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ESR and Magnetic Susceptibility Evidence of Thermally Accessible Electron-transferred Species in $U_2Cl_{10}[\phi_3As]$*

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For understanding the magnetic behavior of 5f electrons in complexes and compounds of actinide metal ions, pentavalent uranium (U^{5+}) is most useful because of its simple configuration of $[Rn]5f^1$. This configuration can enable us to compare experimental observations with theoretical estimates without any consideration of electron-correlation interaction. However, there are only a few reports on complexes containing U^{5+} because of difficulties in their preparation. The present authors have directly studied by electron spin resonance (ESR) measurements, U^{5+} intermediates in photo- and electrolytic reduction processes of uranyl complexes in organic solutions [1].

Recently, transition metal complexes with a series of substituted phosphines have been of interest in the direct interaction between the metal ions and phosphorus [2]. For uranium, only complex formations between uranium and substituted ligands with atoms of the nitrogen family, with a *g*-value of about 2 (observed by ESR spectra) have been reported [3]. But a study of the interaction between uranium and various substituted ligands with atoms of the nitrogen family has not yet been reported. The present authors have succeeded in interpreting consistently the ESR and magnetic susceptibility (χ) of $UCl_5[\phi_3P]$ (ϕ = phenyl) by assuming a thermally accessible intramolecular electron-transfer mechanism [4].

In order to examine the appropriateness of such a mechanism, the magnetic susceptibility of powdered $U_2Cl_{10}[\phi_3As]$ was measured from room temperature to the b.p. of liquid helium and its ESR measurement was carried out from room temperature continuously down to 137 K and at the b.p. of liquid nitrogen. The results obtained by both measurements were analysed consistently with each other, based on thermally accessible intramolecular electron-transfer equilibrium between the uranium ion and triphenylarsine. It is found that this mechanism is applicable to the present complex.

Experimental

Materials

The chemicals used were reagent grade purity and were used after drying and/or degassing by a usual method. Since pentavalent uranium compounds are extremely sensitive to atmospheric oxygen and moisture, all preparations were performed in glass vessels under argon atmosphere. UCl_5tcac (tcac = trichloroacrylylchloride, $Cl_2C{=}CClCOCl$) [5] was dissolved in toluene and a slight excess of triphenylarsine in toluene was added to this solution. A pale greenish complex precipitated immediately. After stirring for 3 h, the precipitates were washed several times with toluene and vacuum-dried overnight.

The uranium content was determined gravimetrically by an ammonium method [6]. Hydrogen and carbon contents were determined with a Yanagimoto CHN coder MT-2. *Anal.* Calc. for $U_2Cl_{10}[\phi_3As]$ ($H_{15}C_{18}Cl_{10}AsU_2$): H, 1.30; C, 19.71; U, 41.89. Found: H, 1.84; C, 19.71; U, 42.13%.

Measurements

Measurement of magnetic susceptibility was carried out on the powdered sample sealed in a quartz tube by the Faraday method from room temperature to the b.p. of helium. For the calibration of the magnetic susceptibility, $HgCo(NCS)_4$ [7] was used as a reference. In order to confirm that the sample was free from ferromagnetic impurity, the dependence of the magnetic susceptibility on the intensity of the magnetic field was measured in the range from 0.1 to 1 T. The values of the magnetic susceptibility obtained were corrected for a diamagnetic susceptibility, $\chi_{dia}(U_2Cl_{10}[\phi_3As]) = -430.17 \times 10^{-6}$ cgs emu/mol.

The ESR spectra were recorded on a JES-ME-2X spectrometer from room temperature down to 137 K and also at the b.p. of liquid nitrogen. The *g*-value was determined with reference to the signal of Mn^{2+} doped into MgO.

Results and Discussion

The magnetic susceptibility of the sample of $U_2Cl_{10}[\phi_3As]$ *versus* temperature is shown in Fig. 1, with a tentative molecular structure for this com-

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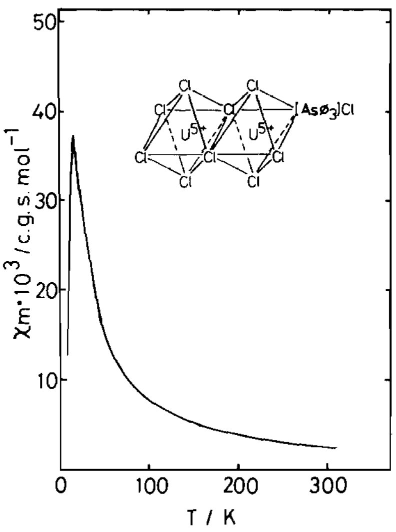

Fig. 1. Temperature dependence of the magnetic susceptibility of $U_2Cl_{10}[\phi_3As]$.

