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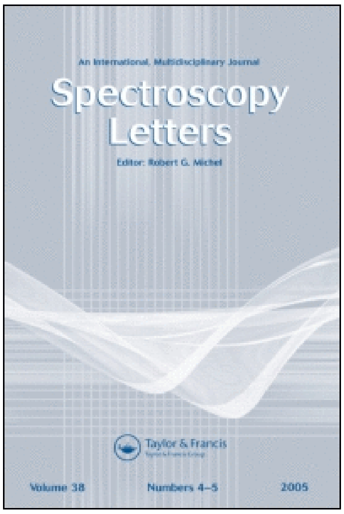

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A HIGH RESOLUTION LUMINESCENCE STUDY OF SILVER DIETHYLENETRIAMINEPENTAACETATOEUROPATE(III) MONOHYDRATE

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

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ABSTRACT

A low-temperature high-resolution luminescence study of $Ag_2Eu(DTPA)\cdot H_2O$ 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 $^7F_{0\text{-}6}$ ground state manifolds and from the $^5D_1$ excited state to the $^7F_{0\text{-}2}$ 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 C_{2v} symmetry with distortion towards C_2 or lower symmetry. Results from the analysis are compared with previously reported X-ray crystallographic results. In addition, the transition energies exhibited in the emission spectrum have been used to calculate the relative energies of the electronic levels characteristic of Eu^{3+} ions in the title compound.

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 ($^5D_0$ to $^7F_{0,1,2,4}$). However in some cases, determination of the position and allowedness of transitions in other manifolds has proven helpful in assigning both energies and spectroscopic character to the electronic levels; which is often required for the complete characterization of the site symmetry.[6] The 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 have been 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 compound is unique in that the emmision 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 $^7F_{0,1,2,4}$ manifolds along with the less intense emissions corresponding to transitions from the $^5D_0$ to the $^7F_{3,5,6}$ manifolds and from the $^5D_1$ to the

$^7F_{0,1,2}$ manifolds. 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.

EXPERIMENTAL

Synthetic Procedure The title compound was synthesized according to the general procedure described by Moeller *et al.*[11] 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 DTPA (Aldrich Chemical Company) was heated at 85°C until the solution cleared. After the solution cooled to room temperature, 2.28 mmol of $AgNO_3$ (Aldrich Chemical Company) was added. The solutions pH was then adjusted to 3.5 using 0.5 M NaOH. The solution was constantly stirred for 15 minutes, at which time a fine white powder precipitated. The precipitate was collected and sealed in a glass capillary tube. Elemental analysis has showed a Eu/DTPA 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 The spectral analysis of the site symmetry occupied by the Eu^{3+} ion in the title compound is based on the intensity and degeneracy of the observed transitions. Given a specfic 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.[12,13] 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.

The strong intensity of the $^5D_0$ to $^7F_0$ transition at 17223 cm^{-1} (Figure 1), relative to the $^5D_0$ to $^7F_{1,2}$ transitions, indicates that the transition is 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. The presence of a transtion in the $^5D_0$ to $^7F_0$ manifold indicates that the site symmetry of the Eu^{3+} ion can be no greater than C_{nv} or C_n. The three observed transitions (16940, 16839 and 16769 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 be deduced any further than C_{nv} or C_n.

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 four allowed transitions (16255, 16250, 16212, and 16083 cm^{-1}) and one partially allowed transition (16122 cm^{-1}). Inspection of the $^5D_0$ to $^7F_4$ manifold(Figure 2) shows nine transitions of which two (14335 and 14117 cm^{-1}) are considered to be partially allowed. A splitting pattern of four allowed $^5D_0$ to $^7F_2$ transitions and seven allowed $^5D_0$ to $^7F_4$ transitions is indicative of a C_{2v} site symmetry. The presence of partially allowed lines in each of these manifolds suggests that the site symmetry is distorted from a true C_{2v} symmetry and is moving toward lower symmetry of C_2.

Due to the relative weak intensity of the lines in the $^5D_0$ to $^7F_3$ manifold (Figure 2), it is not possible to identify all the transitions present in this region. There are five allowed transitions and at least one partially allowed transition in the manifold. This interpretation is consistent with a distorted C_{2v} symmetry moving toward a C_2 symmetry.

