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Lanthanide(III) Complexes with 2-Quinolinecarboxylic Acid in the Neutral Form

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Introduction

The coordination of trivalent lanthanides with the carboxylato functional group has been the object of several studies; complexes with carboxylic acids acting as neutral ligands, although in the zwitterion form, have been also reported [1, 2]. To our knowledge, no complex of lanthanides with carboxylic acids acting as neutral ligands through the oxygen atom of the carbonyl is known.

The 2-quinolinecarboxylic acid exists in the solid state prevalently as dipolar ion; on the other hand, spectroscopic data indicate that in non-aqueous solvents the neutral form predominates. Lanthanide(III) 2-quinolinecarboxylates and lanthanide(III) complexes with this acid in the zwitterion form have been previously prepared and studied [3, 4]. As part of a systematic study on the complexes with neutral ligands of lanthanide salts having weakly or non-coordinating anions, the synthesis and properties of the complexes of lanthanide(III) nitrates, perchlorates and trifluoromethanesulphonates with this acid in the neutral form and acting as O-monodentate ligand are reported here.

Experimental

The 2-quinolinecarboxylic acid is a commercially available product (2-HAN); it was recrystallized from methylcyclohexane. Lanthanide(III) trifluoromethanesulphonates were prepared following previous procedure [5]; they were heated for 1 h at 130 °C under reduced pressure ($\sim 10^{-2}$ mmHg) and immediately dissolved in anhydrous ethanol.

The complexes were obtained by refluxing 1 mmol of the lanthanide(III) nitrate, perchlorate or trifluoromethanesulphonate in 50 ml of anhydrous ethanol mixed with 4–8 mmol of the acid in 100–200 ml of the same solvent. Copious microcrystalline products slowly formed; they were filtered off, washed with anhydrous ethanol and dried *in vacuo* at room temperature over $CaCl_2$.

Thermal analysis, electrolytic conductivity, vibrational and electronic (absorption and emission) spectra were performed as previously described [5]. Water content was determined by the Karl Fischer method.

Results and Discussion

The complexes are soluble in alcohols and acetonitrile; they are also soluble in water with decomposition. Molar conductivity values in acetonitrile and ethanol indicate non-electrolytic behaviour for the nitrate complexes and 1:3 electrolytes for the perchlorate and trifluoromethanesulphonate complexes. The thermogravimetric (TG) and differential thermal analysis (DTA) curves of the lanthanum to europium perchlorate and trifluoromethanesulphonate complexes do not show any mass-loss until decomposition begins endothermically around 200 °C. The TG and

TABLE I. Selected Analytical Data, Electrolytic Conductivity and Temperature of Thermal Decomposition of Lanthanide(III) Complexes with 2-quinolinecarboxylic Acid in the Neutral Form (2-HAN). In Parentheses the Calcd. Values.

Complex	% C	% H	% N	% Ln	Λ_M[a]		t, °C
					EtOH	MeCN	
$La(2\text{-}HAN)_8(ClO_4)_3$	53.28(52.72)	3.18(3.10)	6.30(6.15)	7.58(7.62)	160	385	200
$Nd(2\text{-}HAN)_8(ClO_4)_3$	52.98(52.57)	3.12(3.09)	6.18(6.13)	7.84(7.89)		403	205
$Nd(2\text{-}HAN)_8(CF_3SO_3)_3$			5.71(5.67)	7.42(7.30)	155	394	200
$Nd(2\text{-}HAN)_3(NO_3)_3(H_2O)$	40.03(41.52)	2.80(2.67)	9.45(9.69)	16.09(16.62)	25	18	160*
$Eu(2\text{-}HAN)_8(ClO_4)_3$	51.86(52.34)	3.20(3.08)	6.28(6.10)	8.31(8.28)	157	382	190
$Eu(2\text{-}HAN)_8(CF_3SO_3)_3$			5.57(5.65)	7.80(7.66)	160	372	190
$Eu(2\text{-}HAN)_2(NO_3)_3(H_2O)_2$	32.85(33.32)	2.61(2.52)	9.60(9.72)	20.68(21.10)	15	22	170*
$Tb(2\text{-}HAN)_7(ClO_4)_3(H_2O)$	50.90(49.82)	2.98(3.05)	6.05(5.81)	9.37(9.42)		397	185

[a] ohm^{-1} cm^2 M^{-1}, at 25 ± 0.1 °C; c = 09–2.0·10^{-3} *M*. *± 10.

DTA curves of the nitrate complexes show an endothermic step with mass-loss around 110 °C; however, before this process is completed the decomposition begins endothermically around 170 °C.

