Correlation between intermolecular hydrogen bonds and melting points of uranyl nitrate complexes with cyclic urea derivatives

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ABSTRACT

To clarify requirements for forming $UO_2(NO_3)_2(CU)_2$ (CU: cyclic urea derivative) and $UO_2(NO_3)_2(NRP)_2$ (NRP: N-alkylated pyrrolidone derivative) with high melting points (mps), molecular and crystal structures of $UO_2(NO_3)_2(\mathbf{0a})_2$ (**0a**: 2-imidazolidone), $UO_2(NO_3)_2(\mathbf{0b})_2$ (**0b**: tetrahydro-2-pyrimidone) and $UO_2(NO_3)_2(\mathbf{1a})_2$ (**1a**: 1-methyl-2-imidazolidone) were determined by means of single crystal X-ray analysis. Melting points (mps) of these complexes were compared with each other and those of other $UO_2(NO_3)_2(CU)_2$ and $UO_2(NO_3)_2(NRP)_2$. As a result, the uranyl nitrate complexes with **0a**, **0b** and **1a** exhibit typical structural properties of $UO_2(NO_3)_2L_2$ (L: unidentate ligand); i.e., hexagonal bipyramidal coordination geometry, and two bidentate NO_3^- and two CUs located at *trans* positions in an equatorial plane of UO_2^{2+} ion. Several intermolecular N–H···O hydrogen bonds (HBs) were found in the crystal structures of $UO_2(NO_3)_2(\mathbf{0a})_2$, $UO_2(NO_3)_2(\mathbf{0b})_2$ and $UO_2(NO_3)_2(\mathbf{1a})_2$. In contrast, no intermolecular C–H···O HBs were formed in these crystal structures. The intermolecular HBs were discussed in connection with mps of $UO_2(NO_3)_2(CU)_2$ and $UO_2(NO_3)_2(NRP)_2$ including those reported previously. The mp tends to increase as the number of N–H···O HBs per molecule increases, whereas effects of C–H···O HBs on the mps is not very significant. These results suggest that the intermolecular N–H···O HBs strongly contribute to form a uranyl nitrate complex with high mps.

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1. Introduction

Uranyl nitrate complexes with unidentate ligands (L) such as H_2O [1], ureas [2,3], amides [4–6], alkyl phosphates and phosphine oxides [7–12] generally have a composition, $UO_2(NO_3)_2L_2$, which exhibits hexagonal bipyramidal coordination geometry around U. Four oxygen atoms from two bidentate NO_3^- and two donating atoms from Ls are bound to U at the *trans* positions in the equatorial plane of the UO_2^{2+} ion. This general formula is commonly found in both fundamental chemistry of uranium and nuclear engineering processes like spent nuclear fuel reprocessing [13–20].

In our previous study, we have found that *N*-cyclohexyl-2-pyrolidone (NCP) selectively precipitates UO_2^{2+} from a HNO_3 aqueous solution [21]. From the single crystal X-ray analysis, the

chemical formula of precipitates was found to be $UO_2(NO_3)_2(NCP)_2$ with the typical structural properties of $UO_2(NO_3)_2L_2$ mentioned above [22]. On the basis of UO_2^{2+} precipitation ability of NCP, we proposed a reprocessing method for the spent nuclear fuels produced from fast breeder reactors [23–26], and assessed various pyrrolidone derivatives (NRP) as UO_2^{2+} precipitants in this process. As a result, it was clarified that the UO_2^{2+} precipitation ability depends on hydrophobicity of NRP and packing efficiency of $UO_2(NO_3)_2(NRP)_2$ in the crystal structures [25,26]. In our recent works [24,27,28], hydrophilic cyclic urea derivatives (CUs, Fig. 1) such as 2-imidazolidone (**0a**), tetrahydro-2-pyrimidone (**0b**), 1,3-dimethyl-2-imidazolidone (**2a**), and 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidone (**2b**) were also found to precipitate UO_2^{2+} from the HNO_3 solution. Especially, the UO_2^{2+} precipitation abilities of **0a** and **0b** are comparable to that of NCP in spite of their low hydrophobicity. Comparing precipitation behavior of UO_2^{2+} through addition of CUs and NRPs together with other physical traits, we have inferred that the high precipitation ability of **0a** and **0b** is likely to arise from high melting points

