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Syntheses, Characterization and Biochemical Behaviour of Tungsten Complex

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ABSTRACT: The synthesis of new tungsten(V) dimeric thio complex with disulphido µ-sulphido bridge is reported Moreover, dithiocarbamate ligand is known to form stable Complex with many transition metals. The complex is of interest arises because of its versatile structure and biological activity. The tungsten complex was optimized and a description of the structural parameters is given. Finally the complex was examined as potential antimicrobial agents.

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INTRODUCTION

The field of tungsten complex containing dithiocarbamate ligand is broad and diverse. The preparation and characterization of tungsten complex based on different carriers with appropriate functional groups is one of the promising and interesting research fields in polymer and pharmaceutical chemistry that significantly broadens the prospective practical application of these materials. In the present investigation complexes of tungsten with o-, m-, þ-Ammonium toludinyl dithiocarbamates have been proposed. In this paper, the synthesis, characterization and biological studies of tungsten (V) complex with containing dithiocarbamate group have been discussed.

MATERIALS AND METHODS

Most of the chemicals used were of AR grade. Laboratory grade chemicals, whenever used were purified by standard methods, while the solvents were purified and double distilled before use C,H,N and S contents were determined by Perkin Elmer 2400 elemental analyser, IR spectra were recorded in the range 4000 cm^{-1} – 100 cm^{-1} with a Bruker IFS 66V in KBr and polyethylene medium for compound. The molar conductance of the complex in DMF ($l0^{-3}$M) solution was measured at 27 ±3°C with an Elico Model Conductivity meter. UV-visible spectra were recorded in DMF with Perkin - Elmer Lambda 35 spectrophotometer NMR spectra on Bruker Advance lll 400 MHz spectrometer. Ligand and metal complex were investigated for antibacterial and antifungal against Staphylococcus aureus and Bacillus species as gram positive bacteria and Escherichia Coli and Proteus species as Gram negative and the fungi Candida albicans and Aspergillus fumigatus by using disc - agar diffusion method was followed to determine the activity of the synthesized compounds against the bacterial and fungal species. The antibiotic chloramphenicol, tetracycline and clotrimazole were used as standard reference for in the case of Gram negative, Gram positive and antifungal species. The tested compounds were dissolved in DMF(which have no inhibition activity) to get a concentration of 100µg/mL incubation period for bacterial species 36h at 27°c and for Fungal species 48h at 24°c inhibition of the organism which evidenced by clear zone surround each disk was measured and used to calculate mean of inhibition zone. The anticancer activities of the ligand and its metal complex against the Breast cancer cell line (BT474) and Lung cancer cell line (HOP62) were screened using MTT assay. The results were analyzed by cell viability curves and expressed as IC_{50} values.

Ligand Ammonium, - Toluidinyl dithiocarbamate and metal salts of Ammonium tetrathiotungstate were prepared by standard reported procedure. Synthesis of metal complex : 6.51 g (10.00 mmol) of o-, m-, p- toludinyl dithiocarbamate and 3.47g (10.00 mmol) of Ammonium tetrathiotungstate

were dissolved separately in minimum quantity of double distilled water. Next, both the solutions were mixed together and the mixture was kept for 60-70 minutes on water bath at 80-90 ºC. The precipitate was filtered off wasted with 1:1ethanol:water mixture followed by ether and desiccated under vacuum. A yellow colored complex was obtained with 68.5% yield. The resulting metal Complex was insoluble in common solvents such as water, benzene, chloroform, dichloromethane etc. but it was soluble in DMF and DMSO.

$$CH_3C_6H_4NH_2 + CS_2 + NH_3 \rightarrow CH_3C_6H_4NHCSSNH_4$$

$$Na_2WO_4 + 2NH_3 + 2H_2O + 4H_2S \rightarrow (NH_4)_2WS_4 + 2NaOH + 4H_2O$$

RESULTS AND DISCUSSION

The result of elemental analysis are in good agreement with the calculated values. The metal contents of the complexes were determined according to literature methods.

