Vol. 90 (1996) *ACTA PHYSICA POLONICA A* No. 1

Proceedings of the 2nd Winter Workshop S&SRES'96, Polanica Zdrój 1996

ELECTRONIC STRUCTURE OF ORGANOMETALLIC COMPLEXES OF *f* ELEMENTS. ARE MOLECULAR ORBITAL CALCULATIONS A USEFUL TOOL FOR SPECTROSCOPISTS?

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The crystal field parameters of base-free $(Me_3SiC_5H_4)_3Pr$, $(C_5H_5)_3Pr{\cdot}NCCH_3$, $(C_5H_5)_3La(NCCH_3)_2$:Pr, $[Pr(C_8H_8)]^+$ and $Nd[N(SiMe_3)_2]_3$ as model compound for $Nd[CH(SiMe_3)_2]_3$ were inserted into the corresponding energy matrices of a model spin-free f^1 system. Diagonalizing these matrices the crystal field splitting patterns of the *f* orbitals were calculated. These experimentally based molecular orbital schemes are compared with the results of previous model calculations.

PACS numbers: 03.65.Sq, 71.70.Ch

1. Introduction

Homoleptic organometallics of the *f* elements may be separated into complexes with a σ bond between the central ion and one carbon atom of the ligand and into compounds with bonds between the central ion and the π orbitals of the ligand [1,2]. Ligands of π type may have open structures like η^3-allyl or η^5-(2,4-dimethyl)pentadienyl or cyclic structures like η^5-cyclopentadienyl (Cp), η^6-arene, η^7-cycloheptatrienyl or η^8-cyclooctatetraenyl (COT). During the latest decades the interest of synthetic chemists, spectroscopists and theorists was mainly focused on *f* element organometallics with unsubstituted, permethylated and trimethylsilyl substituted Cp and COT ligands [1–5].

Usually, Cp and COT complexes of the lanthanides and actinides are obtained as powders or poorly crystallizing oils. Thus their optical properties can be studied only in solution, as mulls or as pellets. For this reason the additional information of optical measurements of oriented single crystals is missing and enormous assignment problems of the observed signals arise. In principle these problems may be overcome:

(a) by applying advanced spectroscopic methods like magnetic circular dichroism (MCD) spectroscopy to liquids, viscous oils or solutions [6],

(b) by growing single crystals (where the individual molecules in the unit cell have to be aligned) and recording their linear dichroism [7], and if these experimental assignment procedures cannot be applied,

(c) by performing more or less complicated model calculations [8–10].

Numerous quantum chemical approaches have been applied to organometallics of the f elements [8–10]. The methods range from simple angular overlap (AOM) and INDO via quasi relativistic DV-X$_\alpha$ calculations to complex relativistic core potential spin–orbit CI studies [8–10].

It is the principal purpose of this paper to check whether the results of model calculations would be a useful tool for interpreting the optical spectra of organometallics of the rare earths. In order to do so, we plan to derive the crystal field (CF) splitting patterns of selected complexes by applying the above-mentioned experimental methods. Subsequently the parameters of an empirical Hamiltonian (see Sec. 2.2) will be fitted to the experimentally derived CF splitting patterns. The applicability of the results of molecular orbital (MO) calculations for assignment purposes will be examined in cases:

(a) where the number of CF parameters is equal to the number of linearly independent energy differences of f type orbitals, by extracting the CF parameters from calculated MO schemes and to compare these parameters with those of the fits,

(b) where the number of CF parameters is greater than the number of linearly independent energy differences, by comparing calculated and experimentally based MO schemes.

2. Procedure

2.1. Selection rules

Usually, the appearance of a "cold" band in the absorption spectra of liquids, viscous oils, solutions or sublimed films provides little information on the nature of initial and terminal levels. The corresponding signal of Faraday A type in the MCD spectrum, however, frequently allows the identification of the terminal level, if both the wave function of the initial CF state and the sign of Faraday A term are known [11]. Likewise the wave function of an excited initial CF state can be estimated if the wave function of the terminal level and the sign of the Faraday A term of this transition are known.

