



NOTE

Complexes of Praseodymium(III) and Neodymium(III) Nitrate with Mepazine

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(Received: 6 September 2010;

Accepted: 28 March 2011)

AJC-9781

10-[(1-Methyl-3-piperidyl)methyl]phenothiazine (mepazine) is demonstrated as a bidentate ligand. Its donor sites is heterocyclic nitrogen atom and tertiary nitrogen atom of the side chain. Praseodymium(III) and neodymium(III) nitrate form the complexes with the general formula $[Ln(MZ)_2(NO_3)_2]NO_3$ where Ln = Pr and Nd; MZ = mepazine. These complexes have been characterized by analytical, conductance, infrared, electronic and magnetic studies. The complexes show 1:1 electrolytic behaviour. Only two of the nitrate groups are co-ordinated bidentately to the central metal ion while the other remains uncoordinated. These conclude metal complexes formed as eight-coordinated lanthanide(III) nitrate complex. The values of various bonding parameters suggest a weak covalency for metal-ligand bond.

Key Words: Mepazine, Van-Vleck values, Nephelauxetic-ratio(b), IR, ESR.

Lanthanide compounds have been used as MRI agents in the last 20 years. It has enhanced its importance^{1,2}. Phenothiazine derivatives possess various biological activities^{3,4}. These are used in industry and chemical analysis⁵. In present studies the complexes of praseodymium(III) nitrate and neodymium(III) nitrate with mepazine is reported.

Praseodymium nitrate and neodymium nitrate were purchased from Indian Rare Earths Ltd. and mepazine hydrochloride was obtained from Byk Gulden Pharmaceutica. methanol, ether, DMF and DMSO all were of AnalaR grade.

Preparation of complexes: A mixture of aqueous solution of praseodymium nitrate or neodymium nitrate (2.5 mmol) with methanolic solution of mepazine hydrochloride (6 mmol) was made. The reaction mixture was refluxed on a water bath for ca. 2 h and then cooled in an ice bath. The resulting solid complexes were washed with methanol and dried under reduced pressure over fused calcium chloride. The metal content was determined by complexometric EDTA titration⁶ and ionic nitrate gravimetrically using Nitron reagent⁷. Magnetic moment was determined by Gouy method at room temperature using $Hg[Co(SCN)_4]$ as the calibrant. Molar conductance of the complexes were measured using systronics conductivity meter bridge in 1×10^{-3} M DMF solution. Carbon, hydrogen and nitrogen content were obtained by the Courtsy of CDRI Lucknow.

IR spectra (KBr) were recorded on a shimadzu FT-IR 470 spectrophotometer and electronic spectra in DMF 10^{-3} M

solution on a JASCO-UVIDEC-610 spectrophotometer. Thermal analysis were carried out with a liner heating rate of 10^9 min^{-1} in static air. These IR, ESR and thermal analytical studies and their values were obtained by the Courtesy of Deptt. of Special Centre for Molecular Biology, Jawahar Lal Nehru University, New Delhi.

The molar conductances values of the complexes in DMF ($82-90 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) indicate 1:1 electrolytic behaviour. The stoichiometry of the complexes is supported by analytical, magnetic and molar conductance (Table-1). Both complexes are stable at room temperature, non-hygroscopic and do not possess sharp melting points. These are soluble in DMF and DMSO, but insoluble in water, alcohol and other common organic solvents.

Compound	Ln (%)	μ_{eff}	NO_3^- (ionic)
$[Pr(MZ)_2(NO_3)_2]NO_3$	14.72 (14.86)	3.64	0.0308 (0.0327)
$[Nd(MZ)_2(NO_3)_2]NO_3$	14.94 (15.16)	3.76	0.0326 (0.0326)

Both complexes gave satisfactory C, H and N analysis. Sample taken for determination = 0.5 g; MZ = mepazine.

The μ_{eff} values show paramagnetic nature of the complexes. The measured magnetic moments show a little deviation from Van Vleck values⁸ thereby indicating that the 4f electrons don't

