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Influence of the Nature of the Ligands on the Electronic Ground State of Organouranium(V) Compounds, Studied by Electron Paramagnetic Resonance

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Organouranium(V) amide compounds were studied by electron paramagnetic resonance in frozen solution. Their *g*-tensors were quantitatively interpreted by assuming that dialkylamide, C_8H_8, C_5H_5, C_5Me_5, and THF ligands interact only weakly with 5f orbitals of the central U(V) atom, so that the total angular momentum $J = 5/2$ remains a good quantum number for the description of the electronic ground state of these complexes (weak-field approximation). In the absence of THF ligands, the ground state is predominantly made of $|M_J| = {}^1/_2$ states, with a significant admixture of $|M_J| = {}^5/_2$ states independent of the symmetry of the complex. Thus 5f orbitals are essentially nonbonding, and the metal ligand bonding should involve mainly uranium 6d orbitals. A THF ligand induces a significant admixture of $|M_J| = {}^3/_2$ states. Substitution of amide ligands by alkoxide ligands is characterized by strong U(V)(5f)−OR interactions, which breaks the weak-field approximation. This sensitivity to oxygen ligands indicates that 5f orbitals contribute to the U(V)−oxygen bonding.

Introduction

Uranium(V) compounds are rather uncommon, because of their lack of stability due to disproportionation and reduction.[1] Most of our knowledge of the magnetic behavior (magnetic susceptibility and electron paramagnetic resonance (EPR)) of uranium in this oxidation state was essentially limited to the halides UX_5 (X = F, Cl) or MUF_6 (M = Li, Na, Cs)[2] and the oxides U_2O_5, MU_2O_6 (M = Mg, Ca, La), MUO_3 (M = Li, K), and Li_3UO_4, for example.[3] The EPR spectra of these compounds are consistent with what is expected for an ion with a $5f^1$ configuration which is perturbed by spin−orbit coupling and an octahedral (or cubic) crystal field. In this case the *g*-factors of U(V) may theoretically vary between 2.00 and −1.43, with experimental values mostly in the range −0.2 to −0.7.[4]

More recently, some pentavalent uranium complexes with metal−nitrogen bonds have been synthesized: the complex $(MeC_6H_4C\{NSiMe_3\}_2)_2UCl_3$,[5] the two bis(trimethylsilyl)amide complexes $[\{(Me_3Si)_2N\}_3UX]$ (X = O or NR),[6] and the phosphino amide complex $[\{(R_2PCH_2CH_2)_2N\}_3UCl_2]$ (R = Et, *i*-Pr);[7] the latter gave a very weak EPR signal ($g = 2.0039$) at 77 K, but this free electron spin line could also be due to a radical impurity. The EPR spectrum of the cationic bis(porphyrin)uranium(IV) complex $[(TPP)_2U][SbCl_6]$ (TPP = tetraphenylporphyrin)[8] is characterized by an axial *g*-tensor with $g_{\parallel} = 3.175$ and $g_{\perp} = 1.353$. This spectrum was not interpreted, but it was suggested that the metal center could be partially in the V oxidation state.

The few known organouranium(V) compounds have been reported since 1985. Oxidation of trivalent precursors by pyridine oxide or organic azides afforded the oxo derivatives $[(\eta^5\text{-}C_5Me_5)_2U(OC_6H_3\text{-}i\text{-}Pr_2\text{-}2,6)(O)]$[9] and a few imido complexes of the type $[(\eta^5\text{-}C_5H_4Me)_3U(NR)]$;[10] the latter gave no EPR signal at 4 K. We found that the dialkylamido ligand NR_2 was able to stabilize cationic and neutral uranium(V) complexes; mono- and bis(pentamethylcyclopentadienyl), monocyclooctatetraene, and mixed-ring derivatives have been synthesized by electron transfer from their U(IV) parents.[11]

Here we present an EPR investigation of organouranium(V) amide compounds in dilute frozen solution. These complexes

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(12) Spectra were simulated with a home-made program and with the WIN-EPR Sim Fonia simulation program from Bruker.

