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Structural Configuration of Hexamethylphosphoramide Complexes of Uranium Tetrahalides by Magnetic Susceptibility

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Abstract

Magnetic susceptibilities of UX_4hmpa_2 (where $X = Cl^-$, Br^- and I^-; hmpa = hexamethylphosphoramide) were measured from the b.p. of liquid helium to room temperature. The temperature dependence of the magnetic susceptibilities indicates that UI_4hmpa_2 has a *trans*-configuration, as have UCl_4hmpa_2 and UBr_4hmpa_2. Analysis of the magnetic susceptibilities on the basis of the ligand-field theory shows the distortion of the ligand field around the central uranium ion from O_h symmetry in the following order: $UCl_4hmpa_2 < UBr_4hmpa_2 < UI_4hmpa_2$.

Introduction

Among the many neutral oxygen-donor ligand complexes of uranium tetrachloride and tetrabromide, six-coordinated complexes of the type UX_4L_2 ($X = Cl^-$ and Br^-; L = a neutral monodentate oxygen-donor ligand) have been extensively studied from the viewpoint of spectral and structural chemistry. Complexes with this type can exist either in *trans*- or *cis*-configurations which have D_{4h} or C_{2v} symmetries, respectively. The configurations of all complexes of the UX_4L_2 type reported have been assigned to a *trans*-configuration, except UCl_4tppo_2 (tppo = triphenylphosphine oxide) [1]. In the *trans*-configuration, the difference in intensities between the ligand field around the central uranium ion formed by the ligand L and that by the halogen X leads to a measure of distortion from the octahedral symmetry of the complexes. The relationship between the ligand-field strength of L and the degree of distortion has been discussed by considering the U–O (O = donor oxygen atom of L) and U–X distances in complexes with various kinds of L [2]. On the other hand, it is interesting to note the effect of the ligand-field strength of X when the halogen changes from Cl^- to I^-, keeping the neutral ligand constant.

Six-coordinated UI_4 complexes had not been isolated because of difficulties in their preparation until two of the present authors successfully isolated $UI_4(Mecn)_4$ [3] which can be used as a new starting material for the preparation of UI_4 complexes. There are very few reports about a series of complexes which have a complete set of halogen ions from Cl^- to I^- with a common ligand, L. No crystal structures of UI_4 complexes have ever been determined by X-ray diffraction analysis, except for $UI_4(tmu)_2$ (tmu = *N,N,N',N'*-tetramethylurea) [4]. The distortion of UI_4 complexes cannot, therefore, be compared crystallographically with those of UCl_4 and UBr_4 complexes.

In the present study, the magnetic susceptibility of $UX_4(hmpa)_2$ ($X = Cl^-$, Br^- and I^-; hmpa = hexamethylphosphoramide, $[(CH_3)_2N]_3P{=}O$) was measured from the b.p. of liquid helium to room temperature. These results were analysed on the basis of the ligand-field theory. By comparing their magnetic susceptibilities with each other, we first discuss the geometrical configuration of the *cis* or *trans* forms of $UI_4(hmpa)_2$ and, secondly, the order of magnitude of the tetragonal distortion from octahedral symmetry for all the complexes.

Experimental

Preparation of the Complexes

$UCl_4(hmpa)_2$ and $UBr_4(hmpa)_2$ were prepared according to the method of Bagnall *et al.* [5]. $UI_4(hmpa)_2$ was prepared as described previously [6].

Analyses

The uranium content was determined gravimetrically by an ammonia precipitation method [7], and the halogen content by potentiometric titration with standard silver nitrate solution. Hydrogen, carbon and nitrogen contents were determined with a Yana-

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TABLE I. Elemental Analyses of UX_4hmpa_2 (%)[a]

Complex	H	C	N	X	U
UCl_4hmpa_2	4.92	19.72	11.29	19.1	32.1
$C_{12}H_{36}N_6P_2O_2Cl_4U$	(4.93)	(19.52)	(11.38)	(19.21)	(32.24)
UBr_4hmpa_2	3.9	15.5	9.2	34.7	25.7
$C_{12}H_{36}N_6P_2O_2Br_4U$	(3.97)	(15.73)	(9.17)	(34.89)	(25.98)
UI_4hmpa_2	3.2	13.1	7.5	45.6	21.2
$C_{12}H_{36}N_6P_2O_2I_4U$	(3.30)	(13.05)	(7.61)	(45.98)	(21.56)

[a] Calculated values are given in parentheses.

gimoto CHN Coder MT-2. The results of the analyses of the complexes are shown in Table I.