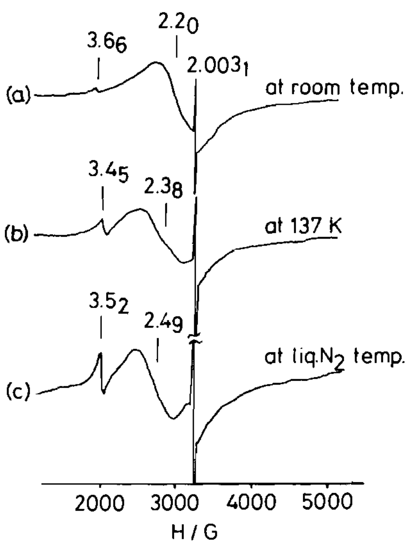

Fig. 2. Change of ESR spectra of $U_2Cl_{10}[\phi_3As]$ with temperature.

pound. The maximum clearly appears at 13 K, in contrast to the monotonically increasing curve of the U_2Cl_{10} dimer [8]. Therefore, in the present U_2Cl_{10}-$[\phi_3As]$, a magnetic superexchange interaction is expected to operate between U^{5+} via chlorine and/or arsenic, probably because of a delocalization of 5f electrons through the introduction of triphenylarsine. Moreover, the observed magnetic susceptibility shown in Fig. 1 cannot be explained by only the U^{5+} dimer having a magnetic exchange interaction. The paramagnetic susceptibility due to the U^{5+} dimers is, in principle, too small to explain such a large paramagnetic susceptibility as shown in the Figure.

Figures 2a to 2c show ESR absorption spectra at room temperature, 137 K and liquid nitrogen temperature, respectively. There are in all four kinds of paramagnetic species responsible for ESR as seen from the Figures. The sharp signal at the center of the spectra is easily assigned to an organic radical from its linewidth of 5.17 G and g-value of 2.00 ((a), (b) and (c)). The existence of such a free radical in U_2Cl_{10}-$[\phi_3As]$ indicates a redox reaction in the sample, although its concentration is very low. This signal corresponds to that of the paramagnetic species reported by Selbin *et al.* [3].

The weak signal overlapping with the sharp signal of the organic radical becomes stronger with decreasing temperature. The ESR signals due to U^{5+} in a dimer with magnetic exchange interaction between them are often observed in the range of $g = 2$–3.5 [9]. The ESR signals of U^{5+} complexes with negligibly small exchange interaction appear at about the value of $g \approx 1$ [5, 10]. The weak signal is attributable to the dimer of U^{5+} having a magnetic exchange interaction.

On the other hand, the weak signal at the lower magnetic field side of a g-value of 3.6(6) and with linewidth of 56 G can be observed from room temperature to liquid nitrogen temperature, as seen in Fig. 2. This signal can be attributed to the U^{4+} species, because its g-value agrees with that of U^{4+}-cupferrate [11], in which a crystalline field around the uranium ion has the same tetragonal symmetry as that in the present sample. The broad and strong signals in the left-hand side of the sharp signal at the center become weaker with decreasing temperature, as seen from the Figures. The signal is considered to be due to a complex, $U^{5+}Cl_5{\cdot}U^{4+}Cl_5{\cdot}[\phi_3As]^{+\cdot}$, produced by an intramolecular electron-transfer as described in the following section. The values of $g = 2.2(0)$–$2.3(8)$ are intermediate between $g = 3.6(6)$ and 2.005(4) and the intensity of the signals is stronger at higher temperature. Thus, this complex, $U^{5+}Cl_5{\cdot}U^{4+}Cl_5{\cdot}[\phi_3As]^{+\cdot}$, is considered to have the weak magnetic interaction among spins of U^{5+}, U^{4+} and $[\phi_3As]^{+\cdot}$, producing the broad and strong signal with $g = 2.2(0)$–$2.3(8)$. The signals with g-values of 3.6(6) and 2.005(4) are due to U^{4+} and $[\phi_3As]^{+\cdot}$, respectively, produced by dissociation of $U^{5+}Cl_5U^{4+}Cl_5{\cdot}[\phi_3As]^{+\cdot}$, although the concentrations of these species are negligibly small. With regard to the $U^{5+}Cl_5$ fraction, it is actually very difficult to observe its signal.

In order to interpret these results, we introduce here an electron-transfer equilibrium, indicated as eqn. (1), taking into account the value of the magnetic susceptibility and the unusual temperature behavior of the ESR signals:

$$U^{5+}Cl_5{\cdot}U^{5+}Cl_5{\cdot}[\phi_3As] \rightleftharpoons U^{5+}Cl_5{\cdot}U^{4+}Cl_5{\cdot}[\phi_3As]^{+\cdot} \qquad (1)$$

The left-hand side of eqn. (1) shows the state of this complex in a lower temperature region and the right-hand side shows the state of this complex in the higher temperature region. The complex on the right-hand side dissociates further into $U^{5+}Cl_5$, $U^{4+}Cl_4$ and $Cl[\phi_3As]^{+\cdot}$ in so small a degree that their contributions to the magnetic susceptibility are negligibly small, but in the ESR spectra their signals are observable.

