# Synthesis, Characterization and Crystal Structures of Lanthanide Phenoxyacetate Complexes with 1,10-Phenanthroline

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**Three new lanthanide phenoxyacetate complexes with 1,10-phenanthroline, $[Nd(POA)_3(phen)]_2 \cdot 2C_2H_5OH$ (1), $[Eu(POA)_3(phen)]_2 \cdot 2C_2H_5OH$ (2) and $[Sm(POA)_2(DMSO)(phen)]_2(ClO_4)_2$ (3) (POA = phenoxyacetate, phen = 1,10-phenanthroline, DMSO = dimethyl sulfoxide), were synthesized and characterized by elemental analyses, IR, UV-vis and FAB-MS spectra. Their structures were determined by single crystal X-ray diffraction analysis. In complexes 1 and 2, the carboxylate groups are bonded to $Ln^{3+}$ ion in three modes: the chelating bidentate, the bridging bidentate and the bridging tridentate. In complex 3, the carboxylate groups are bonded to $Sm^{3+}$ ion only involved in one mode: the bridging bidentate. The luminescence behavior of complex 2 was also studied by means of emission spectra.**

**Keywords** lanthanide complex, coordination polymer, crystal structure

## Introduction

There has been considerable interest in the coordination chemistry of lanthanide complexes with carboxylate ligands due to their potential application in molecular assemblies and luminescent probes in systems of biological relevance.[1-4] Of the numerous lanthanide complexes that have been widely studied,[5-9] most of them are found to exhibit a variety of dimeric or infinite chain structure. Recently we have reported polymeric $Lu(POA)_3(phen)$ compound in which lutetium ions form infinite chain along the *b*-axis direction through the coordination of bridging carboxylate groups.[10] As a part of our series of works, we describe here the synthesis and crystal structure determination of three new lanthanide phenoxyacetate complexes with 1,10-phenanthroline, $[Nd(POA)_3(phen)]_2 \cdot 2C_2H_5OH$ (**1**), $[Eu(POA)_3(phen)]_2 \cdot 2C_2H_5OH$ (**2**) and $[Sm(POA)_2(DMSO)(phen)]_2(ClO_4)_2$ (**3**) (POA = phenoxyacetate, phen = 1,10-phenanthroline, DMSO = dimethyl sulfoxide). This affords an opportunity to observe variations of the bonding forms of carboxylate anions. Luminescence properties of the europium complex have also been studied.

## Experimental

### *Chemicals*

The perchlorate lanthanide(III) salts (Nd, Eu, Sm) were prepared by dissolving the corresponding oxides (99.99%) in a slight excess of perchloric acid. The solutions were evaporated and the resulted precipitates were recrystallized from methanol. Other chemicals were commercially available and used without further purification.

### *Physical measurements*

The analyses (C, H and N) were performed using a Perkin-Elmer 240Q elemental analyser. Infrared spectra were obtained with a Shimadzu FT IR-8300 spectrophotometer and KBr discs. UV-vis spectra were recorded on a Shimadzu MPS-2000 spectrophotometer. Emission spectra was obtained for complex **2** in the solid state at room temperature with a Shimadzu RF-2000 spectrofluorometer and fast atomic bombardment mass spectra (FAB-MS) were obtained on a VG ZAB-HS spectrometer in a 3-nitrobenzyl alcohol matrix.

### *Preparations of complexes*

$[Nd(POA)_3(phen)]_2 \cdot 2C_2H_5OH$ (**1**) HPOA (3 mmol, Scheme 1) and phen (1 mmol) were dissolved in 60% $C_2H_5OH$ (20 mL). The mixture was adjusted to pH 7.0 with 2 $mol \cdot L^{-1}$ NaOH. To the resulting clear solution was added $Nd(ClO_4)_3$ solution (1 mmol dissolved in 10 mL of

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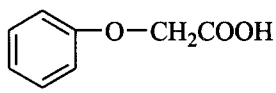
60% $C_2H_5OH$) dropwise. A purple precipitate was filtered off, washed with diethyl ether (3 × 5 mL), then dried at 50 ℃ *in vacuo*. Crystals were obtained by using dimethyl sulfoxide as solvent and slow diffusion of absolute ethanol into the solution. Yield 84%. FAB-MS *m/z*: 733 ($[M+1]^+$). Anal. calcd for $C_{38}H_{35}N_2O_{10}Nd$: C 55.40, H 4.28, N 3.40; found C 55.47, H 4.16, N 3.50.

