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Synthesis, structure and luminescence properties of samarium (III) and dysprosium (III) complexes with a new tridentate organic ligand

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Abstract

A novel organic ligand, 6-diphenylamine carbonyl 2-pyridine carboxylic acid (HDPAP), and the corresponding lanthanide complexes, tris(6-diphenylamine carbonyl 2-pyridine carboxylato) samarium (III) (Sm-DPAP) and tris(6-diphenylamine carbonyl 2-pyridine carboxylato) dysprosium (III) (Dy-DPAP) have been designed and synthesized. The crystal structures and photoluminescence of Sm-DPAP and Dy-DPAP have been studied. The results showed that the lanthanide complexes have electroneutral structures, and the solid samarium complex emits characteristic red fluorescence of Sm (III) ions at room temperature while the dysprosium complex emits the DPAP ligand phosphorescence. The lowest triplet level of DPAP ligand was calculated from the phosphorescence spectrum of Gd-DPAP in *N*,*N*-dimethyl formamide dilute solution determined at 77 K, and the energy transfer mechanisms in the lanthanide complexes were discussed. © 2003 Elsevier B.V. All rights reserved.

Keywords: X-ray crystallography; Samarium complex; Dysprosium complex; Luminescence property; Synthesis

1. Introduction

Since a brightly photoluminescence europium complex was firstly reported by Weissman in 1942 [1], great achievement has been gained in research of lanthanide organic complexes. Complexes of lanthanide ions with organic ligands have been doped in polymers for optical amplification [2,3], and luminescent lanthanide complexes have been used in medical diagnosis in reality, where they are used to detect small amounts of biomolecules that can tell about the physical state of a patient [4,5]. Presently organic electroluminescence (OEL) has been studied extensively for its opportunities of low drive voltage, suitability for integrated circuit and potential application for large flat panel display [6,7]. Several ternary lanthanide complexes have been applied to prepare OEL devices that showed weak visible emission and low electroluminescence efficiency [8-11]. In principle, electroneutral metal complexes may form uniform thin film in vacuum vapor deposition and are reasonably stable to heat, which is required for OEL displays [12]. Investigating the relationship between the structures of organic ligands and the energy levels of lanthanide ions will give evidences for designing high luminescent lanthanide organic complexes. In this paper, a novel organic ligand, 6-diphenylamine carbonyl 2-pyridine carboxylic acid (HDPAP), and the corresponding samarium and dysprosium complexes, Sm-DPAP and Dy-DPAP, were synthesized, and the structures and luminescence properties for the lanthanide complexes have been investigated.

2. Experimental

2.1. Preparation of 6-diphenylamine carbonyl 2-pyridine carboxylic acid

2,6-Dichlorocarbonyl pyridine (DCP) was prepared by a reaction of 2,6-pyridine dicarboxylic acid (H₂DPA) and thionyl chloride [13] with high yield of 95%. To 5.0 g of DCP dissolved in dried benzene was slowly added 4.14 g of diphenylamine dissolved in dried benzene, and stirring was continued for 5 h at 50 °C. The mixture was then cooled to

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room temperature and filtered out to remove the white precipitate. The benzene solution was concentrated in vacuum and then hydrolyzed at 40 °C for 2 h. The pH value of the solution was adjusted to 9.5 using 2.0 mol/l aqueous NaOH; the mixture was filtered and the pH value of the filtrate was adjusted to 3.0 using 2.0 mol/l HCl, giving a white precipitate. The white precipitate was recrystallized in 95% ethanol:acetone (1:1, v:v), giving 2.8 g of HDPAP with yield 35% and mp 74–77 °C.

The synthesis route is expressed as follows:





Sm(DPAP)₃·12H₂O complex was prepared by adding 12.0 mmol of HDPAP dissolved in ethanol to an aqueous solution containing 4.0 mmol SmCl₃, which was obtained by a reaction of Sm₂O₃ (99.95%, Zhu–jiang smeltery Co.) and HCl (6.0 mol/l). The pH value of the mixture was adjusted to 5 by adding an aqueous solution of sodium hydroxide, and the mixture solution was stirred for 12 h at 40 °C. A colorless cubic crystal was precipitated from the solution after deposited for 96 h at room temperature, and the precipitate was filtered out and washed with deionized water and 95% ethanol. A hydrated complex Sm(DPAP)₃·12H₂O was obtained with yield of 66%.