Elemental analysis: Calc W= 42.76, C = 22.33, H = 1.86 N=3.25, S = 29.77 Found Mo, 42.80, C 22.00, H= 1.80, N=3.18, S= 29.40. The electrolytic nature of the complex is measured in DMF, at to 10^{-3}M The conductivity value was found to be 15.6 Ω^{-1} cm^{-1} mol^{-1}. Thus, the prepared complex is non electrolytic in nature and there is no ion present in the out of the coordination sphere spectral studies: There is no coordination through nitrogen atom because there is almost no shifting of the band position of nitrogen centres in the IR spectra of metal complex as shown in **Figure 1**. The complex shows additional band in the region of 498 cm^{-1} indicating the presence W-S terminal bond. Due to the reaction of tungstate with the dtc ligand there arises W-S bridging bond which is present of at 445 cm^{-1}. The additional important band is also present at 380 cm^{-1} suggesting the presence of W-S-W bond. The electronic absorption spectra of metal complex as shown in **Figure 2** in the visible region shows two transition bands in the region around 23000 and 25000 cm^{-1} respectively. The diffuse reflectance spectrum of the tungsten complex shows the d-d transition bands around 14700 and 12500 cm^{-1} which are assigned to transitions

$^3E \longrightarrow {}^1A_1$ and $^1E \longrightarrow {}^1A_1$ respectively .The above mentioned bands are probably a combination of the sulfur to metal transition S⟶W charge Transfer band. The NMR spectra of the complex was recorded in DMSO-d_6 as shown in **Figure 3**. The absence of S-H protons and a slight downfield Shift of the Protons in The NMR spectra of complex, with respect to corresponding ligand was observed. This indicates that the ligand is coordinated to tungsten through sulfur atom in the metal complex. In the ^{13}C NMR spectrum for complex the signal of NCS_2 carbon atom moiety at the regions 53.50,21.12,27.90 and 23.70 ppm were observed which belong to the dithiocarbamate ligand. The signals of carbon due to aryl group were observed at the regions 30.10 to 37.00 ppm in the spectrum of tungsten complex indicating that the chemical environments of the CS_2 moieties of the two dithiocarbamate ligands bound to the W_2 centre. Further a singlet observed in the parent dithiocarbonic acid and assigned for SH Proton is found to be absent in the spectra of corresponding complex indicating the deprotonation of SH group and the formation of W-S bond (**Figure 4**) [13-16].

