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The Electronic Structure of Organometallic Complexes of the f Elements. XIX. Parametrization of the Crystal Field Splitting Patterns of Quasi Trigonal Bi-pyramidal Anionic Complexes Involving the Tris(η^5-cyclopentadienyl)-uranium(IV) Moiety*

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Recently we reported the absorption and magnetic circular dichroism (MCD) spectra of pseudo-trigonal bipyramidal uranium(IV) complexes of the type $[Cp_3UX_2]^q$ ($X = NCS^-$, $NCBH_3^-$, D_2O; $q = +1, -1$) [1]. Arguments were also presented which showed the ground crystal-field state is of Γ_1 symmetry and separated by ~500 cm^{-1} from the next higher state. The selection rules for induced electric dipole transitions allow only $\Gamma_1 \rightarrow \Gamma_4$ or Γ_6 transitions for the approximate D_{3h} symmetry of the metal ion. The selection rules of MCD spectroscopy, however, allow transitions only to excited Γ_6 levels [2, 3]. The wave functions of the levels of Γ_6 symmetry are described to first order by $|\pm 2>$ (if $J < 4$) or $a|\pm 4> + b|\mp 2>$ (where the number in the ket is the J_z value). If the wave function is given by $|\pm 2>$ or if $4a^2 < 2b^2$, a positive Faraday A term should be observed [1–3]. If $4a^2 > 2b^2$ a negative Faraday A term should be observed. Thus using the selection rules and the observed signs of the Faraday A terms, the symmetry and the main J_z components of the eigenvectors of various excited levels have been given [1]. These levels are shown in Table I with the band numbering as given in ref. 1.

In this communication the parameters of a semi-empirical Hamiltonian have been fitted to the levels assigned previously for $[Cp_3U(NCS)_2]^-$ and $[Cp_3U(NCBH_3)_2]^-$. These parameters allow us to compare

TABLE I. Energy Levels and Eigenvectors for $Cp_3U(NCS)_2^-$

Energy levels			Transition[b]	Eigenvectors	
Calculated (cm^{-1})	Observed (cm^{-1})	Diff.[a] (cm^{-1})		Symmetry	Components[c]
0	0			Γ_1	93 $^3H(4,0)$
547	475	72	d	Γ_5	84 $^3F(4,1)$
4423	4107	316	1	Γ_6	57 $^3F(2,2)$ + 23 $^3H(5,2)$
6383	6297	86	2	Γ_6	62 $^3H(5,-4)$ + 27 $^3H(5,2)$
6432	6549	−117	3	Γ_4	39 $^3H(5,3)$ + 39 $^3H(5,-3)$
7221	7740	−519	4	Γ_6	39 $^3H(5,2)$ + 27 $^3H(5,-4)$
9081	9050	31	e	Γ_4	32 $^3F(3,3)$ + 32 $^3F(3,-3)$
9235	9515	−280	5	Γ_6	36 $^3F(4,-4)$ + 30 $^3H(6,-4)$
9784	10020	−236	8	Γ_6	54 $^3F(3,2)$ + 24 $^1G(4,2)$
10221	10288	−67	10	Γ_6	30 $^3F(3,2)$ + 23 $^3F(4,2)$
10721	10695	26	e	Γ_4	26 $^3F(4,3)$ + 26 $^3F(4,-3)$
11401	11211	190	11	Γ_6	74 $^3H(6,2)$
12694	12285	344	12	Γ_6	47 $^3H(6,-4)$ + 24 $^1G(4,-4)$
13470	13550	−80	13	Γ_4	36 $^3(H(6,-3)$ + 36 $^3H(6,3)$
14780	14837	−57	14	Γ_6	49 $^1D(2,2)$ + 13 $^3F(4,2)$
15775	15674	101	e	Γ_6	42 $^3F(4,2)$ + 28 $^1G(4,2)$
16641	16393	248	15	Γ_6	36 $^1G(4,-4)$ + 34 $^3F(4,-4)$
16877	17123	−246	16	Γ_4	24 $^1G(4,-3)$ + 24 $^1G(4,3)$
20613	20492	121	19	Γ_4	41 $^1I(6,-3)$ + 41 $^1I(6,3)$
20765	20921	−156	20	Γ_6	48 $^1I(6,2)$ + 29 $^1I(6,-4)$
21127	21142	−15	21	Γ_6	64 $^1I(6,-4)$ + 26 $^1I(6,2)$
23359	23256	103	27	Γ_6	62 $^3P(2,2)$ + 25 $^1D(2,2)$

[a]Difference = calculated − observed. [b]Numbering of the transitions from ref. 1. [c]Percentage of largest components only, nomenclature is $^{2S+1}L(J,J_z)$. [d]From a 'hot' transition. [e]These weak transitions were detected by a closer inspection of the spectra.

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the experimentally derived crystal-field splittings with that predicted for the Cp_3U^+ moiety by Tatsumi and Nakamura on the basis of extended Hückel calculations [4, 5].

