

# Synthetic, Structural, and Spectroscopic Studies on Solids Containing Tris(dipicolinato) Rare Earth Anions and Transition or Main Group Metal Cations

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The synthesis and basic characterisation are reported for 85 new solids of the general formula  $[\text{ML}_x][\text{Ln}(\text{dipic})_3]_n\text{H}_2\text{O}$  ( $M = \text{Cr}$  or  $\text{Co}$ ;  $L = \text{urea}$ , ammonia, and various amines;  $\text{Ln} = \text{La-Lu}$ , plus  $\text{Y}$ ;  $\text{dipic} = \text{pyridine-2,6-dicarboxylate}$ ). Syntheses of some seven  $\text{Cs}_3[\text{Ln}(\text{dipic})_3]$  and  $[\text{N}(\text{C}_2\text{H}_5)_4]_3[\text{Ln}(\text{dipic})_3]$  species are also given. Low-temperature luminescence measurements on a variety of these compounds and full X-ray crystallographic structure determinations for  $\text{Cs}_3[\text{Eu}(\text{dipic})_3] \cdot 9\text{H}_2\text{O}$  (orthorhombic, space group  $C222_1$ ;  $a = 10.165(2)$ ,  $b = 18.164(4)$ ,  $c = 18.724(4)$  Å;  $Z = 4$ ;  $R_1 = 0.041$  for 1573 "observed" reflections) and  $[\text{Co}(\text{sar})][\text{Eu}(\text{dipic})_3] \cdot 13\text{H}_2\text{O}$  (monoclinic, space group  $P2_1/n$ ;  $a = 10.611(4)$ ,  $b = 26.500(10)$ ,  $c = 17.583(7)$  Å;  $\beta = 91.97(3)^\circ$ ;  $Z = 4$ ;  $R_1 = 0.037$  for 7695 "observed" reflections) are described to illustrate the range and complexity of the physical properties of these new materials. Both  $\text{Cr}(\text{III})$  and  $\text{Co}(\text{III})$  act as very efficient quenchers of the normally strong  $[\text{Eu}/\text{Tb}(\text{dipic})_3]^{3-}$  luminescence, though in at least one system it appears that  $\text{Cr}(\text{III})$  may act to transfer excitation energy to  $\text{Ln}$  excited states from its own higher levels while simultaneously deactivating the  $\text{Ln}$  ion through its lower (doublet) states.

## Introduction

Electronic energy transfer between luminescent rare earth (lanthanide) metal ion complexes and both organic and inorganic quenchers has been widely studied in liquid phases<sup>1–3</sup> and to a more limited extent in solids,<sup>4,5</sup> though extensive work has been conducted on mixed rare earth/transition metal ceramics and glasses.<sup>6</sup> The phenomenon is of general interest in regard to the exploitation of rare earth luminescence in practical devices.<sup>7</sup> There is always a problem in the interpretation of any solution measurements in that the exact separation and relative orientation of any two centers involved in energy exchange are not readily established. This is not true of a crystalline solid provided the crystal structure is known, and it is for this reason that we have commenced a systematic synthetic, structural, and spectroscopic study of several series of compounds which are solids containing normally strongly luminescent rare earth complex ions in the presence of both transition and main group metal ions of widely different electronic structures. In this paper we present our

primary observations on salts containing some tris(dipicolinato)-lanthanide(III) anions (dipicolinate = pyridine-2,6-dicarboxylate) along with transition and main group metal cations.

## Experimental Section

**Synthesis.** The sodium salts of the tris(dipicolinato)lanthanide(III) anions,  $\text{Na}_3[\text{Ln}(\text{dipic})_3] \cdot x\text{H}_2\text{O}$  were all prepared by essentially the literature method for the Yb compound,<sup>8</sup> which involves reacting the freshly precipitated, gelatinous metal(III) hydroxide with the appropriate amounts of dipicolinic acid and sodium hydroxide. For the lighter lanthanides (La–Gd), the metal(III) oxides, where conveniently available, can be substituted for the hydroxide. As observed in some related syntheses,<sup>9,10</sup> the rate of reaction of the oxides with acid decreases markedly across the lanthanide series. All the sodium salts were recrystallized from water by the addition of ethanol.  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ,<sup>11</sup>  $[\text{Co}(\text{en})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ ,<sup>12,13</sup>  $[\text{Co}(\text{sen})_3]\text{Cl}_3$ ,<sup>14</sup>  $[\text{Co}(\text{NO}_2)_2\text{sar}]\text{Cl}_3$ ,<sup>15</sup>  $[\text{Co}(\text{NH}_2)_2\text{sar}]\text{Cl}_3$ ,<sup>15</sup>  $[\text{Co}(\text{sar})_3]\text{Cl}_3$ ,<sup>15</sup>  $[\text{Cr}(\text{en})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ ,<sup>16,17</sup>  $[\text{Cr}(\text{NH}_2)_2\text{sar}]\text{Cl}_3$ ,<sup>18</sup>  $[\text{Cr}(\text{sar})_3]\text{Cl}_3$ ,<sup>18</sup>  $[\text{Cr}(\text{urea})_6]\text{Cl}_3$ ,<sup>19</sup> and  $[\text{Rh}(\text{en})_3]\text{Cl}_3$ <sup>20</sup> were prepared (and, in some cases, resolved) by literature methods. (See below for explanation of the ligand name abbreviations.)

**$\text{Cs}_3[\text{Ln}(\text{dipic})_3] \cdot n\text{H}_2\text{O}$ ,  $\text{Ln} = \text{Eu, Gd, Tb, and Dy}$ .** The preparative procedure used was based on that of the sodium salts (vide supra), and

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for the 4 metal ions was essentially identical once the Ln(III) hydroxide or oxide had been obtained. Hence, it is described in detail only for the Eu compound:

Eu<sub>2</sub>O<sub>3</sub> (1.7 g) and dipicolinic acid (5.3 g) were heated and stirred in boiling water (50 mL) for 30 min. Cs<sub>2</sub>CO<sub>3</sub> (5.3 g) was gradually added to the hot solution, almost complete clarification thereby occurring. More Cs<sub>2</sub>CO<sub>3</sub> was added until all solids had dissolved and the solution pH was ~6. The solution was then filtered and left at room temperature for 18 h. The crystalline solid deposited (6.6 g) was collected by filtration, and the filtrate was diluted with ethanol (100 mL) to cause precipitation of further material (3.0 g). Recrystallization from hot water (5 mL/g) by cooling at room temperature for 24 h provided tablets with a just perceptibly pink color.

(The Dy compound after recrystallization was just perceptibly yellow, while the Gd and Tb compounds were completely colorless by eye.)

[N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>3</sub>[Ln(dipic)<sub>3</sub>]<sub>n</sub>H<sub>2</sub>O, Ln = Eu, Gd, Tb. Again, the preparative procedure followed that of the sodium salts, and details here are given only for the Tb compound:

Tb<sub>4</sub>O<sub>7</sub> (0.68 g) was dissolved in an excess of hot, concentrated HCl and the solution evaporated to dryness on a steam bath. The crystalline residue was dissolved in water (400 mL) and gelatinous Tb(OH)<sub>3</sub> precipitated by the addition of dilute NaOH solution until a pH value > 10 was attained. The precipitate was collected by filtration, washed well with water, and then slurried in water (20 mL) with dipicolinic acid (2.0 g) while being heated on a steam bath for 5 min. Ethanolic tetraethylammonium hydroxide was then added to the warm slurry until a clear solution had formed and the solution pH was ~6. The solution was evaporated under vacuum to a viscous oil, which was converted to a slightly discolored (pinkish), crystalline solid (3.6 g) by being slurried with a mixture of ethanol and acetone. This crude product was heated in boiling methanol (40 mL) and the solution filtered to remove a small amount of insoluble white solid. The filtrate was diluted with acetone (100 mL), and the small amount of flocculent precipitate immediately formed was again removed by filtration. Addition of more acetone (100 mL) then led to the slow deposition of thin, colorless plates of the desired product.

