Inorganic−Organic Hybrid Compounds: Synthesis and Structures of New Metal Organic Polymers Synthesized in the Presence of Mixed Dicarboxylates

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A hydrothermal reaction of a mixture of 1,2-dicyanobenzene (1,2-DCB), 1,4-benzene-dicarboxylic acid (1,4-BDC) along with the corresponding lanthanide salts at a pH of ≈ 5, gives rise to a new series of carboxylate coordination polymers, $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$, (M = La, Pr, Gd, Dy, and Y), which are three-dimensional in structure. The 1,2-DCB oxidized to the corresponding dicarboxylic acid, phthalic acid (1,2-BDC), during the reaction. The structures are of two types with the larger La and Pr lanthanides forming type-1 and the smaller ones, Gd, Dy, and Y, forming type-2. While La and Pr have an idealized D_{3h} triply capped trigonal prism coordination environment, Gd, Dy, and Y have a distorted dodecahedral arrangement with respect to the oxygen atoms. The three-dimensional structure consists of a column of M atoms connected through the 1,2-BDC, and is cross-linked through 1,4-BDC giving rise to rhombic one-dimensional channels. The water molecules, bound to the M atoms, project into the channels. The compounds also illustrate the lanthanide contraction principle. The compounds have been characterized using powder X-ray diffraction, TGA, IR, and photoluminescence measurements. Our continuing investigations clearly reveal that related compounds can be formed with all the rare earth metal ions.

Introduction

Design and synthesis of three-dimensional (3D) coordination polymers with well-defined pores is of current topical interest.[1−5] Large numbers of three-dimensional coordination polymers with porous structures and interesting adsorption properties have been prepared and characterized using a variety of benzene carboxylates.[6−25] Of these, benzene-1,4-dicarboxylic acid (H_2BDC) with a 180° separation between the two carboxylic groups and benzene-1,3,5-tricarboyxlic acid (H_3BTC) with a 120° separation have been proven to yield interesting structures. Recent studies have shown that it is profitable to explore mixed metal benzene dicarboxylates.[26–31] Hetero-bimetallic coordination polymers have traditionally been investigated for their many interesting properties, such as dimensionality and magnetism.[32] In addition, the variations in the coordination environment between the two different metals might also give rise to different structures. Though a large number of mixed metal carboxylates have been prepared, work on the use of mixed dicarboxylates is slow to emerge. Recently, H_2BDC and H_3BTC were used for the preparation of the first example of a Zn coordination polymer built-up from two different carboxylic acids.[21]

Most of the metal-organic frameworks reported in the literature have been prepared employing hydrothermal methods. The hydrothermal method, in some cases, gives rise to unexpected products due to side reactions.[33] We have been interested in the use of hydrothermal methods for the preparation of mixed carboxylate polymers, which invariably lead to uncharacterized dense precipitates. It is known that cyano groups on the phenyl ring are easily converted into carboxylic acid groups by hydrolysis.[34−36] Recently the use of 1,4-dicyanobenzene has been shown to give rise to a series of terephthalate coordination polymers under hydrothermal conditions.[36] In the present study, we have used 1,2-dicyanobenzene and 1,4-terephthalic acid in a hydrothermal system along with a series of lanthanide salts to produce new metal-organic polymers of the general formula, $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$, (M = La, Pr, Gd, Dy, and Y) with three-dimensional structures. In addition, the present system with the rare earth elements of different ionic radii provide us with an opportunity to examine the established lanthanide contraction, and its role on the coordination of the lanthanide ion and the structure. The 1,2-benzene dicarboxylate (isophthalate), found in the products, has been obtained by the hydrolysis of 1,2-dicyanobenzene, under hydrothermal conditions. This is only the second example of the preparation of a metal-organic framework containing two different multi-carboxylates as

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organic linkers. The first report was a Zn coordination polymer, $[Zn_3BDC{\cdot}2BTC{\cdot}2NH(CH_3)_2{\cdot}2NH_2(CH_3)_2]$, with three-dimensional connectivity.[21] In this paper, we report the synthesis, structure and characterization of the compounds.

Results

The title compounds, $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$, (M = La, Pr, Gd, Dy, and Y) can be grouped into two distinct classes based on the coordination environment around the central metal ion and the connectivity with the carboyxlate units. Thus, $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$, M = La and Pr, form type-1, and M = Gd, Dy, and Y, form type-2.

Structure of $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$ M = La and Pr (Type-1)

The asymmetric unit of type-1 compounds contains 44 non-hydrogen atoms, of which two M atoms are crystallographically independent (Figure 1, a). The structure is built up by the connectivity involving M (M = La and Pr) and the carboxylate units. Each M atom is coordinated by two carboxylate ligands [C(1) and C(31)] and [CC(11) and C(21)] in an *O,O′* manner and also coordinated in a monodendate way by three other carboxylate ligands. The M atoms also possess two terminal oxygen atoms, which are found to be water molecules. In addition, two oxygen atoms, [O(1) and O(9)], connect the M atoms through a three-coordinate bond, a μ_3 connection, leading to an effective nine-coordination for the central metal. The coordination environment around M atoms is an idealized D_{3h} triply capped trigonal prism (Figure 1, b). The M atoms have distances in the range 2.397(6)−2.923(5) Å (average 2.568 Å for La and 2.531 Å for Pr). The longer M−O distances are associated with the oxygen atoms, [O(1) and O(9)], having the μ_3 connection, which link the two M centers and a carbon atom. The other bond lengths, C−O, C−C, have the expected values observed in many similar compounds.[6−25] The O−M−O bond angles for M = La and Pr are in the range 46.81(15)−151.25(18)°. The various structural parameters observed in type-1 compounds are in the range expected for this type of bonding. Both the M atoms in the asymmetric unit have two terminal M−O linkages with an average distances of 2.521 Å, which are water molecules. Selected bond lengths are listed in Table 1.

