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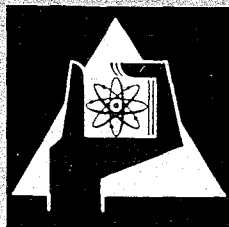
NUCLEAR MAGNETIC RESONANCE SHIFTS
OF PARAMAGNETIC ORGANOMETALLIC ACTINIDE COMPLEXES

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NUCLEAR MAGNETIC RESONANCE SHIFTS
OF PARAMAGNETIC ORGANOMETALLIC ACTINIDE COMPLEXES.
(I) ^{1}H-NMR STUDIES OF URANIUM(IV)TETRACYCLOPENTADIENIDE

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The isotropic ^{1}H-NMR shift of the tetrahedral uranium(IV)tetracyclopentadienide complex has been obtained and the mechanism of the transferred hyperfine interaction between the 5f electrons and the ligands is discussed.

The organometallic actinide complex uranium-(IV)tetracyclopentadienyl $U(C_5H_5)_4$ = "UCp$_4$" [1] should be an interesting object of NMR studies, combining (i) a complex of almost perfect tetrahedral structure, (ii) sufficient chemical stability and (iii) satisfactory solubility even in approximately unpolar solvents with (iv) the existence of two unpaired electrons. According to recent magnetochemical and spectroscopical studies [2], the two unpaired electrons may be considered strongly localized in the apparently still intact 5f shell of the central U(IV) ion. Any observable NMR line positions of the ligand nuclei should therefore be governed by transferred hyperfine (= thf-) interaction effects involving essentially the Fermi contact mechanism.

^{1}H-NMR spectra were throughout taken at room temperature and a frequency of 90 MHz on a Spectrospin spectrometer model HFX, equipped with a Bruker magnet. All samples were prepared and handled under a dry argon atmosphere.

The ring proton shifts of UCp$_4$ and ThCp$_4$ [3] observed in various solvents are given in table 1.

Due to limited solubility, only almost saturated solutions were studied*. All shifts occur upfield from the benzene signal and the high field

* Saturation concentration of e.g. UCp$_4$ in benzene: about 0.9 mg/ml.

Table 1
Chemical shifts of the Cp-protons of UCp$_4$ and ThCp$_4$ (in ppm from internal benzene)

Solvent	UCp$_4$	ThCp$_4$
benzene	20.36	– –
benzene-d$_6$	20.42	1.10
tetrahydrofuran	20.20	0.93
chloroform	– –	0.9 ($\tau = 3.6$) [3]

tetrahydrofuran signal, respectively, which also served as internal standards.

UCp$_4$ shows like ThCp$_4$ only one signal. If we adopt the view that the two lowest crystal field-(= CF-) levels $^1\Gamma_1$ and $^3\Gamma_5$ lie rather close to each other, as derived from the temperature dependence of the magnetic moment [2], the difference of the chemical shifts $[\Delta H(\text{UCp}_4) - \Delta H(\text{ThCp}_4)]/H \equiv \delta$ may be attributed exclusively to the paramagnetic fraction of UCp$_4$ molecules populating the $^3\Gamma_5$ state. At about room temperature, a constant 1:3 mixture** of singlet and triplet state molecules will be approached, the two species probably undergoing very rapid interconversion.

** Contrary to cases definitely dominated by *chemical* equilibria [4], we assume here that the ratio of the two species is essentially given by Boltzmann distribution.

Taking the line position of $ThCp_4$ as representative for that of the diamagnetic UCp_4 molecules, too, by simple linear extrapolation the chemical shift of a fictive sample containing only triplet state molecules should amount to four thirds[*] the difference δ.

Similar to previous results on some paramagnetic Np(V)-systems [6] with the same ground configuration $[Rn]5f^2$, the linewidth of the UCp_4 signal is rather small (around 10 Hz). Narrow NMR-lines of chemically stable paramagnetic samples are usually expected in case of very short electronic relaxation times, in good agreement with the idea of two closely spaced low-lying CF-levels in UCp_4.

