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Synthesis, Spectroscopic, and Antimicrobial Studies of the Bivalent Zinc and Mercury Complexes of Thiosemicarbazide[1]

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Abstract—A series of metal complexes of Zn(II) and Hg(II) having the general composition $[ML_2]X_2$ with thiosemicarbazide have been prepared and characterized by elemental chemical analysis, molar conductance, and spectral (IR and mass) studies. The IR spectral data suggest the involvement of sulfur and terminal amino nitrogen in coordination to central metal ion. On the basis of spectral studies, a tetrahedral geometry has been assigned for the Zn(II) and Hg(II) complexes. Thiosemicarbazide and its metal complexes have been tested in vitro against a number of microorganisms in order to assess their antimicrobial properties.

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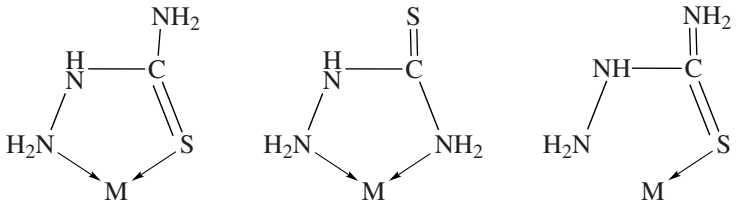
INTRODUCTION

Sulfur compounds have been the subject of interest in coordination chemistry. Thiosemicarbazide–based compounds have been extensively studied over the last couple of decades [1–3]. The various Schiff bases of thiosemicarbazide (thiosemicarbazones) and their corresponding complexes have attracted much attention due to their wide biological activities, such as antitumor [4], antibacterial [5], and antifungal activities [6]. Coordination of these compounds with metal ions, such as copper, nickel, and iron, often enhances their activity [7–9]. Although in recent years a number of structures of thiosemicarbazone complexes have been reported, there have been few structures of the precursor thiosemicarbazides or their complexes [10]. Thiosemicarbazide is an ambidentate ligand capable of forming five-membered metallocycles (**A, B**) during coordination or monodentate bonding (**C**) through sulfur as shown below [11]:



In view of the above applications, the present work relates to the synthesis, spectroscopic, and antimicrobial studies of the Zn(II) and Hg(II) complexes of thiosemicarbazide.

EXPERIMENTAL

All the chemicals were of analytical grade and were procured from Sigma Aldrich and Fluka. Metal salts were purchased from E. Merck and used as received.

Synthesis of complexes. A hot ethanolic solution (20 ml) of thiosemicarbazide (1.8 g, 0.02 mol) and a hot ethanolic solution (20 ml) of the corresponding metal salt (0.01 mol) were refluxed for 3–4 h at 60°C. On cooling colored complexes were precipitated out. They were filtered off, washed with 50% ethanol, and dried under vaccum over P_4O_{10}.

The C, H, and N were analyzed on a Carlo-Erba 1106 elemental analyzer. The nitrogen content of the complexes was determined using Kjeldahl's method.

[1] The article is published in the original.

Table 1. Elemental analysis data and physical properties of the complexes

Complex	Atomic mass found (calcd)	Yield,%	Color	M.p.,°C	Contents (found/calcd), %			
					C	H	N	M
$[Zn(L)_2]Cl_2$	318(320)	74	White	185	7.54/7.35	3.14/3.32	26.41/25.31	20.40/20.55
$[Zn(L)_2](NO_3)_2$	372(371)	60	White	240	6.45/6.56	2.68/2.51	30.10/30.27	17.47/17.40
$[Zn(L)_2]SO_4$	344(345)	61	White	180	6.97/6.80	2.90/2.97	24.41/24.63	18.89/18.79
$[Hg(L)_2]Cl_2$	453(454)	80	White	220	5.29/5.33	2.20/2.12	18.54/18.58	44.37/44.39
$[Hg(L)_2](NO_3)_2$	507(506)	60	Brown	190	4.73/4.65	1.97/1.91	22.09/22.20	39.64/39.71
$[Hg(L)_2]SO_4$	479(478)	54	Mustard	180	5.01/5.12	2.08/2.04	7.53/17.64	41.96/41.81

Table 2. IR spectral data of the metal complexes

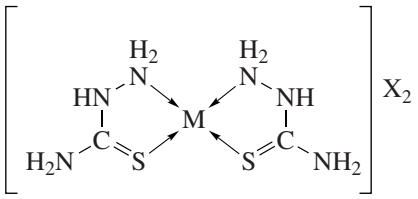
Compound	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\delta(NH_2)$	ν(C=S)	ν(M–N)	ν(M–S)
CH_5N_3S (L)	3365	3263	1642	800		
$[Zn(L)_2]Cl_2$	3338	3247	1633	675	430	350
$[Zn(L)_2](NO_3)_2$	3355	3158	1632	700	431	360
$[Zn(L)_2]SO_4$	3300	3153	1617	700	486	380
$[Hg(L)_2]Cl_2$	3330	3255	1628	700	443	390
$[Hg(L)_2](NO_3)_2$	3341	3258	1624	678	458	390
$[Hg(L)_2]SO_4$	3344	3342	1623	699	408	340

Molar conductance was measured with the ELICO (CM82T) conductivity bridge. The electronic impact mass spectrum was recorded on a JEOL, JMS-DX-303 mass spectrometer. IR spectra (KBr) were recorded on a FTIR spectrum BX-II spectrophotometer. The molecular weights of the complexes were determined cryoscopically in benzene.