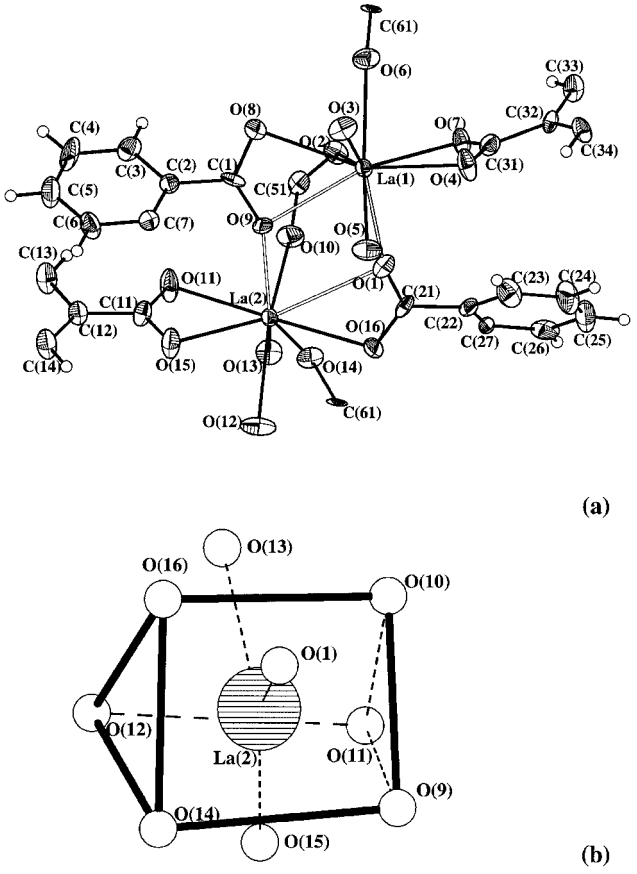


Figure 1. (a) ORTEP diagram showing the asymmetric unit for $[La_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$. Thermal ellipsoids are given at 50% probability. The three-coordinate oxygen atoms connecting the La atoms are shown in open tubular bonds. (b) The coordination environment around La(2) showing the D_{3h} triply capped trigonal prism

Table 1. Selected bond lengths in $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$, (M = La, Pr). Symmetry transformations used to generate equivalent atoms: #1 $x-1, y+1, z$; #2 $x+1, y, z$; #3 $-x+2, -y+1, -z+1$; #4 $x-1, y, z$; #5 $-x, -y+2, -z$

Bond	Distance (Å) La	Pr	Bond	Distance (Å) La	Pr
M(1)−O(1)	2.475(6)	2.430(4)	M(2)−O(1)	2.923(5)	2.923(4)
M(1)−O(2)	2.527(5)	2.493(4)	M(2)−O(9)	2.563(5)	2.530(4)
M(1)−O(3)	2.516(5)	2.473(4)	M(2)−O(10)	2.397(6)	2.361(5)
M(1)−O(4)	2.561(5)	2.514(5)	M(2)−O(11)	2.519(6)	2.479(4)
M(1)−O(5)	2.572(6)	2.535(5)	M(2)−O(12)	2.523(6)	2.486(5)
M(1)−O(6)	2.522(6)	2.484(4)	M(2)−O(13)	2.547(5)	2.519(4)
M(1)−O(7)	2.597(5)	2.560(4)	M(2)−O(14)	2.526(5)	2.480(4)
M(1)−O(8)	2.643(5)	2.601(4)	M(2)−O(15)	2.555(5)	2.516(4)
M(1)−O(9)	2.681(5)	2.653(4)	M(2)−O(16)	2.571(5)	2.526(4)
O(1)−C(21)	1.257(9)	1.259(7)	O(9)−C(1)	1.260(9)	1.278(8)
O(2)−C(51)	1.261(9)	1.249(7)	O(10)−C(51)	1.253(10)	1.252(7)
O(4)−C(31)	1.257(10)	1.242(8)	O(11)−C(11)	1.250(10)	1.249(8)
O(6)−C(61)#1	1.259(9)	1.258(7)	O(14)−C(61)	1.264(9)	1.277(7)
O(7)−C(31)	1.261(9)	1.283(8)	O(15)−C(11)	1.267(10)	1.266(8)
O(8)−C(1)	1.265(9)	1.249(8)	O(16)−C(21)	1.267(9)	1.246(7)

The structure of the type-1 compounds, $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$ M = La and Pr, has two types of 1,2-BDC and 1,4-BDC acids. Thus, C2−C7 forms the benzene ring with C1 and C51 as the carboxylate units, and C22−C27 forms the benzene ring with C21 and C61 forming the carboxylate units completing the two 1,2-BDC. The 1,4-acid has an inversion center in the plane of the benzene ring (C12−C14 and C32−C34) with C11 and C31 being the carboxylate units. Of the carboxylate units, C1, C11, and C31 are bidentate and C51, C21, and C61 are monodentate, respectively, with respect to individual M ions. The framework structure of the type-1 compounds can

be understood in terms of simpler building units. Thus, two three-coordinate oxygen atoms, [O(1) and O(9)], connect two M atoms to give rise to an edge-shared M_2O_{16} dimer. The 1,2-BDC connects the dimers giving rise to a sheet of

