

Synthesis and Elucidation of Some Mixed Ligand Complexes of Th(IV) with N-(1-morpholinobenzyl)semicarbazide

M. VISWANATHAN

Department of Chemistry, Amrita School of Arts and Sciences, Amritapuri Campus, Amrita Vishwa Vidyapeetham University, P.O. Clappana, Kollam-690 525, India

Corresponding author: E-mail: viswanathanm@am.amrita.edu; drmviswanath@gmail.com

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Some mixed ligand complexes of Th(IV) with Mannich base N-(1-morpholinobenzyl)semicarbazide (MBS) and various anions like chloride, nitrate, acetate, thiocyanate and perchlorate have been synthesized and characterized. Their probable structures have been elucidated by elemental analysis, determination of molar mass, measurement of molar conductance, spectral and X-ray diffraction studies. The complexes exhibit formulae: $[\text{Th}(\text{MBS})_3\text{X}]$, where $\text{X} = \text{NO}_3^-$, Cl^- , CH_3COO^- , SCN^- or ClO_4^- . In all these complexes, N-(1-morpholinobenzyl)semicarbazide acts as a bidentate ligand and anions act as unidentate ligands. The antimicrobial activities of ligand and metal chelates against *E. coli*, *S. aureus*, *K. pneumoniae* and *P. aeruginosa* were also studied.

Keywords: Thorium(IV), Mixed ligand complexes, Morpholinobenzyl semicarbazide.

INTRODUCTION

Literature survey reveals that metal chelates of benzaldehyde based Mannich bases have been studied extensively in recent years because of the sensitivity and selectivity of the ligand towards various metal ions [1-5]. The semicarbazide compounds containing amide moiety have a strong ability to form metal chelates. A search through the literature shows that a Mannich base, N-(1-morpholinobenzyl)semicarbazide has been prepared by the condensation of morpholine, semicarbazide and benzaldehyde and its complexes with some transition metals like Cu(II), Ni(II), Co(II) and Zn(II) have been synthesized [6]. In these metal complexes, the ligand is bidentate via the N and O of semicarbazide. The present communication reports the synthesis of some mixed ligand complexes of the Mannich base N-(1-morpholinobenzyl) semicarbazide (Fig. 1) with acetate, chloride, nitrate, perchlorate and thiocyanate of Th(IV). The complexes have been characterized by various physico-chemical techniques like, elemental analysis, magnetic measurements, determination of molar conductivity, spectral and X-ray diffraction studies. The ligand and the metal complexes have biological activities against various microbes like *S. aureus*, *E. coli*, *P. aeruginosa* and *K. pneumoniae*.

EXPERIMENTAL

All the chemicals used were of Merck products. Organic solvents were purified by standard methods. The ligand N-(1-

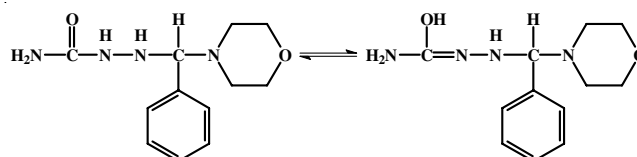


Fig. 1. Structure of N-(1-morpholinobenzyl)semicarbazide

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 neutralized solution, morpholine (0.9 mL, 10 mmol) was added drop by drop with constant stirring to get a clear solution. To this benzaldehyde (1 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 nitrate and perchlorate complexes were prepared by refluxing an alcoholic solution containing N-(1-morpholinobenzyl)semicarbazide and thorium(IV) salt in the 2:1 ratio for about 3 h. The resulting solution was concentrated to one third of its volume and cooled. The solid thorium complexes formed were filtered, washed with methanol or ethanol and dried *in vacuo*. The preparation of thiocyanato and acetato complexes involved two steps. In the first step, the nitrate complex was prepared. In the second step, the nitrate complex was dissolved in methanol and was mixed with stoichiometric quantity of

aqueous methanolic solution of ammonium thiocyanate (or sodium acetate). The resulting reaction mixture in each case was refluxed for about 3 h to replace the nitrate ions with the thiocyanate or acetate ions. The resulting solution was concentrated to one third of its volume and cooled, the solid complexes formed were filtered, washed with ethanol or methanol and dried *in vacuo*.