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exhibit a more or less distorted tetrahedral or trigonal bipyramidal geometry, which is an interesting situation since very few experimental data on U(V) ($5f^1$ configuration) in nonoctahedral symmetry have been reported so far.[4] In particular, it has been demonstrated that octahedral coordination leads to ligand field splittings of the same order of magnitude as the spin−orbit interaction (intermediate-field approximation),[13] which has been verified by EPR on a series of octahedral U(V) complexes.[4] The situation of organouranium(V) amide compounds is particular since the variety of ligands and geometries of these complexes can lead to different energy level schemes, and thus to a variety of EPR spectra, according to the more or less bonding/nonbonding/antibonding character of the 5f−ligand interactions. The intermediate-field approach may be used if these interactions exhibit a significant covalent character. This situation should in principle dominate since 5f orbitals are subject to less shielding than 4f orbitals of lanthanides and, therefore, overlap more strongly with ligand orbitals. The ligand field acts on $|(5f^1),L,S,M_l,M_s\rangle$ metallic states, where L and S are the orbital and spin momentum and M_l and M_s their corresponding z-components. Interactions with ligands lead to a partial or total removal of the $2L + 1$ degeneracy of the ground state. The corresponding EPR spectra are characterized by low $|g|$ values generally smaller than 1.[4] Alternatively, if the interaction between 5f and ligand orbitals is weak, the situation may be treated in the weak-field approximation (interactions with ligand smaller than the spin−orbit coupling) since the ground state exhibits an almost purely metallic character. In that case the ligand field acts on $|(5f^1),L,S,J,M_J\rangle$ states (in the Russell−Saunders approximation), where $J = L + S, L + S - 1, ..., |L - S|$ and M_J are the total angular momentum and their z-components. The small metal−ligand interaction removes the $2J + 1$ degeneracy into Kramers doublets. This situation is very similar to that of the lanthanide $4f^1$ analogue (Ce^{III}) where the small radial distribution of the 4f orbitals prevents strong overlap with ligand orbitals. The EPR spectra of organouranium(V) compounds with nonbonding 5f orbitals should thus be very similar to those of Ce^{III} compounds. The EPR investigation of a series of organouranium(V) amide complexes offers the opportunity to study precisely the influence of the coordination geometry and the nature of the ligands on the electronic ground state of these compounds.

Experimental Section

Syntheses of the mono- and bis(pentamethylcyclopentadienyl) complexes $[(\eta^5\text{-}C_5Me_5)U(NMe_2)_3(THF)][BPh_4]$ (**II**) and $[(\eta^5\text{-}C_5Me_5)_2U(NEt_2)_2][BPh_4]$ (**IV**) are described in ref 11b; preparation of the monocyclooctatetraene compounds $[(\eta^8\text{-}C_8H_8)U(NEt_2)_2(THF)][BPh_4]$ (**I**), $[(\eta^8\text{-}C_8H_8)U(NEt_2)_3]$ (**III**), $[(\eta^8\text{-}C_8H_8)(C_5H_5)U(NEt_2)_2]$ (**V**), and $[(\eta^8\text{-}C_8H_8)U(O\text{-}i\text{-}Pr)_3]$ (**VI**) are reported in ref 11c. Attempts to prepare the compounds $[(\eta^8\text{-}C_8H_8)U(NEt_2)_{3-x}(O\text{-}i\text{-}Pr)_x]$ ($x = 1, 2$) by treatment of **III** with a stoichiometric quantity of 2-propanol were unsuccessful: reaction of **III** with 1 equiv of alcohol gave only a 2:1 mixture of **III** and **VI**.

Frozen solution EPR spectra were recorded at 15 K with a Bruker 220D X-band spectrometer equipped with the standard TE_{102} cavity; ca. 1−5 mg of the complexes was dissolved in 0.4 mL of a 90:10 mixture of THF and methyl-THF. The temperature was controlled with an Oxford Instrument ESR-9 continuous flow helium cryostat.

Results

Figures 1−5 show the experimental and simulated EPR spectra of compounds **I**−**V**. Their shapes are definitely different from those usually encountered for U(V) complexes or U(V) impurities in solids.[4] With the exception of compound **VI** (Figure 6), all of the spectra exhibit the same powder shape with three turning points characteristic of a rhombic g-tensor. In addition to these features, one often observes a narrow line at $g = 2.002$ (marked by an asterisk) due to a nonidentified radical impurity (Figures 1, 2, and 5). The spectrum in Figure 6 also exhibits a broad line due to the EPR cavity. Spectra of compounds **I**−**IV** could be accurately simulated with a rhombic g-tensor and Gaussian line shape functions.[12] The simulation parameters are given in Table 1. Despite the fact that **II** exhibits only two turning points, the simulation unambiguously showed that a third turning point (g_z-component) exists at a field $B_0 >$ 810 mT, which gives an upper limit $g_z < 0.80$ for this component.

