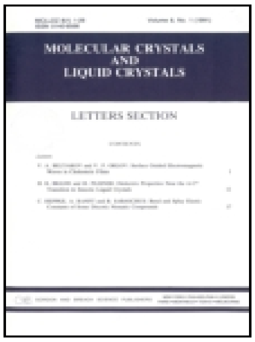

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Xia Yin, Jin-Niu Tang, Gang-Hong Pan, Wei-Man Tian, Wen-Jia Xu & Zhong-Jing Huang (2015) Hydrothermal Synthesis, Structure, Properties of a Novel Supramolecular Complex: [LaCd(bpy)$_4$(NO$_3$)$_5$], Molecular Crystals and Liquid Crystals, 606:1, 208-215, DOI: 10.1080/15421406.2014.905318

To link to this article: http://dx.doi.org/10.1080/15421406.2014.905318

Mol. Cryst. Liq. Cryst., Vol. 606: pp. 208–215, 2015

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.905318

Hydrothermal Synthesis, Structure, Properties of a Novel Supramolecular Complex: [LaCd(bpy)$_4$(NO$_3$)$_5$]

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A novel lanthanum cadmium complex [LaCd(bpy)$_4$(NO$_3$)$_5$] (where bpy = 2,2′-Bipyridine) has been synthesized and structurally characterized by X-ray diffraction method, elemental analysis, spectral method (IR), powder X-ray diffraction (XRD), electronic spectra (UV–vis) and photoluminescence properties. The complex crystallizes in the monoclinic space group P21/c *with unit cell parameters* a = *16.883(2) Å,* b = *14.382(2) Å,* c = *18.981(3) Å, β = 96.806(2),* V = *4576.5(11) Å^3, and* Z = *4. The complex is completed by two crystallographically and chemically independent, octahedrally coordinated Cd(II) ion and icosahedronly coordinated La(III) ion. The electronic spectra and photoluminescence of the complex has been described.*

[Supplemental materials are available for this article. Go to the publisher's online edition of Molecular Crystals and Liquid Crystals to view the free supplemental file.]

Keywords Crystal structure; electronic spectra; hydrothermal synthesis; lanthanum cadmium complex; photoluminescence

Introduction

Lanthanide ions and their complexes with organic ligands have generated a continuously growing interest over the last decades. These elements show typical electronic properties that potentially give great advantages to the complexes they form with organic ligands. In the trivalent state, they are hard Lewis acids that have interesting applications in catalysis in the fields of polymer synthesis [1–5], organic chemistry [6–13], and bioinorganic chemistry [14–20].

For various reasons, Lewis bases such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) are being studied. First, both of these are chelating ligands that are known to readily coordinate in a bidentate fashion with lanthanide cations [21–23] making them

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ideal candidates to incorporate into our materials. Second, and more importantly, both ligands are known to participate in metal ligand charge transfer (MLCT) and thus enhance emission of lanthanide (acceptor) cations via ligand (donor) excitation. In the case of bpy [24–26], MLCT and enhancement of luminescence intensity has been attributed to ligand chelation to the Ln^{3+} ion, which can effectively increase the rigidity of coordination polymers and reduce the loss of energy by radiationless decay. Additionally, enhancement in the excited-state lifetime has been observed [27].

Herein, we report on a novel lanthanum cadmium complex that incorporate bpy auxiliary ligands $[LaCd(bpy)_4(NO_3)_5]$. The synthetic route, structures, Electronic Spectra and Fluorescent properties are discussed.

Experimental

All chemicals were commercial materials of analytical grade and used without purification. Elemental analysis for C, H, and N was carried out on a Perkin-Elmer 2400 II elemental analyzer. The FT-IR spectrum was obtained on a PE Spectrum One FT-IR Spectrometer Fourier transform infrared spectroscopy in the 4000–400 cm^{-1} regions, using KBr pellets. Powder X-ray diffraction patterns were obtained using a pinhole camera (Anton Paar) operating with a point focused Ni-filtered Cu Kα radiation in the 2θ range from 5° to 50° with a scan rate of 0.08° s^{-1}. The optical properties were analyzed by the UV–vis diffuse reflectance spectroscopy (DRS) using a UV–vis spectrophotometer (Cary-500, Varian Co.), in which $BaSO_4$ was used as the internal standard.