The thorium content of the complexes were determined by oxalate-oxide method [7]. The carbon, hydrogen and nitrogen contents were determined by microanalytical method. The anions present in the complexes were also analyzed wherever possible [8]. The nitrate content of the complex was determined as nitron-nitrate by using nitron reagent [8]. The thiocyanate content was determined as AgSCN [7] from alkali thiocyanate solution by using AgNO₃ solution in presence of nitric acid. The perchlorate content was determined by Kurz's method [9]. The molar conductance of the complexes in acetonitrile, DMF, nitrobenzene and methanol (about 10⁻³ M solutions) were measured at room temperature by using an ELICO conductivity bridge type CM82T with a dip type conductivity cell having platinum electrodes (cell constant = 0.94 cm⁻¹). Magnetic susceptibilities were measured at room temperature. The infrared spectra of the ligand and the complexes were recorded in the range 4000-400 cm⁻¹ employing the KBr disc technique. The mass spectra were recorded on a Finnigan MAT 8230 mass spectrometer. The X-ray powder patterns were recorded by using Philips diffractometer (Model PW 1710). The antimicrobial studies of the complexes at various concentration were done by well diffusion method.

RESULTS AND DISCUSSION

The analytical data and molar masses of the complexes are presented in Tables 1a and 1b. All the complexes are moderately soluble in methanol, acetonitrile, nitrobenzene and DMF. The molar conductance values (Table-2) of the complexes in the above solvents were compared with the data available for standard substances to see whether the anions are coordinated or not [10,11]. It was observed that all complexes behave like non-electrolytes in all the solvents used suggesting that the anions present in the thorium(IV) salts have been coordinated with the metal ions. The comparatively high values of conductance for the complexes in methanol are due to the partial displacement of the coordinated anions by polar methanol molecules [12].

All the thorium(IV) complexes with MBS are diamagnetic as expected in view of the noble gas configuration of Th(IV).

In the infrared spectrum of MBS, bands appear in the regions 3260 and 1620 cm⁻¹, which are assigned to $\nu(\text{N-H})$ and $\nu(\text{C=O})$,

TABLE-1a
ANALYTICAL AND MOLAR MASS DATA OF
THE COMPLEXES OF Th(IV) WITH MBS

Complex/ Compound	Elemental analysis (%): Found (calcd.)				Molar mass
	Th	C	H	N	
C ₁₂ H ₁₈ N ₄ O ₂	—	57.2 (57.58)	6.82 (7.25)	21.70 (22.38)	250.3
[Th(MBS) ₃ (OAc)]	22.12 (22.33)	43.42 (43.89)	5.02 (5.24)	15.98 (16.17)	1032.44 (1038.94)
[Th(MBS) ₃ (ClO ₄)]	21.04 (21.49)	39.78 (40.02)	4.54 (4.72)	15.14 (15.56)	1070.86 (1079.39)

TABLE-1b
ANALYTICAL AND MOLAR MASS DATA OF
THE COMPLEXES OF Th(IV) WITH MBS

Complex	Th(%)	Anion(%)	Molar Mass
[Th(MBS) ₃ (NO ₃)]	22.04 (22.26)	5.72 (5.95)	1035.42 (1041.9)
[Th(MBS) ₃ Cl]	22.56 (22.84)	3.26 (3.49)	1008.46 (1015.39)
[Th(MBS) ₃ (NCS)]	22.12 (22.35)	5.34 (5.59)	1031.92 (1038.01)

TABLE-2
MOLAR CONDUCTANCE DATA OF
Th(IV) COMPLEXES WITH MBS

Complex	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)			
	Methanol	Acetonitrile	Nitrobenzene	DMF
[Th(MBS) ₃ Cl]	24	8	6	3
[Th(MBS) ₃ (NO ₃)]	22	5	4	3
[Th(MBS) ₃ (NCS)]	28	7	5	2
[Th(MBS) ₃ (OAc)]	26	4	3	2
[Th(MBS) ₃ (ClO ₄)]	30	9	4	3

respectively. The bands due to $\nu(\text{C=O})$ and $\nu(\text{C=N})$ are located in the regions 1140 and 1670 cm⁻¹, respectively [13,14]. In the spectra of the complexes, the band corresponding to $\nu(\text{C=O})$ mode of free ligand, MBS is not observed which indicates the enolization of C=O followed by deprotonation and complexation with metal ions. The $\nu(\text{C=N})$ mode of the ligand is shifted to lower frequency regions indicating the complexation of azomethine nitrogen to the central metal ion. The band at 3260 cm⁻¹ due to $\nu(\text{N-H})$ of the ligand is absent in the spectra of the complexes, suggesting deprotonation of N-H of the ligand prior to coordination to thorium metal. Based on this, it may be concluded that MBS acts as a monobasic bidentate ligand in the complexes. The additional bands in the spectra of the complexes at 535-475 and 460-415 cm⁻¹ may be assigned to $\nu(\text{Th-O})$ and $\nu(\text{Th-N})$ modes, respectively. The dipole moment change in the vibration of Th-O band is larger compared to that in Th-N band. Thus the band due to $\nu(\text{Th-O})$ occurs in higher frequency [15] region and is stronger and sharper than $\nu(\text{Th-N})$.

