# Luminescence and structural properties of lanthanide complexes of Schiff bases derived from pyridoxal and amino acids<sup>†</sup>‡

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Lanthanide complexes of Schiff bases (SBs) with 1 : 1 and 1 : 2 (M : Lig) stoichiometric ratios were prepared by condensation of pyridoxal (PL) and aspartic acid (Asp) or L-histidine (His), respectively, in the presence of the appropriate metal chloride as a templating agent. These complexes were studied by optical spectroscopy and single crystal X-ray diffraction techniques. Crystallographic studies of 1 : 1 ([Eu(PL-Asp)(H<sub>2</sub>O)<sub>4</sub>](H<sub>2</sub>O)) and 1 : 2 ([Eu(PL-His)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl(H<sub>2</sub>O)<sub>4</sub>) complexes show that Eu<sup>III</sup> is eight-coordinate in both structures, in a distorted square antiprism environment formed by the phenolic oxygen of PL, the nitrogen atom of carbon–nitrogen double bond, oxygen atoms of the carboxylate groups of His or Asp, and oxygen atoms of the water molecules. The main species formed in aqueous solutions containing these SBs have been determined by analysis of the luminescence spectra, lifetimes of Eu<sup>III</sup> excited states and vibronic interaction as well as structural features of the Eu<sup>III</sup> coordination sphere. Possible tetradentate coordination function of SBs in aqueous solutions with relatively high concentrations as well as the potential application of the lanthanide SB complexes as new luminescence materials are discussed.

## Introduction

Lanthanide complexes of Schiff bases derived from pyridoxal and amino acids are very attractive subjects for investigation due to two aspects of their potential applications, namely luminescent and biological ones. In view of the former, the luminescence of lanthanide coordination compounds, supramolecules and polymers has been widely investigated because of the strong emission important for luminescent and laser materials.1 Owing to the structural features of Schiff bases (SBs) their lanthanide complexes have some advantages for luminescence research.<sup>2</sup> First, the SB ligands can be tetradentate which greatly stabilizes the complex in solution relative to bi- and tridentate ligands and strongly minimizes the probability of solvent molecule coordination (that is especially important for water molecules) for 1:2 complexes which results from the predisposition of lanthanide ions towards high coordination numbers (CN = 8-9). Second, the high extinction coefficients of many SB ligands in the near ultraviolet-visible range provide effective absorption of excitation energy which promotes more effective energy transfer to the lanthanide ion. Therefore numerous types of lanthanide SB complexes have been prepared

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including macrocyclic SBs,<sup>3</sup> anhydrous SBs,<sup>4</sup> SB complexes with liquid crystal properties<sup>5</sup> *etc*. However, in the case of tetradentate SBs, many of which have a -2 charge (for example, H<sub>2</sub>salen<sup>6</sup> intensively investigated),<sup>7</sup> Ln<sup>III</sup> ions usually form complexes with the formula Ln<sub>2</sub>L<sub>3</sub> and exhibit less quantum yield in comparison with LnL<sub>2</sub> complexes.<sup>2</sup> As a result Schiff bases derived from pyridoxal and amino acids (Asp and His) were chosen as potential tetradentate ligands containing chromophore groups and the ability to form one centered lanthanide complexes.

A second aspect of interest concerns the biological relevance of compounds containing metal ions and amino acids. Schiff bases of pyridoxal 5'-phosphate (PLP) and its analogues with amino acids have been extensively studied because of their important biological role in the metabolism of amino acids.8 Research concerning lanthanide complexes of SBs with amino acids also sheds light on the coordination function of amino acid radicals. The precipitation of lanthanide ions at alkali pH prevents investigation of the coordination of amino acids whereas in complexes with SBs lanthanide ions do not hydrolyze until  $pH = 10.^9$  Despite the large interest in metal ion containing model systems which reproduce some of the transformations of amino acids effected by pyridoxal-dependent enzymes, most of the studies have been carried out in solution, and only a limited number of Schiff base chelates related to pyridoxal catalysis have been isolated. Basically, the majority of studies reported so far focused either on SBs derived from pyridoxal or on their metal complexes. There are many papers describing crystal structures of pyridoxal SB complexes with copper(II)<sup>10</sup> and cobalt(III)<sup>11</sup> while there are none for analogous complexes with lanthanide ions according to the best of our knowledge. On the other hand Zolin et al. have found that complexes of the Schiff base derived from pyridoxal and aspartic acid can be used as lanthanide shift reagents (LSR) for investigation of derivatives of amino acids and nucleotides in aqueous solutions.12 However the study of the luminescence

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<sup>&</sup>lt;sup>‡</sup> Electronic supplementary information (ESI) available: Additional tables and pictures of X-ray data as well as luminescence data including the crystal-field splitting of the Eu<sup>III</sup> spin–orbit levels in **1** and **2** complexes. See DOI: 10.1039/b706020c

properties of this system is incomplete and further work in the LSR field was not performed due to the lack of structural characterization. The absence of information on Schiff bases of Lhistidine, notwithstanding the biological importance of this amino acid as a metal binding site, was noted in 1981.<sup>13</sup>

In view of this, we report here two europium complexes  $([Eu(PL-Asp)(H_2O)_4](H_2O)(1)$  and  $[Eu(PL-His)_2(H_2O)_2]Cl(H_2O)_4$ (2)) synthesized and structurally characterized by spectroscopic and single crystal X-ray diffraction techniques. Combined analysis of the luminescence, phosphorescence and vibronic spectra has been used to describe the photophysical properties of the europium SB complexes. The differences between the structural properties of the complexes considered in the solid state and in solution are discussed based on the analysis of lifetimes of Eu<sup>III</sup> excited states and luminescence spectra.

## **Results and discussion**

#### Synthesis and structural characterisation

Lanthanide complexes of Schiff bases with 1 : 1 and 1 : 2 (Ln : Lig) stoichiometric ratios (Ln = La, Eu, and Gd) were prepared by the typical condensation reaction of pyridoxal (PL) and racemic aspartic acid (Asp) or L-enantiomeric histidine (His), respectively, in the presence of the appropriate metal chloride as a templating agent (Scheme 1).<sup>14</sup> Single crystals of the [Eu(PL-Asp)(H<sub>2</sub>O)<sub>4</sub>](H<sub>2</sub>O) (1) and [Eu(PL-His)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl(H<sub>2</sub>O)<sub>4</sub> (2) complexes obtained were studied by single crystal X-ray diffraction methods (Table 1).