From the extrapolated contact shift $\frac{4}{3}\delta$, the thf-interaction parameter A of the triplet state molecule is obtained, see ref. [7], by:

$$\frac{4}{3}\delta = -A \cdot \frac{\gamma_e \cdot g \cdot \beta \cdot S'(S'+1)}{\gamma_H \cdot 3kT} . \tag{1}$$

In eq. (1), γ_e and γ_H are the magnetogyric ratios of the electron and the proton, respectively; β is the Bohr magneton and k Boltzmann's constant. Neglecting small deviations from the Russell-Saunders coupling, the spectroscopic splitting factor g of the lowest $^3\Gamma_5$ state of U(IV) is 2.00 [8]. The effective spin quantum number S' is 1.00 for any spin triplet state. Thence, A for C_6D_6-solution amounts to -0.131 gauss.

In a recent study of the contact shifts of certain dicyclopentadienyl complexes of the 3d-elements [9], a negative sign of A has been associated with unpaired electrons in molecular orbitals composed to a considerable extent of ligand contributions. Considering, however, the apparently still unquenched orbital angular momenta of the 5f-electrons in UCp_4 [2], some properties more specific for f-electron systems might account for the negative sign of A.

For some rare earth complexes, it has been pointed out that the mechanism of the thf-coupling effects may indeed differ considerably from that generally assumed for systems of the nd elements. In particular, a mechanism involving primarily the polarization of outer closed shells such as the 5s and 5p shells rather than a direct 4f-ligand overlap contribution appears important [10]. The situation is likely to be similar in 5f-complexes where again outer closed shells of the central metal may participate in transferring spin density to the ring carbon atoms.

Concerning the spin transfer from each ring carbon atom to its closest proton, in cyclic π-electron systems a mechanism involving configurational interaction (= CI-) is usually assumed. Applying McConnel's familiar equation (2) with the semiempirical

$$A = \frac{Q \cdot \rho_C}{2S'} \tag{2}$$

with proportionality factor $Q = -22.5$ gauss [7], a *positive* spin density $\rho_C = 0.012$ will result for each ring carbon atom, leading to a total spin delocalization over the four Cp-ligands of 24%. A 5f *electron* delocalization of that order seems not readily compatible with the almost unchanged orbital angular momenta of the unpaired electrons. Moreover, both the rather long U - C distance of probably $\geqslant 2.74$ Å (deduced from the corresponding distance known for Cp_3UCl [11]) as compared with e.g. an Fe - C distance in ferrocene of only 2.03 Å [12] and the generally very contracted radial distribution of f-orbitals [13] do not appear favorable for sufficiently strong $5f_U - 2p_C$ overlap[**].

Keeping in mind that Fermi contact shifts towards higher fields $(A < 0)$ will generally result from an odd number of single spin reversal steps (either due to CI- or to polarization mechanism), whereas shifts towards lower fields $(A > 0)$ may be associated both with an even number of spin reversals or any number of direct contact steps (or occasionally of both), the two alternative experimental situations I and II may be visualized schematically as in fig. 1.
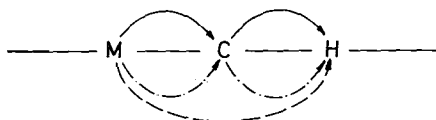
Situation II which obviously applies to UCp_4 may thus alternatively be understood in terms of a predominant polarization step producing first a negative spin density at the ring carbon atoms, and followed by an essentially direct transfer $C \rightarrow H$. Due to the breakdown of a reasonable σ-π-separability to be expected for cyclic π-electron systems fixed in metal complexes, eq. (2) would no longer be rigorously applicable.

A final decision between the two mechanisms in question should, however, be only possible as soon as ^{13}C-NMR spectra will be available.

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[*] Recent examples (some iron(II)-poly(pyrazolyl)-borates [5]) show that the above assumption of exact linearity may be somewhat idealized.
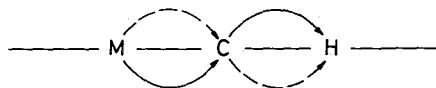
[**] Further support of this view is provided by an analysis of the corresponding group overlap integrals [14]. Recently, however, evidence for a direct spin transfer even in a rather unexpected situation has been reported [15].

