

Synthesis, Characterization and Crystal Structure of New 3-D Supramolecular Metal-Organic Framework Structure of *Bis*(1,10-phenanthroline- k^2N,N')-(isonicotinate- k^2O,O')-(nitrate- k^2O,O')diaqua-neodymium(III) Isonicotinate

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For exploring the novel rare earth ions contained luminescent materials, aromatic ligands of isonicotinic acid (HIN) and 1,10-phenanthroline (phen) were used as antenna groups to construct luminescent molecule. This research lead to the synthesis and the structure determination of the title compound, Nd(IN)(NO₃)(phen)₂(H₂O)₂(IN) (**1**), which was obtained by a solution reaction at room temperature. Two phen and one IN⁻ anion ligands both chelated on the center Nd³⁺ ion, while the other IN⁻ anion is dissociative from the coordinated molecule. The Nd³⁺ ion exhibits a 10-coordinated NdO₆N₄ geometry consisting of two O atoms derived from a IN⁻ ligand, two atoms from NO₃⁻, another two O atoms from two coordinated water molecules and four N atoms from two phen ligands. This mono-nuclear molecule and discrete isonicotinate anion are connected each other with O-H...N hydrogen bonds and π - π stacking interactions to form the 3-D metal-organic frameworks.

Keywords: Crystal structure, π - π Stacking interaction, Hydrgen bond, Metal organic frameworks, Supramolecular framework.

INTRODUCTION

During the past few decades, supramolecular compounds have received much more attentions due to their importance for the study of biological systems and their potential applications in material research, as sensors, gas storage, *etc.*¹⁻⁵. Usually, in all supramolecular systems, hydrogen bonding and aromatic stacking interactions are two main cohesions to form supramolecules. In the past two decades, the design and synthesis of metal organic frameworks (MOFs) by self-assembly of organic ligands as linkers and metal ions as connecting points have afforded a great deal of interest among the family of polymers, inorganic materials and supramolecular architectures⁶⁻¹². Of them, the character of supramolecular assembly is the use of well-defined molecules or macromolecules and intermolecular forces to create larger, more complex chemical systems with new and unique properties^{13,14}. On the efforts to pursue the synthetic strategies for supramolecular framework, some noncovalent interactions have been emphasized repeatedly, such as hydrogen bonding, π - π stacking and anion- π and C-H... π interactions. These secondary interactions may

be very important for different aspects such as molecular recognition and catalysis and so on^{1-5,15}. For exploring the novel rare earth ions contained luminescent materials, aromatic ligands of isonicotinate acid (HIN) and 1,10-phenanthroline (phen) were used as antenna groups to construct luminescent supramolecular structure. Here, we report a three-dimensional supramolecular MOFs compound Nd(IN)(NO₃)(phen)₂(H₂O)₂ (**1**) (Fig. 1), which is assembled from isonicotinic acid (HIN) and 1,10-phenanthroline (phen) ligands and Nd³⁺ ion.

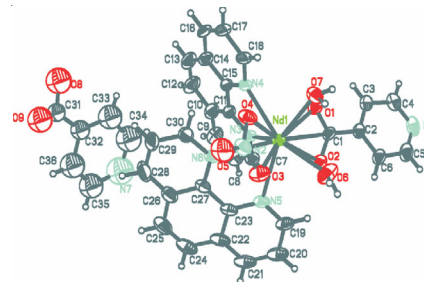


Fig. 1. Structure and labeling of the title compound, with displacement ellipsoids drawn at the 30 % probability level and H atoms shown as small spheres of arbitrary radii

EXPERIMENTAL

All chemicals were obtained from commercial sources and used as received. Elemental analysis for C, H and N were performed on an Elementar Vario MICRO analytic instrument.

Synthesis of Nd(IN)(NO₃)(phen)₂(H₂O)₂ (1): The title compound **1** was synthesized by a solution reaction from isonicotinic acid (HIN) and 1,10-phenanthroline (phen) and Nd³⁺. Isonicotinic acid (75 mg, 0.6 mmol) and NaOH (25 mg, 0.6 mmol) was dissolved in 10 mL of water. To this solution was added a 5 mL aqueous solution of Nd(NO₃)₃·6H₂O (133 mg, 0.3 mmol) at room temperature. After stirred several minutes, a 5 mL alcohol solution of 1,10-phenanthroline·H₂O (120 mg, 0.6 mmol) was added into the above solution. Then the final solution was filtered and stayed at room temperature. Amount of pale purple crystals were obtained after the filtration was slowly evaporated at room temperature for several days. Yield: 52 %. Anal. calcd. (%) for C₃₆H₂₈N₇O₉Nd: C, 51.06; H, 3.33; N, 11.58; O, 17.00. Found (%): C, 51.57; H, 3.11; N, 11.03; O, 17.45.

