

Review

PARAMAGNETISM IN ORGANOLANTHANIDE COMPLEXES

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Introduction

The organometallic chemistry of the lanthanide elements has developed rapidly in recent years [1–5] and each year the number of reports in the literature increases. Since most of the lanthanide ions are paramagnetic, many of these studies include magnetic data. Although several excellent reviews of the organolanthanide field are available [1–7], none contains a comprehensive compilation of the experimentally observed magnetic data currently available on organolanthanide complexes. This review was written to fill this gap.

Detailed analysis of the magnetic susceptibility of a lanthanide compound is complex [8–11]. As originally explained by Van Vleck [8], the moments and populations of the contributing energy states of the metal must be considered as well as the effect of the ligands on these states. Variable temperature studies including low temperature measurements are necessary to fully define the paramagnetic properties of a given complex and few generalizations can be made [9].

However, at room temperature the magnetic moments of many lanthanide complexes often can be approximated by the simple expression $\mu_J = g[J(J+1)]^{1/2}$ (where $g = [S(S+1) - L(L+1) + 3J(J+1)]/[2J(J+1)]$) [10–15], a relationship originally reported by Hund [8,10]. This expression arises directly from the Van Vleck equation for magnetic susceptibility [8] when certain special conditions are met by the system. Specifically $\mu_J = g[J(J+1)]^{1/2}$ applies only when the $^{2S+1}L_J$ ground state is the only state with a significant population, when the crystal field splitting is small compared to kT , and when no higher lying states contribute to the susceptibility via temperature independent second order Zeeman effects. For many lanthanide complexes, these conditions fortuitously are met at room temperature. This expression is not appropriate for complexes of Eu^{3+} , Sm^{3+} , and Sm^{2+} , for which the separation in J states is comparable to kT at room temperature, and the complete Van Vleck equation must be used.

TABLE 1
 MAGNETIC MOMENTS (BM) OF ORGANOLANTHANIDE COMPLEXES

Complex ^a	$\mu(\mu_B)$	T (K) ^b	X-ray ^c	Reference
<i>Ce^{III}</i>				
$[(C_8H_8)_2Ce]K$	1.88	RT	yes	20
$[(C_8H_8)CeCl(THF)_2]_2$	1.79	RT	yes	20
$(C_8H_8)_3Ce_2(THF)_2$	1.86	RT	an	21
$(C_8H_8)Ce(O-i-Pr)(AlEt_2)(C_7H_8)_{0.25}$	2.04	RT	—	22
$(C_5H_5)_3Ce$	2.46	295,194,77	an	23
$(C_5H_5)_3Ce(THF)$	2.30	RT	an	24
$[C_5H_4(CH_2)_3C_5H_4]CeCl$	2.005	306.23	—	25
	1.684	48.84		
<i>Pr^{III}</i>				
$[(C_8H_8)_2Pr]K$	2.84	RT	an	20
$[(C_8H_8)PrCl(THF)_2]_2$	3.39	RT	an	20
$(C_5H_5)_3Pr$	3.61	295,77.	an	23
	3.59	194		
$[C_5H_4(CH_2)_3C_5H_4]PrCl(THF)$	3.50	291	—	26
<i>Nd^{III}</i>				
$[(C_8H_8)_2Nd]K$	2.98	RT	an	20
$[(C_8H_8)NdCl(THF)_2]_2$	3.37	RT	an	20
$(C_8H_8)_3Nd_2(THF)_2$	3.20	RT	yes	21
$(C_5H_5)_3Nd$	3.63	295,77	an	23
	3.62	194		
$(C_5H_5)_3Nd(CNC_6H_{11})$	3.4	300	an	27
$(C_5H_5)_2NdCN$	3.1	300	—	28
	2.5	50		
$[C_5H_4(CH_2)_3C_5H_4]NdCl(THF)$	3.33	291	—	26
$(C_5Me_5)_2NdCl_2Li(THF)_2$	3.5	RT	an	29
$(C_5Me_5)_2Nd(S_2CNEt_2)$	2.75	5–50	an	30
$(Me_2C_5H_5)_3Nd$	3.58	RT	yes	31
<i>Sm^{III}</i>				
$[(C_8H_8)_2Sm]K$	1.42	RT	an	20
$[(C_8H_8)SmCl(THF)_2]_2$	1.36	RT	an	20
$(C_5H_5)_3Sm$	1.54	194	an	23
$(C_5H_7)_3Sm(THF)$	1.55	RT	—	32
$(C_5H_5)_2SmCl$	1.60	300	an	33
	1.34	195		
$[(MeC_5H_4)_2Sm(C\equiv CMe_3)]_2$	1.9	299	yes	34
$(MeC_5H_4)_2Sm(PPh_2)$	1.8	299	—	34
$(C_5Me_5)_2SmI(THF)$	1.86	297	yes	35
$[(C_5Me_5)_2Sm]_2O$	1.8	RT	yes	36
$(C_5Me_5)_2Sm(C_6H_5)(THF)$	1.6	299	yes	37
$(C_5Me_4Et)_2Sm(C_6H_5)(THF)$	1.7	299	an	37
$[(C_5Me_5)_2(Ph_3PO)Sm]_2(OCHCHO)$	1.9	295	yes	38
$[(C_5Me_5)_2SmH]_2$	1.4	RT	yes	39
$[(C_5Me_5)_2Sm]_2C_2Ph_2$	1.7	290	—	39
$[(C_5Me_5)_2Sm]_2N_2Ph_2$	1.9	298	yes	40
$(C_5Me_5)_2(THF)SmCo(CO)_4$	1.76	299	—	41
$[(Me_3C)_4Sm][Li(THF)_4]$	2.1	280	an	42
$[(Me_3CC\equiv C)_4Sm][Li(THF)_4]$	1.66	298	—	43