Detailed analyses of the magnetochemical and optical properties of pseudo(ψ)-trigonal planar $(Me_3SiCp)_3Pr$, ψ-trigonal pyramidal $(C_5H_5)_3Pr\cdot NCCH_3$, ψ-trigonal bipyramidal $Cp_3La(NCCH_3)_2$:Pr, and ψ-trigonal pyramidal $Pr[N(SiMe_3)_2]_3$ have shown that the wave functions of the CF ground states of all these compounds are approximately described by $J_z = 0$ [12–15]. The CF state of Γ_1 symmetry which arises from $^3P_0$ is also described by $J_z = 0$ [16].

Applying the selection rules for forced electric dipole transitions in the MCD spectrum [17]:

right circularly polarized radiation: $J_z(\text{terminal}) - J_z(\text{initial}) = -1 - q$, (1)

$$\text{left circularly polarized radiation: } J_z(\text{terminal}) - J_z(\text{initial}) = +1 - q \qquad (2)$$

($q = \pm 3$ for D_{3h} symmetry; $q = 0, \pm 3, \pm 6$ for C_{3v} symmetry [18]), terminal levels of cold as well as initial levels of hot transitions terminating at $\Gamma_1(^3P_0)$ of the above-mentioned complexes may be easily identified if they give rise to positive or negative Faraday A terms.

If single crystals are available (where the molecules in the unit cell are aligned) usually different selection rules hold for α, σ and π orientation of the principal molecular axis, the propagation direction of electromagnetic radiation and the direction of electric field vector [19].

2.2. Crystal field model

In the framework of the so-called "phenomenological" or "parametric" model the free parameters of an empirical Hamiltonian $\hat{H}$ are fitted to the experimentally derived energies of CF levels. $\hat{H}$ is usually split into two terms $\hat{H}_{\Pi}$ and $\hat{H}_{\mathrm{CF}}$ which consider the interactions within the central ion [20] and the effects of the CF [21], respectively. The CF Hamiltonians for C_{3v} and D_{3h} symmetry which are of interest in this work are given by

$$\hat{H}_{\mathrm{CF}}(C_{3v}) = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_3^4 (C_{-3}^{(4)} - C_3^{(4)}) + B_0^6 C_0^{(6)}$$
$$+ B_3^6 (C_{-3}^{(6)} - C_3^{(6)}) + B_6^6 (C_{-6}^{(6)} + C_6^{(6)}), \qquad (3)$$

$$\hat{H}_{\mathrm{CF}}(D_{3h}) = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_0^6 C_0^{(6)} + B_6^6 (C_{-6}^{(6)} + C_6^{(6)}). \qquad (4)$$

The B_q^k represent the free CF parameters and the $C_q^{(k)}$ — the irreducible tensor operators [21].

The parameter

$$\frac{N_v}{\sqrt{4\pi}} = \sqrt{\sum_{k,q} \frac{1}{2k+1} (B_q^k)^2} \qquad (5)$$

may be considered as a measure of the relative CF strengths of ligand surrounding the metal ion [22].

2.3. "Experiment based MO schemes" in the f range

By inserting the CF parameters of the fits into the energy matrices of the corresponding spin-free f^1 system and diagonalizing these matrices the "experimentally based MO scheme" in the f range [8] were obtained.

In case of systems with higher symmetry (D_{8h}, C_{8v}, D_{3h}) the number of linearly independent energy differences of f type orbitals in the MO scheme is equal to the number of free CF parameters. In these cases "calculated" CF parameters can be extracted from the calculated MO scheme by setting the differences of calculated f orbital energies equal to the differences of eigenvalues obtained from the energy matrix of the corresponding spin-free f^1 system [8].

2.4. Results of model calculations

The results of MO calculations used here were either taken from published tables or obtained upon request from the authors. In some rare cases, where the numerical values were not available, the energies of *f* type orbitals were extracted from published graphs.

3. Results

3.1. π complexes

3.1.1. Complexes derived from the tris(η^5-cyclopentadienyl)lanthanide(III) (Cp_3Ln) moiety

3.1.1.1. Basefree substituted Cp_3Ln

Basefree unsubstituted Cp_3Ln and $(MeCp)_3Ln$ complexes, respectively, crystallize as polymeric or oligomeric species [1,2]. However, by introducing one or two considerably bulkier substituents than the methyl group such as *t*-butyl or trimethylsilyl (Me_3Si), monomeric pseudotrigonal planar (ψ-D_{3h}) species are formed [23,24].