I. Shifts to lower fields

M —▸C and C—▸H: spin reversal

M —▸H : direct transfer " through-space"

M —▸C and C—▸H : direct transfer

II. Shifts to higher fields

M —▸C : direct transfer; C—▸H: spin reversal

M —▸C : spin reversal by polarization;

C —▸H: direct transfer

Fig. 1. Schematic representation of possible thf-mechanisms M → C → H. (Arrows above MCH line: $A > 0$; below MCH line: $A < 0$.)

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NUCLEAR MAGNETIC RESONANCE SHIFTS OF PARAMAGNETIC
ORGANOMETALLIC ACTINIDE COMPLEXES.
II. URANIUM(IV)-TRISCYCLOPENTADIENYL-BOROHYDRIDE.

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In a recent study (1) we have compared the isotropic PMR

shifts of the rather symmetric paramagnetic uranium(IV)-tetra-

cyclopentadienide (UCp_4) with that of its diamagnetic thorium(IV)

homologue. In the present note we are considering the PMR spec-

tra of the two related triscyclopentadienyl-borohydride complexes

of U and Th. Due to the presence of the BH_4-ligand, the Cp_3MBH_4

compounds are expected to exhibit signals specific for Cp-ring

protons and for BH_4 protons, respectively, providing independent

information of possibly supplementary character.

EXPERIMENTAL DETAILS AND RESULTS

The two new actinide compounds Cp_3UBH_4 (2) and Cp_3ThBH_4 were

prepared from related halide complexes according to details to

be described separately (3). For further comparison with Cp_3UBH_4,

the diamagnetic zirconium compound $Cp_2Zr(BH_4)_2$ was also prepared,

following exactly ref. 4. At room temperature, all three compounds

are sufficiently soluble in tetrahydrofuran (THF) and even
in deuterobenzene to yield well-resolved spectra as summarized
in table 1.

All further experimental details were essentially the same as
described in (1). Each signal position in table 1 is referred
to benzene as internal standard.

DISCUSSION

1. Cp-Protons

As for the symmetric MCp_4 complexes, also for the borohydride
derivatives only one rather narrow ring proton signal is observed.
This seems to be a general feature of all Cp_3U-X compounds so
far known (5). From the relative intensities found for a
variety of alkoxy-derivatives (5) may be concluded that all
15 ring protons are indeed represented by a single sharp line.
The two experimental intensity ratios listed in table 1 are in
good accordance with these results. As a matter of fact, for
a structure with three <u>centrally</u> bonded Cp-rings as proved by
a crystallographic X-ray study of Cp_3UCl (6), all 15 protons
should be chemically indentical.

Contrary to UCp_4, in all Cp_3UX compounds magnetic dipolar
(=pseudocontact) interactions should become operative in addition
to the isotropic contact mechanism. In any internally rigid
Cp_3UX molecule no unique angle ϑ will be enclosed by the UX-
axis and the individual vectors pointing from the central atom

Table 1

PMR-Shifts of Several Cyclopentadienyl-Borohydride Complexes

Compound	Solvent	PMR-Signal					Intensity ratio of the two bands[d]
		Group I (Cp)		Group II (BH_4)			
		Shift (ppm)	Line-width (c/sec)	Shift (ppm)	Line-width (c/sec)	$|J_{H-B}|$ (c/sec)	
$ZrCp_2(BH_4)_2$	C_6D_6	1.53	–	6.44	29	83.9±1.5	7.5:10 (8.0:10)
$ThCp_3BH_4$	C_6D_6	1.12	–	3.76	14	85.8±1.5	c)
UCp_3BH_4	THF	13.41	2.9	b)	–	–	–
	C_6D_6	13.77	2.4	67.2	20	86.5±1.5	3.75:15 (4.0:15)
$Al(BH_4)_3$ (8)	C_6H_6	–	–	7.0[a]	–	87	–

a) Shift for liquid water as reference
b) BH_4-signal lost in solvent bands
c) Here intensities could not be determined accurately
d) Intensity ratios in parentheses referring to completely equivalent Cp- and BH_4-protons, respectively.

to the ring protons. Thus, due to the geometric factor $3\cos^2 \vartheta - 1$ in the general expression for the dipolar interaction (7), not all 15 ring protons should experience the same overall shift[x].

The appearance of only one sharp line at room temperature suggests therefore a nonrigid structure, allowing fairly rapid ring rotation around the three five-fold axes.