Physical Measurements

Infrared absorption

Infrared spectra of the powdered samples were recorded on a JASCO IR-2 spectrophotometer by the KBr disc method. (4000–400 cm^{-1}) Far-infrared spectra were recorded on a Hitachi Perkin-Elmer Model 225 spectrophotometer as Nujol mulls mounted between CsI cells (400–240 cm^{-1}).

Magnetic susceptibility

Measurements of magnetic susceptibility were carried out on powdered samples using a Faraday-type torsion magnetometer from the b.p. of liquid helium to room temperature. $HgCo(NCS)_4$ [8] was used as a calibrant of susceptibilities. In order to confirm that the sample was free from ferromagnetic impurities, the dependence of the magnetic susceptibility on the intensity of the magnetic field was measured in the range from 0.1 to 1 T. Diamagnetic susceptibility corrections for all samples were made by using Pascal's constants and the value for tetravalent uranium [9]. The values were given as follows: $UCl_4(hmpa)_2$, −324.2; $UBr_4(hmpa)_2$, −364.2; $UI_4(hmpa)_2$, −428.2 ($\times 10^{-6}$ cgs emu).

Results and Discussion

Magnetic susceptibilities of UX_4hmpa_2 ($X = Cl^-$, Br^- and I^-) are shown in Fig. 1. The magnetic susceptibilities of all the complexes increase with decreasing temperature from room temperature, and have a plateau below 100 K, 80 K and 50 K for UCl_4hmpa_2, UBr_4hmpa_2 and UI_4hmpa_2, 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. The order of magnitude of the magnetic susceptibilities for all the complexes in the measured temperature range is given as follows:

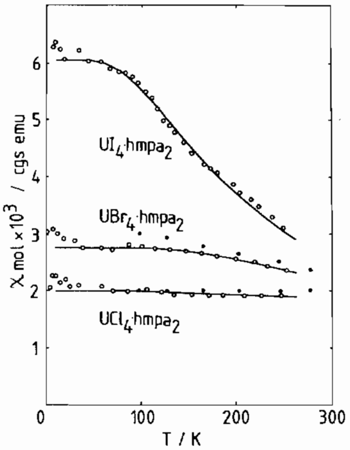

Fig. 1. Temperature dependence of the magnetic susceptibility of UX_4hmpa_2: (○), present measurement; (●), plotted from the values in ref. 5.

$$(UCl_4hmpa_2) < (UBr_4hmpa_2) < (UI_4hmpa_2)$$

The magnetic susceptibilities of UCl_4hmpa_2 and UBr_4hmpa_2 agree with previous results [5] within experimental error.

The infrared spectra of these complexes are very similar to one another. The relevant frequencies, ν(P=O), observed here and their differences from that of the free hmpa molecule (1207 cm^{-1}), $\Delta\nu$(P=O), are given in Table II. In the infrared spectra of UX_4tppo_2 ($X = Cl^-$ and Br^-) [10], the frequency of ν(P=O) shifts to the lower energy region in comparison to that of the free tppo molecule when the oxygen donor atom coordinates to the uranium ion. The ν(P=O) of all the complexes studied here shifts to the lower energy region. Hmpa ligand is, therefore, considered to coordinate to the uranium ion through an oxygen donor atom in all complexes, and the bands of the U–O stretching vibration are observed in the far-infrared region. In the low frequency region (400–240 cm^{-1}, see Fig. 2), only the vibration of the U–Cl bond can be detected and those of U–Br and U–I are out of the measured range.

The paramagnetic susceptibility of tetravalent uranium complexes which have a ligand field with regular octahedral symmetry does not have a con-

TABLE II. Data of Physical Measurements of UX$_4$hmpa$_2$

Complex	Infrared and far-infrared (cm^{-1})				Energy difference ΔE (cm^{-1})
	ν(P=O)	$\Delta\nu$(P=O)	ν(U–O)	ν(U–X)	
UCl$_4$hmpa$_2$	1035	172	386	258	735
UBr$_4$hmpa$_2$	1020	187	381	[a]	545
UI$_4$hmpa$_2$	995	212	377	[a]	245

[a] Out of measured range.

