

I-1. PROJECT RESEARCHES

Project 5

Chemical and electronic properties of Actinide compounds and their applications

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INTRODUCTION: Actinide compounds show a unique chemical and electronic nature due to the partial and insufficient shield of 5f orbital electrons as inner transition elements. We have a deep interest in the aspect of the electronic properties of the actinide compounds and formed the group consisting of three major fields: (1) inorganic and coordination chemistry, (2) electronic properties and (3) theoretical chemistry and its users. Such research environments to handle actinide elements are extremely difficult to build in ordinary university institutes. The hot laboratory of the KURNS offers unique opportunities for the above-mentioned characteristic re-search activities.

EXPERIMENTS and RESULTS: The first fiscal year of the project has been devoted to the setting up the experimental environment and initial test experiments. Each of research fields has made their progress as followings: (1) S. Kambe has investigated "Hidden ordering" in URu₂Si₂ by NMR spectroscopy (¹⁰¹Ru NQR) under zero field without uni-axial stress indicating that 4-fold crystal symmetry remains in the hidden ordered state. (2) Y. Haga et al. has investigated ThRh₆Ge₄ identified as LiRh₆P₄-type structure. The electronic structure of ThRh₆Ge₄ was experimentally determined from the quantum oscillation measurements. This information will help understanding the electronic structure of a correlated material CeRh₆Ge₄ where a phase transition from Ce³⁺ to Ce⁴⁺ is assumed across the quantum phase transition [1]. (3) M. Abe et al. has developed new programs for calculating electronic states and properties of actinide compounds with high accuracy, based on the X2C relativistic Hamiltonian, the initial development of the CASPT2/RASPT2 program and are preparing to make our code publicly available on the GitHub webpage free of charge [2]. We conducted benchmark calculations for the ground and excited states of the UO₂²⁺ molecule using our software. (4) M. Nakase et al. selected phthalocyanine (Pc) as the basic structure for extractants according to the CHON principle and scrutinized its properties. With regard to solubility prediction, a basic regression model for solubility prediction using other chemical parameters was tested this year using HSPiP software based on Hansen Solubility Parameters (HSP). (5) K. Shirasaki et al. has synthesized some uranium(III) BDI complexes through synthesis of BDI potassium salt. (6) N. Ishikawa et al. has measured temperature and magnetic-field-dependent magnetic circular dichroism (HT-VH-MCD) spectroscopy. Similar interaction was confirmed in the sandwich bilayer complex [Pc₂Ln] and the monolayer complex [PcLn(cyclen)]. [3] The peak top of the absorption spectrum in the visible region shifted to the short wavelength side by addition of salen. Obtained compound showed a typical spectrum of metal phthalocyanines with a sharp characteristic band, Q-band, at λ_{max} = 687nm. (7) The dissolution method of ThO₂ by thermochemical conversion has been studied by T. Suzuki et al. The removal of thorium from the precipitate is not sufficient because the amount of thorium is higher than that of radium. An additional method for separating radium from thorium needs to be added before the precipitation method. (8) M. Nogami et al. has examined diamide compounds and synthesized a resin with a diamide structure, *N,N,N',N'*-tetramethylmalonamide (TMMA) as the functional group. [3]

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Electronic structure of ThRh₆Ge₄ with non-centrosymmetric crystal structure

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INTRODUCTION: Actinide intermetallic compounds have long been studied because of their unusual physical properties. In the context of condensed matter physics, electron correlations between charge carriers responsible for electrical transport and those carrying magnetic moments, and local symmetry of those electrons play crucial roles. In this study we demonstrate that the electronic structure of a thorium compound with the characteristic symmetry can precisely be determined by quantum oscillations experiments and the band structure calculations. ThRh₆Ge₄ crystallizes in the hexagonal LiRh₆P₄-type structure. It belongs to the space group P-6m2 which lacks center of inversion. It is also isostructural to an intriguing compound CeRh₆Ge₄ which undergoes ferromagnetic to heavy fermion quantum phase transition under hydrostatic pressure [1]. It is therefore important to identify the electronic structure of this compounds.

EXPERIMENTS : We tried to synthesize ThRh₆Ge₄ using arc-melting the stoichiometric mixture of each element. Czochralski-pulling technique was successfully applied to grow single crystals. Electron microprobe analysis and X-ray diffraction for both powder and single crystals successfully identified LiRh₆P₄-type structure. The sample was characterized by electrical resistivity, specific heat and magnetization measurements. The quantum oscillation was measured using the field-modulation technique at low temperatures. Theoretical band structure calculations were performed using the software package Elk.