**Scheme 1** Chemical structure of the ligand HPOA



$[Eu(POA)_3(phen)]_2 \cdot 2C_2H_5OH$ (**2**) This complex was synthesized in the manner identical to that described for $[Nd(POA)_3(phen)]_2 \cdot 2C_2H_5OH$, with 1 mmol of $Eu(ClO_4)_3$ in place of $Nd(ClO_4)_3$. Yield 79%. FAB-MS *m/z*: 740 ($[M+1]^+$). Anal. calcd for $C_{38}H_{35}N_2O_{10}Eu$: C 54.95, H 4.25, N 3.37; found C 54.87, H 4.20, N 3.45.

$[Sm(POA)_2(DMSO)(phen)]_2(ClO_4)_2$ (**3**) This complex was synthesized in the manner identical to that described for $[Nd(POA)_3(phen)]_2 \cdot 2C_2H_5OH$, with $Sm(ClO_4)_3$ in place of $Nd(ClO_4)_3$. Yield 72% FAB-MS *m/z*: 789 ($[M-ClO_4]^+$) and 689 ($[M-2ClO_4]^{2+}$). Anal. calcd for $C_{32}H_{34}ClN_2O_{12}S_2Sm$: C 43.22, H 3.83, N 3.15; found C 43.54, H 3.72, N 3.19.

**Caution**: Perchlorate complexes are potential explosives. Handling of these complexes must be in small quantity with great care.

*Crystallography*

The crystals data collection were performed on a Siemens P4 diffractometer with Mo Kα radiation ($\lambda = 0.072073$ nm) by the ω-scan method, within the limits $1.94° < \theta < 25.00°$ (**1**, **2**) and $1.79° < \theta < 25.00°$ (**3**). Empirical absorption correction was applied in all cases. The coordinates of the heavy atom were determined from direct methods, and the position of all the other non-hydrogen atoms were found by the usual Fourier methods. The refinement of the structure was done by full-matrix least-squares on $F^2$. All the calculations were carried out on IBM-586 computer using a SHELXTL P4/PC system.[11] A summary of crystal data and structure refinement parameters is given in Table 1. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC) Nos. 176725, 176726, 176727 for complexes **1**, **2** and **3**, respectively.

## Results and discusion

*Crystal structure of* $[Nd(POA)_3phen]_2 \cdot 2C_2H_5OH$ (**1**) *and* $[Eu(POA)_3phen]_2 \cdot 2C_2H_5OH$ (**2**)

The two complexes are isostructural and their ORTEP[12] diagrams are shown in Fig. 1 and Fig. 2. Each Ln atom is

**Table 1** Crystal data and structure refinement parameters for complexes **1**, **2** and **3**

| Complexes | 1 | 2 | 3 |
|---|---|---|---|
| Formula | $C_{38}H_{35}N_2O_{10}Nd$ | $C_{38}H_{35}N_2O_{10}Eu$ | $C_{32}H_{34}ClN_2O_{12}S_2Sm$ |
| Formula weight | 823.92 | 830.63 | 888.53 |
| Color | Purple | Colorless | Colorless |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1/n$ |
| $a$ (nm) | 1.4804(3) | 1.4799(4) | 1.2864(3) |
| $b$ (nm) | 1.2518(3) | 1.2451(4) | 1.3045(2) |
| $c$ (nm) | 1.9661(7) | 1.9665(6) | 2.1488(3) |
| $\beta$ (°) | 101.72(3) | 101.61(3) | 93.85(3) |
| $V$ ($nm^3$) | 3.5675(4) | 3.5494(4) | 3.5978(4) |
| $Z$ | 4 | 4 | 4 |
| $F(000)$ | 1668 | 1676 | 1788 |
| Temperature (K) | 296(2) | 273(2) | 297(2) |
| $\mu$ ($mm^{-1}$) | 1.516 | 1.828 | 1.886 |
| $\theta$ Range (°) | 1.94 to 25.00 | 1.94 to 25.00 | 1.79 to 25.00 |
| Independent reflections and $R$(int) | 6273, 0.0156 | 6254, 0.0424 | 6350, 0.0188 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0299 | 0.0439 | 0.0324 |
| $wR_2$ [$I > 2\sigma(I)$] | 0.0690 | 0.0904 | 0.0759 |
| Goodness of fit: $S$ | 0.930 | 0.873 | 0.934 |
| Largest diff. peak and hole ($e \cdot nm^{-3}$) | 1021/−470 | 1481/−686 | 745/−610 |

