

## **I-1. PROJECT RESEARCHES**

### **Project 7**

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## INTRODUCTION:

Actinide compounds shows 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. These studies will be also useful for application research area such as the handling of the 1F debris and developments of nuclear medicines.

Such research environments to handle actinides elements are extremely difficult to build in ordinary university institutes. The hot laboratory of the KURNS offers unique opportunities for the above-mentioned characteristic research activities.

## EXPERIMENTS:

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. Kanbe and Y. Haga *et al.*, has investigated the molten salt flux (MSF) method as a route to grow high-quality single crystals of UTe<sub>2</sub> with minimal U vacancies. The single-crystalline samples of this compound have been investigated by the measurements of crystallographic and thermodynamic properties.

(2) 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.

(3) M. Nakase *et al.* has studied properties of Phthalocyanine (Pc) as a ligand for an effective extraction of U. Moreover, they tried to construct the prediction models from the complex structure.

(4) N. Shirasaki *et al.* has synthesized some uranium(III) halide complexes, and a commercially unavailable BDI potassium salt to obtain the starting material. The procedure to synthesize BDI potassium salt improved regarding stoichiometry and reflux time [3].

(6) N. Ishikawa *et al.* has measured VT-VH-MCD in the visible energy region for the monolayer Pc complex of U(IV) as well as that of Th(IV), structure of which is PcAn(acac)<sub>2</sub> (An=U or Th), to investigate magnetic

interaction between the (5f)<sup>2</sup> system and the ligand  $\pi$ -conjugate system in a photo excited state.

(7) T. Suzuki *et al.* has the investigated dissolution of CeO<sub>2</sub> as simulant material of ThO<sub>2</sub> and searched the optimum condition of dissolution. 4 kinds of halides are used as reactant chemicals for thermochemical conversion.

(8) M. Nogami *et al.* has examined applicability of the factor “formation of planner five-coordinated complexes” to monoamide compounds.

## RESULTS:

(1) Crystallographic parameters demonstrated that the main source of impurity in UTe<sub>2</sub> is the uranium defects. It hinders not only superconductivity but also the normal state electronic/magnetic excitations of UTe<sub>2</sub> as demonstrated by specific heat measurements [1]. Having established this, the possible route to prepare higher quality UTe<sub>2</sub> samples is to prevent uranium deficiency [2].

(2) The electronic ground state of UO<sub>2</sub><sup>2+</sup> in the gas phase was used for this test with small basis sets. They confirmed that the parallelization was successfully accomplished, and the CPU times linearly scaled up to around 32/128 cores in CASCI/CASPT2 calculations. For instance, a single-core calculation of CASPT2 took five and a half hours, while using 128 cores reduced the time to only four minutes.

(3) A simple regression model of the solubility prediction by other chemicals was tested on the KNIME software (with Python modules), which enables machine learning in a low-code environment.

(4) They investigated the obtained complexes by ICP-AES (uranium ratio), CHN elemental analysis, and XRD spectrum. Although purification of the complexes for single crystal structure analysis are desired in the future, they have obtained fundamental knowledge of the preparation of uranium trivalent complexes through this series study.

(6) Temperature dependence of MCD spectra of complexes were showed that clear evidence for the existence of a magnetic interaction between the (5f)<sup>2</sup> system and the photo-excited circular  $\pi$  conjugation.

(7) They found that the almost all CeO<sub>2</sub> can be dissolved by the thermochemical conversion method using CCl<sub>4</sub>, CCl<sub>3</sub>CCl<sub>3</sub>, and CBr<sub>4</sub> as reactant. Moreover, they also confirmed that almost all ThO<sub>2</sub> can be dissolved by thermochemical conversion method. The highest percentage of dissolution was obtained in the case of CBr<sub>4</sub> as reactant and dissolution by HCl.

(8) Their study suggests that formation of five-coordinated complexes by monoamide compounds may be possible if realization of preferential coordination of other ligands than NO<sub>3</sub><sup>-</sup> to UO<sub>2</sub><sup>2+</sup> is achieved.

## REFERENCES:

- [1] Y. Haga *et al.*, J. Phys.: Condens. Matter, **34**, (2022) 175601.
- [2] H. Sakai *et al.*, Phys. Rev. Mater., **6** (2022) 073401.
- [3] W. Clegg *et al.*, Inorg. Chem., **37** (1998) 2317-2319.

## PR7-1 Effect of uranium deficiency in unconventional superconductor UTe<sub>2</sub>

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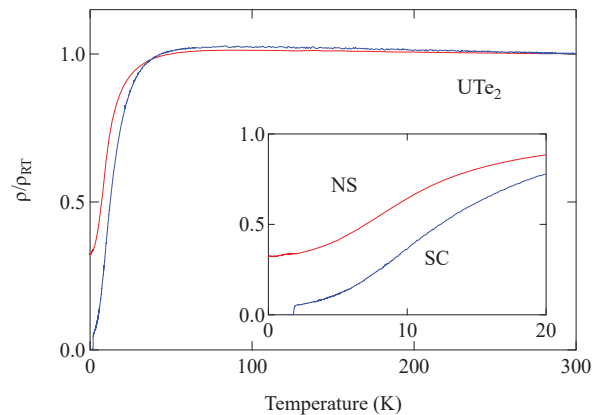
**INTRODUCTION:** Since the discovery of superconductivity in UTe<sub>2</sub>, extremely unconventional aspects of physical properties are investigated both experimentally and theoretically [1]. Experimentally, however, the strong sample dependence on superconducting properties is now recognized as a serious problem to elucidate its intrinsic behavior. In this study, we report the origin of strong sample dependent behavior in UTe<sub>2</sub>. We report detailed analysis on crystallographic structure and discuss the electronic property of this compound.

