. 60%. $C_{13}H_{22}Cd_2N_4O_6$ (554.8): calcd. C 28.14, H 3.96, N 10.09; found C 27.89, H 3.68, N 9.67. IR (KBr pellet): $\tilde{\nu}$ = 3227 (s, sh), 3136 (m, sh), 3112 (m, sh), 3058 (m), 2967 (m), 2858 (m), 1562 (vs), 1498 (m), 1411 (s), 1340 (m), 1329 (m), 1073 (s), 1015 (m), 943 (m), 882 (s), 822 (m), 772 (m), 670−621 (m) cm^{-1}.

[Cd(im)$_2$]$_\infty$ (3): Cd(OAc)$_2$·2H$_2$O (1.33 g, 5 mmol), anhydrous piperazine (0.43 g, 5 mmol) and imidazole (0.68 g, 10 mmol) were added to 30 mL of 3-methyl-1-butanol, and after being stirred at room temperature for 12 h, this heterogeneous mixture was placed into a Teflon-lined autoclave (34 mL). The autoclave was sealed and heated at 160 °C for 24 hours. After cooling to room temperature, colorless crystals were collected and washed with 3 × 15 mL of ethanol and dried in vacuo to give 0.50 g of **3**; yield 40%. $C_6H_6CdN_4$ (246.4): calcd. C 29.22, H 2.44, N 22.73; found C 29.60, H 2.20, N 22.38. IR (KBr pellet): $\tilde{\nu}$ = 3130 (w), 1586 (w), 1482 (vs, sh), 145 (s, sh), 1315 (m), 1244 (s, sh), 1164 (m, sh), 1087 (vs, sh), 943 (s, sh), 818 (m), 756 (s, sh), 746 (s, sh), 664 (vs, sh) cm^{-1}.

X-ray Crystallographic Study: The X-ray single-crystal structure determination was carried out using an Enraf Nonius-CAD4SDP44 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The unit-cell parameters were based on 25 carefully centered reflections in the range 4.42° < 2θ < 51.96°. An absorption correction was applied using ψ-scan data. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXS-97 (version 5.1).[13] All non-hydrogen atoms 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 $R = (||F_o| - |F_c||)/|F_o|$ and $wR = \{w[(|F_o|^2 - |F_c|^2)^2]/w[(|F_o|^2)^2]\}^{1/2}$ $\{w = 1/[\sigma^2(|F_o|^2) + (aP)^2 + bP]$, where $P = (|F_o|^2 + 2|F_c|^2)/3\}$ were used. The crystallographic data are summarized in Table 2, and selected bond lengths and bond angles of the compound **2** and **3** are listed in Table 3. CCDC-149555 (**2**) and -212355 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystal data collection and structure refinement

	2	**3**
Empirical formula	$C_{13}H_{22}N_4O_6Cd_2$	$C_6H_6N_4Cd$
Mol. mass	555.51	246.55
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	*Pcab*
a (Å)	8.2430(16)	9.931(2)
b (Å)	9.883(2)	10.739(2)
c (Å)	12.471(3)	14.622(3)
α (°)	107.89(3)	90.00
β (°)	92.56(3)	90.00
γ (°)	100.87(3)	90.00
V (Å^3)	943.7(3)	1559.4(5)
Z	2	8
F (000)	544	944
$\rho_{calcd.}$ (g cm^{-3})	1.954	2.100
μ (mm^{-1})	2.288	2.735
R_1 [$I > 2\sigma(I)$]	0.0245	0.0296
wR_2 [$I > 2\sigma(I)$]	0.0631	0.0639
R_1 [all data]	0.0410	0.0700
wR_2 [all data]	0.0680	0.0732
GOF	1.064	1.035

Table 3. Selected bond lengths [Å] and angles [°] for **2** and **3**[a]