The general view of complex 1 along with the atom numbering scheme is shown in Fig. 1. Selected bond lengths and angles



Scheme 1 Schematic presentation of Schiff bases used.

are listed in Table 2. Although complex 1 is homochiral it crystallizes in a racemic space group (C2/c). The nitrogen atom N(2) of the C=N bond as well as carbon atoms C(8), C(9), C(10) of the dicarboxylate moiety containing the chiral center C(9) are disordered by two positions (Fig. S1, ESI<sup>‡</sup>). Such disorder corresponds to superposition of two enantiomers in a ratio of 0.802(6) : 0.198(6). The total ratio of enantiomers is 1 : 1 due to centrosymmetric packing in the crystal despite enantiomer excess in the independent part. The europium ion possesses a distorted square antiprism geometry and is coordinated to the phenolic oxygen atom O(1), the nitrogen atom of the C=N double bond N(2), two oxygen atoms of the carboxylate groups O(5) and O(3) and four oxygen atoms of water molecules (O(4w), O(2w), O(3w), O(1w)). One of the antiprism bases is formed

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		Complex 1	Complex 2	
	Empirical formula	$C_{12}H_{21}EuN_2O_{11}$	$C_{28}H_{42}ClEuN_8O_{14}$	
	Formula weight	521.27	902.11	
	Crystal colour, habit	Yellow, prism	Yellow, plate	
	Crystal size/mm	$0.14 \times 0.16 \times 0.23$	$0.04 \times 0.08 \times 0.11$	
	Temperature/K	100(2)	100(2)	
	Crystal system	Monoclinic	Orthorhombic	
	Space group	C2/c	C222 <sub>1</sub>	
	a/Å	15.418(1)	7.268(2)	
	b/Å	8.4575(5)	20.816(5)	
	c/Å	26.016(2)	23.403(6)	
	β/°	90.6985(12)	90	
	V/Å <sup>3</sup>	3392.1(4)	3540.7(16)	
	Z(Z')	8(1)	4(0.5)	
	F(000)	2064	1832	
	$D_{\rm calc}/{\rm g}~{\rm cm}^{-1}$	2.041	1.692	
	Linear absorption, $\mu/cm^{-1}$	37.61	19.25	
	$T_{\rm min}/T_{\rm max}$	0.4783/0.6210	0.8162/0.9270	
	Scan type	$\omega$ (8 s exposure per frame)	$\omega$ (50 s exposure per frame)	
	$\theta$ range/°	2.64-29.0	1.57-27.00	
	Completeness of dataset (%)	99.9	100.0	
	Reflections measured	15841	15989	
	Independent reflections	$4496 [R_{int} = 0.0309]$	$3859 [R_{int} = 0.1654]$	
	Observed reflections $[I > 2\sigma(I)]$	3965	2833	
	Parameters	263	236	
	Final $R(F_{hkl})$ : $R_1$	0.0272	0.0626	
	$wR_2$	0.0587	0.1268	
	GOF	1.063	1.041	
	$\Delta  ho_{ m max}, \Delta  ho_{ m min}/{ m e} { m \AA}^{-3}$	1.019, -0.997	1.158, -1.508	

Table 1 Summary of crystallographic data and experimental details for [Eu(PL-Asp)(H<sub>2</sub>O)<sub>4</sub>](H<sub>2</sub>O) (1) and [Eu(PL-His)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl(H<sub>2</sub>O)<sub>4</sub> (2) complexes<sup>†</sup>

**Table 2** Selected bond lengths (Å) and bond angles (°) in the crystal of  $[Eu(PL-Asp)(H_2O)_4](H_2O)$  (1)

Eu(1)–O(1)	2.259(2)	Eu(1) - O(1W)	2.459(2)
Eu(1) - O(3)	2.389(2)	Eu(1) - O(2W)	2.413(2)
Eu(1) - O(5)	2.416(2)	Eu(1) - O(3W)	2.416(2)
Eu(1)-N(2)	2.504(3)	Eu(1)–O(4W)	2.443(2)
$O(1) = F_{11}(1) = O(3)$	135 (19(8))	$O(3W) = F_{11}(1) = O(4W)$	70 55(8)
O(1) = Eu(1) = O(3)	82 45(8)	O(1) = Fu(1) = O(1W)	80 68(8)
O(3) = Eu(1) = O(2W)	13844(8)	O(3) - Eu(1) - O(1W)	72 27(8)
O(1) = Eu(1) = O(2W)	103.44(8)	O(2W) = Eu(1) = O(1W)	1/3 56(8)
O(1) = Eu(1) = O(5) O(2) = Eu(1) = O(5)	78 10(0)	O(2W) = Eu(1) = O(1W)	140.15(8)
O(3) = Eu(1) = O(3)	76.10(9)	O(3) = Eu(1) = O(1W)	140.13(8)
O(2w) = Eu(1) = O(5)	/5.34(8)	O(3W) - Eu(1) - O(1W)	105.92(8)
O(1) - Eu(1) - O(3W)	153.74(8)	O(4W)– $Eu(1)$ – $O(1W)$	71.69(8)
O(3) - Eu(1) - O(3W)	70.03(7)	O(1)-Eu(1)-N(2)	69.33(9)
O(2W) - Eu(1) - O(3W)	77.51(8)	O(3)-Eu(1)-N(2)	71.73(10)
O(5)-Eu(1)-O(3W)	87.81(8)	O(2W) - Eu(1) - N(2)	121.62(10)
O(1)-Eu(1)-O(4W)	88.26(8)	O(5)-Eu(1)-N(2)	63.97(9)
O(3)-Eu(1)-O(4W)	115.06(8)	O(3W) - Eu(1) - N(2)	136.22(9)
O(2W) - Eu(1) - O(4W)	75.75(8)	O(4W) - Eu(1) - N(2)	147.65(9)
O(5) - Eu(1) - O(4W)	146.95(8)	O(1W) - Eu(1) - N(2)	81.58(10)



Fig. 1 The general view of  $[Eu(PL-Asp)(H_2O)_4](H_2O)$  (1) with atoms represented by thermal ellipsoids (p = 50%). The disorder is omitted for clarity.

by three water molecules (O(1w), O(3w) and O(4w)) and the carboxylate oxygen O(3) while the second is composed of O(1), O(2w), O(5) and N(2) atoms (Fig. S2, ESI<sup>‡</sup>). The coordination number of the europium ion is eight. The distortion of the Eu<sup>III</sup> coordination polyhedron in the above enantiomers is different. For the predominant component the mean deviation for the two antiprism bases are 0.08 and 0.11 Å with a dihedral angle between them equal to 1°. For another component the mean deviation of atoms for the O(1)–O(2w)–O(5)–N(2) base is ~0.25 Å and the corresponding dihedral angle is 6.2°. The Eu–N(2) bond lengths are equal to 2.504(3) and 2.545(13) Å for two components of the disordered group. The Eu–O bond lengths of PL-Asp vary in the range of 2.259(2)–2.416(2) Å and the Eu–O bonds of the coordinated water molecules are systematically elongated (2.413(2)–2.459(2) Å).

The general view of the cation complex **2** along with the atomnumbering scheme is shown in Fig. 2. Selected bond lengths and angles are listed in Table 3. Complex **2** crystallizes in the homochiral space group  $C222_1$  (the europium ion occupies the special position—two-fold axis). The coordination geometry can be described as a distorted square antiprism similar to complex **1**. The Eu<sup>III</sup> is coordinated by two PL-His ligands, the oxygen atom O(3) of the carboxylate group, the nitrogen atom N(2) of the



**Fig. 2** The general view of  $[Eu(PL-His)_2(H_2O)_2]Cl(H_2O)_4$  (2) with atoms represented by thermal ellipsoids (p = 50%).

