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The Chemistry of Uranium. Part XIX. Theoretical Interpretation of the Magnetic Susceptibilities of Uranium(IV) Ions in Crystalline Fields of D_{4h} and C_{2v} Symmetry

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Magnetic susceptibility data on some six coordinated U^{IV} complexes having trans- *and* cis-*configurations are discussed using a crystal field approach. The wave functions required for an explicit evaluation of low- and high-frequency matrix elements were constructed by utilizing projection operator methods. Information about the relative positions of the energy levels arising from a $^3H_4$ state is obtained graphically and conclusions regarding the nature of the levels participating in the observed susceptibilities are presented. A qualitative interpretation of the experimental data was made in the light of the theoretical treatment and recent structural data.*

Introduction

The magnetic properties of $UX_4 \cdot 2L$ species where X = Cl or Br and L represents $O{=}ER_3$ (E = P and As and R = phenyl and ethyl) have previously been interpreted on the assumptions that these complexes have D_{4h} symmetry and that the tetragonal distortion is greater for an arsine oxide than a phosphine oxide ligand and for a bromo complex than a chloro complex. The assignment of *trans*-configurations was based on infra-red spectral data [1].

Recent crystallographic data, however, proved some of these assumptions to be in error, *e.g.* $UCl_4 \cdot 2tppo$ (tppo = triphenylphosphine oxide) has a *cis*-configuration [2] and $UBr_4 \cdot 2hmpa$ (hmpa = hexamethylphosphoramide) is distorted in the opposite direction as assumed when compared to $UCl_4 \cdot 2hmpa$ [3]. On the other hand the arsine oxide complex, $UCl_4 \cdot 2teaso$ [4] (teaso = triethylarsine oxide), is more tetragonally distorted *i.e.* shorter U–O and longer U–Cl bonds than typical UCl_4 complexes of phosphine oxides, *e.g.* $UCl_4 \cdot 2hmpa$ [3] and $UCl_4 \cdot 2ptpa$ [5] (ptpa = phenyltetramethylphosphoramide) and therefore in agreement with the earlier assumption.

In an effort to clarify the magnetic properties of $UX_4 \cdot 2L$ species a crystal field model was used to describe the behaviour of both the *cis* and *trans* configurations theoretically. The experimental behaviour was then interpreted in terms of these results and in the light of previous work in this field.

Theoretical Section

In order to obtain a theoretical interpretation of the magnetics of the abovementioned complexes a crystal field model is applied and methods developed elsewhere [6–8] extended. This is done for both *trans*- and *cis*-configurations.

Trans-configurations

This case can be discussed by regarding the D_{4h} symmetry as resulting from a tetragonal distortion $\Delta V_{D_{4h}}$ applied to an O_h symmetry.

$$V_{D_{4h}} = V_{O_h} + \Delta V_{D_{4h}}$$

Using the expressions for $V_{D_{4h}}$ and V_{O_h} applicable to f systems results in the final expression for $\Delta V_{D_{4h}}$ as

$$\Delta V_{D_{4h}} = Sr^2\ Y_{2,0} + Tr^4 Y_{4,0} + VY_{6,0}$$

where S, T and V are constants depending on the ligand charges and metal–ligand distances.

The splitting of the $^3H_4$ ground term of the U^{IV} ion caused by O_h and D_{4h} perturbations can be represented as in the diagram.

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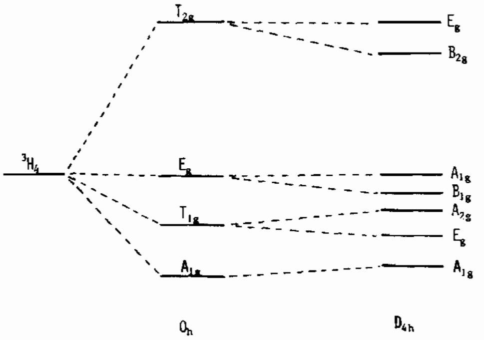
TABLE I. Octahedron Energies and Eigenstates.

