Structural configuration of uranium tetrahalide complexes by magnetic susceptibility
III. Determination of the configuration of UI$_4$hmpa$_m$ (m = 3, 4, 5)

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Abstract

Magnetic susceptibilities of UI$_4$hmpa$_m$ (m = 3, 4, 5) were measured from the b.p. of liquid helium to room temperature. On the basis of the ligand field theory, analysis of the results of magnetic susceptibility, along with IR and solid reflection spectra shows that UI$_4$hmpa$_m$ (m = 3, 4 or 5) has a six-coordinated structure as formula, [UI$_{6-m}$(hmpa)$_m$]I$_{m-2}$ (m = 3, 4 or 5). [UI$_3$(hmpa)$_3$]I has a *fac* configuration with C_{3v} symmetry, and does not have an auto-ionized structure as in the case of [UCl$_4$(dmso)$_3$]. [UI$_2$(hmpa)$_4$]I$_2$ has a *trans* configuration with D_{4h} symmetry, while [UI(hmpa)$_5$]I with C_{4v} symmetry has no geometrical isomer. Taking into account the magnitude of magnetic susceptibility of Br and I complexes with the same configuration, the distortion from the octahedral symmetry in I complexes is larger than that in Br complexes.

Introduction

UX$_4$L$_2$ complexes (X = a halogen or a pseudo halogen; L = a neutral oxygen-donor ligand) have been extensively studied from the view-point of spectral and structural chemistry. The configuration of all complexes of the UX$_4$L$_2$ type has been assigned to *trans* configuration except for UCl$_4$tppo$_2$ (tppo = triphenylphosphine oxide) [1]. Complexes of UX$_4$hmpa$_2$ (X = Cl$^-$, Br$^-$ or I$^-$, hmpa = hexamethylphosphoramide) also have *trans* configuration, where the ligand field around the central uranium ion has a tendency of tetragonal distortion from the regular octahedral symmetry, increasing from Cl$^-$ to I$^-$ [2]. This tendency may be due to the softer and/or bulkier iodine ion than the others. Therefore, the behavior of the ligand field distortion in UI$_4$ complexes is an interesting problem.

UX$_4$L$_n$-type complexes (n = 3–8) have been reported to take various structures. For example, UCl$_4$dmso$_3$ was elucidated to exist in an auto-ionized structure as [UCl$_2$(dmso)$_6$]$^{2+}$[UCl$_6$]$^{2-}$ (dmso is dimethylsulfoxide) by X-ray diffraction [3] and magnetic susceptibility [4] analyses. The structures of UI$_4$urea$_8$ and UCl$_4$MA$_4$ (MA = methylacetamide) have been reported to be eight-coordinated [5] and a dimer [6], respectively. The structure of complexes of the UX$_4$L$_n$-type with a bulky ligand would be of interest, but only a few studies have been carried out, in particular, for the UI$_4$L$_n$-type.

One of the present authors successfully isolated UI$_4$(Mecn)$_4$ [7] which is applicable as a new starting material for the preparation of UI$_4$ complexes and prepared UI$_4$hmpa$_m$ (m = 3, 4, 5). The configuration of the tetraiodineuranium(IV)–hmpa complexes was assigned by analysis of IR, solid reflectance spectra, etc. [8].

In the present study, the magnetic susceptibility of UI$_4$hmpa$_m$ (m = 3, 4, 5) was measured from the b.p. of liquid helium to room temperature. These results were analysed on the basis of the ligand field theory. The structural configurations of these complexes are discussed along with the results of IR and solid reflection spectra. The bonding between uranium and iodine in the present complexes is compared to that between uranium and bromine in the Br complexes reported previously [9].

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TABLE 1. Elemental analyses and infrared spectra

Complex	Analysis (%)[a]			$\nu(P=O)$ (cm^{-1})	$\Delta\nu(P=O)$ (cm^{-1})
	H	C	N		
[UI$_3$(hmpa)$_3$]I	4.30 (4.24)	16.59 (16.83)	9.51 (9.82)	988sh	219
[UI$_2$(hmpa)$_4$]I$_2$	5.06 (4.96)	19.25 (19.70)	11.08 (11.49)	–[b]	
[UI(hmpa)$_5$]I$_3$	5.45 (5.52)	22.85 (21.94)	13.1 (12.79)	–[b]	

[a]Calculated values are given in parentheses.   [b]$\nu(P=O)$ is overlap with other bands. sh: shoulder.

Experimental

UI$_4$hmpa$_m$ ($m = 3, 4, 5$) were prepared as described previously [8].

