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The effects of hydration on the luminescence spectra of trisodium tris(2,6-pyridinedicarboxylato)europium(III) compounds

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Abstract

Luminescence spectra of the hydrated and anhydrous salts of trisodium tris(2,6-pyridinedicarboxylato)europium(III) compounds have been measured at high resolution (better than 1.0 cm^{-1}) and at low temperature (77 K). The alterations in the crystal field splittings, linewidths and relative intensities, as produced by the influence of crystal hydration, are examined and are discussed in detail.

Introduction

Perhaps the most useful property of the luminescence spectra of many lanthanide compounds is their characteristically narrow features. These features are the result of intra-4f electronic transitions which are allowed due to mixing with vibrations and/or other electronic states of opposite parity. Although the spectra of many purely inorganic lanthanide compounds have been routinely investigated at high resolution (0.05 nm) and low temperatures (2 to 77 K) [1, 2], most investigations of lanthanide chelate compounds have been carried out with less resolution (in the order of a nanometer) at ambient temperature [3]. The few low temperature spectra from lanthanide chelates have generally not permitted the determination of much detail in many of the features. In a recent paper by one of the present authors, a detailed study of several luminescence bands produced by a series of europium chelates was presented [4]. This effort emphasized that by changing inorganic counter-ions the local site symmetry experienced by the europium ion could be changed significantly. In the low temperature luminescence spectra which are the subject of this investigation, several manifolds of a series of europium(III) compounds are explored in some detail, with emphasis on the effects of crystal hydration on the crystal field splittings.

Experimental

The compounds prepared for this investigation were tris chelates employing the diprotic ligand dipicolinic acid (2,6-pyridinedicarboxylic acid = DPA). This ligand was chosen because it forms stable tris complexes with lanthanide ions [5] and transfers some of the radiant energy it absorbs to appropriate coordinated lanthanide ions which then fluoresce. Synthesis of the 15 hydrate was achieved by the following method. Dipicolinic acid (3.00 mmol) was added to 50.0 ml of boiling water and allowed to dissolve. Next, $EuCl_3$ (1.00 mmol) was added to the boiling solution and dissolved. Sodium hydroxide was added until the pH of the resultant solution was approximately 8. If, at this point, the solution was cloudy, 1.0 M HCl solution was added dropwise until the solution cleared. Then the solution was allowed to evaporate slowly (over a period of several days) to produce large transparent crystalline plates. The plates were stored in contact with the mother liquor to prevent efflorescence.

Another method was used for the synthesis of the anhydrous sodium salt. An aqueous solution of $EuCl_3$ (1.00 mmol) was heated to near dryness and then allowed to dry in ambient air. The whole was redissolved in 10.0 ml of hot (near boiling) anhydrous methanol. To this solution was added a hot solution of 3.00 mmol of dipicolinic acid in 10.0 ml of anhydrous methanol, producing a cloudy solution whose

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pH was *c.* 6. This solution was kept heated to near boiling as a saturated solution of sodium hydroxide in anhydrous methanol was added dropwise, with continuous monitoring of the solution pH. The solution became clear at a pH of about 10 and subsequent heating or addition of sodium hydroxide produced a precipitate. This precipitate was collected by filtration, dried in a 150 °C oven for 5 min and sealed in dry quartz capillaries. It was observed that even when the compound was left in ambient air for 30 min, there was no increase in weight and no change in its luminescence spectrum, indicating that the compound was not extremely hygroscopic. However, if the compound was exposed to ambient air for an extended time (about 1 day), its luminescence spectrum was different from that obtained from the anhydrous compound. These spectral changes were in the form of additional peaks, peaks in different positions and general broadening of spectral features. The compounds exhibiting intermediate stages of hydration were isolated in dry quartz tubes after limited exposure of the anhydrous compound to warm moist air.

Chemicals used in the above syntheses included the following: 2,6-pyridinedicarboxylic acid, 99% (DPA), purchased from Aldrich Chemical Company and europium oxide, 99.9%, purchased from Alfa Products. These chemicals were used without any further purification.

