The Electronic Structure of Organometallic Complexes of the f Elements. 17. Assignment of the Observed Signals in the Absorption and Magnetic Circular Dichroism Spectra of Quasi-Trigonal-Bipyramidal Complexes Involving the Tris(η^5-cyclopentadienyl)uranium(IV) Moiety

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Received February 25, 1986

The absorption and magnetic circular dichroism (MCD) spectra of the general type $[Cp_3UX_2]^q$ (Cp = η^5-C_5H_5; X = D_2O, SCN^-, $NCBH_3^-$; q = 1+, 1–) were studied at room and low temperatures. For a crystalline field of D_{3h} symmetry the magnetochemically well-confirmed existence of a ground state of Γ_1 symmetry allows in absorption only electric dipole transitions to excited Γ_4 and Γ_6 levels. Both types of transition could be discriminated by using the selection rules of MCD spectroscopy. In addition, the observed signs of the Faraday A terms allow the identification of those Γ_6 levels, the crystal field eigenfunctions of which are dominated by $J_z = \pm 2$ and $J_z = \pm 4$, respectively.

Introduction

Since the fundamental work by Reynolds and Wilkinson[1] the existence of both pseudotetrahedral (ψ-T_d) Cp_3UX and pseudo-trigonal-bipyramidal (tbp) $[Cp_3UX_2]^q$ (q = 1+, 0, 1–) Cp_3U derivatives has been confirmed by numerous structural and spectroscopic results.[2–6]

In 1976 Amberger[7,8] and Amberger and Sienel[9] have attempted to correlate the electronic absorption spectra of various Cp_3UX systems (X = η^5-Cp, η^3-BH_4, Cl) with a calculated crystal field (CF) splitting pattern, assuming an effective CF of T_d symmetry. However, a that time satisfactory arguments for an unambiguous assignment of the observed transitions were lacking. The only criterion in favor of a successful assignment was based on the fact that the energies of the calculated levels did not deviate significantly from the corresponding observed maxima.

It is the aim of this contribution to assign for the first time the CF levels of an organometallic actinide complex on a purely experimental basis. For this first study we preferred the tbp complex type $[Cp_3UX_2]^q$ to the ψ-T_d type because a CF of D_{3h} symmetry notably restricts the number of the allowed forced electric dipole transitions of f–f character.

The $[Cp_3UX_2]^q$ complexes exhibited for different ligands X and charges q, respectively, the same general features in their absorption and MCD spectra, but depending upon the ligand X the individual spectra displayed ranges of different quality. For this reason several anionic, neutral, and cationic $[Cp_3UX_2]^q$ complexes were examined.

The absorption spectra of the ions $[Cp_3U(H_2O)_2]^{+1}$ and $[Cp_3U(D_2O)_2]^+$ (1) exhibit at room temperature relatively broad absorption bands which are frequently accompanied

by weaker and partly resolved vibronic satellites. In order to obtain a better resolution, we studied first of all the low-temperature spectra of several $[Cp_3UX_2]^-$ complexes (X = NCS^- (2), $NCBH_3^-$ (3)) which are soluble in 2-methyltetrahydrofuran (MeTHF) or n-butyronitrile. These solvents freeze as glasses and remain almost transparent down to liquid He temperature.

Experimental Section

Reagents. UCl_4 was prepared by the method of Sutter[10] starting from U_3O_8 and hexachloropropene. Cp_3UCl was prepared by the method of Anderson.[11] Cp_3UNCS and Cp_3UNCBH_3 were synthesized according to a procedure by Fischer et al.[12] by reacting Cp_3UCl with KSCN or $NaNCBH_3$ in degassed H_2O. The tbp complexes [n-Bu_4N][Cp_3UX_2] were synthesized according to ref 12 by reaction of Cp_3UX (X = NCS^- or $NCHB_3^-$) in THF with n-Bu_4NX (X = NCS^- or $NCBH_3^-$). The crude products were purified by washing with air-free water and finally dried at high vacuum. The green cation $[Cp_3U(D_2O)_2]^+$ was produced by dissolving Cp_3UCl in deoxygenated and N_2-saturated D_2O.

Physical Measurements. The absorption spectra were recorded on a Cary Model 17, and the MCD spectra were run within

Table I. Transformation Properties of the Wave Functions of the f^2 System Exposed to a CF of D_{3h} Symmetry

compositn of the eigenvector	J_{even}			J_{odd}		
	a	$\bar{\mu}$	$\bar{\nu}$	a	$\bar{\mu}$	$\bar{\nu}$
		b			b	
		singlets				
$\lvert 0 \rangle$	Γ_1	0	0	Γ_2	0	1
$\lvert +3 \rangle + \lvert -3 \rangle$	Γ_3	3	1	Γ_4	3	0
$\lvert +3 \rangle - \lvert -3 \rangle$	Γ_4	3	0	Γ_3	3	1
$\lvert +6 \rangle + \lvert 0 \rangle + \lvert -6 \rangle$	Γ_1	0	0			
$\lvert +6 \rangle - \lvert -6 \rangle$	Γ_2	0	1			
		doublets				
$\lvert \pm 1 \rangle$	Γ_5	±1		Γ_5	±1	
$\lvert \pm 2 \rangle$	Γ_6	±2		Γ_6	±2	
$\lvert \pm 4 \rangle \pm \lvert \mp 2 \rangle$	Γ_6	±2		Γ_6	±2	
$\lvert \pm 5 \rangle \pm \lvert \mp 1 \rangle$	Γ_5	±1		Γ_5	±1	

a Irreducible representation. *b* Hellwege's crystal quantum numbers.

