group in **3d** reduce the basicity of the phosphorus at the opposite end of the cage.

Uv Spectra. The uv absorption spectra of compounds **1a'**, **1a**, **2a**, **3a**, and **3d** were analyzed using the program LOGFIT[15] and the relevant parameters are listed in Table III. Although the spectra for **1a'** and **1a** generally resembled those reported earlier,[5] the present analysis indicates the presence of additional bands. Compounds **2a'** and **3d'**, in accordance with their previously described instability, decomposed so rapidly in ether or THF solutions that meaningful spectra could not be obtained.

The greater electron-withdrawing character of **2** and **3** relative to that of **1** is undoubtedly responsible for the hypsochromic shift in the spectra of compounds **2a**, **3a**, and **3d** compared to those of compound **1a**. A similar absorption shift toward higher energies from aniline to the anilinium ion has been ascribed to the absence of a nitrogen lone-pair interaction with the aromatic π system in the latter.[24] In the present cases, the decreased availability of the imido nitrogen lone pair(s) for this electron interaction in **2a** and **3a** could arise from lower σ basicity and/or the higher π acidity of **2** and **3**, respectively.

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Registry No. $(Me_2N)_3P$, 1608-26-0; $(Me_2N)_3P{=}NPh$, 35589-04-9; $(Me_2N)_3P{=}NN{=}NPh$, 55215-22-0; $(Me_2N)_3P{=}NP(O)(OPh)_2$, 56727-71-0; $(Me_2N)_3P{=}NP(O)Ph_2$, 56727-72-1; $MeC(CH_2NMe)_3P$, 14418-26-9; $MeC(CH_2NMe)_3P{=}NPh$, 56727-73-2; $MeC(CH_2NMe)_3P{=}NN{=}NPh$, 56727-74-3; $MeC(CH_2NMe)_3P{=}NP(O)(OPh)_2$, 56727-75-4; $MeC(CH_2NMe)_3P{=}NP(O)Ph_2$, 56727-76-5; $P(NMeNMe)_3P$, 3478-74-8; $PhN{=}P(NMeNMe)_3P{=}NPh$, 42975-97-3; $(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$, 56727-77-6; $Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$, 42975-98-4; $P(NMeNMe)_3P{=}NPh$, 56727-78-7; $P(NMeNMe)_3P{=}NN{=}NPh$, 56727-79-8; $Ph_2P(O)N_3$, 4129-17-3; PhN_3, 622-37-7; $(PhO)_2P(O)N_3$, 26386-88-9; ^{31}P, 7723-14-0.

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Contribution from the Department of Chemistry,
University College, Cardiff, Wales, United Kingdom

Ligand Field Theory of Metal Sandwich Complexes. Magnetic Properties of f^x Configurations

KEITH D. WARREN

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The magnetic behavior of the bis(cyclooctatetraene) derivatives of the lanthanide and actinide series is discussed in terms of a pseudoaxial ($C_{\infty v}$) ligand field model. A molecular orbital approach is used to deduce the ordering of the dominantly f-orbital levels and to estimate the required ligand field parameters. The temperature dependence and anisotropy of the magnetic moments are thereby calculated for the f^1, f^2, f^3, and f^4 configurations and compared with the experimental results.

Introduction

In 1968 the first proposed f-orbital aromatic system, bis(cyclooctatetraene)uranium(IV), U(COT)$_2$, was synthesized by Streitwieser and Müller-Westerhoff.[1] Since then U(COT)$_2$ and its 5f analogues have been extensively studied[2-8] and bis(cyclooctatetraene) derivatives of the An^{IV} elements are now also known for Th, Pa, Np, and Pu, while for U, Np, and Pu a number of alkyl-substituted bis(cyclooctatetraene) species have been investigated.[9-11] These studies have mostly been directed toward elucidating the nature of the interaction between the An^{IV} f orbitals and the π systems of the formally aromatic cyclooctatetraenyl dianion rings, chiefly by NMR and magnetic susceptibility measurements, and the state of knowledge concerning the bonding in U(COT)$_2$ has recently been summarized by Streitwieser et al.[8]

Bis(cyclooctatetraene)uranium(IV) belongs[12] to the point group D_{8h} and the principal f orbital–π ligand interaction was considered to be that between the ligand e_{2u} combination and the f_{xyz}, $f_{z(x^2-y^2)}$ orbitals of the metal, this being similar in character to the e_{1g} ligand–d_{xz}, d_{yz} metal interaction known to be important for the metallocenes. In a molecular orbital description the basis set for the actinide elements should include the 5f, 6d, 7s, and 7p levels, but it seems probable that only the lowest of these—the 5f orbitals—are appreciably involved in bonding in U(COT)$_2$ and its analogues.[1,8] In D_{8h} symmetry the π-type orbitals of the two cyclooctatetraene rings

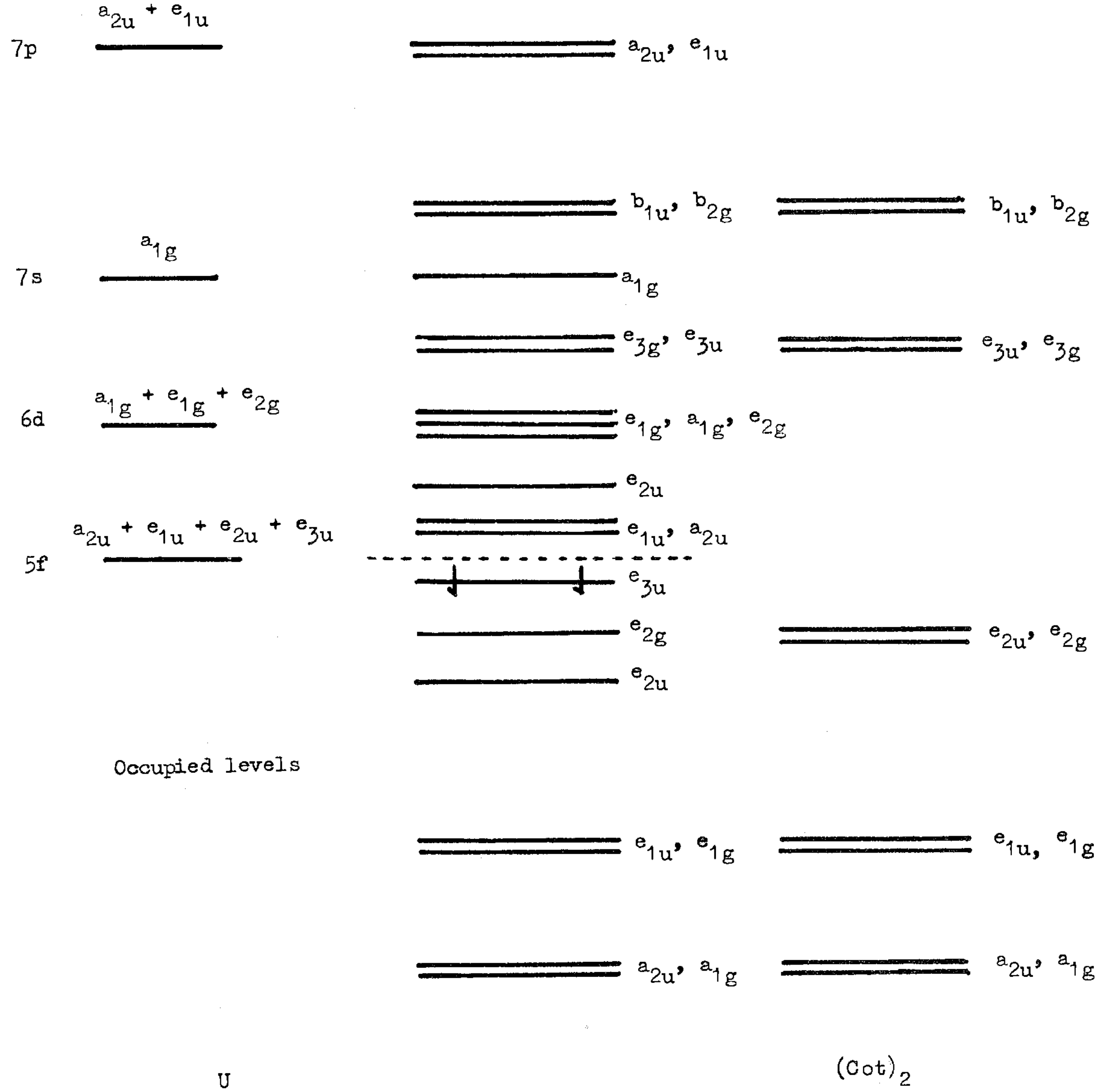

Figure 1. Molecular orbital scheme for bis(cyclooctatetraene)actinide(IV) complexes.

yield the ligand symmetry orbital combinations a_{1g}, a_{2u}, e_{1u}, e_{1g}, e_{2u}, e_{2g}, e_{3u}, e_{3g}, b_{1u}, and b_{2g}, and using the energy ordering deduced by Fischer[13] the approximate molecular orbital scheme shown in Figure 1 may be obtained. The 20 electrons of the two cyclooctatetraenyl dianion rings and the two electrons of U^{IV} ($5f^2$) may then be accommodated as shown, with the last two electrons occupying the e_{3u} level of dominantly f-orbital character, thus suggesting that a ligand field treatment of the properties of the highest occupied, mainly f orbital, levels might be fruitful.

