Magnetic-superexchange Interactions of Uranium(IV) Chloride-addition Complexes with Amides. II. Complexes with Lactams

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The magnetic susceptibilities of five cyclic amide (lactam)-addition complexes of uranium(IV) chloride were measured between room temperature and 2 K. Magnetic-exchange interaction was found only for *N*-methyl-substituted amide complexes, and a dimer structure was assumed for them on the basis of their chemical properties. Treating interdimer interaction with a molecular-field approximation, the magnetic susceptibilities were calculated to be in good agreement with the experimental results in the temperature region of the maxima in χ_A. The transmission of antiparallel spin coupling *via* the π orbitals of the bridging amide ligands is proposed to explain the strong intradimer superexchange interaction for the uranium(IV) chloride–amide complexes with the magnetic-susceptibility maximum.

In the preceding paper,[1] a series of amide-addition complexes of uranium(IV) chloride, $UCl_4 \cdot nL$ (L= $R_1CONR_2R_3$), were prepared, and their magnetic susceptibilities measured. Among the complexes studied, six showed a magnetic-exchange interaction and their magnetic-exchange parameters were calculated, assuming a dimer structure from their chemical properties. The effects of substituents on the bridging amide ligands were discussed.

To elucidate further the effects of the substituents, five uranium(IV) chloride-addition complexes were prepared with lactam (cyclic amide) ligands. Magnetic-exchange interactions were found only for complexes with a methyl group substituted with hydrogen on the amide nitrogen. This paper will report on the magnetic-susceptibility results, and a mechanism for the transmission of spin-exchange coupling in the complexes with *N*-methyl substituents is proposed.

Experimental

Reagents. Reagent-grade 5-, 6-, and 7-membered lactams and *N*-methyl-substituted 5- and 7-membered lactams were purchased from the Nakarai Chemical Industry Co., Ltd., and were used without further purification. Uranium(IV) chloride was prepared by passing carbon tetrachloride vapor over uranium dioxide at 500 °C in a vacuum.[2]

Preparations. Uranium(IV) chloride-γ-butyrolactam (1/4), $UCl_4 \cdot 4BuL$, and uranium(IV) chloride-*N*-methyl-γ-butyrolactam (1/2.5), $UCl_4 \cdot 2.5MBuL$: An oily product was obtained from an acetone solution of anhydrous uranium(IV) chloride by adding, successively, an excess acetone solution of the ligand and isopentane. After washing with ethyl acetate, the precipitates were rapidly dried in a vacuum and then kept over P_2O_5 for about a week.

Uranium(IV) chloride–δ-valerolactam (1/4), $UCl_4 \cdot 4Val$,[3] uranium(IV) chloride–ε-caprolactam (1/4), $UCl_4 \cdot 4CaL$,[4] and uranium(IV) chloride–*N*-methyl-ε-caprolactam (1/2.5), $UCl_4 \cdot 2.5MCaL$,[4] were synthesized according to the methods previously reported.

Analytical. The uranium content was determined gravimetrically as U_3O_8.[5] The chlorine content was determined by potentiometric titration with a standard $AgNO_3$ solution. The carbon, hydrogen, and nitrogen contents were determined with a Yanagimoto CHN coder MT-2. The analytical results are shown in Table 1.

Magnetic Measurements. The magnetic susceptibilities were measured by the Faraday method from 2 to 300 K on powder samples sealed in quartz tubes. The apparatus was calibrated with $Co[Hg(SCN)_4]$ as a standard.[6] The temperature was measured with a Au-Co/Cu thermocouple for temperature above 20 K and with a carbon resistor below 32 K. The dependence of the magnetic susceptibility on the mangetic-field strength was measured at field strengths of 400, 1470, 3320, 5400, and 7200×10^{-4} T at room temperature, the temperature of liquid nitrogen, and the temperature of liquid helium. No dependence of the susceptibilities on the magnetic field was found. The experimental values for magnetic susceptibilities were corrected for the diamagnetism of the sample using the values reported by Dawson,[7] Pascal's constants, and their constitutive correction.[8] The values of the diamagnetic corrections are listed in Table 2.

