Indian Streams Research Journal
ISSN 2230-7850
Impact Factor : 2.1506(UIF)
Volume-4 | Issue-6 | July-2014
Available online at www.lbp.world

STUDY OF MAGNETIC MOMENT OF SELECTED LANTHENIDE COMPLEXES

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ABSTRACT

Recent trade is found to be of great interest in structural study of complexes which are derived from organic compounds containing oxygen and nitrogen donar atom. The ligand [LH_2] was synthesized and its complexes with some of the rare earth metal Sm, Gd and Dy were prepared by usual method. The complexes are found to be paramagnetic while that of La complex shows diamagnetic behavior. The experimental values of magnetic moments for Sm, Gd and Dy complexes when compared with the magnetic moments of Sm, Gd and Dy complexes in literature these values are found more close to the values of tetradentate type of the complexes. The slight lower values of magnetic moment may be attributed to anti ferromagnetic exchange interaction between paramagnetic transition metal ion and the ligand mostly in the semi-quinone form. The observed magnetic moment values for the complexes are closer to the values of tetradentate type of structures.

KEY WORD: magnetic moment, lanthanide complex, imperical formula.

1. INTRODUCTION

Forty years ago, very little was known about lanthanide complexes. By analogy with the d-block metals, it was often assumed that lanthanides were generally six coordinate in their complexes. We now know that this is not the case, that lanthanides (and actinides) show a wider variety of coordination number than do the d-block metals.

With the exception of La^{3+} and Lu^{3+} (and of course Y^{3+}) the Ln^{3+} ions all contain unpaired electrons and are paramagnetic. Their magnetic properties are determined entirely by the ground state (with two exceptions we shall encounter), as the excited states are so well separated from the ground state (owing to spin–orbit coupling) and are thus thermally inaccessible.

The magnetic moment of the Ln^{3+} ions is essentially independent of environment, so that one cannot distinguish between coordination geometries as is sometimes possible for transition metals – in the case of octahedral and tetrahedral Co^{2+} complexes, for example. The

magnetic moments in the second half of the series are greater than the moments in the first half, as $J = L + S$ for a shell greater than half-filled and $J = L - S$ for a less than half-filled shell.

2. MATERIALS AND METHODS

Synthesis of the lanthanide complexes, ligand and details regarding analysis are given below,

Synthesis of Lanthanide complexes :

The lanthanide(III) chlorides, nitrates and thiocyanates were synthesized using methanolic solution of the ligand LH_2 (0.001 mol), and was added upon by a methanolic solution of the Ln(III) salt (0.001 mol) in a dropwise manner with constant stirring on a magnetic stirrer. The pH of the reaction mixture was adjusted to 7- 8 by adding 10% liquor ammonia followed by refluxing the reaction mixture for 10 hours. The resulting solution was preconcentrated to one third of its original volume and kept on standing overnight. The precipitated metal complex was then filtered using Whatmann filter paper no. 41, washed with methanol and finally dried in a vacuum desiccator.

Synthesis of the ligand:

The Ligand(LH_2) was synthesized by making the condensation reaction to take place between acetoacetanilide and 1,3-diaminopropane in 2:1 molar ratio by refluxing in acetone as a solvent.

Analysis of the Complexes:

The complexes were decomposed with a mixture of concentrated hydrochloric-, nitric-, and perchloric acids in the ratio 3:1:l.

The lanthanide metals and C, H, N in the complexes were determined gravimetrically.

Magnetic measurement :

Magnetic susceptibility measurements were carried out on finely powdered solid samples using a simple Gouy – type magnetic balance at room temperature. The magnetic moment was measured by magnetometer.

RESULT AND DISCUSSION:

Magnetic Behavior

The magnetic moment values of the complexes are tabulated in Table 1. All the lanthanide complexes synthesized were paramagnetic due to the presence of unpaired electrons in their elsctronic configuration and the experimental magnetic moment values of Gd(III) (7.14-7.85 BM) and Dy(III) (10.53-10.67 BM) complexes are in tune with the calculated ones except that of Sm(III) which showed marginal deviation from the calculated values. This indicates that the 4f electrons are not much perturbed by the strength of ligand field generated by the Schiff base. The deviation of the magnetic moment values of Sm(III) complexes (1.54-

1.66 BM) could be attributed to low J-J separation, which leads to the thermal excitation and thereby increase in population density of higher energy levels.

Table no. 1- Analytical data

Sr. no.	Complex	Color	Magnetic moment B.M	% Contribution				M.P. (^{0}C)
				M	C	H	N	
1	$[Sm(LH_2)(Cl)_3]$	Greenish With white tinge	1.55	23.46 (23.15)	42.75 (42.54)	4. 45 (4.36)	8.37 (8.64)	285
2	$[Sm(LH_2)(NO3)_3]$	Murky white	1.64	20.67 (20.64)	36.84 (37.91)	3.56 (3.86)	13.53 (13.45)	289
3	$[Sm(LH_2)(NCS)_3]$	Murky white	1.67	21.24 (20.96)	43.30 (43.56)	4.11 (3.95)	13.40 (13.67)	279
4	$[Gd(LH_2)(Cl)_3]$	Reddish With yellow tinge	7.77	24.44 (23.97)	42.18 (42.10)	4.50 (4.30)	8.43 (8.54)	295
5	$[Gd(LH_2)(NO3)_3]$	Reddish Laced with yellow	7.86	21.45 (21.37)	37.65 (37.55)	3.60 (3.84)	13.40 (13.33	294
6	$[Gd(LH_2)(NCS)_3]$	Reddish yellow	7.16	22.00 (21.72)	43.42 (43.13)	3.55 (3.90)	13.48 (13.54)	287
7	$[Dy(LH_2)Cl_3]$	Reddish With brown tinge	10.50	23.86 (24.57)	41.53 (41.77)	4.45 (4.27)	8.51 (8.47)	293
8	$[Dy(LH_2)(NO3)_3]$	faint brown	10.66	22.01 (21.93)	37.08 (37.28)	3.53 (3.81)	13.21 (13.23)	289
9	$[Dy(LH_2)(NCS)_3]$	faint brown	10.5	22.24 (22.28)	42.78 (42.82)	3.44 (3.66)	13.56 (13.45)	291

CONCLUSION

Lanthanide complexes of Sm, Gd and Dy have been synthesized and it is corroborated with the analytical data which show that all the complexes have the empirical formula base in its composition as $[M(LH_2)(X)_3]$, where M = Sm(III), Gd(III), Dy(III) and X = Cl^-, NO_3^- and NCS^-. The magnetic moment values suggest the complexes are paramagnetic due to presence of unpaired electrons.

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