Luminescence and Raman spectra were obtained by using a Ramanor HG.2S Raman spectrophotometer, Jobin Yvon, Instruments SA. The spectrophotometer is equipped with a Nicolet model 1174 multichannel analyzer for signal averaging. Three excitation sources were employed. One was a model UVS-11 UVP shortwave hand lamp purchased from Fisher Scientific Company. The one used most often was a Spectra-Physics model 165 argon ion laser. When a tunable source was required, excitation was supplied by a Chromatix model CMX-4 tunable flashlamp excited dye laser. Refrigeration of the samples was provided by a model CSW-204 Displex closed-cycle refrigeration system from Air Products and Chemicals, Inc. or by immersion in a dewar containing liquid nitrogen.

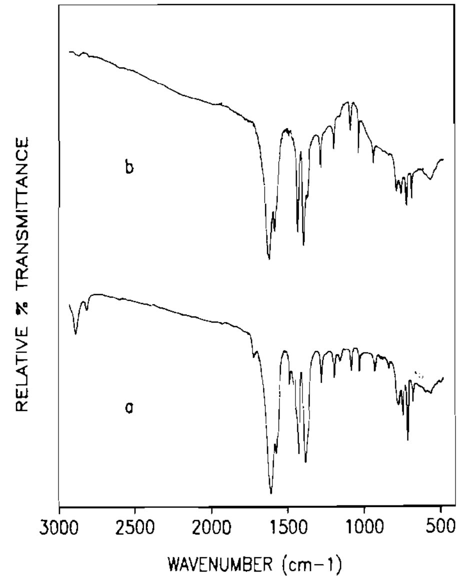

Fig. 1. Infrared spectra of: (a) anhydrous $Na_3[Eu(DPA)_3]$; (b) $Na_3[Eu(DPA)_3] \cdot 15H_2O$.

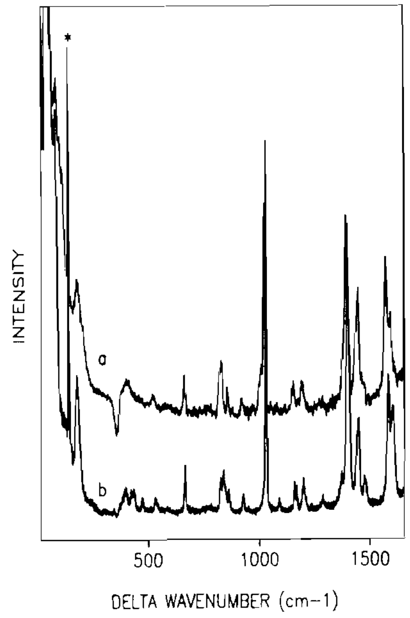

Fig. 2. Raman spectra of: (a) anhydrous $Na_3[Eu(DPA)_3]$; (b) $Na_3[Eu(DPA)_3] \cdot 15H_2O$ excited at 514.5 nm. The asterisk denotes a laser plasma line of the argon ion laser.

Results and discussion

The infrared spectra of the anhydrous and 15 hydrate compounds, prepared as KBr pellets, are given in Fig. 1. Examples of the Raman spectra of the anhydrous and 15 hydrate compounds are given in Fig. 2. The negative deflection at about 365 cm^{-1}, in the Raman spectra, corresponds to a $^7F_0 \rightarrow {}^5D_1$ europium(III) ion absorbance of the broad band ligand luminescence. The results of the elemental analysis performed by Desert Analytics (Tucson, AZ) on the anhydrous compound are: Found: C, 35.06; H, 2.21; N, 5.52. Calc.: C, 35.22; H, 1.26; N, 5.87%. The slightly high value for hydrogen in this elemental analysis may be due to residual sodium hydroxide coprecipitated with the compound. The identification of the 15 hydrate was verified by X-ray powder diffraction analysis.

A prior single crystal X-ray determination of the structure of the neodymium analogue of the 15 hydrate compound studied in this work was reported by Albertsson [6]. His study revealed a distorted D_3 symmetry for the coordination polyhedron around the neodymium ion. The ideal geometry for a nine coordinate complex would be the tricapped trigonal prism coordination polyhedron with site symmetry D_{3h}. Albertsson's study also provided X-ray powder photographs which indicated an 'almost identical' [6] triclinic structure for the homologous series of compounds with Ce through Dy. His single crystal X-ray determination, however, did not locate five of the fifteen water molecules associated with the compound. These water molecules were assigned to disordered positions in cavities in the crystal.

