## Special Issue Article

# Synthesis, Structural Characterization, and Chiroptical Studies of Bidentate Salen-Type Lanthanide (III) Complexes

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*ABSTRACT* The salen-type ligand prepared with (*R*,*R*) diphenylethan-1,2-diamine and salicylaldehyde provides stable and inert complexes KLnL<sub>2</sub> upon simple reaction with lanthanide halides or pseudohalides LnX<sub>3</sub> (Ln = Tb<sup>3+</sup>-Lu<sup>3+</sup>; X = Cl<sup>−</sup> or TfO<sup>−</sup>) of its potassium salt. All the complexes were completely characterized through nuclear magnetic resonance (NMR), electronic circular dichroism (ECD) in the UV and some (Er<sup>3+</sup>, Tm<sup>3+</sup>, Yb<sup>3+</sup>) also with Near-IR ECD (NIR-ECD) and luminescence (Tb<sup>3+</sup>, Tm<sup>3+</sup>). Careful analysis of the NMR shifts demonstrated that the complexes are isostructural in solution and afforded an accurate geometry. This was further confirmed by means of Density Functional Theory (DFT) optimization of the Lu<sup>3+</sup> complex, and by comparing the ligand-centered experimental and time-dependent TD-DFT computed UV-ECD spectra. As final validation, we used the NIR-ECD spectrum of the Yb<sup>3+</sup> derivative calculated by means of Richardson's equations. The excellent match between calculated and experimental ECD spectra confirm the quality of the NMR structure. *Chirality 27:857–863, 2015.* © 2015 Wiley Periodicals, Inc.

KEY WORDS: salen-type ligand; electronic circular dichroism; near-IR circular dichroism; TD-DFT calculation; paramagnetic NMR

Chiral lanthanide complexes are interesting for their applications including enantioselective catalysis, <sup>1–3</sup> detection of bio-analytes, <sup>4–6</sup> circularly polarized light emitting devices, <sup>7,8</sup> and metal organic frameworks.<sup>9</sup> The organic ligands define the Ln<sup>3+</sup> coordination sphere, modulating the access of further chemical species to the ion and making it soluble, stable, and persistent in various environments. Furthermore, the ligand may provide the necessary conditions to sensitize the ion's photo- (or electro-) luminescence.<sup>10</sup> In this context, salen-type ligands (*N*,*N*-bis(salicylidine)diamine) have shown promising properties especially in binding late lanthanides and promoting Near-IR luminescence of Yb<sup>3+</sup> complexes.<sup>11–15</sup>

With the exception of La<sup>3+</sup> and Lu<sup>3+</sup>, all Ln<sup>3+</sup> ions induce characteristic paramagnetic NMR shifts, which can be used to determine accurate solution structures.<sup>16–19</sup> Gd<sup>3+</sup> may induce a relevant contact shift, which is, however, hardly detectable owing to the severe line broadening brought about by this ion. The introduction of chirality elements into Ln<sup>3+</sup> complexes' architecture opens the possibility to investigate their structure with electronic circular dichroism (ECD) in an extended range of energies (Near-IR, UV-vis). Additionally, ECD spectra may be simulated by various approaches. For example, ligand-centered ECD may be evaluated by means of time-dependent Density Functional Theory (TD-DFT),<sup>20</sup> while a simple approach based on Richardson's equations<sup>21,22</sup> provides an estimate of the metal-centered Near-IR ECD of Yb<sup>3+</sup>. The predicted spectra may then be compared with the experimental data, validating the solution geometry obtained from paramagnetic nuclear magnetic resonance (NMR) analysis.23-25

In the following, we discuss  $Ln^{3+}$  complexes with a bis (salicylaldimine)-type ligand, derived from enantiopure (*1R*,*2R*)-1,2-diphenylethylene-1,2-diamine (H<sub>2</sub>L), prepared according to Scheme 1.

Complexes with the general formula  $KLnL_2$  ( $Ln = Tb^{3+}$ ,  $Dy^{3+}$ ,  $Ho^{3+}$ ,  $Er^{3+}$ ,  $Tm^{3+}$ ,  $Yb^{3+}$  and  $Lu^{3+}$ ) were readily obtained following Scheme 2, and fully characterized in chloroform solution by means of (paramagnetic) NMR, as well as of chiroptical and emission spectroscopies.