RESULTS: The electronic structure of ThRh₆Ge₄ was experimentally determined from the quantum oscillation measurements. The results are well described by the band structure calculations. These results define the electronic structure of the compounds with a tetravalent actinide site. This information will help understanding the electronic structure of a correlated material CeRh₆Ge₄ where a phase transition from Ce³⁺ to Ce⁴⁺ is assumed across the quantum phase transition. Further investigation is in progress on this respect. [2]

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Development of relativistic multireference electron correlation methods for actinide compounds

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INTRODUCTION: Understanding the properties of actinide compounds is crucial for both engineering and academic research. Theoretical calculations, alongside experimental approaches, play a vital role in elucidating their characteristics and facilitating safe verification studies. However, accurately handling relativistic and electron correlation effects is essential for theoretical investigations of actinide compounds. As the atomic number Z increases, the relativistic effect becomes significant, challenging the accuracy of conventional scalar relativistic treatments or perturbative corrections of spin-orbit interactions. Rigorous relativistic effects demand the application of four-component Dirac or exact two-component (X2C) relativistic Hamiltonians. Moreover, because all s, p, d, and f orbitals serve as valence orbitals for actinide atoms, static electron correlation cannot be neglected, limiting the efficacy of conventional single reference methods like density functional theories. Multi-reference electron correlation theory becomes necessary but poses computational challenges due to its complexity. Our group has developed new quantum chemistry programs based on the X2C relativistic Hamiltonian to accurately calculate electronic states and properties of actinide compounds. Specifically, we have created a program for the CASPT2/RASPT2 method, employing multiconfigurational wave functions (CASCI/RASCI) as the 0th-order state of perturbation. CASPT2/RASPT2 is a well-established perturbation theory in the non-relativistic framework [1].

METHODS: The Hartree-Fock and molecular orbital integral transformation with the X2C relativistic Hamiltonian can be executed using the free software DIRAC [2,3]. Consequently, we have developed a CASPT2/RASPT2 program that utilizes molecular orbital information computed by the DIRAC software.

RESULTS: This year, we have nearly completed the initial development of the CASPT2/RASPT2 program and are preparing to make our code publicly available on the GitHub webpage free of charge [4]. We conducted benchmark calculations for the ground and excited states of the UO_2^{2+} molecule using our software. Fig. 1 illustrates the potential energy curves obtained at the RASPT2 level. Although no experimental data exist for this system, numerous previous calculation reports are accessible. Overall, our optimized U-O bond length and excitation energies align with some prior works, indicating successful program implementation. Consequently, we plan to utilize our program for other actinide molecules to explore the electronic state properties further.

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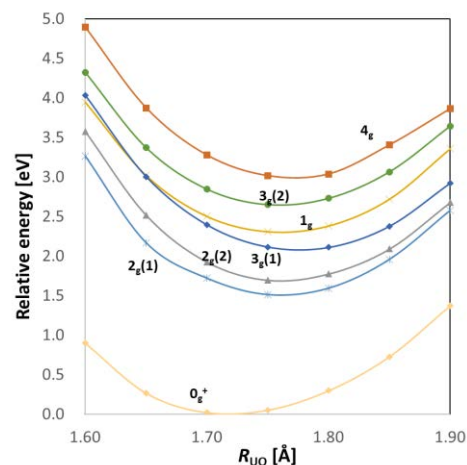


Fig. 1. Potential energy curves for the ground and low-lying excited states for UO_2^{2+}

Synthesis of novel phthalocyanine derivatives and effect of substituent on recognition of light actinide and chemical property-4

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INTRODUCTION: Understanding actinide chemistry is crucial in areas like nuclear fuel reprocessing, Fukushima waste treatment, and medical uses of actinium. My focus is on the thorium (Th) fuel cycle, which avoids producing heavy actinides like americium (Am) and curium (Cm), instead dealing with lighter actinides such as Th, protactinium (Pa), and uranium (U). This cycle requires separating U from Th and other fission products in spent Th fuel. Recently, CHON principle-compliant extractants like monoamides have been explored for U/Th separation. We chose phthalocyanine (Pc) as the base extractant structure and studied its properties. Efforts are ongoing to make Pc soluble in organic solvents and develop a purification method.