Rusults and Discussion

Unsubstituted lactams form $UCl_4 \cdot 4L$ complexes (L= BuL, VaL, and CaL), and the U(IV) ion probably has a coordination number of eight, the most common coordination number for U(IV) complexes. *N*-methyl-substituted lactams coordinate to form $UCl_4 \cdot 2.5L$ complexes (L=MBuL and MCaL), in which the lactam ligands probably bridge between U(IV) ions.

Figure 1 shows the magnetic susceptibility *vs.* temperatue curves for the five lactam complexes. $UCl_4 \cdot$

Table 1. Elemental analyses

Complex	C(%)		H(%)		N(%)		Cl(%)		U(%)	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
$UCl_4 \cdot 4BuL$	25.25	26.67	2.81	3.89	7.42	7.78	21.68	19.70	33.60	33.06
$UCl_4 \cdot 2.5MBuL$	24.64	23.91	3.60	3.59	5.83	5.58	21.93	22.60	36.95	37.94
$UCl_4 \cdot 4VaL$	29.27	31.10	4.37	4.15	6.50	7.26	19.00	18.37	31.95	30.84
$UCl_4 \cdot 4CaL$	35.65	34.62	5.46	5.29	6.27	6.73	16.11	17.05	26.78	28.61
$UCl_4 \cdot 2.5MCaL$	31.37	30.12	4.85	4.66	4.91	5.02	19.71	20.34	33.35	34.13

Table 2. Diamagnetic susceptibility corrections

Complex	$\chi_{dia} \times 10^6$/emu
$UCl_4 \cdot 4BuL$	−340.0
$UCl_4 \cdot 2.5MBuL$	−291.5
$UCl_4 \cdot 4VaL$	−387.5
$UCl_4 \cdot 4CaL$	−442.0
$UCl_4 \cdot 2.5MCaL$	−353.0

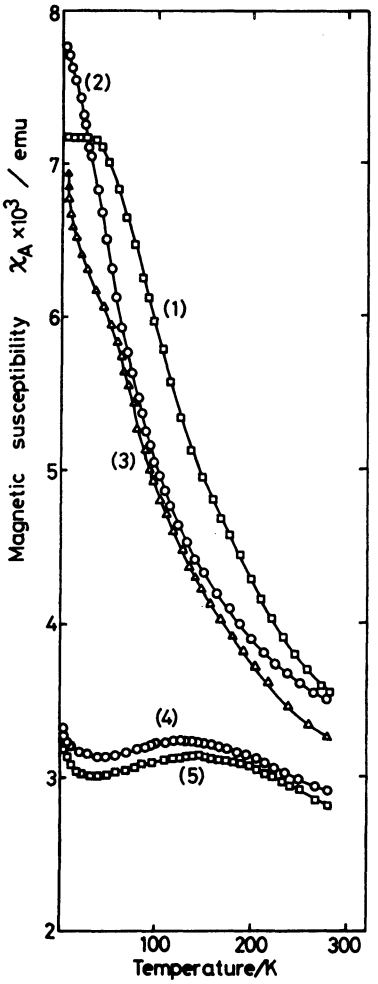

Fig. 1. Temperature dependence of magnetic susceptibility per gram atom. (1), $UCl_4 \cdot 4CaL$; (2), $UCl_4 \cdot 4BuL$; (3), $UCl_4 \cdot 4VaL$; (4), $UCl_4 \cdot 2.5MBuL$; (5), $UCl_4 \cdot 2.5MCaL$.

2.5MBuL and $UCl_4 \cdot 2.5MCaL$ differ from the other three complexes having broad susceptibility maxima at 127 and 146 K respectively. Unsubstituted lactam complexes show different magnetic behavior at lower temperature, but show increasing susceptibilities with a decrease in the temperature from room temperature down to the temperature of liquid helium. Their paramagnetism can be explained by a model based on the crystalline field on the U(IV) ion.

