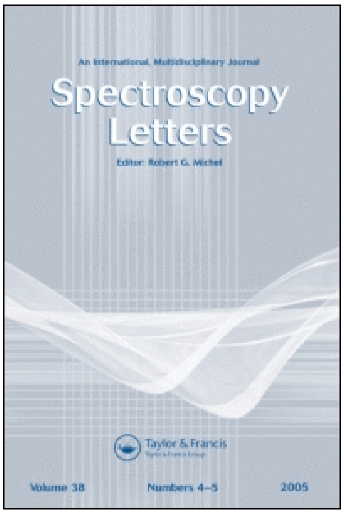

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Synthesis and Spectral Study of Several Solid M_3[Eu(2,6-Pyridinedicarboxylate)$_3$] Salts (M=Li , Na , K , Rb , Cs , NH_4 , and Pyridinium)

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SYNTHESIS AND SPECTRAL STUDY OF SEVERAL SOLID $M_3[Eu(2,6\text{-PYRIDINEDICARBOXYLATE})_3]$ SALTS ($M=Li^+$, Na^+, K^+, Rb^+, Cs^+, NH_4^+, and Pyridinium$^+$)[*]

Key Words: Eu^{3+} luminescence, 2,6-pyridinedicarboxylate, counterion effect

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ABSTRACT

Salts of the $[Eu(2,6\text{-pyridinedicarboxylate})_3]^{3-}$ complex anion and various monovalent inorganic and organic counterions (Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, and pyridinium$^+$) have been synthesized and studied by emission spectroscopy. The Eu^{3+} ion emission spectra exhibited by these salts have been observed with high resolution (less than 1.0 cm^{-1}) and at low temperature (77 K). The emission

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spectra of these compounds indicate that changing the attached counterion does not affect the site symmetry observed by the europium ion beyond slight distortions indicated by small shifts in the energies of the Eu^{3+} electronic levels.

INTRODUCTION

It is well known that the ligand field surrounding a lanthanide ion will perturb to a small degree the electronic spectrum of that ion relative to that of the free ion.[1] The degree of this perturbation is dependent upon the conformation and strength of that ligand field. Slight changes in the compound's stoichiometry or structure, which result in changes in the ligand field, will be observable as alterations of the electronic spectrum of that compound. These spectral changes can be of use in the determination of electronic, magnetic, and structural characteristics of the lanthanide ion-containing compound.

The small number of spectroscopic emission studies concerned with the effects observed upon the replacement of counterions precipitated with a Eu^{3+} containing complex anion can be partially attributed to the difficulty in reproducing solid-state salts with purity of Eu^{3+} ion sites. The trisodium salts of the tris(2,6-pyridinedicarboxylate) [dipicolinate or DPA^{2-}] chelate complexes of lanthanides have been well studied[2-6] because of the ease and reproducibility of their synthesis, their well-behaved emission characteristics, and their well-known crystal structures. These attributes indicate that a series of these compounds might be employed for a spectroscopic study of the counterion effects upon the electronic levels of complexed Eu^{3+} ions.

Recently, we have reported the results of our studies of inorganic counterion effects with Eu^{3+} complex anions of benzoylacetonate[7] and ethylenedinitrilotetraacetate.[8] It has been shown that replacement of inorganic counterions can give rise to large shifts in the observed Eu^{3+} ion emission spectra, even to the point of changing the site symmetry encountered by the Eu^{3+} ion. In both of these studies,[7-8] the chelating ligands did not coordinatively saturate the nine coordination positions commonly associated with Eu^{3+} ions. The vacant coordination positions were, in some cases, filled with complexed solvent molecules and, in others, left empty such that the Eu^{3+} ion exhibited eight coordinate geometry. In the present title compounds, three tridentate ligands attach[9] to fill nine coordination positions and thus saturate the first coordination sphere of the Eu^{3+} ion.

