

SYNTHESIS, CRYSTAL STRUCTURE AND THERMAL DECOMPOSITION OF A NOVEL PRASEODYMIUM SUPERMOLECULAR COMPLEX

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A novel complex, [Pr(5-nip)(phen)(NO₃)(DMF)] (5-nip: 5-nitroisophthalic acid; phen: 1,10-phenanthroline, DMF: N,N-dimethylformamide), was prepared and characterized by single crystal X-ray diffraction, elemental analysis, IR spectrum and DTG-DSC techniques. The results show that the crystal is monoclinic, space group P2(1)/n with $a=11.0876(6)$ Å, $b=12.8739(7)$ Å, $c=16.9994(8)$ Å; $\beta=91.193(4)^\circ$, $Z=4$, $D_c=1.822$ Mg m⁻³, $F(000)=1320$. Each Pr(III) ion is nine-coordinated by one chelating bidentate and two monodentate bridging carboxylate groups, one chelating bidentate nitril group, one DMF molecule and one 1,10-phenanthroline molecule. The complex is constructed with one-dimensional ribbons featuring dinuclear units and the one-dimensional ribbons are further assembled into two-dimensional networks by strong π - π stacking interactions. The complex has high stability up to 500°C. The enthalpy change of formation of the compound in DMF was measured using an RD496-III type microcalorimeter with the value of -9.214 ± 0.173 kJ mol⁻¹.

Keywords: crystal structure, enthalpy change of formation of the compound in DMF, 5-nitroisophthalic acid, praseodymium complex, thermal analysis

Introduction

Supermolecular construction from small molecular carboxylic acids ligands and metal ions has been developed remarkably as one of hotspots in coordination chemistry, supermolecular chemistry and material science fields. The π -stacking interaction is a significant intermolecular interaction in constructing supermolecular architectures [1–3]. Small molecular aromatic carboxylic acids 1,2,4,5-benzenetetracarboxylic acid [4], 1,3,5-benzenetricarboxylic acid [5], and 1,4-benzenedicarboxylic acid [6] are used extensively in the synthesis of coordination polymers for their versatile coordination modes. And the 2,2'-bipylike ligands involving 2,2'-bipyridine, 1,10-phenanthroline are inclined to form π -stacking interaction to enhance the stability of the supermolecular polymers [7, 8]. A great deal of lanthanide coordination polymers with aromatic polycarboxylic acid are reported in hydrothermal synthesis for their high coordination numbers and large ion radii differing from the transition metals complexes [9, 10]. In this paper, we prepared a new coordination polymer of holmium and 5-nitroisophthalic acid with 1,10-phenanthroline in DMF, and studied the crystal structural, thermal stability and measured the enthalpy change of formation of the compound in DMF using an RD496-type microcalorimeter.

Experimental

All the reagents used were Analar grade and used without further purification.

Pr(NO₃)₃·6H₂O (0.4352 g), 5-H₂nip (0.2113 g) and 1,10-phen (0.1980 g) were dissolved in 5 mL DMF, respectively, and the DMF solution of Pr(NO₃)₃ was added dropwise to the mixture DMF solution of the two ligands. Then a pellucid green solution was obtained. After 6 months placed in air, some green block crystals were recovered in the DMF solution and the structure of the suitable crystal for measurement was established by X-ray crystallography. These crystals were washed with anhydrous alcohol for 3 times and dried at room temperature (82% yield based on praseodymium).

Elemental analyses (C, H, N) were performed on an Elemental Vario EL III CHNOS analyzer. The content of praseodymium was checked using EDTA titration method. The IR spectra were recorded with a BEQ VZNDX-550 FTIR spectrometer using the KBr pellets technique over the range 4000–400 cm⁻¹. X-ray diffraction data collection was performed on an Apple Smart-CCD diffractometer with graphite-monochromated MoK α ($\lambda=0.71073$ Å) radiation in the phi and omega scanning mode at 273 K. 4322 Unique data ($R_{\text{int}}=0.0806$) were used to solve the structure by direct methods and refined on F^2 by the full-matrix least-squares methods using the SHELXL-97 (Sheldrick,

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Table 1 Crystallographic data and structure refinement for [Pr(5-nip)(phen)(NO₃)(DMF)]_n

