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Synthesis and Characterization of Mixed Metal Complexes of Fe-W with Schiff Bases Of Diethylene Triamine

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ABSTRACT

Mixed metal complexes of Fe-W have been synthesized with Schiff bases of diethylene triamine (dien) formed from acetophenone, benzaldehyde, acetyl acetone and salicylaldehyde. The complexes were characterized by elemental and thermal analysis, IR, UV-Vis spectral studies and magnetic susceptibility studies. The anti-bacterial and anti-cancer activities of dien salicylaldehyde Schiff base complex were studied which indicates potential application of tungsten based complexes in biological field .

Keywords: Fe –W dien Schiff base complex, antibacterial, anti-cancer activities of Fe-W mixed metal complexes.

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INTRODUCTION

In search of cheaper methods for industrial nitrogen fixation, as compared to the Haber-Bosch process, a number of chemists have attempted at synthesis of several metal clusters [1-14]. Studies on Schiff base complexes of metals fascinate inorganic chemists even today because of extensive applications in different fields, ease of synthesis and use as biological models [15-19]. There are not many studies on tungsten based complexes nor are there reports about applications of tungsten complexes in biological field. This is one factor which prompted us to venture on Fe -W complexes .Here in, we report the synthesis and characterization of mixed metal complexes of Fe-W with Schiff bases of diethylene triamine (dien) formed from acetophenone, benzaldehyde, acetyl acetone and salicylaldehyde.

EXPERIMENTAL

All reagents and solvents used were of analytical grade and used without purification. The complexes were prepared as follows. In the synthesis of diethyleneTriamine based Fe-W complex with salicylaldehyde, 0.00482 mol of Ferric ammonium sulphate in water was taken in a RB flask and then added 0.00482 mol of diethylene triamine and 0.00969 mol of salicylaldehyde simultaneously along with a further addition of 20 ml of rectified spirit. The mixture was stirred and refluxed continuously using a magnetic stirrer for about 1.5 hours. Then added 0.00482 mol of Sodium tungstate in water, when a maroon coloured complex separated out . The complex was filtered using hot water and rectified spirit as wash liquid. The complex thus formed was then dried at 50° C in an air oven. In the preparation of other complexes with acetophenone,benzaldehyde,acetylacetone, 0.00482 mol of Ferric ammonium sulphate in water was taken in a RB flask and then added 0.00482 mol of diethylene triamine and 0.00969 mol of acetophenone/ acetylacetone/ benzaldehyde simultaneously along with a further addition of 20 ml of rectified spirit. The mixture was stirred and refluxed continuously using a magnetic stirrer for about 1.5 hours. Then added 0.00721 mol of Sodium tungstate in water, a yellow coloured complex separated out. The complex was filtered using hot water and rectified spirit as wash liquid. The complex thus formed was then dried at 50° C in an air oven.

The iron in the complexes was determined by optical emission spectroscopy using ICP-OES Perkin Elmer optima 5300 DV Spectrometer and Nitrogen was estimated by Kjelhdhal 's method. Tungsten in the sample was precipitated as tungstic acid, which was later incinerated and estimated as WO_3. TG/DTA were recorded in nitrogen medium using NETZSCH STA 409 C/CD thermal analyzer with a heating rate of 10°C/min. Magnetic susceptibility studies were carried out using Vibrating magnetometer EG and GPARC model 155. UV –Visible absorption spectra were done using Varian Cary Spectrophotometer 5E – UV-Vis-NIR. The IR spectra were recorded in KBr using Schimadzu IR spectrometer. Antibacterial activities of salicylaldehyde-dien Schiff base complex were studied using a minimum modification of the disc diffusion method originally described by Bauer [20] . The invitro cytotoxicity of the prepared coordination complex was determined by MTT-based assay in human A549 lung carcinoma cell line. The MTT based assay measures the mitochondrial dehydrogenase activity as an indication of cell viability. The MTT assay [21] is

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based on the ability of live but not dead cells to reduce the yellow tetrazolium dye to a purple formazan product. Cells were maintained in DMEM medium, supplemented with 10% Fetal Bovine Serum, at 37^{o}C in humidified atmosphere with 5% CO_2.