C=N double bond, the oxygen atom O(1) of pyridoxal and the oxygen atom O(1w) of water. The europium coordination number is eight. The symmetrically related antiprism bases are composed of O(1), O(1w), O(3) and N(2) atoms (Fig. S2, ESI‡). The mean displacement of atoms from the antiprism base and the dihedral angle between bases are 0.10 Å and 4.9°, respectively. The Eu–O bond lengths of PL-His vary in the interval 2.316(7)–2.377(7) Å, the Eu–O(1w) bond length is 2.417(6) Å, and the Eu–N(2) bond length is 2.562(8) Å. The pyridine rings of PL-His ligands are almost parallel to each other (the dihedral angle is 4.2°) with the shortest contacts C(2) ··· C(2A) and N(1) ··· N(1A) equal to 3.03 and 3.24 Å, respectively. Such disposition as well as shortened distances between rings serves as direct evidence of a rather strong intramolecular  $\pi$ -stacking interaction.<sup>15</sup>

In summarizing the features of the molecular structures of complexes 1 and 2 it is worth emphasizing that the bonds formed by europium are longer in complex 2 probably owing to steric hindrances. However, the formal charge of the ligands in the complexes are principally different. In complex 1 the PL-Asp ligand is characterized by a formal charge of -3 formed by

**Table 3** Selected bond lengths (Å) and bond angles (°) in the crystal of  $[Eu(PL-His)_2(H_2O)_2]Cl(H_2O)_4$  (2)

Eu(1)–O(1) Eu(1)–O(3)	2.316(7) 2.377(7)	Eu(1)–O(1W) Eu(1)–N(2)	2.417(6) 2.562(8)
$\begin{array}{l} O(1A)-Eu(1)-O(1)\\ O(1A)-Eu(1)-O(3A^{a})\\ O(1)-Eu(1)-O(3A)\\ O(1)-Eu(1)-O(3)\\ O(3A)-Eu(1)-O(3)\\ O(1A)-Eu(1)-O(1WA)\\ O(1)-Eu(1)-O(1WA)\\ O(3)-Eu(1)-O(1WA)\\ O(3)-Eu(1)-O(1WA)\\ O(3)-Eu(1)-O(1WA)\\ O(1W)-Eu(1)-O(1WA) \end{array}$	$\begin{array}{c} 78.7(3) \\ 113.5(2) \\ 141.0(2) \\ 113.5(2) \\ 81.0(3) \\ 69.8(2) \\ 137.3(2) \\ 78.3(2) \\ 79.6(2) \\ 150.9(3) \end{array}$	O(1A)-Eu(1)-N(2) O(1)-Eu(1)-N(2) O(3)-Eu(1)-N(2) O(1WA)-Eu(1)-N(2) O(1W)-Eu(1)-N(2) O(3)-Eu(1)-N(2A) O(1WA)-Eu(1)-N(2A) O(1W)-Eu(1)-N(2A) N(2)-Eu(1)-N(2A)	87.4(2) 70.2(2) 65.0(3) 80.1(2) 107.3(2) 143.2(3) 107.3(2) 80.1(2) 151.2(4)

<sup>*a*</sup> Atoms with the label A are obtained from base one by the symmetry operation -x + 1, y, -z + 3/2.

the deprotonated hydroxyl group of PL and two deprotonated carboxylate groups. In complex 2 both PL-His ligands are characterized by a formal charge of -1 owing to the deprotonated hydroxyl group of PL, deprotonated carboxylate group of His and the protonated N(1) atom of pyridoxal ring. The latter is unambiguously reflected in the pronounced increase of the C(1)-N(1)-C(5) angle from 118.7(2) to 125.6(1.5)°. The above increase of the C-N-C angle upon protonation agrees well with available structural data for similar complexes of transition metals. Indeed according to the Cambridge Structural Database (Ver. 5.28, November 2006) in 34 complexes with protonated pyridoxal ring the value of the corresponding C-N-C angle varies in the range of 123.4–125.4°. Hence complex 1 is neutral while complex 2 is a cation with a chloride as the counterion owing to the difference in the charges of the coordinated ligand. The chloride anions in crystal of complex 2 form H-bonds with two solvate water molecules (O  $\cdots$  Cl separation varies in the range of 2.88–3.02 Å) and all cation ... anion contacts are rather long, in particular the shortest  $Cl(1) \cdots Eu(1)$  contact is as large as 7.268(5) A.

The crystal packing in both complexes is related to the presence of hydrogen bonds and  $\pi$ - $\pi$  interactions. Molecules of complex **1** in the crystal are assembled into centrosymmetric dimers (Fig. 3). These pairs are held together by intermolecular stacking interactions of moderate strength between the pyridoxal ring and the C=N double bond of the coordinated PL-Asp ligands with the shortest C...C and C...N contacts equal to 3.33–3.48 and ~3.50 Å, respectively. In addition these dimers are assembled into 3-dimensional frameworks by numerous O-H...O (O...O 2.68– 2.90 Å) and O-H...N (O...N 2.77 Å) hydrogen bonds.

The cation complexes 2 in the crystal are assembled into infinite chains by intermolecular stacking interactions of strength similar to the above mentioned intramolecular stacking interactions (the shortest contacts  $C(3) \cdots C(3) (-x, y, 3/2 - z)$  and  $C(5) \cdots C(5) (-x, y, 3/2 - z)$  amount to 3.31 and 3.23 Å, respectively) but the type of cycle overlap is different in principle. Moreover the O-H  $\cdots$  N hydrogen bonds formed by water molecules coordinated with the nitrogen atom of histidine can be anticipated (N(4)  $\cdots$  O(3w) 2.79 Å). The said chains are interlinked into the cationic layers by rather strong CO<sub>2</sub>  $\cdots$  H–N(1) hydrogen bonds (N(1)  $\cdots$  O(4) is 2.682(2) Å), Fig. 4. These layers are parallel to the crystallographic *bc* plane and thus are perpendicular to the polar axis 2<sub>1</sub>. The solvate water molecules and (H<sub>2</sub>O)  $\cdots$  Cl  $\cdots$  (H<sub>2</sub>O) anionic aggregates assemble the layers into a 3-dimensional



Fig. 3 The 3-dimensional H-bonded framework in the crystal of  $[Eu(PL-Asp)(H_2O)_4](H_2O)$  (1).



Fig. 4 Cationic chains interlinked by  $\pi$ - $\pi$  stacking interactions and O-H···N bonds in crystal of [Eu(PL-His)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl(H<sub>2</sub>O)<sub>4</sub> (2).

supramolecular framework by means of N–H···O and O–H···O hydrogen bonds. Thus the supramolecular organization in the crystal of complex **2** formed by inter- and intramolecular stacking interactions can be described as separated cationic layers with anionic (H<sub>2</sub>O)···Cl···(H<sub>2</sub>O) filling (Fig. 5).



Fig. 5 The crystal packing of  $[Eu(PL-His)_2(H_2O)_2]Cl(H_2O)_4$  (2) illustrating alternation of cationic layers and anionic filling.

#### Luminescence studies of 1 and 2 complexes

The europium complexes of Schiff bases investigated exhibit the characteristic luminescence spectrum of the Eu<sup>III</sup> ion at both low and ambient temperatures. Two different types of luminescence spectra were obtained (Fig. 6). Stark components of the  ${}^5D_0 \rightarrow {}^7F_J$  transitions (J = 0-4) in the luminescence spectra of the europium complexes recorded at 77 K under broad-band excitation point to low site symmetry of Eu<sup>III</sup>. Judging from the ratio of the integrated intensities of the  ${}^5D_0 \rightarrow {}^7F_J$  (J = 0, 2-6) transitions to the  ${}^5D_0 \rightarrow {}^7F_1$  transition (Table 4) the site symmetry of Eu<sup>III</sup> is slightly nearer to the inversion centre for 1 than for 2. Intensity of the  ${}^5D_0 \rightarrow {}^7F_2$  transition, dependent on  $T_2$  (Judd–Ofelt intensity parameter)<sup>16</sup> and sensitive to the structure of lanthanide surroundings, is 1.6 times higher for complex 2 which indicates the lower symmetry of complex 2 compared to complex 1. A



