Polyhedron 29 (2010) 2048–2052

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis, crystal structures and luminescent properties of an isotypic series of rare-earths complexes with a dialdehyde ligand

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ARTICLE INFO

Article history:
Received 22 December 2009
Accepted 23 March 2010
Available online 27 March 2010

Keywords:
Lanthanides
Coordination complexes
X-ray structures
Photoluminescence
Emission spectra
2,6-Bis(2-formylphenoxymethyl)pyridine (*L*)

ABSTRACT

A series of mononuclear complexes based on lanthanide ions has been synthesized and X-ray characterized. The compounds $[\mathrm{Ln^{III}}L_2(\mathrm{NO_3})_3(\mathrm{H_2O})_2]$ (Ln = La, Ce, Pr, Nd, Sm, Gd and Tm; *L* = 2,6-bis(2-formylphenoxymethyl)pyridine) are found to be isomorphous and isostructural. Ligand *L* systematically coordinates through one carbonyl functionality, and the resulting complexes are placed on a twofold axis in crystals belonging to *C*2/*c* space-group. Emission spectra for Ln = La, Pr, Nd revealed a correlation between the Ln–O coordination bond length and the photoluminescent properties of the complexes, in line with a Förster–Dexter mechanism for intramolecular energy transfer. Ligand *L* is therefore a suitable sensitizer for lanthanide ions.

1. Introduction

Coordination chemistry gives the opportunity to explore different ways in order to synthesize new compounds with the hope to obtain advanced materials having magnetic, optical, luminescent or electrochemical properties [1–3]. On the other hand, it is well known that dialdehydes and diamines derivatives are important precursors in the synthesis of macrocyclic ligands. For instance, 2,6-bis(2-formylphenoxymethyl)pyridine (*L* hereafter), has been used as a precursor to obtain macrocyclic systems including pendant arms, which have the ability to complex metal ions [4,5]. A number of related multidentate molecules also served as building blocks for cryptands, for which host properties have been extensively probed [6].

The aim of this research is to extend the study of *L* as a donor to lanthanide ions to achieve materials with photoluminescent properties. We assume that these materials are potentially luminescent because *L* contains both chromophore and aryl groups with π electrons, which are required for the effective intramolecular transfer of excitation energy from the resonance levels of the chromophore groups to $\mathrm{Ln^{3+}}$ (antenna effect) [7]. The expected function of the ligand is to increase the luminescent properties toward visible and infrared ranges [8,9]. We report here on the synthesis of an isotypic series of new complexes where ligand *L* coordinates to lanthanides: $\mathrm{La^{III}}$, $\mathrm{Ce^{III}}$, $\mathrm{Pr^{III}}$, $\mathrm{Nd^{III}}$, $\mathrm{Sm^{III}}$, $\mathrm{Gd^{III}}$ and $\mathrm{Tm^{III}}$. The crystallographic characterization of the free ligand *L* and complexes $[\mathrm{Ln^{III}}L_2(\mathrm{NO_3})_3(\mathrm{H_2O})_2]$, as well as the luminescent properties of some of these complexes are discussed.

2. Experimental

2.1. Synthesis

All the reactants used to obtain the ligand and the lanthanide complexes were analytic grade from Sigma–Aldrich Chemical Company Inc., USA. IR spectra were measured on an IR-FT Nicolet 550 Model Magna-IR Spectrometer and ATR-FT Perkin Elmer Spectrum 1. ESI-TOF mass spectra were obtained with a Bruker Daltonics Data Analysis 3.3, and elemental analyses (C, H, N) were performed using a Perkin Elmer Instruments Series II 2400 CHNS-O. Single crystals diffraction data were collected on a Siemens P4 diffractometer. The excitation and emission spectra were obtained on a Luminescence Spectrometer Perkin Elmer LS55.

2,6-Bis(2-formylphenoxymethyl)pyridine (L). The ligand was prepared *via* Williamson condensation between the sodium salt of salicylaldehyde and 2,6-bis(bromomethyl)pyridine in a 2:1 ratio, under N_2 atmosphere, by using a modified literature method [10] (the detailed preparation is transferred to the supplementary material). Colorless crystals, mp. 141–142 °C; Micro *Anal.* Calc. for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.94; N, 4.03. Found: C, 72.25; H, 4.67; N, 4.23%. IR (KBr pellets, $\mathrm{cm^{-1}}$): 1683 ($\nu_{\mathrm{C=O}}$), 1591 ($\nu_{\mathrm{C=N}}$) and 1237 ($\nu_{\mathrm{C-O-C}}$).