**EXPERIMENTS:** Single crystals of UTe<sub>2</sub> were grown either from chemical vapor transport method using iodine as a transport agent. Samples were characterized using an electron probe microanalysis for the stoichiometry and homogeneity. Crystallographic parameters were determined using single-crystal X-ray diffraction techniques. Superconductivity was verified by electrical resistivity measurements using the four-probe method. Specific heat was measured using a home-built calorimeter in a <sup>3</sup>He cryostat.

**RESULTS:** Figure 1 shows the typical data on the temperature dependence of electrical resistivity measured on superconducting (SC) and non-superconducting (NS) samples. The data are normalized at room temperature. Apparently, SC sample showing a resistance drop at 1.8 K corresponding to superconducting transition has low residual resistivity than NS sample, demonstrating that SC sample shows less impurity scattering and therefore higher quality.

Crystallographic parameters determined for both NS and SC samples are shown in Table 1. Here, UTe<sub>2</sub> crystallizes in the orthorhombic cell with space group Immm. There are three fractional coordinate parameters U (0 0 z), Te1 (1/2 0 z) and Te2 (0 y 1/2). There is no significant difference in these parameters. However, the equivalent isotropic atomic displacement parameter  $B_{eq}$  for the uranium site of NS sample is abnormally large. It is even larger than Te sites with lower atomic number. Detailed analysis of scattering intensity strongly suggests that uranium site occupancy for NS sample is strongly deviated from full occupancy. By treating uranium site occupancy as a fitting parameter, the best fit was obtained at U<sub>0.962(2)</sub>Te<sub>2</sub>. This result is fully consistent with the composition analysis using EPMA. Note also that the lattice parameter of NS is slightly smaller than that of SC sample, in consistent qualitatively with X-ray diffraction. However, the reduction of the volume is too small from the expected value if uranium deficiency is substituted by tellurium. It is therefore suggested that 4 % of uranium sites are left vacant in NS samples. [2]

The present results demonstrated that the main source of impurity in UTe<sub>2</sub> is the uranium defects. It hinders not only superconductivity but also the normal state electronic/magnetic excitations of UTe<sub>2</sub> as demonstrated by specific heat measurements [2]. Having established this, the possible route to prepare higher quality UTe<sub>2</sub> samples is to prevent uranium deficiency. Recent improvements of crystal growth technique using molten salt flux technique successfully achieved this and resulted in extremely high-quality single crystals [3].



**Fig. 1.** Temperature dependence of electrical resistivity normalized at room temperature for UTe<sub>2</sub>.

	NS	SC
$a$	4.1600(2)	4.1618(5)
$b$	6.1219(4)	6.1355(7)
$c$	13.9476(9)	13.9698(13)
U ( $z$ )	0.13545(5)	0.13520(4)
Te1 ( $z$ )	0.29755(5)	0.29780(10)
Te2 ( $y$ )	0.24895(5)	0.24910(3)
$B_{eq}$ (U)	0.687	0.513
$B_{eq}$ (Te1)	0.562	0.576
$B_{eq}$ (Te2)	0.515	0.529

**Table 1.** Crystallographic parameters of UTe<sub>2</sub> for NS and SC samples.

### REFERENCES:

- [1] D. Aoki *et al.*, J. Phys.: Condens. Matter, **34** (2022) 243002.
- [2] Y. Haga *et al.*, J. Phys.: Condens. Matter, **34** (2022) 175601.
- [3] H. Sakai *et al.*, Phys. Rev. Mater., **6** (2022) 073401.

## PR7-2 Development of relativistic multireference electron correlation methods for actinide compounds

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**INTRODUCTION:** Elucidating the properties of actinide compounds is important for both engineering and academic research. Theoretical calculations along with experimental approaches can aid in clarifying their properties and conducting safe verification studies.

For theoretical studies of actinide compounds, precise handling of relativistic and electron correlation effects is essential. As atomic number  $Z$  increases, the relativistic effect becomes significant, and conventional scalar relativistic treatment or perturbative correction of spin-orbit interaction may not be accurate. To account for rigorous relativistic effects, the four-component Dirac or the exact two-component (X2C) relativistic Hamiltonians should be applied. Additionally, since all  $s$ ,  $p$ ,  $d$ , and  $f$  orbitals are valence orbitals for actinide atoms, static electron correlation may not be negligible, which limits the effectiveness of conventional single-reference methods such as density functional theories. Multi-reference electron correlation theory is necessary, but its computational complexity poses a challenge.

Our group has developed new programs for calculating electronic states and properties of actinide compounds with high accuracy, based on the X2C relativistic Hamiltonian. Specifically, we have developed programs for the CASCI-CASPT2 and DMRG-CASPT2 methods, which employ multiconfigurational wave functions (CASCI/DMRG) as the 0th-order state of perturbation. CASPT2 is a well-established perturbation theory in non/quasi-relativistic frameworks [1].