Fig. 6 Luminescence spectra of  $[Eu(PL-Asp)(H_2O)_4](H_2O)$  (1) (a) and  $[Eu(PL-His)_2(H_2O)_2]Cl(H_2O)_4$  (2) (b) recorded by a low resolution spectrometer at 77 K.

general splitting of  ${}^{7}F_{1}$ ,  ${}^{7}F_{2}$  and  ${}^{7}F_{4}$  levels amounts to 260, 250 and 405 cm<sup>-1</sup> and 125, 150 and 290 cm<sup>-1</sup> for complexes 1 and 2, respectively. These values are determined by the asymmetric charge environment of Eu<sup>III</sup> in the former complex, where two of the three charges belong to one base of the square antiprism, and the more symmetric charge environment of Eu<sup>III</sup> in the latter complex (three charges belong to one base of square antiprism and the other three charges to the other base). Such large general splittings are also evidence that the effect of JJ'mixing has to be taken into account upon the analysis of Stark components.<sup>17</sup> The mono-exponential luminescence decay of the Eu( ${}^{5}D_{0}$ ) level obtained for 1 and 2 complexes reveals the equivalent europium environments in both complexes (Table 5). The  $\tau$  values

**Table 4** Relative integral intensity of  ${}^{5}D_{0}$ -F<sub>1</sub> (J = 0, 2–6) electronic transitions in luminescence spectra of compounds investigated upon ligand excitation at 77 K ( $\lambda_{exc} = 365 \text{ nm}$ )

Compounds	${}^{5}D_{0}-{}^{7}F_{0}$	${}^{5}D_{0} - {}^{7}F_{2}$	${}^{5}D_{0}-{}^{7}F_{3}$	${}^{5}D_{0}-{}^{7}F_{4}$	${}^{5}D_{0}-{}^{7}F_{5}$	${}^{5}D_{0}-{}^{7}F_{6}$	
$\begin{array}{l} [Eu(PL-Asp)(H_2O)_4](H_2O)\ (1)\\ [Eu(PL-His)_2(H_2O)_2]Cl(H_2O)_4\ (2)\\ [Eu+\ (PL-Asp)]\ (solution\ s1)\\ [Eu+\ (PL-His)_2]\ (solution\ s2) \end{array}$	0.55 0.18 0.26 0.20	5.45 8.63 6.44 6.38	0.29 0.36 0.28 0.23	3.02 5.13 2.98 2.90	0.25 0.23 0.14 0.16	0.76 1.07 0.55 0.51	

**Table 5** Position of  ${}^{5}D_{0} - {}^{7}F_{0}$  electronic transition in the luminescence spectra and lifetime ( $\tau$ ) of the metal-centered luminescence upon ligand excitation at 77 K ( $\lambda_{exc} = 365 \text{ nm}$ )

Compounds	$^{5}D_{0}-^{7}F_{0}/cm^{-1}$	τ/ms
$\begin{split} & [Eu(PL-Asp)(H_2O)_4](H_2O)(1) \\ & [Eu(PL-His)_2(H_2O)_2]Cl(H_2O)_4 \ \textbf{(2)} \\ & \text{Solutions, concentration/M} \end{split}$	17 259 17 212	$\begin{array}{c} 0.22 \pm 0.02 \\ 0.75 \pm 0.03 \end{array}$
$\begin{array}{l} [{\rm Eu}+({\rm PL-Asp})],3.5\times10^{-3}({\rm s1})\\ [{\rm Eu}+({\rm PL-Asp})],3.5\times10^{-4}\\ [{\rm Eu}+({\rm PL-His})],7.6\times10^{-3}\\ [{\rm Eu}+({\rm PL-His})_2],9.7\times10^{-3}({\rm s2}) \end{array}$	17 224 17 247 17 250 17 215	$\begin{array}{c} 0.83 \pm 0.03 \\ 0.38 \pm 0.02 \; (80\%) \; 0.83 \pm 0.03 \; (20\%) \\ 0.33 \pm 0.02 \\ 0.42 \pm 0.02 \; (50\%) \; 0.88 \pm 0.03 \; (50\%) \end{array}$

 $(0.22 \pm 0.02 \text{ and } 0.75 \pm 0.03 \text{ ms})$  are well adjusted with four and two water molecules coordinated, respectively.

Parts of the high resolution luminescence spectrum of complex 1 in the region of europium electronic transitions and the crystalfield splitting of the Eu<sup>III</sup> spin-orbit levels are presented in Fig. 7 and Table S1 (ESI<sup>‡</sup>), respectively. The asymmetric two component peak corresponding to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  transition along with the broadened first component of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition and excess number of Stark components of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition reveal the presence of nonequivalent luminescence centers. According to Xray data the structure of complex 1 is disordered by two positions one of which is the nitrogen atom of the C=N bond (Fig. S1, ESI<sup>‡</sup>). The length of the Eu-N bond is different in these enantiomers and as a result two luminescence centers were observed. High resolution luminescence data obtained for complex 2 revealed one luminescence center in line with the X-ray experiment and were used for obtaining the crystal-field splitting of the Eu<sup>III</sup> spin-orbit levels (Fig. S1 and Table S1, respectively, ESI<sup>‡</sup>).



Fig. 7 Parts of high resolution luminescence spectrum of  $[Eu(PL-Asp)-(H_2O)_4](H_2O)$  (1) in the region of europium electronic transitions at 77 K.

**Vibronic interaction.** Since vibronic satellites are produced by a dependence of the 4f wavefunctions on the vibrational motions of the bound ligands they can reveal the features of the lanthanide coordination sphere and allow for the estimation of interaction intensity of a lanthanide ion with ligands. IR spectra published previously for PL-Asp<sup>14</sup> and PL-His<sup>13</sup> were used to assign the satellites observed. A row of vibronic satellites associated with the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0.2}$  transitions appears in the luminescence spectrum of complex 1 at 77 K (Table 6). The stretching symmetrical (1323 cm<sup>-1</sup>) and asymmetrical (1654 cm<sup>-1</sup>) vibrations of carboxylate groups are observed in the vibronic sideband of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of the Eu<sup>III</sup> ion (15 100–14 600 cm<sup>-1</sup> region). Their splitting amounts to ~320 cm<sup>-1</sup> and corresponds to the monodentate coordination function of carboxylate groups.<sup>18,19</sup> The

Table 6 Vibronic satellites observed in the luminescence spectra of  $[Eu(PL-Asp)(H_2O)_4](H_2O)$  (1) and  $[Eu(PL-His)_2(H_2O)_2]Cl(H_2O)_4$  (2) at 77 K

Assignment	Frequencies for complex 1/cm <sup>-1</sup>	Frequencies for complex $2/cm^{-1}$
v(M–Lig)	_	180
$\delta(COO^{-})$	745	570, 670, 740
$\delta$ (CH) ring		1220
$\nu$ (C–OH)	_	1280
$v_{\rm s}(\rm COO^{-})$	1323, 1370	1320
v(C=C, C=N)	1425, 1575	1435, 1585
$v_{\rm as}({\rm COO^-})$	1654	1652

vibration with frequency  $\sim 1370 \text{ cm}^{-1}$  in the vibronic sideband of the  ${}^5D_0 \rightarrow {}^7F_0$  transition (17050–15000 cm<sup>-1</sup> region) could be assigned to the stretching symmetrical vibration of another carboxylate group taking into account that the PL-Asp ligand contains two carboxylate groups having Eu–O bonds of different length (Table 2).

