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Synthesis, Characterization and Antibacterial Studies of Pr(III), Nd(III), Gd(III), Sm(III) and Dy(III) Complexes with N-(1-Morpholinobenzyl)semicarbazide

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A series of chelate complexes of the lanthanide ions Pr(III), Nd(III), Gd(III), Sm(III) and Dy(III) with a Mannich base, N-(1-morpholinobenzyl)semicarbazide (MBS) have been synthesized and characterized. The structures of these complexes have been elucidated by the analytical, magnetic, electrical conductivity and spectral studies. The complexes exhibit the general formula $[Ln(MBS)_3]$ where Ln = Pr^{3+}, Nd^{3+}, Gd^{3+}, Sm^{3+} and Dy^{3+} and MBS = morpholinobenzyl semicarbazide. The biological activities of the ligand and the complexes against *E. coli, S. aureus, K. pneumoniae* and *P. aeruginosa* were also studied. The metal chelates have higher activity than that of the free ligand, N-(1-morpholinobenzyl)semicarbazide.

Keywords: N-(1-Morpholinobenzyl)semicarbazide, Lanthanide(III) complexes, Antibacterial study.

INTRODUCTION

Literature survey shows that the metal complexes of Mannich bases have been studied extensively in recent years. It is evident that the compounds containing amide moiety have a strong ability to form metal complexes and they exhibit a wide range of biological activities [1-3]. In an amide group there are two potential binding sites, *i.e.*, oxygen and nitrogen for complexation. For neutral amide groups both protonation and metal ion binding will be at the amide oxygen [4]. On deprotonation the binding shifts to the amide nitrogen [5]. It is evident from the literature that semicarbazide compounds containing the amide moiety have a strong ability for complexation. The synthesis of some transition metal complexes of this type of Mannich base have been reported [6]. The present communication reports the synthesis and characterization of some lanthanides like Pr(III), Nd(III), Gd(III), Sm(III) and Dy(III) complexes with the Mannich base N-(1-morpholinobenzyl)semicarbazide (Fig. 1). The antibacterial activity of the ligand and the complexes are also described in this communication.

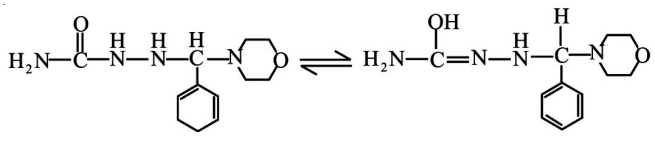

Fig. 1. Structure of N-(1-morpholinobenzyl)semicarbazide

EXPERIMENTAL

All the reagents used for the synthesis of the ligand and the complexes were AnalaR or GR (Merck) grade. Organic solvents were purified by standard methods.

The ligand N-(1-morpholinobenzyl)semicarbazide (MBS) was prepared by reported method [6]. Semicarbazide hydrochloride (1.11 g, 10 mmol) in 20 mL of ethanol was neutralized with ammonia. To this solution, morpholine (0.9 mL, 10 mmol) was added drop by drop with constant stirring for about 5 min. The colourless solid formed was filtered and recrystallized from ethanol (yield 81 %, m.p. 217 °C).

The lanthanide nitrates were prepared from corresponding oxides [7]. The lanthanide oxides were dissolved in 50 % nitric acid and the salt formed was crystallized after concentrating the solution in a steam bath.

All the lanthanide(III) complexes were prepared by the following general procedure [8-10]. An alcoholic solution containing the ligand (MBS) and the metal salt in 3:1 mole ratio is magnetically stirred and warmed for 0.5 h. Then it is transferred into a flask and refluxed for 3 h. It was then concentrated and the volume of the solution is reduced to half of its original volume. The solid thus separated is filtered, washed with methanol and dried over calcium chloride in a desiccators.

The metal contents of the complexes were determined by gravimetric methods [11]. The elemental analysis (carbon,

TABLE-1
ANALYTICAL AND MOLAR MASS DATA OF THE COMPLEXES OF MBS WITH THE NITRATES OF LANTHANIDE(III) IONS

Complex/Compound	Molar mass: Found (calcd.)	Elemental analysis (%): Found (calcd.)			
		Ln	C	H	N
$C_{12}H_{18}N_4O_2$	(250.30)	–			
$[Pr(MBS)_3$	881.6 (888.80)	15.30 (15.85)	48.01 (48.60)	5.81 (5.74)	18.18 (18.90)
$[Sm(MBS)_3]$	891.7 (898.26)	17.11 (16.86)	48.34 (48.09)	5.50 (5.68)	18.08 (18.70)
$[Nd(MBS)_3]$	887.1 (892.14)	15.83 (16.26)	48.81 (48.42)	5.51 (5.72)	19.11 (18.83)
$[Gd(MBS)_3]$	893.8 (905.15)	16.88 (17.37)	47.45 (47.73)	5.32 (5.63)	18.08 (18.56)
$[Dy(MBS)_3]$	901.1 (910.40)	17.05 (17.85)	48.10 (47.45)	5.95 (5.60)	18.71 (18.45)