In the present study the influence of water molecules, in or about the coordination sphere of the europium(III) ion, is explored by comparison of the luminescence spectrum of a hydrated chelate compound to the luminescence spectrum of the corresponding anhydrous chelate compound. The transitions considered in detail are those where the differences in the luminescence spectra of the hydrated and anhydrous compounds can be sufficiently resolved to be clearly observed. Band assignments were made by consideration of the calculated free ion energy levels given in Dieke [2] and calculations on coordination compounds by Filipescue *et al.* [7]. In the cases of $^7F_1 \leftarrow {}^5D_0$ and the $^7F_2 \leftarrow {}^5D_0$ manifolds of europium(III), overlapping transitions can be expected from the $^7F_3 \leftarrow {}^5D_1$ and the $^7F_4 \leftarrow {}^5D_1$ manifolds, respectively [2, 8]. Such overlapping manifolds should yield transitions of less intensity due to the fact that the upper $^5D_1$ level can decay to the $^5D_0$ level by non-radiative means.

The determination of crystal field site symmetries by the examination of lanthanide ion luminescence band splittings is generally well understood. The method employed in this paper for the determination of the band splittings that result from crystal field splittings of the free ion energy levels is the group theoretical approach introduced by Bethe [9]. The aspects of this method as applied especially to lanthanide ions is described in more detail by Wybourne [10]. As an example, the $^7F_2 \leftarrow {}^5D_0$ luminescence transition of the europium(III) ion in a crystal symmetry of D_{3h} will be described. When a lanthanide ion is placed in a crystal field, the free ion levels will split into a number of sublevels that can be characterized by the irreducible representation of the appropriate point group describing the crystal field symmetry. In D_{3h} symmetry, $J=0$ yields an A_1' representation and $J=2$ yields an A_1' and two E' representations. A transition between states of $J=0$ and $J=2$ is allowed by the electric dipole selection rule [10], which possesses the same symmetry representations as translations along the three-dimensional coordinate axes, the A_2'' and E' representations. In order for the transition to occur, the product of the ground state, the transition dipole and the excited state must contain the completely symmetric representation A_1'. This results in a single description for the two transitions expected in the $^7F_2 \leftarrow {}^5D_0$ manifold, $E' \leftarrow A_1'$ (note that if polarized light is used to excite the europium(III) ion, then the E vector of the luminescence will be polarized perpendicularly to the E vector of the exciting light). Slight distortions of this D_{3h} symmetry, due to steric effects from the bulky ring group of the ligand or crystal packing considerations, may result in a very small splitting of degenerate transitions. The intensity of the transitions, to the first order, is directly proportional to the degeneracy of the active symmetry representation for the transition. In the case of europium(III), when the excited state being considered is the $^5D_0$ level, which is described by the totally symmetric representation, the intensity is dependent only on the degeneracy of the lower state crystal field level. The intensity of the observed transition will be affected by vibrational interactions, so it is necessary to refrigerate the sample being investigated.

The first compound to be discussed is the anhydrous europium(III) chelate. Examination of Fig. 3 reveals luminescence originating from the $^5D_0$ level of the europium ion. Luminescence originating from the $^5D_1$ and $^5D_2$ levels, observed at higher energies, was less intense and not used for this work. Since the $^5D_0$ state ($J=0$) does not split in a crystal field, the splittings observed are due only to those of the lower level. The splittings expected for these transitions for various possible nine-fold coordination polyhedra are summarized in Table 1. Entries in Table 2 reveal that a feature, corresponding to the $^7F_0 \leftarrow {}^5D_0$ transition, is observed outside of the wavelength range of Fig. 3. The relative intensity of this feature is so small that it should be considered symmetry disallowed. In Fig. 3 the $^7F_1 \leftarrow {}^5D_0$ manifold consists of three distinct peaks of near equal intensity with the two peaks at lower energy split by about 20 cm^{-1} and the third peak split about 60 cm^{-1} from the barycenter of the other two. This pattern is consistent with symmetry designations of one non-degenerate and one doubly degenerate feature, where the degeneracy has been relaxed due to a slight distortion of site symmetry. In the area of the $^7F_0 \leftarrow {}^5D_0$ manifold

