

# NMR study of chemical species extracted and ligand-exchange reaction in the lanthanide(III)(NO<sub>3</sub>)<sub>3</sub>-CMPO system

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## Abstract

Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) is used in the TRUEX process. <sup>31</sup>P and <sup>13</sup>C NMR measurements were carried out to study the behavior of coordination of Ln(III)-CMPO complexes and the ligand exchange reaction for Eu(III) and Gd(III)-CMPO systems. It was found that CMPO molecules locate in the equatorial region with respect to the magnetic axis of the Ln<sup>III</sup> ions and they coordinate to the central Ln<sup>III</sup> ions in a bidentate manner with Ln<sup>III</sup>...O=P and Ln<sup>III</sup>...O=C. Although several isomers for Ln(III)-CMPO complexes co-exist in CDCl<sub>3</sub>, a rapid intramolecular interconversion occurs at room temperature. The numbers of CMPO molecules coordinated to Eu<sup>III</sup> and Gd<sup>III</sup> ion were estimated to be 3 and 2, respectively, in CDCl<sub>3</sub> solution. The kinetic parameters, Δ*H*<sup>\*</sup> and Δ*S*<sup>\*</sup> for the ligand exchange reactions were evaluated. These ligand exchange reactions seem to proceed through a dissociative (D) mechanism.

## 1. Introduction

Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide, CMPO, is used as an extractant substituted for TBP in the TRUEX process [1] for a generic transuranic element extraction. CMPO can extract not only quadrivalent and hexavalent actinides but also trivalent actinides such as Am<sup>III</sup> and Cm<sup>III</sup>, which are poorly recovered by TBP, from a wide concentration range of HNO<sub>3</sub>. The extraction chemistry of CMPO is generally explainable by the basic properties of the phosphoryl group, the intramolecular buffering effect and the induced and steric effects of substituent groups [2]. However, there are few studies concerned with the behavior of CMPO in solution. In this work, the coordination behavior and the ligand exchange reaction of lanthanide(III)-CMPO systems were studied by NMR, magnetic susceptibility and infrared absorption measurements.

## 2. Experimental details

### 2.1. Materials

Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO), purchased from M&T Chemical Inc., was used without further purification. Hydrated lanthanide(III) nitrate and other materials were reagent

grade. The lanthanide(III)(NO<sub>3</sub>)<sub>3</sub>-CMPO complexes were synthesized as described previously [3]. The empirical formulae of lanthanide(III)(NO<sub>3</sub>)<sub>3</sub>-CMPO complexes were found to be Ln(NO<sub>3</sub>)<sub>3</sub>·3CMPO for La, Ce, Pr and Nd, and Ln(NO<sub>3</sub>)<sub>3</sub>·2CMPO for Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb, by elemental analysis.

### 2.2. NMR measurements

The NMR spectra were recorded on a JEOL-JNM-GSX 400 NMR spectrometer, operating at 161.8 MHz for <sup>31</sup>P and 100.4 MHz for <sup>13</sup>C, with an internal deuterium lock (CDCl<sub>3</sub>). <sup>31</sup>P and <sup>13</sup>C NMR chemical shifts were measured relative to 85% (v/v) D<sub>3</sub>PO<sub>4</sub>/D<sub>2</sub>O as an external reference and TMS as an internal reference, respectively. The assignments of <sup>13</sup>C NMR signals for free CMPO and its complexes, Ln(NO<sub>3</sub>)<sub>3</sub>·3CMPO (Ln: La, Ce, Pr, Nd) were performed using C-H COSY 2D-NMR and DEPT spectra. The solution used for NMR line broadening measurements was prepared by weighing out a given amount of Ln(NO<sub>3</sub>)<sub>3</sub>·2CMPO (Ln: Eu and Gd) in a 5-ml volumetric flask and adding the appropriate amount of CMPO and CDCl<sub>3</sub>. The concentration of lanthanide(III)-CMPO complex was approximately 0.2 mol l<sup>-1</sup>. The longitudinal relaxation time *T*<sub>1</sub> was determined using an inversion recovery method with the 180°-τ-90° pulse sequence. The relaxation time *T*<sub>1</sub> for the lanthanide(III)-CMPO complexes was corrected for the diamagnetic contribution by that of La(NO<sub>3</sub>)<sub>3</sub>·3CMPO complex. The transverse

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relaxation time  $T_2$  was obtained from the linewidth at half-height from the relation  $1/T_2 = \pi\Delta\nu_{1/2}$ .