The $Dy(DPAP)_3 \cdot 12H_2O$ was prepared as the synthesis method of $Sm(DPAP)_3 \cdot 12H_2O$ with yield of 58%.

2.3. Crystal structure determination

Diffraction intensities for the complexes were collected at 20 °C on a Siemens R3m diffractometer using the ω -scan technique. Lorentz-polarization and absorption corrections were applied [14]. The structures were solved with the direct method and refined with full-matrix least-squares using the SHELXS-97 and SHELXL-97 programs, respectively [15,16]. Anisotropic displacement parameters were applied to all non-hydrogen atoms, and the organic hydrogen atoms were generated geometrically (C–H 0.96 Å); the aqua hydrogen atoms were located from difference maps and refined with isotropic displacement factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [17]. Crystal data as well as details of data collection and refinement for the complex are summarised in Table 1. Selected bond distances and bond angles for $Sm(DPAP)_3$ ·12H₂O and $Dy(DPAP)_3$ ·12H₂O are listed in Tables 2 and 3, respectively. Drawings were produced with SHELXTL [18].

2.4. Measurements and apparatus

Elemental analysis for the samples was carried out with an Elementar vario EL elemental analyzer. IR spectra in the region of 4000-400 cm⁻¹ were recorded on a Bruker infrared spectrophotometer using conventional KBr method.



Table 1

FAB-MS spectra were performed on a VG ZAB-HS spectrometer. The ¹H NMR spectra were recorded on a USA Varian UNITYINOVA-500 spectrometer (500 MHz).

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Crystallographic	data	for	$Sm(DPAP)_3{\cdot}12H_2O$	and	$Dy(DPAP)_3 \cdot 12H_2O$
complexes					

Complexes	Sm-DPAP	Dy-DPAP
Formula	C57H63N6O21Sm	C ₅₇ H ₆₃ N ₆ O ₂₁ Dy
Formula weight	1318.47	1330.62
Temperature (K)	293	293
Radiation (Mo Ka) (Å)	0.71073	0.71073
Crystal system	Cubic	Cubic
Space group	Pa3	Pa3
Unit cell	a = 22.8778(7)	a = 22.9178(8)
dimensions (Å)		
Volume (Å ³)	11,974.1(6)	12,037.0(7)
Ζ	8	8
Density (calculated)	1.436	1.442
$(g \text{ cm}^{-3})$		
Absorption coefficient	10.61	13.21
(cm^{-1})		
<i>F</i> (000)	5224	5256
Crystal size (mm ³)	$0.2 \times 0.2 \times 0.2$	$0.3 \times 0.3 \times 0.3$
$2\theta_{\rm max}$ (degrees)	55	55
Index ranges	-29 < h < 22,	-29 < h < 28,
	-29 < k < 25,	-29 < k < 27,
	-29 < l < 29	-29 < l < 25
Reflections collected	68,634	68,087
Independent	$4608(R_{\rm int} = 0.1044)$	$4611(R_{\rm int} = 0.0607)$
reflections		
Data/restraints/	4608/0/257	4611/0/257
parameters		
Goodness-of-fit on F^2	1.001	1.003
Final R indices	$R_1 = 0.0422,$	$R_1 = 0.0337,$
$[I > 2\sigma(I)]$	$\omega R_2 = 0.1164$	$\omega R_2 = 0.0964$
Largest diff.	0.696 and	0.646 and
peak and hole	$-0.534 \text{ e}\text{\AA}^{-3}$	$-0.587 \text{ e}\text{\AA}^{-3}$
Parameter Δ	6.09	5.89