In this contribution we focus on $(Me_3SiCp)_3Pr$. At very low temperatures this compound exhibits temperature independent paramagnetism, thus indicating a nonmagnetic singlet CF ground state. The observed low intensities of the absorption transition which starts at the CF ground state and terminates at Γ_1 ($^3P_0$), and of the corresponding inverse luminescence transition are consistent with a CF ground state of Γ_1 symmetry [12]. Applying the selection rules for forced electric dipole transitions [17–19] to the observed low temperature absorption and MCD spectra, respectively a couple of excited CF states of Γ_4 and Γ_6 symmetry could be identified and associated with their dominant component of $\pm J_z$ in the eigenvector.

Whereas the luminescence spectra of most Pr^{III} organometallics are dominated by transitions which initiate from $^3P_0$ [13,14], the most intense group of $(Me_3SiCp)_3Pr$ corresponds to the transitions from 13 $\Gamma_6(^1D_2) \rightarrow {}^3H_4$. With an initial Γ_6 state induced electric dipole transitions are allowed to terminal states of Γ_1, Γ_2, Γ_5 and Γ_6 symmetry [19]. For this reason the energies of CF states of these symmetries arising from $^3H_4$ could be extracted with high precision from the cold luminescence spectrum.

The parameters of the above-mentioned empirical Hamiltonian were fitted to the energies of 24 CF states to give a root mean square derivation of 21.4 cm^{-1}. Although this value looks excellent, we believe that the CF parameters are only poorly defined, as essentially only the energies of excited Γ_4 and Γ_6 states were fitted.

On the basis of the CF parameters obtained (see Table I) we calculated the CF pattern of the corresponding fictive spin-free f^1 system. In Fig. 1 this experiment based CF splitting pattern is compared with the results of calculations for fictive trigonal planar Cp_3Pr [25]. Obviously, the calculated total splitting of *f* orbitals is a factor of 2 greater than the experimental one.

If one extracts the CF parameters from the MO scheme one arrives at $B_0^2 = -3486\ cm^{-1}$, $B_0^4 = 3044\ cm^{-1}$, $B_0^6 = 825\ cm^{-1}$ and $B_6^6 = -5919\ cm^{-1}$. The

TABLE I

Parameter values for (Me$_3$SiCp)$_3$Pr, Cp$_3$Pr·NCCH$_3$, Cp$_3$La(NCCH$_3$)$_2$:Pr and [Pr(COT)]$^+$. All values in cm^{-1}.

Parameter	(Me$_3$SiCp)$_3$Pr[a]	Cp$_3$Pr·NCCH$_3$[b]	Cp$_3$La(NCCH$_3$)$_2$:Pr[c]	[Pr(COT)]$^+$[d]
F^2	66268	66010	66546	66241
F^4	48718	49092	49017	49254
F^6	33016	32506	32459	32507
ζ_{4f}	746	743	748.5	748.8
α	(23.1)[e]	21.1	(22.9)	21.1
β	(−757)	(−757)	(−674)	(−757)
γ	(1534)	(1534)	(1520)	(1534)
M^0	(1.76)	(1.76)	(1.76)	(1.76)
M^2	(0.99)	(0.99)	(0.99)	(0.99)
M^4	(0.67)	(0.67)	(0.67)	(0.67)
P^2	(275)	(275)	(275)	(275)
P^4	(206)	(206)	(206)	(206)
P^6	(138)	(138)	(138)	(138)
B_0^2	−2485	−1310	−654	−25
B_0^4	1323	1424	2114	−3731
B_0^6	555	756	1853	248
B_3^4	–	190	–	–
B_3^6	–	610	–	–
B_6^6	−1956	−2178	−2078	–
$N_v/\sqrt{4\pi}$	1322	1003	1086	1246

[a] From Ref. [12]. [b] From Ref. [13]. [c] From Ref. [14]. [d] From Ref. [34]. [e] Values in brackets were not freely varied.