Table 3 lists the Weiss contants and the effective Bohr magnetons in the temperature region where the data fit the Curie-Weiss law. The magnetic susceptibilities of $UCl_4 \cdot 2.5MBuL$ and $UCl_4 \cdot 2.5MCaL$ show maxima, indicating an antiferromagnetic-exchange interaction.

Table 3. Curie-Weiss constants and effective Bohr magnetons

Complex	Temperature range/K	θ/K	μ_{eff}/μ_B
$UCl_4 \cdot 4BuL$	100 —r.t.	−257	2.76
$UCl_4 \cdot 2.5MBuL$	200 —r.t.	−804	2.52
$UCl_4 \cdot 4VaL$	100 —r.t.	−238	2.67
$UCl_4 \cdot 4CaL$	75 —r.t.	−164	2.79
$UCl_4 \cdot 2.5MCaL$	230 —r.t.	−387	2.47

a) Curie-Weiss law as $\chi_A = \frac{C}{T-\theta}$.

A dimeric structure for these complexes was assumed from their composition and the dimeric structures of complexes with similar compositions. $UCl_4 \cdot 2.5DMA$ has been considered to have a dimeric structure from its composition and from the measurement of its electric conductivity.[9–12] For the three bridges between two uranium ions, these are considered to be one ligand bridge and two chlorine ion bridges by Bagnall *et al.*,[12] while three ligand bridges are proposed by Gans.[13] Uranium(IV) chloride–*N*,*N*-dimethyl-α,α-diphenylacetamide (1/2.5) shows the temperature-independent paramagnetism characteristic of hexacoordinate U(IV) compounds; a dimeric structure with one ligand, dimethyl-diphenyl-acetamide, and two chlorine ions bridging two U(IV) ions has been proposed to account for the magnetic susceptibility.[4] Some transition-metal chloride complexes with lactam are considered to have dimer structures.[14,15] A dimer model is, therefore, assumed for complexes that have a magnetic-exchange interaction.

For the intradimer magnetic-exchange interaction, it is appropriate to use the isotropic spin Hamiltonian:

$$H_{ex} = -2J_{ex}\vec{S_1}\cdot\vec{S_2}, \quad (1)$$

where J_{ex} is the exchange integral for the interaction between uranium ions with spin operators $\vec{S_1}$ and $\vec{S_2}$. As each uranium(IV) ion has two unpaired spins, the spin angular momentum $S_1=S_2=1$. By substituting the energy levels obtained from the spin Hamiltonian (1) into the well-known van Vleck equation,[16] the magnetic susceptibility per gram of the atom is given as:

$$\chi_A = \frac{Ng^2\mu_B^2}{kT}\frac{5+\exp(-4J_{ex}/kT)}{5+3\exp(-4J_{ex}/kT)+\exp(-6J_{ex}/kT)} + N\alpha. \quad (2)$$

The value of $N\alpha$ is estimated by extrapolating the magnetic-susceptibility curve to the higher-temperature region. Then, the value of J_{ex} can be obtained from the temperature of maximum susceptibility. Susceptibilities calculated using these values, and assuming $g=2$ as in Part I, did not agree with the experimental results. Therefore, the effect of interdimer interaction was considered further.

For the complex that has a low symmetry field and $S>1/2$, zero-field splitting must be considered. Ginsberg *et al.* considered the effects of single-ion zero-field splitting on the magnetic susceptibility of nickel dimers.[17] They dealt with interdimer interactions by means of a molecular-field approximation. The Hamiltonian for this interaction is taken as $-2Z'J'_{ex}$

