Magnetic Susceptibilities of Octacoordinated Uranium(IV) Complexes

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Magnetic susceptibility measurements were carried out on octacoordinated uranium(IV) complexes, such as tetrakis(acetylacetonato)uranium(IV), tetrakis(trifluoroacetylacetonato)uranium(IV), tetrakis(benzoylacetonato)-uranium(IV), tetrakis(dibenzoylmethanato)uranium(IV), tetrakis(thenoyltrifluoroacetonato)uranium(IV), tetrakis(cupferronato)uranium(IV), and uranium(IV)tetrachloride, in the temperature range from room temperature to the temperature of liquid nitrogen or liquid helium. The Curie-Weiss law holds above the temperature of liquid nitrogen, with a magnetic moment of 3.5—2.92 BM. For the latter two complexes, a temperature-independent paramagnetism was observed in the low temperature range; the other complexes also seemed to show the same trend. We tried to interpret the magnetic behavior on the basis of the crystal-field model of the square antiprism structure or the dodecahedron structure of the complexes.

The measurement of the magnetic behavior is one of the most useful and effective methods for the study of the electronic state of a complex. Particularly, the temperature-independent paramagnetism (TIP) at low temperatures often gives decisive information on the ground state of the central metal ion being studied. The configuration of the valence electrons of the uranium ion was early considered to be $(6d)^2$, because uranium dioxide magnetically diluted with thorium dioxide had a magnetic moment nearly equal to the spin-only value. Indeed, the quenching of the orbital angular momentum leading to the contribution only of the spin angular momentum to the observed magnetic momentum is, in many cases, characteristic of the d-electron, while in lanthanoid ions, which have unfilled 4f shell, the Russell-Saunders coupling has been found to be more feasible. Hutchison and Candela have, however, shown that the configuration $(5f)^2$ of the uranium ion (IV) with the $^3H_4$ term as the ground state is also capable of giving a magnetic moment near the spin-only value if the ion is influenced by the crystal field with cubic symmetry.[1)] The TIP of the octahedral Cs_2UCl_6 at low temperatures could be reasonably explained by this scheme, taking into consideration the high-frequency interaction between the ground singlet state $^1\Gamma$ of the $^3H_4$ term and the lowest excited state (about 1 kcm^{-1} above the former). If the configuration be assumed to be $(6d)^2$, the ground state resulting from the splitting of $^3F_2$ in the octahedral crystal field would be the triplet $^3\Gamma_4$, which does not show the TIP at low temperatures. Recently, Mulak and Czopnik measured the magnetic susceptibility of $U(SO_4)_2\cdot 4H_2O$ and $U(CH_3COCHCOCH_3)_4$ and explained the observed TIP on the basis of the splitting behavior of the $^3H_4$ term in a crystal field of a slightly distorted archimedian antiprism symmetry.[2)] In the present study, the magnetic susceptibility of octacoordinated uranium (IV) complexes with the structure of dodecahedron as well as that of square antiprism is measured in the range from room temperature to the temperature of liquid nitrogen or liquid helium, and the results are interpreted on the basis of the crystal field theory.

