The Electronic Structure of Organometallic Complexes of the f Elements. XXI. The Crystal Field Splitting Pattern of Perdeuterated Tris(η^5-cyclopentadienyl)uranium(IV) Chloride in the Low Energy Range*

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Abstract

The absorption and magnetic circular dichroism spectra of the transitions $^3H_4 \rightarrow {}^3F_2$, $^3H_5$ $^3F_3$, $^3F_4$ and $^3H_6$ of (Cp-d_5)$_3$UCl have been measured at room and low temperatures. Preliminary crystal field calculations allowed the assignment of many transitions. On the basis of the crystal field eigenfunctions and eigenvalues obtained from these calculations, the temperature dependence of the paramagnetic susceptibility was calculated. For an orbital reduction factor of $k = 0.93$, a satisfactory agreement of experimental and calculated values was achieved.

Introduction

It is well known that several Lewis bases form mono and bis adducts with the tris(η^5-cyclopentadienyl)uranium(IV) moiety producing crystal fields (CF) of C_{3v} and D_{3h} symmetry, respectively, at the U ion site [1–5]. Recently we obtained the CF splitting patterns of various [Cp$_3$UX$_2$]^q (q = +1, −1; X = D$_2$O, NCS$^-$, NCBH$_3^-$, NCCH$_3$) complexes on the basis of magnetochemical, magnetooptical and optical experiments [6, 7], and fitted the parameters of a semiempirical Hamiltonian to the low lying CF splitting patterns of the anionic species [Cp$_3$UX$_2$]$^-$ (X = NCS$^-$, NCBH$_3^-$) [8].

It is the aim of this paper to obtain the CF splitting patterns of the representative mono adduct Cp$_3$UCl by using the same experimental methods as described earlier and to fit the parameters of a phenomenological Hamiltonian (using the C_{3v} sym-

metry of the CF) to this CF splitting pattern. With the CF eigenfunctions and eigenvalues derived on the basis of the above procedure we present a calculation of the temperature dependence of the paramagnetic susceptibility.

Earlier Amberger assumed T_d symmetry for Cp$_3$UCl [9] (and Kanellakopulos *et al.* made the same assumption for Cp$_3$NpCl [10]) and performed similar calculations. However, the optical spectra as well as the temperature dependence of the paramagnetic susceptibility of the Cp$_3$AnCl complexes indicated that the deviation from the ideal T_d symmetry is relatively pronounced [9–14]. For this reason it is highly desirable to consider the actual C_{3v} symmetry of the effective CF [5]. However, it is relatively difficult to derive the CF splitting pattern of Cp$_3$UCl because of the following reasons:

The first and the second excited CF levels are not well separated from the CF ground state [9–14]. Therefore, in the absorption spectrum measured at room temperature, the transitions from the CF ground state are frequently obscured by 'hot' transitions. Usually, well resolved low temperature absorption spectra of organometallic f element complexes can be obtained if the sample of interest is dissolved in the solvent 2-methyltetrahydrofuran which forms a glass at low temperature [15]. Unfortunately, this solvent reacts with Cp$_3$UCl producing spectra of the Cp$_3$UX$_2$ type [7, 16]. The inert solvent methylcyclohexane also forms a glass at low temperature, but most Cp$_3$UX complexes are not sufficiently soluble in this solvent or exhibit a strong temperature dependence of the solubility. Addition of toluene (ratio 1:1) increases the solubility remarkably, but this procedure has the disadvantage that the glass exhibits many cracks at very low temperatures. For this reason we measured the absorption spectra at ~40 K and the MCD spectra at ~150 K. At these temperatures the first excited level is somewhat thermally populated so that hot bands may arise.

If we assume a T_2 CF ground state and strict T_d symmetry of the CF, ~33 transitions of induced electric dipole character are expected in the low temperature absorption spectrum in the range 4000–40 000 cm^{-1} [9]. The highest three or four levels may be obscured because of a strong charge transfer band which starts ~530 nm, so ~30 levels should be observable. For the actual C_{3v} symmetry of the CF and assuming an A_1 ground state (*vide infra*) some 40 transitions should arise. In the low temperature absorption spectrum of Cp$_3$UCl, however, only 25 strong bands and numerous weak signals could be detected. Usually, one assumes that the stronger bands correspond to induced electric dipole transitions and the weaker signals are due to vibronic or hot transitions. Additionally the possibility exists that some weaker signals are caused by transitions $A_1 \rightarrow A_2$ which are forbidden in strict C_{3v} symmetry, but may become weakly allowed when the geometry of the 5-membered Cp rings is considered. However the small number of strong transitions suggests that some accidental degeneracies take place and/or several of the weaker signals are due to forced electric dipole transitions.

The low temperature absorption spectrum of Cp$_3$UCl may be separated phenomenologically into a well resolved low energy region (between 750 and 2300 nm) and a high energy region (between 750 and 400 nm) with a mass of signals which are partly superimposed on a strong charge transfer band. As this charge transfer transition also gives rise to a broad MCD signal, it is very difficult to recognize the nature of the MCD signals of f–f origin [6, 7].

Because no reliable assignments based on MCD spectra can be made in the high energy range at the present, we focus on the transitions at low energies. The CF energies (with respect to the CF ground state) of the levels derived from the multiplets $^3H_{4,5,6}$ and $^3F_{2,3,4}$, respectively, are not very sensitive to the choice of the Slater parameters, which are not well known for covalent uranium(IV) complexes. This simplifies the fitting procedure of the low lying levels considerably.

