

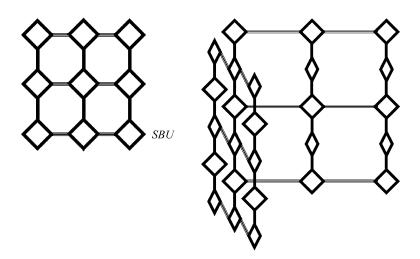
Article

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# Assembly of a Secondary Building Unit (SBU) into Two- and Three-Dimensional Structures in Lanthanide Benzenedicarboxylates

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**ABSTRACT:** Two series of lanthanide benzenedicarboxylates of the general framework formula  $[M_2(2,2'-bipy)_2(C_8H_4O_4)_3]$  (M = Y, Gd, and Dy) have been prepared employing hydrothermal methods, and their structures were determined by single-crystal X-ray diffraction. Both the structure types contain only one type of secondary building units (SBU), which are connected differently giving rise to two- and three-dimensional (2- or 3-D) structures. While the 2-D structure is related to an augmented square lattice, the 3-D one closely resembles the CdSO<sub>4</sub> structure. This is the first observation, to our knowledge, of a CdSO<sub>4</sub> structure in the coordination polymers containing the rare earth ions. The formation of these structures has been rationalized from the connectivity between the building units, which clearly indicates that the framework structures are related. All the compounds have been characterized by powder X-ray diffraction, elemental analysis, infrared (IR) spectroscopic, thermogravimetric analysis (TGA), and photoluminescence studies.

#### Introduction

Metal-organic framework (MOFs) compounds have attracted the attention of synthetic chemists because of their applications in the areas of catalysis, sorption, separation, luminescence, nonlinear optics, etc. 1-5 Intense research during the past decade or so resulted in a large number of MOF compounds with novel structures and interesting properties. Most of these compounds have been prepared employing hydrothermal methods. One of the recent developments in this area has been the use of retrosynthesis,6 modular chemistry,7 and supramolecular chemistry<sup>8</sup> approaches for stabilizing novel MOF compounds. Of particular interest is the use of reticular synthesis employing discrete metals or metal clusters as nodes and multifunctional organic ligands as linkers to form secondary building units (SBU), which are further connected to result in inorganic default structures.9-11 In many MOF compounds, especially those belonging to 3d transition elements, the commonly observed SBU has been a paddle wheel. The 4f systems, on the other hand, appear to have more than one type of building unit, presumably due to the higher coordination preferences of the lanthanide ions. 12

In the area of MOF compounds, there has been a growing interest in studying polymorphic structures.<sup>13</sup> The topologies of the polymorphic structures appear to be governed by many factors,<sup>14</sup> such as the geometry around the metal ion,<sup>15</sup> the conformational flexibility of the ligands,<sup>16,17</sup> the solvent,<sup>18</sup> and the various weak interactions.<sup>19,20</sup> In addition, the effect of additives in the reaction mixtures on the ensuing polymorphic structures has also been investigated recently.<sup>21</sup> We have been investigating the formation of new inorganic framework structures based on 4f elements. In synthesizing new benzenecarboxylates of lanthanide ions, we sought to employ a secondary ligand, such as 2,2'-bipyridne (2,2'-bipy), to effectively reduce the available coordination sites for bonding with carboxylate anions. During the course of such investigations, we have now discovered two new isophthalate coordination compounds, [M<sub>2</sub>-

 $(2,2'-bipy)_2(C_8H_4O_4)_3$  (I) and  $[M_2(2,2'-bipy)_2(C_8H_4O_4)_3] \cdot H_2O$ (II) (M = Y, Gd, and Dy), with 2- and 3-D structures. The structures of both compounds are unique and appear to be topologically related, formed by the same SBUs. The two structures are the result of the use of different secondary amines in the otherwise similar synthetic compositions. While I possess an augmented square lattice structure with a (4,4) net topology, II forms with the CdSO<sub>4</sub> type structure. The CdSO<sub>4</sub> structure has been discussed at length in the literature in recent years<sup>22–24</sup> and is related to the mercuric sulfate structure.<sup>25</sup> Both compounds have only one type of building unit and may be considered a special case of polymorphism of the framework structure, since the total formulas between the compounds are different. To our knowledge, this is the first time a CdSO<sub>4</sub> structure has been realized in a 4f element system. In this paper, the synthesis, structure, and the structural relationship between I and II are presented.