Bis(cyclooctatetraene) derivatives are however also known for the lanthanide elements and species of the general formula $[Ln^{III}(COT)_2]^-$ have been prepared as the potassium salts[14,15] where Ln = La, Ce, Pr, Nd, Sm, Gd, and Tb. These complexes too possess an eightfold rotation axis of symmetry, and the $K[Ce(COT)_2]$ salt belongs[16] to the point group D_{8d}, but they are even less stable than the $An(COT)_2$ systems and chemically behave very much as Ln^{3+} compounds. Consequently the $[Ln^{III}(COT)_2]^-$ complexes may be treated by a similar molecular orbital approach, though with a much weaker metal f–π ligand interaction, and should also be amenable to a description of their f^x configurations by a ligand field approach.

However, for neither the 4f nor the 5f species are values of the appropriate ligand field splitting parameters available from spectroscopic data, and estimates for these quantities are now obtained for both series using an elementary molecular orbital treatment. The purpose of the present paper is therefore to use these calculated parameters to interpret the available magnetic susceptibility data in terms of a ligand field model and to indicate areas in which further experimental results would be of value.

Theory and Calculations

For systems belonging to the point groups C_n, C_{nh}, C_{nv}, D_n, D_{nd}, and D_{nh} it was shown by Scott and Matsen[17] that the properties of d^x configurations could be treated in terms of a field of effectively axial, $C_{\infty v}$, symmetry as long as $n \geq 5$. Generalization of their conclusions indicates that pseudoaxial symmetry will result for l^x configurations for $n \geq 2l + 1$, and consequently $4f^x$ and $5f^x$ configurations in D_{8d} and D_{8h} symmetry respectively may also be considered in terms of a $C_{\infty v}$ ligand field.

In both the 4f and 5f series the spin–orbit and interelectronic repulsion terms appreciably exceed the ligand field splittings, and thus for both f^x series a weak-field basis set is the more appropriate and specific inclusion of spin–orbit coupling is essential. The required functions are therefore the $|LSJM_J\rangle$

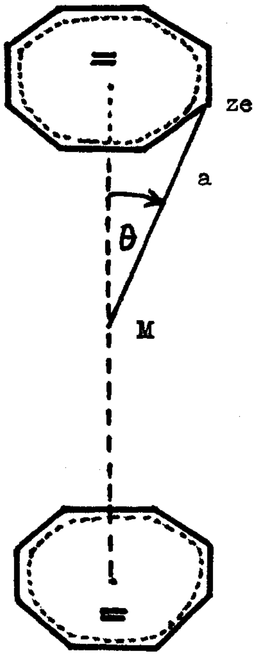

Figure 2. Crystal field model for bis(cyclooctatetraene) derivatives.

set, obtained from the $|LSM_LM_S\rangle$ set via the familiar Clebsch–Gordan coefficients. For the 4f series calculations in the weak-field basis show that J is generally a good quantum number, and although the larger ligand field for the 5f elements leads to greater J mixing, the ground states are usually of quite high purity in the $|LSJM_J\rangle$ representation. For both series therefore the magnetic susceptibility properties of the various f^x configurations may be reasonably well evaluated in that basis, using the first-order ground-state wave functions.

In the absence of a magnetic field the appropriate perturbation Hamiltonian, H', is given by

$$H' = \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_i (r_i) l_i \cdot s_i + \sum_i V_{\mathrm{LF}}(r_i)$$

and the effectively axial ligand field operating on the f-orbital basis set may be written as $V_{\mathrm{ax}} = c_1Y_0^0 + c_2Y_2^0 + c_3Y_4^0 + c_4Y_6^0$ where the Y_k^q terms are spherical harmonics of order q and degree k. The term in Y_0^0 will not split the f-orbital set, and, because $q = 0$ throughout, the ligand field will not mix orbitals of different m_l values, and the V_{ax} contributions will be diagonal in the m_l representation. Consequently the f-orbital set yields four irreducible representations and one may define the ligand field parameters $\langle 0|V_{\mathrm{ax}}|0\rangle = \sigma$, $\langle \pm1|V_{\mathrm{ax}}|\pm1\rangle = \pi$, $\langle \pm2|V_{\mathrm{ax}}|\pm2\rangle = \delta$, and $\langle \pm3|V_{\mathrm{ax}}|\pm3\rangle = \phi$.

For a field of pseudoaxial symmetry, when spin–orbit coupling is explicitly included, the wave functions of the $|LSJM_J\rangle$ set are characterized[18] according to the irreducible representations of the double group $C_\infty{}^*$, these being here defined by the relevant M_J values. Thus $M_J = 0$ corresponds to the representations Σ^+ (J even) or Σ^- (J odd), and $M_J = \pm1, \pm2, \pm3, \ldots$, to the representations Π, Δ, Φ, ..., while for the half-integral M_J values $\pm{}^1/_2$, $\pm{}^3/_2$, $\pm{}^5/_2$, ..., the correspondence is to the representations Π^*, Δ^*, Φ^*, ..., as defined previously.[18]

Although the classical electrostatic crystal field model is known to be inadequate for the evaluation of the matrix elements of V_{ax} (see for example ref 19), it can nevertheless be used in a purely phenomenological sense to describe the relative energies of the f-orbital set in terms of three independent parameters. The ionic model of Figure 2 is therefore adopted in which each carbon atom of the two cyclooctatetraenyl dianion rings bears a negative charge, z_i, of $^1/_4$. Thus, with $V_{\mathrm{ax}} = \sum_{i=1}{}^{16} z_ie^2/r_{ij}$, expansion in spherical harmonics about the origin yields

$$(r_{ij})^{-1} = (\pi/5)^{1/2}(r^2/a^3)(3\cos^2\theta_i - 1)Y_2{}^0 + (\pi/9)^{1/2}(r^4/a^5)(35\cos^4\theta_i - 30\cos^2\theta_i + 3)Y_4{}^0 + (\pi/13)^{1/2}(r^6/a^7)(231\cos^6\theta_i - 315\cos^4\theta_i + 105\cos^2\theta_i - 5)Y_6{}^0$$

Defining the parameters $Ds = (8/15)(\langle r^2\rangle/a^3)(3x^2 - 1)ze^2$, $Dt = (2/33)(\langle r^4\rangle/a^5)(35x^4 - 30x^2 + 3)ze^2$, and $Du = (5/429)(\langle r^6\rangle a^7)(231x^6 - 315x^4 + 105x^2 - 5)ze^2$, where $x = \cos\theta$, one obtains the results $\langle 0|V_{\mathrm{ax}}|0\rangle = 4Ds + 6Dt + 20Du$, $\langle \pm1|V_{\mathrm{ax}}|\pm1\rangle = 3Ds + Dt - 15Du$, $\langle \pm2|V_{\mathrm{ax}}|\pm2\rangle = -7Dt + 6Du$, and $\langle \pm3|V_{\mathrm{ax}}|\pm3\rangle = -5Ds + 3Dt - Du$.

Following the procedure of Elliott and Stevens[20] the splittings may also be expressed in terms of the $A_k{}^q\langle r^k\rangle$ parameters (see also ref 21). Thus, using the relationships between the $A_k{}^q\langle r^k\rangle$ and $B_q{}^k$ parameters listed by Wybourne,[22] the Ds, Dt, and Du parameters are related to the familiar $B_q{}^k$ quantities by the expressions $B_0{}^2 = 15Ds$, $B_0{}^4 = 33Dt$, and $B_0{}^6 = (429/5)Du$.