### 2.3. IR measurement

IR spectra were recorded on IRA-2 in the range from 4000 to 400 cm<sup>-1</sup>.

### 2.4. Magnetic susceptibility measurement

The magnetic susceptibility was measured with a Faraday-type torsion magnetometer from 77 K to room temperature at 0.7 T on samples sealed in a quartz tube.

## 3. Results and discussion

### 3.1. Coordination structure of lanthanide(III)(NO<sub>3</sub>)<sub>3</sub>-CMPO complexes in solution

Lanthanide-induced-shifts,  $\Delta_{\text{obsd}}$ , consist of a contact shift and a pseudocontact shift,

$$\Delta_{\text{obsd}} = \Delta_c + \Delta_{\text{pc}} \quad (1)$$

where  $\Delta_{\text{obsd}}$  needs to be corrected for any contributions caused by the complexation, that is, by subtracting the measured shifts for a diamagnetic La(III) complex. The contact shift,  $\Delta_c$ , is proportional to the spin expectation value,  $\langle S_z \rangle$ , of the paramagnetic lanthanide(III) ions and the hyperfine coupling constant,  $A$ , while the pseudocontact shift,  $\Delta_{\text{pc}}$ , is proportional to a magnetic constant,  $D$ , characteristic of each lanthanide(III) ion, and a term  $(A_2^0G + A_2^2G')$  dependent on the geometry of the nucleus. When lanthanide(III) complexes have an axial symmetry, or an internal reorientation in the complexes occurs, the pseudocontact shift is proportional to  $G$  [4].

In order to deduce the structure of lanthanide(III) complexes, the separation of the observed lanthanide-induced shifts (LIS) into contact and pseudocontact components must be achieved. Reilly's method [5] for this purpose relies upon a linear least-square analysis of the LIS data by eqn. (2) rearranged from eqn. (1).

$$\frac{\Delta_{\text{obsd}}}{D} = A \frac{\langle S_z \rangle}{D} + (A_2^0G + A_2^2G') \quad (2)$$

If the experimental LIS data fit eqn. (2) with a high degree of confidence, the lanthanide complexes under consideration will have axial symmetry or become axially symmetric as a result of intramolecular motions or rearrangements. Figure 1 shows plots of the <sup>31</sup>P LIS data for Ln(NO<sub>3</sub>)<sub>3</sub>·*q*CMPO (*q*=2 or 3) according to eqn. (2). As shown in Fig. 1, the observed LIS data are divided into two groups, the one containing the lighter lanthanide(III) complexes with the value of *q*=3 and the other the heavier lanthanide(III) complexes with the value of *q*=2. Since both linear relations have