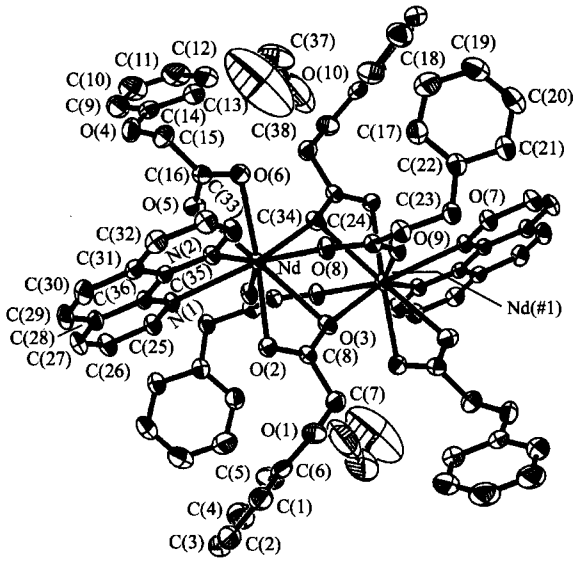



**Fig. 1** An ORTEP drawing of $[Nd(POA)_3(phen)]_2 \cdot 2C_2H_5OH$ (**1**).

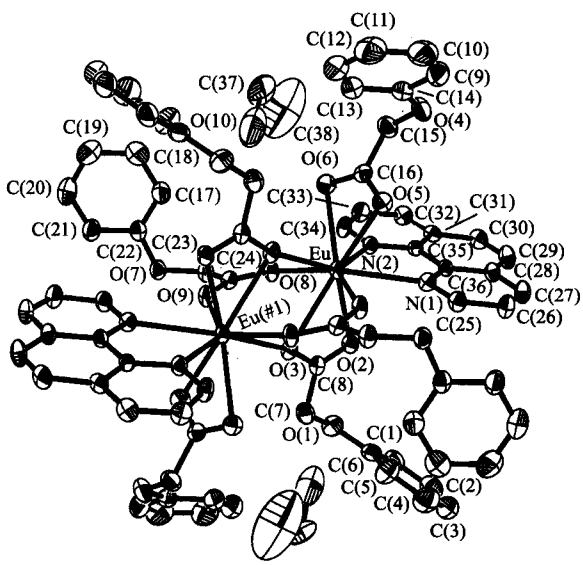



**Fig. 2** An ORTEP drawing of $[Eu(POA)_3(phen)]_2 \cdot 2C_2H_5OH$ (**2**).

nine-coordinated and has a deformed tricapped trigonal-prismatic geometry, where seven oxygen atoms of five carboxylate ligands and two nitrogen of phen molecule are bound to the Ln atom. A representative coordination geometry of the Nd center in complex **1** is presented in Fig. 3. The phenoxy oxygen atoms of ligands are not coordinated to the metal atom due to steric influence. In complexes **1** and **2**, the two Ln atoms are linked by the four carboxylate groups, the bridging carboxylate groups are involved in three different coordination modes: a common bidentate chelating mode, a bidentate bridging mode as well as a tridentate bridging mode, resulting in a dimeric unit with centrosymmetry.

