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Synthesis, Characterization and Antifungal Studies of Some As(III), Sb(III) and Bi(III) Complexes with *o*-Tolyl Ammonium Dithiocarbamate

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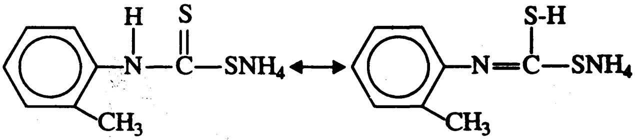
ML_3XY, ML_2XY_2 and $M_2LX_5Y_2$ stoichiometry containing As(III), Sb(III) and Bi(III) complexes with *o*-tolyl ammonium dithiocarbamate has been prepared and characterised using various physico-chemical techniques such as microanalytical, magnetic measurement, conductometric studies, infrared spectroscopy, UV and visible spectral data and ^1H NMR studies. The ligand and its metal complexes are screened for their antifungal activities against two fungi (*A. niger* and *C. albicans*) and some metal complexes exhibited promising results. However, the presence of a chloride atom attached with the metal system is probably responsible for the increasing activity of complexes.

Key Words: Synthesis, Arsenic, Antimony, Bismuth, Complexes, *o*-Tolyl ammonium dithiocarbamate, Antifungal activity.

INTRODUCTION

In recent years, there has been intensive activity involving the synthesis and evaluation of the biological activities of nitrogen and sulphur containing substituted mercapto compounds and their metal complexes[1–3]. Biological, pharmacological and medicinal significance of many coordination complexexs has been studied by several workers[4, 5]. The toxic action of arsenic, antimony and bismuth in living cells is believed to be due to their combination with some sulphydryl compounds present in protoplasm and in all such cases a chelate is formed as some essential enzymes[6]. The present work aims to study the isolation, stereochemical analysis and anti fungal activity of metal complexes of tautomerised *o*-tolyl ammonium dithiocarbamate (Fig. 1) with As(III), Sb(III) and Bi(III) metal ions.



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EXPERIMENTAL

All chemicals used in this work were of AR or CP grade. *o*-Tolyl ammonium dithiocarbamate was prepared in our laboratory by the methods described in the chemical literature[7, 8]. The complexes were prepared in acidic (at pH *ca.* 4 to 6), basic (at pH *ca.* 8 to 9) and neutral media by the general method as given below:

0.01 Mole of metal salts was dissolved in 50 mL of water followed by a few drops of conc. HCl. It was mixed with 50 mL of hot ethanolic solution of 0.03 mole of ligand and it was refluxed in 250 mL quick fit flask at desired pH using dilute ammonium hydroxide and HCl for about 3–4 h. The contents were cooled in ice bath and the solid complex was recrystallized by means of hot ethanol. It was dried at 80°C in an air oven.

The melting points were determined in open capillaries and are uncorrected. The IR, electronic and ^1H NMR spectra of ligand and metal complexes were recorded at CDRI, Lucknow. Microanalysis of the metal complexes was done in the Department of Chemistry, Patna University, Patna by means of multi-channel computerised automatic C, H and N-analyser. Physical properties of complexes are given in Table-1.