Empirical formula	C ₂₃ H ₁₈ N ₅ O ₁₀ Pr
Formula mass	665.33
Temperature/K	273(2)
Crystal system	monoclinic
Space group	P2(1)/n
<i>a</i> /Å	11.0876(6)
<i>b</i> /Å	12.8739(7)
<i>c</i> /Å	16.9994(8)
β/°	91.193(4)
<i>V</i> /Å ³	2426.0(2)
<i>Z</i>	4
<i>F</i> (000)	1320
<i>D</i> _{calc} /Mg m ⁻³	1.822
Absorption coefficient/mm ⁻¹	2.077
Crystal size/mm	0.310×0.129×0.092
Range <i>h k l</i> collected	-13≤ <i>h</i> ≤11 -15≤ <i>k</i> ≤13 -20≤ <i>l</i> ≤19
Reflections collected	14735
Independent reflections	4322 [<i>R</i> _{int} =0.0806]
Completeness to θ (=26.00°)	99.9%
Data/restraints/parameters	4322/0/354
Goodness-of-fit on <i>F</i> ²	0.868
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ =0.0382, <i>wR</i> ₂ =0.0740
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0739, <i>wR</i> ₂ =0.0810
Largest different peak and hole/e Å ⁻³	1.078 and -0.860

1997) program package [11]. All non-hydrogen atoms were refined anisotropically and all the H atoms attached to the carbon were placed geometrically. The crystal data and refinement details of the complex are summarized in Table 1.

The TG-DSC curves were obtained with a Perkin Elmer thermogravimetric analyzer in air atmosphere with a heating rate of 10°C min⁻¹. The calorimetric experiments were performed with an RD496-III type microcalorimeter [12]. The calorimetric constants at 25.15°C was determined by the Joule effect before experiment, which is 63.901±0.030 μV mW⁻¹. The enthalpy of dissolution of KCl (spectral purity) in deionized water was measured to be 17.238±0.048 kJ mol⁻¹, which was in good agree-

ment with the value of 17.241±0.018 kJ mol⁻¹ from [13]. The accuracy was 0.02% and the precision was 0.3%, which indicates that the calorimetric system was accurate and reliable.

Results and discussion

The analysis data of the element content are shown in Table 2. From these values, we can find that the experimental data are consistent with the calculated values.

The band of the COOH group for 5-nitroisophthalic acid ligand at 1709 cm⁻¹, completely vanishes in the spectrum of the complex. 1627 and 1465 cm⁻¹ are assigned to asymmetric and symmetric vibrations of the COO⁻ group, indicating that the carboxyl group is coordinated to Pr(III) ion in two coordination modes [14], which is confirmed by X-ray diffraction analysis. The bands of the nitro group for the ligand at 1556 and 1349 cm⁻¹ do not moved and suggested the group is not involved in coordinated. The bands at 1299, 1036, 794 and 733 cm⁻¹ emerge, which could be considered as the coordinated group with C_{2v} symmetry [15]. A strong band appears at 1653 cm⁻¹, which could be attributed to the carboxyl group of the DMF molecule and a lower moving proves the coordination of the group to holmium ion [16]. IR spectrum of the complex is consistent with the structure analysis from the X-ray diffraction.

In Table 3 the final atomic coordinates and thermal parameters for the title complex are showed. Selected bond lengths and angles are listed in Table 4. In the asymmetric unit, there are a 5-nitroisophthalic acid ligand, a phen ligand, a NO₃⁻ ion and a DMF molecule as showed in Fig. 1. The nine-coordinated praseodymium ion lies in a distorted tricapped triangular prism environment (Fig. 2), in which the two faces comes from N(1), O(1), O(9) and O(2), O(3), O(7) as the sections, and O(4), O(8) and N(2) as the three capstones. The average Pr–O distance is 2.510 Å and the mean bond length of Pr–N is 2.655 Å. In the complex, 5-nip ligand acts in only a chelate-bidentate coordination mode.

Each pair of holmium ions is bridged by a pair of *syn-syn* 5-nip carboxylate groups into a dimeric subunit with an intradimer Pr...Pr distance of 5.669(1) Å. The different adjacent dimmers are doubly interlinked by the 5-nip ligands to form an infinite ribbon. The