For $[\mathrm{Ce(COT)_2}]^-$ the crystallographic results[16] give $a = 2.742$ Å and $\theta = 40.85°$, which with the $\langle r^2\rangle$, $\langle r^4\rangle$, and $\langle r^6\rangle$ values for $\mathrm{Ce^{3+}}$ of 1.20, 3.455, and 21.226 au, respectively, given by Freeman and Watson[23] yield the values 2713, −275, and −55.8 cm^{-1} for the $B_0{}^2$, $B_0{}^4$, and $B_0{}^6$ parameters. Comparison with the experimental $B_q{}^k$ quantities listed by Wybourne[22] for various $\mathrm{LnCl_3}$ species shows that the calculated $B_0{}^2$ is some 30 times as large as the empirical value, $B_0{}^4$ is of the same order of magnitude, and $B_0{}^6$ is roughly 10 times too small. These results are strikingly similar to those found by Hutchings and Ray[19] for $\mathrm{PrCl_3}$ and underline the quantitative inadequacy of the electrostatic model. For $\mathrm{U(COT)_2}$ the crystallographic data, $a = 2.647$ Å and $\theta = 43.40°$, with the $\langle r^2\rangle$, $\langle r^4\rangle$, and $\langle r^6\rangle$ values given for $\mathrm{U^{4+}}$ by Lenander[24] (1.68, 5.00, and 24.20 au, respectively), lead to the values 3440, −541, and −57.5 cm^{-1} for $B_0{}^2$, $B_0{}^4$, and $B_0{}^6$. The limited experimental data available for the 5f series suggest that here the electrostatic model somewhat overestimates $B_0{}^2$ and appreciably underestimates $B_0{}^4$ and $B_0{}^6$.

An approximate molecular orbital calculation was therefore carried out to estimate more realistically the f-orbital splitting for the bis(cyclooctatetraene) complexes of the 4f and 5f series. Jorgensen's[25] variant of the Wolfsberg–Helmholz procedure was used to treat the interaction of the metal f orbitals with the appropriate ligand symmetry orbital combinations: the two original orbitals, Ψ_i and Ψ_j, are orthogonalized by the Schmidt procedure such that $\Psi_i(\mathrm{orthog}) = \Psi_i$ and $\Psi_j(\mathrm{orthog}) = (\Psi_j - S_{ij}\Psi_i)/(1 - S_{ij}{}^2)^{1/2}$, thus making ordinary second-order perturbation methods applicable. Taking the original diagonal core terms as H_{ii} and H_{jj} and assuming the usual Wolfsberg–Helmholz approximation, $H_{ij} = S_{ij}(H_{ii} + H_{jj})$, the orthogonalized off-diagonal element becomes $S_{ij}H_{jj}/(1 - S_{ij}{}^2)^{1/2}$ which for small values of S_{ij} is satisfactorily approximated as $S_{ij}H_{jj}$. Thus, writing the metal and ligand core terms as H_{M} and H_{L}, respectively, and the group overlap integral between the given f orbital and the appropriate ligand symmetry orbital combination as G_{ML}, the bonding or antibonding tendencies of the dominantly f-orbital levels are given as $\Delta E = G_{\mathrm{ML}}{}^2H_{\mathrm{L}}{}^2/(H_{\mathrm{M}} - H_{\mathrm{L}})$, assuming $G_{\mathrm{ML}}{}^2 << 1$.

For the ligand symmetry orbitals of a (σ), e_1 (π), e_2 (δ), and e_3 (ϕ) symmetry the H_{L} terms have been estimated by Fischer[13] as −15, −13, −9, and −5 eV, respectively, but the appropriate H_{M} terms for the metals are difficult to determine since data for ionization potentials either are frequently highly configuration dependent or are lacking altogether. However, the photoelectron spectra of a series of tris(cyclopentadiene)lanthanide species reveal[26] that the f-orbital ionization

Table I. Molecular Orbital Calculations for $[\mathrm{Ce(COT)_2}]^-$ and $\mathrm{U(COT)_2}$

f orbital	G_{ML}	H_{L}, eV	$H_{\mathrm{L}}^2 G_{\mathrm{ML}}^2/(H_{\mathrm{M}}-H_{\mathrm{L}})$, cm^{-1}	Effective splitting	Eigenvectors	
					c_{M}	c_{L}
$[\mathrm{Ce(COT)_2}]^-$: $S_\sigma = 0.0226, S_\pi = 0.0149, H_{\mathrm{M}} = -7$ eV, $\theta = 40.85°$						
σ	0.0327	−15	+243	+29.3	0.9981	−0.0610
π	−0.0235	−13	+125	−88.1	0.9987	0.0507
δ	−0.0406	−9	+538	+324.5	0.9847	0.1742
ϕ	−0.0194	−5	−38	−251.1	0.9988	−0.0482
$Ds = 25.0, Dt = -39.3, Du = 8.3$ cm^{-1} ($B_0{}^2 = 374.9, B_0{}^4 = -1296.3, B_0{}^6 = 707.9$ cm^{-1}); charge on Ce = +2.86						
$\mathrm{U(COT)_2}$: $S_\sigma = 0.0409, S_\pi = 0.0287, H_{\mathrm{M}} = -8$ eV, $\theta = 43.40°$						
a_{2u} (σ)	0.0699	−15	+1238	+27.7	0.9897	−0.1429
e_{1u} (π)	−0.0268	−13	+195	−1015.3	0.9976	0.0691
e_{2u} (δ)	−0.0735	−9	+3530	+2319.7	0.8845	0.4666
e_{3u} (ϕ)	−0.0401	−5	−108	−1318.3	0.9978	−0.0659
$Ds = 85.7, Dt = -274.4, Du = 66.5$ cm^{-1} ($B_0{}^2 = 1286.1, B_0{}^4 = -903.6, B_0{}^6 = 5709.1$ cm^{-1}); charge on U = +3.08						

energy remains fairly constant between 7 and 7.5 eV for the early members of the series, and the value of −7 eV was therefore taken for the H_{M} term for Ce. For the 5f series Hayes and Edelstein,[7] in a standard Wolfsberg–Helmholz calculation, adopted with some misgivings a figure of −8 eV for H_{M} for uranium. However, this value appears amply vindicated by its approximate equality[27] to the first f-orbital ionization energy for uranium(I) and is therefore used here also. For $\mathrm{U(COT)_2}$ the primitive $2p_\sigma$–5f and $2p_\pi$–5f overlaps there quoted[7] were used in calculating the necessary group overlap integrals, while for $[\mathrm{Ce(COT)_2}]^-$ the primitive $2p_z$–$4f_{z^3}$ (S_σ) and $2p_x$–$4f_{xz^2}$ (S_π) overlap integrals were calculated from the expressions given in the Appendix[28] using the self-consistent-field 4f wave functions of Freeman and Watson[23] for $\mathrm{Ce^{3+}}$ and the double-ζ 2p C orbitals listed by Clementi.[29]

In evaluating the G_{ML} quantities ligand–ligand overlap was neglected and the angular dependence of the primitive overlaps obtained according to Clack and Smith.[30] Using the ligand symmetry orbitals for the cyclooctatetraenyl dianion given by Cotton[31] and the relationships

$$\sum_{m=0}^{n-1} \cos^2 m(2\pi/n) = \sum_{m=0}^{n-1} \sin^2 m(2\pi/n) = n/2$$

the following group overlaps were derived. (For convenience only the symmetry designations for D_{8h} and $C_{\infty v}$ are given.)

$$G(\mathrm{a_{2u}}, \sigma) = 6^{1/2} \sin^2 \theta(4 - 5 \sin^2 \theta)S_\pi - 2 \cos^2 \theta(2 - 5 \sin^2 \theta)S_\sigma$$

$$G(\mathrm{e_{1u}}, \pi) = 2^{-1/2} \sin \theta \cos \theta\, [(15 \sin^2 \theta - 4)S_\pi - 6^{1/2}(4 - 5 \sin^2 \theta)S_\sigma]$$

$$G(\mathrm{e_{2u}}, \delta) = {}^1\!/\!_2(10^{1/2}) \sin^2 \theta\, [2^{1/2}(1 - 3 \cos^2 \theta)S_\pi - 2(3^{1/2})(\cos^2 \theta)S_\sigma]$$

$$G(\mathrm{e_{3u}}, \phi) = -{}^1\!/\!_2(10^{1/2}) \sin^3 \theta \cos \theta\, [3^{1/2}S_\pi + 2^{1/2}S_\sigma]$$

These results differ essentially from those of Fischer[13] in that the relative signs of the S_σ and S_π contributions are here reversed. Thus for $\mathrm{U(COT)_2}$ the data used in the present calculation predict $|G_{\mathrm{ML}}|$ to increase in the order $\pi < \phi < \sigma < \delta$, as opposed to Fischer's order of $\phi < \sigma < \delta < \pi$. Moreover, no choice of θ would permit the G_{ML} values of Hayes and Edelstein[7] to be reproduced (although the present results do not differ too greatly therefrom), and the cause of this discrepancy remains obscure.