EXPERIMENTS: The experimental setup for distillation purification of Pc-U was upgraded, as shown in **Fig. 1**. The aluminum frame was newly installed to reinforce and enhance safety in experiments. The electric power supply was installed on the top, and the pump was set under the tube, making the space needed for experiments smaller. Such ingenuity is essential for experiments in a limited controlled area.



Figure 1 Updated distillation apparatus

SOLUBILITY PREDICTION: Predicting the solubility of the complexes in an organic solvent for solvent extraction is an essential step for minimizing experimental tests and reducing waste generation. Hence, our efforts have been directed towards constructing prediction models based on complex structures, as we started last year. We tested a basic regression model for solubility prediction utilizing HSPiP software, which can predict the physicochemical properties of chemicals based on the Hansen Solubility Parameter (HSP). The HSP is a set of empirical parameters that predict the solubility behavior of substances in different solvents. HSP characterizes the three primary forces involved in solvation: dispersion forces (related to London dispersion forces), polar forces (related to dipole-dipole interactions), and hydrogen bonding forces. Each substance and solvent can be assigned a set of HSP values corresponding to these forces. By comparing the HSP values of solvents, we can predict whether the substance can dissolve in that solvent. The HSP values are typically represented as points in a three-dimensional space, with axes corresponding to the three forces. Solvents close together in the space are expected to dissolve similar substances. Conversely, substances with HSP values distant from those of a solvent are less likely to dissolve well in that solvent. The HSP parameters can be predicted from chemical structures such as SMILES, where characters represent atoms and bonds. Atoms are represented by their atomic symbols (e.g., C for carbon, O for oxygen), and bonds between atoms are indicated by various symbols (e.g., single bonds are usually implicit, double bonds are represented by "=", triple bonds by "#"). We tested such a scheme and tested it shortly.

PLANS: In the next fiscal year, our efforts will extend to validating the prediction model regarding the solubility of U-Pc complexes, emphasizing rigorously testing its predictive capabilities. Additionally, we plan to incorporate supplementary data from pertinent literature sources to enhance our understanding and prediction of complex characteristics.

Fundamental preparation study to access functional uranium(III) complexes: Investigation of β -diketoiminate ligand preparation

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INTRODUCTION: The electron configuration of uranium(III) is $5f^3$ whose electrons are influenced by the shielding effects of $5s$ and $5p$ less than $4f$, thus the complexes with uranium(III) often have unique properties in contrast to other oxidation states. In 2013, King et al. synthesized uranium(III) β -diketoiminate (BDI) complex such as (BDI)U₂ [1] and in 2020, Boreen et al. reported that the single molecule magnet (SMM) behavior was observed in low temperature using (BDI)U(OAr)₂ (OAr = 2,6-Diisopropylphenyl) [2]. Because of the steric hindrance of BDI ligands, low-coordination complexes with BDI ligands are relatively easy to achieve. The purpose of this study is to investigate suitable preparation method of uranium complexes with BDI ligands and its derivatives and to characterize low valent uranium BDI complexes. Here, we synthesized a commercially unavailable BDI derivative potassium salt for the starting materials of uranium(III) complexes.

EXPERIMENTS: The procedure to synthesize BDI potassium salt was followed by the one reported by Cleg with fine modifications regarding stoichiometry and reflux time [3] and described as follows. The BDI ligand was synthesized by dehydration reaction using a Dean-Stark apparatus (Fig. 1). Acetylacetone 15 ml and 2,6-diisopropylaniline were dissolved in 150 ml of toluene. The volume of 2,6-diisopropylaniline was 55 ml for condition 1 and 30 ml for condition 2. In addition, about 1 g of *p*-toluenesulfonic acid was mixed as a catalyst. After the freeze-pump-thaw method (3 times), refluxing was carried out as heating for 48 h (condition 1) or 1.5 h (condition 2). After that, the reaction mixture was distilled under reduced pressure and obtained residuals. Recrystallization was performed for the target substance. Hexane was used as the solvent, and the compound was recovered after being dissolved at 30°C and allowed to stand at -15°C for 2 days for condition 1 and 2 weeks for condition 2. KN(SiMe₃)₂ (toluene solution, 0.5 mol/L) was added at one stoichiometric ratio to the compound obtained in both conditions.