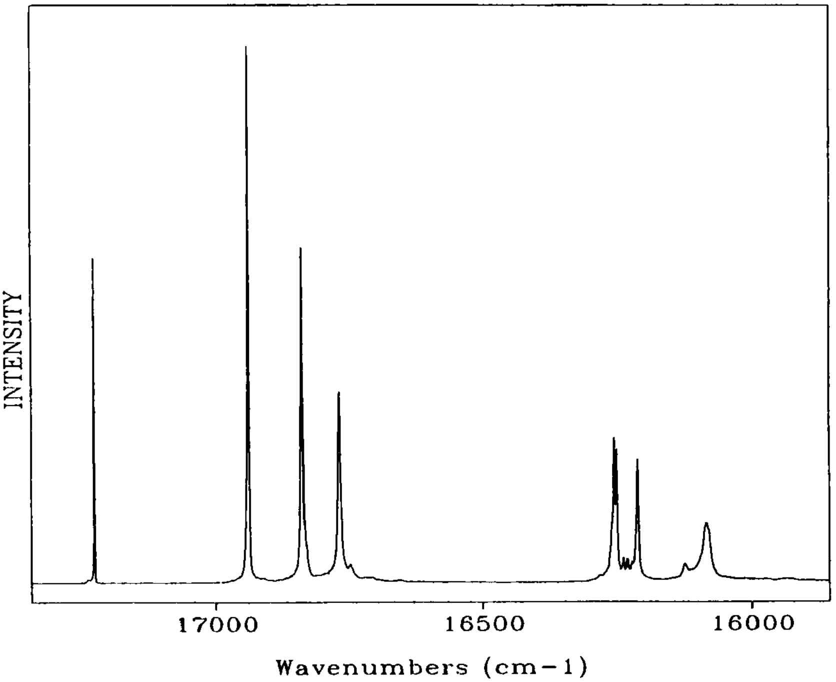

FIG. 1. Eu^{3+} ion emission spectrum exhibited by $Ag_2Eu(DTPA)\cdot H_2O$ over the spectral range including transitions from the $^5D_0$ excited state to the $^7F_{0,1,2}$ states.

The spectral quality of the $Ag_2Eu(DTPA)$ complex is such that the $^5D_0$ to $^7F_{5,6}$ manifolds and the $^5D_1$ to $^7F_{0-2}$ manifolds could also be obtained. For a C_{2v} site symmetry, group theory predicts eight allowed transitions in the $^5D_0$ to $^7F_5$ manifold and ten allowed transitions in the $^5D_0$ to $^7F_6$ manifold. Six transitions are observed in the $^5D_0$ to $^7F_5$ manifold in Figure 3. Two additional transitions (13470 and 13451 cm^{-1}) of the $^5D_0$ to $^7F_5$ manifold are observed in the lower energy section of the spectral scan of the $^5D_0$ to $^7F_{3,4}$ manifolds and are not seen in Figure 2. Due to the broadness of the spectral features in the $^5D_0$ to $^7F_6$ manifold, only five distinct transitions can be identified. The remaining allowed transitions are assumed to be unresolved in the broad features of the manifold.

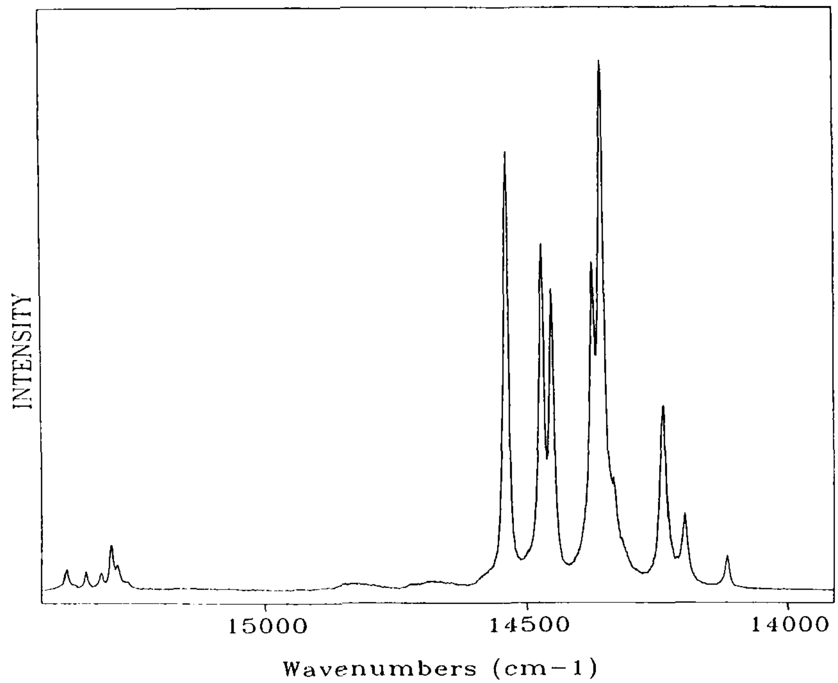

FIG. 2. Eu^{3+} ion emission spectrum exhibited by $Ag_2Eu(DTPA)\bullet H_2O$ over the spectral range including transitions from the $^5D_0$ excited state to the $^7F_{3,4}$ states.