[M(saturated amine)][Ln(dipic)<sub>3</sub>]<sub>n</sub>H<sub>2</sub>O (M = Cr, Co, Rh; Saturated Amine = Ammonia, 1,2-Ethanediamine (en), 1,1,1-Tris-(((2-aminoethyl)amino)methyl)ethane (sen), Sarcophagine (3,6,10,13,19-Hexaazabicyclo[6.6.6]icosane, sar), 1,8-Dinitrosarcophagine ((NO<sub>2</sub>)<sub>2</sub>sar), 1,8-Diaminosarcophagine ((NH<sub>2</sub>)<sub>2</sub>sar) and [Cr(urea)<sub>6</sub>][Ln(dipic)<sub>3</sub>]<sub>n</sub>H<sub>2</sub>O. All the compounds prepared in these series, whether from optically inactive or (where appropriate) active reactants, were extremely insoluble in water and could be obtained quantitatively by simply mixing aqueous solutions of the transition metal complex cation as its chloride salt and the tris(dipicolinato)lanthanide anion as its sodium salt. Precipitates formed almost immediately even from hot solutions and were collected by filtration and washed well with water, and then ethanol and ether. In some cases, prolonged standing of the precipitate in contact with its supernatant solution resulted in an increase in crystal size, though for the Cr(III) complexes this was accompanied by decomposition except with those involving cage amine ligands. A recrystallization procedure found to work well with the [Co(en)<sub>3</sub>]<sup>3+</sup> salts was to dissolve the compound in dilute HCl and then add urea and heat the solution for several hours on a steam bath to slowly raise the pH through urea hydrolysis (though a large excess of urea must be avoided as it appears to convert the rare earth complex to some unidentified but possibly cationic species which does not form a precipitate).

Table Sup. 1 (supplementary material) contains a listing of the particular compounds prepared from the very numerous possible sets along with microanalytical data obtained after vacuum desiccation of each for 12 h. In most cases it appears that at least some water of crystallization is quite readily lost, so that crystals become opaque on storage and the composition deduced from crystal structure solutions commonly has more water molecules than in the composition deduced from the elemental analyses.

**Spectroscopy.** Procedures for the performance of low-temperature (77 K) measurements on the luminescence of powdered (microcrystalline) solids have been described previously.<sup>21-23</sup>

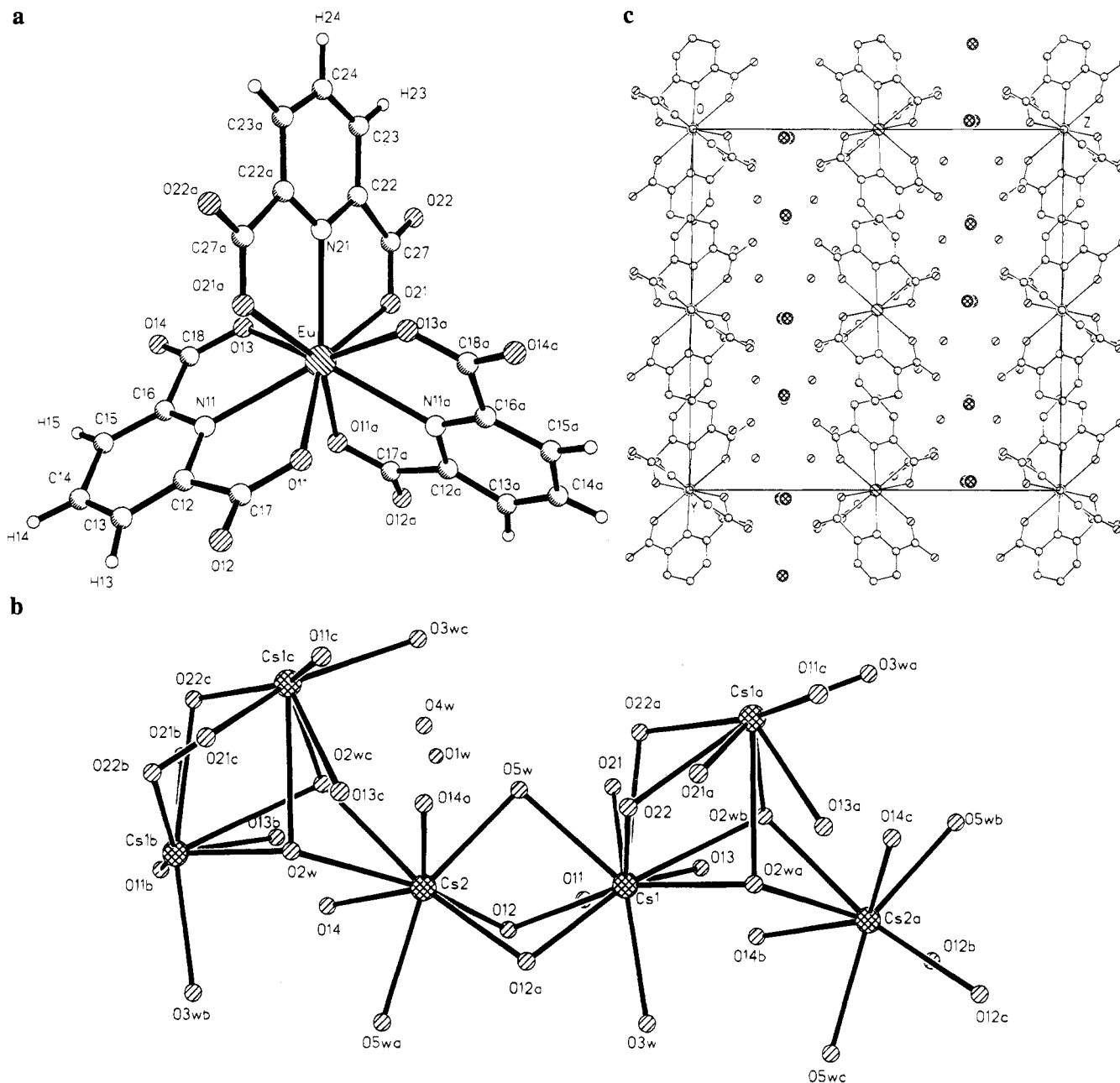
**Structure Determinations.** Unique diffractometer data sets (Siemens P4 diffractometer, 2θ<sub>max</sub> 50°, 2θ/θ scan mode, filtered Mo Kα radiation, λ 0.71073 Å) were measured at 293(2) K for Cs<sub>3</sub>[Eu(dipic)<sub>3</sub>]<sub>9</sub>H<sub>2</sub>O and [Co(sar)][Eu(dipic)<sub>3</sub>]<sub>13</sub>H<sub>2</sub>O. In each case, of the *N* independent reflections obtained, *N*<sub>o</sub> with *I* > 3σ(*I*) were considered "observed" and used in the full-matrix least squares refinements on |*F*| (Cs<sub>3</sub>[Eu(dipic)<sub>3</sub>]<sub>9</sub>H<sub>2</sub>O) or *F*<sup>2</sup> ([Co(sar)][Eu(dipic)<sub>3</sub>]<sub>13</sub>H<sub>2</sub>O) after absorption corrections. Anisotropic thermal parameters were refined for the non-hydrogen atoms. The structures were solved with SHELXS-86<sup>24</sup> and refined using SHELXL-93.<sup>25</sup> Pertinent results are given in Figures 1 and 2 and Tables 1-5; material deposited comprises tables of bond lengths, bond angles and anisotropic thermal parameters for both compounds and tables of all atoms introduced at calculated coordinates as well as full details of the structure determination and refinement procedures. Crystals of [Co(sar)][Eu(dipic)<sub>3</sub>]<sub>13</sub>H<sub>2</sub>O were obtained by allowing the initially precipitated solid obtained as described above to stand in contact with the supernatant solution for 2 days. Crystals of Cs<sub>3</sub>[Eu(dipic)<sub>3</sub>]<sub>9</sub>H<sub>2</sub>O were obtained by slow evaporation of an aqueous solution of the solid initially obtained by the addition of ethanol to its aqueous solution.

## Results and Discussion

**Syntheses.** All the mixed rare earth/transition metal materials presently described are remarkably simple to prepare because of their very low solubilities in water, though this does also mean that purification and crystal growth for those salts formed from hydrolytically sensitive cations are difficult. The insolubility may be considered an example of the principle of charge matching,<sup>26</sup> further illustrated by the difficulty in obtaining salts of cations such as [Ni(en)<sub>3</sub>]<sup>2+</sup> and [Ru(bipy)<sub>3</sub>]<sup>2+</sup>, though it is worthy of note that cations such as [Cr(dmsO)<sub>6</sub>]<sup>3+</sup> and [Co(phen)<sub>3</sub>]<sup>3+</sup> do not precipitate [Ln(dipic)<sub>3</sub>]<sup>3-</sup> from water, so that an explanation of the seemingly high lattice energies of the insoluble compounds cannot be trivial, though the two structures presently described (below) show that hydrogen bonds between coordinated amino protons and dipicolinate oxygen atoms are important in at least these cases. All the isolated solids appear to be hydrated, and again as illustrated by the structures presently described, this water of crystallization may play a complicated role in determining the structure. Another interesting feature of these two structures indicating the subtlety of their determinants is the fact that the achiral hydrated cesium ion forms an optically active crystal with [Eu(dipic)<sub>3</sub>]<sup>3-</sup> whereas the chiral [Co(sar)]<sup>3+</sup> cation gives a racemic compound.

