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Original article

Synthesis, crystal structures and luminescence properties of europium and terbium picolinamide complexes

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ABSTRACT

The novel coordination structures of europium and terbium chloride-picolinamide complexes ($EuCl_3{\cdot}(C_6H_6N_2O)_2{\cdot}5H_2O$, Eu-pa and $TbCl_3{\cdot}(C_6H_6N_2O)_2{\cdot}5H_2O$, Tb-pa) are reported. The crystal structures in the solid state are characterized by X-ray single crystal diffraction, FTIR, Raman, FIR, THz and luminescence spectroscopy. In the crystal structures, the pyridyl nitrogen and carbonyl oxygen atoms in picolinamide are coordinated to the metal ions to form a five-membered ring structure. The experimental results indicate the similar coordination structures of Eu and Tb-pa complexes and the changes of hydrogen bonds and conformation of the ligands induced by complexation. The results provide models for the coordination structures of lanthanide ions with ligands having amide groups.

1. Introduction

The luminescent and magnetic properties of lanthanide complexes have attracted much attention for decades. Lanthanide ions are critical for a variety of applications, such as chromophores for LEDs and as probes and labels in a variety of biological and chemical applications. For example, lanthanide complexes were used for the imaging of cancer [1] and the detection of proteins and nucleic acids [2]. The probes based on europium and terbium ions are of special interest because of the particularly suitable spectroscopic properties of these ions. For example, a new and rapid fluorescence stain method for histologic sections was developed using Eu and Tb complexes [3]. The interactions between the lanthanide ions and biomolecules are involved in these applications of lanthanide ions. The carboxamide group is an important moiety in the primary structure of proteins and a versatile donor in coordination chemistry [4,5], so the binding modes of lanthanide ions with ligand having amide groups is of great interest.

For investigation on the interactions between lanthanide ions and amide groups, picolinamide (denoted as pa) is selected as a model ligand. Besides its importance in living organisms, picolinamide is an interesting ligand in inorganic chemistry [6–15]. It is used as N, O-bidentate or N, O, O-tridentate ligand (the carbonyl oxygen coordinates with two metal ions). The crystal structures of $[Ag(pia)_2](NO_3){\cdot}H_2O$, $[Zn(H_2O)_2(picolinamide)_2]I_2$, $[Co(H_2O)_2(picolinamide)_2](NO_3)_2$, $[Cu_{1.5}(picolinamide)_3](H_2O)_6$, $[Co(picolinamide)_2(H_2O)_2]{\cdot}Cl_2$ and $SrCl_2{\cdot}C_6H_6N_2O{\cdot}H_2O$ have been reported [6–10]. In these metal complexes, pa acts as an efficient competitive ligand toward halides or nitrate ions for coordination sites of these metal centers.

Here we report the synthesis of europium and terbium complexes with pa. Their structural characterization has been carried out by spectroscopic and X-ray diffraction analysis to compare the coordination differences of two lanthanide ions.

2. Experimental

The lanthanide chlorides were prepared and crystallized from the corresponding rare earth oxide of high purity (99.99%) with HCl. Picolinamide was purchased from J&K Company in China. The preparation of these metal complexes was as follows: 3 mmol of the ligand and 3 mmol or 6 mmol of metal chlorides were

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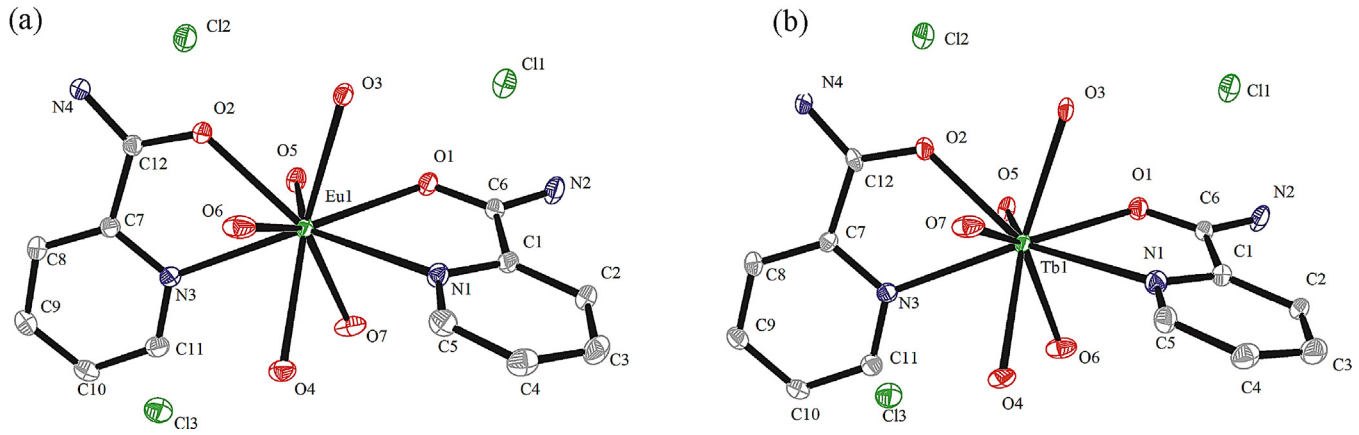

Fig. 1. The crystal structures of Eu-pa and Tb-pa.

dissolved in H_2O/ethanol and the mixture was heated on a water bath to prepare saturated solutions of metal–ligand complexes, then the concentrated solutions were filtered and cooled for crystallization. Anal. calcd. for Eu-pa ($EuCl_3{\cdot}(C_6H_6N_2O)_2{\cdot}5H_2O$): C, 24.32; H, 3.74; N, 9.45. Found: C, 24.16; H, 3.70; N, 9.43. Anal. calcd. for Tb-pa ($TbCl_3{\cdot}(C_6H_6N_2O)_2{\cdot}5H_2O$): C, 24.04; H, 3.70; N, 9.34. Found: C, 24.32; H, 3.66; N, 9.29.