(1) Reynolds, L. T.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *2*, 246.
(2) Wong, C.; Yen, T.; Lee, T. *Acta Crystallogr.* **1965**, *18*, 340.
(3) Fischer, R. D.; Klähne, E.; Kopf, J. *Z. Naturforsch., Anorg. Chem., Org. Chem.* **1978**, *33B*, 1393.
(4) Bombieri, G.; Benetollo, F.; Bagnall, K. W.; Plews, M. J.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1983**, 45.
(5) Bombieri, G.; Benetollo, F.; Klähne, E.; Fischer, R. D. *J. Chem. Soc., Dalton Trans.* **1983**, 1115.
(6) Jahn, W.; Yünlü, K.; Oroschin, W.; Amberger, H.-D.; Fischer, R. D. *Inorg. Chim. Acta* **1984**, *95*, 85.
(7) Amberger, H.-D. *J. Organomet. Chem.* **1976**, *110*, 59.
(8) Amberger, H.-D. *J. Organomet. Chem.* **1976**, *116*, 219.
(9) Amberger, H.-D.; Sienel, G. R. *Z. Naturforsch., B.: Anorg. Chem., Org. Chem.* **1976**, *31B*, 769.

(10) Hermann, J. A.; Sutter, J. F. *Inorg. Synth.* **1957**, *5* 143.
(11) Anderson, M.; Crisler, L. R. *J. Organomet. Chem.* **1969**, *17*, 345.
(12) Fischer, R. D.; Yünlü, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1369.

Table II. Assignment Procedure of the Terminal Levels of the Observed Transitions

occurrence of a band in the absorption spectrum	occurrence of a Faraday A term	sign of the Faraday A term	symmetry of the excited level	further specification of the excited level
yes	no		Γ_4	
yes	yes	+	Γ_6	$4\alpha^2 > 2\beta^2$
yes	yes	−	Γ_6	$|\pm 2\rangle$; $4\alpha^2 < 2\beta^2$

the ranges 420–1000 and 1000–2000 nm, respectively, by means of the JASCO dichrographs J-500 C and J-200 D in combination with an electromagnet with the maximum field of 13.5 kG. For cooling down the solutions, we used an Air Products LT-3-110 cryostat. In order to prove that the above-mentioned solvents MeTHF and n-butyronitrile did not react with the complexes of interest, we ran the absorption spectra of their KBr pellets at room as well as at low temperature. In general, both types of spectra were almost identical; however, the spectra of the glasses were somewhat better resolved.

Results

General Symmetry Considerations. The $5f^2$ system U^{4+} gives rise to the manifolds $^3H_{4,5,6}$, $^3F_{2,3,4}$, $^3P_{0,1,2}$, $^1G_4$, $^1D_2$, and $^1S_0$, respectively. If the free U^{4+} ion is exposed to a CF of D_{3h} symmetry, these manifolds are split into various CF levels. In table I the composition of the eigenvectors of the resulting CF levels is indicated and correlated with the irreducible representations of the point group D_{3h}. For the sake of completeness, these levels are also characterized in terms of their crystal quantum numbers $\bar{\mu}$ and $\bar{\nu}$,[13] respectively.

With the assumption of both D_{3h} symmetry and an energetically isolated Γ_1 CF ground state (vide infra), only forced electric dipole transitions to excited Γ_4 and Γ_6 levels are allowed in absorption.[13]

Görller–Walrand and Godemont have given the MCD selection rules for right (rcp) and left circulary polarized (lcp) radiation,[14] respectively:

rcp: J_z(terminal) − J_z(initial) = −1 − ρ

lcp: J_z(terminal) − J_z(initial) = +1 − ρ

In the case of D_{3h} symmetry, ρ adopts ± 3.[15] These selection rules may be used to determine the sign of the Faraday A term if the wave function of the initial and the terminal state are known. On the other hand, this relation may also be used to estimate the predominant J_z values of the wave function of the terminal state provided that both the wave function of the initial state and the sign of the Faraday A term are known.