RESULTS: The precipitate from condition 1 was identified as C₂₉H₄₁N₂K (molecular weight 391.375) using ICP-AES and CHN elemental analysis (Table 1). The compound weight was 0.83 g and the yield throughout the experiment was 47.7%. Addition of KN(SiMe₃)₂ to the precipitate obtained under experimental condition 2 yielded a derivative of KBDI, C₁₇H₂₄NOK (molecular weight 298.29). The yield of the compound in total was 64.8%.

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Fig. 1. Dean-Stack apparatus used for preparation of BDI and its derivatives.

Table 1 Elemental analysis results of KBDI salt

	Calculated [%]	Obtained(Difference) [%]
C	73.60	73.30(-0.30)
H	9.26	8.52(-0.74)
N	7.15	7.24(+0.09)
K	9.98	8.54(-1.44)

Study of Heavy Fermion Superconductor URu₂Si₂ ¹⁰¹Ru-NQR study

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INTRODUCTION: Understanding of "Hidden ordering" in URu₂Si₂ is fairly progressed recently [1], whereas the definitive answer is still missing. This issue is very exciting since the hidden ordering is supposed to be new spontaneous symmetry breaking. Considering the recent experimental results, few possible space groups of hidden order symmetry have been selected previously [2,3]. If the hidden order symmetry is once determined, corresponding multipolar order parameter is spontaneously determined.

EXPERIMENTS: In this study, the local symmetry of Ru site is determined in the hidden order state without uni-axial stress and with uni-axial stress along the [100] and [110] directions [4], by means of precise Ru-NQR measurements. These measurements again support the 4-fold symmetry at Ru site in the hidden order state without uni-axial stress. Furthermore, certain cases can be excluded from the previously proposed possible ones. In this year, the Ru-NQR measurements without uni-axial stress are performed.

RESULTS: As shown in Fig. 1, ¹⁰¹Ru NQR spectra under zero field without uni-axial stress in the hidden ordered state at 4.2K. There is no splitting of spectra under uniaxial pressure, indicating that there is no internal magnetic field appearing in the hidden ordered state. As ¹⁰¹Ru is $I=5/2$ nuclei, there are two NQR peaks are observed *i.e.* ν_{1Q} ($I = \pm 3/2 \leftrightarrow I = \pm 1/2$) and ν_{2Q} ($I = 5/2 \leftrightarrow I = \pm 3/2$). In the present case, the ratio ν_{2Q}/ν_{1Q} is exactly 2 within the experimental errors, indicating that the 4-fold symmetry at Ru site holds in the hidden order state, which also indicates that 4-fold crystal symmetry remains in the hidden ordered state.

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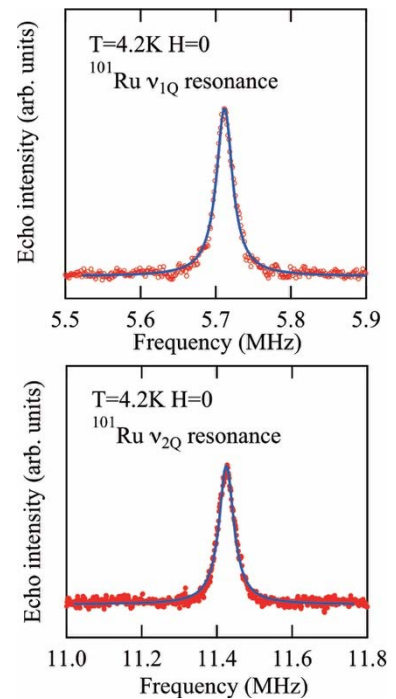


Fig. 1. ¹⁰¹Ru NQR spectra at 4.2 K under zero field. Two resonance spectra: ν_{1Q} ($I = \pm 3/2 \leftrightarrow I = \pm 1/2$) and ν_{2Q} ($I = 5/2 \leftrightarrow I = \pm 3/2$) have been observed.

Exploration of new interactions between actinide 5f electron systems and photo-excited organic π -electron systems

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INTRODUCTION: Metal complexes of actinide as well as those of lanthanide have high magnetic anisotropy due to the orbital angular momentum component in the total angular momentum of the f-electronic systems. In contrast to 4f electrons, 5f electrons are characterized by a large covalency involved in chemical bonding.

Another type of electronic angular momentum is known to be generated on a cyclic π -conjugated system of macrocyclic ligands, such as phthalocyanines (Pc) or porphyrins, by photo-excitation into degenerate π - π^* excited states.

