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Europium(III) Complexes with 2,2′,2″-Terpyridine-1,1′,1″-Trioxide

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Aromatic N-oxides behave as strongly basic ligands with a-type acceptor cations and normally give rise to well defined stoichiometry compounds. The number of reported complexes of this type of ligand with lanthanides is, however, scanty and the information on their properties fragmentary [1, 2]. To our knowledge no complex of lanthanides with 2,2′,2″-terpyridine-1,1′,1″-trioxide has been prepared. We report in this paper the synthesis and fluorescence spectra of the complexes of europium(III) nitrate and perchlorate with this ligand.

Experimental

Materials

2,2′,2″-Terpyridine-1,1′,1″-trioxide (terpyO_3) was prepared by the method of Case [3]. As a starting material for the preparation of the perchlorate complex, anhydrous europium(III) perchlorate complex with DMSO was employed.

Preparation of the complexes

1 mmol of europium(III) nitrate pentahydrate in 10 ml of acetonitrile or anhydrous europium(III) perchlorate complex with DMSO in 30 ml of absolute ethanol was added to a suspension of 2 mmol (nitrate) or 3.5 mmol (perchlorate) of terpyO_3 in 100–200 ml of a mixture of acetonitrile or absolute ethanol and tetrahydrofuran (2:1). Microcrystalline products slowly formed on boiling the clear solution. They were filtered off, washed with acetonitrile or absolute ethanol, diethylether and dried *in vacuo* at room temperature.

Physico-chemical measurements were performed following previous procedures [2].

Results and Discussion

Cation–ligand 1:1 and 1:3 molar ratio was found for the nitrate and perchlorate complex, respectively. Both complexes are soluble in hot methanol and acetonitrile. Thermal analysis shows that the dehydration of the perchlorate complex begins at relatively low temperature (Table I) and is practically complete at 100 °C. Molar conductivity values measured for the complexes in acetonitrile indicate non-electrolytic (nitrate) or 1:3 electrolytic (perchlorate) behaviour [4]. In methanol the conductivity of the nitrate complex is 105 $\text{ohm}^{-1}\ \text{cm}^2\ M^{-1}$ (Table I). This value is, however, approximately the same as measured for the europium(III) nitrate pentahydrate in the same solvent and indicates in both cases ionization of one nitrate group.

IR spectra indicated that the oxygen atoms of terpyO_3 are involved in bonding the cation. The free terpyO_3 exhibits strong doublet at 1258 and 1245 cm^{-1} assigned to NO stretching mode. An intense band showing three or four peaks between 1250 and 1220 cm^{-1} is exhibited by both complexes. The shift, though small, clearly indicates a ligand to cation coordination. It is, however, smaller than those observed for 2,2′-bipyridine-1,1′-dioxide (bipyO_2) complexes and suggests weaker cation-ligand bond. On the other hand, the increased splitting of this mode compared with the free ligand suggests non-equivalence of the Ln–O bonds. This effect probably arises from the non-coplanarity of the three oxygens in the terpyO_3 molecule owing to the formation of highly distorted conformation or polymeric

TABLE I. Analytical Data and Molar Conductivity of Europium Complexes with 2,2′,2″-Terpyridine-1,1′,1″-Trioxide (terpyO_3) (in parentheses the calcd. values).

Complex	%C	%H	%N	%Eu	Λ_M[a]		t_i, °C[b]
					MeOH	CH_3CN	
$Eu(terpyO_3)(NO_3)_3 \cdot H_2O$	28.91(28.27)	2.13(2.06)	12.80(13.19)	24.33(23.85)	105	26	260(90)
$Eu(terpyO_3)_3(ClO_4)_3 \cdot 2H_2O$	39.83(40.63)	2.87(2.80)	9.26(9.48)	11.08(11.43)	295	402	290(65)

[a] $\text{ohm}^{-1}\ \text{cm}^2\ M^{-1}$, at 25 ± 0.1 °C; c = 2–4·10^{-4} *M*. Λ_M for $Eu(NO_3)_3 \cdot 5H_2O$ in MeOH is 91 $\text{ohm}^{-1}\ \text{cm}^2\ M^{-1}$ (c = 6.0·10^{-4} *M*).
[b] Temperature of incipient thermal decomposition (in parentheses the temperature of incipient dehydration).

structures. The NO bending mode at 870 and 862 cm^{-1} in the free ligand appears slightly affected upon complexation showing about 10 cm^{-1} shift to lower frequencies.