The values obtained from the above equations for the $\mathrm{a_{2u}}$, $\mathrm{e_{1u}}$, $\mathrm{e_{2u}}$, and $\mathrm{e_{3u}}$ (σ, π, δ, and ϕ) group overlap integrals are shown in Table I for $\mathrm{U(COT)_2}$ and $[\mathrm{Ce(COT)_2}]^-$, together with the corresponding calculated bonding or antibonding ΔE values. Expressing these in terms of an f-orbital splitting pattern, values are calculated for the parameters Ds, Dt, and Du (and $B_0{}^2$, $B_0{}^4$, and $B_0{}^6$); for $[\mathrm{Ce(COT)_2}]^-$ the dominantly f orbitals follow the energy sequence $\phi < \sigma < \pi < \delta$ and for $\mathrm{U(COT)_2}$ the order $\phi < \pi < \sigma < \delta$, but in both cases the salient features are the same. The ϕ level lies lowest and is overall bonding while the δ level shows the strongest interaction with the ligands and is the most antibonding in character. (This result follows naturally from the assumption that the metal f orbitals lie higher in energy than the ligand $\mathrm{e_{2u}}$ level but below the ligand $\mathrm{e_{3u}}$ level (vide infra).) For $[\mathrm{Ce(COT)_2}]^-$ the $B_0{}^2$, $B_0{}^4$, and $B_0{}^6$ parameters deduced are quite comparable with experimental results for other 4f systems,[22] and the few data available for 5f species (e.g., the $\mathrm{PaCl_6{}^{2-}}$ and $\mathrm{UCl_6{}^{2-}}$ anions[32,33]) suggest that this is true for $\mathrm{U(COT)_2}$ also.

The eigenfunctions derived from the molecular orbital treatment (Table I) indicate that for $\mathrm{U(COT)_2}$ the δ level contains some 22% ligand character, thus supporting Streitwieser's[1,8] supposition concerning the importance of the $\mathrm{e_{2u}}$ π ligand interaction, but for $[\mathrm{Ce(COT)_2}]^-$, due to the smaller overlap integrals, this, the largest ligand admixture, is only some 3%. Being derived from a rather crude approximation, these results are necessarily tentative, but they do provide some semiquantitative guide to the extent of the metal f–π ligand interaction.

With the ligand field parameters derived for $[\mathrm{Ce(COT)_2}]^-$ and $\mathrm{U(COT)_2}$ the energy level patterns which result for the f^x configurations of the 4f and 5f series are readily found, assuming that the $B_q{}^k$ parameters remain of similar magnitude throughout the lanthanide and actinide series, respectively. For the f^1 and f^2 systems the full $|LSJM_J\rangle$ basis sets are easily constructed and the complete ligand field matrices are given in the Appendix.[28] For f^3 and higher configurations evaluation of the matrix elements via the wave functions becomes impracticable and these results are best derived by the tensor operator techniques described by Wybourne.[22]

In the $|LSJM_J\rangle$ basis the free-ion ground states of $4\mathrm{f}^x$ systems (x = 1–4) usually show a purity of not less than about 97%, but because of the stronger intermediate coupling, somewhat lower purities are found for the 5f series, ranging from about 95% for $5\mathrm{f}^2$ to 81% for $5\mathrm{f}^4$. For the configurations treated—f^1, f^2, f^3, and f^4—the weak-field ground states are respectively ${}^2\mathrm{F}_{5/2}$, ${}^3\mathrm{H}_4$, ${}^4\mathrm{I}_{9/2}$, and ${}^5\mathrm{I}_4$, which in the 4f series are usually separated by not less than 2000 cm^{-1} from the first excited state. Consequently the separation of the ground J state from higher lying states is large compared with kT and the first-order ground-state manifold wave functions should be sufficient to give an excellent account of the magnetic susceptibility properties. For the 5f series a larger separation between the ground and excited states is found, due to the greater spin–orbit coupling constants, but because of the stronger spin–orbit mixing the first-order ground-state wave functions will not give quite such a good account of the magnetic behavior, especially for the f^3 and f^4 systems.

For all of the f^x configurations the first-order ground-state

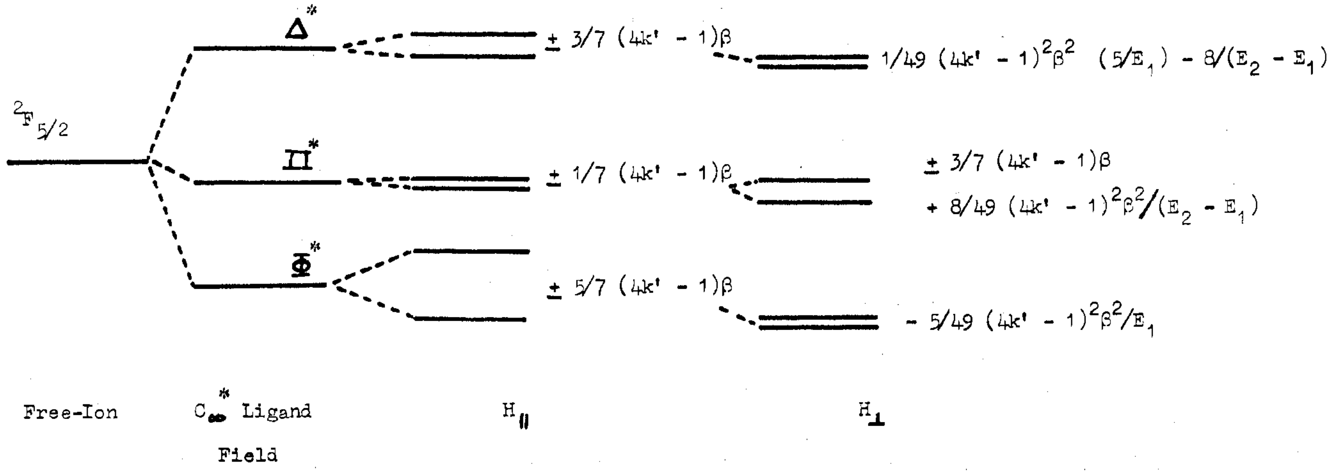

Figure 3. Energy level diagram for f^1 systems in C_∞* symmetry; $E_1 = \Delta^* - \Phi^*, E_2 = \Pi^* - \Phi^*$.

splittings produced by the pseudoaxial ligand field are easily derived via the operator-equivalent method of Elliott and Stevens,[20] and the values obtained for the 4f and 5f series using the B_q^k parameters of Table I are listed in Table II. In the derivation of expressions for the magnetic susceptibilities the orbital reduction factor, k', was introduced in an attempt to allow for any delocalization of electrons out of the f orbitals onto the ligand atoms, and the nonvanishing matrix elements of the Zeeman operators, $k'L_z + 2S_z$ and $k'L_x + 2S_x$, were determined within the various ground-state manifolds assuming for simplicity a single isotropic value of k'. It must however be noted that this use of k' is less satisfactory than for the sandwich complexes of the 3d series (for which pseudoaxial symmetry also obtains) since the ground-state wave functions there correspond closely to pure strong-field configurations. Thus, for ground states showing orbital contributions to the moment, the terms involving k' are there restricted to the L_z operator and relate only to the particular degenerate level from which the orbital contribution actually arises. In the present weak-field basis however terms involving k' occur for both the L_z and the L_x (L_y) operators, and the $|LSJM_J\rangle$ states are in general functions of all the $|m_l|$ values. Consequently the assumption of a single isotropic k' is tantamount to neglecting any differences in metal–ligand mixing for the real f orbitals of differing $|m_l|$. The derived values of k' must therefore be treated with circumspection, but this approach was preferred to the more cumbrous procedure in which four parameters relating to the different $|m_l|$ values would be required.