X-ray structural studies of the trisodium salts of the tris(DPA) complex of several lanthanides have shown a geometric polyhedron surrounding the Eu^{3+} ion that can be approximated by a tricapped trigonal prism.[10-13] In this polyhedron the three nitrogen atoms occupy the equatorial positions on the three faces of the prism. The other six positions are filled with a single oxygen, one from each of the six carboxylate groups. This results in a helical positioning of the chelated ligands which appears to set the Eu^{3+} ion in a D_3 site symmetry.[2-6] However, recent optical studies of the trilithium salt of this complex anion have shown that the site symmetry exhibited by the complexed Eu^{3+} ion appears to be a slightly distorted form of D_{3h} symmetry.[14] The expected symmetry for an "undistorted" tricapped trigonal prism would be D_{3h}. This apparent contradiction is attributable to the insensitivity of the Eu^{3+} ion emission spectrum to some slight structural distortions. This insensitivity has been encountered in other similar cases such as those of the trichloride and trihydroxide of Eu^{3+}.[15-16] For the title compounds in a triclinic form, the distortion is approximated by the rotation of the ends of the trigonal prisms about 15° in opposite directions.[10-13] Although this may seem to be a large distortion, the Eu^{3+} ion fails to see its effects beyond slightly increasing the allowed nature of a few of the still forbidden transitions.

Other distortions of equal importance are also observed in the crystal structures described by single crystal X-ray analysis.[10-13] These distortions result in the loss of the coplanar nature of the three triangles making up the geometric polyhedron and the loss of the equilateral nature of the individual triangles. These distortions have the effect of starting to lower the site symmetry of the Eu^{3+} ion towards C_2 or lower site symmetry. This may be observed in the splitting of normally degenerate transitions and in the increasing of the "allowedness" of several normally disallowed transitions.

EXPERIMENTAL DETAILS

A stock solution of 0.284 M europium chloride was prepared by the dissolution of 25.0 g europium oxide (Johnson Matthey/ALFA Products) in a slight excess of hydrochloric acid (Mallinckrodt Incorporated) and dilution to 500 mL. 1 M hydroxide solutions were prepared from 1 mole of the appropriate hydroxide (Johnson Matthey/ALFA Products), which was dissolved in and diluted to 1 L volume with deionized water. The 2,6-pyridinedicarboxylic acid (Aldrich Chemicals) was weighed and used as received.

Approximately 2 mL of the appropriate metal(I) hydroxide or aqueous amine solution was added to 1 mL of the europium stock solution. The precipitated hydroxide was then washed three times with 5 mL aliquots of deionized water. Next, 0.15 g of the solid ligand (H_2DPA) was mixed with the europium hydroxide, diluted to about 5 mL, and heated to a gentle boil. The metal(I) hydroxide or aqueous amine was then added dropwise to the boiling solution until a solution pH above 8 was reached. Dissolution produced a strongly luminescent solution, which upon concentration, yielded clear luminescent crystals. In the case of the tripyridinium salt, the crystals were allowed to air dry before being sealed into a glass capillary. In the other cases, a small amount of the precipitate along with a small amount of the saturated solution was sealed into a glass capillary. Phonon Raman spectra of the trilithium and trisodium salts exhibited the pattern of peaks characteristic of the triclinic crystal structure as described previously.[17]

Excitation of the title compounds was accomplished through the use of the 457.9 nm line of a six-watt argon-ion laser (Coherent Radiation model number Innova 300; 500 milliwatts of power was available at this wavelength). The sample was cooled to reduce vibrational broadening of the emission lines by immersion of the sealed capillary containing the sample into liquid nitrogen. The emitted light was collected at 90° from the incident laser light and focused onto the entrance slit of a 1-meter double monochromator having a resolution of 0.5 cm^{-1} at 514 nm (Ramanor Spectrophotometer, Jobin Yvon-Instruments SA, model number HG.2S). A photon-counting detection system and multichannel analysis system (Nicolet, model 1170) completed the light collection module of the apparatus. The data were processed by means of an AT personal computer using "Spectra Calc" software (Galactic Industries Corp.).

RESULTS

The 457.9 nm excitation source was used to non-resonantly excite the compounds by a phonon assisted route. Non-resonant excitation was employed rather than the near-resonant 465.8 nm argon-ion laser line (which corresponds to the $^7F_0$ to $^5D_2$ absorption transition of the Eu^{3+} ion) to avoid fully resonant excitation of minor constituents. The $^5D_0$ to $^7F_1$, $^7F_2$, and $^7F_4$ manifolds of the Eu^{3+} ion emission spectra exhibited by the studied compounds are shown in Figures 1a, 1b, and 1c, respectively. These three manifolds along with the $^5D_0$ to $^7F_0$ manifold (which is disallowed in this case) have proven to be the most useful in the identification of the Eu^{3+} ion site symmetry, in that their intensity is usually one to two orders of magnitude greater than those of most other observable manifolds. The energies observed for the transitions making up these three manifolds are listed in Table 1.