I R	Energy	Degeneracy	Eigenstates
A_{1g}	$-14a - 20b$	1	$\sqrt{\frac{1}{12}}[\sqrt{7}\vert 0> + \sqrt{\frac{5}{2}}(\vert 4> + \vert\bar{4}>)]$
T_{1g}	$-7a + b$	3	$\sqrt{\frac{1}{2}}(\vert 4> - \vert\bar{4}>)$
			$\sqrt{\frac{1}{8}}(\vert 3> + \sqrt{7}\vert\bar{1}>)$
			$-\sqrt{\frac{1}{8}}(\vert\bar{3}> + \sqrt{7}\vert 1>)$
E_g	$-2a + 16b$	2	$\sqrt{\frac{1}{2}}(\vert 2> + \vert\bar{2}>)$
			$-\sqrt{\frac{1}{12}}[\sqrt{5}\vert 0> - \sqrt{\frac{7}{2}}(\vert 4> + \vert\bar{4}>)]$
T_{2g}	$13a - 5b$	3	$\sqrt{\frac{1}{2}}(\vert 2> - \vert\bar{2}>)$
			$\sqrt{\frac{1}{8}}(\sqrt{7}\vert 3> - \vert\bar{1}>)$
			$\sqrt{\frac{1}{8}}(\vert 1> - \sqrt{7}\vert\bar{3}>)$



Hence the actual energies of the levels resulting from the $^3H_4$ level in a D_{4h} environment can be calculated by regarding $\Delta V_{D_{4h}}$ as a perturbation of V_{O_h}. This is done by using the known energies [5] of the O_h levels concerned and their symmetry adapted wave functions [9] in a first order perturbation approach [10, 11]. These are given in Table I.

In Table I a and b are positive constants containing $<r^4>$, $<r^6>$, ligand charges and the metal–ligand distance.

The final energies corresponding to the D_{4h} levels in Diagram I are found to a first order approximation and are expressable in terms of the positive parameters a, b, s, t and v. As follows

$$E_{A_{1g}} = -14a - 20b - 0.07s + 0.04t + 0.11v$$

$$E_{E_g} = -7a + b - 0.06s + 0.01t + 0.05v$$

$$E_{A_{2g}} = -7a + b - 0.08s + 0.03t + 0.1v$$

$$E_{B_{1g}} = -2a + 16b - 0.03s - 0.03t - 0.06v$$

$$E_{A_{1g}} = -2a + 16b - 0.07s + 0.04t + 0.1v$$

$$E_{B_{2g}} = 13a - 5b - 0.03s - 0.03t - 0.06v$$

$$E_{E_g} = 13a - 5b + 0.01s - 0.04t + 0.001v$$

Here s, t and v depend, amongst others, on the parameters $<r^2>$, $<r^4>$ and $<r^6>$ respectively.

In order to assess the relative behaviour of the above energies as a function of the parameters a, b, s, t and v numerous graphs were drawn with various values of b/a, v/s and b/s. Fig. 1 is typical of the results obtained throughout.

From these graphs it is seen that only for extreme values of t/s can the ground state be other than the non-degenerate A_{1g} *i.e.* B_{1g} or the degenerate E_g level. However, as was pointed out elsewhere [7, 12] $v/s < t/s < 1$ is a reasonable limitation to the physically accessable ranges of the parameters s, t and v. Hence the possibility of a ground state other than A_{1g} can be ruled out.

