February, 1983] © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* **56**, *607—613 (1983)*

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

Chie Miyake,* Yukio Hinatsu, and Shosuke Imoto
Department of Nuclear Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565

(Received December 7, 1981)

Studies of magnetic susceptibility, χ, from 300 to 2 K on seventeen UCl_4–amide complexes showed that six complexes had maxima in χ between 155 and 82 K. This unusual magnetic behavior occurred only with *N*-methyl or ethyl-substituted amide complexes. Infrared and chemical evidence indicates that these six complexes probably have dimeric structure, in which two U(IV) ions are bridged by the amide ligands. Assuming a dimer structure and a two-spin Heisenberg model with $-2J_{ex}$ of about 90 cm^{-1} for the dimer, the magnetic susceptibilities for the six complexes were calculated in good agreement with the experimental results in the temperature region of the maxima in χ.

Magnetic-exchange interactions at low temperatures in polynuclear complexes of transition metals, especially of dimeric copper(II) complexes, have been extensively studied for thirty years.1) Similar magnetic behavior of complexes of actinoid ions has been reported previously. Tetrakis(diethylamido)uranium(IV)2) and tris[bis(*N,N'*-dimethylethylenediamido)]uranium(IV)3) have dimer and trimer structures respectively, as determined by X-ray-diffraction analysis. In these complexes, magnetic-exchange interactions might be expected to occur, but their magnetic susceptibility increases down to the temperature of liquid helium without showing any magnetic susceptibility maxima. Recently, the superexchange phenomena have been first observed by us on uranium(IV) chloride-addition complexes with amides.4)

This paper will report on the temperature-dependent magnetic susceptibilities of uranium(IV) chloride-addition complexes with seventeen amide molecules, among which six complexes showed a maximum in their magnetic susceptibility-*versus*-temperature curves that indicates intradimer superexchange interaction. Some results of the infrared-absorption measurements are reported.

Experimental

Table 1 lists the full names of the complexes studied, the abbreviated formula, and the substituents on the carbon and nitrogen atoms of each amide.

Materials. Reagent-grade amides were used as purchased without any further purification. The anhydrous uranium tetrachloride was synthesized by the solid-vapor-phase reaction of uranium dioxide and carbon tetrachloride at 500 °C.5) The cesium hexachlorouranate was obtained as a crystalline powder by dissolving cesium chloride in a hydrochloric acid solution of uranium tetrachloride and by then slowly evaporating the water.6)

Preparation of Complexes. *$UCl_4\cdot 2.5DEA$*: A five-fold excess of diethylacetamide was added to a hot acetone solution of Cs_2UCl_6, thus precipitating cesium chloride. After filtering the precipitates, the oily product was obtained by adding isopentane to the filtrate. The oil was dissolved in hot acetone and then precipitated again with isopentane. After several repetitions of this procedure, a green solid was obtained: it was

Table 1. Formulae for uranium (IV) chloride–amide complexes

Complex	Abbreviation of complex	Substituents a)		
		R_I	R_{II}	R_{III}
Uranium(IV)chloride–*N,N*-Dimethylacetamide (1/2.5)	$UCl_4\cdot 2.5$ DMA	CH_3	CH_3	CH_3
Uranium(IV)chloride–*N,N*-Diethylacetamide (1/2.5)	$UCl_4\cdot 2.5$ DEA	CH_3	C_2H_5	C_2H_5
Uranium(IV)chloride–*N,N*-dimethylformamide (1/2.5)	$UCl_4\cdot 2.5$ DMF	H	CH_3	CH_3
Uranium(IV)chloride–*N,N*-Dimethylbenzamide (1/3)	$UCl_4\cdot 3$ DMBA	Ph	CH_3	CH_3
Uranium(IV)chloride–*N*-Methylacetanilide (1/3)	$UCl_4\cdot 3$ MAA	CH_3	CH_3	Ph
Uranium(IV)chloride–*N,N*-Diphenylacetamide (1/3)	$UCl_4\cdot 3$ DPA	CH_3	Ph	Ph
Uranium(IV)chloride–*N*-Methylformanilide (1/3)	$UCl_4\cdot 3$ MFA	H	CH_3	Ph
Uranium(IV)chloride–Benzamide (1/4)	$UCl_4\cdot 4$ BAM	Ph	H	H
Uranium(IV)chloride–Benzanilide (1/4)	$UCl_4\cdot 4$ BAN	Ph	Ph	H
Uranium(IV)chloride–Acetanilide (1/4)	$UCl_4\cdot 4$ AAN	CH_3	Ph	H
Uranium(IV)chloride–*N,N*-Diphenylformamide (1/4)	$UCl_4\cdot 4$ DPF	H	Ph	Ph
Uranium(IV)chloride–*N*-Methylacetamide (1/4)	$UCl_4\cdot 4$ MA	CH_3	CH_3	H
Uranium(IV)chloride–*N*-Ethylacetamide (1/4)	$UCl_4\cdot 4$ EA	CH_3	C_2H_5	H
Uranium(IV)chloride–*N*-Methylformamide (1/4)	$UCl_4\cdot 4$ MF	H	CH_3	H
Uranium(IV)chloride–Acetamide (1/6)	$UCl_4\cdot 6$ AA	CH_3	H	H
Uranium(IV)chloride–Acrylamide (1/6)	$UCl_4\cdot 6$ AcA	CH_2CH	H	H
Uranium(IV)iodidedichloride–*N,N*-Dimethylacetamide (1/5)	$UI_2Cl_2\cdot 5$ DMA	CH_3	CH_3	CH_3

