Crystal Field Strengths, Nephelauxetic Effects, and Experimentally Based Molecular Orbital Schemes (in the f Range) of Selected Cyclopentadienyl Complexes of Samarium(III)[‡]

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The absorption and luminescence spectra of pseudo (ψ) trigonal planar $[Sm(\eta^5\text{-}C_5H_4tBu)_3]$ (**1**), low symmetric $[Sm(\eta^5\text{-}Cp)(\eta^3\text{-}Tp^{Me_2})(\eta^2\text{-}Tp^{Me_2})]$ (Cp = η^5-cyclopentadienyl; Tp^{Me_2} = hydrotris(3,5-dimethylpyrazolyl)borato) (**2**) as well as ψ trigonal pyramidal $[Sm(\eta^5\text{-}C_5H_4tBu)_3(THF)]$ (**3**), $[Sm(\eta^5\text{-}Cp)_3(THF)]$ (**4**) and $[Sm(\eta^5\text{-}Cp)_3(CNC_6H_{11})]$ (**5**) have been measured at room and low temperatures. From the spectra obtained, truncated crystal field (CF) splitting patterns of these compounds could be derived, and simulated by fitting the parameters of a phenomenological Hamiltonian. On the basis of the CF parameters used, the global CF strengths experienced by the Sm^{3+} central ions of complexes **1**–**5**, as well as the individual CF strength associated with one $C_5H_4tBu^-$ ligand are estimated. The obtained Slater parameters F^2 and the spin-orbit coupling parameters ζ_{4f} allow the insertion of compounds **1**–**5** into truncated nephelauxetic and relativistic nephelauxetic series. Besides, the experimentally based non-relativistic and relativistic molecular orbital schemes (in the f range) of complexes **1** and, partly, **3** are set up and compared with the results of quantum chemical model calculations.

Introduction

After a successful parametric analysis of the experimentally derived crystal field (CF) splitting pattern, the global CF strength $[N_v/(4\pi)^{1/2}]$ experienced by the central ion of a lanthanide [Ln(III)] compound may be calculated by the relation[2]

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

where the B^k_q 's represent the phenomenological CF parameters used in the fit.[3−6] The individual CF strength associated with one single ligand L^- of homoleptic neutral LnL_3 or anionic $[LnL_p]^{3-p}$ complexes is obtained by dividing $N_v/(4\pi)^{1/2}$ by three or the number of ligands (p), respectively (method A).

Alternatively, the individual CF strength of the ligand L^- of neutral $LnLL'_2$ or anionic $[LnLL'_q]^{2-q}$ complexes is nearly equal to the global CF strength if the CF strength associated with the ligands L'^- may be safely neglected (method B).

In recent years, we have parametrized the CF splitting patterns of a number of monomeric homoleptic LnL_3 [L = $C_5H_4SiMe_3^-$,[7] $N(SiMe_3)_2^-$,[8−10] $CH(SiMe_3)_2^-$,[11,12] $OC_6H_3tBu_2\text{-}2,6^-$[13]] complexes and — using method A — we found enormous individual CF strengths. By combining these ligands L with those producing weak CF strengths, the individual CF strength of the ligand L may also be estimated by means of method B.

Some years ago, we compared the absorption spectra of $[Nd(COT)(Tp^{Me_2})]$ [COT = η^8-cyclooctatetraenyl; Tp^{Me_2} = hydrotris(3,5-dimethylpyrazolyl)borato] and $[Nd(COT)(I)(THF)_3]$ and observed only minor differences.[14] As the CF strengths of I^- and THF are relatively small,[15] we concluded that this holds also for the Tp^{Me_2} ligand. Applying method B, the large global CF strengths found for $[Ln(COT)(Tp^{Me_2})]$ (Ln = Pr, Nd, Sm)[16−19] were considered to be approximately equal to the individual CF strength of the COT ligand.

Up to now, the results of both methods (with the central Ln^{3+} ion as well as the ligand L^- fixed) have not been cross-checked. Because of the existence of Sm^{III} and Sm^{II} precursors, the variety of organosamarium(III) complexes is

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[‡] Electronic structures of organometallic complexes of f elements, 57. Part 56: Ref.[1]

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extremely well developed. In the framework of the present and some following estimations of the CF strengths of the strong ligands L adopting methods A and B, respectively, we will focus on the combination of the Sm^{3+} ion and (substituted) η^5-cyclopentadienyl (Cp) ligands. In this first study, we select from the series of hitherto described homoleptic [$SmCp'_3$] [Cp′ = $C_5H_4tBu^-$, $C_5H_3(1,3\text{-}SiMe_3)_2^-$, $C_5Me_5^-$, $C_5HMe_4^-$, $C_5Me_4Et^-$, $C_5H_4SiEt_3^-$, $C_5H_4CH(SiMe_3)_2^-$][20–27] and monomeric [$SmCp'L'_2$] (Cp′ = Cp^-, $C_5H_4tBu^-$, $C_5H_4Me^-$, $C_5Me_5^-$, $C_5H_4SiMe_3^-$, $C_5Me_4CH_2Ph^-$; L′ = Cl^-, $acac^-$, I^-, Tp^{Me_2})[28–32] complexes the combination [$Sm(C_5H_4tBu)_3$] (**1**)/[$Sm(Cp)(Tp^{Me_2})_2$] (**2**).

For the purpose of demonstrating that the CF strengths associated with the $C_5H_4tBu^-$ and Cp ligand, respectively, are comparable, it is planned to additionally analyze the absorption spectra of [$Sm(C_5H_4tBu)_3(THF)$] (**3**) and [$Sm(Cp)_3(THF)$] (**4**). In order to study spectroscopic and nephelauxetic effects associated with the isocyanide and nitrile ligand, respectively, we wish to compare the result of a CF analysis on [$Sm(Cp)_3(CNC_6H_{11})$] (**5**) with that of a previous one on [$Sm(Cp)_3(NCCH_3)$].

Organometallic π complexes of f elements usually have poor crystallizing properties, and additionally the principal rotation axes of the individual molecules in the unit cell are frequently not aligned. Even if they were aligned as in the case of low symmetric crystal systems, it is difficult to orientate these rotation axes with respect to outer homogeneous or vector fields. For this reason, the optical properties of organo-f element complexes are usually studied in solution or as pellets, thus missing the additional information obtainable from optical polarization measurements. A way out of these difficulties would be to extract a first rough set of parameters from the results of quantum chemical calculations on the compound of interest.

In order to check the predictions of previous model calculations on model pseudo (ψ) trigonal planar [$Ln(\eta^5\text{-}Cp)_3$] (Ln = Sm, Pr, Ce)[33–35] as well as of real ψ trigonal pyramidal [$Pr(\eta^5\text{-}Cp)_3(B)$] (B = THF, CNC_6H_{11})[35] and [$Gd(\eta^5\text{-}Cp)_3(THF)$],[36] we wish to compare the calculated non-relativistic and relativistic molecular orbital (MO) schemes (in the f range) of these compounds with our experimentally based results.

Results and Discussion

General Symmetry Considerations, Selection Rules and the Phenomenological Hamiltonian

The crystal and molecular structure of compound **1** is unknown, however, the optical spectra of this complex exhibits the same features as those of [$Sm(C_5Me_5)_3$] or [$Sm(C_5HMe_4)_3$],[37] where the three Cp centroids describe a trigonal planar geometry around the Sm^{3+} ion.[23,24] Thus for **1**, we assume an effective CF of D_{3h} symmetry.

A single-crystal X-ray study of complex **2** revealed a symmetrical η^5-bonding of the Cp ring and an η^3- as well as an η^2-bonding mode of the two Tp^{Me_2} ligands[32] (Figure 1).