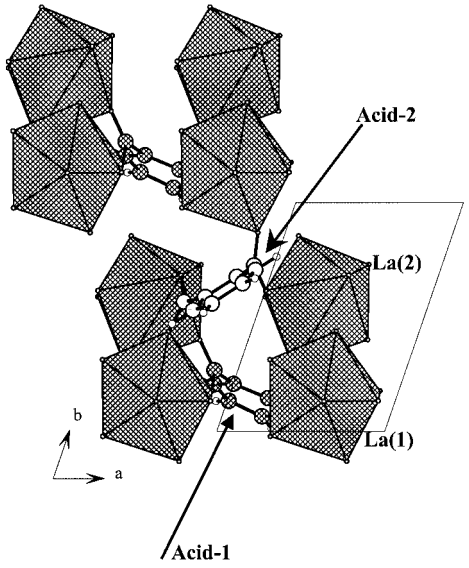


Figure 2. Figure showing the connectivity between La and the two 1,2BDC acids in the *ab* plane. Note that one of the 1,2BDC (acid 1) connects two La atoms forming an edge-shared La-dimer and the other (acid 2) connects the two such dimers together to form a column

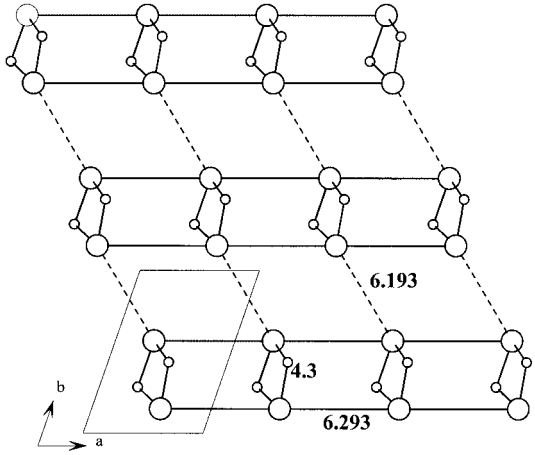


Figure 3. Figure shows the M-dimers, formed by the three-coordinate oxygen atoms, and its connectivity in the *ab* plane in Type-1 compounds. The connecting 1,2-BDC acids are not shown

M-carboxylate networks in the *ab* plane (Figures 2 and 3). While one 1,2-BDC connects a pair of M_2O_{16} dimers the second 1,2-BDC connects two different pairs forming a ladder-like arrangement. The arrangement of ladders and their connectivity gives rise to a corrugated sheet with steps in the *ab* plane. If we connect the M atom, the corrugated sheet is seen very clearly (Figure 3). The M−M atoms are separated by 4.3 Å within the dimer and 6.293 Å between the dimers in the same ladder. The distance between the two M dimers of different ladders is 6.193 Å (Figure 3). The corrugated sheets are cross-linked by the 1,4-BDC completing the three-dimensional structure as shown in Figure 4. The connectivity between the M, 1,2-BDC and 1,4-BDC gives rise to rhombic one-dimensional channels as shown in Figure 5. The two water molecules bound to the M ions (M = La and Pr) projects into the channels.

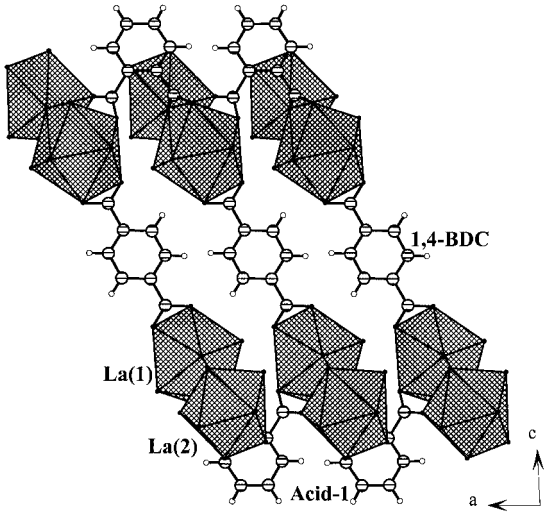


Figure 4. The view of the structure of the type-1 compound in the *ac* plane. The figure also shows the connectivity between two columns of dimers through 1,4-BDC. Only one of the 1,2-BDC acids is shown for clarity

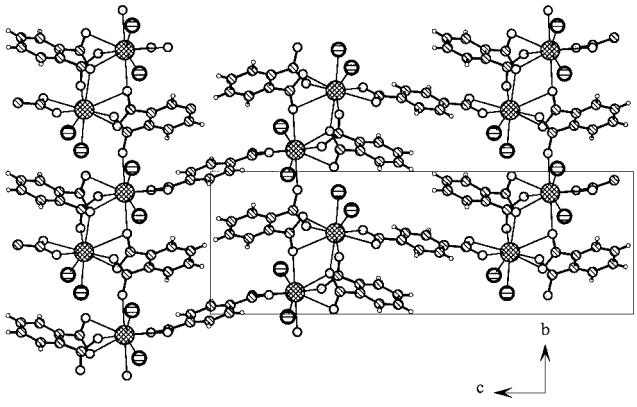


Figure 5. View of the structure of type-1 compound along the *bc* plane. The bonded water molecules are shown as large circles. Note that the bonded water molecule projects into the large channels

Structure of $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$ M = Gd, Dy, and Y (Type-2)

The asymmetric unit of the type-2 compounds $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$ M = Gd, Dy, and Y, have 21 non-hydrogen atoms, of which one M atom is independent (Figure 6, a). The M atoms are eight-coordinated with oxygen atoms that have M−O distances in the range 2.262(4)−2.509(4) Å (av. 2.381 for Gd, 2.411 Å for Dy, and 2.370 Å for Y). The coordination environment around the central M atom is a distorted dodecahedron. The C−O, C−C bond lengths show typical values.[6−25] The O−M−O bond angles for M = Gd, Dy, and Y are in the range

52.50(12)−154.89(13)°. The various structural parameters observed in type-2 compounds are in the range expected for this type of bonding. The M atom has two terminal M−O linkages with an average distance of 2.405 Å, which are water molecules. Selected bond lengths are listed in Table 2.