Hydrogen, carbon and nitrogen contents were determined with a Yanagimoto CHN Coder MT-2. Infrared spectra of the powdered samples were recorded on a JASCO IR-2 spectrophotometer by the KBr disk method (4000–400 cm^{-1}). Results of elemental analyses and infrared spectra are shown in Table 1.

Measurements of magnetic susceptibility were carried out using a Faraday type torsion magnetometer from the b.p. of liquid helium to room temperature. HgCo(NCS)$_4$ was used as a calibrant of susceptibility [10]. In order to confirm that the sample was free from a ferromagnetic impurity, the dependence of magnetic susceptibility on the intensity of magnetic field was measured in the range 0.1–0.7 T. Diamagnetic susceptibility corrections for all samples were made by using Pascal's constants and the values were given as follows; UI$_4$hmpa$_3$, -522.6; UI$_4$hmpa$_4$, -616.9; UI$_4$hmpa$_5$, -711.3; ($\times 10^{-6}$ in cgs emu units).

Results and discussion

Figures 1, 2 and 3 show the dependence of the magnetic susceptibility on temperature for UI$_4$hmpa$_3$, UI$_4$hmpa$_4$ and UI$_4$hmpa$_5$, respectively. The magnetic susceptibilities of all complexes increase with decreasing temperature from room temperature, and have a plateau below 80, 100 and 150 K, for UI$_4$hmpa$_3$, UI$_4$hmpa$_4$ and UI$_4$hmpa$_5$, respectively. Slight increases in magnetic susceptibilities at temperatures below 10 K seem to be due to very small paramagnetic impurities which could be present in the complexes. Their contributions in the higher temperature region are negligibly small.

For UI$_4$hmpa$_3$, the P=O stretching frequency, $\nu(P=O)$, is observed at 988 cm^{-1}, as a shoulder of
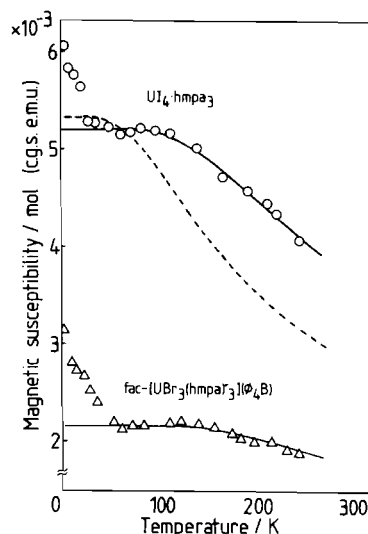

Fig. 1. Temperature dependence of magnetic susceptibility of UI$_4$hmpa$_3$: (O), observed; (——), calculated for C_{3v} symmetry; (– – –), calculated for auto-ionized structure, $\frac{1}{2}$[UI$_2$(hmpa)$_6$]$^{2+}$[UI$_6$]$^{2-}$. For UBr$_3$(hmpa)$_3$(ϕ_4B): ($\triangle$), observed; (——), calculated for C_{3v} symmetry.

other strong bands, showing the shift to the lower energy side from that of free hmpa molecule (1207 cm^{-1}). For UI$_4$hmpa$_4$ and UI$_4$hmpa$_5$, the P=O stretching band cannot be observed, and strong bands are observed at this region. If the hmpa does not coordinate to the uranium ion, the $\nu(P=O)$ of hmpa in these complexes should be observed with the same frequency as that of the free hmpa molecule. Since the absorption band of free hmpa cannot be observed, $\nu(P=O)$ for both complexes probably overlap with the other strong bands, i.e. $\nu(P=O)$ for both complexes may shift to the low energy side. In UI$_4$hmpa$_m$ ($m = 3$, 4 or 5), all hmpa ligands seem to coordinate to uranium ion through the oxygen atom.

