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Magnetic Moments of Lanthanide 3-, 4-Nitrobenzoates and 3,4-Dinitrobenzoates

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Summary. The magnetic moments for lanthanide 3-nitro and 4-nitrobenzoates were determined at 298 K and those for 3,4-dinitrobenzoates of rare earth elements over the temperature range 77 – 296 K. The complexes of 3,4-dinitrobenzoates of rare earths were found to obey the Curie-Weiss law. The values of μ calculated for all complexes (except that for europium 3,4-dinitrobenzoates) are close to those obtained for Ln^{3+} ions by Hund and Van Vleck. The results reveal that irrespective of the kind of ligands (3-nitro, 4-nitro or 3,4-dinitrobenzoates) no influence of their field on lanthanide ions occurs.

Keywords. Magnetic moments of lanthanide nitrobenzoates; Magnetic susceptibilities of 3-, 4-nitro- and 3,4-dinitrobenzoates of rare earth elements; Magnetic moments of rare earth element nitrobenzoates; Magnetic moments of nitrocomplexes.

Magnetische Momente von Lanthaniden-3-nitro-, -4-nitro- und -3,4-dinitrobenzoaten

Zusammenfassung. Die magnetischen Momente von Lanthaniden-3-nitro und -4-nitrobenzoaten wurden bei 298 K untersucht, die von -3,4-dinitrobenzoaten im Temperaturbereich von 77 – 296 K. Die Komplexe entsprechen der Curie-Weiss-Regel. Die für alle Komplexe gefundenen μ-Werte (ausgenommen das 3,4-Dinitrobenzoat von Eu) sind sehr nahe den von Hund und Van Vleck erhaltenen. Es wurde also kein Einfluß des Ligandenfeldes auf die Lanthanid-Ionen festgestellt.

Introduction

In our previous papers [1 – 6] we have presented the manner of the preparation of 3- and 4-nitrobenzoates and 3,4-dinitrobenzoates of rare earth elements, their quantitative composition, IR and X-ray spectra, thermal stabilities and solubilities in water at 298 K.

The aim of the present paper was to investigate the magnetic properties of 3-, 4-nitrobenzoates and 3,4-dinitrobenzoates of rare earth elements, which have not been measured so far, and to try to give an interpretation of the obtained results.

Experimental

Magnetic susceptibilities of polycrystalline samples of 3-, 4-nitrobenzoates and 3,4-dinitrobenzoates of rare earth elements were measured by the Gouy method using a sensitive Gahn RM-2 electronic

Table 1. Magnetic data for lanthanide 3- and 4-nitrobenzoates ($L = C_7H_4NO_4$)

Ln^{3+}	Ground term	Calcd. Hund μ_{eff}	Van Vleck μ_{eff}	3-Nitrobenzoates of *Ln*	Experimental μ_{298} [B. M.]	4-Nitrobenzoates of *Ln*	Experimental μ_{298} [B. M.]
La^{3+}	$^1S_0$	0	0	$LaL_3 \cdot 2.5\,H_2O$	0	$LaL_3 \cdot 3\,H_2O$	0
Ce^{3+}	$^2F_{5/2}$	2.54	2.56	$CeL_3 \cdot 2.5\,H_2O$	2.50	$CeL_3 \cdot 3\,H_2O$	2.50
Pr^{3+}	$^3H_4$	3.58	3.62	$PrL_3 \cdot 2\,H_2O$	3.66	$PrL_3 \cdot 3\,H_2O$	3.65
Nd^{3+}	$^4J_{9/2}$	3.62	3.68	$NdL_3 \cdot 2\,H_2O$	3.51	$NdL_3 \cdot 3\,H_2O$	3.56
Sm^{3+}	$^6H_{5/2}$	0.84	1.55 – 1.65	$SmL_3 \cdot 2\,H_2O$	1.82	$SmL_3 \cdot 3\,H_2O$	1.84
Eu^{3+}	$^7F_0$	0	3.40 – 3.51	$EuL_3 \cdot 2\,H_2O$	3.24	$EuL_3 \cdot 3\,H_2O$	3.45
Gd^{3+}	$^8S_{7/2}$	7.94	7.94	$GdL_3 \cdot 2\,H_2O$	7.80	$GdL_3 \cdot 3\,H_2O$	7.84
Tb^{3+}	$^7F_6$	9.70	9.70	$TbL_3 \cdot 2\,H_2O$	9.70	$TbL_3 \cdot 3\,H_2O$	9.68
Dy^{3+}	$^6H_{15/2}$	10.60	10.60	$DyL_3 \cdot 2\,H_2O$	10.40	$DyL_3 \cdot 3\,H_2O$	10.40
Ho^{3+}	$^5J_8$	10.60	10.60	$HoL_3 \cdot 2\,H_2O$	10.60	$HoL_3 \cdot 3\,H_2O$	10.60
Er^{3+}	$^4J_{15/2}$	9.60	9.60	$ErL_3 \cdot 2\,H_2O$	9.56	$ErL_3 \cdot 3\,H_2O$	9.54
Tm^{3+}	$^3H_6$	7.60	7.60	$TmL_3 \cdot 2\,H_2O$	7.59	$TmL_3 \cdot 3\,H_2O$	7.62
Yb^{3+}	$^2F_{7/2}$	4.50	4.50	$YbL_3 \cdot 2\,H_2O$	4.40	$YbL_3 \cdot 3\,H_2O$	4.51
Lu^{3+}	$^1S_0$	0	0	$LuL_3 \cdot 2\,H_2O$	0	$LuL_3 \cdot 3\,H_2O$	0