**Structure Determinations.** The Cs<sup>+</sup> and [Co(sar)]<sup>3+</sup> salts of the [Eu(dipic)<sub>3</sub>]<sup>3-</sup> anion were chosen as materials suitable for initial structural studies because they were readily crystallized, contained an anion known usually to show strong visible luminescence, and were anticipated to show markedly different properties due to the difference in cations. In fact, the spectroscopic properties of the two solids are very different (see below) and the structure determinations indicate several possible origins of this. Atomic coordinates for the cesium compound are given in Table 2, and the cesium and europium coordination environments are shown in Figure 1. The two cations can be

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**Figure 1.** (a)  $[\text{Eu}(\text{dipic})_3]^{3-}$  entity found in  $\text{Cs}_3[\text{Eu}(\text{dipic})_3]\cdot 9\text{H}_2\text{O}$ , showing atom numbering within the dipicolinate ligands. (b) Part of the chain of bridged eleven- and eight-coordinate cesium atoms found within  $\text{Cs}_3[\text{Eu}(\text{dipic})_3]\cdot 9\text{H}_2\text{O}$ . Water oxygen atoms are indicated by the subscript w. (c) View of the unit cell of  $\text{Cs}_3[\text{Eu}(\text{dipic})_3]\cdot 9\text{H}_2\text{O}$  with hydrogen bonds and coordinate bonds to cesium omitted. The cesium atoms are shown as hatched circles.

considered to be bridged by the dipicolinate carboxylate groups, though the complete coordination spheres around cesium are considerably more complicated to describe than is the expected,<sup>8</sup> quite regular tricapped trigonal prismatic coordination sphere of the  $[\text{Eu}(\text{dipic})_3]^{3-}$  moiety. Two types of cesium ion, bridged by both carboxylate and water oxygen atoms, are found as part of a chain extending throughout the crystal. The chain can actually be considered as pairs of (bridged) eleven-coordinate cesium ions linked through bridging coordination to single eight-coordinate cesium ions. Six water molecules per formula unit of  $\text{Cs}_3[\text{Eu}(\text{dipic})_3]\cdot 9\text{H}_2\text{O}$  are involved in coordination to  $\text{Cs}^+$ , though all water molecules are involved in hydrogen bonding either to other water molecules or to the oxygen atoms of dipicolinate ligands. Hydrogen bonding parameters are given in Table 3. Although the space group is chiral and the crystal therefore optically active, the representation of the configuration of the complex anion as  $\Delta$  in Figure 1 is arbitrary, since

refinement did not allow definite assignment of the absolute configuration. Metal-metal separations are of course significant with regard to electronic interactions affecting luminescence behavior; the shortest  $\text{Cs}\cdots\text{Eu}$  separation is 4.584 Å, while the shortest  $\text{Eu}\cdots\text{Eu}$  separation is 10.165 Å. Deviations of the  $[\text{Eu}(\text{dipic})_3]^{3-}$  anion from  $D_3$  symmetry, despite the fact that the ion is situated on a twofold axis, are extremely small; the angles between the planes through the mid-point of the triangle  $\text{O}(11)-\text{O}(13)-\text{O}(21)$ , Eu and each of the coordinated oxygens are 60.4, 59.7 and 59.9°, while the dihedral angle between planes  $\text{O}(11)-\text{O}(13)-\text{O}(21)$  and  $\text{O}(11)-\text{O}(13)-\text{O}(21)$  is only 0.7°. The centroids of these planes are separated by 3.8 Å.

The chirality of the  $[\text{Co}(\text{sar})]^{3+}$  complex<sup>15</sup> means that two forms, a racemic compound and a racemic mixture, of the salt formed with the chiral (and labile)  $[\text{Eu}(\text{dipic})_3]^{3-}$  anion are possible. The material presently isolated is the racemic compound in which the two enantiomeric forms of the cation

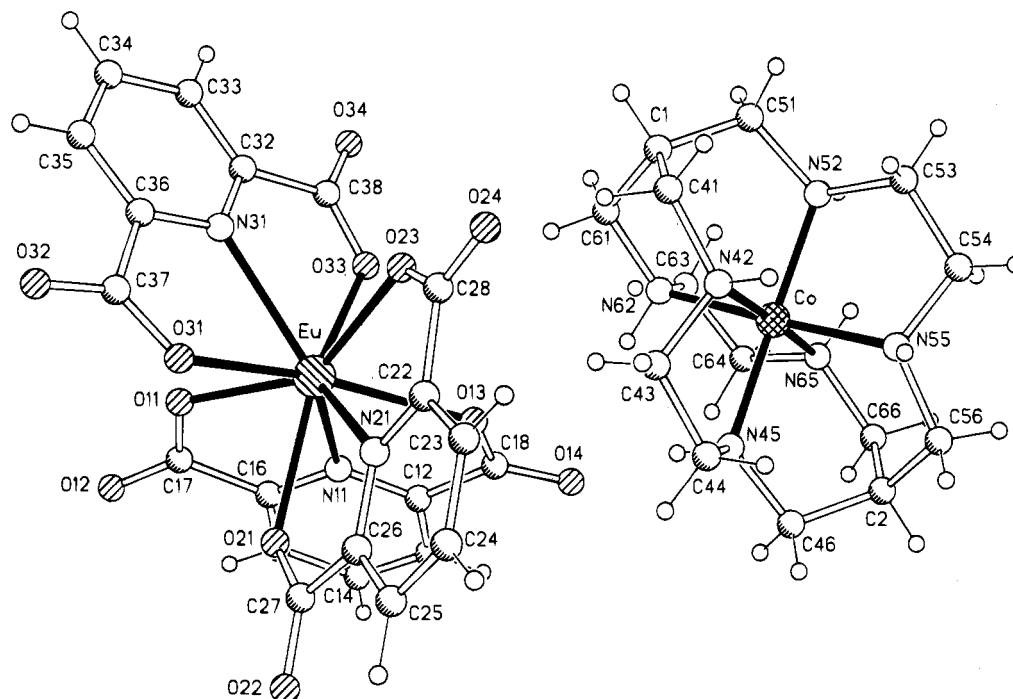


Figure 2.  $\Delta$ -Cation/ $\Lambda$ -anion pair present (along with its mirror image) in  $[\text{Co}(\text{sar})][\text{Eu}(\text{dipic})_3] \cdot 13\text{H}_2\text{O}$ .

Table 1. Crystallographic Data<sup>a</sup> for  $\text{Cs}_3[\text{Eu}(\text{dipic})_3] \cdot 9\text{H}_2\text{O}$  (1) and  $[\text{Co}(\text{sar})][\text{Eu}(\text{dipic})_3] \cdot 13\text{H}_2\text{O}$  (2)

$\text{C}_{21}\text{H}_{27}\text{Cs}_3\text{EuN}_3\text{O}_{21}$ (1)	$M = 1208.2$
orthorhombic	space group $C222_1$
$a = 10.165(2) \text{ \AA}$	$T = 293(2) \text{ K}$
$b = 18.164(4) \text{ \AA}$	$\lambda = 0.7107_3 \text{ \AA}$
$c = 18.724(4) \text{ \AA}$	$\rho_{\text{calc}} = 2.32 \text{ g cm}^{-3}$
$V = 3460(1) \text{ \AA}^3$	$\mu = 50.1 \text{ cm}^{-1}$
$Z = 4$	$R = 0.041$
	$R_w = 0.044$
$\text{C}_{35}\text{H}_{67}\text{CoEuN}_9\text{O}_{25}$ (2)	$M = 1224.9$
monoclinic	space group $P2_1/n$
$a = 10.611(4) \text{ \AA}$	$T = 293(2) \text{ K}$
$b = 26.500(10) \text{ \AA}$	$\lambda = 0.7107_3 \text{ \AA}$
$c = 17.583(7) \text{ \AA}$	$\rho_{\text{calc}} = 1.65 \text{ g cm}^{-3}$
$\beta = 91.97(3)^\circ$	$\mu = 16.8 \text{ cm}^{-1}$
$V = 4941(3) \text{ \AA}^3$	$R_1 = 0.0372$
$Z = 4$	$wR_2 = 0.0961$