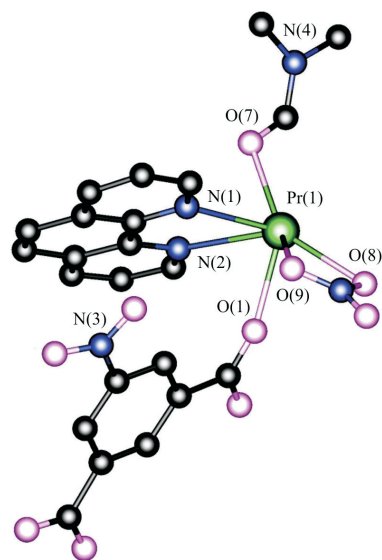
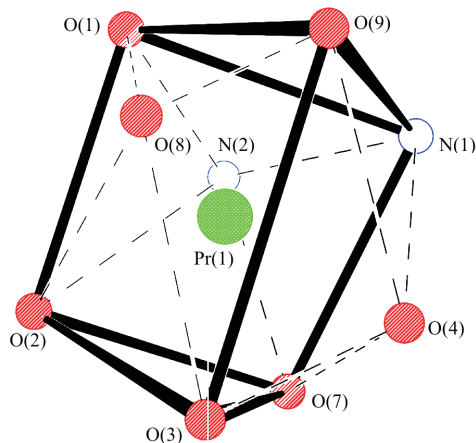
Table 2 The analysis data of the element content for [Pr(5-nip)(phen)(NO₃)(DMF)]_n (%)

Complex [Pr(5-nip)(phen)(NO ₃)(DMF)] _n	Mass fraction/%			
	C	H	N	Pr
Experimental data	42.05	2.56	10.33	20.95
Calculated values	41.52	2.73	10.53	21.18

Table 3 Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \cdot 10^3$) for the title complex

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Pr(1)	6584(1)	3647(1)	9207(1)	33(1)
O(1)	4572(3)	4323(3)	9051(2)	39(1)
O(2)	3178(3)	5169(3)	9716(2)	48(1)
O(3)	-1199(3)	4286(3)	9226(2)	42(1)
O(4)	-1644(3)	2943(3)	8469(2)	51(1)
O(5)	1595(5)	954(5)	7275(3)	104(2)
O(6)	3343(4)	1613(4)	7213(3)	76(2)
O(7)	7723(4)	2549(3)	10153(2)	56(1)
O(8)	6705(4)	5127(3)	8197(3)	51(1)
O(9)	6029(4)	3692(4)	7697(2)	53(1)
O(10)	6137(5)	5074(4)	6966(3)	82(2)
N(1)	5791(4)	1809(3)	8763(3)	37(1)
N(2)	5040(4)	2653(3)	10136(3)	37(1)
N(3)	2329(5)	1613(4)	7453(3)	55(2)
N(4)	9642(5)	2469(4)	10610(3)	54(1)
N(5)	6277(5)	4632(5)	7600(4)	53(1)
C(1)	6192(5)	1360(5)	8119(3)	47(2)
C(1)	5706(6)	442(5)	7805(4)	53(2)
C(1)	4779(6)	-16(5)	8172(4)	55(2)
C(1)	4348(5)	409(5)	8869(4)	43(2)
C(1)	3413(6)	-83(5)	9324(4)	60(2)
C(1)	3083(6)	322(5)	10012(4)	59(2)
C(1)	3600(5)	1265(5)	10308(3)	44(2)
C(1)	3319(6)	1678(5)	11053(4)	53(2)
C(1)	3869(5)	2566(5)	11307(4)	50(2)
C(1)	4709(5)	3036(5)	10828(3)	48(2)
C(1)	4510(5)	1773(4)	9875(3)	37(1)
C(1)	4889(5)	1327(4)	9155(3)	35(1)
C(1)	2531(5)	3849(4)	8845(3)	33(1)
C(1)	2859(5)	3074(4)	8318(3)	36(1)
C(1)	1953(5)	2451(4)	8003(3)	37(1)
C(1)	771(5)	2565(4)	8161(3)	37(1)
C(1)	425(4)	3369(4)	8656(3)	31(1)
C(1)	1314(4)	3977(4)	9004(3)	33(1)
C(1)	3506(5)	4494(4)	9228(3)	32(1)
C(1)	-887(5)	3547(5)	8795(3)	36(1)
C(1)	10642(6)	2984(6)	11012(4)	72(2)
C(1)	9852(7)	1436(6)	10306(5)	87(2)
C(1)	8608(6)	2915(5)	10501(3)	48(2)

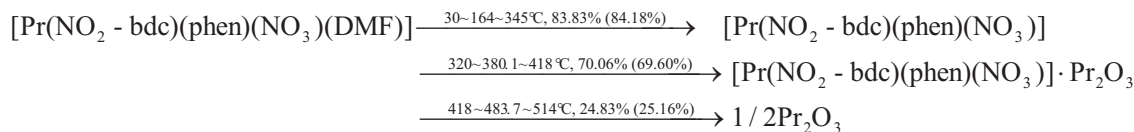
phen ligands are extended in a parallel fashion on both sides of the 1D ribbon at a face to face distance of 7.504 Å to give a spatial arrangement that is suitable for aromatic intercalation. So the adjacent ribbons interact strongly through π - π stacking interaction between the lateral slanted phen ligands at an offset

**Fig. 1** The asymmetry unit of the complex. H atoms are omitted for clarity**Fig. 2** The tricapped-triangular prism environment of praseodymium ion

face-to-face distance of ca. 3.31 Å in offset fashion into 2D wavelike layers. The 2D layers are arranged in an \cdots ABAB \cdots fashion along *c* axis into 3D framework.

