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RESEARCH ARTICLE

SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL STUDIES OF HETEROBINUCLEAR IRON (III) – TUNGSTEN (V) COMPLEXES OF DITHIOCARBAMATES

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ABSTRACT

The heterobinuclear complexes [FeWO₂(L)₄(H₂O)] (L=dithiocarbamates) were prepared by the interaction of Iron tungstate with the respective ligands in aqueous DMF. The magnetic moment (6.71 and 6.66 BM) and EPR studies suggested the presence of tungsten in the pentavalent state. The FT-IR spectral bands suggested the presence of $\nu(\text{W}=\text{O})$ (900cm⁻¹) and $\nu(\text{Fe}-\text{O}-\text{W})$ (790cm⁻¹) and bidentate dithiocarbamate ligands (1500 and 960 cm⁻¹) in the molecule. The FT-IR and thermal decomposition studies confirmed the presence of a coordinated water molecule. The ¹H NMR chemical shifts indicated non-identical environment of protons coming closer due to rigidity in rotation around C–N bond of dithiocarbamate ligand and coordination to the heterometal atoms. The proposed structure consists of a tetrahedral Iron (III) and octahedral tungsten (V) bridged by an oxo group. The antimicrobial activities of the complexes were determined by disc diffusion and well diffusion method.

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INTRODUCTION

Dori *et al.* (1981) studied the complexes of tungsten(V) are monomeric [W₂O₄(EDTA)]²⁻, WCl₃(OR)₂] (R = Me, Et), M[WCl₄(OR)₂] and M[WCl₅(OR)] (M = tetra alkyl ammonium; R = Me, Et). Yamamoto *et al.* (1983) studied the purification of first naturally occurring tungstoenzymes, from one of the acetogens. Sung *et al.* (2000) studied the tungstoenzymes belong to *aldehyde oxidoreductases* (AOR), *formate dehydrogenases* (FDH) and *N-formylmethanofuran dehydrogenases* (FMDH). The crystal structures of two enzymes isolated from *pyrococcus furiosus*, *aldehyde oxidoreductase* and *formaldehyde oxidoreductase*, have been determined by Rees *et al.* (Rees1997). The possibility emerges that active FMDH enzymes resemble rhodobacter sphaeroides DMSO reductase (DMSOR) by having two pterin dithiolenes and one endogenous protein ligand in the W(IV) oxidation state. Johnson *et al.* (1996). studied that Tungsten plays a key role in the biological activity of enzymes like *pyrococcus furiosus*, *Thermococcus litoralis*, *clostridium thermoautotrophicum* and *pelobacter acetylenicus*, Chirila *et al.* (2000).

Studied several Fe-W-S and Cu-W-S heterobimetallic complexes and the binuclear oxo bridges in iron-tungsten and manganese-tungsten complexes. Morrow *et al.*⁷ studied some mixed olefin-alkyne complexes of molybdenum and tungsten dithiocarbamate. We hereby present the preparation, characterization and antibacterial studies of Iron-tungsten complexes of dithiocarbamates, which may be used as bench models in the bioinorganic chemistry of tungsten. Sodium tungstate, Iron(III) sulphate, sodium diethyldithiocarbamate, solvents and chemicals used are of pure G.R. grade. The ligands of 4-morpholinyldithiocarbamate and 1-piperidinyldithiocarbamate were prepared by the solution route procedures. FeWO₄ was prepared by mixing Iron sulphate (1.9g) in water (20cm³) with sodium tungstate (1.65g) in water (20cm³). Iron tungstate was filtered and dried. FeWO₄.H₂O (0.5g) was dissolved in DMF (20cm³) and conc. HCl (2.0cm³) digested over a water bath for 0.5h. The solution was filtered and an aqueous solution of sodium diethyldithiocarbamate (1.6g) in water (80cm³) was added with constant stirring under ice-cold conditions. The brown colored complex was filtered, washed with water and MeOH and dried. The CHN analyses were carried out on a Heraeus CHN-O-Rapid analyzer. Iron and tungsten were determined by wet chemical analyses. TG-DTA measurements were carried out on Seiko SII thermal

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analyzer. The samples were heated in air at a rate of $6^{\circ}\text{C min}^{-1}$ in Pt crucibles. The TLC measurements were carried out on a silica gel plate using a mixture of CH_2Cl_2 and CH_3OH (2:1) as eluants, which were developed in an iodine chamber. The conductivity measurements of the complexes in DMF were carried out on a METZER 440 digital conductivity bridge.