Atom	Atom	Distance	Atom	Atom	Distance		
Sm(1)	O(2)	2.379(3)	Sm(l)	O(3)	2.446(3)		
Sm(1)	N(1)	2.575(4)	O(1)	C(I)	1.231(6)		
O(2)	C(1)	1.280(6)	O(3)	C(7)	1.237(5)		
Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O(2)	Sm(1)	O(3)	125.6(1)	O(2)	Sm(1)	O(3) ^{#2}	150.6(1)
O(2)	Sm(1)	$O(2)^{#2}$	79.8(1)	O(2)	Sm(1)	$O(3)^{\#1}$	89.8(1)
O(2)	Sm(1)	N(1)	64.3(1)	O(3)	Sm(1)	N(l)	61.6(1)
N(1)	Sm(1)	$N(I)^{\#I}$	118.37(4)	O(2)	Sm(1)	$N(I)^{#1}$	84.1(1)
O(3)	Sm(1)	$N(I)^{\#1}$	126.5(1)	O(2)	Sm(1)	$N(I)^{#2}$	142.7(1)
O(3)	Sm(1)	N(I) ^{#2}	66.6(1)	O(3)	Sm(1)	O(3)	74.0(1)
C(1)	O(2)	Sm(1)	126.0(3)	C(2)	N(1)	Sm(1)	115.6(3)
C(6)	N(l)	Sm(1)	120.6(3)	C(7)	O(3)	Sm(1)	126.9(3)

Table 2 Some bond lengths (Å) and angles (degree) for Sm(DPAP)_3 $\cdot 12H_2O$ complex

Symmetry transformations used to generate equivalent atoms: (#1) y,z,x; (#2) z,x,y.

The excitation and emission spectra were recorded on a Aminco Bowman Series fluorescence spectrophotometer with both excitation and emission slits at 8.0 nm with a PMT at 700 V. The relative emission intensity was recorded from the highest emission peak under the optimum excitation wavelength. Phosphorescence spectra were recorded on SPEX 1934D phosphorescence spectrometer at 77 K, with both excitation and emission slits at 4.0 mm, with the light pulse width of 1.0 ms and pulse interval of 0.001 ms. UV spectra were recorded on a Varlan UV-vis spectrophotometer.

3. Results and discussion

3.1. Elemental analysis and IR absorption

The elemental analysis data for $C_{19}H_{14}N_2O_3$ (HDPAP) are: found (calcd) C 71.48 (71.69), H 4.43 (4.43), and N 8.89 (8.80). IR (KBr) ν_{max} (cm⁻¹): 3238.2, 3078.0, 1754.8,

Table 3 Some bond lengths (Å) and angles (degrees) for $Dy(DPAP)_3{\cdot}12H_2O$ complex

1653.2, 1591.4, 1489.8, 1373.6, 756.5, 695.5. ¹H NMR in CD₃SOCD₃: 13.084 (1H, s), 7.921 (1H, t, ${}^{3}J = 7.5$ Hz), 7.893 (1H,d,d, ${}^{3}J = 8.0$ Hz, ${}^{4}J = 2.0$ Hz), 7.768 (1Hd,d, ${}^{3}J = 7.25$ Hz, ${}^{4}J = 1.75$ Hz), 7.284 (8H,s), 7.204 (2H,s). FAB-MS: *m/z* 319 ([M + H]⁺).

The complexes were verified by elemental analysis, IR spectroscopy and X-ray crystal analysis. The elemental analysis results for Sm-DPAP are: found (calcd for SmC₅₇-H₆₃N₆O₂₁) C 51.43 (51.92), H 4.60 (4.82), N 6.13 (6.37), Sm 11.28 (11.40). IR (KBr) ν_{max} (cm⁻¹): 3421.5 (s, ν_{HO-H}), 3104.9, 3064.3 (w, ν_{C-H}), 1491.6 (m, $\nu_{skeleton}$), 699.7 (s, δ_{C-H}), 1620.8 (s, ν_{as} (COO⁻)), 1565.5 (s, $\nu_{C=O}$), 1379.6 (s, ν_{s} (COO⁻)), 1270.2 (m, ν_{C-N}). The elemental analysis results for Dy-DPAP are: found (calcd for DyC₅₇H₆₃N₆O₂₁) C 50.85 (51.45), H 4.62 (4.77), N 6.13 (6.32), Dy 12.79 (12.21). IR (KBr) ν_{max} (cm⁻¹): 3390.6 (s, ν_{HO-H}), 3109.8, 3057.5 (w, ν_{C-H}), 1619.1 (s, ν_{as} (COO⁻)), 1565.1 (s, $\nu_{C=O}$), 1374.9 (s, ν_{s} (COO⁻)).