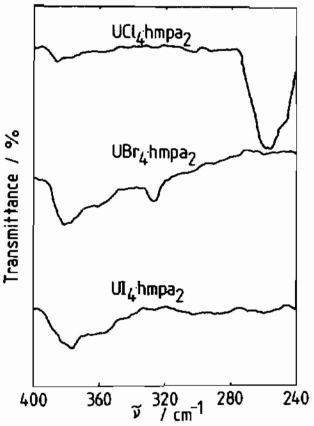

Fig. 2. Far-infrared spectra of UX$_4$hmpa$_2$.

tribution from the first-order Zeeman term and is independent of temperature. Their magnetic susceptibility is attributable to the high frequency term arising from mixing of the A$_1$ (^{3}H$_4$) ground state with the T$_1$ (^{3}H$_4$) excited state [11]. UCl$_4$hmpa$_2$ [12, 13] and UBr$_4$hmpa$_2$ [13] were reported to have a *trans*-octahedral structure. In the *trans*-configuration, the symmetry around the uranium ion decreases from O_h to D_{4h}, and both the first- and the second-order Zeeman effects contribute to its magnetic susceptibility. The magnetic susceptibility of *trans*-UX$_4$L$_2$ complexes increases with decreasing temperature and shows a plateau at the lower temperature. Such a type of magnetic susceptibility *versus* temperature curve is characteristic of this configuration. If the UX$_4$L$_2$ complex has a *cis*-configuration, the symmetry around the central uranium ion further decreases to C_{2v}. In this case, the contribution from the first-order Zeeman term vanishes, and only the high-frequency term gives rise to the temperature-independent paramagnetic susceptibility. Therefore, the geometrical configuration, *cis* or *trans*, of UX$_4$L$_2$ complexes can be elucidated from the behaviour of the magnetic susceptibility.

It is clear from Fig. 1 that the magnetic susceptibility of UBr$_4$hmpa$_2$ increases and that of UCl$_4$hmpa$_2$ also slightly increases, with decreasing temperature, although the magnetic susceptibility of UCl$_4$hmpa$_2$ has been reported to be independent of temperature over the range 98–305 K [5]. Therefore, it is probable that both complexes have a ligand field with D_{4h} symmetry and a *trans*-configuration. The geometrical configuration of these complexes, therefore, agree with these obtained by X-ray diffraction analyses [12, 13]. The larger temperature dependence of the magnetic susceptibility of UI$_4$hmpa$_2$, more so than those of UCl$_4$hmpa$_2$ and UBr$_4$hmpa$_2$, suggests that UI$_4$hmpa$_2$ may also have a *trans*-octahedral configuration with a ligand field of D_{4h} symmetry. Calculated magnetic susceptibilities of tetravalent uranium with a ligand field of D_{4h} are shown as a solid line in Fig. 1. These were calculated with the well-known van Vleck equation [14] by putting a given energy difference, ΔE, between the ground state A$_1$ and the first excited state E$_1$ where the latter is a result of a splitting of the T$_1$ state. Close agreement between observed and calculated values was obtained for all complexes. It, therefore, may be concluded that the symmetry of the ligand field around uranium in UI$_4$hmpa$_2$ is D_{4h}, and that it also has a *trans*-octahedral configuration. The values of ΔE which fit best are listed in Table II.

The splitting of the ^{3}H$_4$ ground term of tetravalent uranium caused by crystalline fields of O_h and D_{4h} symmetries is presented in Fig. 3. The energy difference ΔE decreases with an increase in the magnitude of tetragonal distortion [15]. Thus the order of magnitude of the tetragonal distortion can be seen from the order of ΔE obtained from the observed magnetic

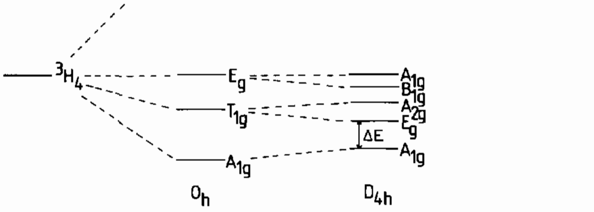

Fig. 3. Energy diagrams of the ^{3}H$_4$ ground term of U^{IV} in O_h and D_{4h} environments.

susceptibility. As listed in Table II, the order of energy difference ΔE is given as follows:

$$\Delta E(UCl_4hmpa_2) > \Delta E(UBr_4hmpa_2) > \Delta E(UI_4hmpa_2)$$

Therefore, the order of tetragonal distortion from the octahedral symmetry is:

$$UCl_4hmpa_2 < UBr_4hmpa_2 < UI_4hmpa_2$$

The X-ray diffraction analyses of UCl_4hmpa_2 and UBr_4hmpa_2 show that the U–O distance in UBr_4hmpa_2 is shorter than that of UCl_4hmpa_2 [12, 13]. It is probable that UI_4hmpa_2, which has a greater degree of distortion than UBr_4hmpa_2, has a shorter U–O distance than UBr_4hmpa_2. A similar tendency of relative changes of U–O and U–X distances in going from Cl^- to I^- is also observed in UX_4tmu_2 ($X = Cl^-$, Br^- and I^-) [4].

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