Experimental

Magnetic susceptibility measurements in the range from room temperature to the temperature of liquid nitrogen were carried out with a torsion magnetometer of the Faraday type in the magnetic field of 5.0 kOe, and the measurements from the temperature of liquid nitrogen to that of liquid helium, with the Torsion Magnetic balance MB2 of the Shimadzu Seisakusho Ltd. in 10.66 and 8.685 kOe. The temperature was measured using an Au-Co/Cu thermocouple or a carbon-resistance thermometer. The value of the magnetic susceptibility was calibrated by using $NiCl_2$ powder as the standard. The measurements were made for seven complexes: tetrakis(acetylacetonato)uranium(IV) ($U(acac)_4$), tetrakis(trifluoroacetylacetonato)uranium(IV) ($U(tfac)_4$), tetrakis(benzoylacetonato)uranium(IV) ($U(bac)_4$), tetrakis-(dibenzoylmethanato)uranium(IV) ($U(dbm)_4$), tetrakis-(thenoyltrifluoroacetonato)uranium(IV) ($U(TTA)_4$), tetrakis (cupferronato) uranium(IV) ($U(cupf)_4$), and uranium(IV) tetrachloride (UCl_4); the methods of preparation have been described elsewhere.[3)] UCl_4 is so deliquescent that it was sealed into a glass tube in a vacuum; the correction for the glass tube was made by measuring the magnetic susceptibility of the empty glass tube under the same conditions as were used for the specimen. Correction for diamagnetism was made for the U(IV) ion and the chloride ion by using the value reported by Dawson;[4)] for H_2O and the acetylacetonato ion, by using the value reported by Earnshaw,[5)] for benzoylacetone, by using the value reported by the Handbook,[6)] and for all others, by using the value of Pascal's constant. The values of the diamagnetic increment used for the correction were as follows: $U(acac)_4$, −240; $U(tfac)_4$, −280; $U(bac)_4$, −404; $U(dbm)_4$, −592; $U(TTA)_4$, −368; $U(cupf)_4$, −315; UCl_4, −123 ($\times 10^{-6}$ cgs emu).

Results

Figure 1 shows the relationships between the reciprocal molar magnetic susceptibility and the temperature for $U(acac)_4$, $U(tfac)_4$, $U(bac)_4$, $U(dbm)_4$, $U(TTA)_4$, and $U(cupf)_4$. These complexes are found to follow the Curie-Weiss law over the temperature range measured except for the lowest part, where a slight positive deviation from the straight line is observed. The magnetic moment and the Weiss constant calculated from the straight line are shown in Table 1. Figure 2 represents the temperature dependence of the magnetic susceptibility for $U(cupf)_4$ and UCl_4 in the

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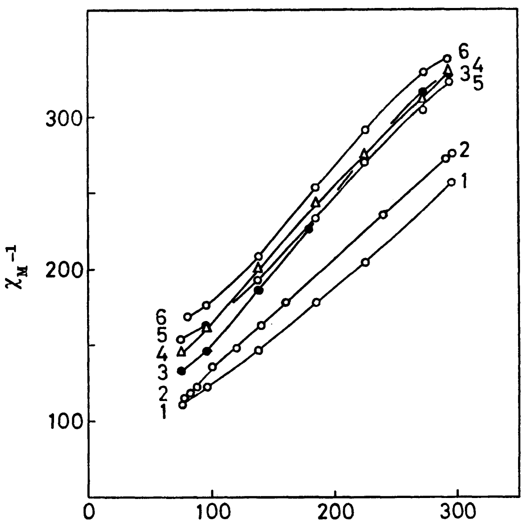


Fig. 1. Reciprocal susceptibility of complexes as a function of temperature.
1: U(dbm)$_4$, 2: U(cupf)$_4$, 3: U(acac)$_4$, 4: U(tfac)$_4$, 5: U(bac)$_4$, 6: U(TTA)$_4$.

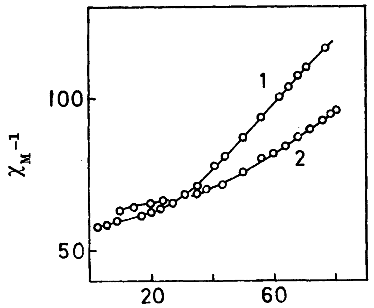


Fig. 2. Reciprocal susceptibility of complexes as a function of temperature.
1: U(cupf)$_4$. 2: UCl$_4$.