**METHODS:** The free software DIRAC [2,3] already provides the Hartree-Fock and molecular orbital integral transformation with the X2C relativistic Hamiltonians. Therefore, we have developed CASCI-CASPT2 and DMRG-CASPT2 programs, which can be implemented subsequently to the DIRAC software. The primary aim of this research is to develop the X2C-DMRG-CASPT2 method. DMRG (density matrix renormalization group) [4] is a more suitable method than CASCI for dealing with a larger active space, albeit at the cost of high computational complexity.

The study will be conducted in three phases: (1) developing the X2C-CASCI-CASPT2 method, (2) developing the X2C-DMRG method, and (3) integrating the first two phases into the X2C-DMRG-CASPT2 method. Phases 1 and 2 will be carried out concurrently and merged into the third phase when sufficient progress has been made.

In the current year, we have completed Phase 1 by implementing an interface program from DIRAC to CASCI-CASPT2. Furthermore, we have accomplished the parallelization of the CASCI-CASPT2 program, enabling us to conduct large-scale calculations using supercomputers.

**RESULTS:** Figure 1 shows the scheme of the current programming in the left panel, and the CPU times of parallelized calculations in CASCI and CASPT2 in the right panel. The electronic ground state of  $\text{UO}_2^{2+}$  in the gas phase was used for this test with small basis sets. We confirmed that the parallelization was successfully accomplished, and the CPU times linearly scaled up to around 32/128 cores in CASCI/CASPT2 calculations. For instance, a single-core calculation of CASPT2 took five and a half hours, while using 128 cores reduced the time to only four minutes. This allows us to perform computations for more realistic systems with larger active spaces, which will be addressed in the coming year.

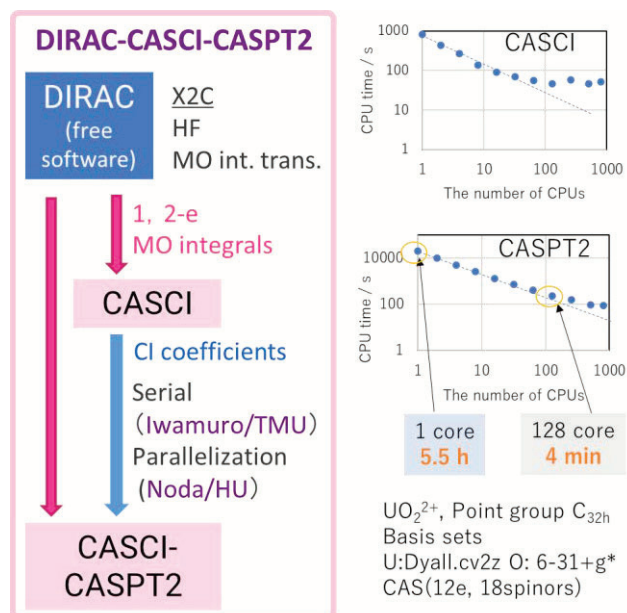


Fig. 1. Scheme of phase 1 programming and computation CPU time for parallelization in  $\text{UO}_2^{2+}$ .

### REFERENCES:

- [1] K. Anderson *et al.*, *J. Phys. Chem.*, **94** (1990) 5483-5488.
- [2] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC22 (2022), written by H. J. Aa. Jensen *et al.*
- [3] T. Saue *et al.*, *J. Chem. Phys.*, **152** (2020) 204104.
- [4] S. R. White, *Phys. Rev. Lett.*, **69** (1992) 2863.

## PR7-3 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 essential in any aspect, including the reprocessing of spent nuclear fuels, treatment of wastes generated in Fukushima Daiichi Nuclear Power Station, medical use of Actinium, and so on. I am especially interested in the Th fuel cycle, which does not produce heavy actinides such as Am and Cm. Instead, understanding the chemistry of light actinides such as Th, Pa, and U is essential. The Th fuel cycle needs an effective separation of U from Th and other fission products in spent Th fuels. To enable such separation, the thorium–uranium extraction (THOREX) process, like the plutonium–uranium redox extraction (PUREX) process, has been studied [1]. In the THOREX process,  $\text{UO}_2^{2+}$  is extracted by tri-*n*-butyl phosphate (TBP) with  $\text{Al}(\text{NO}_3)_3$ . Some other extractants which consist of C, H, O, and N atoms (CHON principle), such as monoamide, are recently reported for U/Th separation [2]. In this study, Phthalocyanine (Pc) was selected as the main structure of the extractant, which also satisfies the CHON principle, and intensively studied their characteristics. The Pc derivatization is ongoing to make the Pc soluble in an organic solvent. The purification technique suitable for Pu-Actinide complexes was investigated, and the Pc-Zn complex was synthesized as reference species previously. Next, we aim to synthesize the Pc-U complexes in the organic solvent. In FY2023, we prepared the pure U(IV) and implemented the synthesis of U(IV) acetylacetonate.

