

Mössbauer spectra of Eu(III) and Gd(III) complexes of phosphine oxides with chelating perchlorate

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Abstract The reaction of $\text{Ln}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$ with triphenylphosphine oxide (TPPO) in methanol has led to the formation of $[\text{Ln}(\text{ClO}_4)_2(\text{tppo})_4]\text{ClO}_4 \cdot \text{MeOH}$ ($\text{Ln} = \text{Nd}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Yb}$), in which the perchlorate anion acts as a symmetric bidentate. The emission spectra of Eu(III)-TPPO complexes, showing enhancement in the intensity due to the phenyl group, indicate an isotropic electron distribution for the nitrate complex $[\text{Eu}(\text{NO}_3)_3(\text{tppo})_2(\text{EtOH})]$. ^{151}Eu and ^{155}Gd Mössbauer spectra of the TPPO complexes also lead to the same conclusion.

Keywords Lanthanide complex · Phosphine oxide · Perchlorate complex · Emission spectra · Mössbauer spectra

1 Introduction

Phosphine oxides and organophosphates have been known as excellent synergistic coextractants for lanthanide and actinide ions. The coordination behavior of weakly coordinating anions is interesting in connection with the solvent extraction. Recently some actinide pertechnetate and perrehenate complexes have been obtained in the presence of phosphine oxides or organophosphate, an analogous condition to the PUREX process [1, 2]. Interestingly the coordination of triflate anion is also reported in the presence of phosphine oxide [3]. In this paper we have characterized the lanthanide perchlorate complexes carrying phosphine oxides using x-ray crystallography, emission spectra and ^{151}Eu and ^{155}Gd Mössbauer spectroscopy.

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2 Experimental

2.1 Preparation

$\text{Ln}(\text{ClO}_4)_3(\text{tppo})_4\text{MeOH}$ $\text{Ln}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$ (0.125 mmol) and TPPO (triphenylphosphine oxide; 139 mg, 0.500 mmol) were stirred in methanol (30 mL) for 1 h at room temperature. Ethanol (5 mL) was added and the solution was concentrated gently to yield a white crystalline powder. Eu complex: yield 125 mg, 63%. FAB-MS: $m/z = 1463$ $[\text{M} - \text{ClO}_4 - \text{MeOH}]^+$. Gd complex: yield:156 mg,79%. FAB-MS: $m/z = 1468$ $[\text{M} - \text{ClO}_4 - \text{MeOH}]^+$.

$\text{Ln}(\text{NO}_3)_3(\text{tppo})_2\text{EtOH}$ These complexes were prepared similarly starting from $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ [4].

2.2 Measurements

Emission and excitation spectra of CH_2Cl_2 solutions were recorded on a SPEX Fluorolog-3 (Horiba Jobin Yvon) at room temperature. X-ray diffraction data were collected on a SMART APEX (Bruker) fitted with monochromated Mo $\text{K}\alpha$ X-ray radiation at 173 K. The data were processed as routine.

^{151}Eu Mössbauer spectra were measured on a Wissel Mössbauer system (DFG-1200 and MDU-1200H) at 77 K using a $^{151}\text{Sm}/\text{SmF}_3$ source. ^{155}Gd Mössbauer spectra were measured using Wissel 1200 Mössbauer system (MDU-1200, DFG-1200, MVC-1200). Both the absorber (100 mgGd cm^{-2}) and the source ($^{155}\text{Sm}/\text{Pd}_3^{154}\text{Sm}$) were kept at 12 K [5].

3 Results and discussion

X-ray structural determinations show that $\text{Ln}(\text{ClO}_4)_3(\text{tppo})_4 \cdot \text{MeOH}$ with Ln = Nd, Eu, Gd, Dy, Yb are isostructural, indicating no change in coordination number across the 4f block. The crystal consists of $[\text{Ln}(\text{ClO}_4)_2(\text{tppo})_4]^+$, counter anion and solvated MeOH. $[\text{Gd}(\text{ClO}_4)_2(\text{tppo})_4]^+$ has a distorted dodecahedron configuration. Two perchlorate anions coordinate to Gd^{3+} symmetrically as a bidentate, and Gd–O bond lengths (253.4 pm in average) are longer than those of Gd–O_{tppo} (227.5 pm). Two GdO₂Cl chelate planes are almost orthogonal (dihedral angle = 88.4°). The electrospray mass spectra of the methanol solutions of the complexes suggest retention of coordinated ClO_4^- . The nine-coordinate complex $\text{Gd}(\text{NO}_3)_3(\text{tppo})_2 \cdot \text{EtOH}$ is isostructural to the Eu(III) complex [6].

Figure 1 shows the excitation and emission spectra of Eu complexes in CH_2Cl_2 at room temperature. Hereafter we use the abbreviation Ln-L-X showing lanthanide centre (Ln), phosphine oxide (L), and coordinating anion (X). In the excitation spectra monitored at $\lambda = 614$ (nitrate complex) and 617 nm (perchlorato complexes), maxima are observed at 248 and 280 nm (Eu-tppo- ClO_4), 248 and 278 (Eu-tppo- NO_3), and 243 nm (Eu-tbpo- ClO_4 ; tbpo = tributylphosphine oxide). The λ_{max} around 243–248 and 278–280 nm are assigned to $n-\pi^*$ and $\pi-\pi^*$, respectively, which are in good agreement with λ_{max} of absorption spectra of these complexes. In the emission spectra, a strong antenna effect of phenyl group was observed while

