Title

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Abstract

The absorption spectrum of $Cp_3Sm{\cdot}CNC_6H_{11}$ has been measured at room and low temperatures in a hydrocarbon glass and in a KBr pellet. EPR and magnetic susceptibility measurements are also reported in this paper. The observed optical bands were assigned based on calculations which assumed the crystal field parameters of the Sm complex were the same as for the previously analyzed $Cp_3Pr{\cdot}CNC_6H_{11}$. The parameters of an empirical Hamiltonian were fit to the energies of 39 levels to give an r.m.s. deviation of 21 cm^{-1}. On the basis of the wave functions of the crystal field ground state obtained from the fit, the ground state g values and the temperature-dependent magnetic susceptibility were calculated and compared to the experimental values.

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Introduction

Though the optical and magnetochemical properties of adducts derived from tris(η^5-cyclopentadienyl)-lanthanide(III) ($Cp_3Ln{\cdot}X$) have been studied extensively for more than three decades, only the crystal field (CF) splitting patterns of the first three members of the lanthanide series are understood in detail [1-6]. The CF parameters of these complexes turned out to be rather similar, so we were encouraged to use these parameters with the energy matrices of the f^8 - f^{13} systems (assuming a CF of C_{3v} symmetry) in order to analyze the optical and magnetochemical properties of $Cp_3Ln{\cdot}X$ complexes of the second half of the 4f series [7,8]. However, the calculated CF splitting patterns were quite different from the experimental patterns [7,8]. These findings suggest that one should approach the problem of the CF parameters of $Cp_3Ln{\cdot}X$ adducts of the second half series more gradually, i.e., it is better to analyze the CF splitting patterns of the $4f^4$ - $4f^7$ complexes before turning to the second half of the lanthanides. In this paper we present a preliminary analysis of the optical spectra and magnetic properties of the $Cp_3Sm{\cdot}CNC_6H_{11}$ complex.

Experimental Details

The synthesis of $Cp_3Ln{\cdot}CNC_6H_{11}$ adducts has been described previously [9]. The optical spectra, EPR and susceptibility measurements were carried out as described in refs. 1, 2, 10 and 11.

Results

We have recorded the absorption spectrum of $Cp_3Sm{\cdot}CNC_6H_{11}$ at ambient temperature and at approximately 90 and 30 K, respectively. In addition we have measured the magnetic susceptibility in the temperature range 5 - 300 K and the electron paramagnetic resonance (EPR) spectrum at ~ 5 K.

The 4f → 4f transition energies of the observed low temperature spectrum which are well separated from the charge transfer transition are given in Table 1. Two further CF levels of the ground manifold at approximately 230 and 540 cm^{-1} could be inferred from the absorption spectrum run at ambient temperature.

The observed EPR spectrum of Sm^{3+}: $Cp_3La{\cdot}CNC_6H_{11}$ could be approximately fit by the spin Hamiltonian parameters $|g_{\|}|_1 = 1.16$, $|g_{\|}|_2 = 1.21$ and $|g_{\perp}| = 1.07$.

The measured magnetic susceptibility data (plotted as μ_{eff}^2) are shown in Fig. 1.

(Insert Fig. 1)

Analysis

In order to fit the optical data we have assumed that the CF parameters obtained for $Cp_3Pr{\cdot}CNC_6H_{11}$ [2] will give the correct ordering of the levels for $Cp_3Sm{\cdot}CNC_6H_{11}$. On this basis we can assign the absorption spectrum of $Cp_3Sm{\cdot}CNC_6H_{11}$ as shown in Table 1. Subsequently, a least-squares adjustment of free ion [12] and CF parameters [13] 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 Sm^{3+}: $LaCl_3$ [14]. The remaining parameters were allowed to vary. For 39 levels the r.m.s. deviation was 21 cm^{-1}. Table 2 gives the final values of the free ion and crystal field parameters. For comparison purposes parameters for $Cp_3Pr{\cdot}CNC_6H_{11}$ [2] and Sm^{3+}: $LaCl_3$ [14] are also listed.

Insert Table 1, Table 2

Using the eigenvectors of the Kramers' degenerate CF ground state, the calculated spectroscopic splitting factors $g_{\|}$ and $g_{\perp}$ are -0.84 and 1.08, respectively.