RESULTS AND DISCUSSION

The elemental analysis data on the complexes Table -I confirm the proposed composition $[(Dien\text{-}4H)(CHC_6H_4OH)(CHC_6H_4O)Fe\ (WO_4)]_2$, $[[(Dien\text{-}4H)\ (CHC_6H_5)_2(H_2O)Fe]_2\ (WO_4)_3]$, $[[(Dien\text{-}4H)\ (CCH_3C_6H_5)_2(H_2O)Fe]_2(WO_4)_3]$ and $[(Dien\text{-}4H)\ (CH_3\ CCH_2\ COCH_3\ )_2Fe]_2(WO_4)_3]$. The salicylaldehde based complex was sparingly soluble in DMSO, ethanol and water while the other complexes were insoluble in all available laboratory solvents. The thermal analysis data from TGA and DTA on the four complexes are furnished in Table-II. The thermograms were run only upto 1000◦ C and the final residue corresponds to a mixtures of Fe_2O_3 and WO_3. The decomposition is incomplete in complex formed with acetophenone based Schiff base even at a temperature of 1000˚C. The final decomposition is accompanied by endotherms and exotherms leading to final oxide formation. The theoretical values are slightly lower than experimental values indicating the decomposition is incomplete. But higher temperatures could not be done due to possibility of formation of tungsten nitrides. IR spectral data on the complexes and assignment of the bands are given in Table-III. υ_{NH} in the complexes appears around 3400 cm^{-1}. $\upsilon_{C=N}$ and $\upsilon_{c=c}$ do not appear distinct and hence assigned together in the region 1500-1636 cm^{-1}. $\upsilon_{W=O}$ and υ_{W-O} of the complexes appear around 980 and 830 cm^{-1} respectively [22]. $\upsilon_{C=O}$ in acetyl acetonato complex appears around 1640 cm^{-1} due to coordination.$\boldsymbol{\upsilon_{Fe-O}}$ of the complexes appear in the region 440-472 cm^{-1}. This corresponds to iron oxygen stretching seen in ferric low spin complexes [23] in concurrence with magnetic susceptibility studies on salicylaldehyde Schiff base complex indicated a magnetic moment of 0.578 BM. Such a very low value of 0.578 BM indicates strong anti ferromagnetic coupling between the two Fe (III) atoms present in the complex. This also shows that the Fe (III) atoms are in low spin state. The electronic spectral data Table-I indicate complexes show three bands around 245, 350 and 460nm as observed for low spin octahedral Ferric systems which may be assigned to $^2A_{2g} \rightarrow {}^2E_g$, $^2A_{2g} \rightarrow {}^2T_{1g}$ and a spin forbidden transition [24,25]. The diameter of the inhibitory zone from anti bacterial studies are presented in the Table IV As the concentration of the complex increases, the diameter of the inhibitory zone also increases indicating an increased activity. Antibacterial activities of salicylaldehyde-trien Schiff base complex studied using the disc diffusion method indicated that the complexes are active against all the five bacterias studied namely Staphylococcus aureus, Streptococcus mutans, Bacillus subtilis, E. coli and Pseudomonas aeruginosa. The anticancer activity of the salicylaldehyde schiff's base complex of diethylenetetramine was done using the MTT assay (Mossman, 1983), which is based on the ability of The live but not dead cells to reduce the yellow tetrazolium dye to a purple formazan product. A549 (lung cancer cell line) were incubated with different concentrations of the extract (diethylene triamine salicylaldehyde complex dissolved in DMSO (250,500,750 and 1000µg) for 24 hours. The dien salicylaldehyde based Schiff base Fe-W complex showed reasonable activity towards cancerous cells Table-V. A simultaneous work with a normal human cell indicated very less toxicity.The benzaldehyde and acetophenone complexes may tentatively proposed a structure with a tungstate bridging two iron(III) in turn coordinated to a water molecule and two O^- of the tungstate ion.The carbonyl O may be involved in the acetyl acetonato complex instead of O of water

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molecule.In the salicylaldehyde complex,each iron may be linked to two imine N ,to a tungstate thro two O^- and OH oxygen and O^- oxygen of salicylaldehyde part .