<sup>a</sup>  $R$  factors defined as follows:  $R_1 = \frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|}$ ,  $R_w = \frac{\sum (|F_o| - |F_c|)^2}{\sum (|F_o| + |F_c|)^2}$ ,  $wR_2 = \frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2 + F_c^2)]^2}$ ,  $w = \frac{1}{\sigma^2(F) + 0.00003F^2}$ ,  $wR_2 = \frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2 + F_c^2)]^2}$ ,  $w = \frac{1}{\sigma^2(F) + (0.0445P)^2 + 10.67P}$ , where  $P = (\max(F_o^2, 0) + 2F_c^2)/3$ .

have the expected<sup>15,27</sup>  $D_3$   $lel_3$  structure with all nitrogen donor atoms of a given cation having the same configuration. Atomic coordinates for the salt are given in Table 4, and a  $\Delta$ -Co/ $\Lambda$ -Eu cation-anion pair is shown in Figure 2. Bond lengths and bond angles within the cation are closely similar to those observed in several related species,<sup>27-30</sup> and the parameters for the anion closely match those for the anion in its cesium salt, though the precision of the determination is inferior in the latter case. Water molecules within the lattice of the Co/Eu compound form a

Table 2. Atomic Coordinates/ $\text{\AA}$  and Temperature Factors/ $\text{\AA}^2$  for  $\text{Cs}_3[\text{Eu}(\text{dipic})_3] \cdot 9\text{H}_2\text{O}$

atom	$x$	$y$	$z$	$U^a$
Cs(1)	0.2436(1)	0.47610(6)	0.74347(7)	0.05039(3)
Cs(2)	0.50000	0.2621(1)	0.75000	0.0490(7)
Eu	0.2479(1)	0.50000	0.50000	0.0219(3)
O(11)	0.4168(8)	0.4809(5)	0.5917(5)	0.031(3)
O(12)	0.5412(11)	0.4056(9)	0.6577(7)	0.041(4)
O(13)	0.1872(9)	0.4138(6)	0.4046(5)	0.035(3)
O(14)	0.2237(14)	0.3138(7)	0.3390(6)	0.056(5)
N(11)	0.3710(9)	0.3784(6)	0.4951(6)	0.025(3)
C(12)	0.4608(12)	0.3609(7)	0.5463(7)	0.027(4)
C(13)	0.5293(17)	0.2968(9)	0.5467(9)	0.049(6)
C(14)	0.5041(26)	0.2473(10)	0.5037(21)	0.062(6)
C(15)	0.4098(18)	0.2637(9)	0.4413(8)	0.047(6)
C(16)	0.3467(14)	0.3308(8)	0.4435(8)	0.034(5)
C(17)	0.4759(12)	0.4210(10)	0.6027(8)	0.029(5)
C(18)	0.2451(18)	0.3537(8)	0.3919(8)	0.034(4)
O(21)	0.1408(9)	0.5775(6)	0.4118(5)	0.033(3)
O(22)	-0.0345(12)	0.6067(8)	0.3443(6)	0.043(4)
N(21)	0.0002(16)	0.50000	0.50000	0.028(4)
C(22)	-0.0669(12)	0.5391(9)	0.4523(7)	0.031(4)
C(23)	-0.2030(14)	0.5402(12)	0.4506(8)	0.049(6)
C(24)	-0.2638(22)	0.50000	0.50000	0.024(5)
C(27)	0.0187(15)	0.5776(9)	0.3962(9)	0.031(5)
O(1)w	0.50000	0.2524(7)	0.50000	0.024(6)
O(2)w	-0.0393(15)	0.4134(11)	0.3210(8)	0.076(7)
O(3)w	0.5542(19)	0.5871(10)	0.6749(10)	0.098(8)
O(4)w	0.2514(21)	0.1647(11)	0.6122(11)	0.136(10)
O(5)w	0.2236(20)	0.6955(10)	0.3265(13)	0.150(11)

<sup>a</sup> Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

complicated hydrogen-bonded network, eight molecules per formula unit being found in fully occupied sites and being hydrogen bonded to one another and dipicolinate oxygens, while five molecules per formula unit are disordered over sites found within a channel formed by separate stacks of cations and anions. This channel lies almost parallel to  $a$  and the water molecules within it appear to have considerable freedom of motion, so that it is not possible to give an exact description of the nature of the bonding. Basic hydrogen bond characteristic parameters are given in Table 5, population parameters being included in Table 4. Aside from  $\text{OH} \cdots \text{O}$  bonding involving

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**Table 3.** Hydrogen Bond Parameters for  $\text{Cs}_3[\text{Eu}(\text{dipic})_3]\cdot 9\text{H}_2\text{O}$ 

DH...A	sym transformation of A	D-H/Å	H...A/Å	D...A/Å	angle DHA/deg
O(2w)H(21w)...O(2w)	$-x, y, 0.5 - z$	0.85	1.99	2.777	153
O(2w)H(22w)...O(13)	$x, y, z$	0.85	2.13	2.785	134
O(3w)H(31w)...O(1w)	$x, 1 - y, 1 - z$	0.85	2.59	3.283	140
O(3w)H(32w)...O(11)	$x, y, z$	0.85	2.00	2.848	173
O(4w)H(41w)...O(3w)	$-0.5 + x, -0.5 + y, z$	0.85	1.87	2.717	180
O(4w)H(42w)...O(2w)	$0.5 + x, 0.5 - y, 1 - z$	0.85	2.00	2.848	180
O(5w)H(51w)...O(21)	$x, y, z$	0.85	1.95	2.804	176
O(5w)H(52w)...O(21)	$x, 1 - y, 1 - z$	0.85	1.96	2.801	170

**Table 4.** Atomic coordinates/Å and Equivalent Isotropic Displacement Parameters/Å<sup>2</sup> for  $[\text{Co}(\text{sar})][\text{Eu}(\text{dipic})_3]\cdot 13\text{H}_2\text{O}$ 

