

Synthesis, Crystal Structures and Magnetic Properties of Two Lanthanide Coordination Polymers with 3-Carboxyphenoxyacetatic Acid

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Two lanthanide(III) coordination polymers: $[Ln(3-CPOA)_{1.5}(phen)]_n$ (Ln = Ce (1), Pr (2), $3-H_2CPOA = 3$ -carboxyphenoxyacetatic acid, phen = 1,10-phenanthroline) have been hydrothermally synthesized and characterized by single crystal X-ray diffraction and magnetic measurements. Both polymers are isostructrural and crystallize in monoclinic space group P2₁/c. Single-crystal X-ray diffraction studies show that two complexes possess 3D framework structures based on a binuclear unit. Magnetic studies for two complexes show a stronger magnetic coupling between the lanthanide ions. (CCDC: 895012 for 1; 895013 for 2).

Keywords: Coordination polymer, Lanthanide, 3-Carboxyphenoxyacetatic acid, Magnetic properties.

INTRODUCTION

In the past decade, the rational design and syntheses of lanthanide coordination polymers have attracted increasing attention in material research due to their many superior functional properties and actual or potential applications¹⁻⁶. However, it is a great challenge to control structures with desired properties because many factors affect the result, such as central metal ions, organic ligands, solvents, pH value and so on. The most effective approach to overcome this problem is the appropriate choice of the well-designed organic bridging ligands. Many multi-carboxylate or heterocylic carboxylic acids are used for this purpose¹⁻⁸. In order to extend our investigation in this field, we chose 3-H₂CPOA as a functional ligand, which based on the following considerations: (1) 3-H₂CPOA is a flexible ligand that not only includes rigid carboxylate groups but also bearing a flexible -OCH₂- spacer, which allows more flexibility and may result in rich topologies^{9,10}. (2) It can acts not only as hydrogen-bond acceptor but also as hydrogenbond donor which depend upon the number of deprotonated carboxy group, which is beneficial for the construction of coordination polymers. (3) To our best of knowledge, 3-H₂CPOA has not been adequately explored in the construction of lanthanide coordination polymers.

Taking into account these factors, we herein report the synthesis, crystal structures, magnetic properties of Ce(III) and Pr(III) compounds with 3-CPOA ligands.

EXPERIMENTAL

All chemicals and solvents were of A.R. grade and used without further purification. Carbon, hydrogen and nitrogen were determined using an Elementar Vario EL elemental analyzer. IR spectra were recorded using KBr pellets and a Bruker EQUINOX 55 spectrometer. Thermogravimetric analysis (TGA) data were collected on a LINSEIS STA PT1600 thermal analyzer with a heating rate of 10 °C min⁻¹. Magnetic susceptibility data were collected in the 2-300 K temperature range with a Quantum Design SQUID Magnetometer MPMS XL-7 with a field of 0.1 T. A correction was made for the diamagnetic contribution prior to data analysis.

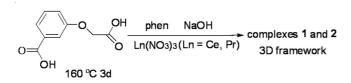
Synthesis: A mixture of Ce(NO₃)₃·6H₂O (0.1302 g, 0.3 mmol), 3-H₂CPOA (0.088 g, 0.45 mmol), phen (0.060 g, 0.3 mmol), NaOH (0.024 g, 0.6 mmol) and H₂O (10 mL) was stirred at room temperature for 15 min and then sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C h⁻¹. Yellow block-shaped crystals of complex **1** were isolated manually and washed with distilled water. Yield: 60 % (based on Ce). Anal. Calcd for C_{25.5}H₁₇N₂O_{7.5}Ce (%): C 50.08, H 2.80, N 4.58; found: C 50.41, H 2.56, N 4.81. IR (KBr, v_{max}, cm⁻¹): 1635s, 1585m, 1406s, 1338m.