**EXPERIMENTS:** U(IV) acetylacetonate was synthesized following the procedure prepared in the Yamamura lab at Kyoto University. The black  $\text{UO}_2$  powder was first added to the concentrated HCl, and the mixture was heated to 100 C to dissolve. The solution was filtrated, and the green filtrate was forwarded to the next step. The electrochemical reduction to U(III) was implemented with Pt and Hg electrodes. After the reduction to U(III), the color of the solution became dense, and finally, pale red with the incandescent lamp was seen, as shown in **Figure 1 (a)**. Then the oxidation to U(IV) occurs at room temperature, which gives the green color as shown in **Figure 1(b)**. Then, the excess acetylacetonate was added to the U(IV) solution while heating at 50 C. The pH was adjusted to about 6 by dropwise addition of 3 M NaOH, and precipitation was formed. The precipitation contains some impurities, such as unreacted acetylacetonate and hydrated U; recrystallization by methanol was imple-

mented. Finally, the U(IV)-acetylacetonate complex was obtained. The U(IV)-acetylacetonate complex is the precursor of other Pc-U complexes. The final U(IV) acetylacetonate is shown in **Figure 2**



**Fig. 1.** Prepared U solution; (a) U(III) and (b) U(IV) in HCl solution.



**Fig. 2.** The synthesized U(IV) acetylacetonate.

**SOLUBILITY PREDICTION:** If a prediction of the solubility of the complexes is possible, it can effectively minimize the number of experiments, and the minimization of the radioactive waste generation becomes possible. Therefore, we tried to construct the prediction models from the complex structure. This year, a simple regression model of the solubility prediction by other chemicals was tested on the KNIME software (with Python modules), which enables machine learning in a low-code environment. The solubility data of Pc and U-Pc complexes must be accumulated from the literature or experiments.

**PLANS:** We will synthesize the U(IV)-Pc complex in the next fiscal year with newly synthesized Pc derivatives. The synthetic work was halted due to the maintenance and change in the layout of the chemical Lab in Tokyo Tech. The chemical lab upgrade was finished, and gradually, the synthesis was restarted. The prediction model of the solubility of U-Pc complexes will be further tested, and obtaining the complementary data from the literature and prediction of the characteristics will be implemented.

### REFERENCES:

- [1] R. H. Rainey and J. G. Moore, Nucl Sci Eng., **10(4)** (1961) 367-371.
- [2] P.N. Pathak, Solv Ext Ion Exch, **20(3)** (2002) 293-311.

## PR7-4 Fundamental preparation study to access functional uranium(III) complexes

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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. On the other hand, uranium(III) is easily oxidized and changed into uranium(IV) or uranyl(VI). Thus, to maintain the oxidation state, limited ligands are required to use for complexation with uranium(III). In 2013, King et al. synthesized uranium(III)  $\beta$ -diketoiminate (BDI) complex such as (BDI)U<sub>2</sub> [1] and in 2020, Boreen et al. reported that the single molecule magnet (SMM) behavior was observed in low temperature using (BDI)U(OAr)<sub>2</sub> (OAr = 2,6-Diisopropylphenyl) [2]. Because of the steric hindrance of BDI ligands, low-coordination complexes with BDI ligands are relatively easy to achieve. Of course, BDI ligands can be the supporting ligands not only for uranium(III) but also for uranium(IV), uranyl(V), and uranyl(VI) complexes [3].

The purpose of this study is to investigate suitable preparation method of uranium complexes with BDI ligands and to characterize low valent uranium BDI complexes. We also synthesized a commercially unavailable BDI potassium salt to obtain the starting material.

**EXPERIMENTS:** uranyl(VI) chloride solution (1M) was reduced into uranium(III) through an electrolytic reduction in 1M hydrochloric acid 20ml for approximately 3 hours. Subsequently, the solution evaporated and the purple compound, presumably UCl<sub>3</sub> · (H<sub>2</sub>O)<sub>3.85</sub> was obtained. It was estimated by ICP-AES (uranium ratio) and CHN elemental analysis. On the other hand, uranium iodide was achieved by reaction in ethanol. This reaction route required to use very thin uranium metal and iodine. After stirring vigorously for 7 days, the reaction didn't be finished completely. At that time, we collected the red brown powder which was rendered at that reaction. The uranium ratio was 38.45% which was close to the uranium ratio of U<sub>2</sub>I<sub>3</sub>.

The procedure to synthesize BDI potassium salt was followed by the one reported by Clegg in 1998 with fine modifications regarding stoichiometry and reflux time [4]. On top of that, a similar compound also can be synthesized by using the same equipment.

**RESULTS:** BDI potassium salt is soluble in THF and according to past reports, uranium (IV) trichloride BDI complex is not soluble in THF. Unfortunately, there was no residue after stirring solution, so the reaction products with uranium chloride hydrate seem to be soluble. It is necessary to use different solvents or an additional step if

the uranium chloride hydrate use as starting material. In the case of uranium iodide, to prevent oxidization of low valent uranium ion, carbon tetrachloride was used as the solvent. After stirring about 12 hours, the solution was removed from the residue, and washing by toluene to extract potassium iodide. The obtained brown powder was measured by XRD equipment (MiniFlex II, Rigaku). To know the difference between uranium BDI compound and lanthanide BDI compound, the attempt to react BDI potassium salt (Fig. 1, lower) with cerium compound was done. Unlike uranium, the lanthanide trichloride hydrates didn't dissolve in most polar solvents. Therefore, cerium nitrate hexahydrate was used in this experiment and consequently pink powder can be obtained.