Data for the metal complexes were collected on a Rigaku Saturn 724 spectrometer (Eu-pa) equipped with a graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) or Saturn 724+ spectrometer using rotate target (λ = 0.71073 Å) at 173(2) K (Tb-pa). The structures were resolved by the direct methods with SHELX-97 and refined using the full-matrix least-squares on F^2 method. Empirical absorption corrections were applied and anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model [16].

The mid-IR spectra were measured on a Nicolet Magna IN10 spectrometer using micro-IR method at 4 cm^{-1} resolution. Element analyses were carried out on an Elementar Vario EL spectrometer. The THz absorption spectra were recorded on the THz time-domain device of Capital Normal University of China, based on photoconductive switches for generation and electro-optical crystal detection of the far-infrared light [17]. The far-IR spectra of the molecules in the 650–50 cm^{-1} region were measured using the commonly used Nujol mull method and were taken on a Nicolet Magna-IR 750 II Spectrometer at 8 cm^{-1} resolution and 128 scans. The Raman spectra were recorded on a Nicolet 6700 FTIR NXR FT-Raman module at 4 cm^{-1} resolution and 256 scans. The luminescence spectra of Eu-pa and Tb-pa were measured on a Hitachi F4500 luminescence spectrometer.

3. Results and discussion

3.1. The crystal structures of Eu-pa and Tb-pa

The crystal structures of Eu-pa and Tb-pa complexes are shown in Fig. 1. Crystal data and structure refinements of the metal complexes are listed in Table 1. The selected bond lengths and bond angles are listed in Table S1 in Supporting information. For Eu-pa and Tb-pa complexes ($[Ln(C_6H_6N_2O)_2(H_2O)_5]Cl_3$), crystallized in a monoclinic system, $C2/c$ space group, Ln^{3+} is 9-coordinated to two carbonyl oxygen atoms and two pyridyl nitrogen atoms from two pa ligands and five water molecules. Pa is an N, O-bidentate ligand here to form a five-membered ring structure. Chloride ions are only involved in forming hydrogen bonds. The Ln–O distances are between 2.371 and 2.497 Å (Eu), and 2.343 and 2.496 Å (Tb). The average Ln–O distances are 2.436 (Eu) and 2.410 Å (Tb). The Ln–N distances are 2.615 and 2.644 Å (Eu), 2.581 and 2.618 Å (Tb). The Ln–O, average Ln–O and Ln–N distances decreased along with the increase of atomic number, which is consistent with the lanthanide contraction effect. The changes of the O–C–N angles related to amide groups are as follows: 121.7(4)° and 121.9(4)° for Eu-pa, 123.0(8)° and 122.9(8)° for Tb-pa, which indicate the different degree of changes of pa conformation in the two complexes.

The torsion angles of O2–C12–C7–N3, O1–C6–C1–N1 and C2–C3–C4–C5 are −3.3(6)° (−1.6(12)°), −1.3(6)° (−2.3(12)°), 3.7(7)° (3.8(14)°) for Eu-pa (Tb-pa). The results indicate the torsion angles are within 5°, the pyridyl ring and the amide group are nearly coplanar and Eu and Tb ions cause different level of deviation from

Table 1
Crystal data and structure refinement for ten lanthanide-pa complexes.

	Eu-pa	Tb-pa
CCDC No.	918188	918189
Chemical formula	$EuCl_3{\cdot}(C_6H_6N_2O)_2{\cdot}5H_2O$	$TbCl_3{\cdot}(C_6H_6N_2O)_2{\cdot}5H_2O$
Formula weight	592.65	599.61
T (K)	173(2)	173(2)
Cryst syst	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
A (Å)	28.642(6)	28.575(6)
B (Å)	7.7281(15)	7.7257(15)
C (Å)	19.533(4)	19.463(4)
α (°)	90	90
β (°)	104.00(3)	104.02(3)
γ (°)	90	90
V (Å^3)	4195.1(14)	4168.7(14)
Z	8	8
D_{calcd} (g cm^{-3})	1.877	1.911
μ (Mo Kα) (mm^{-1})	3.412	3.817
F(0 0 0)	2336	2352
Crystal size (mm^3)	0.21 × 0.18 × 0.10	0.13 × 0.13 × 0.10
θ range for data collection (°)	1.47–27.49	1.47–27.47
Limiting indices	$-37 \le h \le 37$, $-9 \le k \le 10$, $-25 \le l \le 25$	$-36 \le h \le 36$, $-10 \le k \le 9$, $-25 \le l \le 25$
Reflections collected/unique	17,889/4800	16,443/4739
R_{int}	0.0437	0.0530
Completeness to θmax	99.9%	99.6%
Data/restraints/parameters	4800/0/244	4739/14/286
GOF on F^2	1.317	1.238
$R1$ [$I > 2\sigma(I)$]	0.0342	0.0609
$wR2$ [$I > 2\sigma(I)$]	0.1037	0.1424
$R1$ (all data)	0.0363	0.0640
$wR2$ (all data)	0.1101	0.1437
Largest diff. peak and hole (e Å^{-3})	0.831 and −0.957	4.392 and −1.683