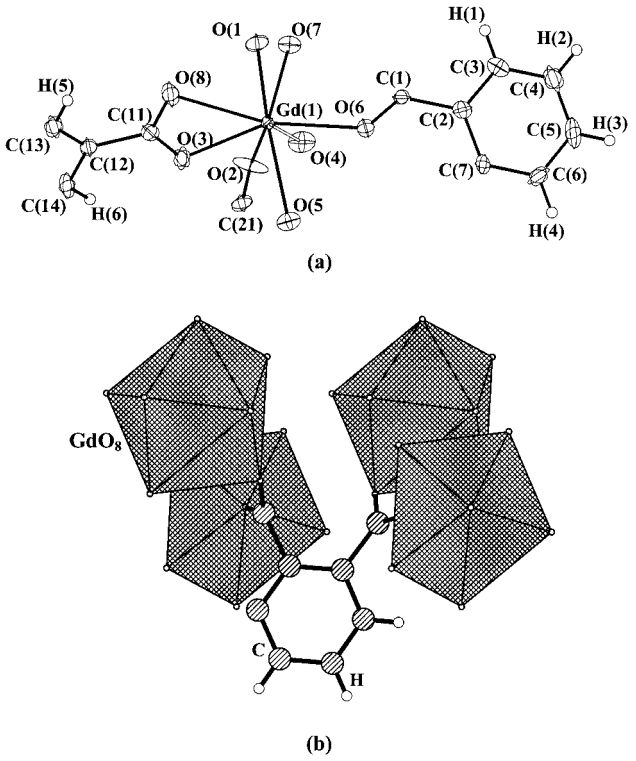


Figure 6.(a) ORTEP diagram showing the asymmetric unit for $[Gd_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$. Thermal ellipsoids are given at 50% probability. (b) Figure showing the connectivity between the 1,2-BDC and Gd. Note that the acid has a monodendate connectivity with the distorted dodecahedrally coordinated Gd atoms

Table 2. Selected bond lengths for $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$ (M = Gd, Dy, and Y). Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 1, -z + 1$; #2 $-x, -y + 2, -z + 1$

Bond	Distance (Å)		
	Gd	Dy	Y
M(1)−O(2)	2.272(4)	2.314(4)	2.262(4)
M(1)−O(1)	2.306(4)	2.336(4)	2.285(4)
M(1)−O(6)	2.371(4)	2.409(3)	2.359(3)
M(1)−O(5)	2.398(4)	2.423(3)	2.389(3)
M(1)−O(4)	2.401(4)	2.426(4)	2.391(3)
M(1)−O(3)	2.406(4)	2.430(4)	2.395(3)
M(1)−O(7)	2.422(4)	2.441(3)	2.415(3)
M(1)−O(8)	2.475(4)	2.509(4)	2.461(4)
O(1)−C(1)#1	1.243(7)	1.244(7)	1.252(6)
O(2)−C(21)	1.247(7)	1.249(6)	1.238(6)
O(3)−C(11)	1.243(7)	1.242(7)	1.250(6)
O(6)−C(1)	1.263(6)	1.286(6)	1.261(6)
O(7)−C(21)#2	1.265(6)	1.258(6)	1.264(6)
O(8)−C(11)	1.289(7)	1.282(7)	1.276(6)

Unlike type-1, type-2 compounds have only one type of 1,2-BDC and 1,4-BDC acids. Thus, C2−C7 forms the benzene ring with C1 and C21 forming the carboxylate units for the 1,2-BDC, while the 1,4-BDC has an inversion center in the plane of the benzene ring (C12−C14) with C11 being part of the carboxylate unit. While 1,2-BDC only has monodendate connectivity through all the oxygen atoms, that of 1,4-BDC has bidentate bonding with respect to the M atoms. In Figure 6, b the monodendate connectivity between the M atoms and 1,2-BDC is shown. The connectivity between the M atoms and the 1,2-BDC acid, similar to type-1 compounds, gives rise to a corrugated step-like ladder arrangement. If the M atoms are connected, it gives

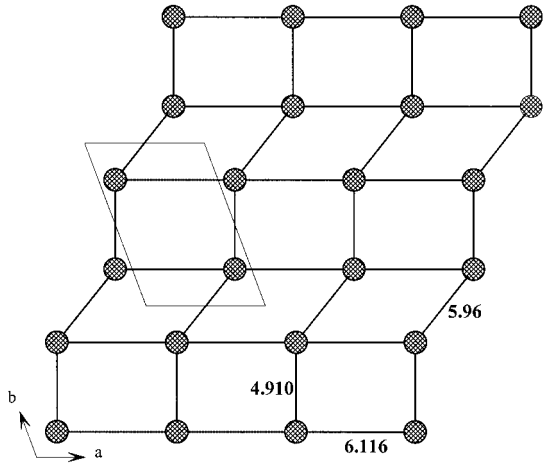


Figure 7. Figure shows the M atoms and its connectivity in Type-2 compounds. The connecting 1,2-BDC acids are not shown. Note that the M atom connectivity forms a corrugated four-connected net

rise to a four-connected network as shown in Figure 7. Similar to the type-1 compounds, the distance between the M atoms in the four-connected net varies between 4.910−6.116 Å (Figure 7). The connectivity between the 1,2-BDC, 1,4-BDC and the M atoms gives rise to rhombic one-dimensional channels (Figure 8). The two water mol-