The spectrum of **V** is not as well characterized as the others. It is composed of four features in addition to the extra line, which indicates that we are dealing with at least two different paramagnetic species. Most probably, **V** was partially decomposed, and the tentative simulation was made by considering the two sharp features (g_x and g_y) similar to those found in other spectra, associated with the broad line (g_z-component?) at high field. Despite the fact that the g-values deduced from the

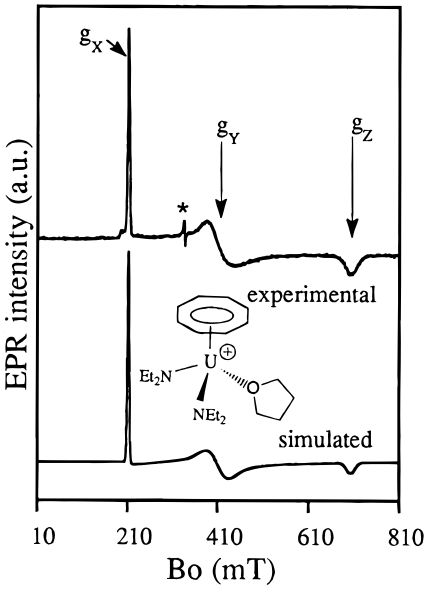

Figure 1. EPR spectrum of $[(\eta^8\text{-}C_8H_8)U(NEt_2)_2(THF)][BPh_4]$ (**I**).

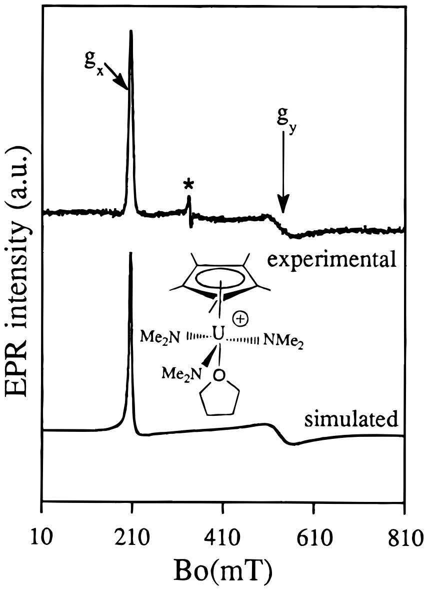

Figure 2. EPR spectrum of $[(\eta^5\text{-}C_5Me_5)U(NMe_2)_3(THF)][BPh_4]$ (**II**).

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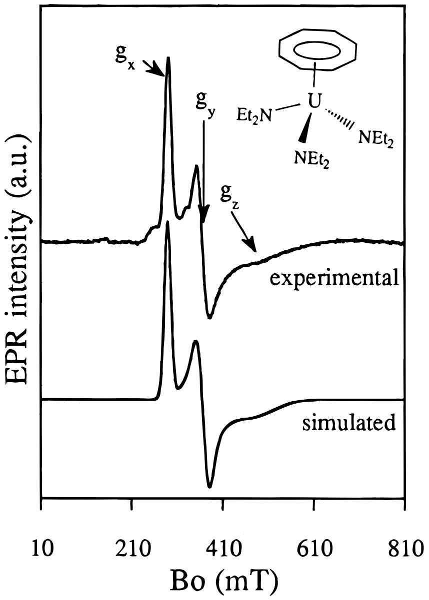

Figure 3. EPR spectrum of [(η^8-C_8H_8)U(NEt_2)$_3$] (**III**).

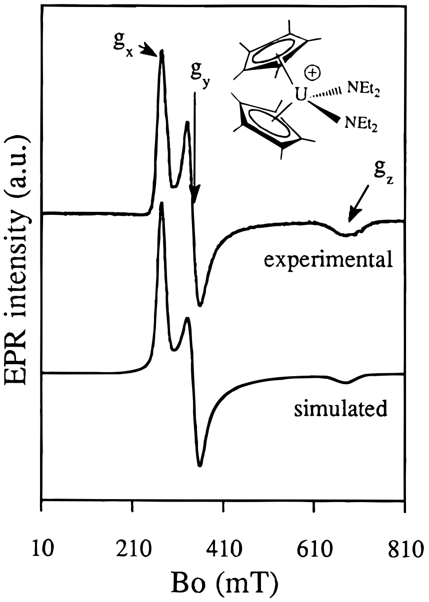

Figure 4. EPR spectrum of [(η^5-C_5Me_5)$_2$U(NEt_2)$_2$][BPh_4] (**IV**).

simulation seem acceptable, they should be considered as rough approximations.