For the $^5D_1$ to $^7F_{0-2}$ manifolds (Figures 4 and 5) in either a C_{2v} or C_2 site symmetry, group theory predicts 3, 9 and 15 transitions, respectively. Therefore no additional insight into the site symmetry of the Eu^{3+} ion in the complex can be gained from a symmetry analysis of these manifold and it is concluded that the Eu^{3+} ion occupies an approximate C_{2v} site symmetry with distortions leading to a C_2 or lower site symmetry. A compilation of the experimentally observed transitions as compared to the predicted number of transitions from a symmetry analysis for a C_{2v} and C_2 site symmetry is given in Table 1.

Relationship to Structure Due to the nature of the $Ag_2Eu(DTPA)\bullet H_2O$ complex (a fine powder), the structure of the title compound could not be determined by X-ray analysis. However, certain

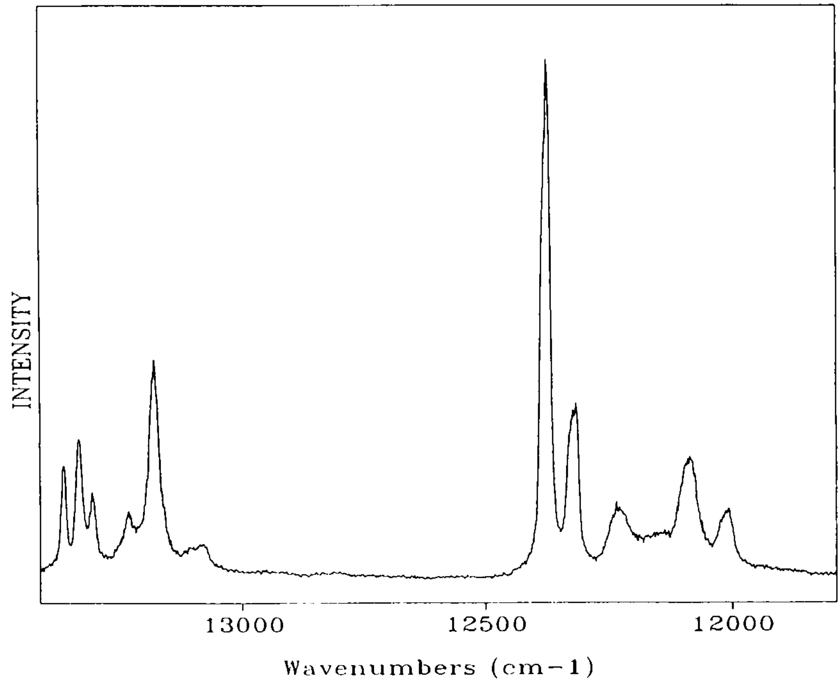

FIG. 3. Eu^{3+} ion emission spectrum exhibited by $Ag_2Eu(DTPA)•H_2O$ over the spectral range including transitions from the $^5D_0$ excited state to the $^7F_{5,6}$ states.

implications can be drawn from the emission spectrum that has been obtained. The base symmetry of C_{2v} and the hydrated form of the sample would imply that the compound is likely to be nine coordinate and occupying a geometric polyhedron that approaches a monocapped square antiprism. It is proposed that the three amino nitrogens and five carboxylic oxygens of the DTPA ligand form a square antiprism around the Eu^{3+} ion, while the coordinated water molecule forms the cap of the antiprism. The proposed geometric arrangement is possible if the three amino nitrogens and one carboxylic oxygen from a terminal amino nitrogen form the base of the square antiprism and the remaining four carboxylic oxygens form the top of the square antiprism. This proposed geometric arrangement is consistent with that observed by X-ray analysis for $Na_2Gd(DTPA)•H_2O$[14] in which