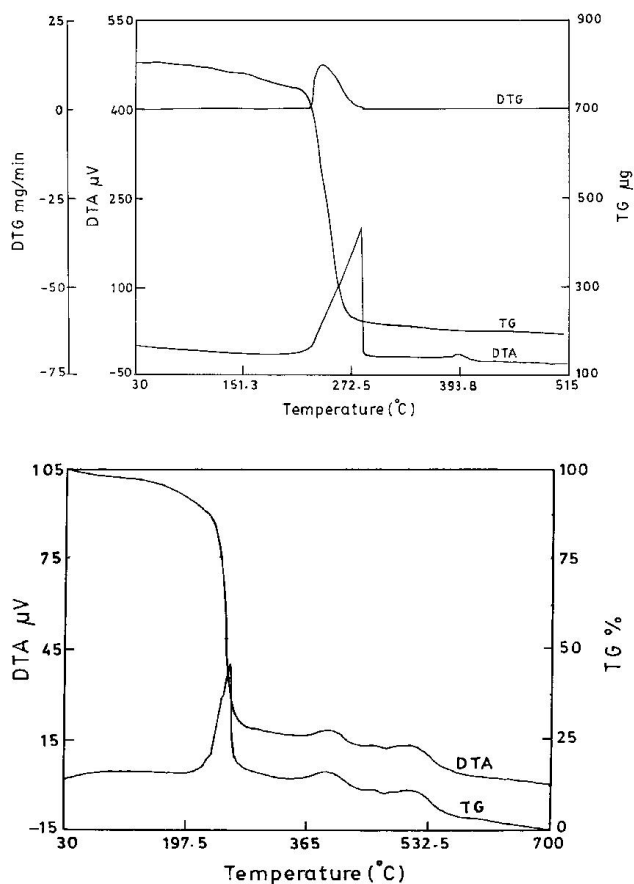


Fig. 1. TG curves of $[\text{FeWO}_2(\text{L})_4(\text{H}_2\text{O})]$ dithiocarbamate complexes

The redox titrimetric procedure was adopted to assign the oxidation state of tungsten. The magnetic susceptibility measurements of the powder complexes were determined at room temperature using VSM technique. The EPR spectra of the complexes were recorded in powder form at room temperature on a Varian E-4 X-band EPR spectrometer in quartz tubes. The g values are calculated using DPPH as the standard ($g = 2.0036$). The FT-IR spectra for the complexes were recorded as KBr matrix on BRUKER IFS 66V FT-IR spectrometer. The ^1H NMR of complex 1 was studied using a Hitachi R-600 high resolution NMR spectra-photometer. Antibacterial activity was assayed using the agar well diffusion test and disc diffusion method. Antibacterial activity was assayed using the agar well diffusion test technique. Muller Hinton Agar Medium (MHA) was prepared, and then sterilized by autoclaving at 121°C and 15 lbs pressure for 15 minutes. 20 ml of the sterilized media was poured into sterilized Petri dish and allowed to solidify at room temperature. A sterile cotton swab was used for spreading the test microorganism from the 24 hours inoculated broth evenly on the MHA plates. Similarly swabbing was done separately for each test microorganism on the MHA plates and left for few minutes to allow complete absorption of the inoculum. In

each of these plates 7mm diameter wells were made using an appropriate size sterilized cork borer. Each complex extract was added to the respective wells on the MHA plates. The extract loaded plates were kept for incubation at 37°C for 24 hours. After incubation, a clear zone was observed around the well which was evidence of the presence of antibacterial active compounds in the complexes. Diameters of the zone of inhibition were measured in millimeters (including the diameter of the well).

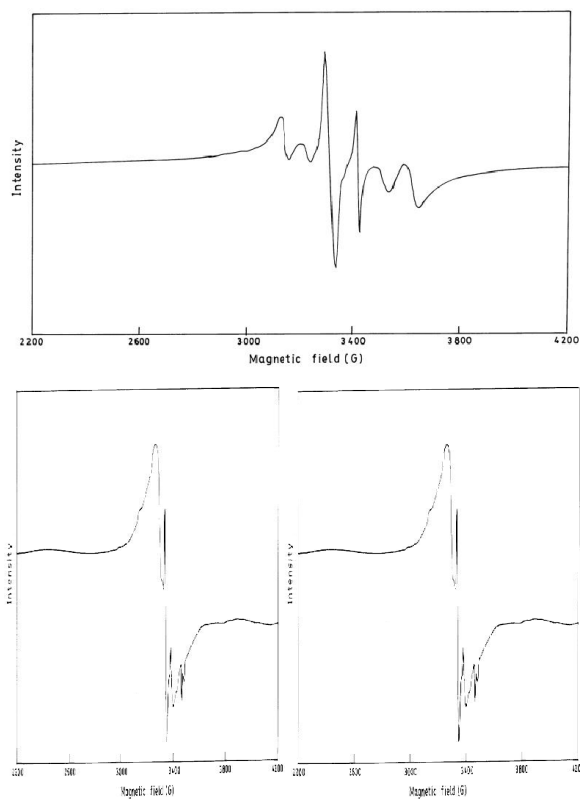


Fig. 2. EPR spectra of $[\text{FeWO}_2(\text{L})_4(\text{H}_2\text{O})]$ dithiocarbamate complexes

