Complexation of Ho(III) with Tetraalkyl-diglycolamide in Aqueous Solutions and a Solid State Compared in Organic Solutions of Solvent Extraction

Fei Kou,^a Suliang Yang,^{*a} Lihua Zhang,^a Simon J. Teat^{*b} Guoxin Tian,^{*a,c}

^aRadiochemistry Department, China Institute of Atomic Chemistry, Beijing 102413, China

^bAdvanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

^cCollege of Nuclear Science and Technology, Harbin Engineering University, Harbin, Heilongjiang 150001, China

ABSTRACT The complexation of Ho(III) with tetramethyl-diglycolamide (TMDGA) and N,N'-dimethyl-N,N'-dioctyl-diglycolamide (DMDODGA) were investigated with spectrophotometry and X-ray crystallography. Single crystals of a solid compound $\text{HoL}_3(\text{ClO}_4)_3$ (L = TMDGA) were grown from aqueous solutions by slow evaporation. The crystal structure of $\text{HoL}_3(\text{ClO}_4)_3$ shows that in the solid compound Ho(III) is coordinated by nine oxygen atoms from three tridentate TMDGA molecules in a distorted tricapped trigonal prism (*TCTP*) geometry. In aqueous solution, three successive complex species, HoL^{3+} , HoL_2^{3+} , and HoL_3^{3+} (L = TMDGA) were identified and their stability constants were determined to be 2.20 ± 0.09 , 4.48 ± 0.18 , 5.88 ± 0.18 , respectively, with spectral titration method at 25°C and 1 M ionic strength (1 M NaNO_3). The UV-Vis absorption/reflection spectra of the 1:3 species HoL_3^{3+} (L = TMDGA) in aqueous solution/solid state $\text{HoL}_3(\text{ClO}_4)_3$ compound were very well comparable to the absorption spectra of the extracted samples of Ho(III) with DMDODGA in various organic solvents in solvent extraction. The similarity in the spectra suggest that Ho(III) in the extracted samples is also coordinated by three tridentate DMDODGA with similar coordination geometry as that in HoL_3^{3+} (L = TMDGA) in aqueous solution/solid $\text{HoL}_3(\text{ClO}_4)_3$ compound. In the organic phase of solvent extraction with DMDODGA as extractant, the

nitrate anions do not directly bond to Ho(III) in the extracted complex but just act as far away counter-ion to neutralize the positive charge of HoL_3^{3+} ($\text{L} = \text{DMDODGA}$), and the diluents do not have much influence on the formation of the extracted Ho(III)-DMDODGA complex.

Lanthanides as a major component of the fission product of fissile materials, such as U-235 and Pu-239, co-exist with minor actinides (MAs, mainly Np, Am, and Cm) in spent nuclear fuel. Minor actinides in spent nuclear fuel, which are mainly produced by the multiple neutron capture of the fertile materials such as U-238 in nuclear reactors, contribute the most of the long-term radioactive hazards to high level radioactive waste (HLW). To reduce the volume of HLW generated during the reprocessing of spent nuclear fuel, a partitioning-transmutation strategy (P-T) has been developed. In the P-T strategy, the small amount of long-lived MAs and radioactive fission products are separated from other non-radioactive components in HLW, and are further transmuted into short-lived or stable isotopes in nuclear reactors or dedicated accelerators. For the partitioning, three separation tasks have to be accomplished. The first is to separate Ln(III) and An(III) from other components of HLW; the second is to separate An(III) from Ln(III); and the third is to separate Am(III) from Cm(III). However, due to the very similar chemical properties of An(III) and Ln(III), the last two tasks are extremely challenging.

To partition actinide ions from HLW, N,N,N',N'-tetraalkyl-diglycolamide (TRDGA) molecules (Scheme 1), have been developed for the extraction of actinide and lanthanide ions from acidic solutions.[1-12] The promising application of TRDGA molecules

originates from their ability of selectively bonding actinides (An) in a wide range of oxidation states (+3, +4, +5, and +6) as well as the trivalent lanthanides in aqueous solutions and solvent extraction systems.[2,4]

Scheme 1 The structure of the related ligands. Left: TRDGA; middle: TMDGA; right: DMDODGA.

The water-insoluble TRDGA ligands have been developed as extractants for selectively separating actinide ions from acidic aqueous solutions and are being further refined for this purpose. Recently, it was found that water-soluble TRDGA ligands with small alkyl groups might serve as masking reagents in the separation of Am(III) and Cm(III) from each other. [8,10]

Despite the significant progress made in last two decades,[12] to develop separation processes for nuclear industry may require more optimization based on a comprehensive understanding of the interaction between the TRDGA ligands and the metal ions at molecular level. In this work, an investigation with spectroscopy and crystallography on the complexation of Ho(III) with TMDGA and DMDODGA was conducted in aqueous solutions, in various organic phases of solvent extraction, and in a solid state compound.