With the assumption of a Γ_1 CF ground state, described by $J_z = 0$ (vide infra), and application of the above-mentioned selection rules, MCD transitions may only be observed if the terminal states are described by the eigenvector $|\pm 2\rangle$ or by the linear combination $\alpha|\pm 4\rangle \pm \beta|\mp 2\rangle$. According to Table I, these functions transform like Γ_6. If $|4\alpha^2| > |2\beta^2|$, the Faraday A curve has a positive sign, while a negative Faraday A term is expected for $|4\alpha^2| < |2\beta^2|$.[13]

Identification of the CF Ground State. The temperature dependence of the paramagnetic susceptibility of $[n\text{-Bu}_4N][Cp_3U(NCS)_2]$ and $[n\text{-Bu}_4N][Cp_3U(NCBH_3)_2]$ has been determined by Kanellakopulos[16] and Edelstein,[17] respectively. Both samples display temperature-inde-

pendent paramagnetism up to ca. 250 K. This feature is indicative of an energetically more isolated singlet ground state than in corresponding ψ-T_d systems.[8,18]

The assumption of an isolated CF ground state is also supported by our observations according to which only a few isolated "hot" bands disappear in the absorption and MCD spectra of **2** and **3** when the solutions are cooled down to liquid He temperature. The ^1H NMR spectra of various tbp complexes are, moreover, in accordance with the existence of a nonmagnetic ground state in that the isotropic shifts of the Cp ring protons are notably smaller than for the ψ-T_d-shaped parent Cp_3UX systems.[6,12,19] Furthermore, the isotropic shifts of the tbp complexes are only weakly temperature-dependent.[6,12,19]

The ground multiplet $^3H_4$ of the free U^{4+} ion is split by a CF of D_{3h} symmetry beside some doublets into the nonmagnetic singlets of Γ_1, Γ_3, and Γ_4 symmetry, respectively (Table I).

In our earlier CF calculations of $Cp_3U^{IV}X^{7-9}$ and $Cp_3Pr^{III}\cdot B$ (B = a neutral base)[20-22] complexes of C_{3v} symmetry, the CF ground states were formulated to first order as $\gamma|+3\rangle + \theta|0\rangle - \gamma|-3\rangle$, with $\theta \gg \gamma$. As in D_{3h} symmetry $|0\rangle$ and $|\pm 3\rangle$ functions cannot be intermixed, it seems most suggestive to ascribe a $|0\rangle$ function of Γ_1 symmetry to the ground state of tbp systems (Table I). Interestingly, the ground states of the corresponding $4f^2$ systems $Cp_3Pr\cdot NCCH_3$ and $Cp_3Pr(NCCH_3)_2$, respectively, are also of Γ_1 symmetry, and the transition from C_{3v}- to D_{3h}-shaped systems makes the ground state energetically even more isolated.[23]

Analysis of the Absorption and MCD Spectra. Forced electric dipole transitions from a Γ_1 ground state are only allowed to excited Γ_4 and Γ_6 states.[13] The MCD selection rules,[14] however, admit only transitions of Faraday A type from Γ_1 to Γ_6. As a Γ_6 eigenfunction is, to first order, described either by $|\pm 2\rangle$ or by a linear combination of the type $\alpha|\pm 4\rangle \pm \beta|\mp 2\rangle$, a positive Faraday A term should correspond to $4\alpha^2 > 2\beta^2$. Hence, a negative Faraday A term should indicate that the final Γ_6 level is described either by $|\pm 2\rangle$ or should result from $4\alpha^2 < 2\beta^2$.

Following these criteria, all "cold" transitions in the absorption and MCD spectra were attributed to either of the three categories as mentioned in Table II.

The entire absorption spectrum may be divided into three sections which will be discussed separately.

2500–2200 nm. To avoid in this spectral range any interference with binary, and even ternary, vibrational combination bands[24] which appear even in the case of perdeuterated solvents, KBr pellets of the samples were

(13) Hüfner, S. *Optical Spectra of Transparent Rare Earth Compounds*; Academic: New York, 1978.

(14) Görller-Walrand, C.; Godemont, J. *J. Chem. Phys.* **1977**, *66*, 48.

(15) Görller-Walrand, C.; Beyens, Y.; Godemont, J. *J. Chem. Phys.* **1979**, *76*, 190.

(16) Kanellakopulos, B., private communications. Yünlü, K. Ph.D. Thesis, Universität Hamburg, 1983, p 123.

(17) Edelstein, N. M., private communication.

(18) Aderhold, C.; Baumgärtner, F.; Dornberger, E.; Kanellakopulos, B. *Z. Naturforsch., A: Phys. Chem., Kosmophys.* **1978**, *33A*, 1268.

(19) Bagnall, K. W.; Plews, M. J.; Brown, D.; Fischer, R. D.; Klähne, E.; Landgraf, G. W.; Sienel, G. R. *J. Chem. Soc., Dalton Trans.* **1982**, 1999.

(20) Amberger, H. D.; Jahn, W.; Edelstein, N. *Spectrochim. Acta, Part A* **1985**, *41A*, 465.

(21) Amberger, H.-D.; Schultze, H.; Edelstein, N. M. *Spectrochim. Acta, Part A* **1985**, *41A*, 713.

(22) Amberger, H.-D.; Yünlü, K.; Edelstein, N. M. *Spectrochim. Acta, Part A* **1986**, *42A*, 27.

(23) Kanellakopulos, B. Lecture, International Rare Earth Conference, Zürich, March 4–8, 1985.