Adopting an orbital reduction factor k = 0.95 the temperature dependence of μ_{eff}^2 was calculated on the basis of the eigenfunctions and eigenvalues obtained from the fit. The experimental and calculated data are compared in Fig. 1.

Discussion

Based on the assumption that the empirical parameters of $Cp_3Pr{\cdot}CNC_6H_{11}$ will reproduce the correct ordering of the energy levels of $Cp_3Sm{\cdot}CNC_6H_{11}$ we are able to fit the "assigned" optical levels of the latter compound quite well. The fit of $g_{||}$ and the temperature dependence of μ^2_{eff} was less satisfactory. It is well-known that the energy levels of the first excited manifold ($^6H_{7/2}$) greatly affect the magnetic data of Sm III compounds. The levels of this manifold have not been observed in the IR spectrum, even at low temperatures. Future work will try to extract the energies of these and other low-lying levels from luminescence spectra.

Acknowledgements

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14. W.T. Carnall, H. Crosswhite and H.M. Crosswhite, *Energy Level Structure and Transition Probabilities in the Spectra of the Trivalent Lanthanides in LaF_3*, ANL-Report, 1977 (unpublished), Appendix I. Table I.

Table 1. Experimental and calculated energy levels for $Cp_3Sm{\cdot}CNC_6H_{11}$ (in cm^{-1})

State*	E_{obs}	E_{calc}
1 1/2	0	0
1 3/2	230	230
2 1/2	540	543
3 1/2		895
4 1/2		1440
5 1/2		1589
2 3/2		1614
3 3/2		2370
6 1/2		2377
7 1/2		2617
4 3/2		2795
8 1/2		2870
9 1/2		3569
5 3/2		3610
10 1/2		3819
11 1/2		4021
6 3/2		4129
12 1/2		4258
13 1/2	4850	4861
14 1/2	4993	4962
15 1/2	5092	5083
7 3/2	5115	5110
16 1/2	5482	5503
8 3/2	5516	5529
17 1/2	5624	5635
9 3/2	6105	6111
18 1/2	6361	6355
19 1/2	6489	6476
10 3/2	6549	6567
20 1/2	6653	6643
21 1/2	6743	6738
11 3/2	6892	6897
22 1/2	7018	7017
23 1/2	7082	7065
12 3/2	7163	7181
24 1/2	7252	7281
25 1/2	7315	7354
26 1/2	7530	7537
13 3/2	7553	7540
27 1/2	8150	8190
14 3/2	8285	8258
28 1/2	8319	8286
29 1/2	8396	8348
30 1/2	9311	9312

* The states are classified by the crystal quantum number μ and are ordered in ascending energy.

31 1/2	9337	9349
15 3/2	9337	9361
32 1/2	9506	9463
16 3/2	9506	9483
33 1/2	10604	10603
17 3/2	10604	10626
34 1/2	10650	10663
35 1/2	10730	10732
18 3/2	10858	10836
36 1/2	11050	10983

Table 2
Parameter values for $Cp_3Sm{\cdot}CNC_6H_{11}$, $Cp_3Pr{\cdot}CNC_6H_{11}$ and Sm^{3+}:$LaCl_3$ (in cm^{-1})

