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Lanthanide perrhenate complexes with δ-valerolactam: synthesis, characterization and structure

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Abstract

Complexes of the general formula $Ln(ReO_4)_3.8(VL)$ (Ln=Pr, Nd, Sm, Eu; VL=δ-valerolactam) and $Ln(ReO_4)_3.7(VL)$ (Ln=Tb) were synthesized and characterized by elemental analysis, infrared absorption spectroscopy, Raman spectroscopy, visible absorption spectroscopy (for the Nd complex), emission spectroscopy (for the Eu and Tb compounds) and single-crystal X-ray diffraction (for the Eu compound). These techniques provide evidence that the anions are not coordinated, as well as the fact that the valerolactams coordinate through their carbonyl oxygens. The metal–ligand bonds are essentially electrostatic. The symmetry of the coordination polyhedron in the Eu complex is D_{4d} (square antiprism). The compound is isomorphous with the corresponding perchlorate octa-coordinated complexes.

Keywords: Lanthanide; Perrhenate; δ-valerolactam

1. Introduction

Lanthanide complexes containing eight equal ligands have been described [1–3] and their coordination polyhedra are square antiprisms, sometimes with distortions [1]. The synthesis and characterization of δ-valerolactam complexes with lanthanide trifluoromethanesulfonate [4] and perchlorates [5] have been described. In the former, compounds of formula $Ln(CF_3SO_3)_3.8(VL)$ were obtained, while in the latter, $Ln(ClO_4)_3.8(VL)$, for Ln=La–Ho and $Ln(ClO_4)_3.7(VL)$, for Ln=Er–Lu. In order to study the behavior of this ligand with a heavier non-coordinating anion, as well as the spectroscopy of these complexes, this work involved the synthesis and characterization of δ-valerolactam complexes with lanthanide perrhenates (Ln=Pr, Nd, Sm, Eu and Tb).

2. Experimental

The complexes were synthesized by reaction of the ligand with the corresponding lanthanide perrhenates in ethanol. The precipitates were filtered, washed with ethanol and dried in vacuo. Slow evaporation of the solution of the Eu compound yielded the crystals used in the X-ray diffraction experiment.

The characterization of the compounds was carried out by elemental analysis; performed on a Perkin–Elmer 240 elemental analyzer, and titrations with EDTA, using Xylenol Orange as indicator. Infrared absorption spectra were recorded on a Nicolet FTIR-510 spectrometer, using Nujol mulls between KBr windows.

The Raman spectrum of the Pr compound (solid) was recorded on a Renishaw spectrometer, using a Coherent He–Ne laser at 632.8 nm for irradiation. The visible absorption spectrum of the Nd compound was recorded on a Zeiss DMR-10 spectrophotometer, using a silicone mull. Emission spectra of the Eu and Tb compounds were recorded on a Hitachi Perkin–Elmer MPF4 spectrofluorimeter. This equipment has a resolution better than 0.3 nm. X-ray single crystal diffraction analysis was performed on an Enraf–Nonius FR 590 diffractometer, using Mo Kα (λ=0.71073 Å) radiation, graphite monochromated. No calculations were necessary, since the Eu compound was found to be isomorphous to a previously studied substance.

3. Results and discussion

Table 1 displays the analytical data for the compounds synthesized. These data indicate the stoichiometries

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Table 1
Analytical data (%) for the complexes

Ln	Analysis							
	Lanthanide		Carbon		Hydrogen		Nitrogen	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
Pr	9.1	9.1	28.5	28.5	4.3	4.3	6.6	6.5
Nd	8.5	8.6	28.5	28.5	4.3	4.5	6.6	6.3
Sm	8.9	8.8	28.4	28.9	4.3	4.1	6.6	6.6
Eu	9.0	8.9	28.3	28.3	4.3	4.4	6.6	6.6
Tb	9.9	10.0	26.2	26.1	3.9	3.7	6.1	6.0

$Ln(ReO_4)_3.8(VL)$ for the Pr, Nd, Sm and Eu compounds (molecular formulae $C_{40}H_{72}N_8O_{20}Re_3Ln$) and $Ln(ReO_4)_3.7(VL)$ for the Tb compound.

