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Electronic structures of organometallic complexes of f elements. XLIV. Parametrization of the crystal field splitting pattern of $[(MeCp)_3PrCl]^-$

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Abstract

The absorption and magnetic circular dichroism spectra of $[N(n\text{-}Bu)_4]^+[(MeCp)_3PrCl]^-$ dissolved in 2-MeTHF were measured at room and at low temperatures. On the basis of these spectra the crystal field splitting pattern could be derived. The parameters of an empirical Hamiltonian were fitted to the energies of 42 levels to give an r.m.s. deviation of 23 cm^{-1}. From the crystal field parameters obtained the crystal field strength of the ligand collective was estimated. Compared with neutral $Cp_3Pr{\cdot}B$ complexes the crystal field strength of the anionic $[(MeCp)_3PrCl]^-$ moiety is unusually low. © 1998 Elsevier Science S.A.

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1. Introduction

During the latest decade we parametrized the crystal field (CF) splitting patterns of a number of neutral adducts derived from the tris (η^5-cyclopentadienyl)lanthanide (Cp_3Ln) moiety assuming an effective CF of C_{3v} symmetry [1,2]. However, up to now, $[Cp_3PrNCS]^-$ is the only anionic $[Cp_3LnX]^-$ complex, where a successful CF analysis of the optical spectra has been reported [3]. Interestingly, the CF parameter B_0^2 of this anionic complex is reduced by approximately 30%, but the remaining CF parameters are nearly identical with those of $Cp_3Pr{\cdot}$MeTHF [3,4]. In order to examine if this finding is accidental or a more general property of anionic $[Cp_3LnX]^-$ complexes we plan to parametrize the experimentally derived CF splitting patterns of various anionic $[Cp_3LnX]^-$ complexes ($X{=}Hal^-$, OMe^-, Me^-, $C_6H_5^-$).

In the framework of this contribution we focus on $[N(n\text{-}Bu)_4]^+$ $[(MeCp)_3PrCl]^-$ (**1**) as this compound is not only more stable than $[N(Me)_4]^+[Cp_3PrCl]^-$ but is also soluble in polar solvents such as 2-MeTHF, DMSO or CH_2Cl_2. The concentration of **1** dissolved in the above-mentioned solvents is sufficient for recording magnetic circular dichroism (MCD) spectra, which allow a correlation of the observed signs of Faraday A terms with the composition of the wave functions of initial and terminal levels of the transitions under consideration [5].

2. Experimental details

Compound **1** was synthesized according to the procedure of Breitbach [6] by reacting 2.2 mmol of $(MeCp_3)Pr$ dissolved in 25 ml toluene with 2 mmol of $[N(n\text{-}Bu_4)]Cl$. After stirring for 3 h at room temperature the precipitated **1** was filtered, washed with 5 ml of toluene and dried for 1 h under high vacuum. Because of the extreme air and moisture sensitivity of **1** the synthesis, as well as the handling (preparation of solutions, pressing of pellets, loading of the cryostat), was done in a glove box.

The absorption and MCD measurements were performed as described elsewhere [4,5].

3. Symmetry considerations

All previously analyzed neutral $Cp_3Pr{\cdot}B$ adducts (B= neutral base) as well as $[Cp_3PrNCS]^-$ had a CF ground state of A_1 symmetry the wave function of which is described to first order by $A|0\rangle \pm B|\pm 3\rangle (A \gg B)$ [1,3–5]. Thus we assume that this holds also for **1**.