Table 2. Detailed magnetic data for the light lanthanide 3,4-dinitrobenzoates ($L = C_7H_3N_2O_6$)

$CeL_3 \cdot 2H_2O$ $\Theta = -46$ K			$PrL_3 \cdot 2H_2O$ $\Theta = -42$ K			$NdL_3 \cdot 2H_2O$ $\Theta = -25$ K			$SmL_3 \cdot 2H_2O$ $\Theta = -83$ K			$EuL_3 \cdot 2H_2O$ $\Theta = -724$ K			$GdL_3 \cdot 2H_2O$ $\Theta = -7$ K		
T[K]	$\chi_M \cdot 10^6$	μ[B.M.]	T[K]	$\chi_M \cdot 10^6$	μ[B.M.]	T[K]	$\chi_M \cdot 10^6$	μ[B.M.]	T[K]	$\chi_M \cdot 10^6$	μ[B.M.]	T[K]	$\chi_M \cdot 10^6$	μ[B.M.]	T[K]	$\chi_M \cdot 10^6$	μ[B.M.]
77	7 430	2.72	77	15 400	3.83	77	17 900	3.83	77	2 330	1.72	77	5 980	6.15	77	94 100	7.23
125	5 180	2.67	130	10 600	3.82	132	11 300	3.77	129	1 800	1.69	129	5 580	6.13	131	55 800	7.42
137	4 880	2.68	142	10 000	3.84	140	10 700	3.76	139	1 700	1.68	139	5 520	6.16	141	52 400	7.48
146	4 540	2.66	151	9 510	3.83	151	10 200	3.79	150	1 650	1.68	151	5 440	6.15	148	48 800	7.40
163	4 210	2.65	161	9 030	3.83	162	9 550	3.78	161	1 590	1.67	158	5 380	6.12	160	44 700	7.38
171	4 020	2.65	165	8 790	3.82	173	9 060	3.79	173	1 570	1.67	169	5 350	6.15	166	42 500	7.34
180	3 870	2.66	175	8 280	3.79	184	8 580	3.79	185	1 530	1.68	179	5 270	6.13	177	40 100	7.37
183	3 840	2.67	183	8 140	3.83	194	8 170	3.79	199	1 470	1.70	190	5 220	6.17	187	37 800	7.36
196	3 660	2.65	195	7 710	3.83	203	7 840	3.78	202	1 380	1.69	198	5 170	6.13	195	36 600	7.41
211	3 390	2.66	205	7 380	3.82	213	7 540	3.79	208	1 330	1.70	208	5 090	6.11	205	34 900	7.42
220	3 310	2.68	208	7 290	3.82	229	7 060	3.79	220	1 290	1.72	217	5 070	6.14	215	33 300	7.40
230	3 230	2.65	218	7 050	3.82	239	6 800	3.79	230	1 250	1.67	228	5 000	6.17	225	31 400	7.39
240	3 060	2.65	229	6 800	3.84	249	6 580	3.80	240	1 200	1.71	238	4 940	6.14	234	30 300	7.41
251	2 950	2.67	238	6 570	3.84	257	6 350	3.79	251	1 180	1.80	248	4 890	6.11	242	29 200	7.40
260	2 890	2.68	245	6 360	3.82	266	6 170	3.79	257	1 130	1.80	255	4 870	6.13	249	28 200	7.38
271	2 810	2.66	255	6 160	3.83	276	5 970	3.79	268	1 100	1.60	265	4 810	6.16	259	27 100	7.38
277	2 730	2.66	265	5 980	3.83	294	5 650	3.80	292	1 080	1.57	276	4 760	6.13	267	26 100	7.36
295	2 630	2.68	293	5 440	3.82							295	4 700	6.19	296	23 500	7.36

