

Magneto Spectra Studies of Lanthanide Nitrate Complexes of 2-Methyl Benzothiazole N-Oxide

Abstract

2-Methyl benzothiazole N-Oxide (MBTNO) complexes of Lanthanide nitrates of the formulae $\text{Ln}(\text{NO}_3)_3(\text{MBTNO})_3$ (where Ln = La,Ce,Pr,Sm, Gd,Dy or Yb) have been prepared in non aqueous media and characterized by elemental analysis, magnetic susceptibility, molar conductance and IR spectral data. Conductance data of the complexes suggest that all three nitrate ions are within the coordination spectra.

Keywords: Magneto Spectra, benzothiazole N-Oxide.

Introduction

The last two decades have witness considerable interest in coordination compounds of aromatic amines N-oxide with various metal ions in term of donor-acceptor relationship (1-4).

Objective of the Study

IR Data indicates that MBTNO is bonded to the metal through only the N-oxygen atom and bidentate nitrate groups in the complexes.

Review of Literature

A literature survey clearly indicates that the coordination behavior of 2-methyl benzothiazole N-Oxide (MBTNO) has not been studied earlier. Thus it is worthwhile to study the Lanthanide nitrate complexes of MBTNO.

Experimental

Reagents

2-Methyl benzothiazole was procured from Aldrich chemicals and its N-Oxidation was carried out by Ochiai method (S), Lanthanide nitrates were obtained from Rare earth products Ltd. India and were used with a further purification.

Preparation and Analysis of Complexes

Lanthanide nitrate (2m mole) were dissolve in Methanol and mixed with Ligand (4m mole) solution in Acetone. The reaction mixture was kept overnight and excess of solvent was evaporated at room temperature. The product obtained were recrystallised with Acetone and dried over P_2O_5 in vacuum desiccator.

All these complexes were analyzed for Metal,Carbon,Hydrogen and Nitrogen. The physical measurements were made as reported earlier (6).

Result and Discussion

Analytical data (table-1) of the complexes shows that the Lanthanide (III) nitrate complexes have the general formula $[\text{Ln}(\text{MBTNO})_3(\text{NO}_3)_3]$ (Where Ln = La.,Cr,Pr,Sm,Gd,Dy or Yb).

S.K. Gupta

Assistant Professor
Deptt.of Chemistry,
P.G.V. College,
Jiwaji Ganj, Lashkar,
Gwalior

V.K. Jain

Assistant Professor & HOD,
Deptt.of Chemistry,
Ambah P.G. College,
Ambah, Morena



Brajesh Sharma

Sr. Executive,
Deptt.of Chemistry,
Ambah P.G. College,
Ambah, Morena

Complexes	% Found (Calculated)				Ω mohm ⁻¹ , cm ² mole ⁻¹	Electrolytic nature	Molecular Weight Found (Calculated)
	M	C	H	N			
La(NO ₃) ₃ (MBTNO) ₃	17.08	35.22	2.67	10.32	4.49	Non electrolyte	814 820
	16.95	35.12	2.56	10.24			
Ce(NO ₃) ₃ (MBTNO) ₃	17.18	35.19	2.67	10.33	4.42	Non electrolyte	816 821
	17.05	35.08	2.55	10.23			
Pr(NO ₃) ₃ (MBTNO) ₃	17.29	35.16	2.65	10.30	5.01	Non electrolyte	812 822
	17.15	35.04	2.55	10.22			
Sm(NO ₃) ₃ (MBTNO) ₃	18.26	34.77	2.63	10.21	4.47	Non electrolyte	820 832
	18.15	34.61	2.52	10.10			
Gd(NO ₃) ₃ (MBTNO) ₃	18.92	34.43	2.59	10.11	4.01	Non electrolyte	831 839
	18.83	34.33	2.50	10.01			
Dy(NO ₃) ₃ (MBTNO) ₃	19.33	34.28	2.59	10.05	5.11	Non electrolyte	834 843.5
	19.26	34.14	2.49	9.96			
Yb(NO ₃) ₃ (MBTNO) ₃	20.34	33.83	2.55	9.99	4.48	Non electrolyte	843 854
	20.26	33.72	2.45	9.84			

All these complexes are non hygroscopic solids soluble in polar solvents like Methanol, Ethanol, Acetone, and Acetonitrile but insoluble in non polar solvents like Benzene, Carbon tetra chloride and Chloroform.