With an A_1 CF ground state, transitions to terminal

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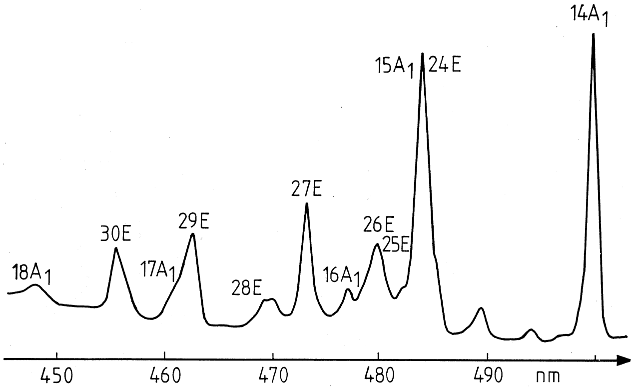

Fig. 1. The low temperature (30 K) absorption spectrum of [N(n-Bu)$_4$][(MeCp)$_3$PrCl] dissolved in 2-MeTHF within the range 445–503 nm.

levels of A_1 and E symmetry are allowed in the low temperature absorption spectrum [7]. In Ref. [8] we indicated the crude composition of the wave functions of E levels for an f^2 system exposed to a CF of C_{3v} symmetry. Additionally, we gave the correlation of the observed signs of the Faraday A terms in the MCD spectrum with the composition of the terminal E levels, provided the initial level of A_1 symmetry is described by the above-mentioned wave function [8].

4. Results

4.1. Absorption and MCD spectra

Comparing the absorption spectra of powdered **1** and **1** dissolved in polar solvents such as CH$_2$Cl$_2$, DMSO and 2-MeTHF only slight differences can be detected. As the latter solvent is freezing as a glass and thus allows the recording of low temperature absorption (s. Fig. 1) and MCD spectra (cf. Fig. 2) of solutions we focus on **1** dissolved in 2-MeTHF. However, due to binary CH

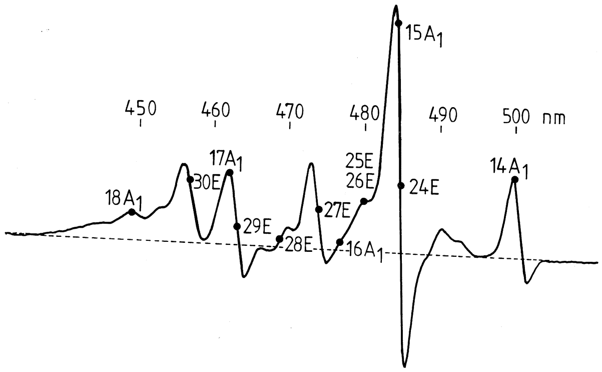

Fig. 2. The low temperature (90 K) MCD spectrum of [N(n-Bu)$_4$][(MeCp)$_3$PrCl] dissolved in 2-MeTHF within the range 432–510 nm. The observed maxima in the absorption spectrum are indicated by dots.

Table 1
Calculated and experimental energy levels for [N(n-Bu)$_4$][Cp$_3$PrCl] dissolved in 2-MeTHF

