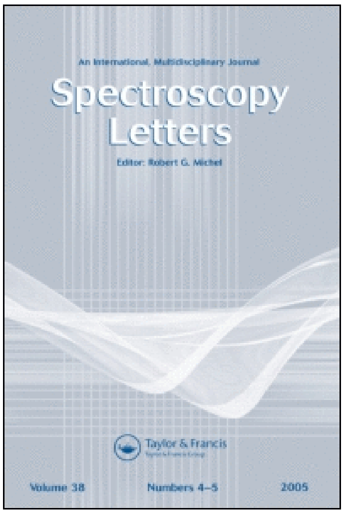

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Pesterfield, L. L. , Coker, N. A. and Stump, N. A.(2000) 'A High Resolution Luminescence Study of two Novel Salts of the Triethvlenetetraaminehexaacetatoeuropate(III) Anion', Spectroscopy Letters, 33: 4, 585 — 594
To link to this Article: DOI: 10.1080/00387010009350141
URL: http://dx.doi.org/10.1080/00387010009350141

SPECTROSCOPY LETTERS, 33(4), 585–594 (2000)

A HIGH RESOLUTION LUMINESCENCE STUDY OF TWO NOVEL SALTS OF THE TRIETHYLENETETRAAMINEHEXAACETATOEUROPATE(III) ANION

Key Words: Lanthanide luminescence; Coordination chemistry; Site symmetry analysis

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ABSTRACT

A low-temperature high-resolution luminescence study of $K_3Eu(TTHA)\bullet H_2O$ and $Tl_3Eu(TTHA)\bullet H_2O$ has been carried out. The Eu^{3+} luminescence spectrum was recorded over the spectral range which includes transitions from the $^5D_0$ excited state to the $^7F_{0\text{-}4}$ ground state manifolds. The observed spectral patterns are analyzed using group theoretical methods so as to deduce the site symmetry of the Eu^{3+} ion in the complex. The analysis shows that the Eu^{3+} ion occupies a spectroscopic site symmetry that approaches a D_2 symmetry with distortion towards a C_2 or lower symmetry in the potassium salt and a site symmetry of a C_3 in the thallium salt. These salts illustrate the potential of the counterion to markedly influence the effective site symmetry of the Eu^{3+} ion.

INTRODUCTION

The luminescence spectrum of the Eu^{3+} ion ($4f^6$) has been studied in a wide variety of compounds ranging from inorganic halides[1] to polyaminomacrocycles.[2] Some of the most intensely studied compounds have been Eu^{3+} ion complexes with aminocarboxylic acid ligands, such as: nitrolotriacetic acid (NTA),[3] ethylenediaminetetraacetic acid (EDTA),[4] and 2,6-pyridinedicarboxylic acid (DPA).[5] Due to the relative simplicity of the luminescence spectrum of the Eu^{3+} ion, the degeneracy and allowedness of the emission features can often be used to identify the structural environment of the Eu^{3+} ion. In selected cases the spectral pattern can be used along with group theoretical methods to determine the site symmetry of the Eu^{3+} ion. The sensitivity of the emission spectrum to the near environment of the lanthanide ion can also permit investigation of the effects of variations in both the first and second coordination sphere and the resulting modifications in the structure of the complex. A site symmetry analysis can often be accomplished through the investigation of four major Eu^{3+} emission manifolds[6] ($^5D_0$ to $^7F_{0,1,2,4}$). This technique has been most successfully applied to relatively simple inorganic complexes of europium, for example $Cs_2NaEuCl_6$[7] and $Eu(OH)_3$[8]. Our laboratories are interested in the application of the technique to deduce the site symmetry of the Eu^{3+} ion in organic chelate complexes with aminocarboxylic acid ligands[9,10] Organic chelate complexes are challenging in that the complexity of the organic chelate often results in slight variations in the structural environment surrounding the Eu^{3+} ion which, in turn, is reflected as broad unresolvable features in the luminescence spectrum. The luminescence spectrum of the title compounds are unique in that the emission features are sufficiently narrow and intense so as to permit analysis of the spectrum and deduction of the site symmetry of the Eu^{3+} ion. The emission spectrum has been recorded for the intense transitions from the $^5D_0$ to the $^7F_{0,1,2,4}$. The positions of the spectral features can be used to determine the energies of the various electronic levels, while the patterns that develop can identify the site symmetry of the Eu^{3+} ion.

