

# On the Bonding Properties of Trivalent Actinide and Lanthanide Ions: U(III)-Cl, Np(III)-Cl and Ce(III)-Cl Bonding in a LiCl-KCl Eutectic Melt at 450 °C: Spectroscopic Evidences from Their *f-d* and *f-f* Electronic Transitions

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## 1. Introduction

Studies of chloride complexes of trivalent actinide and lanthanide elements have received growing attention recently because of their implications in the long term safety of high level nuclear waste and pyrochemical processing of spent nuclear fuel.

While studying the chemical behavior of actinide ions in the chloride based molten salt, we recognized the importance of the *5f-5d* transitions of the actinide ions in interpreting the bonding properties of the An-Cl complexes. We aimed to explain the nature of chemical bonding in the U(III)-Cl and Np(III)-Cl and Ce(III)-Cl focusing on interpretation of their electronic absorption spectra.

## 2. Experimental

All experiments were carried out in a controlled glove box system. The inert atmosphere was maintained by purging with purified Ar gas to avoid exposure to oxygen and water. The O<sub>2</sub> and H<sub>2</sub>O level were maintained at less than 1 ppm. The electrochemical/spectroscopic integrated measurement units interfaced with a glove box-furnace system were designed and set up for spectro and electrochemical measurements simultaneously in high temperature molten salt media. The experimental details of the spectro-electrochemical measurement are described in our recent paper[1].

## 3. Results and Discussions

### 3.1 Measurements of the *5f-6d* and *5f-5f* transition lines of the U(III) and U(IV) ions in a LiCl-KCl at 450 °C

Figure 1-(a),(b),(c) show the electronic absorption spectrum of U(III),Np(III),Ce(III)-Cl species in a LiCl-KCl at 450 °C. It consists of two main peaks in the wavelength range of 300 – 600 nm which are mainly attributable to the inter-configurational *5f-6d* transitions of U(III) and Np(III) ions. For Ce(III) ion, it appears in a UV region.

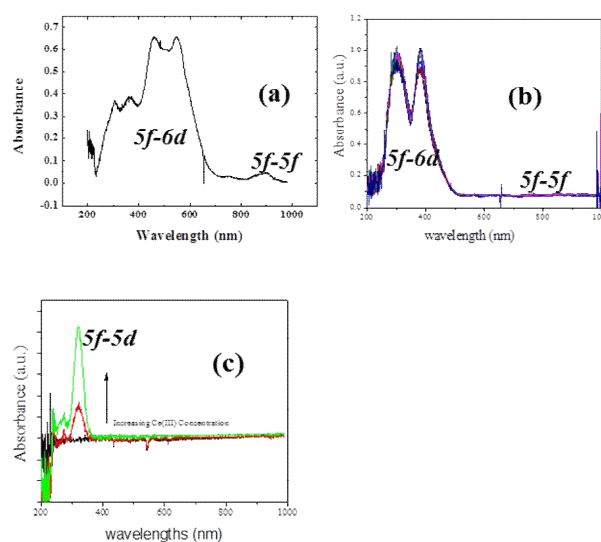


Fig. 1. Electronic absorption spectra of U<sup>III</sup>(a), Np<sup>III</sup>(b), Ce<sup>III</sup> (c) ions in a LiCl-KCl eutectic melt.

### 3.2 Evidences of covalent bond formation in the U(III)-Cl and Np(III)-Cl and ionic bonding in Ce(III)-Cl complexes from their electronic absorption spectra

The accessibility of *f-d* transition data may provide clues for the covalency in U-Cl, Np-Cl and Ce-Cl bonding. Figure 2 schematically shows the covalent bonding effect on the UV-VIS spectral pattern in metal-Cl complexes. The smaller the *f-d* / *f-f* intensity ratio is, the greater the tendency of the covalent bond formation. Uranium ions have a greater tendency toward covalent bond formation than that of lanthanides, including a complex formation with electron donating chloride ligands[2]. Several divalent lanthanide ions such as Eu,Sm,Yb and trivalent Ce exhibit *4f-5d* transition lines in a normal UV range. In particular, early actinides such as uranium may provide more

electrons for covalent bonding with ligands. The UV-VIS spectra reflect the formation of covalent bonding. As a metal ion participates in chemical bonding, it loses its pure electronic state, and as a result, the selection rule for electronic transitions is broken by the orbital mixing depending on the strength of the bonding formation. Figure 2 accounts for the changes in spectral intensities upon covalent bonding formation of An/Ln(III) ions with the surrounding chloride ligands. The intensity of the allowed  $5f-6d$  lines was significantly decreased (lower than 100), on the other hand, the intensities from the forbidden  $5f-5f$  transitions contributed significantly to the spectrum. Simply, the intensity ratio of  $5f-6d/5f-5f$  may be regarded as an indirect measure of covalent bond formation. For the U(III) and Np(III) ions, the intensities of  $5f-5f$  transitions are about one order of magnitude larger than  $4f-4f$  transitions in lanthanide ions. And the  $5f-6d$  transitions are about less intense than  $4f-5d$  transitions in the lanthanide ions. Spectral analysis shows the bonding strength between metal and ligand as  $U(III)-Cl > Np(III)-Cl \gg Ce(III)-Cl$ . Recent EXAFS studies provided structural and bonding information of around uranium ion in high temperature molten salt media, supporting covalent bond formation in our study[3].

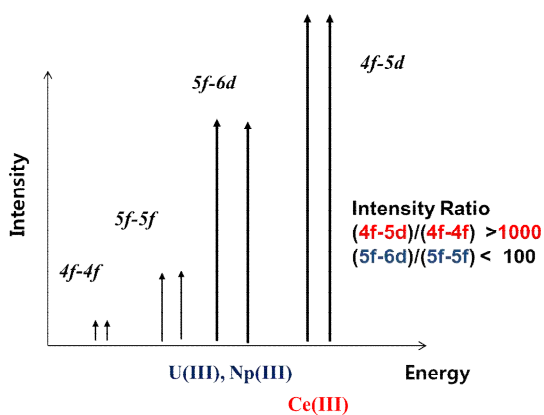


Fig.2. Schematic diagram of UV-VIS spectral intensities and positions of  $5f-6d$ ,  $4f-5d$  and  $5f-5f$ ,  $4f-4f$  transitions of U(III), Np(III) and Ce(III) ions in a LiCl-KCl melt at 450 °C.

## 4. Conclusions

The  $5f-6d$  transition lines in an actinide ions ( $4f-5d$  for lanthanides) can be used as a sensitive probe for monitoring the actinide metal-ligand bonding. Spectral analysis shows the bonding strength of metal-ligand as  $U(III)-Cl > Np(III)-Cl \gg Ce(III)-Cl$ .

## Acknowledgement

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