

Synthesis, Characterization & Biological Activity of Some New Schiff Base Complexes Derived From Thiosemicarbozone

KEYWORDS	Thiosemicarbazone / Schiff bases/ Mo (V) and W (VI) / Biological Activity).								
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ABSTRACT The Schiff bases anisaldehyde thiosemicarbazone (ATC), 3-4, dimethoxy benzaldehyde thiosemicarbazone (DMBTC), thiophene-2 aldehyde thiosemicarbazone (TATC), 2-acetyl pyridine thiosemicarbazone (APTC) and acetyl acetone thiosemicarbazone (AATC) were prepared by standard methods and characterised by M.P. & I.R. Spectra. Their complexes with Molybdinum {(Mo ATC), (Mo DMBTC), (Mo TATC), (Mo ATC), (Mo ATC), Tungsten {(W ATC), (W DMBTC), (W TATC), (W ATC), (W ATC)} have been prepared by standard method and characterised by elemental analyses, electrical conductance, magnetic susceptibility, IR and electronic spectral studies molar conductance & T.G.A.. Both the ligands and their complexes have been screened for their fungicidal & bactericidal activities and the results indicate that they exhibit significant antimicrobial properties.

INTRODUCTION:

The Schiff base compounds have been used as fine chemicals and medical substrates in the field of coordination chemistry. Schiff bases and their metal complexes have been studied for their application in biological, clinical and pharmacological areas.⁽¹⁻⁴⁾ The chemistry of molybdenum has aroused considerable interest in view of its biological importance⁽⁵⁾. The effect of MO(V) and W(VI) metal compounds on biological systems has evoked considerable interest ⁽⁶⁻⁹⁾. Keeping in view these facts we have synthesised and characterised the complexes of these metals with ATC, DMBTC, TATC, APTC and AATC. The obtained results are reported here.

MATERIALS AND METHODS :

Materials used in the preparation of ligands (schiff bases) were different aldehydes and ketons. All used chemicals were of analytical grade and purchased from (Sigma/Aldrich). The aldehydes used were anisaldehyde (BDH), 3,4-dimethoxy benzaldehyde (sigma), thiophene-2-aldehyde (Fluka), 2-acetyl pyridine (BDH) and ketone was acetyl acetone (BDH) and thiosemicarbazide (Aldrich). Metals used in the preparation of complexes were molybdenum and tungsten. Molybdenum used as molybdenum (V) chloride (Sigma) and tungsten as tungsten VI chloride (Fluka).

Instrumentation :

Elemental analyses were carried out at R.S.I.C. Dept. C.D.R.I. Lucknow. Conductivity measurements were carried out at Philips conductivity bridge model PR 9500, with a dip type conductivity cell at department of chemistry B.C.B. The conductances of the complexes were measured in methanol, dimethyl formamide and dimethyl sulphoxide at 10⁻³ M dilution at 30°C. The infra red studies of the complexes were made with Perkin-Elmer spectrophotometer model 651 (U.S.A.) in KBR as well as Nuzol phase from 4000 cm⁻¹ to 200 cm⁻¹ at R.S.I.C. Department C.D.R.I. Lucknow. Magnetic susceptibility of the complexes was determined by the Gouy method at the dept of chemistry, University of Roorkee, Roorkee. The sample tube was calibrated with CuSO₄. TGA analysis was carried out at the chem. deptt. G.N.D. University. Amritsar Visible spectra were recorded with Backman DV-2 spectrophotometer in the range of 300 cm⁻¹ to 750 cm⁻¹ at Deptt. of Chemistry, Bareilly College, Bareilly.

PREPARATION OF LIGANDS :

The Schiff bases were prepared by the condensation of respective aldehyde/ketone with thiosemicarbazide. The amino compound was dissolved in ethanol and refluxed for

about half an hour. The requisite amount of the respective aldehyde/ketone was then added to the flask. The mixture was then refluxed for about six hours. The reaction mixture was kept for 24 hours. The crystals of the ligand were obtained which were purified by recrystallization. The purity of the ligands were characterised by elemental analyses, Milting Point and IR spectra.

PREPARATION OF COMPLEXES

Preparation of Oxomolybdenum (V) Complexes:

A methanolic solution of metal chloride was added in small quantities with stirring to a hot solution of the ligand in methanol. The pH of the reaction mixture was adjusted to 6 NaOAc/HOAc buffer and stirring condinued for 10-15 min. The solid complex that separated was washed with aq. methanol and dried over P_4O_{10} under vacuum.