Table 1. Structure and magnetic constants of octacoordinated U(IV) complexes

Complexes	Structure	μ	Weiss const. (K)	Ref.
U(dbm)$_4$	DH	3.43	− 77	
U(cupf)$_4$		3.5	−120	
U(acac)$_4$	SA	2.92	− 68	
U(tfac)$_4$		3.16	−116	
U(bac)$_4$		3.08	− 91	
U(TTA)$_4$		3.01	−101	
UCl$_4$	DH	3.29	− 62	4
UF$_4$	SA	3.30	−102	4
UF$_4$ in ThF$_4$	SA	2.92	− 25	4
γ-Na$_2$UF$_6$	cube	3.18	− 86	8
(NH$_4$)$_4$UF$_8$	SA			
U(SO$_4$)$_2$·4H$_2$O	SA	3.14[a]	−125	2
UO$_2$	cube	3.11	−208	9
UO$_2$ in ThO$_2$	cube	2.86	− 42	9
K$_4$U(NCS)$_8$	cube	3.26	−119	10

a) Estimated from the figure in Ref. 2.

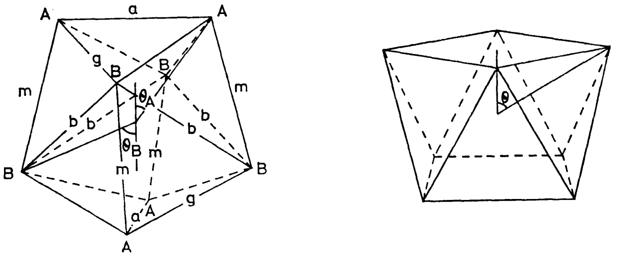
temperature range from the temperature of liquid nitrogen to the temperature of liquid helium.[7] TIP is suggested for both complexes from the curved χ^{-1} *vs.* T relationships at low temperatures. The magnetic moment and the Weiss constant of U(cupf)$_4$ and UCl$_4$, as estimated from the linear part of the curve in the higher temperature range, are also given in Table 1.

Discussion

Among the octacoordinated uranium(IV) complexes studied in the present experiment, only U(acac)$_4$, U(dbm)$_4$, and UCl$_4$ have been elucidated as to the structure around the central uranium ion. In Table 1 we have summarized the structures and the magnetic moments of the octacoordinated uranium(IV) compounds already determined, together with those obtained in the present study. From the table, it seems that the complexes with the square antiprism structure show relatively lower magnetic moments than do those with dodecahedron structure.

Dodecahedron. In UCl$_4$ and U(dbm)$_4$ the nearest surrounding anions around the central U(IV) ion are known to form a dodecahedron and to produce a tetragonal crystal field with D$_{2d}$ symmetry. The ground state of the uranium ion with the ground term of $^3H_4$ in the configuration (5f)^2 is then split into five singlets and two doublets under the influence of the electric field. From his study of the visible absorption spectra of UCl$_4$ at the temperature of liquid helium, McLaughlin inferred that the ground state is the singlet, $^1\Gamma_{t4}$, with the lowest excited state of $^1\Gamma_{t1}$, spaced 551 cm^{-1} above.[11] However, the TIP observed in the present experiment does not agree with this scheme, because such a large splitting as 551 cm^{-1} would give rise to TIP in the temperature range below about 500 K.

Another example of the analysis of the absorption spectra for the complex of dodecahedron coordination has been given in the case of ZrSiO$_4$ doped with the U(IV) ion, where the ground state was also assigned to be $^1\Gamma_{t4}$, but where the lowest excited state was estimated to be the doublet, $^2\Gamma_{t5}$ 155 cm^{-1}, above the singlet.[12] Recently Troc *et al.* carried out a detailed analysis of the magnetic susceptibility measured for uranium compounds with a Th$_3$P$_4$-type structure, in which each cation is surrounded by eight nearest anions, thus forming an octaverticon with the point symmetry D$_{2d}$.[13] According to these results, the ground



Dodecahedron

Square Antiprism

Fig. 3.

state for U_3P_4 was found to be composed of two close-spaced singlets, ${}^1\Gamma_{t3}$ and ${}^1\Gamma_{t2}$, with a separation of 8.9 cm^{-1}.