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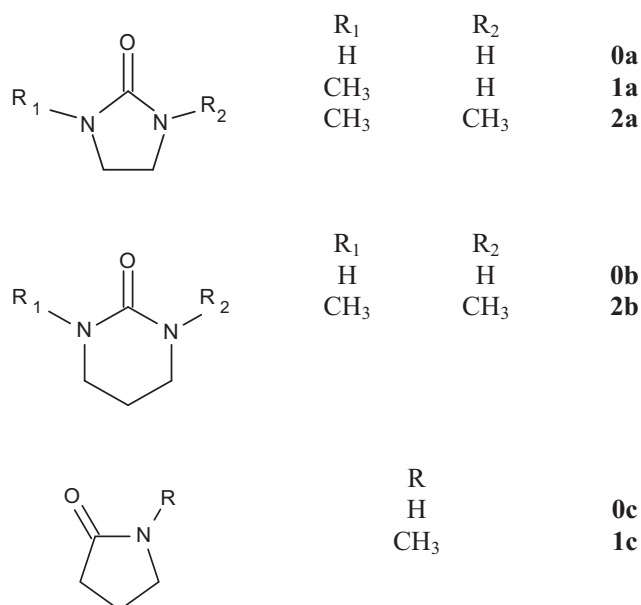**Fig. 1.** Schematic formulae of cyclic urea and pyrrolidone derivatives.

(mps) of $UO_2(NO_3)_2(\mathbf{0a})_2$ and $UO_2(NO_3)_2(\mathbf{0b})_2$ [28]. Thus, there should be some correlation between the precipitation ability of L and mp.

However, it is still unclear what determines mps of $UO_2(NO_3)_2(CU)_2$ and $UO_2(NO_3)_2(NRP)_2$. In the previous studies [26,27], we have reported that $UO_2(NO_3)_2(\mathbf{0c})_2$ (see Fig. 1) involving the imino group shows higher mp than $UO_2(NO_3)_2(NRP)_2$ with *N*-alkylation despite the lower molecular weight. In the crystal structure of $UO_2(NO_3)_2(\mathbf{0c})$, intermolecular hydrogen bonds (HBs) are present in between the imino group and the carbonyl oxygen atom of the neighboring molecule, and therefore, presence of the N–H···O HBs should be correlated with the high mp. On the basis of this insight, $UO_2(NO_3)_2(\mathbf{0a})_2$ and $UO_2(NO_3)_2(\mathbf{0b})_2$, which have two imino groups as shown in Fig. 1, are expected to form more intermolecular N–H···O HBs in their crystal structures and to realize the high mps. To examine this hypothesis, it is necessary to compare the molecular and crystal structures of the uranyl nitrate complexes with different Ls listed in Fig. 1.

For this purpose, we performed the single crystal X-ray analyses for $UO_2(NO_3)_2(\mathbf{0a})_2$, $UO_2(NO_3)_2(\mathbf{0b})_2$ and $UO_2(NO_3)_2(\mathbf{1a})_2$ (**1a**: 1-methyl-2-imidazolidone) in this study. Although crystal structures of $UO_2(NO_3)_2(\mathbf{2a})_2$, $UO_2(NO_3)_2(\mathbf{2b})_2$, $UO_2(NO_3)_2(\mathbf{0c})_2$ and $UO_2(NO_3)_2(\mathbf{1c})_2$ have already determined in our previous studies [23,24,26,29], they are revisited here to systematically discuss correlations between mps and intermolecular HBs present in $UO_2(NO_3)_2L_2$ (L = CU, NRP; Fig. 1).

2. Experimental

2.1. Chemicals

2-Imidazolidone (**0a**), tetrahydro-2-pyrimidone (**0b**) and 1,3-dimethyl-2-imidazolidone (**2a**) were purchased from Tokyo Chemical Industry, Kanto Chemical or Sigma–Aldrich Co., Ltd. All chemicals were used without further purification. 1-Methyl-2-imidazolidone (**1a**) was prepared as described elsewhere [30], and characterized by ^{1}H NMR [(CDCl$_3$, TMS, ppm): 2.79 (s, 3H, N-CH$_3$), 3.42 (t, 4H, –(CH$_2$)$_2$–), 4.80 (s, 1H, N-*H*)]. $UO_2(NO_3)_2(\mathbf{2a})_2$ was synthesized according to the reported methods [24].