In addition, previous studies[10,11] have shown that while the site symmetry of the Eu^{3+} ion is primarily determined by the coordinating ligands(first coordination sphere), counterions(second coordination sphere) can markedly influence the effective site symmetry of the Eu^{3+} ion. The potassium and thallium salts clearly illustrate the potential of counterions to perturb the luminescence spectrum.

EXPERIMENTAL

Synthetic Procedure The title complexes were synthesized according to the general procedure described by Moeller *et al.*[12] for the preparation of Eu-EDTA salts. A 30 ml aqueous suspension of 0.570 mmol Eu_2O_3 (Johnson Matthey-ALFA Products) and 1.14 mmol TTHA (Aldrich Chemical Company) was heated at 85°C until the solution cleared. The solution was allowed to cool to room temperature, then 2.28 mmol of either KNO_3 or $TlNO_3$ (Aldrich Chemical Company) was added. The pH was then adjusted to 3.5 using 0.05 M NaOH. Both salts precipitated from solution after allowing the solvent to partially evaporate overnight at room temperature. The precipitates were collected and sealed in a glass capillary tube. Elemental analysis has shown a Eu/TTHA mole ratio for the precipitate of 1.00.

Instrumentation The luminescence spectrum was obtained using the 465.8 nm line of a six-watt argon ion laser (Coherent Radiation, Innova 300) as the excitation source. The 465.8 nm line corresponds to the resonant absorption band associated with the $^7F_0$ to $^5D_2$ transition in the Eu^{3+} ion. Samples were cooled by immersion in liquid nitrogen (77 K) to reduce vibrational broadening of the emission lines. The luminescence was collected at 90° to the incident laser beam and focused onto the entrance slit of a one meter double monochromator having a resolution of 0.5 cm^{-1} at 514 nm (Jobin Yvon-Instruments SA, Ramanor Spectrophotometer HG.2S). The monochromator was equipped with a cooled red sensitive PMT (Hamamatsu, type 636). The PMT pulses were processed by a PARR amplifier/discriminator then recorded with a Nicolet 1170 signal averager. The data were subsequently processed by a personal computer employing "Spectra Calc" software (Galactic Industries Corp.).

RESULTS AND DISCUSSION

Spectral Analysis Background The spectral analysis of the site symmetry occupied by the Eu^{3+} ion in the title compounds is based on the intensity and degeneracy of the observed transitions. Given a specific site symmetry, group theoretical methods can be used to predict the allowedness and degeneracy of transitions within a manifold. Tables have been compiled for the Eu^{3+} ion which predict the number of observable transitions in the luminescence spectrum given the site symmetry of the ion.[13,14] By comparing the observed splitting patterns in the luminescence spectrum with these compilations, the site symmetry of the metal ion in an emitting species can be deduced.

Spectral Analysis of the Potassium Salt The weak intensity of the $^5D_0$ to $^7F_0$ transition at 17231 cm^{-1} (Figure 1), relative to the $^5D_0$ to $^7F_{1,2}$ transitions, indicates that the transition is only partially allowed. Due to the singly degenerate nature of both the $^5D_0$ and the $^7F_0$ levels, the presence of a single observable transition in this manifold suggests that the Eu^{3+} ion occupies a single site symmetry in the complex. If the single transition in the $^5D_0$ to $^7F_0$ manifold is treated as being allowed, then the site symmetry of the Eu^{3+} ion can be no greater than C_{nv} or C_n. However, if the single transition in the $^5D_0$ to $^7F_0$ manifold is treated as being only partially allowed, then higher symmetries are possible. The three observed transitions (16963, 16823 and 16775 cm^{-1}) in the $^5D_0$ to $^7F_1$ manifold (Figure 1) can be treated as either three singlets or as a singlet and a split E. In either case the possible site symmetry can not be deduced any further.