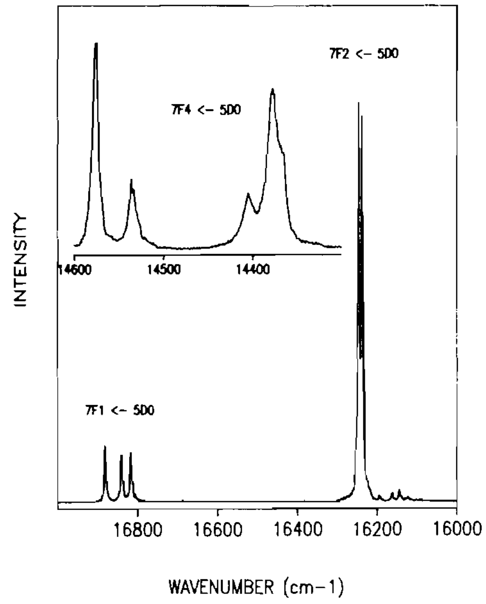

Fig. 3. Luminescence spectrum of anhydrous $Na_3[Eu(DPA)_3]$ excited at 465.8 nm.

are two very intense peaks of nearly identical intensity which are split by about 10 cm^{-1} and several very weak peaks at lower energy. These splitting patterns are consistent with either two, doubly degenerate features or, due to the hypersensitive nature of this transition, one , doubly degenerate feature that is split slightly by a small distortion of the site symmetry. At this point in the analysis it is apparent that the splitting patterns observed in the three previous transition manifolds are consistent with either D_3 or C_{3h} point symmetry. In order to differentiate unambiguously between these two site symmetries, it is necessary to examine one additional manifold. The $^7F_3 \leftarrow {}^5D_0$ manifold is very weak due to being disallowed by both the electric dipole selection rule ($\Delta J = \pm 2,4,6$) and the magnetic dipole selection rule ($\Delta J = 0, \pm 1$, not $0 \leftrightarrow 0$). It is therefore not readily accessible for point symmetry analysis. The $^7F_4 \leftarrow {}^5D_0$ manifold is electric dipole allowed and exhibits peaks at five different frequencies. The splitting pattern is consistent with three, doubly degenerate features, one slightly split and overlapping another, and one, non-degenerate feature. Thus the transitions and splitting patterns observed for the anhydrous compound are consistent with a slightly distorted D_3 site symmetry because there exists a non-degenerate peak in the $^7F_4 \leftarrow {}^5D_0$ manifold.

In the analysis of the observed splitting patterns of the hydrated europium compound, as viewed under moderate resolution, results similar to those discussed above for the anhydrous compound are obtained. Again, this is indicative of a predominantly distorted D_3 site symmetry. One of the obvious differences in the hydrated compound's spectrum, displayed in

TABLE 1. Symmetry relations between coordination polyhedra and luminescence transitions for europium(III)-containing compounds

Coordination polyhedron (CN)[b]	Site symmetry	Active representations[a]			
		$^7F_4 \leftarrow {}^5D_0$	$^7F_2 \leftarrow {}^5D_0$	$^7F_1 \leftarrow {}^5D_0$	$^7F_0 \leftarrow {}^5D_0$
Square antiprism (8)	D_{4d}	B_2, E_1	E_1	A_2	none
	D_4	A_2, 2E	E	A_2, E	none
	D_2	$2B_1$, $2B_2$, $2B_3$	B_1, B_2, B_3	B_1, B_2, B_3	none
Triangulated dodecahedron (8)	D_{2d}	B_2, 2E	B_2, E	A_2, E	none
	D_2	$2B_1$, $2B_2$, $2B_3$	B_1, B_2, B_3	B_1, B_2, B_3	none
	S_4	2B, 2E	2B, E	A, E	none
Tricapped trigonal prism (9)	D_{3h}	3E′	2E′	A_2'	none
	D_3	A_1, 3E	2E	A_2, E	none
	S_6	$2A_u$, E_u	E_u	A_g	none
	C_{3h}	3E′	E′	A′, E″	none
	C_3	3A, 3E	A, 2E	A, E	A
Monocapped square antiprism (9)	C_{4v}	$2A_1$, 2E	A_1, E	A_2, E	A_1
	C_4	3A, 2E	A, E	A, E	A
	C_2	5A, 4B	3A, 2B	A, 2B	A
Bicapped square antiprism (10)	D_{4d}	B_2, E_1	E_1	A_2	none
	D_{2d}	B_2, 2E	B_2, E	A_2, E	none
	D_2	$2B_1$, $2B_2$, $2B_3$	B_1, B_2, B_3	B_1, B_2, B_3	none