Among all complexes under study, which constitute a homogeneous series, compound **VI** provides a striking exception since its spectrum is only composed of a broad and poorly resolved signal at high field. This latter can be simulated by an axial g-tensor with $|g_\perp| = 0.91$ and $|g_\parallel| = 0.74$. Despite the fact that the $g_\parallel$ turning point of **VI** is not completely seen, the general aspect of the simulated spectrum is strongly affected by small variations of $g_\parallel$, so that the determination of this parameter is relatively precise. It should be noted that **III** and **VI** have exactly the same tetrahedral arrangement, but with the NR_2 ligands in **III** replaced by O-i-Pr ligands in **VI**. The fact that their EPR spectra are dramatically different shows that the determining factor of the electronic ground state is indeed the nature of the ligands. Although a certain similarity exists between the spectrum of **VI** and the EPR spectra of U(V) species previously described in the literature and interpreted with the intermediate-field approximation,[4] it appears that the spectra of compounds **I**−**V** are without precedent to the best of our knowledge.

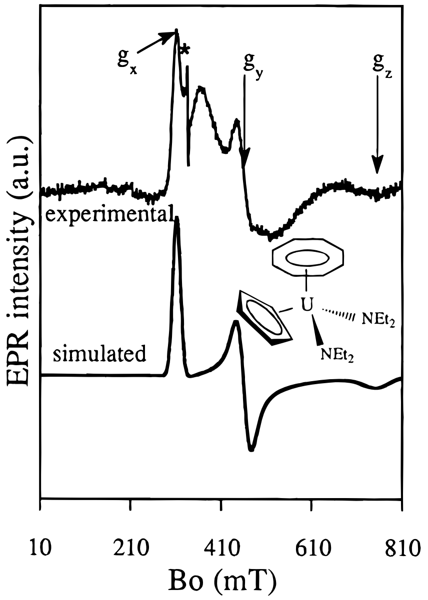

Figure 5. EPR spectrum of [(η^8-C_8H_8)(η^5-C_5H_5)U(NEt_2)$_2$] (**V**).

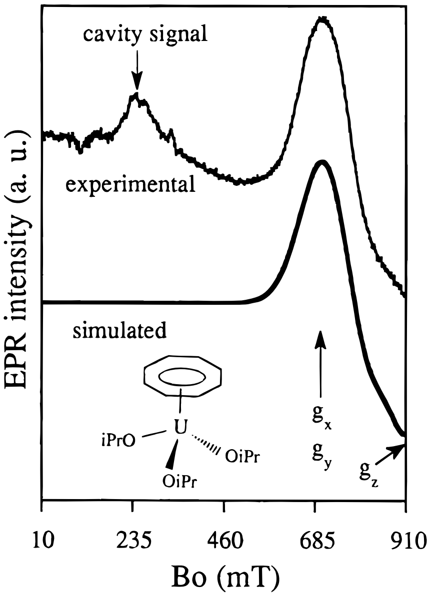

Figure 6. EPR spectrum of [(η^8-C_8H_8)U(O-i-Pr)$_3$] (**VI**).

Electronic Ground State of Organouranium(V) Compounds. For U(V) element in an octahedral environment, characterized by ligand field interactions of the same order of magnitude as the spin−orbit interaction, the $|g|$-values are always smaller than 2. This situation has been extensively studied by EPR and theoretical calculations.[3,4,13] All of the organouranium(V) amide compounds studied in this work are characterized by $|g|$-values in the range 3.3−0.7. Compounds **I**, **III**, **IV**, and **V** exhibit pseudotetrahedral geometries, whereas **II** exhibits a trigonal bipyramidal arrangement. In this work we show that U(5f)−ligand interactions are much smaller than the spin−orbit splitting $7\lambda/2 = 7608$ cm^{-1} between the $^2F_{5/2}$ ground state and the $^2F_{7/2}$ excited state.[14] In this case the effect of the metal−ligand interactions is only to remove the degeneracy of the atomic $^2F_{5/2}$ ground state, without significant mixing with the $^2F_{7/2}$ excited state and with ligand orbitals. As a consequence, we may consider that the total angular momentum $J = {}^5/_2$ is a good quantum number and thus that the different states of the complexes can be accurately