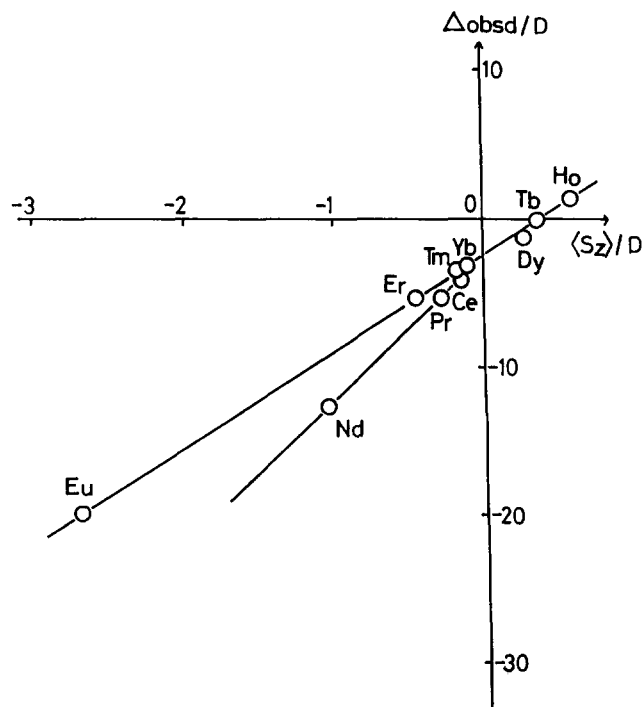


Fig. 1. A plot of  $\Delta_{\text{obsd}}/D$  versus  $\langle S_z \rangle/D$  for <sup>31</sup>P NMR chemical shifts of lanthanide(III)-CMPO complexes in CDCl<sub>3</sub>.

a high degree of confidence (their correlation coefficients  $R=0.999$ ), these shifts conform to the axially symmetric model. Moreover, it is seen that the slopes of the two subgroups are considerably different from each other, suggesting that the difference in the *q* value gives rise to a significant change in the hyperfine coupling constant, that is, the spin density at the phosphorus atom in coordinated CMPO. The negative sign of intercept,  $A_2^0G$ , for both subgroups of lanthanide(III)-CMPO complexes indicates that the phosphorus atoms lie in the equatorial region with respect to the principal magnetic axis.

Since lanthanide(III)-CMPO complexes appear to be axially symmetric, the geometrical factors (*r*,  $\theta$ ) of the atom of a CMPO molecule can be estimated from the following relationship:

$$\Delta_{\text{pc}} = (A_2^0G)D = - \frac{2\langle r_e^2 \rangle \langle A_2^0 \rangle \beta^2}{60(kT)^2} \frac{3 \cos^2\theta - 1}{r^3} D' \quad (3)$$

where  $\langle r_e^2 \rangle$  is the expectation value of the square radius of a 4f orbital,  $\langle A_2^0 \rangle$  is the crystal field parameter,  $\beta$  is the Bohr magneton,  $k$  is the Boltzman constant,  $D'$  is so-called "Bleaney factor" and  $\theta$  is the angle between the vector of length *r* joining the nucleus to the metal ion and the principal axis of symmetry. Once the distance between the observed nucleus and lanthanide(III) ion, *r*, is estimated by an approximate method, the angle  $\theta$  can be calculated according to eqn. (3).

In this study, *r* was elucidated by measuring the longitudinal relaxation time ( $T_{1m}$ ) for lanthanide(III)-

CMPO complexes. Concerning the paramagnetic lanthanide(III)-complexes except for Gd<sup>III</sup>,  $r$  is related to  $T_{1m}$  [6] by

$$\frac{1}{T_{1m}} = \frac{4(\mu_0/4\pi)^2 \gamma_N^2 \mu_{\text{eff}}^2 \beta^2 T_e}{3r^6} \quad (4)$$