Synthesis of $[LaCd(bpy)_4(NO_3)_5]$

The reagents of $3CdSO_4 \cdot 8H_2O$ (0.2565 g, 0.33 mmol), La_2O_3 (0.1626 g, 0.5 mmol), bpy (0.3126 g, 2 mmol), nitric acid (0.15 mL) and 15 mL water were placed in a reactor and the mixture was stirred for 0.5 hr. The resulting mixture was sealed in a 25 mL Teonlined stainless reactor, kept under autogenous pressure at 130°C for 72 hr and then slowly cooled to room temperature and filtered. The filtrate was allowed to slowly concentrate at room temperature and after one month colorless crystals of 1. The colorless block crystals suitable for X- ray diffraction were isolated directly, yield: 45%, based on La. Anal. Calcd. for $C_{40}H_{32}CdLaN_{13}O_{15}$ (%): C,40.51; H, 2.72; N, 15.35. Found: C, 40.37; H, 2.76; N, 15.53. IR data (KBr pellets, cm^{-1}): 2488 (m), 2388 (w), 1596 (m), 1456 (s), 1324 (s), 1177 (w), 1038 (s), 1011 (m), 904 (m), 816 (s), 765 (m), 740 (m), 644 (w), 598 (w), 484 (w), 443 (w).

Crystal Structure Determination

Single crystal of the complex was mounted on glass fibers and measured on a Bruker SMART CCD area detector at 298 K using graphite mono-chromated Mo Ka radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied using the SADABS program [28]. The structure was solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXTL program [29]. All non-hydrogen atoms were refined anisotronically. A summary of the crystallographic data and structure refinement is shown in Table 1, selected bond lengths and angles of the complexes are listed in Table 2.

Table 1. Experimental data for complex

Empirical formula	$C_{40}H_{32}CdLaN_{13}O_{15}$
Formula weight	1186.10
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *P21/c*
a (Å)	16.883(2)
b (Å)	14.382(2)
c (Å)	18.981(3)
β (°)	96.806(2)
Volume (Å^3)	4576.5(11)
Z	4
$D_{\text{calc.}}$ (mg m^{-3})	1.721
Absorption coefficient (mm^{-1})	1.469
F(000)	2352
Crystal size	0.26 × 0.24 × 0.21
θ range for data collection (°)	1.21–25.00
Reflections collected	24432
Unique reflections	8061 [$R_{(\text{int})} = 0.0338$]
Completeness to $\theta = 25.00$	99.9%
Absorption correction	Semi-empirical
Max. and min. transmission	0.735 and 0.689
Data/restraints/parameters	8061/0/631
Goodness-of-fit on F^2	1.027
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0284$, $wR_2 = 0.0685$
R indices (all data)	$R_1 = 0.0409$, $wR_2 = 0.0750$
Largest diff. peak and hole (e Å^{-3})	0.316 and −0.621

Results and Discussion

Description of the Structure

Single crystal X-ray diffraction analysis shows that the asymmetric unit of complex consists of one Cd(II) ion, one La(III) ion, four bpy ligand and five bidentate nitrates. As depicted in Fig. 1, the structure of complex [$LaCd(bpy)_4(NO_3)_5$] is most readily described as two crystallographically and chemically independent, octahedrally coordinated Cd(II) ion and icosahedronly coordinated La(III) ion. The coordination environment around the Cd(II) center is best portrayed as a distorted [CdN6] octahedral geometry, ligated by six nitrogen atoms from three bpy ligand, the La(III) ion possesses a distorted [LaN2O10] icosahedron geometry which is completed by two nitrogen atoms from one bpy and ten oxygen atoms from five bidentate nitrates. Thus, we have two chemically distinct species separated from each other and from neighboring molecules by ordinary van der Waals distances (C—H· · ·O non-classical hydrogen bonding). The Cd–N bond lengths vary from 2.291 (3) to 2.376 (3) Å, while the La–N bond lengths are from 2.740 (2) to 2.786 (2) Å. The La–O bond lengths are vary from 2.630 (2) to 2.792 (3) Å. As expected the N–Cd–N angles within the chelate ring are less than 90°, ranging from 70.33 (10) to 71.41 (11)° with no obvious reason for

Table 2. The selected bond lengths (Å) and angles (°)