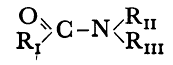
a)

$$\mathrm{O{=}C(R_I){-}N(R_{II})(R_{III})}$$

Table 2. Elemental analyses

Complex	C(%)		H(%)		N(%)		Cl(%)		U(%)	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
UCl_4·2.5DMA	20.04	20.09	4.11	3.77	5.76	5.86	23.18	23.74	40.01	39.85
UCl_4·2.5DEA	26.32	26.97	4.72	4.87	5.50	5.25	20.98	21.25	36.67	35.67
UCl_4·2.5DMF	16.50	16.01	3.23	3.11	6.36	6.22	25.02	25.22	40.62	42.33
UCl_4·3DMBA	37.21	39.19	3.86	3.99	4.98	5.08	18.55	17.15	28.59	28.79
UCl_4·3MAA	38.51	39.18	4.14	3.99	4.48	5.08	17.60	17.17	30.00	28.78
UCl_4·3DPA	50.06	49.76	3.79	3.85	3.81	4.15	14.07	14.00	24.37	23.50
UCl_4·3MFA	35.93	37.00	3.42	3.44	5.44	5.35	18.31	18.07	30.96	30.33
UCl_4·4BAM	37.61	38.90	3.37	3.24	6.61	6.48	17.72	16.42	28.02	27.55
UCl_4·4BAN	53.79	53.43	3.61	3.77	4.69	4.80	13.01	12.14	18.90	20.38
UCl_4·4AAN	41.41	41.75	3.80	3.91	6.11	6.09	15.71	15.42	25.60	25.88
UCl_4·4DPF	53.08	53.43	3.65	3.77	4.69	4.80	12.06	12.14	18.92	20.38
UCl_4·4MA	21.30	21.43	4.11	4.17	8.30	8.34	20.79	21.11	35.04	35.43
UCl_4·4EA	25.26	26.38	4.60	4.95	7.44	7.69	19.00	19.48	33.75	32.70
UCl_4·4MF	15.47	15.59	3.11	3.25	8.88	9.09	22.88	23.03	40.19	38.65
UCl_4·6AA	19.96	19.62	3.82	4.09	11.33	11.45	19.03	19.32	32.61	32.43
UCl_4·6AcA	27.64	26.81	3.72	3.73	10.57	10.42	17.74	17.60	28.54	29.54
UI_2Cl_2·5DMA	23.72	24.06	4.38	4.51	6.89	7.02	32.15	32.55	23.05	23.85
							(Cl+I)			

Table 3. Diamagnetic susceptibility corrections

Complex	$\chi_{dia} \times 10^6$/emu
UCl_4·2.5DMA	−275.0
UCl_4·2.5DEA	−334.3
UCl_4·2.5DMF	−245.3
UCl_4·3DBMA	−416.8
UCl_4·3MAA	−416.8
UCl_4·3DPA	−530.6
UCl_4·3MFA	−372.7
UCl_4·4BAM	−421.6
UCl_4·4BAN	−618.3
UCl_4·4AAN	−469.1
UCl_4·4DPF	−639.8
UCl_4·4MA	−303.6
UCl_4·4EA	−353.5
UCl_4·4MF	−258.6
UCl_4·6AA	−325.3
UCl_4·6AcA	−349.1
UI_2Cl_2·5DMA	−479.2

(emu $mol^{-1} \times 4\pi \times 10^{-6} \rightarrow m^3 \times mol^{-1}$)

dried over P_2O_5.

UCl_4·3DPA: Oily solids were obtained from an acetone solution of anhydrous uranium tetrachloride by adding, successively, a dichloromethane solution of the ligand and then petroleum ether. The precipitates were dried under a vacuum.

UCl_4·3MFA and UCl_4·4BAN: Oily solids were obtained from acetone solutions of anhydrous uranium tetrachloride by adding an acetone solution of the ligand. Then the precipitates were dried under a vacuum.

