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Research Article

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Synthesis, characterization and biological evaluation of novel dithiocarbamate metal complexes

M. Musthak Ahamad, R. Mallikarjuna Rao, E. V. Suresh Kumar, A. Jayaraju, T. Noorjahan Begum and J. Sreeramulu*

Department of Chemistry, Srikrishnadevaraya University, Anantapur, India

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ABSTRACT

A series of new bidentate ligands are dithiocarbamates of 4-Amino anti-pyrene and 2-aminothiozole (AADTC, ATDTC) were prepared by new synthetic methods, as the sodium salt. In the reaction of Chloroauric acid and Ruthenium Chloride with aadtc and atdtc the corresponding complexes were prepared. The complexes was characterized by Elemental Analysis, IR, ESR, H ^{1}NMR and TGA-DTA.

Keywords: 4-Amino antipyrine, 2-Amino thiazole Chloroauric acid , Ruthenium chloride, dithiocarbamates.

INTRODUCTION

Dithiocarbamates are organosulphur compounds. Dithiocarbamates and their metal complexes have invited much research attention due to their diverse applications and interesting biological, structural, magnetic, electrochemical and thermal properties[1-7] They are used as accelerators in vulcanization, as high-pressure lubricants and as fungicides and pesticides. Also, dithiocarbamates are often used for the synthesis of transition metal complexes.[8-13] As the dithiocarbamates themselves, dithiocarbamate-metal complexes have been used in agriculture for controlling insects and fungi[14], in the treatment of alcoholism, *etc*. The dithiocarbamate ligands reported in only the dithiocarboxy group as the ligator 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]We report in this article a new bidentate ligand dithiocarbamates of 4-Amino anti-pyrene and 2-aminothiozole (AADTC, ATDTC) were prepared, as the sodium salt. In the reaction of Chloroauric acid and Ruthenium Chloride with AADTC and ATDTC the to form corresponding complexes.

EXPERIMENTAL SECTION

Auricchloride anhydrous was obtained from Fluka. 4-Antipyrine , 2-aminothazole 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. [Au(AADTC)2Cl$_2$] and [Ru(ATDTC)$_2$Cl$_2$] were prepared by the procedures described in the literature [23]. Conductivity measurements of the above Au and Ru complexes were carried out on a Systronics conductivity bridge 305, using a conductivity cell of cell constant 1.0. Doubly distilled water was used as solvent. Electronic absorption spectra of this metal complexes were measured on a JAS.CO UV/VIS-7850 recording spectrophotometer. Infrared spectra of the metal complexes were recorded on a

JAS.CO-460 Plus FT-IR spectrophotometer in the range of 4000-400 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. ^{1}H NMR spectra were recorded on a Brucker DRX- 500 Advance spectrometer at 500 MHz in DMSO-d6 using tetramethylsilane as internal reference. Melting points were measured on a Unimelt capillary melting point apparatus and reported uncorrected

Preparation of sodium salt of dithiocorbamate ligands.

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

Preparation of Au(II) and Ru (III)complexes,

Synthesis of [Au (AADTC)$_2$)Cl$_2$]

The aqueous solution of 0.05 mol of Auric Chloride was added with constant stirring to an aqueous solution of 0.1mol of Sodium salt of 4-Amino antipyrine dithiocarbamate ligand. The reaction mixture was stirred at room temperature for 2 hours. The colored precipitates were obtained. The precipitates were filtered and washed with water and then with Methanol and dried over calcium chloride in a desiccator's. Yield:(68%) and decomposes at 110 °C. Anal. Calcd. For C, 33.59; H,2.58; N,9.79, Au.22.95%. Found: C, 32.55. H, 2.52; N,9.50.

Synthesis of [Ru(ATDTC)$_2$)Cl$_2$]

The aqueous solution of 0.1 mol of Ruthenium chloride was added with constant stirring to an aqueous solution of 0.2mol of Sodium salt of 4-Amino antipyrine dithiocarbamate ligand. The reaction mixture was stirred at room temperature for 10 hours. The black precipitates were obtained. The precipitates were filtered and washed with water and then with Methanol and dried over calcium chloride in a desiccators. Yield :(78%) and decomposes at 110 °C. Anal. Calcd. for: C, 17.22; H, 1.08; N,10.04%. Found: C, 17.21; H, 1.10; N,10.0

RESULTS AND DISCUSSION

Electronic absorption spectrum

The solid reflectance spectral data for the Au and Ru of amino thiazole and antipyrine metal complexes. The complexes Au(AADTC)$_2$ and Ru(ATDTC)$_2$ complexes exhibits magnetic property and has an electronic spectrum which can be assigned to low-spin Au(III) and Ru (III) in an octahedral environment. Intraligand $\pi \rightarrow \pi^*$ electronic transition in the N…C…S and S…C…S chromophores of the dithiocarbamate moiety Thus the peak at 646.7 nm and the shoulder at 499 nm arise from 1A1g_1T1g and 1A1g_1T2g transitions, respectively. The other lower peaks are probably charge-transfer in origin. transition in the ethyl salicylaldiminate moiety. Charge transfer bands.

