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The electronic structure of organometallic complexes of the f elements
XXXVI. Parameterization of the crystal field splitting pattern of $(CH_3OCH_2CH_2C_5H_4)_3Sm^{III}$

C. Qian and B. Wang
Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200 032 (China)

N. Edelstein
Chemical Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720 (USA)

H. Reddmann, C. Hagen and H.-D. Amberger*
Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg (Germany)

Abstract

The absorption and luminescence spectra of $(CH_3OCH_2CH_2C_5H_4)_3Sm^{III}$ (Cp'_3Sm) in hydrocarbon glasses and in KBr pellets have been measured at room and low temperatures. The bands were assigned assuming comparable crystal field splitting patterns for Cp'_3Sm and for the previously analyzed $Cp_3Sm(NCCH_3)_2$. The parameters of an empirical Hamiltonian were fitted to the energies of 42 levels to give an rms deviation of 42 cm^{-1}. Making use of the calculated wave functions and eigenvalues, the experimentally determined low temperature magnetic susceptibility of powdered Cp'_3Sm could be simulated.

1. Introduction

Whereas bis base adducts of the tris(η^5-cyclopentadienyl)uranium(IV) moiety (Cp_3U^+) have been known for more than four decades [1,2], bis nitrile adducts derived from Cp_3Ln (Ln = La, Ce, Pr) were first described in 1985 [3–5]. Large single crystals of $Cp_3Nd(NCCH_3)_2$ have been grown [6]; however, these crystals decompose within approximately 1 week, when sealed under an inert atmosphere (He, Ar, N_2) [6]. Recently, it was found that $Cp_3Sm(NCCH_3)_2$ could be chemically stabilized by diluting a $Cp_3La(NCCH_3)_2$ matrix with some 20% of $Cp_3Sm(NCCH_3)_2$ [7].

In 1992, Qian *et al.* synthesized Cp'_3Ln complexes ($Cp' = CH_3OCH_2CH_2C_5H_4$; Ln = La–Yb), where two of the three Cp′ groups coordinate almost axially the pseudotrigonal plane Cp_3Ln moiety *via* the oxygen atoms [8,9]. In contrast to the bis nitrile adducts, these complexes are also stable in inert solvents such as glassy freezing mixtures of methylcyclohexane and toluene in the ratio 1:1.

In the framework of this contribution, we derive the crystal field (CF) splitting pattern on the basis of absorption and luminescence measurements, and the parameters of an empirical Hamiltonian are fitted to the experimentally derived splitting pattern. On the basis of the eigenfunctions and eigenvalues obtained, the temperature dependence of the paramagnetic susceptibility is calculated and compared with experimental data.

2. Experimental details

The synthesis of Cp'_3Ln has been described previously [8,9]. The optical spectra and susceptibility measurements were carried out as described in refs. 10–12.

3. Results

3.1. Absorption spectrum

The low temperature absorption spectrum of Cp'_3Sm dissolved in methylcyclohexane/toluene (1:1)

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*Author to whom correspondence should be addressed.

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exhibits essentially the same features as that of $Cp_3La_{0.8}Sm_{0.2}(NCCH_3)_2$ [7]; however, numerous additional weak signals appear. Most of these signals are probably of vibronic origin, but some of them have energies which are comparable to the calculated energies of higher-lying Γ_8 states (see Table 1). As the CF ground state is of Γ_8 symmetry, transitions to terminal Γ_8 states are forbidden in strict D_{3h} symmetry [7,13]. Because of the slightly different Ln–O distances of Cp'_3Ln compounds (274 and 284 pm in the case of the Pr compound [8]) and the deviation of the O–Ln–O angle (174.8° for the Pr complex [8]) from the ideal 180° value, $\Gamma_8 \rightarrow \Gamma_8$ transitions may become weakly allowed. Some weak transitions have been assigned accordingly.

3.2. Luminescence spectrum

The vibrational Raman and luminescence transitions are energetically well separated upon excitation by the 476 nm line of an Ar^+ laser. In the range 17 600–11 180 cm^{-1}, numerous luminescence signals of very different intensity appeared. The existence of the more sharp and intense signals can be rationalized by assuming an initial state at 17 541 cm^{-1} and terminal states arising from the manifolds ^6H_J ($J = 5/2$–$13/2$).