Preparation of dioxotungsten (VI) Complexes :

The solution of metal salt was dissolved in 10 ml of NaOH solution by heating on a water bath and was filtered. The Schiff base was dissolved in 20 ml of NaOH solution. The solution of the Schiff base was added to the above solution of metal salt. The precipitate so obtained was filtered washed with water followed by ether and dried in vacuum over silica gel.

RESULT AND DISCUSSION:

The elemental analyses of the complexes indicate that Mo(V) reacts with ligand in the molar ratio of 1:2. On this basis, the composition of the complexes comes out to be [MoO(L)₂ Cl₂]. The molar conductance in MeOH, DMSO & DMF at 10⁻³M dilution indicate the non-electrolytic nature of the complexes ⁽¹⁰⁾. The elemental analyses of the complexes reveals that dioxotungsten reacts with ligand in the molar ratio of 1:2 and the complexes appears to have the composition of [WO₂(L)₂Cl₂]. The molar conductance value of the complexes in DMF at 10⁻³ M dilution shows that the complexes were non electrolyte⁽¹¹⁾.

Oxomolybdenum (V) Complexes Electronic Spectra :

The electronic spectra of oxomolybdenum (V) complexes were best considered as octahedral with a strong tetragonal distortion resulting from molybdenum oxygen bond. The complex exhibit three distinct absorption bands in the ligand field region⁽¹²⁾. The low intensity absorption peaks in the long wave length region were possibly due to first crystal field transition ²B₂ ²E (dxy dxz, dyz). This transition were observed at 12820 - 16000 cm⁻¹. The second crystal field transition were obs

RESEARCH PAPER

served at 18750 - 21000 cm⁻¹ due to transition ${}^{2}B_{2} \, {}^{2}B_{1}$ (dxy dx²-y²). The third peak appeared at 22000 - 30000 cm⁻¹ and was due to transition ${}^{2}B_{2} \, {}^{2}A_{1}$ (dxy dz²) The spectral band at 15151 cm⁻¹ indicates octahedral geometry for the complexes in agreement with Ballhausen Gray Scheme⁽¹³⁾.

Magnetic Moment :

The oxomolybdenum (V) complexes show magnetic moment value of 1.63 - 1.68 B.M. which correspond to the spin only value (1.73 B.M.) expected for oxomolybedum (V) complex showing the absence of any Mo-Mo interaction. Thus the complexes were found to be paramagnetic as expected for a d¹- system⁽¹⁴⁾.

I.R. Spectra :



Acetyl acetone thiosemicarbazone molybdenum (V) chloride

The I.R. spectra of the ligand and its metal complexes have been recorded. The comparison of the IR spectral bands of free ligands & the metal complexes indicates that in the complexes both n (C=N) & n(C=S) have appeared with lowering of n(C=N) by ~15 cm⁻¹ and n(C=S) by ~ 80 cm⁻¹. These shifts indicates the co-ordination through nitrogen of azomethine group and sulphur of (C=S) group(15). It appears therefore, in these complexes the ligand functions in a bidentate manner bonding through nitrogen and sulphur. The IR spectra of the complexes also exhibited two more bands which may due to (Mo=O) stretching and (Mo-Cl) bond^(16,17).

Volume : 4 | Issue : 2 | Feb 2014 | ISSN - 2249-555X

Dioxotungsten (VI) Chloride

Electronic & Magnetic Moment Spectra :

The electronic spectra of the complexes show a strong band at 24850 cm⁻¹. This may be due to ligand to metal charge transfer transition between the highest occupied ligand molecular orbital and the lowest empty tungsten d orbital⁽¹⁸⁾. The magnetic moment data indicate its diamagnetic nature⁽¹⁹⁾ as expected for d⁰ system and the stabilization of higher oxidation through complex formation.

I.R. Spectra :

In the IR spectra of the ligands show two important bands which may be due to n(C=N) group & n(C=S) group. On complexation these bands have shifted to lower frequencies indicating the coordination through nitrogen of (C=N) group and sulphur of (C=S) group. The ligand appears to behaving in bidentate manner. The IR spectra of the complexes also exhibited two more bands which may be due to (W=O) stretching and the presence of (W-Cl) bond⁽²⁰⁾.



