

NOTE**Synthesis and Crystal Structure of a New La(III) Coordination Polymer Assembled from 2,4'-Diphenic Acid and Auxiliary Ligands**

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A new metal coordination polymer $\{[\text{La}_2(\text{dpa})_3(2,2'\text{-bipy})_2(\text{H}_2\text{O})]\text{H}_2\text{O}\}_n$ (H_2dpa = 2,4'-biphenyl-dicarboxylic acid and 2,2'-bipy = 2,2'-bipyridine) has been synthesized and structurally characterized by elemental analysis and X-ray diffraction. The crystal is triclinic, P-1 group with $a = 9.594(5)$ Å, $b = 13.472(5)$ Å, $c = 22.475(5)$ Å, $\alpha = 104.079^\circ$, $\beta = 90.007^\circ$, $\gamma = 101.209^\circ$, $M_r = 1394.87$, $V = 2760.5(19)$ Å³, $D_c = 1.678$ g/cm³, $F(000) = 1388$ and $Z = 2$. In the present compound, the two La(III) ions are in different coordination environments. Two La(III) are linked together through dpa ligand, give rise to a binuclear La(III) cluster and form a 2-D (4,4) net.

Key Words: Synthesis, Crystal structure, La(III), Coordination polymer, 2,4'-Diphenic acid.

The rational design and syntheses of metal-organic frameworks (MOFs) is the current interest in chemical research and materials science, stemming from their potential applications in magnetism, nonlinear optics, gas absorption and luminescence¹⁻⁶. The most common strategy used to obtain coordination polymers is to employ appropriate bridging ligands capable of binding to several metal centers through direct bond formation. Diphenic acid (H_2dpa) as O-donor ligand has received much more attention in the designed synthesis of coordination polymers because the two functional groups may have different coordination modes and the carboxylate group can adopt versatile coordination conformations which endow them with the ability to generate metal-oxygen chains or clusters⁷⁻⁹.

All reagent and solvents employed were commercially available and used as received without further purification. Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic element analyzer.

Synthesis of the La(III) coordination polymer compound: A mixture of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 2,4'-dpa (1.5 mmol), 2,2'-bpy (1 mmol) and distilled water (15 mL) was heated in a 25 mL stainless steel reactor with a Teflon liner 160 °C for 96 h, followed by slow cooling to room temperature. Yellow crystals of the compound formed. Anal. calcd. (%) for $\text{C}_{66}\text{H}_{44}\text{N}_4\text{O}_{14}\text{La}_2$: C, 56.83; H, 3.18; N, 4.02. Found (%): C, 55.97; H, 3.24, N, 4.05.

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X-Ray crystallography: A suitable yellow block crystal with dimensions of 0.30 mm × 0.25 mm × 0.20 mm was mounted on a glass fiber and data were collected on a Bruker Smart 1000 CCD diffractometer with a MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K by using an ω scan mode in the range of $2.30^\circ < \theta < 27.50^\circ$. All non-hydrogen atoms were located by geometrical calculations and their positions and thermal parameters were fixed during the structure refinement. The highest and lowest residual peaks in the final difference Fourier map are 1.164 and $-0.470 e/\text{\AA}^3$, respectively. All calculations were performed by the SHELXTL 97 program¹⁰. The selected bond lengths and bond angles are listed in Table-1. CCDC:779391.

TABLE-1
SELECTED BOND LENGTHS (\AA) AND ANGLES ($^\circ$) FOR COMPOUND

La(2)-O(6)	2.447(3)	La(1)-O(5 ⁱⁱ)	2.475(3)
La(2)-O(8)	2.482(3)	La(1)-O(12)	2.470(3)
La(2)-O(1W)	2.512(3)	La(1)-O(3)	2.510(3)
La(2)-O(9)	2.514(3)	La(1)-O(2)	2.535(3)
La(2)-O(4 ⁱ)	2.529(3)	La(1)-O(7 ⁱⁱ)	2.620(3)
La(2)-O(10)	2.581(3)	La(1)-O(11 ⁱⁱⁱ)	2.671(3)
La(2)-N(4)	2.702(4)	La(1)-N(2)	2.720(3)
La(2)-N(3)	2.728(4)	La(1)-N(1)	2.758(3)
La(2)-O(3 ⁱ)	2.771(3)	La(1)-O(8 ⁱⁱ)	2.765(3)
O(6)-La(2)-O(8)	84.00(9)	O(8)-La(2)-O(10)	136.65 (9)
O(6)-La(2)-O(1W)	135.22(10)	O(1W)-La(2)-O(10)	71.86(9)
O(6)-La(2)-O(1W)	72.19(10)	O(9)-La(2)-O(10)	51.21(9)
O(6)-La(2)-O(9)	91.53(9)	O(4 ⁱ)-La(2)-O(10)	72.58(9)
O(8)-La(2)-O(9)	161.14(10)	O(6)-La(2)-N(4)	133.87(11)
O1W-La(2)-O(9)	122.00(9)	O(8)-La(2)-N(4)	78.88 (10)
O(6)-La(2)-O(4 ⁱ)	85.12(11)	O(1W)-La(2)-N(4)	78.62(12)
O(8)-La(2)-O(4 ⁱ)	119.77(9)	O(9)-La(2)-N(4)	91.34(11)
O(1W)-La(2)-O(4 ⁱ)	75.37(11)	O(4 ⁱ)-La(2)-N(4)	140.22(11)
O(9)-La(2)-O(4 ⁱ)	77.89(10)	O(10)-La(2)-N(4)	71.00(10)

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$; (iii) $x+1, y-1, z$.

The local coordination geometry of polymer $\{[\text{La}_2(\text{dpa})_3(2,2'\text{-bipy})_2(\text{H}_2\text{O})]\text{H}_2\text{O}\}_n$ with atomic numbering scheme is depicted in Fig. 1. It is shown that the asymmetry unit of the molecule consists of two La(III) ions. The bond lengths and bond angles are given in Table-1 and the bonds distance of La-O carboxylate is from 2.447(3)-2.771(3) \AA . La1(III) is surrounded by nine coordinate atoms from 2,4'-dpa and 2,2'-bipy ligands and La2(III) is coordinated by eight atoms. In compound, the 2,4'-dpa ligands adopt four coordination modes to link metal ions: $\mu_2\text{-}\eta^1\text{:}\eta^1$, $\mu_1\text{-}\eta^1\text{:}\eta^0$, $\mu_2\text{-}\eta^2\text{:}\eta^1$ and $\mu_1\text{-}\eta^1\text{:}\eta^1$. Each of pair of La(III) atoms is linked by two dpa²⁻ anions with a La...La separation of 4.226 \AA . Dihedral angles between two phenyl rings in dpa²⁻ ligands are 57.67°, 48.96° and 44.68°. Two La(III) polyhedra are linked together through carboxylate groups which lead to form binuclear La(III) cluster