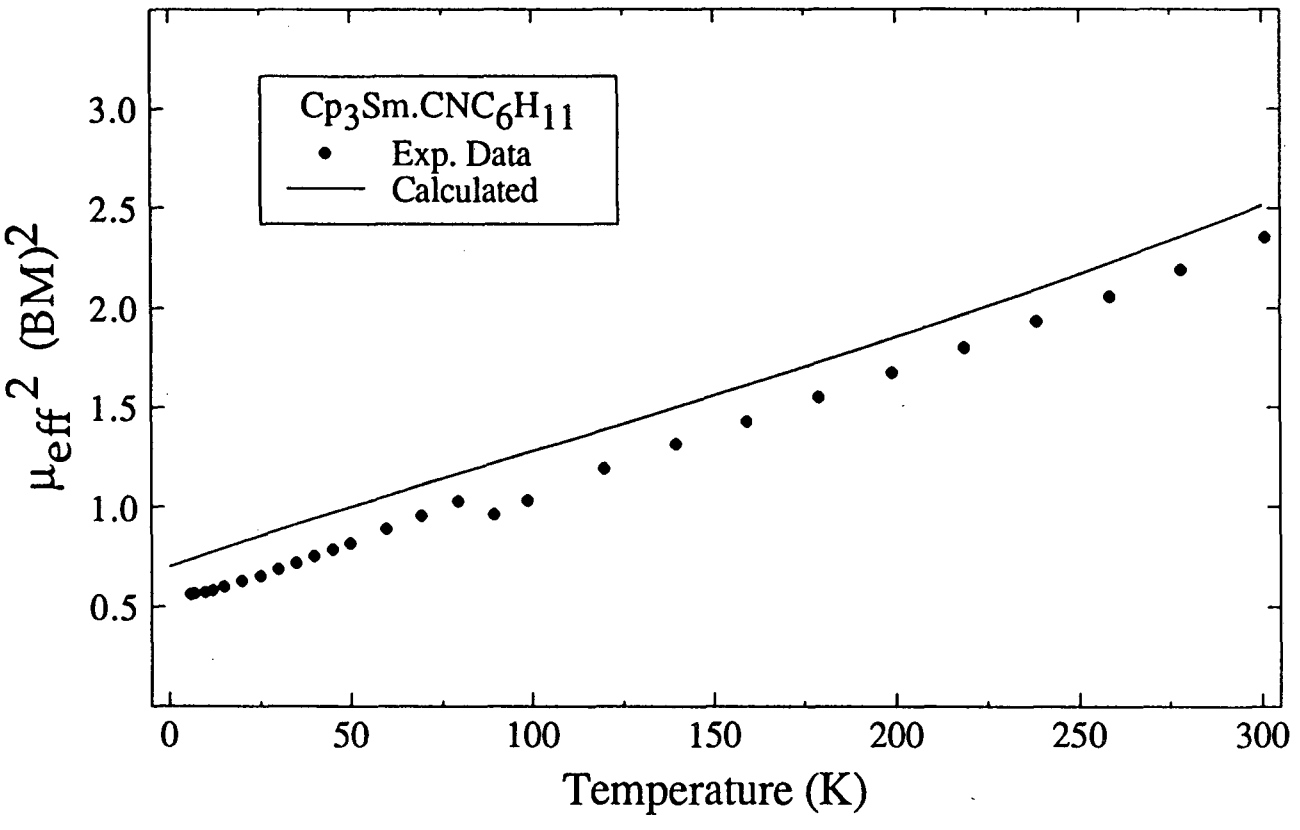
Parameter	$Cp_3Sm{\cdot}CNC_6H_{11}$	$Cp_3Pr{\cdot}CNC_6H_{11}$[a]	Sm^{3+}:$LaCl_3$[b]
F^2	75174	65575	78125
F4	54490	47985	56809
F^6	38049	32070	40091
ζ_{4f}	1149	737	1168
α	(21.6)[c]	21.8	21.6
β	(-724)	-698	-724
γ	(1700)	(1534)	(1700)
T^2	(291)	-	291
T^3	(13)	-	13
T^4	(34)	-	34
T^6	(-193)	-	-193
T^7	(288)	-	288
T^8	(330)	-	330
M^0	(2.40)	(1.76)	2.40
M^2	(1.34)	(0.99)	(1.34)
M^4	(0.91)	(0.67)	(0.91)
P^2	(341)	(275)	341
P^4	(256)	(206)	(256)
P^6	(171)	(138)	(171)
B_0^2	-1499	-1372	186
B_0^4	1456	1625	-270
B_0^6	1326	792	-623
B_3^4	1470	98	-
B_3^6	485	889	-
B_6^6	-2205	-2395	470

[a]From ref. 2.

[b]From ref. 14.

[c]Values in brackets were not freely varied.

Figure 1. μ_{eff}^2 vs. T for $Cp_3Sm{\cdot}CNC_6H_{11}$. The experimental data are given as points. The curve is drawn for k = 0.95.


$Cp_3Sm.CNC_6H_{11}$
Exp. Data
Calculated
μ_{eff}^2 (BM)^2
3.0
2.5
2.0
1.5
1.0
0.5
0
50
100
150
200
250
300
Temperature (K)

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