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Synthesis, characterization and biological evaluation of novel dithiocarbamate metal complexes

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ABSTRACT

A series of novel bidentate dithiocarbamate ligand of 2-Amino-2-methyl 1-propanol (AMPDTC) was prepared by new synthetic method. The synthetic sodium salt of 2-Amino-2-methyl 1-propanol dithiocarbamate ligand is followed by the reaction of Copper and Manganese Chlorides to get corresponding complexes. These forming complexes were characterized by Elemental Analysis, IR, ^1H NMR, ESR TGA-DTA and anti microbial analysis.

Keywords: 2-Amino 2-methyl 1-propanol, dithiocarbamate ligand, Elemental Analysis, Copper and Manganese Chlorides.

INTRODUCTION

There is currently a growing interest dithiocarbamate complexes of dithiolates [1–4]. Dithio carbamates, in particular, are versatile chelating agents with diverse applications in industry, agriculture and medicine [5, 6]. Although complexes of dithiocarbamates with monodentate and polydentate ligands have been prepared and characterized [7–14] The dithiocarbamate ligands reported in only the dithiocarboxy group as the ligand group, so they behave like bidentate ligands in complexes. Dithiocarbamates have been found to act almost as uninegative bidentate ligands, coordinating through both Sulphur atoms, and both tetra and hexa-coordinated complexes of many transition metal ions have been isolated. [15-16] In this article we report the synthesis, characterization and antimicrobial activity of Copper(II) and Mn(II) Complexes of dithiocarbamates.

MATERIALS AND METHODS

Copper chloride anhydrous was obtained from Fluka, 2-Amino, 2-methyl 1-propanol and carbon disulfide were purchased from Aldrich. Other chemicals used were of analytical reagent or higher purity grade. Solvents used were of reagent grade and purified before use by the standard methods. Conductivity measurement was carried out by a Systronics conductivity bridge 305, using a conductivity cell of cell constant 1.0 doubly distilled water was used as solvent. Electronic absorption spectra on JAS.CO UV/VIS-7850 recording spectrophotometer. Infrared spectra was recorded on a JAS.Co-460 plus FT-IR spectrophotometer in the range of $4000\text{--}400\text{ cm}^{-1}$ in KBr pellets. Micro chemical analysis of carbon, hydrogen and nitrogen for the complexes were carried out on a Herause CHNO-Rapid elemental analyzer. ^1H NMR spectra were recorded on a Bruker DRX-500 Advance spectrometer at 500MHz in DMSO-d₆ using tetramethylsilane as internal reference standard. Melting points were measured on a unimelt capillary melting Point apparatus and reported uncorrected.

Preparation of Sodium salt of dithiocarbamate ligands.

0.05 mol of amine was dissolved in 30 ml of absolute alcohol in a clean beaker which was placed in ice bath. To this cold solution add 5 ml of Sodium hydroxide (10N) solution, and then add Pure carbon disulphide (0.05ml) in drop wise with constant stirring. The contents were stirred mechanically for about 30 min, sodium salt of dithiocarbamate precipitated out. It was dried over and recrystallized from ethanol.

Preparation of Cu (II) and Mn (II) Complexes,**Synthesis of [Cu (AMPDTC)₂]Cl₂**

The aqueous solution of 0.05 mol of Copper Chloride was added with constant stirring to an aqueous solution of 0.01 mol of Sodium salt of 2-Amino 2-Methyl 1-Propanol dithiocarbamate ligand. The reaction mixture was stirred at room temperature for 2 hours. The colored (yellow) precipitates were obtained. The precipitates were filtered and washed with water and then with methanol and dried over calcium chloride in desiccator's Yield:78% and decomposes at 110 C.