atom	x	y	z	$U^a$	occ	atom	x	y	z	$U^a$	occ
Eu	0.10371(2)	0.24461(1)	0.19259(1)	0.031(1)*	1.0	C(41)	0.1829(6)	0.4341(2)	0.3440(4)	0.061(2)*	1.0
O(11)	0.0101(3)	0.1904(1)	0.0927(2)	0.050(1)*	1.0	N(42)	0.3218(4)	0.4297(2)	0.3326(2)	0.043(1)*	1.0
O(12)	0.0361(5)	0.1444(2)	-0.0112(3)	0.088(2)*	1.0	C(43)	0.3632(5)	0.3763(2)	0.3265(3)	0.047(1)*	1.0
O(13)	0.2715(3)	0.3070(1)	0.1782(2)	0.041(1)*	1.0	C(44)	0.4972(5)	0.3765(2)	0.3031(3)	0.051(1)*	1.0
O(14)	0.4116(3)	0.3483(1)	0.1097(2)	0.044(1)*	1.0	N(45)	0.5042(4)	0.4082(1)	0.2339(2)	0.040(1)*	1.0
N(11)	0.2048(4)	0.2480(1)	0.0643(2)	0.035(1)*	1.0	C(46)	0.6376(5)	0.4176(2)	0.2110(4)	0.060(2)*	1.0
C(12)	0.3024(4)	0.2786(2)	0.0529(3)	0.037(1)*	1.0	C(51)	0.1493(6)	0.5171(2)	0.2775(4)	0.064(2)*	1.0
C(13)	0.3697(5)	0.2768(2)	-0.0129(3)	0.052(1)*	1.0	N(52)	0.2883(4)	0.5265(2)	0.2717(2)	0.047(1)*	1.0
C(14)	0.3338(6)	0.2420(2)	-0.0683(3)	0.061(2)*	1.0	C(53)	0.3464(7)	0.5521(2)	0.3391(3)	0.058(2)*	1.0
C(15)	0.2337(6)	0.2105(2)	-0.0565(3)	0.055(1)*	1.0	C(54)	0.4860(6)	0.5519(2)	0.3300(3)	0.058(2)*	1.0
C(16)	0.1715(5)	0.2141(2)	0.0112(3)	0.042(1)*	1.0	N(55)	0.5249(4)	0.4985(2)	0.3169(2)	0.048(1)*	1.0
C(17)	0.0639(5)	0.1803(2)	0.0318(3)	0.051(1)*	1.0	C(56)	0.6609(6)	0.4943(2)	0.2941(4)	0.067(2)*	1.0
C(18)	0.3319(4)	0.3146(2)	0.1186(3)	0.033(1)*	1.0	C(61)	0.1348(5)	0.4358(2)	0.2028(3)	0.057(1)*	1.0
O(21)	0.2575(3)	0.1774(1)	0.1816(2)	0.051(1)*	1.0	N(62)	0.2651(4)	0.4423(2)	0.1750(2)	0.042(1)*	1.0
O(22)	0.4256(3)	0.1334(2)	0.2196(3)	0.069(1)*	1.0	C(63)	0.2712(6)	0.4756(2)	0.1066(3)	0.052(1)*	1.0
O(23)	0.0703(3)	0.2961(1)	0.3055(2)	0.044(1)*	1.0	C(64)	0.4053(6)	0.4835(2)	0.0900(3)	0.051(1)*	1.0
O(24)	0.1135(4)	0.3184(2)	0.4258(2)	0.066(1)*	1.0	N(65)	0.4686(4)	0.5030(1)	0.1610(2)	0.041(1)*	1.0
N(21)	0.2500(3)	0.2282(1)	0.3076(2)	0.038(1)*	1.0	C(66)	0.6098(6)	0.5040(2)	0.1562(3)	0.059(1)*	1.0
C(22)	0.2364(5)	0.2541(2)	0.3713(3)	0.044(1)*	1.0	O(1w)	0.3560(3)	0.6025(1)	0.1619(2)	0.047(1)*	1.0
C(23)	0.3157(6)	0.2457(2)	0.4362(3)	0.060(2)*	1.0	O(2w)	0.1333(4)	0.3744(2)	0.0258(3)	0.085(1)*	1.0
C(24)	0.4076(6)	0.2097(3)	0.4320(4)	0.067(2)*	1.0	O(3w)	-0.3765(4)	0.0779(2)	0.2807(4)	0.096(2)*	1.0
C(25)	0.4206(5)	0.1824(2)	0.3658(4)	0.060(2)*	1.0	O(4w)	0.8775(5)	0.3723(2)	0.3120(3)	0.094(2)*	1.0
C(26)	0.3396(4)	0.1924(2)	0.3047(3)	0.045(1)*	1.0	O(5w)	-0.1295(5)	0.1011(2)	0.4541(3)	0.093(2)*	1.0
C(27)	0.3416(4)	0.1653(2)	0.2299(3)	0.046(1)*	1.0	O(6w)	-0.3825(5)	0.3822(3)	-0.0078(3)	0.120(2)*	1.0
C(28)	0.1323(5)	0.2927(2)	0.3688(3)	0.045(1)*	1.0	O(7w)	-0.1271(7)	0.4532(2)	0.0333(4)	0.128(2)*	1.0
O(31)	0.0050(3)	0.1784(1)	0.2673(2)	0.044(1)*	1.0	O(8w)	0.5408(7)	0.0444(2)	0.4189(4)	0.123(2)*	1.0
O(32)	-0.1623(3)	0.1345(1)	0.3015(2)	0.057(1)*	1.0	O(9w)	0.2535(14)	0.3530(6)	0.5574(8)	0.112(4)	0.5
O(33)	-0.0016(3)	0.3164(1)	0.1294(2)	0.042(1)*	1.0	O(10w)	0.3589(17)	0.4613(6)	0.4934(10)	0.148(5)	0.5
O(34)	-0.1746(3)	0.3582(1)	0.0903(2)	0.054(1)*	1.0	O(11w)	0.6028(14)	0.4472(5)	0.4599(8)	0.124(4)	0.5
N(31)	-0.1345(3)	0.2475(1)	0.1987(2)	0.033(1)*	1.0	O(12w)	0.2775(17)	0.3770(7)	0.5451(10)	0.142(6)	0.5
C(32)	-0.1995(4)	0.2838(2)	0.1617(3)	0.035(1)*	1.0	O(13w)	0.5075(22)	0.1097(9)	0.0756(13)	0.124(7)	0.33
C(33)	-0.3295(5)	0.2839(2)	0.1569(4)	0.054(1)*	1.0	O(14w)	0.3738(25)	0.0666(10)	0.9537(14)	0.145(9)	0.33
C(34)	-0.3922(5)	0.2458(2)	0.1934(4)	0.071(2)*	1.0	O(15w)	0.3086(24)	0.0852(8)	0.9583(12)	0.100(6)	0.33
C(35)	-0.3257(5)	0.2087(2)	0.2311(4)	0.059(2)*	1.0	O(16w)	0.4578(15)	0.1291(6)	0.0453(9)	0.082(4)	0.33
C(36)	-0.1955(4)	0.2107(2)	0.2324(3)	0.038(1)*	1.0	O(17w)	0.2575(28)	0.4850(10)	0.5227(15)	0.161(9)	0.33
C(37)	0.1126(4)	0.1709(2)	0.2707(3)	0.040(1)*	1.0	O(18w)	0.5711(44)	0.0285(17)	0.0747(26)	0.127(14)	0.17
C(38)	-0.1197(4)	0.3230(2)	0.1242(3)	0.038(1)*	1.0	O(19w)	0.1445(40)	0.4704(14)	0.5435(22)	0.107(11)	0.17
Co	0.39566(6)	0.46782(2)	0.24838(3)	0.033(1)*	1.0	O(20w)	0.4633(10)	0.4526(4)	0.4693(6)	0.118(3)	0.67
C(1)	0.1166(5)	0.4615(2)	0.2779(4)	0.057(1)*	1.0	O(21w)	0.5836(40)	0.0810(17)	0.1084(24)	0.121(12)	0.17
C(2)	0.6747(5)	0.4725(2)	0.2163(3)	0.054(1)*	1.0	O(22w)	0.2417(37)	0.0773(14)	0.9579(20)	0.090(10)	0.17

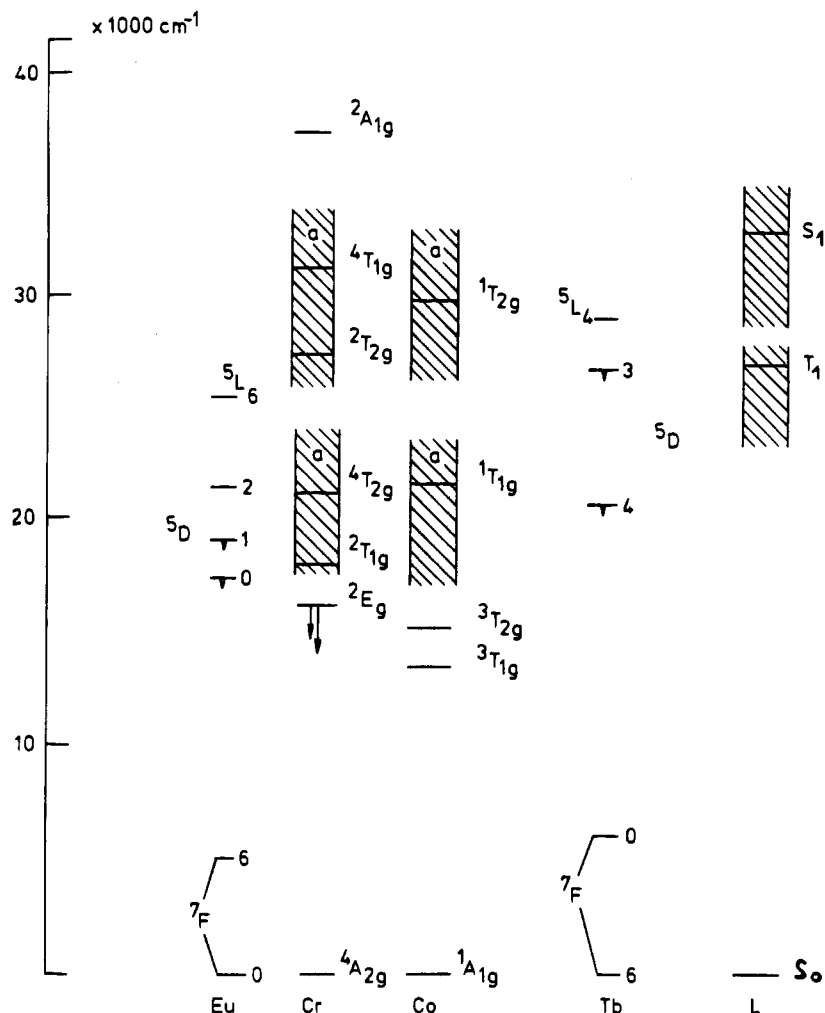
<sup>a</sup> Asterisk indicates  $U_{eq}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 5.** Hydrogen Bond Parameters for  $[\text{Co}(\text{sar})][\text{Eu}(\text{dipic})_3]\cdot 13\text{H}_2\text{O}$ 