Table II. Diagonal Ligand Field Matrix Elements and Calculated Energies for f^x Configurations in C_∞* Symmetry[a]

	Ds	*Dt*	*Du*	*E*(4f)	*E*(5f)
		f^1, $^2F_{5/2}$; Multiply All Entries by (1/7)			
Φ*	−30	11	0	−168.8	−798.6
Δ*	6	−33	0	206.6	1366.9
Π*	24	22	0	−37.8	−568.3
				Δ = 375.4	Δ = 2165.5
		f^2, $^3H_4$; Multiply All Entries by (2/165)			
Γ	260	−270	−680	3.3	429.8
Φ	221	−135	34	−235.4	−1608.3
Δ	104	165	748	27.8	162.7
Π	−91	315	−578	134.6	706.1
Σ⁺	−364	−210	136	139.3	619.6
				Δ = 374.7	Δ = 2314.4
		f^3, $^4I_{9/2}$; Multiply All Entries by (1/4719)			
H*	−8190	−8568	−14535	2.5	144.4
Γ*	−2730	10472	53295	−8.4	93.1
Φ*	1365	8092	−48450	−144.8	−1128.8
Δ*	4095	−1428	−29070	−17.3	−252.5
Π*	5460	−8568	38760	168.0	1143.8
				Δ = 312.9	Δ = 2272.6
		f^4, $^5I_4$; Multiply All Entries by (1/4719)			
Γ	7644	6664	7752	−1.4	−139.2
Φ	1911	−9996	−32946	35.7	151.2
Δ	−2184	−5236	42636	106.6	865.9
Π	−4641	4284	1938	−56.9	−306.0
Σ	−5460	8568	−38760	−168.0	−1143.8
				Δ = 274.6	Δ = 2009.7

[a] All values in cm⁻¹. Splittings are in terms of ligand field parameters. Energies were calculated via parameters of Table I.

For the f^1 and f^2 configurations the required Zeeman matrix elements are readily found from the appropriate $|LSJM_J\rangle$ functions, but for all f^x configurations the results for the general case, $k' \neq 1$, are easily derived via the Clebsch–Gordan coefficients using the expressions given in the Appendix,[28] wherein are also listed the resulting matrix elements of $k'L_z + 2S_z$ ($H\|$) and of $k'L_x + 2S_x$ ($H\perp$) within the ground state manifolds. The elements of $H\|$ are entirely diagonal and those of $H\perp$ entirely off-diagonal, and in the latter case the eigenvalues are obtained by second-order perturbation theory as before.[34] The susceptibility may then be found via the familiar Van Vleck equation

$$\chi_\alpha = \frac{N\sum_i [E^{\mathrm{I}}_i/kT) - 2E^{\mathrm{II}}_i]e^{-E_i^0/kT}}{\sum_i e^{-E_i^0/kT}}$$

where $E^{\mathrm{I}}_i = \langle\psi_i|k'L_\alpha + 2S_\alpha|\psi_i\rangle\beta$, and $E^{\mathrm{II}}_i = \sum_j(\langle\psi_i|k'L_\alpha + 2S_\alpha|\psi_j\rangle\beta)^2/(E^0_i - E^0_j)$, with $i \neq j$ and $\alpha = z$ ($H\|$) or x, y ($H\perp$). The effective magnetic moments are obtained from the Curie formula, $\chi = N\mu_{\mathrm{eff}}^2/3kT$, and the average, $\langle\mu\rangle$, from the z and x, y components using $\langle\mu\rangle = [^1/_3(\mu_x^2 + \mu_y^2 + \mu_z^2)]^{1/2}$. In Figure 3 these calculations are illustrated for the example of the f^1 system; the energy level diagram shows the C_∞* ligand field splitting of the free-ion $^2F_{5/2}$ ground state together with the effects produced by the application of $H\|$ and $H\perp$ magnetic fields. Similar diagrams for the other f^x systems are however omitted since the calculations follow the same pattern as for the previously discussed 3d sandwich complexes,[34] apart from the use of a weak-field rather than a strong-field basis set.

In Table III are listed the expressions derived for $\mu\|$ and $\mu\perp$ for the f^1, f^2, f^3, and f^4 systems, from which the temperature dependence of the average moment and its components may be found, and the results are shown for the 4f and 5f complexes in Figures 4–7. Here kT varies from zero to 200 cm⁻¹, i.e., from 0 K to ambient temperature. The expressions given are valid for any axial field splitting of the ground states but are presented in the most convenient form for use with the calculated 4f ordering of the M_J levels. Since the B_q^k values are theoretical and not experimental quantities,

Table III. Magnetic Moments for f^x Configurations in C_∞^* Symmetry

$$f^1,\ {}^2F_{5/2};\ \alpha = (\Delta^* - \Phi^*)/kT,\ \beta = (\Pi^* - \Phi^*)/kT$$

$$\mu_\parallel = \frac{3^{1/2}(4k' - 1)}{7}\left\{\frac{25 + 9e^{-\alpha} + e^{-\beta}}{1 + e^{-\alpha} + e^{-\beta}}\right\}^{1/2}$$

$$\mu_\perp = \frac{3^{1/2}(4k' - 1)}{7}\Big\{[10(1 - e^{-\alpha})\alpha^{-1} + 16(e^{-\beta} - e^{-\alpha})(\alpha - \beta)^{-1} + 9e^{-\beta}][1 + e^{-\alpha} + e^{-\beta}]^{-1}\Big\}^{1/2}$$

$$f^2,\ {}^3H_4;\ \alpha = (\Gamma - \Phi)/kT,\ \beta = (\Delta - \Phi)/kT,\ \gamma = (\Pi - \Phi)/kT,\ \delta = (\Sigma^+ - \Phi)/kT$$

$$\mu_\parallel = \frac{2(6^{1/2})(3k' - 1)}{5}\left\{\frac{9 + 16e^{-\alpha} + 4e^{-\beta} + e^{-\gamma}}{e^{-\delta} + 2(1 + e^{-\alpha} + e^{-\beta} + e^{-\gamma})}\right\}^{1/2}$$

$$\mu_\perp = \frac{2(6^{1/2})(3k' - 1)}{5}\Big\{[4(1 - e^{-\alpha})\alpha^{-1} + 7(1 - e^{-\beta})\beta^{-1} + 9(e^{-\beta} - e^{-\gamma})(\gamma - \beta)^{-1} + 10(e^{-\gamma} - e^{-\delta})(\delta - \gamma)^{-1}][e^{-\delta} + 2(1 + e^{-\alpha} + e^{-\beta} + e^{-\gamma})]^{-1}\Big\}^{1/2}$$

$$f^3,\ {}^4I_{9/2};\ \alpha = (H^* - \Phi^*)/kT,\ \beta = (\Gamma^* - \Phi^*)/kT,\ \gamma = (\Delta^* - \Phi^*)/kT,\ \delta = (\Pi^* - \Phi^*)/kT$$

$$\mu_\parallel = \frac{3^{1/2}(7k' - 3)}{11}\left\{\frac{25 + 81e^{-\alpha} + 49e^{-\beta} + 9e^{-\gamma} + e^{-\delta}}{1 + e^{-\alpha} + e^{-\beta} + e^{-\gamma} + e^{-\delta}}\right\}^{1/2}$$

$$\mu_\perp = \frac{3^{1/2}(7k' - 3)}{11}\Big\{[32(1 - e^{-\beta})\beta^{-1} + 42(1 - e^{-\gamma})\gamma^{-1} + 18(e^{-\beta} - e^{-\alpha})(\alpha - \beta)^{-1} + 48(e^{-\gamma} - e^{-\delta})(\delta - \gamma)^{-1} + 25e^{-\delta}][1 + e^{-\alpha} + e^{-\beta} + e^{-\gamma} + e^{-\delta}]^{-1}\Big\}^{1/2}$$

$$f^4,\ {}^5I_4;\ \alpha = (\Gamma - \Sigma^+)/kT,\ \beta = (\Phi - \Sigma^+)/kT,\ \gamma = (\Delta - \Sigma^+)/kT,\ \delta = (\Pi - \Sigma^+)/kT$$

$$\mu_\parallel = \frac{6^{1/2}(7k' - 4)}{5}\left\{\frac{16e^{-\alpha} + 9e^{-\beta} + 4e^{-\gamma} + e^{-\delta}}{1 + 2(e^{-\alpha} + e^{-\beta} + e^{-\gamma} + e^{-\delta})}\right\}^{1/2}$$

$$\mu_\perp = \frac{6^{1/2}(7k' - 4)}{5}\Big\{[4(e^{-\alpha} - e^{-\beta})(\beta - \alpha)^{-1} + 7(e^{-\beta} - e^{-\gamma})(\gamma - \beta)^{-1} + 9(e^{-\delta} - e^{-\gamma})(\gamma - \delta)^{-1} + 10(1 - e^{-\delta})\delta^{-1}][1 + 2(e^{-\alpha} + e^{-\beta} + e^{-\gamma} + e^{-\delta})]^{-1}\Big\}^{1/2}$$