When it comes to XRD spectrum in uranium BDI complex and cerium BDI complex, same peaks can be found. One of the different points was that the number of peaks of uranium BDI complex (Fig. 1, upper) was many more than that of cerium BDI compound.

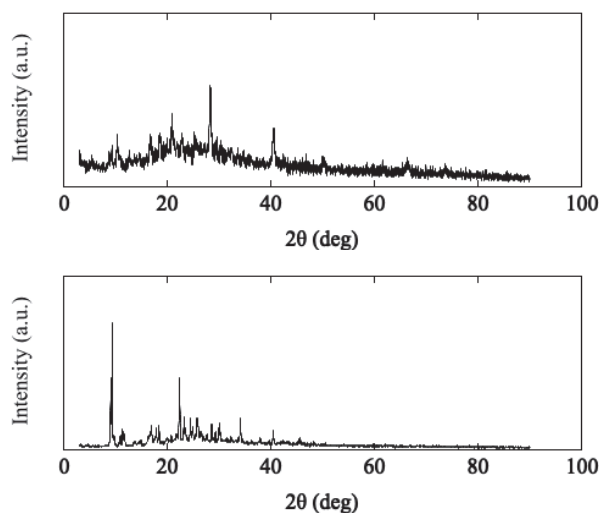


Fig. 1. XRD patterns obtained from uranium BDI complex (upper) and potassium BDI complex (lower).

Although purification of the complexes for single crystal structure analysis are desired in the future, we have obtained fundamental knowledge of the preparation of uranium trivalent complexes through this series study.

### REFERENCES:

- [1] D. M. King *et al.*, *Angew. Chem. Int. Ed.*, **52** (2013) 4921-4924.
- [2] M. A. Boreen *et al.*, *Dalton Trans.*, **49** (2020) 7938-7944.
- [3] P. Waldschmidt *et al.*, *Inorg. Chem.*, **62** (2023) 2013-2023.
- [4] W. Clegg *et al.*, *Inorg. Chem.*, **37** (1998) 2317-2319.

## PR7-5 Synthesis of ultra-pure UTe<sub>2</sub> by molten salt flux method

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**INTRODUCTION:** Uranium ditelluride (UTe<sub>2</sub>) has attracted considerable attention since the compound exhibits a number of novel superconducting (SC) features. Ran *et al.* [1] first reported that UTe<sub>2</sub> exhibits an unconventional superconductivity below  $T_c = 1.6$  K, and extremely large upper critical field  $H_{c2}$  exceeding the Pauli-limiting field. In this paper, we report the molten salt flux (MSF) method as a route to grow high-quality single crystals of UTe<sub>2</sub> with minimal U vacancies. Such stoichiometric UTe<sub>2</sub> crystals grown by the MSF method exhibit the highest  $T_c$  of 2.1 K with a remarkably large RRR  $\sim 1000$ , which is much better than that grown by chemical vapor transition (CVT) method.

**EXPERIMENTS:** In the MSF method, an equimolar mixture of sodium chloride and potassium chloride (NaCl + KCl) was chosen, which has a eutectic melting point of about 650 °C [2]. In each growth procedure, a piece of lightly etched U metal and granule of Te metal were weighed to adjust the target molar ratio of Te/U. Then, the metals were placed together in the bottom of a carbon crucible. The carbon crucible filled with the metals and salt mixture was placed in a quartz tube with an inner and outer diameter of 15 and 18 mm, respectively. It was heated at 200 °C for several hours under dynamic vacuum to dehydrate the contents. Then, the carbon crucible was vacuum-sealed into the quartz tube. The sealed quartz tube was inserted into a home-built vertical electric tube furnace. First, it was preheated at 450 °C for 24 h, then raised to 950 °C over 24 h, and kept for 24 h to produce a uniform melt. Then, the temperature was slowly lowered to a final-step temperature ( $T_f$ ) with a ramp rate of 0.02–0.03 °C per min. The temperature was maintained at  $T_f$  for 24 h for annealing. After cooling down, the molten salts were easily dissolved in water, and the millimeter-sized crystals were picked up, washed with ethanol, and immediately dried in a vacuum atmosphere.

**RESULTS:** Figure 1 shows the temperature dependence

of normalized resistivity  $\rho(T)/\rho(300\text{ K})$  along the a axis for the representative single crystals of non-superconducting (NS), superconducting SC1, and SC2. The RRR value was estimated using the  $\rho(0)$  obtained by fitting to  $\rho(T) = AT^2 + \rho(0)$  in the range of  $T_c < T < 4\text{ K}$ , assuming a Fermi liquid state just above  $T_c$ . The  $\rho(0)$  of the NS crystal in Fig. 1 was  $2.2\mu\Omega\text{cm}$ , whereas that of the SC2 was  $34\mu\Omega\text{cm}$ . The considerably higher residual resistivity of the NS crystal indicates higher density of its scattering centers. U<sub>1- $\delta$</sub> Te<sub>2</sub> may be described as U<sup>4+1- $\delta$</sup> [VU] <sub>$\delta$</sub> U<sup>5+ $\delta$</sup> Te<sub>2</sub>, where [VU] means the vacancies of U sites. A [VU] of  $\sim 4\%$  in the NS crystal significantly changes the 5f electron count because of the simultaneous generation of U<sup>5+</sup> and U vacancies which cause strong scattering of conduction electrons. Therefore, even if the uranium deficiency of the SC crystals is less than 1%, extra electron scattering may occur, and/or the corresponding residual density of states may exist in the SC state.