Group theory can be employed to predict the number of transitions which should be exhibited by a lanthanide ion in a given symmetry. If these predictions

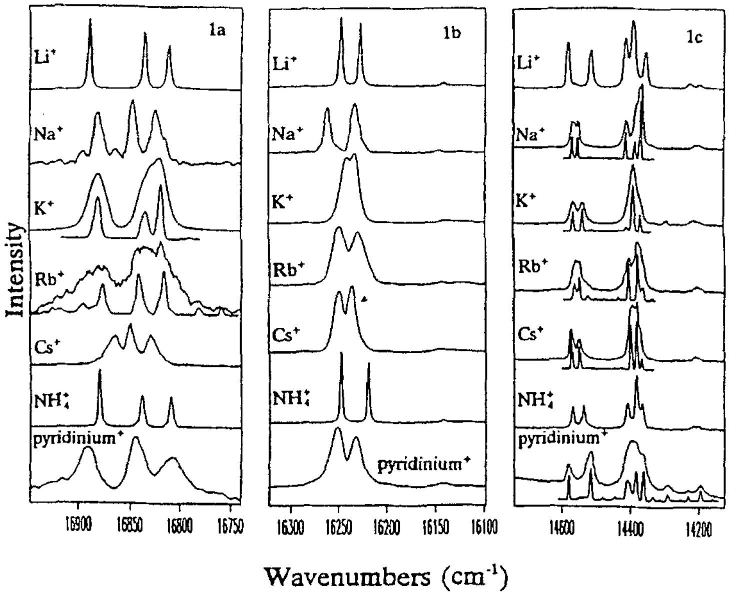

FIG. 1. Spectral features arising from transitions between the $^5D_0$ and $^7F_1$ (FIG. 1a), the $^5D_0$ and $^7F_2$ (FIG. 1b), and the $^5D_0$ and $^7F_4$ (FIG. 1c) Eu^{3+} ion electronic levels in several $M_3[Eu(DPA)_3]$ salts. The inset spectra are deconvolutions of the original spectra generated by the SSRes option in the "Spectra Calc" Software.

are made for all possible symmetries, they can be employed to predict the symmetry around the ion from which the electronic transitions are observed. A compilation of the predicted transitions for the symmetries which are possible for a Eu^{3+} ion in a tricapped trigonal prism is given in Table 2.

The splitting patterns, and therefore the site symmetries of the Eu^{3+} ion, appear to remain constant throughout this series of salts. In each case the transition found in the $^5D_0$ to $^7F_0$ manifold is effectively disallowed, since it was found to be between two and four orders of magnitude less intense than other observed transitions. The low intensity of this transition indicates a Eu^{3+} ion symmetry which is greater than C_n or C_{nv} (which rules out C_2 or lower symmetries

TABLE 1

Energies(cm^{-1}) of the Allowed Transitions Between the $^5D_0$ and $^7F_{1,2,\text{ and }4}$ Eu^{3+} Ion Electronic Levels

Transition Manifold	^7F levels[a]	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+	Pyridinium$^+$
		Transition Energy (cm^{-1})						
$^5D_0 \downarrow {}^7F_4$	E',	14355	14367	14366	14364	14367	14371	14362
	E',	14389	14384	14388	14379	14380	14387	14383
	A_2''	14412	14410	14388	14405	14397	14411	14407
		14513	14550	14536	14548	14546	14531	14514
		14579	14567	14563	14562	14570	14560	14577
$^5D_0 \downarrow {}^7F_2$	E'	16226	16231	16232	16230	16236	16218	16232
		16246	16260	16240	16249	16249	16246	16251
$^5D_0 \downarrow {}^7F_1$	E',	16811	16823	16819	16816	16829	16808	16809
	A_2''	16834	16847	16835	16842	16851	16838	16844
		16889	16882	16881	16878	16865	16880	16892

