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Synthesis, structures and luminescence properties of nine lanthanide complexes with triphenylphospine oxide and phenanthroline

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ABSTRACT

Nine new lanthanide complexes, $[Ln(OPPh_3)_2(phen)(NO_3)_3]$ (**1**–**5**) ($OPPh_3$ = triphenylphosphine oxide, phen = 1,10-phenanthroline, Ln = Ce, Gd, Tb, Ho, Eu) and $[Ln(OPPh_3)_2(C_2H_5OH)(NO_3)_3]$ (**6**–**9**) (Ln = Tb, Ho, Er, Tm), have been synthesized by the reactions of lanthanide nitrates, the $OPPh_3$ ligand and phen in acetonitrile (**1**–**4**) or ethanol (**5**–**9**) in the air. These title complexes were characterized by IR, elemental analyses, single-crystal X-ray diffraction analysis, luminescence, thermogravimetric analysis, ^1H NMR and ^{31}P NMR spectroscopy. Structure analysis shows complexes **1**–**9** consist of one Ln^{3+} cation and three NO_3^- anions, with the Ln ion being ten-coordinated (**1**–**5**) or nine-coordinated (**6**–**9**). In complexes **1**–**5**, two forms of $\pi\ldots\pi$ interactions exist between the phen rings and benzene rings from the $OPPh_3$ ligand. Robust $R_2^2(12)$ hydrogen bonds exist in complexes **6**–**9**. Solid luminescence spectra of compounds **5**, **3** and **6** are assigned to the emission of Eu^{3+}, Tb^{3+}. The emission lifetimes (1.14 ms of $^5D_0$ for compound **5**, 1.10 and 0.97 ms of $^5D_4$ for compounds **3** and **6**) and absolute emission quantum yields (26.88% for compound **5**, 11.36% and 2.16% for compounds **3** and **6**) were also determined.

1. Introduction

Complexes containing lanthanide metals are of great interest because of their technological importance in physicochemical, biochemical and medical applications [1–5]. In recent years they have attracted great attention for their function as catalysts for organic reactions [6,7]. Increasing interest in lanthanide PO-based complexes has been received over a few decades because of their attractive luminescent properties (narrow band emission, high quantum yields, long lifetimes) and their process ability, which are useful in a wide range of applications [8,9]. In f-element chemistry, phosphine oxides are ubiquitous ligands because of their strong coordination ability to lanthanide ions [10]. The solid coordination complexes of lanthanide compounds with $OPPh_3$ have previously been investigated by infrared and electronic spectroscopy, elemental analysis, luminescence and in solution by conductivity [11,12].

We are interested in the coordination chemistry of P═O ligands and their coordination capabilities. In our previous work, we have created some lanthanide complexes with the bidentate ligand tetrakis(O-isopropyl)methylenediphosphonate ($(iPrO)_2P(O)CH_2$-$P(O)(OiPr)_2$) [13], and the complex $[Y(Ph_3PO)_4(NO_3)_2][NO_3]$ with the ligand $OPPh_3$ [14].

In addition, 1,10-phenanthroline (phen) is often chosen as a nitrogen ancillary ligand because it is a bidentate chelating ligand with strong steric hindrance, which can enhance the luminescence quantum yields of lanthanide complexes [15–17]. In this work, by the reaction of lanthanide nitrates, triphenylphosphine oxide ($OPPh_3$) and 1,10-phenanthroline (phen) in acetonitrile (**1**–**4**) and ethanol (**5**–**9**) in the air, two series of nine new lanthanide complexes, $[Ln(OPPh_3)_2(phen)(NO_3)_3]$ (**1**–**5**) ($OPPh_3$ = triphenylphosphine oxide, phen = 1,10-phenanthroline, Ln = Ce, Gd, Tb, Ho, Eu) and $[Ln(OPPh_3)_2(C_2H_5OH)(NO_3)_3]$ (**6**–**9**) (Ln = Tb, Ho, Er, Tm) have been synthesized. All these complexes have luminescence properties, which is reported for the first time for lanthanide complexes with the $OPPh_3$ ligand. Among these complexes, **5**, **3** and **6** have attractive solid luminescence properties (narrow band emission, high quantum yields, long lifetimes) due to the emission of $Eu^{3+}$and Tb^{3+}. More intriguingly, complexes **3** and **5** have high quantum yields and long luminescence lifetimes compared with **6** due to the existence of the ancillary ligand phen. Moreover, the low prices of the $OPPh_3$ and phen ligands make it possible to make more economical luminescent devices. In the following text, we report the synthesis and a structural comparison of complexes **1**–**9**.