In this electron-transfer equilibrium, the paramagnetic species are the $U^{5+}\cdot U^{5+}$ dimer, $U^{5+}\cdot U^{4+}$ dimer and the triphenylarsine cation radical. Magnetic susceptibilities of these three paramagnetic species are calculated at first as follows. When U^{5+} is in the dimer with a magnetic exchange interaction, it can be dealt with as the ion with $S = 1/2$ [12]. Then, the magnetic susceptibility per $U^{5+}\cdot U^{5+}$ dimer molecule is given as:

$$\chi_{\mathrm{mol}}(U^{5+}\cdot U^{5+}) = 2\left(\frac{Ng^2\beta^2}{3kT}\right) \times \left(\frac{1}{1 + \frac{1}{3}\exp(-2J_{\mathrm{ex}}/kT)}\right) + \chi_{\mathrm{t.i.p.}} \qquad (2)$$

where J_{ex} is the exchange integral for the intradimer interaction and can be obtained in relation to the maximum temperature of the magnetic susceptibility, and $\chi_{\mathrm{t.i.p.}}$ is the temperature-independent paramagnetic susceptibility. Putting $-2J_{\mathrm{ex}}$ as 15 cm^{-1} (corresponding to 13 K, $g = 2$ and $\chi_{\mathrm{t.i.p.}} = 0$) into eqn. (2), the magnetic susceptibilities are calculated as shown in Fig. 3 by solid squares. The other dimer containing U^{5+} and U^{4+} has magnetic susceptibility as given in eqn. (3) [12]:

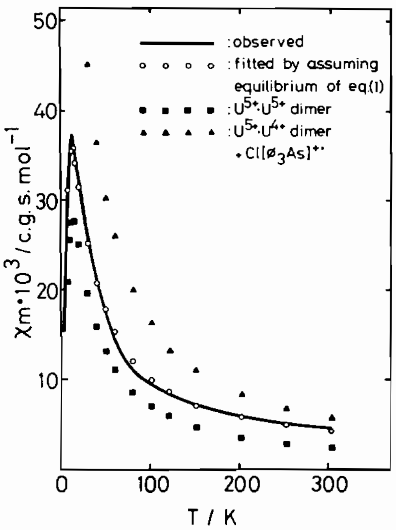

Fig. 3. Magnetic susceptibility–temperature curves of paramagnetic species.

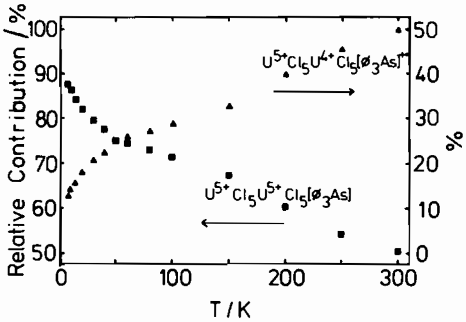

Fig. 4. Temperature dependence of relative contributions from both species in eqn. (1) obtained by fitting magnetic susceptibility.

$$\chi_{\mathrm{mol}}(U^{5+}\cdot U^{4+}) = \left(\frac{Ng^2\beta^2}{kT}\right) \times \left(\frac{10 + \exp(-3J_{\mathrm{ex}}/kT)}{8 + 4\exp(-3J_{\mathrm{ex}}/kT)}\right) + \chi_{\mathrm{t.i.p.}} \qquad (3)$$

assuming $S_1 = 1/2$ for U^{5+} and $S_2 = 1$ for U^{4+}. On the right-hand side of the equilibrium (1) there is another paramagnetic species of triphenylarsine cation radical. Then, the paramagnetic susceptibility of the right-hand side is the sum of the magnetic susceptibility of the $U^{5+}\cdot U^{4+}$ dimer and that of the cation radical, which can be obtained by assuming that Curie's law is obeyed (solid triangle in Fig. 3).

Finally, the observed solid line can be fitted by considering the contributions from paramagnetic species of both sides in balance in the electron-transfer equilibrium. Figure 4 shows a relative contribution from both sides under a good fitting condition. The contribution from the left side reaches closer to 100% as the temperature decreases, while at room temperature the ratio of contributions from both sides equals about 1:1. The enthalpy change of this electron-transfer equilibrium can be estimated to be 0.024 kcal/mol (99 J/mol) from the temperature dependence of the obtained equilibrium constant in the range below 100 K.

Concerning electron spin resonance spectra, the proposed electron-transfer equilibrium can explain qualitatively the behavior of ESR absorption spectra with temperature. Thus, it should be said that in our case an intramolecular electron transfer between the metal ion (uranium) and its ligand (ϕ_3As) is thermally accessible.

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