Here we shall apply the crystal field theory straightforwardly to the octacoordinated U(IV) complexes with a dodecahedron environment. The dodecahedron is characterized by two angles, θ_A and θ_B, as is shown in Fig. 3. As the values of θ_A and θ_B for several known complexes all fall into a relatively narrow range, that is, $\theta_A=34$—$37°$ and $\theta_B=72$—$74°$, it will be assumed in the following calculation that $\theta_A=35°$ and $\theta_B=73°$. The potential function of the crystal field is given by:

$$V = B_2^0O_2^0 + B_4^0O_4^0 + B_4^4O_4^4 + B_6^0O_6^0 + B_6^4O_6^4,$$

where O_2^0, O_4^0, O_4^4, O_6^0, and O_6^4 are equivalent operators, and where

$$B_2^0 = e^2Z(3\cos^2\theta_A+3\cos^2\theta_B-2)\alpha\langle r^2\rangle/a^3$$

$$B_4^0 = e^2Z(35\cos^4\theta_A+35\cos^4\theta_B-30\cos^2\theta_A -30\cos^2\theta_B+6)\beta\langle r^4\rangle/16a^5$$

$$B_4^4 = -35e^2Z(\sin^4\theta_A+\sin^4\theta_B)\beta\langle r^4\rangle/16a^5$$

$$B_6^0 = e^2Z(231\cos^6\theta_A+231\cos^6\theta_B-315\cos^4\theta_A -315\cos^4\theta_B+105\cos^2\theta_A+105\cos^2\theta_B-10)\cdot \gamma\langle r^6\rangle/64a^7$$

$$B_4^6 = -63e^2Z[(11\cos^2\theta_A-1)\sin^4\theta_A+(11\cos^2\theta_B-1)\cdot \sin^4\theta_B]\gamma\langle r^6\rangle/64a^7.$$

The α, β, and γ are the multiplying factors and are given for the ${}^3H_4$ term as $\alpha=-2.10\times10^{-2}$, $\beta=-7.346\times10^{-3}$, and $\gamma=6.099\times10^{-5}$. The U–O distance, a, was taken as 2.32 A, the value determined for tetrakis(acetylacetonato)uranium(IV), and the mean values of the n-th power of the radial distance of the 5f electron, $\langle r^2\rangle$, $\langle r^4\rangle$, and $\langle r^6\rangle$, were taken from the literature; $\langle r^2\rangle=1.68$, $\langle r^4\rangle=5.00$ and $\langle r^6\rangle=24.4$ a.u.[14] Z is the charge of the anion ligated to the central metal ion. The values of the coefficients, B_n^m, assuming that $Z=2$, are then given in cm^{-1} as follows: $B_6^0=-49.53$, $B_4^0=2.54$, $B_4^4=123.37$, $B_6^0=-1.97$, and $B_6^4=-16.67$. The splitting scheme of the ${}^3H_4$ term calculated on the basis of this potential function is shown in Fig. 4. This scheme shows that the ground state is the singlet, ${}^1\Gamma_{t3}$, with the lowest excited state, ${}^1\Gamma_{t2}$, located 23 cm^{-1} (33 K) above. A similar calculation showed the splitting to be 45 cm^{-1} if the two characteristic angles were taken to be $\theta_A=37°$ and $\theta_B=74°$.