Cd(1)-N(13)	2.291(3)	Cd(1)-N(8)	2.329(3)
Cd(1)-N(9)	2.351(3)	Cd(1)-N(12)	2.358(3)
Cd(1)-N(11)	2.371(3)	Cd(1)-N(10)	2.376(3)
La(1)-O(8)	2.630(2)	La(1)-O(14)	2.640(2)
La(1)-O(5)	2.646(2)	La(1)-O(10)	2.659(2)
La(1)-O(4)	2.677(2)	La(1)-O(11)	2.680(2)
La(1)-O(1)	2.681(2)	La(1)-O(2)	2.689(2)
La(1)-O(13)	2.690(3)	La(1)-O(7)	2.792(3)
La(1)-N(1)	2.740(2)	La(1)-N(2)	2.786(2)
N(13)-Cd(1)-N(8)	97.70(10)	N(13)-Cd(1)-N(9)	114.65(9)
N(8)-Cd(1)-N(9)	70.33(11)	N(13)-Cd(1)-N(12)	71.41(10)
N(8)-Cd(1)-N(12)	106.74(11)	N(9)-Cd(1)-N(12)	173.32(10)
N(13)-Cd(1)-N(11)	104.00(10)	N(8)-Cd(1)-N(11)	156.16(11)
N(9)-Cd(1)-N(11)	91.45(10)	N(12)-Cd(1)-N(11)	89.64(10)
N(13)-Cd(1)-N(10)	162.35(10)	N(8)-Cd(1)-N(10)	90.98(10)
N(9)-Cd(1)-N(10)	82.72(10)	N(12)-Cd(1)-N(10)	91.41(10)
N(11)-Cd(1)-N(10)	70.99(10)	O(8)-La(1)-O(14)	126.44(8)
O(8)-La(1)-O(5)	164.47(7)	O(14)-La(1)-O(5)	67.90(7)
O(8)-La(1)-O(10)	108.21(8)	O(14)-La(1)-O(10)	112.01(8)
O(5)-La(1)-O(10)	66.47(8)	O(8)-La(1)-O(4)	128.65(8)
O(14)-La(1)-O(4)	65.10(8)	O(5)-La(1)-O(4)	47.71(8)
O(10)-La(1)-O(4)	110.55(8)	O(8)-La(1)-O(11)	73.21(8)
O(14)-La(1)-O(11)	111.19(9)	O(5)-La(1)-O(11)	108.88(8)
O(10)-La(1)-O(11)	47.67(7)	O(4)-La(1)-O(11)	156.55(8)
O(8)-La(1)-O(1)	67.84(7)	O(14)-La(1)-O(1)	120.10(8)
O(5)-La(1)-O(1)	100.60(7)	O(10)-La(1)-O(1)	115.63(7)
O(4)-La(1)-O(1)	65.66(7)	O(11)-La(1)-O(1)	127.38(8)
O(8)-La(1)-O(2)	98.95(7)	O(14)-La(1)-O(2)	125.77(8)
O(5)-La(1)-O(2)	65.64(7)	O(10)-La(1)-O(2)	72.51(7)
O(4)-La(1)-O(2)	63.41(7)	O(11)-La(1)-O(2)	109.06(7)
O(1)-La(1)-O(2)	47.44(6)	O(8)-La(1)-O(13)	123.04(8)
O(14)-La(1)-O(13)	47.40(8)	O(5)-La(1)-O(13)	70.18(8)
O(10)-La(1)-O(13)	70.98(8)	O(4)-La(1)-O(13)	100.85(8)
O(11)-La(1)-O(13)	66.32(9)	O(1)-La(1)-O(13)	166.15(8)
O(2)-La(1)-O(13)	130.85(7)	O(8)-La(1)-N(1)	71.38(8)
O(14)-La(1)-N(1)	65.26(8)	O(5)-La(1)-N(1)	115.38(8)
O(10)-La(1)-N(1)	174.53(8)	O(4)-La(1)-N(1)	73.00(7)
O(11)-La(1)-N(1)	128.05(7)	O(1)-La(1)-N(1)	69.47(7)
O(2)-La(1)-N(1)	112.96(7)	O(13)-La(1)-N(1)	104.51(8)
O(8)-La(1)-N(2)	64.81(8)	O(14)-La(1)-N(2)	66.86(8)
O(5)-La(1)-N(2)	130.70(8)	O(10)-La(1)-N(2)	114.98(8)
O(4)-La(1)-N(2)	122.76(8)	O(11)-La(1)-N(2)	71.27(8)
O(1)-La(1)-N(2)	118.39(7)	O(2)-La(1)-N(2)	163.30(8)
O(13)-La(1)-N(2)	65.25(8)	N(1)-La(1)-N(2)	59.73(8)

(Continued on next page)

Table 2. The selected bond lengths (Å) and angles (°) (Continued)