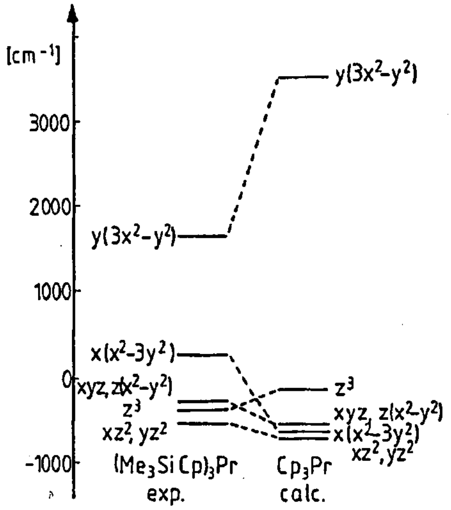

Fig. 1. Comparison of the calculated MO scheme of fictive ψ-trigonal planar Cp$_3$Pr with the experimentally based MO scheme of (Me$_3$SiCp)$_3$Pr.

signs of the CF parameters are the same as those concluded from experiment (see Table I). However, the absolute values of the calculated parameters are approximately 45% greater for the parameters B_0^2 and B_0^4 and off factors of some 2.3 and 3, respectively, for the parameters B_0^6 and B_6^6.

3.1.1.2. Mono base adducts derived from Cp_3Ln ($Cp_3Ln{\cdot}B$)

$Cp_3Pr{\cdot}MA$ (MA = methylacetate) has an orthorhombic [26] and $Cp_3Pr{\cdot}BA$ (BA = *n*-butylacetate) a nearly orthorhombic ($\beta = 91.58°$) unit cell [27]. As the four molecules in the unit cell are nearly aligned, optical polarization measurements of oriented single crystals are possible, in principle. Indeed, at room temperature we observed nice polarization effects and by applying the selection rules for α, σ and π orientation we could separate several terminal levels of Γ_1 and Γ_3 symmetry, for transitions from CF ground state [7,26–28]. Presumably because of a phase transition the crystals cracked at low temperatures thus preventing the observation of linear dichroism at low temperatures.

$Cp_3Pr{\cdot}B$ complexes have an energetically isolated singlet CF ground state which is roughly described by $J_z = 0$ [6]. Therefore cold transitions to excited singlet and doublet terminal levels can be separated by performing MCD measurements. Moreover, the observed signs of Faraday A terms allow the identification of the main component of J_z in the eigenvectors of terminal states.

On this basis the CF splitting patterns of $Cp_3Pr{\cdot}B$ (B = MeTHF, CNC_6H_{11}, $NCCH_3$, BA) were derived and the parameters of the empirical Hamiltonian were fitted to the energies of the CF states [7,13].

Using the CF parameters of $Cp_3Pr{\cdot}MeTHF$ we calculated the CF splitting pattern of *f* orbitals of the corresponding spin-free f^1 system. Unfortunately, no results of model calculations on $Cp_3Pr{\cdot}B$ complexes have been published up to now. However, some theorists communicated to us the results of two preliminary INDO calculations on $Cp_3Gd{\cdot}THF$ and of a preliminary DV-X_α calculation on $Cp_3Gd{\cdot}OH_2$. One INDO calculation leads to a total splitting of *f* type orbitals which is only one eighth of the experimentally based one, and the other is a factor of four too large. In both cases the relative ordering of *f* type orbitals is completely different from that concluded from experiment.

The calculated splitting of the DV-X_α calculation is also off a factor of 4. Additionally, an unrealistic strong mixing of *f* type orbitals results and moreover the degeneracy of *e* levels is strongly lifted.

The CF parameters of $Cp_3Pr{\cdot}CNC_6H_{11}$ have been estimated on the basis of the AOM. Apart from the parameter B_6^6 an unexpected agreement of experimentally based and calculated CF parameters was obtained [29].

3.1.1.3. Bis base adducts derived from Cp_3Ln (Cp_3LnB_2)

Neat ψ-trigonal bipyramidally coordinated Cp_3LnB_2 complexes can only be synthesized as solids for Ln = La–Nd by using sterically non-demanding bases like acetonitrile or propionitrile [30]. In contrast to the extremely labile Nd and Pr compounds $Cp_3La(NCCH_3)_2$ is rather stable. Cp_3LnB_2 compounds of the higher lanthanides can be stabilized by doping a $Cp_3La(NCCH_3)_2$ matrix with Ln (up to now only checked for Ln = Sm [31] and Tb [32]) or by making use of the chelate effect. For example, in case of $(MeOCH_2CH_2Cp)_3Ln$ where two of the three ether oxygen atoms coordinate axially [33], the whole Ln series is known.