Infrared absorption spectroscopy data for the Sm and Tb complexes show that the νCO bands are shifted towards lower wavenumbers (1622 cm^{-1} Sm, 1628 cm^{-1} for Tb) as compared to the free ligand (1665 cm^{-1}). On the other hand, the ReO_4 ν_3 vibration appeared at 915 cm^{-1} (Sm) and 916 cm^{-1} (Tb).

The Raman spectrum of the Pr compound (non-luminescent) showed the ν_2 band of ReO_4 at 350 cm^{-1}, as well as ν_4 at 335 cm^{-1}. This result, as well as the frequency values of the IR absorption bands in the Sm and Tb compounds, suggest that the ReO_4^- anions are non-coordinated, since for this case the expected values for these vibrational frequencies are 915, 350 and 311 cm^{-1} [5,6]. These results also evidence that the valerolactams are bonded through their carbonyl oxygens.

The visible absorption spectrum of the Nd compound at room temperature shows the hypersensitive $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ and $^2P_{1/2}$ transitions. From these absorption bands the parameters: nephelauxetic [7], $\beta=0.993$; covalence factor [8] $b^{1/2}=0.0592$ and Sinha's covalence parameter [9], $\delta=0.0705$ were calculated. The values of these parameters suggest an essentially electrostatic character for the metal–ligand bonds.

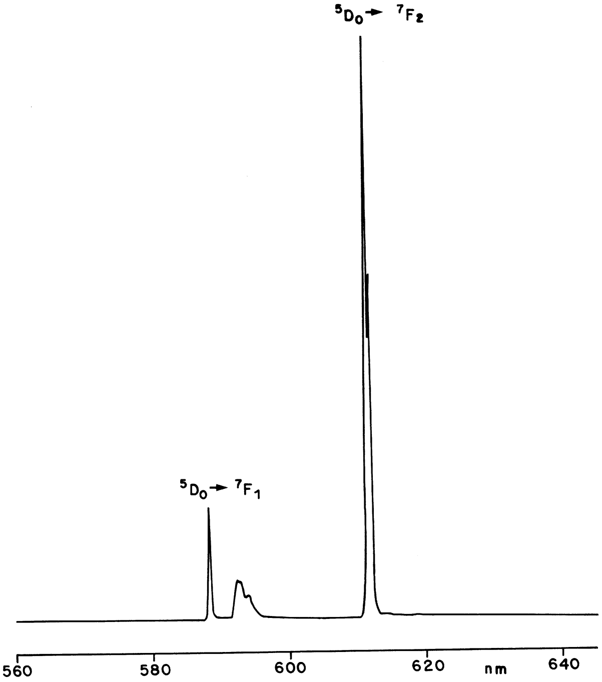

Fig. 1. Emission spectrum of the europium complex.

Emission spectra were recorded for the Eu and Tb compounds, the only ones to present luminescence. The Tb spectrum shows $^5D_4 \rightarrow {}^7F_J$ ($J=6$, 5, 4, 3) transitions.

The Eu emission spectrum at 77 K is shown in Fig. 1. The absence of a $^5D_0 \rightarrow {}^7F_0$ band; the presence of three $^5D_0 \rightarrow {}^7F_1$ peaks, due to one A_2 (magnetically allowed) and one E species (doubly degenerate, electrically allowed); the existence of two $^5D_0 \rightarrow {}^7F_2$ peaks, due to one E species (electrically allowed), suggest a D_{4d} symmetry for this compound [10] identical to the corresponding perchlorate complex [4].

Table 2 shows the unit cell parameters of the Eu compound, determined by single-crystal X-ray diffraction, compared to those of $Nd(ClO_4)_3.8(VL)$ [4]. As can be observed, the values are very similar (within experimental error), showing that the compounds are isomorphous, or, in other words, that also in this case the ligands are disposed in a D_{4d} symmetry (square antiprism) around the central ion.

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Table 2
Crystal parameters (X-ray single crystal diffraction)

Space group	$Nd(ClO_4)_3.8(VL)$ [4] $P2_1/n$	$Eu(ReO_4)_3.8(VL)$ (this work) $P2_1/n$
a (Å)	25.491(4)	25.549(4)
b (Å)	16.074(3)	15.781(4)
c (Å)	13.051(3)	13.599(4)
β (°)	90.15 (3)	90.22 (3)

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