DH...A	sym transformation of A	D-H/Å	H...A/Å	D...A/Å	angle DHA/deg
O(1w)H(1wa)...O(6W)	$-x, 1 - y, -z$	0.85	1.95	2.764	159
O(1w)H(1wb)...O(31)	$0.5 - x, 0.5 + y, 0.5 - z$	0.85	1.92	2.764	170
O(2w)H(2wa)...O(8W)	$-0.5 + x, 0.5 - y, -0.5 + z$	0.85	2.21	3.000	155
O(2w)H(2wb)...O(5W)	$0.5 + x, 0.5 - y, -0.5 + z$	0.85	2.08	2.926	179
O(3w)H(3wa)...O(8W)	$-1 + x, y, z$	0.85	1.91	2.759	179
O(3w)H(3wb)...O(22)	$-1 + x, y, z$	0.85	1.90	2.752	178
O(4w)H(4wa)...O(15W)	$0.5 + x, 0.5 - y, -0.5 + z$	0.85	2.15	2.925	152
O(4w)H(4wb)...O(23)	$1 + x, y, z$	0.85	2.03	2.878	180
O(5w)H(5wa)...O(2W)	$-0.5 + x, 0.5 - y, 0.5 + z$	0.85	2.12	2.926	142
O(5w)H(5wb)...O(6W)	$0.5 + x, 0.5 - y, 0.5 + z$	0.85	1.87	2.719	178
O(7w)H(7wa)...O(8W)	$-0.5 + x, 0.5 - y, -0.5 + z$	0.85	2.06	2.734	137
O(8w)H(8wb)...O(7W)	$0.5 - x, -0.5 + y, 0.5 - z$	0.85	1.94	2.709	149
O(8w)H(8wa)...O(3W)	$1 + x, y, z$	0.85	1.91	2.759	180

the complex anion and water, the cation-anion interactions appear to involve a contribution from  $\text{NH}\cdots\text{O}$  bonding, the closest distance of approach of one coordinated secondary amino

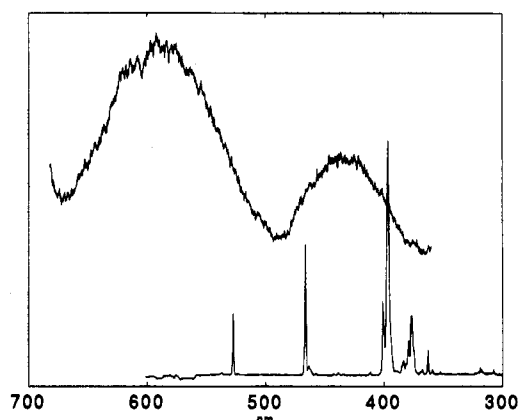
group proton to an uncoordinated carboxylate group oxygen being 1.80 Å. The shortest  $\text{Eu}\cdots\text{Co}$  separation in the lattice is 7.41 Å, and the shortest  $\text{Eu}\cdots\text{Eu}$  separation is 10.12 Å.



**Figure 3.** Energy level diagram showing 3d states (Cr(III), Co(III)) and 4f states (Eu(III), Tb(III)) and indicating the overlap of broad transition metal bands with sharp lanthanide bands. "a" denotes a spin-allowed transition.

Deviations of the anion symmetry from  $D_3$  are again very small, though significantly larger than in the cesium salt; the angles between the planes including the midpoint of the triangle O(11)–O(21)–O(31), Eu, and those between the midpoint of the triangle O(13)–O(23)–O(33), Eu and those bonded oxygens are 61.6, 59.7, and 58.7°, and those between the midpoint of the triangle O(11)–O(21)–O(31) and O(13)–O(23)–O(33) planes is 3.7°, and the centroids of the planes are 3.33 Å apart.

**Photophysical Properties of Microcrystalline  $[\text{Ln}(\text{dipic})_3] \cdot n\text{H}_2\text{O}$  ( $\text{Ln} = \text{Eu(III)}, \text{Tb(III)}$ ;  $\text{M} = \text{Cr(III)}, \text{Co(III)}, \text{Rh(III)}, \text{Cs(I)}, \text{N}(\text{C}_2\text{H}_5)_4^+$ ).** (a) **Emission Spectroscopy.** Excitation of the Cr- and Co-containing complexes of this series through the first excited state of Eu(III),  $^5D_0$ , of Tb(III),  $^5D_4$ , or of the dipicolinate ligand results in a very weak, sometimes even undetectable, luminescence from the lanthanide ions. This is due to the resonance between the Ln(III) excited levels and the broad d states of the Cr(III) and Co(III) ions (Figures 3 and 4). The absorption bands of the transition metal ions overlap the spectral range of the narrow line emission spectra of Eu(III) and Tb(III), resulting in an efficient quenching of the Ln luminescence, as shown by the rather short luminescence lifetimes (Table 6). In contrast, Cs(I), Rh(III), and  $\text{N}(\text{C}_2\text{H}_5)_4^+$  are cations which do not possess low-lying energy levels able to quench the Ln luminescence and the Eu(III) compounds containing these countercations therefore display an intense red emission (Figure 5).



**Figure 4.** Excitation spectra at 77 K for (a) Cr(III) doublet emission from  $[\text{Cr}(\text{urea})_6][\text{Eu}(\text{dipic})_3]$  (upper trace) and (b) Eu(III)  $^5D_0-^7F_0$  emission from  $\text{Cs}_3[\text{Eu}(\text{dipic})_3]$  (lower trace).

The crystallographic data given above for both the Eu(III)-containing complexes  $\text{Cs}_3[\text{Eu}(\text{dipic})_3] \cdot 9\text{H}_2\text{O}$  and  $[\text{Co}(\text{sar})][\text{Eu}(\text{dipic})_3] \cdot 13\text{H}_2\text{O}$  reveal that numerous water molecules are incorporated in the unit cell in disordered positions. Murray et al.<sup>4</sup> have investigated the effect of the degree of hydration on the luminescence spectra of different  $\text{Na}_3[\text{Eu}(\text{dipic})_3] \cdot n\text{H}_2\text{O}$  hydrates and have found that different arrangements of the hydrate molecules result in different crystal field splittings, clearly reflected in the emission spectra. Similar effects have been found in most of the presently examined compounds.

**Table 6.** Eu( $^5D_0$ ), Tb( $^5D_4$ ), and Cr( $^2E_g$ ) Luminescence Lifetimes (77 K) in [Ln(dipic) $_3$ ] $^{3-}$  Salts

salt	$\lambda_{exc}/nm$	$\lambda_{em}/nm$	$\tau_f^{Cr}/\mu s$	$\tau_f^{Eu}/\mu s$	$\tau_f^{Tb}/\mu s$
[(+) $Cr(en)_3$ ][Eu(dipic) $_3$ ]	308	671	106 $\pm$ 3		
	581.2	671	98 $\pm$ 4		
[Cr(en) $_3$ ][Eu(dipic) $_3$ ]	308	671	94 $\pm$ 2		
	581.2	671	92 $\pm$ 2		
[Cr(urea) $_6$ ][Eu(dipic) $_3$ ]	581	700	103 $\pm$ 10		
[Cr(en) $_3$ ][La(dipic) $_3$ ]	308	675.5	103 $\pm$ 3		
[Cr(urea) $_6$ ][Tb(dipic) $_3$ ]	308	700	259 $\pm$ 4		
	488	700	248 $\pm$ 9		
[Cr((NH $_2$ ) $_2$ sar)[Tb(dipic) $_3$ ]	308	682	167 $\pm$ 3		
[(+) $Cr(en)_3$ ][Eu(dipic) $_3$ ]	581.2	615.6		21 $\pm$ 2	
	581	617.7		94 $\pm$ 3	
[Cr((NH $_2$ ) $_2$ sar)[Eu(dipic) $_3$ ]	308	594.3		2020 $\pm$ 40	
[N(C $_2$ H $_5$ ) $_4$ ] $_3$ [Eu(dipic) $_3$ ]	580.9	594.3		1860 $\pm$ 40	
	580.9	615		1900 $\pm$ 30	
	488	616.5		1780 $\pm$ 20	
[Rh(en) $_3$ ][Eu(dipic) $_3$ ]	581.6	616.5			4.60 $\pm$ 0.03
[Cr(urea) $_6$ ][Tb(dipic) $_3$ ]	308	543			4.37 $\pm$ 0.08
	488	543			
[Cr((NH $_2$ ) $_2$ sar)[Tb(dipic) $_3$ ]	308	545			60 $\pm$ 2
	488	545			47 $\pm$ 4