#### **Experimental Section**

Both I and II were prepared by hydrothermal methods employing 1,3-benzenedicarboxylic acid (isophthalic acid, 1,3-BDC) in the presence of different secondary amines (SA). An SA is generally required, presumably, to help in the deprotonation of the benzenedicarboxylic acid. Typically, a mixture of the composition M(NO<sub>3</sub>)<sub>3</sub>/2(1,3-BDC)/ 3(2,2'-bipy)/3(SA)/555H<sub>2</sub>O at 180 °C for 72 h in a 23 mL PTFE-lined stainless steel autoclave yielded a crop of pure single crystals (yield  $\sim$ 80%). In the present synthesis, the use of piperidine as the SA resulted in I, while piperazine or NaOH led to the formation of II. The Y compound in both I and II was found to be a mixture of phases. For the single-crystal structure analysis of the Y compound, we carefully selected the crystal which closely resembled that of Gd and Dy. We have not been able to prepare a single phase material containing Y, despite many repeated attempts. The initial characterizations, in both cases, were carried out using powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), and infrared (IR) spectroscopic studies. The powder XRD patterns were recorded on crushed single crystals in the  $2\theta$  range  $5-50^{\circ}$  using Cu K $\alpha$  radiation. The XRD patterns indicated, in the case of Gd and Dy, that the products were new materials; the patterns were entirely consistent with simulated patterns based on the structures determined using the single-crystal X-ray diffraction. Elemental analysis: for **I**, calcd(obsd) for Gd, C = 47.17(47.11), N = 5.00(4.91), H = 2.50(2.46); for Dy, C = 46.74-(46.58), N = 4.96(4.83), H = 2.45(2.34) and for **II**, for Gd; C = 46.43-

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Table 1. Crystal Data and Structure Refinement Parameters for I,  $[M_2(C_{10}N_2H_8)_2(C_8H_4O_4)_3]$  (M = Y, Gd, and Dy)

structure parameter	Y	Gd	Dy
empirical formula	$C_{44}H_{28}Y_2N_4O_{12}$	$C_{44}H_{28}Gd_2N_4O_{12}$	$C_{44}H_{28}Dy_2N_4O_{12}$
formula weight	982.54	1119.23	1129.73
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$ , (No. 2)	$P\bar{1}$ , (no. 2)	$P\overline{1}$ , (no. 2)
a./Å	11.4060(2)	11.4366(2)	11.3878(2)
b/Å	11.9991(1)	12.0522(3)	11.9894(1)
c /Å	16.5355(4)	16.6213(3)	16.5173(3)
α /°	92.0110(10)	91.8000(10)	91.9420(10)
β /°	106.7560(10)	107.1070(10)	106.8140(10)
γ /°	105.9300	106.0700(10)	105.9680(10)
$V/\text{Å}^3$	2067.68(7)	2088.15(8)	2059.62(6)
Z	2	2	2
$D \text{ (calc) /g cm}^{-3}$	1.578	1.780	1.822
$\mu$ /mm <sup>-1</sup>	2.862	3.217	3.670
λ (Mo Kα) /Å	0.71073	0.71073	0.71073
F(000)	988	1088	1096
2θ range /°	2.6-46.6	2.6-46.4	2.6-46.6
total data collected	8555	8742	8667
unique data	5790	5862	5798
observed data $[I > 2\sigma(I)]$	4392	5004	4805
$R_{\text{merg}}$	0.0355	0.0201	0.0253
R indexes $[I > 2\sigma(I)]$	$R_1 = 0.0399^a$ ; $wR_2 = 0.0868^b$	$R_1 = 0.0232^a$ ; $wR_2 = 0.0561^b$	$R_1 = 0.0237^a$ ; $wR_2 = 0.0752$
R indexes [all data]	$R_1 = 0.0625^a$ ; $wR_2 = 0.0972^b$	$R_1 = 0.0309^a$ ; $wR_2 = 0.0589^b$	$R_1 = 0.0311^a$ ; $wR_2 = 0.0775$
largest difference map peak and hole/e Å <sup>-3</sup>	0.679 and -0.812	0.437 and -0.865	0.545 and $-1.116$

 ${}^{a}R_{1} = \sum ||F_{0}| - |F_{c}|| \sum |F_{0}|. \ {}^{b}wR_{2} = \{\sum [w(F_{0}^{2} - F_{c}^{2})^{2}] \sum [w(F_{0}^{2})^{2}]\}^{1/2}. \ w = 1/[\sigma^{2}(F_{0})^{2} + (aP)^{2} + bP], \ P = [\max(F_{0}^{2}, 0) + 2(F_{c})^{2}]/3, \text{ where } a = 0.0265$ and b = 0 for Gd, a = 0.0378 and b = 0 for Dy, and a = 0.0354 and b = 0 for Y.

(46.25), N = 4.92(4.73), H = 2.64(2.47); for Dy; C = 43.17(42.81), N = 4.88(4.73), H = 2.61(2.56).

Thermogravimetric analysis (TGA, Metler-Toledo) was carried out in oxygen atmosphere (flow rate = 50 mL/min) in the temperature range 30 to 900 °C (heating rate = 5 °C/min). The studies indicate one weight loss for I and two weight losses for II. For I, the observed total weight loss of 70.7% for Gd and 70.5% for Dy in the range 340-480 °C corresponds to the loss of 2,2'-bipy and isophthalate groups [calc. 71.9% (Gd) and 71.2% (Dy)]. For II, the small initial weight loss in the range 170-250 °C corresponds to the loss of the lattice water, and the second weight loss of 70.9 for Gd and 70.9 for Dy corresponds to the loss of 2,2'-bipy and isophthalate groups [calc. 72.4% (Gd) and 71.7% (Dy)]. In all cases, the calcined samples were found to be crystalline, and the powder XRD lines match well with the corresponding pure oxides [JCPDS No. 43-1014 (Gd) and 43-1006