RESULTS AND DISCUSSION

The Heterobinuclear Iron - Tungsten dithiocarbamate complexes with Fe(III) is synthesized by the interaction of the respective metal tungstates with dithiocarbamates in DMF by the addition of conc. HCl or conc. HNO_3 . The complexes are insoluble in water and common organic solvents, but soluble in DMF. Based on the analytical data Iron-Tungsten dithiocarbamate complexes are formulated as $\text{FeWO}_2(\text{L})_4\text{H}_2\text{O}$ L=4-morpholinyl dithiocarbamate or 1-piperidinyl dithiocarbamate. The elemental analyses suggested the proposed composition of the complexes. A lower molar electrical conductivity value $8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in DMF suggested the non-ionic nature of the complexes. A single spot obtained in TLC indicated that the complexes are pure and discrete in nature. Thermal decomposition data of the complexes 1-3 in the first step indicated the loss of one coordination water molecule in the temperature range $90\text{--}130^{\circ}\text{C}$. The first stage of decomposition of complex 1 (Fig. 1) occurs in the range of $70\text{--}210^{\circ}\text{C}$ and a weight loss of 2.16% was observed corresponding to the loss of one molecule of water resulting in $[\text{FeWO}_2(4\text{-morphdte})_4 \text{H}_2\text{O}]$ phase. Second stage of decomposition begins at 210°C and proceeds up to

290°C recording a weight loss of 57.97%, which agrees well with the calculated weight loss of 57.36% resulting in WS_2 and $FeSO_4$. The third stage of decomposition takes place in the temperature range of 290–520°C recording a weight loss of 76.37% resulting in the formation of WO_3 and FeO . The first stage of decomposition of complex **2** takes place in the range of 60–210°C and a weight loss 1.96% was observed corresponding to the loss of one molecule of water resulting in $[FeWO_2(1-pipdte)_4 H_2O]$ phase, endorsed by an endotherm at 208°C. Second stage of decomposition begins at 210°C and proceeds up to 290°C recording a weight loss of 57.85% which agrees well with the calculated weight loss of 56.70% resulting in WS_2 and $FeSO_4$. The third stage of decomposition takes place in the temperature range of 290–695°C recording a weight loss of 75.91% resulting in the formation of WO_3 and FeO .