Considering the above results and conclusions the observed susceptibilities of the D_{4h} complexes under discussion can be interpreted qualitatively by using Van Vleck's equation in the well-known form

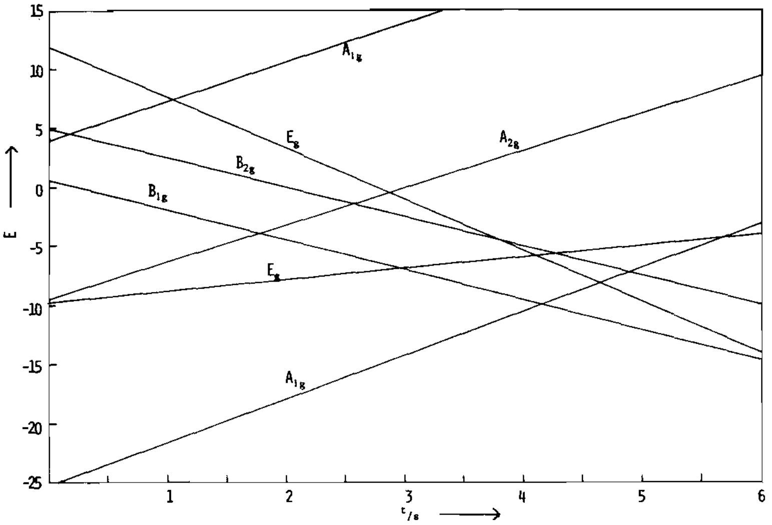


Figure 1. Typical parameter dependence of the electrostatic energies of an ion in a $^3H_4$ state when perturbed by a D_{4h} environment. b/a = ½ and v/s = ½.

$$\chi = \frac{N\Sigma_i(W_i^{(1)2}/kT - 2W_i^{(2)})}{\Sigma_i e^{-Wi/kT}}$$

where $W_i^{(1)} = \beta < \psi_i | gJ_z | \psi_i >$ and

$$W_i^{(2)} = \Sigma_m' \frac{\beta^2 |<\psi_i | g\, J_z | \psi_m>|^2}{W_i^0 - W_m^0}$$

with $g = 4/5$ for levels arising from $^3H_4$.

In order to study the matrix elements in $W_i^{(1)}$ and $W_i^{(2)}$ the symmetry adapted wave functions corresponding to the levels concerned must be constructed. This can be done by projection operator methods [13] and results in

$$A_{1g} : \psi_1 = \sqrt{\frac{7}{12}}|0> + \sqrt{\frac{5}{24}}(|4> + |\bar{4}>)$$

E_g :

$$\psi_2 = -i\left[\sqrt{\frac{1}{16}}(|3> + |\bar{3}>) + \sqrt{\frac{7}{16}}(|1> + |\bar{1}>)\right]$$

$$\psi_3 = \sqrt{\frac{1}{16}}(|3> - |\bar{3}>) - \sqrt{\frac{7}{16}}(|1> - |\bar{1}>)$$

$$A_{2g} : \psi_4 = -i\sqrt{\frac{1}{2}}(|4> - |\bar{4}>)$$

$$B_{1g} : \psi_5 = \sqrt{\frac{1}{2}}(|2> + |\bar{2}>)$$

$$A_{1g} : \psi_6 = -\sqrt{\frac{5}{12}}|0> + \sqrt{\frac{7}{24}}(|4> + |\bar{4}>)$$

$$B_{2g} : \psi_7 = -i\sqrt{\frac{1}{2}}(|2> - |\bar{2}>)$$

E_g :

$$\psi_8 = i\left[\sqrt{\frac{7}{16}}(|3> + |\bar{3}>) - \sqrt{\frac{1}{16}}(|1> + |\bar{1}>)\right]$$

$$\psi_9 = -\sqrt{\frac{7}{16}}(|3> - |\bar{3}>) - \sqrt{\frac{1}{16}}(|1> - |\bar{1}>)$$

Using these wave functions it is easily verified that all diagonal matrix elements vanish while the only non-diagonal elements are

$$<\psi_4 | \frac{4}{5} J_z | \psi_1>$$

$$<\psi_3 | \frac{4}{5} J_z | \psi_2>$$

$$<\psi_9 | \frac{4}{5} J_z | \psi_2>$$

$$<\psi_8 | \frac{4}{5} J_z | \psi_3>$$

$$<\psi_6 | \frac{4}{5} J_z | \psi_4>$$

$$<\psi_7 | \frac{4}{5} J_z | \psi_5>$$

$$<\psi_7 | \frac{4}{5} J_z | \psi_8>$$

This then indicates that only high-frequency terms contribute to the susceptibility of the D_{4h} complexes under consideration. In contrast to a previous interpretation [1] our results exclude a high-frequency contribution due to interaction between the A_{1g} ground state and E_g excited state since the matrix element concerned actually vanishes. An interaction between the A_{1g} ground state and A_{2g} excited state is suggested instead. This is also justified by the relative position of these two levels as displayed in Fig. 1.

