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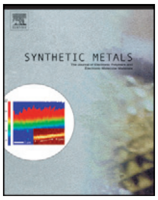

Lanthanide imidodiphosphinate complexes
Synthesis, structure and new aspects of electroluminescent properties

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ABSTRACT

The lanthanide imidodiphosphinate complexes Ln(pip)$_3$ (Ln = Ce, Nd, Tb, Ho) were prepared from the corresponding Ln[N(SiMe$_3$)$_2$]$_3$ with [Ph$_2$P(O)]$_2$NH in a quantitative yield. X-ray single structure analysis of Ce(pip)$_3$ has revealed that the lanthanide ion in these compounds coordinated by three bidentate [Ph$_2$P(O)NP(O)Ph$_2$]$^-$ ligands and THF molecule. With respect to the organic light emitting diodes (OLED) application, the simple electroluminescent (EL) devices with a multilayer configuration ITO/TPD/Ln(pip)$_3$/Yb, ITO/CBP/Ln(pip)$_3$/Yb, ITO/TPD/Ln(pip)$_3$/Alq$_3$/Yb, ITO/TPD/Alq$_3$/Ln(pip)$_3$/Yb were fabricated. It was found that the lanthanide imidodiphosphinate complexes possess the hole-blocking and electron-transporting ability and it was also observed the exciplex emission between these complexes and TPD.

1. Introduction

The lanthanide metals are unique elements which fascinating luminescent properties stipulated their outstanding role in lighting and light conversion technologies [1]. In the past decade the main attention was focused on the application of lanthanide complexes as electroluminescent (EL) materials for organic light emitting diodes (OLED) [2,3]. One of the most important problems in this field is a selection of suitable ligands which would provide the high efficiency of these complexes. Up to now the main research were concerned on the lanthanide β-diketonate complexes which are limited in terms of practical applications because their poor photo and electro stability [4,5]. Recently, as an alternative to these complexes, lanthanide imidodiphosphinate complexes were suggested and in particular the terbium imidodiphosphinate Tb[Ph$_2$P(O)NP(O)Ph$_2$]$_3$ Tb(pip)$_3$ has been studied in OLED [6]. In this case the much bulkier imidodiphosphinato ligand was used as the inorganic analogue of the β-diketonate ligand. However, it should be noted that significantly much attention was turned out to photoluminescent properties of such imidodiphosphinate lanthanide complexes [7–10]. It was shown that these ligands are suitable for sensitizing metal-centered emission in the visible range for the ions Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+} [7,10] and in near-infrared range for Nd^{3+}, Er^{3+} and Yb^{3+} [8–10]. These data prompted us to investigate the electroluminescent properties of imidodiphosphinate complexes of Ce, Nd and Ho and compare them with the properties of Tb analogue prepared under the same conditions. Here we describe the synthesis of Ln(pip)$_3$ (Ln = Ce, Nd, Tb and Ho) by a new way and electroluminescent properties of OLED devices consisted of exclusively vacuum deposited layers using ITO glass as the anode, N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) as the hole-transporting layer, Ln(pip)$_3$ (Ln = Ce, Nd, Tb and Ho) as the active layers and Yb as the cathode. It was found that lanthanide imidodiphosphinate complexes possess the hole-blocking ability and it was also observed the exciplex formation between these complexes and TPD.

2. Experimental

2.1. General

N,*N*′-diphenyl-*N*,*N*′(di(m-tolyl)benzidine (TPD), 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl (CBP), tris(8-quinolinolate)aluminum (Alq$_3$) and Yb were purchased from Sigma–Aldrich. The synthesis of imidodiphosphinate complexes Ln(pip)$_3$ was carried out in vacuum using standard Schlenk techniques. Tris(trimethylsilylamide)

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complexes Ln$[N(SiMe_3)_2]_3$ (Ln = Ce, Nd, Tb, Ho) [11] and imidodiphosphine $[Ph_2P(O)]_2NH$ [12] were prepared according the published procedure. IR spectra were recorded in the region from 4000 cm^{-1} to 450 cm^{-1} on a PerkinElmer 577 spectrometer. The samples were prepared as a Nujol mull on KBr plates.

