Magnetic susceptibilities of lanthanide(III)–CMPO complexes and lanthanide(III) oxalate complexes

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Abstract

Lanthanide(III)-CMPO complexes with nitrate ion as counter-ion and lanthanide(III)-oxalate complexes were synthesized. The former complexes were identified as $Ln(NO_3)_3 \cdot 3CMPO$ for La(III), Ce(III), Pr(III) and Nd(III), whereas $Ln(NO_3)_3 \cdot 2CMPO$ were formed for Sm(III), Eu(III) and Gd(III). The latter were identified as $Ln_2(C_2O_4)_3 \cdot 9H_2O$ for complexes of La(III) and Ce(III), and as $Ln_2(C_2O_4)_3 \cdot 10H_2O$ for Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III). From the dependence of magnetic susceptibility on temperature in the range from room temperature to liquid nitrogen, the effective numbers of the Bohr magneton were estimated as 1.9, 2.9, 2.8 and 7.9 for Ln(III)-CMPO complexes and 1.9, 3.2, 2.6 and 8.3 for Ln(III)-oxalate complexes, (Ln:Ce, Pr, Nd and Gd) respectively.

1. Introduction

Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) employed in the TRUEX process [1] can extract trivalent actinides, Am(III) and Cm(III), which are hardly recovered by TBP from a solution of HNO₃ or HCl. Magnetic susceptibility is one of the most important properties as regards future application of superconducting technology for spent fuel reprocessing. It is important to investigate the magnetic properties of complexes of the lanthanide series because the results obtained can be used to substitute for the actinide series due to the similarity between the two series. In the present study, Ln(III)-CMPO complexes with nitrate ions as counter-ion were synthesized and their magnetic susceptibilities were measured. Moreover, since oxalic acid can form complex compounds under strongly acidic conditions, Ln(III)-oxalate complexes were synthesized and their magnetic susceptibilities were also measured for comparison.

2. Experimental details

Octyl (phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) purchased from M&T Chemicals Inc. was used without further purification. Hydrated lanthanide(III) nitrate, oxalic acid dihydrate, ethanol and other materials were reagent grade.

Lanthanide(III)-CMPO complexes (Ln: La, Ce, Pr, Nd, Sm, Eu and Gd) were synthesized by mixing

hydrated lanthanide(III) nitrate and excess CMPO in ethanol and stirring for 1 h at room temperature. After evaporating the ethanol, the complexes were recrystallized from either diethylether/*n*-pentane or diethylether/*n*-heptane.

Lanthanide(III)-oxalate complexes (Ln: La, Ce, Pr, Nd, Sm, Eu and Gd) were synthesized by mixing 1 N HNO₃ solution containing hydrated lanthanide(III) nitrate and an aqueous solution containing (COOH)₂·2H₂O and stirring for 1 h at room temperature. Further, the pH of the mixture was adjusted to 2 by addition of ammonia. After the precipitates produced were filtered under suction, they were washed with water and dried under a vacuum desiccator.

Microanalysis for carbon, hydrogen and nitrogen was performed using a Yanagimoto CHN corder. The magnetic susceptibility measurement was carried out with a Faraday-type torsion magnetometer from 77 K to room temperature at 0.6 T on the samples sealed into a quartz tube. Corrections for the diamagnetism of the ligand were made using Pascal's constants. Infrared spectra of CMPO complexes of lanthanide(III) were obtained by the KBr method using a Japan Spectroscopic Co. Ltd IRA-2. NMR spectra for an Ln(III)–CMPO complex in CDCl₃ solution were recorded with a JEOL JNM GSX-400 spectrometer operating at room temperature.

3. Results and discussion

The elemental analytical data revealed that the empirical formulae of Ln(III)-CMPO complexes are



Fig. 1. Temperature dependence of magnetic susceptibility for lanthanide(III)-CMPO complexes.

Ln(NO₃)₃·3CMPO for La(III), Ce(III), Pr(III) and Nd(III), and Ln(NO₃)₃·2CMPO for Sm(III), Eu(III) and Gd(III). The analytical values of these compounds agreed with the theoretical values of the assumed chemical formula with an accuracy better than 2%. For Ln(III)–CMPO complexes, infrared spectra show absorption bands at about 1590 cm⁻¹ and 1150 cm⁻¹, which are assigned to carbonyl and phosphoryl stretches by comparison with ν (C=O) and ν (P=O) of free CMPO, respectively. These low frequency shifts of carbonyl and phosphoryl groups on complexation suggest that the



Fig. 2. Temperature dependence of magnetic susceptibility for lanthanide(III)-oxalate complexes.

lanthanide ions interact with both carbonyl and phosphoryl groups of CMPO ligand in the bidentate coordination mode.