Furthermore the observation that displacement of the chloride ions by bromide ions results in higher paramagnetism is in accordance with the present interpretation.

Finally the approximate temperature independence observed at lower temperatures (Fig. 3) supports the conclusion that only high-frequency elements contribute; only at higher temperatures do the Boltzman factors associated with the excited states become appreciable and hence the temperature dependence of the susceptibility at these temperatures.

Cis-*configurations*

If the symmetry is decreased from D_{4h} to C_{2v}, as is the case for $UCl_4 \cdot 2tppo$, the D_{4h} levels arising from the $^3H_4$ free ion level are split as shown below.

D_{4h}	C_{2v}
A_{1g}	$A_1^{(1)}$
A_{1g}	$A_1^{(2)}$
B_{1g}	$A_1^{(3)}$
A_{2g}	$A_2^{(1)}$
E_g	$B_1^{(1)} \dotplus B_2^{(1)}$
B_{2g}	$B_2^{(2)}$
E_g	$A_2^{(2)} \dotplus B_1^{(2)}$

This indicates that for *cis*-configurations only non-degenerate levels exist and hence no non-zero low frequency terms are expected to contribute to the paramagnetic susceptibility [14, 15]. In order to study the relevant high-frequency contributions the symmetry adapted wave functions belonging to the C_{2v} levels were constructed, using projection operators, and found to be [16]

$$A_1^{(1)} : \psi_1 = |0>$$

$$A_1^{(2)} : \psi_2 = \frac{1}{\sqrt{2}}(|4> + |\bar{4}>)$$

$$A_1^{(3)} : \psi_3 = \frac{1}{\sqrt{2}}(|2> - |\bar{2}>)$$

$$A_2^{(1)} : \psi_4 = \frac{1}{\sqrt{4}}[(|3> - |\bar{3}>) - i(|3> + |\bar{3}>)]$$

$$A_2^{(2)} : \psi_5 = \frac{1}{\sqrt{4}}[(|1> - |\bar{1}>) + i(|1> + |\bar{1}>)]$$

$$B_1^{(1)} : \psi_6 = \frac{1}{\sqrt{2}}(|4> - |\bar{4}>)$$

$$B_1^{(2)} : \psi_7 = \frac{1}{\sqrt{2}}(|2> + |\bar{2}>)$$

$$B_2^{(1)} : \psi_8 = \frac{1}{\sqrt{4}}[|3> - |3> + i(|3> + |-\bar{3}>)]$$

$$B_2^{(2)} : \psi_9 = \frac{1}{\sqrt{4}}[|1> - |\bar{1}> - i(|1> + |1>)]$$

Using these wave functions it is easily verified that the only non-zero high frequency elements stem from interactions between the level pairs $A_1^{(2)}$–$B_1^{(1)}$, $A_1^{(3)}$–$B_1^{(2)}$, $A_2^{(1)}$–$B_2^{(1)}$ and $A_2^{(2)}$–$B_2^{(2)}$

In order to obtain an estimate of the relative importance of these interactions to the susceptibility the positions of the levels relative to each other have to be studied. This is again done by applying first order perturbation theory in the context of a crystal field theory. The potential used here for f systems was found from crystallographic data [2] and an estimate for the relative ligand strength to be reducible to

$$V_{C_{2v}} = 3.0r^2Y_{2,0} + 2.0r^4Y_{4,0} + 0.1r^4(Y_{4,4} + Y_{4,-4}) + 0.2r^6Y_{6,0} - 0.2r^6(Y_{6,4} + Y_{6,-4})$$