The IR spectrum of the acid in xylene exhibits a strong band at 1750 cm^{-1} assigned to the C = O stretching mode. A broad band showing more than one peak and assigned to the intramolecular hydrogen bonded OH stretching mode appears between 2800 and 2400 cm^{-1}. A very weak band at 1700 cm^{-1} and a strong one at 1590 cm^{-1} appear in the spectrum of 2-HAN in the solid state and assigned respectively to the C = O stretching and carboxylato asymmetric stretching and ring modes. The spectra are consistent with the acid in the neutral form in xylene and prevalently as zwitterion in the solid state. The IR spectra of the lanthanum to europium perchlorate and trifluoromethanesulphonate complexes are free from bands between 3500 and 3200 cm^{-1}; otherwise a broad band associated with the H_2O stretching modes appears in this region of the spectra. The broad band between 2800 and 2400 cm^{-1} and the medium intensity ones at 1628 and 1598 cm^{-1} are the same that appear in the spectra of the acid in xylene and of the N-protonated species (2-HANH$^+$). Two very strong bands appear at 1665–1660 and 1380–1375 cm^{-1}; they are assigned to stretching modes of the un-ionized carboxylic group. This spectral pattern is consistent with the acid in the neutral form and bound to the cation through the oxygen atom of the carbonyl. Two un-split and strong bands assigned respectively to the ν_3 and ν_4 modes of the perchlorate group (T_d symmetry) appear at 1095 and 620 cm^{-1} in the spectra of the perchlorate complexes indicating that deviation from the tetrahedral geometry does not occur. The spectra of the trifluoromethanesulphonate complexes show three un-split and strong bands at 1285–1280, 1038–1035 and 645–642 cm^{-1} assigned respectively to the stretching $\nu_4(E)$, $\nu_1(A_1)$ and deformation $\nu_3(A_1)$ modes of the C_{3v} symmetry $-SO_3$ group [5]. Only bands associated with the C_{2v} symmetry nitrate group appear in the spectra of the nitrate complexes indicating coordination of the three nitrate groups in all complexes. On the other hand, only ionic perchlorate and trifluoromethanesulphonate groups act in these complexes. On this ground eight-coordination can be suggested for all the perchlorate and trifluoromethanesulphonate complexes and ten-coordination for all nitrate complexes by the contribution also of water molecules.

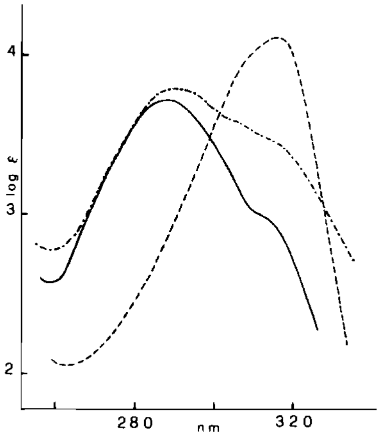

Fig. 1. UV spectra of: (——) 2-HAN in ethanol; (– – –) 2-HAN in water; (– • – •) Nd(2-HAN)$_8$(CF$_3$SO$_3$)$_3$ in ethanol.

The UV spectrum of 2-HAN shows a group of intense bands between 260 and 330 nm with ϵ_{max} at 288 nm in ethanol and 318 nm in water. It has been suggested that changes undergone by the spectrum when the pH is reduced from 7 to 4 are due to the transformation of the basic pyridine nitrogen into the pyridinium ion [6, 7] (Fig. 1). The UV spectra of the complexes resemble in the band shape that shown by the free acid in ethanol; the group of bands undergoes, however, a generalized shift (4–6 nm) to lower frequencies while the intensity increases. This trend is in line with IR data and can be associated with the formation of ligand-cation bond through the oxygen atom of the carbonyl. The f–f spectra of neodymium and holmium complexes, recorded in the region of the hypersensitive transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}$ in Nd^{3+} ion and $^5I_8 \rightarrow {}^5G_6$ in Ho^{3+} ion, show changes in the band shape and intensity with respect to the aquo-ion; the intensity increases about three, respectively six times while the barycentre of the band group shifts to lower frequencies. Both these effects have been correlated with covalency. The values of the Sinha's parameter, δ, [8] are positive in any case but smaller than unity (δ = +0.70–0.80 for neodymium complexes; δ = +0.60–0.75 for holmium complexes). This parameter has been proposed as semi-empirical measure of covalency; if this correlation is effective it indicates weak covalent bonding. The number of the principal bands observed in the region of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transitions in the neodymium complexes is greater than five and excludes in any case cubic site symmetries.