Single crystal structure determination: X-Ray intensity data for **1** were collected on a red prism crystal (0.24 mm × 0.20 mm × 0.13 mm) at 293(2) K on a Rigaku RAXIS-RAPID CCD area detector diffractometer using graphite monochromated MoK_α radiation (λ = 0.071075 nm). The structure was solved using direct methods and refined by full-matrix least-squares techniques. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. All hydrogen atoms were added at calculated positions and refined using a riding model. The structure was refined on F² using SHELXTL-97 software package¹⁶ without any unusual events. The crystal and refinement details for compound **1** are listed in Table-1. Selected bond lengths and angles are given in Table-2.

TABLE-1
CRYSTAL DATA, COLLECTION AND STRUCTURE
REFINEMENT PARAMETERS FOR COMPOUND **1**

Empirical formula	C ₃₆ H ₂₈ N ₇ O ₉ Nd
Formula weight	846.89
Crystal system	Triclinic
Space group	P-1
a (Å)	11.368(2)
b (Å)	12.766(3)
c (Å)	13.227(3)
α (°)	63.85(3)
β (°)	85.96(3)
γ (°)	75.29(3)
Volume (Å ³)	1664.7(6)
Z	2
ρ _{calc} (mg/mm ³)	1.690
μ (mm ⁻¹)	1.629
F ₍₀₀₀₎	850.0
2θ range for data collection	6.02–54.86°
Reflections collected	16460
Independent reflections	7518 [R _{int} = 0.0273, R _{sigma} = 0.0376]
Data/restraints/parameters	7518/15/437
Goodness-of-fit on F ²	1.116
Final R indexes [I ≥ 2σ(I)] [#]	R ₁ = 0.0524, wR ₂ = 0.1473
Final R indexes [all data]	R ₁ = 0.0720, wR ₂ = 0.1757

$$^{\#} R_1 = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}; wR_2 = \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right\}^{0.5}$$

TABLE-2
SELECTED BOND LENGTHS OF THE COMPOUND **1**

Nd1-O7	2.470(5)	Nd1-O2	2.525(5)
Nd1-O6	2.543(7)	Nd1-O1	2.568(4)
Nd1-O4	2.592(5)	Nd1-N4	2.621(6)
Nd1-N5	2.628(5)	Nd1-O3	2.655(6)
Nd1-N3	2.658(6)	Nd1-N6	2.710(5)

RESULTS AND DISCUSSION

We have synthesized the supramolecular compound Nd(IN)(NO₃)(phen)₂(H₂O)₂(IN) (**1**) (Fig. 2). In this compound, the Nd³⁺ ion has a 10-coordinated NdO₆N₄ geometry consisting of two O atoms derived from an IN⁻ ligand, two atoms from NO₃⁻, another two O atoms from two coordinated water molecules and four N atoms from two phen ligands (Fig. 3). By virtue of π-π stacking interactions between two phen ligands from neighbour molecules, these discrete molecules are fused to form a supramolecular chain along [101] direction (Fig. 4)^{4,5}. And then, adjacent chains are joined together through O7-H7WA...N1 hydrogen bond and give out a supramolecular sheet which is along the bc plane (Fig. 5)¹⁻³. Regarding the Nd³⁺ ion as a node, the sheet exhibit a (6,3) topology⁵. Finally, these sheets are further connected each other *via* two hydrogen bonds of O6-H6WA...O8 and O7-H7WB...O9 and a supramolecular 3-D metal organic framework is formed (Table-3).