Unfortunately, the CH combination vibrations of the common solvents as well as of the Cp ligands coincide accidentally with transitions to the excited multiplets $^3F_2$ and $^3H_5$ [17]. In order to avoid these coincidences we studied the optical properties of (Cp-d$_5$)$_3$UCl as pellets and dissolved in a mixture of methylcyclohexane-d$_{14}$/toluene-d$_8$ (ratio 2:1).

Experimental

Reagents

The starting compounds UCl$_4$ and C$_5$D$_6$ were prepared following standard methods [18, 19]. Cp$_3$UCl and (Cp-d$_5$)$_3$UCl were synthesized according to a procedure by Anderson and Crisler [20].

Physical Measurements

The absorption spectra were recorded on a Cary model 17, and the MCD spectra were run within the ranges 750–1000 and 1000–2000 nm, respectively, by means of the JASCO dichrographs J-500 C and J-2000 D in combination with an electromagnet with the maximum field of 13.5 kG. For cooling down the solutions and the pellets we used an Air Products LT-3-110 cryostat. The Raman spectrum was recorded by means of a Cary model 82, using the exciting line of 514.5 nm of an Ar$^+$ laser (model 165 of Spectra Physics), and the FIR spectrum by means of the Bruker model IFS 112 V.

Results

The Vibrational Spectra of Cp$_3$AnCl (An = U, Th)

In order to discriminate between vibronic and accidentally weak induced electric dipole transitions or the transitions $A_1 \rightarrow A_2$ (which are forbidden in strict C_{3v} symmetry, but may become weakly allowed in lower symmetry when the exact geometry of the five-membered Cp rings is considered) it is necessary to know the vibrational spectrum of Cp$_3$UCl in the skeletal range. For strict C_{3v} symmetry of the Cp$_3$UCl moiety one expects six skeletal vibrations which are all IR and Raman allowed. Cp$_3$UCl, however, exhibited only two broad transitions with maxima at 240 and 272 cm^{-1}, and no signals in the Raman spectrum. In order to detect the four missing bands we also measured the Raman spectrum of the white and thus much better scattering Cp$_3$ThCl.

Only four well resolved signals with maxima at 110, 135, 241, and 275 cm^{-1} could be observed. We therefore assume that the missing two signals coincide accidentally with the observed bands.

In order to assign the observed transitions, we assume that weak signals which are separated from strong bands by ~110, ~135, ~241 and ~275 cm^{-1}, and combinations or overtones of these energies may be of vibronic origin.
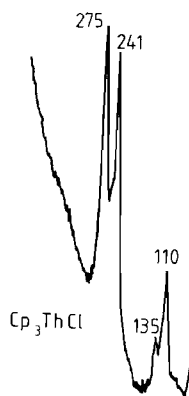

Fig. 1. The Raman spectrum of Cp$_3$ThCl within the range 50–450 cm^{-1}.

General Symmetry Considerations and Selection Rules

The free ion U^{4+} gives rise to multiplets $^{2S+1}L_J$ with $0 \leqslant J \leqslant 6$. If the U^{4+} ion is placed in a CF of C_{3v} symmetry, these multiplets are split into various CF levels. Table I lists the composition of the CF eigenvectors and correlates them with the irreducible representations of the C_{3v} point group.

TABLE I. Transformation Properties of the Wave Functions of the f^2 System with a CF of C_{3v} Symmetry

Composition of the eigenvector	J_{even}	J_{odd}
Singlets		
$|0\rangle$	A_1	A_2
$A|+3\rangle + B|0\rangle - A|-3\rangle$	A_1	A_2
$\dfrac{1}{\sqrt{2}}|+3\rangle + \dfrac{1}{\sqrt{2}}|-3\rangle$	A_2	A_1
$C|+6\rangle - D|+3\rangle + E|0\rangle - D|-3\rangle + C|-6\rangle$	A_1	A_2
$F|+6\rangle - G|+3\rangle - G|-3\rangle - F|-6\rangle$	A_2	A_1
Doublets		
$|\pm1\rangle$	E	E
$a|\pm2\rangle \mp b|\mp1\rangle$	E	E
$c|\pm4\rangle \pm d|\pm1\rangle + e|\mp2\rangle$	E	E
$f|\pm5\rangle + g|\pm2\rangle \mp h|\mp1\rangle$	E	E

With the exception of the transitions $A_1 \rightarrow A_2$ and $A_2 \rightarrow A_1$ each forced electric dipole transition within the CF levels A_1, A_2 and E is allowed by symmetry [21].

Görller–Walrand and Godemont have given the MCD selection rules for right and left circularly polarized radiation [22], respectively:

r.c.p. $J_z(\text{terminal}) - J_z(\text{initial}) = -1 - \rho$

l.c.p. $J_z(\text{terminal}) - J_z(\text{initial}) = +1 - \rho$

In case of C_{3v} symmetry, ρ has the values 0, ±3 or ±6 [23]. These relations may be used to estimate the predominant J_z value of the wave function of the terminal level, provided that both the wave function of the initial level and the sign of the Faraday A term are known.