[a] Magnetic-dipole selection rules were employed for the $^7F_1 \leftarrow {}^5D_0$ transition, and electric-dipole rules for the others.
[b] CN = coordination number.

TABLE 2. Luminescence transitions of anhydrous $Na_3[Eu(dipicolinate)_3]$

Energy (cm^{-1} in air)	Wavelength (nm)	FWHM (cm^{-1})	Relative intensity	Transition assignment
17214	580.92	2	0.3	${}^7F_0 \leftarrow {}^5D_0$
16881	592.38	5	41	${}^7F_1 \leftarrow {}^5D_0$
16840	593.82	5	33	
16816	594.67	6	35	
16245	615.57	4	100	${}^7F_2 \leftarrow {}^5D_0$
16236	615.92	4	90	
14576	686.06	10	5.6	${}^7F_4 \leftarrow {}^5D_0$
14535	687.99	10	2.5	
14407	694.11	10	12.3	
14377	695.56	10		
14366	696.09	10		

TABLE 3. Luminescence transitions of $Na_3[Eu(dipicolinate)_3] \cdot 15H_2O$

Energy (cm^{-1} in air)	Wavelength (nm)	FWHM (cm^{-1})	Relative intensity	Transition assignment
17215	580.89	3	0.50	${}^7F_0 \leftarrow {}^5D_0$
16897	591.82	3		${}^7F_1 \leftarrow {}^5D_0$
16884	592.28	5	0.58	
16878	592.49	5	0.37	
16862	593.05	5	2.56	
16851	593.44	unresolved		
16847	593.58	≈5	0.50	
16839	593.86	8	3.56	
16833	594.07	unresolved		
16827	594.28	unresolved	8.12	
16819	594.57	≈5		
16816	594.67	≈5		
16245	615.57	6	81	${}^7F_2 \leftarrow {}^5D_0$
16236	615.92	8	100	
14568	686.44	≈17	0.49	${}^7F_4 \leftarrow {}^5D_0$
14551	687.24	11	1.60	
14412	693.87	13	1.40	
14380	695.41	≈11	0.62	
14370	695.89	≈10	0.20	
14366	696.09	≈10	0.96	

Fig. 4 (Table 3), is the magnitude of the splitting of the hypersensitive ${}^7F_2 \leftarrow {}^5D_0$ manifold. The splitting of the two features in this manifold has been increased from about 10 cm^{-1} in the anhydrous compound to almost 30 cm^{-1} in the hydrated compound. Concomitant with the change in the magnitude of the splitting is an increase in the linewidth from about 4 cm^{-1} to 6 and 8 cm^{-1}, respectively. A closer examination of the ${}^7F_2 \leftarrow {}^5D_0$ manifold (Fig. 5) also reveals an observable asymmetry to the line shapes of the two features produced by the hydrated compound. Inspection of the ${}^7F_1 \leftarrow {}^5D_0$ manifold for the hydrated compound suggests that the europium(III) ion is being subjected to several distinctly different but similar environments. Different arrangements of the hydration sphere have resulted in the distinct and resolvable features which appear in this manifold when viewed under high resolution (Fig. 6). Although these spectral differences are easily obtained, it is difficult to ascribe them to any particular structural change without additional information.