TABLE 1 (continued)

Complex ^a	μ (μ_B)	T (K) ^b	X-ray ^c	Reference
<i>Sm^{III}</i>				
$[(C_5H_5)_2Sm(THF)]_n$	3.6	298	—	44
$(C_5Me_5)_2Sm(THF)_2$	3.6	296	yes	37
$(C_5Me_5)_2Sm$	3.5	296	yes	37
$[(C_5Me_5)SmI(THF)_2]_2$	3.6	298	yes	45
$(C_5Me_4Et)_2Sm(THF)_2$	3.8	298	an	37
$(C_5Me_4Et)_2Sm$	3.6	298	an	37
$(C_5Me_5)_2Sm(OPPh_3)(THF)$	3.7	295	—	36
<i>Eu^{III}</i>				
$(C_5H_5)_3Eu$	3.74	298	an	46
$(C_5H_5)EuCl_2(THF)_3$	4.24	300, 194	an	47
<i>Eu^{II}</i>				
$(C_5H_5)_2Eu$	7.63	300, 80	—	48
$(C_5Me_5)_2Eu(Et_2O)(THF)$	7.99	5–50	an	49
$(C_5Me_5)_2Eu(THF)$	7.99	298	an	50
“PhEuI”	7.5	295	—	51
<i>Gd^{III}</i>				
$(C_5H_5)_3Gd$	7.98	295	an	23
	7.95	194, 77		
$(C_9H_7)_3Gd(THF)$	7.89	RT	—	32
$(C_5H_5)_2GdCl$	8.86	301	an	33
$(C_5H_5)_2GdCl$	7.7	65–291	an	52
$(C_5H_5)_2GdCl(THF)$	8.18	65–294	an	52
$(C_5H_5)_2Gd(C\equiv CPh)$	7.98	RT	—	53
$(C_5H_5)_2GdPh$	7.69	RT	—	53
$[C_5H_4(CH_2)_3C_5H_4]GdCl(THF)$	8.15	291	—	26
<i>Tb^{III}</i>				
$[(C_8H_8)_2Tb]K$	9.86	RT	an	20
$(C_5H_5)_3Tb$	8.9	300, 85	an	48
$(C_5H_5)_3Tb(CNC_6H_{11})$	10.1	300	an	27
$(C_9H_7)_3Tb(THF)$	9.43	RT	—	32
$(Me_3SiCH_2)_3Tb(THF)_2$	9.12	RT	—	54
<i>Dy^{III}</i>				
$(C_5H_5)_3Dy$	10.0	295, 194, 77	an	23
$(C_9H_7)_3Dy(THF)$	9.95	RT	—	32
$(C_5H_5)_2DyCl$	10.6	300, 195	an	33
$[(C_5H_5)_2DyMe]_2$	9.9	RT	an	55
$[C_5H_4(CH_2)_3C_5H_4]DyCl(THF)$	11.32	291	—	26
$(C_5H_5)DyCl_2(THF)_3$	11.81	300, 194	an	47
<i>Ho^{III}</i>				
$(C_5H_5)_3Ho$	10.2	300, 85	an	48
$(C_5H_5)_3Ho(CNC_6H_{11})$	10.6	300	an	26
$(C_5H_5)_2HoCl$	10.3	300, 95	an	33
$[(C_5H_5)_2HoMe]_2$	10.0	RT	an	55
$(C_5H_5)_2Ho(C\equiv CPh)$	10.14	295	an	53
$[C_5H_4(CH_2)_3C_5H_4]HoCl(THF)$	10.9	291	—	26
$(C_5H_5)Ho(C\equiv CPh)_2$	10.48	295	—	53

continued

TABLE 1 (continued)