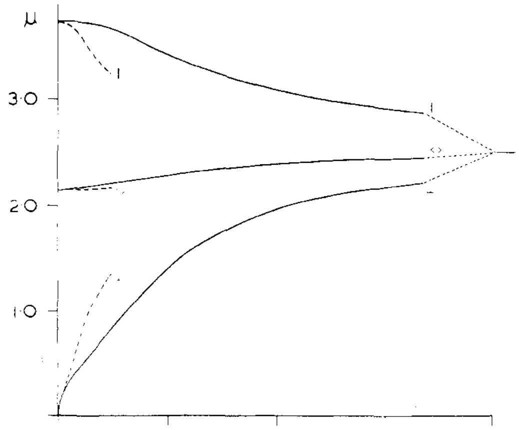

Figure 4. Temperature dependence of magnetic moment for f^1 systems in C_∞^* symmetry. (Here and in Figures 5–7 the 4f results are shown as full lines and the 5f results as broken lines.)

the temperature dependence of the moments is shown in terms of kT/Δ, rather than of T, where Δ is the overall ground-state splitting. Thus, even if the calculated Δ is incorrect, the μ vs. kT/Δ plots will remain of the same form if the ratios of the

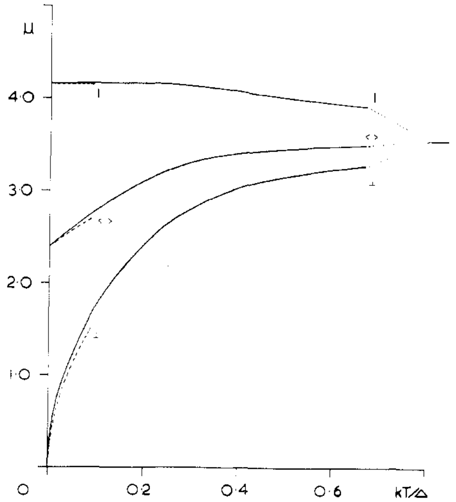

Figure 5. Temperature dependence of magnetic moment for f^2 systems in C_∞^* symmetry.

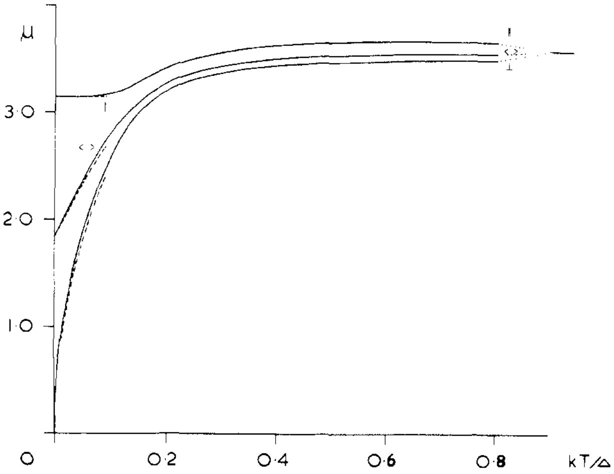

Figure 6. Temperature dependence of magnetic moment for f^3 systems in C_∞^* symmetry.

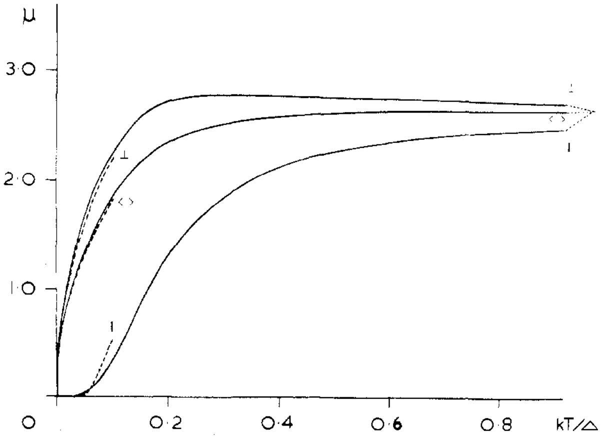

Figure 7. Temperature dependence of magnetic moment for f^4 systems in C_∞^* symmetry.

B_0^2, B_0^4, and B_0^6 parameters are unchanged. In Table III are listed the isotropic free-ion μ values $[=g(J(J+1))^{1/2}]$ for the f^x configurations, which are approached as $kT/\Delta \to \infty$, and the limiting values of $\mu_\parallel$, $\mu_\perp$, and $\langle\mu\rangle$ $(=gM_J)$ for $kT/\Delta \to 0$, $k' = 1$ being assumed throughout. The values for $kT/\Delta \to 0$ will be correct only for the M_J component assumed to lie lowest and will be reduced for $k' < 1$.

Finally, errors occasioned by the use of first-order ground-state functions are considered. In the free-ion situation

Table IV. Calculated and Experimental Magnetic Moments (BM) for $M(COT)_2$ Systems

Limiting calcd magnetic moments					Exptl magnetic moments (temp range, K)	
		$kT/\Delta \rightarrow 0$				
Confign; ground state	($k' = 1$) Free ion value	$\mu_\parallel$	$\mu_\perp$	$\langle\mu\rangle$	4f	5f
f^1, $^2F_{5/2}$; Φ^*	$3(5^{1/2})/7^{1/2}$	$15\sqrt{3}/7$	0	15/7	1.88 (room temp)[a]	
f^2, $^3H_4$, Φ	$8/5^{1/2}$	$12\sqrt{3}/5$	0	12/5	2.84 (room temp)[a]	2.3, 2.4 (4.2–45),[b,c] 2.6 (10–300)[c]
f^3, $^4I_{9/2}$; Φ^*	$12/11^{1/2}$	$20\sqrt{3}/11$	0	20/11	2.98 (room temp)[a]	1.8, 1.64 (3–60)[b,c]
f^4, $^5I_4$; Σ^+	$6/5^{1/2}$	0	0	0		Diamagnetic (4.2–45)[b,c]

[a] K. O. Hodgson, F. Mares, D. F. Starks, and A. Streitwieser, *J. Am. Chem. Soc.*, 95, 8650 (1973). [b] D. G. Karraker, *Inorg. Chem.*, 12, 1105 (1973). [c] D. G. Karraker, J. A. Stone, E. R. Jones, and N. Edelstein, *J. Am. Chem. Soc.*, 92, 4841 (1970).

the inclusion of matrix elements of the form $\langle J|L + 2S|J \pm 1\rangle$ which connect states of different J values leads to only small amounts of mixing, and Golding[35] has shown that the calculated Ce^{3+} ($4f^1$) free-ion μ value is increased by less than 0.03 BM over the $g(J(J + 1))^{1/2}$ value. Much more significant however is the mixing of states of different J values due to the ligand field, i.e., by matrix elements of V_{ax} which connect states of the same M_J but different J. For the f^1 and f^2 configurations the ligand field will mix the $^2F_{5/2}$ and $^2F_{7/2}$ and the $^3H_4$ and $^3H_5$ states, respectively, and the connecting matrix elements and those for the upper levels are listed also in the Appendix.[28] For these systems the second-order ground-state wave functions may be obtained using the off-diagonal matrix elements of V_{ax}, assuming the $(J + 1)$ state to lie $(J + 1)\xi/2S$ higher, as given by the Landé rule. The matrix elements of the Zeeman operators involving the $^2F_{7/2}$ and $^3H_5$ states are given in the Appendix,[28] and the corrected f^1 and f^2 Zeeman matrices were thus found and the moments evaluated for both the 4f and 5f series.