## MATERIALS AND METHODS General

Unless otherwise indicated, all materials were purchased from Sigma-Aldrich (St. Louis, MO) and were used without further purification. All the lanthanide salts were stored in a dessicator with  $P_2O_5$ .

NMR measurements were performed on a Varian (Palo Alto, CA) INOVA 600 spectrometer operating at 600 MHz for <sup>1</sup>H. The temperature was controlled to  $\pm 0.1$  °C. CDCl<sub>3</sub> was used as the solvent and the (residual) solvent signal (7.26 ppm for <sup>1</sup>H and 77.16 ppm for <sup>13</sup>C) was used to reference the spectra.

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Scheme 1. Preparation of ligand H<sub>2</sub>L.



**Scheme 2.** Preparation of lanthanide complexes with salen-type ligand KLnL<sub>2</sub> and atom-labeling (see Supporting Information for details and yields).

UV-vis spectra were recorded using a Varian Cary 4E UV-vis spectrophotometer at room temperature and using a cylindrical quartz cell with an optical path of 0.01 cm.

UV-vis ECD spectra were recorded with a Jasco (Tokyo, Japan) J710 spectropolarimeter at room temperature using the following settings: 0.01 cm optical path; bandwidth 1.0 nm; response 4 s; speed 20 nm/min. All spectra were recorded in commercial CHCl<sub>3</sub> at concentrations around 2.5 mM.

The emission spectra were collected only for  $\text{Tm}^{3+}$  and  $\text{Tb}^{3+}$ , which show emission bands respectively in the region of blue ( $\text{Tm}^{3+}$ ) and green ( $\text{Tb}^{3+}$ ). The spectra were recorded using a Horiba Fluorolog-3 Fluorimeter at room temperature and at a concentration of 0.695 mM ( $\text{Tm}^{3+}$ ) and 0.496 mM ( $\text{Tb}^{3+}$ ) in CHCl<sub>3</sub> as the solvent, using a 1 cm cell. The following parameters were employed: excitation wavelength 348 nm, integration time 0.3 s, slits opening 1 nm, 5 accumulations.

Near-IR ECD spectra were recorded at room temperature on a Jasco J200D spectropolarimeter, operating between 750 and 1350 nm, modified by a tandem detector Si/InGaAs with dual photomultiplier amplifier and using a "semimicro" square cell with optical path of 1 cm. The following set of parameters was employed: sensitivity  $1 \text{ m}^{\circ}/\text{cm}$  (Yb<sup>3+</sup>, Er<sup>3+</sup>) and sensitivity  $20 \text{ m}^{\circ}/\text{cm}$  (Tm<sup>3+</sup>); scan speed 2 cm/min; time constant 1 sec; bandwidth 3.2 nm. A 1 cm quartz cell was used and for each sample 20 accumulations were collected (averaged by means of a Jasco DP-500 N data processor). Solutions (1.3 mM) were prepared in reagent-grade CHCl<sub>3</sub>.

#### Synthesis of H<sub>2</sub>L

The salen-type ligand H<sub>2</sub>L was prepared by condensation of the diamine with the salicaldehyde in ethanol heated at reflux (Scheme 1), following a reported literature procedure.<sup>26,27</sup> A 100 mL three-neck flask equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel was loaded with 0.35 g of 2-hydroxybenzaldehyde (1, 2.90 mmol), 0.83 g of K<sub>2</sub>CO<sub>3</sub> (6.00 mmol) and deionized water (4 mL). The mixture was stirred until complete dissolution of the solids, then ethanol (15 mL) was added. The resulting turbid mixture was stirred at reflux for 2 h, and then a solution of 1.23 g of (1R, 2R)-1,2-diphenylethane-1,2diamine (2, 5.80 mmol) in 7 mL of EtOH was added dropwise over 30 min. The obtained yellow slurry was stirred at reflux for 2 h and then cooled at room temperature. Subsequently, water (150 mL) was added and the solution was cooled at 0-5 °C: this allowed the crude product to precipitate within 2 h. The product was then collected by filtration and washed with ethanol. The crude solid was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (12 mL), washed with water  $(2 \times 7.5 \text{ mL})$  and brine (2.5 mL), and the solvent was evaporated affording 2.17 g of 2,2'-(((1R, 2R)-1,2-diphenylethane-1,2diyl)-bis(azanylylidene))-bis(metanylylidene))-diphenol (H<sub>2</sub>L) as a yellow solid (isolated yield = 89%) which was used without further purification (for the <sup>1</sup>H-NMR see Supporting Information).