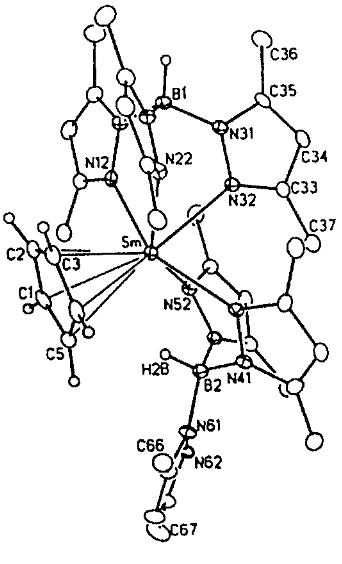

Figure 1. Molecular structure of [$Sm(\eta^5\text{-}Cp)(\eta^3\text{-}Tp^{Me_2})(\eta^2\text{-}Tp^{Me_2})$] from a single-crystal analysis[32]

In order to simplify the parametrization of the experimentally derived energy level scheme of this low symmetric compound, we adopt the following two approaches: in analogy with our previous treatments of the CF splitting patterns of [$Ln(COT)(Tp^{Me_2})$] (Ln = Pr, Nd, Sm)[16–19] we only consider the influence of the Cp ligand, which leads to C_{5v} symmetry. Alternatively, we approximate the real molecular geometry by a pentagonal sandwich complex (D_{5h} symmetry of the effective CF).

The electrostatic potentials of seven- and higher-membered aromatic ring ligands, experienced by f electrons, are equivalent to circles,[38] thus the effective CFs of [$Ln(COT)$]$^+$ fragments[16–19] are of $C_{\infty v}$ symmetry. Theoretically, in the case of lower membered aromatic ligands such as Cp, the actual C_{5v} symmetry of the [$Sm(Cp)$]$^{2+}$ moiety has to be considered. However, a number of previous studies of ψ trigonal pyramidal[39] and ψ trigonal bipyramidal[40] Cp complexes of rare earths showed that the five-membered Cp rings disturb the pseudo symmetry only weakly. Therefore, in the framework of this approach instead of the actual molecular C_{5v} the higher $C_{\infty v}$ symmetry is assumed. Effective CFs of D_{5h} and $C_{\infty v}$ symmetry have the same CF Hamiltonians (vide infra), thus both approaches are equivalent from the aspect of CF theory.

Single-crystal X-ray analyses of numerous mono base adducts of the type [$Ln(Cp')_3(B)$] (Cp′ = Cp, alkylated or silylated Cp, B = THF, CNC_6H_{11}, $NCCH_3$) revealed a ψ trigonal pyramidal structure,[20] suggesting an effective CF of C_{3v} symmetry for adducts **3–5**.

The free Sm^{3+} ion gives rise to multiplets $^{2S+1}L_J$ with $1/2 \leq J \leq 21/2$.[41] If the Sm^{3+} ion is placed into CFs of D_{3h}, $D_{5h}/C_{\infty v}$ or C_{3v} symmetry, respectively, these multiplets are split into various CF levels.[6] The wavefunctions of these levels are described to first order by $\pm M_J$ for $D_{5h}/C_{\infty v}$ symmetry, whereas different $\pm M_J$ functions with $\Delta M_J = 6$

mix for D_{3h}, and $\Delta M_J = 3$ for C_{3v} symmetry. Table 3 of ref.[42] lists the composition of the CF eigenvectors of f^n systems (with an odd number of f electrons) exposed to a CF of D_{3h} symmetry, and correlates them with the irreducible representations (irreps) Γ_7, Γ_8 and Γ_9 of the D_{3h}' double group. In this table the convention of Koster et al.[43] is used. The convention suggested by Hüfner[44] interchanges Γ_7 and Γ_8.

In the case of $D_{5h}/C_{\infty v}$ symmetry, the CF states are sufficiently characterized by their M_J quantum numbers, and in the case of C_{3v} symmetry, the CF states transform like the irreps Γ_4 and $\Gamma_{5/6}$.

The electric dipole selection rules (odd number of f electrons) for powdered or dissolved species with an effective CF of D_{3h} symmetry are given in Table A 5.2. of ref.[6] This table shows that the only forbidden transitions for adduct **1** are of the type $\Gamma_7 \rightarrow \Gamma_7$ and $\Gamma_8 \rightarrow \Gamma_8$, respectively.

In the case of compound **2**, the ideal $D_{5h}/C_{\infty v}$ symmetry is noticeably distorted, thus we expect that each $^{2S+1}L_J$ multiplet splits into J + 1/2 levels, and all transitions are allowed. According to Table A 5.3. of ref.[6], all transitions in C_{3v} symmetry are allowed for dissolved and powdered adducts **3**−**5**.

The energy levels within f^n configuration in D_{3h}, $D_{5h}/C_{\infty v}$ and C_{3v} symmetry can be written in terms of the atomic free ion (H_{FI}) and crystal field (H_{CF}) Hamiltonians as follows:

$$H = H_{FI} + H_{CF}\text{, where}$$

$$H_{FI} = \sum_{k=0,2,4,6} f_k F^k(nf,nf) + a_{so}\zeta_{4f} + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + {}_{i=2,3,4,6,7,8}\Sigma\, t_i T^i + \sum_{k=0,2,4} m_k M^k + \sum_{k=2,4,6} p_k P^{k\,[4]}\text{, and}$$

$$H_{CF}(D_{3h}) = B^2_0\, C^{(2)}_0 + B^4_0\, C^{(4)}_0 + B^6_0\, C^{(6)}_0 + B^6_6\, (C^{(6)}_{-6} + C^{(6)}_6)\ (\text{Ref.}^{[6]}\text{, p. 242}).$$

$$H_{CF}(D_{5h}/C_{\infty v}) = B^2_0\, C^{(2)}_0 + B^4_0\, C^{(4)}_0 + B^6_0\, C^{(6)}_0\ (\text{Ref.}^{[6]}\text{, p. 242/245}).$$

$$H_{CF}(C_{3v}) = B^2_0 C^{(2)}_0 + B^4_0 C^{(4)}_0 + B^4_3(C^{(4)}_{-3} - C^{(4)}_3) + B^6_0 C^{(6)}_0 + B^6_3(C^{(6)}_{-3} - C^{(6)}_3) + B^6_6(C^{(6)}_{-6} + C^{(6)}_6)\ (\text{Ref.}^{[6]}\text{, p. 245}).$$

The $F^k(nf,nf)$'s and ζ_{4f} terms represent, respectively, the radial parts of the electrostatic and spin-orbit interactions between f electrons, while f_k and a_{so} are the angular parts of these interactions. α, β and γ are the parameters associated with the two-body effective operators of configuration interaction, and the T^i's are the corresponding three-body effective operators. The M^k parameters represent the spin-spin, and spin-other-orbit interactions, while the P^k parameters arise from electrostatic spin-orbit interactions with higher configurations.[4] The CF interaction for the above symmetries is represented by the B^k_q parameters and the tensor operators $C^{(k)}_q$.[3]

Optical Spectra of [Sm(C_5H_4tBu)$_3$]

Homoleptic base-free SmL_3 complexes with alkylated or silylated ligands are usually deeply colored[20−27] because of an energetically low-lying charge-transfer transition of the type $Sm^{III}(L^-)_3 \rightarrow Sm^{II}(L_3)^{2-}$. Thus these compounds show either no or a few luminescence transitions (on the basis of which the CF splitting patterns of Sm^{III} compounds in the low energy range < 5000 cm^{-1} are usually derived).[45] For this reason the energies of the low-lying levels of compound **1** have to be extracted mainly from "hot" transitions and IR/NIR spectra, where, however, fundamental vibrations as well as binary and ternary C−H combination vibrations and overtones are severely disturbing.

In order to partly separate stronger bands of f-f transitions from weaker vibrational signals, we also recorded the absorption spectrum of "optically empty" [La(C_5H_4tBu)$_3$] in the IR/NIR range. As the NIR spectrum of this compound was poorly resolved, we also used [La($C_5H_4SiMe_3$)$_3$] (oil at room temperature) for the above purpose.

Comparing the low-temperature IR spectra of **1** and the corresponding La compound, we could not detect any differences, thus the energies of low-lying levels have to be concluded from "hot" transitions in the UV/Vis/NIR range and the rare transitions of the luminescence spectrum. In the low temperature Vis/NIR spectrum of complex **1** some "hot" signals (with $\Delta E \approx 486$ cm^{-1} from the corresponding "cold" bands) that appear in the room temperature spectrum are missing, thus indicating an excited level at about 486 cm^{-1}.