Recently we parameterized the CF splitting pattern of $Cp_3La(NCCH_3)_2$:Pr and $(CH_3OCH_2CH_2Cp)_3Pr$ [14] (cf. Table I).

Results of more advanced model calculations on Cp_3LnB_2 complexes have not come to our attention. However, in order to get a first idea of the numerical values of CF parameters for $(Me_3SiCp)_3Pr$ and $Cp_3La(NCCH_3)_2$:Pr, respectively, we performed simple calculations in the framework of the AOM (see Table II). The free AOM parameters e_σ, e'_σ, e''_σ, e_π, e'_π and e''_π consider the influence of Cp rings of the base-free compound, mono and bis adduct, respectively, and e^*_σ and e^{**}_σ the effects of $NCCH_3$ ligand(s) of $Cp_3 \cdot NCCH_3$ and $Cp_3La(NCCH_3)_2$:Pr.

TABLE II

B^k_q parameters for $(Me_3SiCp)_3Pr$, $Cp_3Pr \cdot NCCH_3$ and $Cp_3La(NCCH_3)_2$:Pr calculated in the framework of the AOM.

Parameter	$(Me_3SiCp)_3Pr$	$Cp_3Pr \cdot NCCH_3$	$Cp_3Pr(NCCH_3)_2$
B^2_0	$-3.652e_\sigma - 0.581e_\pi$	$-3.163e'_\sigma - 0.555e'_\pi$ $+0.714e^*_\sigma$	$-3.652e''_\sigma - 0.581e''_\pi$ $+1.429e^{**}_\sigma$
B^4_0	$1.532e_\sigma + 0.474e_\pi$	$1.408e'_\sigma + 0.41e'_\pi$ $+1.286e^*_\sigma$	$1.532e''_\sigma + 0.474e''_\pi$ $+2.571e^{**}_\sigma$
B^6_0	$1.357e_\sigma - 0.996e_\pi$	$0.940e'_\sigma - 0.34e'_\pi$ $+1.857e^*_\sigma$	$1.357e''_\sigma - 0.996e''_\pi$ $+3.714e^{**}_\sigma$
B^4_3	–	$0.657e'_\sigma - 0.49e'_\pi$	–
B^6_3	–	$0.755e'_\sigma + 0.227e'_\pi$	–
B^6_6	$-2.073e_\sigma + 1.034e_\pi$	$-1.926e'_\sigma + 1.007e'_\pi$	$-2.073e''_\sigma + 1.034e''_\pi$

If one assumes for the sake of simplicity that the numerical values of all these e_σ and e_π are comparable and positive, the AOM predicts the following trends. Going from $(Me_3SiCp)_3Pr$ via $Cp_3Pr \cdot NCCH_3$ to $Cp_3La(NCCH_3)_2$:Pr the CF parameter B^2_0 should move to less negative values, B^4_0 and B^6_0 should become more positive and B^6_6 should be rather constant within this series. Besides, the parameter B^6_3 for $Cp_3Pr \cdot NCCH_3$ should be greater than B^4_3. All these predicted trends are confirmed by the fits (cf. Table I).

3.1.2. Complexes derived from the (η^8-cyclooctatetraenyl)lanthanide(III) cation

Numerous model calculations of rather different grades of difficulty have been performed on sandwich complexes of the stoichiometries $K[Ln^{III}(COT)_2]$, $Ce^{IV}(COT)_2$ and $An^{IV}(COT)_2$ [10, 34]. These calculations produced rather different orderings of *f* orbitals [34]. An experimental check of these results was hitherto not possible, because the unpaired electrons of sandwich systems with n membered rings experience a CF of $D_{\infty h}$ symmetry if $n \geq 2l$ (l = orbital angular momentum number of the unpaired electrons) [35]. A CF of $D_{\infty h}$ symmetry is centrosymmetric, thus *f–f* transitions of induced electric dipole character are strictly Laporte forbidden for $K[Ln(COT)_2]$ and $An(COT)_2$ complexes. Moreover, wide ranges of the absorption spectra of these series of compounds are hampered by strong broad bands of charge transfer or *f–d* origin.