$[\mathrm{Ln^{III}}L_2(\mathrm{NO_3})_3(\mathrm{H_2O})_2]$. The complexes were synthesized by the reaction of the appropriate $\mathrm{Ln^{III}}$ salt (Ln = La, Ce, Pr, Nd, Sm, Gd and Tm, 0.5 mmol) and *L* (1 mmol), in refluxing acetonitrile

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doi:10.1016/j.poly.2010.03.018

(50 mL) for 5 h. The mixture was cooled and the volume reduced by evaporation under reduced pressure, to give the expected complex as product. The crude solid was recrystallized from acetonitrile, affording air-stable crystals suitable for X-ray structural analysis.

$[\mathrm{La}L_2(\mathrm{NO_3})_3(\mathrm{H_2O})_2]$ orange crystals; mp. 153–154 °C (dec.); *Anal.* Calc. for $C_{42}H_{38}N_5O_{19}La$: C, 47.78; H, 3.63; N, 6.63. Found: C, 47.87; H, 3.11; N, 6.93%. IR (KBr pellets): 3457 (ν_{O-H}), 1661 ($\nu_{C=O\ free}$), 1642 ($\nu_{C=O-La}$), 1481 (ν_{NO3}), 1296, 1038, 818, 730 cm^{-1}.

$[\mathrm{Ce}L_2(\mathrm{NO_3})_3(\mathrm{H_2O})_2]$ yellow crystals; mp. 156 °C; *Anal.* Calc. for $C_{42}H_{38}N_5O_{19}Ce$: C, 47.73; H, 3.62; N, 6.63. Found: C, 47.5; H, 3.51; N, 7.01%. IR (KBr pellets): 3458 (ν_{O-H}), 1665 ($\nu_{C=O\ free}$), 1643 ($\nu_{C=O-Ce}$), 1461 (ν_{NO3}), 1301, 1057, 818, 733 cm^{-1}.

$[\mathrm{Pr}L_2(\mathrm{NO_3})_3(\mathrm{H_2O})_2]$ yellow crystals; mp. 163–164 °C; *Anal.* Calc. for $C_{42}H_{38}N_5O_{19}Pr$: C, 47.64; H, 3.63; N, 6.61. Found: C, 47.72; H, 3.11; N, 6.91%. IR (KBr pellets): 3457 (ν_{O-H}), 1661 ($\nu_{C=O\ free}$), 1642 ($\nu_{C=O-Pr}$), 1459 (ν_{NO3}), 1296, 1056, 818, 760 cm^{-1}.

$[\mathrm{Nd}L_2(\mathrm{NO_3})_3(\mathrm{H_2O})_2]$ pink crystals; mp. 157–158 °C (dec.); *Anal.* Calc. for $C_{42}H_{38}N_5O_{19}Nd$: C, 47.55; H, 3.61; N, 6.60. Found: C, 47.63; H, 3.10; N, 6.89%. IR (KBr pellets): 3457 (ν_{O-H}), 1664 ($\nu_{C=O\ free}$), 1634 ($\nu_{C=O-Nd}$), 1464 (ν_{NO3}), 1302, 1054, 822, 761 cm^{-1}.

$[\mathrm{Sm}L_2(\mathrm{NO_3})_3(\mathrm{H_2O})_2]$ colorless crystals; mp. 159 °C (dec.); *Anal.* Calc. for $C_{42}H_{38}N_5O_{19}Sm$: C, 47.73; H, 3.62; N, 6.63. Found: C, 47.50; H, 3.51; N, 7.01%. IR (KBr pellets): 3461 (ν_{O-H}), 1665 ($\nu_{C=O\ free}$), 1634 ($\nu_{C=O-Sm}$), 1487 (ν_{NO3}), 1305, 1057, 817, 761 cm^{-1}.

$[\mathrm{Gd}L_2(\mathrm{NO_3})_3(\mathrm{H_2O})_2]$ yellow crystals; mp. 156 °C; *Anal.* Calc. for $C_{42}H_{38}N_5O_{19}Gd$: C, 46.97; H, 3.57; N, 6.52. Found: C, 47.03; H, 4.11; N, 5.96%. IR (KBr pellets): 3462 (ν_{O-H}), 1662 ($\nu_{C=O\ free}$), 1646 ($\nu_{C=O-Gd}$), 1446 (ν_{NO3}), 1309, 1021, 817 cm^{-1}.