Vibronic satellites of  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transitions found in the luminescence spectrum of complex 2 at 77 K in the regions 17050-15000 and 15100-14600 cm<sup>-1</sup>, respectively, are presented in Table 6 and Fig. S4 (ESI<sup>‡</sup>). Judging from the higher number of vibronic satellites observed in this spectrum than in the luminescence spectrum of complex 1 as well as from their intensities, the vibronic interaction is remarkably stronger in the former. This can be conditioned by the presence of intraligand charge transfer originating with two negative oxygen atoms and one protonated nitrogen atom of PL. The vibronic satellites found indicate the monodentate coordination function of the carboxylate groups similar to complex 1 as well as the coordination of pyridoxal ring through the hydroxyl oxygen atom ( $\nu$ (C–OH) is  $\sim$ 1280 cm<sup>-1</sup>). The appearance of three frequencies attributed to  $\delta(\text{COO}^-)$  correlates with the presence of the shortest bond between the Eu<sup>III</sup> ion and the carboxylate group in complex 2(2.377(7)) and 2.389(2)–2.417(3) Å for 2 and 1 complexes, respectively).

In order to both obtain additional information on excited states of the systems studied and to estimate the potential of their luminescent applications the phosphorescence spectra of the lanthanum complexes were also considered. It is well-known that the energy transfer from ligand excited states to the resonance states of Ln<sup>III</sup> in complexes can occur in different ways. The favored simplified mechanism involves ligand excitation by the absorption of ultraviolet energy to an excited singlet state, followed by energy migration *via* nonradiactive intersystem crossing to a ligand triplet state ( $E_1 = E(S_1-T)$ ) and energy transfer from the triplet state to a resonance state of Ln<sup>III</sup> ion, from which the emission occurs ( $E_2 = E(T)-E({}^{s}D_0)$ ). Therefore there is no doubt that the singlet and triplet states of the ligand play an important role in the effective energy transfer in lanthanide systems.<sup>20</sup>

The triplet states of sodium salts of PL-Asp and PL-His are located at 19 200 and 22 400 cm<sup>-1</sup> at 77 K, respectively (Table 7). The triplet energy state is affected by complexation in the La<sup>III</sup> complexes and sustains a blue shift in 1 (+2100 cm<sup>-1</sup>) and a red shift in 2 (-1500 cm<sup>-1</sup>) up to 21 300 and 20 900 cm<sup>-1</sup>, respectively. The relatively low energy of the triplet state of the former sodium salt and uncommon blue shift of this state upon complexation may be explained by complicated supramolecular assemblies formed by PL-Asp anions. The singlet state emission was observed at

**Table 7** Energy of singlet and triplet states upon ligand excitation ( $\lambda_{exc} = 365 \text{ nm}$ )

	$S_1/cm^{-1}$	T/cm <sup>-1</sup>			
[PL-Asp], ss	а	19 200			
[La(PL-Asp)], ss	a	21 300			
[PL-His], ss	a	22 400			
[La(PL-His) <sub>2</sub> ], ss	a	20 900			
[La(PL-Asp)], sol	23 700	20 200			
[La(PL-His) <sub>2</sub> ], sol	24 200	22 800			
<sup><i>a</i></sup> State was not detected; ss = solid state; sol = solution.					

300 K as a weak shoulder for all solid state compounds and so the energy of this state could not be determined unambiguously. Contrary to the solid state case the  $\pi\pi^*$  state was detected in aqueous solutions of the lanthanum SBs with PL-Asp and PL-His (Table 7). The energy gap  $E_1$  is relatively small (about 1400–1830 cm<sup>-1</sup>) which points to ineffective intersystem crossing processes. To estimate the luminescence efficiency for europium complexes the energy gap  $E_2$  was also calculated on the basis of the values obtained. The  $E_2$  amounts to ~4100 and 3700 cm<sup>-1</sup> for 1 and 2 complexes, respectively. These values are near to optimal for the high luminescence intensity of europium complexes according to published data<sup>21</sup> with some advantage for complex 2. The absence of any residual luminescence of excited ligand states for both complexes is evidence of the effective energy transfer from excited ligand states to Eu<sup>III</sup> resonance levels and is in the line with this estimation.

## Luminescence studies of SB complexes in solution

Since the SB complexes studied are soluble in water their photophysical properties were also investigated in solution. It is worth noting that this luminescence analysis sheds light on some features of the main Eu<sup>III</sup> species only although various species formed in solution. The luminescence decay used for this analysis is sufficiently informative<sup>22</sup> except in the case where the species formation had a very short lifetime of the excited state. The emission spectra of water frozen solutions of europium chloride containing one or two molar equivalents of PL-Asp (s1) or PL-His (s2), respectively, with concentrations similar to those used in the synthesis are given in Fig. 8. Stark splittings of Eu<sup>III</sup> electronic transitions in both solutions are quite similar and remarkably different from the corresponding values for complexes 1 and 2. The values of relative integrated intensities of Eu<sup>III</sup> electronic transitions for these solutions are also similar (Table 4). The Eu<sup>III</sup> site symmetry is slightly nearer to the inversion centre in these solutions than in the corresponding solid state complexes.

The luminescence decay obtained for the Eu( ${}^{5}D_{0}$ ) level in the solution s2 (~9.7 × 10<sup>-3</sup> M) is a bi-exponential function and corresponding lifetimes amount to 0.42 ± 0.02 and 0.88 ± 0.03 ms. This indicates the presence of at least two types of Eu<sup>III</sup> chemical environments. To identify these species the luminescence spectrum of the aqueous solution containing europium chloride with one molar equivalent of PL-His (~7.6 × 10<sup>-3</sup> M) was recorded (Fig. 8c). This spectrum is characterized by: (i) another type of Stark splitting in comparison with solution s2; (ii) the mono-exponential luminescence decay of the Eu( ${}^{5}D_{0}$ ) level with the corresponding lifetime amounting to 0.33 ± 0.02 ms; and



**Fig. 8** Luminescence spectra of water solutions of PL-His with two (9.7 ×  $10^{-3}$  M) (a) and one (7.6 ×  $10^{-3}$  M) (c) molar equivalents of europium chloride as well as solutions of PL-Asp with one molar equivalent of europium chloride at 3.5 ×  $10^{-3}$  (b) and 3.5 ×  $10^{-4}$  M (d) at 77 K.

(iii) the position of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  transition at  $\sim 17250 \text{ cm}^{-1}$ . Analysis of the latter can be useful upon the description of the europium coordination sphere owing to the correlation between the frequency of the  ${}^5D_0 \rightarrow {}^7F_0$  transition and the sum of the derived nephelauxetic parameters of the coordinating atoms obtained by Frey and Horrocks.23 Based on this correlation the frequency shift of the  ${}^5D_0 \rightarrow {}^7F_0$  transition from 17215 to 17250 cm<sup>-1</sup> could be explained by the presence of both the 1:2 and 1:1 species in solutions containing two and one molar equivalent of PL-His, respectively. These data allow the formation of the 1 : 1 species in solution s2 to be excluded at least in a quantity detectable by the luminescence spectroscopy. In view of this the bi-exponential luminescence decay observed in solution s2 seems to be determined by the distinctions in the coordination sphere of the Eu<sup>III</sup> 1 : 2 species. The longer lifetime probably corresponds to a Eu<sup>III</sup> environment devoid of O-H vibrations or with one water molecule coordinated, whereas the shorter lifetime corresponds to a metal ion bound to several water molecules.<sup>22,24</sup> Taking into account these types of Eu<sup>III</sup> environment and its high coordination number one can surmise the coordination of the nitrogen atom of His. Similar coordination of His was found in several cases.<sup>25</sup> Hence PL-His is a tetradentate ligand in solution s2. The luminescence spectrum corresponding to the 1:1 species was not observed even upon the 30-fold dilution of solution s2. This behaviour is probably determined by the intense intramolecular  $\pi$ - $\pi$  stacking which can remarkably increase the stability constant of the 1 : 2 species<sup>26</sup> (cf. crystallographic section) and/or by the tetradentate coordination function of PL-His.