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Table 1. Simulation Parameters for Compounds **I−VI**[a]

parameter	**I**	**II**	**III**	**IV**	**V**	**VI**
$\lvert g_x \rvert$	3.170 ± 0.005	3.270 ± 0.005	2.310 ± 0.005	2.460 ± 0.005	2.160 ± 0.005	0.910 ± 0.005
$\lvert g_x \rvert$	1.640 ± 0.005	1.260 ± 0.005	1.820 ± 0.005	1.950 ± 0.005	1.460 ± 0.005	0.910 ± 0.005
$\lvert g_x \rvert$	0.960 ± 0.005	<0.80	1.36 ± 0.01	0.99 ± 0.01	0.90 ± 0.01	0.74 ± 0.01
ΔB_x	4	4	14	16	17	130
ΔB_y	40	40	22	21	27	130
ΔB_z	20		90	40	60	70

[a] Line widths ΔB_i ($i = x, y, z$) are given in millitesla.

described by functions of the type $|(5f^1),L,S,J,M_J\rangle = |(5f^1),3,{}^1/_2,{}^5/_2,M_J\rangle$, hereafter noted $|J,M_J\rangle = |{}^5/_2,M_J\rangle$ or more simply $|M_J|$. With this scheme, U(V) (5f^1) should be equivalent to its 4f^1 lanthanide partner (Ce^{III}). The second consequence of dealing with weak U(V)−ligand interactions is that we may safely use the crystal field theory to describe these interactions, where the different ligands are considered as point charges which influence the electronic structure of U(V) compounds through their symmetry. The crystal field Hamiltonian is written as[15]

$$H_c = \sum_{k=0}^{2J} \sum_{q=-k}^{+k} B_k^q O_k^q \tag{1}$$

where B_k^q and O_k^q are respectively the crystal field coefficients and the equivalent operators.[15] The crystal field Hamiltonian (1) splits the $^2F_{5/2}$ ground state into three Kramers doublets. If the splitting is much larger than *kT*, so that only the lowest doublet is thermally populated, the system may be treated as for an effective spin $\tilde{S} = {}^1/_2$. The two normalized wave functions $|\alpha\rangle$ and $|\beta\rangle$ of a Kramers doublet are written as linear combinations of states with different M_J values:[15]

$$|\alpha\rangle = \sum_{M_J} a_{M_J} |J,M_J\rangle$$

$$|\beta\rangle = \sum_{M_J} (-1)^{J-M_J} a_{M_J}^* |J,-M_J\rangle \tag{2}$$

with

$$\sum_{M_J} |a_{M_J}|^2 = 1 \tag{3}$$

where $a_{M_J}^*$ is the complex conjugate of a_{M_J} and the nonzero values of a_{M_J} in the summation are determined by the symmetry of the complex. The residual degeneracy of the Kramers doublets is lifted by the external magnetic field B_0, with the corresponding Zeeman Hamiltonian of this effective spin $\tilde{S} = {}^1/_2$ written as

$$H = \beta(g_x B_x \tilde{S}_x + g_y B_y \tilde{S}_y + g_z B_z \tilde{S}_z) \tag{4}$$

where the components g_x, g_y, and g_z of the *g*-tensor are determined by the values of the coefficients a_{M_J} in expression 2. A particularly simple situation occurs when the crystal field symmetry is such that the three Kramers doublets are characterized by only one value of M_J, i.e., when expressions 2 are reduced to

$$|{}^{\alpha}_{\beta}\rangle = |J,\pm M_J\rangle$$

Each doublet is characterized by an axial *g*-factor with components $g_{\parallel}$ and $g_{\perp}$ given by[15]

$$\begin{gathered}
|{}^5/_2,\pm{}^1/_2\rangle \\
g_{\parallel} = g_J = 0.86 \\
g_{\perp} = 3g_J = 2.57 \\
|{}^5/_2,\pm{}^3/_2\rangle \\
g_{\parallel} = 3g_J = 2.57 \\
g_{\perp} = 0 \\
|{}^5/_2,\pm{}^5/_2\rangle \\
g_{\parallel} = 5g_J = 4.29 \\
g_{\perp} = 0
\end{gathered} \tag{5}$$