Complex ^a	$\mu(\mu_B)$	$T(K)$ ^b	X-ray ^c	Reference
<i>Er^{III}</i>				
(C ₈ H ₈) ₃ Er ₂ (THF) ₂	9.31	RT	an	21
(C ₅ H ₅) ₃ Er	9.45	295, 77	an	23
	9.44	194		
(C ₅ H ₅) ₂ ErCl	9.79	300, 195	an	33
[(C ₅ H ₅) ₂ ErMe] ₂	9.5	RT	an	55
	9.41	RT	an	53
[(C ₅ H ₅) ₂ ErC≡CPh] ₂	9.64	RT	an	53
(C ₅ H ₅) ₂ ErGePh ₃	9.7	RT	–	56
(C ₅ H ₅) ₂ ErSnPh ₃	7.2	RT	–	56
(C ₅ H ₅) ₂ Er(C ₆ H ₄ Cl- <i>p</i>)	11.09	291, 195	–	57
	11.04	77		
(C ₅ H ₅) ₂ Er(C ₆ H ₄ Me- <i>p</i>)	9.27	291	–	57
	9.28	195		
	9.30	77		
[C ₅ H ₄ (CH ₂) ₃ C ₅ H ₄]ErCl(THF)	10.59	291	–	26
(MeC ₅ H ₄) ₂ Er(C ₆ H ₄ Me- <i>p</i>)	9.23	291	–	57
	9.21	195		
	9.22	77		
(C ₅ H ₅)ErCl ₂ (THF) ₃	9.68	300, 194	yes	47
[(Me ₃ C) ₄ Er][Li(THF) ₄]	9.7	280	an	42
[(Me ₃ CC≡C) ₄ Er][Li(THF) ₄]	9.79	RT	–	43
(Me ₃ SiCH ₂) ₃ Er(THF) ₃	9.82	RT	–	54
<i>Tm^{III}</i>				
(C ₅ H ₅) ₃ Tm	7.1	300, 85	an	48
[(C ₅ H ₅) ₂ TmMe] ₂	7.5	RT	an	55
<i>Yb^{III}</i>				
(C ₅ H ₅) ₃ Yb	4.00	295, 194, 77	an	23
(C ₅ H ₅) ₃ Yb(CNC ₆ H ₁₁)	4.4	300	an	27
[(C ₅ H ₅) ₃ Yb] ₂ (N ₂ C ₄ H ₄)	3.48	4–100	yes	58
(C ₉ H ₇) ₃ Yb(THF)	4.1	RT	–	32
[(C ₅ H ₅) ₂ YbCl] ₂	4.81	301, 195	an	33
	4.53	66–294		52
(C ₅ H ₅) ₂ YbCl(THF)	4.85	66–295	an	52
[(C ₅ H ₅) ₂ YbMe] ₂	4.0	RT	an	55
	4.14	RT		53
[(C ₅ H ₅) ₂ Yb(C≡CPh)] ₂	4.31	RT	an	53
(C ₅ H ₅) ₂ YbPh	3.86	RT	–	53
(C ₅ H ₅) ₂ Yb(C ₆ H ₄ Me- <i>p</i>)	3.96	291	–	57
	3.97	195, 77		
(C ₅ H ₅) ₂ YbCN	4.0	300	–	28
	3.6	50		
[C ₅ H ₄ (CH ₂) ₃ C ₅ H ₄]YbCl(THF)	4.12	291	–	26
(C ₅ Me ₅) ₂ YbCl(THF)	4.2	301	an	59
(C ₅ Me ₅) ₂ YbCl ₂ Na(OEt ₂) ₂	3.91	4–45	an	59
(C ₅ Me ₅) ₂ Yb(O ₂ CCMe ₃)	3.29	5–35	–	30
(C ₅ Me ₅) ₂ Yb(S ₂ CNEt ₂)	3.39	5–55	an	30
(C ₅ Me ₅) ₄ Yb ₃ (C≡CPh) ₄	4.53	90–300	yes	60
	3.58	5–30		
(C ₅ Me ₅) ₂ (THF)Yb(OC)Co(CO) ₃	4.1	303	yes	61
[(C ₅ Me ₅) ₂ Yb] ₂ [Fe ₃ (CO) ₁₁]	3.91	4–60	yes	62
(C ₅ Me ₅) ₂ Yb[Mn(CO) ₅](MePh) _{0.25}	4.237	80–300	yes	63
	3.57	5–20		

TABLE 1 (continued)

Complex ^a	μ (μ_B)	T (K) ^b	X-ray ^c	Reference
<i>Yb^{III} (continued)</i>				
(C ₃ H ₅)YbCl ₂ (THF) ₃	4.33	300, 194	an	47
[(Me ₃ C) ₄ Yb][Li(THF) ₃]	4.6	280	an	42
(Me ₃ SiCH ₂) ₃ Yb(THF) ₂	4.64	RT	—	54

^a For polymetallic complexes, the μ listed applies to each metal center. ^b RT = room temperature.