The level energies can be expressed in terms of the parameters $\alpha = <r^2>$, $\beta = <r^4>$ and $\gamma = <r^6>$:

$$E_{A_1}^{(1)} = 2.2\alpha - 14.9\beta - 0.2\gamma$$

$$E_{A_1^{(2)}} = -3\alpha - 0.5\beta - 0.1\gamma = E_{B_1^{(1)}}$$

$$E_{A_1^{(3)}} = \alpha - 3.7\beta + 0.4\gamma$$

$$E_{A_2^{(1)}} = 0.8\alpha - 12\beta - 0.1\gamma = E_{B_2^{(1)}}$$

$$E_{A_2^{(2)}} = 1.8\alpha - 9.8\beta - 0.1\gamma = E_{B_2^{(2)}}$$

$$E_{B_1^{(2)}} = 0.8\alpha - 4.5\beta + 0.5\gamma$$

A typical plot of the parameter dependence of the energies is given in Fig. 2.

It is seen that the ground state is the non-degenerate $A_1^{(1)}$ level for which no interaction with excited levels exists. Hence the susceptibility is expected to become appreciable only at higher temperatures where the interactions between the excited levels assume importance.

Discussion of Experimental Results

The temperature dependence of the magnetic susceptibilities of a number of uranium(IV) complexes are given in the curves in Fig. 3. The interpretation of the magnetic behaviour of these $UX_4 \cdot 2l$ complexes (X = Cl, Br and l = neutral oxygen donor ligands) must now be modified in the light of the above theoretical treatment and recent X-ray structural data.

The temperature independent paramagnetic behaviour of $UCl_4 \cdot 2tppo$ (curve (a)), which has C_{2v} sym-

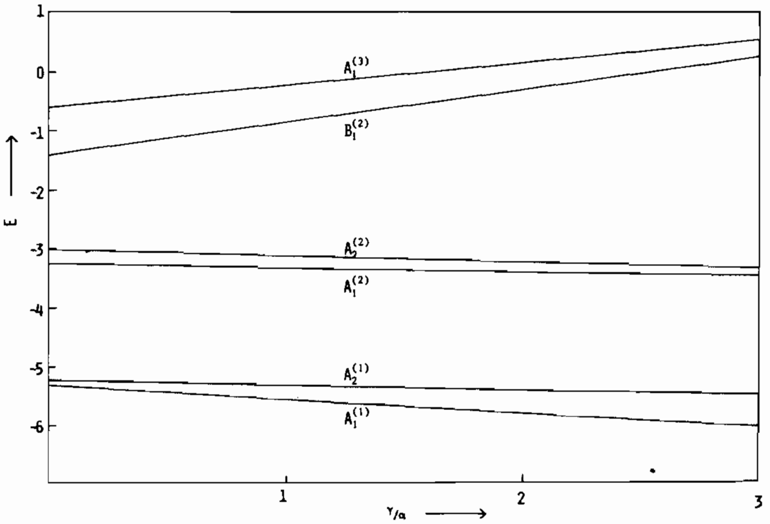


Figure 2. Typical parameter dependence of the electrostatic energies of an ion in a $^3H_4$ state when perturbed by a C_{2v} environment. $\beta/\alpha = \frac{1}{2}$.

