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Research Article

SYNTHESIS AND CHARACTERISATION OF MIXED METAL COMPLEXES OF Fe-W WITH SCHIFF BASES OF TRIETHYLENE TETRAMINE

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ABSTRACT

Mixed metal complexes of Fe-W have been synthesized with Schiff bases of triethylene tetra amine (trien) 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 trien salicylaldehyde Schiff base complex were studied which indicates potential application of tungsten based complexes in biological field.

Keywords: Schiff base complex, anticancer activities of Fe-W mixed metal complexes.

INTRODUCTION

The chemist's interest to develop cheaper methods for industrial nitrogen fixation, as compared to the Haber-Bosch process has led to the synthesis of several novel metal clusters[1-14]. Studies on Schiff base complexes of metals fascinate inorganic chemists even today because of their extensive application in diverse fields, ease of synthesis and use as biological models[15-19]. Next, Mo figures in antineoplastic activities as MoS_4^{2-}, and has been well studied[20]. There are not much studies on tungsten complexes with potential application in biological field. This is another factor which prompted us to venture on Fe -W complexes .Herein we report the synthesis and characterization of mixed metal complexes of Fe-W with Schiff bases of triethylene tetraamine (trien) 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 trien salicylaldehyde Schiff base complex were studied which indicates potential application of tungsten based complexes in biological field.

MATERIALS AND METHODS

All reagents and solvents used were of analytical grade and used without purification. The complexes were prepared as follows. 0.00661 mol of Ferric ammonium sulphate in water was taken in a RB flask and then added 0.00666 mol of triethylene tetramine and 0.01335 mol of salicylaldehyde / benzaldehyde / acetophenone / acetyl acetone simultaneously to the RB flask 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 0.0099 mol of Sodium tungstate in water, a maroon coloured complex separated out when salicylaldehde was used and yellow coloured complexes in all other cases. The complexes were filtered using hot water and rectified spirit as wash liquid. The complexes thus formed were 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-trien Schiff base complex were studied using a minimum modification of the disc diffusion method originally described by Bauer[21]. 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 (Mossman, 1983)[22] is 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°C in humidified atmosphere with 5% CO_2.

RESULTS AND DISCUSSION

The elemental analysis data on the complexes Table -1 confirm the proposed composition $[[(Trien\text{-}4H)(CHC_6H_4OH)_2Fe]_2(WO_4)_3]$,$[[(Trien\text{-}4H)(CHC_6H_5)_2Fe]_2(WO_4)_3]$,$[[(Trien\text{-}4H)(CCH_3C_6H_5)_2Fe]_2(WO_4)_3]$,$[[(Trien\text{-}4H)(CH_3CCH_2COCH_3)_2Fe]_2(WO_4)_3]$. The salicylaldehde based complex was sparingly soluble in DMF, DMSO 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-2. The thermograms were run only upto 1000◦ C and the final residue corresponds to a mixtures of Fe_2O_3 and WO_3. 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. The decomposition is accompanied by several endotherms and exotherms leading to final oxide formation. IR spectral data on the complexes and the assignment of the bands are given in Table-3 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 1520-1635 cm^{-1}. $\upsilon_{W=O}$ and υ_{W-O} of the complexes appear around 960 and 840 cm^{-1} respectively[23] . $\boldsymbol{\nu_{Fe-O}}$ of the complexes appear in the region 460-510 cm^{-1}. This corresponds to iron oxygen stretching seen in ferric low spin complexes in concurrence with magnetic susceptibility studies[24]. The magnetic susceptibility of triethylenetetramine salicylaldehyde based schiff's base complex showed a very low value of 0.61 BM. This 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-1 also confirm the presence of Fe(III) in low spin state[25] . The diameter of the inhibitory zone are presented in the Table 4 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 triethylenetetramine was done using the MTT assay (Mossman, 1983), which is based on the ability of 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 (triethylene salicylaldehyde complex dissolved in DMSO) (250,500,750 and 1000µg) for 24 hours. The Trien salicylaldehyde based Schiff base Fe-W complex showed reasonable activity towards cancerous cells Table 5. Based on the studies done , the complexes are assigned a structure with a tungstate ion bridging two iron coordinated to trien moiety through two imino and two N-H nitrogen and a tungstate through two O^- .