TABLE-2
ELECTRONIC SPECTRAL DATA AND RELATED BONDING PARAMETERS IN COMPLEXES

S. No.	M(III)	λ_{\max} (cm ⁻¹)		J-level	(1- β)	β	b ^{1/2}	η
		Ln(NO ₃) ₃	Complex					
1	Pr(III)	Pr(NO ₃) ₃	[Pr(Mz) ₂ (NO ₃) ₂]NO ₃	³ H ₄ → ³ P ₂	0.0055	0.9945	0.0524	0.0027
		22220	22110	³ H ₄ → ³ P ₁	0.0067	0.9933	0.0578	0.0033
		21275	21135	³ H ₄ → ³ P ₀	0.0098	0.9902	0.0700	0.0049
		20408	20210	³ H ₄ → ¹ D ₂	0.0082	0.9918	0.0608	0.0037
2	Nd(III)	Nd(NO ₃) ₃	[Nd(Mz) ₂ (NO ₃) ₂]NO ₃	⁴ I _{9/2} → ² G _{9/2}	0.0050	0.9950	0.0494	0.0024
		19600	19512	⁴ I _{9/2} → ⁴ G _{5/2} , ² G _{7/2}	0.0082	0.9918	0.0640	0.0040
		17240	17105	⁴ I _{9/2} → ² S _{3/2} , ⁴ F _{7/2}	0.0070	0.9930	0.0610	0.0036
		13512	13410	⁴ I _{9/2} → ⁴ F _{5/2} , ⁴ H _{9/2}	0.0080	0.9920	0.0650	0.0040
		12500	12400					

participate in bond-formation. The data also suggest non metal-metal interaction or spin-spin coupling.

The thermal studies indicate that complexes are stable upto 260 °C showing absence of any coordinated water molecule and solvent molecules. The complexes undergo two stage decomposition one at 270-340 °C with weight loss of 63-65 % due to the organic moiety and another at 360-750 °C with weight loss of 17-18 % due to nitrate as then metal oxides form. The residue becomes constant at 770 °C. Both the decomposition range are clearly exothermic processes.

Infrared spectra: Ligand shows a broadband at 2560-2500 cm⁻¹. It corresponds to CH₂C₅H₉NCH₃H⁺ combined with Cl⁻ ion. But in the spectra of metal complexes, these bands reduce to a small hump showing that tertiary nitrogen atom of the side chain is a site of co-ordination. A band at 2860-2810 cm⁻¹ in ligand corresponds to presence of heterocyclic nitrogen attached with alkyl group. This band disappears in the spectra of metal complexes. It suggests co-ordination of metal ion through heterocyclic nitrogen atom. This shows that mepazine acts as a bidentate chelating agent with heterocyclic nitrogen atom and tertiary nitrogen atom of the side chain as two coordination sites. The sharp band at 760 cm⁻¹ (CSC)⁹ observed in the spectra of ligand remains unaffected in the spectra of the metal complexes supporting the non coordination of heterocyclic sulphur atom.

IR spectra of the lanthanide nitrate complexes exhibit four bands around 1486-1478, 1280-1270, 1040-1030 and 820-815 cm⁻¹. This can be assigned to the vibrational modes of the coordinated (C_{2v}) nitrate groups. The magnitude of splitting of two bands at higher energies (200-190 cm⁻¹) suggests that the nitrate groups are present as bidentate ligands¹⁰.

The bands at 1390-1380 cm⁻¹ in both complexes are due to ionic nitrate present in the complex¹⁰. The far-IR spectra of the complexes contain a band at 450-440 cm⁻¹ assignable to $\nu(\text{Ln-N})$ bonding¹¹. This shows that these complexes have both ionic and coordinated nitrate groups.

Electronic spectra: Ligand has $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition observable at 31746 and 39370 cm⁻¹, respectively. In the corresponding complexes the $n \rightarrow \pi^*$ is shifted to 32780-32460 cm⁻¹ and $\pi \rightarrow \pi^*$ is shifted to 38000-36760 cm⁻¹. The electronic spectra of $f-f$ transitions for Pr(III) and Nd(III) complexes in the visible region and their tentative assignments¹² are given

in Table-2. These bands show an appreciable red-shift with respect to the corresponding aqua-ions. Various bonding parameters have been calculated using proper equations¹².

Nephelauxetic ratio value (β) are less than unity and the values of bonding parameter (b^{1/2}) and covalency angular parameter (η) suggest covalency in metal ligand bonding¹³. These parameters also indicate of course a weak covalency for metal ligand bond¹⁴.

Conclusion

Lanthanide(III) ions undertaken form complexes exhibiting coordination number eight with two mepazines and two nitrate groups. These two ligands behave as bidentate ligands. One NO₃⁻ group remains in outer coordination sphere. Hence complexes may be formulated as [Ln(Mz)₂(NO₃)₂]NO₃.

ACKNOWLEDGEMENTS

The authors express thanks to CDRI Lucknow, Special Center for Molecular Biology, J.N.U. and deep sense of gratitude to Prof. L.K. Mishra, Science College, Patna for providing useful data and suggestions. One of the authors (BGT) thanks to UGC for providing major research project.

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