Previously, our group revealed the existence of a magnetic interaction between these two angular momenta (J-L interaction) in rare-earth Pc complexes by temperature- and magnetic-field-dependent magnetic circular dichroism (HT-VH-MCD) spectroscopy [1][2]. This interaction has been observed in sandwich-type bilayer complexes [Pc₂Ln] (Ln=Tb, Dy) and monolayer complexes [PcLn(cyclen)]. Similar interaction was confirmed in the sandwich bilayer complex [Pc₂Ln] and the monolayer complex [PcLn(cyclen)].[3][4]

Last year, we reported measurement of VT-VH-MCD in the visible energy region for the monolayer Pc complex of U(IV) as well as that of Th(IV) to investigate magnetic interaction between the (5f)² system and the ligand π -conjugate system in a photo excited state.

This year, we conducted preliminary experiments for the synthesis of a new type of Pc-uranium complex having a different second ligand, namely salen (N,N'-Bis(2-hydroxybenzylidene)ethylenediamine).

EXPERIMENTS: The precursor [PcUCl₃]Li(THF)₄ was synthesized according to Ref [5]. Dilithium phthalocyanine, UCl₄, and dehydrated triglyme were placed in a flask in a glove box and THF was added. The mixture was heated outside the glove box in a sealed condition using an oil bath. After cooling to room temperature, hexane was added, and the precipitate was collected by filtration. Salen was dissolved in DMSO and Triethylamine was added. To this solution, a DMSO solution of [UPcCl₃]Li(THF)₄ was mixed a small amount at a time, and the mixture was shaken well.

RESULTS: The peak top of the absorption spectrum in the visible region shifted to the short wavelength side by addition of salen. The addition was stopped when the absorption peak of salen increased. Thus obtained compound showed a typical spectrum of metal phthalocyanines with a sharp characteristic band, Q-band, at $\lambda_{\text{max}} = 687\text{nm}$.

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Fundamental Study on Extraction/Separation of Actinides and Their Decay Products for Medical Nuclide Production - Precipitation Method by using Magnesium Carbonate -

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INTRODUCTION: Many amounts of decay products are generated from uranium and/or thorium chemicals which are stored in long term. If these decay products are extracted and/or transmuted, we can obtain the several kinds of nuclides and can apply them to many fields such as medicine. While, concern of nuclear therapy using α -nuclides recently increases. Especially, ^{225}Ac is one of the most concerning α -nuclides. However, since ^{225}Ac don't exist in nature, it must be generated artificially. We have proposed $^{229}\text{Th}/^{225}\text{Ac}$ generator, ^{229}Th is generated by $^{228}\text{Ra}(n,\gamma)$ reaction. Our plan of obtaining ^{228}Ra is recovery of decay products from Th. We have plan to use the residue of rare earth ore and/or long storage ThO_2 . For obtaining this type generator, development of the dissolution method of thorium compounds, extraction of Ra-228 from thorium and other decay products, manufacturing of stable target, irradiation of neutron, and separation of ^{229}Th , etc. are required. In the last year, we investigated the dissolution method of ThO_2 by thermochemical conversion. In this year, we investigated the precipitation methods for the radium extraction from solution. We carried out the co-precipitation experiment of radium in thorium solution by magnesium carbonates.

EXPERIMENTS: We use 4 types of thorium solutions; dissolution of ThO_2 in HCl or HNO_3 after thermochemical conversion using CCl_3CCl_3 or CBr_4 . The chemical conversion was carried out by heating of capsule within 0.1g of ThO_2 and 1g of halides at 300°C in 12h. The chemical converted thorium samples were dissolved 30mL of concentrated HCl or HNO_3 . The solutions were filtrated using 20mL of deionized water. The obtained solutions were neutralized by adding Na_2CO_3 , after neutralization, we added 8mL of 1M Na_2CO_3 , and finally added 2mL of 1M MgCl_2 . We immediately obtained white precipitation after adding MgCl_2 solution. After waiting 1 hour, the precipitations were filtrated. The filtrates were measured by Ge γ -ray spectrometer and ICP-MS. The determination of activity of ^{228}Ra was evaluated by using the measurement of radioactivity of ^{228}Ac under the radiation equilibrium. ^{232}Th was detected and measured by ICP-MS.