Assuming an A_1 CF ground state, described by $J_z = 0$ (*vide infra*), and applying the above selection rules, Faraday A terms may only be observed if the terminal levels contain contributions of $|\pm1\rangle$, $|\pm2\rangle$, $|\pm4\rangle$ or $|\pm5\rangle$. According to Table I these functions transform like E. A positive sign of the Faraday A curve is expected when the terminal level is $|\pm1\rangle$ or if $b^2 > 2a^2$, $(4c^2 + d^2) > 2e^2$, $h^2 > (5f^2 + 2g^2)$, whereas a negative sign is expected if $2a^2 > b^2$, $2e^2 > (4c^2 + d^2)$ and $(5f^2 + 2g^2) > h^2$ (*cf.* wave functions of Table I).

Identification of the CF Ground State

Kanellakopulos *et al.* determined the temperature dependence of the paramagnetic susceptibility of numerous Cp_3UX complexes [12]. He interpreted his data for Cp_3UCl by assuming a CF ground state of A_1 symmetry which is described to first order by $0.44|+3\rangle - 0.12|0\rangle + 0.44|-3\rangle$ and a first excited level of A_1 symmetry some 180 cm^{-1} higher [14]. In contrast to this interpretation we explained the same data one decade ago by assuming a CF ground state of A_1 symmetry with dominant $|0\rangle$, a first excited level of E symmetry which is dominated by $|\pm1\rangle$ and a second excited level of E symmetry with large contributions of $|\pm2\rangle$ in the eigenvector [9]. As the latter sequence of CF levels agrees with that of the $4f^2$ systems Cp_3PrX (X = 2-MeTHF, CNC_6H_{11}) [24, 25] and with that of $[Cp_3UX_2]^-$ (X = NCS$^-$, NCBH$_3^-$) [8] we assume this partial splitting pattern to be more plausible.

Analysis of the Absorption and MCD Spectra

We assign the observed signals in the MCD and absorption spectra, respectively, by a combination of experimental information (*cf.* section 'Selection Rules') and the preliminary results of a CF calculation. As a starting basis for the free ion parameters we used the Slater parameters $F^2 = 45\,000$, $F^4 = 42\,000$, $F^6 = 23\,000$, $\zeta_{5f} = 1750$, α, β, γ and Ms and Ps as found for $U(BD_4)_4$:$Hf(BD_4)_4$ [26]. For CF parameters we chose the mean values of the CF parameters of UCp_4 [27] and $[Cp_3U(NCS)_2]^-$ [8]. The calculated CF energies as well as the predicted signs of the spectroscopic splitting factors (compared with the signs of the observed Faraday A terms) allowed the identification of most of the excited CF levels. The parameters of the semiempirical Hamiltonian [24–26] were then fitted to the assigned energy levels. The final calculated eigenvalues and major components of the eigenvectors are listed in Table II.

$^3H_4$

At room temperature the absorption spectrum of Cp_3UCl has many bands which are absent or are only weakly observable in the spectrum at 40 K. These 'hot' bands are separated from the corresponding 'cold' signals by ~210 and 450 cm^{-1}, respectively.

The preliminary CF calculation produces a CF ground state of A_1 symmetry ($|0\rangle$ dominant) and two (210 and 471 cm^{-1}) excited levels of E symmetry with $|\pm1\rangle$ and $|\pm4\rangle$ dominant. This calculated sequence of the CF levels agrees with our previous interpretation of the temperature dependence of the paramagnetic susceptibility [9] and with the energy differences extracted from the optical spectra. The identification of the first excited level is further supported by the MCD spectrum: in several cases, where the cold bands correspond to Faraday B terms the 'hot' signals ($E = 210$ cm^{-1}) give rise to positive

TABLE II.