Compound **2** was obtained as yellow block-shaped crystals in a manner similar to that used to obtain complex **1**, except using $Pr(NO_3)_3 \cdot 6H_2O$ instead of $Ce(NO_3)_3 \cdot 6H_2O$. Yield: 55 % (based on Pr). Anal. Calcd for $C_{25.5}H_{17}N_2O_{7.5}Pr$ (%): C 50.02, H 2.80, N 4.57; found: C 49.69, H 3.06, N 4.93. IR (KBr, v_{max} , cm⁻¹): 1634s, 1587m, 1406s, 1340m. The compounds are insoluble in water and common organic solvents, such as methanol, ethanol, acetone and DMF.

Structure determinations: Single-crystal data of compounds **1** and **2** were collected at 296(2) K on a Bruker Smart Apex 1000 CCD diffractometer with MoK_{α} radiation ($\lambda = 0$. 71073 Å). A summary of the crystallography data and structure refinement is given in Table-1 and selected bond lengths and angles of the compounds are listed in Table-2. The structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL-97 system¹¹.

RESULTS AND DISCUSSION

Synthesis and characterization of the compounds: Both compounds 1 and 2 were obtained by hydrothermal reactions (Scheme-I). The pH values of the solutions were 4-5. The reaction route as follows:



Scheme-I: Synthetic routes for compounds 1 and 2

Description of the structure: Single-crystal X-ray diffraction analysis reveals that complexes **1** and **2** are isostructrural 3D frameworks based on a binuclear unit and the structure of **2** is selected and described. Complex **2** crystallizes in monoclinic space group P2₁/c. The asymmetrical unit of the cell of compound **2** contains one crystallographically unique Pr(III) atom, one and a half 3-CPOA²⁻ ligands, one phen ligand. The 3-CPOA²⁻ ligand takes two centrosymmetric orientations, which results in disordered positions. As shown in Fig. 1, the Pr(III) center is eleven-coordinated by two N atoms of one phen ligand, nine carboxylate O atoms from seven different 3-CPOA²⁻ ligands. The distances of Pr-O and Pr-N bonds span the range of 2.245(15)-2.879(14) Å and 2.649(8)-2.670(7) Å, which are in good with the bond lengths observed in other Pr(III) complexes^{3,4,8}.

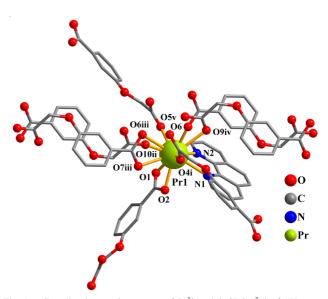


Fig. 1. Coordination environments of Pr^{3+} and 3-CPOA²⁻ in **2** (H atoms were omitted for clarity). Symmetry code: (i) -x + 2, y-1/2, -z + 3/2; (ii) x, y + 1, z; (iii) -x + 1, -y + 1, -z + 1; (iv) -x + 2, -y, -z + 1; v: x, -y + 3/2, z-1/2

TABLE-1 CRYSTAL DATA FOR COMPOUNDS 1 AND 2					
Compound	1	2			
Molecular formula	C _{25.5} H ₁₇ N ₂ O _{7.5} Ce	C _{25.5} H ₁₇ N ₂ O _{7.5} Pr			
Molecular weight	611.53	612.32			
Crystal system	Monoclinic	Monoclinic			
Space group	P2 ₁ /c	P2 ₁ /c			
a/Å	9.827(8)	9.827(8)			
b/Å	11.406(10)	11.406(10)			
c/Å	21.158(19)	21.158(19)			
β/(°)	90.574(9)	90.574(9)			
V/Å ³	2371(4)	2371(4)			
Z	4	4			
F(000)	1208	1212			
Crystal size/mm	$0.28 \times 0.26 \times 0.24$	$0.28 \times 0.27 \times 0.25$			
θ range for data collection	2.03-26.55	2.63-26.37			
Limiting indices	$-12 \le h \le 12, -14 \le k \le 14, -24 \le 1 \le 26$	$-12 \le h \le 12, -12 \le k \le 14, -26 \le 1 \le 2$			
Reflections collected/unique (R _{int})	18050/4864 (0.0980)	17675/4797 (0.0724)			
$D_c/(Mg \cdot cm^{-3})$	1.713	1.715			
μ/mm^{-1}	1.971	2.106			
Data/restraints/parameters	4864/206/376	4797/12/376			
Goodness-of-fit on F ²	1.042	1.020			
Final R indices $[(I \ge 2\sigma(I))] R_1, \omega R_2$	0.0679, 0.1264	0.0648, 0.1159			
R indices (all data) R_1 , ωR_2	0.1281, 0.1523	0.1027, 0.1314			
Largest diff. peak and hole/(e·Å ⁻³)	1.832 and -1.672	2.128, -1.894			