Atom	Atom	Distance	Atom	Atom	Distance		
Dy(l)	O(2)	2.343(3)	Dy(l)	O(3)	2.404(3)		
Dy(l)	N(I)	2.530(3)	O(1)	C(I)	1.231(5)		
O(2)	C(I)	1.282(5)	O(3)	C(7)	1.244(4)		
Atom	Atom	Atom	Distance	Atom	Atom	Atom	Distance
O(2)	Dy(l)	$O(2)^{\#1}$	79.2(1)	O(2) ^{#2}	Dy(l)	O(3)	89.6(1)
C(2)	Dy(l)	$O(3)^{\#1}$	148.52(9)	O(2)	Dy(l)	$N(I)^{#1}$	142.3(1)
O(2)	Dy(l)	O(3)	127.78(9)	$O(2)^{\#2}$	Dy(l)	N(1)	81.83(9)
O(2)	Dy(1)	N(1)	65.4(1)	O(3)	Dy(l)	N(1)	62.57(9)
O(3)	Dy(l)	$N(I)^{\#1}$	66.81(9)	O(3)	Dy(l)	$O(3)^{\#1}$	74.1(1)
$O(3)^{#2}$	Dy(l)	N(l)	127.4(1)	C(7)	O(3)	Dy(l)	126.8(2)
N(I) ^{#2}	Dy(l)	N(1)	118.71(3)	C(1)	O(2)	Dy(l)	125.7(3)
C(2)	N(3)	Dy(l)	115.6(2)	C(6)	N(1)	Dy(l)	120.9(2)

Symmetry transformations used to generate equivalent atoms: (#1) y,z,x; (#2) z,x,y.



Fig. 1. Crystal structure of Sm(DPAP)3:12H2O complex.

3.2. Crystal structure

The crystal structure of Sm(DPAP)₃·12H₂O consists of the mononuclear Sm(DPAP)3 molecules and lattice water molecules. As shown in Fig. 1, the Sm(III) atom is coordinated in a tri-capped trigonal prism geometry with three nitrogen atoms [Sm(1)-N(1) 2.575(4) Å] in pyridine ring, three carboxylate oxygen atoms [Sm(1)-O(2)]2.379(3) Å; $O(2)-Sm(1)-N(1) 64.3(1)^{\circ}$ and three carbonyl oxygen atoms [Sm(1)-O(3) 2.446(3) Å, O(3)-Sm(1)-N(1) $61.5(1)^{\circ}$ from three different DPAP ligands. The coordination number of central Sm(III) atom here is 9, reaching its saturated state, therefore, the lattice water molecules only form donor hydrogen bonds with the carboxylate oxygen atoms. Thus, compared with the ternary lanthanide-βdiketonato-base complexes [19,20], where the coordination numbers are 6 or 8, the mononuclear Sm(DPAP)₃ molecules in this structure would have better chemical thermodynamic stability.

The crystal structure of Dy(DPAP)₃·12H₂O is similar to that of Sm(DPAP)₃·12H₂O, and a little differences of the bond lengths and bond angles between the two complexes have been observed. The Dy(III) atom is coordinated in a tri-capped trigonal prism geometry with three nitrogen atoms [Dy(1)-N(1) 2.530(3) Å] in pyridine ring, three carboxylate oxygen atoms [Dy(1)-O(2) 2.343(3) Å; O(2)-Dy(1)-N(1) 65.4(1)°] and three carbonyl oxygen atoms $[Dy(1)-O(3) 2.404(3) \text{ Å}, O(3)-Dy(1)-N(1) 62.57(9)^{\circ}]$ from three different DPAP ligands.