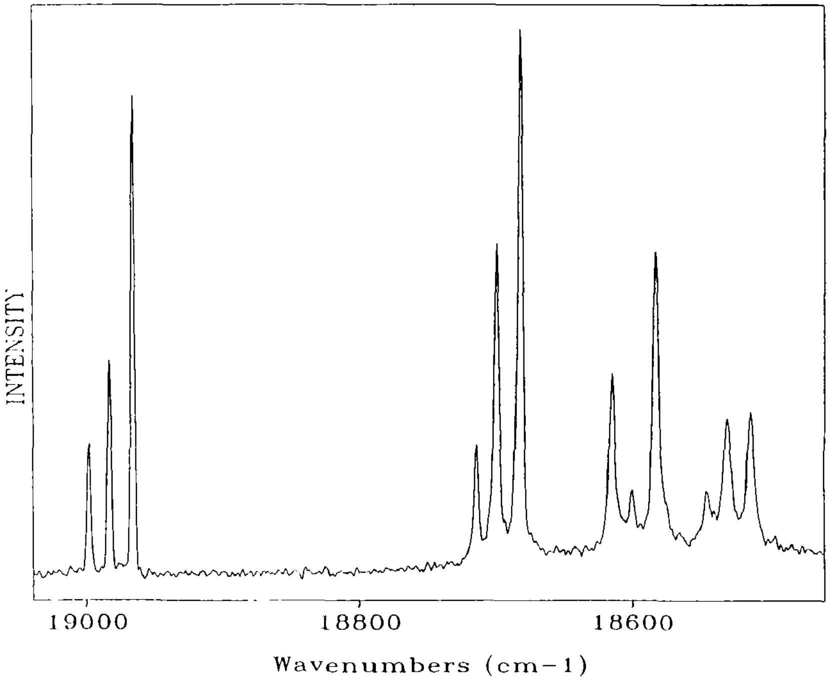

FIG. 4. Eu^{3+} ion emission spectrum exhibited by $Ag_2Eu(DTPA)\bullet H_2O$ over the spectral range including transitions from the $^5D_1$ excited state to the $^7F_{0,1}$ states.

the Gd^{3+} ion is described as residing in a distorted capped square antiprism. Distortion towards a C_2 or lower site symmetry can then be ascribed to variations in the microcrystalline structure of the Eu-DTPA complex due to differences in the size of the counter-ions(Na^+: 98 pm and Ag^+: 113 pm) and to some extent differences in the size of the central ion(Eu^{3+}: 98 pm and Gd^{3+}: 97 pm).

Determination of the Electronic Energy Levels If the $^7F_0$ electronic ground state is assigned a relative energy of zero, the energies of other states can be determined relative to the ground state. It is then possible to predict the energy of transitions in the $^5D_1$ to $^7F_{1,2}$ manifolds and compare the results with the experimentally observed transition energies. Inspection of Figure 4 shows three transitions in the $^5D_1$ to $^7F_0$ manifold and nine transitions in the $^5D_1$ to $^7F_1$ manifold. Examination of