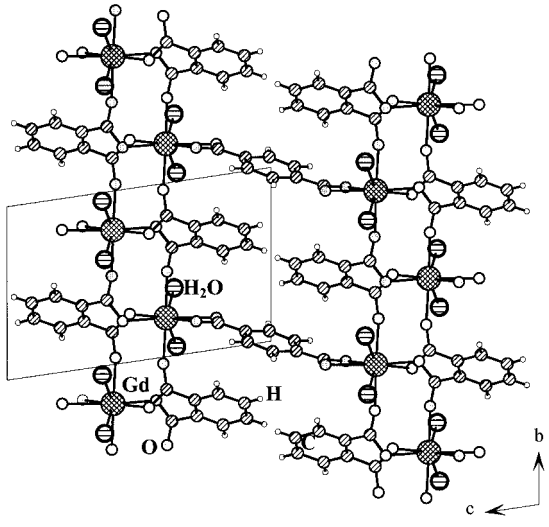


Figure 8. Structure of type-2 compound, $[Gd_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$ in the *bc* plane. Note that the 1,2-acid and La form a ladder-like arrangement connected by 1,4-acids giving rise to rhombic-like channels. The bound water molecules are shown as large circles

ecules bound to the M atoms project into these channels.

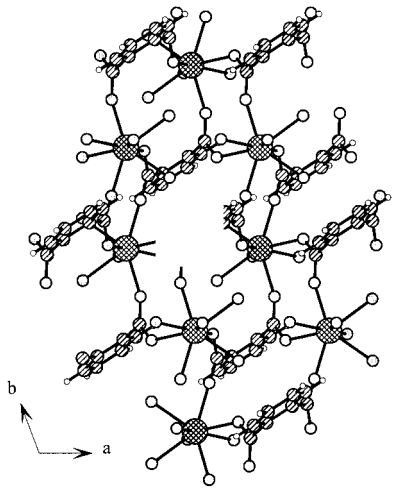
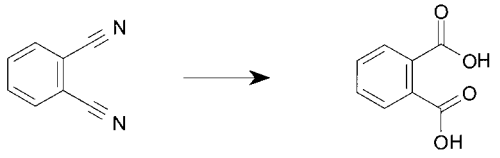


Figure 9. Structure of $[Gd_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$ in the *ab* plane showing the arrangement of the benzene rings of the acid

The packing diagram in the *ab* plane is shown in Figure 9. The arrangement of the benzene carboxylates in the *ab* plane clearly indicates that direct π···π interactions have been avoided.

Discussion

Five new compounds have been synthesized with the general formula, $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$, M = La, Pr, Gd, Dy, and Y, employing mild condition hydrothermal reactions. The compounds have been prepared using 1,2-dicyanobenzene (1,2-DCB), but the final product contained benzene-1,2-dicarboxylic acid (phthalic acid). The 1,2-DCB compound has been hydrolyzed under the hydrothermal synthesis conditions to give rise to phthalic acid.



Since the product contained pthalic acid, we have made attempts to prepare the title compounds using pthalic acid in the starting synthesis mixture in place of 1,2-DCB. The experiments resulted in the desired product, but it was in the powder form with no single crystals being obtained. It is likely that the slow hydrolysis of 1,2-DCB to 1,2-BDC is needed to give rise to good quality single crystals of the coordination polymers described in this work.

All the compounds have been obtained as good quality single crystals and their structures were determined using single-crystal X-ray diffraction. Though the overall structure of the compounds appears to have close resemblance amongst them, there are minor differences between those formed with La and Pr and those formed with Gd, Dy, and Y. One of the differences is the absence of three-coordinate oxygen atoms (μ_3 connection) in the latter. The presence of three-coordinate oxygen atoms leads to the formation of M−O−M linkages and a dimer (M = La, Pr). Such a μ_3 connection of the oxygen atom in the M−O−M bridge is an electrostatic valence requirement of the bridging oxygen atoms. The μ_3 connections of the oxygen atoms are, probably, needed to accommodate the higher coordination of the large M ions.

The present study consists of a family of rare earth compounds with similar formulae and different structures. It appears that the size of the lanthanide ion possibly has a role in the final structure. In Figure 10, we have plotted the unit cell volume as a function of the covalent radii. We have considered the unit cell volume for the type-2 compounds to be double in order to be consistent with the formula. It is clear that there are two distinct slopes. The larger La and Pr appear to form a group while the smaller Gd, Dy, and Y belong to the other. This shows that there is a lanthanide contraction effect on the structure. Similar behavior has been noted in many compounds involving lanthanide ions, especially in intermetallic compounds.[37] The differences in the size of the lanthanide ions also results in different coordination for the M ions, which probably also leads to the observed differences in the structure.