^c "Yes" indicates the complex was characterized by X-ray diffraction. "an" indicates the structure of an analog of the same formula has been determined by X-ray diffraction.

We were interested in determining how the recently acquired magnetic data on organolanthanide complexes compare with the μ_J approximation. We also wanted to know the range of experimentally observed values for comparison with magnetic data on complexes to be synthesized in the future. Accordingly, we have assembled the available data.

Summary of available data

Table 1 contains a listing, by element and oxidation state, of the magnetic moment data reported in the literature on organometallic complexes of paramagnetic lanthanide ions in well defined oxidation states. The effective magnetic moment, the temperature of the measurement when specified, and the reference are listed. When the complex or a closely related analog has been structurally analyzed by X-ray diffraction, this is also noted. Values for organometallic complexes in

TABLE 2

COMPARISON OF EXPERIMENTAL AND THEORETICAL MAGNETIC MOMENTS

Metal	Number of different complexes	Range of room temperature (290–310 K) values in Table 1	Average observed value	$\mu_J = g[J(J+1)]^{1/2}$
Ce ^{III}	7	1.8–2.5	2.0	2.54
Pr ^{III}	3	2.8–3.6	3.3	3.58
Nd ^{III}	8	2.98–3.7	3.3	3.62
Sm ^{III}	16	1.36–1.9	1.7	0.84
Sm ^{II}	7	3.5–3.8	3.6	0
Eu ^{III}	2	3.7–4.2	4.0	0
Eu ^{II}	3	7.6–8.0	7.8	7.94
Gd ^{III}	7	7.7–8.9	8.0	7.94
Tb ^{III}	5	8.9–10.1	9.5	9.72
Dy ^{III}	6	9.9–11.8	10.6	10.63
Ho ^{III}	7	10.0–10.6	10.4	10.60
Er ^{III}	15	7.2–11.1 ^a	9.6	9.57
Tm ^{III}	2	7.1–7.5	7.3	7.63
Yb ^{III}	19	3.8–4.9	4.3	4.5

^a Twelve of fifteen listed complexes are in the narrower range 9.2–9.8.

which the oxidation state is uncertain [16–19] have not been included. In Table 2 the range of experimentally observed values in Table 1 is compared with the simple $\mu_J = g[J(J + 1)]^{1/2}$ estimate.

Discussion of data

Some useful generalizations can be made from the data in Tables 1 and 2. First, the observed room temperature magnetic moments for organometallic complexes of a given lanthanide tend to fall in a rather narrow range. With the exceptions of Dy^{III} and Er^{III}, the range of observed μ values for a given metal in a specific oxidation state is no greater than 1.2 μ_B . Erbium(III) is an exception due to three extreme values which make the 7.2–11.1 μ_B range larger than normal. Twelve of the fifteen room temperature magnetic moments fall in the much narrower range of 9.2–9.8 μ_B . For Dy^{III}, there are only six values available. Of these, four fall in the narrower 9.9–10.6 μ_B range. Hence, in general, a room temperature magnetic moment for an organolanthanide complex of a given metal in a given oxidation state will fall in a narrow, predictable range. Room temperature magnetic moments therefore can be used along with other data to identify a given metal and oxidation state.

The specific complexes which gave the extreme high and low values for each ion were listed to see if a pattern was present, e.g., does one type of complex consistently have higher magnetic moments. No single class of complex consistently displayed the extreme values.

Another generalization which can be made from the data is that the room temperature magnetic moments follow the theoretical value of μ_J except for complexes of Eu³⁺, Sm³⁺, and Sm²⁺. As discussed above, these ions do not meet the boundary conditions which allow the μ_J expression to apply. Hence, the μ_J from a single ground state J level is not a valid estimate of the magnetic moment. For the other ions, the average magnetic moments are within -0.5 to $0.1 \mu_B$ of the theoretical μ_J value. The averages are almost always lower than μ_J and the range of values lies to the low side of μ_J . Hence, μ_J is a reasonable first approximation for an upper limit of a room temperature magnetic moment of an organolanthanide complex with the exception of complexes of Eu³⁺, Sm³⁺, and Sm²⁺.

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