The infrared spectrum of the nitrate complex shows three additional bands at 1464, 1340 and 1024 cm⁻¹ which are assigned to ν_4 , ν_1 and ν_2 modes of the coordinated nitrate ions [16-18]. Since the difference between ν_4 and ν_1 is about 124 cm⁻¹, it is suggested that the nitrate ions are coordinated unidentately to the thorium(IV) [19].

The thiocyanato complex of thorium(IV) exhibits three additional bands at 2052, 864 and 460 cm⁻¹ which are attributed to $\nu(\text{CN})$, $\nu(\text{CS})$ and $\delta(\text{NCS})$ modes of coordinated thiocyanate ion, respectively. It has been well established that $\nu(\text{CN})$ occurs at lower frequency around 2050 cm⁻¹ in N-bonded complexes compared to the position in the case of S-bonded complexes [20] appearing around 2100 cm⁻¹. For N-bonded complexes $\nu(\text{CS})$ mode appears in the range of 860-780 cm⁻¹ while it appears in the range 760-720 cm⁻¹ for S-bonded complexes. In addition to these a single sharp band around 480 cm⁻¹ corresponding to $\delta(\text{NCS})$ mode appears in the case of N-bonded

complexes. On the other hand, in the case of S-bonded complexes several bands with lower intensities appear around 420 cm^{-1} . Thus, it is evident that the thiocyanate ion is coordinated unidentately to the thorium ion through N atom.

In the IR spectrum of acetato complex two additional bands are present at 1671 and 1322 cm^{-1} corresponding to asymmetric and symmetric stretching vibrations of carboxylate group. The ν_{asym} and ν_{sym} modes of the carboxylate ion in the free acid appears at 1560 and 1420 cm^{-1} , respectively. But, in the spectrum of the complex $\nu_{\text{asym}}(\text{OCO})$ mode is shifted to higher frequency, 1671 cm^{-1} whereas $\nu_{\text{sym}}(\text{OCO})$ is shifted to lower frequency, 1322 cm^{-1} . Thus, the separation between the two $\nu(\text{OCO})$ bands increases which indicates the unidentate coordination of acetate ion to thorium ion. The nonelectrolytic conductance value of the complex agrees with this conclusion.

The infrared spectrum of the perchlorato complex exhibits three additional bands at 1102 , 1082 and 621 cm^{-1} corresponding to ν_4 , ν_1 and ν_3 modes of coordinated perchlorate ion. This indicates the unidentate coordination of ClO_4^- to Th(IV) ion. The non-electrolytic conductance value of the complex agrees with this conclusion.

The ^1H NMR spectra of MBS and $[\text{Th}(\text{MBS})_3\text{Cl}]$ were recorded in $\text{DMSO}-d_6$ solution. The ligand exhibits a multiplet signal at δ 6.96-7.82 ppm which is due to the presence of aromatic protons. Signals at δ 6.62 ppm due to CH group, at δ 6.14 due to NH proton, at δ 2.3 due to morpholine $-\text{N}-\text{CH}_2$, at δ 3.8 ppm due to morpholine $\text{O}-\text{CH}_2$. The singlet at δ 10.8 ppm is due to $-\text{N}=\text{C}-\text{OH}$ group. In the metal chelates, the multiplet at δ 7.16-7.20 ppm and at δ 7.9-8.08 ppm is due the presence of aromatic protons. The downfield shifting of $-\text{CH}$ and $-\text{NH}$ protons indicates the coordination of azomethine nitrogen. The missing of the peak at δ 10.8 ppm of MBS in the complex confirms that the ligand is in enol form and it undergoes deprotonation followed by coordination of the carboxyl oxygen with the metal.