Infrared (IR) spectroscopic studies (Bruker IFS-66v) were carried out in the mid-IR region as a KBr pellet. The results indicated characteristic sharp lines with almost similar bands. Minor variations in the bands were noticed between the compounds. We observed the IR bands for the water molecules in the case of II. The observed bands are 3600-3660(s) cm<sup>-1</sup> -  $\nu_s$ OH, 3066(w) cm<sup>-1</sup> -  $\nu_s$ (C-H)<sub>aromatic</sub>,  $1606(\text{w}) \text{ cm}^{-1} - \delta_s \text{H}_2 \text{O}, 1523(\text{s}) \text{ cm}^{-1} - \nu_s \text{(C=O)}, 1469(\text{s}) \text{ cm}^{-1} - \delta_s \text{(COO)}, 1409(\text{s}) \text{ cm}^{-1} - \delta \text{(OH)}, \text{ and } \delta \text{(CO)}, 1145(\text{s}) \text{ cm}^{-1} - \delta \text{(COO)}, 1409(\text{s}) \text{ cm}^{-1} - \delta \text{(OH)}, \text{ and } \delta \text{(CO)}, 1145(\text{s}) \text{ cm}^{-1} - \delta \text{(COO)}, 1409(\text{s}) \text{ cm}^{-1} - \delta \text{(OH)}, \text{ and } \delta \text{(COO)}, 1409(\text{s}) \text{ cm}^{-1} - \delta \text{(OH)}, \text{ cm}^{-1} - \delta \text{(O$  $\delta(CH_{aromatic})_{in-plane}$ , 746(s) and 843(s) cm<sup>-1</sup> –  $\delta(CH_{aromatic})_{out-of-plane}$ .

Room temperature solid-state photoluminescence studies were performed on powdered samples (Perkin-Elmer spectrometer (LS-55) with a single beam setup equipped with a xenon lamp (50 W) as the source and a photomultiplier tube as the detector.

Single-Crystal Structure Determination. A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a thin glass fiber. Crystal structure determination by X-ray diffraction was performed on a Siemen's Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo K $\alpha$  radiation,  $\lambda = 0.71073$ Å) operating at 40 kV and 40 mA. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program.<sup>26</sup> The structure was solved and refined using the SHELXTL-PLUS suite of program.<sup>27</sup> All the hydrogen atoms of the carboxylic acids were initially located in the difference Fourier maps, and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. Final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares refinement against  $|F|^2$  was carried out using the SHELXTL-PLUS<sup>27</sup> suite of programs. Details of the structure solution and final refinements for compounds I and II (M = Y, Gd, and Dy) are given in Tables 1

CCDC 268101 – 268106 contain the supplementary crystallographic data for all the compounds. The data can be obtained free of charge from the Cambridge Crystallographic Data Center, Cambridge, UK via www.ccdc.cam.ac.uk/data\_request/cif.

# **Results and Discussion**

The structure of I consists of a network of  $MO_6N_2$  (M = Y, Gd, and Dy) distorted dodecahedral units, 2,2-bipy ligands and 1,3-BDC anions. The dodecahedral units are linked through the carboxylate anions giving rise to a 2-D layered structure with the 2,2'-bipy ligands hanging into the interlamellar spaces from the metal center. The M-O bond distances are in the range 2.248(3)-2.478(3) Å (av. 2.348 Å for Y, 2.392 Å for Gd, and 2.359 Å for Dy), and the M-N bond distances have an average distance of 2.572 Å for Y, 2.607 Å for Gd, and 2.574 Å for Dy. The O/N-M-O/N bond angles are in the range 52.91-(9)-148.2(2)°. All the C-O, C-N, and C-C distances and angles are in the ranges expected for this bonding. The selected bond distances are listed in Table 3.

The structure of I can be described based on simple SBUs. Thus, two MO<sub>6</sub>N<sub>2</sub> units are connected by the carboxylate anions forming a paddle wheel-like SBU as shown in Figure 1a. The SBU is formed by two 2,2'-bipy ligands and six carboxylate linkers. All the six carboxylates linkers have the same type of connectivity with the metal centers. To understand the structure, it is preferable to differentiate the isophthalates as acid-1 and acid-2, respectively. It may be noted that, of the six vertices of the paddle wheel-like SBU, only four vertices are available for bonding with neighboring SBUs as two vertices are bonded to terminal 2,2'-bipy ligands (Figure 1a). Thus, each paddle wheel unit is connected to four other paddle wheel units involving six 1,3-BDC anion linkers (two acid-1 and four acid-2). This gives rise to two SBUs being connected by two 1,3-BDC units (acid-2), and the remaining two by one 1,3-BDC unit each (acid-1). This kind of bonding gives rise to a 2-D structure with apertures (Figure 1b). As can be noted, the connectivity

Table 2. Crystal Data and Structure Refinement Parameters for II, [M<sub>2</sub>(C<sub>10</sub>N<sub>2</sub>H<sub>8</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)<sub>3</sub>]·H<sub>2</sub>O (M = Y, Gd, and Dy)