The molar conductance data (table1) of the complex in nitrobenzene shows the non-electrolytic

behavior of these complexes (7). The observed magnetic moment of these complexes agree well with the Van Vleck and Frank values (8), which suggest that the 4f electron in these complexes do not participate in bond formation.

The important IR spectral bands of the complexes are presented in table 2

Complex	$\bar{\nu}$ (N-C)	$\bar{\nu}$ (C-H) out of plane deformation	δ (NO)	$\bar{\nu}$ (C-S)	$\bar{\nu}$ (M-O)
2-methylbenzothiazole N-oxide	1235	1080, 1025, 910	840	760	-
La(NO ₃) ₃ (MBTNO) ₃	1195	1090, 1040, 905	825	755	400
Ce(NO ₃) ₃ (MBTNO) ₃	1190	1092, 1035, 910	830	758	390
Pr(NO ₃) ₃ (MBTNO) ₃	1198	1085, 1035, 908	832	750	390
Sm(NO ₃) ₃ (MBTNO) ₃	1205	1085, 1030, 900	825	765	395
Gd(NO ₃) ₃ (MBTNO) ₃	1202	1095, 1025, 895	822	760	398
Dy(NO ₃) ₃ (MBTNO) ₃	1205	1088, 1028, 899	830	752	402
Yb(NO ₃) ₃ (MBTNO) ₃	1200	1090, 1030, 900	835	750	395

The ligands MBTNO possesses to possible sites for coordination amine N-oxygen and sulphur of the Thiazole ring . the main absorption frequencies of MBTNO namely N-O stretching , C-S stretching and C-H out of plane bending expected to be the influenced on complexes (9,10).

The most important mode of vibration in the spectra of MBTNO is N-O stretching which appears at 1235cm⁻¹ in free ligand (1) undergoes a significant negative shift on complexation (9,10), which attribute to oxygen. Coordination of MBTNO to lanthanide ion (table 1). A strong absorption observed at δ 840 cm⁻¹ for N-O bending (11). Because of coordination from oxygen atom of the N-O group to metal atom, a noticeable shift of N-O bend is expected. The data

summarized in table 2 shows that only a slightly shift in the vibration observed.

Also a strong bend appears in the spectrum of MBTNO at 760 cm⁻¹ for $\bar{\nu}$ (C-S) which does not show any effect on complexation indicates that sulphur atom do not participate in bond formation.

The positive shift of the C-N of the plane vibration of ligands in all complexes is indicative of the drainage of electron density from aromatic ring to the metal ion. In the 370-400 cm⁻¹ region a new band appears in all the complexes which is assignable to $\bar{\nu}$ (M-O) (12).

The nature of binding of nitrate groups to the metal can be predicted by Ekamming. The combination band in the 1700-1800 cm⁻¹ region (table 3) (13,14).

Table 3 IR absorption frequencies (cm⁻¹) of nitrate ion in lanthanide complexes of 2-methyl benzotiazole N-oxide

Complex	($\bar{\nu}_2 + \bar{\nu}_5$)	$\bar{\nu}_2 + \bar{\nu}_6$	($\bar{\nu}_2 - \bar{\nu}_5$) - ($\bar{\nu}_2 + \bar{\nu}_6$)	$\bar{\nu}_4$	$\bar{\nu}_1$	$\bar{\nu}_2$	$\bar{\nu}_6$	$\bar{\nu}_3$	$\bar{\nu}_5$
La(NO ₃) ₃ (MBTNO) ₃	1790	1735	55	1520	1310	1030	815	735	710
Ce(NO ₃) ₃ (MBTNO) ₃	1775	1730	45	1525	1315	1030	820	740	715
Pr(NO ₃) ₃ (MBTNO) ₃	1785	1740	45	1520	1310	1045	820	732	712
Sm(NO ₃) ₃ (MBTNO) ₃	1780	1730	50	1515	1312	1050	810	745	705
Gd(NO ₃) ₃ (MBTNO) ₃	1788	1742	46	1518	1320	1035	818	736	708
Dy(NO ₃) ₃ (MBTNO) ₃	1785	1735	40	1525	1318	1040	810	740	715
Yb(NO ₃) ₃ (MBTNO) ₃	1782	1732	50	1520	1320	1035	815	738	708

The spectra of these complexes contains only two combination bands with a separation of 45 cm⁻¹ which lie in the rang 29-54 cm⁻¹ reported for bidentate nitro groups (13) reveals bidentate bonding of nitrate group in these complexes.

Conclusion

In conclusion, the IR data of those complexes along with non-electrolytic behavior of compounds suggest a coordination number 9 for Lanthanide ions in those complexes.

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