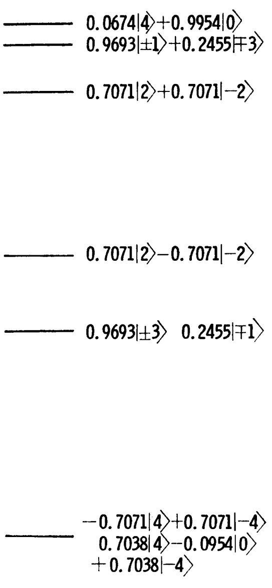


Fig. 4,

The magnetic susceptibility is written in the form:

$$\bar{\chi} = N\mu^2\mu_B^2/3kT(1-\exp(-\delta/kT))/ (1+\exp(-\delta/kT))2kT/\delta \qquad (1)$$

where δ is the splitting between ${}^1\Gamma_{t2}$ and ${}^1\Gamma_{t3}$ and where μ_B is the Bohr magneton. The magnetic moment is given by $\mu=\sqrt{32}\,pg$, where g is the spectroscopic splitting factor and where p is the coefficient of $1\pm4\rangle$ in the eigenvector of the ${}^1\Gamma_{t3}$ state. The value of p is $1/\sqrt{2}$ for $\delta=0$; it is slightly decreased with an increase in δ, but it hardly reaches 0.69 in the present model. The spectroscopic splitting factor is 0.8 for the pure ${}^3H_4$ term, but is calculated to be 0.83 in the intermediate coupling scheme; this gives $\mu=3.27$—3.32 within the range of $p=0.696$—0.707. The temperature dependence of Eq. (1) with $\mu=3.30$ is presented in Fig. 5, where it may be seen that the reciprocal susceptibility shows a marked deviation from the straight line below about $T=\delta/2k$, suggesting the TIP at lower temperatures. The apparent magnetic moment gained from this figure is $\mu=3.43$, which is about 5% larger than that obtained in the higher temperature range, $\delta\ll kT$. Thus, the magnetic behavior of octacoordinated U(IV) complexes which would show TIP at low temperatures (below about 100 K (70 cm^{-1})) and which have the apparent magnetic moment of $\mu=3.4$—3.5 seems likely to be explained by the present scheme. From the values in Table 1, U(cupf)$_4$ is also considered to belong to this group along with U(dbm)$_4$ and UCl$_4$; it seems very possible that dodecahedron is the coordination polyhedron of U(cupf)$_4$.

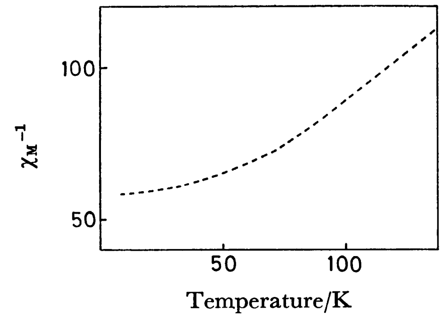


Fig. 5. Reciprocal susceptibility theoretically obtained as a function of temperature.
μ: 3.3, δ: 108 cm^{-1}, δ/k: 160

Square Antiprism. For the complexes having the coordination polyhedron of archimedian antiprism with the octahedral symmetry of D_{4d}, the energy level scheme was calculated by Mulak and Czopnik using the c/a ratio as a parameter, and it was shown that either the singlet state, $|0\rangle$, or the doublet states, $|\pm4\rangle$ and $|\pm3\rangle$, can be the ground state, according to the value of c/a.[2] They assumed that the ground state was $|\pm3\rangle$, which would be split into two closely-spaced singlets under the distortion of the rhombic or lower symmetry. However, the value of c/a determined by X-ray analysis for Zr(acac)$_4$, which is isomorphous with U(acac)$_4$, is 0.908; this value leads to the ground state being $|0\rangle$, with the lowest excited level being $|\pm1\rangle$. According to Lippard and Russ, the polyhedron of Zr(acac)$_4$ is a distorted square antiprism; it is approximately formed by twisting the perfect square antiprism around the 8 axis by 10—20 degrees.[15] This twisting gives rise to the splitting of the $|\pm2\rangle$ state and markedly lowers the $1/\sqrt{2}(|2\rangle-|-2\rangle)$ state. The calculation carried out along the lines of the analysis by Mulak and Czopnik, with the value of $c/a=0.908$, showed that the splitting between $|0\rangle$ and $|\pm1\rangle$ is about 30 cm^{-1} and that the $1/\sqrt{2}(|2\rangle-|-2\rangle)$ state is located near the $|\pm1\rangle$ doublet if the twisting angle is 10—15 degrees, as is shown in Fig. 3. We shall show that this energy level scheme can also be used in explaining the magnetic behavior of octacoordinated U(IV) complexes with a distorted square antiprism structure.