$\vec{S}_z\langle\vec{S}_z\rangle$. Here, $\vec{S}_z$ is the operator for the Z compounent of the dimer total spin, J'_{ex} is the effective interdimer exchange integral, and Z' is the coordination number of the dimer lattice. Therefore, the magnetic susceptibility per gram of the atom is:

$$\chi_A = \frac{Ng^2\mu_B^2}{3k}\left\{\frac{F_1}{T-4Z'J'_{ex}F_1} + \frac{2F'}{1-4Z'J'_{ex}F'}\right\} + N\alpha, \quad (3)$$

where

$$F' = F_2/D + 3C_2^2F_3/(3J_{ex}-\delta) + 3C_1^2F_4/(3J_{ex}+\delta),$$
$$F_1 = \{1 + \exp(4J_{ex}/kT) + 4\exp(4J_{ex}/kT)\exp(D/kT)\}/F_5,$$
$$F_2 = \{2\exp(4J_{ex}/kT)\exp(D/kT) + \exp(D/kT) - 1 - 2\exp(4J_{ex})/kT)\}/F_5,$$
$$F_3 = \{\exp(4J_{ex}/kT) - \exp(J_{ex}/kT)\exp(\delta/kT)\}/F_5,$$
$$F_4 = \{\exp(4J_{ex}/kT) - \exp(J_{ex}/kT)\exp(-\delta/kT)\}/F_5,$$
$$F_5 = 2 + \exp(D/kT) + \exp(J_{ex}/kT)\exp(-\delta/kT) + \exp(J_{ex}/kT)\exp(\delta/kT) + 2\exp(4J_{ex}/kT) + 2\exp(4J_{ex}/kT)\exp(D/kT),$$
$$\delta = [(3J_{ex} + D)^2 - 8J_{ex}D]^{1/2},$$
$$C_1 = 2(2)^{1/2}D/[(9J_{ex}-D+3\delta)^2+8D^2]^{1/2},$$
$$C_2 = (9J_{ex}-D+3\delta)/[(9J_{ex}-D+3\delta)^2+8D^2]^{1/2}.$$

The single-ion zero-field splitting parameter, D, was assigned an initial value of 10 cm^{-1}. The magnetic susceptibilities calculated by Eq. 3 using the parameters listed in Table 4 are shown in Fig. 2. Table 4 also lists the exchange parameters for UCl_4·2.5DMA and UCl_4·2.5DEA. In the temperature region of χ_{max}, the calculated values agreed well with the experimental magnetic susceptibilities. The discrepancy at lower temperatures is partly due to paramagnetic impurities, such as monomers. The calculation of the magnetic susceptibilities was not further refined, since the aim of this work was not a precise fit of the calculations with the experimental results, but the determination of the relation of the magnitude of the exchange parameter with the substituents on the ligand in the amide-addition complexes of UCl_4. It is noteworthy that UCl_4·2.5MBuL, whose χ_{max} temperature is lower than that of UCl_4·2.5MCaL; has a larger χ_{max} than the latter. This fact suggests that intradimer-exchange interaction is antiferromagnetic.

When a hydrogen bonded to a ligand-nitrogen atom is replaced by a methyl group, the number of lactam ligands coordinated with UCl_4 changes from 4 to 2.5 and the magnetic properties suggest intradimer-exchange interaction. Both complexes with half an integer-lactam molecule must be bridged dimers. The methyl group donates electron density to the nitrogen atom of the lactam ligand, so both the nitrogen and the oxygen atoms can bond to the U(IV) ion and the lactam ligand provides a path for the intradimer magnetic-super-exchange interaction.

Table 4. Magnetic-exchange interaction parameters and TIP[a] susceptibilities for complexes

Complex	$2J_{ex}/cm^{-1}$	$Z'J'_{ex}/cm^{-1}$	$N\alpha$
UCl_4·2.5DMA[b]	−82.6	−64.0	970×10^{-6}
UCl_4·2.5DEA[b]	−77.0	−74.0	1240×10^{-6}
UCl_4·2.5MBuL	−86.8	−34.0	1010×10^{-6}
UCl_4·2.5MCaL	−99.4	−26.0	1000×10^{-6}

a) TIP: Temperature-independent paramagnetic. b) *Cf.* Part I.