SLJ comp.[a]	CF state[b]	E_{calc} (cm^{-1})	E_{obs} (cm^{-1})
$^3H_4$	1A$_1$	0	0
$^3H_4$	1E	51	52[c,d]
$^3H_4$	1A$_2$	172	
$^3H_4$	2E	197	199[c]
$^3H_4$	3E	516	486[c]
$^3H_4$	2A$_1$	647	641[c]
$^3H_5$	2A$_2$	2145	
$^3H_5$	4E	2169	
$^3H_5$	5E	2257	
$^3H_5$	3A$_1$	2300	
$^3H_5$	6E	2505	
$^3H_5$	3A$_2$	2619	
$^3H_5$	7E	2630	
$^3H_6$	4A$_1$	4193	4184[d]
$^3H_6$	8E	4221	
$^3H_6$	4A$_2$	4269	
$^3H_6$	9E	4322	4310[d]
$^3H_6$	5A$_1$	4485	
$^3H_6$	10E	4661	4675[d]
$^3H_6$	5A$_2$	4721	
$^3H_6$	11E	4894	4892
$^3H_6$	6A$_1$	4977	5008
$^3F_2$	12E	5040	5051
$^3F_2$	13E	5254	5243
$^3F_2$	7A$_1$	5344	5320
$^3F_3$	6A$_2$	6171	
$^3F_3$	14E	6436	6443
$^3F_3$	15E	6596	6530
$^3F_3$	8A$_1$	6622	6653
$^3F_3$	7A$_2$	6632	
$^3F_4$	16E	6489	6835
$^3F_4$	9A$_1$	6883	6854
$^3F_4$	17E	6958	6958
$^3F_4$	10A$_1$	6967	6958
$^3F_4$	18E	7003	6998
$^3F_4$	8A$_2$	7078	
$^1G_4$	19E	9583	9597
$^1G_4$	11A$_1$	9665	9662
$^1G_4$	20E	9805	9794
$^1G_4$	12A$_1$	9841	9872
$^1G_4$	21E	10 237	10 215
$^1G_4$	9A$_2$	10 426	
$^1D_2$	22E	16 323	16 289
$^1D_2$	23E	16 428	16 426
$^1D_2$	13A$_1$	16 597	16 603
$^3P_0$	14A$_1$	20 014	20 008
$^3P_1$	10A$_2$	20 450	20 437
$^3P_1$	24E	20 656	20 661
$^1I_6$	15A$_1$	20 673	20 661
$^1I_6$	25E	20 742	20 747
$^1I_6$	26E	20 875	20 842
$^1I_6$	16A$_1$	20 936	20 964
$^1I_6$	11A$_2$	21 010	
$^1I_6$	27E	21 093	21 133
$^1I_6$	28E	21 326	21 313
$^3P_2$	29E	21 631	21 622
$^1I_6$	17A$_1$	21 691	21 706
$^1I_6$	12A$_2$	21 786	
$^3P_2$	30E	21 955	21 954
$^3P_2$	18A$_1$	22 285	22 321
$^1S_0$	19A$_1$	45 393	

[a] Largest eigenvector component. [b] CF state (C_{3v} symmetry). [c] From 'hot' transitions. [d] From the absorption spectrum of a pellet.

combination vibrations this solvent absorbs strongly at higher wavelengths than 2250 nm. For this reason the relatively weak signals of the transition $^3H_4 \rightarrow {}^3H_6$ are partly obscured. In this range we extract the band positions from the absorption spectrum of a KBr pellet of **1**.

The absorption and MCD spectra of **1** resemble closely, at both low and high temperatures, those of neutral $Cp_3Pr\cdot B$ adducts [4,5]; however, the individual groups of f–f transitions extend over a considerably narrower range. This finding is a strong hint that essentially the same ordering of CF levels is maintained, but the CF strength is noticeably reduced if one replaces a neutral by an anionic base.

4.2. Simulation of the CF splitting pattern

Assuming strict C_{3v} symmetry of the effective CF and making use of the selection rules for absorption transitions and the observed signs of the Faraday A terms in the MCD spectra (see Section 3) the experimental CF splitting pattern as given in Table 1 could be derived.

The parameters of an empirical Hamiltonian $H=H_{FI}+H_{CF}$ were fitted to this experimental CF splitting pattern. Details of H_{FI} are given elsewhere [9], and H_{CF} is defined by $H_{CF}=B_0^2C_0^{(2)}+B_0^4C_0^{(4)}+B_3^4(C_{-3}^{(4)}-C_3^{(4)})+B_0^6C_0^{(6)}+B_3^6(C_{-3}^{(6)}-C_3^{(6)})+B_6^6(C_{-6}^{(6)}+C_6^{(6)})$ [10], where the B_q^k values represent the free CF parameters and the $C_q^{(k)}$ values the tensor operators, respectively. In order to limit the number of free parameters α, β, γ, the M^k and P^k parameters were fixed at the values used for the analysis of $Cp_3Pr\cdot MeTHF$ [4]. The remaining parameters were allowed to vary. For 42 assignments the r.m.s. deviation was 23 cm^{-1}. Table 2 gives the final values for the free ion and CF parameters. For comparison purposes parameters for the Pr^{3+} free ion [11], $Cp_3Pr\cdot MeTHF$ [4] and $[Cp_3Pr\cdot NCS]^-$ [3] are also listed.