4. Analysis

In order to fit the optical data, we have assumed that the CF parameters obtained for $Cp_3La_{0.8}Sm_{0.2}(NCCH_3)_2$ [7] will give the correct ordering of levels for Cp'_3Sm. On this basis, we can assign the absorption and luminescence spectrum of Cp'_3Sm as shown in Table 1. Subsequently, a least-squares adjustment of free ion [14] and CF parameters [15] was performed. In order to limit the number of free parameters, α, β, γ, the T^i, M^k and P^k parameters were fixed at the values used for the analysis of $LaCl_3$:Sm [16]. The remaining parameters were allowed to vary. For 42 levels, the rms deviation was 42 cm^{-1}.

Table 2 gives the final values of the free ion and CF parameters. For comparison purposes, parameters for $Cp_3La_{0.8}Sm_{0.2}(NCCH_3)_2$ [7] and $LaCl_3$:Sm [16] are also listed.

Approximately 16 mg of material was available for magnetic measurements. For small amounts of air-sensitive material, container corrections become a significant fraction of the measured susceptibility at higher temperatures. In this case, only measurements at and below 12 K are considered reliable. The data for 0.5 and 4 T were fit with the Curie–Weiss formula $\chi = C/(T-\theta)$ with the following values: $C = 0.109 \pm 0.004$ emu K mol^{-1}, $\theta = -1.1 \pm 0.6$ K and $\mu_{eff} = 0.93 \pm 0.02$ BM

TABLE 1. Experimental and calculated energy levels for (Cp'_3Sm)

SLJ comp.[a]	CF state[b]	E_{obs} (cm^{-1})	E_{calc} (cm^{-1})
$^6H_{5/2}$	$1\Gamma_8$	0	0
$^6H_{5/2}$	$1\Gamma_9$		88
$^6H_{5/2}$	$1\Gamma_7$		300
$^6H_{7/2}$	$2\Gamma_8$	870	835
$^6H_{7/2}$	$2\Gamma_7$		1289
$^6H_{7/2}$	$3\Gamma_8$		1364
$^6H_{7/2}$	$2\Gamma_9$	1578	1603
$^6H_{9/2}$	$4\Gamma_8$		2176
$^6H_{9/2}$	$3\Gamma_9$	2358	2315
$^6H_{9/2}$	$3\Gamma_7$		2380
$^6H_{9/2}$	$4\Gamma_9$	2749	2705
$^6H_{9/2}$	$5\Gamma_8$	2773	2784
$^6H_{11/2}$	$5\Gamma_9$		3418
$^6H_{11/2}$	$4\Gamma_7$	3586	3604
$^6H_{11/2}$	$6\Gamma_8$		3743
$^6H_{11/2}$	$5\Gamma_7$		3766
$^6H_{11/2}$	$6\Gamma_9$		3919
$^6H_{11/2}$	$7\Gamma_8$		4175
$^6H_{13/2}$	$6\Gamma_7$	4849	4825
$^6H_{13/2}$	$7\Gamma_7$	4956	4923
$^6H_{13/2}$	$8\Gamma_8$	(5015)[c]	5006
$^6H_{13/2}$	$7\Gamma_9$	5098	5060
$^6H_{13/2}$	$8\Gamma_9$	5328	5297
$^6H_{13/2}$	$8\Gamma_7$	5328	5354
$^6H_{13/2}$	$9\Gamma_8$	5455	5455
$^6H_{15/2}$	$9\Gamma_9$	6127	6196
$^6H_{15/2}$	$10\Gamma_9$	6341	6331
$^6H_{15/2}$	$9\Gamma_7$	6341	6380
$^6H_{15/2}$	$10\Gamma_7$	6443	6471
$^6H_{15/2}$	$10\Gamma_8$	(6481)	6474
$^6H_{15/2}$	$11\Gamma_7$	6655	6657
$^6H_{15/2}$	$11\Gamma_8$		6828
$^6F_{3/2}$	$11\Gamma_9$	6868	6893
$^6F_{3/2}$	$12\Gamma_7$	6868	6930
$^6F_{15/2}$	$12\Gamma_9$	6975	6999
$^6F_{15/2}$	$13\Gamma_7$	7109	7200
$^6F_{5/2}$	$12\Gamma_8$	(7336)	7338
$^6F_{5/2}$	$14\Gamma_7$	7510	7465
$^6F_{5/2}$	$13\Gamma_9$	7555	7554
$^6F_{7/2}$	$14\Gamma_9$	8116	8143
$^6F_{7/2}$	$13\Gamma_8$	(8183)	8166
$^6F_{7/2}$	$15\Gamma_7$	8291	8248
$^6F_{7/2}$	$14\Gamma_8$	(8347)	8333
$^6F_{9/2}$	$16\Gamma_7$	9144	9217
$^6F_{9/2}$	$15\Gamma_8$		9307
$^6F_{9/2}$	$15\Gamma_9$	9276	9336
$^6F_{9/2}$	$16\Gamma_8$	(9398)	9438
$^6F_{9/2}$	$16\Gamma_9$	9492	9438
$^6F_{11/2}$	$17\Gamma_8$	(10565)	10591
$^6F_{11/2}$	$17\Gamma_9$	10586	10618
$^6F_{11/2}$	$18\Gamma_8$		10632
$^6F_{11/2}$	$17\Gamma_7$	10672	10645
$^6F_{11/2}$	$18\Gamma_8$	10820	10754
$^6F_{11/2}$	$18\Gamma_7$	11019	10936
$^4G_{5/2}$	$19\Gamma_8$	(17541)	17528
$^4G_{5/2}$	$19\Gamma_7$	17808	17871
$^4G_{5/2}$	$19\Gamma_9$	18015	18036
$^4F_{3/2}$	$20\Gamma_9$	18801	18839