UCl_4·4BAM: Oily solids were precipitated from an acetone solution of anhydrous uranium tetrachloride by adding, successively, a small excess of benzamide in the acetone solution and then petroleum ether. The product was dried under a vacuum and stored in a vessel with P_2O_5.

UCl_4·4AAN: An excess of an acetone solution of acetanilide was added to the acetone solution of uranium tetrachloride, and the product was precipitated by adding isopentane. The precipitates were dried under a vacuum.

UCl_4·4MF: Precipitates were obtained from an ethyl acetate solution of anhydrous uranium tetrachloride by adding an ethyl acetate solution of the ligand. After washing with ethyl acetate, the precipitates were dried in a vacuum.

UCl_4·6AcA: An acetone solution of the ligand and then isopentane was added to an acetone solution of anhydrous uranium tetrachloride to precipitate the product. The precipitates were dried in a vacuum.

UCl_4·2.5DMA,7) UCl_4·2.5DMF,8) UCl_4·3DMBA,9) UCl_4·3MAA,9) UCl_4·4DPF,9) UCl_4·4MA,10) UCl_4·4EA,11) UCl_4·6AA,7) and UI_2Cl_2·5DMA12) were synthesized according to the methods previously reported.

Chemical Analysis. The uranium content was determined gravimetrically by the ammonium method,13) while the chlorine content was determined by potentiometric titration with a standard $AgNO_3$ solution. The carbon, hydrogen, and nitrogen contents were determined with the Yanagimoto CHN coder, MT-2. The results of elemental analyses are listed in Table 2.

Magnetic Measurement. The magnetic susceptibilities were measured with a torsion balance from room temperature down to 2 K, using powdered $Co[Hg(SCN)_4]$ as a standard14) and with $\chi_g = 16.44 \times 10^{-6}$ emu g^{-1} (emu $g^{-1} \times 4\pi 10^{-3} \rightarrow m^3\ kg^{-1}$) at 20 °C. The temperature was measured with a Au–Co/Cu thermocouple for the range from room termperature to 20 K and with a carbon resistor below 32 K. To test for ferromagnetic impurities in the samples, the dependence of the magnetic susceptibility on the magnetic field was measured at 400, 1470, 3320, 5400, and 7200 Oersted at room temperature, 77 and 4.2 K.

Table 3 lists the values of the diamagnetic-susceptibility correction used in calculating the paramagnetic susceptibility of complexes from the experimentally measured values.15)

Infrared Absorption. The infrared-absorption spectra were recorded on HITACHI-225 Spectrophotometer using a prism disk of KRS-5 (TlBr–TlI), either as neat compounds or as Nujol mulls. The spectra were also measured in 0.1% CCl_4 solution, if required.

Results and Discussion

Figure 1 shows the magnetic susceptibility *versus*

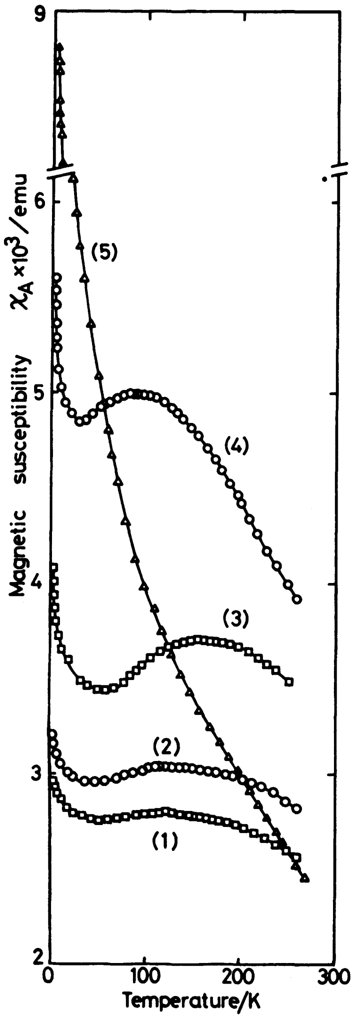


Fig. 1. Temperature dependence of magnetic susceptibility per gram atom.
(1): UCl_4·2.5DMA, (2): UCl_4·2.5DEA, (3): UCl_4·4MA, (4): UCl_4·4EA, (5): UCl_4·3DPA. (emu mol^{-1} × 4π × 10^{-6}→m^3 mol^{-1}).