Table 3. Detailed magnetic data for the heavy lanthanide 3,4-dinitrobenzoates ($L = C_7H_3N_2O_6$)

TbL_3·2 H_2O $\Theta = -6$ K			DyL_3·2 H_2O $\Theta = -3$ K			HoL_3·2 H_2O $\Theta = -6$ K			ErL_3·2 H_2O $\Theta = -2$ K			TmL_3·2 H_2O $\Theta = -4$ K			YbL_3·2 H_2O $\Theta = -41$ K		
T[K]	$\chi_M \cdot 10^6$	μ[B.M.]	T[K]	$\chi_M \cdot 10^6$	μ[B.M.]	T[K]	$\chi_M \cdot 10^6$	μ[B.M.]	T[K]	$\chi_M \cdot 10^6$	μ[B.M.]	T[K]	$\chi_M \cdot 10^6$	μ[B.M.]	T[K]	$\chi_M \cdot 10^6$	μ[B.M.]
77	153 000	10.13	77	164 000	10.30	77	165 000	10.52	77	144 000	9.29	77	78 800	7.16	77	26 500	5.00
120	102 000	10.25	130	101 000	10.40	124	106 000	10.53	129	85 200	9.30	129	51 200	7.39	120	19 400	5.00
134	91 900	10.18	136	96 700	10.40	133	99 500	10.55	139	78 300	9.26	139	46 000	7.26	131	18 100	4.99
144	85 300	10.15	145	90 900	10.40	145	92 000	10.57	149	73 200	9.27	150	42 900	7.28	141	17 100	4.99
153	81 100	10.18	156	84 200	10.38	155	87 000	10.61	159	68 800	9.29	159	40 800	7.30	149	15 600	4.87
166	74 500	10.15	170	77 200	10.36	168	79 200	10.52	169	65 200	9.33	169	38 200	7.28	164	15 000	4.96
177	70 100	10.15	178	74 500	10.41	179	74 600	10.53	182	58 900	9.21	178	36 400	7.28	174	14 400	4.98
185	67 300	10.16	190	69 800	10.40	188	70 900	10.51	193	56 500	9.29	202	32 300	7.29	181	13 800	4.95
192	64 600	10.14	199	66 800	10.41	198	68 000	10.56	203	53 300	9.25	214	30 400	7.29	196	13 000	4.97
206	60 800	10.18	208	63 400	10.37	208	63 900	10.48	213	51 500	9.36	222	29 400	7.29	205	12 400	4.94
221	56 700	10.17	219	60 400	10.38	224	60 200	10.54	223	49 300	9.33	231	28 300	7.30	216	12 000	4.97
233	54 000	10.18	227	58 900	10.43	237	56 800	10.52	232	46 600	9.26	248	26 800	7.35	227	11 400	4.94
238	52 700	10.16	237	55 900	10.38	249	54 400	10.55	242	44 900	9.28	250	26 000	7.27	237	11 100	4.97
246	50 500	10.11	247	53 500	10.57	260	52 400	10.58	252	42 900	9.26	260	24 900	7.25	247	10 700	4.97
255	49 500	10.18	257	51 700	10.39	276	49 300	10.56	262	41 500	9.29	270	24 200	7.29	261	10 200	4.96
267	47 600	10.21	268	49 200	10.34	296	45 800	10.53	272	39 900	9.28	274	23 500	7.23	270	9 900	4.98
277	45 400	10.15	278	48 000	10.40				282	38 400	9.27	296	22 000	7.27	280	9 600	4.98
296	42 300	10.12	291	45 900	10.41				296	36 700	9.29				295	9 200	4.98