Infrared spectrum

Two regions in the IR spectrum of the Au(AADTC)$_2$ and Ru(ATDTC)$_2$ complex shave proven valuable in arguments concerning the electronic and structural characteristics of this compound. The presence of the thioureido band between 1530–1430cm–1 suggest a considerable double bond character in the C...N bond vibration of the S2C–NR2 group. The band present in the 940cm–1 range is attributed to the prevailing contribution of (C...S) Vibrations in these ranges have been used effectively indifferentiating between monodentate and bidentate dithiocarbamate ligands. The presence of only one strong band supports bidentate coordination of the dithio ligand, whereas a doublet is expected in the case of monodentate coordination. The-(C...S) and (C...N) stretching frequencies fall in the 1032 cm–1 (1001 cm–1 for the free ligand) and 1473 cm–1, respectively. The methyl group in the complex, as a medium strong bands in the 2960 cm–1 range, can be related to the asymmetric CH3 stretching vibration, while bands at 1725cm–1 are due to the vibrations of the carbonyl group of antipyrine.

$$AuCl_3+R_2NH_2+CS_2 \ +NaoH \xrightarrow{C2H5OH} [Au(Rdtc)_2Cl_2] +H_2O$$

$$RuCl_3+R_2NH_2+CS_2 \ +NaoH \xrightarrow{C2H5OH} [Ru(Rdtc)_2Cl_2] +H_2O$$

R=ANTIPYRENE AND THIAZOLE RINGS

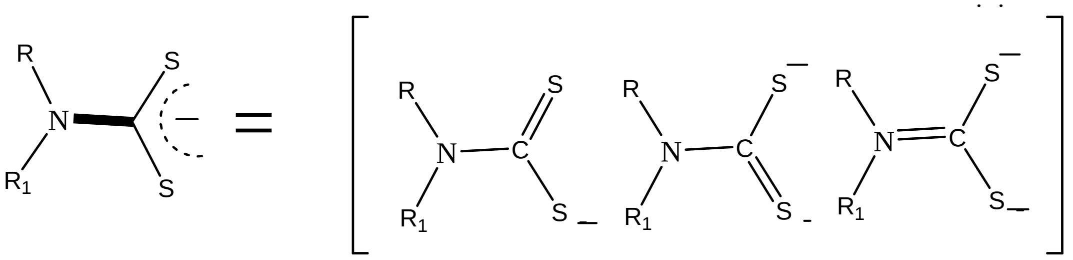
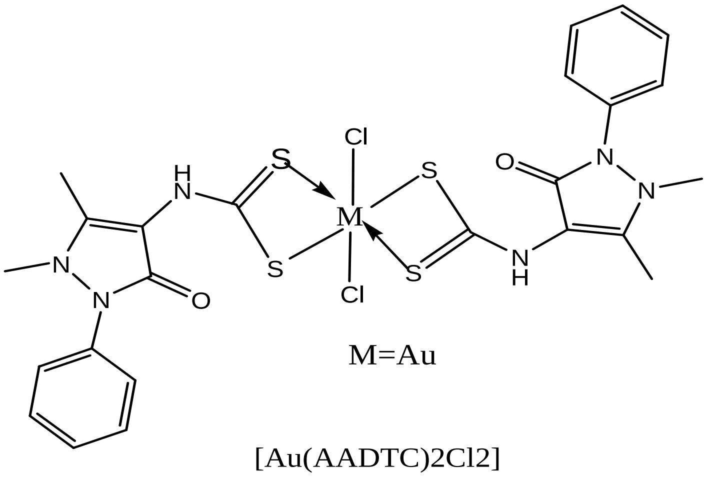


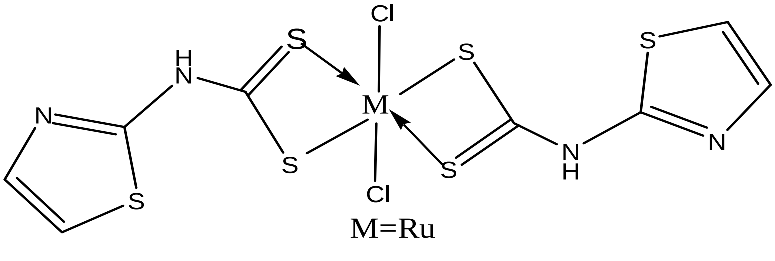
Fig-Resonence form of dithiocorbamate metal complexes

1H -NMR spectra

The 1H-NMR spectrum of Au(AADTC)$_2$ and Ru(ATDTC)$_2$ complexes showed a pattern at 6.9-7.5 ppm, which may be assigned to the aromatic protons. The peak at 7.8-7.95 attributed to NH protons of thiouroid nitrogens in both complexes in other signals is also appeared in the region of 1.2, 2.3, 2.6 and 4.6ppm.



[Au(AADTC)2Cl2]



[Ru(ATDTC)2Cl2]

Antimicrobial Activity

Antimicrobial test was performed on four bacterias (*Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa,*) and two fungis (*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 oC 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 oC for the bacteria and 27 oC 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 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 innoculated media with the aid of sterile forceps. The plates innoculated with bacteria were incubated at 37 oC for 24 hours, and those inoculated with fungi were incubated at 27 oC 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 Au(III) and Ru(III) 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.)

Table-1

Growth inhibition zone in millimeters (mm)						
BACTERIA					FUNGUI	
	Gram +Ve		Gram -Ve			
	S. aur	*B. subt*	*E. coli*	*P. aerug*	*C. alb*	*C. trop*
Au(AADTC)$_2$	12	14	13	15	13	15
Ru(ATDTC)$_2$	10	15	---	15	16	14
FLU					15	15
DMSO	12	14	_	_	---	---

CONCLUSION

Au(III) and Ru (III) complexes of various dithiocarbamates with have been synthesized and characterized. The two ligand moieties exhibit a bidentate coordination mode in the Au(III) and Ru (III) 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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