The ³¹P NMR spectrum shows a singlet signal at 46.4, 67.9, 104.6, 98.6, 51.52 and -32.5 ppm relative to D₃PO₄ for La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Eu(III), respectively. These resonances are downfield or upfield from that of free CMPO, 39.4 ppm. Any resonance for Gd(III) was not observed owing to its large electronic spin. The ¹³C NMR for Ln(III)–CMPO complexes shows signals at 167.3, 172.4

Compound	$\chi_{\mathfrak{m}}(\mathrm{emu} \mathrm{mol}^{-1})$ (×10 ³)	$\mu_{\rm eff/Ln^{3+}}$	θ	$g\sqrt{J(J+1)}$
La(NO ₃) ₃ ·3CMPO	Diamagnetic	_	_	0
Ce(NO ₃) ₃ ·3CMPO	2	1.9	6	2.54
Pr(NO ₃) ₃ ·3CMPO	12	2.9	-3	3.58
Nd(NO ₃) ₃ ·3CMPO	6	2.8	2	3.62
Sm(NO ₃) ₃ ·2CMPO	2	_		(0.84)
Eu(NO ₃) ₃ ·2CMPO	4	_	-	(0)
Gd(NO ₃) ₃ ·2CMPO	25	7.9	-2	7.94
$La_2(C_2O_4)_3 \cdot 9H_2O$	Diamagnetic	-	-	0
$Ce_2(C_2O_4)_3 \cdot 9H_2O$	2	1.9	13	2.54
$Pr_2(C_2O_4)_3 \cdot 10H_2O$	10	3.2	25	3.58
$Nd_2(C_2O_4)_3 \cdot 10H_2O$	7	2.6	10	3.62
$Sm_2(C_2O_4)_3 \cdot 10H_2O$	1	_	-	(0.84)
$Eu_2(C_2O_4)_3 \cdot 10H_2O$	5	_	-	(0)
$Gd_2(C_2O_4)_3 \cdot 10H_2O$	50	8.3	2	7.94

TABLE 1. Magnetic data for complexes of lanthanide(III) with CMPO and oxalate

 χ_m : molar magnetic susceptibility at room temperature

 $\mu_{\text{eff}/\text{Ln}^{3+}}$: effective number of Bohr magneton per Ln³⁺

 θ : Weiss' constant defined as $\chi_m = C/(T-\theta)$

J: quantum number of total angular momentum, g: g value.

and 167.6 ppm relative to TMS, which are assigned to the carbonyl carbon, for La(III), Ce(III) and Sm(III) respectively. These resonances are downfield from that of free CMPO, 165.90 ppm. Concerning other Ln(III)--CMPO complexes any signals assignable to carbonyl carbon are not detected. In addition, resonances were observed for each carbon environment in the isobutyl, *n*-octyl, phenyl and bridging methylene groups. These downfield and upfield shifts in the ³¹P and ¹³C NMR spectra also support the participation of carbonyl and phosphoryl groups in bond.

The elemental analytical data suggested that the chemical formulae of Ln(III)-oxalate complexes are $Ln_2(C_2O_4)_3 \cdot 9H_2O$ for complexes of La(III) and Ce(III), and are $Ln_2(C_2O_4)_3 \cdot 10H_2O$ for complexes of Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III). The analytical values of these compounds agreed with the theoretical values of the assumed chemical formula with an accuracy better than 2%.

Figures 1 and 2 show the dependence of magnetic susceptibility on temperature for complexes of Ln(III) with CMPO and oxalate respectively. Complexes of Ce(III), Pr(III), Nd(III) and Gd(III) with CMPO and oxalate show paramagnetism following the Curie–Weiss law. On the contrary, complexes of Sm(III) and Eu(III) show rather temperature independent paramagnetism caused by thermal distribution of electron spin to excited states, giving rise to the second Zeeman effect as a

result of the mixing of excited states in the ground state. Complexes of La(III) are diamagnetic. The magnetic data are summarized in Table 1. The values of μ_{eff} for both complexes of Ln(III) with CMPO and oxalate are less than the theoretical values except for complexes of Gd(III). This suggests that a 4f electron is affected by the ligand field of CMPO and oxalate, leading to an orbital reduction. In the CMPO complex, both functional groups, carbonyl and phosphoryl groups, strongly coordinate to lanthanide(III) ions.

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