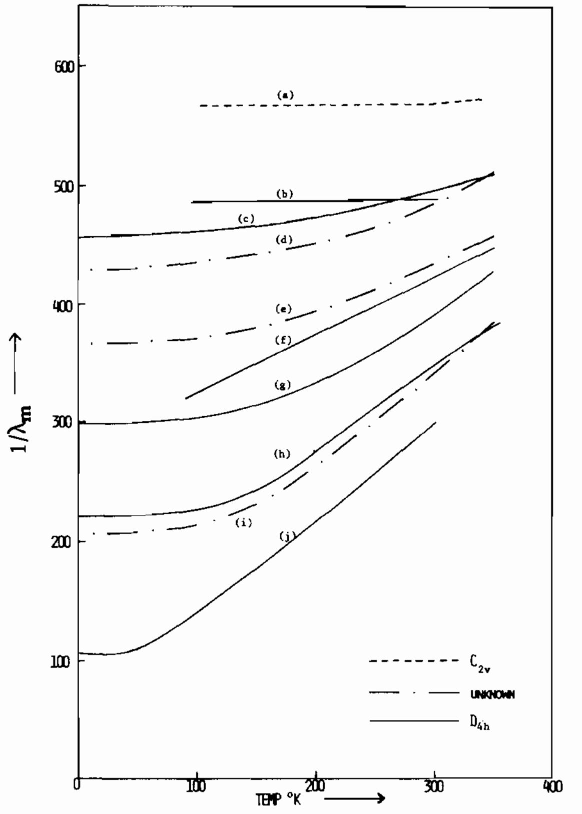


Figure 3. Temperature dependence of the magnetic susceptibilities of some uranium(IV) complexes. (a) $UCl_4 \cdot 2$tppo; (b) $UCl_4 \cdot 2$-hmpa; (c) $UCl_4 \cdot 2$tepo; (d) $UBr_4 \cdot 2$tppo; (e) $UCl_4 \cdot 2$tpaso; (f) $UBr_4 \cdot 2$hmpa; (g) $UBr_4 \cdot 2$tepo; (h) $UCl_4 \cdot 2$teaso; (i) $UBr_4 \cdot 2$tpaso; (j) $UBr_4 \cdot 2$teaso (curves c, d, e, g, h, i and j as from ref. 1.).

metry [2], is in good agreement with the theory where it was seen that the ground state is a non-degenerate A_1 level for which no interaction with excited levels exists (see under theoretical). Although some doubt exists about the exact structures of the triphenyl arsine/phosphine oxide complexes *i.e.* $UBr_4 \cdot 2$tppo and $UX_4 \cdot 2$tpaso ($X = Cl$ and Br) as to whether these have *cis* or *trans* configurations, the other $UX_4 \cdot 2$l complexes almost certainly have D_{4h} symmetry as has already been indicated for $UCl_4 \cdot 2$l (l = hmpa [3], ptpa [5] and teaso [4]) and $UBr_4 \cdot$2hmpa [3].

There are two types of tetragonal distortions operative in these complexes, firstly, as a result of the difference in ligand field effect between equitorial (chloride and bromide) and axial (oxygen donor) ligands and, secondly, a structural distortion where the U–O bonds become relatively shorter and U–X bonds relatively longer.

The increasingly greater temperature dependence of the $UCl_4 \cdot$2l species in the direction hmpa, tepo, tpaso and teaso is in agreement with this interpretation (see also Fig. 1). In the case of the hmpa complex the ligand field distortion is small since chloride and hmpa are very similar in this respect [17]. It may therefore be regarded as of approximate O_h symmetry which would explain the observed temperature independent susceptibility of this complex [6]. Both the ligand field [1] and the structural distortions increase in the direction indicated above. In the case of $UCl_4 \cdot$2teaso the structural distortion is already prominent [4].

The molar susceptibility of the $UBr_4 \cdot$2hmpa complex (curve f) is much more temperature dependent than that of its chloro analogue (curve b). A recent structural determination [3] indicated that there are only small structural differences between these compounds and that the slight distortion is in the opposite direction than expected earlier, *i.e.* U–O bonds somewhat longer and U–Br bonds shorter. This suggests that the "ligand field distortion" is more important than the structural distortion in the bromo complexes. The latter will also be significant especially in the cases of the arsine oxide ligands where U–O bond shortening and U–Br bond lengthening are expected.

Conclusion

The above theoretical treatment together with the recent crystallographic data provide a satisfactory interpretation of the temperature dependence of the magnetic susceptibilities of the complexes concerned. The relative positions of the curves for the susceptibilities (from a to j) can also be qualitatively understood in the light of the foregoing theory and the interpretation of distortion as being due to structural as well as ligand effects.

Acknowledgments

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