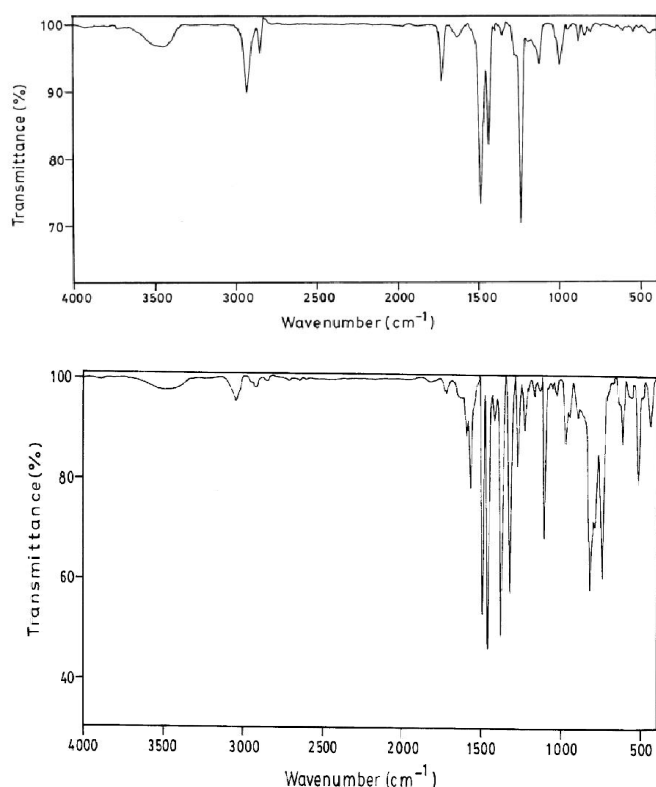


Fig. 3. FT-IR spectra of $[FeWO_2(L)_4(H_2O)]$ dithiocarbamate complexes

It is important to prove the discrete nature of the complexes as the synthesis involves two metal centers, which possesses the possibility of the formation of individual metal complexes. Several solvent systems were attempted and a mixture of $CH_2Cl_2:CH_3OH$ (4:1 by volume) was found to be effective in carried out TLC measurement for all complexes. TLC measurements were carried out on a silica gel plate using $CH_2Cl_2:CH_3OH$ as the eluant. Heterobinuclear complexes gave colour spots in which case the plates were developed in an iodine chamber. The chromatogram of all the complexes showed a single spot, which suggested the discrete nature of the complexes. The R_f values are in the range of 0.68 & 0.59. No splitting in the spots observed even solvent mixtures were used. The ligand dithiocarbamate was taken in slightly large excess than the metal tungstates so that no individual complex formation resulted. The synthetic procedure was adopted when

less dithiocarbamate ligand was used, where mixture of complexes are found by TLC. Coordination complexes can be categorized into cationic, anionic or non-ionic complexes. Electrical conductivity measurements in solution provide valuable information about the nature of the complexes. The electrical conductivity of 10^{-4} M solutions of the complexes in DMF at 27°C was measured. The molar conductivity (λ_M) values obtained after correcting for the solvent were found to be in the range of $8-20 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. The very low λ_M values suggest the non-ionic nature of the heterometal tungsten complexes. Magnetic moment values of the heterometal tungsten complexes are measured at room temperature. The magnetic moment values were obtained after applying necessary diamagnetic corrections and for temperature independent paramagnetism (TIP). The Fe–W complexes also exhibited a magnetic moment of 6.71 and 6.66 BM. This is in accordance with the fact that iron is in the trivalent state (d^5) and W in the pentavalent state (d^1), which contribute to a net magnetic moment of $(5.92+1.73) 7.65 \text{ BM}$.

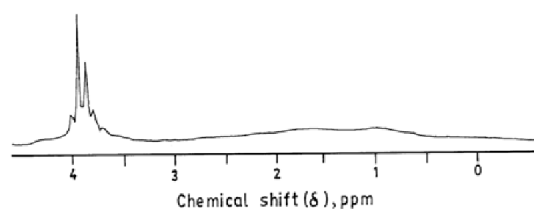


Fig. 4. 1H NMR spectra of $[FeWO_2(L)_4(H_2O)]$ dithiocarbamate complexes

The powder EPR spectrum of complex **1** and **2** are indicative of the fact that Iron is in the trivalent state and tungsten in the pentavalent state. The nuclear spin (I) of ^{57}Fe and ^{184}W are $1/2$ and $1/2$ respectively. The spectrum showed a broad signal due to Fe^{3+} with a g value of 1.998 and 1.982. (Fig. 2). The lower value of the magnetic moment in **2** may be due to the magnetic interactions between the adjacent paramagnetic centers in the complex. The redox titration of the complexes with $KMnO_4$ solution suggested the involvement of one electron oxidation of tungsten (V) to tungsten (VI). The Fourier transform infrared spectra of the complexes were recorded as KBr matrix. The infrared spectra of the metal-tungsten complexes are reproduced in figure 3. The weak broad band observed around 3450 cm^{-1} is assigned to $\nu(OH)$ indicating the presence of coordinated water molecule. The band observed at 1600 cm^{-1} is attributed to $\delta(H_2O)$. The presence of coordinated water is also supported by thermo gravimetric data. The band around 1000 cm^{-1} in the complexes is attributed to $\nu(CS)$ of the bidentate dithiocarbamates⁴⁰. The results indicate that the univalent dithiocarbamate ligand is coordinated through two sulphur atoms in a bidentate fashion resulting in a four number chelate. An intense band observed around 960 cm^{-1} is assigned to $\nu(W=O_t)$ stretching⁴¹ and this peak is a fingerprint of tungsten-oxygen terminal stretching. The complexes exhibit infrared absorptions around 820 cm^{-1} and 620 cm^{-1} , which are attributed⁴² to $M-O_b-W_{(asym)}$ and $M-O_b-W_{(sym)}$ stretching vibrations respectively. The band around 500 cm^{-1} is due to $\nu(M-OH_2)$ and around 450 cm^{-1} is due to $\nu(W-S)$. Thus the infrared spectra of all complexes show the presence of coordinated water molecule as well $W=O_t$ and $M-O_b-W$ bonds. The 1H -NMR spectra (Fig. 4) of the $[FeWO_2(4\text{-morphdte})_4(H_2O)]$ complex was recorded in $CDCl_3$ using TMS