Band		E_{calc}[b] (cm^{-1})	E_{obs} (cm^{-1})	Eigenvector composition $(2S+1)_{LJ}$[c]
Number	State			
	1A$_1$	0	0	86.1 $^3H_4$ + 9.1 $^1G_4$
	1E	235	210	84.7 $^3H_4$ + 9.2 $^1G_4$
	2E	493	450	89.6 $^3H_4$ + 6.9 $^1G_4$
	3E	1006		81.8 $^3H_4$ + 9.7 $^1G_4$
	1A$_2$	1007		89.7 $^3H_4$ + 6.0 $^1G_4$
	2A$_1$	1938		77.8 $^3H_4$ + 15.3 $^1G_4$
	4E	3585		60.9 $^3F_2$ + 25.2 $^3H_5$
1	5E	4413	4425	72.8 $^3F_2$ + 11.6 $^1D_2$
2	3A$_1$	4528	4530	78.3 $^3F_2$ + 10.6 $^1D_2$
3	2A$_2$	5661	5290*	93.2 $^3H_5$ + 3.0 $^3F_3$
4	6E	5805	5824	81.8 $^3H_5$ + 5.6 $^3F_2$
5	7E	6092	6039	92.7 $^3H_5$ + 2.2 $^3H_6$
6	4A$_1$	6207	6277	84.6 $^3H_5$ + 5.5 $^3F_2$
7	8E	7040	7090	73.1 $^3H_5$ + 12.9 $^3F_2$
	3A$_2$	7047	7090	85.9 $^3H_5$ + 9.1 $^3F_3$
8	9E	7335	7770*	78.7 $^3H_5$ + 8.2 $^3F_4$
9	4A$_2$	8263	8264	83.0 $^3F_3$ + 14.8 $^3H_6$
10	5A$_1$	8483	8475	28.7 $^3F_3$ + 28.1 $^3H_6$
11	5A$_2$	8564	8510	77.5 $^3F_3$ + 7.3 $^3H_5$
12	10E	8589	8606	50.4 $^3F_3$ + 14.5 $^1G_4$
13	11E	8695	8703	77.2 $^3F_3$ + 6.2 $^1G_4$
14	6A$_1$	8856	8850	38.3 $^3F_4$ + 35.9 $^1G_4$
15	12E	9299	9346	28.6 $^3F_4$ + 27.9 $^1G_4$
16	13E	9549		36.5 $^3F_4$ + 19.5 $^3F_3$
	6A$_2$	9824		40.4 $^3F_4$ + 22.5 $^1G_4$
18	14E	9921		47.3 $^3F_4$ + 32.0 $^1G_4$
17	7A$_1$	9961	9970	44.4 $^3F_3$ + 15.5 $^3F_4$
19	15E	10800	10803	83.6 $^3H_6$ + 3.6 $^1I_6$
	7A$_2$	10819	10803	73.5 $^3H_6$ + 10.2 $^3F_3$
20	16E	11112	10905*	72.5 $^3H_6$ + 7.7 $^3F_3$
21	8A$_1$	11129	11136	58.5 $^3H_6$ + 24.2 $^1G_4$
22	9A$_1$	11598		75.4 $^3H_6$ + 11.8 $^3F_3$
	8A$_2$	12262		65.8 $^3H_6$ + 14.4 $^3F_3$
23	17E	12451	12453	70.8 $^3H_6$ + 9.7 $^1G_4$
	10A$_1$	12510	12453	72.1 $^3H_6$ + 11.1 $^1G_4$
24	18E	12848	12821	71.0 $^3H_6$ + 10.9 $^3F_3$
	19E	14912		31.3 $^1D_2$ + 27.3 $^3F_4$
	11A$_1$	15074		28.0 $^1D_2$ + 21.0 $^3F_4$
	20E	15137		48.9 $^1D_2$ + 22.3 $^3P_2$
	21E	15414		31.4 $^3F_4$ + 21.7 $^1D_2$
	12A$_1$	15696		32.1 $^3F_4$ + 20.9 $^1D_2$
	13A$_1$	16078		51.2 $^3F_4$ + 29.0 $^1G_4$
	22E	16307		42.5 $^1G_4$ + 37.2 $^3F_4$
	14A$_1$	16434		79.4 $^3P_0$ + 7.0 $^1S_0$
	23E	17133		42.2 $^1G_4$ + 32.7 $^3F_4$
	9A$_2$	17220		50.9 $^1G_4$ + 35.5 $^3F_3$
	10A$_2$	18535		97.2 $^3P_1$ + 0.9 $^3H_6$
	24E	18978		94.8 $^3P_1$ + 1.4 $^1D_2$
	15A$_1$	20037		88.8 $^1I_6$ + 8.4 $^3H_6$
	25E	20486		82.8 $^1I_6$ + 6.1 $^1G_4$
	26E	20812		88.8 $^1I_6$ + 3.4 $^1G_4$
	11A$_2$	21082		88.8 $^1I_6$ + 5.4 $^1G_4$
	27E	21147		72.8 $^1I_6$ + 18.9 $^3P_2$
	16A$_1$	21262		92.3 $^1I_6$ + 4.7 $^3H_6$
	28E	21343		77.4 $^1I_6$ + 15.1 $^3P_2$
	17A$_1$	22024		51.0 $^1I_6$ + 40.0 $^3P_2$
	12A$_2$	22638		94.2 $^1I_6$ + 4.1 $^3H_6$
	29E	22804		60.0 $^3P_2$ + 27.4 $^1D_2$
	30E	23613		42.9 $^3P_2$ + 30.4 $^1D_2$
	18A$_1$	24853		36.4 $^1I_6$ + 31.2 $^1D_2$
	19A$_1$	39343		90.9 $^1S_0$ + 6.8 $^3P_0$

(continued)

[a]These numbers correspond to the numbers in the Figures.   [b]Parameters given in column Calculation B in Table III.   [c]Only the largest two components are listed. An asterisk indicates assigned level but not used in this fit.

Faraday A terms. For this reason the first excited level is assigned to E symmetry with either the $|\pm1\rangle$ or $|\pm4\rangle$ component dominant.

$^3F_2$

Binary CH combination vibrations of the Cp ligands coincide with the transition $^3H_4 \rightarrow {}^3F_2$ [17]. Reid et al. studied the NIR spectrum of ThCp$_4$ (where no f–f transitions can take place) and observed signals of vibrational origin at 3937, 4110, 4175, 4224, 4376, 4478 and 4545 cm^{-1} [17]. With the exception of band 2 all signals of Cp$_3$UBr (Fig. 2) coincide with the reported vibrations of ThCp$_4$. When the temperature is lowered, the intensity of bands 1' and 2' (which are separated by 230 cm^{-1} from the corresponding cold signals 1 and 2) decreases. For this reason bands 1, 1', 2, and 2' are of electronic origin and the remaining signals presumably of vibrational origin. This is confirmed by the low temperature absorption spectrum of (Cp-d$_5$)$_3$-UCl, where one strong band at 4530 and a weaker at 4425 cm^{-1} can be observed (cf. Fig. 3).