From the TGA studies, it is clear that the bound water molecules leave at around 170−210 °C. In order to understand the thermal stability of these compounds, especially after the release of bound water molecules, we have performed careful experiments by heating the sample at different temperatures. For this purpose, we have selected the Y compound and heated the sample at each temperature in air for 120 min and the XRD patterns were recorded in the 2θ range of 5−30°. The results are shown in Figure 11. The samples appear to retain their structure only up to 150 °C, after which new peaks corresponding to yttrium oxide start appearing. From this, it is clear that the structure collapses after the loss of bound water of crystallization, unlike in

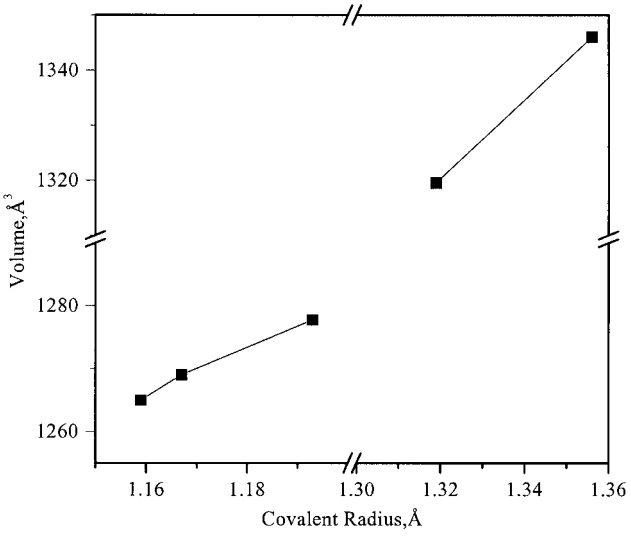


Figure 10. The variation of the crystal volume as a function of covalent radii of the lanthanide ions

some of the lanthanide coordination polymers reported recently.[38]

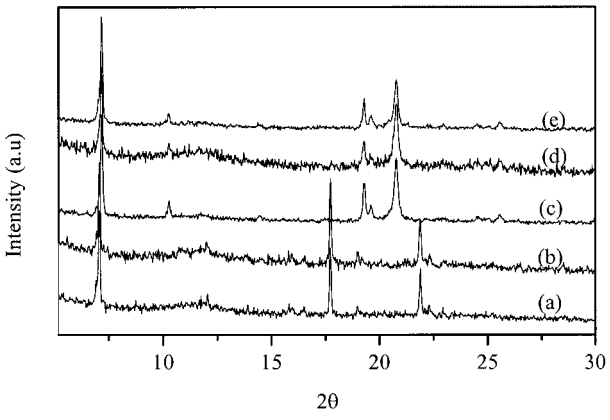


Figure 11. The XRD pattern of the $[Y_2(H_2O)_4\{(1,2BDC)_2$-$(1,4BDC)\}]$ as a function of temperature (a) 100, (b) 150, (c) 200, (d) 250, (e) 300 °C

The optical properties of the benzene carboxylates have been investigated since they involve the 4f orbitals, which are generally well shielded from their chemical environments by $5s^2$ and $5p^6$ electrons. The f-f transitions are parity forbidden, which leads to unfavorable excitation of the lanthanide ions. The photoluminescence studies indicate that both the acids, 1,2-BDC and 1,4-BDC, show photoluminescence (Figure 12). The main emission peak for the acids is located at the same position, at 240 nm. The emission bands for the acids, which also act as ligands in these compounds, may be attributable to the $\pi^*\rightarrow n$ transitions. Interestingly, the emission spectrum for the lanthanide coordination polymer shows a main peak at ≈ 400 nm. This peak corresponds to the intra-ligand fluorescent emission. In addition, the samples also exhibit additional emission bands when excited at 235 nm. These bands correspond to some of the expected $^5D_4\rightarrow{}^7F_n$ transitions. The observed transitions are: $^5D_4\rightarrow{}^7F_6$ = 508 (Gd), 494 (Dy), 483(Y); $^5D_4\rightarrow{}^7F_5$ = 544 (Gd), 539 (weak, Dy), 542 (weak, Y); $^5D_4\rightarrow{}^7F_4$ = 573, 592 (Gd), 584 (Dy), 574 (Y); $^5D_4\rightarrow{}^7F_3$ = 616 (Gd). Similar behavior has been observed in many lanthanide coordination polymers.[8,39] As representative examples, the photoluminescence behavior for the acids along with Gd, Dy, and Y are given in Figure 12.

The pH of the initial reaction mixture also appears to play an important role in the formation of the compounds. A reaction mixture with a pH of ≈ 3 recrystallizes the 1,4-BDC acid and no other product was obtained. A reaction of a mixture of the 1,2-BDC and 1,4-BDC acids with a pH of ≈3 also recrystallizes only the acids. A starting reaction mixture containing both the acids at a pH of ≈ 5−6, however, gives rise to the desired product, but only in the powder form (very poor yield ≈ 5−10%) with no single crystals being obtained. In order to establish the pH conditions, we have also carried out reactions with piperidine and piperazine as the secondary base in place of NaOH, which resulted in the formation of the title compounds. From this, it appears that a pH of ≈ 5 is, probably, necessary to deprotonate the acid as the final product is devoid of any of the amine used in the synthesis, i.e., NaOH, piperidine, or piperazine.