$[\mathrm{Tm}L_2(\mathrm{NO_3})_3(\mathrm{H_2O})_2]$ yellow crystals; mp. 158 °C; *Anal.* Calc. for $C_{42}H_{38}N_5O_{19}Tm$: C, 46.64; H, 3.53; N, 6.45. Found: C, 45.24; H, 3.51; N, 6.69%. IR (KBr pellets): 3424 (ν_{O-H}), 1664 ($\nu_{C=O\ free}$), 1634 ($\nu_{C=O-Tm}$), 1448 (ν_{NO3}), 1291, 1028, 811, 748, 721 cm^{-1}.

2.2. X-ray diffraction

Pertinent crystal data and other crystallographic parameters are listed in Table 1. Diffraction data were collected at room temperature (294–298 K) using the Mo Kα radiation ($\lambda = 0.71073$ Å), through standard procedures [11]. Raw data were corrected for absorption effects, either using suitable Ψ-scans data [12], or a Gaussian face-indexed correction, if available [13]. The refinement of the organic ligand did not present special difficulties. In contrast, space-group determination for the lanthanide complexes is not so straight. Diffraction patterns systematically afford intensity statistics in line with a non-centrosymmetric space-group, *Cc*. However, the final structures clearly display a twofold symmetry (see *infra*), consistent with space-group *C*2/*c*, which was eventually retained. The main disadvantage of such a choice is that the nitrate ion placed on the twofold axis presents high thermal displacements. Attempts to resolve disordered sites (*i.e.* considering that this ion belongs to *Cc* rather than *C*2/*c*) were unsuccessful, and the final refinements [13] were carried out with restraints applied on anisotropic displacement parameters for N3, O9 and O10 sites (see deposited CIF). C-bonded H atoms were placed in idealized positions and refined as riding to their carrier C atoms. H atoms for the coordinated water molecule were found in a difference map, and refined freely, although the geometry was regularized through soft restraints: O–H = 0.85(1) and H···H = 1.34(2) Å.

2.3. Preliminary study of the photoluminescent properties of the complexes

The study of the photoluminescent properties was realized by irradiating at 254 and 366 nm the ligand *L*, lanthanides salts used as starting materials, and the synthesized complexes. Ligand and complexes were studied both in the solid-state and as DMF solutions, at 4.5×10^{-3} M concentration. Afterward, their UV–Vis spectra were recorded, in order to know the wavelength of maximum absorption, and the emission and excitation spectra were eventually measured for solid and solution samples.