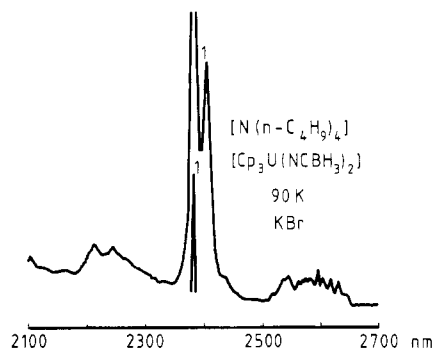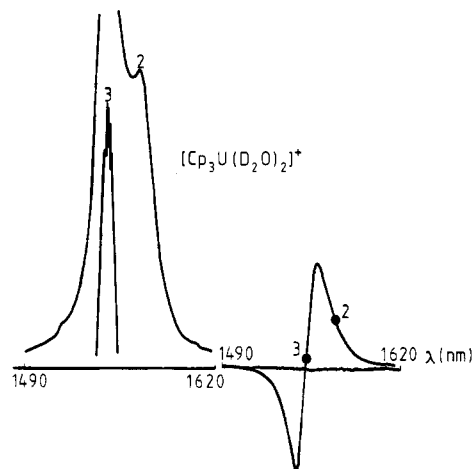(24) Reid, A. F.; Scaife, D. E.; Wailes, P. C. *Spectrochim. Acta* **1964**, *20*, 1257.

Figure 1. The absorption spectrum of [N(n-C$_4$H$_9$)$_4$][Cp$_3$U-(NCBH$_3$)$_2$] within the range 2100–2700 nm (KBr pellet, temperature 90 K).
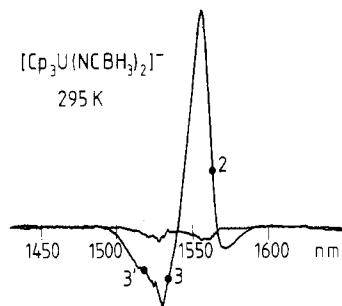

Figure 2. The room-temperature absorption and MCD spectrum of [Cp$_3$U(D$_2$O)$_2$]$^+$ within the range 1490–1620 nm. The dots in the MCD spectrum refer to maxima in the corresponding absorption spectrum. This holds also for Figures 3, 5, 6, 7 and 8.

Figure 3. The room-temperature MCD spectrum of [Cp$_3$U-(NCBH$_3$)$_2$]$^-$ within the range 1430–1650 nm.

Figure 4. The low-temperature (150 K) MCD spectrum of [Cp$_3$U(NCS)$_2$]$^-$ within the range 1450–1650 nm.

Figure 5. The room-temperature absorption and MCD spectrum of [Cp$_3$U(NCBH$_3$)$_2$]$^-$ within the range 1200–1330 nm.
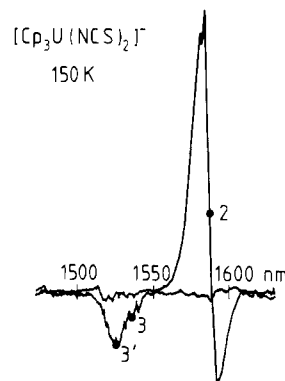
preferred to solutions. MCD studies were prevented both by instrumental limitations and the use of pellets.

At room temperature we observed in the case of samples **2** and **3** one broad, asymmetric band of high intensity along with some weak signals which should correspond to CH combination vibrations of the Cp ring.[24] After being cooled to 90 K, two sharp, intense signals appeared instead of the original broad one which we attribute to the transition $\Gamma_1(^3H_4) \rightarrow {}^3F_2$. With the assumption of a CF of strict D_{3h} symmetry, the excited manifold $^3F_2$ gives only rise to levels of Γ_1, Γ_5, and Γ_6 symmetry. Therefore, the observed intense doublet must be assigned to the transition $\Gamma_1(^3H_4) \rightarrow \Gamma_6(^3F_2)$. Some deviation from ideal D_{3h} symmetry apparently splits the twofold degenerate Γ_6 level into two close-lying components.
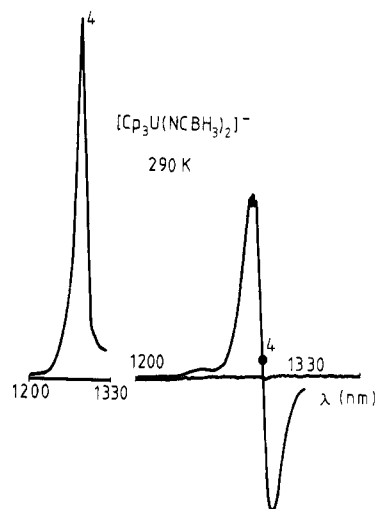
1620–1200 nm. All tbp species exhibit at room temperature two or three very intense bands between 1500 and 1600 nm which are characteristic of this type of coordination.[25] In the case of **1**, band 2 (See Figure 2) has no counterpart in the MCD spectrum, whereas signal 3 corresponds to a negative Faraday A term. For this reason bands 2 and 3 have to be assigned to the transitions $\Gamma_1(^3H_4) \rightarrow \Gamma_4$ and $\Gamma_1(^3H_4) \rightarrow \Gamma_6$, respectively. The Γ_6 wave function should be dominated by $|\pm 2\rangle$. In the case of **3**, the MCD curve of the 1500–1600 nm absorption is relatively diffuse: signal 2 may be explained by a superposition of a strong negative Faraday B term and a weak positive A term, while signals 3 and 3′ seem to correspond to a positive Faraday B term. The MCD spectrum of **2** clearly proves this ten-

tative interpretation. Considering the MCD curves of **2** and **3**, the final states of the transitions 3 and 2 should be correlated with Γ_4 and Γ_6 symmetry, respectively, the Γ_6 state being dominated by $|\pm 4\rangle$. Virtually, this latter assignment seems to contradict the above-mentioned assignment of the transitions 2 and 3.