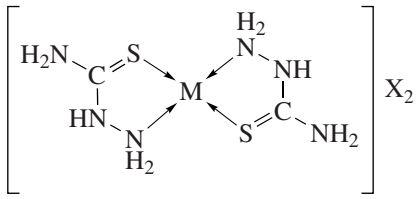
In vitro antimicrobial screening was performed by the agar disc diffusion method [12, 13]. All the test organisms were obtained from Microbial Type Culture Collection and Gene Bank (Institute of Microbial Technology, Chandigarh, India). The sterile discs impregnated with the test compounds were placed on the seeded plates. The zone of inhibition around the disc indicated the antimicrobial activity of the test compounds.

RESULTS AND DISCUSSION

The complexes were synthesized by reacting thiosemicarbazide with metal ion in a 2 : 1 molar ratio in an ethanolic medium. The ligand behaves as bidentate and coordinates through the terminal N and S atoms. Elemental analysis of the complexes corresponds to the composition as shown in Table 1. The molar conductance measurements of the complexes in DMF lie in a range of 116–138 Ohm^{-1} cm^2 mol^{-1}, indicating their 1 : 2 electrolytic behavior. Thus, the complexes may be formulated as $[M(L)_2]X_2$, (where M = Zn(II) and Hg(II); L = thiosemicarbazide, X = Cl^-, NO_3^- and $1/2SO_4^{2-}$). The complexes containing SO_4^{2-} and NO_3^- are produced in the *cis* form (**D**), while the *trans* form (**E**) is obtained when Cl^- is the anion as shown below:



(D)



(E)

All complexes are diamagnetic. The assignments of the significant IR spectral bands of thiosemicarbazide and its metal complexes are presented in Table 2. Ideally, five N–H stretching frequencies would be

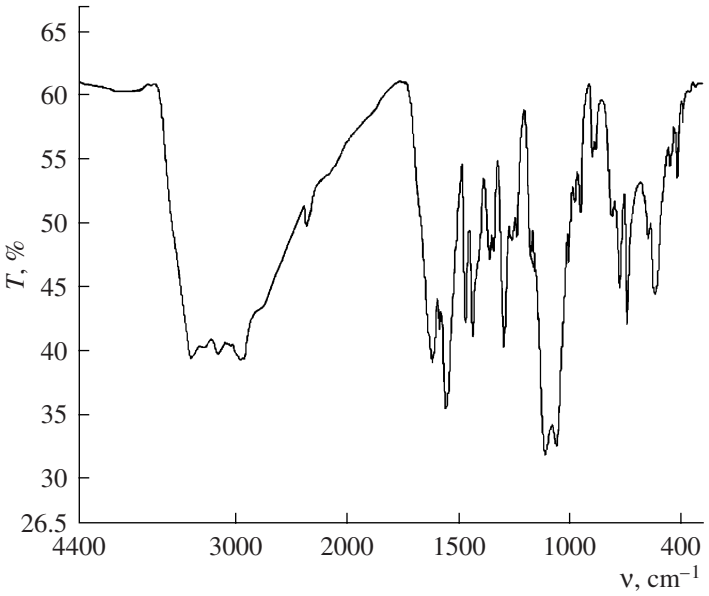


Fig. 1. IR spectra of *cis*-$[Zn(L)_2]SO_4$.

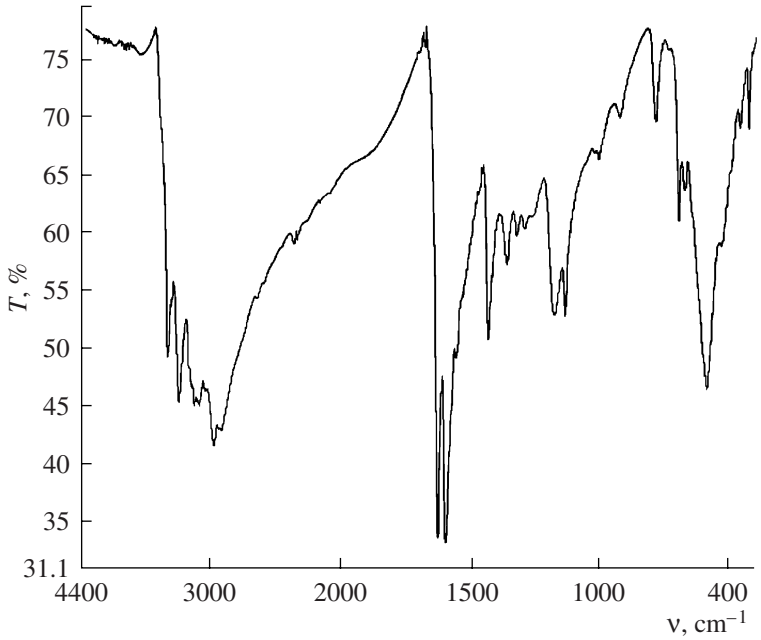


Fig. 2. IR spectra of *trans*-$[Zn(L)_2]Cl_2$.