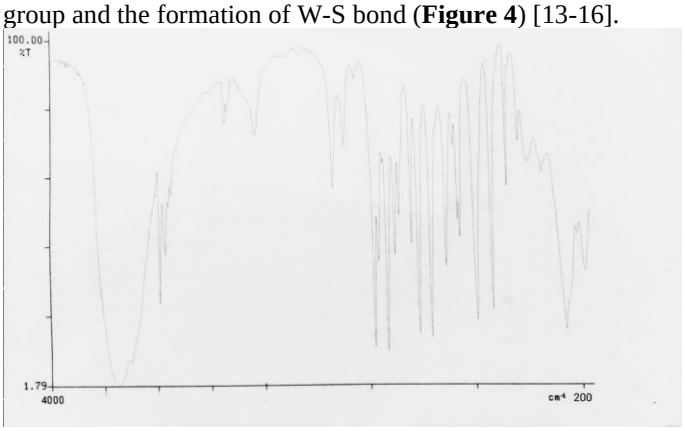

Figure 1 IR spectra of metal complex

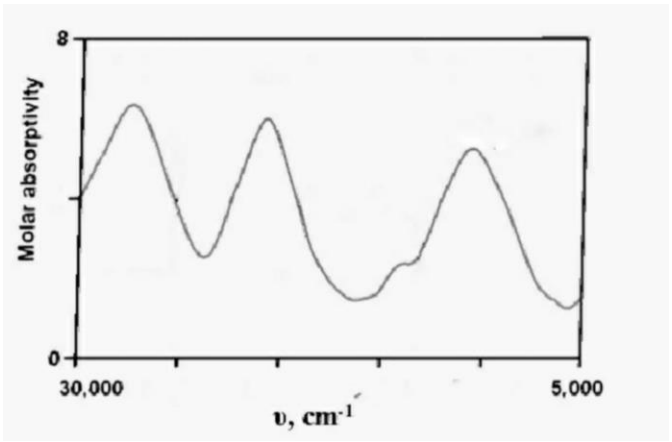

Figure 2 Electronic absorption spectra of metal complex

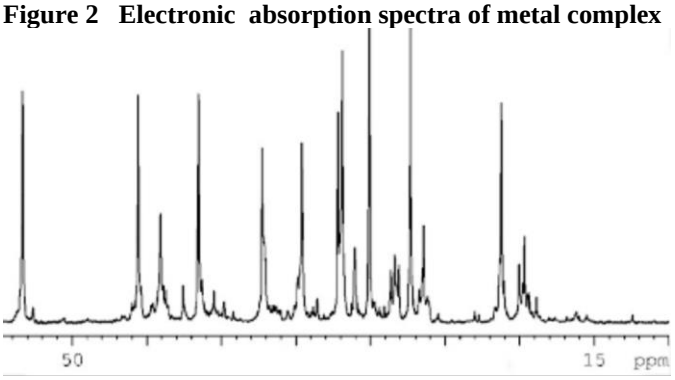

Figure 3 ^{13}C NMR spectra of metal complex

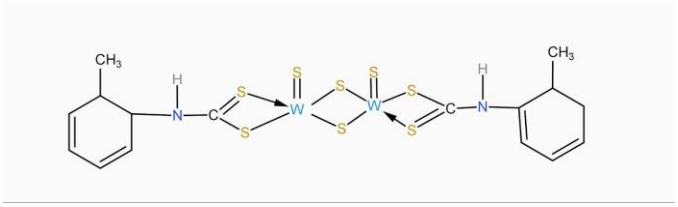

Figure 4 The proposed coordination mode of the metal complex

Antimicrobial Studies: The results show that the metal complex is more active than the parent ligand dithiocabamate. The enhanced activity of the metal complex compared to free ligand can be ascribed to increased lipophilic nature of the tungsten complex arising due to chelation. The solubility of the compound also plays an important role in ascertaining the degree of inhibition. metal complex of the ligand having sulfur as a donor atom was found to be more potent than those without sulphur. It has been proposed that the ultimate action of structurally non-specific toxicants is the denaturation of one or more proteins of the cell. Chelating agents are often powerful inhibitors of metalloenzymes, so it is evident from data **Table I** that activity significantly increases on coordination [21-26].

Table 1: Antibacterial activity of ligand and metal complex

	Sample	Bacteria				Fungi	
		Gram +ve		*Gram -ve*			
		S.aureus	*Bacillus Sp.*	*E.coli*	*Proteus Sp.*	*C.albicans*	*A. fumigatus*
1.	Tetracycline	25	27	-	-	-	-
2.	Chloramphenicol	-	-	28	29	-	-
3.	Clotrimazole	-	-	-	-	23	21
4.	$C_8H_{12}N_2S_2$	14	12	16	17	15	16
5.	$W_2C_{16}H_{16}N_2S_8$	18	19	20	19	18	18

Inhibition Zone in mm Concentration 100 µg/mL

The anticancer activities of the ligand and its metal complex against the Breast cancer (BT474) and Lung cancer (HOP62) cell lines were screened using MTT assay. The results were analyzed by cell viability curves and expressed as IC_{50} values. The maximal inhibition concentration given in **table 2** showed that the cytotoxicity efficiencies of the compounds under the investigation follow the order tungsten (V) complex > dithiocarbamate ligand from the result it is evident that the tungsten complex exhibited higher in vitro cytotoxicity against both the selected cell lines when compared to the ligand compared with that of the standard drug cisplatin. The cytotoxicity of tungsten complex is depending on their ability to bind DNA and damage its structure resulting in the impairment of its function which is followed by the replication and transcription processes inhibition and eventually cell death. Thus the relatively higher toxicity exhibited by the tungsten(V) complex as compared to the ligand may be due to the stronger binding ability of the complex with DNA.

Table 2: Anticancer Studies of the dithiocarbamate ligand and its tungsten Complex[a]

S.No.	Compound	Cell Lines	
		BT474	**HOP62**
1.	$C_8H_{12}N_2S_2$	25 ± 1.2	28 ± 1.4
2.	$W_2C_{16}H_{16}N_2S_8$	18 ± 1.5	21 ± 1.7
3.	Cisplatin	13 ± 0.5	12 ± 0.9

[a]IC_{50} Concentration of the drug required to inhibit growth of 50% of the cancer cells (µM) the data are mean ± SD of three replicants each.

CONCLUSION

In the present study the bridging complex of tungsten with Ammonium dithiocarbamate was prepared and characterized by physico-chemical methods. The antibacterial and anticancer activity data given for the compounds presented in this paper allowed to state that metal complex showed enhanced activity as compared to ligand fragment.

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CONFLICT OF INTEREST

Author declares that there is no conflict of interest regarding the publication of this paper.

DATA AVAILABILITY

Available on request

FUNDING SOURCE

Not applicable

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