Additional insight into the site symmetry of the Eu^{3+} ion can be gained by inspection of the $^5D_0$ and $^7F_{2,4}$ manifolds. The $^5D_0$ and $^7F_2$ manifold (Figure 1) is interpreted as containing three allowed transitions (16280, 16244 and 16182 cm^{-1}) and two partially allowed transitions (16265 and 16091 cm^{-1}). If the manifold is interpreted this way, the assignable site symmetries are reduced to D_2 and D_{2d}. Inspection of the $^5D_0$ to $^7F_4$ manifold (Figure 2) shows nine transitions of which three (14437, 14344 and 14118 cm^{-1}) are considered to be partially allowed. The remaining six transitions (14556, 14475, 14385, 14362, 14248 and 14202 cm^{-1}) are considered to be allowed based on intensity considerations. Under this interpretation, the most probable site symmetry occupied by the Eu^{3+} ion is D_2. However, if all the lines in the $^5D_0$ and $^7F_{2,4}$ manifolds are considered to be allowed, the Eu^{3+} ion occupies a site symmetry no greater than C_2. The weak intensity of the $^5D_0$ to $^7F_0$ transition does not indicate the assignment of a C_2 site symmetry. However, the presence of partially allowed lines

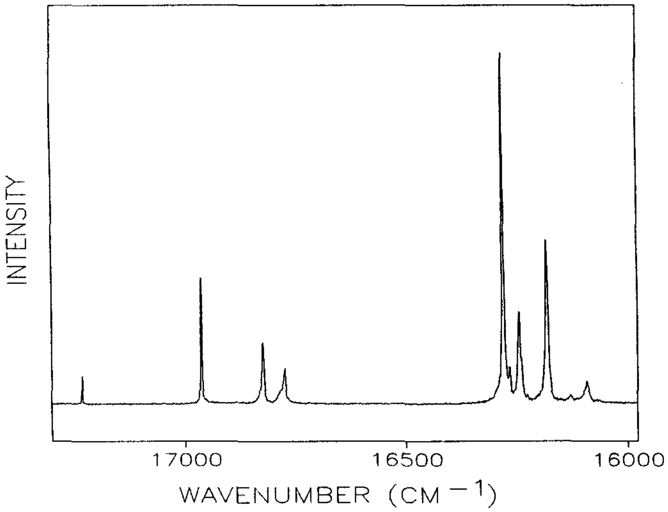

FIG. 1. Eu^{3+} ion emission spectrum exhibited by $K_3Eu(TTHA)\bullet H_2O$ over the spectral range including transitions from the $^5D_0$ excited state to the $^7F_{0,1,2}$ states.

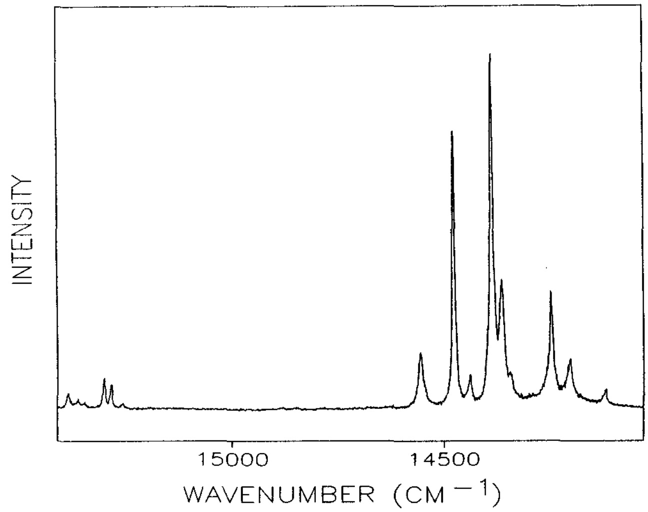

FIG. 2. Eu^{3+} ion emission spectrum exhibited by $K_3Eu(TTHA)\bullet H_2O$ over the spectral range including transitions from the $^5D_0$ excited state to the $^7F_{3,4}$ states.