The observed maxima of bands 1 and 2 are close to the calculated energies of the levels 5E and 3A$_1$
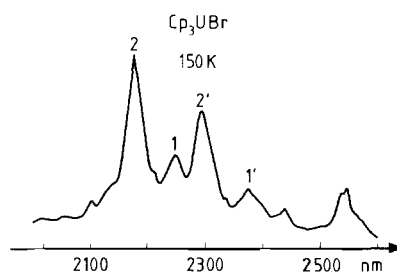

Fig. 2. The absorption spectrum of Cp$_3$UBr within the range 2000–2600 nm (teflon pellet, temperature: 150 K). Bands with one or two primes, respectively, refer to hot transitions starting from the first and second excited state. This holds also for Figs. 3–10.
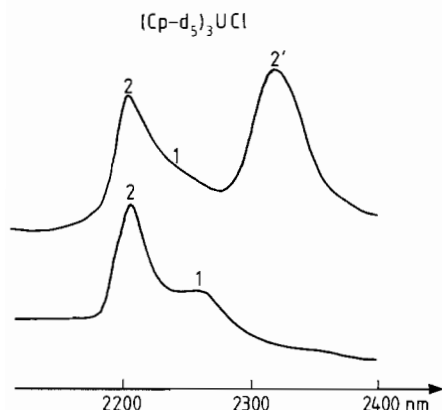
Fig. 3. The absorption spectrum of $(Cp-d_5)_3UCl$ within the range 2100–2400 nm. Upper curve: teflon pellet, room temperature; lower curce: KBr pellet, 30 K.

and the corresponding terminal levels are so assigned. Commercial dichrographs do not work in this energy range so no magnetooptical measurements are available.

$^3H_5$

In this energy range CH combination vibrations of the solvent and of the Cp ligands are also expected [17]. For this reason we studied the absorption spectrum of $(Cp-d_5)_3UCl$ dissolved in a mixture of perdeuterated solvents. At room temperature a complex band structure can be observed, which is simplified considerably by lowering the temperature. The two weaker signals 3′ and 3″ at 5080 and 4837 cm^{-1} have no cold counterparts. They are assigned to transitions from the first two E states at 210 and 450 cm^{-1}. Thus we assign a level of symmetry A_2 at 5290 cm^{-1}. Signal 4 (at 5824 cm^{-1}) in the absorption spectrum corresponds to a negative Faraday A curve.

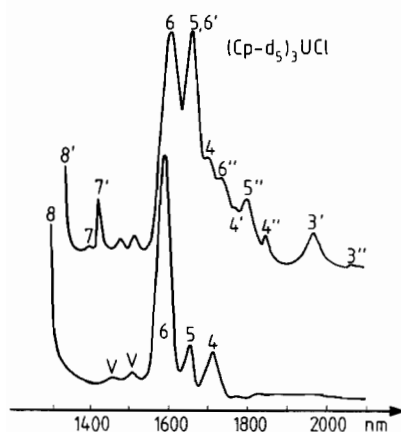Fig. 4. The absorption spectrum of $(Cp-d_5)_3UCl$ dissolved in methylcyclohexane-d_{14}/toluene-d_8. This mixture of solvents was also used in Figs. 6 and 9. Upper curve: room temperature; lower curve: 40 K.
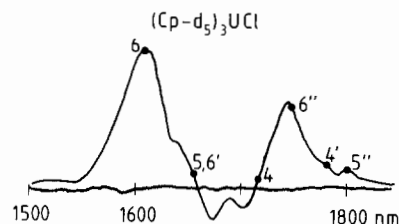

Fig. 5. The low temperature (150 K) MCD spectrum of $(Cp-d_5)_3UCl$ within the range 1500–1830 nm. The dots in the spectrum refer to maxima in the corresponding absorption spectrum. This holds also for Figs. 6 and 9.

This means that the condition $(5f^2 + 2g^2) > h^2$ holds for the eigenvector of the terminal level of this transition. The preliminary CF calculation predicts the level 6E (which meets this condition) at 5733 cm^{-1}.

At higher temperatures the hot band 6′ coincides with signal 5 which has an energy of 6039 cm^{-1} in the absorption spectrum run at 30 K. In the MCD spectrum run at 150 K a positive Faraday A term appears. We believe this signal is produced by the stronger (at 150 K) hot and not by the cold transition, but we are unable to make any assignments based on MCD measurements. The CF calculation predicts the level 7E at 6101 cm^{-1} which is close to the experimental value. For this reason we assign the terminal level of this transition with 7E.

Signal 6 at 6277 cm^{-1} in the absorption spectrum corresponds to a Faraday B term. This means that the terminal level of this transition should be of A_1 symmetry. As the preliminary CF calculation predicts the level $4A_1$ at 6135 cm^{-1} we assign the terminal level of this transition with $4A_1$. In the room temperature absorption spectrum one strong and three weak signals can be observed on the high energy side of band 6 which have no distinct counterparts in the MCD spectrum. At 40 K only the signals at 6628 and 6825 cm^{-1} remain. The energy separations of 351 and 548 cm^{-1} of both signals from band 6 can be explained by a combination of the vibrations at 241 and 110 cm^{-1} and the overtone of the fundamental vibration at 275 cm^{-1}. For this reason both signals are presumably due to vibronic transitions.