balance. Measurements were made at a magnetic field strength of 9.9 kOe. The calibrant employed was $CoHg(SCN)_4$ for which the magnetic susceptibility was taken $16.44 \cdot 10^{-6}$ ($cm^3 g^{-1}$) [7]. The correction for diamagnetism of the constituent atoms was calculated by use of Pascal's constants [8]. The magnetism of the samples was found to be field independent. The temperature-independent paramagnetism of rare earth ions was assumed to be zero. The magnetic moments were calculated from the equations:

$$\mu = 2.83\,(\chi_M \cdot T)^{1/2}, \tag{1}$$

$$\mu = 2.83\,[(\chi_M(T - \Theta)]^{1/2}. \tag{2}$$

The obtained results are given in Tables 1 – 3 and Figs. 1 and 2.

Results and Discussion

The magnetic susceptibilities of lanthanide 3-nitro- and 4-nitrobenzoates were determined at 298 K whereas those for 3,4-dinitrobenzoates over the temperature range 77 – 296 K. The values of Weiss constants, Θ, determined for each complex of 3,4-dinitrobenzoates (Tables 2 and 3) were found to be of both sign. For most of the 3,4-dinitrobenzoates of rare earth elements they show negative values whereas for gadolinum and erbium 3,4-dinitrobenzoates positive values were found. A positive value of Θ may be caused by ferromagnetic spin interactions while a negative one may probably arise from antiferromagnetic spin interactions or a crystal field splitting of the paramagnetic spin states [9 – 12].

The relatively small absolute value of Θ for 3,4-dinitrobenzoates of Gd – Tm are in the range 2 – 7 K, while the greater ones for cerium, praseodymium, neodymium, samarium, and ytterbium are ranging from 25 K to 83 K. Only for europium 3,4-dinitrobenzoate a very high value of 724 K was observed (Table 2).

From the literature it follows that weak interaction between atoms or ions causes small values of Θ. In the complexes of 3,4-dinitrobenzoates the paramagnetic central ions remain practically unaffected by the diamagnetic ligands coordinated

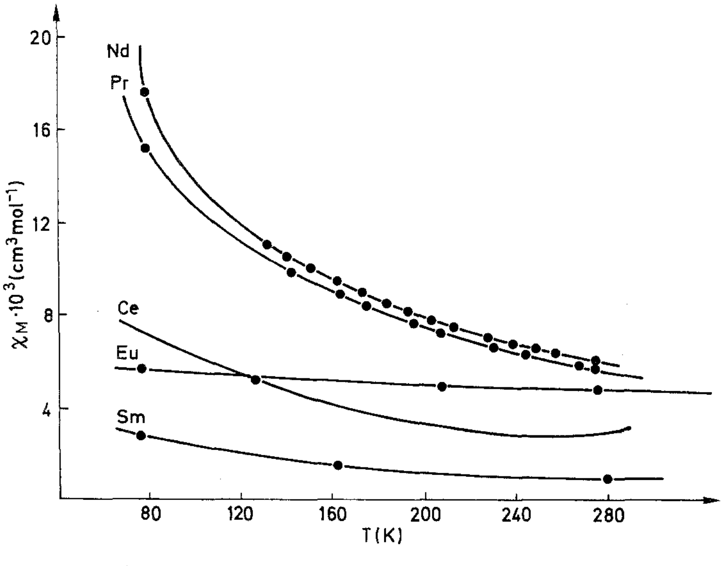

Fig. 1. The dependence between χ_M and T for 3,4-dinitrobenzoates of Ce, Pr, Nd, Sm, and Eu