The MSF method is a promising technique for crystal growth of SC UTe<sub>2</sub> to control the  $T_c$  value and prevent any disorder caused by uranium vacancies. The MSF method would also be useful for various uranium chalcogenides because it is applicable at relatively low temperatures to avoid volatilization of the constituent chalcogens. This will be certainly useful for nuclear fuel technology in future.

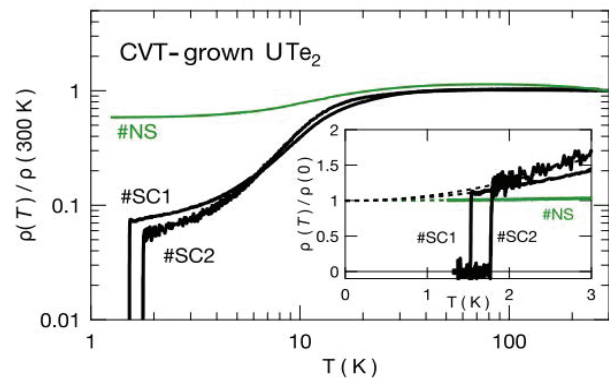


Fig. 1. Temperature dependence of normalized resistivity [3],  $\rho(T)/\rho(300\text{ K})$ , for the CVT-grown single crystals of UTe<sub>2</sub>. The resistivity is measured along the a axis. The inset shows the enlarged plot of  $\rho(T)/\rho(0)$  with regard to  $\rho(0)$  in the low-temperature part. The value of  $\rho(0)$  was estimated by fitting to  $\rho(T) = AT^2 + \rho(0)$  in the range of  $T_c < T < 4\text{ K}$ .

### REFERENCES:

- [1] S. Ran *et al.*, *Science*, **365** (2019) 684.
- [2] D. Coleman and P. Lacy, *Mater. Res. Bull.*, **2** (1967) 935.
- [3] H. Sakai *et al.*, *Phys. Rev. Mat.*, **6** (2022) 073401.

## PR7-6 Exploration of new interactions between actinide 5f electron systems and photo-excited organic $\pi$ -electron systems

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**INTRODUCTION:** Lanthanide and actinide complexes have high magnetic anisotropy due to the orbital angular momentum component in the total angular momentum of the f-electronic systems. Unlike 4f electrons, 5f electrons are characterized by a large covalency involved in chemical bonding. On the other hand, phthalocyanine (Pc), one of the representative macrocyclic ligands, has a cyclic  $\pi$ -conjugated system and acquires orbital angular momentum in the  $\pi$ - $\pi^*$  excited state.

Our group has confirmed 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.

Previously, our group has identified 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 [Pc<sub>2</sub>Ln] (Ln=Tb, Dy) and monolayer complexes [PcLn(cyclen)]. Similar interaction was confirmed in the sandwich bilayer complex [Pc<sub>2</sub>Ln] and the monolayer complex [PcLn(cyclen)].[3][4]

In this study, we measured VT-VH-MCD in the visible energy region for the monolayer Pc complex of U(IV) as well as that of Th(IV), structure of which is shown in Fig.1, to investigate magnetic interaction between the (5f)<sup>2</sup> system and the ligand  $\pi$ -conjugate system in a photo excited state.

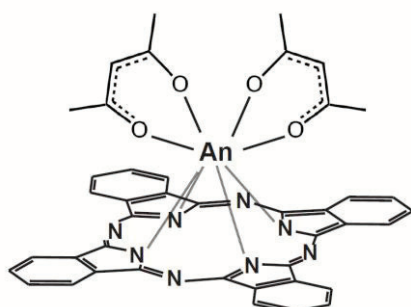


Fig. 1. Structure of PcAn(acac)<sub>2</sub> (An=U or Th).

**EXPERIMENTS:** Bisacetylacetonatophthalocyaninouranium(IV), PcU(acac)<sub>2</sub>, was prepared according to the literature method from lithiumphthalocyanine and tetraacetylacetonatouranium(IV), latter of which was provided by Dr Yamamura (Institute for Integrated Radiation and Nuclear Science, Kyoto University). MCD measurements were performed using a J-Spectroscopy J-720 circular dichroism dispersometer equipped with an

Oxford SM4000 superconducting magnet cryostat. The uranium complex was doped in a thin film of polymethyl methacrylate (PMMA) and subjected to measurements. VT measurements were performed in the temperature range from 1.5K to 100K under the magnetic field of 1T and VH measurements were in the magnetic field from 0T to 6T at 1.5K.

