Inorganica Chimica Acta, 44 (1980) L89–L92
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Fluorescence Spectra of Europium Quinolinecarboxylates

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Received September 11, 1979

Lanthanide(III) quinolinecarboxylates having stoichiometry $Ln(n\text{-}AN)_3 \cdot mH_2O$ (n = 2, 4, 6; m = 0–4; HAN = quinolinecarboxylic acid) have been prepared and characterized [1, 2]. Vibrational and electronic spectra indicated O-bidentate structures for the 4- and 6-quinolinecarboxylates and N,O-chelate structures for the 2-quinolinecarboxylates. Dehydration of the hydrated species or dissolution in organic solvents caused only small changes in the band shape and intensity of the hypersensitive transitions. On the other hand, transitions that occur between low J-values in europium(III) ion are very sensitive to changes in the environment and are thus able to give useful information on the nature of the chromophoric group and symmetry of the complex.

Results and Discussion

Europium(III) fluorescence arises from ligand-to-cation energy transfer and almost totally from the $^5D_0$ level. Fluorescence arising from the $^5D_1$ level is very weak, the spectra showing only bands associated with the various $^5D_1 \rightarrow {}^7F_J$ transitions the intensity of which is lesser than 2% the most intense $^5D_0 \rightarrow {}^7F_2$ transition.

It will be seen from the spectra of the europium (III) 2-quinolinecarboxylate trihydrate (Fig. 1 and Table I) that the degeneracy of the $^7F_{1,2}$ levels is removed and that three and four components of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$, respectively, transitions appear in the relative regions. The $^5D_0 \rightarrow {}^7F_0$ transition is allowed and appears as a relatively intense line at 578.2 nm. Only slight change in the relative intensity occurs on lowering the temperature from 300 to 77 K. This spectral pattern suggests C_{2v} site symmetry for the europium(III) ion in this compound. The appearance in the spectra of numerous broad components of the $^5D_0 \rightarrow {}^7F_{3,4}$ transitions agrees with the postulated C_{2v} symmetry. The spectra show that the splitting of terms, baricenter and relative intensity of the various bands do not undergo any significant change on dehydration or dissolution of the various species in DMSO or methanol. This indicates that the N,O-chelate conformation of this ligand secures to the cation sixfold coordinated arrangement of the $[LnN_3O_3]$ type; if additional interactions occur they are, in this case, of the outer-sphere type only.

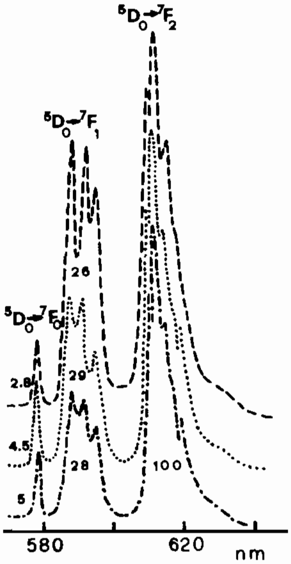

Fig. 1. Emission spectra at 77 K of: (–.–.) $Eu(2\text{-}AN)_3 \cdot 3H_2O$; (...) $Eu(2\text{-}AN)_3$; (– – –) $Eu(2\text{-}AN)_3$ in DMSO. Assignments and relative intensity (%) are also shown.

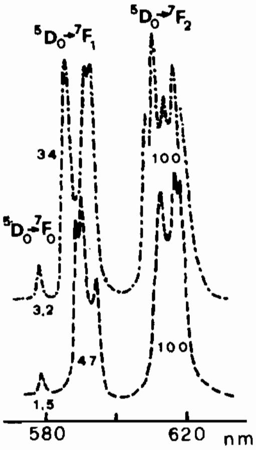

Fig. 2. Emission spectra at 77 K of: (– – –) $Eu(4\text{-}AN)_3 \cdot 3H_2O$; (–.–.) $Eu(4\text{-}AN)_3$. Assignments and relative intensity (%) are also shown.

The emission spectra of the europium(III) 4-quinolinecarboxylate trihydrate agree with D_{2d}, distorted towards C_{4v}, site symmetry for the europium(III) ion (Fig. 2 and Table I); the spectra of the 6-quinolinecarboxylate tetrahydrate suggest C_{4v} site symmetry (Fig. 3 and Table I). It will be seen that the dehydration of these two species causes such a modification of the

TABLE I. Details of the Observed Fluorescence Transitions of the Europium(III) Quinolinecarboxylates. In parenthesis are the relative intensity values (%).

Eu(2-AN)$_3$·mH$_2$O				Eu(4-AN)$_3$·mH$_2$O				Eu(6-AN)$_3$·mH$_2$O				Assignment
m = 3		m = 0		m = 3		m = 0		m = 4		m = 0		
18947	(<0.2)	18939	(<0.2)									$^5D_1 \rightarrow {}^7F_0$
17295	(5.0)	17289	(4.5)	17274	(1.5)	17265	(3.2)	17277	(3.5)	17271	(4.0)	$^5D_0 \rightarrow {}^7F_0$
16998 16898 16801	(28)	16992 16900 16807	(29)	16898 16869 16818	(47)	17030 16855 16829	(34)	16955 16915 16849	(32)	16941 16858	(34)	$^5D_0 \rightarrow {}^7F_1$
16327 16221 16202 16021	(100)	16321 16234 16213 16026	(100)	16255 16171 16158	(100)	16308 16234 16147 16127	(100)	16292 16268 16181 16103	(100)	16367 16276 16134	(100)	$^5D_0 \rightarrow {}^7F_2$
15373 15314	(<0.2)	15385 15337	(<0.2)	very weak		15349	(<0.4)	15361 15337	(<0.2)	very weak		$^5D_0 \rightarrow {}^7F_3$
14556 14472 14388 14286	(<0.1)	14535 14472 14388 14306	(<0.1)	14472 14388 14265	(<0.1)	14451 14368 14286	(<0.1)	14493 14368 14245	(<0.1)	very weak		$^5D_0 \rightarrow {}^7F_4$