At room temperature, **1** shows two absorption bands in the range 1250–1300 nm, whereas **2** and **3** exhibit only one signal. After being cooled to liquid He temperature, this signal is split in case of some Cp$_3$UXY complexes but is preserved in the case of **2** and **3**. Band 4 displays a positive Faraday A term and must therefore be ascribed to the transition $\Gamma_1(^3H_4) \rightarrow \Gamma_6$ with dominant $|\pm 4\rangle$.

According to our former tentative CF calculations,[7-9] the absorption bands of organometallic U^{IV} complexes within the range 1620–1200 nm correspond to the transition $^3H_4 \rightarrow {}^3H_5$. Multiplets with $J = 5$ are split by a CF of D_{3h}

(25) Klähne, E. Ph.D. Thesis, Universität Hamburg, 1982.

Table III. Assignment of the Observed "Cold" Absorption and MCD Transitions

band no. in the "cold" absorpn spectrum	occurrence of a Faraday A term in the MCD spectrum	sign of the Faraday A term	terminal state	dominant $|\pm J_z\rangle$
1, 1′			Γ_6	$|\pm 2\rangle$
2	yes	+	Γ_6	$|\pm 4\rangle$
3	no		Γ_4	
4	yes	+	Γ_6	$|\pm 4\rangle$
5			Γ_6	$|\pm 4\rangle$
6	yes	+		
7				
8, 8′	a	$-^a$	$\Gamma_6{}^a$	$|\pm 2\rangle^a$
9				
10				
11	yes	–	Γ_6	$|\pm 2\rangle$
12	yes	+	Γ_6	$|\pm 4\rangle$
13	a	a	a	a
14	yes	–	Γ_6	$|\pm 2\rangle$
15	yes	+	Γ_6	$|\pm 4\rangle$
16	no		Γ_4	
17–26	a			
27	yes	–	Γ_6	$|\pm 2\rangle$

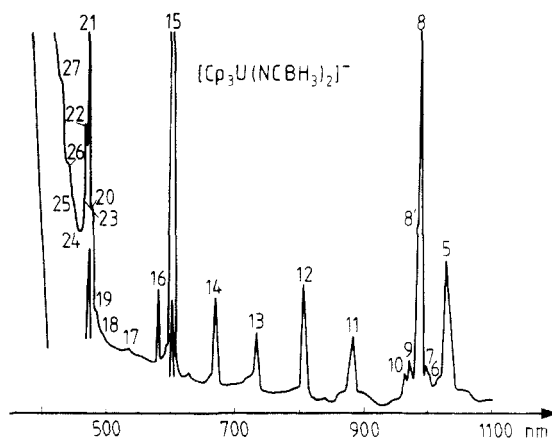^{a}These MCD curves are diffuse, and their nature is unsure. For a more detailed discussion see text.

Figure 6. The low-temperature absorption spectrum (90 K) of [Cp₃U(NCBR₃)₂]⁻ within the range 400–1100 nm.

symmetry into the levels $\Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5 + 2\Gamma_6$ (cf. Table I). One of the two Γ_6 levels is dominated by $|\pm 4\rangle$ and the other by $|\pm 2\rangle$. As signal 4 has to be associated definitely with the final Γ_6 level with dominant $|\pm 4\rangle$ (vide supra), we correlate signal 3 (in Table II) with the Γ_6 level dominated by $|\pm 2\rangle$. This is in accordance with the MCD spectrum of 1 and several other Cp₃UXY complexes, but in contradiction with the MCD spectrum of 2 and 3.

1125–700 nm. Between 1125 nm and the onset of the strong charge-transfer transition, the observed f–f bands are not grouped (Figure 6). We divide this remaining spectral section rather artificially into groups between 1125 and 700 and between 700 and 400 nm, as a change of the detector of the dichrograph J-500 C is necessary around 700 nm.

In the room-temperature absorption spectrum of the tbp species two close-lying weak bands can be observed in the range 1090–1120 nm, the corresponding MCD feature of which resembles a negative Faraday A curve. As both absorptions disappear at low temperatures, they have not been considered in Table III. With the tentative assumption of the same final level for both these bands and the cold signal 5, the initial levels should have an energy separation of some 600 cm⁻¹ from the CF ground state.