**RESULTS:** The U and Th complexes show very similar absorption spectra in the visible energy region due to the ligand centered  $\pi$ - $\pi^*$  transition. Both complexes exhibit a sharp absorption band called Q band at around 14000-15000 cm<sup>-1</sup>, which is typical for monolayered Pc complexes. MCD spectrum of this band shows a characteristic differential profile called A-term MCD. This indicates that the excited state is doubly degenerate and split by Zeeman effect. The Th complex with no 5f electron showed no temperature dependence in the MCD spectrum. On the other hand, the U complex with (5f)<sup>2</sup> system showed a significant temperature dependent MCD, as shown in Fig. 2. This is clear evidence for the existence of a magnetic interaction between the (5f)<sup>2</sup> system and the photo-excited circular  $\pi$  conjugation.

In order to quantify this interaction, a numerical simulation analysis was performed. Currently, an assumption that lowest substate in the J=4 multiplet is Jz=4 gives the best agreement to the experimental result. Quantum-chemical RASSCF-RASSI calculation has been performed to evaluate the validity of the assumption and the numerical model used.

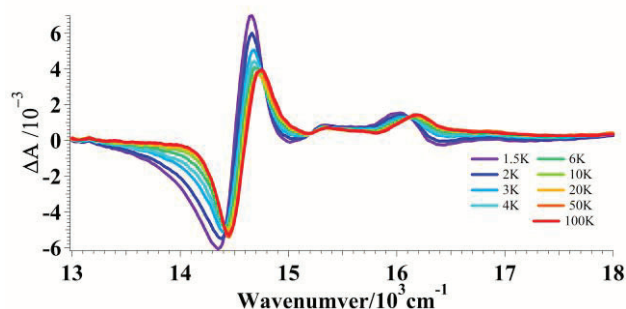


Fig. 2. Temperature dependence of MCD spectra of PcU(IV)(acac)<sub>2</sub> in visible range at the temperatures from 1.5K to 100K under magnetic field of 1T.

### REFERENCES:

- [1] K. Kizaki *et al.*, *Chem. Commun.*, **53** (2017) 6168-6171.
- [2] T. Fukuda *et al.*, *CHEM.-EUR. J.*, **23**(64) (2017) 16357-16363.
- [3] K. Kizaki *et al.*, *Inorg. Chem.*, **60**(3) (2021) 2037-2044.
- [4] K. Kizaki *et al.*, *Inorg. Chem. Front.*, **10** (2023) 915-925.



**PR7-7 Fundamental Study on Extraction/Separation of Actinides and Their Decay Products for Medical Nuclide Production – Dissolution Methods of ThO<sub>2</sub> by Thermochemical Conversion –**

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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  $\alpha$ -nuclides recently increases. Especially, Ac-225 is one of the most concerning  $\alpha$ -nuclides. However, Ac-225 don't exist in nature, because it is nuclide in Np decay series. There are several kinds of generation methods of Ac-225, e.g.,  $^{226}\text{Ra}(n,2n)^{225}\text{Ra} \rightarrow ^{225}\text{Ac}$ . We have proposed  $^{229}\text{Th}/^{225}\text{Ac}$  generator, Th-229 is generated by  $^{228}\text{Ra}(n,\gamma)$  reaction. Our plain of obtaining Ra-228 is recovery of decay products from thorium. We have plan to use the residue of rare earth ore and/or long storage thoria, because the old thorium under the condition of radioactive equilibrium is desirable. 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 Th-229, etc. are required. In this year, we investigated the dissolution method of ThO<sub>2</sub> by thermochemical conversion.

**EXPERIMENTS:** Firstly, we investigated dissolution of CeO<sub>2</sub> as simulant material of ThO<sub>2</sub> and searched the optimum condition of dissolution. 4 kinds of halides are used as reactant chemicals for thermochemical conversion. Weight ratio of CeO<sub>2</sub>/halides was 1/10. These mixtures were put into Swagelok capsule and heated. After heating, the obtained products were dissolved by conc. HCl or HNO<sub>3</sub>. After filtration, the concentrations of Ce were measured by ICP-MS, and the dissolution percentage were calculated. The dissolution experiments of ThO<sub>2</sub> were carried out by the same procedures as CeO<sub>2</sub>, but temperature and heating time were kept to one condition, 300°C, and 4h.

**RESULTS:** The dissolution results of CeO<sub>2</sub> are shown in Fig. 1. We confirmed that the dissolution rate by HCl is higher than HNO<sub>3</sub>, and temperature affects the dissolution rate. We found that the almost all CeO<sub>2</sub> can be dissolved by the thermochemical conversion method using CCl<sub>4</sub>, CCl<sub>3</sub>CCl<sub>3</sub>, and CBr<sub>4</sub> as reactant. By the way, the experiments using CCl<sub>4</sub> was carried out as reference experiments, because CCl<sub>4</sub> was forbidden the engineering

use. The dissolution results of ThO<sub>2</sub> are shown in Fig. 2. We also confirmed that almost all ThO<sub>2</sub> can be dissolved by thermochemical conversion method. The highest percentage of dissolution was obtained in the case of CBr<sub>4</sub> as reactant and dissolution by HCl.