The hot signal 7′ at 6880 cm^{-1} has only a very weak cold signal. This means that an A_2 level should be located at 7090 cm^{-1}, which is close to the predicted $3A_2$ level at 7119 cm^{-1}. However the preliminary calculation also predicts the level 8E at 7048 cm^{-1}.

The very strong band 8 at 7770 cm^{-1} gives rise to a positive Faraday A term. Thus the condition $(4c^2 + d^2) > 2e^2$ holds for the eigenvector of the terminal level of this transition. This condition is met for the level 9E which is predicted at 7361 cm^{-1}.

On the high energy side of band 8 one strong and one weak signal appear which are separated by ~125 and 410 cm^{-1} from band 8. As no CF levels are
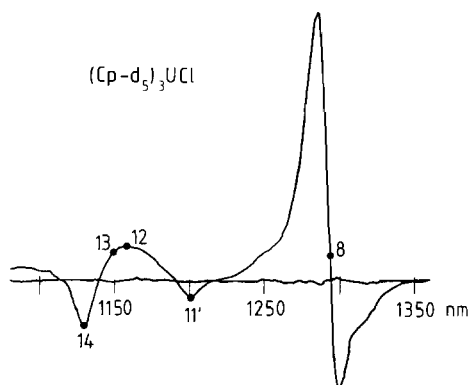
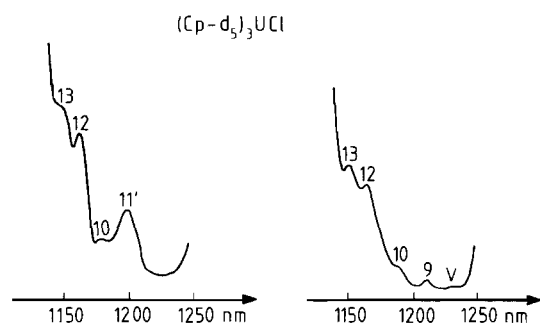Fig. 6. The low temperature (150 K) MCD spectrum of $(Cp-d_5)_3UCl$ within the range 1100–1350 nm.

Fig. 7. The absorption spectrum of $(Cp-d_5)_3UCl$ within the range 1150–1250 nm. Left hand side: solvent as in Fig. 4, 90 K. Right hand side: KBr pellet, 50 K.

predicted in this region, we assume that these signals are due to vibronic transitions. The first energy separation may be explained either by the coupling of the skeletal vibration at 110 or 135 cm^{-1} and the second by the coupling of the combination vibrations at 135 and 275 cm^{-1}.

$^3F_3$

The manifold $^3F_3$ is split by a CF of C_{3v} symmetry into five levels, two of which are of A_2 symmetry. For this reason only three signals are expected in the low temperature absorption spectrum. At room temperature only one broad asymmetric band 11′ with the maximum at 8300 cm^{-1} appears. Band 11′ cannot be observed in the absorption spectrum, run at 40 K, so the corresponding cold band is missing. We conclude that an A_2 level must be present at 8510 cm^{-1}. This is in good agreement with the CF calculation which predicts the level $5A_2$ at 8534 cm^{-1}.

No hot bands can be detected which may be correlated with the transitions 1E, 2E → 4A$_2$. However a very weak signal 9 appears at 8264 cm^{-1} besides three somewhat stronger bands 10, 12, 13 in the absorption spectrum of $(Cp-d_5)_3UCl$ run at 50 K

(KBr pellet). This transition would match the predicted energy of 4A$_2$ (8241 cm^{-1}). Similarly, the signals 10, 12, and 13 match the CF energies of the levels $5A_1$, 10E and 11E very well and the terminal levels of these transitions are thus tentatively assigned. The possibility that bands 12 and 13 are of hot electronic or vibronic origin can be ruled out as they appear also in the absorption spectrum of Cp$_3$UCl (dissolved in toluene/methylcyclohexane) run at 20 K. Unfortunately a CH combination vibration of the solvent obscures signal 10 in this spectrum.

No distinct MCD signals were observed in this energy range which could be used for verification of these assignments.

In contrast to the $(Cp_3UX_2)^-$ (X = NCS$^-$, NCBH$_3^-$) series, where no transitions to terminal CF levels derived from the $^3F_3$ were detected, several weak transitions can be observed in the case of Cp$_3$UCl.
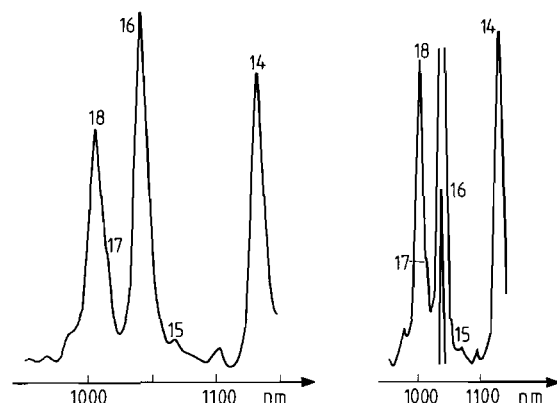
Fig. 8. Left hand side: the absorption spectrum of $(Cp-d_5)_3$-UCl within the range 950–1050 nm (KBr pellet, 50 K). Right hand side: the low temperature (20 K) absorption spectrum of Cp$_3$UCl dissolved in methylcyclohexane/toluene.
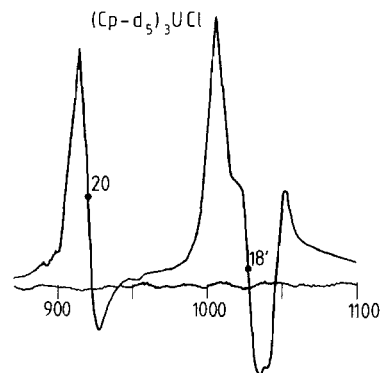
Fig. 9. The low temperature (150 K) MCD spectrum of $(Cp-d_5)_3UCl$ within the range 870–1100 nm.