In the 4f series the corrections due to J mixing prove to be negligible, but for the 5f complexes reductions in $\langle\mu\rangle$ of ca. 0.1 and 0.2 BM, respectively, are found for the f^1 and f^2 systems. Although $\mu_\perp$ is barely changed, $\mu_\parallel$ is significantly reduced, this being largely due to the reduction in the diagonal $k'L_z + 2S_z$ terms for the respectively lowest lying Φ^* and Φ ($M_J = \pm\ ^5/_2$ and ± 3) levels. However, the perturbation treatment probably overestimates these corrections since the J and $(J + 1)$ states are usually separated by somewhat more than the Landé interval, and the differences in the diagonal V_{ax} terms for the M_J components of the upper and lower states should also be considered. For $5f^1$ the diagonal V_{ax} term for $^2F_{5/2}$ (Φ^*) is calculated as -799 cm^{-1} and that for $^2F_{7/2}$ (Φ^*) as $+1800$ cm^{-1}, thus increasing the separation by nearly 2600 cm^{-1}. Similarly for $5f^2$ the diagonal V_{ax} term for $^3H_4$ (Φ) is -1608 cm^{-1} and that for $^3H_5$ (Φ) only -513 cm^{-1}, thus increasing the separation of the mixing states by almost 1100 cm^{-1}. In both cases therefore the separation of the J and $(J + 1)$ states will be underestimated and the extent of J mixing exaggerated; consequently the corrections (which are also tabulated in the Appendix[28]) will be appreciably too great, and the values obtained by a simple treatment of the ground state should thus provide a working basis for the interpretation of the experimental magnetic susceptibilities.

Discussion

As shown in Figures 4–7 the anticipated anisotropy of the calculated magnetic moments is very considerable for all of the f^x configurations studied. Since the crystallographic data[12,16] show that both $U(COT)_2$ and $[Ce(COT)_2]^-$ belong to monoclinic space groups, it would in principle be possible to determine this anisotropy experimentally, but the extreme instability of the $An(COT)_2$ and $[Ln(COT)_2]^-$ species presents formidable difficulties. Thus, although such data would be of great value, only values of the average moments, $\langle\mu\rangle$, are currently available.

However, using the calculated B_q^k parameters, the temperature dependence of $\langle\mu\rangle$ varies significantly from one f^x configuration to another in both the 4f and 5f series. Thus for f^1 systems $\langle\mu\rangle$ shows little dependence on temperature, and, although the f^2 average moment shows more variation, in both cases $\mu_\parallel$ and $\mu_\perp$ vary in a contrary sense with temperature, leading to only a small overall temperature dependence of $\langle\mu\rangle$. For f^3 and more especially f^4 systems, however, both $\mu_\parallel$ and $\mu_\perp$ decrease with decreasing temperature, thus producing a much larger total variation of $\langle\mu\rangle$. Nevertheless, because of the much greater ground-state splittings anticipated for the 5f as compared with the 4f series, the predicted temperature dependence of $\langle\mu\rangle$ shows considerable differences in the two series.

Unfortunately, experimental data are still scarce (see Table IV) and for the lanthanide complexes only room-temperature measurements in THF solution have been reported.[14,15] As well as the values listed, results for the Sm, Gd, and Tb complexes were also recorded, but of these the Gd^{III} salt should show a $^8S_{7/2}$ ground state with an isotropic, J-only, moment, while for Sm^{III} any treatment restricted to the f^5, $^6H_{5/2}$, ground state would be inadequate because of the $^6H_{7/2}$ level lying only about 1000 cm^{-1} higher. These systems have not therefore been treated, and although the f^8, $^7F_6$, Tb^{III} complex is amenable to the present approach, the $C_{\infty}{}^*$ ligand field splits the ground level into seven components and the results are therefore confined to the Appendix.[28] The $4f^4$ system $[Pm(COT)_2]^-$ has nevertheless been treated, although not yet prepared, since there seems no reason to doubt its accessibility, and the temperature dependence of $\langle\mu\rangle$ for the f^4 species, with the predicted Σ^+ ground component, should afford a good test of the validity of the ligand field treatment.

For the 5f series the data are similarly sparse. Thus no magnetic data have been reported for the recently synthesized[3,4] $5f^1$ system $Pa(COT)_2$, and studies of the U and Np derivatives have largely been confined to the very low-temperature region. Moreover, for $Pu(COT)_2$ an anomalous and unexplained diamagnetism, increasing sharply with decrease in temperature, has been found which effectively obscures any trend in the magnetic moment along the lines here predicted. This diamagnetism is however at least qualitatively consistent with the prediction that the Σ^+ component of $5f^4$, $^5I_4$, should lie lowest.

Nevertheless, the reported 4f data are of considerable interest. Thus, despite the assertion of Streitwieser et al.[15] that the moments correspond closely with the free-ion quantities, the values of $\langle\mu\rangle$ for the Ce, Pr, and Nd species are respectively 0.65, 0.74, and 0.64 BM lower than the J-only $[g(J(J + 1))^{1/2}]$ free-ion values and some 0.5–0.6 BM lower than the values quoted[15] for $Ln(SO_4)_3 \cdot 8H_2O$ salts. The observed values of $\langle\mu\rangle$ are thus substantially smaller than those usually encountered for Ln^{3+} species and for $[Ce(COT)_2]^-$ the measured moment is actually lower than the limiting value ($kT/\Delta \rightarrow 0$) of 2.143 BM predicted for the Φ^* component of $^2F_{5/2}$ lying lowest. Thus, to accommodate the reported value for $[Ce(COT)_2]^-$, one must postulate an orbital reduction factor, k', at least as small as 0.91, together with a substantially larger ligand field; however, the very small metal–ligand mixing indicated in Table I and the demonstrably[14,15] ionic character of $[Ce(COT)_2]^-$ render this rather improbable.

Moreover, escape from this dilemma by assuming that the Φ^* level is not the lowest component also seems unlikely. Thus, for $[Ce(COT)_2]^-$ to approximate to a $4f^1$ situation the 4f level must lie between the ϕ and δ ligand symmetry levels in the molecular orbital picture adopted. Were the 4f level to lie below the ligand δ level, this would correspond to the location of more than one electron in the dominantly f-orbital levels, while if the 4f level were to lie higher than the ligand ϕ orbital, the highest lying electron of the complex would be located in a dominantly ligand type orbital, neither of which appears at all reasonable. Thus, since the Φ^* level is composed mainly (85.7%) of ϕ character, all acceptable choices for the f-orbital splitting parameters lead to the Φ^* level lying lowest in the $^2F_{5/2}$ manifold. Similarly the $\langle\mu\rangle$ values reported for the Pr and Nd complexes indicate either a ligand field some 4–5 times as large as that calculated or k' values of 0.87 and 0.90, respectively, or some combination of $k' < 1$, plus a larger ligand field. Again, none of these possiblities seems very likely.

Finally there remains the possibility of distortion from the eightfold, pseudoaxial symmetry. For f^2 systems the ground state is a doubly degenerate Φ level, which could be split by a reduction in symmetry, possibly of Jahn–Teller origin, thereby yielding an effectively twofold, D_{2h} or D_{2d}, situation. However, Jahn–Teller effects would be expected to be small in such a weakly bonding system, and in any case the ground states for the f^1 and f^3 systems are Kramers doublets which cannot be split by descent in symmetry, while the f^4 ground level is the nondegenerate Σ^+ component. Since we lack information about the nature of any low-symmetry field, further speculation is inappropriate, but it is possible that solvation of the $[Ln(COT)_2]^-$ anions by THF molecules may be responsible for the observed moment values. Thus THF is known[15] to solvate the bis(cyclooctatetraene) complexes of the lanthanide series, and it is possible that in solution this may result in the destruction of the pseudoaxial symmetry.

The interpretation of the measured moments is therefore less than satisfactory for the 4f series, and further measurements, preferably on solid samples over a wide temperature range, are essential. In particular, ESR studies of the Kramers doublet f^1 and f^3 species would be of the utmost value in providing independent evidence about the lowest lying components of the ground states.

In the 5f series the agreement between theory and experiment is more satisfactory. Thus, the low-temperature (<45 K) moment of 2.3–2.4 BM found[5,11] for $U(COT)_2$ can be reproduced with the calculated $B_q{}^k$ parameters, assuming $k' \approx 0.97$, and the predicted increase of about 0.3 BM at ambient temperature is consistent with the reported[6] effective moment of 2.6 BM for the range 10–300 K. In the recently studied lower part of the temperature range[11] (4–10 K) a discontinuity in the $1/\chi$ vs. T plot at about 9 K was ascribed to a lifting of the degeneracy of the Φ ground level by a low-symmetry ligand field, due to the monoclinic crystal lattice. Alternatively a Jahn–Teller effect could operate but, as noted above, only f^2 systems of the f^x configurations studied may show such splittings.