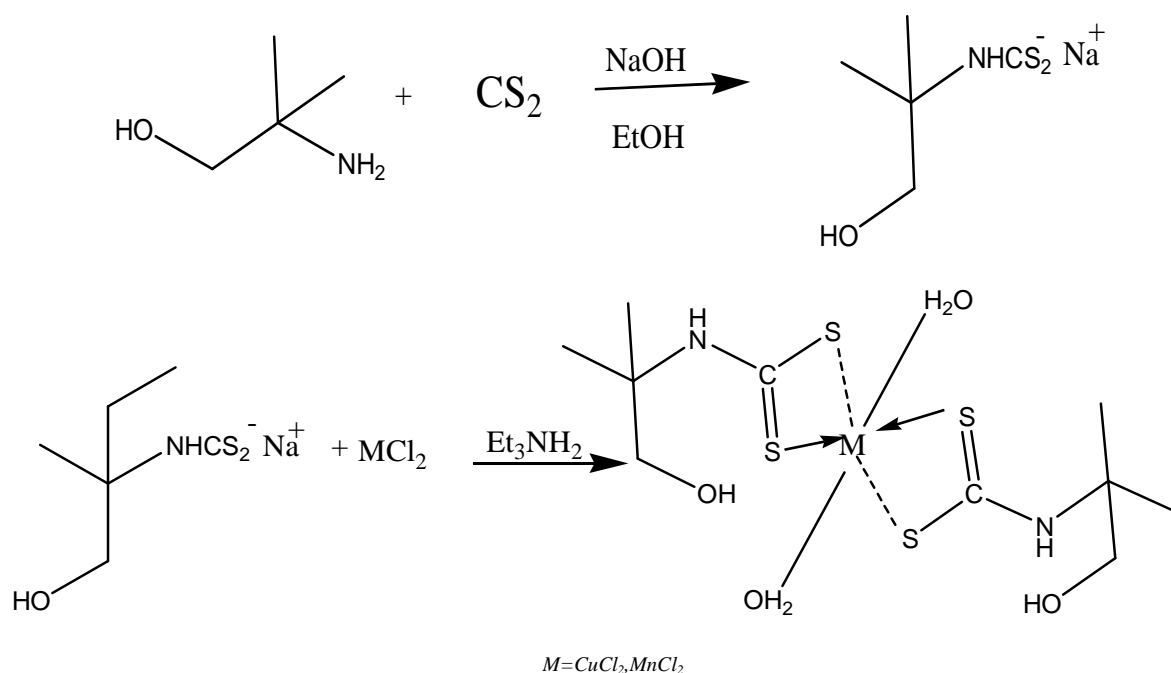
Anal. Calcd. For C, 25.94; H, 4.35; N, 6.05; Cl, 15.35; Cu, 13.73; Found: C, 24.92; H, 3.96; N, 5.9; Cl, 14.35; Cu, 12.98;

Synthesis of [Mn (AMPDTC)Cl₂]

The aqueous solution of 0.05 mol of Manganese Chloride was added with constant stirring to an aqueous solution of 0.01 mol of Sodium salt of 2-Amino 2-Methyl 1-Propanol dithiocarbamate ligand in the presence of small quantity of triethylamine. The reaction mixture was stirred at room temperature for 2 hours. The colored (gray) precipitates were obtained. The precipitates were filtered and washed with water and then with methanol and dried over calcium chloride in desiccator's Yield:80% and decomposes at 110 C. Anal. Calcd. For C, 26.43; H, 4.44; N, 6.17; Cl, 15.60; Mn, 12.09 Found: C, 25.53; H, 4.4; Cl, 15.2; Mn, 11.99; N, 5.99.

RESULTS AND DISCUSSION

The solid reflectance spectra data for the Cu and Mn of 2- amino 2- methyl 1-propanol metal complexes. The complexes [Cu(AMPDTC)₂]Cl₂ and [Mn(AMPDTC)₂]Cl₂ complexes exhibits magnetic property and has an electronic spectrum which can be assigned to low spin Cu (II) and Mn(II) in an Octahedral Environment. Intra ligand electronic transition in then...C...S...S and S...C...S chromophores of the dithiocarbamate moiety. Thus the peak at 646 nm and the shoulder at 499 nm arise from 1A_{1g}-1T_{1g} and 1A_{1g}-1T_{2g} transitions, respectively. The other lower peaks are probably charge-transfer in origin.