$^3F_4$

Five transitions starting from the CF ground state are allowed by symmetry, but only three strong transitions can be observed in the absorption spectrum of $(Cp-d_5)_3UCl$ in this energy range at 50 K. Two weak signals at the high energy side of band 14 are separated by some 260 and 495 cm^{-1} from the main band. These energy separations may be explained by the coupling of the vibrations at 275 or 241 cm^{-1} or the overtone of the vibration at 241 cm^{-1}, so these signals may be of vibronic origin. But the weak signal 15 at 9346 cm^{-1} would also match the calculated energy of 11E (9285 cm^{-1}) in a satisfactory manner. A close inspection of the absorption spectrum reveals that band 18 is rather asymmetric. In the absorption spectrum of Cp$_3$UCl run at 20 K, a shoulder 17 appears; additionally signal 15 becomes more distinct.

In the MCD spectrum, band 14 (8850 cm^{-1}) clearly corresponds to a negative Faraday B term. For this reason the terminal level of this transition has to be correlated with an A_1 level. The preliminary CF calculation predicts the level 6A$_1$ at 8807 cm^{-1}. Band 18 (9970 cm^{-1}) in the absorption spectrum corresponds clearly to a positive Faraday B term. This means that the terminal level of this transition must be of A_1 symmetry. The tentative CF calculation predicts the level 7A$_1$ at 9988 cm^{-1} which is in good agreement with the experimental energy. Transition 18′ gives rise to a distinct positive Faraday A term, but the nature of signal 16 is uncertain. Inspection of the MCD spectra of Cp$_3$UBr and Cp$_3$UI did not resolve this problem. It corresponds either to (a) a negative Faraday A or (b) a positive Faraday B term.

For (a): The eigenvector of the terminal level of this transition must fulfill the condition $(4c^2 + d^2) < 2e^2$. This condition is met by level 14E, which would be separated some 400 cm^{-1} from the experimental energy. This assignment would also mean that the transition to the level 13E is missing and the existence of shoulder 17 cannot be explained.

For (b): In this case the terminal level of this transition should be of A_1 symmetry or the $g_\|$ value of an excited E level is accidentally very low. The preliminary CF calculation predicts no A_1, but only the level 13E (at 9610 cm^{-1}) in this range. Though there would be good agreement of the calculated and experimental energies, the calculated eigenvector for this level gives rise to $|g_\|| = 1.808$. Furthermore the composition of the eigenvector suggests a positive Faraday A term.

$^3H_6$

The preliminary CF calculation predicts that the CF levels of this multiplet should extend between 10 800 and 12 900 cm^{-1}. At room temperature various signals can be detected, but at 20 K only the strong band 20 (at 10 905 cm^{-1}) and several diffuse
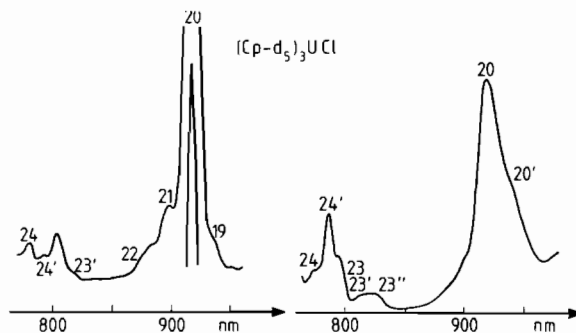

Fig. 10. The absorption spectrum of $(Cp-d_5)_3UCl$ within the range 750–960 nm. Left hand side: glass, 90 K; right hand side: solution, room temperature.

signals survive. More information can be obtained from the spectrum run at 90 K, where the hot signals 23′ and 24′ together with the corresponding cold bands can be observed.

The strong band 20 corresponds to a positive Faraday A term in the MCD spectrum. This means that the relation $(4c^2 + d^2) > 2e^2$ holds for the eigenvector. This condition is met for level 16E which is predicted at 11 145 cm^{-1}. The weaker signals 19, 21–24 do not give rise to distinct MCD transitions. For this reason they cannot be assigned on a purely experimental basis, but signals 19, 21, 23 and 24 are not too far from the calculated energies of levels 8A$_1$, 17E/10A$_1$ and 18E (*cf.* Table II). Shoulder 19 has an energy separation of 205 cm^{-1} from signal 22 and may therefore correspond to a hot transition. But this shoulder also appears in the absorption spectrum, run at 20 K. This means that signal 19 in Fig. 10 (left hand side, 90 K) may be due to both the hot transition 1E → 16E and the cold transition 1A$_1$ → 15E. Signal 21 which has an energy separation of 231 cm^{-1} from band 20 may also be of vibronic origin, as the existence of this signal may be explained by the coupling of the vibration of 241 cm^{-1}. This is true also for signal 22, as its energy separation of 550 cm^{-1} from band 20 may be interpreted by the coupling of the overtone of the vibration at 275 cm^{-1}.