as the reference. The spectrum has a quartet peak due to $-N-(CH_2)_2$, having δ values of 3.55, 3.58, 3.62 and 3.66 ppm as expected. Due to resonance in the dithiocarbamate ligands, the C-N bond acquires partial double bond character and as a result, the free rotation over C-N bond is restricted⁴³. Given the geometry of the molecule, due to restriction in free rotation, the environment around the terminal $-CH_2-CH_2-$ groups are not the same and hence a multiplet is observed⁴⁴. Further, since the dithiocarbamate are attached to two different metal atoms, the electronic factors would vary and thereby bringing difference in the chemical environments of the protons.

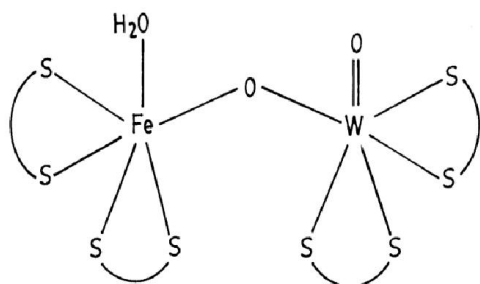


Fig. 5. Proposed structure of $[FeWO_2(L)_4(H_2O)]$ dithiocarbamate complexes

composition of the synthesized complexes are $[FeWO_2(L)_4(H_2O)]$ where (L= morphdct, pipdct). TLC and conductivity measurements showed that the complexes are discrete and non-ionic nature. Magnetic moment and EPR conclusively shows the presence of trivalent iron and pentavalent tungsten in the dithiocarbamate complexes. TG and IR studies indicated the presence of coordinated water in the complexes in heterobinuclear complexes iron(III) and tungsten(V) have coordination number six with octahedral geometry. The metal atom is coordinated by aqua, bidentate dithiocarbamate and oxo bridge to tungsten, with tungsten having a terminal oxygen atom⁴⁵ (Fig. 5).

Micro organisms used for antimicrobial activity are Escherichia coli. The antibacterial activity performance of complex particles was done by using disc diffusion method (Fig. 6). The disc diffusion method for antibiotic susceptibility testing is the Kirby-Bauer method. The agar used is Muller-Hinton agar that is rigorously tested for composition and pH. Further the depth for agar in the plate is a factor to be considered in the disc diffusion method. This method is well documented and standard zones of inhibition have been determined for susceptible and resistant values. There is also a zone of intermediate resistant indicating that some inhibition occurs using this antimicrobial but it may not be sufficient inhibition to eradicate the organism from the body. The zone of inhibition increases with the increase in complex particle concentration and decrease in particle size.

Conclusions

The heterobinuclear complexes were prepared and characterized by antibacterial studies. The ¹H NMR chemical shifts indicated non-identical environment of protons coming closer due to rigidity in rotation around C-N bond of dithiocarbamate ligand and coordination to the heterometal atoms. The proposed structure consists of a tetrahedral Iron(III) and octahedral tungsten(V) bridged by an oxo group. The present study concluded that heterobinuclear complex prepared by using dithiocarbamates are having potential sources of bioactive compounds and can be used as source for antibacterial agent.

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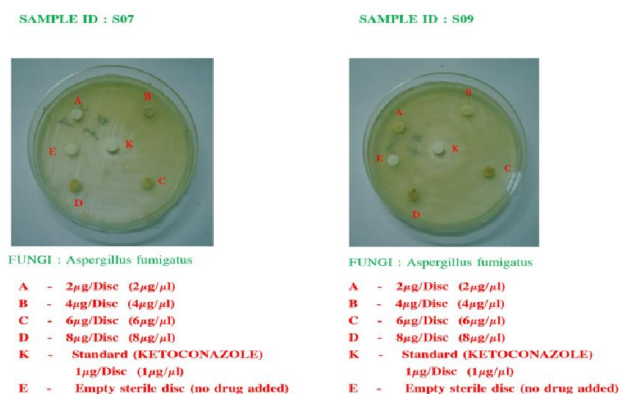


Fig. 6. Antibacterial activity studies of dithiocarbamate complexes

The dithiocarbamate or dithiolate ligands may probably coordinate to tungsten in AOR-type form hyperthermophilic archaea, which grow at high temperatures in sulfur-rich environments. Model complexes with dithiolate chelates are more relevant to biological W centers, and as expected, this removes the axial symmetry, resulting in rhombic EPR signals. Thus, the present complexes may act as bench models for AOR-type tungstoenzyme.