The luminescence spectrum of water solution s2 contains a limited number of vibronic satellites at 77 K with: (i) frequency 700 cm<sup>-1</sup> in the range 16 640–16 540 cm<sup>-1</sup> assigned to  $\delta$ (COO<sup>-</sup>), (ii) frequency 1390 cm<sup>-1</sup> in the range 15 840–15 850 cm<sup>-1</sup> assigned to  $v_s$ (COO<sup>-</sup>), and (iii) frequency 1410 cm<sup>-1</sup> assigned to stretching vibration of imidazolium ring as vibronic repetition of the

 ${}^{5}D_{0}-{}^{7}F_{2}$  transition in the range 15000-14750 cm<sup>-1</sup>. The latter vibronic satellites are evidence in favour of the coordination of the His ring by the Eu<sup>III</sup> ion. This coordination leads to weakened bonds between Eu<sup>III</sup> and ligands due to steric hindrances and as a consequence the vibronic interaction decreases. The vibronic satellites found also confirm the preservation of the coordination of carboxylate groups upon the transition from solid state to solution.

Let us to return to the question of similarity of the luminescence spectra of s1 and s2 solutions taking into account that PL-His is a tetradentate ligand and forms mainly Eu<sup>III</sup> 1:2 species in solution s2. The emission spectrum of the solution s1 (3.5  $\times$  10<sup>-3</sup> M) (Fig. 8b) is quite different when compared to the luminescence of the complex 1: (i) the position of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  transition is shifted from 17 259 to 17 224 cm<sup>-1</sup> upon the transition from complex 1 to solution s1, (ii) the relative intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  transition is twice as small in solution, and (iii) Stark components of electronic transitions are very different. In addition a single exponential decay is observed for solution s1 and the corresponding lifetime amounts to  $0.83 \pm 0.03$  ms (Table 5). The latter is unlikely for the europium 1:1 species with a tetradentate ligand due to its high CN. These data can be explained by an assumption about the formation of a 1 : 2 complex  $[Eu(PL-Asp)_2]^{3-}$  as the main species detected in solution s1. The residual europium chloride could not be registered as another species in this case owing to the short luminescence decay;  $\tau$  for europium chloride amounts to  $0.22 \pm 0.02$  ms in the solid state.<sup>27</sup> Vibronic satellites found in the emission spectrum of solution s1 indicate the presence of two types of coordinated carboxylate groups and the splitting between  $v_s(COO^-)$  and  $v_{as}(COO^-)$  indicates that the monodentate coordination function of the carboxylates is preserved. In order to provide a rationale for the above assumption, the solution s1 was diluted 10-fold and a luminescence spectrum of another type was observed (Fig. 8d). The behaviour of Stark components of the Eu<sup>III</sup> electronic transitions in this spectrum is similar to complex 1 as well as the magnitudes of general splittings of the electronic transitions (148, 139, 384 cm<sup>-1</sup> for  ${}^{7}F_{1}$ ,  ${}^{7}F_{2}$  and  ${}^{7}F_{4}$  levels, respectively). A ratio of general splitting of the  ${}^{7}F_{1}$ level to the <sup>7</sup>F<sub>2</sub> level smaller than 1 along with doublets in the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition point to the triangle as a model of Eu<sup>III</sup> charge surroundings according to mathematical modelling of the luminescence spectra of europium complexes in solutions performed by Zolin et al.<sup>28</sup> Therefore one can suppose that the luminescence spectrum recorded for the diluted solution belongs mainly to the 1:1 species. The bi-exponential luminescence decay of the Eu( ${}^{5}D_{0}$ ) level and corresponding lifetimes 0.38  $\pm$  0.02 and  $0.83 \pm 0.03$  ms were observed in the diluted solution (Table 5). The shorter lifetime, which contributes  $\sim 80\%$  to the decay, probably corresponds to the 1:1 species with coordinated water molecules and the longer lifetime indicates the formation of 1:2 species with an Eu<sup>III</sup> environment basically devoid of O-H vibrations owing to the tetradentate coordination function of PL-Asp. Thus the Eu<sup>III</sup> 1:1 and 1:2 species coexist in solution containing one equivalent of PL-Asp with predominant contribution of the 1 : 1 species to the luminescence when the concentration is  $\sim 10^{-4}$  M. The stability of the 1:2 species in diluted solution is possibly connected with the  $\pi$ -stacking interaction between ligands through pyridoxal rings similar to the case of solution s2. The formation of predominantly  $Eu^{III}$  1 : 2 species in solution (with relatively high concentration)

and the possibility of tetradentate coordination of both SBs lead to similar luminescence spectra for **s1** and **s2** solutions.

### Conclusions

Two europium SB complexes derived from pyridoxal and amino acids, *viz* Eu(PL-Asp)(H<sub>2</sub>O)<sub>4</sub>](H<sub>2</sub>O) (1) and [Eu(PL-His)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl(H<sub>2</sub>O)<sub>4</sub> (2), were characterized by single crystal X-ray techniques as the first case of lanthanide SBs derived from pyridoxal. The europium polyhedron in complexes 1 and 2 is an antiprism with a considerable degree of distortion due to the different nature of bonded atoms and bond length variation. Disorder in the crystal of complex 1 was found by X-ray diffraction and the difference between the coordination centres was apparent mainly in the Eu–N bond lengths (2.504(3) and 2.536(9) Å). High resolution luminescence experiments for this complex also showed the presence of two nonequivalent luminescence centers owing to high efficiency of Eu<sup>III</sup> ion as a luminescence probe for the chemical environment<sup>29</sup> and allowed a scheme of Eu<sup>III</sup> electronic levels for both systems considered to be obtained.

In the solid state, complex 2 forms supramolecular networks *via* relatively strong intra- and intermolecular  $\pi$ - $\pi$  stacking and H-bonding interactions, complexes 1 are arranged in the crystal by dimers via intermolecular stacking interaction of moderate strength. This strong intramolecular  $\pi$ - $\pi$  stacking interaction promotes the formation of the Eu<sup>III</sup> 1 : 2 species and the increase of stability constants of these species in aqueous solutions upon the relatively high concentrations of ligands ( $\sim 10^{-3}$  M) for both europium SBs. Moreover these SBs demonstrate the tetradentate coordination function in solution which includes the coordination of the nitrogen atom of histidine for the PL-His ligand. The analysis of the vibronic interaction also enables some features of the Eu<sup>III</sup> coordination sphere in solution to be revealed. The vibrations assigned to the carboxylate groups with monodentate coordination function were found in the solution containing PL-Asp whereas the vibronic satellites attributed to both carboxylates and the histidine ring were observed in solutions containing PL-His.

The analysis performed on the scheme of ligand energy levels as well as detected lifetimes of Eu<sup>III</sup> excited states reveal the relatively effective intramolecular energy transfer from the ligands to europium ion. This factor together with the stability of the Eu<sup>III</sup> 1 : 2 species in solution and good solubility of lanthanide SB complexes in water make them possible prospective candidates for luminescence materials for biological and medical applications.