in each of the manifolds suggests that the site symmetry is distorted from a true D_2 symmetry and is moving toward a lower symmetry of C_2.

Spectral Analysis of the Thallium Salt The strong intensity of the $^5D_0$ to $^7F_0$ transition at 17229 cm^{-1} (Figure 3), relative to the $^5D_0$ to $^7F_{1,2}$ transitions, indicates that the transition is allowed and that the site symmetry of the Eu^{3+} ion can be no greater than C_{nv} or C_n. The three observed transitions (16915, 16897 and 16756 cm^{-1}) in the $^5D_0$ to $^7F_1$ manifold (Figure 3) are considered to be a singlet and a split E.

Once again additional insight into the site symmetry of the Eu^{3+} ion can be gained by inspection of the $^5D_0$ and $^7F_{2,4}$ manifolds. The $^5D_0$ and $^7F_2$ manifold is interpreted as containing five allowed transitions (16306, 16300, 16234, 16147 and 16138 cm^{-1}) consisting of a singlet and two slightly split E's. Inspection of the $^5D_0$ to $^7F_4$ manifold(Figure 4) shows nine allowed transitions (14554, 14449, 14502, 14433, 14436, 14391, 14296, 14291 and 14226 cm^{-1}) consisting of three singlets and three slightly split E's. Under this interpretation, the most probable site symmetry occupied by the Eu^{3+} ion is C_3. A compilation of the experimentally observed transitions for both the potassium and thallium salts are listed in Table 1.

Relationship to Structure Due to the nature of the potassium and thallium(a fine powder), the structure of the salts could not be determined by X-ray analysis. However, certain implications can be drawn from the emission spectra that have been obtained. Working from a base symmetry of D_2, it is likely that the TTHA ligand is nine coordinate with the Eu^{3+} ion occupying a geometric polyhedron that approaches a tricapped trigonal prism. It is proposed that the two terminal amino nitrogens and the four terminal carboxylic oxygens of the TTHA ligand form the top and bottom of the trigonal prism around the Eu^{3+} ion, while the remaining two carboxylic oxygens and the coordinated water molecule form the caps of the prism. The proposed geometric arrangement implies that the two central amino nitrogens do not coordinate to the Eu^{3+} ion. The same situation has been observed in $K[La(EDTA)(H_2O)_3]\bullet 5H_2O$[15] where the X-ray crystal structure shows that the La^{3+} ion lies above the amino nitrogens of the EDTA^{4-} anion.

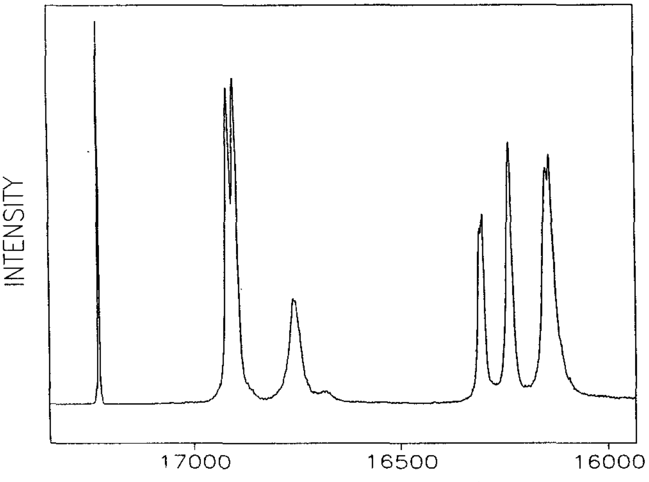

FIG. 3. Eu^{3+} ion emission spectrum exhibited by $Tl_3Eu(TTHA)•H_2O$ over the spectral range including transitions from the $^5D_0$ excited state to the $^7F_{0,1,2}$ states.