where  $(\mu_0/4\pi)$  is the magnetic permeability under vacuum)  $\gamma_N$  is the gyromagnetic ratio of the observed nucleus and  $T_e$  is the relaxation time of electron spin of the lanthanide(III) ion. The obtained geometrical factors are shown in Table 1 together with  $T_{1m}$  and  $\mu_{\text{eff}}$  which was estimated by the dependence of the magnetic susceptibility on temperature. It is seen that the phosphorus atoms of CMPO are located at an angle of approximately 60° with respect to the principal axis at a distance of 3.1–3.3 Å from the central lanthanide(III) ions. The distance of Ce<sup>III</sup>-P (3.34 Å) is nearly equal to that of Ce<sup>III</sup>-C(carbonyl) (3.12 Å), resulting in that CMPO coordinates to Ce<sup>III</sup> ion in a bidentate manner in CDCl<sub>3</sub>. This is consistent with the observation in the IR spectrum of Ce(NO<sub>3</sub>)<sub>3</sub>·3CMPO that the phosphoryl and carbonyl stretching frequencies, 1178 and 1614 cm<sup>-1</sup>, of free CMPO decrease by 26 and 21 cm<sup>-1</sup>, respectively, on complexation, indicating that the Ce<sup>III</sup> ion is bonded to both the phosphoryl and carbonyl oxygens. Moreover, the IR spectrum of Ce(NO<sub>3</sub>)<sub>3</sub>·3CMPO exhibits absorption bands at 1490, 1290 and 1030 cm<sup>-1</sup>, which are assigned to  $\nu_4$ ,  $\nu_1$  and  $\nu_2$  vibrations of coordinating nitrate ion. It is difficult to know whether nitrate ion coordinates to Ce<sup>III</sup> ion in a monodentate manner or in a bidentate manner. In any case, the coordination number is in the range 8–10 for Ce(NO<sub>3</sub>)<sub>3</sub>·3CMPO. In addition, from the dependence of <sup>31</sup>P NMR spectra for Nd(NO<sub>3</sub>)<sub>3</sub>·3CMPO and Er(NO<sub>3</sub>)<sub>3</sub>·2CMPO on temperature (10, -10 and -30 °C), a single resonance at room temperature splits into several resonances at low temperature in both spectra. These suggest that several isomers appear in CDCl<sub>3</sub> due to the bidentate mode of coordination of the unsymmetrical CMPO. At the higher temperature region, a rapid intramolecular interconversion in lan-

thanide(III)-CMPO complexes occurs and the first coordination sphere of lanthanide(III)-CMPO complexes is considerably fluxional in solution.

### 3.2. Ligand exchange reaction in the lanthanide(III)-CMPO systems

Figure 2 shows the <sup>31</sup>P NMR spectra of Eu(III)-CMPO solutions prepared by dissolving hydrated Eu(NO<sub>3</sub>)<sub>3</sub> and CMPO into CDCl<sub>3</sub>, together with that of Eu(NO<sub>3</sub>)<sub>3</sub>·2CMPO. In all spectra with excess CMPO, two signals are observed, the one at downfield (40 ppm) is assigned to free CMPO and the other at upfield (-52 and -58 ppm) to coordinated CMPO. The behavior of <sup>31</sup>P NMR signals for Eu(III)-CMPO solutions shows that CMPO exchange is slow with respect to the <sup>31</sup>P NMR time scale. Under the conditions (B), (C) and (D), where the concentration of free CMPO is much higher than that of Eu(NO<sub>3</sub>)<sub>3</sub>, the ratios of the integrated areas for the free CMPO and the coordinated CMPO are equal to those expected for the case where Eu(NO<sub>3</sub>)<sub>3</sub>·3CMPO is the dominant chemical species. For spectrum (A), the ratio of the integrated resonance areas for the free CMPO and the coordinated CMPO suggests that the species like Eu(NO<sub>3</sub>)<sub>3</sub>·2CMPO coexists with Eu(NO<sub>3</sub>)<sub>3</sub>·3CMPO. Then, the <sup>31</sup>P NMR chemical shift, -52 ppm, for (A) is different from the -58 ppm for (B), (C) and (D). Consequently, the number of CMPO molecules coordinated to the Eu<sup>III</sup> ion,  $q$ , is 3 in the presence of excess CMPO.

For the Gd(III)-CMPO system, it is impossible to determine the value of  $q$  from the ratio of the integrated resonance areas for the free CMPO and the coordinated CMPO because the signal of coordinated CMPO cannot be observed due to extensive line broadening. Therefore, in this study, the value of  $q$  was estimated by lanthanide-induced relaxation enhancement (LIRE) measurement. When a ligand coordinates to a Gd<sup>III</sup> ion,  $q$  is related to the observed longitudinal relaxation time  $T_1$  given by eqn. (5) [7]:

$$(T_1)^{-1} = (1-pq)T_{1f}^{-1} + pq(T_{1m} + \tau_m)^{-1} \quad (5)$$

where  $p$  is the fraction of coordinated ligand,  $\tau_m$  is the lifetime of ligand in the first coordination sphere, and  $T_{1f}$  and  $T_{1m}$  are the longitudinal relaxation time of the free ligand and the coordinated ligand, in the absence of chemical exchange. The value of  $T_{1m}$  was estimated by