No band assigned to the D_{3h} symmetry nitrate group appears in the IR spectrum of the solid nitrate complex. This indicates that no ionic nitrate group acts in this complex. Two un-split and strong bands at 1095 and 627 cm^{-1} appear in the IR spectrum of the perchlorate complex, which are assigned to the ν_3 and ν_4, modes of T_d symmetry perchlorate group, respectively. This spectral pattern indicates the presence of only ionic perchlorate groups in this complex.

Both complexes exhibit strong fluorescence when excited at 320 nm. Fluorescence arises from ligand to cation energy transfer and mainly from the lowest resonance level. Emission originated at the $^5D_1$ level is also valuable. Fluorescence spectral data of europium(III) complexes are normally used to draw out useful information concerning the nature of the ligand to cation bond and symmetry of the complex [5].

The complex Eu(terpyO$_3$)(NO$_3$)$_3$·H$_2$O in the solid state exhibits two very weak bands at 533.5 and 536.5 nm and two ones at 554.0 and 558.8 nm assigned to the $^5D_1 \rightarrow {}^7F_1$ and $^5D_1 \rightarrow {}^7F_2$ transitions, respectively. The $^5D_1 \rightarrow {}^7F_0$ transition is not observed. A weak line appears at 579.2 nm arising from the $^5D_0 \rightarrow {}^7F_0$ transition. The predominantly magnetic dipole allowed $^5D_0 \rightarrow {}^7F_1$ transition shows two components: the former appears as a line at 589.7 nm, the latter is observed at 592.8 nm with a shoulder around 593.4 nm (E-component). The $^5D_0 \rightarrow {}^7F_2$ transition mainly consists of a very intense line at 613.3 nm; two weaker ones at 617.9 and 619.2 nm are associated also with this transition and probably arise from an E-component. The splitting is relatively high (34 cm^{-1}) but this can be reasonably assigned to a second order effect arising from the non-coplanarity of the three pyridine N-oxide rings. The $^5D_0 \rightarrow {}^7F_3$ transition consists of a broad band at 650.3 nm and and a very weak one around 657.5 nm. The $^5D_0 \rightarrow {}^7F_4$ transition is very weak and poorly resolved; nevertheless four broad components can be observed at 681.5, 686, 695 and 701 nm. This complex was heated at 150 °C for 1 h under reduced pressure (~10^{-2} mmHg) and the thermal analysis showed that at this temperature complete dehydration occurred.

No change in the number of components and relative intensity of the various transitions was, however, observed in the emission spectrum; this demonstrates unequivocally that the water molecule is of the outer-sphere type. Both from analytical and spectroscopic data there is little doubt that this complex consists of the EuO$_9$ chromophore acquired by three bidentate nitrate groups and one tridentate terpyO$_3$ molecule.

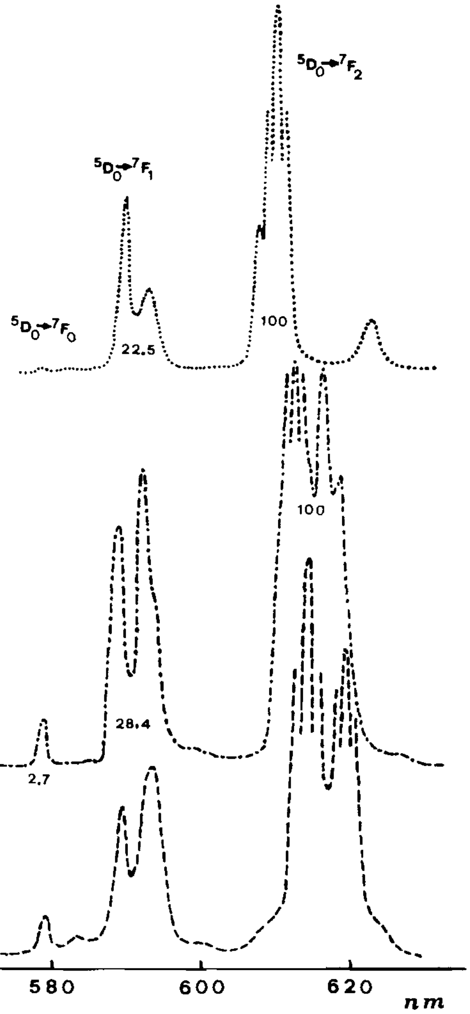

Fig. 1. Fluorescence spectra at 77 K of europium complexes with 2,2',2''-terpyridine-1,1',1''-trioxide (terpyO$_3$): (–·–·–) Eu(terpyO$_3$)(NO$_3$)$_3$·H$_2$O (solid); (·······) Eu(terpyO$_3$)$_3$(ClO$_4$)$_3$·2H$_2$O (solid); (– – –) Eu(terpyO$_3$)$_3$(ClO$_4$)$_3$·2H$_2$O (in methanol). Attribution and relative intensity (%) are also shown.