5. Discussion

Comparing the parameters of **1** with those of $[Cp_3Pr\cdot NCS]^-$ and $Cp_3Pr\cdot MeTHF$ (see Table 2) it becomes apparent that B_0^2 of the anionic complexes is indeed unusually low. The remaining CF parametes of **1**, however, differ noticeably from those of $[Cp_3Pr\cdot NCS]^-$ or $Cp_3Pr\cdot MeTHF$. Thus, the scarcely varying B_q^k parameters (with the exception of B_0^2) of the two latter compounds is only accidental.

The parameter

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

is considered as a relative measure of the CF strength of the collective of ligands [12]. Inserting the CF parameters

Table 2
Parameter values[a] for $[(MeCp)_3PrCl]^-$, $[Cp_3PrNCS]^-$, $Cp_3Pr\cdot MeTHF$ and Pr^{3+} as the free ion (in cm^{-1})

Parameter	$[(MeCp)_3PrCl]^-$	$[Cp_3PrNCS]^{-}$ [b]	$Cp_3Pr\cdot MeTHF$ [c]	Pr^{3+} [d]
F_2	66 153	66 200	66 207	71 822
F_4	49 086	49 457	49 148	51 827
F_6	32 244	32 677	32 546	33 890
ζ_{4f}	743.0	741.7	742	766
α	(23.1)	(23.1)	(23.1)	23.9
β	(−757)	(−757)	(−757)	−599
γ	(1534)	(1534)	(1534)	(1400)
M^0	(1.76)	(1.76)	(1.76)	—[e]
M^2	(0.99)	(0.99)	(0.99)	—[e]
M^4	(0.67)	(0.67)	(0.67)	—[e]
P^2	(275)	(275)	(275)	166
P^4	(206)	(206)	(206)	—[e]
P^6	(138)	(138)	(138)	—[e]
B_0^2	−840	−868	−1200	
B_0^4	808	1218	1301	
B_0^6	163	519	486	
B_3^4	310	294	290	
B_3^6	942	742	842	
B_6^6	−1849	−2010	−2032	
$N_v/\sqrt{4\pi}$	948	1030	1148	
β	0.921	0.922	0.922	
β'	0.970	0.968	0.969	

[a] Values in parentheses were not freely varied.
[b] From Ref. [3].
[c] From Ref. [4].
[d] From Ref. [11].
[e] Values for these parameters not given in Ref. [11].

of **1**, $[Cp_3Pr\cdot NCS]^-$ and $Cp_3Pr\cdot MeTHF$ into this relation one ends up with considerably lower

$$\frac{N_v}{\sqrt{4\pi}}$$

values for the anionic complexes (see Table 2). The nephelauxetic and relativistic nephelauxetic parameters β and β' (defined by $\beta = F^2(\text{complex})/F^2(\text{free ion})$, and $\beta' = \zeta_{4f}(\text{complex})/\zeta_{4f}(\text{free ion})$), however, are nearly identical for all three compounds (see Table 2).

6. Conclusions

With $[(MeCp)_3PrCl]^-$ a compound has been analyzed, where the LnX bond is of predominant ionic character. $[(MeCp)_3PrF]^-$ exhibits comparable optical spectra, but those of $[Cp_3PrCH_3]^-$ and $[Cp_3PrC_6H_5]^-$ are noticeably different (C. Guttenberger, B. Unrecht, H.-D. Amberger, unpublished results). Possibly, this is a first experimental confirmation of the results of previous model calculations on Cp_3UCH_3, where a predominant ionic UCp, but an essentially covalent UCH_3 bond has been claimed [13].

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