Table 1: Elemental analysis data of Trien Schiff base complexes

Complexes	% N (theo) Exp	%Fe (theo) Exp	% W (theo) Exp	Λ_{max}
$[[(Trien4H)(CHC_6H_4OH)_2Fe]_2(WO_4)_3]$	(7.14)7.79	(7.16)7.14	(35.26)36.40	250,340,490
$[[(Trien\text{-}4H)(CHC_6H_5)_2Fe]_2(WO_4)_3]$	(7.46)7.15	(7.44)8.05	(36.76)36.73	255,300,485,550
$[[(Trien\text{-}4H)(CCH_3C_6H_5)_2Fe]_2(WO_4)_3]$	(7.19)6.54	(7.18)6.88	(35.44)36.02	250,350,460,540
$[[(Trien4H)(CH_3CCH_2COCH_3)_2Fe]_2(WO_4)_3]$	(7.59)6.87	(7.57)7.02	(37.36)35.82	250,350,480,580

Table 2: Thermal analysis data

Complexes	% Residue TGA (Theo) Exp	DTA PeaksQ	
		Endothermic	Exothermic
$[[(Trien4H)(CHC_6H_4OH)_2Fe]_2(WO_4)_3]$	(54.67) 63.31	590.1,783,800, 862,918	508.9,795, 839 880, 691
$[[(Trien-4H)(CHC_6H_5)_2Fe]_2(WO_4)_3]$	(57.00) 67.97	358.5, 554	470,524.5,667, 320.5
$[[(Trien-4H)(CCH_3C_6H_5)_2Fe]_2(WO_4)_3]$	(54.95) 65.23	516,806.5, 841.5	475,694.1,836
$[[(Trien4H)(CH_3CCH_2COCH_3)_2Fe]_2(WO_4)_3]$	(57.93) 60.97	362, 658, 764.5	316.5,541,641.5, 758,854.5

Table 3: IR spectral data of complexes (υ cm^{-1})

Complexes	υ_{NH}	$\upsilon_{CH(ali)}$, $\upsilon_{CH(ar)}$	$\upsilon_{C=N}$, $\upsilon_{C=C}$	$\upsilon_{W=O}$	υ_{W-O}	$\upsilon_{Fe=O}$
$[[(Trien4H)(CHC_6H_4OH)_2Fe]_2(WO_4)_3]$	3417, 3407	2938	1622, 1614, 1537	924	846	598, 460
$[[(Trien-4H)(CHC_6H_5)_2Fe]_2(WO_4)_3]$	3542, 3522, 3393, 3371	3045	1500, 1525	923	841	466
$[[(Trien-4H)(CCH_3C_6H_5)_2Fe]_2(WO_4)_3]$	3406, 3240	3137, 2933,	1634, 1619, 1530, 1575	936	854	550, 580
$[[(Trien4H)(CH_3CCH_2COCH_3)_2Fe]_2(WO_4)_3]$	3413	2938	1622, 1527, 1570	932	840	575

Table 4: Antibacterial studies data

ORGANISM	Gram positive/ negative	STD	10µg	15µg	30µg
Staphylococcus aureus	positive	39	22	26	30
Streptococcus mutans	positive	38	20	25	31
Bacillus subtilis	positive	39	22	27	32
E. coli	negative	38	19	23	28
Pseudomonas aeruginosa	negative	39	18	21	26

STD streptomycin 30µg

Table 5: Anticancer activity of the complex I on A549 cell line

Conc	Absorbance at 570nm			Average	SD	% of viability	% of toxicity
Control	1.31	1.32	0.020	1.32	0.02	100	0
250µg	0.81	0.71	0.1	0.71	0.1	53.7879	46.2121
500µg	0.74	0.65	0.09	0.65	0.09	49.2424	50.7576
750µg	0.67	0.59	0.08	0.59	0.08	44.6970	55.3030
1000µg	0.6	0.53	0.07	0.53	0.07	40.1515	59.8485

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