Three Ho(III) complex species with TMDGA were identified and their stability constants were determined in 1M NaNO₃ to help optimize the separation processes using TMDGA as an chelate in aqueous phase. Single crystals just containing one Ho(III) complex species, HoL₃³⁺ (L = TMDGA), were prepared for the first time, and the diffuse reflectance spectrum of the compound was collected. Based on the relevance of the absorption spectra of Ho(III) to the coordination geometry in the related complexes, the composition and coordination geometry of the extracted complex of Ho(III) with DMDODGA were illustrated to be a 1:3 complex species of Ho(III) with DMDODGA, which is similar as HoL₃³⁺ (L = TMDGA) in the aqueous solutions and in the solid state compound.

Figure 1 shows a representative set of absorption spectra from a titration of Ho(III) with TMDGA. The titrations are necessarily performed in 1 M NaNO₃ instead of 1 M NaClO₄ due to the limited solubility of a complex in 1 M NaClO₄. Also in most studies and industrial processes nitrate is often used as background electrolyte. To correct the effect of the weak coordination between nitrate and Ho(III) on the absorption spectrum, the standard spectrum and stability constant of Ho(NO₃)₂⁺ were obtained from separate sets of spectrophotometric titrations of Ho(III) with nitrate. The value of the stability constant, log β , for Ho(NO₃)₂⁺ was determined to be -0.59 ± 0.03 in aqueous solution of 1 M ionic strength (1M NaClO₄) at 25°C. Then to fit the data from the titrations of Ho(III) with TMDGA in 1 M NaNO₃, the obtained reference spectrum of Ho(NO₃)₂⁺ was input as known and its stability constant was also included. Three Ho(III) complex species with TMDGA in 1 M NaNO₃ solutions were identified, and their stability constants were determined with spectrophotometric titration method.[13,14] In the titrations, the

absorption spectra of Ho(III) change as the concentration of the ligand increases in the solutions. Analyses with the Hyperquad program [14] suggests that the change in the absorption spectra during the Ho(III)-TMDGA titrations can be ascribed to the successive formation of the three Ho(III) complex species. The differences in the Ho(III) absorption spectra of the complexes is clearly illustrated by the deconvoluted spectra of the complexes. For the 1:1, 1:2, and 1:3 Ho(III)-TMDGA complexes, the stability constants, $\log\beta$, are calculated to be 2.20 ± 0.09 , 4.48 ± 0.18 , and 5.88 ± 0.18 , respectively.

Figure 1 A representative spectrophotometric titration of Ho(III)-TMDGA complexation. Upper: normalized spectra collected during a titration; middle: molar absorption spectra from deconvolution; lower: speciation of Ho(III) during the titration. Starting solution: $C_{\text{Ho(III)}} = 0.0913 \text{ M}$ in 1 M NaNO_3 of pH 3; titrant solution: 0.45 M TMDGA in 1 M NaNO_3 of pH 3; volume of the totally added titrant solution: 1.300 mL .

The complexation of Ln(III) ions with oxygen donors is mainly governed by the electrostatic interaction following the lanthanide contraction. Without steric effect from the ligands, the stability constants for the complexes of Ln(III) with a given ligand usually should increase across the whole Ln(III) series. The lower stability constants of the Ho(III) complexes with TMDGA than those (3.53 ± 0.10 , 5.84 ± 0.19 , 6.80 ± 0.19) of Nd(III) and those (3.71 ± 0.12 , 5.95 ± 0.21 , 6.93 ± 0.34) of Am(III) complexes might be ascribed to the stronger hydration of Ho(III) due to its much smaller size.[13a,b]

With the procedure developed in our previous work on Nd(III) and Am(III),[13a,b] a solid compound, $\text{HoL}_3(\text{ClO}_4)_3$, was prepared in the form of single crystals suitable for x-ray diffraction analysis. Like its analogues of Nd(III) and Am(III) complexes, the 1:3 Ho(III) compound crystalizes in monoclinic space group $C2/c$. The three TMDGA molecules are triple-helically coordinated to the Ho(III) center. The Ho(III) ion is surrounded by a distorted tricapped trigonal prism (*TCTP*) with six carbonyl oxygen atoms at the corners and three ether oxygen atoms capped on the three quadrilateral faces. It is noteworthy that the Ho(III) is completely wrapped by the three TMDGA molecules, so the charge density of the complex is much lower than that of Ho(III) aqua ion. With the less easily polarized six methylene groups on the ligand backbones and six dimethyl

amide groups pointing outside the complex, it does not have definitely oriented interaction with the counterion, ClO_4^- , which is also with very low charge density due to its big size and high symmetry (Figure 2). Subsequently, the structure is essentially comprised of the isolated complexes with the very disordered perchlorate counterions sitting in the voids among the complexes. This feature in the structure provides an unique model for studying the extracted complexes of Ho(III) with water-insoluble TRDGA ligands.