TABLE-2

SEL	ECTED BOND D	TABLE-2 ISTANCES (Å) AND BOND AN	NGLES (°) FOR CON	IPOUNDS 1 AND 2	
		1			
Ce(1)-O(1)	2.529(6)	Ce(1)-O(2)	2.496(7)	Ce(1)-O(4)#2	2.439(7)
Ce(1)-O(5)#3	2.451(7)	Ce(1)-O(6)	2.287(12)	Ce(1)-O(6)#4	2.879(13)
Ce(1)-O(7)#4	2.739(12)	Ce(1)-O(9)#5	2.741(13)	Ce(1)-O(10)#1	2.264(15)
Ce(1)-N(1)	2.685(7)	Ce(1)-N(2)	2.669(8)	-	-
O(10)#1-Ce(1)-O(6)	87.4(4)	O(10)#1-Ce(1)-O(4)#2	78.7(4)	O(6)-Ce(1)-O(4)#2	70.7(3)
O(10)#1-Ce(1)-O(5)#3	71.0(4)	O(6)-Ce(1)-O(5)#3	74.0(4)	O(4)#2-Ce(1)-O(5)#3	134.0(2)
O(10)#1-Ce(1)-O(2)	95.5(4)	O(6)-Ce(1)-O(2)	155.9(3)	O(4)#2-Ce(1)-O(2)	86.4(2)
O(5)#3-Ce(1)-O(2)	129.5(2)	O(10)#1-Ce(1)-O(1)	91.6(4)	O(6)-Ce(1)-O(1)	152.6(3)
O(4)#2-Ce(1)-O(1)	135.8(2)	O(5)#3-Ce(1)-O(1)	79.8(2)	O(2)-Ce(1)-O(1)	51.4(2)
O(10)#1-Ce(1)-N(2)	146.0(4)	O(6)-Ce(1)-N(2)	92.7(4)	O(4)#2-Ce(1)-N(2)	133.1(2)
O(5)#3-Ce(1)-N(2)	76.4(2)	O(2)-Ce(1)-N(2)	97.9(2)	O(1)-Ce(1)-N(2)	73.2(2)
O(10)#1-Ce(1)-N(1)	152.3(4)	O(6)-Ce(1)-N(1)	94.9(4)	O(4)#2-Ce(1)-N(1)	76.1(2)
O(5)#3-Ce(1)-N(1)	136.1(2)	O(2)-Ce(1)-N(1)	71.7(2)	O(1)-Ce(1)-N(1)	98.5(2)
N(2)-Ce(1)-N(1)	61.6(3)	O(10)#1-Ce(1)-O(7)#4	35.6(4)	O(6)-Ce(1)-O(7)#4	118.5(4)
O(4)#2-Ce(1)-O(7)#4	75.8(3)	O(5)#3-Ce(1)-O(7)#4	96.7(3)	O(2)-Ce(1)-O(7)#4	60.1(3)
O(1)-Ce(1)-O(7)#4	72.0(3)	N(2)-Ce(1)-O(7)#4	145.2(3)	N(1)-Ce(1)-O(7)#4	124.9(3)
O(10)#1-Ce(1)-O(9)#5	121.1(5)	O(6)-Ce(1)-O(9)#5	34.7(4)	O(4)#2-Ce(1)-O(9)#5	87.2(3)
O(5)#3-Ce(1)-O(9)#5	80.1(3)	O(2)-Ce(1)-O(9)#5	140.6(3)	O(1)-Ce(1)-O(9)#5	132.5(3)
N(2)-Ce(1)-O(9)#5	60.4(3)	N(1)-Ce(1)-O(9)#5	69.0(3)	O(7)#4-Ce(1)-O(9)#5	153.1(4)
O(10)#1-Ce(1)-O(6)#4	11.6(4)	O(6)-Ce(1)-O(6)#4	75.8(4)	O(4)#2-Ce(1)-O(6)#4	74.4(3)
O(5)#3-Ce(1)-O(6)#4	68.9(3)	O(2)-Ce(1)-O(6)#4	105.8(3)	O(1)-Ce(1)-O(6)#4	102.2(3)
N(2)-Ce(1)-O(6)#4	145.2(3)	N(1)-Ce(1)-O(6)#4	150.5(3)	O(7)#4-Ce(1)-O(6)#4	45.8(3)