The overall shift $\delta_1 = \Delta H_{C-H}(Cp_3UBH_4 - Cp_3ThBH_4)$ of the ring protons is positive as for UCp_4, but reduced by a factor of ca. 2/3. It is interesting that the line positions of the four Cp_3U-halide complexes are found in a very similar region (5), being possibly due to some pseudo-halide character of the BH_4 ligand. A more detailed discussion of the proton line shifts will be postponed to a forthcoming paper.

2. BH_4-Protons

All three organometallic borohydride complexes show a clear 1:1:1:1 quartet signal unambiguously to be assigned to the BH_4-protons. As far as this quartet structure is concerned, the spectra resemble strongly those of well-known borohydride compounds of main group elements such as $Al(BH_4)_3$ (8) or $LAl(BH_4)_3$ (9, 10), L symbolizing various Lewis Bases. The fine structure of the signal arising from the coupling with the ^{11}B nucleus (I = 3/2) has been explained to simulate four <u>equivalent</u> borohydride protons. Thus, also in the present case, very rapid

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[x] Magnetically non-equivalent protons exist in principle also in any rigid <u>diamagnetic</u> MCp_n complex (n ≥ 3), although the order of magnitude of the dipolar interaction between the ^1H-nuclei of different Cp-ligands turns out to be negligibly small (1).

intramolecular opening and new   formation of M-H-B bonds, most probably via a tunnelling mechanism (8) may be suggested. The almost constant value of the _average_ coupling parameter $|J_{H-B}|$ (table 1), in spite of the very different central atoms, appears likely to confirm this view. The overall shifts of the quartet centers, however, reflect the presence of different central atoms.

It seems, on the other side, premature to conclude from the present results that the lowest minima of the potential hypersurface for the formal BH_4-motion relative to the Cp_3M-group should correspond to a structure involving two M-H-B bridging bonds, as has been established for the aluminium borohydrides (9). Unfortunately, the rather restricted solubility of the three organometallic compounds in conventional solvents prevents at present reasonable PMR-studies at lower temperatures and direct ^{11}B-NMR spectroscopy, respectively.

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PROTON MAGNETIC RESONANCE STUDIES OF PARAMAGNETIC
4f AND 5f SYSTEMS CONTAINING THE CYCLOPENTADIENYL
LIGAND[x].

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While for some paramagnetic cyclopentadienyl complexes of
uranium(IV) the appearance of surprisingly sharp proton
resonance signals has been reported (1, 2), comparable
^{1}H-NMR studies of related organometallic lanthanide complexes
have so far not been performed at all. The purpose of this note
is to give a first brief survey over the results obtained on
solutions of the following systems at room temperature:

(i)   Some adducts Cp_3LnB (where Cp denotes the cyclopentadienyl
ligand C_5H_5, Ln a trivalent rare earth ion and B a neutral
Lewis base molecule);

(ii)   Three base-free Cp_3Ln-complexes which are sufficiently
soluble in benzene or cyclohexane even without the aid
of an additional ligand B;

(iii) Ytterbium complexes of the type $(Cp_2YbL)_2$ where L is
either Cl or NH_2;

(iv)   A number of novel actinide complexes similarly composed
like those mentioned under (1).

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[x] Communication III of the series on "Nuclear Magnetic Resonance
Studies of Paramagnetic Organometallic Actinide Complexes".