In order to avoid the difficulties which are associated with a quasi-centrosymmetric structure and in order to investigate the unperturbed CF splitting effects of COT ring, it is recommended to study half-sandwich complexes of the stoichiometries (COT)LnY or (COT)AnZ$_2$, where Y and Z represent ligands, the ligand field strengths of which are nearly negligible.

During the last few years Edelmann and co-workers have synthesized a number of (COT)LnY(THF)$_x$ complexes (Y = [HBpz$_3$]$^-$ (pz = pyrazol-1-yl), [HB(3,5-Me$_2$pz)$_3$]$^-$, I$^-$, [C$_6$H$_5$C(NSiMe$_3$)$_2$]$^-$, [(C$_6$H$_5$)$_2$P(NSiMe$_3$)$_2$]$^-$, x = 0–3) [36–38] which might meet partly the above-mentioned condition.

We have studied the optical spectra of the corresponding Pr, Nd and Sm complexes of the (COT)LnY series. In case of Y = [HBpz$_3$]$^-$, [HB(3,5-Me$_2$pz)$_3$]$^-$ and (THF)$_3$I$^-$ we noticed that the selection rules for C_{8v} are essentially considered. In case of (COT)Pr[HB(3,5-Me$_2$pz)$_3$] the perturbing trigonal field of [HB(3,5-Me$_2$pz)$_3$]$^-$ ligand produces a splitting of levels (which are twofold degenerate in C_{8v} symmetry) by 10–25 cm^{-1} on average [39]. For (COT)Pr[HBpz$_3$] these values are even smaller, but for (COT)Pr(THF)$_3$I somewhat larger. Thus all these compounds can be considered as [Pr(COT)]$^+$ to a good approximation.

Recently we succeeded in parameterizing the CF splitting patterns of (COT)Pr[HB(3,5-Me$_2$pz)$_3$] [34, 39] and of (COT)Nd[HB(3,5-Me$_2$pz)$_3$] [40]. Thus we have for the first time the chance to check the results of more than 30 years of model calculations on [Ln(COT)$_2$]$^-$ and An(COT)$_2$ complexes.

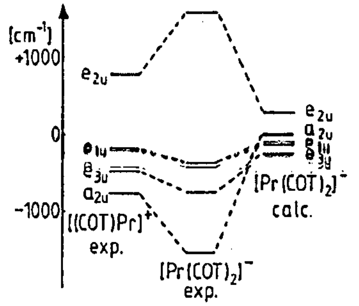

Fig. 2. Comparison of the calculated MO scheme of [Pr(COT)$_2$]$^-$ with the experimentally based ones of [Pr(COT)]$^+$/[Pr(COT)$_2$]$^-$.

The experimentally based energy sequence of f orbitals of [Pr(COT)]$^+$ [34] does not agree with the results of earlier MO calculations on [Ln(COT)$_2$]$^-$ [35] (cf. Fig. 2) but is in agreement with more recent MO calculations for U(COT)$_2$ [41, 42]. In order to check not only the ordering of f orbitals but also the magnitude of the CF splitting effects, we have assumed that to a first approximation the CF splitting of the full sandwich [Pr(COT)$_2$]$^-$ complex is twice as large as that of the half-sandwich [Pr(COT)]$^+$. If one accepts this rough approximation the $N_v/\sqrt{4\pi}$ parameter for [Pr(COT)$_2$]$^-$ is 2492 cm^{-1} and those extracted from the MO calculations of Boerrigter et al. [41] and Chang and Pitzer [42] are 9700 cm^{-1} and 7856 cm^{-1}, respectively [34]. Going from a Pr$^{\text{III}}$ to the corresponding U$^{\text{IV}}$

compound the CF strength increases frequently by a factor of three [34]. Thus the calculated magnitudes of the CF splitting effects for $U(COT)_2$ seem to be realistic. The CF parameters of $U(COT)_2$ as extracted from the calculations of Boerrigter et al. [41] and Chang and Pitzer [42] are compared in Table III with those of $[Pr(COT)_2]^-$. As can be seen from this table in all three cases the parameter B_0^4 is dominant.