[a] The $^5D_0$ excited J-state is made up of a single electronic level with an assigned representation of A_1'. The representations described for the ^7F levels include only those for which allowed transitions between that level and the $^5D_0$ level result for a Eu^{3+} ion in D_{3h} site symmetry.

as a possible assignment). Three transitions are observed in the $^5D_0$ to $^7F_1$ manifold, which denotes a low symmetry. Two singly degenerate transitions are seen in the $^5D_0$ to $^7F_2$ manifold and can be assigned as such through the observation of the transitions to the $^7F_2$ level from the $^5D_1$ level[14] (these transitions were previously misassigned as two doubly degenerate transitions in the study of the Na^+ salt[18]). Five transitions are encountered in the $^5D_0$ to $^7F_4$ manifold and are assigned as singly degenerate transitions by methods similar to those employed for the analysis of the $^5D_0$ to $^7F_2$ transitions.

TABLE 2

Compilation of Allowed Transitions Originating in the $^5D_0$ Electronic Level of Eu^{3+} Ions in a Distorted Tricapped Trigonal Prism Coordination Polyhedron

Experimentally Observable Transitions				Site Symmetry[a]	Crystal System[b]
$^7F_0 \leftarrow {}^5D_0$	$^7F_1 \leftarrow {}^5D_0$	$^7F_2 \leftarrow {}^5D_0$	$^7F_4 \leftarrow {}^5D_0$		
NONE*	$A_1' \rightarrow A_2'$ $A_1' \rightarrow E^{*}$	$A_1' \rightarrow E''^{*}$	$A_1' \rightarrow A_2''^{*}$ $A_1' \rightarrow 2\,E'$	D_{3h}	Hexagonal
NONE*	$A' \rightarrow A'$ $A' \rightarrow E^{*}$	$A' \rightarrow E''^{*}$	$A' \rightarrow 2\,A''^{*}$ $A' \rightarrow 2\,E'$	C_{3h}	
$A_1 \rightarrow A_1$	$A_1 \rightarrow A_2$ $A_1 \rightarrow E$	$A_1 \rightarrow A_1$ $A_1 \rightarrow 2\,E$	$A_1 \rightarrow 2\,A_1^{*}$ $A_1 \rightarrow 3\,E$	C_{3v}	Trigonal
NONE*	$A_1 \rightarrow A_2$ $A_1 \rightarrow E$	$A_1 \rightarrow 2\,E^{*}$	$A_1 \rightarrow A_2^{*}$ $A_1 \rightarrow 3\,E$	D_3	
$A \rightarrow A$	$A \rightarrow A$ $A \rightarrow E$	$A \rightarrow A$ $A \rightarrow 2\,E$	$A \rightarrow 3\,A^{*}$ $A \rightarrow 3\,E$	C_3	
$A_1 \rightarrow A_1$	$A_1 \rightarrow A_2$ $A_1 \rightarrow B_1$ $A_1 \rightarrow B_2$	$A_1 \rightarrow 2\,A_1^{*}$ $A_1 \rightarrow B_1$ $A_1 \rightarrow B_2$	$A_1 \rightarrow 3\,A_1^{*}$ $A_1 \rightarrow 2\,B_1$ $A_1 \rightarrow 2\,B_2$	C_{2v}	Rhombic
$A \rightarrow A$	$A \rightarrow A$ $A \rightarrow 2\,B$	$A \rightarrow 3\,A$ $A \rightarrow 2\,B$	$A \rightarrow 5\,A$ $A \rightarrow 4\,B$	C_2	Monoclinic
$A' \rightarrow A'$	$A' \rightarrow A'$ $A' \rightarrow 2\,A^{*}$	$A' \rightarrow 3\,A'$ $A' \rightarrow 2\,A^{*}$	$A' \rightarrow 5\,A'$ $A' \rightarrow 4\,A^{*}$	C_s	
$A \rightarrow A$	$A \rightarrow 3\,A$	$A \rightarrow 5\,A$	$A \rightarrow 9\,A$	C_1	Triclinic

[*] These manifolds contain other transitions which are vibronically allowed to varying degrees (10 to 100 times less in intensity than an electronic or magnetic dipole allowed transition).