3. Results and discussion

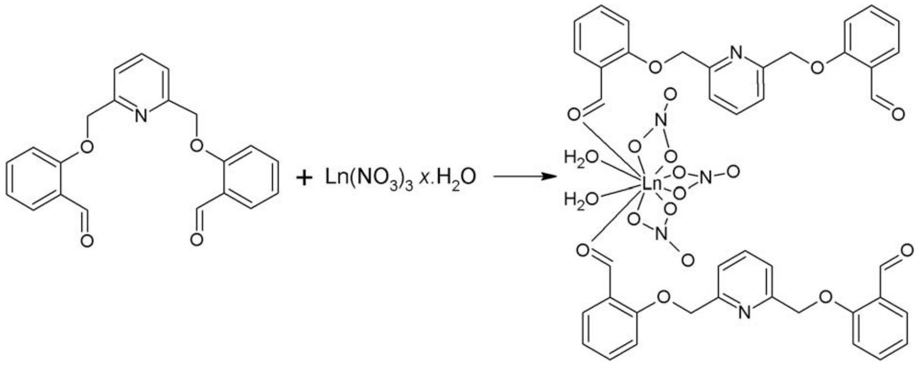
3.1. Synthesis

Complexes $[\mathrm{Ln^{III}}L_2(\mathrm{NO_3})_3(\mathrm{H_2O})_2]$ were successfully prepared (Scheme 1) and spectroscopic studies are consistent with the proposed formula. Similar IR spectra are obtained along the series, featuring two carbonyl vibrations, for example at 1661 and 1642 cm^{-1} in the case $Ln^{III} = Pr^{III}$ (Fig. S1, Supplementary material), suggesting that one carbonyl group coordinates the metal while the other remains free. Strong IR vibrations at 1459 and 1296 cm^{-1} ($Ln^{III} = Pr^{III}$) are assigned to coordinated nitrate ions, and the stretching signal at 3457 cm^{-1} accounts for water molecules included in the coordination sphere. Elemental analyses agree with the 1:2 ratio for Ln:*L*, and the formula was finally confirmed by mass spectrometry. All ESI-TOF mass spectra exhibit a base peak (100%) corresponding to the free ligand ($L\mathrm{H}^+$, *m*/*z* 348) and peaks of smaller intensity for $\mathrm{Ln}L\mathrm{H}^+$ and $\mathrm{Ln}L(\mathrm{NO_3})_2\mathrm{H}^+$ species.

Table 1
X-ray parameters.

Complex	*L*	La	Ce	Pr	Nd	Sm	Gd	Tm
Chemical formula	$C_{21}H_{17}NO_4$	$C_{42}H_{38}LaN_5O_{19}$	$C_{42}H_{38}CeN_5O_{19}$	$C_{42}H_{38}N_5O_{19}Pr$	$C_{42}H_{38}N_5NdO_{19}$	$C_{42}H_{38}N_5O_{19}Sm$	$C_{42}H_{38}GdN_5O_{19}$	$C_{42}H_{38}N_5O_{19}Tm$
Fw	347.36	1055.68	1056.89	1057.68	1061.01	1067.12	1074.02	1085.70
Color	pale yellow	orange	yellow	yellow	pale pink	colorless	yellow	yellow
Space-group	$P2_1/n$	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	8.710(4)	20.802(3)	20.724(6)	20.682(4)	20.613(6)	20.676(6)	20.646(5)	20.606(6)
b (Å)	18.002(7)	9.2209(12)	9.214(3)	9.222(2)	9.205(3)	9.223(3)	9.242(3)	9.277(4)
c (Å)	11.038(5)	22.875(2)	22.747(7)	22.712(6)	22.581(6)	22.603(7)	22.545(6)	22.546(10)
β (Å)	95.89(2)	103.683(8)	103.772(14)	103.72(2)	103.822(12)	103.766(18)	103.825(14)	103.86(3)
V (Å^3)	1721.8(14)	4263.2(9)	4219(2)	4208.2(17)	4161(2)	4186(2)	4177(2)	4185(3)
Z	4	4	4	4	4	4	4	4
2θ Range (°)	3–55	4–60	4–55	4–52.5	4–60	4–55	4–55	4–55
μ (mm^{-1})	0.093	1.090	1.168	1.247	1.338	1.493	1.678	2.210
R Indices $[I > 2\sigma(I)]^a$	0.048, 0.121	0.029, 0.076	0.033, 0.083	0.027, 0.066	0.037, 0.093	0.041, 0.104	0.036, 0.079	0.040, 0.102
R indices (all data)^a	0.084, 0.156	0.033, 0.076	0.040, 0.090	0.034, 0.072	0.048, 0.101	0.050, 0.114	0.042, 0.086	0.053, 0.113
$D_{calc.}$ (g cm^{-3})	1.340	1.645	1.664	1.669	1.694	1.693	1.708	1.723
Data/parameters	3948/236	6184/310	4822/310	4261/310	6058/310	4790/310	4792/310	4765/310
S^a	1.054	1.066	1.047	1.085	1.082	1.050	1.081	1.076

[a] $R_1 = \frac{\sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert}{\sum \lvert F_o\rvert}$, $wR_2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$, $S = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\text{data} - \text{parameters}}}$.



Scheme 1. Synthetic route for lanthanide complexes.

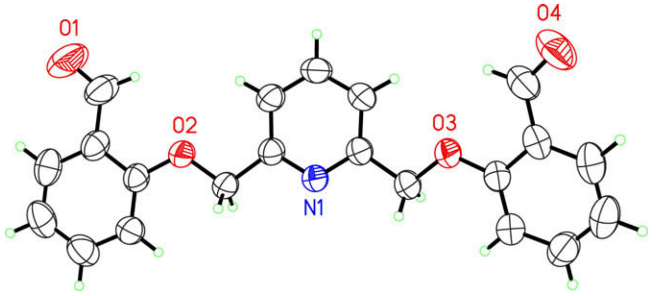


Fig. 1. Molecular structure of ligand *L*. Displacement ellipsoids are shown at the 30% probability level.