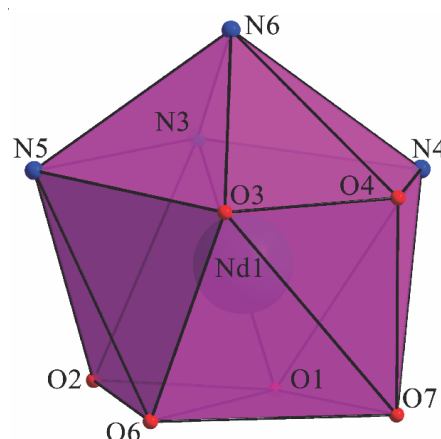


Fig. 2. 10-Coordinated NdO₆N₄ geometry coordination polyhedron

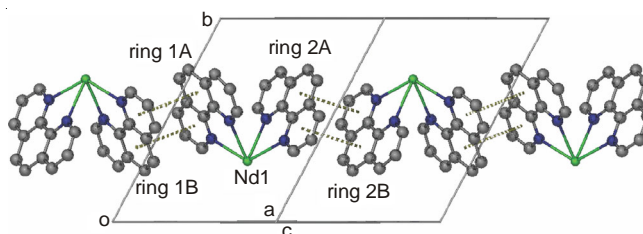


Fig. 3. Supramolecular chain along [101] direction by π-π stacking interaction of phen ligands. The dash lines mean the interactions

TABLE-3
HYDROGEN-BOND GEOMETRY (Å, °) IN THE COMPOUND **1**

D-H...A	D-H	H...A	D...A	D-H...A
O6-6WA...O8i	0.88	1.86	2.591(15)	139
O7-7WA...N1ii	0.89	1.94	2.771(8)	153
O7-WB...O9iii	0.89	2.18	2.716(14)	118

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

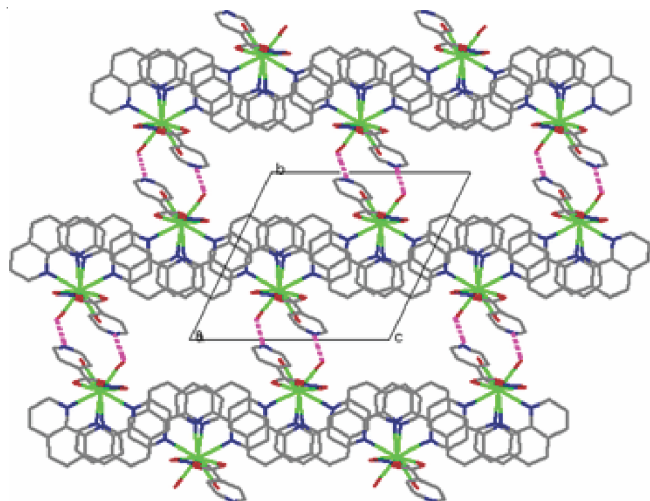


Fig. 4. Supramolecular sheet along the bc plane. The purple dash lines mean the hydrogen bond of O7-H7WA...N1

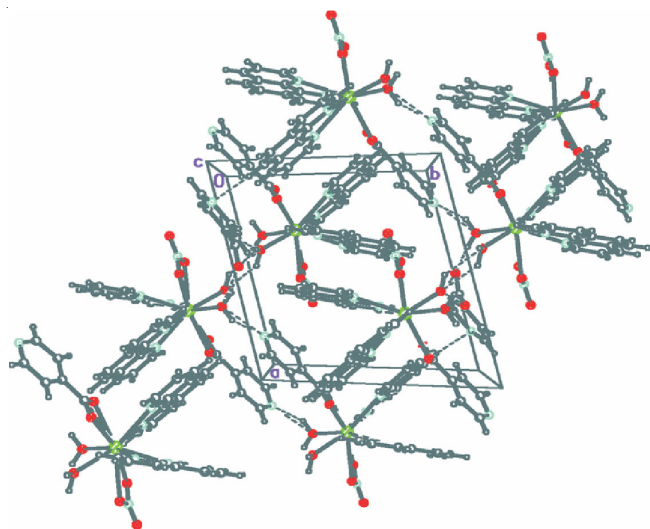


Fig. 5. Packing diagram viewed along the c-direction, Nd: green diagonal; O: red cross; N: blue inner dot; C: black circles; and H: small green circles

Conclusion

We have synthesized the supramolecular compound $\text{Nd}(\text{IN})(\text{NO}_3)(\text{phen})_2(\text{H}_2\text{O})_2 \cdot (\text{IN})$. The Nd^{3+} ion exhibits a

10-coordinated NdO_6N_4 geometry consisting of two O atoms derived from a IN^- ligand, two atoms from NO_3^- , another two O atoms from two coordinated water molecules and four N atoms from two phen ligands. This mono-nuclear molecule and discrete isonicotinic anion are connected each other with O-H...N hydrogen bonds and π - π stacking interactions to form the 3-D metal-organic frameworks.

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