Luminescence transitions of organometallic Sm^{III} compounds usually initiate at the lowest CF level of $^4G_{5/2}$,[45,46] which is found at 17489 cm^{-1} in the room temperature absorption spectrum of complex **1** dissolved in methylcyclohexane. In the luminescence spectrum of solid **1**, we could not detect a single luminescence transition, but a methylcyclohexane solution showed a signal at 16591 cm^{-1} (using the exciting line at 476.5 nm) which suggests the existence of a CF level at 898 cm^{-1}.

In the range 4000−4650 cm^{-1} of the IR/NIR spectrum (pellet) the expected transitions $^6H_{5/2} \rightarrow {}^6H_{11/2}$ are partially obscured by strong C−H combination vibrations and overtones, but in the remaining part of this spectrum a number of f-f transitions could be clearly identified (Figure 2, Table 1).

The UV/Vis part of the low temperature absorption spectrum is dominated by a strong broad charge-transfer band. On the low-energy side of this band one strong (17486 cm^{-1}) and three diffuse signals at approximately 18282, 19245 and 19485 cm^{-1} appeared (Table 1).

Optical Spectra of [Sm(Cp)(Tp^{Me_2})$_2$]

In order to separate bands of f-f and vibrational origin in the absorption spectrum of compound **2**, we could not make use of the corresponding "optically empty" La, Gd,

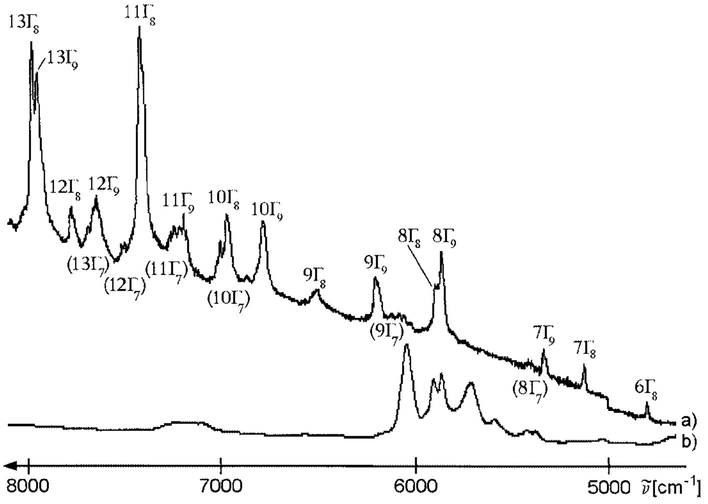

Figure 2. Absorption spectra in the range 4700−8100 cm^{-1}: a) [Sm(C$_5$H$_4$*t*Bu)$_3$], pellet, ca. 80 K; b) [La(C$_5$H$_4$SiMe$_3$)$_3$], oil, room temperature

Table 1. Calculated and experimental energy values for [Sm(C$_5$H$_4$*t*Bu)$_3$]; all values in cm^{-1}

Multiplet [a]	CF level		E (calcd.)	E (exp.)[b]	Multiplet	CF level		E (calcd.)	E (exp.)
$^6H_{5/2}$	$1\Gamma_7$[c]	±5/2[d]	0	0	$^6H_{15/2}$	$12\Gamma_8$	±1/2	7752	7760
$^6H_{5/2}$	$2\Gamma_9$	±3/2	493	486[e]	$^6F_{5/2}$	$13\Gamma_9$	±3/2	7930	7932
$^6H_{7/2}$	$2\Gamma_7$	±7/2	910	898[f]	$^6F_{5/2}$	$13\Gamma_8$	±1/2	7934	7960
$^6H_{5/2}$	$1\Gamma_8$	±1/2	977		$^6F_{7/2}$	$14\Gamma_7$	±7/2	8517	
$^6H_{7/2}$	$3\Gamma_7$	±5/2	1634		$^6F_{7/2}$	$14\Gamma_8$	±1/2	8607	8618
$^6H_{7/2}$	$2\Gamma_9$	±3/2	1873		$^6F_{7/2}$	$14\Gamma_9$	±3/2	8635	8618
$^6H_{7/2}$	$2\Gamma_8$	±1/2	1950		$^6F_{7/2}$	$15\Gamma_7$	±5/2	8659	(8669)
$^6H_{9/2}$	$3\Gamma_9$	±9/2	2523		$^6F_{9/2}$	$15\Gamma_8$	±1/2	9605	9616
$^6H_{9/2}$	$4\Gamma_7$	±7/2	2704		$^6F_{9/2}$	$15\Gamma_9$	±3/2	9660	
$^6H_{9/2}$	$3\Gamma_8$	±1/2	3004		$^6F_{9/2}$	$16\Gamma_7$	±5/2	9668	
$^6H_{9/2}$	$4\Gamma_9$	±3/2	3095		$^6F_{9/2}$	$16\Gamma_9$	±9/2	9835	9816
$^6H_{9/2}$	$5\Gamma_7$	±5/2	3107		$^6F_{9/2}$	$17\Gamma_7$	±7/2	9836	
$^6H_{11/2}$	$4\Gamma_8$	±11/2	3616		$^6F_{11/2}$	$16\Gamma_8$	±1/2	10874	(10772)
$^6H_{11/2}$	$5\Gamma_9$	±9/2	3853		$^6F_{11/2}$	$17\Gamma_9$	±3/2	10886	(10903)
$^6H_{11/2}$	$6\Gamma_7$	±7/2	4160		$^6F_{11/2}$	$18\Gamma_7$	±5/2	10929	
$^6H_{11/2}$	$5\Gamma_8$	±1/2	4431		$^6F_{11/2}$	$19\Gamma_7$	±7/2	11040	
$^6H_{11/2}$	$6\Gamma_9$	±3/2	4492		$^6F_{11/2}$	$18\Gamma_9$	±9/2	11212	(11216)
$^6H_{11/2}$	$7\Gamma_7$	±5/2	4570		$^6F_{11/2}$	$17\Gamma_8$	±11/2	11438	(11531)
$^6H_{13/2}$	$6\Gamma_8$	±13/2	4806	4795	$^4G_{5/2}$	$20\Gamma_7$	±5/2	17486	17486
$^6H_{13/2}$	$7\Gamma_8$	±11/2	5093	5118	$^4G_{5/2}$	$19\Gamma_9$	±3/2	18278	18282
$^6H_{13/2}$	$7\Gamma_9$	±9/2	5319	5320	$^4G_{5/2}$	$18\Gamma_8$	±1/2	18344	
$^6H_{13/2}$	$8\Gamma_7$	±7/2	5400	(5399)[g]	$^4F_{3/2}$	$20\Gamma_9$	±3/2	19210	(19245)
$^6H_{13/2}$	$8\Gamma_9$	±3/2	5872	5851	$^4F_{3/2}$	$19\Gamma_8$	±1/2	19459	(19485)
$^6H_{13/2}$	$8\Gamma_8$	±1/2	5881	5880	$^4G_{7/2}$	$21\Gamma_7$	±7/2	19855	
$^6H_{13/2}$	$9\Gamma_7$	±5/2	6097	(6104)					
$^6H_{15/2}$	$9\Gamma_9$	±15/2	6202	6190					
$^6H_{15/2}$	$9\Gamma_8$	±13/2	6507	6509					
$^6H_{15/2}$	$10\Gamma_9$	±9/2	6760	6768					
$^6H_{15/2}$	$10\Gamma_7$	±7/2	6955	6956					
$^6F_{1/2}$	$10\Gamma_8$	±1/2	6992	6993					
$^6H_{15/2}$	$11\Gamma_7$	±7/2	7196	(7210)					
$^6F_{3/2}$	$11\Gamma_9$	±3/2	7224	7176					
$^6F_{3/2}$	$11\Gamma_8$	±1/2	7388	7399					
$^6H_{15/2}$	$12\Gamma_7$	±5/2	7542	(7492)					
$^6H_{15/2}$	$12\Gamma_9$	±3/2	7631	7632					
$^6F_{5/2}$	$13\Gamma_7$	±5/2	7692	(7669)					

[a] Dominating Russell-Saunders multiplet $^{2S+1}L_J$. [b] From absorption measurements. [c] CF states (D_{3h}' double group) ordered in ascending energy. [d] Largest eigenvector component ±M$_J$. [e] From hot transitions. [f] From luminescence measurements. [g] Values in brackets (which are presumably due to forbidden $\Gamma_7 \rightarrow \Gamma_7$ transitions) were not fitted.