2.2. Preparation of $UO_2(NO_3)_2(CU)_2$

2.2.1. $UO_2(NO_3)_2(\mathbf{0a})_2$ and $UO_2(NO_3)_2(\mathbf{0b})_2$

A stock solution of UO_2^{2+} ([UO_2^{2+}] = 0.1 M for $UO_2(NO_3)_2(\mathbf{0a})_2$ or 0.05 M for $UO_2(NO_3)_2(\mathbf{0b})_2$, M: mol/dm^3) was prepared by dissolving $UO_2(NO_3)_2·6H_2O$ in 3.0 M HNO$_3$ aq. After addition of twice molar amount of **0a** or **0b** to [UO_2^{2+}], CH$_3$OH (1 mL) was added to these reaction mixtures. Each of the mixtures gave crystals suitable for X-ray diffraction after standing for a week in the refrigerator. IR Data (KBr, cm^{-1}): $UO_2(NO_3)_2(\mathbf{0a})_2$: 920, 928 (O=U=O asymmetric stretching, ν_3), 1647 (C=O stretching in CU, $\nu_{C=O}$), 3383, 3418 (N–H stretching in CU, ν_{N-H}). $UO_2(NO_3)_2(\mathbf{0b})_2$: 906, 926 ($\nu_3$), 1623 ($\nu_{C=O}$), 3404 ($\nu_{N-H}$).

2.2.2. $UO_2(NO_3)_2(\mathbf{1a})_2$

A solution containing UO_2^{2+} (0.2 M) and **1a** (0.4 M) was prepared by dissolving $UO_2(NO_3)_2·6H_2O$ and **1a** in CH$_3$OH (1 mL). After addition of diethyl ether (1 mL), this solution was stood in the refrigerator. Crystals suitable for X-ray diffraction deposited within 1 week. $UO_2(NO_3)_2(\mathbf{1a})_2$: 917 ($\nu_3$), 1636 ($\nu_{C=O}$), 3436 ($\nu_{N-H}$).

Although these uranyl nitrate complexes are newly reported here, their elemental analyses have not been performed yet because of unavailability of such an instrument in our control area dedicated for treatment of nuclear fuel materials like uranium.

2.3. X-ray crystallography

Molecular and crystal structures of uranyl nitrate complexes of **0a**, **0b** and **1a** were determined at 223 K by means of single crystal X-ray diffraction. The yellow crystal of each compound was mounted on a glass fiber. Intensity measurements were carried out on a Rigaku RAXIS RAPID diffractometer with Mo Kα radiation (λ = 0.71075 Å). The structures were solved by direct method (SIR92) and expanded by using Fourier techniques [31]. Non-hydrogen atoms were anisotropically refined by SHELXL-97 [32]. Hydrogen atoms were refined as riding on their parent atoms with $U_{iso}(H)$ = 1.2 $U_{eq}(C, N)$. The final cycle of full-matrix least-squares refinements on F^2 were based on observed reflections and variable parameters, and converged with unweighted and weighted agreement factors (R and wR, respectively). All calculations were performed by the CrystalStructure crystallographic software package [33].

The number of HBs in each uranyl complex was determined by using PLATON software using CIF files of $UO_2(NO_3)_2(CU)_2$ or $UO_2(NO_3)_2(NRP)_2$ [34]. The following three criteria were utilized to assign HBs: (1) if distance between hydrogen donor (D) and acceptor (A) atoms (D) is less than ($\sum r_{vdw}$ + 0.5) Å (r_{vdw}: van der Waals radius), (2) if an A···H distance (d) is less than ($\sum r_{vdw}$ − 0.12) Å, and (3) if D–H···A angle (θ) is larger than 100° [35].

2.4. Infrared spectroscopy

IR samples were prepared by mixing each uranyl nitrate complex with dry KBr, and their IR spectra were measured by using a diffuse reflectance method with Shimadzu FTIR-8400S spectrometer. The data collection for each sample was performed in the range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1}, and repeated 36 times and merged.

2.5. Determination of melting point

Melting points of $UO_2(NO_3)_2(\mathbf{1a})_2$ and $UO_2(NO_3)_2(\mathbf{2a})_2$ were recorded by ASONE ATM-02 mp apparatus. For this experiment, powdered uranyl complexes (ca. 1 mg) were loaded in a glass capillary filled with Ar gas, followed by sealing with hot melting. The