(*continued*)

TABLE 1. (*continued*)

SLJ comp.[a]	CF state[b]	E_{obs} (cm^{-1})	E_{calc} (cm^{-1})
$^4F_{3/2}$	$20\Gamma_7$	18986	18957
$^4G_{7/2}$	$20\Gamma_8$	(19798)	19730
$^4G_{9/2}$	$21\Gamma_9$	19890	19919
$^4G_{7/2}$	$21\Gamma_8$	(19902)	19933
$^4G_{7/2}$	$21\Gamma_7$	20058	20018
$^4G_{7/2}$	$22\Gamma_9$	20120	20086
$^4G_{9/2}$	$22\Gamma_8$	(20189)	20221
$^4I_{15/2}$	$22\Gamma_7$	20226	20235
$^4G_{9/2}$	$23\Gamma_9$	(20275)	20278
$^4G_{9/2}$	$23\Gamma_8$	20341	20292

[a] Largest eigenvector component. [b] Crystal field state (D_{3h} symmetry). [c] Levels in parentheses were not fitted.

TABLE 2. Parameter values[a] for Cp'_3Sm, $Cp_3La_{0.8}Sm_{0.2}(NCCH_3)_2$ and $Sm^{3+}:LaCl_3$ (in cm^{-1})

Parameter	Cp'_3Sm	$Cp_3La_{0.8}Sm_{0.2}$ $(NCCH_3)_2$	$Sm^{3+}:LaCl_3$[b]
F^2	76602	77702	78125
F^4	57162	56124	56809
F^6	39329	39832	40091
ζ_{4f}	1156	1155	1168
α	(21.6)	(21.6)	21.6
β	(−724)	(−724)	−724
γ	(1700)	(1700)	(1700)
T^2	(291)	(291)	291
T^3	(13)	(13)	13
T^4	(34)	(34)	34
T^6	(−193)	(−193)	−193
T^7	(288)	(288)	288
T^8	(330)	(330)	330
M^0	(2.40)	(2.40)	2.40
M^2	(1.34)	(1.34)	(1.34)
M^4	(0.91)	(0.91)	(0.91)
P^2	(341)	(341)	341
P^4	(256)	(256)	(256)
P^6	(171)	(171)	(171)
B^2_0	−1077	−953	186
B^4_0	1177	1882	−270
B^6_0	2588	1903	623
B^6_6	−1865	−2038	470
$N_v/\sqrt{4\pi}$	1081	1083	249

[a] Values in parentheses were not freely varied. [b] From ref. 16.

(T=5–12 K). The calculated value of μ_{eff} at 0 K and 10 K are 0.85 BM and 0.90 BM, respectively. Since the sample mass was small and the susceptibility quite weak, we consider this agreement satisfactory.

5. Discussion

Compared with our previous fits of the CF splitting patterns of mono and bis adducts derived from the Cp_3Ln moiety, the present fit for Cp'_3Sm is less satisfactory. We think this reflects the comparatively drastic deviation of Cp'_3Sm from the ideal D_{3h} symmetry on which the fit was based.

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