A cursory examination of the spectrum of the hydrated europium(III) compound can be misleading. Structural information about the hydration influence requires a careful examination and comparison of the corresponding luminescence spectra of the hy-

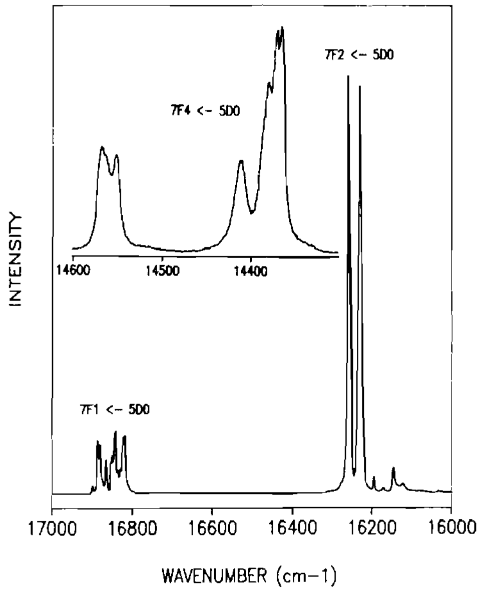

Fig. 4. Luminescence spectrum of $Na_3[Eu(DPA)_3]\cdot 15H_2O$ excited at 465.8 nm.

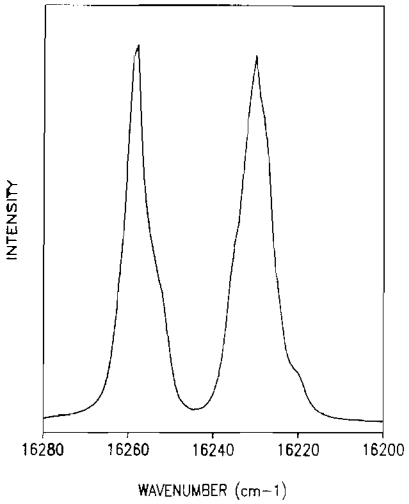

Fig. 5. Expanded view of the $^7F_2 \leftarrow {}^5D_0$ manifold of the luminescence spectrum of $Na_3[Eu(DPA)_3]\cdot 15H_2O$ excited at 465.8 nm.

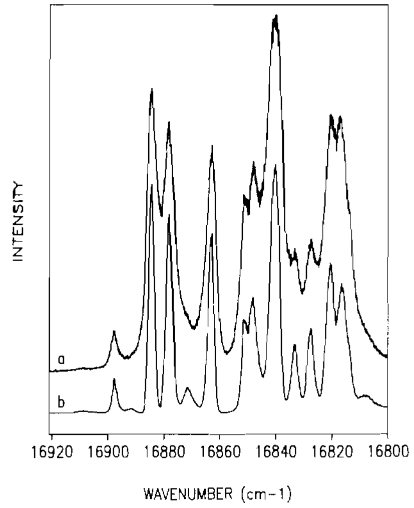

Fig. 6. Expanded (a) view and (b) deconvolution of the $^7F_1 \leftarrow {}^5D_0$ manifold of the luminescence spectrum of $Na_3[Eu(DPA)_3]\cdot 15H_2O$ excited at 465.8 nm.

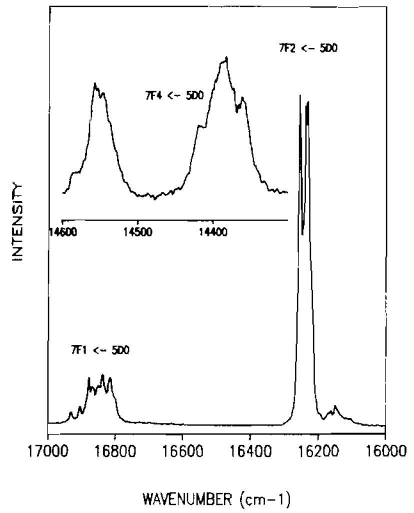

Fig. 7. Luminescence spectrum of $Na_3[Eu(DPA)_3]\cdot H_2O$ excited at 465.8 nm.