The energy levels within an f^2 configuration in D_{3h} symmetry can be written in terms of a free-ion (H_{FI}) and a crystal-field (H_{CF}) Hamiltonian as follows

$$\mathcal{H} = H_{FI} + H_{CF}$$

where

$$H_{FI} = \sum_{k=0,2,4,6} f_k F^k(nf, nf) + \zeta_f a_{so} + \alpha L(L+1)$$
$$+ \beta G(G_2) + \gamma(R_7) + \sum_{k=0,2,4} m_k M^k +$$
$$+ \sum_{k=2,4,6} P_k P^k$$

and

$$H_{CF} = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_0^6 C_0^{(6)} + B_6^6 [C_6^{(6)} + C_{-6}^{(6)}]$$

Details of H_{FI} have been described in ref. 6 and of H_{CF} in ref. 7.

The assignments given previously were fitted to the parameters of the above Hamiltonian by a least-squares routine. In order to limit the number of free parameters, α, β, γ, the M^k and the P^k parameters were fixed at the values used for the analysis of $U(BD_4)_4$ in $Hf(BD_4)_4$ [8]. The remaining parameters were allowed to vary. For 18 levels the r.m.s. deviation was ~300 cm^{-1} for both $[Cp_3U(NCS)_2]^-$ and $[Cp_3U(NCBH_3)_2]^-$. The energy levels for $[Cp_3U(NCS)_2]^-$ are given in Table I and the free-ion and crystal-field (CF) parameters for both compounds are given in Table II.

TABLE II. Hamiltonian Parameters for $[Cp_3U(NCS)_2]^-$ and $[Cp_3U(NCBH_3)_2]^-$ [a]

Parameters	$[Cp_3U(NCS)_2]^-$	$[Cp_3U(NCBH_3)_2]^-$
F^2	45391	45609
F^4	44494	46116
F^6	19446	20780
ζ	1659	1664
α	[31][a]	[31]
β	[−644]	[−644]
γ	[1200]	[1200]
M^0	[0.99]	[0.99]
M^2	[0.55]	[0.55]
M^4	[0.38]	[0.38]
P^2	[500]	[500]
P^4	[500]	[500]
P^6	[500]	[500]
B_0^2	−2795 ± 670	−3121 ± 824
B_0^4	3039 ± 1100	3554 ± 1526
B_0^6	7659 ± 968	7250 ± 1658
B_6^6	−3064 ± 723	−2872 ± 817

[a] All parameters are in cm^{-1}. [b] Values of parameters in [ ] are held fixed at $U(BD_4)_4$ values (ref. 8).

The fit as shown in Table I is poor, and the free-ion parameters are not well defined. However the CF parameters are relatively insensitive to changes in the free-ion parameters and, given the assignments listed in Table I, appear to be of the correct sign and order of magnitude.

The magnetic susceptibility of $(C_4H_9)_4N[Cp_3U(NCBH_3)_2]$ was measured from 5–300 K; the data are shown in Fig. 1. From the appearance of 'hot' transitions the first excited state in this compound was located at ~600 cm^{-1} and is calculated to be of E symmetry. We have fixed the energy of this level to 600 cm^{-1} and calculated the magnetic susceptibility from 2–302 K with the wavefunctions obtained from the parameters given in Table II. The calculated susceptibility, with an orbital reduction factor of $k = 0.90$, is shown as the continuous line in Fig. 1 and agrees quite well with the experimental data.

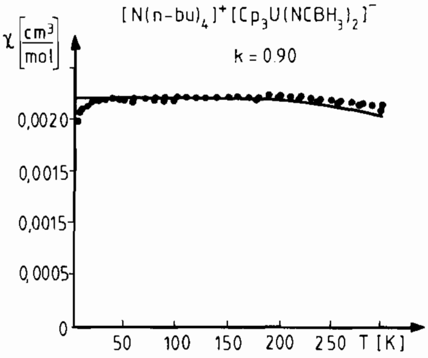

Fig. 1. The magnetic susceptibility of $[(C_4H_9)_4N][Cp_3U(NCBH_3)_2]$ as a function of temperature. The line represents the calculated values, the points represent the experimental data.

The empirical crystal-field parameters may be compared with those obtained from the extended Hückel orbital energies calculated by Tatsumi and Nakamura for the quasi-planar moiety Cp_3U^+ [4, 5]. From these energies the following crystal-field parameters are found: $B_0^2 = -3660$, $B_0^4 = 2970$, $B_0^6 = 3250$, and $|B_6^6| = 6830$ (all in cm^{-1}). The influence of the axial ligands may be estimated by use of the angular overlap model [9, 10]. If we arbitrarily set the value of e_σ of axial ligands at 750 cm^{-1} (1.5 times the value used for $Cp_3Pr{\cdot}CNC_6H_{11}$), we obtain the values $B_0^2 = -2600$, $B_0^4 = 4860$, $B_0^6 = 5940$, (all in cm^{-1}) and $|B_6^6|$ is unaffected. Thus the rather straightforward Hückel calculations agree in sign and magnitude with our empirically derived crystal-field parameters for these organouranium complexes. It appears the results of the Tatsumi's extended Hückel-calculations on lower symmetry complexes of the type Cp_3UX can be used for initial parameters for further empirical crystal-field analyses.

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