Selected bond lengths and angles of complexes **1**, **2** are listed in Table 2. The Ln···Ln distances are 0.4015 and 0.3982 nm for complexes **1** and **2**, respectively. The average Ln—N distances are 0.2624 and 0.2584 nm for complexes **1** and **2**, respectively. In complexes **1** the average Ln—O

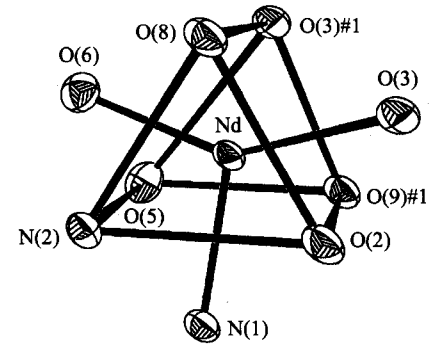



**Fig. 3** Coordination geometry of the metal center in $[Nd(POA)_3(phen)]_2 \cdot 2C_2H_5OH$ (**1**).

[Ln—O(8), Ln—O(3) # 1, Ln—O(9) # 3] distances found in $\mu_3$-O bridge and the average Ln—O [Ln—O(2), Ln—O(3), Ln—O(5), Ln—O(6)] distances found in the chelating carboxylate group are 0.2414 and 0.2564 nm, respectively; as to complex **2**, they are 0.2366 and 0.2531 nm, respectively. The Ln—O (carboxylate) distances are in the order Ln—O (chelating) > Ln—O ($\mu_3$). As revealed from the above data, we can found that the Eu—O and Eu—N distances are all shorter than the corresponding Nd—O and Nd—N distances. This indicates that interactions between the metal ion and the oxygen atoms as well as nitrogen atoms in complex **2** are stronger than those in complex **1**.

*Crystal structure of* $[Sm(POA)_2(DMSO)(phen)]_2(ClO_4)_2$ (**3**)

Due to the smaller ionic radius of $Sm^{3+}$ in comparison with that of $Nd^{3+}$ and $Eu^{3+}$, the crystal structure of complex **3** exhibits some different features, as illustrated in Fig. 4. A notable feature of the crystal is that two tridetate bridging