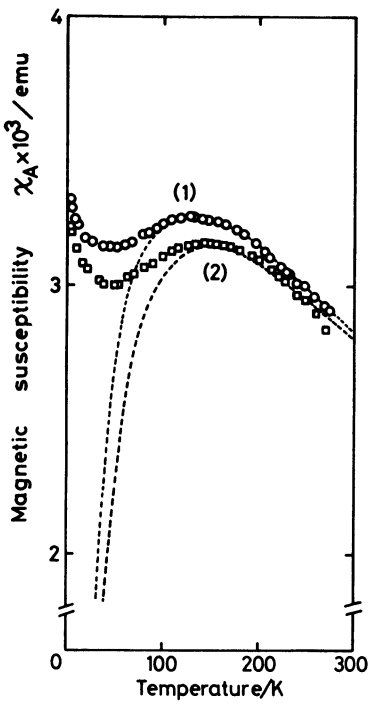

Fig. 2. Magnetic susceptibility *versus* temperature curve. (1), UCl_4·2.5MBuL; (2), UCl_4·2.5MCaL. ○, □; Experimental, ------; calculated.

Table 5. Effect of the substituent of the amide molecule on the magnetic behavior

Complexes in right-side column have the maximum of magnetic susceptibility *versus* temperature curve, while those on the left side are normally paramagnetic. Groups in parentheses are substituents.

UCl_4·4BuL (H)	⟷	UCl_4·2.5MBuL	(CH_3)
UCl_4·4CaL (H)	⟷	UCl_4·2.5MCaL	(CH_3)
UCl_4·6AA (H, H)	⟷	UCl_4·2.5DMA[a]	(CH_3, CH_3)
UCl_4·4AAN (Ph, H)	⟷	UCl_4·2.5DEA[a]	(C_2H_5, C_2H_5)
	⟷	UCl_4·4MA[a]	(CH_3, H)
UCl_4·3DPA (Ph, Ph)	⟷	UCl_4·4EA[a]	(C_2H_5, H)
UCl_4·4BAM (H, H)	⟷	UCl_4·3DMBA[a]	(CH_3, CH_3)
UCl_4·4BAN (Ph, H)	⟷	UCl_4·3DMBA[a]	(CH_3, CH_3)
UCl_4·4AAN (H, Ph)	⟷	UCl_4·3MAA[a]	(CH_3, Ph)
UCl_4·3DPA (Ph, Ph)	⟷	UCl_4·3MAA[a]	(CH_3, Ph)

a) These complexes have been studied in Part I.

Table 5 lists complexes where magnetic-exchange interactions were found in the right-side column, and the remainder of the amide complexes on the left. Table 5 shows the correlation between *N*-methyl (ethyl) substitution and a magnetic-exchange interaction. The carbonyl oxygen of the amide ligand is the principal donor site, and the nonbonding electron pair on the nitrogen delocalizes into a π-molecular orbital involving oxygen, carbon, and nitrogen atoms. When a methyl group is substituted for a hydrogen on the nitrogen atom, the electron density on the nitrogen increases because of the electron-donating property of the methyl group.

For a large metal ion such as uranium, both oxygen and nitrogen coordinate and the amide ligand acts as a bridging group. As the electron-donating power of a methyl group is greater than that of an ethyl group, the temperature of the χ_{max} values of complexes with *N*-methyl-substituted amides is expected to be higher than that of complexes with *N*-ethyl-substituted amides. The experimental results coincide with this expectation. (Compare $UCl_4 \cdot 4MA$ and $UCl_4 \cdot 4EA$ and/or $UCl_4 \cdot 2.5DMA$ and $UCl_4 \cdot 2.5DEA$ in Part I.) It has been reported, on the basis of the vibrational and NMR spectra, that simultaneous coordination through both carbonyl oxygen and amide nitrogen may be present in $[Co(DMA)_6](ClO_4)_2$.[18]

The exchange interaction originates from an overlap of the wave functions of the unpaired electrons. Here, the superexchange interaction through the amide molecule between uranium ions must be considered.