3.3. UV absorption spectra

UV absorption spectra for 2.5×10^{-5} mol/l HDPAP, $1.0 \times 10^{-5} \text{ mol/l} \text{ Sm}(\text{DPAP})_3$ and $1.0 \times 10^{-5} \text{ mol/l}$ Dy(DPAP)₃ ethanol solutions were determined at the same

Table 4
The photophysical properties of Sm(DPAP) ₃ and Dy(DPAP) ₃ complex

Sample	UV al	osorption	Fluorescence		
	λ_{\max} (nm)	$\varepsilon \times 10^{-4} \text{ mol}^{-1}$ dm ³ cm ⁻¹	λ_{ex} (nm)	λ_{em} (nm)	I (a.u.)
2.5 × 10 ⁻⁵ 14 HDDAD	077	1.4			
2.5×10^{-1} mol/l HDPAP	211	1.4			
1.0×10^{-4} mol/l Sm-DPAP	294	2.30 ^a	346	388	2.84
1.0×10^{-5} mol/l Dy-DPAP	292	2.37			
Sm(DPAP) ₃ ·12 H ₂ O			353	601	3.99
Dy(DPAP) ₃ ·12 H ₂ O			354	484	2.08

^a The UV spectrum for 1.0×10^{-5} mol/1Sm(DPAP)₃ ethanol solution was determined.

conditions, and the maximum absorption wavelengths and molar absorption coefficients are given in Table 4. The absorption bands for Sm(DPAP)3 and Dy(DPAP)3 dilute solutions shifted to longer wavelengths compared with that of HDPAP ligand, which was attributed to expansion of π conjugated system caused by the metal coordination.

3.4. Fluorescence spectra

The excitation spectra for the original Sm(DPAP)₃·12-H₂O complex and 1.0×10^{-4} mol/l Sm(DPAP)₃ ethanol solution are shown in Fig. 2, monitored at 601 and 361 nm, respectively. 300-400 nm wide band centered at 353 nm was observed on the excitation spectrum for the solid Sm(DPAP)₃·12H₂O complex, and two excitation bands for the samarium complex ethanol dilute solution were located at 277 and 346 nm.

The emission spectrum of solid Sm-DPAP complex consists of four main lines at 565 nm (${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$), 601 nm (${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$), 645 nm (${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$), 712 nm $({}^{4}G_{5/2} \rightarrow {}^{6}H_{11/2})$ (Fig. 2(b)). Different from the ternary Sm- β -diketone-base complexes [21] with the electronic dipole transition (${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$) as the strongest emission



Fig. 2. Excitation and emission spectra for (a) 1.0×10^{-4} mol/l $Sm(DPAP)_3$ ethanol solution and (b) solid $Sm(DPAP)_3 \cdot 12H_2O$ at room temperature.



Fig. 3. Excitation and emission spectra for solid $Dy(DPAP)_3$.12H₂O at room temperature.

band, the magnetic dipole transition $({}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2})$ was the strongest emission band for the solid Sm-DPAP complex, due to the different symmetry of Sm³⁺ ions in the two kinds of samarium complexes. Weak characteristic emission peaks of Sm³⁺ ions and strong broad DPAP ligand fluorescence emission band centered at 388 nm were observed on the emission spectrum for 1.0×10^{-4} mol/1 Sm(DPAP)₃ ethanol solution at room temperature (Fig. 2(a)).

The excitation and emission spectra for the original $Dy(DPAP)_3$ ·12H₂O is shown in Fig. 3. A broad excitation band (300–400 nm) centered at 354 nm was observed on the excitation spectrum for solid $Dy(DPAP)_3$ ·12H₂O, and the emission spectrum for the solid dysprosium complex showed a wide phosphorescence emission band centered at 484 nm at room temperature, which was attributed to the DPAP ligand emission. Due to the OH quenching effect, the DPAP ligand phosphorescence emission was not observed for 1.0×10^{-4} mol/l Dy(DPAP)₃ ethanol solution at room temperature.