O(9)#5-Ce(1)-O(6)#4	109.7(4)	Ce(1)-O(6)-Ce(1)#4	104.2(4)	-	-
		2			
Pr(1)-O(1)	2.518(6)	Pr(1)-O(2)	2.486(6)	Pr(1)-O(4)#3	2.432(6)
Pr(1)-O(5)#2	2.426(6)	Pr(1)-O(6)	2.267(12)	Pr(1)-O(6)#5	2.879(14)
Pr(1)-O(7)#5	2.725(10)	Pr(1)-O(9)#4	2.724(11)	Pr(1)-O(10)#1	2.245(15)
Pr(1)-N(1)	2.670(7)	Pr(1)-N(2)	2.649(8)	-	-
O(10)#1-Pr(1)-O(6)	87.6(4)	O(10)#1-Pr(1)-O(5)#2	71.1(5)	O(6)-Pr(1)-O(5)#2	74.3(4)
O(10)#1-Pr(1)-O(4)#3	78.0(5)	O(6)-Pr(1)-O(4)#3	70.4(4)	O(5)#2-Pr(1)-O(4)#3	133.48(17)
O(10)#1-Pr(1)-O(2)	94.9(5)	O(6)-Pr(1)-O(2)	155.4(3)	O(5)#2-Pr(1)-O(2)	129.5(2)
O(4)#3-Pr(1)-O(2)	86.2(2)	O(10)#1-Pr(1)-O(1)	91.9(5)	O(6)-Pr(1)-O(1)	153.0(3)
O(5)#2-Pr(1)-O(1)	80.0(2)	O(4)#3-Pr(1)-O(1)	135.80(19)	O(2)-Pr(1)-O(1)	51.47(18)
O(10)#1-Pr(1)-N(2)	146.2(5)	O(6)-Pr(1)-N(2)	92.8(4)	O(5)#2-Pr(1)-N(2)	76.5(2)
O(4)#3-Pr(1)-N(2)	133.5(2)	O(2)-Pr(1)-N(2)	98.4(2)	O(1)-Pr(1)-N(2)	73.0(2)
O(10)#1-Pr(1)-N(1)	151.8(5)	O(6)-Pr(1)-N(1)	94.8(4)	O(5)#2-Pr(1)-N(1)	136.5(2)
O(4)#3-Pr(1)-N(1)	76.4(2)	O(2)-Pr(1)-N(1)	71.8(2)	O(1)-Pr(1)-N(1)	98.2(2)
N(2)-Pr(1)-N(1)	61.8(2)	O(10)#1-Pr(1)-O(9)#4	121.2(5)	O(6)-Pr(1)-O(9)#4	34.5(4)
O(5)#2-Pr(1)-O(9)#4	80.7(3)	O(4)#3-Pr(1)-O(9)#4	86.7(3)	O(2)-Pr(1)-O(9)#4	140.7(3)
O(1)-Pr(1)-O(9)#4	132.9(3)	N(2)-Pr(1)-O(9)#4	60.9(3)	N(1)-Pr(1)-O(9)#4	68.9(3)
O(10)#1-Pr(1)-O(7)#5	34.4(5)	O(6)-Pr(1)-O(7)#5	118.3(4)	O(5)#2-Pr(1)-O(7)#5	95.0(3)
O(4)#3-Pr(1)-O(7)#5	76.6(3)	O(2)-Pr(1)-O(7)#5	60.5(3)	O(1)-Pr(1)-O(7)#5	71.7(3)
N(2)-Pr(1)-O(7)#5	144.6(3)	N(1)-Pr(1)-O(7)#5	126.0(3)	O(9)#4-Pr(1)-O(7)#5	152.6(3)
O(10)#1-Pr(1)-O(6)#5	12.6(6)	O(6)-Pr(1)-O(6)#5	75.0(5)	O(5)#2-Pr(1)-O(6)#5	68.0(3)
O(4)#3-Pr(1)-O(6)#5	74.2(3)	O(2)-Pr(1)-O(6)#5	106.3(3)	O(1)-Pr(1)-O(6)#5	103.0(3)
N(2)-Pr(1)-O(6)#5	144.4(3)	N(1)-Pr(1)-O(6)#5	150.6(3)	O(9)#4-Pr(1)-O(6)#5	108.7(4)
O(7)#5-Pr(1)-O(6)#5	46.0(3)	Pr(1)-O(10)-Pr(1)#4	102.8(6)	-	-