At room temperature three relatively broad bands appear in the absorption spectrum between 1050 and 950 nm and two Faraday A terms of different sign in the MCD spectrum. At 90 K the three absorption bands could be
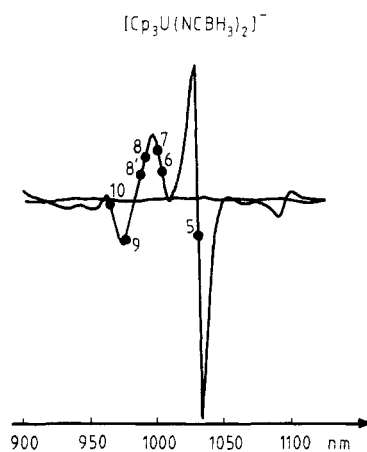

Figure 7. The low-temperature MCD spectrum of [Cp₃U-(NCBH₃)₂]⁻ within the range 850–1070 nm.

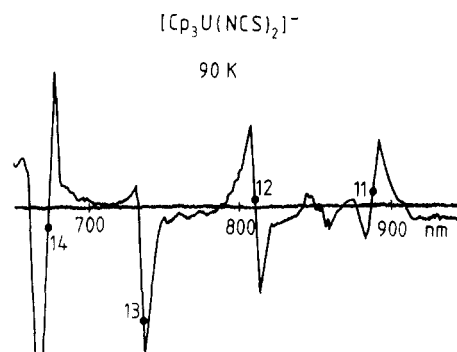**Figure 8.** The low-temperature (90 K) MCD spectrum of [Cp₃U(NCS)₂]⁻ within the range 650–1070 nm.

resolved into at least seven signals, whereas the resolution of the broad *negative* Faraday A term could not be improved considerably at 150 K. Nevertheless, it became more apparent that the weak signal 10 might correspond to a positive Faraday A term, which overlaps partly with the broad negative Faraday A term of 8/8′. According to preliminary CF calculations one Γ_4 and three Γ_6 levels (one with $|\pm 2\langle$ and two with $|\pm 4\rangle$ dominant in the eigenvector) are expected along with three other levels in this range. We tentatively assume that the final level which is responsible for the appearance of 8 and 8′ is split into two components due to small deviations from ideal D_{3h} sym-
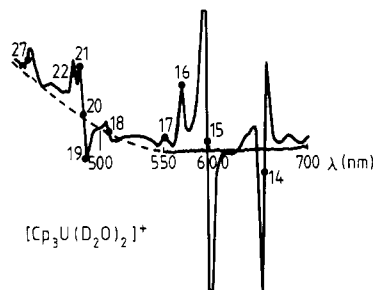
Figure 9. The room-temperature MCD spectrum of [Cp₃U-(D₂O)₂]⁺ within the range 400–700 nm.

Figure 10. The low-temperature (90 K) MCD spectrum of [Cp₃U(NCBH₃)₂]⁻ within the range 420–560 nm.

metry. In the case of sample 3, band 6 has energy separations of 125 and 173 cm^{-1} from 8 and 8′, respectively, band 7 of 130 cm^{-1} from 8′, and band 9 of 126 cm^{-1} from 8′ and of 178 cm^{-1} from 8. These findings may be rationalized if one assumes that the existence of the weak bands 6, 7, and 9 is caused by vibronic coupling effects. For this reason only the signals 5, 8/8′, and 10 have been tentatively assigned in Table III.

Signal 11 appears in absorption as well as in MCD. At room temperature it was difficult to recognize the type of the MCD curve. The low-temperature spectra of 2 and 3 indicate clearly that it corresponds to a negative Faraday term. This means that the final state of this transition must be of Γ_6 symmetry with dominant $|\pm2\rangle$.

Similarly, band 12 can be observed clearly in the absorption spectrum of 1, but only very vaguely in the room temperature MCD spectrum. From the low-tempeature MCD spectra of 2 and 3 it becomes apparent that a positive Faraday A term has to be associated with this transition. This means that the terminal level is of Γ_6 symmetry with a high contribution of $|\pm4\rangle$ in the eigenvector. Band 13 in the absorption spectrum corresponds to a diffuse signal in the MCD spectra of 1, 2, and 3, even at 90 K (in the case of 2 and 3). It may be associated with a positive Faraday A or negative B term.

700–420 nm. Between signals 13 and 14 a weak band could be observed in the room-temperature absorption spectra of 2 and 3 which disappeared at liquid N_2 temperature. With the tentative assumption that this band and signal 14 have the same terminal level, the initial level of this transition should lie some 600 cm^{-1} above the CF ground state.

Band 14 in the absorption spectrum is associated with a negative Faraday A term. According to Table II, it has to be correlated with a transition to a terminal Γ_6 level with a large contribution of $|\pm2\rangle$.

In the room-temperature absorption spectra of 1, 2, and 3 several weaker signals can be observed between the bands 14 and 15. At low temperatures only two of these signals survive. Again, the hot bands are separated some 600 cm^{-1} from the corresponding cold transitions. One of these hot bands gives rise to a positive Faraday A term.

The comparatively strong absorption band 15 has been stated to be highly characteristic of a tbp coordination of the Cp₃U⁺ unit.[25] As this signal corresponds to a positive Faraday A term, it has to be correlated with the transition $\Gamma_1(^3H_4) \rightarrow \Gamma_6$ with dominant $|\pm4\rangle$.

Band 16 in the absorption spectrum corresponds to a negative Faraday B term. In view of Table II, this signal should be due to the transition $\Gamma_1(^3H_4) \rightarrow \Gamma_4$.