Table 2. Calculated and experimental energy values for [Sm(Cp)(Tp^{Me_2})$_2$]; all values in cm^{-1}

Multiplet [a]	CF level[b]	E (calcd.)	E (exp.)[c]	E (exp.)[d]	Multiplet [a]	CF level [b]	E (calcd.)	E (exp.) [c]	E (exp.) [d]
$^6H_{5/2}$	±5/2	0	0	0	$^6F_{5/2}$	±5/2	7244		7223
$^6H_{5/2}$	±3/2	296	230		$^6F_{5/2}$	±3/2	7263		7271
$^6H_{5/2}$	±1/2	447	406		$^6F_{5/2}$	±1/2	7274		7329
$^6H_{7/2}$	±7/2	1062	1052		$^6F_{7/2}$	±1/2	8105		8104
$^6H_{7/2}$	±5/2	1270	1234		$^6F_{7/2}$	±5/2	8113		8104
$^6H_{7/2}$	±3/2	1359	1382		$^6F_{7/2}$	±3/2	8116		8123
$^6H_{7/2}$	±1/2	1440	1480		$^6F_{7/2}$	±7/2	8139		8180
$^6H_{9/2}$	±9/2	2253	2294		$^6F_{9/2}$	±1/2	9247		9170
$^6H_{9/2}$	±7/2	2428	2388		$^6F_{9/2}$	±3/2	9249		9255
$^6H_{9/2}$	±5/2	2508	2482		$^6F_{9/2}$	±5/2	9269		9255
$^6H_{9/2}$	±3/2	2583	2578		$^6F_{9/2}$	±7/2	9314		9320
$^6H_{9/2}$	±1/2	2632	2706		$^6F_{9/2}$	±9/2	9350		9363
$^6H_{11/2}$	±11/2	3536	3574		$^6F_{11/2}$	±1/2	10585		10526
$^6H_{11/2}$	±9/2	3704	3674		$^6F_{11/2}$	±3/2	10602		10628
$^6H_{11/2}$	±7/2	3792	3800		$^6F_{11/2}$	±5/2	10633		10628
$^6H_{11/2}$	±5/2	3866	3834		$^6F_{11/2}$	±7/2	10675		10692
$^6H_{11/2}$	±3/2	3926	3892		$^6F_{11/2}$	±9/2	10725		10692
$^6H_{11/2}$	±1/2	3960	4046		$^6F_{11/2}$	±11/2	10786		10811
$^6H_{13/2}$	±13/2	4880	4910	4912	$^4G_{5/2}$	±5/2	17769	17732	
$^6H_{13/2}$	±11/2	5045	5052	5056	$^4G_{5/2}$	±3/2	18013		
$^6H_{13/2}$	±9/2	5156	5152	5149	$^4G_{5/2}$	±1/2	18177		
$^6H_{13/2}$	±7/2	5242	5228	5230	$^4F_{3/2}$	±3/2	18935		18904
$^6H_{13/2}$	±5/2	5306	5260	5263	$^4F_{3/2}$	±1/2	18956		18975
$^6H_{13/2}$	±3/2	5351	5340	5345	$^4G_{7/2}$	±7/2	19876		19927
$^6H_{13/2}$	±1/2	5373	5420	5423	$^4G_{7/2}$	±5/2	20045		20041
$^6H_{15/2}$	±15/2	6261	6212	6213	$^4G_{7/2}$	±3/2	20184		
$^6H_{15/2}$	±13/2	6403	6436	6437	$^4G_{7/2}$	±1/2	20261		
$^6F_{1/2}$	±1/2	6494	6491	6489					
$^6H_{15/2}$	±11/2	6557	6543	6553					
$^6H_{15/2}$	±9/2	6673		6660					
$^6F_{3/2}$	±3/2	6732		6743					
$^6H_{15/2}$	±7/2	6749		6750					
$^6F_{3/2}$	±1/2	6789		6791					
$^6H_{15/2}$	±5/2	6795		6791					
$^6H_{15/2}$	±3/2	6820		6826					
$^6H_{15/2}$	±1/2	6832		6826					

[a] Dominating Russell-Saunders multiplet $^{2S+1}L_J$. [b] Largest eigenvector component $\pm M_J$. [c] From luminescence measurements. [d] From absorption measurements.

Y, Lu compounds as these don't exist at this point, but as a proxy we used the combined vibrational energies of NaCp and KTp^{Me_2}. The wavenumbers of the thus separated signals of presumable f-f origin in the Vis/NIR spectrum are given in Table 2 (Figure 3).

By using all of the exciting lines of an Ar$^+$ laser, the best signal-to-noise ratio in the luminescence spectrum of compound **2** was observed by applying the line at 476.5 nm. Using this line, the vibrational Raman signals are well separated from the luminescence transitions.[45,46] The observed

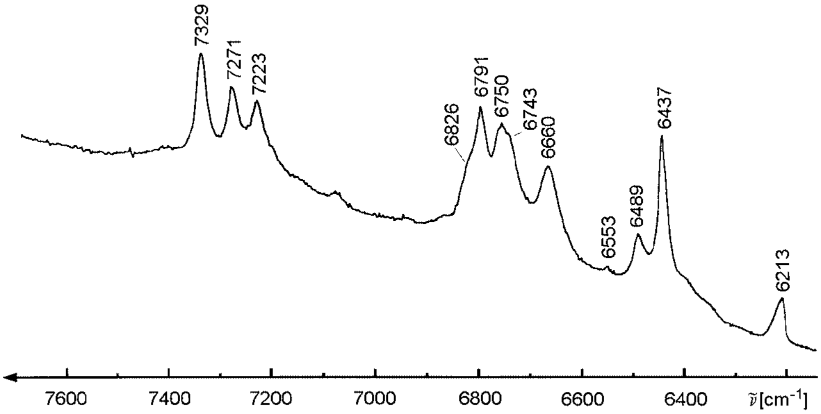

Figure 3. Absorption spectrum of [Sm(Cp)(Tp^{Me_2})$_2$] in the range 6150−7700 cm^{-1}, pellet, ca. 80 K

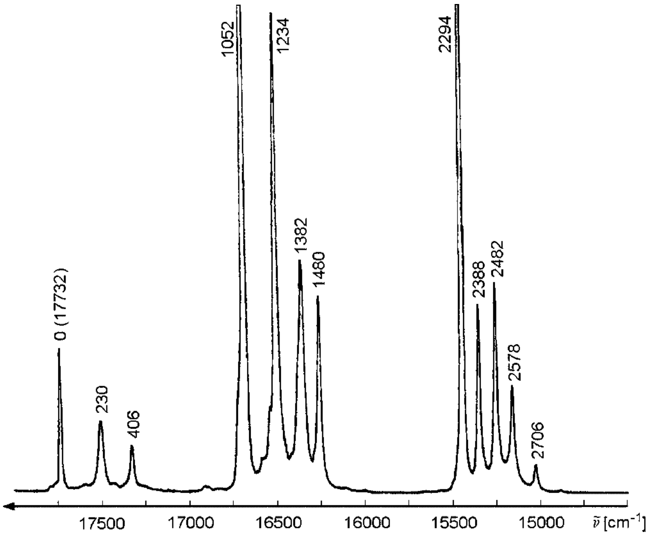

Figure 4. Luminescence spectrum of [Sm(Cp)(Tp^{Me_2})$_2$] in the range 14500−18000 cm^{-1}, powder, ca. 90 K; the value in brackets denotes the absolute wavenumber of the fluorescing level, and those without brackets the derived CF energies.

low temperature luminescence spectrum (Figure 4) can be rationalized by identifying the fluorescing level at 17732 cm^{-1} with the lowest CF state of the multiplet $^4G_{5/2}$, and the terminal levels arising from the multiplets ^6H_J (J = 5/2, 7/2, 9/2, 11/2, 13/2, 15/2) and $^4F_{1/2}$. On this basis, the CF splitting pattern of **2** in the low-energy range could be derived (Table 2). In the overlapping region, the CF energies directly observed in the absorption spectrum and concluded from the luminescence spectrum, agree nicely (cf. Table 2).