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## Preparation of KLnL<sub>2</sub> Lanthanide Complexes

The synthesis of lanthanide complexes (KLnL<sub>2</sub>) has been optimized for  $Yb^{3+}$  starting from an already reported procedure for M[Ln(Salen)<sub>2</sub>] complexes<sup>28</sup> and then extended to the preparation of all the other terms of the series (Tb<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup> and Lu<sup>3+</sup>). See the Supporting Information for the isolated yields of the various KLnL<sub>2</sub>.

## Synthesis of KYbL<sub>2</sub> and General Method for KLnL<sub>2</sub>

In a 10 mL two-neck flask, 0.01 g (0.50 mmol) of (H<sub>2</sub>L) were dissolved in 1 mL of anhydrous diethylether under nitrogen atmosphere. Then 0.17 g of Yb(TfO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.25 mmol) was added at once, which resulted in a turbid suspension. Finally, 1.20 mL of KOH solution (1.10 mmol in 2 mL of MeOH) was added: an immediate change of color (from off-white to bright yellow) was appreciated, followed by the precipitation of the metal chelate. The solution was stirred for 2 h at 80 °C, then it was cooled, filtered, and the precipitate washed several times with diethyl ether to remove traces of unreacted ligand. Then the pale yellow solid was dried (0.01 g, yield 90%) and characterized through <sup>1</sup>H NMR (see Supporting Information).

#### **Computational Section**

DFT and TD-DFT calculations were run with Gaussian '09<sup>29</sup> with default grids and convergence criteria, using the functionals M06<sup>30</sup> and CAM-B3LYP.<sup>31</sup> Ahlrichs TZVP<sup>32</sup> basis set was employed for geometry optimization and TD-DFT calculations for all atoms except Lu, for which the SDD basis set and MWB60 effective core potential (ECP) were used.<sup>33</sup> The input structure for DFT geometry optimizations was obtained by the routine PERSEUS<sup>34</sup> by means of NMR data analysis. The number of excited states considered was 150 for single-molecule calculations. UV and CD spectra were generated using the program SpecDis<sup>35</sup> by applying a Gaussian band shape with  $\sigma$ =0.24 eV exponential half-width.

## RESULTS AND DISCUSSION NMR Characterization

An NMR titration of the deprotonated ligand L in CDCl<sub>3</sub> with the Ln salt reveals the full disappearance of the free ligand resonances at L:Ln<sup>3+</sup> = 2:1 stoichiometry. At this point, the <sup>1</sup>H and <sup>13</sup>C-NMR spectra (CDCl<sub>3</sub>) show a unique set of eight (relatively) narrow resonances, which confirms KLnL<sub>2</sub> as the main species in solution, characterized by an effective  $D_Z$  symmetry.

Except for La<sup>3+</sup>, Gd<sup>3+</sup>, and Lu<sup>3+</sup> ions, all other Ln<sup>3+</sup> ions possess unpaired electrons and this paramagnetism induces remarkable shifts of nuclear resonances (Lanthanide Induced Shift or LIS effect) with respect to the diamagnetic terms (lutetium derivative in this study). In the principal system of Ln<sup>3+</sup> magnetic susceptibility tensor ( $\chi^{Ln}$ ), under the assumption that the unpaired electron(s) cloud can be effectively described as a point (i.e., that the 4f-electron radial distribution is small compared to the Ln-H or Ln-C distances), one can write well-established relationships<sup>16,18</sup>

$$\delta_{ij}^{\exp} = \delta_i^{dia} + \delta_{ij}^{para} = \delta_i^{dia} + \delta_{ij}^{FC} + \delta_{ij}^{PCS} \tag{1}$$

$$\delta_{ij}^{FC} = -\frac{A_i}{\hbar} \frac{\langle S_Z \rangle_j}{\gamma_I B_0} = F_i \langle S_Z \rangle_j \tag{2}$$

$$\delta_{ij}^{PCS} = D_{I,j} \frac{3\cos^2\theta_i - 1}{r_i^3} + D_{II,j} \frac{\sin^2\theta_i \sin^2\Omega_i - 1}{r_i^3} = D_{I,j}G_i + D_{II,j}H_i$$
(3)