Cd(1)-N(13)	2.291(3)	Cd(1)-N(8)	2.329(3)
O(8)-La(1)-O(7)	46.87(7)	O(14)-La(1)-O(7)	171.36(8)
O(5)-La(1)-O(7)	119.48(7)	O(10)-La(1)-O(7)	69.55(8)
O(4)-La(1)-O(7)	122.85(8)	O(11)-La(1)-O(7)	63.11(8)
O(1)-La(1)-O(7)	64.54(7)	O(2)-La(1)-O(7)	62.86(8)
O(13)-La(1)-O(7)	128.75(9)	N(1)-La(1)-O(7)	112.39(8)
N(2)-La(1)-O(7)	104.63(8)		

this difference, and we attribute it to intermolecular or interligand contacts. The N–La–N angles within the chelate ring is 59.73 (8)° is smaller than the N–Cd–N angles, relative to the La(III) ion has a high coordination number.

XRD Patterns

Simulated and experimental powder X-ray diffraction patterns of the complex is shown in Fig. S1. All the peaks in the recorded curves approximately match those in the simulated curves generated from single-crystal diffraction data, which confirms the phase purity of the as-prepared products. The difference in reflection intensity between the simulated and experimental patterns is due to ascertain degree of preferred orientation of the powder samples during data collection.

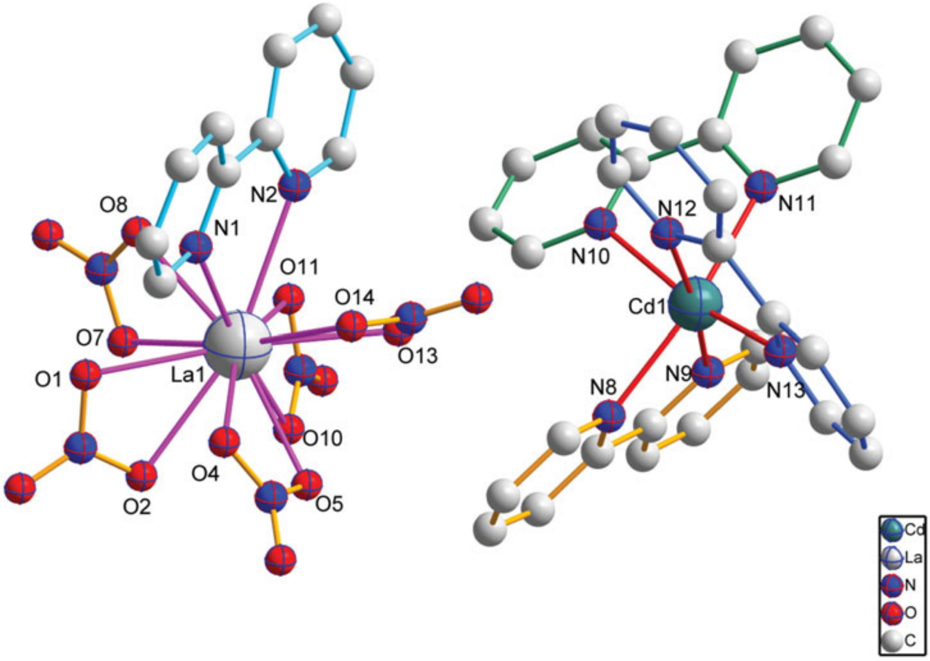

Figure 1. The coordination environment of the complex with hydrogen atoms omitted for clarity.

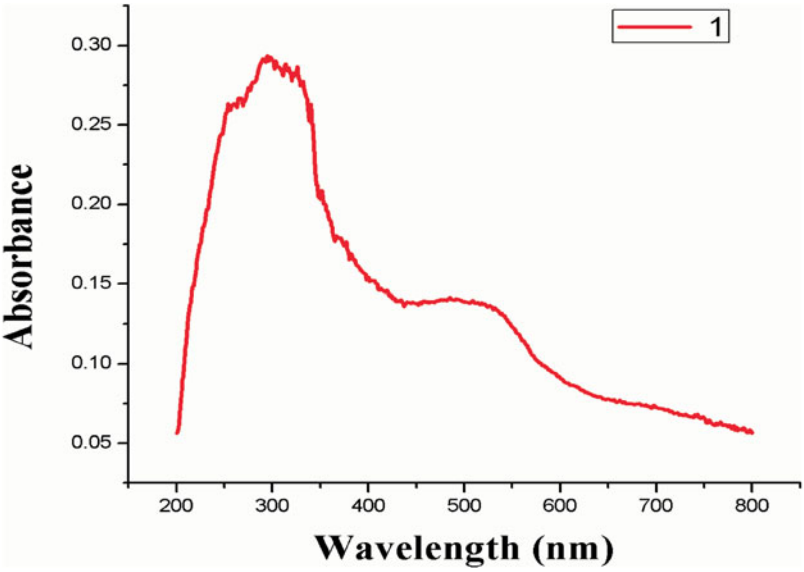

Figure 2. Diffuse reflectance UV–vis spectra of complex.