7 L 2(-10 2 0)2(-0 4-4)3 2- ( ))					
structure parameter	Y	Gd	Dy		
empirical formula	C <sub>44</sub> H <sub>30</sub> Y <sub>2</sub> N <sub>4</sub> O <sub>13</sub>	C <sub>44</sub> H <sub>30</sub> Gd <sub>2</sub> N <sub>4</sub> O <sub>13</sub>	C <sub>44</sub> H <sub>30</sub> Dy <sub>2</sub> N <sub>4</sub> O <sub>13</sub>		
formula weight	1000.55	1137.24	1147.74		
crystal system	monoclinic	monoclinic	monoclinic		
space group	C2/c (No. 15)	C2/c (No. 15)	C2/c (No. 15)		
a /Å	17.4993(3)	17.6083(10)	17.5479(8)		
b /Å	13.1290	13.0496(8)	13.1130(6)		
c /Å	18.7591(3)	18.8475(11)	18.7783(8)		
α /°	90	90	90		
β/°	111.8950(10)	112.0740(10)	112.1020(10)		
γ /°	90	90	90		
$V/Å^3$	3999.00(10)	4013.4(4)	4003.5(3)		
Z	4	4	4		
D (calc) /gcm <sup>-3</sup>	1.662	1.882	1.904		
$\mu / \text{mm}^{-1}$	2.963	3.351	3.779		
λ (MoKα) /Å	0.71073	0.71073	0.71073		
F(000)	2016	2216	2232		
$2\dot{\theta}$ range /°	4.0-46.6	4.0-46.6	4.0-46.6		
total data collected	8037	8105	8303		
unique data	2863	2887	2875		
observed data $[I > 2\sigma(I)]$	2476	2472	2638		
$R_{ m merg}$	0.0285	0.0289	0.0374		
R indexes $[I > 2\sigma(I)]$	$R_1 = 0.0273^a$ ; $wR_2 = 0.0617^b$	$R_1 = 0.0200^a$ ; $wR_2 = 0.0414^b$	$R_1 = 0.0200^a$ ; $wR_2 = 0.0494^b$		
R indexes [all data]	$R_1 = 0.0353^a$ ; $wR_2 = 0.0653^b$	$R_1 = 0.0273^a$ ; $wR_2 = 0.0436^b$	$R_1 = 0.0222^a$ ; $wR_2 = 0.0501^b$		
largest difference map peak and hole/eÅ <sup>-3</sup>	0.287 and -0.400	0.307  and  -0.436	0.823 and $-0.985$		

 ${}^{a}R_{1} = \sum ||F_{0}| - |F_{c}||/\sum |F_{0}|. \ {}^{b}wR_{2} = \{\sum [w(F_{0}^{2} - F_{c}^{2})^{2}]/\sum [w(F_{0}^{2})^{2}]^{1/2}. \ w = 1/[\sigma^{2}(F_{0})^{2} + (aP)^{2} + bP], \ P = [\max(F_{0}^{2}, 0) + 2(F_{c})^{2}]/3, \text{ where } a = 0.0165$ and b = 0.2035 for Gd, a = 0.0160 and b = 0 for Dy, and a = 0.0287 and b = 4.5321 for Y.

Table 3. Selected Bond Distances for I  $[M_2(C_{10}N_2H_8)_2(C_8H_4O_4)_3]$ 

$(M = Gd, Dy, and Y)^a$				
	distance (Å)			
bond	Y	Gd	Dy	
M(1)-O(1)	2.257(3)	2.318(3)	2.274(4)	
M(1) - O(2)	2.323(3)	2.376(3)	2.337(4)	
M(1) - O(3)	2.360(3)	2.413(3)	2.368(4)	
M(1) - O(4)	2.365(3)	2.402(3)	2.377(4)	
M(1) - O(5)	2.380(3)	2.431(3)	2.391(4)	
M(1) - O(6)	2.430(3)	2.460(3)	2.439(4)	
M(1)-N(2)	2.526(4)	2.563(3)	2.526(5)	
M(1)-N(1)	2.631(4)	2.663(4)	2.634(5)	
M(2)-O(7)#2	2.248(3)	2.292(3)	2.266(4)	
M(2) - O(8)	2.280(3)	2.319(3)	2.286(4)	
M(2)-O(10)#3	2.329(3)	2.374(3)	2.338(4)	
M(2)-O(9)#4	2.333(3)	2.379(3)	2.346(4)	
M(2) - O(12)	2.432(3)	2.478(3)	2.440(4)	
M(2) - O(11)	2.435(3)	2.464(3)	2.442(4)	
M(2)-N(4)	2.551(4)	2.585(4)	2.548(5)	
M(2)-N(3)	2.579(4)	2.618(4)	2.587(5)	
O(1) - C(48)	1.274(5)	1.273(5)	1.268(6)	
O(2)-C(21)#1	1.266(5)	1.259(5)	1.263(6)	
O(3)-C(48)#1	1.252(5)	1.262(5)	1.257(6)	
O(4)-C(21)	1.253(5)	1.259(5)	1.252(6)	
O(5)-C(31)	1.273(5)	1.271(5)	1.283(7)	
O(6)-C(31)	1.263(5)	1.258(5)	1.238(7)	
O(7) - C(38)	1.242(5)	1.248(5)	1.248(7)	
O(8) - C(28)	1.263(5)	1.264(5)	1.261(7)	
O(9) - C(38)	1.263(5)	1.261(5)	1.256(7)	
O(11)-C(41)#2	1.255(5)	1.257(5)	1.241(7)	
O(12)-C(41)#2	1.267(5)	1.266(5)	1.266(7)	
N(1)-C(1)	1.336(6)	1.352(6)	1.330(8)	
N(1)-C(5)	1.349(6)	1.349(6)	1.349(7)	
N(2)-C(6)	1.346(6)	1.351(6)	1.339(8)	
N(2)-C(10)	1.337(6)	1.345(6)	1.343(8)	
N(3)-C(11)	1.325(7)	1.330(7)	1.324(9)	
N(3)-C(15)	1.341(6)	1.335(7)	1.348(9)	
N(4)-C(20)	1.332(7)	1.336(7)	1.329(10)	
N(4)-C(16)	1.343(7)	1.344(7)	1.354(10)	