The coordination number for the U(IV) ion is usually eight or six, but if the complex is hexacoordinate, it will have a constant paramagnetic susceptibility from room temperature corresponding to temperature-independent paramagnetism. When the complex has the coordination number of eight, it will show temperature-dependent paramagnetism. This magnetic behavior of uranium(IV) complexes can be explained on the basis of the crystalline-field theory. Thus, the present complexes are probably octacoordinated. Octacoordinated U(IV) complexes have either a dodecahedral or square antiprismatic field around the U(IV) ion, with the dodecahedral field occurring more often. Assuming a cubic coordination on the U(IV) ion, a probable structure for the $UCl_4 \cdot 3L$ complexes is shown in Fig. 3. In a field of cubic symmetry, seven 5f orbitals are split into a singlet, a_{2u}, and two triplets, t_{1u} and t_{2u}. The t_{1u} orbital is the lowest in energy. Each of the a_{2u}, t_{1u}, and t_{2u} orbitals has charge-density maximum in a certain direction. The t_{1u} orbital has a charge-density maximum in the direction toward the center of the cube-face, and this charge-density maximum is the largest among the three kinds of orbitals[19] (see Fig. 4). The t_{1u} orbital does not participate in the π-overlap with the coordinated oxygen or nitrogen atoms of the ligand, for this orbital is directed toward the center of the cube-face. However, the t_{1u} orbital is favored for the π-overlap with p_z, and this tendency is enhanced when the cubic coordination of the ligands actually becomes dodecahedral by up and down displacements of the corner oxygen and nitrogen atoms, as is shown in Fig. 3. The antiferromagnetic coupling of unpaired electrons of the U(IV) ions can be explained by the bridging of the amide ligands. The high temperature of χ_{max} suggests that the exchange interaction occurs *via* the π orbitals shown in Fig. 3, since the polarized spins in a π-system can couple at a distance with little attenuation[17] and can lead to strong superexchange interaction. A similar transmission of antiparallel spin coupling was found, for example, in the royal-blue modification of anhydrous copper(II) formate.[20] A proton-magnetic-resonance experiment now planned can provide evidence regarding the proposed π-system.[21]

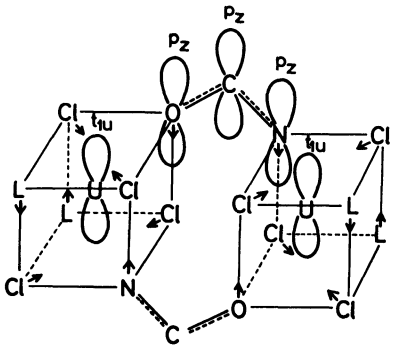

Fig. 3. Presumed structure for $UCl_4 \cdot 3L$ type complex in idealized form. For bridging amide molecules, only O=C–N is drawn, otherwise amide molecules are represented as L. If all ligands move to the directions shown by arrows, coordination polyhedron turns from cube to dodecahedron.

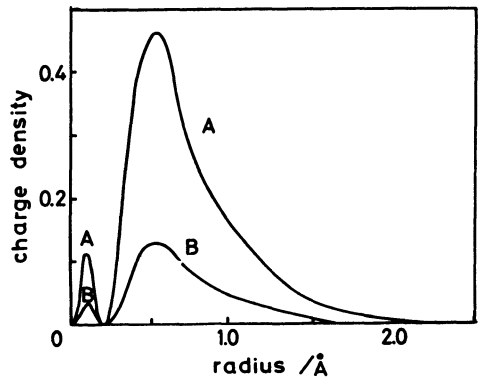

Fig. 4. Charge density distribution of 5f orbitals.
A: t_{1u} in the direction toward the center of cube-face,
B: a_{2u} in the direction toward the corner of cube and t_{2u} in its direction of charge density maximum.[19]

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