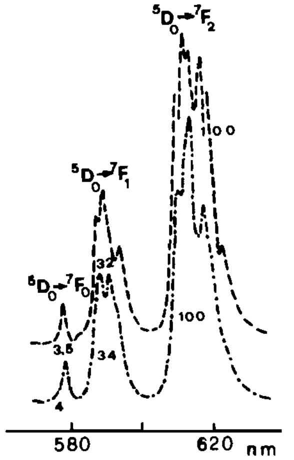

Fig. 3. Emission spectra at 77 K of : (– – –) Eu(6-AN)$_3$·4H$_2$O; (–.–.) Eu(6-AN)$_3$. Assignments and relative intensity (%) are also shown.

TABLE II. Partial Energy Level Scheme for Europium Quinolinecarboxylates in the Solid State at 77 K. The values refer to the baricenter of the band group. In parenthesis are the values for the hydrates (cm^{-1}, ±6).

Level	Eu(2-AN)$_3$	Eu(4-AN)$_3$	Eu(6-AN)$_3$
$^5D_2$	21496	21515	21515
$^5D_1$	18947	19025[a]	19006[a]
$^5D_0$	17289	17265	17271
$^7F_4$	2925[a]	2877[a]	
$^7F_3$	1935[a]	1930[a]	1935[a]
$^7F_2$	989(985)	1021(1040)	1018(1045)
$^7F_1$	371(368)	393(385)	390(376)
$^7F_0$	0	0	0

[a] ± 10.

TABLE III. Intensity, as Oscillator Strength (10^6 P), of the $^4I_{9/2} \to {}^4G_{5/2}$ in Nd^{3+} Ion and $^5I_8 \to {}^5G_6$ in Ho^{3+} Ion Hypersensitive Transitions. In parenthesis is the baricenter of the band group (in kK).[a]

Solvent	Ln(2-AN)$_3$		Ln(4-AN)$_3$		Ln(6-AN)$_3$	
	Nd	Ho	Nd	Ho	Nd	Ho
DMSO	20.41 (17.12)	22.35 (22.03)	23.92 (17.18)	25.97 (22.07)	24.74 (17.18)	26.53 (22.07)
C_2H_5OH	20.38 (17.14)	22.96 (22.03)	24.05 (17.18)	b	24.87 (17.18)	b
Pyridine	20.80 (17.12)	22.07 (22.03)	24.36 (17.18)		25.03 (17.18)	

[a] See also ref. [1]. [b] Scarcely soluble.

spectral patterns that structural rearrangement through release of the hydrogen bondings acting between the pyridine nitrogen and the water molecules of adjacent entities [3] must be postulated. IR and UV spectra indicated [1] that replacement of the cation–water interactions by pyridine nitrogen–cation interactions through formation of polymeric species does not occur; on this ground sixfold coordinated arrangements of the [LnO$_6$] type can be assigned to both the dehydrated compounds. The cation is in these compounds in a non-centrosymmetric ligand field; in this case both the $^5D_0 \to {}^7F_{1,2}$ transitions are allowed by selection rules. On the other hand, the efficiency of the intramolecular energy transfer from the ligand to the cation is increased the more covalent the complex; it happens, moreover, that the $^5D_0 \to {}^7F_2$ transition, among the various transitions that occur between low J-values in europium(III) ion, is more sensitive to the surroundings than the $^5D_0 \to {}^7F_1$ transition. The intensity ratio ($^5D_0 \to {}^7F_2$):($^5D_0 \to {}^7F_1$) values (η) measured for these compounds are in any case relatively low and do not differ appreciably from one another. Moreover, the low-energy diagram constructed from the results of both the absorption and emission spectra shows that the values measured for the 4- and 6-quinolinecarboxylates are approximately identical (Table II); these values are, on the other hand, comparable with those measured for the europium (III) ethylsulphate [4]. This trend agrees with the absorption spectra from which approximately the same values were measured for the oscillator strength of the $^4I_{9/2} \to {}^4G_{5/2}$ and $^5I_8 \to {}^5G_6$ hypersensitive transitions in the neodymium, respectively holmium compounds (Table III); both spectra suggest low-covalency in the Ln–ligand bondings.

Experimental

Lanthanide(III) n-quinolinecarboxylates (n = 2, 4, 6) were prepared following previous procedures [1, 2]. The 2-quinolinecarboxylates were recrystallized from methanol; the 4- and 6-quinolinecarboxylates are soluble in methanol, but rapidly reprecipitate as insoluble species. All compounds are soluble in DMSO. Samples were treated under reduced pressure ($\sim 10^{-2}$ mm Hg) at 150 °C for 1 h. Thermoanalytical measurements and IR spectra indicated that dehydration occurred almost totally.

IR and electronic spectra and thermal analysis were performed following previous procedures [1]. The fluorescence spectra were obtained by a Perkin-Elmer MPF-3L fluorescence spectrophotometer from solid compounds and methanol or DMSO solutions at room and liquid nitrogen temperatures exciting with 330–350 nm radiations. The resolution was better than 10 cm^{-1}.

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