in which the index *i*-th refers to the considered resonant nucleus and the *j*-th index to the lanthanide;  $\delta^{dia}_{ij}$  is the chemical shift in a reference diamagnetic compound ( $j = La^{3+}$  or  $Lu^{3+}$ );  $\delta^{FC}_{ij}$  is the Fermi contact shift and  $\delta^{PCS}_{ij}$  is the pseudocontact

shift;  $A_i/\hbar$  is the hyperfine coupling constant;  $\gamma_1$  is the gyromagnetic ratio of the observed nucleus and  $B_0$  is the applied magnetic field;  $\langle S_z \rangle_j$  is the expectation value of  $S_z$  operator for the specific lanthanide;  $G_i$  and  $H_i$  are geometrical factors of the *i*-th nucleus, dependent on  $(r_i, \theta_i, \Omega_i)$ , its spherical coordinates in a polar system centered on the metal ion;  $D_{I_j}$ and  $D_{II,j}$  are respectively the axial and rhombic term of  $\chi^{Ln}$ .

Paramagnetism enhances longitudinal,  $\rho_1$ , and transverse,  $\rho_2$ , relaxation rates according to<sup>18</sup>

$$\rho_{(1,2),ij}^{\exp} = \rho_{(1,2),ij}^{dia} + \rho_{(1,2),ij}^{para}$$
(4)

where the superscripts *dia* and *para* refer to diamagnetic and paramagnetic contributions, similarly to what we said above for the shift equations. Grossly estimating the term  $\rho_1^{dia} = 1 \text{ s}^{-1}$ , we can write

$$\rho_{1,ij}^{para} = \rho_{1,ij}^{\exp} - 1 = \frac{K_{1,j}}{r_i^6} \tag{5}$$

in which  $K_1$  is constant for all nuclei of the *j*-th lanthanide complex. Equation 5 is particularly helpful for assigning the



**Fig. 1.** Longitudinal relaxation rate  $\rho_{I,ij}^{\text{para}}$  vs.  $r_i^{-6}$  for KYbL<sub>2</sub> complex.

<sup>1</sup>H-NMR spectrum of a complex with strongly shifted resonances: taking the distances  $r_i$  from a roughly optimized (by molecular mechanics, MM) structure, one can seek the best linear trend in a  $\rho_{I,ij}^{\text{para}}$  vs.  $r_i^{-6}$  plot. In this specific case, because of the effective  $D_2$  symmetry, this preliminary operation can be performed on a model structure including only  $\frac{1}{2}$  of the salen ligand. The result for KYbL<sub>2</sub> starting with an MM model of the complex is shown in Figure 1.

With the aid of <sup>1</sup>H relaxation rates, of homo- and heteronuclear correlation spectra, and following a protocol based on eqs. (1–5) described elsewhere,  $^{16,19,36,37}$  we obtained the complete assignment of the NMR spectrum of KYbL<sub>2</sub>.

Linearity of  $\delta_i^{para,Yb}$  vs.  $\delta_i^{para,Ln}$  reveals isostructurality between the Yb<sup>3+</sup> and the Ln-compounds,<sup>37</sup> which is indeed the case for all systems from Tb<sup>3+</sup> to Tm<sup>3+</sup>. This condition ensures that separation of Fermi contact and pseudocontact shifts can be obtained through the method described in previous work,<sup>37</sup> with the results displayed in Tables 1 and 2.

## From PCSs to PERSEUS Structure

Once isostructurality in solution has been demonstrated and pseudocontact shifts are available, one can use our routine PERSEUS<sup>19</sup> to determine the accurate solution geometry of KLnL<sub>2</sub>. To this end, in a first run we used only the <sup>1</sup>H data obtaining an agreement factor (see the caption to Figure 2) A.F. = 1%, which is completely satisfactory. Second, we introduced also the <sup>13</sup>C paramagnetic shifts for KYbL<sub>2</sub>, on the assumption that the contact contribution for this ion is negligible, as indeed witnessed by the <sup>1</sup>H data shown in Table 1. The resulting A.F. = 7% is extremely good. The principal values of magnetic anisotropy for Yb<sup>3+</sup>, D<sub>I</sub> and D<sub>II</sub>, are respectively –3980.19 and –1602.05 ppm · Å<sup>3</sup> (see eq. 3 in the above section).