where g_J is the Lande factor:

$$g_J = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \tag{6}$$

Let us now consider the distorted tetrahedral geometry of U(V) amide compounds. We may analyze the hierarchy of the different terms of the crystal field Hamiltonian for a typical amide complex such as **III**, for example. For an isolated U(V)−(C$_8$H$_8$) fragment, the purely axial crystal field contains only terms with $q = 0$:

$$H_c = B_2^0 O_2^0 + B_4^0 O_4^0 = B_2^0[3J_z^2 - J(J+1) + x(35J_z^4 - 30J(J+1)J_z^2 + 25J_z^2 - 6J(J+1) + 3J^2(J+1)^2)] \tag{7}$$

with $x = B_4^0/B_2^0$.

Since operators O_2^0 and O_4^0 are only functions of J_z, they have only diagonal terms for the six pairs of states $|J,\pm M_J\rangle$. Consequently this axial crystal field gives three Kramers doublets $|J,\pm M_J\rangle$ with their *g*-factors given by expression 5. At this stage, it can be checked that the experimental values of g_x, g_y, and g_z for compounds **I−V** are characterized by $g_z < 1.4$ and $g_{\perp} > 2$, which indicates that the lowest Kramers doublet has a major contribution from the states $|{}^5/_2,\pm{}^1/_2\rangle$ since the other two pairs of states are characterized by $g_{\perp} = 0$. This situation is possible for a dominant positive B_2^0 or a dominant negative B_4^0 term in eq 7. The results of crystal field and molecular orbital calculations[17] on uranocene support the second alternative.

For the low symmetries (C_{2v} or C_s) of complexes **I−V**, due to the contribution of ligands NR$_2$, η^8-C$_8$H$_8$, η^5-C$_5$H$_5$, η^5-C$_5$-

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Table 2. Coefficients *a*, *b*, and *c* of the Ground State (Expression 9) and the Corresponding *g*-Values Calculated in the Weak-Field Approximation

compd	*g*-tensor exptl	*g*-tensor calcd	*a*	*b*	*c*	$a^2 + b^2 + c^2$
I	$g_x = 3.170$	$g_x = 3.170$	0.932	0.259	0.169	0.965
	$g_y = 1.640$	$g_y = 1.640$				
	$g_z = 0.960$	$g_z = 0.960$				
II	$g_x = 3.270$	$g_x = 3.270$	0.964	−0.154	0.215	1.000[a]
	$g_y = 1.260$	$g_y = 1.260$				
	$g_z < 0.80$	$g_z = 0.779$				
III	$g_x = 2.310$	$g_x = 2.309$	0.914	−0.390	0.055	0.990
	$g_y = 1.820$	$g_y = 1.820$				
	$g_z = 1.36$	$g_z = 1.360$				
IV	$g_x = 2.460$	$g_x = 2.460$	0.936	−0.239	0.056	0.938
	$g_y = 1.950$	$g_y = 1.950$				
	$g_z = 0.99$	$g_z = 0.990$				
V	$g_x = 2.160$	$g_x = 2.158$	0.858	−0.256	0.083	0.808
	$g_y = 1.460$	$g_y = 1.462$				
	$g_z = 0.90$	$g_z = 0.894$				
VI	$g_x = 0.910$	no solutions				
	$g_y = 0.910$					
	$g_z = 0.74$					

[a] Imposed in the calculation.

Me_5, and THF, the crystal field Hamiltonian admixes terms with $q = 2$:

$$H_c = B_2^0(O_2^0 + xO_4^0) + B_2^2O_2^2 + B_4^2O_4^2 \tag{8}$$

Operators O_2^2 and O_4^2 mix states differing by 2, so that the ground state Kramers doublet is written as

$$|^{\alpha}_{\beta}\rangle = a|^5/_2,\pm^1/_2> + b|^5/_2,\pm^5/_2\rangle + c|^5/_2,\mp^3/_2\rangle \tag{9}$$

Since the components of the *g*-factor are very sensitive to the value of M_J (see expression 5), the experimental *g*-values should reflect the exact $|M_J|$ composition of the ground state. The principal values of the *g*-tensor for the ground state eigenfunction (9) are given by the following expressions:[16]

$$\begin{aligned} g_x &= \pm^6/_7(2\sqrt{5}bc + 4\sqrt{2}ac + 3a^2) \\ g_y &= \pm^6/_7(2\sqrt{5}bc - 4\sqrt{2}ac + 3a^2) \\ g_z &= \pm^6/_7(5b^2 + a^2 - 3c^2) \end{aligned} \tag{10}$$