## Experimental

#### Synthesis

All solvents were of analytical grade and used without further purification. Pyridoxal hydrochloride (PL), DL-aspartic acid, and L-histidine dihydrochloride (Sigma) were used as received. The lanthanide chlorides (Ln = La, Eu, Gd) were prepared from their oxides in the usual way.<sup>30</sup> The content of compounds synthesized was confirmed by elemental analyses. Lanthanide Schiff bases of pyridoxal with Asp and L-His were prepared by template synthesis according to a previously described method.<sup>14</sup> Sodium Schiff bases of pyridoxal with Asp and L-His were prepared in a similar way to the lanthanide case.

## Complex 1:1

An aqueous solution (2 ml) of PL (0.0509 g; 0.25 mmol) was prepared as well as an aqueous solution (2 ml) of Asp (0.0333 g; 0.25 mmol) with 0.33 ml of NaOH (0.04 g; 1.0 mmol) added to obtain a pH of  $\sim$ 6. These solutions were mixed to form a yellow solution. An aqueous solution (1 ml) of EuCl<sub>3</sub>·6H<sub>2</sub>O (0.0916 g; 0.25 mmol) was added dropwise to the mixture. A small quantity of precipitate appeared right away. The mixture was stirred for 3 h at rt. The yellow precipitate obtained the next day was filtered, washed with 0.5 ml isopropyl alcohol and dried. Yields: La (50 mg, 70%), Eu (116 mg, 66%), Gd (96 mg, 60%). LaC<sub>12</sub>N<sub>2</sub>O<sub>12</sub>H<sub>23</sub> (526.23): (Found: C, 27.18; H, 4.22; N, 5.27%. Calc.: C 27.39, H 4.41, N 5.32%);  $EuC_{12}N_2O_{11}H_{21}$  (521.27): (Found: C, 27.52; H, 4.16; N, 5.22%. Calc.: C 27.65, H 4.06, N 5.37%); GdC<sub>12</sub>N<sub>2</sub>O<sub>11</sub>H<sub>21</sub> (526.56): (Found: C, 27.22; H, 3.90; N, 5.30%. Calc.: C 27.37, H 4.02, N 5.32%). Single crystals suitable for X-ray analysis were obtained by slow diffusion of an ethanol-water solution.

## Complex 1:2

An aqueous solution (1 ml) of PL (0.0407 g; 0.2 mmol) was prepared as well as an aqueous solution (1 ml) of L-His (0.0383 g; 0.2 mmol) with 0.2 ml of NaOH (0.024 g; 0.6 mmol) added to obtain a pH of  $\sim$ 6. These solutions were mixed to form a yellow solution. An aqueous solution (0.5 ml) of EuCl<sub>3</sub>·6H<sub>2</sub>O (0.0366 g; 0.1 mmol) was added dropwise to the mixture. Right away the complex began to precipitate out. The mixture was stirred for 3 h at rt. The yellow precipitate obtained the next day was filtered, washed with 0.2 ml EtOH and dried for 2 h at 40 °C. Yields: La (54 mg, 55%), Eu (81 mg, 70%), Gd (64 mg, 58%). LaClC $_{28}N_8O_{14}H_{42}$  (889.05): (Found: C, 37.58; H, 4.42; N, 12.56%. Calc.: C 37.83, H 4.76, N 12.60%); EuClC<sub>28</sub>N<sub>8</sub>O<sub>14</sub>H<sub>42</sub> (902.11): (Found: C, 37.08; H, 4.32; N, 12.20%. Calc.: C 37.28, H 4.69, N 12.42%); GdClC<sub>28</sub>N<sub>8</sub>O<sub>13</sub>H<sub>40</sub> (889.37): (Found: C, 37.64; H, 4.36; N, 12.54%. Calc.: C 37.81, H 4.53, N 12.60%). Single crystals suitable for X-ray analysis were obtained by a slow evaporation method of aqueous solutions.

## X-Ray crystallography†

X-Ray diffraction experiments were carried out with a Bruker SMART APEX II CCD area detector, using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 100 K. Reflection intensities were integrated using SAINT software and the absorption correction was applied semi-empirically using SADABS program. The sufficiently high value of  $R_{int}$  for Eu(PL-His)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>Cl (2) is a consequence of extremely small crystal dimensions and weak reflection power. The structures were solved by direct methods and refined by the full-matrix least-squares against  $F^2$  in anisotropic approximation for non-hydrogen atoms.

The analysis of Fourier density synthesis revealed that in complex 1 the nitrogen atom of the C=N bond as well as the carbon atoms of the dicarboxy moiety (chiral center) are disordered by two positions. Such disorder corresponds to superposition of two enantiomers in ratios of 0.802(6) and 0.198(6) (Fig. S1, ESI‡). The refinement of self occupancies factors (s.o.f.) for C(8), C(9), C(10) and C(8'), C(9') and C(10') was carried out with constraints on the anisotropic displacement parameters (ADP) values of each pair of atoms (EADP instruction). The bond lengths for C(9)–C(10) and C(9')-C(10'); C(8)-N(2) and C(8')-N(2'), C(9')-N(2') and C(9)-N(2); C(11)–C(9') and C(11)–C(10); C(8)–C(3) and C(8')–C(3) were refined to be equal for each pair using the free variables. In addition to the above fragment the solvate water molecule (O(5w)) in 1 is also disordered by two positions with equal occupancies. The ADP of O(5w) and O(5w') atoms were refined with EADP instructions. In 2 analysis of the atomic displacement parameters of the chloride anion have revealed that despite of its general position its occupancy is equal to 0.5. Observed occupancy of the chlorine anion coincides well with the charge of the cationic part as well as with the intermolecular contacts of chlorine anion. Indeed the Cl(1) form in the crystal had an unrealistically shortened contact equal to 3.06 Å. It should be noted that such an occupancy of Cl(1) is not a symmetry imposed one and was observed in the case of monoclinic space groups with the cation in a general position. The positions of hydrogen atoms of water molecules and amino groups were located from Fourier density synthesis while for all other hydrogen atoms positions were calculated geometrically.

We have to emphasize that chlorine can be treated not only as chlorine (s.o.f. 0.5) but also as oxygen or even potassium with s.o.f. equal to 1.0. The latter is unfavorable from the point of view of interatomic contacts formed by the atom (coordination 3 is too unusual for potassium). Of course the main reason to treat that atom as chlorine is the overall charge of the complexes. The discrepancy factor (*R*1) can serve as an additional independent justification of this mode. Thus for chlorine the *R*-factor value is the lowest one (0.0626) while for oxygen with an s.o.f. 1.00 it is slightly higher 0.0634.

The positions of the hydrogen atoms of the water molecules and amino groups were located from Fourier density synthesis while for all other hydrogen atoms positions were calculated geometrically. Taking into account that for two positions of O(5w) only one set of hydrogen atoms was located and any of the available AFIX instructions is suitable, the O–H bond lengths for O(5w) and O(5w') were refined using a DFIX instruction.

Crystal data and structure refinement parameters for 1 and 2 complexes are given in Table 1. All calculations were performed using the SHELXTL software.<sup>31</sup>

#### Luminescence measurements

The luminescence spectra of the compounds investigated were measured with a LOMO DFS-12 spectrometer (high resolution) and LOMO UM-2 monochromator (low resolution) at 300 and 77 K. DRSh-250 and 500 mercury high-pressure lamps were used as an excitation source for these experimental set-ups, respectively. The intense Hg 365 nm line of this lamp was isolated by UV filters. Registration of phosphorescence spectra as well as measurements of the luminescence decay were carried out by a low resolution set-up. The lifetimes of europium excited states were obtained as averages of at least three independent measurements and were analyzed with Origin 7.0.