Electronic Spectra

The bands in the UV region were attributed to the intraligand transition mainly centered in bpy ligand. The intraligand bands are sufficiently intense to mask a metal ligand charge-transfer band involving dπLa(III)–π^*(bpy) and dπCd(II)–π^*(bpy) which is observed in the 303 nm region as assigned in a UV–vis spectrum of [LaCd(bpy)$_4$(NO$_3$)$_5$] (Fig. 2). The

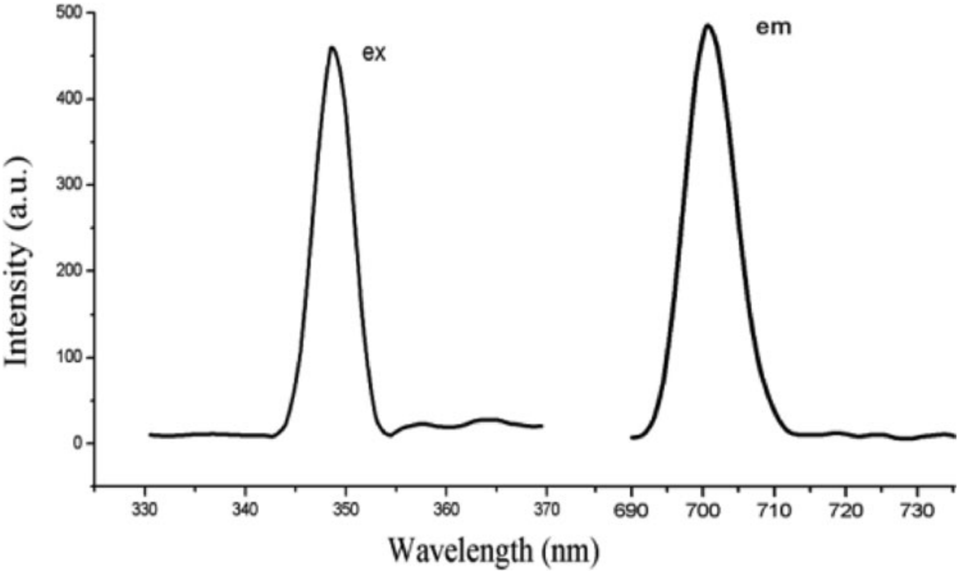

Figure 3. Excitation and emission spectra of the complex in the solid state.

intensity is much larger and simpler than the ligand itself. From the spectral behavior, the visible bands may be assigned to the MLCT transitions.

Photoluminescence Properties

The photoluminescence properties of the complex were studied in the solid state at room temperature (298 K) (Fig. 3). The luminescence spectrum shows a strong emission located at 701 nm with an excitation wavelength of 348 nm, while a intense excitation located at 348 nm with an emission wavelength of 701 nm. The spectra clearly indicate that an energy transfer occurred from the bpy to the metal ions, resulting in both the emission and excitation are only a strong absorption band. The ligand systems in these compounds also act as light absorbing antennae to sensitize the lanthanide luminescence. 2,2′-bipyridine are known to coordinate lanthanide ions and sensitize their emission via energy transfer [30].

Conclusions

A novel lanthanum cadmium compound [LaCd(bpy)$_4$(NO$_3$)$_5$], has been prepared and structurally characterized. The structural analyses revealed that the compound is zero-dimensional ionic salts containing cationic La(III) complex and octahedrally coordinated cationic Cd(II). The electronic spectra and photoluminescence of the complex has been investigated. The latter measurements indicate that a sensitization process involving bpy absorption followed by energy transfer to the metal cations is present in the compound.

Acknowledgments

The authors thank the NO.2 Middle School of Dongkou Hunan, the National Natural Science Foundation of China (20761002), P.R. China and the Natural Science Foundation of Guangxi (053020), P.R. China.

Supplementary Material

CCDC 892404 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. www.t&fonline.com/GMCL_A_905318.

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