Thermal gravimetric analysis (DTG-DSC) for the crystal sample was performed from 30 to 1000°C at a heating rate of 10°C min⁻¹ under a static air atmosphere (Fig. 3) and the thermal decomposed procedure are deduced as Scheme 1.

For the title complex, the thermal decomposition procedure is divided into three stages. At the first stage, the mass loss of 11.18% corresponds to the loss of the DMF molecule (ca. 11.13% for one DMF), which is consistent with the absence of the expected 1652 cm⁻¹ for the carbonyl of DMF molecule in IR spectrum of the middle product 1 at 320°C (Fig. 4). The DMF molecule leaving process is an endothermal one with the value of 66 J g⁻¹ from the DSC curve in Fig. 3. The further mass decrease from 320 to 418°C



Scheme 1 Thermal decomposed procedure for the title complex

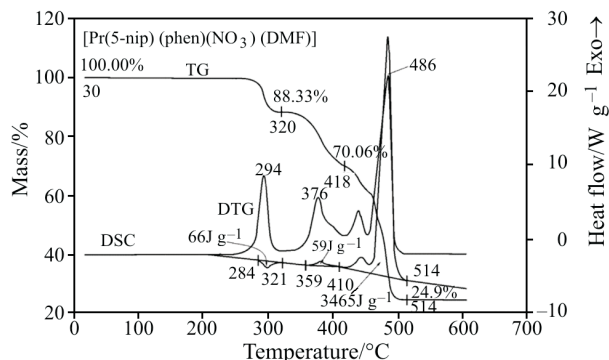


Fig. 3 Thermal gravimetric curves for the title complex

suggests the stepwise decomposition of the compound and partly decomposition to Pr_2O_3 , which could be proved by the IR spectrum of the middle product 2 for all the other characterized bands existed, expect for the 1652 cm^{-1} for DMF molecule disappeared (Fig. 4). Similarly, the heat of this process could be estimated by DSC experiment as 59 J g^{-1} . Finally, the compound

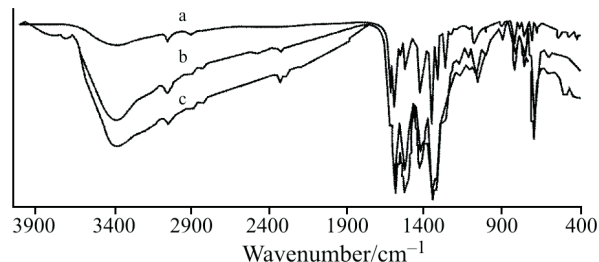


Fig. 4 The IR spectra for the a – title complex, b – middle product 1 and c – middle product 2

is completely converted to Pr_2O_3 of 24.83% (ca. 25.16%) at 514°C , and the metal content is analyzed using the EDTA titration with 84.96% (ca. 85.45%). The heat sent out in the second stage is measured as the value of 3465 J g^{-1} from DSC experiment. These results show the complex has high stability partly due to strong supramolecular interactions.

The enthalpy change of formation of the title complex in DMF can be represented as:

Table 4 Selected bond lengths (Å) and angle (°) for the complex

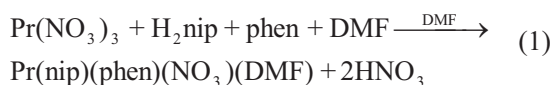
Pr(1)–O(2) #1	2.392(4)	Pr(1)–O(3) #2	2.591(3)
Pr(1)–O(1)	2.404(3)	Pr(1)–O(9)	2.628(4)
Pr(1)–O(7)	2.469(4)	Pr(1)–N(1)	2.629(4)
Pr(1)–O(4) #2	2.522(4)	Pr(1)–N(2)	2.679(4)
Pr(1)–O(8)	2.570(4)		
O(2) #1–Pr(1)–O(1)	86.62(12)	O(4) #2–Pr(1)–O(9)	72.02(13)
O(2) #1–Pr(1)–O(7)	79.62(15)	O(8)–Pr(1)–O(9)	49.11(14)
O(1)–Pr(1)–O(7)	137.72(13)	O(3) #2–Pr(1)–O(9)	102.04(13)
O(2) #1–Pr(1)–O(4) #2	122.36(12)	O(2) #1–Pr(1)–N(1)	145.43(14)
O(1)–Pr(1)–O(4) #2	143.73(12)	O(1)–Pr(1)–N(1)	89.41(13)
O(7)–Pr(1)–O(4) #2	74.02(14)	O(7)–Pr(1)–N(1)	80.49(14)
O(2) #1–Pr(1)–O(8)	91.88(14)	O(4) #2–Pr(1)–N(1)	78.06(13)
O(1)–Pr(1)–O(8)	73.71(12)	O(8)–Pr(1)–N(1)	119.81(14)
O(7)–Pr(1)–O(8)	145.76(14)	O(3) #2–Pr(1)–N(1)	126.93(13)
O(4) #2–Pr(1)–O(8)	83.24(13)	O(7)–Pr(1)–N(2)	70.70(13)
O(2) #1–Pr(1)–O(3) #2	72.47(12)	O(2) #1–Pr(1)–N(2)	85.12(13)
O(1)–Pr(1)–O(3) #2	139.86(12)	O(1)–Pr(1)–N(2)	68.57(13)
O(7)–Pr(1)–O(3) #2	72.62(13)	O(7)–Pr(1)–N(2)	70.55(13)
O(4)–Pr(1)–O(3) #2	51.09(12)	O(4) #2–Pr(1)–N(2)	129.45(14)
O(8)–Pr(1)–O(3) #2	73.19(13)	O(8)–Pr(1)–N(2)	142.27(13)
O(2) #1–Pr(1)–O(9)	138.88(14)	O(3) #2–Pr(1)–N(2)	139.63(13)
O(1)–Pr(1)–O(9)	71.71(12)	O(9)–Pr(1)–N(2)	116.51(14)
O(7)–Pr(1)–O(9)	139.03(14)	N(1)–Pr(1)–N(2)	61.61(14)

*Symmetry transformations used to generate equivalent atoms for compound: #1 – $-x+1, -y+1, -z+2$, #2 – $-x+1, y, z$

Table 5 Experimental data of the liquid phase formation reaction for the title complex

Q_1/mJ	Q_2/mJ
-428.352	32.603
-428.732	32.542
-427.963	32.018
-428.015	32.332
-428.629	32.722
-427.981	32.397
-428.279±0.140	32.436±0.101

In the table, Q_1 is the heat of formation reaction of the complex in 0.5 mL DMF including 0.1 mol L⁻¹ Pr(NO₃)₃ and 1.0 mL mixed DMF solution of 0.1 mol L⁻¹ H₂nip and 0.1 mol L⁻¹ phen; Q_2 is the diluted heat of 0.5 mL DMF added into 1.0 mL mixed DMF solution of 0.1 mol L⁻¹ H₂nip and 0.1 mol L⁻¹ phen



The calorimetric experiments were performed according to [17–19]. The heat of formation reaction Q_1 and the solvent diluted heat Q_2 were measured for six times in DMF at 25.15°C (Table 5). The first process is an exothermic one, while the second process is an endothermic one at 25.15°C. Thus, the enthalpy changes of formation reaction of the complex in DMF, $\Delta_r H_m^\theta$, could be obtained from Q_1 and Q_2 according to Eq. (2):

$$\Delta_r H_m^\theta = (Q_1 - Q_2) / n \quad (2)$$

Finally, $\Delta_r H_m^\theta = -9.214 \pm 0.173 \text{ kJ mol}^{-1}$ (n is the molar number of praseodymium ion in the reaction).

Conclusions

We have prepared successfully the title complex [Pr(5-nip)(phen)(NO₃)(DMF)]. The crystal structure of the complex was determined by single crystal X-ray diffraction. In the complex each praseodymium(III) ion is nine-coordinated. There exists strong π - π stacking supramolecular interactions between two adjacent ribbons, resulting in the high stability of the title complex. The thermal decomposition procedure of the title complex could be expressed by the scheme shown in Scheme 1 and witnessed by IR spectra of the middle products. The enthalpy change of formation of the title complex in DMF was obtained with the value of $-9.214 \pm 0.173 \text{ kJ mol}^{-1}$.

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