The parameter $N_v/\sqrt{4\pi} = 1246\ \mathrm{cm}^{-1}$ for $[Pr(COT)]^+$ and $1322\ \mathrm{cm}^{-1}$ for $(Me_3SiCp_3)Pr$ (cf. Table I). This means that the CF strength of one COT ring is nearly three times greater than that of one Cp ring. Even if one focuses on the CF strength of one single C atom the CF strength of C_{COT} ($156\ \mathrm{cm}^{-1}$) is considerably greater than that of C_{Cp} ($88\ \mathrm{cm}^{-1}$). These findings may be explained by the noticeably shorter distance of LnC_{COT} (259.5 pm for (COT) $Sm[HBpz_3]$ [43] as compared with LnC_{Cp} (276.3 pm for triclinic $Cp_3Sm{\cdot}NCCH_3$ [44]).

TABLE III

Comparison of fitted CF parameters for $[Pr(COT)]^+/[Pr(COT)_2]^-$ and calculated ones for $[Ce(COT)_2]^-$, $U(COT)_2$. All values in cm^{-1}.

	B_0^2	B_0^4	B_0^6	$N_v/\sqrt{4\pi}$
$[Pr(COT)]^{+a}$	−21	−3732	+254	1246
$[Pr(COT)_2]^{-a}$	−42	−7464	+508	2492
$[(Ce(COT)_2]^{-b}$	+375	−1296	+708	503
$U(COT)_2^c$	−440	−23558	+5810	7856
$U(COT)_2^d$	+223	−28440	+7465	9700

[a] From Ref. [34]. [b] From Ref. [35]. [c] From Ref. [42]. [d] From Ref. [41].

3.2. σ complexes

To the best of our knowledge neither CF analyses nor model calculations have been performed on organometallics of the lanthanides with σ bonds between the central ion and the ligands. The most well-known representatives of σ complexes are the ψ-trigonal pyramidal $Ln[HC(SiMe_3)_2]_3$ compounds [45]. Both spectroscopists and theorists consider the isostructural and isoelectronic $Ln[N(SiMe_3)_2]_3$ complexes [46] as ideal model compounds for these methanides [47]. The amides crystallize as needles, and the trigonal principal axes of the two molecules per unit cell are aligned along the needle axis of the single crystal [48]. Thus it should be no problem to record the low temperature σ and π absorption spectra of this class of compounds.

In case of the Pr complex the CF ground state of Γ_1 and the first excited state of Γ_3 symmetry are only separated by approximately $50\ \mathrm{cm}^{-1}$ [15] thus obscuring the observation of distinct polarization properties. For this reason we changed to the Nd complex.

The appearance of a signal in the 5 K EPR spectrum of $Nd[N(SiMe_3)_2]_3$ confirms a CF ground state which is roughly described by $J_z = \pm 1/2$. In C_{3v} symmetry $J_z = \pm 1/2$ transforms like the irreducible representation Γ_4. Applying the selection rules for σ and π orientation [19] a number of signals in the 50 K absorption spectrum could be assigned to terminal levels of Γ_4 and $\Gamma_{5/6}$ symmetry, respectively [49].

The CF parameters of the optimal fit [49] lead to the following experimentally based MO scheme (in cm^{-1}): $z^3 = -749$, $xz^2/yz^2 = -459$, $xyz/z(x^2-y^2) = -234$, $x(x^2-3y^2) = 964$, $y(3x^2-y^2) = 1170$.

Model calculations in the framework of the INDO approximation have been performed on $Ln[N(SiMe_3)_2]_3$, (Ln = Eu, Yb) [50] and *ab initio* calculations on $U^{III}(NH_2)_3$ [47]. The results of the INDO calculations are in complete disagreement with experiment. The numerical values of the *ab initio* calculations were requested from the authors, but did not arrive before this paper was concluded.

4. Conclusions

It is generally accepted that the results of model calculations on organometallics of the *f* elements describe the type of bonding in a satisfactory manner and provide valuable hints for the interpretation of photoelectron spectra [9, 10]. In the framework of this study we checked for the first time whether the results of model calculations on organometallics of the lanthanides would be a useful tool for assigning energy levels extracted from optical spectra. It seems that the results of earlier Wolfsberg–Helmholtz MO or INDO calculations are not very helpful, whereas more complex but computer time consuming approaches [9, 10] may provide valuable starting parameter sets for fitting experimentally derived CF splitting patterns.

Acknowledgments

H.-D. A. wants to thank several cited and non-cited theorists for communicating the results of their calculations prior to publication and the Fonds der Chemischen Industrie for financial support.

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