hydrogen and nitrogen) were carried out using HCE 1108 CHN analyzer. The molar masses of the complexes were determined by the Rast camphor method [12]. The molar conductance of the complexes in methanol, acetonitrile, DMF and nitrobenzene (about 10^{-3} M solutions) were determined at room temperature. Magnetic susceptibilities of the complexes were determined by the Gouy method. The infrared spectra of the ligand and the complexes were recorded in the range 4000-400 cm^{-1} employing the KBr disc technique. The X-ray powder patterns were recorded using Philips diffractometer (Model PW 1710) for the complexes of Nd(III) and Sm(III). The antimicrobial studies of the complexes were also done by well diffusion method [13] by using bacteria like *Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa* and *Klebsiella pneumonia*.

RESULTS AND DISCUSSION

Five complexes of lanthanide metal ions with N-(1-morpholinobenzyl)semicarbazide (MBS) have been isolated. The analytical results (Table-1) indicate 1:3 (metal:ligand) stoichiometry for all the lanthanide(III) complexes. The molar conductance values (Table-2) of the lanthanide(III) complexes reveal them to non-electrolytes [14]. The room temperature magnetic moments (Table-3) of these complexes with MBS are compared with theoretical spin orbit coupling values [15] (the Hund values) of the respective lanthanide ions. Except for samarium ions they agree with each other. However, the experimental values of the complexes including those of samarium agrees with the theoretical values calculated from van Vleck formula [16]. The discrepancies are attributed to the fact that the first excited states *J* of the Sm^{3+} are sufficiently close to their ground state so that these states can mix with each other even at room temperature to cause an increase in magnetic moments. It is observed that the magnetic moments of the present complexes exhibit only very little deviation from the van Vleck values. This shows the nonparticipation of 4*f* electrons in the bond formation with the ligands.

TABLE-2
MOLAR CONDUCTANCE DATA OF THE COMPLEXES

Complex	Molar conductance (ohm^{-1} cm^2 mol^{-1})			
	Methanol	Acetonitrile	Nitrobenzene	DMF
$[Pr(MBS)_3]$	7.1	4.8	5.0	3.5
$[Sm(MBS)_3]$	6.5	3.9	4.4	4.1
$[Nd(MBS)_3]$	5.9	4.1	3.9	4.2
$Gd(MBS)_3]$	4.8	3.6	3.6	4.3
$Dy(MBS)_3]$	5.6	4.2	4.1	3.5

TABLE-3
MAGNETIC MOMENTS (μ_{eff}) OF THE COMPLEXES OF MBS WITH LANTHANIDE IONS AT ROOM TEMPERATURE

Complex	Magnetic moments (BM)		
	Observed	Hund value	van Vleck value
$[Pr(MBS)_3]$	3.55	3.58	3.62
$[Sm(MBS)_3]$	1.60	0.84	1.65
$[Nd(MBS)_3]$	3.56	3.62	3.68
$Gd(MBS)_3]$	7.90	7.94	7.94
$Dy(MBS)_3]$	10.30	10.61	10.61

The mode of binding of the ligand MBS with the lanthanide ions in complex formation was studied by comparing the IR spectra of the ligand with those of the complexes. In the IR spectrum of the ligand, bands are observed in the regions 3260 and 1620 cm^{-1}, which are assigned to ν(N-H) and ν(C=O), respectively. The bands obtained in the regions 1140 and 1670 cm^{-1} are due to ν(C-O) and ν(C=N) respectively [17,18]. In the spectra of the complexes, the band corresponding to ν(C=O) mode of free MBS is missing. This shows the enolization of the C=O group followed by deprotonation and complex formation with the lanthanide ions. The band due to ν(C=N) mode of MBS is shifted to lower frequency regions indicating the complexation of the azomethine nitrogen to the lanthanide ions. In the far infrared region of the spectra of the complexes, bands are observed at 540-480 and 465-410 cm^{-1} which may be assigned to ν(Ln-O) and ν(Ln-N) modes, respectively. The dipole moment change in the vibration of M-O band is larger in comparison to that in the case of Ln-N band. As a result, the band due to ν(Ln-O) appears in higher frequency region [19] and is sharper and stronger than ν(Ln-N).

The mass spectrum of MBS shows the molecular ion peak at *m/z* 250. The neodymium complex ($C_{36}H_{51}N_{12}O_6Nd$) shows the molecular ion peak at *m/z* 892. The ligand, MBS as well as the complex show the base peak at *m/z* 164 due to the fragment, $C_8H_{10}N_3O$. From the data, the stoichiometry of the metal chelates can be confirmed as being of the $[ML_3]$ type.