<sup>&</sup>lt;sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1 - x+2, -y, -z + 1; #2 - x + 2, -y, -z; #3 - x + 2, -y - 1, -z; #4 x, y -

resembles the (4,4) net topology commonly observed in many MOF compounds. The 2,2'-bipy ligands, connected to the M<sup>3+</sup> ions, project into the interlamellar region, giving rise to considerable intralayer  $\pi \cdots \pi$  interactions between the 2,2'-bipy ligands and interlayer  $CH \cdots \pi$  interactions.

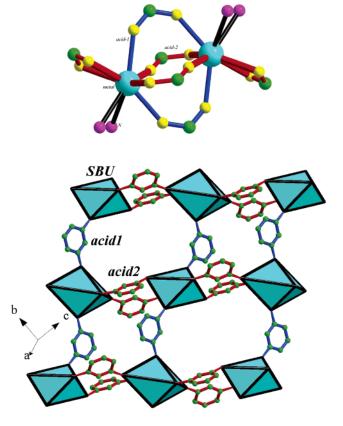


Figure 1. (a) Figure shows the paddle wheel secondary building unit (SBU) observed in  $\mathbf{I}$  and  $\mathbf{II}$ . (b) The structure of  $\mathbf{I}$  in the bc plane. Since the compound possesses only six nodes for connection with the 1,3-BDC anions, the SBU unit is represented as an octahedra. acid-1 and acid-2 represent the two types of 1,3-BDC anion connectivity (see text). Note that the amine molecules occupy only one type of aperture within the layer.

The structure of **II** consists of a network of  $MO_6N_2$  (M = Y, Gd, and Dy) distorted dodecahedral units, 2,2-bipy ligands and 1,3-BDC anions. The M-O bond distances are in the range 2.281(2)-2.543(3) Å (ave 2.352 Å for Y, 2.387 Å for Gd, and

Table 4. Selected Bond Distances for II,  $[M_2(C_{10}N_2H_8)_2(C_8H_4O_4)_3]\cdot H_2O (M = Gd, Dy, and Y)^a$ 

		distance (Å)	
bond	Y	Gd	Dy
M(1)=O(5)	2.281(2)	2.322(2)	2.297(2)
M(1) - O(1)	2.308(2)	2.340(2)	2.321(2)
M(1) - O(2)	2.329(2)	2.362(2)	2.340(2)
M(1) - O(4)	2.328(2)	2.369(2)	2.343(2)
M(1) - O(3)	2.341(2)	2.387(2)	2.358(2)
M(1) - O(6)	2.526(2)	2.543(3)	2.535(2)
M(1)-N(2)	2.548(3)	2.589(3)	2.566(3)
M(1)-N(1)	2.569(2)	2.595(3)	2.567(3)
O(1)-C(11)	1.255(3)	1.256(4)	1.257(4)
O(2)-C(28)	1.268(4)	1.257(4)	1.259(4)
O(3)-C(21)	1.255(3)	1.252(4)	1.250(4)
O(4)-C(11)#1	1.265(3)	1.266(4)	1.264(4)
O(5)-C(21)#1	1.260(3)	1.256(4)	1.263(4)
O(6)-C(28)	1.257(4)	1.262(4)	1.255(4)
N(1)-C(1)	1.338(4)	1.338(5)	1.333(5)
N(1)-C(5)	1.344(4)	1.342(4)	1.355(4)
N(2)-C(10)	1.334(4)	1.338(5)	1.339(5)
N(2)-C(6)	1.355(4)	1.347(5)	1.345(4)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1 - x, -y + 2, -z.