In general, the low energy absorption band around 1800 nm is sensitive to the number and the type of ligands. This absorption band in solid reflectance spectra is observed for all present complexes as in
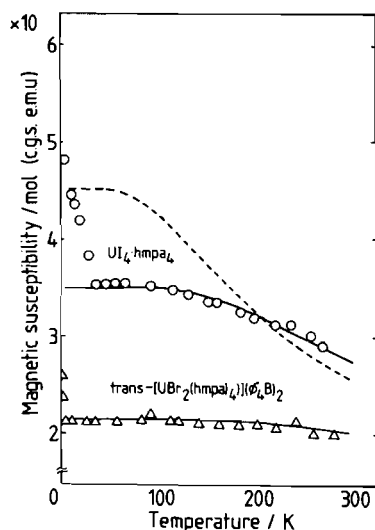
Fig. 2. Temperature dependence of magnetic susceptibility of UI_4hmpa_4: (O), observed; (——), calculated for D_{4h} symmetry. For $UBr_2(hmpa)_4(\phi_4B)_2$: (△), observed; (——), calculated for D_{4h} symmetry.
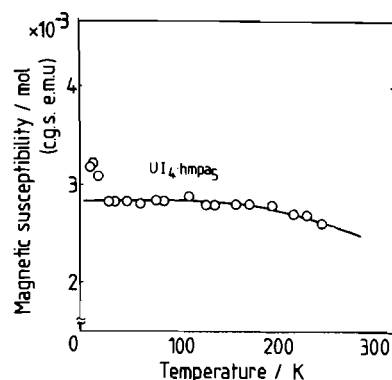

Fig. 3. Temperature dependence of magnetic susceptibility of UI_4hmpa_5: (O), observed; (——), calculated for C_{4h} symmetry.

the case of the Br complexes. The solid reflectance spectra around 1800 nm for UI_4hmpa_3 and UI_4hmpa_4 are similar in shape to those of $[UBr_3hmpa_3](\phi_4B)$ and $[UBr_2hmpa_4](\phi_4B)_2$, respectively, suggesting that I complexes, $[UI_{6-m}(hmpa)_m]I_{m-2}$ ($m = 3, 4, 5$), may have the same configuration as Br complexes which have a six-coordinated structure, $[UBr_{6-n}hmpa_n](\phi_4B)_{n-4}$ ($n = 2, 3$) [9].

Structure of UI_4hmpa_3

According to the results of IR and solid reflectance spectra, this complex may be formulated as follows

$$UI_4hmpa_3 \longrightarrow [UI_3hmpa_3]I \qquad (1)$$
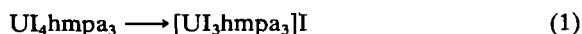
where three iodine ions and three hmpa ligands coordinate to the uranium(IV) ion, and the remaining iodine ion exists as a counter-ion.

On the other hand, some complexes have been reported with the formula as UX_4L_m (m stands for an integer or half integer of 3 to 8) having the auto-ionized structure. For example, UCl_4dmso_3 exists in the auto-ionized structure as $[UCl_2(dmso)_6]^{2+}[UCl_6]^{2-}$ [5, 6] and $UCl_4depa_{2.5}$ as $[UCl_5depa]^+[UCl_3depa_4]^-$ [11] (depa is diethylpropionamide).

If UI_4hmpa_3 exists as the auto-ionized structure, it is shown as follows.

$$UI_4hmpa_3 \longrightarrow \tfrac{1}{2}[UI_2(hmpa_6]^{2+}[UI_6]^{2-} \qquad (2)$$
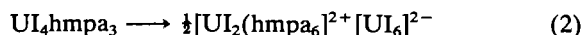
In this structure, the six-coordinated anion complex and the absence of uncoordinated hmpa ligand have very similar results for IR and solid reflectance spectra as that of the octahedral structure as shown eqn. (1). One of the differences of both structures, however, is the coordination number of the cation complexes, i.e. $[UI_3hmpa_3]^+$ and $[UI_2(hmpa)_6]^{2+}$ are six-coordinated and eight-coordinated, respectively, giving rise to the difference in the symmetry around the uranium ion in these complexes. The symmetry around the uranium ion is a key factor in determining the structure of the complexes by magnetic susceptibility measurements. In the case of the auto-ionized structure of eqn. (2), the complex cation, $[UI_2(hmpa)_6]^{2+}$, probably has an eight-coordinated configuration with a distorted C_{2v} symmetry, and the complex anion, $[UI_6]^{2-}$, has a regular octahedral configuration. The configuration and the symmetry of cation and anion complexes are shown in Fig. 4. Assuming eqn. (2), the observed magnetic susceptibility should be the sum of the contribution from the cation, $[UI_2(hmpa)_6]^{2+}$ and that from the anion, $[UI_6]^{2-}$, that is,

$$\chi_{observed} = \tfrac{1}{2}\chi([UI_2(hmpa)_6]^{2+}) + \tfrac{1}{2}\chi([UI_6]^{2-})$$

The anion, $[UI_6]^{2-}$, has a temperature-independent paramagnetic susceptibility of approximately 2.1×10^{-3} cgs emu [12]. On the other hand, the splitting of the $^3H_4$ ground term of uranium(IV) ($5f^2$ configuration) caused by eight-coordinated ligands
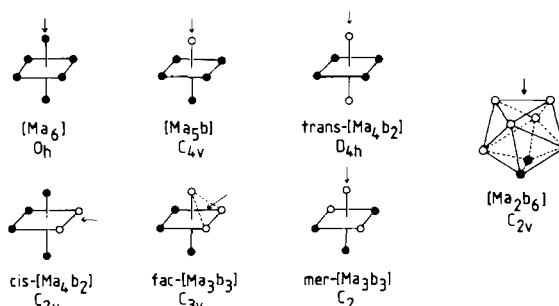

Fig. 4. Geometrical isomers and their point groups of six-coordinated structures and the dodecahedron structure.