TABLE 1. Experimental paramagnetic shifts  $\delta_{i,Ln}^{para}$ , pseudocontact  $\delta_{i,Ln}^{PCS}$ , and Fermi Contact  $\delta_{i,Ln}^{FC}$  contributions for KLnL<sub>2</sub> series (in ppm)

(a)	Tb <sup>3+</sup>			Dy <sup>3+</sup>			Ho <sup>3+</sup>			
$^{1}\mathrm{H}$	$\delta^{\text{para}}$	$\delta^{PCS}$	$\delta^{FC}$	$\delta^{\text{para}}$	$\delta^{PCS}$	$\delta^{FC}$	$\delta^{\text{para}}$	$\delta^{PCS}$	$\delta^{FC}$	
3	27.76	43.38	-11.48	44.19	54.10	-10.30	21.66	27.94	-8.16	
5	38.54	50.46	-10.38	53.89	62.93	-9.31	26.00	32.50	-7.38	
6	8.22	32.69	-17.55	26.24	40.77	-15.74	12.54	21.05	-12.48	
i	81.58	85.83	-12.24	89.43	107.04	-10.98	45.95	55.27	-8.71	
bz	-159.90	-129.25	-17.67	-168.58	-161.19	-15.85	-93.11	-83.24	-12.57	
0	-79.27	-97.78	4.50	-128.13	-121.94	4.03	-61.84	-62.97	3.20	
m	-28.74	-35.13	1.86	-45.49	-43.82	1.66	-22.01	-22.63	1.32	
р	-23.86	-28.87	1.87	-36.65	-36.00	1.67	-17.77	-18.59	1.33	
(b)		Er <sup>3+</sup>			Tm <sup>3+</sup>			$\mathbf{Yb}^{3_{+}}$		Lu <sup>3+</sup>
$^{1}\mathrm{H}$	$\delta^{\text{para}}$	$\delta^{PCS}$	$\delta^{FC}$	$\delta^{\text{para}}$	$\delta^{PCS}$	$\delta^{FC}$	$\delta^{\text{para}}$	$\delta^{PCS}$	$\delta^{FC}$	$\delta^{dia}$
3	-13.28	-8.93	-5.55	-21.75	-18.42	-2.96	-8.36	-8.44	-0.93	6.47
5	(*)	(*)	(*)	-16.67	-21.43	-2.68	-8.40	-9.82	-0.85	6.94
6	(*)	(*)	(*)	(*)	(*)	(*)	-3.40	-6.36	-1.43	6.51
i	-22.17	-17.66	-5.91	-40.29	-36.45	-3.16	-15.71	-16.70	-1.00	7.52
bz	16.47	26.60	-8.54	51.12	54.90	-4.56	23.46	25.15	-1.44	6.04
0	24.25	20.12	2.17	41.73	41.53	1.16	21.09	19.03	0.37	7.4
m	8.83	7.23	0.90	15.00	14.92	0.48	7.55	6.84	0.15	7.29
р	7.37	5.94	0.90	12.50	12.26	0.48	6.14	5.62	0.15	7.18

In the last column the diamagnetic shifts  $\delta_{i,Ln}^{dia}$  for  $Lu^{3+}$  are also reported. \*Values are not experimentally available.

TABLE 2. Total observed <sup>13</sup>C shifts for Lu<sup>3+</sup> and Yb<sup>3+</sup>

<sup>13</sup> C	$\delta^{\mathrm{obs, \ Lu}}$	$\delta^{\mathrm{obs, Yb}}$
3	121.02	101.69
5	132.74	86.07
6	134.79	106.79
i	162.49	100.42
bz	74.8	(*)
0	130.08	139.63
m	128.65	125.69
р	127.05	122.37

\*Values are not experimentally available.

In this structure the salen ligand is twisted (NCCN dihedral angle) by  $-54^{\circ}$ , which is close to the value found on a heteroleptic Dy<sup>3+</sup> complex containing the same ligand.<sup>15</sup>

## UV-vis and ECD Spectra

The UV–vis spectrum of the free ligand  $H_2L$  (see Supporting Information) exhibits two absorption peaks at 248 nm and 312 nm, due to the transitions of conjugated cromophores.<sup>38–40</sup>

UV-vis absorption and CD spectra for the salen-type complexes are shown in Figures 3 and 4. Compared with the absorption peak of the ligand, one can note a bathochromic shift by 20 nm, indicating the deprotonation of the ligand and its coordination to  $\text{Ln}^{3+}$  ions.