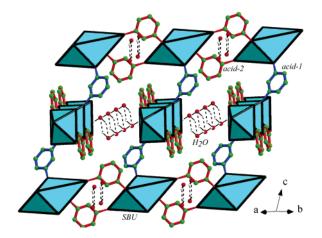
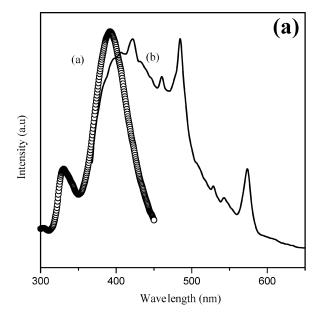


Figure 2. Structure shows the connectivity between the SBUs in II. The water molecules occupy the channel spaces and form a 1-D ladderlike structure. Note the similarity in the connectivity involving the two types of 1,3-BDC anions in I and II. The secondary layer going in a direction perpendicular to the first layer is also shown. This arrangement of layers is similar to that observed in the CdSO<sub>4</sub> structure (see text).

2.366 Å for Dy), and the M-N bond distances have an average distance of 2.558 Å for Y, 2.592 Å for Gd, and 2.566 Å for Dy. The O/N-M-O/N bond angles are in the range 53.01-(9)-149.67(9)°. All the C-O, C-N, and C-C distances and angles are in the ranges expected for this bonding. The selected bond distances are given in Table 4.

The structure of II also possesses identical paddle wheellike secondary building units as I. In II, the connectivity between the SBUs through the 1,3-BDC units gives rise to similar (4,4) 2-D nets. The observed 3-D structure of **II**, then, is due to the presence of a second identical 2-D layer in a direction perpendicular to the first layer (Figure 2). The water molecules occupy the channel spaces within the structure (Figure 2). More importantly, strong hydrogen-bond interactions exist between the water molecules giving rise to a pseudo one-dimensional (1-D) ladder-like arrangement. It is highly likely that the position of the water molecules and its hydrogen-bond interactions with the framework oxygen atoms would have resulted in the formation of a 3-D structure with interpenetrating 2-D layers. This cross-linking of the (4,4) 2-D net gives rise to an unusual



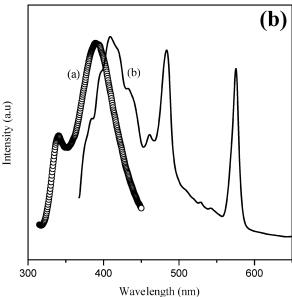
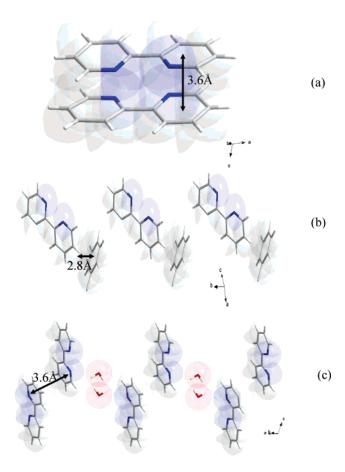


Figure 3. Room temperature solid-state photoluminescence spectra for (a)  $\mathbf{I}$  and (b)  $\mathbf{II}$ .  $\mathbf{M} = \mathbf{Gd}$  (a) and  $\mathbf{Dy}$  (b).

arrangement and a novel structure. This unique structure can be described as a "Lincoln log" arrangement.2 Whitesides and co-workers<sup>28</sup> described the mesoscale assembly of polyurethane rods in which adjacent rods lie at right angles to each other as Lincoln logs. This orthogonal stacking of the (4,4) augmented square nets in **II** is identical to the CdSO<sub>4</sub> network (Figure 2).

The room temperature solid-state photoluminescence properties for all the compounds of  $\mathbf{I}$  and  $\mathbf{II}$  were investigated. The studies clearly indicate that all the compounds show similar photoluminescence behavior (Figure 3). When excited at 252 nm, the Gd compound exhibited a shoulder at 340 nm and a main peak at 390 nm. The emission peak at 390 nm can be assigned to the intraligand  $\pi^* \to \pi$  or  $\pi^* \to n$  transitions of the 1,3-BDC units or the 2,2'-bipy ligands. To test this assignment of the emission bands, we have carried out the photoluminescence studies on the sodium salt of 1,3-BDC, which also exhibited similar emissions at 390 nm. Hence, this emission cannot be assigned as ligand-to-metal-charge-transfer (LMCT) or metal-to-ligand-charge-transfer (MLCT). 12,29 The Dy



**Figure 4.** (a) The  $\pi \cdots \pi$  interactions observed in **I**. (b) The CH $\cdots \pi$ interactions observed in **I**. (c) The  $\pi \cdots \pi$  interactions observed in **II**.

compound exhibits a main peak at 410 nm along with peaks at 470 and 570 nm, when excited at 351 nm (Figure 3). Like the Gd compound, the main emission peak corresponds to the  $\pi^*$  $\rightarrow \pi$  or  $\pi^* \rightarrow$  n transitions and the smaller peaks corresponds to the Dy3+ ion centered emission peaks. The peaks at 470 and 570 nm can be assigned to  ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$  (~470 nm) and  ${}^4F_{9/2}$  $\rightarrow$  <sup>6</sup>H<sub>13/2</sub> (~570 nm) transitions.<sup>30</sup>