	2		
Cd(1)−N(4)	2.315(4)	Cd(1)−N(1)$1	2.237(3)
Cd(1)−O(2)	2.389(3)	Cd(1)−O(5)$2	2.378(3)
Cd(1)−O(1)	2.434(3)	Cd(1)−O(5)	2.414(3)
Cd(1)−C(4)	2.750(4)	Cd(1)−O(6)	2.543(4)
Cd(2)−N(3)	2.277(4)	Cd(2)−N(2)	2.192(3)
Cd(2)−O(4)$3	2.373(3)	Cd(2)−O(3)	2.349(3)
Cd(2)−O(4)	2.490(4)	Cd(2)−O(1)	2.409(3)
N(1)$1−Cd(1)−N(4)	171.87(13)	N(1)−Cd(1)$4	2.237(3)
N(1)$1−Cd(1)−O(2)	88.64(12)	N(4)−Cd(1)−O(5)$2	80.82(13)
O(5)$2−Cd(1)−O(2)	89.13(11)	N(4)−Cd(1)−O(2)	96.97(12)
N(4)−Cd(1)−O(5)	83.86(12)	N(1)$1−Cd(1)−O(5)	89.30(12)
O(2)−Cd(1)−O(5)	166.35(11)	O(5)$2−Cd(1)−O(5)	77.53(13)
N(4)−Cd(1)−O(1)	94.68(12)	N(1)$1−Cd(1)−O(1)	93.38(12)
O(3)−Cd(2)−O(1)	98.20(11)	N(3)−Cd(2)−O(1)	74.44(13)
N(3)−Cd(2)−O(4)	93.43(13)	N(2)−Cd(2)−O(4)	110.74(13)
O(1)−Cd(2)−O(4)	145.95(11)	O(3)−Cd(2)−O(4)	52.79(12)
N(2)−Cd(2)−O(4)$3	88.56(13)	N(3)−Cd(2)−O(3)	102.77(14)
O(3)−Cd(2)−O(4)$3	125.42(9)	N(3)−Cd(2)−O(4)$3	93.00(13)
O(5)−Cd(1)−O(6)	52.26(11)	N(2)−Cd(2)−O(1)	87.48(9)
N(2)−Cd(2)−N(3)	155.26(14)	O(1)−Cd(1)−O(6)	87.59(10)
O(2)−Cd(1)−O(1)	53.93(10)	N(2)−Cd(2)−O(3)	96.31(14)
N(4)−Cd(1)−O(6)	91.01(12)	O(5)−Cd(1)−O(1)	139.69(10)
O(2)−Cd(1)−O(6)	141.11(11)		
	3		
Cd(1)−N(4)#1	2.188(4)	Cd(1)−N(1)	2.190(4)
Cd(1)−N(2)#2	2.199(5)	Cd(1)−N(3)	2.219(5)
N(1)−C(1)	1.327(7)	N(1)−C(2)	1.342(8)
N(2)−C(1)	1.308(7)	N(2)−C(3)	1.334(8)
N(4)#1−Cd(1)−N(1)	111.80(18)	N(1)−Cd(1)−N(2)#2	114.27(9)
N(4)#1−Cd(1)−N(3)	106.06(9)	N(1)−Cd(1)−N(3)	99.80(17)
N(2)#2−Cd(1)−N(3)	113.24(9)		

[a] Symmetry transformations used to generate equivalent atoms: **2:** $1 *x* − 1, *y*, *z*; $2 −*x*, −*y* + 1, −*z* + 1; $3 −*x* + 1, −*y* + 1, −*z*; $4 *x* + 1, *y*, *z*; $5 −*x*, −*y* + 1, −*z*; $6 −*x* + 1, −*y* + 1, −*z* + 1; **3:** #1 *x* − 1/2, −*y* + 1, −*z* + 3/2; #2 −*x* + 1/2, *y* + 1/2, −*z* + 1; #3 −*x* + 1/2, *y* − 1/2, −*z* + 1; #4 *x* + 1/2, −*y* + 1,− *z* + 3/2.

Acknowledgments

This work was supported by the State Key Project of Fundamental research (No. G200077500) and the National Science Foundation of China (No. 90101028).

---

[1] [1a] J. M. Lehn, *Supramolecular Chemistry*; VCH: Weinheim,**1995**. [1b]S. R. Batten, R. Roberson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1460−1494. [1c] C. N. R. Rao and B. Raveau, in *Colossal Magnetoresistance, Charge Ordering and Related Properties of Rare Earth Manganese Oxides*, World Scientific: Singapore, **1998**. [1d]A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem. Int. Ed.* **1999**, *38*, 3268−3292. [1e] O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474−484. [1f] Z.-Y. Fu, X.-T. Wu, J.-C. Dai, S.-M. Hu, W.-X. Du, H.-H. Zhang, R.-Q. Sun, *Eur. J. Inorg. Chem.* **2002**, 2730−2735.

[2] B. Moulton, M. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629−1658.

[3] L. Yu, G. A. Stephenson, C. A. Mitchell, C. A. Bunnell, S. V. Snorek, J. J. Bowyer, T. B. Borchardt, J. G. Stowell, S. R. Byrn, *J. Am. Chem. Soc.* **2000**, *122*, 585−591.

[4] N. Masciocchi, S. Bruni, E. Cariati, F. Cariati, S. Galli, A. Sironi, *Inorg. Chem.* **2001**, *40*, 5897−5905.

[5] [5a] Y.-Q. Tian, C.-X. Cai, Y. Ji, X.-Z. You, S.-M. Peng, G.-H. Lee, *Angew. Chem. Int. Ed.* **2002**, *41*, 1384−1386. [5b] Y.-Q. Tian, C.-X. Cai, X.-M. Ren, C.-Y. Duan, Y. Xu, S. Gao, X.-Z. You, *Chem. Eur. J.* **2003**, *9*, 5673−5685.

[6] M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke, O. M. Yaghi, *J. Solid State Chem.* **2000**, *152*, 3−20.

[7] S. R. Betten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1460−1494.

[8] D. Rendell, *Fluorescence and phosphorescence*, John Wiley & Sons, New York, **1987**.

[9] R. Szostak, in *Molecular Sieves*, **1998**, 2nd Ed., Blackie Academic & Professional, imprint of Thomson Science, London, UK.

[10] The unpublished results of two isomorphic coordination polymers of cobalt imidazolate: $[Co_2(im)_4 \cdot DMA]_\infty$ (**6** in space group *Pbca* and **7** in space group $P2_1/n$; DMA = *N*,*N*-dimethylacetylamide).

[11] O. M. Yaghi, M. O'Keffee, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705−714.

[12] N. Masciocchi, G. A. Ardizzoia, S. Brenna, F. Castelli, S. Galli, A. Maspero, A. Sironi, *Chem. Commun.* **2003**, 2018−2019.

[13] G. M. Sheldrick, *SHELXTL-Plus V5.1 Software Reference Manual*; Bruker AXS Inc.: Madison, WI. **1997**.

Received August 12, 2003
Early View Article