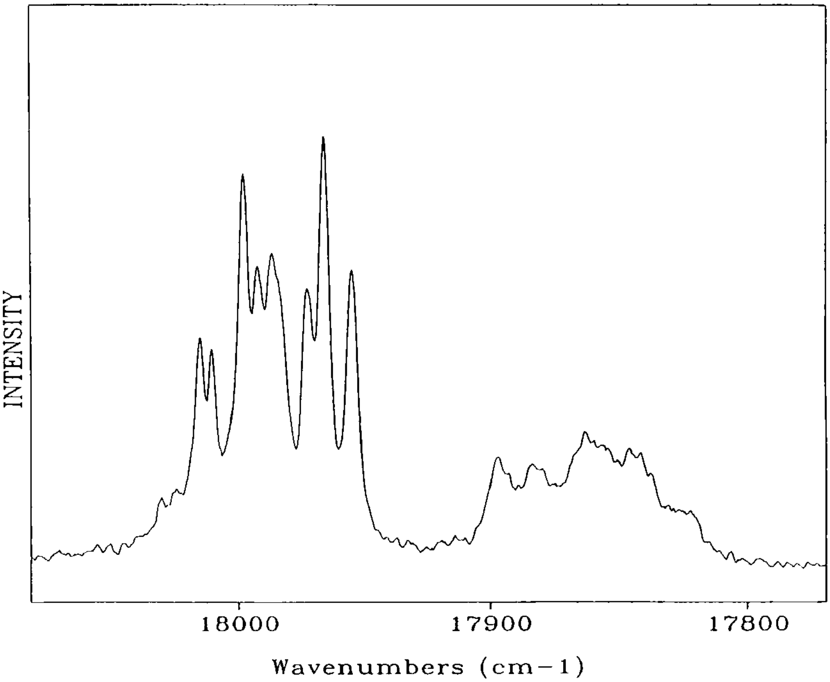

FIG. 5. Eu^{3+} ion emission spectrum exhibited by $Ag_2Eu(DTPA)\bullet H_2O$ over the spectral range including transitions from the $^5D_1$ excited state to the $^7F_2$ state.

the $^5D_1$ to $^7F_2$ manifold (Figure 5) reveals that only 13 of the 15 transitions predicted for this manifold can be clearly identified. From the experimental data, the three $^7F_1$ ligand-field levels are 283, 384 and 454 cm^{-1} above the $^7F_0$ level and the five $^7F_2$ ligand-field levels are 968, 973, 1011 1101 and 1140 cm^{-1} above the $^7F_0$ level. The calculated and experimentally observed transition energies are listed in Table 2. Comparision of the calculated and experimental values indicates that it is possible to predict the approximate transition energy of allowed transtions in upper manifolds. It is interesting to note that transitions in the first part the $^5D_1$ to $^7F_2$ manifold (higher energy) appear to arise from transitions between the $^5D_1$ level and the first three ligand-field levels of the $^7F_2$ level. While the second half of

TABLE 1

Group Theoretically Allowed Transitions for C_{2v} and C_2 Site Symmetries and the Corresponding Observed Transition Energies in $Ag_2Eu(DTPA)\bullet H_2O$

Transition manifold	Number of allowed transitions		Observed transition energies (cm^{-1})		
	C_{2v}	C_2			
$^5D_0$ to $^7F_6$	10	13	12372	12317	12235
			12089	12012	
$^5D_0$ to $^7F_5$	8	11	13470	13451	13368
			13338	13309	13238
			13184	13087	
$^5D_0$ to $^7F_4$	7	9	14540	14475	14457
			14380	14363	14335
			14245	14205	14117
$^5D_0$ to $^7F_3$	5	7	15386	15348	15318
			15299	15288	
$^5D_0$ to $^7F_2$	4	5	16255	16250	16212
			16122	16083	
$^5D_0$ to $^7F_1$	3	3	16940	16839	16769
$^5D_0$ to $^7F_0$	1	1	17223		
$^5D_1$ to $^7F_2$	15	15	18031	18026	18017
			18013	17999	17994
			17987	17974	17956
			17897	17883	17868
			17857		
$^5D_1$ to $^7F_1$	9	9	18717	18702	18685
			18616	18601	18583
			18546	18531	18513
$^5D_1$ to $^7F_0$	3	3	19000	18985	18968

TABLE 2

Calculated and Experimentally Observed Transition Energies of the $^5D_1$ to $^7F_{1,2}$ Manifolds

Transition manifold	Calculated transition energies (cm^{-1})			Experimentally observed transition energies (cm^{-1})		
$^5D_1$ to $^7F_1$	18717	18702	18685	18717	18702	18685
	18616	18601	18584	18616	18601	18583
	18546	18531	18514	18546	18531	18513
$^5D_1$ to $^7F_2$	18032	18017	18000	18031	18017	17999
	18027	18012	17995	18026	18013	17994
	17989	17974	17957	17987	17974	17956
	17899	17884	17867	17897	17883	17868
	17860	17845[a]	17828[a]	17857		

[a] Corresponding experimental transition was not identifiable in the spectrum.

the $^5D_1$ to $^7F_2$ manifold appears to arise from transitions between the $^5D_1$ level and the last two ligand-field levels of the $^7F_2$ level.

CONCLUSION

Analysis of the low temperature emission spectrum exhibited by $Ag_2Eu(DTPA)\bullet H_2O$ has revealed a metal ion symmetry that can be approximated by a C_{2v} metal ion site that is distorted towards a probable C_2 site. The site symmetry may be interpreted to indicate a nine coordinate Eu^{3+} ion occupying a distorted monocapped square antiprismatic geometric polyhedron., which is consistent with prevoius X-ray studies. The energy associated with the electronic levels of the Eu^{3+} ion have been determined relative to the $^7F_0$ ground state and compared with the experimentally observed energies.

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