^1H NMR spectrum of MBS and $Nd(MBS)_3$ complex was recorded in DMSO-d_6 solution. The ligand shows a multiplet signal at δ 6.62 ppm due to CH group, at δ 6.14 due to the NH proton, at δ 2.3 due to morpholine-N-CH_2 and at δ 3.8 ppm due to morpholine O-CH_2. The singlet at δ 10.8 ppm is due to –N=C-OH group. In the complexes, the multiplet at δ 7.16-7.20 ppm and at δ 7.90-8.08 ppm is due to aromatic protons. Shifting of –CH and –NH protons to the downfield indicates the coordination of azomethine nitrogen. The peak at δ 10.8 ppm in the MBS was found to be missing in the complex which confirms that the ligand is in enol form and it undergoes

deprotanation and then the carbonyl oxygen coordinates with the metal.

The X-ray powder patterns were recorded for Nd(III) and Sm(III) complexes. The diffraction patterns were indexed by the method developed by Hesse [20] and Lipson [21,22]. Both of these complexes were found to be orthorhombic. The cell parameters have been calculated by using the equation:

$$Sin^2\theta\ (hkl) = Ah^2 + Bk^2 + Cl^2$$

where, $A = \frac{\lambda^2}{4a^2}, B = \frac{\lambda^2}{4b^2}$ and $C = \frac{\lambda^2}{4c^2}$.

For the complex of Nd(III) the lattice constants are: A = 0.0042, B = 0.0088 and C = 0.0820. The unit cell dimensions are: a = 18.0020 Å, b = 15.2092 Å and c = 10.6994 Å. Thus, the cell volume of the complex is given as, V = abc = 2.929×10^{-21} cm^3. The density of the complex is 1.011 g cm^{-3} and the molar mass is 892.14. From this $n = \frac{dN_0V}{M} = 1.999 \approx 2.$ Thus, the number of molecules per unit cell is two. For the complex of Sm(III), the lattice constants are: A = 0.004926, B = 0.0114 and C = 0.0948. Hence, a = 20.998 Å, b = 18.314 and c = 12.6972. Thus, the cell volume is V = abc = 4.882×10^{-21} cm^3. Its density is 1.178 g cm^{-3} and the molar mass is 898.26. From this, $n = \frac{dN_0V}{M} = 3.8542 \approx 4.$ Thus, the number of molecules per unit cell is 4.

The antimicrobial studies of the ligand, MBS and the complexes of it with the lanthanide metals were done using four different bacteria, *viz., S. aureus, K. pneumoniae, P. aeruginosa* and *E. coli* by well diffusion method. The values of zone of inhibition of the ligand and the complexes are given in Table-4. All the complexes were found to be active towards these bacteria. The metal chelates are found to be more active than the free ligand and the control (ampicillin). The order of activity towards *S. aureus* is Sm > Nd > Gd > Dy > Pr. In the case of *P. aeruginosa* the order of activity is Sm > Gd > Nd > Dy > Pr. For *K. pneumoniae* and *E. coli* the order of activity is Sm > Gd > Nd > Pr > Dy.

TABLE-4
ANTIBACTERIAL ACTIVITY OF THE LIGAND (MBS) AND ITS COMPLEXES

Compound	Zone of inhibition (mm)			
	S. aureus	*E. coli*	*P. aeruginosa*	*K. pneumoniae*
Ampicillin	10	12	15	12
MBS	9	10	8	7
$[Sm(MBS)_3]$	20	24	22	23
$[Nd(MBS)_3]$	16	17	16	18
$[Pr(MBS)_3]$	11	14	12	15
$Gd(MBS)_3]$	15	18	19	19
$Dy(MBS)_3]$	13	11	14	12

Based on the above studies, the complexes may be represented as in Fig. 2 in which the coordination number of lanthanide ion is six.

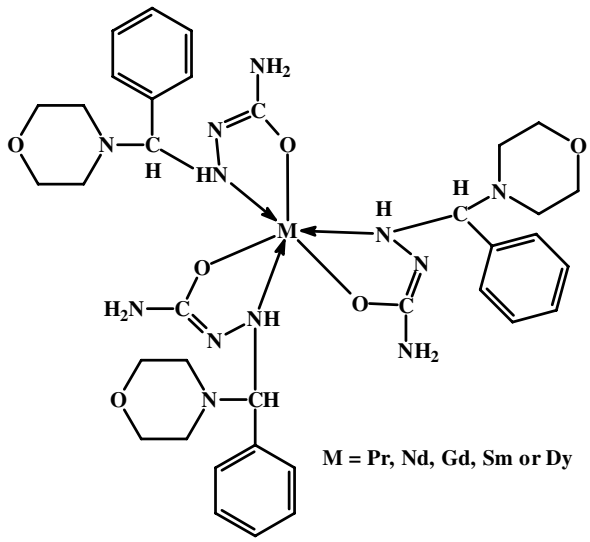

Fig. 2. Structure of the complexes of MBS with lanthanides

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