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2. Experimental

2.1. Materials and measurements

The reagents cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$), europium nitrate ($Eu(NO_3)_3{\cdot}6H_2O$), gadolinium nitrate ($Gd(NO_3)_3{\cdot}6H_2O$), terbium nitrate ($Tb(NO_3)_3{\cdot}6H_2O$), holmium nitrate ($Ho(NO_3)_3{\cdot}6H_2O$), erbium nitrate ($Er(NO_3)_3{\cdot}6H_2O$), thulium nitrate ($Tm(NO_3)_3{\cdot}6H_2O$), triphenylphosphine oxide ($OPPh_3$) and $C_{12}H_8N_2$ (phen) were purchased from Jinan Henghua Sci. & Tec. Co., Ltd. and used as received. All other materials were of analytical grade and used without further purification. All experiments were performed at ambient temperature. Elemental analyses (C, H) were performed on a Flash EA 1112 analyzer. IR spectra were recorded from KBr pellets on a Bruker EQUINOX 55 FT-spectrometer operating in the 4000–600 cm^{-1} region. Emission spectra were recorded on a Hitachi F-4500 Luminescence spectrophotometer. The lifetime measurements were performed with an Edinburgh Instruments FLS920 transient/steady-state luminescence spectrometer at room temperature. NMR experiments were carried out on a VNMRS-600 spectrometer using $CDCl_3$ as the solvent.

2.2. Synthesis of complexes **1**–**9**

2.2.1. Synthesis of complexes **1**–**4**

Complex **1**: $Ce(NO_3)_3{\cdot}6H_2O$ (0.2 mmol, 0.0868 g) was dissolved in CH_3CN (10 ml). After the mixture was stirred for 10 min, 1,10-phenanthroline (0.2 mmol, 0.0396 g) and triphenylphosphine oxide (0.4 mmol, 0.2224 g) was added to this mixture. Stirring was continued for 6 h at ambient temperature. After this time, any insoluble residues were removed by filtration, and the filtrate was evaporated slowly at room temperature for about one month to yield colorless crystalline products. Complexes **2**–**4** use the same method as **1**, only replacing $Ce(NO_3)_3{\cdot}6H_2O$ with $Gd(NO_3)_3{\cdot}6H_2O$, $Tb(NO_3)_3{\cdot}6H_2O$, $Ho(NO_3)_3{\cdot}6H_2O$ respectively.

$[Ce(OPPh_3)_2(phen)(NO_3)_3]$ (**1**), 54% yield. *Anal.* Calc. for $C_{48}H_{38}CeN_5O_{11}P_2$: C, 54.54; H, 3.65; N, 6.52. Found: C, 54.19; H, 3.58; N, 6.59%. IR (KBr disc, cm^{-1}): 3435m, 3057w, 2318w, 1590w, 1468s, 1438s, 1309s, 1153s, 1121s, 1091m, 1030m, 998w, 850w, 815w, 749m, 725s, 693s, 540vs, 460w.

$[Gd(OPPh_3)_2(phen)(NO_3)_3]$ (**2**), 57% yield. *Anal.* Calc. for $C_{48}H_{38}GdN_5O_{11}P_2$: C, 53.63; H, 3.55; N, 6.42. Found: C, 53.33; H, 3.52; N, 6.48%. IR (KBr disc, cm^{-1}): 3434m, 3057w, 2024w, 1590w, 1468s, 1438s, 1309s, 1152s, 1121s, 1092m, 1030m, 997w, 850w, 815w, 749m, 724s, 693s, 541vs, 460w, 415w.

$[Tb(OPPh_3)_2(phen)(NO_3)_3]$ (**3**), 60% yield. *Anal.* Calc. for $C_{48}H_{38}TbN_5O_{11}P_2$: C, 53.73; H, 3.61; N, 6.42. Found: C, 53.25; H, 3.51; N, 6.47%. IR (KBr disc, cm^{-1}): 3435m, 3054w, 2320w, 1590w, 1468s, 1437s, 1308s, 1153s, 1121s, 1092m, 1029m, 997w, 849w, 815m, 748s, 725s, 692s, 541vs, 460w, 416w.

$[Ho(OPPh_3)_2(phen)(NO_3)_3]$ (**4**), 56% yield. *Anal.* Calc. for $C_{48}H_{38}HoN_5O_{11}P_2$: C, 53.15; H, 3.51; N, 6.41. Found: C, 52.96; H, 3.49; N, 6.44%. IR (KBr disc, cm^{-1}): 3434m, 3057w, 2024w, 1625w, 1590w, 1468s, 1438s, 1309s, 1153s, 1121s, 1092m, 1030m, 997w, 850w, 815w, 749m, 725s, 693s, 541vs, 460w.