Infrared Spectrum

Two regions in the IR spectrum of the [Cu (AMPDTC)₂Cl₂] and [Mn(AMPDTC)₂Cl₂] complex have proven valuable in arguments concerning the electronic and structural characteristics of this compound. The presence of the thiouride band between 1545-1430 cm⁻¹ suggest a considerable double bond character in the C...N bond vibration of the S₂C-NR₂ group. The band present in the 967 cm⁻¹ range is attributed to the prevailing contribution of (C...S) Vibrations in these ranges have been used defectively in differentiating between monodentate, bidentate dithiocarbamate ligands. The presence of only one strong band supports bidentate coordination of the dithioligands, where as a doublet is expected in the case of monodentate coordination. The (C...S) and (C..N) Stretching frequencies fall in the 1035 cm⁻¹ (1001 cm⁻¹ for the free ligand) and 1478 cm⁻¹ respectively. The methyl group in the complex, as medium strong bands in the 2960 cm⁻¹ range can be related to the asymmetric CH₃ stretching vibration.

¹H-NMR Spectra

The NMR spectrum of the [Cu(AMPDTC)₂Cl₂] and [Mn(AMPDTC)₂Cl₂] complexes showed at 2.3-2.4 ppm, which may be assigned to the hydroxyl protons. The peak at 7.9-7.98 attributed to NH protons of thiourid nitrogens in both complexes. In other signals is also appeared in the region 0.98, 1.5, 3.8 ppm.

Antimicrobial Activity

Antimicrobial test was performed on four bacteria (Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa,) and two fungus (Candida albicans and Candida tropicalis). The media used were prepared by dissolving separately 2 g of the nutrient broth powder and 38 g of the Mueller Hinton agar powder in 250 ml and 1 L of deionized water, respectively. The two media were sterilized in an autoclave at 121°C for 15 minutes and then stored overnight in a refrigerator after cooling. Cultures of the microorganisms were prepared in sterile nutrient broth and incubated for 24 hours at 37°C for the bacteria and 27°C for the fungi. 0.1 ml of each of the overnight cultures in sterile test tubes with caps were made up to 10 ml with 9.9 ml of sterile deionized water.

To give 1:100 or 10⁻² dilution of the microorganisms. The technique used for the study was agar-well diffusion. Solutions of concentration 10 mg/ml of the compounds

Growth inhibition zone in millimeters (mm)						
	BACTERIA				FUNGUS	
	Gram +Ve		Gram -Ve		<i>C.alb</i>	<i>C.trop</i>
	<i>S.aur</i>	<i>B.subt</i>	<i>E.coli</i>	<i>P.aerug</i>		
Cu(AMPDTC) ₂	14	14	15	14	14	15
Mn(AMPDTC) ₂	13	15	14	114.5	16	14
FLU			----	----	15	15
DMSO	12	14	15	16	----	---

were made in dimethylsulphoxide (DMSO). DMSO was also used as the negative control. The positive controls for bacteria and fungi were discs of commercial antibiotics manufactured by Abtek Biological Limited and Fluconazole dissolved in DMSO. The discs were carefully placed on the inoculated media with the aid of sterile forceps. The plates inoculated with bacteria were incubated at 37°C for 24 hours, and those inoculated with fungi were incubated at 27°C for 72 hours. After wards, the zones of inhibition of microbial growth that appeared around the wells of the compounds were examined and the diameters measured and recorded in millimeters (mm). Antimicrobial activity of the Cu(II) and Mn(II) complexes was evaluated *in vitro* against Gram positive bacteria- Staphylococcus aureus and Bacillus subtilis, Gram negative bacteria- Escherichia coli, Pseudomonas aeruginosa, and fungi, Candida albicans, Candida tropicalis. The results for the complexes and commercial antibiotics used as positive controls are listed in (Table 1.)

CONCLUSION

Cu (II) and Mn (II) complexes of 2-Amino 2-Methyl 1-propanoldithiocarbamate with have been synthesized and characterized. The ligand moiety exhibit a bidentate coordination mode in the Cu (II) and Mn (II) complexes. Solid reflectance spectra and magnetic data indicate that the complexes are Paramagnetic and Octahedral. The complexes show selective activity towards some of the test microorganisms.

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