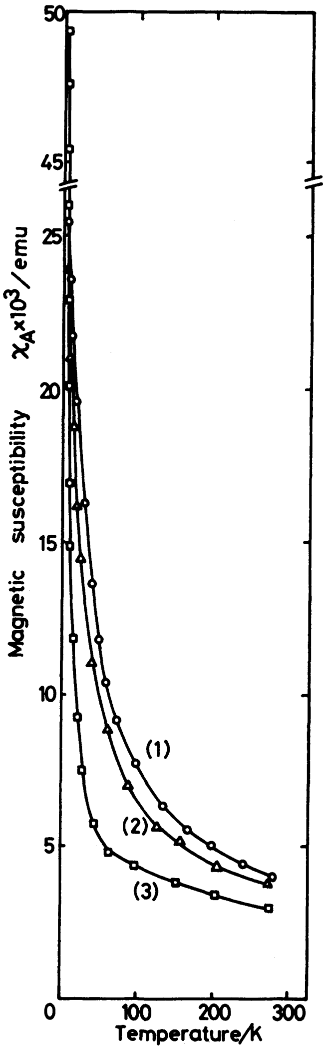


Fig. 2. Temperature dependence of magnetic susceptibility per gram atom.
(1): UCl_4·6AcA, (2): UCl_4·6AA, (3): UI_2Cl_2·5DMA.

temperature curves for UCl_4·2.5DMA, UCl_4·2.5DEA, UCl_4·4MA, UCl_4·4EA, and UCl_4·3DPA. Figure 2 also shows the magnetic susceptibility *versus* temperature curves for UCl_4·6AcA, UCl_4·6AA, and UI_2Cl_2·5DMA. Figure 3 presents the magnetic susceptibility *versus* temperature curves for UCl_4·3DMBA, UCl_4·3MAA, UCl_4·4BAN, UCl_4·4BAM, and UCl_4·4AAN. As may be seen from Fig. 1, broad but clearly distinguishable maxima appear at 121.8, 112.0, 155.1, and 81.8 K for UCl_4·2.5DMA, UCl_4·2.5DEA, UCl_4·4MA, and UCl_4·4EA respectively, while for UCl_4·3DMBA and UCl_4·3MAA of Fig. 3, the maxima appear at 134.2 and 142.0 K respectively. For the other eleven complexes, the magnetic susceptibilities monotonically increase down to the temperature of liquid helium (see also Fig. 6). The magnetic-susceptibility maxima shown in Figs. 1 and 3 have not previously been observed for uranium(IV) complexes and can not be explained by the usual concept of paramagnetic susceptibility. As has previously been reported,[4)] magnetic-exchange interaction is believed to occur between uranium ions in these complexes. The additional maximum at a temperature lower than the 134.2 K of the curve of UCl_4·3DMBA in Fig. 3 might be due to the existence of another kind of magnetic-exchange interaction between uranium ions. According to Bagnall *et al.*, the series of *N*,*N*-dimethylacetamide addition complexes of uranium(IV) are probably dimers, judging from their behavior in preparation and the measurements of their electric conductivities.[7,12,16)] Bagnall proposed that UCl_4·2.5DMA is a dimer with one ligand bridge and two chlorine ion bridges,[12)] while Gans proposed that it had three ligand bridges.[17)] Uranium(IV) chloride-*N*,*N*-dimethyl-*a*,*a*-diphenylacetamide (1/2.5) shows temperature-independent paramagnetism; this result can be explained by considering a dimeric structure with one ligand bridge and two chlorine-ion bridges per dimer.[9)] Although the crystal structure of UCl_4-addition complexes of amides has not yet been determined by X-ray diffraction, UCl_4·2.5DMA and UCl_4·2.5DEA should have polynuclear structures, probably a dimer structure, judging from their molecular formula. On the other hand, UCl_4·3Me_2SO is known

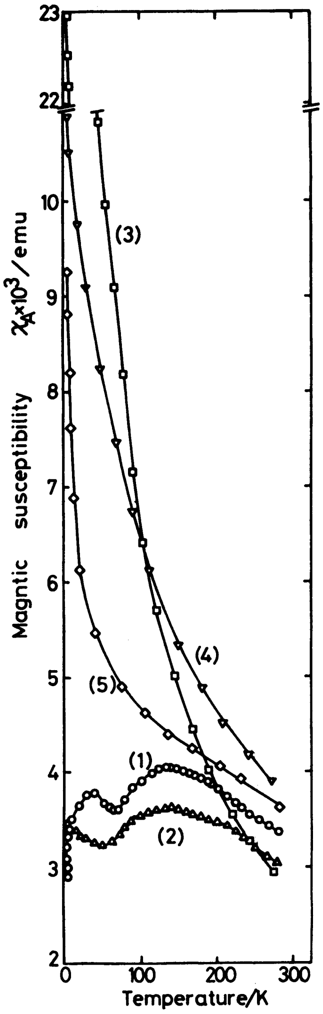


Fig. 3. Temperature dependence of magnetic susceptibility pre gram atom.
(1): UCl_4·3DMBA, (2): UCl_4·3MAA, (3): UCl_4·4BAN, (4): UCl_4·4BAM, (5): UCl_4·4AAN.