$$(T_{1m})^{-1} = (2/5)(\mu_{\text{eff}}\beta\gamma_P)^2\tau_R/r_{\text{Gd-P}}^6 \quad (6)$$

where  $\tau_R$  is the reorientational correlation time of the electron spin-nuclear spin vector,  $\mu_{\text{eff}}$  is the effective number of Bohr magnetons,  $\beta$  is the Bohr magneton,  $\gamma_P$  is the gyromagnetic ratio of <sup>31</sup>P,  $r_{\text{Gd-P}}$  is the distance between the Gd<sup>III</sup> ion and the <sup>31</sup>P nucleus under consideration. According to eqns. (5) and (6), the value

TABLE 1. Geometrical factors ( $r$ ,  $\theta$ ),  $T_{1m}$  and  $\mu_{\text{eff}}$  for lanthanide(III)-CMPO complexes

Ln <sup>III</sup>	Atom	$r$ (Å)	$\theta$ (°)	$T_{1m}$ (ms)	$\mu_{\text{eff}}$
Ce <sup>III</sup>	$\overline{P=O}$	3.34	57.5	193	1.9
	$\overline{C-CH_2-P}$	3.08	55.3	113	1.9
	$\overline{C=O}$	3.12	55.1	377	1.9
	$\overline{P-CH_2(\alpha)}$	3.11		146	1.9
Nd <sup>III</sup>	$\overline{P=O}$	3.13	57.0	57	2.8
Tm <sup>III</sup>	$\overline{P=O}$	3.22	57.6	5	6.1
Yb <sup>III</sup>	$\overline{P=O}$	3.17	57.5	28	3.7

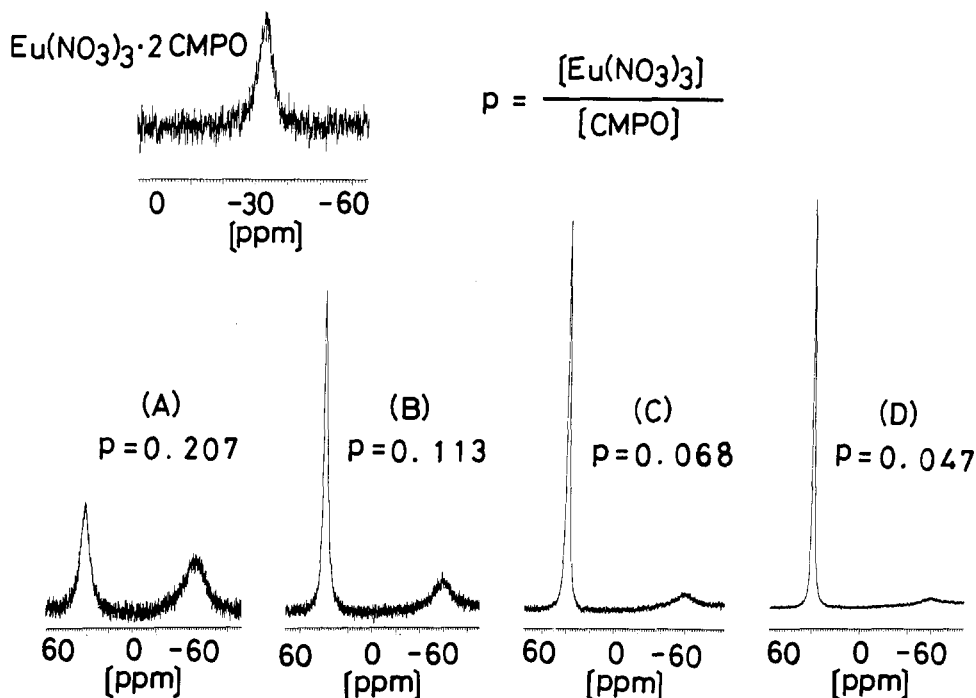


Fig. 2. <sup>31</sup>P NMR spectra of Eu(NO<sub>3</sub>)<sub>3</sub>·2CMPO and the Eu(III)-CMPO system in CDCl<sub>3</sub> (25 °C).

of  $q=2$  gives rise to a distance  $r_{\text{Gd-P}}=3.3 \text{ \AA}$ , while  $q=3$  gives  $3.6 \text{ \AA}$ . The former value appears to be reasonable for the distance  $r_{\text{Gd-P}}$  in lanthanide(III)-CMPO complexes, which was discussed in the previous section. Therefore, here we take  $q=2$  for the Gd<sup>III</sup>-CMPO system.

