## **8–4** Discovery of Thermochromic Uranium Complexes

Coordination Chemistry in Ionic Liquids Using Time-Resolved Laser-Induced Fluorescence Spectroscopy



**Fig.8-10 Thermochromic behavior of** [C4mim]s[UO2(NCS)5] Reversible change in color: solid (left, -196 °C) to sol (right, 90 °C). An orange uranium complex is uncommon.



**Fig.8-12 Time-resolved luminescence spectra of [C₄mim]₃[UO₂(NCS)₅] recorded under UV irradiation** The weak luminescence at 90 °C (thin line) becomes enhanced at -196 °C (bold line).

Inductively coupled plasma mass spectrometry or other mass spectrometric methods are used in chemical analysis of actinides in water or organic solvents instead of radiation measurements. These techniques, however, are inapplicable to in-situ observations of the dissolved chemical species. In contrast, time-resolved laser-induced fluorescence spectroscopy (TRLFS) enables qualitative analysis of solutions. Investigating the energy dissipation processes after irradiation by laser pulses is of necessity our approach to studying the chemistry of actinide complexes.

Observation of dissolved metal ions at high concentrations using TRLFS has revealed the coordination structure of the uranium complex, which has remained unknown in water or organic solvents. Ionic liquids are a series of salts that are composed entirely of ions and melt at room temperature. Because they are stable at 100 °C, novel physical properties of these solvents at higher temperatures can be designed. We performed a dissolution test of uranyl ions (UO2<sup>2+</sup>) in 1-butyl-3-methyl imidazolium thiocyanate ([C4mim][NCS]; the structure is shown in Fig.8-11), which formed a liquid at very high concentrations. Further addition of uranium affords a metal salt with a [UO2<sup>2+</sup>]:[NCS<sup>-</sup>] composition ratio of 1:5, which remains a sol at room temperature. Surprisingly, this substance reveals



**Fig.8-11 Crystal structure around**  $[UO_2(NCS)_5]^3$  (-196 °C) There are five NCS<sup>-</sup> ions on the equatorial plane coordinated to a uranyl ion  $(UO_2^{2^+})$ , surrounded by three 1-ethyl-3methylimidazolium cations. This salt forms a bright yellow solid at -196 °C. The symbols are as follows: oxygen: red, nitrogen: blue, carbon: black, sulfur: yellow, and hydrogen: pink. The chemical structure of the ionic liquid is shown above.

thermochromism, that is, temperature-dependent color changes due to external stimuli (Fig.8-10). There have been no studies describing this property of uranium complexes; this salt becomes yellow on solidification when cooled at the liquid nitrogen temperature, whereas it melts on heating, becoming red.

To understand this phenomenon, the thermochromic ionic liquid was crystallized at low temperature, resulting in the crystal structure shown in Fig.8-11, where the coordination number around uranium on the equatorial plane at low temperature is five. In addition, the luminescence spectrum under irradiation by ultraviolet light is shown in Fig.8-12; it exhibits quenching of luminescence at room temperature. The symmetrical structure around the U moiety, therefore, affects the spectrum by reducing the coordination number on heating. The orange or red U<sup>VI</sup>O<sub>2</sub><sup>2+</sup> compounds are uncommon, so a coordination number of four is attributed to the local environment between the uranyl and the ligand as well as to cation–anion interactions.

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## Reference

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