drated and anhydrous compounds. This effort is greatly aided by comparison to intermediately hydrated compounds which were obtained by briefly exposing the anhydrous compound to a moist atmosphere. One example of the luminescence spectra of the intermediately hydrated compounds is seen in Fig. 7. The numerical data from this spectrum are presented in Table 4. The spectrum of this compound reveals an obvious change in point symmetry for the europium(III) ion. When this spectrum is analyzed by the method outlined above the result is a pattern suggesting D_{2d} point symmetry. This point symmetry is consistent with a ten-coordinate monohydrate exhibiting a bicapped square antiprismatic coordination polyhedron. The narrow linewidths (4 cm^{-1} FWHM) of the features in this spectrum are about the same as those exhibited by the anhydrous compound and hence suggest an extremely well-ordered compound. In addition, the splitting of the hypersensitive $^7F_2 \leftarrow {}^5D_0$ manifold in this compound is about 35 cm^{-1}, which is similar to the splitting observed in the luminescence spectrum of the 15 hydrate compound. These two observations

TABLE 4. Luminescence transitions of $Na_3[Eu(dipicolinate)_3] \cdot H_2O$

Energy (cm^{-1} in air)	Wavelength (nm)	FWHM (cm^{-1})	Relative intensity	Transition assignment
17212	580.99	2	0.5	$^7F_0 \leftarrow {}^5D_0$
16866	592.91	5	16	$^7F_1 \leftarrow {}^5D_0$
16851	593.44	5	16	
16811	594.85	6	14	
16260	615.01	4	44	$^7F_2 \leftarrow {}^5D_0$
16225	616.33	4	100	
14576[a]	686.06	10	0.5	$^7F_4 \leftarrow {}^5D_0$
14554	687.10	10	5	
14431	692.95	12	0.6	
14350	696.86	16	7	

[a] This feature is suspected to be from residual anhydrous compound.

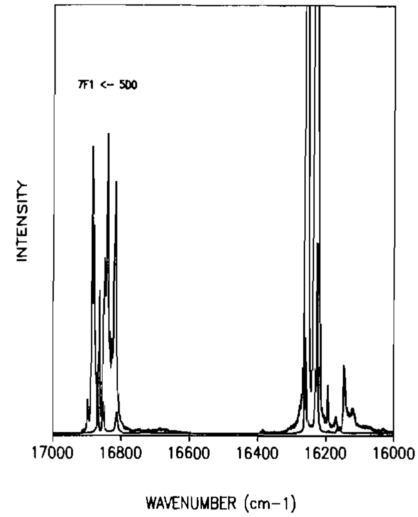

Fig. 8. The luminescence spectrum of $Na_3[Eu(DPA)_3] \cdot H_2O$ (below) inserted in the luminescence spectrum of $Na_3[Eu(DPA)_3] \cdot 15H_2O$ (above) showing the relative positions and suspected small contribution of the monohydrate to the spectrum of the 15 hydrate (excited at 465.8 nm).

support the suggested ten-coordinate structure. As expected, when the luminescence spectrum of this monohydrated form is inserted into the spectrum of the 15 hydrate in the manner of a 'key in a lock', it appears that it is a very minor contributor to the spectrum of the 15 hydrate (Fig. 8). When this partially hydrated compound was left exposed to the laboratory atmosphere overnight, the luminescence spectrum obtained the next day was essentially the same as in Fig. 8, except the linewidths had about doubled. This suggests that migration of additional water into the coordination sphere of the europium(III) ion is slow and/or that the influence of lattice water is being observed.

A luminescence spectrum of a sample of the anhydrous compound which was exposed to ambient air for an extended period is presented in Fig. 9. This spectrum reveals an increased number of luminescence lines due to a suspected increase in the number of hydrated species. Deconvolution of the spectrum into representations of each individual hydrate species would require assignment of groups of lines by line intensities. This method would only be viable if all the species were of essentially the same point symmetry, because other point symmetries could produce different numbers and/or degeneracies of lines. However, due to the dramatic differences in the spectrum of the anhydrous compound from that of the suspected monohydrate, it is reasonable to state two general observations. First, the presence of water seems to cause a dramatic increase in the magnitude of the splitting of the hypersensitive $^7F_2 \leftarrow {}^5D_0$ manifold, as observed in the spectra of the 15 hydrate as well as in that of the monohydrate. Second, the position of the central peak in the $^7F_2 \leftarrow {}^5D_0$ manifold shifts to higher energy in sites of D_{2d} site symmetry. Thus we would argue that both point symmetries are exhibited by the europium(III) ions in the sample whose spectrum is given in Fig. 9. Because the lines in the $^7F_2 \leftarrow {}^5D_0$ manifold are hypersensitive, it is not possible to use their intensities as a guide to the predominance of a species of a particular point symmetry. This leaves the $^7F_1 \leftarrow {}^5D_0$ manifold as the main indicator of the relative abundance of species present. These considerations suggest that as the extent of hydration

