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Synthesis, characterization and study of compounds between hydrated lanthanide (III) perrhenates and 4-methylmorpholine-*N*-oxide (MMNO)

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Abstract

Complexes between hydrated lanthanide(III) perrhenate salts and the ligand MMNO were prepared following the stoichiometry $Ln(ReO_4)_3 \cdot (MMNO)_6$ (Ln=La, Nd, Eu, Er, Yb and Y). They were characterized by conductance measurements in acetonitrile, powder X-ray diffraction patterns, IR vibrational spectroscopy, Raman and electronic absorption spectroscopy.

Keywords: Lanthanide; Perrhenate; 4-Methylmorpholine-*N*-oxide

1. Introduction

4-Methylmorpholine-*N*-oxide is found in both anhydrous and monohydrated forms belonging to the monoclinic $P2_{1/n}$ and $P2_{1/c}$ systems, respectively, both structures are consistent with chair-conformation morpholine rings, with minor differences involving the nitrogen atom [1].

The main characteristics of the perrhenate ion are: possession of a heavy metal central atom, high molecular weight, formation of a strong acid in aqueous solution, high thermal stability and spectroscopic properties very similar to the perchlorate anion and, finally, to behave as both mono- or bidentate ligand towards the metal ion [2–4]. The studies of Claasen and Zielen [4] had shown that the perrhenate ion has a regular tetrahedron structure with Td symmetry and nine vibrational degrees of freedom distributed along four normal vibration modes. Vibrations ν_3 and ν_4 are IR active and all four modes are Raman active [5]. On coordination the perrhenate ion changes from ionic character to coordinate, lowering the Td symmetry to C_{3v} or C_{2v} according to the number of coordinated oxygen atoms. The lowering of the symmetry decomposes the degenerate vibrations turning active some IR inactive ones.

2. Experimental

The complexes were synthesized from the methanol solution under gentle heating of hydrated salts and MMNO in ethanol (molar ratio 1:6). The compounds were characterized by complexometric titration with EDTA [6], C, H, N microanalysis (Table 1), and conductance measurements using milimolar solutions of acetonitrile and methanol employing a Leeds and Northrup equipment. Cell conductivity was $K_c = 0.11597$ cm^{-1}. IR spectra were obtained in a Bomem FTIR MB-102 spectrophotometer using dispersions in nujol between CsI plates. Raman spectra were registered in an interferometric Bomem DAB-16 apparatus at 1064 nm. Absorption spectra (in solution) of the neodymium and erbium compounds were obtained on a Hitachi U-3000 spectrophotometer. Refraction indexes were measured in an Abbé type Bausch and Lomb refractometer. Emission spectra, both at 298 and 77 K, were measured in an adapted Hitachi/Perkin–Elmer MPF-4 spectrofluorimeter with a resolution of 0.5 nm. X-ray diffraction patterns (powder method) were determined in a PW1710 (Philips) diffractometer employing Cu Kα (1.5418 Å) radiation.

3. Results and discussion

Table 1 presents the analytical results compatible with

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Table 1
Analytical results and electrolytic conductance data for $[Ln(ReO_4)(MMNO)_6](ReO_4)_2$

Ln	%M		%C		%H		%N		Conductance, Δ_M^a	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Acetonitrile	Methanol
La	8.72	9.01	22.68	22.74	4.18	4.25	5.28	5.37	234	158
Nd	9.03	9.37	22.55	22.62	4.16	4.75	5.26	5.72	243	160
Eu	9.47	9.62	22.44	22.60	4.14	4.01	5.23	5.43	237	188
Er	10.32	10.47	22.23	22.44	4.10	4.19	5.19	5.23	257	183
Yb	10.64	10.76	22.15	22.32	4.09	4.21	5.17	5.27	239	170
Y	5.76	6.03	23.36	23.67	4.31	4.54	5.45	5.81	279	160

[a] Ω^{-1} cm^2 mol^{-1}.

the stoichiometry $Ln(ReO_4)_3 \cdot (MMNO)_6$ (Ln=La, Nd, Eu, Er, Yb and Y). Electrolytic conductances are in agreement with a 1:2 electrolyte behaviour, indicating a general formula $[Ln(ReO_4)(MMNO)_6](ReO_4)_2$ (Ln=La, Nd, Eu, Er, Yb and Y) in acetonitrile solution [7].