Symmetry transformations used to generate equivalent atoms: (1) #1: x, y + 1, z; #2: -x + 2, y-1/2, -z + 3/2; #3: x, -y + 3/2, z-1/2; #4 -x + 2, -y + 1, -z + 1; #5: -x + 2, -y, -z + 1; (2) #1: x, y + 1, z; #2: x, -y + 3/2, z-1/2; #3: -x + 2, y -/2, -z + 3/2; #4: -x + 2, -y, -z + 1; #5: -x + 2, -y + 1, -z + 1

The two carboxylate groups of the 3-CPOA²⁻ ligand adopt three different coordination modes: μ_1 - η^1 : η^1 bidentate mode, μ_2 - η^1 : η^1 bidentate mode and μ_2 - η^1 : η^2 tridentate mode, respectively. Two crystallographically equal Pr(III) centers are bridged by two O atoms of carboxylate groups from two different 3-CPOA²⁻ ligands and two carboxyl groups from two individual 3-CPOA²⁻ ligands in bidentate mode into a binuclear unit (Fig. 2) with a Pr-Pr distance of 4.099(3) Å, which is joined by 3-CPOA²⁻ ligands to form a 2D sheet (Fig. 3). Then, the sheets further assembled into a 3D metal-organic supramolecular framework by the coordination interactions of 3-CPOA²⁻ ligands and Pr(III) ions (Fig. 4).

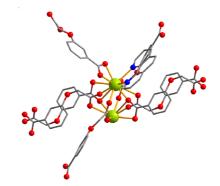


Fig. 2. Dinuclear unit in compound 2 (H atoms were omitted for clarity)

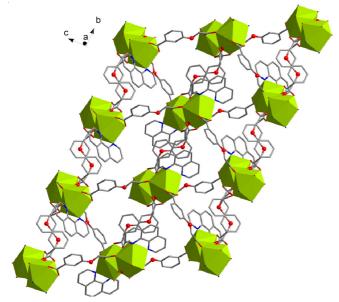


Fig. 3. View of 2D sheet of the compound **2** along the a axis (H atoms were omitted for clarity)

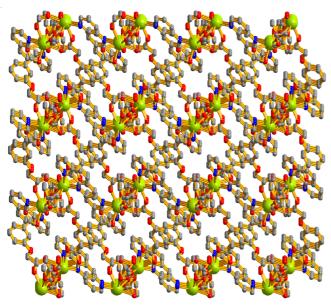


Fig. 4. A perspective of 3D framework along the bc plane

Thermogravimertric analyses: In order to examine the thermal stability of the networks, thermogravimertric analyses (TGA) were carried out for crystalline samples of compounds **1** and **2** in the temperature range 20-800 °C. Two complexes show similar thermal behavior owing to their isomorphous structures. As shown in Fig. 5, complexes **1** and **2** were stable up to 385 °C and 390 °C, respectively and then began to decompose.