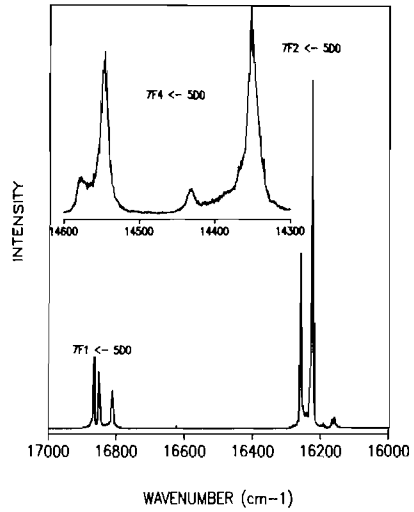

Fig. 9. The luminescence spectrum of a sample of anhydrous $Na_3[Eu(DPA)_3]$ (excited at 465.8 nm) after extended exposure to moist air.

proceeds, the predominant europium(III) ion site symmetry returns to distorted D_3. Foster and Richardson have presented the magnetically circularly polarized luminescence spectrum of the aqueous $Eu(DPA)_3^{3-}$ anion at room temperature and concluded that the Eu(III) ion resided in a site with D_3 symmetry [11]. This is consistent with the frozen solution spectrum at 77 K.

Application of a line intensity deconvolution to the 15 hydrate compound yields 12 distinct features in the $^7F_1 \leftarrow {}^5D_0$ manifold, which implies at least four different site symmetries for the europium(III) ion. From the positions of these features in comparison to those observed in the anhydrous and monohydrate compounds, it is apparent that both D_3 and D_{2d} species are likely. Also, from the intensities presented by these features, it is suspected that the D_3 site is the majority contributor. This supposition is supported by the two features present in the $^7F_2 \leftarrow {}^5D_0$ manifold, whose linewidths and shapes suggest the presence of two different europium(III) ion sites.

Another method available for the characterization of the hydration of lanthanide crystal compounds is through the correlation of the number of inner sphere coordinated water molecules with luminescence decay times. The rationale for this method involves comparison of the lifetimes of two compounds that differ only in being synthesized with H_2O versus D_2O. If the water of hydration is inner sphere, then the deuterated compound should have a longer luminescence decay time than the undeuterated compound due to less efficient vibrationally coupled relaxation. Horrocks and Sudnick reported reciprocal lifetime values for many hydrated Eu(III) compounds and included the dipicolinate compounds as examples of compounds with no inner sphere coordinated water [12]. Lifetime measurements made on the 15-hydrate compounds in this study ($\tau_{1/2} = 1.3$ ms for the H_2O compound and 2.1 ms for the D_2O compound) differed only slightly from the values referenced above. Although the differences in the two lifetimes are insufficient to verify an average of one coordinated water molecule per Eu(III) ion, the difference is sufficient to suggest that there are some hydrated metal ions in the inner sphere. This is in accord with the suggestion that the D_{2d} species that was identified in the present work is only a minor contributor to the overall luminescence spectrum.

Conclusions

It is apparent from these experimental results that a wealth of structural information is present in the luminescence spectra produced by europium(III) ions. This information can be used in conjunction with X-ray structure determinations to describe more completely the structures of europium(III) compounds where more than one hydrated species may be present. It is seen that information pertaining to the outer coordination sphere of lanthanide ions is present in the splittings of the crystal field levels. Such a spectral–structural correlation can also be useful in the determination of coordination polyhedra for compounds not amenable to study by single crystal X-ray methods. The extension of this method of analysis to europium(III)-doped compounds should follow.

Acknowledgements

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