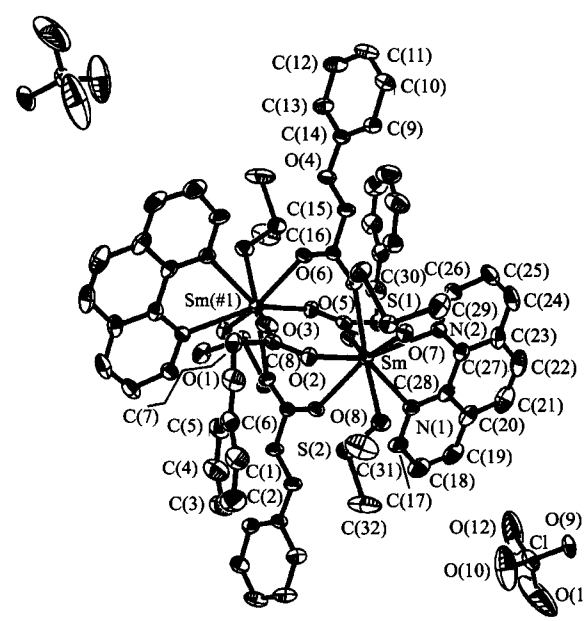



**Fig. 4** An ORTEP drawing of $[Sm(POA)_2(DMSO)(phen)]_2(ClO_4)_2$ (**3**).

**Table 2** Selected bond lengths (nm) and bond angles (°) of complexes **1**, **2** and **3**

| **1** | | **2** | | **3** | |
|---|---|---|---|---|---|
| | | Bond lengths | | | |
| Nd—O(2) | 0.2516(3) | Eu—O(2) | 0.2470(4) | Sm—O(3) # 1 | 0.2355(3) |
| Nd—O(3) | 0.2663(3) | Eu—O(3) | 0.2651(4) | Sm—O(5) | 0.2381(3) |
| Nd—O(5) | 0.2532(3) | Eu—O(5) | 0.2490(4) | Sm—O(6) # 1 | 0.2393(3) |
| Nd—O(6) | 0.2546(3) | Eu—O(6) | 0.2512(4) | Sm—O(8) | 0.2412(3) |
| Nd—O(8) | 0.2429(3) | Eu—O(8) | 0.2386(4) | Sm—O(7) | 0.2422(3) |
| Nd—N(1) | 0.2633(3) | Eu—N(1) | 0.2602(4) | Sm—O(2) | 0.2429(3) |
| Nd—N(2) | 0.2615(3) | Eu—N(2) | 0.2567(4) | Sm—N(1) | 0.2614(4) |
| Nd—O(3) # 1 | 0.2397(2) | Eu—O(3) # 1 | 0.2342(4) | Sm—N(2) | 0.2612(3) |
| Nd—O(9) # 1 | 0.2416(2) | Eu—O(9) # 1 | 0.2371(4) | | |
| | | Bond angles | | | |
| O(3) # 1-Nd-O(9) # 1 | 76.03(9) | O(3) # 1-Eu-O(9) # 1 | 76.26(13) | O(3) # 1-Sm-O(5) | 74.42(11) |
| O(3) # 1-Nd-O(8) # 1 | 75.81(9) | O(3) # 1-Eu-O(8) # 1 | 75.90(14) | O(3) # 1-Sm-O(6) # 1 | 75.25(10) |
| O(9) # 1-Nd-O(8) | 135.84(8) | O(9) # 1-Eu-O(8) | 136.03(13) | O(5)-Sm-O(6) # 1 | 126.06(10) |
| O(3) # 1-Nd-O(2) | 124.82(9) | O(3) # 1-Eu-O(2) | 124.95(14) | O(3) # 1-Sm-O(8) | 140.28(11) |
| O(9) # 1-Nd-O(2) | 88.22(10) | O(9) # 1-Eu-O(2) | 88.18(15) | O(5)-Sm-O(8) | 147.28(11) |
| O(8)-Nd-O(2) | 80.80(10) | O(8)-Eu-O(2) | 80.79(14) | O(6) # 1-Sm-O(8) | 75.31(10) |
| O(3) # 1-Nd-O(5) | 88.88(10) | O(3) # 1-Eu-O(5) | 88.52(15) | O(3) # 1-Sm-O(7) | 140.81(10) |
| O(9) # 1-Nd-O(5) | 81.06(9) | O(9) # 1-Eu-O(5) | 80.52(15) | O(5)-Sm-O(7) | 74.65(10) |
| O(8)-Nd-O(5) | 131.30(9) | O(8)-Eu-O(5) | 131.58(14) | O(6) # 1-Sm-O(7) | 143.61(10) |
| O(2)-Nd-O(5) | 140.94(9) | O(2)-Eu-O(5) | 140.98(14) | O(8)-Sm-O(7) | 74.07(10) |
| O(3) # 1-Nd-O(6) | 78.70(9) | O(3) # 1-Eu-O(6) | 78.25(14) | O(3) # 1-Sm-O(2) | 121.66(12) |
| O(8)-Nd-O(6) | 80.43(9) | O(8)-Eu-O(6) | 79.90(14) | O(5)-Sm-O(2) | 81.95(10) |
| O(2)-Nd-O(6) | 144.51(9) | O(2)-Eu-O(6) | 144.42(14) | O(6) # 1-Sm-O(2) | 77.55(10) |
| O(5)-Nd-O(6) | 51.08(9) | O(5)-Eu-O(6) | 51.90(14) | O(8)-Sm-O(2) | 76.50(11) |
| O(3) # 1-Nd-N(2) | 139.85(9) | O(3) # 1-Eu-N(2) | 140.01(15) | O(7)-Sm-O(2) | 76.60(10) |
| O(9) # 1-Nd-N(2) | 142.09(9) | O(9) # 1-Eu-N(2) | 141.75(14) | O(3) # 1-Sm-N(2) | 78.23(10) |
| O(8)-Nd-N(2) | 77.30(9) | O(8)-Eu-N(2) | 77.26(14) | O(5)-Sm-N(2) | 78.01(10) |
| O(2)-Nd-N(2) | 78.79(9) | O(2)-Eu-N(2) | 78.51(15) | O(6) # 1-Sm-N(2) | 135.94(11) |
| O(5)-Nd-N(2) | 86.96(9) | O(5)-Eu-N(2) | 87.61(15) | O(8)-Sm-N(2) | 106.13(11) |
| O(6)-Nd-N(2) | 67.83(9) | O(6)-Eu-N(2) | 68.25(15) | O(7)-Sm-N(2) | 72.29(11) |
| O(3) # 1-Nd-N(1) | 150.12(9) | O(3) # 1-Eu-N(1) | 149.30(14) | O(2)-Sm-N(2) | 146.43(11) |
| O(9) # 1-Nd-N(1) | 79.52(9) | O(9) # 1-Eu-N(1) | 78.57(13) | O(3) # 1-Sm-N(1) | 74.92(14) |
| O(8)-Nd-N(1) | 134.05(9) | O(8)-Eu-N(1) | 134.79(14) | O(5)-Sm-N(1) | 134.04(11) |
| O(2)-Nd-N(1) | 70.71(9) | O(2)-Eu-N(1) | 71.05(15) | O(6) # 1-Sm-N(1) | 76.61(11) |
| O(5)-Nd-N(1) | 70.44(9) | O(5)-Eu-N(1) | 70.14(15) | O(8)-Sm-N(1) | 72.77(12) |
| O(6)-Nd-N(1) | 102.35(9) | O(6)-Eu-N(1) | 103.21(15) | O(7)-Sm-N(1) | 111.91(10) |
| N(2)-Nd-N(1) | 62.58(9) | N(2)-Eu-N(1) | 63.20(15) | O(2)-Sm-N(1) | 143.83(11) |
| O(3) # 1-Nd-O(3) | 75.07(9) | O(3) # 1-Eu-O(3) | 74.40(16) | N(2)-Sm-N(1) | 62.78(11) |