A Spectrospin spectrometer model HFX operating at 90 Mc/sec was
used for all measurements, and all samples were prepared and
handled under a dry argon atmosphere. Although proton-carrying
ligands B or L usually give rise to various different resonance
signals, in the tables 1 and 2 only the signals of the Cp-ligands
are considered. The quantity δ is the difference ΔH(sample) -
ΔH(reference) between the actual overall proton shift of the
compound in question and the shift of a diamagnetic reference
sample. For the U(IV)- and Np(IV)-compounds the corresponding
diamagnetic Th(IV) homologues were chosen, and Cp_3Y(III) for
all other systems. Since all attempts to prepare also a Cp_3Th(IV)-
cation have so far been unsuccessful, the signal of the Cp_3U(IV)-
cation in aqueous solution (3) was referred to that of Cp_3ThCl
dissolved in THF, too. All adducts denoted in table 1 by an
asterisk have been prepared only recently according to standard
procedures (4), and further properties will be published else-
where.
The following abbreviations were used in the tables:
Nic = (-)-nicotine, N-Me-Pyrr = N-methyl-pyrrolidine, Pyr =
pyridine, THF = tetrahydrofuran and 2-Me-THF = 2-methyl-tetra-
hydrofuran (CNC_6H_{11} = cyclohexyl-isonitrile).
From all 4f- and 5f-systems so far investigated only Cp_3Gd,
$NpCp_4$ (5) and $PaCp_4$ (6) did not show any detectable resonance
at all. All other systems give rise to only one ring proton
signal, indicating that at least at room temperature fairly
rapid internal ring rotation must be assumed, unless the magnetic
dipolar interactions are negligibly small. The total of signals
listed in table 1 varies over more than two orders of magnitude
both as far as the δ-values and the line widths are concerned.
While within each series of adducts Cp_3LnB with one fixed Ln-ion
noticeably similar absorption parameters occur for different
ligands B, it seems to depend very individually on the central
ion whether or not remarkable changes go along with the transi-
tion : Cp_3Ln $\longrightarrow$ Cp_3LnB. It may be deduced from the data

Table 1

Cp-Proton Shifts of Systems with three Cp-Ligands

f^n	Metal 4f	5f	Ligand other than Cp	Solvent	δ(ppm)	Line width (c/sec)
f^2	Pr(III)	-	-	THF	-7.73	4.3
	"		-	2-Me-THF	-7.88	3.0
	"		Nic[x)	C_6H_6	-7.58	6.0
		U(IV)	F (7)	C_6D_6	+12.6	3.2
		"	Cl (3)	"	+ 9.56	1.5
		"	Br (7)	"	+ 9.79	1.1
		"	J (7)	"	+10.4	1.3
		U(IV)$^\oplus$	- (3)	H_2O	+ 6.40	1.0
f^3	Nd(III)		-	THF-d_8	+ 3.22	27
	"		N-Me-Pyrr[x)	C_6H_6	+ 3.22	34
	"		CNC_6H_{11} (4)	"	+ 3.32	27
	"		Nic[x)	"	+ 3.33	26
		Np(IV)	Cl (8)	C_6D_6	+27.4	30
f^5		Pu(III)	- (9)	THF	- 5.24	66
		"	Nic[x)	C_6D_6	- 5.61	76
f^{10}	Ho(III)		-	C_6D_6	-197	200
	"		CNC_6H_{11} (4)	"	-137	145
	"		-	THF	-134	130
f^{12}	Tm(III)		-	C_6D_6	+164	220
	"		-	THF-d_8	+ 69	160
	"		Nic[x)	C_6D_6	+ 60.5	65
	"		CNC_6H_{11} (4)	"	+ 55.1	65

Table 1 continued

| f^n | Metal | | Ligand | Solvent | δ(ppm) | Line |
	4f	5f	other than Cp			width (c/sec)
f^{13}	Yb(III)		-	C_6D_{12}	+59	300
	"		-	C_6D_6	+56	290
	"		-	THF	+54	280
	"		Pyr (10)	C_6D_6	+52	270
	"		CNC_6H_{11} (4)	"	+51	290

Table 2

Cp-Proton Shifts of Systems $(Cp_2YbL)_2$

Ligand L	Solvent	δ(ppm)	Line width (c/sec)
NH_2	THF	+ 21.4	50
NH_2	C_6D_6	+ 24.0	45
Cl	THF	+ 47.8	245
Cl	C_6D_6	+ 74.0	260

in table 1 that in THF- and 2-Me-THF-solution throughout adduct
formation with the cyclic ether has taken place. It is particularly
surprising that all Yb(III)-complexes containing three Cp-ligands
give rise to fairly similar proton shifts, whereas by changing L
in $(Cp_2YbL)_2$-complexes, or simply by variation of the solvent, both
parameters are noticeably affected. For all groups of compounds

with almost constant ^{1}H-NMR-line positions also remarkably similar electronic absorption spectra are found in the region of the f-f-transitions. The reverse is true for Cp_3Tm and its derivatives Cp_3TmB as well as for the corresponding Ho(III)-systems.

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