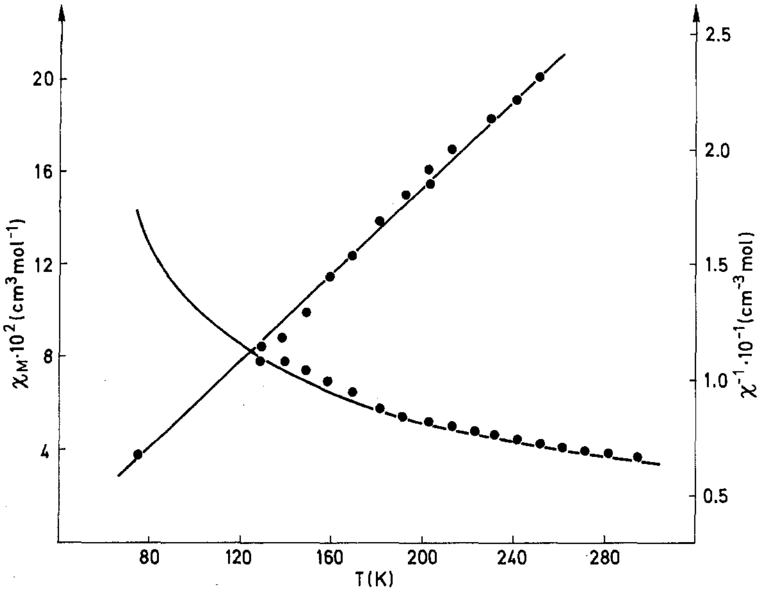

Fig. 2. The relationship of χ_M and χ_M^{-1} versus T for erbium 3,4-dinitrobenzoates

around them and the f electrons causing their paramagnetism are well separated from outside influences. The higher value of Θ may suggest the interaction of the crystal field of ligands with the central ion. The values of μ determined for all complexes (except that for europium 3,4-dinitrobenzoate) are close to those calculated for Ln^{3+} ions by Hund and Van Vleck (Tables 1 – 3), which is connected with the electron configuration of lanthanide ions. In rare earth ions 4f electrons are in an inner shell characterized by a radius $\sqrt{\langle r^2 \rangle} \cong 0.35$ Å [13]. This value is very small in comparison with the radius of the $5s^2 5p^6$ closed shell (~ 1 Å) and the distance between rare earth ions, which is in fact about 10 times larger. So the 4f electrons interact only weakly with the electrons of the surrounding atoms. Then the intra-atomic interactions are much stronger than the inter-atomic ones and the width of the 4f band is entirely negligible because the overlap between different 4f wave functions is extremely small.

The f electrons of the lanthanide ions are almost unaffected by the chemical environment and the energy levels are the same as in the free ions due to the very effective shielding by the overlying $5s^2 5p^6$ shell. For most of the lanthanide ions the ground state is separated by many hundreds of cm^{-1} from the next higher lying state. Thus the magnetic properties can be taken as those of the ground state alone, making lanthanide ions in a compound act in the same way as the free ion as far as the f electrons are concerned. The energy levels of a free rare earth ion are only slightly modified when it is placed in a crystal.

The complexes of 3,4-dinitrobenzoates of rare earth elements obey the Curie-Weiss law. A plot of the inverse of the magnetic susceptibility, χ_M determined for all compounds yields a straight line. In Figs. 1 and 2 the relationships between χ_M and T for 3,4-dinitrobenzoates of Ce, Pr, Nd, Sm, and Eu and also χ_M (and χ_M^{-1}) and T for 3,4-dinitrobenzoates of Er are presented. Taking into account the obtained results it is possible to conclude that in the complexes of 3-, 4-nitrobenzoates and

3,4-dinitrobenzoates of rare earth elements (with the exception of 3,4-dinitrobenzoate of europium), irrespective of the kind of ligands, no influence of their field on the lanthanide ions occurs. The higher value of μ for europium 3,4-dinitrobenzoate compared to that given by Hund, on one hand, may suggest the interaction of the ligand field with the central ion or, on the other hand, may probably be connected with the multiplet splitting in the case of the europium ion. The first excited J state is sufficiently close in energy to the ground state (and in the case of Eu^{3+} even the second and third excited state as well), to be appreciably populated at room temperature [14–19]. Since these excited states have higher J values than the ground state, the actual magnetic moment is higher than those calculated by the use of the value of J for the ground state. With the exceptions of samarium and europium the multiplet widths of lanthanides are very wide compared to kT at room temperature, while those for Sm and Eu are comparable to kT [14, 17].

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