Acetyl acetone thiosemicarbazone dioxotungsten (VI) chloride

CONCLUSION :

On the basis of above discussions, it appears that the ligands acts in a bidentate manner coordinated through nitrogen & sulphur. The complexes may be assigned an octahedral geometry with a slight distortion. Out of its six position four are occupied by two ligand molecules and two by chlorine atom.

Table-1 CHARACTERIZATION OF OXOMOLYBDENUM (V) COMI	PLEXES
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SI.	Name and Molecular For-	Colour	M.P./	Elemental Analyses						or Conductance <u>1⁻¹ Cm² Mol⁻¹</u>		Magnetic
No. n	mula of the complex	Colour	D.T. ℃	С%	Н%	N%	S%	Pd%	Meth- anol	DMF	DMSO	B.M.
1.	Acetyl acetone thio- semicarbazone oxomo- lybdenum (V) chloride {MoO(C ₅ H ₉ N ₃) ₂ Cl ₂]	Yellow	275	30.16 (29.20)	4.25 (3.65)	18.79 (17.04)	14.45 (13.01)	20.27 (19.47)	7	13	16	1.68
2.	Bis (anisaldehyde) thio- semicarbazone oxomo- lybdenum (V) chloride {MoO(C ₁₇ H ₁₇ N ₃ O ₂ S) ₂ Cl ₂]	brown	259	49.06 (48.74)	5.51 (4.06)	11.26 (10.03)	8.13 (7.64)	11.15 (11.47)	5	9	12	1.66
3.	Bis (3,4-dimethoxy benzaldehyde) thio- semicarbazone oxomo- lybdenum (V) chloride {MoO(C ₁₉ H ₂₁ N ₃ O ₄ S) ₂ Cl ₂]	Orange	225	48.29 (47.65)	4.98 (4.38)	9.19 (8.77)	7.21 (6.68)	11.94 (10.03)	8	10	15	1.65
4.	Bis (thiophene-2-aldehyde) thiosemicarbazone oxo- molybdenum (V) chloride {MoO(C ₁₁ H ₉ N ₃ S ₃) ₂ Cl ₂]	Pale Yellow	255	36.53 (35.62)	3.19 (2.43)	12.09 (11.34)	26.33 (25.91)	13.92 (12.95)	10	9	16	1.64
5	Bis (2-acety pyridine) thiosemicarbazone oxomolybdenum(V) chloride {MoO(C, FH, N, S), Cl,]	Red	295	47.06 (46.33)	4.12 (3.86)	19.22 (18.02)	9.39 (8.23)	13.93 (12.35)	13	8	15	1.63
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Figures in parenthesis are calculated values.

Table-2

CHARACTERIZATION OF DIOXO TUNGSTEN (VI) COMPLEXES

Sl. No.	Name and Molecular For- mula of the complex	Colour	.⊤ °C	Elementa	l Analyses		Molor Conductance Ohm ⁻¹ Cm ²	Magnetic Mo-		
			M.P./ D	С%	Н%	N%	S%	Pd%	DMF	
1.	Acetyl acetone thio- semicarbazone di- oxotungsten (VI) chloride $[WO_2(C_5H_9N_3)_2Cl_2]$	Oran- geYellow	252	23.38 (22.74)	3.11 (2.84)	14.68 (13.27)	11.88 (10.11)	30.56 (29.06)	1.9	dia magnetic
2.	Bis (anisaldehyde) thio- semicarbazone dioxo- tungsten (VI) chloride [WO ₂ (C ₁₇ H ₁₇ N ₂ O ₂ S) ₂ Cl ₂]	Dark Yel- low	202	42.47 (41.76)	4.85 (3.48)	9.12 (8.60)	7.46 (6.55)	19.24 (18.83)	-	dia magnetic
3.	Bis (3,4-dimethoxy benzal- dehyde) thiosemicarbazone dioxotungsten (VI) chloride [WO ₂ (C ₁₉ H ₂₁ N ₃ O ₄ S) ₂ Cl ₂]	Brown	235	42.69 (41.56)	4.09 (3.83)	8.28 (7.66)	6.92 (5.83)	17.72 (16.77)	1.8	dia magnetic
4.	Bis (thiophene-2-aldehyde) thiosemicarbazone di- oxotungsten (VI) chloride [WO ₂ (C ₁₁ H ₉ N ₃ S ₃) ₂ Cl ₂]	Yellow	260	30.02 (29.96)	2.93 (2.04)	10.51 (9.53)	22.32 (21.79)	21.06 (20.89)	2.1	dia magnetic
5	Bis (2-acetyl pyridine) thiosemi- carbazone dioxotungsten (VI) chloride [WO ₂ (C ₁₅ H ₁₅ N ₅ S) ₂ Cl ₂]	Brownish Yellow	265	40.24 (39.08)	4.77 (3.26)	16.25 (15.21)	7.86 (6.95)	20.76 (19.98)	2.2	dia magnetic