ORTEP-style views are given for ligand *L* and complex [LaL_2(NO_3)$_3$(H_2O)$_2$] in Figs. 1 and 2, respectively. Complete geometric parameters may be consulted from the archived CIF file, and diffraction data are available on request to authors.

The free ligand is stabilized in the solid-state in a nearly planar arrangement (Fig. 1), characterized by dihedral angles between the central pyridine ring (N1/C9···C13) and benzene rings (C2···C7 and C15···C20) of 5.75(9)° and 26.19(8)°. The molecule thus approximates C_{2v} point symmetry, with the carbonyl functional groups oriented in the same direction with respect the core pyridine ring. This conformation is reminiscent of that previously described, for instance, for 2,6-bis(phenoxymethyl)pyridine [14]. The observed arrangement for heteroatoms in *L* seems to be unfavorable for its use as a chelating ligand. However, the possibility for different conformations in solution should not be ruled out, as rotations about methoxy C–O bonds are not sterically impeded. Indeed, a very different conformation was described for closely related ligands, where aldehyde groups are replaced by dimethoxymethyl or hydroxylmethyl substituents [15]. In these cases, bent conformations are stabilized, with a benzene ring almost perpendicular to the rest of the molecule. In the same way, formal substitution of aldehyde functional groups in ***L*** by hydroxyl groups affords an actual podant ligand, stabilized by soft intramolecular hydrogen bonds. This molecule has been shown to have complexing ability towards Na^+, involving all heteroatoms in coordination bonds [16].

Lanthanide complexes are all isostructural and isomorphous (Table 1). A previous report about the Ce(III) complex was published [17]. We however included this complex in this work, because the former refinement was of limited resolution and was not deposited with the CCDC. On the other hand, for comparison purposes, it is preferable to have all diffraction patterns measured in the same conditions and refinements carried out with identical models.

Complexes are formulated [$Ln^{III}L_2$(NO_3)$_3$(H_2O)$_2$], where *L* is the ligand above described, and Ln^{III} is a lanthanide ion (Ln = La, Ce, Pr, Nd, Sm, Gd, Tm; following geometric parameters are given for Ln = La). The molecule lies on a twofold axis, with atoms Ln, N3 and O9 placed in special positions. As mentioned in Section 2, nitrate anion N3 is probably disordered across the C_2 axis, as reflected in the prolate thermal ellipsoid of O9. The nitrate ions behave as bidentate ligands, as frequently observed in lanthanide complexes [18,19]. Ligand *L* is monodentate, using a single carbonyl group for coordination. The conformation of this ligand is indeed close to that found in the free molecule: the ligand is quite planar, the dihedral angle between the pyridine and benzene rings being 11.04(14)° and 8.36(15)°. As a consequence of the molecular symmetry, both ligands *L* in the molecule are almost perpendicular, the angle between corresponding mean planes being 86.35(2)°. The coordination environment is completed by two water molecules, giving a 10-coordinated metal center. The coordination geometry (Fig. 2, inset) is best described as a distorted bicapped square antiprism [20], approaching D_{4d} symmetry [21].