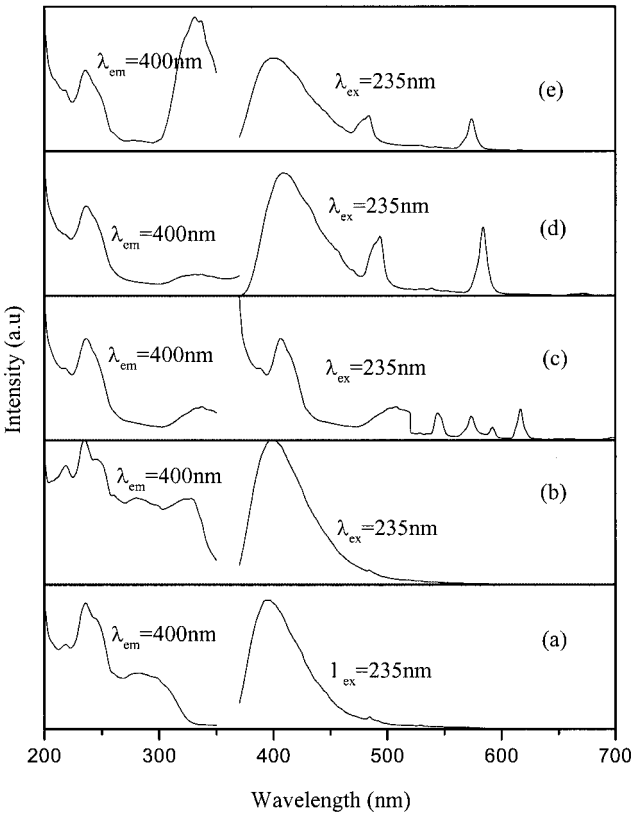


Figure 12. The photoluminescence spectra of the compounds along with the two acids. (a) 1,2-BDC, (b) 1,4-BDC, (c) Gd (d) Dy and (e) Y

Conclusions

A new series of coordination polymers of the general formula, $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$, M = La, Pr, Gd, Dy, and Y, have been prepared and characterized employing hydrothermal methods. The large lanthanides show a higher coordination compared with the smaller ones. The structure consists of a column of M−O formed by the connectivity between 1,2-BDC and M atoms and are interconnected by 1,4-BDC to give rise to the three-dimensional structure. The secondary coordinated water molecule does not appear to be reversibly adsorbed. The photoluminescence studies show some of the expected $^5D_4\rightarrow{}^7F_n$ transitions. It is likely that related compounds encompassing other lanthanide ions with similar structures can be prepared. We are currently pursuing research in this direction.

Experimental Section

Synthesis and Initial Characterization: All the compounds have been prepared by employing hydrothermal methods. In a typical synthesis for the lanthanum coordination polymer, $LaCl_3$ (0.245 g)

was dissolved in 5 mL of MilliQ water. 1,2-Dicyanobenzene (0.128 g) and terephthalic acid, [HOOC(C_6H_4)COOH; 1,4-BDC] (0.169 g) were then added to this under continuous stirring. Finally the pH was adjusted to ≈ 5 by the addition of 0.4 mL of 5 M NaOH and the mixture was homogenized for 30 min at room temperature. The final mixture with the composition, $LaCl_3$:1,2$(NC)_2C_6H_4$:1,4-BDC:2NaOH:278H_2O, was sealed in a 23 mL PTFE-lined acid digestion bomb and heated at 180 °C for 72 h under autogenous pressure. The pH after the reaction did not show an appreciable change. The resulting product contained rod-like crystals admixed with very small quantities of white powder were filtered under vacuum and dried at ambient temperature. The crystals were easily separated under an optical microscope and later by ultrasonification for further characterization. The yield of the single crystals was about ≈ 80% based on the La compound. The white powder was found to be amorphous by powder X-ray diffraction. The same compound can also be synthesized starting from other salts of La, [for ex. $La(NO_3)_3$], as well as by carrying our reactions in smaller capacity acid-digestion bombs (7 mL). Identical composition and synthesis conditions have been employed for the preparation of other compounds. In the case of the Gd and Dy compounds only good quality single crystals resulted from the reaction. The yield of the product in all the cases was 75−80%. The initial characterizations were carried out using elemental analysis, powder X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Infra Red (IR) spectroscopy for all the compounds. Elemental analysis: for La, C 35.92% (34.20%), H 2.58% (2.37%); for Pr, C 34.38% (34.03%), H 2.47% (2.36%); for Gd, C 32.34% (32.76%), H 2.35% (2.27%); for Dy, C 32.61%(32.38%), H 2.11% (2.25%); and for Y, C 39.55% (38.80%), H 2.69% (2.94%). The powder XRD patterns were recorded on crushed single crystals in the 2θ range 5−50° using Cu *K*α radiation (Rich-Seifert, 3000TT). The XRD patterns indicated that the products were new materials; the patterns were entirely consistent with the structures determined using the single crystal X-ray diffraction.

Thermogravimetric analysis (TGA) has been carried out (Metler-Toledo) under an oxygen atmosphere (flow rate = 50 mL/min) in the temperature range 25 to 700 °C (heating rate = 10 °C/min). The studies show identical results for all the compounds with two sharp weight losses. The initial weight loss of 10% in the range 170−210 °C corresponds to the loss of four water molecules bound to La (calcd. 8.2%) and the second weight loss of 52.9% in the range 450−475 °C corresponds to the loss of the benzene carboxylates (calcd. 56%). The calcined sample was crystalline and the powder XRD lines match well with the corresponding pure oxides in all the cases.

Infra Red (IR) spectroscopic studies have been carried out in the mid-IR region as a KBr pellet (Bruker IFS-66v). The results indicate characteristic sharp lines with almost similar bands. Minor variations between the bands have been noticed between the compounds. The observed bands are: 3485−3620 (s) cm^{-1} − ν_{as}OH, 3292−3405 (s) cm^{-1} − ν_sOH, 3061 (w) cm^{-1} − ν_s(C−H)$_{aromatic}$, 1646−1669 (m) cm^{-1} − ν_s(C=O), 1605 (w) cm^{-1} − $\delta_s H_2O$, 1543(s) − (C−C)$_{skeletal}$, 1425 (s) cm^{-1} − δ_s(COO), 1405 (s) cm^{-1} − δ(OH), 1289−1294 (s) cm^{-1} − δ(CO), 1150 (s) cm^{-1} − δ(CH$_{aromatic}$)$_{in\text{-}plane}$, 750 (s) and 843 (s) cm^{-1} − δ(CH$_{aromatic}$)$_{out\text{-}of\text{-}plane}$.