The europium(III) perchlorate hydrate is weakly fluorescent by excitation to the $^5L_6$ level. The emission spectrum consists mainly of two poorly resolved bands associated with the $^5D_0 \rightarrow {}^7F_{1,2}$ transitions; the spectrum does not show any marked change on passing from the ethanolic to the aqueous solution in which the ion probably possesses a centre of inversion [9]. A decacoordinated LnO_{10} chromophore acquired by three bidentate nitrate groups and four water molecules in bicapped dodecahedral geometry has been established for hydrated lanthanide(III) nitrates in the solid state [10]. The complexes Eu(2-HAN)$_8$X$_3$ (X = ClO_4, CF_3SO_3) and the complex Eu(2-HAN)$_2$(NO$_3$)$_3$(H$_2$O)$_2$ strongly fluoresce when

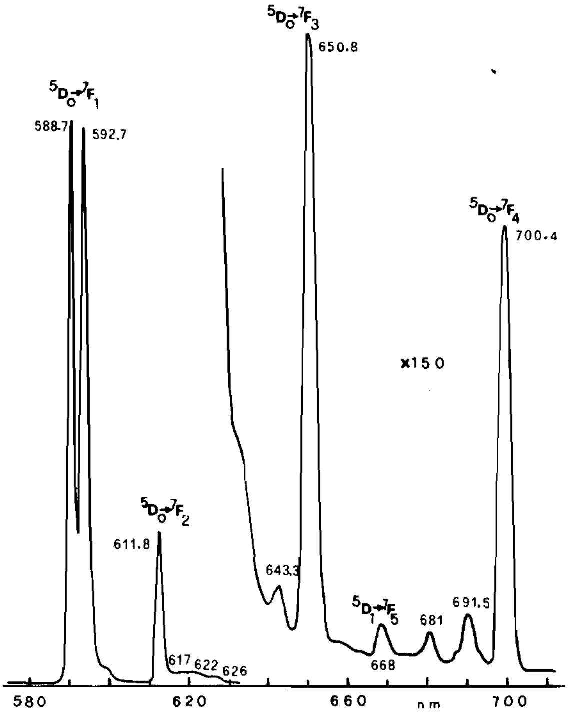

Fig. 2. Emission spectrum of $Eu(2\text{-}HAN)_8(ClO_4)_3$ from solid at 77 K. Excitation with 365 nm radiation.

excited with near ultraviolet radiations. Emission arises almost totally from the lowest resonance level ($^5D_0$); bands associated with transitions originating at the $^5D_1$ level are very weak. The three spectra are practically superimposable on one another showing only slight and insignificant differences in the energy and relative intensity of the various transitions. In Fig. 2 is depicted only the emission spectrum of the perchlorate complex. The $^5D_0 \to {}^7F_0$ transition can be taken as forbidden, the spectra showing in the relative region a line the intensity of which is less than 0.5% the most intense $^5D_0 \to {}^7F_1$ transition. The $^5D_0 \to {}^7F_1$ transition consists of only two almost equal intensity lines. In the region of the $^5D_0 \to {}^7F_2$ transition appear a line the intensity of which is less than 10% the $^5D_0 \to {}^7F_1$ transition and three much weaker components at lower frequencies. The $^5D_0 \to {}^7F_{3,4}$ transitions consist certainly of two components each while the weak band appearing at 668 nm can be reasonably assigned to the $^5D_1 \to {}^7F_5$ transition. This spectral pattern is consistent with a rather high symmetry for the electrostatic field; however, the two lines associated with the $^5D_0 \to {}^7F_1$ transition indicate that the Eu(III) ion is not located in all cases at a site with cubic symmetry. The two dominant geometries for eight coordination are the square antiprism (D_{4d}) and the tetragonal dodecahedron (D_{2d}); for decacoordination the bicapped square antiprism (D_{4d}) and the bicapped dodecahedron (D_2 or C_{2v}). The emission spectra of these europium complexes agree with D_{4d} symmetry at the europium(III) site. The appearance of a discrete line in the region of the $^5D_0 \to {}^7F_2$ transition may be due to distorsion of the idealized polyhedron.

References

1 R. A. Chupakhina and V. V. Sebebrennikov, *Russ. J. Inorg. Chem.*, 1406 (1962).
2 J. Kay, J. W. Moore and M. D. Glick, *Inorg. Chem.*, *11*, 2818 (1972).
3 A. Seminara and A. Musumeci, *J. Inorg. Nucl. Chem.*, *39*, 599 (1977).
4 A. Seminara, *Inorg. Chim. Acta*, *44*, L89 (1980).
5 A. Seminara and E. Rizzarelli, *Inorg. Chim. Acta*, *40*, 249 (1980).
6 P. Lumme, *Ann. Acad. Scient. Fennicae, A II 68* (1955).
7 L. E. Lyons, *J. Proc. Roy. Soc. N. S. W.*, *83*, 75 (1949).
8 S. P. Sinha, *Spectrochim. Acta*, *22*, 57 (1966).
9 G. S. Ofelt, *J. Chem. Phys.*, *37*, 511 (1962).
10 I. M. Rumanova, G. F. Volodina and N. V. Belov, *Crystallography (Soviet. Phys.)*, *9*, 545 (1965).