For the $5f^3$ complex $Np(COT)_2$ moments of 1.81 and 1.64 BM have been recorded[5,11] for the temperature ranges 4.2–45 and 3–60 K, respectively. The average of these determinations can be reproduced with the calculated $B_q{}^k$ parameters, using $k' \approx 0.94$, but a small temperature dependence over the range studied is predicted, together with an increase of some 0.9 BM between 0 K and room temperature.

For the weakly interacting 4f complexes k' should be very close to unity, but rather smaller values might be expected for the more strongly bonded $An^{IV}(COT)_2$ systems. Moreover, although k' values should be interpreted with the caution enjoined earlier, it is possible to estimate k' semiquantitatively for $U(COT)_2$ and $Np(COT)_2$ from the composition of the wave functions of the lowest lying components of the $^3H_4$ and $^4I_{9/2}$ ground states. Thus, the magnetic behavior, especially at low temperatures, will depend largely upon the nature of the Φ and Φ^* components, respectively, and using the eigenvectors of Table I, which show about 22% and 2% ligand character in the δ and σ levels, respectively, the Φ and Φ^* components of the f^2 and f^3 systems are found to contain overall about 2% and 5% of ligand character ($k' = 0.98$ and 0.95). For $Np(COT)_2$ NMR data[9] suggest that the extent of covalency is slightly less than for $U(COT)_2$, so that 5% is perhaps an overestimate, but the smaller calculated k' for the Np derivative arises from the appreciably greater proportion of δ character in the Φ^* level, as opposed to the Φ level of the U complex. The empirical k' values are slightly smaller than the calculated quantities, but these are of the right order of magnitude and correctly predict $k'(Np(COT)_2) < k'(U(COT)_2)$. Moreover, these results tend further to support the ground component deduced by Hayes and Edelstein[7] and appear to argue against the Γ ground level earlier proposed,[5] for which $k' \approx 0.8$ is required.

Unfortunately only very limited spectroscopic data have been reported for the bis(cyclooctatetraene) derivatives of either the 4f or the 5f series, so that experimental $B_q{}^k$ values cannot be derived therefrom for comparison. The fragmentary data[15] provide some very slight evidence suggesting that the calculated $B_q{}^k$ values may be rather too small, but the spectra are not extensive enough to permit further analysis.

After the bulk of this work was completed, the magnetic properties of the $[An^{III}(COT)_2]^-$ complexes of Np and Pu in the low-temperature range were reported.[36] For the Pu^{III} complex a moment of 1.25 BM was found between 2.2 and 80 K, but for this f^5 system a treatment of magnetic properties based on the lowest lying J state alone may well be inadequate and is not therefore pursued. The f^4 Np^{III} complex however shows temperature-independent paramagnetism between 2.2 and 5.5 K, and Curie–Weiss plots corresponding to moments of 1.04 and 1.39 BM, respectively, between 5.5 and 19° and between 19 and 80 K. This behavior is certainly consistent with a $J_z = 0$ (Σ^+) ground component and is in general accordance with the predictions for f^4 systems but serves thereby only to underline the mystery attaching to the anomalous diamagnetism of the f^4 Pu^{IV} complexes.

Registry No. $[Ce(COT)_2]^-$, 51705-68-1; $U(COT)_2$, 11079-26-8.

Supplementary Material Available. The Appendix, containing tables of weak ligand field matrices and Zeeman matrix elements for f^1 and f^2, $C_{\infty}{}^*$, systems, results for the $4f^8$ system, J mixing corrections for $5f^1$ and $5f^2$ systems, and expressions for 4f–2p overlap integrals, will appear following these pages in the microfilm edition of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50114D-12-75.

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Contribution from Bell Telephone Laboratories, Inc., Murray Hill, New Jersey 07974,
and the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Nonparameterized Molecular Orbital Calculations of Ligand-Bridged $Fe_2(CO)_6X_2$-Type Dimers Containing Metal–Metal Interactions[1,2]

BOON KENG TEO, MICHAEL B. HALL, RICHARD F. FENSKE, and LAWRENCE F. DAHL*

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Parameter-free molecular orbital calculations via the Fenske–Hall model have been carried out on representative Fe_2B_2-bridged complexes of the $Fe_2(CO)_6X_2$-type dimer (viz., those where X_2 denotes both the (B···B)-nonbonded $(SCH_3)_2$ and $(NH_2)_2$ ligands and the corresponding (B—B)-bonded S_2 and *cis*-$CH_3N{=}NCH_3$ ligands) and of the $[Fe_2(CO)_6(PR_2)_2]^n$ series (n = 0, 1−, 2−). These comparative calculations reveal that the above systematic variation of the bridging ligands (with and without direct B–B bonds) does not markedly affect the nature of the Fe–Fe interactions. The orbital character of the a_1 HOMO in each natural species is found to correspond closely to the classical "bent" Fe–Fe bond with the b_2 LUMO being its antibonding counterpart. Furthermore, the determined MO energy-level ordering and associated eigenvectors for the phosphido-bridged dimers with n = 1− and 2− are consistent with the monoanion possessing one electron and the dianion two electrons in this $4b_2$ MO of predominantly antibonding diiron character, corresponding formally to a "net" one-electron Fe–Fe bond and a "net" no-electron Fe–Fe bond, respectively. The results of this molecular orbital study, which provides the first detailed description of the electronic structure and bonding characteristics of this important dimeric metal cluster system, are evaluated and correlated with the available spectroscopic and crystallographic data.

Introduction

A large number of structurally related diiron hexacarbonyl complexes of general formula $Fe_2(CO)_6X_2$ containing Fe_2B_2-bridged systems (where B denotes the metal-attached bridging atom of ligand X) have been characterized by X-ray diffraction. These ligand-bridged diamagnetic species, which each possess an electron-pair Fe–Fe interaction, may be classified into the following two general groups: (a) dimers with no B–B bonds exemplified by either *two* separate, bridging X ligands, which are identical in the cases of NH_2,[3a] SR (with R = C_2H_5,[3b] C_6H_5[3c]), and PRR′ (with R = C_6H_5, R′ = CH_3 or H)[3d] and different as found for X = $P(p\text{-}CH_3C_6H_4)_2$, X′ = OH,[3e] or for one bidentate X_2 group such as $(NR)_2C{=}O$ (with R = CH_3,[3f] C_6H_5[3g]), $(NR)_2C{=}NR$ (with R = C_6H_{11}),[3h] RNC_6H_4NR' (with R = H, R′ = C_6H_5),[3i] $S_2C_2R_2$ (with R = C_6H_5),[3j] and $As_4(CH_3)_4$;[3k] (b) dimers with direct B–B bonds for which X_2 = $(NCH_3)_2$,[4a] $N_2C_{12}H_8$,[4b] $N_2C_5H_8$,[4c] and S_2.[4d] In all of these nitrogen-, sulfur-, phosphorus-, and arsenic-bridged dimers the local coordination about each iron atom may be described (with the neglect of Fe–Fe bonding) as a distorted tetragonal pyramid with two carbonyl ligands and the two bridging B atoms located in the basal plane and one axial carbonyl. The dimeric molecule, formally arising from the junction of the basal planes of the two tetragonal pyramids along the common B–B line, has a highly nonplanar Fe_2B_2 core with sharply acute Fe–B–Fe angles and a short Fe–Fe distance in the single-bond range. An important observed structural feature in these homologous complexes (Figure 1) is the general occurrence (in the absence of abnormal steric effects)[5] of a symmetrical Fe_2B_2-bridged fragment having idealized C_{2v} geometry with analogous Fe–Fe distances and resembling Fe–B–Fe angles for similar X ligands.

An electron-pair coupling interaction between the two Fe(I) atoms is necessary in order for each iron to attain a closed-shell electronic configuration in accord with the diamagnetic character of the compounds. In order to rationalize the basic geometry of these dimers, a *distinct* "bent" Fe–Fe bond was proposed[3a,b,4d] which was conceptually viewed as completing an octahedral-like coordination about each iron atom. Although this postulation of a *distinct* Fe–Fe bond in such complexes has gained general acceptance, its directional nature is still a subject of some controversy. From qualitative symmetry considerations Braterman[6] subsequently suggested that the nature of bonding in $Fe_2(CO)_6X_2$-type complexes is presumably closely related (on the basis of electronic bookkeeping) to that in the geometrically similar $Co_2(CO)_8$. Despite the absence of any simple conclusive argument, Braterman[6] felt drawn to the straight-bond model of $Co_2(CO)_8$