Two idealized geometries have been proposed for nonacoordinated polyhedra: the monocapped square antiprism (C_{4v}) and the tricapped trigonal prism (D_{3h}) [6]. D_{3h} symmetry does not allow the $^5D_0 \rightarrow {}^7F_0$ transition. The presence in the emission spectrum of a line associated with this transition agrees with C_{4v} (or C_4) site symmetry for the europium(III) ion. This symmetry, on the other hand, allows the $^5D_0 \rightarrow {}^7F_2$ transition with only two components, one non-degenerate and the other doubly degenerate. The $^5D_0 \rightarrow {}^7F_1$ transition should appear also as a singlet and a doublet.

The complex Eu(terpyO$_3$)$_3$(ClO$_4$)$_3$·2H$_2$O fluoresces both from $^5D_0$ and $^5D_1$ levels. A relatively intense

TABLE II. Partial Energy Level Scheme for Solid Europium(III) Complexes with 2,2',2''-Terpyridine-1,1',1''-Trioxide (terpyO_3). The Values Refer to the Baricenter of the Band Group (cm^{-1}, ±7).

Complex	$^7F_1$	$^7F_2$	$^7F_3$	$^7F_4$	$^5D_0$	$^5D_1$	η^a
$Eu(terpyO_3)(NO_3)_3 \cdot H_2O$	367	1044	1895	2641^b	17265	19048	3.52
$Eu(terpyO_3)_3(ClO_4)_3 \cdot 2H_2O$	355	889	1924	^{c}	17250	19008	4.45

^{a}See text. ^{b}±10 cm^{-1}. ^{c}Very weak.

line at 535. 0 nm with a shoulder at about 537 nm is associated with the $^5D_1 \rightarrow {}^7F_1$ transition while two weaker components of the $^5D_1 \rightarrow {}^7F_2$ transition appear at 551.3 and 563 nm. A line appears at 579.7 nm assigned to the $^5D_0 \rightarrow {}^7F_0$ transition; its intensity is, however, less than 1% the $^5D_0 \rightarrow {}^7F_1$ transition and it can be taken as forbidden. A line at 591.0 nm and a broader one at 593.3 nm are associated with the $^5D_0 \rightarrow {}^7F_1$ transition. A very intense line at 611.0 nm and a weak one at 609.5 nm arise from the $^5D_0 \rightarrow {}^7F_2$ transition; a weak component of this transition also appears as broad band centered at 623.2 nm. The $^5D_0 \rightarrow {}^7F_3$ consists of two weak and broad components appearing at 653 and 660 nm with a shoulder around 650 nm. The $^5D_0 \rightarrow {}^7F_4$ transition is very weak and does not offer useful information. So as the corresponding nitrate this complex does not show any significant change in the spectral patten when dehydrated. All data indicate that this complex also consists of nonacoordinated LnO_9 type arrangement acquired by three tridentate terpyO_3 molecules to form mono- or polymeric structure. The emission spectrum suggests D_{3h} (or D_6) site symmetry for the europium(III) ion in tricapped trigonal prismatic geometry. On the other hand, it is not possible, on the basis of these spectral data only, to exclude D_3 one. This complex is soluble in methanol, but solvolysis or destruction of polymeric species, whether existing, occurs. The appearance of a line at 579.6 nm ($^5D_0 \rightarrow {}^7F_0$ transition), change in splitting and intensity of the various $^5D_{0,1} \rightarrow {}^7F_{0-4}$ transitions indicate structural rearrangement and change in symmetry (Fig. 1).

No significant change in the relative intensity of the various transitions occurs for both complexes on lowering the temperature from 300 to 77 K. The intensity ratio ($^5D_0 \rightarrow {}^7F_2$)/($^5D_0 \rightarrow {}^7F_1$) ($\eta$) values are relatively high (Table II), but, remarkably lower than those measured for europium(III) bipyO_2 complexes [2]. Fluorescence intensity depends, also, on the probability that the resonance levels in the ion have to receive energy from the ligand. It is expected that the efficiency of the intramolecular energy transfer is increased the more covalent is the complex. Unless different internal radiationless processes occur, this increase corresponds, among the various transitions that occur between low J-values, in the $^5D_0 \rightarrow {}^7F_2$ transition probability and reflects increase in the intensity of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ and $^5I_8 \rightarrow {}^5G_6$ hypersensitive transitions in the corresponding neodymium and holmium complexes, respectively [7].

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