Comparing the different Ln-adducts along the series, the absorption spectra show consistent similarities in the 200–330 nm range, while some differences can be found in the 330–450 nm region for  $\text{Er}^{3+}$  and  $\text{Tb}^{3+}$ . In the UV region there are two strong bands at 260 nm and 220 nm. Above 300 nm, two weaker and broader absorptions are observed around 400 nm and 320 nm for  $\text{Dy}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Lu}^{3+}$ ,  $\text{Tm}^{3+}$ , and  $\text{Yb}^{3+}$ . In this region, the behavior of  $\text{Er}^{3+}$  and  $\text{Tb}^{3+}$  derivatives appears different, as the longer-wavelength band is red-shifted by 50 nm in comparison with the other terms of the series.

The ligand-centered UV-vis ECD spectra show no variation along the series and several consistent features may be observed (approximate wavelength in nm, sign and strength are indicated): 400 (+, weak); 370 (-, medium); 350 (+, medium); 330 (-,weak); 270 (-, medium); 260 (+, strong); 230 (-, strong); 210 (+, strong). These bands are allied with the electronic transitions centered on the ligand moieties, each containing two salicylidiimine moieties and two phenyl rings. Since ECD spectra are very sensitive to the structure, the consistent profile observed for all complexes further confirms the isostructurality for all the Ln<sup>3+</sup> species considered, at least in terms of relative orientation between the various chromophores.

## Ligand-Centered ECD Calculations

TD-DFT is currently recognized as one of the methods with the best cost/efficiency compromise to simulate the UV-vis and CD spectra of medium-size transition metal complexes.<sup>20,41–43</sup> The isostructurality we observed along the series allows us to extrapolate the geometry and to extend it to the Lu<sup>3+</sup> derivative, which is a closed-shell system, amenable to a TD-DFT/DFT protocol to calculate the ligandcentered ECD spectrum<sup>44</sup>.

Starting from the PERSEUS structure, this latter was reoptimized with DFT using the M06 functional and TZVP basis set for all atoms except Lu, for which the SDD basis set and MWB60 effective core potential (ECP) were used (see Supporting Information).<sup>33</sup> The final structure possesses  $D_2$ symmetry (in agreement with NMR data) and Lu-O e Lu-N distances equal respectively to 2.445 e 2.700 Å (in keeping with the literature for similar cases).<sup>45</sup> No axial coordination or solvent effects were considered in the geometry optimization and in the following ECD calculations. The DFToptimized geometry is reported in Figure 5 and appears very similar to the NMR one, confirming our structural determination (R.M.S. deviation = 0.21 Å; see distance comparison in the Supporting Information).

ECD calculations were run on the DFT-optimized structure with the TD-DFT method using the CAM-B3LYP functional and the same set of basis and ECP discussed above, and the result is shown in Figure 6. The nice agreement with the experimental ECD spectrum confirms the quality of the NMR-derived and DFT-optimized structures, in terms of interchromophoric arrangement.

## Near-IR Electronic CD

Finally, we took advantage of the Near-IR ECD spectrum associated with the monoelectronic  $Yb^{3+}$  transitions  ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ .<sup>17</sup> The Near-IR ECD spectrum of the  $Yb^{3+}$  complex, displayed in Fig. 7 (dashed blue line), consists



Fig. 2. Solution structure of KYbL<sub>2</sub>, as determined through the analysis of paramagnetic NMR data. The agreement factor is defined as A.F. =  $[(\Sigma_i(\delta_i^{\text{pcs,calc}} - \delta_i^{\text{pcs,calc}})^2/\Sigma_i(\delta_i^{\text{pcs,exp}})^2)]^{1/2}$ .



Fig. 3. Ligand-centered UV-vis spectra of KLnL<sub>2</sub> complexes (CHCl<sub>3</sub> solution).



Fig. 4. Ligand-centered ECD spectra of KLnL<sub>2</sub> complexes (CHCl<sub>3</sub> solution).



**Fig. 5.** Comparison between DFT-refined structure of  $LuL_2^-$  (hue in blue) and PERSEUS output for KYbL<sub>2</sub> (hue in pink).

of an intense and broad positive band at 970 nm and a weak one at 960 nm.