The line broadening method developed by Swift and Connick [8] was used to determine the kinetic parameters of ligand exchange reactions for Eu(III) and Gd(III)-CMPO systems. The observed transverse relaxation time,  $T_{2p}$ , is given by

$$(T_{2p})^{-1} = \frac{pq}{\tau_m} \frac{(T_{2m})^{-2} + (\tau_m T_{2m})^{-1} + (\Delta\omega_m)^2}{(\tau_m^{-1} + T_{2m}^{-1})^2 + (\Delta\omega_m)^2} \quad (7)$$

where  $\tau_m$  is the lifetime of the ligand in the first coordination sphere,  $T_{2m}$  is the transverse relaxation time of the coordinated ligand and  $\Delta\omega_m$  is the difference in chemical shifts in Hertz between the free and the coordinated ligands. The determination of  $\tau_m$  can be achieved by analyzing the negative slope portion of the semilog plot of  $(T_{2p})^{-1}$  versus  $T^{-1}$ . The relationship between  $\tau_m$  and the first-order exchange rate constant  $k_{\text{ex}}$  is given by the Eyring relation

$$k_{\text{ex}} = (\tau_m)^{-1} = kTh^{-1} \exp(-\Delta H^*/RT + \Delta S^*/R) \quad (8)$$

The kinetic parameters obtained from the dependence of the ligand exchange rate constant  $k_{\text{ex}}$  on temperature are given in Table 2. The value of  $k_{\text{ex}}$  for the Eu(III)-CMPO system at 298 K ( $1.1 \times 10^3 \text{ s}^{-1}$ ) agrees with the fact that the ligand exchange reaction is slow with respect to the NMR time scale (approximately

TABLE 2. Kinetic parameters of ligand exchange reactions for Eu(III)-CMPO and Gd(III)-CMPO systems

Ln <sup>III</sup>	$k_{\text{ex}}$ (298 K) (sec <sup>-1</sup> )	$\Delta H^*$ (kJ mol <sup>-1</sup> )	$\Delta S^*$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Eu <sup>III</sup>	$1.1(\pm 0.2) \times 10^3$	$37.8 \pm 1.9$	$-59.9 \pm 6.5$
Gd <sup>III</sup>	$1.6(\pm 0.1) \times 10^3$	$41.3 \pm 1.6$	$-44.1 \pm 5.3$

$1.5 \times 10^4 \text{ s}^{-1}$ ), which is estimated from Fig. 2. As to the activation enthalpy change  $\Delta H^*$  and the activation entropy change  $\Delta S^*$ , both ligand exchange systems almost exhibit the same values in an experimental error.

It was found that the first-order exchange rate constants for both Eu(III)-CMPO and Gd(III)-CMPO systems are independent of the concentration of CMPO. This suggests the operation of either a dissociative (D) mechanism or an interchange dissociative (Id) mechanism for the ligand exchange reaction [9]. Since CMPO has a bulky structure and lanthanide(III)-CMPO complexes possess large coordination numbers, the ligand exchange reaction appears to proceed through a D mechanism rather than an Id mechanism. This kind of ligand exchange reaction through a D mechanism in spite of the negative value of entropy change as in the present case, has often been reported up to the present [9,10]. However, it is possible even in this case that any interactions between the active intermediate and CDCl<sub>3</sub>, e.g. the hydrogen bonding between NO<sub>3</sub><sup>-</sup> in the first coordination sphere and CDCl<sub>3</sub> [11], may introduce a considerable ordering into the second co-

ordination sphere, leading to a substantial negative entropy change.

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