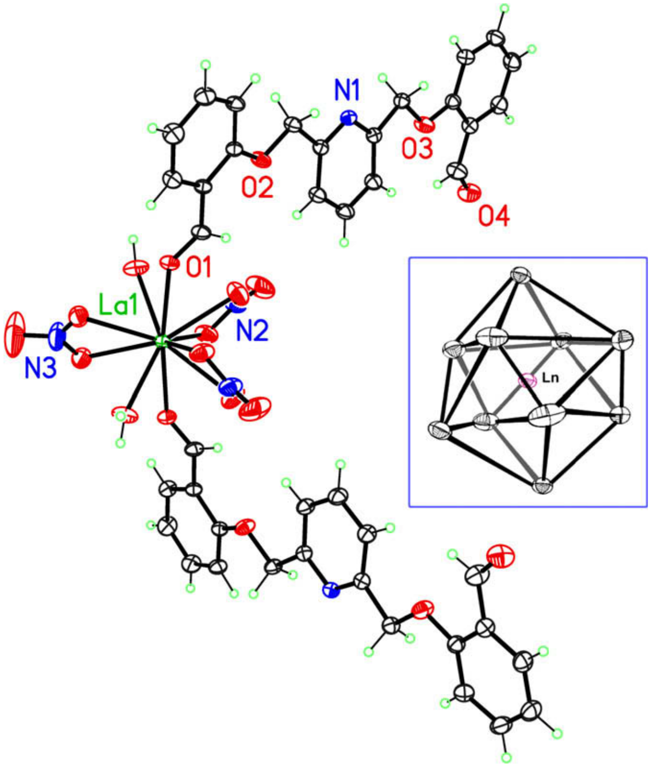


Fig. 2. Molecular structure of complex [LaL_2(NO_3)$_3$(H_2O)$_2$]. Displacement ellipsoids are shown at the 30% probability level. The inset represents the coordination polyhedron around the lanthanide center.

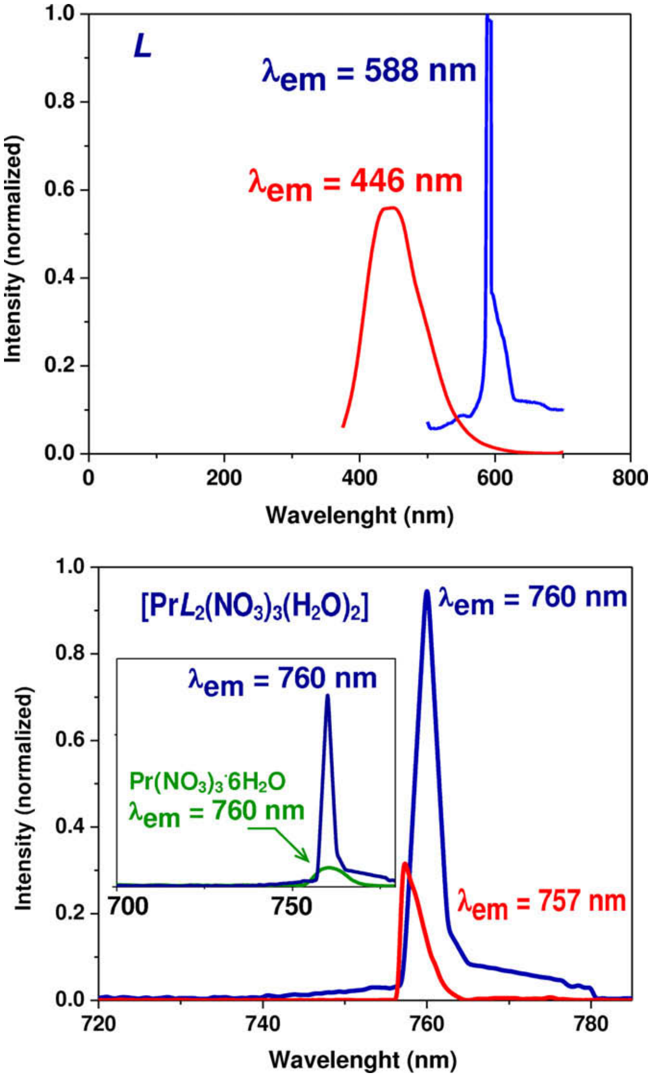


Fig. 3. Normalized emission spectra for free L (top) and Pr complex (bottom). For ligand *L*, λ_{exc} = 350 nm and emission is observed in DMF solution (red line) and in the solid-state (blue line). For the Pr complex, λ_{exc} = 290 nm and emission is observed in DMF solution (red line) and in the solid-state (blue line). The insert compares emissions for $Pr(NO_3)_3{\cdot}6H_2O$ (green line) and $[PrL_2(NO_3)_3(H_2O)_2]$ (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Coordinated water molecules also serve as donor for intermolecular hydrogen bonds with the free aldehyde group and the pyridine N atom of two symmetry-related molecules. The resulting 3D supramolecular network, together with the planar geometry of the main ligand, allows the building of an efficient packing structure in the crystal. Two molecules related by an inversion center have two ligands *L* arranged in a slightly shifted face-to-face configuration, which generates $\pi \cdots \pi$ interactions between aromatic rings. These stabilizing contacts may be characterized by the distance separating two *L* mean planes interacting in the crystal, 3.30 Å, shorter than the distance between planes in graphite, 3.35 Å. The resulting crystal structure displays a high packing index, 0.72 [22], and no residual voids are available for lattice solvent inclusion.