TABLE-1
PHYSICAL PROPERTIES OF METAL-COMPLEXES OF DITHIOCARBAMATE

Metal complexes (Colour)	pH	Analysis %, Found (Calcd.)			
		C	H	N	Metal
$[As(C_8H_8NS_2)_3(NH_3)(H_2O)]$ (Ash coloured)	4	44.5 (43.7)	5.1 (4.3)	8.6 (8.3)	10.6 (10.5)
$[As(C_8H_8NS_2)_3(H_2O)_2]$ (Ash coloured)	7	45.4 (43.7)	3.9 (4.2)	5.5 (5.4)	11.0 (11.5)
$[As(C_8H_8NS_2)_3(NH_3)_2]$ (Brown)	9	44.7 (43.8)	5.7 (4.5)	9.5 (9.8)	9.9 (11.5)
$[Sb(C_8H_8NS_2)_2Cl(H_2O)_2]$ (Light red)	6	33.9 (34.4)	3.4 (3.6)	6.3 (6.1)	21.0 (21.7)
$[Sb(C_8H_8NS_2)_2Cl_3]$ (Red)	7	30.7 (30.0)	3.9 (4.0)	9.2 (9.0)	18.7 (19.4)
$[Sb_2(C_8H_8NS_2)Cl_5(H_2O)_2]$ (Red)	8	12.9 (13.5)	2.6 (2.9)	3.0 (2.5)	40.0 (40.4)
$[Bi_2(C_8H_8NS_2)(H_2O)_3Cl_5]$ (Green)	4	9.3 (11.0)	1.0 (1.5)	1.3 (1.8)	49.4 (50.3)
$[Bi(C_8H_8NS_2)_2Cl(H_2O)_2]$ (Greenish black)	7	24.3 (25.0)	2.9 (3.1)	3.4 (3.7)	30.1 (30.9)
$[Bi_2(C_8H_8NS_2)(NH_3)_2(HO)_5(H_2O)]$ (Black)	9	13.3 (13.0)	2.0 (2.8)	6.0 (6.1)	56.0 (56.9)

Ligand and all the nine metal complexes were screened for antifungal activity against two fungi, *viz.*, *Aspergillus niger* and *Candida albicans* using turbidity method[9]. 0.1 mL of the test compound (200 μg in DMF) in 5 mL of sterilised fungi medium was treated with 3–4 drops of 48 h old culture in a sterilised test tube. The tubes are shaken well and incubated for 48 h at 37°C. The extent of inhibition was determined by measuring the decrease in turbidity in terms of percentage of transmission at 660 mm[9]. Salicylic acid (5%) was used as standard and DMF as solvent control. The results are subjectively graded and summarised in Table-2.

RESULTS AND DISCUSSION

The micro analytical data of the metal complexes correspond to ML_3XY, ML_2XY_2 and $M_2LX_5Y_2$ stoichiometry for ($M = As^{3+}$, $X = H_2O/NH_2$ and $Y = NH_2/H_2O$), ($M = Bi^{3+}/Sb^{3+}$, $X = Cl$ and $Y = H_2O/Cl$) and ($M = Bi^{3+}/Sb^{3+}$, $X = Cl$ and $Y = H_2O$ or $M = Bi^{3+}$, $X = H_2O$ and $Y = NH_3$) respectively. Molecular formulae of As(III) complexes were confirmed by their molecular weight determination in acetone by means of cryoscopic method and these were found as monomer. Molecular weight of Sb(III) and Bi(III) complexes could not be measured due to insolubility in common organic solvent at room temperature. However, all the metal complexes were fairly soluble in DMF (in cold) and ethanol (in hot). The conductometric measurement showed non-conducting behaviour having neutral complexes.

The electronic spectrum of ligand contains absorption bands at 200 nm and 250 nm which may be assigned as $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition respectively. These UV spectral bands of ligands were observed on higher region on complexation at 240 and 260 nm respectively, confirming the bonding of ligand to metal ions through sulphur atom[10].

The IR spectra of the ligand and its metal complexes were compared and a conclusion was drawn from the fact that the ν(C═S) and ν(C—S) bands of the ligand observed at 1200 and 530 cm^{-1} are red shifted to 1190 and 500 cm^{-1} respectively on coordination and this is further supported by the presence of new bands corresponding to ν(M—S) in the far infrared region of the spectrum[11] (Table-2).

The IR spectra of ligands contain strong bands at 3310 cm^{-1} which may be assigned to ν(NH). This band was almost identical in all the metal-complexes suggesting the non-involvement of N—H group of ligand in metal complexes. The NH_4^+ ion bands present in the ligand at 3080, 2040 and 1580 cm^{-1} disappear from all the complexes except $[Sb(C_8H_{12}N_2S_2)_2Cl_3]$.