Figure 2. Upper: structural packing of $\text{HoL}_3(\text{ClO}_4)_3$ viewed down the intercept of a-axis and c-axis, showing the isolated complexes and the disordered perchlorates; lower:

ORTEP drawing (50% probability ellipsoids) of HoL_3^{3+} . L – TMDGA, Ho – light green, oxygen – red, nitrogen – light blue, carbon – gray, hydrogen – light gray.

The corresponding Ho-O bond lengths (average $\text{Ho-O}_{\text{carbonyl}} = 2.343 \text{ \AA}$ and $\text{Ho-O}_{\text{ether}} = 2.460 \text{ \AA}$) well fall into the trend of the ionic radii of Ln(III) series (See supplementary content). Taking into account other Ln(III) complexes with alkyl groups of C2 to C4, the change from C1 to C4 in the alkyl groups does not have much steric effect on the bonding. Even though the 1:1 and 1:2 complexes of Ln(III) with TRDGA have been identified in aqueous solutions, the 1:3 complexes seem to be very preferred in solid state compound. With different TRDGA ligands of C1 to C4 alkyl groups and various anions, so far in the solid state compound only the 1:3 complexes have been successfully prepared.[11, 13b,15]

The diffuse reflectance spectrum of the solid $\text{HoL}_3(\text{ClO}_4)_3$ (L = TMDGA) compound in UV-Vis region was collected in comparison with the absorption spectrum of the 1:3 complex in solution, thereby providing useful information about the relevance between the absorption of Ho(III) and the coordination geometry of the complexes. The shape of the spectrum of the solid $\text{HoL}_3(\text{ClO}_4)_3$ compound is nearly identical to the absorption spectrum of the 1:3 complex in solution, as shown in Figure 3. This indicates the coordination geometries of the 1:3 complexes are nearly the same in the solid state as in solution.

To further get insight of the extraction of Ln(III)/An(III) with TRDGA extractants, four extracted samples of Ho(III) complexes with DMDODGA were prepared and the UV-Vis absorption spectra were recorded. The organic phases were 0.5 M DMDODGA in 1-

octanol, 40/60% (v/v) 1-octanol/kerosene, kerosene, and toluene, respectively; the aqueous solutions were 0.005 - 0.1 M Ho(III) in 1 M HNO₃. The comparable spectra of the extracted samples and HoL₃³⁺ (L = TMDGA) in the solutions and in the solid state (as shown in Figure 3) suggests that the coordination geometry of Ho(III) in the extracted samples with DMDODGA is similar to that in HoL₃³⁺. This similarity in spectra indicates that with excess extractant in the organic phase, the diluents do not have much effect on the composition of the extracted complexes. The nitrate might not directly bond to Ho(III) centers in the solvent extraction system but rather acts as the counterion in the form of ion pair to balance the positive charge of the 1:3 complexes. This result does not support the claim based on solvent extraction that 3 - 4 TODGA molecules are present in the extracted species in non-polar diluents like *n*-dodecane, but there are ~2 TODGA molecules in the extracted species in polar diluents like *n*-octanol, 1,2-dichloroethane, and nitrobenzene. [7,9,12]

Figure 3. Diffuse reflectance spectra of solid HoL₃(ClO₄)₃ compound (black, right axis) in comparison with the absorption spectra of [HoL₃]³⁺ (L = TMDGA) in aqueous solution

(green, left axis), and the normalized absorption spectra of the extracted complexes of DMDODGA in various organic phases (left axis).

In conclusion, single crystals of the $\text{HoL}_3(\text{ClO}_4)_3$ (L= TMDGA) compound were grown from aqueous solution by slow evaporation and analyzed by X-ray diffraction. In the solid compound, the nine-coordinated Ho(III) has a distorted tricapped trigonal prism geometry with six carboxyl oxygen atoms at the corners and three ether oxygen atoms capped on the three faces. Three Ho(III) complex species with TMDGA were identified and the stability constants were determined with spectrophotometry in 1 M NaNO_3 at 25 °C. The similarity of the UV-Vis absorption/reflectance spectra suggests the 1:3 Ho(III)-TMDGA complex exists in solution with a nearly identical geometry as in the solid $\text{HoL}_3(\text{ClO}_4)_3$ (L= TMDGA) compound, and the extracted complex of Ho(III) with DMDODGA might possess a similar coordination geometry, indicating that with excess extractant in the organic phase, the diluents do not have much effect on the composition/formation of the extracted complexes. The nitrate might not directly bond to Ho(III) centers in the solvent extraction system but acts as counterion in the form of ion pair to balance the positive charge of the 1:3 complexes. These results provide fundamental structural information to help understand the complexation of TRDGA-class ligands with Ln(III)/An(III) in solvent extraction systems.

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