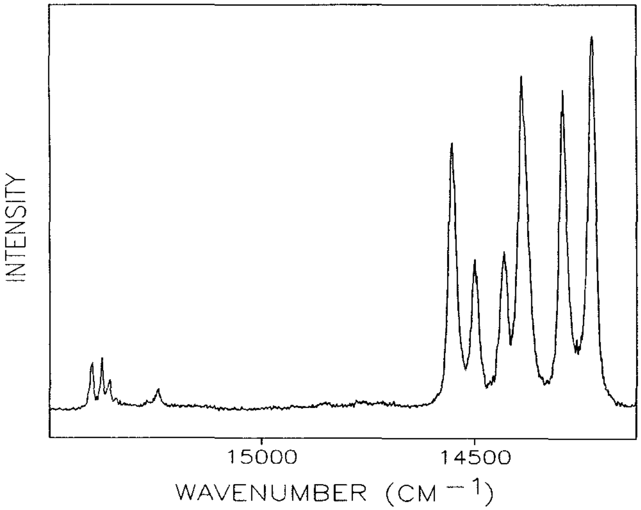

FIG. 4. Eu^{3+} ion emission spectrum exhibited by $Tl_3Eu(TTHA)•H_2O$ over the spectral range including transitions from the $^5D_0$ excited state to the $^7F_{3,4}$ states.

TABLE 1

Experimentally Observed Transitions in $K_3Eu(TTHA) \bullet H_2O$ and $Tl_3Eu(TTHA) \bullet H_2O$

Transition manifold	Observed transition energies (cm^{-1})					
	$K_3Eu(TTHA) \bullet H_2O$			$Tl_3Eu(TTHA) \bullet H_2O$		
$^5D_0$ to $^7F_0$	17231*			17229		
$^5D_0$ to $^7F_1$	16963	16823	16775	16915	16897	16756
$^5D_0$ to $^7F_2$	16280	16265*	16244	16306	16300	16234
	16182	16091*		16147	16138	
$^5D_0$ to $^7F_4$	14556	14475	14437*	14554	14449	14502
	14385	14362	14344*	14433	14436	14391
	14248	14202	14118*	14296	14291	14226

* denotes a transition which is only partially allowed

Using the proposed geometric arrangement, the distortion of the base D_2 site symmetry can then be ascribed to variations in the microcrystalline structure of the Eu-TTHA complex due to differences in the size of the counter-ions(K^+: 133 pm and Tl^+: 149 pm).

CONCLUSION

The low temperature luminescence spectra for $K_3Eu(TTHA) \bullet H_2O$ and $Tl_3Eu(TTHA) \bullet H_2O$ clearly illustrate the dramatic effects counterions can have on the effective site symmetry occupied by the Eu^{3+} ion in the coordination polyhedron. The recorded spectra show that changing the counterion effects both the splitting pattern and line positions observed in the Eu^{3+} ion luminescence spectrum. The observed changes in line position and splitting pattern can be attributed to distortions, caused by the counterions, in the basic site symmetry occupied by the Eu^{3+} ion in the complex.

The next step in our research is to investigate the effects of counterions on the Eu^{3+} ion luminescence spectrum by employing various chelating groups such as, propylenediammine-tetraacetic acid (PDTA) and ethylenediamminetetrapropionic acid (EDTP).

ACKNOWLEDGMENTS

The authors would like to acknowledge the use of the Laser Raman Laboratory at the Transuranium Research Laboratory at the Oak Ridge National Laboratory which is supported by the US Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

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Date Received: February 9, 2000
Date Accepted: April 15, 2000