Since an efficient stacking of molecules in the solid-state is facilitated by the molecular symmetry, it is not surprising that all synthesized complexes are isomorphous. As expected, the density is increased from $_{57}$La (1.645 g/cm^3) to $_{69}$Tm (1.723 g/cm^3), reflecting the ion contraction along the lanthanide series. A similar general trend is observed for unit cell volumes and coordination bond lengths.

3.2. *Luminescence study of La^{III}, Pr^{III} and Nd^{III} complexes*

Under UV irradiation, above described La^{III}, Pr^{III} and Nd^{III} complexes emit light, either in the solid-state or in solution, at different wavelengths compared to emission produced in absence of irradiation. The La-based complex emits in the yellow range, more intensively if irradiation is applied. The Nd^{III} complex emits in the purple region if not irradiated and shifts emission to green under irradiation. Finally, the Pr^{III} complex behaves similarly to the La complex, emitting a bright yellow light under irradiation.

Fig. 3 (upper panel) shows the emission spectra of *L* in the solid-state and dissolved in DMF. After excitation at 350 nm, a Stokes displacement toward the visible range is observed: λ_{em} = 588 nm and λ_{em} = 446 nm in the solid and solution state respectively, indicating that *L* is a good candidate for sensitizing lanthanides. The smallest Stokes shift observed in solution compared to solid-state should be related to the involvement of DMF, which activate vibration modes using UV photons, at expense of the $\pi \leftarrow \pi^*$ transitions in solvated *L*.

For Ln^{III} complexes (Ln = La, Pr, Nd), the emission is found in the visible range, regardless of the lanthanide used. Excitation in the UV region affords emission at 455 nm (La), 760 nm (Pr) and 864 nm (Nd) in the solid-state. Similarly to the free ligand *L*, emission intensity decreases for DMF solutions: λ_{em} = 453, 757 and 862 nm for La, Pr and Nd, respectively. Spectra for Ln = Pr are displayed in Fig. 3 (lower panel).

As expected, the La^{III} emission yield is only slightly enhanced in the antenna-containing complex compared with the starting material $La(NO_3)_2.6\ H_2O$, since the 4*f* shell of La^{III} is empty. For such salts and complexes [23], specific luminescence mechanisms have been invoked [24], like self-trapped exciton luminescence [25]. In contrast, the lanthanide–chromophore interaction affords very efficient energy transfer in Pr^{III} and Nd^{III} complexes (see inset for Ln^{III} = Pr^{III}). Regarding the energy transfer, although a limited series of complexes has been studied, a clear structure–property correlation is observed: the more the Ln–O coordination bond length is short, the more luminescent properties are improved. The Förster–Dexter theory [26] seems thus to be applicable to the present series of complexes, although it would be difficult to resolve unambiguously if the actual mechanism for energy transfer is by exchange interaction (Dexter transfer [27]) or rather through a dipole–dipole interaction mechanism (Förster model [28]).

4. Conclusions

We have synthesized and characterized an isotypic series of air-stable monometallic lanthanide complexes formulated $[LnL_2(NO_3)_3(H_2O)_2]$ using a dialdehyde ligand, *L*. This ligand clearly behaves as an efficient sensitizer for the lanthanide photoluminescence. The antenna effect is probably limited to the benzaldehyde group coordinated to the metal center. Since a site of coordination remains free in the ligand, the reported complexes could be used as building blocks for the preparation of more sophisticated binuclear devices [29], allowing the design of sensors with tunable photoluminescent properties. In a different point of view, these new complexes also deserve further physical characterization. For instance, emission spectra at variable temperature could determine the exact mechanism for energy transfer, since the Dexter mechanism is known to be a temperature-dependent process, while in the Förster model, assuming Coulombic interactions, the energy depends only on the separation between the sensitizer and activator.

Acknowledgment

The authors acknowledge the Facultad de Ciencias Químicas, UANL, and PAYCyT for financial support (project number CA1260–06).

Appendix A. Supplementary material

CCDC 755323, 755324, 755325, 755326, 755327, 755328, 755329 and 755330 contain the supplementary crystallographic data for ligand *L*, Ln = La, Ln = Ce, Ln = Pr, Ln = Nd, Ln = Sm, Ln = Gd and Ln = Tm. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.03.018.

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