[a] as determined by group theory.

[b] as given by Hüfner.[1]

For a tricapped trigonal prism coordination polyhedron, the observed splitting pattern indicates a distorted D_{3h} site symmetry (Table 2). This assignment is discussed in detail in an earlier paper analyzing the emission spectrum obtained from the trilithium salt.[14] In short, there is no symmetry for which two singly degenerate transitions should be allowed in the $^5D_0$ to $^7F_2$ manifold. There is also no symmetry site for which five allowed singly degenerate transitions should be observed in the $^5D_0$ to $^7F_4$ manifold. However, if one assumes that a single doubly degenerate transition can be split slightly by a distortion of the coordination sphere without a complete change in the site symmetry, the two transitions of the $^5D_0$ to $^7F_2$ manifold can be described as a split doubly degenerate transition, and the five transitions of the $^5D_0$ to $^7F_4$ manifold can be described as one singly and two doubly degenerate transitions. If the doubly degenerate transitions are split in these two manifolds, it is probable that they are also split in other manifolds that might contain doubly degenerate transitions, such as the transitions of the $^5D_0$ to $^7F_1$ manifold. Transitions can be split as a result of the distortion described in the introduction towards C_2 or lower symmetry. No indication of a distortion towards D_3 symmetry, as suggested by X-ray diffraction data[10-13] and some previous reports,[2-6,18] is observed here. By this reasoning we believe that D_{3h} distorted towards C_2 or lower symmetry is the only possible assignment for the Eu^{3+} ion site symmetry from the recorded emission spectrum.

The retention of the same Eu^{3+} ion site symmetry throughout this series of compounds is believed to be attributable to the saturation of the coordination sphere by the chelating ligands. This saturation will not allow for the retention of labile solvent molecules within the first coordination sphere of the Eu^{3+} ion. Any waters of hydration found in these systems will be attached to the counterion or located interstitially. The effect of the lability of such water is seen in the broadening of the spectral features of several of the salts and has been described previously for several adducts of the trisodium compound.[18] This broadening is believed to stem from the emission of Eu^{3+} ions in several similar, but not identical, positions.

Because there is no change in the Eu^{3+} ion site symmetry, we have been afforded the opportunity to examine only the effect of a change of counterion upon a single metal ion site symmetry. This effect is most easily observed in the changes in the magnitude with which the doubly degenerate transitions are split. The magnitude of the split is believed to be directly related to the amount of distortion from ideal D_{3h} symmetry towards C_2 or lower symmetry (i.e., the greater the doubly degenerate transition is split, the greater is the distortion from D_{3h} symmetry).

The distortion from D_{3h} symmetry is also seen by the increase in the allowed nature of several electronic transitions which are formally disallowed in D_{3h} symmetries. In all the emission spectra, several very weak transitions are observed in the $^5D_0$ to $^7F_2$ (Figure 1b) and $^5D_0$ to $^7F_4$ (Figure 1c) manifolds of the emission spectrum. In the tripyridinium salt these transitions exhibit much greater intensities, relative to the allowed transitions, than in any of the other emission spectra from this series of salts. This fact indicates that the distortion from which the added intensity arises is the greatest in the pyridinium salt.

CONCLUSIONS

One conclusion drawn from the present work is that the counterion has little effect upon the crystal field of the Eu^{3+} ion in these compounds. This is quite different from other chelate compounds in which the coordination sphere of the Eu^{3+} ion is not saturated by the chelating ligands, and large changes are observed even to the point of changing the crystal structure and symmetry site. This saturation excludes the labile solvent molecules from the inner (first) coordination sphere which predominantly affects the Eu^{3+} ion emission characteristics.

The changes in the electronic emission spectrum are correlated with distortions observed in the crystal structure by X-ray analysis. However, these distortions are not large enough (except possibly in the case of the tripyridinium salt) to force the emission spectrum to indicate a change in the Eu^{3+} ion site symmetry. All the studied compounds appear to show a distorted D_{3h} symmetry site moving towards a C_2 or lower symmetry site. This distortion is greatest in the case of the very large organic pyridinium cation, where, presumably, steric hindrance may have an effect upon the crystal packing of the ions.

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