The possible values of coefficients *a*, *b*, and *c* in the ground state wavefunction are obtained by solving eqs 10 with experimental values of the *g*-tensors. For compounds **I**, **III**, **IV**, and **V**, characterized by a well-defined g_z-component, we retained only the solutions which almost satisfy the normalization condition $a^2 + b^2 + c^2 = 1$. The situation is different for compound **II**, for which we derived only an upper limit $g_z < 0.8$. In that case we solved eqs 10 for g_x and g_y by imposing the normalization condition. In addition to coefficients *a*, *b*, and *c*, this procedure gave an accurate value $g_z = 0.779$ for this compound. In all cases we chose g_x, g_y, $g_z > 0$, which gave real values for coefficients *a*, *b*, and *c*. Negative *g*-values gave imaginary coefficients with the same modulus as for positive *g*-values, and thus a change of the sign of *g* did not modify the $|M_J|$ composition of the ground state. The results are summarized in Table 2, which also shows the comparison of experimental and calculated *g*-values. It is important to note that the U(V) alkoxide compound **VI**, which possesses no amide ligand, gives no solutions for *a*, *b*, and *c* coefficients in eqs 10.

The fact that these coefficients satisfy the normalization condition for amide compounds provides a confirmation that the weak-field approach is well-adapted to the description of the contribution of 5f orbitals to the electronic structure of U(V)−amide complexes. At first sight, this behavior could be explained by the globally tetrahedral arrangement of these complexes, which is supposed to minimize the interactions with the ligands.[13] However, this explanation cannot be retained without some reserve because compounds **II** and **VI** offer exceptions to this simple rule. First of all the geometry of **II** is bipyramidal, not tetrahedral. This has no evident consequence on its electronic ground state, which is similar to that of compounds **I**, **III**, **IV**, and **V**. Second, **VI** is tetrahedral and equivalent with **III**, but with alkoxide instead of amide ligands. The fact that the experimental *g*-values of the U(V) alkoxide compound cannot give solutions for eqs 10 shows that the weak-field approximation is not adapted to these ligands, despite the global tetrahedral arrangement of this compound. Moreover the *g*-tensor of **VI**, characterized by g_x, g_y, $g_z < 1$, bears similarities to those usually found for U(V) in octahedral environments, always interpreted within the framework of the intermediate-field approximation.[4]

Returning to U(V)−amide compounds, it should be stressed that the $|M_J|$ composition of the ground state also reflects the nature of the ligands. All of these complexes exhibit the common feature of having a ground state dominated by the $|^1/_2|$ states, which results from a major contribution of the axial terms B_2^0 or B_4^0 to the crystal field Hamiltonian (8). Coefficient *a* is always larger than 0.9, except for the poorly characterized compound **II** ($a \approx 0.8$), for which only approximate *g*-values are available. This coefficient reaches the value $a = 0.96$ for the strongly axial compound **II** possessing a "linear" moiety C_5Me_5−U−THF. The second important admixture to the ground state is that of the $|^5/_2|$ states, which results from B_2^2 and B_4^2 terms in Hamiltonian 8. The most characteristic ligand-dependent contribution is that of the $|^3/_2|$ states. This admixture remains very small ($c \approx 0.05-0.08$) in amide compounds containing no THF ligands (**III**, **IV**, and **V**). However, it becomes significant in compounds **I** ($c = 0.169$) and **II** ($c \approx 0.215$) possessing a THF ligand.

At this stage, it seems possible to rationalize the results and to derive a general trend for the role of ligands in determining the electronic ground state of U(V) complexes, despite the small number of compounds studied in this work.

(i) Ligands such as η^8-C_8H_8, η^5-C_5H_5, η^5-C_5Me_5, and NR_2 exhibit only very weak interactions with 5f orbitals of the central U(V) atom, so that $J = ^5/_2$ remains a good quantum number for the description of the electronic structure of the complexes. These ligands favor the major contribution of $|M_J| = ^1/_2$ to the ground state wave function, with an additional admixture of $|M_J| = ^5/_2$. The contribution of the $|M_J| = ^3/_2$ states is almost negligible with these ligands. All of these features imply that 5f orbitals are nonbonding, so that the uranium 6d orbitals should play the primary role in the covalent bonding between U(V) and its ligands.