To simulate the same spectrum, we used Richardson's equations, a simplified electrostatic model based on charge and polarizability of atoms and groups of an organic ligand around a lanthanide ion.<sup>22</sup> Charge and polarizability were evaluated respectively by standard natural bond orbital (NBO) analysis (from DFT calculations)<sup>46</sup> and the atombased method by Miller.<sup>47</sup> The CD spectrum was simulated weighting each transition by the Boltzmann population of the starting crystal-field sublevel and applying to each line a



Fig. 6. TD-DFT calculated (continuous red line; red shift=+30 nm;  $\sigma$ =0.024 eV) and experimental (dashed blue line) ECD spectra of KLuL<sub>2</sub> complex.



Fig. 7. Comparison between calculated (continuous red line) and experimental (dashed blue line) Near-IR CD spectra of  $KYbL_2$  complex.

Lorentzian function with  $\Delta v = 50 \text{ cm}^{-1}$ . For details on the procedure, see Ref. 20. The result, shown in Figure 7, is very satisfactory: with the exception of a small red-shift for the highest-energy band, the calculated spectrum matches very well the experimental one, which further validates our structure, this time in terms of crystal field geometry around the lanthanide ion.

Currently, we are not able to compute other lanthanidecentered ECD spectra and consequently we only report the experimental NIR-ECD data of Er<sup>3+</sup> and Tm<sup>3+</sup> (see Supporting Information).

#### **Emission Spectra**

Upon irradiation at 348 nm,  $\text{Tm}^{3+}$  and  $\text{Tb}^{3+}$  derivatives display blue and red luminescence, respectively. Their emission spectra are shown in Figures 8 and 9. We can recognize a broad band in the range 400–480 nm, due to the ligand fluorescence. In addition, we can distinguish the typical narrow bands associated to *f-f* Ln<sup>3+</sup> transitions, which are clearly sensitized by the ligand. The Tm<sup>3+</sup> compound displays blue luminescence when irradiated at 365 nm and its emission spectrum shows only two narrow bands centered respectively *Chirality* DOI 10.1002/chir



**Fig. 8.** Photoluminescence of  $\text{Tb}^{3+}$  ion in  $\text{KTbL}_2$  complex.



Fig. 9. Photoluminescence of Tm<sup>3+</sup> ion in KTmL<sub>2</sub> complex.

at 380 nm  $({}^{1}D_{2} \rightarrow {}^{3}H_{4})$  and 390 nm  $({}^{1}D_{2} \rightarrow {}^{3}H_{5})$ . The Tb<sup>3+</sup> compound shows green luminescence and we can recognize at least five distinct transitions: (a)  ${}^{5}D_{3} \rightarrow {}^{7}F_{6}$  (380 nm, weak); (b)  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$  (490 nm, strong); (c)  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  (540 nm, strong); (d)  ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$  (575 nm, weak); (e)  ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$  (610 nm, weak).

## CONCLUSION

The salen-type ligand H<sub>2</sub>L is very well suited to promptly obtain stable and inert complexes with late lanthanides. Their structure in solution was determined by means of paramagnetic NMR and remains conserved from Tb<sup>3+</sup> to Yb<sup>3+</sup>. We used two widely different computational approaches to account for the ECD spectra in the UV, which is due to ligand-centered electronic transitions, and-for the Yb<sup>3+</sup> compound—in the Near-IR, around 1000 nm, allied to the magnetically allowed transition of this ion. In the former case, we used TD-DFT; in the latter we employed Richardson's equations, based on a simplified electrostatic model describing the interaction between the ligand and Ln<sup>3+</sup>. The match between computed and experimental spectra demonstrates that the quality of our structure is completely satisfactory. It is interesting to observe that the two spectral windows are sensitive to different structural portions, the Chirality DOI 10.1002/chir

UV-vis one to the (relative) orientation of the aromatic ligands, while the NIR one to the crystal field geometry around the lanthanide ion. Therefore, a combined approach based on both methods allows a safer structural assignment than any single method alone. Emission spectra of  $Tb^{3+}$  and  $Tm^{3+}$  derivatives display the expected sharp lines typical for these two metal ions, which emerge over a broad background of ligand-centered emissions.

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## SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article at the publisher's web-site.

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