As the magnetic susceptibility is anisotropic in the tetragonal crystal field, components both parallel to and perpendicular to the symmetry axis should be considered. The parallel component of the magnetic susceptibility is given as follows;

$$\chi_{/\!/} = Ng^2\mu_B{}^2/kT\cdot 2\exp(-\delta/kT)/(1+2\exp(-\delta/kT)) \quad (2)$$

where δ is the splitting between $|0\rangle$ and $|\pm1\rangle$. The $\chi_\perp$ component is given by;

$$\begin{aligned}\chi_\perp = {} & 2Ng^2\mu_B{}^2[10(1-\exp(-\delta/kT))/\delta \\ & +4.5(1-\exp(-\delta/kT))\exp(-\Delta/kT)/\Delta]/ \\ & (1+2\exp(-\delta/kT)+\exp(-(\delta+\Delta)/kT)) \quad (3)\end{aligned}$$

taking into account the high-frequency interaction between $|0\rangle$ and $|\pm1\rangle$ and that between $|\pm1\rangle$ and $1/\sqrt{2}(|2\rangle-|-2\rangle)$, where Δ is the splitting between $|\pm1\rangle$ and $1/\rangle\sqrt{2}(|2\rangle-|-2\rangle)$. When $\Delta \ll kT$,

$$\begin{aligned}\chi_\perp = {} & 2Ng^2\mu_B{}^2[10(1-\exp(-\delta/kT))/\delta \\ & +4.5\exp(-\delta/kT)/kT]/(1+3\exp(-\delta/kT)) \quad (4)\end{aligned}$$

The average magnetic susceptibility, χ, is represented by Eq. (5); at lower temperatures ($Tk \ll \delta$) it becomes $40Ng^2\mu_B{}^2/3\delta$.

$$\bar{\chi} = 1/3\chi_{/\!/} + 2/3\chi_\perp \quad (5)$$

Under these conditions, the only contribution to the paramagnetic susceptibility is the temperature-independent paramagnetism due to the high-frequency interaction between the excited levels, $|\pm1\rangle$, and the ground state of $|0\rangle$. In Fig. 6 are plotted the average magnetic susceptibilities of Eq. (5), with the values of g and Δ/δ being assumed to be 0.827 and 0.1 respectively. TIP is seen at the lower temperatures, and the apparent magnetic moment of 3.24 is obtained from the straight part of the curve. This value is somewhat larger than the values experimentally obtained for U(acac)$_4$, U(bac)$_4$, U(tfac)$_4$, and U(TTA)$_4$, as in the case of the complexes with a dodecahedron structure. Thus, the behavior of magnetic susceptibility observed seems likely to be explained by the crystal field model with D_{2d} or D_{4d} symmetry, corresponding to dodecahedron or square antiprism respectively.

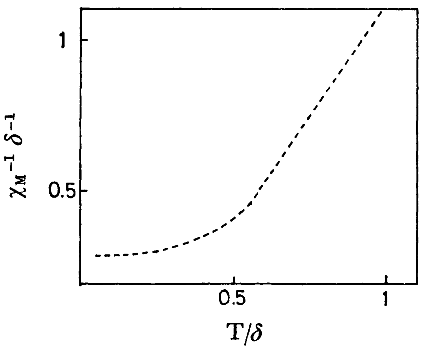


Fig. 6. Reciprocal susceptibility theoretically obtained as a function of temperature measured by energy difference between ground state and first excited state. $g=0.827$, Δ/δ: 0.1.

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