All remaining f–f transitions are, both in absorption and in MCD, superimposed on a strong, broad charge transition band. Here, the experimental base line of the MCD spectrum suffers undoubtedly from the high absorbance of the charge transfer. The estimated base line of the pure
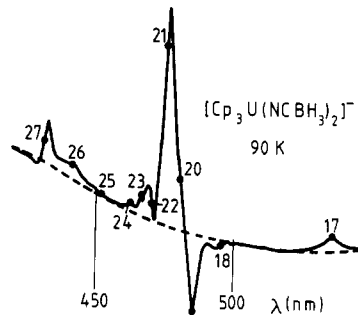
MCD of f–f transitions below 550 nm is indicated as a dotted line. Because of the uncertainty of the base line and the clustering of the CF levels, it is difficult to distinguish the nature of the individual Faraday terms. According to our preliminary CF calculations, only one Γ_4 and three Γ_6 levels (one in which $|\pm4\rangle$, and two in which $|\pm2\rangle$ dominates) are expected within this range. This means that one positive and two negative Faraday A terms, and four allowed absorption bands, respectively, should arise.

In contrast to this expectation only two stronger bands (21 and 27) can be observed aside various shoulders in the absorption spectrum of 3 (90 K). As a few of the shoulders might be of vibronic origin, the absorption spectrum was also run at 30 K in order to detect any thermal depopulation effects of potential hot vibronic bands. However, as the ratios of the intensities of 21 and 20 remained unchanged, transition 20 seems to be of purely electronic origin. This conclusion is further supported by the findings that in the case of 2 signal 20 is distinctly separated from signal 21. The overall MCD curve of the three transitions 19, 20, and 21 may be interpreted either in terms of a positive Faraday A term or of two close-lying Faraday B terms of opposite sign. According to preliminary CF calculations one Γ_4 and two Γ_6 levels (with $|\pm2\rangle$ and $|\pm4\rangle$ dominant) are clustering in this range. Since either interpretation of the MCD curve is consistent with the calculated CF splitting pattern, we are unable to assign any of the signals 19–21 individually. Signal 27 gives rise to a negative Faraday A term and must therefore be correlated with the transition $\Gamma_1(^3H_4) \rightarrow \Gamma_6$ with dominant $|\pm2\rangle$.

Discussion

The optical spectra of [Cp₃UX₂]^q complexes exhibit features comparable to those of the base adducts of the early members of the Cp₃Ln series:[20–22] Strong signals, presumably of forced electric dipole origin, are accompanied by vibronic satellites which are weaker by 1 order of magnitude. Only skeleton vibrations of the Cp₃UX₂ unit seem to be involved in this coupling. Some degenerate levels are split by some 10–30 cm^{-1}, and a few transitions which are strictly forbidden in D_{3h} symmetry are weakly observable, presumably due to weak deviations from this symmetry. Some weak distortion from ideal D_{3h} symmetry has become evident from previous X-ray studies.[3–5]

The results of this paper demonstrate that conclusive assignments of the majority of the spectral transitions of the organoactinide complex type [Cp₃UX₂]^q is not possible in solution until a combined analysis of the pure absorption and the corresponding MCD spectra has been carried out. Essential conditions for such a successful combined treatment are (a) the appearance of well-isolated and unambiguously detectable purely electronic transitions which (b) can reliably be assigned by the selection rules of forced

electric dipole transitions only. In principle, magnetic dipole transitions cannot be ruled out either, but according to all present experience with noncentrosymmetric uranium(IV) systems, their magnetic dipole transitions are by at least 1 order of magnitude weaker than forced electric dipole transitions.[26] The above treatment of various organouranium(IV) systems $[Cp_3UX_2]^q$ seems to provide for the first time[27] a sufficiently large, purely experimental basis for a promising CF analysis with the final aim to

arrive at a better understanding of the still unsolved electronic structure of Cp_3U^{IV} derivatives.] It is hoped to end up in the near future at CF parameter sets which may be optimally correlated with predictions from recently elaborated, purely theoretical treatments.[28]

(26) See: Satten, R. A.; Schreiber, C. L.; Wong, E. Y. *J. Chem. Phys.* 1965, *42*, 162. Nevertheless, in view of the well-established magnetic dipole character of the transition $\Gamma_1(^3H_4) \rightarrow \Gamma_4(^3H_5)$ of Cs_2UX_6 (X = Cl, Br) around 6.300 cm^{-1}, some uncertainty remains for the correct nature of transition 2 in Figures 3 and 4.

(27) We are aware of an earlier, albeit essentially purely descriptive MCD study of uranocene, $(\eta^8\text{-}C_8H_8)_2UIV$, the f–f absorption spectrum of which is, due to the high molecular symmetry, strongly dominated by vibronic satellites: Mowrey, R. L. Ph.D Thesis, University of Virginia, 1976.

(28) Tatsumi, K.; Nakamura, A. *J. Organomet. Chem.* 1984, *272*, 141. Tatsumi, K., personal communication.