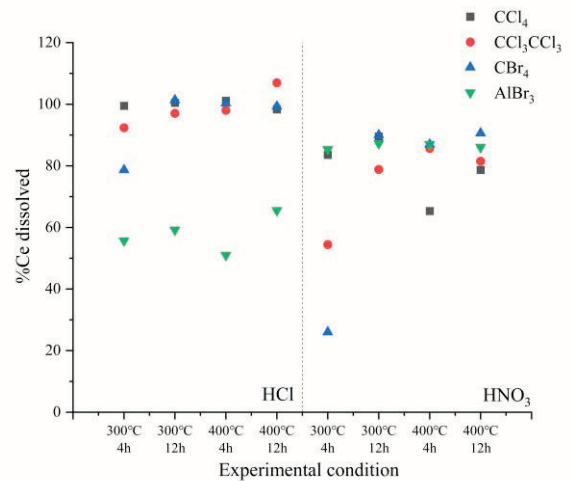


Fig. 1. Dissolution percentage of CeO<sub>2</sub> by thermochemical conversion.

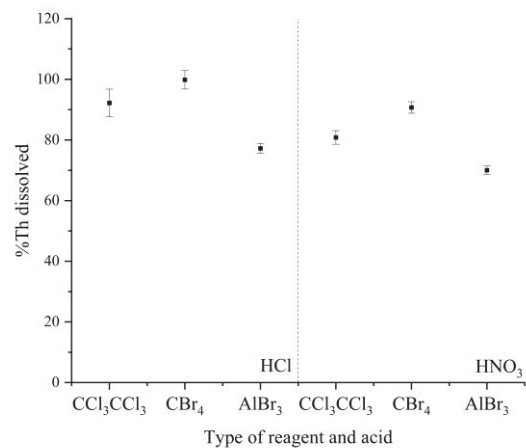


Fig. 2. Dissolution percentage of ThO<sub>2</sub> by thermochemical conversion.

## PR7-8 Potential Another Factor to Give Selective Complex Formation between Monoamide Compounds and 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, considering the possibility of complete incineration of waste compounds (so-called “CHON principle”[1]). 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, we have not found any clear tendency between the chemical structure of functional monoamide and the adsorptivity[2].

Recently we have found that another research group has tried to develop compounds which are selective for uranium(VI) ( $\text{UO}_2^{2+}$ ) species. According to the group,  $\text{UO}_2^{2+}$  ion prefers to form “planar five-coordinated complexes” which are scarcely seen in other metal ions, and based on the knowledge they developed  $\text{H}_2\text{saldian}$ -type ligands[3]. In addition, as one of the application of those ligands, a novel adsorbent for recovery of U in seawater was synthesized, where complex formation occurs outside of main chain of polymer[4]. In this report, applicability of this factor “formation of planar five-coordinated complexes” to monoamide compounds we have examined was discussed.

**RESULTS:** Our main target solvent for using monoamide compounds is nitric acid. A typical coordination style of a monoamide compound to  $\text{UO}_2^{2+}$  in  $\text{HNO}_3$  media is shown in Fig. 1. It can be seen that one  $\text{UO}_2^{2+}$  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. Judging from the figure, it would be difficult to form a five-coordinated complex under usual circumstances.

While, as an example apart from monoamide compounds, we have been investigating one of triphosphine trioxides, 1,1,3,5,5-pentaphenyl-1,3,5-triphosphapentane trioxide (PPTPT : Fig. 2) for a potential versatile extractant [3]. Although PPTPT has high selectivity for U(VI) in  $\text{HNO}_3$  of high concentrations, the most distinguished nature of it would be its unusual high selectivity for U(VI) in  $\text{HNO}_3$  of very low concentrations. Our preliminary structure analysis of an PPTPT- $\text{UO}_2^{2+}$  nitrate complex by single X-ray has revealed that one  $\text{UO}_2^{2+}$  ion is surrounded by two PPTPT molecules by in total four phosphoryl groups and one oxygen atom from  $\text{H}_2\text{O}$ , forming a five-coordinated complex. This suggests that formation of five-coordinated complexes by monoamide

compounds may be possible if realization of preferential coordination of other ligands than  $\text{NO}_3^-$  to  $\text{UO}_2^{2+}$  is achieved. Such an approach may be investigated next year.

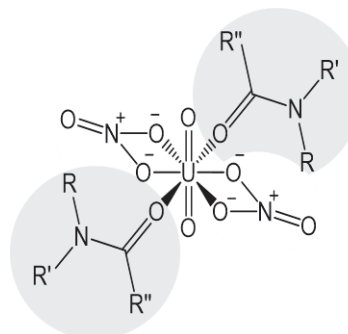


Fig. 1. Typical coordination style of a monoamide compound to  $\text{UO}_2^{2+}$  in  $\text{HNO}_3$

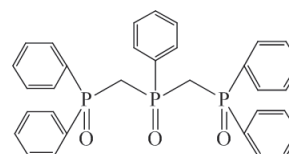


Fig. 2. Chemical structure of PPTPT.

### REFERENCES:

- [1] M. G. B. Drew *et al.*, Dalton Trans., (2007) 244-251.
- [2] M. Nogami *et al.*, KURNS Progress Report 2019, (2020) PR13-5.
- [3] T. Mizumachi *et al.*, Inorg. Chem., **61** (2022) 6175-6181.
- [4] K. Ito *et al.*, 2023 Annual Meeting, Atomic Energy Soc. Jpn, Mar. 2023, 1H08.