2.2.2. Synthesis of complex $[Eu(OPPh_3)_2(phen)(NO_3)_3]$ (**5**)

Compound **5** was prepared in a manner similar to that described for **1**, except that C_2H_5OH (10 ml) was used instead of CH_3CN, and $Eu(NO_3)_3{\cdot}6H_2O$ (0.02 mmol, 0.0892 g) was used instead of $Ce(NO_3)_3{\cdot}6H_2O$. Yield: 46%. *Anal.* Calc. for $C_{48}H_{38}EuN_5O_{11}P_2$: C, 53.96; H, 3.61; N, 6.47. Found: C, 53.60; H, 3.54; N, 6.51%. IR (KBr disc, cm^{-1}): 3436m, 3055w, 2023w, 1625w, 1591w, 1469s, 1438s, 1306s, 1153s, 1121s, 1092m, 1029m, 998w, 849w, 816w, 749m, 724s, 694s, 540vs, 460w, 415w.

2.2.3. Synthesis of complexes **6**–**9**

Complexes **6**–**9** were obtained according to a procedure similar to that for complex **5**.

$[Tb(OPPh_3)_2(C_2H_5OH)(NO_3)_3]$ (**6**), 52% yield. *Anal.* Calc. for $C_{38}H_{36}TbN_3O_{12}P_2$: C, 48.38; H, 3.92; N, 7.33. Found: C, 48.12; H, 3.80; N, 7.39%. IR (KBr disc, cm^{-1}): 3366m, 3058w, 2980w, 2300w, 1591w, 1467vs, 1437s, 1384m, 1310vs, 1169s, 1152vs, 1120s, 1092m, 1030m, 997w, 872w, 815m, 750m, 725s, 691s, 539vs, 461w.

$[Ho(OPPh_3)_2(C_2H_5OH)(NO_3)_3]$ (**7**), 51% yield. *Anal.* Calc. for $C_{38}H_{36}HoN_3O_{12}P_2$: C, 48.27; H, 3.83; N, 7.28. Found: C, 47.82; H, 3.78; N, 7.34%. IR (KBr disc, cm^{-1}): 3118m, 2980w, 2300w, 1567vs, 1496w, 1471m, 1452s, 1383vs, 1306s, 1148vs, 1120vs, 1090s, 1043m, 960w, 884w, 809w, 743s, 691w, 513w.

$[Er(OPPh_3)_2(C_2H_5OH)(NO_3)_3]$ (**8**), 50% yield. *Anal.* Calc. for $C_{38}H_{36}ErN_3O_{12}P_2$: C, 47.92; H, 3.82; N, 7.28. Found: C, 47.70; H, 3.77; N, 7.32%. IR (KBr disc, cm^{-1}): 3367s, 3058m, 2499w, 2354w, 1638s, 1591s, 1469s, 1315s, 1155vs, 1120vs, 1031s, 997m, 872m, 814m, 748s, 724s, 691w, 537vs.

$[Tm(OPPh_3)_2(C_2H_5OH)(NO_3)_3]$ (**9**), 52% yield. *Anal.* Calc. for $C_{38}H_{36}TmN_3O_{12}P_2$: C, 47.68; H, 3.81; N, 7.23. Found: C, 47.62; H, 3.76; N, 7.31%. IR (KBr disc, cm^{-1}): 3415s, 2426w, 2344w, 1638s, 1463s, 1436s, 1384vs, 1306s, 1148vs, 1120vs, 1090s, 1028s, 997m, 871m, 815m, 752s, 724s, 691w, 617w, 539vs.

2.3. Crystal structure determination and refinement

Single-crystal X-ray diffraction studies of complexes **1**–**9** were performed on a Bruker SMART diffractometer equipped with a CCD area detector with a graphite monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo Kα radiation (λ = 0.71073 Å). All data are corrected by semi-empirical method using the SADABS program. The program SAINT was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL-97 package and refined with SHELXL. Metal atom centers were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinements were performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. All the hydrogen atoms were first found in difference electron density maps, and then placed in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they are bonded. Further crystallographic data and experimental details for structural analyses of all the complexes are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations for products **1**–**9** in are given in Tables S1 and 3 respectively.

3. Results and discussion

3.1. Synthesis of the complexes

The nine complexes **1**–**9** were synthesized by the reactions of lanthanide nitrates with triphenylphosphine oxide ($OPPh_3$) and 1,10-phenanthroline (phen) in the solvent of acetonitrile for **1**–**4** or ethanol for **5**–**9** (Scheme 1).

In **1**–**4**, the lanthanide ions are coordinated by $OPPh_3$ and phen, due to the low coordinating ability of acetonitrile. In complex **5**, the lanthanide ion is coordinated by phen and $OPPh_3$, while the lanthanide ions in **6**–**9** are unexpectedly coordinated by ethanol and $OPPh_3$ instead. The different coordination patterns between **5** and **6**–**9** may be explained by four reasons. Firstly, 1,10-phenan-