Using the exciting line at 457.9 nm two "negative bands" with minima at 19927 cm^{-1} and 20041 cm^{-1} appeared. The existence of these signals may be explained by an absorption process from background radiation.[17] The former peak corresponds to a broad asymmetric band with the maximum at ca. 19930 cm^{-1} in the "ordinary" absorption spectrum of a pellet.

Absorption Spectra of [Sm(C$_5$H$_4$*t*Bu)$_3$(THF)], [Sm(Cp)$_3$(THF)] and [Sm(Cp)$_3$(CNC$_6$H$_{11}$)]

The low temperature absorption spectra of dissolved adducts **3−5** and previously analyzed solid [Sm(Cp)$_3$(NCCH$_3$)][45] are nearly identical. The same holds for the luminescence spectra of adducts **4** and **5** and for that of [Sm(Cp)$_3$(NCCH$_3$)][45] For this reason we do not present figures of the recorded spectra and refer the reader to ref.[45] Because of the deep purple color of a glassy frozen solution of compound **3**, we didn't try to record its luminescence spectrum.

CF Analyses

Because of the missing optical polarization measurements of oriented single crystals, and the principle impossi-

Table 3. Parameter values for [Sm(C$_5$H$_4$*t*Bu)$_3$], [Sm(Cp)(Tp^{Me_2})$_2$], [Sm(C$_5$H$_4$*t*Bu)$_3$(THF)], [Sm(Cp)$_3$(THF)], [Sm(Cp)$_3$(CNC$_6$H$_{11}$)], [Sm(Cp)$_3$(NCCH$_3$)] and [La$_{0.8}$Sm$_{0.2}$(Cp)$_3$(NCCH$_3$)$_2$]; all values in cm^{-1}.

Parameter	Cpd. **1**	Cpd. **2**	Cpd. **3**	Cpd. **4**	Cpd. **5**	[Sm(Cp)$_3$(NCCH$_3$)][a]	[La$_{0.8}$Sm$_{0.2}$(Cp)$_3$(NCCH$_3$)$_2$][a]
F^2	73992	78294	75324	75773	75813	76230	77002
F^4	58470	56267	56551	56699	56445	56187	56124
F^6	37391	39760	39503	39311	39382	39636	39832
ζ_{4f}	1143	1159	1149	1149	1151	1148	1155
α	[21.6][b]	[21.6]	[21.6]	[21.6]	[21.6]	[21.6]	[21.6]
β	[-724]	[-724]	[-724]	[-724]	[-724]	[-724]	[-724]
γ	[1700]	[1700]	[1700]	[1700]	[1700]	[1700]	[1700]
T^2	[291]	[291]	[291]	[291]	[291]	[291]	[291]
T^3	[13]	[13]	[13]	[13]	[13]	[13]	[13]
T^4	[34]	[34]	[34]	[34]	[34]	[34]	[34]
T^6	[-193]	[-193]	[-193]	[-193]	[-193]	[-193]	[-193]
T^7	[288]	[288]	[288]	[288]	[288]	[288]	[288]
T^8	[354]	[354]	[354]	[354]	[354]	[354]	[354]
M^0	[2.4]	[2.4]	[2.4]	[2.4]	[2.4]	[2.4]	[2.4]
M^2	[1.34]	[1.34]	[1.34]	[1.34]	[1.34]	[1.34]	[1.34]
M^4	[0.91]	[0.91]	[0.91]	[0.91]	[0.91]	[0.91]	[0.91]
P^2	[341]	[341]	[341]	[341]	[341]	[341]	[341]
P^4	[256]	[256]	[256]	[256]	[256]	[256]	[256]
P^6	[171]	[171]	[171]	[171]	[171]	[171]	[171]
B^2_0	−2809	−1158	−1577	−1523	−1487	−1627	−953
B^4_0	1483	−81	1407	1509	1418	1291	1882
B^6_0	1278	−182	1080	1269	1243	1306	1903
B^4_3	−	−	1076	1135	1213	769	−
B^6_3	−	−	502	317	336	490	−
B^6_6	−2685	−	−2245	−2216	−2217	−2190	−2038
$N_v/(4\pi)^{1/2}$	1749	522	1371	1378	1373	1324	1222
σ	17.5 (25)[c]	35.0 (59)	30.8 (25)	30.4 (51)	25.2 (59)	31 (57)	20 (42)

[a] From ref.[45] [b] Values in square brackets were fixed at the values of [LaCl$_3$:Sm^{3+}].[41] [c] Number of assignments in parentheses.

bility to interpret magnetic circular dichroism measurements of dissolved systems with an odd number of f electrons,[47] the derived sequences of CF levels of compounds **1−5** cannot be assigned on an experimental but only on a calculational (**1**, **2**) or comparative (**3−5**) basis.

In order to get a first idea of the signs and magnitudes of the CF parameters of complexes **1** and **2**, we adopted the CF parameter set of ψ trigonal planar $[Pr(C_5H_4SiMe_3)_3]$[7] for **1**, and for **2**, we divided the CF parameters B^2_0, B^4_0 and B^6_0 of this compound by three. Because of the similarity of the optical spectra of $[Sm(Cp)_3(NCCH_3)]$[45] and those of adducts **3−5**, we used the unchanged CF parameters of $[Sm(Cp)_3(NCCH_3)]$[45] as a starting set for the latter complexes.

Together with the unchanged free-ion parameters of $LaCl_3{:}Sm^{3+}$ [41] for compound **2**, those of $[Sm(Cp)_3(NCCH_3)]$[45] for adducts **3−5** and compound **1** (however, because of presumably increased covalency the Slater parameter F^2 of the latter compound was reduced by 3%), the above mentioned sets of CF parameters were inserted into the energy matrices of the f^5 system exposed to the CFs of D_{3h}, $D_{5h}/C_{\infty v}$ and C_{3v} symmetry, respectively. Diagonalizing these matrices we calculated eigenvalues which were not too different from the experimental energies of CF states, which were thus assigned. On this basis in the framework of subsequent fitting procedures, the parameters of $H_{FI} + H_{CF}$ were fitted to the experimental CF splitting patterns. In order to reduce the number of free parameters, α, β, γ, the T^i, M^k and P^k parameters[4] were fixed at the values used in the CF analyses of $[LaCl_3{:}Sm^{3+}]$[41] and $[Sm(Cp)_3(NCCH_3)]$.[45] The remaining parameters were allowed to vary. For 25, 59, 25, 51 and 59 assignments, the reduced r.m.s. deviations (σ, cf. ref.[6] p.182) for compounds **1−5** were 17.5, 35.0, 30.8, 30.4 and 25.2 cm^{-1}, respectively.

Table 3 gives the final values of the CF and free-ion parameters for compounds **1−5**. For comparison purposes, the parameters of $[Sm(Cp)_3(NCCH_3)]$ and $[La_{0.8}Sm_{0.2}(Cp)_3(NCCH_3)_2]$ are also listed. In Table 1 and 2, experimental and calculated CF splitting patterns of complexes **1** and **2** are compared. Those of adducts **3−5** are not given because of the close similarity of the CF splitting patterns of these compounds and $[Sm(Cp)_3(NCCH_3)]$.[45]

Inserting the CF parameters of compounds **1−5** into the relation below[2] one ends up with $N_v/(4\pi)^{1/2}$ values of 1749, 522, 1371, 1378 and 1373 cm^{-1}, respectively.