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# References

- 1 M. J. Weber, in *Rare Earth Lasers*, North-Holland Publishing Co., Amsterdam, 1979, vol. 4, pp. 275–315.
- 2 R. D. Archer and H. Chen, Inorg. Chem., 1998, 37, 2089-2095.
- 3 H. C. Aspinall, *Chem. Rev.*, 2002, **102**, 1807–1850; U. Casellato, S. Tamburini, P. Tomasin, P. A. Vigato, S. Aime and M. Botta, *Inorg. Chem.*, 1999, **38**, 2906–2916; S. Aime, M. Botta, U. Casellato, S. Tamburini and P. A. Vigato, *Inorg. Chem.*, 1995, **34**, 5825–5831.
- 4 S. A. Schuetz, V. W. Day, R. D. Sommer, A. L. Rheingold and J. A. Belot, *Inorg. Chem.*, 2001, 40, 5292–5295; P. Blech, C. Floriani, A. Chiesivilla and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1990, 3557–3561.
- 5 K. Binnemans and C. Gorller-Walrand, *Chem. Rev.*, 2002, **102**, 2303–2345.
- 6 J. I. Bullock and H. A. Tajmir-Riahi, J. Chem. Soc., Dalton Trans., 1978, 36–39; N. K. Dutt and K. Nag, J. Inorg. Nucl. Chem., 1968, 30, 2779–2781; W. Nowicki and S. Zahara, Spectrosc. Lett., 1992, 25, 593–601.
- 7 H. Chen and R. D. Archer, *Inorg. Chem.*, 1994, **33**, 5195–5202; S. Afshar and J. Bullock, *Inorg. Chim. Acta*, 1980, **38**, 145; N. K. Dutt and K. Nag, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2493–2496.
- 8 D. E. Metzler, M. Ikawa and E. E. Snell, J. Am. Chem. Soc., 1954, 76, 648–652.
- 9 V. F. Zolin and L. G. Koreneva, in *Rare Earth Probe in Chemistry and Biology*, ed. M. E. Zhabotinskii, Nauka, Moscow, ch. 2, pp. 205–207.
- 10 F. Nepveu, J.-J. Bonnet, J.-P. Laurent and M. Massol, J. Coord. Chem., 1981, 11, 185–189; F. Nepveu and J.-J. Bonnet, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 1983, C39, 339–341; R. E. Marsh, Acta Crystallogr., Sect. B: Struct. Sci., 1997, B53, 317–322; I. I. Mathews and H. Manohar, Polyhedron, 1991, 10, 2163–2169.
- K. Jitsukawa, T. Yamamoto, H. Masuda and H. Einaga, *Chem. Lett.*, 1993, 1693; K. Jitsukawa, T. Yamamoto, H. Takahashi, H. Masuda and H. Einaga, *Chem. Lett.*, 1995, 777; A. G. Sykes, R. D. Larsen, J. R. Fischer and E. H. Abbott, *Inorg. Chem.*, 1991, **30**, 2911–2916; M. B. Feerrari, G. G. Fava, M. Lanfranchi, C. Pelizzi and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, 1991, 1951–1957.
- 12 L. M. Vainer, V. F. Zolin, L. G. Koreneva and P. Z. Sagnaev, *Russ. J. Coord. Chem.*, 1975, 1, 1512–1515; V. F. Zolin and L. G. Koreneva, *J. Struct. Chem.*, 1980, 21, 51–55.
- 13 L. Casella and M. Gullotti, J. Am. Chem. Soc., 1981, 103, 6338-6347.

- 14 A. V. Dushkin, V. F. Zolin, L. G. Koreneva, E. G. Ruhadze, G. P. Talyzenkova and V. I. Tsaruyk, *Russ. J. Coord. Chem.*, 1975, 1, 1533– 1541.
- 15 E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem.*, *Int. Ed.*, 2003, 42, 1210–1250.
- 16 B. R. Judd, Phys. Rev., 1962, 127, 750–761; G. S. Ofelt, J. Chem. Phys., 1962, 37, 511–520.
- 17 O. J. Sovers and T. J. Yoshioka, J. Chem. Phys., 1968, 49, 4945–54; O. J. Sovers and T. Yoshioka, J. Chem. Phys., 1968, 51, 5330–5336.
- 18 K. Nakamoto, in Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A. Theory, and Applications in Inorganic Chemistry, John Wiley Interscience Publ., New York, 1997, p. 536.
- 19 L. Puntus, V. Zolin and V. Kudryashova, J. Alloys Compd., 2004, 374(1-2), 330–334.
- 20 N. Sabbatini, M. Guardigli and J.-M. Lehn, Coord. Chem. Rev., 1993, 123, 201–228; J.-C. G. Bunzli, J. Alloys Compd., 2006, 408-412, 934–944.
- 21 F. J. Steemers, W. Verboom, D. N. Reinhoudt, E. B. Vandertol and J. W. Verhoeven, J. Am. Chem. Soc., 1995, 117, 9408–9414; J.-C. G. Bünzli, Met. Ions Biol. Syst., 2004, 42, 39–75.
- 22 P. P. Barthelemy and G. R. Choppin, *Inorg. Chem.*, 1989, 28, 3354– 3357; G. R. Choppin and D. R. Peterman, *Coord. Chem. Rev.*, 1998, 174, 283–299.
- 23 S. T. Frey and W. deW. Horrocks, *Inorg. Chim. Acta*, 1995, 229, 383– 390.
- 24 R. M. Supkowski, W. De and W. Horrocks, *Inorg. Chim. Acta*, 2002, 340, 44–48.
- L. L. Koh, J. O. Ranford, W. T. Robinson, J. O. Svensson, A. L. C. Tan and D. Wu, *Inorg. Chem.*, 1996, **35**, 6466–6472; P. S. Subramanian, E. Suresh, P. Dastidar, S. Waghmode and D. Srinivas, *Inorg. Chem.*, 2001, **40**, 4291–4301; H. M. Dawes and T. N. Waters, *J. Chem. Soc., Chem. Commun.*, 1982, 1390–1391; K. Aoki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 1984, 410–411.
- 26 O. Yamauchi, A. Odani and M. Takani, J. Chem. Soc., Dalton Trans., 2002, 3411–3421.
- 27 L. N. Puntus, K. P. Zhuravlev, K. A. Lyssenko and V. F. Zolin, *Opt. Mater.*, 2007, DOI: 10.1016/j.optmat.2007.02.043.
- 28 V. F. Zolin and L. G. Koreneva, J. Struct. Chem., 1983, 24, 704-710.
- 29 J.-C. G. Bünzli, in Lanthanide Probes in Life, Chemical and Earth Sciences. Theory and Practice, ed. J.-C. G. Bünzli and G. R. Choppin, Elsevier Science Publ. B.V., Amsterdam, 1989.
- 30 J. F. Desreux, in Lanthanide Probes in Life, Chemical and Earth Sciences. Theory and Practice, ed. J.-C. G. Bünzli and G. R. Choppin, Elsevier Science Publ. B.V., Amsterdam, 1989, ch. 2, pp. 43–64.
- 31 G. M. Sheldrick, SHELXTL-97, Version 5.10, Bruker AXS Inc., Madison, WI-53719, USA, 1997.