Table I: Elemental analysis data of Dien Schiff base complexes

Complexes	% N (theo) Exp	%Fe (theo) Exp	% W (theo) Exp	Λ_{max}(nm)
$[(Dien\text{-}4H)(CHC_6H_4OH)(CHC_6H_4O)Fe(WO_4)]_2$	(6.85) 7.15	(9.11) 9.5	(29.98) 28.73	255,,350,510
$[[(Dien\text{-}4H)(CHC_6H_5)_2(H_2O)Fe]_2(WO_4)_3]$	(5.20) 4.97	(6.92) 6.82	(34.2) 35.07	245,355,455
$[[(Dien\text{-}4H)(CCH_3C_6H_5)_2(H_2O)Fe]_2(WO_4)_3]$	(5.03) 5.01	(6.69) 5.82	(33.04) 32.44	255,355,480,540
$[[(Dien\text{-}4H)(CH_3CCH_2COCH_3)_2Fe]_2(WO_4)_3]$	(5.28) 5.87	(7.032) 8.01	(23.14) 24.37	250,325,465,550

Table II: Thermal analysis data of Dien Schiff base complexes

COMPLEXES	% Residue from TGA	DTA peaks ^oC	
		exothermic	endothermic
$[(Dien\text{-}4H)(CHC_6H_4OH)(CHC_6H_4O)Fe(WO_4)]_2$	36.52	237, 307.2, 412, 475	541.4
$[[(Dien\text{-}4H)(CHC_6H_5)_2(H_2O)Fe]_2(WO_4)_3]$	58.46	633, 800, 820.9	666, 600
$[[(Dien\text{-}4H)(CCH_3C_6H_5)_2(H_2O)Fe]_2(WO_4)_3]$	High	75, 296.8	579.2, 587.8, 600
$[[(Dien\text{-}4H)(CH_3CCH_2COCH_3)_2Fe]_2(WO_4)_3]$	69.29	522.8, 653.3, 737, 775	500, 600, 758

Table III : IR Spectral data ofDien Schiff base complexes(cm^{-1})

Complexes	υ_{NH}, υ_{OH}	$\upsilon_{(ali)}$, $\upsilon_{(ar)}$	$\upsilon_{C=N}$, $\upsilon_{C=C}$	$\upsilon_{W=O}$	υ_{W-O}	$\upsilon_{Fe=O}$
$[(Dien\text{-}4H)(CHC_6H_4OH)(CHC_6H_4O)Fe(WO_4)]_2$	3422	3229,3059 2925,2862	1628 1510	980, 945	838	460
$[[(Dien\text{-}4H)(CHC_6H_5)_2(H_2O)Fe]_2(WO_4)_3]$	3420,3414	3135,3050 2925,2857	1627, 1555,1506	948	846	467
$[[(Dien\text{-}4H)(CCH_3C_6H_5)_2(H_2O)Fe]_2(WO_4)_3$	3419,3412	3050 2932,2860,	1636, 1555	975	855	470
$[[(Dien\text{-}4H)(CH_3CCH_2COCH_3)_2Fe]_2(WO_4)_3]$	3427,3423, 3418,3403	2931,2860	1628, 1515	949	849	472, 442

Table IV: Antibacterial studies

ORGANISM	Gram positive/ negative	STD-10µg	10µg	15µg	30µg
Staphylococcus aureus	positive	38	23	28	32
Streptococcus mutans	positive	39	24	27	33
Bacillus subtilis	positive	38	22	26	32
E. coli	negative	39	12	16	19
Pseudomonas aeruginosa	negative	38	16	19	22

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Table V: Anticancer studies data of complex I

sample	Concentration	Absorbance at 570nm			Average	SD	% of viability	% of toxicity
Salicylaldehyde Dien Schiff base complex	Control	1.31	1.35	1.32	1.32	0.020817	100	0
	250µg	1.09	0.81	0.95	0.95	0.14	71.96969697	28.03030303
	500µg	1.02	0.76	0.89	0.89	0.13	67.42424242	32.57575758
	750µg	0.95	0.71	0.83	0.83	0.12	62.87878788	37.12121212
	1000µg	0.88	0.66	0.77	0.77	0.11	58.33333333	41.66666667

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