ligands (carboxylate) have been replaced by two bridging bidentate ligands (carboxylate) and two monodentate ligands (DMSO).

The dinuclear entity is centrosymmetric. Each samarium ions is coordinated by four oxygen atoms of the bridging bidentate carboxylates, two oxygen atoms from two DMSO molecule, as well as two nitrogen atom afforded by a phen molecule, which give a coordination number of eight. The coordination geometries of metal ion can be described as distorted tetragonal antiprismatic (Fig. 5). Instead of being involved in the coordination of the metal ions, the two $ClO_4^-$ ions interact with the complex species $[Sm(POA)_2(DMSO)(phen)]_2^{2+}$ through electrostatic force and keep the molecule neutral.

Selected bond lengths and angles of the complex **3** are listed in Table 3. Two samarium ions are bridged by four carboxyl groups, which are only involved in the bidentate bridg-

ing mode. The separation of the two metal ions is 0.4353 nm. The average Sm—O bond length of carboxylate groups is 0.2390 nm. The average Sm—O bond length of DMSO is 0.2417 nm. The average Sm—N bond length is 0.2613 nm.

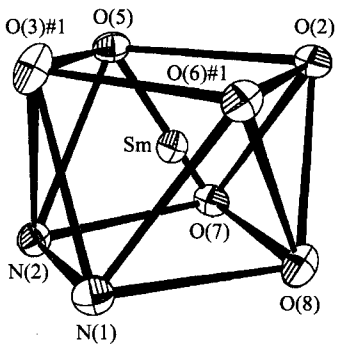



**Fig. 5** Coordination geometry of the metal center in $[Sm(POA)_2(DMSO)(phen)]_2(ClO_4)$ (**3**).

**Table 3** The main absorption band of IR spectra and their assignment

| Compound | Main absorption and their assignment |
|---|---|
| HPOA | 3012 (O—H), 1599 ($COO^-$), 1438 ($COO^-$) |
| phen | 1622 (C=C), 1587 (C=N), 875 (C—H), 738 (C—H) |
| $[Nd(POA)_3(phen)]_2 \cdot 2C_2H_5OH$ | 3445 (O—H), 1625 ($COO^-$), 1428 ($COO^-$), 846 (C—H), 730 (C—H), 426 (Nd—O) |
| $[Eu(POA)_3(phen)]_2 \cdot 2C_2H_5OH$ | 3450 (O—H), 1628 ($COO^-$), 1429 ($COO^-$), 847 (C—H), 731 (C—H), 427 (Eu—O) |
| $[Sm(POA)_2(DMSO)(phen)]_2(ClO_4)_2$ | 1635 ($COO^-$), 1435 ($COO^-$), 1020 (S=O), 847 (C—H), 730 (C—H), 426 (Sm—O) |