RESULTS: The precipitation ratios of ^{228}Ra were calculated the activity difference between before and after precipitation experiment. We confirmed that almost all of ^{228}Ra was coprecipitated regardless of sample solutions. The amounts of ^{232}Th in solution before and after precipitation experiments and the percent precipitation of ^{232}Th were shown in Fig. 1. The precipitation amounts of Th in the case of the dissolution of chemical converted Th with CCl_3CCl_3 by HCl is the least among the all cases. The dependence of the chemical reagents for thermochemical conversion is speculated that the counter anion of the reagent used in the thermochemical conversion may have affected thorium precipitation formation. Although the separation of radium from thorium is available by the coprecipitation method, the removal of thorium from precipitate is not enough since there are much amounts of thorium in comparison with radium. We would have to add the further separation methods of radium from thorium before the precipitation method.

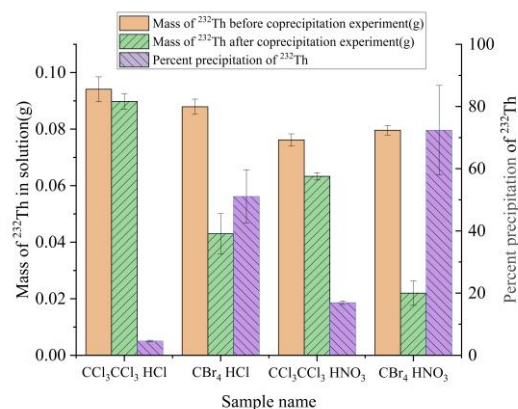


Fig. 1. Mass change of ^{232}Th in the solution before and after the precipitation experiments, and the percent precipitation of ^{232}Th

Consideration of Another Candidate Resins Containing Monoamide Structure with Selectivity for Actinyl Ions

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INTRODUCTION: Development of highly selective compounds for actinyl ions has been important. We have been focusing on monoamide compounds as promising candidates. Earlier we have considered two factors for interaction between monoamides and actinyl ions; one is “chelating effect” of the ring formed by polymer monoamides and actinyl ion(s), and the other is “flexibility” of monoamide. For our synthetic organic resins with a monoamide structure as the functional group, however, we have not found any clear tendency between the chemical structure of functional monoamide and the adsorptivity to uranium(VI) (UO_2^{2+}) species[1]. Separately, last year we mentioned another preferable factor for compounds with selectivity for U(VI), *i.e.*, UO_2^{2+} ions prefer to form “planar five-coordinated complexes” which are scarcely seen in other metal ions[2]. Based on the above knowledge, this year a novel type of resin structure was suggested.

RESULTS: Our main target solvent for using monoamide compounds is nitric acid, and as already discussed, a typical coordination style of a monoamide compound to UO_2^{2+} in HNO_3 media is shown in Fig. 1, *i.e.*, one UO_2^{2+} ion is surrounded by two carbonyl oxygen atoms of two monoamide molecules and in total four oxygen atoms of two nitrate ions, forming a six-coordinated complex[2]. In the past, we have been sticking to the exclusive utilization of monoamide compounds. In case of resins, however, forming such six-coordinated structures or the above-mentioned five-coordinated ones might be difficult spatially. Our novel idea is to use the combination of monoamide and diamide compounds as the bifunctional groups. Diamide compounds are famous for the separation of actinide(III) and lanthanide(III) species as well as actinide(IV) and (VI) ones, and we have already had an experience to synthesize a resin with a diamide structure, *N,N,N',N'*-tetramethylmalonamide (TMMA : Fig. 2) as the functional group[3]. We expect higher possibility of interaction between amide oxygen atoms and U(VI), and also lower possibility of interaction between amide oxygen atoms and lanthanide(III) species by combining monoamide and diamide structures in one resin. In the former case, it may be possible that either of the two amide oxygen atoms in one diamide group is involved in the bonding with U(VI).

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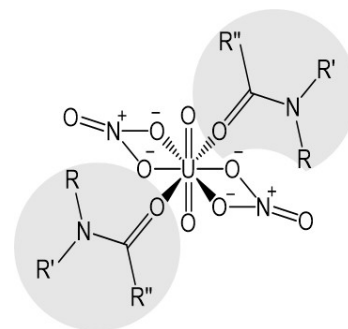


Fig. 1. Typical coordination style of a monoamide compound to UO_2^{2+} in HNO_3 .

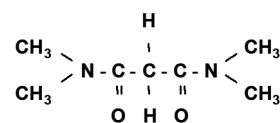


Fig. 2. Chemical structure of TMMA.