TABLE 2 Eigenvalues and eigenvectors for the $^3H_4$ term in the ligand field of point group C_{3v}

Eigenvalue (cm^{-1})	Eigenvector
669 63	$0\,8980|\pm4\rangle+0\,4273|\pm1\rangle+0\,1044|\mp2\rangle$
399 32	$0\,4603|-3\rangle+0\,7591|0\rangle+0\,4603|+3\rangle$
−89 06	$0\,3559|\pm4\rangle-0\,5664|\pm1\rangle-0\,7433|\mp2\rangle$
−264 60	$0\,7071|-3\rangle-0\,7071|+3\rangle$
−337 42	$0\,2585|\pm4\rangle-0\,7047|\pm1\rangle+0\,6607|\mp2\rangle$
−621 06	$0\,5367|-3\rangle-0\,6510|0\rangle+0\,5368|+3\rangle$

Conditions $Z_O = 2\,0$ a u, $Z_I = 0\,85$ a u, $R(U-O) = 2\,16$ Å, $R(U-I) = 3\,01$ Å, $\theta r_1 = 55°$, $\theta r_2 = 62°$

which form a dodecahedron (distorted C_{2v} symmetry) was reported by H Sakurai et al [4] According to the well known van Vleck equation, the magnetic susceptibility of $[UI_2(hmpa)_6]^{2+}$ is calculated with a parameter of an energy difference, ΔE_{dod}, between the ground state and the first excited state Although the parameters for the calculation of the magnetic susceptibility, $\chi([UI_2(hmpa)_6]^{2+})$, were over a wide range, the calculated values did not agree with the observed values A typical example of the calculated magnetic susceptibility is plotted as a broken line in Fig 1, taking the ΔE_{dod} of 190 cm^{-1} for the complex with a dodecahedral structure Since the calculated values are quite different from the observed, the auto-ionized structure corresponding to eqn (2) is not reasonable

Concerning eqn (1), there are two possible geometrical isomers for $[UI_3(hmpa)_3]I$, one is facial (fac) and the other is meridional (mer) These isomers have C_{3v} and C_2 symmetry around the uranium ion, respectively (Fig 4) When the $[UX_3L_3]$-type complex has a mer configuration with C_2 symmetry, the electronic levels of the $^3H_4$ ground term split in the same manner as that of cis-$[UX_4L_2]$- or cis-$[UX_2L_4]$-type complexes with C_{2v} symmetry [13] In this symmetry, the contribution from the first-order Zeeman term vanishes, and only the high-frequency term gives rise to the temperature-independent paramagnetic susceptibility Thus, the meridional configuration leads to the temperature independent paramagnetic susceptibility However, the observed magnetic susceptibility depends on temperature above 80 K, excluding the mer configuration for this complex

In order to further examine the symmetry around the uranium ion, the magnetic susceptibility of the complex was calculated assuming C_{3v} symmetry which corresponds to the fac configuration The electronic levels split from the $^3H_4$ ground term of the uranium(IV) ion in this symmetry are given in Table 2, where it can be seen that the $^3H_4$ term is split

into three singlets and three doublets Taking the lowest two states into account, the calculated magnetic susceptibility using the van Vleck equation with the energy difference, $\Delta E_{C_{3v}} = 330$ cm^{-1}, is shown in Fig 1 (solid line), and closely agrees with the observed value Then, this complex may have a facial configuration with C_{3v} symmetry formulated as fac-$[UI_3(hmpa)_3]I$