Vibrational spectroscopy (IR and Raman (R)) permits the identification of the coordination modes ν_1 (IR, R) and ν_2 (IR, R) indicating existence of mono-coordinated and non-coordinated ReO_4 group. The conductance data suggest that only one of them is coordinated (Table 2) [5].

Fig. 1 shows the absorption spectra of the compounds $Ln(ReO_4)_3 \cdot (MMNO)_6$ and $Ln(ReO_4)_3 \cdot (H_2O)_9$ (Ln=Nd

Table 2
Infrared (IR) and Raman (R) data of $[Ln(ReO_4)(MMNO)_6](ReO_4)_2$ compounds

Ln	Infrared (IR) and Raman (R) vibrational frequencies (cm^{-1}) of ReO_4^-									
	ν_1		ν_2		ν_3		ν_4		ν_6	
	IR	R	IR	R	IR	R	IR	R	IR	R
La	957	964	909	899	—	921	338	332	317	329
Nd	952	—	904	—	921	—	331	—	316	—
Eu	963	960	910	896	924	924	340	333	322	326
Er	952	—	911	—	—	—	332	—	317	—
Yb	956	965	909	896	933	925	336	336	320	—
Y	957	961	910	897	937	924	335	333	317	—

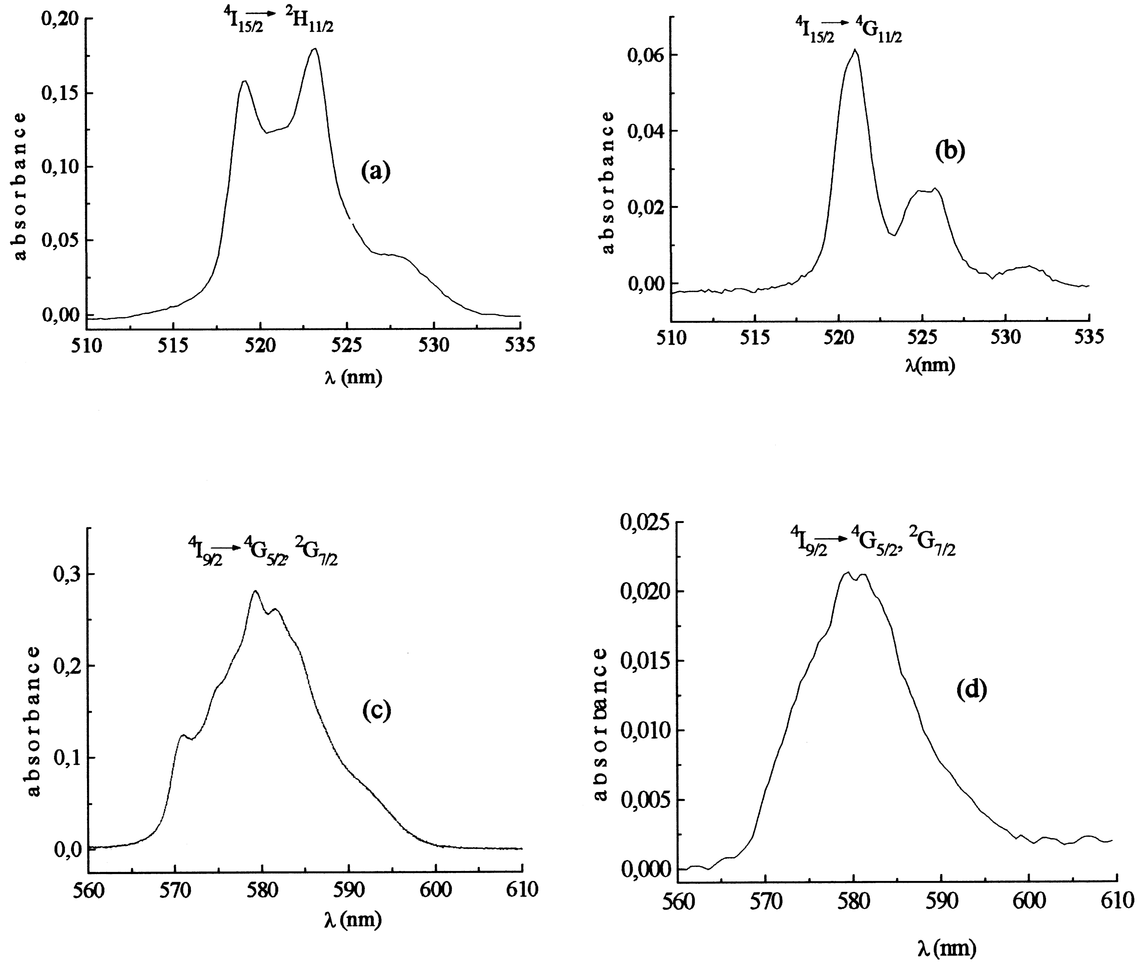

Fig. 1. Absorption spectra of compounds (a) $[Er(ReO_4)(MMNO)_6](ReO_4)_2$; (b) $Er(ReO_4)_3(H_2O)_9$; (c) $[Nd(ReO_4)(MMNO)_6](ReO_4)_2$; and (d) $Nd(ReO_4)_3(H_2O)_9$ at room temperature in methanolic solutions. Translations $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ for Nd(III) and $^4I_{15/2} \rightarrow {}^2H_{11/2}$ for Er(III).

Table 3
Spectroscopic parameters and oscillator strengths of $Ln(ReO_4)_3 \cdot (H_2O)_9$ and $Ln(ReO_4)_3 \cdot (MMNO)_6$ (Ln=Er and Nd), using $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ for Nd(III) and $^4I_{15/2} \rightarrow {}^2H_{11/2}$ for Er(III)

Complex	M ($\times 10^{-3}$)	β	δ	$b^{1/2}$	P ($\times 10^6$)