The mass spectrum of the ligand, MBS exhibits a molecular ion peak at m/z 25. The metal chelate, $[\text{Th}(\text{MBS})_3\text{Cl}]$ shows the molecular ion peak at m/z 1015. The ligand as well as the metal chelate exhibit the base peak at m/z 164 due to the fragment, $\text{C}_8\text{H}_{10}\text{N}_3\text{O}$.

The X-ray powder patterns of the complexes $[\text{Th}(\text{MBS})_3\text{Cl}]$ and $[\text{Th}(\text{MBS})_3\text{NO}_3]$ were recorded on a Rigaku (Japan) PW 1710 X-ray powder diffractometer on a chart recorder. The diffraction patterns were indexed by using the method developed by Hesse [21] and Lipson and Steeple [22]. The complexes were found to be orthorhombic. The unit cell dimensions of the complex, $[\text{Th}(\text{MBS})_3\text{Cl}]$ are : $a = 17.9743\text{ \AA}$, $b = 11.4783\text{ \AA}$ and $c = 8.7975\text{ \AA}$. Thus the cell volume (V) of the complex is $1.8151 \times 10^{-21}\text{ cm}^3$. The density of the complex

is 0.9264 g cm^{-3} . From these values n is given as $\frac{dN_0 V}{M} = 0.9969$. Thus it is evident that the number of molecules per unit cell is one. In the case of the complex, $[\text{Th}(\text{MBS})_3\text{NO}_3]$, the unit cell dimensions were found to be $a = 18.2868\text{ \AA}$, $b = 11.6780\text{ \AA}$ and $c = 8.9505\text{ \AA}$ and the cell volume (V) is $1.8151 \times 10^{-21}\text{ g cm}^{-3}$. Evidently the number of molecules per unit cell, $n = \frac{dN_0 V}{M} = 1.0291$, i.e., one per unit cell.

The metal chelates were tested for their antibacterial activity against *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Escherichia coli* and *Pseudomonas aeruginosa* by well diffusion method [23]. The ligand and the metal chelates were found to be active towards these bacteria. The metal chelates exhibit higher activity in comparison with that of the free ligand or the control (ampicillin). The zone of inhibition values of the ligand and the complexes against the growth microorganisms are summarized in Table-3. The chloro complexes are found to be more active than the acetato and nitrato complexes.

TABLE-3
ANTIBACTERIAL ACTIVITY OF THE
LIGAND AND THE METAL CHELATES

Compound	Zone of inhibition (mm)			
	<i>S. aureus</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>K. pneumoniae</i>
Ampicillin	10	12	15	12
MBS	8	10	9	8
$[\text{Th}(\text{MBS})_3\text{Cl}]$	19	20	21	22
$[\text{Th}(\text{MBS})_3\text{NO}_3]$	16	15	16	13
$[\text{Th}(\text{MBS})_3\text{NCS}]$	17	15	14	15
$[\text{Th}(\text{MBS})_3\text{ClO}_4]$	15	17	16	15
$[\text{Th}(\text{MBS})_3\text{OAc}]$	14	16	15	14

On the basis of the above studies, it is concluded that the present metal chelates have the general structure $[\text{Th}(\text{MBS})_3\text{X}]$ where $\text{X} = \text{NO}_3^-$, Cl^- , SCN^- , CH_3COO^- or ClO_4^- . Thus, the metal chelates may be represented as in Fig. 2 in which the coordination number of thorium is seven.

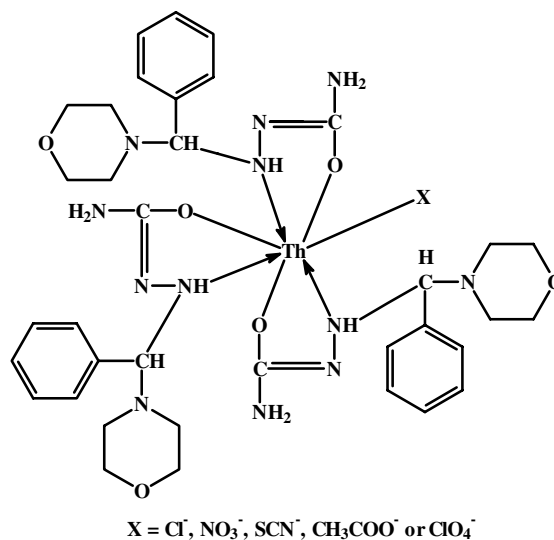


Fig. 2. Structure of complexes of N-(1-morpholinobenzyl)semicarbazide (MBS) with thorium

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