2.2. Synthesis

2.2.1. Tris(tetraphenylimidodiphosphonato-O,O′)-cerium–Ce(pip)$_3$ (**1**)

To a suspension of $[Ph_2P(O)]_2NH$ (0.94 g, 2.25 mmol) in THF (20 ml) was added a solution of Ce$[N(SiMe_3)_2]_3$ (0.47 g, 0.75 mmol) in THF (20 ml). The reaction mixture was stirred for 12 h at room temperature. After removal of volatile components in vacuum a crystalline solid was obtained. The formed pale-blue crystals dried under vacuum and recrystallized from toluene to give 0.96 g (92%) of **1**. The compound is air and moisture stable. Anal. Calc. for $C_{72}CeH_{60}N_3O_6P_6$ (1389.25): C 62.25; Ce 10.09; H 4.35; N 3.02; P 13.38. Found: C 62.17; Ce 10.07; H 4.53; N 3.53; P 13.35. IR (Nujol, cm^{-1}) 3074 (br), 3050 (br), 1592 (w), 1218 (m), 1128 (m), 1086 (m), 1066 (w), 1027 (w), 996 (w), 726 (m), 694 (m), 585 (w), 555 (m), 518 (w).

2.2.2. Tris(tetraphenylimidodiphosphonato-O,O′)-neodymium–Nd(pip)$_3$ (**2**)

The compound was prepared similarly to **1** from Nd$[N(SiMe_3)_2]_3$ (0.47 g, 0.75 mmol) and $[Ph_2P(O)]_2NH$ (0.94 g, 2.25 mmol). Yield of **2**: 0.95 g, 90%. Anal. Calc. for $C_{72}H_{60}N_3NdO_6P_6$ (1393.38): C 62.06; H 4.34; N 3.02; Nd 10.35; P 13.34. Found: C 61.90; H 4.56; N 3.03; Nd 9.70; P 12.96. IR (Nujol, cm^{-1}) 3074 (br), 3050 (br), 1594 (w), 1220 (m), 1129 (m), 1087 (m), 1065 (w), 1025 (w), 997 (w), 725 (m), 694 (m), 583 (w), 554 (m), 518 (w).

2.2.3. Tris(tetraphenylimidodiphosphonato-O,O′)-terbium–Tb(pip)$_3$ (**3**)

The compound was prepared similarly to **1** from Tb$[N(SiMe_3)_2]_3$ (0.48 g, 0.75 mmol) and $[Ph_2P(O)]_2NH$ (0.94 g, 2.25 mmol). Yield of **3**: 0.84 g, 80%. Anal. Calc. for $C_{72}H_{60}N_3O_6P_6Tb$ (1408.06): C 61.42; H 4.29; N 2.98; P 13.20; Tb 11.29. Found: C 61.19; H 4.59; N 2.92; P 13.21; Tb 10.89. IR (Nujol, cm^{-1}) 3074 (br), 3050 (br), 1592 (w), 1218 (m), 1127 (m), 1088 (m), 1066 (w), 1026 (w), 996 (w), 725 (m), 694 (m), 586 (w), 554 (m), 520 (w).

2.2.4. Tris(tetraphenylimidodiphosphonato-O,O’)-holmium–Ho(pip)$_3$ (**4**)

The compound was prepared similarly to **1** from Ho$[N(SiMe_3)_2]_3$ (0.48 g, 0.75 mmol) and $[Ph_2P(O)]_2NH$ (0.94 g, 2.25 mmol). Yield of **4**: 0.96 g, 91%. Anal. Calc. for $C_{72}H_{60}HoN_3O_6P_6$ (1414.06): C 61.16; H 4.28; Ho 11.66; N 2.97; P 13.14. Found: C 61.35; H 4.10; Ho 11.10; N 2.95; P 12.56. IR (Nujol, cm^{-1}) 3074 (br), 3050 (br), 1592 (w), 1219 (m), 1128 (m), 1088 (m), 1065 (w), 1026 (w), 997 (w), 725 (m), 694 (m), 584 (w), 554 (m), 519 (w).