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

The above mentioned global CF strength of 1749 cm^{-1} for base-free compound **1** is the highest global CF strength ever found for a lanthanide compound. This is in agreement with the results of previous and current CF analyses of ψ trigonal planar complexes such as $[Pr(C_5H_4SiMe_3)_3]$, $[Pr(C_5H_4tBu)_3]$, $[Nd(C_5H_4SiMe_3)_3]$ and $[Nd(C_5H_4tBu)_3]$ where $N_v/(4\pi)^{1/2}$ values of 1429, 1497, 1662 and 1651 cm^{-1} were found,[7,48] which are the highest hitherto concluded for Pr^{III} and Nd^{III} compounds.

The CF strengths experienced by the Sm^{3+} central ions decrease from base-free compound **1** via mono adducts **3−5** to the bis adduct $[La_{0.8}Sm_{0.2}(Cp)_3(NCCH_3)_2]$ (Table 3) which is mainly due to the decreasing absolute value of B^2_0 within this series. The results[49] of basic model calculations in the framework of the angular overlap model[50−52] are consistent with the found trend for the above mentioned compounds (Table 3). The enormous decrease of CF strength going from base-free compound **1** to the mono adduct **3** is paralleled by the pair of compounds $[Sm(C_5H_4SiEt_3)_3]$/$[Sm(C_5H_4SiEt_3)_3(NCCH_3)]$ (where the former complex has a comparable CF splitting pattern as compound **1**) which have preliminary $N_v/(4\pi)^{1/2}$ values of 1721 and 1375 cm^{-1}.[53]

Applying method A on compound **1** and method B on complex **2**, $C_5H_4tBu^-$ and unsubstituted Cp produce CF strengths of 583 and 522 cm^{-1}, respectively. Comparing both values, the agreement is not too bad.

The most obvious reason for the discrepancy found would be that it is not allowed to neglect the CF strengths of the two Tp^{Me_2} ligands. Usually, nine-coordinate Ln^{3+} central ions experience low CF strengths.[54] For this reason, it was originally assumed that this also holds for homoleptic nine-coordinate $[Ln(\eta^3\text{-}Tp)_3]$ (Ln = La−Tb)[55,56] and $[Ln(COT)(\eta^3\text{-}Tp^{Me_2})]$ (Ln = Pr, Nd, Sm),[16−19] where the N atoms of the Tp^{Me_2} ligands have only somewhat shorter distances from the Ln central ions[57] as in $[Ln(Tp)_3]$.[55,56] Thus, we neglected the contribution of the Tp^{Me_2} ligand to the global CF strength and identified (adopting method B) the global CF strength of $[Ln(COT)(Tp^{Me_2})]$ (approximately 1250 cm^{-1})[16−19] with the individual CF strength of the COT ligand.

In order to examine the above assumption of a low CF strength of the Tp^{Me_2} or Tp ligand, we recently analyzed the optical spectra of homoleptic $[Ln(\eta^3\text{-}Tp)_3]$ (Ln = Eu, Pr)[56,58] and found averaged CF strengths of 149 cm^{-1} [56] and 194 cm^{-1},[58] respectively, per Tp ligand. In view of the global CF strength of approximately 1250 cm^{-1} of $[Ln(COT)(Tp^{Me_2})]$ complexes it is a somewhat rough but reasonable approximation to neglect the contribution of the Tp^{Me_2} ligand to the global CF strength.

By means of compound **1** and applying method A, the individual CF strength of the $C_5H_4tBu^-$ ligand was estimated to be 583 cm^{-1} (vide supra). This value is approximately three times greater than that of the Tp ligand and thus the contribution of the η^3- and η^2-coordinated Tp^{Me_2} ligands to the global CF strength of complex **1** cannot be neglected. In view of these facts, it is rather surprising that methods A and B, when applied to compounds **1** and **2**, lead to comparable values of the CF strength of η^5-coordinated (substituted) Cp ligands (vide supra). The most simple explanation for this finding would be that opposite effects cancel out in the case of compound **2**, thus giving almost the same individual CF strength of the Cp ligand as found for the substituted Cp ligand of compound **1**.

If one accepts the above rough approximation for [Ln(COT)(Tp^{Me_2})], the individual CF strength of COT ligand is (with about 1250 cm^{-1}) by a factor of 2.1 greater than that which we derived for the $C_5H_4tBu^-$ ligand of compound **1** adopting method A. If one refers to the ligand field strength produced by one coordinated C atom of both ring ligands, one arrives at 156 cm^{-1} (COT) and 116 cm^{-1} (Cp).

The optical spectra of [Sm{CH(SiMe$_3$)$_2$}$_3$] have not been analyzed at this point, but in the case of the corresponding Nd compound we found an individual CF strength of 348 cm^{-1} for the essentially σ bonded $CH(SiMe_3)_2^-$ ligand,[12] which is considerably greater than those associated with one carbon atom of π bonded COT or Cp ligands. These findings may be partly explained by the considerably reduced average Sm−C distance of [Sm{CH(SiMe$_3$)$_2$}$_3$] (2.33 Å)[59] as compared to [Sm(COT)(Tp^{Me_2})] (2.622 Å)[57] and (as a proxy for compound **1**) [Sm(C$_5$H$_3$(1,3-SiMe$_3$)$_2$)$_3$] (2.76 Å).[22]

The CF parameters B^4_0 and B^6_0 of complex **2** have unusual low absolute values as compared to the remaining Cp compounds of Table 3, a fact which contributes mainly to the low global CF strength of this compound. In contrast to B^2_0, which is caused mainly by electrostatic effects the CF parameter B^6_0 is dominated by covalency effects (ref.[44] p.71). Possibly, the low covalency of complex **2** (vide infra) may be partly responsible for the low absolute values of B^4_0 and B^6_0 of this compound.

The Slater parameter F^2 and the spin-orbit coupling parameter of the gaseous Sm^{3+} ion are unknown, thus the nephelauxetic parameter beta = F^2(complex)/F^2(free ion), the relativistic nephelauxetic parameter beta′ = ζ_{4f}(complex)/ζ_{4f}(free ion), and the covalency √b [defined as √b = √(1-beta)/2 [60]] cannot be calculated. Furthermore, the Slater parameters of Sm^{III} compounds are frequently not well defined due to the limited number of ^{2S+1}L terms (with different L or S) considered in the fits. Anyway, the insertion of compounds **1−5** into truncated empiric nephelauxetic and relativistic nephelauxetic series can be seen from Table 4. Evidently, the truncated nephelauxetic series for Sm^{III} compounds in Table 4 is only partly paralleled by the trend of ζ_{4f} values, and thus the relativistic nephelauxetic series.

Obviously, complex **1** has the lowest F^2 value and thus is the most covalent Sm^{III} compound hitherto analyzed, F^2 of adducts **3−5** moves within the typical range of mono adducts, whereas **2** has a relatively low covalency. The observed trends within compounds **1** and **3−5** are paralleled by the corresponding Pr and Nd complexes.[48]

Comparing the found F^2 and $N_v/(4\pi)^{1/2}$ values of adduct **5** and [Sm(Cp)$_3$(NCCH$_3$)] (Table 3), one has to conclude that covalency and global CF strength are more pronounced for the isocyanide than for the nitrile adduct.

The eigenvalues of an energy matrix of the spin-free f^1 system, into which the CF parameters of a parametric analysis of the compound of interest had been inserted, were defined in ref.[49] as the experimentally based non-relativistic MO scheme of this compound in the f range. Likewise, the eigenvalues of an energy matrix of the real f^1 system, into which the spin-orbit coupling as well as the CF parameters had been inserted, were defined as the experimentally based relativistic MO scheme of this compound in the f range.[66]

In Figure 5, the experimentally based non-relativistic MO schemes (in the f range) of complex **1** and [Pr(η^5-C$_5$H$_4$SiMe$_3$)$_3$][52] are compared with the non-relativistic MO scheme of fictive ψ trigonal planar [Sm(η^5-Cp)$_3$] calculated in the framework of the SW-Xα approximation.[33]

Obviously, the calculated splitting of f orbitals is considerably greater than the experimentally based ones. Moreover, the experimentally based sequences of f orbitals are roughly comparable for **1** and [Pr(η^5-C$_5$H$_4$SiMe$_3$)$_3$] (only the close-lying orbitals f_{z^3} and $f_{z(x^2-y^2)}/f_{xyz}$ are interchanged) but at the first glance considerably different from the calculated one for fictive trigonal planar[Sm(Cp)$_3$]. Fitting the free parameters of the phenomenological Hamiltonian of

Table 4. F^2, ζ_{4f} and $N_v/(4\pi)^{1/2}$ values of selected Sm^{III} compounds; all values in cm^{-1}.