3.5. Triplet state of the ligand and energy transfer

The value of the lowest triplet state level for HDPAP ligand is 20,477 cm⁻¹, calculated from the phosphorescence spectrum for Gd(DPAP)₃ complex dimethyl sulfoxide dilute solution determined at 77 K. The lowest triplet state level of the DPAP ligand was higher by 2778 cm^{-1} than the lowest excited state level of Sm^{3+} , ${}^{4}G_{5/2}$, and may be matched with the excitation state levels of the latter according to the energy gap study on the Eu^{3+} and Tb³⁺ organic complexes [22,23]. However, week characteristic emission of Sm^{3+} ions with the DPAP ligand fluorescence were observed on the emission spectrum for the Sm(DPAP)₃ ethanol dilute solution at room temperature, which was attributed to the following factors. First, the energy gap between the lowest excited state level (${}^{4}G_{5/2}$) and the highest ground state level (${}^{6}F_{11/2}$) of Sm³⁺ ions is shorter than that of Eu³⁺ or Tb³⁺ ions, and the samarium complex is apt to be deactivated by the solvent O-H

vibrations. Second, the DPAP ligand fluorescence emission and the energy transfer process from the lowest triplet state level of the ligand to the excited state levels of Sm^{3+} ions are two competitive processes, and the organic ligand with large conjugated structure may not be beneficial to the energy transfer from the ligand to the central metal ions. So, it is proposed that a good organic ligand of rare earth ions should have proper triplet energy levels with mediate conjugated structure.

The excitation spectrum for solid $\text{Sm}(\text{DPAP})_3$ complex showed that most of the excitation energy was mainly absorbed by the ligand, and then some absorbed energy was transferred to the central Sm^{3+} ions, emitting the characteristic fluorescence of the latter, while the ligand keeps its emission itself in shorter wavelengths. The dominant luminescence mechanism for the solid $\text{Sm}(\text{DPAP})_3$ complex was given as luminescence from the triplet state of the ligand to the central samarium ion $(\text{L}^* \rightarrow \text{M})$ (shown in Fig. 4).

It is desirable to mention that the characteristic emission of Sm³⁺ ions for solid Sm(DPAP)₃·12H₂O complex was also observed under light excitation at 442, 466 and 477 nm, respectively. These excitation bands emerged from the direct absorption of some of the Sm³⁺ excited states, e.g. 477 nm due to the ${}^{6}\text{H}_{5/2} \rightarrow {}^{4}\text{I}_{j}$ (j = 9/2, 11/2) transition. The facts showed evidences that there are also directly excitation mechanisms for the Sm³⁺ ions in the solid samarium complex, for example:

$$\operatorname{Sm}^{3+} \xrightarrow{h\nu} \operatorname{Sm}^{3+**}({}^{4}I_{9/2}) \xrightarrow{\operatorname{non-radiative}} \operatorname{Sm}^{3+*}({}^{4}G_{5/2})$$
$$\times \xrightarrow{\operatorname{radiative} 6} H_{i} + hv' \quad (j = 5/2, 7/2, 9/2, 11/2)$$

Only the phosphorescence of the DPAP ligands was observed for the solid dysprosium complex without any characteristic emission of Dy^{3+} ions at room temperature. The lowest triplet energy level of the DPAP ligands was lower than that of the lowest excited state level of Dy^{3+} ions, and the energy could not be transferred to the central dysprosium ions through the triplet energy level of the DPAP ligands (Fig. 4).



Fig. 4. Energy transfer scheme for Sm(DPAP)3 and Dy(DPAP)3 complexes.

4. Conclusions

A novel samarium(III) complex and a novel dysprosium(III) complex, tris(diphenylamine carbonyl 2-pyridine carboxylato) samarium(III) and tris(diphenylamine carbonyl 2-pyridine carboxylato) dysprosium(III), have been synthesized. The crystal structures of the samarium complex and the dysprosium complex showed that they are electroneutral molecules, in which the central Sm³⁺ and Dy³⁺ ions are wrapped by three novel tridentate organic ligands, with some water molecules located around the outer shell of Sm(DPAP)₃ and Dy(DPAP)₃ complexes. The solid samarium complex emits characteristic emission of Sm³⁺ ions. The energy gap between the excited triplet energy levels of the organic ligands [$T^*(L)$] and the lowest excited energy levels of rare earth ions is an important factor to the luminescence of rare earth organic complexes.

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