$Nd(ReO_4)_3(H_2O)_9$	8.07	0.992	0.806	0.0632	4.87
$[Nd(ReO_4)(MMNO)_6](ReO_4)_2$	7.49	0.995	0.503	0.0500	60.6
$Er(ReO_4)_3(H_2O)_9$	2.82	0.999	0.100	0.0224	5.34
$[Er(ReO_4)(MMNO)_6](ReO_4)2$	7.53	0.998	0.200	0.0316	60.5

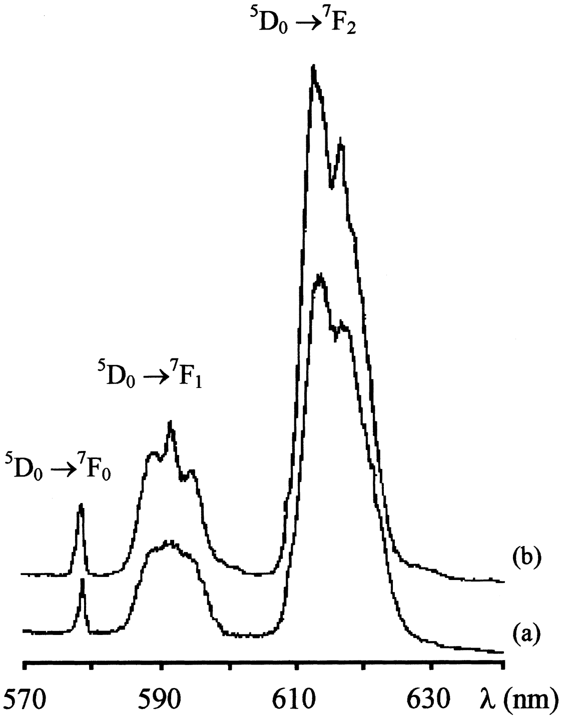

Fig. 2. Fluorescence spectra of $Eu(ReO_4)_3(MMNO)_6$ at (a) 298 and (b) 77 K.

and Er) in the 560–610 and 510–540 nm regions corresponding to the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ and $^4I_{15/2} \rightarrow {}^2H_{11/2}$ transitions. From Simpson's rule [8] it was possible to calculate the nefelauxetic parameter (β) [9], the covalency factor ($b^{1/2}$) [10] and Sinhas's parameter [11] (Table 3). The presence of six MMNO ligands and one ReO_4^- ion in the coordination sphere in substitution to nine water molecules (in the salts) implies considerable perturbation of the chemical environment. The calculated parameters show that the salt is much more ionic in character than the complexes.

The emission spectra at room temperature and 77 K are shown in Fig. 2. They are quite similar, with one peak for the $^5D_0 \rightarrow {}^7F_0$ transition, two peaks and a shoulder for $^5D_0 \rightarrow {}^7F_1$ and three peaks for $^5D_0 \rightarrow {}^7F_2$. Based on the number of peaks and coordination number (7) a microsymmetry C_{3v} is proposed around the europium ion [12]. From X-ray diffraction techniques (powder method) it is possible to observe two isomorphous series, one for the La, Nd, Eu and Er compounds and the other for Yb and Y.

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