Structure of UI_4hmpa_4

Since there is no evidence for the free hmpa ligand in the IR spectrum and the characteristic peak for the octahedral U^{4+} ion is at 1800 nm in the solid reflectance spectrum, UI_4hmpa_4 is considered to have a six-coordinated structure as follows

$$UI_4hmpa_4 \longrightarrow [UI_2(hmpa)_4]I_2 \qquad (3)$$
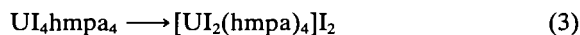
$[UI_2(hmpa)_4]I_2$ has either a trans or cis configuration, with symmetry around the uranium ion of D_{4h} or C_{2v}, respectively (Fig 4) As described previously [2], the magnetic susceptibility behavior is quite different according to the symmetry around the uranium ion If the complex has a trans configuration (D_{4h} symmetry), the magnetic susceptibility increases with decreasing temperature and has a plateau at lower temperature, while the complex with cis configuration (C_{2v} symmetry) is temperature-independent paramagnetic at all temperature regions The observed magnetic susceptibility for $[UI_2(hmpa)_4]I_2$ depends on the temperature above 100 K The values of magnetic susceptibility calculated by the van Vleck equation with wavefunctions reported by J W Gonsalves et al [14] and a parameter, $\Delta E_{D_{4h}} = 485$ cm^{-1}, agree with observed values (solid line in Fig 2) Therefore, the symmetry around the uranium ion is D_{4h} and the complex has a trans configuration

Furthermore, the IR and solid reflectance spectra of UI_4hmpa_4 are very similar to those of trans-$[UBr_2(hmpa)_4](\phi_4B)_2$ except for the absorption bands due to the ϕ_4B^- ion The similarity of the IR spectrum as well as the results of magnetic susceptibility and the solid reflectance spectrum suggests a trans configuration for $[UI_2(hmpa)_4]I_2$

Structure of UI_4hmpa_5

The proposed structure for this complex is the six-coordinated structure as follows

$$UI_4hmpa_5 \longrightarrow [UI(hmpa)_5]I_3 \qquad (4)$$
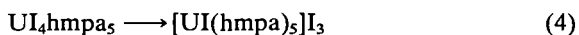
The symmetry of the ligand field around the uranium(IV) ion in a $[UXL_5]$-type complex is tetrahedral with point group C_{4v} The split of the ground term, $^3H_4$, in the ligand field of C_{4v} is the same as that of D_{4h} which belongs to tetrahedral

symmetry The magnetic susceptibility of the $[UXL_5]$-type complex can be calculated by using the similar wavefunctions of the complex with D_{4h} symmetry Taking the lowest two states into account, the calculated magnetic susceptibility using the van Vleck equation with $\Delta E_{C_{4t}} = 595$ cm^{-1} is shown in Fig 3 It is very close to the observed values, indicating tetragonal symmetry around uranium in UI$_4$hmpa$_5$ The results of the IR and solid reflectance spectra also correspond to the six-coordinated structure with a formula of $[UI(hmpa)_5]I_3$ Therefore an octahedral structure is reasonable for this complex

Comparison of I complexes and Br complexes

The magnetic susceptibility of *trans*-$[UI_2(hmpa)_4]I_2$ is larger than that of *trans*-$[UBr_2(hmpa)_4](\phi_4B)_2$ in the measured temperature range (Fig 2) The magnetic susceptibility of *fac*-$[UI_3(hmpa)_3]I$ is also larger than that of *fac*-$[UBr_3(hmpa)_3](\phi_4B)$, of which the symmetry is C_{3v} (Fig 1) This tendency is explained in the same manner as in the case of the order of magnetic susceptibility of *trans*-$[UX_4(hmpa)_2]$ (X = Cl, Br and I) [2] In the D_{4h} and C_{3v} symmetry, the energy difference between the ground state and the first excited states, ΔE, decreases with increasing the tetragonal and trigonal distortion from the regular octahedral symmetry, respectively The distortion is a measure of the difference between the ligand field strength of the hmpa ligand and that of the halogen ligand [9, 14] Since the order of the ligand field strength is O(hmpa) $\gg$ Cl > Br > I, the order of the distortion from the octahedral symmetry is Br complex < I complex As the contributions from the first- and the second-order Zeeman effects to the magnetic susceptibility increase with increasing the distortion of the complex, the order of magnetic susceptibility is given as χ(Br complex) < χ(I complex) This tendency is consistent with the order of the magnetic susceptibility reported previously [2]

Conclusions

In conclusion, it is shown that UI$_4$hmpa$_m$ (m = 3, 4 or 5) complexes have a six-coordinated structure

with the formula, $[UI_{6-m}(hmpa)_m]I_{m-2}$ (m = 3, 4 or 5) $[UI_3(hmpa)_3]I$ has a *fac* configuration, and does not have the auto-ionized structure as observed for $[UCl_4(dmso)_3]$ $[UI_2(hmpa)_4]I_2$ and $[UI(hmpa)_5]I_3$ have a *trans* configuration and octahedral structure, respectively

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