In the coordination polymers of the benzene carboxylates,  $CH\cdots\pi$  and  $\pi\cdots\pi$  interactions appear to play a crucial role in stabilizing the crystal structure. In the present compounds, we observe both  $CH\cdots\pi$  and  $\pi\cdots\pi$  interactions that involve the 1,3-BDC units and the 2,2'-bipy ligands. To have a better insight and to understand the role of such interactions in the stability of I and II, we have performed preliminary calculations using the AM1 parametrized Hamiltonian available in the Gaussian program suite.31 These calculations show two interactions in the 2-D structure, I, and three interactions in the 3-D structure, II (Figure 4a,b)

The 2-D structure of **I** has one  $\pi \cdots \pi$  and one CH $\cdots \pi$ interaction. The calculated  $\pi \cdots \pi$  interaction energy of 4.93 kcal/ mol arises from the interactions between the two antiparallel 2,2'-bipyridine units with a distance of 3.6 Å and an angle of 6.5° between the aromatic rings (antiparallel arrangement) (Figure 4a). The  $CH\cdots\pi$  interaction occurs between the two layers involving the C-H of the 2,2'-bipy and the  $\pi$  ring of the 1,3-BDC with the CH··· $\pi$  distance of 2.8 Å and the interaction angle of 70° (Figure 4b). The calculated energy for this CH··  $\cdot \pi$  interaction is 1.16 kcal/mol. The 3-D structure, **II**, possesses two CH··· $\pi$  and one  $\pi$ ··· $\pi$  interactions. One of the CH··· $\pi$ interactions is between the 1,3-BDC C-H and the  $\pi$  ring of the 2,2'-bipy unit, with a CH··· $\pi$  distance of 2.76 Å and an interaction angle of 53°. The calculated energy for this interaction is 4.16 kcal/mol. The second CH $\cdots \pi$  interaction is between the C-H of the 2,2'-bipy unit and the  $\pi$  ring of the 1,3-BDC with a CH··· $\pi$  distance of 2.9 Å and an interaction angle of 65°. The calculated energy for this interaction is 2.9 kcal/mol. The  $\pi \cdots \pi$  interaction occurs between the 2,2'-bipy units; a distance of 3.6 Å and an angle of 4.5° have been observed between the aromatic rings (Figure 4c). The calculated energy for this interaction is 3.3 kcal/mol.

It may be noted that the structures of I and II appear to be devoid of any appreciable hydrogen-bond interactions, commonly observed in many inorganic-organic hybrid compounds. In the absence of hydrogen-bond interactions, it is clear that the weak CH··· $\pi$  and the  $\pi$ ··· $\pi$  interactions are the dominant interactions existing in both structures, lending some stability to these structures. There is now a general consensus that this interaction falling in the moderate energy scale (3-10 kcal/ mol) acts to bind molecules together in the crystal. It is likely that this interaction would be used as an important parameter in the design of new solids. It is likely that the study of similar systems would open up new avenues for our understanding of the nature of  $CH\cdots\pi$  and the  $\pi\cdots\pi$  interactions and their role in the structural stability.

From the structural point of view, it is important to note that both I and II have identical building units. A careful analysis of the building units reveals that there are orientational differences between the paddle wheel units. The orientational differences in the SBUs appear to be the result of connectivity by the two types of 1,3-BDC units (acid-1 and acid-2). The 1,3-BDC along with the 2,2'-bipy units are arranged to maximize the  $\pi \cdots \pi$  interactions. In **I**, each paddle wheel unit is connected to four other paddle wheel units by six 1,3-BDC linkers (Figure 1a). This is, in a way, similar to the SBU with four vertices as four carboxylate units connect only two SBUs. This arrangement can now be visualized as a (4,4) net with a augmented square lattice as shown schematically in Figure 5a. In II, the four connected networks are further connected orthogonal to each other giving rise to the augmented CdSO<sub>4</sub> structure. A schematic of the arrangement of the two square nets are shown in Figure

From the synthesis point of view, it may be noted that both I and II are formed from the same synthesis mixture, albeit a different secondary amine was employed for deprotonating the 1,3-BDC in **II**. Since both compounds have been prepared from identical synthesis mixtures, it is likely that the same building unit is present in solution in both cases, and a spontaneous assembly of the building units could have facilitated the formation of I and II. Unlike the open-framework phosphate structures,<sup>32</sup> our present understanding of the formation of the MOF phases is poor. It is likely that the secondary amine added during the reaction to facilitate the deprotonation of the acid could have played a subtle role during the assembly of the SBUs into 2- and 3-D structures. This scenario may be compared to the additive induced polymorphism reported in the literature recently.<sup>21</sup> Although the framework formula for both **I** and **II** are different, **II** contains one molecule of water in its framework. As the framework has been formed by only one type of building units in both structures, it can be considered as a special case of polymorphism, wherein the same building units are involved in the formation of two distinct structures of different dimensionalities. The water molecules, present in II, appear to form hydrogen-bonded dimers, which probably influences the arrangement of the 2-D (4,4) nets into three dimensions. The

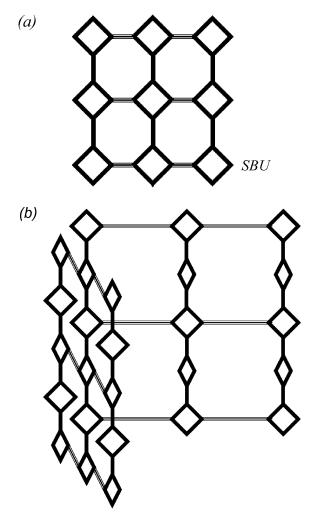


Figure 5. Schematic showing the arrangement of the SBU in I and II. (a) The augmented square lattice and (b) the CdSO<sub>4</sub> lattice.

arrangement of water molecules in **II** is quite unique forming a ladder-like arrangement in two directions that are mutually perpendicular (Figure 2). It is quite clear that the water molecules are important in the formation of the 3-D structure of II. It is likely that the lower-dimensional structure (I) could be the precursor for the higher-dimensional one (II), as such concepts have been well developed in zinc phosphates.<sup>32</sup> Further work is required to understand and unravel the formation of these complex structures.