(29) **Note added in proof**: Preliminary CF calculations indicate that bands 3 of 1 and 2 of 2 and 3 have to be ascribed to the transition $\Gamma_1(^3H_4) \rightarrow \Gamma_6$, whereas bands 2 of 1 and 3 of 2 and 3 should correspond to the transition $\Gamma_1(^3H_4) \rightarrow \Gamma_4$. The calculated *g* value of the Γ_6 level would lead to a positive Faraday *A* term as found for 2 and 3, but not for 1.

Transition-Metal Sulfur Ylide Complexes. 23.[1] Methylene Transfer from Sulfur Ylides to Transition-Metal Complexes: A Parallel between Sulfur Ylides and Diazomethane in Organometallic Chemistry

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Treatment of $(\eta^5\text{-}C_5H_4R^1)Mn(CO)_2(THF)$ (R^1 = H, Me) with $(Me_2N)(R^2)S(O)$=CH$_2$ (R^2 = Me, Ph) in THF afforded the μ-alkylidene complexes $[(\eta^5\text{-}C_5H_4R^1)(CO)_2Mn]_2CH_2(Mn\text{-}Mn)$ and the ethylene complexes $(\eta^5\text{-}C_5H_4R^1)Mn(CO)_2(C_2H_4)$. With $(C_5Me_5)Mn(CO)_2(THF)$ only the ethylene complex was obtained. The mechanism of the transformations is discussed in comparison to the related reactions between the manganese tetrahydrofuran complexes with diazomethane.

Introduction

An ylide complex can be described as a base-stabilized carbene complex.[2] Thus the stability of ylide complexes of
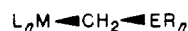
$$L_nM \!\!-\!\!\blacktriangleleft CH_2 \!\!-\!\!\blacktriangleleft ER_n$$

the general type $L_nMCH_2ER_n$ increases with the growing nucleophilicity of the component ER_n and the electron-attracting capability of the transition-metal fragment L_nM.

The reaction of $(CO)_5Cr(CH_2PR_3)$ with tertiary phosphines PR$'_3$ led to CO displacement,[3] whereas sulfur ylide complexes $(CO)_5Cr[CH_2S(O)R^2R^3]$ were converted to phosphonium ylide complexes when treated with PR$_3$.[4] This is rationalized by the inferior donor capacity of a sulfide or sulfoxide in comparison to a phosphine. A kinetic study of the aforementioned reaction revealed that $(CO)_5Cr[CH_2S(O)Me_2]$ underwent irreversible dissociation

into dimethyl sulfoxide and the very reactive carbene complex $(CO)_5Cr$=CH$_2$ which is subsequently trapped by phosphines.[5]

$$(CO)_5Cr[CH_2S(O)Me_2] \xrightarrow[-Me_2SO]{} [(CO)_5Cr\!=\!CH_2] \xrightarrow{+ER_3} (CO)_5Cr[CH_2ER_3]$$
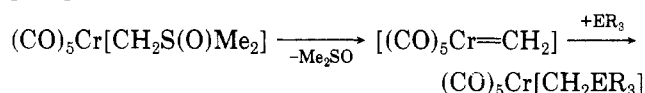
Such a dissociation process should be markedly facilitated when the leaving group tendency of the sulfide component of the sulfur ylide is enhanced as compared to dimethylsulfoxide. Moreover, the generation of a carbene species seems more likely with electron-rich transition-metal fragments which provide additional stabilization to the electron-deficient carbene ligand.[6] In an extreme view it should be possible to generate stable carbene (methylene) complexes from electron-rich metal complexes and stable sulfur ylides.[7]

Here we report on our studies of the reactivity of complexes $(\eta^5\text{-}C_5H_4R^1)(CO)_2Mn(THF)$ (R^1 = H,[8] Me[8]) and

(1) For part 22, see: Weber, L. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* 1985, *B40*, 373.

(2) For reviews see: (a) Weber, L. In The Chemistry of the Metal-Carbon Bond; Hartley, F. R., Patai, S., Eds.; Wiley: Chichester, 1982; p 91. (b) Weber, L. *Angew. Chem.* 1983, *95*, 539; *Angew. Chem., Int. Ed. Engl.* 1983, *22*, 516. (c) Schmidbaur, H. *Angew. Chem.* 1983, *95*, 980; *Angew. Chem., Int. Ed. Engl.* 1983, *22*, 907. (d) Kaska, W. C. *Coord. Chem. Rev.* 1983, *48*, 1.

(3) Knoll, L. *J. Organomet. Chem.* 1979, *182*, 77.

(4) Weber, L. *J. Organomet. Chem.* 1977, *141*, 49.

(5) Fischer, H.; Weber, L. *Chem. Ber.* 1984, *117*, 3340.

(6) For stable Re=CH$_2$ complexes see for example: Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* 1983, *105*, 5804 and references cited herein.

(7) Recently Gladysz demonstrated the reversible formation of the sulfur ylide complex $[(C_5H_5)(NO)(PPh_3)Re\text{-}CH_2SMe_2]^+$ by the addition of Me$_2$S to the cation $[(C_5H_5)(NO)(PPh_3)Re\!=\!CH_2]^+$: McCormick, F. B.; Gladysz, J. A. *J. Organomet. Chem.* 1981, *218*, C57.