by X-ray diffraction to have an ionic-pair structure, $[UCl_2(Me_2SO)_6]^{2+}[UCl_6]^{2-}$.[18] We have recently observed its magnetic susceptibility to increase monotonically down to 4.2 K and explained its magnetic susceptibility as a sum of those of the individual ions on the basis of the crystalline-field theory.[19]

Assuming that the complexes with maxima have dimer structures, and that magnetic-superexchange interaction operates between the central uranium ions, we can propose an explanation for the anomalous magnetic behavior. According to the Heisenberg model, the exchange-interaction Hamiltonian for a two-spin system is expressed by Eq. 1;

$$H = -2J_{ex}\vec{S_1}\cdot\vec{S_2}, \tag{1}$$

where J_{ex} is the exchange integral for the intradimer interaction between uranium ions with spin angular momenta, $\vec{S_1}$ and $\vec{S_2}$. When the uranium(IV) ion has

Table 4. Temperatures with magnetic-susceptibility maximum and magnetic-exchange parameters for complexes

Complex	$T\chi_{max}$/K	$2J_{ex}$/cm^{-1}
UCl_4·3DMBA	134.2	−91.0
UCl_4·3MAA	142.0	−96.6
UCl_4·2.5DMA	121.8	−82.6
UCl_4·2.5DEA	112.0	−77.0
UCl_4·4MA	155.1	−106.4
UCl_4·4EA	81.8	−56.6

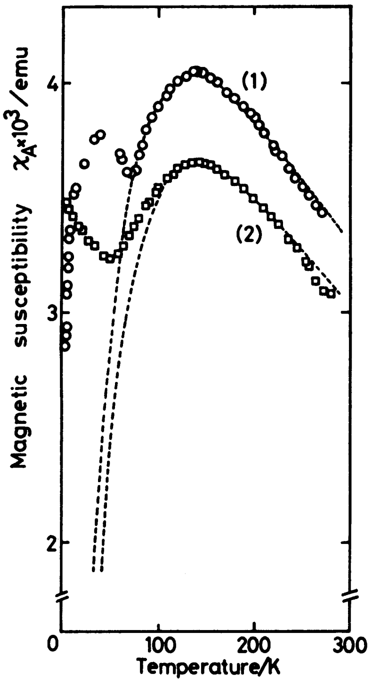


Fig. 4. Magnetic susceptibility *versus* temperature curve.
(1): UCl_4·3DMBA, (2): UCl_4·3MAA. ○, □: Experimental, ------: calculated.

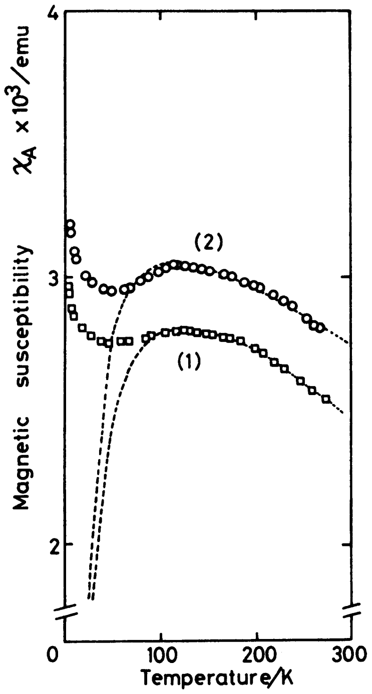


Fig. 5. Magnetic susceptibility *versus* temperature curve.
(1): UCl_4·2.5DMA, (2): UCl_4·2.5DEA. ○, □: Experimental, ------: calculated.

a non-degenerate ground state, $S_1=S_2=1$. From the well-known van Vleck equation[20] and Eq. 1, 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 J_{ex} can be obtained by the relation to the temperature of maximum susceptibility. $N\alpha$ is estimated by extrapolating the magnetic-susceptibility curve to the higher-temperature region (Table 4). Putting values of J_{ex} and $N\alpha$ and $g=2$ in Eq. 2, the magnetic susceptibilities per gram of the atom were calculated: they are shown in Figs. 4 and 5. The calculated curves of Fig. 5 include the effect of the molecular field; they will be discussed in a paper (Part II) to be published later. The discrepancy in the lower-temperature region might be partly due to paramagnetic impurities, such as a monomer, and partly due to the neglect of the orbital contribution. For the temperature region where the data fit the Curie-Weiss law, the Weiss constant and the effective Bohr magneton number are listed in Table 5.