expected in thiosemicarbazide in a high-frequency region of 3400–3000 cm^{-1}. The band due to $\nu_{as}(NH_2)$ at 3365 cm^{-1} in thiosemicarbazide is shifted to lower frequencies in the complexes. Thiosemicarbazide has two bands at 1642 and 1619 cm^{-1}. The former is the deformation mode, $\delta(NH_2)$, of the amine in the hydrazine residue, and the latter is the amide II band of the primary amine. These bands shift toward lower frequencies due to the involvement of one of the group NH_2 in coordination. Strong evidence is the appearance of a 430–459 cm^{-1} band due to ν(M–N). Strong band at 800 cm^{-1} assigned to C=S stretching vibration shifts to lower frequencies in the complexes, indicating the involvement of thioketo sulfur in complex formation. In each complex, two thiosemicarbazide ligands coordinate to the central metal ion through two terminal

Table 3. Antibacterial screening data of thiosemicarbazide and its complexes

Compound	μg/disc	Diameter of zone of inhibition, mm			
		gram positive		gram negative	
		Staphylococcus aureus	*Staphylococcus epidermidis*	*Escherichia coli*	*Pseudomonas aeruginosa*
CH_5N_3S (L)	100				
$[Zn(L)_2]Cl_2$	100	10	08		09
$[Zn(L)_2](NO_3)_2$	100	09	08	08	07
$[Zn(L)_2]SO_4$	100	09	07		
$[Hg(L)_2]Cl_2$	100	26	24	22	22
$[Hg(L)_2](NO_3)_2$	100	24	25	18	20
$[Hg(L)_2]SO_4$	100	23	22	16	14
Amikacin	30	26	22	21	20

hydrazine N atoms and two S atoms. Thus, it is concluded that the ligand acts as a bidentate chelating agent.

The infrared spectra of the *cis* and *trans* complexes show marked differences in certain regions of the spectrum (Figs. 1 and 2). The *trans* isomers show two sharp strong bands in a frequency region of 3400–3000 cm^{-1}. The corresponding *cis* isomers show only broad bands throughout this region. In the region around 1600 cm^{-1} corresponding to NH_2 bending modes, two sharp bands are observed for the *trans* isomer, while a single broad band is observed for the *cis* isomers [14].

The infrared spectra of the nitrate complexes show a sharp band at 1384 cm^{-1} characteristic of the uncoordinated nitrate group [15]. The IR bands in the region of 1408–1426 and 615–622 cm^{-1} characteristic of the uncoordinated sulfate group are seen in the infrared spectra of the sulfate complexes [16]. However, no ν(M–Cl) band is observed in the spectrum of the $[M(L)_2]Cl_2$ complexes, suggesting that the chloride is ionic [17].

Table. 4. Antifungal screening data of thiosemicarbazide and its complexes

Compound	μg/disc	Diameter of zone of inhibition, mm	
		Candida albicans	*Aspergillus niger*
CH_5N_3S (L)	200		
$[Zn(L)_2]Cl_2$	200	08	
$[Zn(L)_2](NO_3)_2$	200	08	08
$[Zn(L)_2]SO_4$	200	09	
$[Hg(L)_2]Cl_2$	200	30	28
$[Hg(L)_2](NO_3)_2$	200	14	12
$[Hg(L)_2]SO_4$	200	10	08
Nystatin	200	26	18

The antimicrobial screening data show that thiosemicarbazide does not exhibit antimicrobial properties. From Tables 3 and 4, it is clear that the Zn(II) and Hg(II) complexes exhibit antibacterial and antifungal activities. The antimicrobial data of the $Hg(L)_2Cl_2$ complexes are very similar to those of standard antibacterial amikacin and antifungal nystatin. The increased activity of the metal chelates can be explained on the basis of the chelation theory [18]. It is known that chelation tends to make the ligand act as more powerful and potent bactericidal agents. It is observed that in a complex the positive charge of metal is partially shared with the donor atoms present in the ligands and there may be π-electron delocalization over the whole chelating. This increases the lipophilic character of the metal chelate and favors its permeation through the lipoid layer of the bacterial membranes. There are other factors which also increase the activity, namely, solubility, conductivity, and bond length between the metal and ligand.

The present study revealed tetrahedral geometry in the Zn(II) and Hg(II) complexes, coordinated to the simple bidentate ligand, thiosemicarbazide, through the terminal hydrazine N atom and the S atom to form five membered chelate rings. Our results are in agreement with the earlier findings that thiosemicarbazide itself does not show biological activity [19]. However, it is important to note that both zinc and mercury metal chelates exhibited potent antibacterial and antifungal activities.

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