On close comparison of the packing of the three complexes, they are very similar to each other. At first, the molecules of complexes pack to form an infinite chain constructed with building block, which are stabilized by weak face-to-face $\pi\cdots\pi$ stacking (the shortest distance between two phen rings 0.33772 nm for **1**, 0.3418 nm for **2** and 0.3281 nm for **3** as shown in Fig. 6). Then adjacent chains are further connected through edge-to-face C—H$\cdots\pi$ interaction [$\pi$ rings are composed of C(9)C(10)C(11)C(12)C(13)C(14), H(18)$\cdots\pi$ 0.3068 nm, C(18)—H(18)$\cdots\pi$ 128.8° for **1** and H(18)$\cdots\pi$ 0.3146 nm, C(18)—H(18)$\cdots\pi$ 129.8° for **2**; H(29)$\cdots\pi$ 0.2796 nm, C(29)—H(29)$\cdots\pi$ 120.8° for **3**], leading to a 2-D network in *ac* plane as illustrated in Fig. 7 for **1**. In addition, solvent ethanol molecules in complexes **1** and **2** are filled between neighboring sheets stabilized by O(10)—H(10)$\cdots$O(6) hydrogen bonds [O(10)$\cdots$O(6) 0.2720 nm for **1**, O(10)$\cdots$O(6) 0.2835 nm for **2**]. The network solid structures are therefore stabilized by this weak inter-molecular interaction.[13,14]

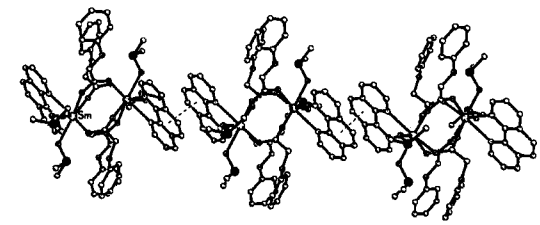


**Fig. 6** 1-D chain stacking of complex **3** along *a*-axis direction.

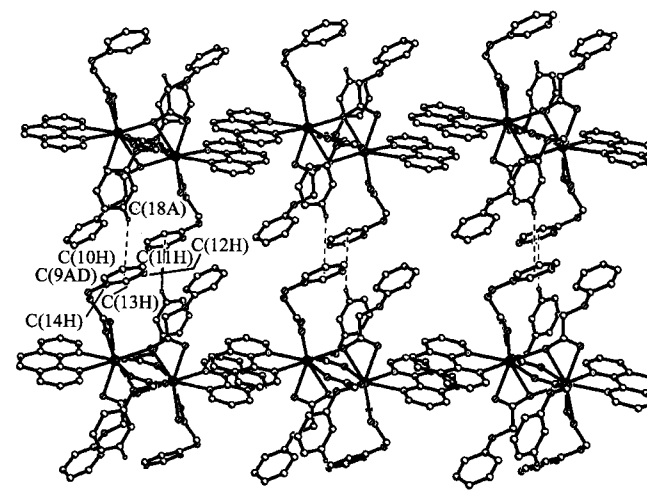



**Fig. 7** 2-D sheet in complex **1** constructed by $\pi\cdots\pi$ stacking and C—H $\cdots\pi$ interactions in *ac* plane.

*Infrared spectra*

The main IR data and their assignments are summarized in Table 3. The "free" HPOA ligand exhibits three characteristic bands at 3012 $cm^{-1}$(OH), 1599 $cm^{-1}$($COO^-$) and 1438 $cm^{-1}$($COO^-$). For all the lanthanide complexes, it is noted that the characteristic band of the HPOA ligand has vanished, two new bands appear at about 1635 and 1428 $cm^{-1}$, which are assigned to asymmetric and symmetric stretching vibration of the carboxyl group, and the $\delta_{C-H}$ band bathochromic has shifted compared with the free phen ligand. This also suggest the phen ligand has bound $Ln^{3+}$.[15] The "free" DMSO exhibits a characteristic band at about 1040 $cm^{-1}$(S=O),[16] and the red shift observed from 1040 to 1020 $cm^{-1}$ in complex **3** is due to binding of DMSO to Sm(III) ion. In complexes **1** and **2** the broad band at 3450 $cm^{-1}$ occurs from the O—H stretching vibrations of ethanol, which is in agreement with X-ray analysis.