As is shown in Table 6(a), the complexes with the maxima in their magnetic susceptibility versus temperature curves have at least one methyl or ethyl substituent on the amide nitrogen. (See the complexes combined by arrows.) Figure 6 shows the dependence of the magnetic susceptibility on the temperature for four complexes having no substituent on the carbon of amide. None of the four complexes exhibits a maximum similar to those shown in Figs. 1 and 3. Substitution on the carbon of amide is apparently necessary for the complexes to exhibit a maximum in the magnetic susceptibility *versus* temperature curve. (Note the relation in Table 6(b) and recall the experimental susceptibility.) The facts that the kind of substituent on the amide ligand is responsible for the magnetic-exchange interaction and that the value of J_{ex} of the amide complexes has some significance in the comparison of the strength of exchange interaction among the complexes suggest that the amide ligand is involved

TABLE 5. CURIE-WEISS CONSTANTS AND EFFECTIVE BOHR MAGNETONS

Complex	Temperature range/K	θ/K	μ_{eff}/μ_B
UCl_4·2.5DMA	210—r.t.	−869	2.35
UCl_4·2.5DEA	240—r.t.	−625	2.46
UCl_4·2.5DMF	150—r.t.	−460	2.48
UCl_4·3DMBA	190—r.t.	−418	2.72
UCl_4·3MAA	235—r.t.	−265	2.59
UCl_4·3DPA	70—r.t.	−175	2.32
UCl_4·3MFA	115—r.t.	−179	2.42
UCl_4·4BAM	4.2—r.t.	−143	2.88
UCl_4·4BAN	4.2—r.t.	−38	2.55
UCl_4·4AAN	35—r.t.	−455	2.83
UCl_4·4DPF	30—r.t.	−85	3.08
UCl_4·4MA	195—r.t.	−875	2.73
UCl_4·4EA	195—r.t.	−276	2.88
UCl_4·4MF	115—r.t.	−120	3.13
UCl_4·6AA	95—r.t.	−90	2.75
UCl_4·6AcA	110—r.t.	−87	2.96
UI_2Cl_2·5DMA	70—r.t.	−273	2.56

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

TABLE 6. EFFECT OF THE SUBSTITUENT OF THE AMIDE MOLECULE ON THE MAGNETIC BEHAVIOR

Complexes with no maximum susceptibility[a]		Complexes with maximum susceptibility[a]
(a) Substituents on the amide nitrogen		
UCl_4·6AA (H, H) UCl_4·4AAN (Ph, H) $UCl_4$3DPA (Ph, Ph)	←→	UCl_4·2.5DMA (CH_3, CH_3) UCl_4·2.5DEA (C_2H_5,C_2H_5) UCl_4·4MA (CH_3, H) UCl_4·4EA (C_2H_5, H)
UCl_4·4BAM (H, H) UCl_4·4BAN (Ph, H)	←→	UCl_4·3DMBA (CH_3, CH_3)
UCl_4·4AAN (H, Ph) UCl_4·3DPA (Ph, Ph)	←→	UCl_4·3MAA (CH_3, Ph)
(b) Substituents on the carbon of amide		
UCl_4·2.5DMF (H)	←→	UCl_4·2.5DMA (CH_3) UCl_4·3DMBA (Ph)
UCl_4·4MF (H)	←→	UCl_4·4MA (CH_3)
UCl_4·3MFA (H)	←→	UCl_4·3MAA (CH_3)

a) The groups in parentheses are the substituent.

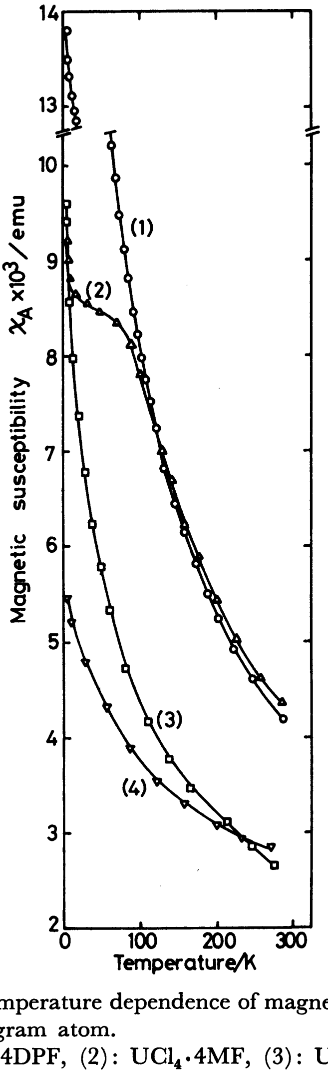


Fig. 6. Temperature dependence of magnetic susceptibility per gram atom.
(1): UCl_4·4DPF, (2): UCl_4·4MF, (3): UCl_4·3MFA, (4): UCl_4·2.5DMF.