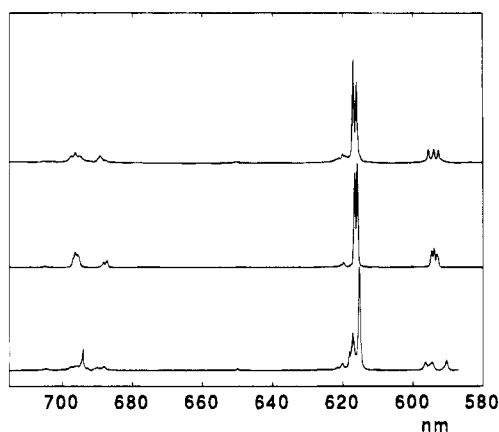
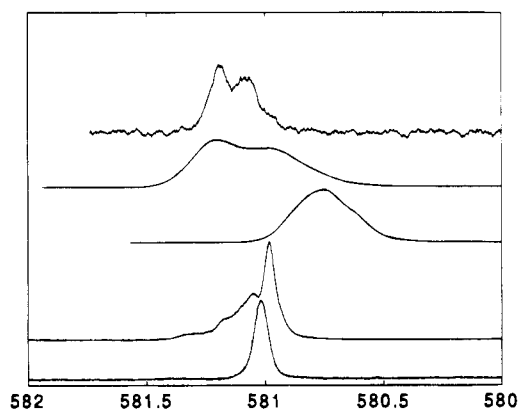
**Figure 5.** Europium(III) emission (77 K) from (a) [Rh(en) $_3$ ][Eu(dipic) $_3$ ],  $\lambda_{exc} = 376.5$  nm (upper trace), (b) Cs $_3$ [Eu(dipic) $_3$ ],  $\lambda_{exc} = 395$  nm (middle trace), and (c) [N(C $_2$ H $_5$ ) $_4$ ] $_3$ [Eu(dipic) $_3$ ],  $\lambda_{exc} = 580.75$  nm (lower trace).**Figure 6.** Eu(III)  $^5D_0-^7F_0$  excitation spectra (77 K) for (from top to bottom) (a) [Co(NH $_3$ ) $_6$ ][Eu(dipic) $_3$ ], (b) [Cr(diamsar)][Eu(dipic) $_3$ ], (c) [N(C $_2$ H $_5$ ) $_4$ ] $_3$ [Eu(dipic) $_3$ ], (d) [Cr(en) $_3$ ][Eu(dipic) $_3$ ], and (e) [Co(en) $_3$ ][Eu(dipic) $_3$ ].

Figure 6 displays Eu ( $^5D_0-^7F_0$ ) excitation spectra obtained by monitoring the Eu ( $^5D_0-^7F_2$ ) transition. The 0-0 transition being unique for a given metal ion environment, the number of its components and its band shape are indicative of the type of structure prevailing in the complex.<sup>31</sup> In all the compounds

examined, the energy of the  $^5D_0-^7F_0$  transition is dependent upon the nature of the [ML $_x$ ] $^{z+}$  cation(s). The narrowest transition is observed for [Co(en) $_3$ ][Eu(dipic) $_3$ ], with a full width at half-height (fwhh) of 2.5  $cm^{-1}$ , typical of one single and well-defined environment for the lanthanide ion. Where different hydrates are present, as appears to be the case with [Cr(en) $_3$ ][Eu(dipic) $_3$ ], 0-0 transitions are found at different energies. When an Eu(III) compound contains a statistical distribution of molecules with somewhat different conformations or when the compound has a polymeric nature, the bandwidth of the 0-0 transition increases considerably.<sup>31</sup> This is observed for [N(C $_2$ H $_5$ ) $_4$ ] $_3$ [Eu(dipic) $_3$ ] and [Cr((NH $_2$ ) $_2$ sar)][Eu(dipic) $_3$ ], suggesting a substantial disorder in the positions of hydrate water molecules and/or the presence of several different hydrates (as suggested by repetitive elemental analyses). In some instances, different batches of the same compound yielded 0-0 excitation spectra displaying different components. Selective laser excitations through the profile of the 0-0 transition reveal significant differences between the emission spectra. In spite of this, most of them clearly display the characteristics of the *pseudo-D* $_3$  symmetry expected for the [Eu(dipic) $_3$ ] $^{3-}$  species. Under this symmetry point group, the  $^5D_0-^7F_1$  and  $^5D_0-^7F_2$  transitions are comprised of two components assigned to  $A_1-E$ ,  $A_1-A_2$ , and  $A_1-E$  (twice), respectively.<sup>31</sup>

Metcalf et al.<sup>2,32</sup> have reported a chiral discrimination in energy transfer between [Ln(dipic) $_3$ ] $^{3-}$  and enantiomerically resolved Co(III) complexes in solution. They assumed that enantioselective quenching in these luminophore-quencher systems reflects intermolecular chiral discrimination that depends on the details of the chiral structure of the Co(III) complexes. They also reported that the strongest optical activity was observed for the  $^5D_0-^7F_1$  transition. In the compounds studied herein, this transition seems to be more sensitive to deviations from  $D_3$  symmetry than the hypersensitive  $^5D_0-^7F_2$  transition, and in most of the compounds, the  $A_1-E$  component splits into two bands. Despite the narrow 0-0 transition observed for [Co(en) $_3$ ][Eu(dipic) $_3$ ], both components of the  $^5D_0-^7F_1$  transition appear as doublets (splittings: 10 and 18  $cm^{-1}$ ). The  $^5D_0-^7F_0$  excitation spectra recorded by setting the analyzing wavelength on each component of the two doublets reveal exactly the same narrow line centered at 17 212  $cm^{-1}$ . We interpret these data as reflecting the sensitivity of the  $^5D_0-^7F_1$  transition to chirality; both [Co(en) $_3$ ] $^{3+}$  and [Eu(dipic) $_3$ ] $^{3-}$  are chiral species, so that two different cation/anion pairs,  $\Delta_C/\Delta_A$

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**Table 7.** Crystal Field Levels ( $\text{cm}^{-1}$ ,  ${}^7F_0$  Origin) for Eu(III) in  $[\text{MN}_6][\text{Eu}(\text{dipic})_3]$ , Identified from Luminescence Spectra at 77 K

level	$[\text{MN}_6] = [\text{Cr}(\text{en})_3]$	$[\text{MN}_6] = [\text{Co}(\text{en})_3]$	$[\text{MN}_6] = [\text{Cr}(\text{NH}_2)_2\text{sar}]$
${}^7F_1$	304	321	323
	401	331	378
	416	386	412
${}^7F_2$	960	955	965
	1010	984	995
		404	

$\Delta_{\text{Eu}} (\Lambda_{\text{Co}}/\Lambda_{\text{Eu}})$  and  $\Delta_{\text{Co}}/\Lambda_{\text{Eu}} (\Lambda_{\text{Co}}/\Delta_{\text{Eu}})$  are possible. If both types of pair are present in the crystalline solid, a question we are presently attempting to answer through further crystallographic studies, then the  ${}^7F_1$  level of the Eu(III) ions would be subject to slightly different crystal fields, thereby resulting in splitting of the  ${}^5D_0-{}^7F_1$  transition and explaining the observed results (Table 7). The effect of this diastereoisomeric difference would then have to be too small to induce observable splitting of the  ${}^5D_0-{}^7F_0$  transition, but we note that its fwhh ( $2.5 \text{ cm}^{-1}$ ) is somewhat larger than is observed for unequivocally defined and rigid metal ion sites ( $1-2 \text{ cm}^{-1}$ )<sup>31</sup> and that complete dehydration of the compound  $\text{Na}_3[\text{Eu}(\text{dipic})_3] \cdot 15\text{H}_2\text{O}$  produces a shift in the  ${}^5D_0-{}^7F_0$  transition of only  $1 \text{ cm}^{-1}$  (from 17 215 to  $17\,214 \text{ cm}^{-1}$ ).<sup>4</sup> The presence of two components in this transition cannot therefore be completely ruled out. The crystal structure of  $[\text{Co}(\text{sar})][\text{Eu}(\text{dipic})_3] \cdot 13\text{H}_2\text{O}$  does not show the presence of inequivalent Eu centers, but Metcalf et al.<sup>2</sup> have demonstrated that seemingly minor variations in the nature of Co(III) hexamine quenchers can have major effects on their quenching efficiency, presumably because of differences in associated-ion structures, so it would be unwise to conclude that solid  $[\text{Co}(\text{en})_3][\text{Eu}(\text{dipic})_3]$  must be similar to  $[\text{Co}(\text{sar})][\text{Eu}(\text{dipic})_3]$ . Nonetheless, if coordinated amine NH to coordinated carboxylate O hydrogen bonding were again to be important in the cation-anion association, the  $\text{Eu} \cdots \text{Co}$  separation would still be close to  $7.5 \text{ \AA}$ .