Fig. 1 Excitation and emission spectra of Eu-tppo-ClO₄, Eu-tppo-NO₃ and Eu-tbpo-ClO₄ in CH₂Cl₂ solution at room temperature

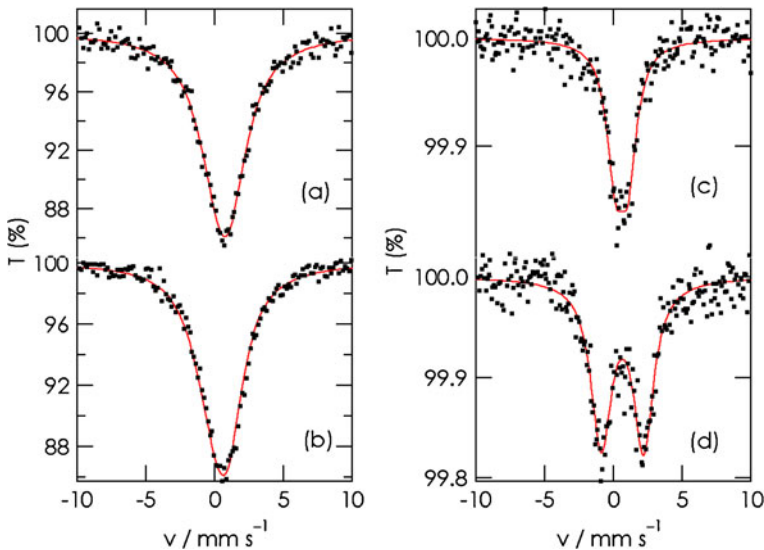
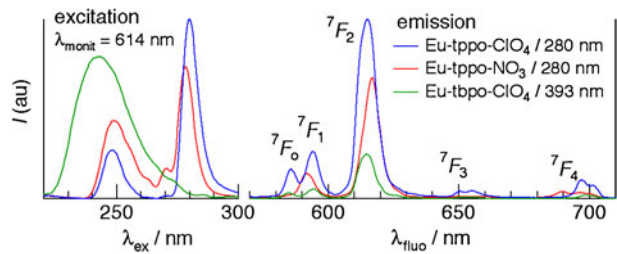


Fig. 2 ¹⁵¹Eu (left) and ¹⁵⁵Gd Mössbauer spectra (right) of Ln-tppo-ClO₄ and Ln-tppo-NO₃. **a** Eu-tppo-NO₃, **b** Eu-tppo-ClO₄, **c** Gd-tppo-NO₃, **d** Gd-tppo-ClO₄

that of P=O group was not so effective. The red emissions are the transitions of ⁵D₀ → ⁷F_j of Eu³⁺ centre. The spectrum of Eu-tppo-NO₃ is slightly different from those of Eu-tppo-ClO₄ and Eu-tbpo-ClO₄. The emission to ⁷F₀ almost disappears in Eu-tppo-NO₃, suggesting high symmetry at the Eu(III) centre. The emission spectrum of solid state Eu-tppo-NO₃ does not show ⁵D₀ → ⁷F₀ transition either.

Figure 2 shows the ¹⁵¹Eu Mössbauer spectra of Eu complexes at 77 K. The parameters are summarized in Table 1. Both the spectra are slightly asymmetric. The quadrupole coupling constant (e^2qQ) values are 5.36 and 3.68 mm s⁻¹ for Eu-tppo-ClO₄ and Eu-tppo-NO₃, respectively, suggesting higher symmetry in the nitrate complex. ¹⁵⁵Gd Mössbauer spectroscopy is more informative. The isomer shift values (δ) are those of eight or nine oxygen-coordinated Gd(III) complexes [7]. Gd-tppo-NO₃ shows a quite small e^2qQ value. Since Gd³⁺ has a half-filled 4f subshell, we may expect a large contribution of a lattice term to the electric field gradient V_{zz} . A quite small e^2qQ value of 1.99 mm s⁻¹ clearly indicates that the electron distribution around the Gd³⁺ atom is much isotropic in Gd-tppo-NO₃. This observation agrees with the results of emission spectra of the Eu(III) complexes.

Table 1 ^{151}Eu and ^{155}Gd Mössbauer parameters. Asymmetric parameter is fixed to be zero

	^{151}Eu parameters at 77 K				^{155}Gd parameters at 12 K			
	δ^a	e^2qQ	Γ_{exp}	V_{zz}	δ^b	e^2qQ	Γ_{exp}	V_{zz}
	mm s^{-1}	mm s^{-1}	mm s^{-1}	10^{21}V m^{-2}	mm s^{-1}	mm s^{-1}	mm s^{-1}	10^{21}V m^{-2}
Ln-tppo-ClO ₄	0.20	5.36	2.19	3.37	0.67	6.63	1.76	3.66
Ln-tppo-NO ₃	0.30	3.68	2.59	2.32	0.61	1.99	1.50	1.10

^arelative to EuF₃ at room temperature, ^brelative to $^{155}\text{Sm}/\text{SmPd}_3$ source

Since Gd(III) and Eu(III) complexes are isostructural, we may compare the V_{zz} values directly. The V_{zz} value of Gd-tppo-ClO₄ agrees very well with that of Eu-tppo-ClO₄. However that of Eu-tppo-NO₃ ($2.32 \times 10^{21} \text{V m}^{-2}$) is obviously larger than that of Gd-tppo-NO₃ ($1.10 \times 10^{21} \text{V m}^{-2}$). This difference may arise from a small unignorable orbital contribution of Eu(III) atom having a hole in the 4f subshell.

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