Table 7. Amide-band frequencies

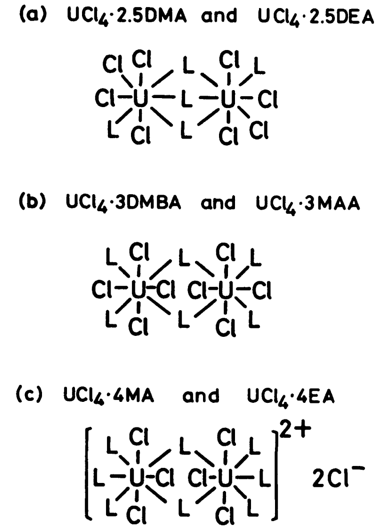
Complex	Amide I ν/cm^{-1}	Amide I Δ	Amide II ν/cm^{-1}	Amide II Δ	Amide III ν/cm^{-1}	Amide III Δ
N-Methylacetamide	1660	−60	1567	−3	1298	−47
$UCl_4\cdot$4MA	1600		1564		1251	
N-Ethylacetamide	1656	−51	1562	−101	1298	−2
$UCl_4\cdot$4EA	1605		1461		1296	
N-Methylformamide	1664	−39	1530	6	1244	7
$UCl_4\cdot$4MF	1625		1536		1251	

Table 8. N–H stretching frequencies

Complex	State	ν(N–H) cm^{-1}	$\Delta\nu$/cm^{-1}
N-Methylacetamide	Gas phase	3473	−253
	Hydrogen-bonded	3290	−70
$UCl_4\cdot$4MA		3220	
N-Ethylacetamide	Gas phase	3459	−182
	Hydrogen-bonded	3298	−21
$UCl_4\cdot$4EA		3277	
N-Methylformamide	Gas phase	3468	−143
	Hydrogen-bonded	3299	26
$UCl_4\cdot$4MF		3325	

in the magnetic-exchange interaction pathway between uranium(IV) ions.

The coordination of the amide molecule was further examined on the basis of the infrared spectra. The amide with the skeleton of RCONHR′ has the characteristic vibration of a peptide, constituted of six amide bands, *i.e.*, amide-band frequencies I—VI. Table 7 shows the results of the measurements of three amide bands, I, II, and III, of free amides and complexes. Amide I absorption is assigned 80% to the C=O stretching vibration; Amide II, 60% to the bending vibration in the plane of N–H and 40% to the C–N stretching vibration, and Amide III, 40% to the C–N stretching vibration and 30% to the bending vibration in the plane of N–H.[21] If the nitrogen of the amide molecule coordinates directly to the uranium ion, the absorptions of Amides II and III are expected to shift toward a lower frequency. In $UCl_4\cdot$4MA and $UCl_4\cdot$4EA (with the magnetic susceptibility maxima), and $UCl_4\cdot$4MF (without the maximum), the directions of the shifts are opposite one another. This indicates a difference in the coordination of amides, suggesting the possibility of coordination through nitrogen in the former case. The N–H absorption for the ligand is known to shift to about 200 cm^{-1} lower than that in the free ligand due to the strong hydrogen bonding. In all three complexes, this absorption shifts to a lower frequency (Table 8). Furthermore, in $UCl_4\cdot$4MA and $UCl_4\cdot$4EA, the absorption shifts to a lower frequency, even compared with the N–H stretching frequency in the hydrogen-bonding state, but in $UCl_4\cdot$4MF the shift is to a higher frequency. Accordingly, in the former two complexes the N–H bonding becomes weaker with complex formation than the strength of N–H bonding, which contributes to the hydrogen bonding. These data also support the possibility of nitrogen coordination. On the other hand, the frequencies of Amide I all shift to lower frequencies, indicating that oxygen coordinates to the uranium ion. In $Co(DMA)_4(ClO_4)_2$, both oxygen and nitrogen of *N*,*N*-dimethylacetamide are reported to coordinate to the central metal ion.[22] Taking the results of magnetic behavior and infrared absorption into account, both oxygen and nitrogen are considered to coordinate to the uranium ion in $UCl_4\cdot$4MA and $UCl_4\cdot$4EA.


(a) $UCl_4\cdot$2.5DMA and $UCl_4\cdot$2.5DEA

(b) $UCl_4\cdot$3DMBA and $UCl_4\cdot$3MAA

(c) $UCl_4\cdot$4MA and $UCl_4\cdot$4EA

Fig. 7. Structural formulas suggested for dimers which are considered to be octa-coordinated, according to the references 7, 12, 17) for (a) and 9, 12) for (c). Amide molecules are represented as L.

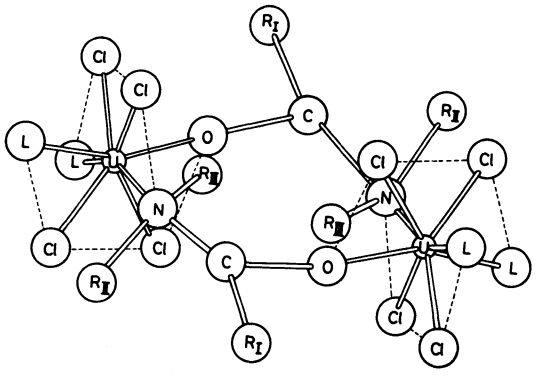


Fig. 8. A coordination diagram for $UCl_4\cdot$3L type complexes by both oxygen and nitrogen atoms. Amide molecules which do not bridge are represented as L. Broken line shows dodecahedral coordination.