Magnetic properties: The magnetic behaviours of 1 are shown in Fig. 6. The $\chi_M T$ value of 0.830 cm³ mol⁻¹ K at room temperature is close to the expected value of 0.806 cm³ mol⁻¹ K for one magnetic isolated Ce(III) ion (S = 1/2, L = 3, 2F_{5/2}, g = 6/7). Upon lowering the temperature, the $\chi_M T$ value decreases continuously. Between 180 and 300 K, the magnetic susceptibilities can be fitted to the Curie-Weiss law, $\chi_M = C_M/$ (T- θ), with C_M = 1.12 cm³ mol⁻¹ K, θ = -104.5 K. These results indicate a stronger magnetic interactions between the neighboring Ce(III) ions.

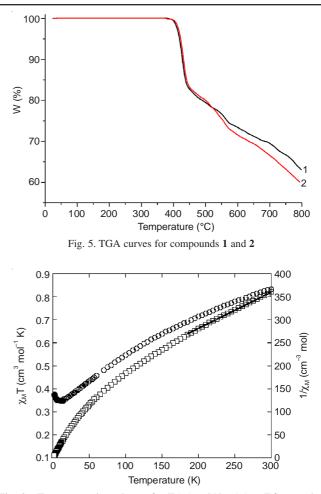


Fig. 6. Temperature dependence of $\chi_M T(\mathbf{O})$ and $1/\chi_M (\Box) vs. T$ for complex **1**. The black line shows the Curie-Weiss fitting

The magnetic behaviours of compound **2** are shown in Fig. 7. The $\chi_M T$ value at room temperature is 1.65 cm³ mol⁻¹ K, which is close to the value expected (1.60 cm³ mol⁻¹ K) for one insulated Pr(III) ion (S = 1, L = 5, {}^{3}H_{4}, g = 4/5). $\chi_M T$ value decreases continuously to a value of 0.088 cm³ mol⁻¹ K at 2 K. Between 150 and 300 K, the magnetic susceptibilities can be fitted to the Curie-Weiss law with $C_M = 1.75$ cm³ mol⁻¹ K, $\theta = -19.8$ K. These results demonstrate a strong magnetic interactions between the adjacent Pr(III) centers.

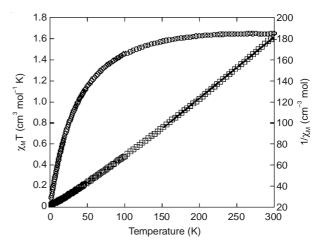


Fig. 7. Temperature dependence of $\chi_M T(\mathbf{O})$ and $1/\chi_M (\mathbf{D})$ *vs.* T for complex **2**. The black line shows the Curie-Weiss fitting

According to the topologies of compounds 1 and 2, because of the long metal-metal distance between the metal centers of dinuclear units, only the coupling interactions between the metal centers within them are considered. There are two set of magnetic exchange pathways within the dinuclear units, which consist of two carboxylate groups in *syn-syn* fashion and two η^2 -O bridges from the μ_2 -carboxylate groups, cooperatively contributed by the magnetic coupling transported by mixed bridges, with large Ln-O-Ln angles (104.2(4)° for 1, 105.0(4)° for 2). The larger magnetic coupling observed in two compounds can be attributed to the small Ln…Ln separations (4.092(4) Å for 1, 4.099(3) Å for 2) in the diametric Ln(III) ions.

Conclusion

In conclusion, we have successfully synthesized and characterized two 3D lanthanide coordination polymers $([Ln(3-CPOA)_{1.5}(phen)]_n$ (Ln = Ce (1), Pr (2)). Magnetic susceptibility measurements indicate that compounds 1 and 2 show a stronger magnetic coupling between the lanthanide ions.

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