Hence, as usual, triangular bipyramidal structures may be assigned to all the monomeric complexes of As(III), Sb(III) and Bi(III), two triangular bipyramids joined by bidentate bridged structure for dimeric Bi(III) complexes and two triangular pyramids joined by two corners may be suggested as the structures of the dimeric Sb(III) complexes.

^1H NMR spectra of As(III) complexes are recorded in $CDCl_3$ using internal indicator TMS. All the As(III) complexes showed a strong multiplet signal at ($\delta = 7.2$ ppm which has integral height of 110 divisions corresponding to 12 phenyl protons[12–14] of the three coordinated ligand molecules which are in equivalent magnetic environment. There is a sharp signal at $\delta = 2.3$ ppm having an integral height of 80 divisions corresponding to 9 protons of the three methyl

TABLE-2
METAL-LIGAND VIBRATIONAL BANDS (cm^{-1}) AND ANTIFUNGAL ACTIVITY DATA

Complexes	ν(M—S)	ν(M—OH_2)	ν(M—OH)	ν(M—Cl)	ν(M—NH_3)	Antifungal activity % transmission (484) *A. niger*	Antifungal activity % transmission (484) *C. albicans*
Ligand [$C_8H_{11}NS_2$]	–	–	–	–	–	+	+
[$As(C_8H_8NS_2)_3(NH_3)(H_2O)$]	250,200	380	–	–	420	+	+
[$As(C_8H_8NS_2)_3(H_2O)_2$]	215, 210, 200	415	–	–	–	++	+
[$As(C_8H_8NS_2)_3(NH_3)_2$]	250, 200	–	–	–	360, 310	+	+
[$Sb(C_8H_8NS_2)_2Cl(H_2O)_2$]	240, 200	420	–	290, 270, 260	–	++	+
[$Sb(C_8H_8NS_2)_2Cl_3$]	240, 200	–	–	330, 320, 310	–	+++	++
[$Sb_2(C_8H_8NS_2)Cl_5(H_2O)_2$]	240, 210	420, 410	–	320, 310, 250	–	+	+
[$Bi_2(C_8H_8NS_2)(H_2O)_3Cl_5$]	210, 200	415	–	255, 245	–	+	+
[$Bi(C_8H_8NS_2)_2Cl(H_2O)_2$]	225, 220, 205	410	–	270, 240	–	++	++
[$Bi_2(C_8H_8NS_2)(NH_3)_2(HO)_5(H_2O)$]	below 200	420	270	–	360	+	+
Sailicyclic Acid	–	–	–	–	–	++++	++++

% Transmission: (–) = 1–25 no activity, (+) 26–50, (++) 51–75, (+++) 76–100, (++++) 100%. Drug-concentration = 200 μg, Solvent = DMF groups of the three coordinated ligand molecules. This also confirms the three magnetic equivalence of the three coordinate molecules. There is a broad signal at $\delta = 7.85$ ppm corresponding to the three protons of the three imino protons[15, 16] of the three coordinated ligand molecules. This result also confirms that the N—H group remained unchanged in each coordinated ligand molecule. The proton signal of coordinated water is most probably embeded in the signal of phenyl protons at δ 7.2 ppm and that of coordinated ammonia is most probably embedded in the signal for methyl protons at $\delta = 2.3$ ppm. These assignments are in good agreement with the previous work done in this field[17]. Similar ^{1}H NMR spectra are also obtained for Sb(III) and Bi(III) monomeric complexes. Hence, the above triangular bipyramidal structure may be assigned to the complexes.

Antifungal Activity

From the results of antifungal screening (Table-2), it is clear that almost all complexes showed nearly same extent of activity. But they are less active compared to standard salicyclic acid. It is interesting to note that due to the presence of chlorine atoms and comparatively faster diffusion of $[Sb(C_8H_{12}N_2S_2)_2Cl_3]$ showed increased fungal activity. It exhibited better activity against *A. niger* (about 85%) other than against *C. albicans* (about 60%). The complex $[Sb(C_8H_{12}N_2S_2)_2Cl_3]$ was found to be an effective antifungal agent.

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