*Absorption spectra*

Absorption spectra of the HPOA, complexes **1**, **2** and **3** were recorded in ethanol (Fig. 8). The free HPOA displays two strong absorption bands in the UV spectral region at 216 and 272 nm, which are attributed to $\pi$-$\pi^*$ transitions. These bands are strongly perturbed upon co-ordination to $Ln^{3+}$ (Nd, Eu, Sm) and blue shift is found for the last band, implying coordination of the ligand. The absorption spectra of complexes **1** and **2** are similar and exhibit two bands (224, 265 nm for

complex **1**; 223, 263 nm for complex **2**). In comparison with complexes **1** and **2**, the difference in the spectrum of complex **3** obviously arose from the coordinated solvent molecules DMSO.

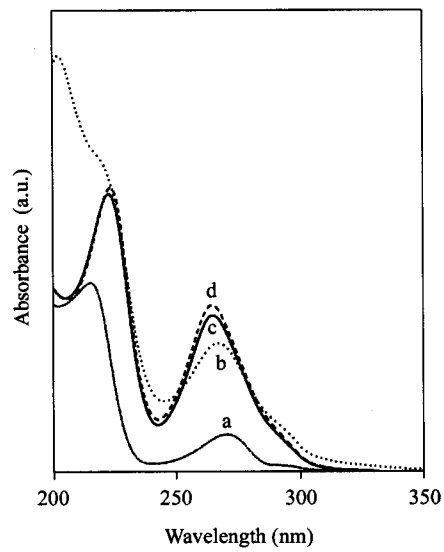



**Fig. 8** UV-vis spectra of HPOA (a, short dot), complex **1** (c, solid), complex **2** (d, dash) and complex **3** (b, dot).

*Emission spectra*

Complex **2** is highly luminescent in the solid state. Its emission spectrum at room temperature is shown in Fig. 9. Excited at 270 nm, this luminescence is typical of the Eu centered transitions from $^5D_0$ levels to the lower $^7F_{0\text{-}4}$ levels of the ground multiplet,[17,18] and five narrow emission peaks centered at 580, 592, 612, 652 and 698 nm are assigned to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$ transitions, respectively. Among the peaks, the relative intensity of the $^5D_0 \rightarrow {}^7F_2$ electronic dipole transition is the strongest, showing that the $Eu^{3+}$ ion does not lie in a centrosymmetric coordination site.[19] Because the forbidden $^5D_0 \rightarrow {}^7F_2$ electronic dipole transition is sensitive to the coordination environment, the asymmetric microenvironment causes the polarization of the $Eu^{3+}$ under the influence of the electric field of the surrounding ligands and thus increases the probability for the electronic dipole transition. This is in good agreement with the results of crystal structure determination.

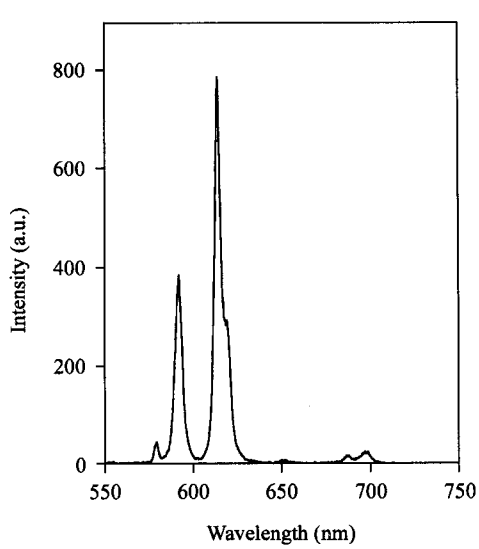



**Fig. 9** Emission spectra of $[Eu(POA)_3(phen)]_2 \cdot 2C_2H_5OH$.

## Conclusion

We have synthesized and characterized a series of lanthanide complexes, which afford interesting examples to exhibit surprising diversity of structures and different coordination modes. The results indicate that even in the similar experimental condition, the complexes of lanthanide are sometimes expected to be different from each other. The differences in the compositions, structures and coordination numbers of the central metal atoms of the complexes are concerned with not only the ionic radius of the relevant $Ln^{3+}$ but also the mutual steric interaction of the ligands.

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