Single Crystal Structure Determination: A suitable single crystal of each 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*α radiation, λ = 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.[40] The structure was solved and refined using the

Table 3. Crystal data and structure refinement parameters for [$M_2(H_2O)_4${(1,2BDC)$_2$(1,4BDC)}] (M = La, Pr)

Structure parameter	La	Pr
Empirical formula	$C_{24}H_{20}La_2O_{16}$	$C_{24}H_{20}Pr_2O_{16}$
Molecular mass	842.16	846.22
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$, (no. 2)
a [Å]	6.2428(2)	6.2221(4)
b [Å]	8.9794(2)	8.9189(5)
c [Å]	25.3905(7)	25.2972(2)
α [°]	88.954(1)	88.730(1)
β [°]	86.896(1)	87.036(1)
γ [°]	70.920(1)	70.76(1)
V [Å^3]	1343.14(6)	1323.69(11)
Z	2	2
D (calc) [gcm^{-3}]	2.063	2.123
μ [mm^{-1}]	3.217	3.718
λ (Mo-K_α) [Å]	0.71073	0.71073
F(000)	796	820
2θ range [°]	1.6−46.6	1.6−46.6
Total data collected	5569	5637
Unique data	3748	3753
Observed data [$I > 2\sigma(I)$]	2868	3205
R_{merg}	0.041	0.0239
R indexes [$I > 2\sigma(I)$]	R_1 = 0.0351[a]; wR_2 = 0.0823[b][b]	R_1 = 0.0296[a]; wR_2 = 0.0820[b]
R indexes [all data]	R_1 = 0.0519[a]; wR_2 = 0.0928[b]	R_1 = 0.0364[a]; wR_2 = 0.0855[b]
Largest difference map peak and hole [e·Å^{-3}]	0.747 and −1.487	0.966 and −1.424

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2(F_c)^2]/3$, where $a = 0.0089$ and $b = 0.0$ for La and $a = 0.00444$ and $b = 0.0$ for Pr.

Table 4. Crystal data and structure refinement parameters for $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$ (M = Gd, Dy, and Y)

Structure parameter	Gd	Dy	Y
Empirical formula	$C_{12}H_{10}GdO_8$	$C_{12}H_{10}DyO_8$	$C_{12}H_{10}YO_8$
Molecular mass	439.45	447.50	371.11
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$, (no. 2)	$P\bar{1}$, (no. 2)	$P\bar{1}$, (no. 2)
a [Å]	6.1107(3)	6.1163(2)	6.1272(1)
b (Å)	8.8045(4)	8.8254(3)	8.8099(3)
c (Å)	12.8764(7)	12.9291(2)	12.8788(4)
α [°]	95.073(2)	94.752(2)	95.060(2)
β [°]	99.116(2)	99.311(2)	99.143(1)
γ [°]	109.958(2)	109.449(2)	110.302(2)
V [Å^3]	635.32(5)	642.36(2)	635.97(3)
Z	1	1	1
D (calcd.) [gcm^{-3}]	2.297	2.299	1.938
μ [mm^{-1}]	5.259	5.855	4.624
λ (Mo-K_α) [Å]	0.71073	0.71073	0.71073
F(000)	420	424	370
2θ range [°]	3.2−46.6	3.2−46.5	3.2−46.4
Total data collected	2677	2703	2652
Unique data	1791	1813	1773
Observed data [$I > 2\sigma(I)$]	1642	1696	1658
R_{merg}	0.0247	0.0215	0.0165
R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0227$[a]; $wR_2 = 0.0564$[b]	$R_1 = 0.0228$[a]; $wR_2 = 0.0611$[b]	$R_1 = 0.0401$[a]; $wR_2 = 0.1073$[b]
R indexes [all data]	$R_1 = 0.0267$[a]; $wR_2 = 0.0572$[b]	$R_1 = 0.0253$[a]; $wR_2 = 0.0619$[b]	$R_1 = 0.0436$[a]; $wR_2 = 0.1092$[b]
Largest difference map peak and hole [e·Å^{-3}]	0.626 and −1.105	0.776 and −1.024	0.835 and −0.958

[a] $wR_1\ \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max.(F_o^2,0) + 2(F_c)^2]/3$, where a = 0.0211 and b = 0.0 for Gd, a = 0.0348 and b = 0.1023 for Dy, and a = 0.0737 and b = 1.0849 for Y.

SHELXTL-PLUS suite of programs.[41] 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. The hydrogen atoms of the water molecules were not located in the difference Fourier maps. 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[41] suite of programs. Details of the structure solution and final refinements for the compounds $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$, (M = La and Pr) are given in Table 3 and for M = Gd, Dy, and Y are given in Table 4. The Selected bond lengths for $[M_2(H_2O)_4\{(1,2BDC)_2(1,4BDC)\}]$, M = La and Pr, are listed in Table 1 and for M = Gd, Dy, and Y in Table 2.

CCDC-214923 to -214927 contain the supplementary crystallographic data for this paper. These data can be obtained from the above, via www.ccdc.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44-1223-336-033, E-mail: deposit@ccdc.cam.ac.uk).

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