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## References

- (1) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. Angew. Chem., Int. Ed. 2004, 43, 1466.
- (2) Moulton B.; Zawarotko, M. J. Chem. Rev. 2001, 101, 1629.
- (3) Jainak, C. Dalton Trans. 2003, 2781.
- (4) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. Science 2003, 300, 1127.

- (5) Evans O. R.; Lin, W. Acc. Chem. Res. 2002, 35, 511.
- (6) Corey, E. J. Chem. Soc. Rev. 1988, 17, 111.
- (7) Ferey, G. J. Solid State Chem. 2000, 152, 37.
- (8) Desiraju, G. R. Crystal Engineering, The Design of Organic Solids; Elsevier: Amsterdam, 1989.
- (9) Eddaoudi, M.; Kim, J.; Vodak, D.; Sudik, A.; Wachter, J.; O'Keeffe M.; Yaghi, O. M. Proc. Natl. Acad. Sci. U.S.A. 2002, 99, 4900.
- (10) Batten S. R.; Robson, R. Angew. Chem., Int. Ed. 1998, 37, 1461.
- (11) O'Keeffe M.; Hyde, B. G. Crystal Structures I. Patterns and Symmetry; Mineralogical Society of America, Washington, DC, 1996.
- (12) Thirumurugan A.; Natarajan, S. Dalton Trans. 2004, 2923.
- (13) Braga, D.; Grepioni, F. Chem. Commun. 2005, 3635.
- (14) Herbstein, F. H. Cryst. Growth Des. 2004, 4, 1419.
- (15) Power, K. N.; Hennigar, T. L.; Zaworotko, M. J. New J. Chem. 1998,
- (16) Senthil Kumar, V. S.; Pigge, F. C.; Rath, N. P. New J. Chem. 2004, 28, 1192.
- (17) Blake, A. J.; Brooks, N. J.; Champness, N. R.; Crew. M.; Deveson, A.; Fenske, D.; Gregory, D. H.; Hanton, L. R.; Hubberstey, P.; Schroder, M. Chem. Commun. 2001, 1432.
- (18) Shin, D. M.; Lee, I. S.; Chung, Y. K.; Lah, M. S. Chem. Commun. 2003, 1036.
- (19) Senthil Kumar, V. S.; Pigge, F. C.; Rath, N. P. New J. Chem. 2003, 27, 1554.
- (20) Xie, Z.; Liu, L.; Yang, B.; Yang, G.; Ye, L.; Li, M.; Ma, Y. Cryst. Growth Des. 2005, 5, 1959.
- (21) Thallapally, P. K.; Jetti, R. K. R.; Katz, A. K.; Carrel, H. L.; Singh, K.; Lahiri, K.; Kotha, S.; Boese, R.; Desiraju, G. R. Angew. Chem., Int. Ed. 2004, 43, 11149.
- (22) Power, K. N.; Hennigar, T. L.; Zaworotko, M. J. Chem. Commun.,1998, 595
- (23) Plater, M. J.; Foreman, M. R. J.; Skakle, J. M. S. Cryst. Eng. 2001, 4, 319
- (24) O'Keeffe, M.; Hyde, B. G. Crystal Structures I. Patterns and Symmetry; Mineralogical Society of America, Washington D. C.,
- (25) Bonefacic, A. Acta Crystallogr. 1961, 14, 116
- (26) Sheldrick, G. M. SADABS Siemens Area Detector Absorption Correction Program; University of Göttingen, Gottingen, Germany,
- (27) Sheldrick, G. M. SHELXTL-PLUS Program for Crystal Structure Solution and Refinement; University of Gottingen, Gottingen, Germany, 1997.
- (28) Oliver, S. R. J.; Clark, T. D.; Bowden, N.; Whitesides, G. M. J. Am. Chem. Soc. 2001, 123, 8119.
- (29) Zhang, L. Y.; Tong, M. L.; Gong, M. L.; Chen, X. M. Eur. J. Inorg. 2003, 2965.
- (30) Blasse, G.; Grabmaier, B. C. Luminescent Materials; Springer, Berline
- (31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.;. Pople, J. A. Gaussian 03, Revision B.05; Gaussian, Inc., Pittsburgh, PA, 2003.
- (32) Rao, C. N. R.; Natarajan, S.; Choudhury, A.; Neeraj, S.; Ayi, A. A. Acc. Chem. Res. 2001, 34, 80.

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