(ii) Oxygen ligands modify this scheme, with two different effects, depending on the nature of the U(V)−O bond. For an oxygen-donor ligand (represented by THF), the U(V)−O bond involves a nonbonding oxygen orbital of this ligand. In this case the interaction with the metal atom remains small compared to the spin−orbit interaction, so that the weak−field approximation is still relevant. The ground state is also of predominantly $|M_J| = ^1/_2$ character as for other amide compounds. However the THF ligand induces a significant admixture of $|M_J| = ^3/_2$ states. This sensitivity of the electronic ground state to the presence of a THF ligand indicates that 5f−THF interactions could exhibit a small covalent character. However, the fact that the weak-field approximation is still well adapted to the problem shows that the U(V)−THF interactions are still dominated by uranium 6d orbitals.

(iii) Alkoxide ligands OR interact more strongly with uranium 5f orbitals, even in tetrahedral geometry, so that the ligand field is not small compared to the spin−orbit splitting between the $^2F_{5/2}$ ground state and the excited $^2F_{7/2}$ state of the free U(V) ion. The weak-field approximation is broken in this case, and the 5f−OR interactions induce a mixing of $J = {}^5/_2$ and $J = {}^7/_2$ states. This interpretation should be confirmed by the study of other U(V)−alkoxide compounds prior to analyze more deeply the electronic ground state of this family of complexes. In this context, we tried to prepare a series of complexes of formula $[(\eta^8\text{-}C_8H_8)U(NEt_2)_{3-x}(O\text{-}i\text{-}Pr)_x]$ ($x = 1, 2$) in order to examine the influence of each additional alkoxide ligand on the measured EPR spectrum. Unfortunately these mixed amide−alkoxide derivatives were found to be unstable toward disproportionation reactions and were readily transformed into mixtures of **III** and **VI**.

It should be noticed that ligands are only considered as point charges in the weak-field approximation used to describe U(V) amide compounds, and covalent admixtures of ligand orbitals to the ground state were not explicitly considered. This is justified by the poor resolution of EPR spectroscopy in frozen solution, which is only sensitive to the strong spin−orbit effect of the central U(V) atom. A direct consequence of a small ligand admixture is to make the sum $a^2 + b^2 + c^2$ slightly smaller than 1. This is the reason why values of a, b, and c coefficients which only approximately satisfy the normalization condition are acceptable (Table 2). However, a direct study of the (small) covalent contribution to 5f−ligand interactions needs the use of electron nuclear double resonance (ENDOR) spectroscopy.

Conclusion

In this work we studied the electronic structure of organouranium(V) amide compounds by EPR in diluted frozen solutions. It was shown that the interactions of 5f orbitals with η^8-C_8H_8, η^5-C_5H_5, η^5-C_5Me_5, THF, and NR_2 ligands are sufficiently small to conserve the ground state quantum number $J = {}^5/_2$ of the free U(V) ion as a good quantum number for the complex, so that the contribution of 5f orbitals to the electronic structure of these compounds is essentially nonbonding. The experimental g-tensors were quantitatively interpreted within the weak-field approximation, and the effect of the nature of ligands was analyzed by their influence on the $|M_J|$ composition of the electronic ground state.

Compounds **I**−**V** are characterize by a predominantly $|{}^1/_2|$ ground state with an admixture of $|{}^5/_2|$, independent of whether they adopt a pseudotetrahedral or trigonal bipyramidal geometry. The effect of the THF ligand in **I** and **II** is to induce a significant admixture of the $|{}^3/_2|$ states, revealing a stronger oxygen 2p−uranium 5f interaction. Replacement of alkylamide ligands by alkoxide ligands has a dramatic effect on the electronic ground state of the complex. The 5f−OR interaction is strong, so that J is no longer a good quantum number and the weak-field approximation is no longer valid.

In conclusion, it appears that bonding with ligands such as η^8-C_8H_8, η^5-C_5H_5, and NR_2 should occur primarily via uranium 6d orbitals, leaving the 5f orbitals nonbonding, while a covalent character appears for the interaction of 5f orbitals with oxygen ligands. The latter remains small for O-donor ligands (THF), but it is much stronger for alkoxide ligands.

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