Compound [a]	F^2	ζ_{4f}	$N_v/(4\pi)^{1/2}$	Ref.
[LaF$_3$:Sm^{3+}]	79805	1176	610	[61]
[Na$_3$[Sm(ODA)$_3$]·2NaClO$_4$·6H$_2$O][b]	79015	1166	755	[62]
[Sm(Cp)(Tp^{Me_2})$_2$]	78293	1159	522	this work
[GdOCl:Sm^{3+}]	78196	1150	640	[63]
[LaCl$_3$:Sm^{3+}]	78125	1168	300	[41]
[Cs$_2$NaSmCl$_6$]	77510	1167	545	[64]
[La$_{0.8}$Sm$_{0.2}$(Cp)$_3$(NCCH$_3$)$_2$]	77002	1155	1222	[45]
[Sm[N(SiMe$_3$)$_2$]$_3$(CNC$_6$H$_{11}$)$_2$]	76676	1169	891	[65]
[Sm(C$_5$H$_4$CH$_2$CH$_2$OCH$_3$)$_3$]	76602	1156	1198	[46]
[Sm[N(SiMe$_3$)$_2$]$_3$]	76388	1164	1179	[9]
[Sm(C$_5$H$_4$SiEt$_3$)$_3$(NCCH$_3$)]	76305	1149	1375	[53]
[Sm(Cp)$_3$(NCCH$_3$)]	76230	1148	1324	[45]
[Sm(Cp)$_3$(CNC$_6$H$_{11}$)]	75813	1151	1373	this work
[Sm(Cp)$_3$(THF)]	75773	1149	1378	this work
[Sm(C$_5$H$_4$tBu)$_3$(THF)]	75324	1149	1371	this work
[Sm(C$_5$H$_4$tBu)$_3$]	73992	1143	1749	this work

[a] Ordered by decreasing Slater parameter F^2. [b] ODA = oxydiacetato.

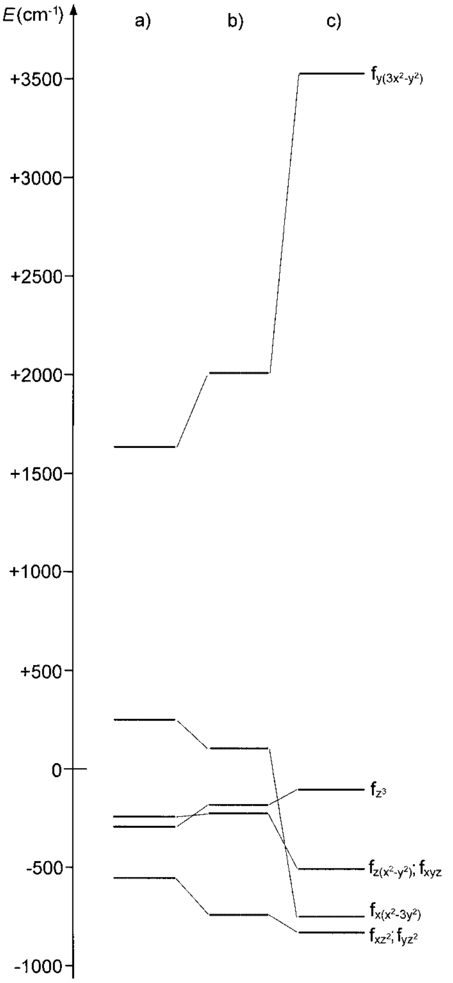

Figure 5. Experimentally based and calculated non-relativistic MO schemes of: a) [$Pr(C_5H_4SiEt_3)_3$] (exp., from ref.[7]); b) [$Sm(C_5H_4tBu)_3$] (exp.); c) fictive ψ trigonal planar [$Sm(Cp)_3$] (calcd. from ref.[33])

the spin-free f^1 system to the calculated energies of f orbitals of the latter complex one arrives at $B^2_0 = -3443\ cm^{-1}$, $B^4_0 = 2817\ cm^{-1}$, $B^6_0 = 1296\ cm^{-1}$ and $B^6_6 = -6033\ cm^{-1}$. Comparing these values with those of compound **1** (Table 4), it becomes evident that first of all the CF parameters B^6_6 (which considers the interactions between the orbitals $f_{x(x^2-3y^2)}$ and $f_{y(3x^2-y^2)}$ within the framework of CF theory) but also B^4_0 are heavily overestimated by the model calculation. If one reduces B^6_6 to a quarter, not only the correct sequence of levels but also the correct total splitting of f orbitals would result. From the aspect of MO theory the required reduction of B^6_6 means that the interaction of $f_{y(3x^2-y^2)}$ with the corresponding symmetry adapted linear combination of ligand orbitals is overestimated and that of $f_{x(x^2-3y^2)}$ is underestimated by the model calculation.

The electronic structure of fictive ψ trigonal planar [$Pr(Cp)_3$] was calculated by means of the SW-Xα[33] as well as the INDO/1[35] approximation. The SW-Xα calculation yielded a comparable MO scheme (in the f range) as for [$Sm(Cp)_3$][33] and the more basic INDO/1 calculation led, astonishingly, to the same energetic sequence[35] as we had concluded for [$Pr(\eta^5\text{-}C_5H_4SiMe_3)_3$] (Figure 5). However, in the case of the INDO/1 approximation the calculated total splitting of f orbitals (1545 cm^{-1} [35]) is noticeably smaller than the experimentally based one (2189 cm^{-1} [7]).

The result of a recent non-relativistic discrete variational (DV)-Xα calculation on ψ trigonal planar [$Ce(Cp)_3$][34] is similar to that of the SW-Xα approximation.[33]

In Figure 6, the result of a previous relativistic DV-Xα calculation on fictive ψ trigonal planar [$Ce(Cp)_3$][34] is compared with the experimentally based relativistic MO schemes of compound **1** and that of a model compound, the CF splitting pattern of which was calculated adopting the spin-orbit coupling parameter used for [$Ce(Cp)_3(NCCH_3)_2$] (610 cm^{-1})[67] and the CF parameters of complex **1**. Obviously, the same sequences of levels exist, but the DV-Xα calculation predicts a total splitting of f levels which is a factor of 1.75 greater than that of the above characterized model compound. This is mainly due to an overestimated spin-orbit coupling parameter of the DV-Xα calculation, which is approximately twice as great (1300 cm^{-1}) as those found in the framework of previous CF analyses of Ce^{III} compounds (cf. ref.[6] p. 127).