2.3. X-ray crystallography study

The X-ray diffraction data were collected on a SMART APEX diffractometer (graphite-monochromated, MoK$_\alpha$-radiation, φ–ω-scan technique, = 0.71073 Å). The intensity data were integrated by SAINT program [13]. SADABS [14] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined on F^2 using all reflections with SHELXTL package [15]. All non-hydrogen atoms were refined anisotropically. H-atoms in [Ce(pip)$_3$(THF)](THF)$_{1.5}$ placed in calculated positions and refined in the “riding-model”. SADABS was used to perform area-detector scaling and absorption corrections. Details of crystallographic, collection and refinement data for [Ce(pip)$_3$(THF)](THF)$_{1.5}$ are shown in Table 1.

Table 1
The details of crystallographic, collection and refinement data for [Ce(pip)$_3$(THF)](THF)$_{1.5}$.

Empirical formula	$C_{40}H_{37}N_4O_6Sc$
Empirical formula	$C_{82}H_{80}CeN_3O_{8.5}P_6$
Formula weight	1569.43
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, *P*-1
Unit cell dimensions	
a (Å)	12.5004(3)
b (Å)	14.1388(4)
c (Å)	23.7501(7)
α (°)	91.9620(10)
β (°)	99.0680(10)
γ (°)	115.2200(10)
Volume (Å^3)	3725.79(18)
Z calculated density (Mg/m^3)	2, 1.399
Absorption coefficient (mm^{-1})	0.799
F(000)	1618
Crystal size (mm)	0.29 × 0.25 × 0.15
θ range for data collection (°)	2.62–26.00
Limiting indices	$-15 \le h \le 14$, $-17 \le k \le 17$, $-29 \le l \le 21$
Reflections collected/unique (R_{int})	22377/14518 (0.0244)
Completeness to θ = 26.50	99.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8895 and 0.8013
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	14518/28/922
Goodness-of-fit on F^2	1.060
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0427$, $wR_2 = 0.1004$
R indices (all data)	$R_1 = 0.0599$, $wR_2 = 0.1065$
Largest diff. peak and hole (eÅ^{-3})	1.523 and −1.447

2.4. Device fabrication

OLED devices were prepared in a vacuum system with different evaporation chambers for different types of organic and metal layers (cluster-tool) [16]. The simple non-doped two-layer devices ITO/TPD/Ln(pip)$_3$/Yb, ITO/CBP/Ln(pip)$_3$/Yb, consisting of N,N’-Diphenyl-N,N’(di(m-tolyl)benzidine (TPD) or 4,4′-bis(N-carbazolyl)-1,1′-biphenyl (CBP) as a hole transport layer, and three-layer devices ITO/TPD/Ln(pip)$_3$/Alq$_3$/Yb, ITO/TPD/Alq$_3$/Ln(pip)$_3$/Yb were fabricated (Fig. 1). A commercial ITO on glass substrate with 100 Ω/sq. was used as anode material (Merck Balzers) and commercial Yb metal (Sigma–Aldrich) as cathode material. The constituent organic (45 nm), lanthanide complex (30 nm), Alq$_3$ (15 nm) and metal (150 nm) layers were deposited using thermal vacuum evaporation (at a base pressure of approximately 10^{-6} mbar) of commercial grade TPD, CBP, Alq$_3$ and Yb metal, freshly synthesized Ln(pip)$_3$ (Ln = Ce, Nd, Tb, Ho). The active area of the devices was a circle with Ø 8 mm. The EL spectra and current–voltage luminescence characteristics were measured with an Ocean Optics USB-2000 fluorimeter and a computer controlled TEC-23 power supply under ambient conditions.

3. Results and discussion

3.1. Synthesis and structure

Previously we presented a convenient synthetic way of preparing metal complexes for OLEDs, which affords neutral mononuclear water- and acid residual-free compounds in high yield [17–18]. This method based on the chemical reactions of lanthanide silylamides Ln$[N(SiMe_3)_2]_3$ with the substrates containing a labile hydrogen atom such as alcohols, thiols, selenols yielding the respective derivatives of Ln(XR)$_3$ type.