It is noteworthy that, in two pairs of a methyl derivative and an ethyl derivative of a given amide, $UCl_4\cdot$2.5DMA and $UCl_4\cdot$2.5DEA, and $UCl_4\cdot$4MA and $UCl_4\cdot$

4EA, the temperatures of the χ_{max} of the methyl derivatives are higher than those of the corresponding ethyl derivatives. This is consistent with the facts that an amide ligand contributes to the pathway between uranium ions and that the effect of the methyl substituent is predominant over the ethyl substituent in electron-releasing property. Concerning the origin of bridging, these facts indicate that, as the electron dinsity on the nitrogen atom is enhanced by the methyl (ethyl) group, in the case of a large metal ion such as uranium, both oxygen and nitrogen can coordinate to the metal ion; this amide molecule then acts as a bridging molecule. The values of the magnetic susceptibility of methyl derivatives are thus smaller than those of the corresponding ethyl derivatives. Furthermore, the value of the magnetic susceptibility of $UCl_4 \cdot 3MAA$ is smaller than that of $UCl_4 \cdot 3DMBA$, and the temperature of χ_{max} is higher in the former than in the latter. This fact can be explained by the existence of an antiferromagnetic interaction in the dimer.

In conclusion, the complexes which have the maximum of magnetic susceptibility *versus* temperatur curve are considered to be dimers (see Fig. 7), and the pathway for the magnetic-superexchange interaction is considered to be a polyatomic bridging of the amide molecule› probably by coordinating in the manner of U–N–C–O–U, as is shown in Fig. 8.

References

1) W. E. Hatfield, "Properties of Magnetically Condensed Compounds," in "Theory and Applications of Molecular Paramagnetism," ed by E. A. Boudreaux and L. N. Mulay, John Wiley and Sons, N. Y. (1976).

2) J. G. Reynolds, A. Zalkin, D. H. Templeton, N. M. Edelstein, and L. K. Templeton, *Inorg. Chem.*, **15**, 2498 (1976).

3) J. G. Reynolds, A. Zalkin, D. H. Templeton, and N. M. Edelstein, *Inorg. Chem.*, **16**, 599 (1977).

4) C. Miyake, Y. Hinatsu, and S. Imoto, *Chem. Phys. Lett.*, **63**, 529 (1979).

5) T. Yoshimura, C. Miyake, and S. Imoto, *J. Nucl. Sci. Technol.*, **8**, 498 (1971).

6) J. Kooi, E. Weisskopt, and D. M. Gruen, *J. Inorg. Nucl. Chem.*, **13**, 310 (1960).

7) K. W. Bagnall, A. M. Deane, T. L. Markin, P. S. Robinson, and M. A. A. Stewart, *J. Chem. Soc.*, **1961**, 1611.

8) P. Gans and B. C. Smith, *J. Chem. Soc.* **1964**, 4177.

9) J. G. H. du Preez, M. L. Gibson, and C. P. J. can Vuuren, *J. South African Chem. Inst.*, **24**, 135 (1971).

10) K. W. Bagnall, D. Brown, P. J. Jones, and P. S. Robinson, *J. Chem. Soc.*, **1964**; 2531.

11) K. W. Bagnall, D. Brown, J. G. H. du Preez, J. Bajorek, L. Bonner, H. Cooper, and G. Segel, *J. Chem. Soc., Dalton Trans.*, **1973**, 2682.

12) K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, *J. Chem. Soc.*, **1965**, 3594.

13) T. Nakai, "Muki Kagaku Zensho XII-I Uranium," Maruzen, Tokyo (1960), p. 69.

14) H. St. Rade, *J. Phys. Chem.*, **77**, 424 (1973).

15) L. N. Mulay, "Definitions and Units for Magnetic Terms," in "Theory and Applications of Molecular Paramagnetism," ed by E. A. Boudreaux and L. N. Mulay, John Wiley and Sons, N. Y. (1976).

16) K. W. Bagnall, D. Brown, and R. Colton, *J. Chem. Soc.*, **1965**, 3594.

17) P. Gans, Ph. D. Thesis, London University (1964).

18) G. Bombieri and K. W. Bagnall, *J. Chem. Soc., Chem. Commum.*, **1975**, 188.

19) H. Sakurai, C. Miyake, and S. Imoto, *J. Inorg. Nucl. Chem.*, **42**, 69 (1980).

20) J. H. van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford Univ. Press, London (1932).

21) T. Miyazawa, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, **29**, 611 (1958).

22) B. B. Wayland, R. J. Fitzgerald, and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 4600 (1966).