Some of the Cr(III) containing compounds display a relatively intense luminescence from the Cr  ${}^2E_g$  level which can be used to determine the symmetry of the coordination polyhedron around the chromium ion. The main emission of Cr(III) normally arises from the spin-forbidden  ${}^2E_g-{}^4A_{2g}$  transition, which usually appears as a narrow doublet. In ruby, in which the Cr(III) ion lies in a  $C_{3v}$  local environment, the doublet is split by  $29.4 \text{ cm}^{-1}$  at  $77 \text{ K}$ .<sup>33</sup> In the  $[\text{Cr}(\text{en})_3][\text{Eu}(\text{dipic})_3]$  complex, the Cr doublet displays a splitting of  $31.2 \text{ cm}^{-1}$ , indicative of trigonal symmetry for the chromium environment. In other compounds, the components of the doublet are much broader, as expected for lower symmetry Cr coordination polyhedra. With the exception of the compounds containing cage amine complexes of Cr(III), all are somewhat sensitive to photodecomposition,<sup>34</sup> so that  $[\text{Cr}(\text{en})_3][\text{Eu}(\text{dipic})_3]$ , for example, quite rapidly changes color from yellow to pink (indicating loss of the amine ligand) when exposed to laser radiation or more slowly when simply stored in normal light.

**(b) Ligand-to-Metal Energy Transfer.** In the absence of quenchers such as Cr(III) or Co(III) amine complexes,  $[\text{Eu}(\text{dipic})_3]^{3-}$  moieties are efficient light-converting devices through ligand-to-metal energy transfer. Even at room temperature they give an intense red emission upon excitation with UV radiation. The maximum of the ligand excitation band lies above  $40\,000 \text{ cm}^{-1}$ , meaning that the light conversion process

involves an efficient multiphonon assistance. The size of the gap between the ligand feeding level and the Eu ( ${}^5D_0$ ) emitting level near  $18\,000 \text{ cm}^{-1}$  shows that a resonance condition is not essential for an efficient ligand-to-metal energy transfer as long as adequate vibronic couplings are at hand. In addition, the location of ligand states at high energy prevents both a mixing of these states with the  $4f$  states and a back-transfer from the excited metal to the ligand, as often observed for Tb(III) compounds,<sup>35</sup> and favors high quantum yields. In some instances, it appears that the  $\nu(\text{C}=\text{O})$  vibrational mode is an efficient relay to gain resonance between the ligand and Eu(III) or Tb(III) levels. Sabbatini, et al.<sup>36</sup> have shown that the  $[\text{Tb}(p\text{-tert-butylcalix}[4]\text{arenetetraamide})]$  complex, where Tb(III) is coordinated to four carbonyl groups (and four ether oxygens), is a very good luminescent stain. In works involving some of the present authors, it has been observed that  $[\text{Tb}_2(p\text{-tert-butylcalix}[8]\text{arene-6H})(\text{dmf})_5]$ , in which each Tb(III) is bound to dmf carbonyl oxygen atoms, shows very efficient ligand-to-metal energy transfer<sup>5</sup> and that Eu(III) mixed-ligand  $\beta$ -diketonate complexes have a particularly high quantum yield upon ligand excitation when the ligand-to-metal charge transfer state lies at high energy.<sup>37</sup> In the  $[\text{Eu}(\text{dipic})_3]^{3-}$  anion, the metal ion is bonded to each dipicolinate ligand through two oxygen atoms of different carboxylate groups and the nitrogen atom of the pyridine moiety. Excitation spectra show that Eu emission is observed for short wavelengths assigned to dipicolinate absorption, suggesting once again that energy transfer from the donor to the acceptor levels is promoted by vibronic coupling involving  $\nu(\text{C}=\text{O})$ .

**(c) Luminescence Lifetimes.** The  $\text{Eu}({}^5D_0)$  and  $\text{Tb}({}^5D_4)$  luminescence decays were found to be monoexponential. Thus, all the emitting species in the macromolecular samples must be identical with respect to both the number of acceptors around the donors and their distance of separation. The luminescence lifetimes are given in Table 6. Compounds without Cr or Co moieties as acceptors have luminescence lifetimes of about 2 ms, showing that, as found in all cases where crystal structures have been determined, "water of crystallization" in the compounds is not coordinated to the  $\text{Ln}^{3+}$  ions but is hydrogen-bonded to the dipicolinate ligands.<sup>5,35</sup> When Cr(III) acceptors are present, the lifetimes decrease drastically to less than 0.1 ms (Table 6), while the Eu and Tb lifetimes are too short to measure for the Co(III)-containing samples. Co(III) complexes are known to have spin-forbidden d-d transitions which are lower in energy than the readily observed  ${}^1A_{1g}-{}^1T_{1g}$  transition (Figure 3), and the weak absorption bands associated with these transitions overlap several  ${}^5D_0-{}^7F_J$  (Eu) and  ${}^5D_4-{}^7F_J$  (Tb) emission manifolds. The immeasurably short Eu and Tb lifetimes in the cobalt(III) amine complex salts therefore indicate that the  ${}^3T_{1g}$  and  ${}^3T_{2g}$  levels play a crucial role as acceptor levels in the  $\text{Ln} \rightarrow \text{Co}$  energy transfer mechanism. Moreover, when lanthanide ions are excited through a ligand band at 308 nm, the luminescence lifetimes are significantly longer. We therefore conclude that the ligand-to-Ln energy transfer process occurs via a long-lived ligand triplet state and perhaps may also involve higher M(III) energy levels which provide a rate-limiting pathway in the overall conversion process. Finally, we note an interesting property of  $[\text{Cr}(\text{urea})_6][\text{Tb}(\text{dipic})_3]$ : the  $\text{Tb}({}^5D_4)$

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lifetime is quite short, despite the intense luminescence of this compound. This we interpret in terms of the  $^5D_4$  state being continuously populated through higher Cr(III) levels while it is simultaneously deactivated by the lower Cr(III) levels.

**Conclusions.** It is apparent that the spin-forbidden d-d transitions of both Cr(III) and Co(III) lie at an energy (which is only slightly dependent to the nature of the bound ligands) such that they provide an efficient pathway for the quenching of luminescence from Eu(III) and Tb(III) tris(dipicolinato) complexes. However, it also appears that spin-allowed transitions, which are, of course, markedly sensitive to the nature of the ligand donor atoms, may, when their energy is appropriate, serve to transfer excitation from the transition metal to the lanthanide ion. For the particular complexes studied in the present work,  $\text{NH}\cdot\cdot\text{O}(\text{carboxylate})$  hydrogen bonding between the two complex ion species<sup>38,39</sup> is probably a critical aspect of the energy transfer processes, and we are directing current synthetic studies toward materials incorporating non-hydrogen-bonding cations in order to explore this hypothesis further. The

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photosensitivity of compounds such as the  $[\text{Cr}(\text{en})_3][\text{Ln}(\text{dipic})_3]$  series suggests that it may be possible to use photolysis to form derivatives in which the amine ligands are lost and carboxylato groups bridge the transition and rare earth metal ions, so enhancing interactions between the two centers at the same time as perturbing the Cr(III) energy levels. Thus, we are also currently investigating thermal as well as photochemical pathways to such materials.

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**Supplementary Material Available:** Tables Sup. 1-9 containing elemental analyses, a summary of crystallographic details, bond lengths, bond angles, anisotropic temperature factors, and calculated hydrogen atom coordinates and  $U$  values for  $\text{Cs}_3[\text{Eu}(\text{dipic})_3]\cdot 9\text{H}_2\text{O}$  and  $[\text{Co}(\text{sar})][\text{Eu}(\text{dipic})_3]\cdot 13\text{H}_2\text{O}$  and figures showing emission spectra of  $[\text{ML}_2][\text{Eu}(\text{dipic})_3]$  (24 pages). Ordering information is given on any current masthead page.

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