To the best of our knowledge, results of model calculations on mono adducts of the $Sm(Cp)_3$ moiety have not been published up to now. However, [$Ln(Cp)_3(THF)$] (Ln = Pr,[35] Gd[36]) and [$Pr(Cp)_3(CNC_6H_{11})$][35] have been the subject of INDO/1 calculations. In the case of [$Pr(Cp)_3(B)$] (B = CNC_6H_{11}, THF), these calculations led to the same

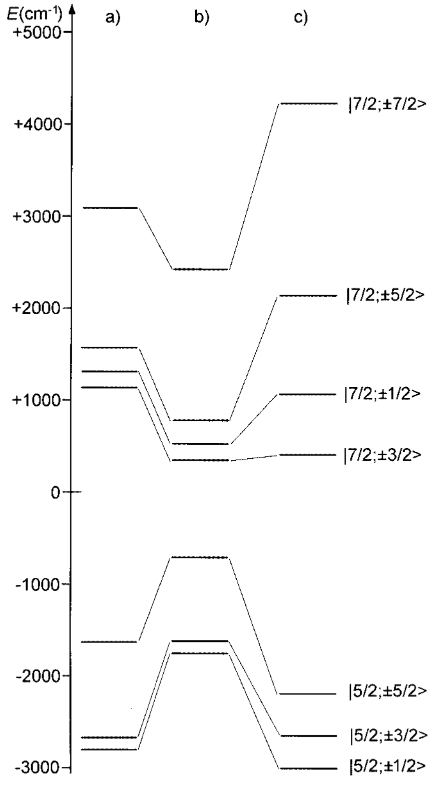

Figure 6. Experimentally based and calculated relativistic MO schemes of: a) [$Sm(C_5H_4tBu)_3$] (exp.); b) calculated, adopting CF parameters of [$Sm(C_5H_4tBu)_3$] and $\zeta_{4f} = 610\ cm^{-1}$; c) ψ trigonal planar [$Ce(Cp)_3$] (calcd., from ref.[34])

energetic sequence of f orbitals as we found on an experimental basis for these compounds[68] as well as for [Sm(Cp)$_3$(NCCH$_3$)][69] and adducts **3−5**. However, the calculated total splitting of f orbitals of [Pr(Cp)$_3$(B)] is with 742 cm^{-1} (B = CNC$_6$H$_{11}$) and 997 cm^{-1} (B = THF) considerably smaller than the experimentally based ones of [Pr(Cp)$_3$(CNC$_6$H$_{11}$)] (1978 cm^{-1}),[68] [Pr(Cp)$_3$(THF)] (1722 cm^{-1} [68]), [Sm(Cp)$_3$(NCCH$_3$)] (1989 cm^{-1} [69]) and compounds **3** (2043 cm^{-1}), **4** (2007 cm^{-1}) and **5** (1988 cm^{-1}).

The above-mentioned INDO calculation for [Gd(Cp)$_3$(THF)] led to the following energetic sequence of f orbitals: $f_{z^3} < f_{xz^2}/f_{yz^2} < f_{z(x^2-3y^2)}/f_{xyz} < f_{x(x^2-3y^2)} < f_{y(3x^2-y^2)}$ (with a total splitting of f orbitals of 230 cm^{-1} [36]) which differs considerably from the experimentally based ones for mono adducts of the [Ln(Cp)$_3$] moiety (Figure 7).

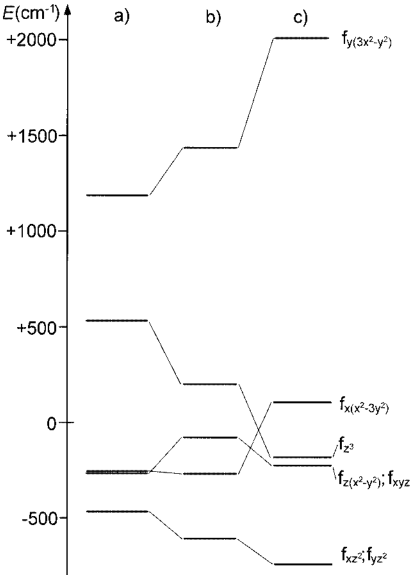

Figure 7. Experimentally based non-relativistic MO schemes of: a) [La$_{0.8}$Sm$_{0.2}$(Cp)$_3$(NCCH$_3$)$_2$]; b) [Sm(C$_5$H$_4$*t*Bu)$_3$(THF)]; c) [Sm(C$_5$H$_4$*t*Bu)$_3$]

To the best of our knowledge model calculations on bis adducts of the [Ln(Cp)$_3$] moiety have not been performed, thus no calculated counterpart of the experimentally derived MO scheme of [La$_{0.8}$Sm$_{0.2}$(Cp)$_3$(NCCH$_3$)$_2$] exists.

Going from the fictive base-free trigonal planar [Ln(Cp)$_3$] complex via a trigonal pyramidal mono to a trigonal bipyramidal bis base adduct, the axially f_{z^3} orbital should be increasingly energetically destabilized adopting the approximation of the angular overlap model.[49] This is nicely demonstrated by the series of compounds **1**, **3** and [La$_{0.8}$Sm$_{0.2}$(Cp)$_3$(NCCH$_3$)$_2$] (Figure 7).

Conclusion

The CF strengths of C$_5$H$_4$*t*Bu$^-$ and Cp ligands estimated by applying method A on compound **1**, and applying method B to **2** differ by some 10%. The main reason for this discrepancy is that it is not justified to neglect the CF strength associated with the Tp^{Me_2} ligand in the case of complex **2**. This finding suggests to apply method B to other [Sm(Cp)(L′)$_2$] compounds such as [Sm(Cp)(acac)$_2$] and [Sm(Cp)(I)$_2$] where the CF strengths produced by the acac$^-$ and I$^-$ ligands are probably weaker than in the case of Tp^{Me_2}.

In this work, the experimentally based MO schemes of compound **1** and the corresponding THF adduct are compared with the results of previous model calculations of different degrees of sophistication. Astonishingly, and perhaps accidentally, basic model calculations in the framework of the INDO/1 approximation on [Pr(Cp)$_3$] and [Pr(Cp)$_3$(B)] (B = THF, CNC$_6$H$_{11}$) would have led to correct signs but to noticeably reduced absolute values of the CF parameters as compared to those of the sets [Pr(C$_5$H$_4$SiMe$_3$)$_3$]/(**1**) and [Pr(Cp)$_3$(B)]/(**3−5**) (B = THF, CNC$_6$H$_{11}$).

Besides, applying the relativistic DV/Xα approximation to fictive ψ trigonal planar [Ce(Cp)$_3$] a sequence of CF levels was calculated which is in agreement with the experimentally based relativistic MO scheme of complex **1**. However, this approximation seriously overestimated mainly the spin-orbit coupling parameter.

It seems that the present approximations of quantum chemistry have to be refined somewhat until they are really helpful for interpreting optical spectra of f element organyls.

Experimental Section

Compounds **1**, **2**, **4** and **5** as well as the "optical empty" reference compounds [La(C$_5$H$_4$SiMe$_3$)$_3$] and [La(C$_5$H$_4$*t*Bu)$_3$(THF)] were synthesized by adopting the procedures of Wayda,[21] Lopes et al.,[32] Birmingham et al.,[70] Fischer et al.[71] and Stults et al.[72] The absorption spectra of compounds **1** and **2** were recorded by means of KBr pellets, and those of adducts **3** and **4** (dissolved in a mixture of MeTHF/THF in the ratio 3:1) as well as those of complex **5** (dissolved in a mixture of methylcyclohexane/toluene in the ratio 3:1) as glassy frozen solutions, making use of a Cary 5e instrument. The luminescence spectra of compounds **1**, **2**, **4** and **5** were run as powders (and that of **1** additionally as methylcyclohexane solution) by means of a Raman spectrometer (Jobin−Yvon, model U 1000) equipped with an Ar$^+$ laser (Coherent model Innova 70). In all optical low temperature measurements the samples were immersed in liquid nitrogen. Using liquid He as coolant didn't change the appearance of the spectra but worsened the signal-to-noise ratio.

The room temperature absorption spectrum of complex **1** dissolved in a mixture of glassy freezing 2-MeTHF and THF in the ratio 3:1 was identical with the data recorded by means of a KBr pellet of **1**. At 77 K, however, the absorption spectrum resembled those of [Sm(Cp)$_3$(B)] (B = THF, NCCH$_3$, CNC$_6$H$_{11}$), thus we assume that the mono THF adduct of complex **1** (i.e. **3**) is formed quantitatively.

In order to confirm the results of the fit of compound **2**, we calculated the temperature dependence of μ^2_{eff} of this complex on the basis of calculated wavefunctions and eigenvalues, and planned to compare these data with the corresponding experimental values.

Unfortunately, compound **2** lost weight in the framework of the susceptibility measurements,[73] thus leading to less reliable experimental μ^2_{eff} values. Nevertheless, the calculated temperature dependence of μ^2_{eff} in the range $77\ \mathrm{K} < T < 280\ \mathrm{K}$ was within the experimental array of curves.

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