Parametric Fitting of the Experimental Data

The energy levels within f^n configuration in C_{3v} symmetry can be written in terms of the atomic free ion (H_{FI}) and crystal field (H_{CF}) Hamiltonians as follows [28]:

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

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

$$H_{CF} = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_3^4 (C_{-3}^{(4)} - C_3^{(4)})$$
$$+ B_0^6 C_0^{(6)} + B_3^6 (C_{-3}^{(6)} - C_3^{(6)}) + B_6^6 (C_{-6}^{(6)} + C_6^{(6)})$$

The $F^k(nf, nf)$s and ζ_f represent, respectively, the radial parts of the electrostatic and spin—orbit interactions between f electrons, while f_k and a_{so} are the angular parts of the interactions. α, β, and γ are the parameters associated with the two-body effective operators of configuration interaction. The M^k parameters represent the spin—spin and spin—other-orbit interactions while the P^k parameters arise from electrostatic-spin—orbit interactions with higher configurations. The crystal field interaction for C_{3v} symmetry is represented by the six B_q^k parameters and the tensor operators $C_q^{(k)}$ [28].

The assigned energy levels were fitted to the parameters of the above Hamiltonian. The α, β, γ, M^k and P^k parameters were fixed at values used for $U(BD_4)_4/Hf(BD_4)_4$. The remaining parameters were allowed to vary. Fitting the 27 experimental energies shown in Table II resulted in an r.m.s. deviation of $\sim$147 cm^{-1}. The parameters for this fit (Calculation A) are given in Table III.

Three levels fit particularly poorly. If we do not use these levels in our fit, we find that for 24 levels,

TABLE III. Parameter Values for Cp_3UCl (cm^{-1})

Parameter	Calculation A	Calculation B
F^2	41676(2249)	45031(931)
F^4	41364(2471)	39700(790)
F^6	19892(5537)	23161(2044)
ζ_{5f}	1734(24)	1760(9)
α	[36.5][a]	[36.5]
β	[−648]	[−648]
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	−1799(350)	−1371(113)
B_0^4	4155(612)	3892(223)
B_0^6	−1675(903)	−1979(324)
B_3^4	−2936(420)	−2086(137)
B_3^6	−2548(678)	−3125(182)
B_6^6	−5213(421)	−4878(157)
No. of levels	27	24
σ	147.1	42.3

[a]Numbers in [ ] fixed at values from ref. 26.

we obtain an r.m.s. deviation of $\sim$43 cm^{-1}. The parameters for this fit, the calculated energies, and the two largest eigenvector components are shown in Table II. The parameters (Calculation B) are given in Table III.

Magnetic Susceptibility Results

The experimentally determined temperature dependence of the reciprocal paramagnetic susceptibility of Cp_3UCl is shown in Fig. 11. This figure also shows the calculated temperature dependence (based on the actual experimental low-lying energy levels and the eigenvectors obtained from our fit) for the orbital reduction factor $k = 0.93$, k being defined by the modified Zeeman Hamiltonian $\langle \psi | kL + 2S | \psi \rangle$. The agreement of the calculated curve with the experimental data is satisfactory.
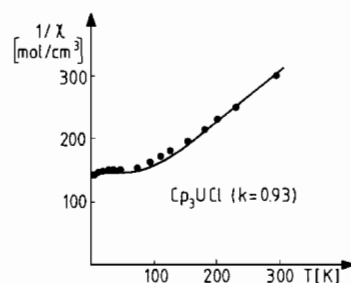

Fig. 11. The inverse magnetic susceptibility of Cp_3UCl as a function of temperature. The line represents the calculated values, the points represent the experimental data.

Discussion

As shown in Table III, the experimental data are not very sensitive to values of the F^k parameters. The reason for this is that we are fitting only the low-lying energy levels which correspond to only a few $L-S$ terms. However the crystal field parameters seem relatively well-fixed. From the Auzel parameter [29]

$$N_v/\sqrt{4\pi} = \left[\sum_{k,q} \left(\frac{1}{2k+1} \right) (B_q^k)^2 \right]^{1/2}$$

we find $N_v/\sqrt{4\pi} = \sim$3000 cm^{-1}. This value is the same order of magnitude as found for $[Cp_3U(NCS)_2]^{-1}$ and $[Cp_3U(NBH_3)_2]^-$ but considerably larger than the values of $\sim$1000 cm^{-1} obtained for the trivalent Pr complexes, $Cp_3Pr\cdot MeTHF$ and $Cp_3Pr\cdot CNC_6H_{11}$.

The analysis using all the experimental data gave a rather poor value of σ, the r.m.s. energy deviation. Three calculated levels fit poorly, but there is no obvious reason to believe they are misassigned. Although the fit improved considerably when these levels were removed, it is still not up to the standard

of $\sigma = \sim 20$ cm^{-1} found for trivalent actinide ions in LaCl$_3$. However it is near the quality found for other U^{4+} ions. Since only energy levels below 15 000 cm^{-1} are assigned here, this work must be considered preliminary.

Acknowledgements

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