Figures in parenthesis are calculated values.

Table-3 INFRARED SPECTRA FOR MOLYBDENUM (V) COMPLEXES

S.No.	Name of the complexes	Bands (Cm ⁻¹)				
	Acetyl acetone thiosemicarbazone	Ligand	3410 (s) 2071 (m) 1157 (w) 665 (m)	3290 (w) 1069 (vs) 1056 (s) 583 (w)	3018 (vw) 1475 (w) 946 (m) 418 (w)	2876 (m) 1286 (m) 824 (vs)
1.	Acetyl acetone thiosemicarbazone oxomolybde- num (V) chloride	Complex	3481 (w) 2071 (m) 1353 (w) 736 (vs)	3316 (w) 1596 (vs) 1229 (m) 574 (m)	3111 (m) 1528 (w) 1068 (m) 335 (s)	2943 (w) 1408(vw) 915 (vs)
2	Bis (anisaldehyde) thiosemicarbazone	Ligand	3400 (s) 2018 (m) 1357 (s) 721 (s)	3286 (w) 1604 (vs) 1081 (w) 597 (m)	3146 (m) 1530 (w) 1013 (s) 512 (s)	2886 (m) 1525 (sh) 820 (vs)
Z	Bis (anisaldehyde) thiosemicarbazone oxomo- lybdenum (V) cholride	Complex	3304 (w) 1583 (vs) 1038 (w) 556 (w)	3081 (vw) 1448 (m) 910 (s) 409 (m)	2850 (m) 1363 (w) 868 (w) 345 (s)	2078 (w) 1246 (m) 759 (vs)
	Bis (3,4-dimethoxy bezaldehyde) thiosemicar- bazone	Ligand	3350 (m) 1809(vw) 1238 (m) 683 (m)	3272 (w) 1630 (vs) 1173 (s) 547 (w)	3049 (m) 1558 (w) 951 (m) 458 (m)	2825 (w) 1337 (w) 835 (vs)
з.	Bis (3,4-dimethoxy bezaldehyde) thiosemicarba- zone oxomolybdenum (V) cholride	Complex	3381 (w) 1601 (vs) 1032 (m) 670 (w)	3121 (m) 1463 (w) 620 (vs) 529 (m)	2966 (w) 1259 (m) 840 (s) 340 (vs)	2226(vw) 1157 (w) 778(vs)
1. 2 3. 4.	Bis (thiophene-2-aldehyde) thiosemicarbazone	Ligand	3486 (m) 2829 (w) 1257 (w) 840 (vs)	3216 (w) 2027 (m) 1138 (s) 698 (m)	3105 (m) 1622 (vs) 1048 (m) 487 (w)	2990 (w) 1418 (m) 942 (vw)
	Bis (thiophene-2-aldehyde) thiosemicarbazone oxomolybdenum (V) chloride	Complex	3320 (w) 1603(vs) 1249 (w) 756 (vs)	3200 (m) 1532 (m) 1043 (m) 550 (m)	3020 (w) 1444 (vw) 915 (vs) 320 (vs)	2976 (m) 1358 (m) 848 (m)

RESE	ARCH PAPER		Volume	: 4 Issue : 2 F	eb 2014 ISSN	I - 2249-555X
F	Bis (2-acetyl pyridine) thiosemicarbazone	Ligand	3515 (m) 2092 (w) 1264 (w) 815 (vs)	3458 (w) 1635 (vs) 1174 (w) 720 (s)	3305 (m) 1546 (w) 1026 (s) 510 (m)	2947 (w) 1320 (m) 949 (w)
5.	Bis (2-acetyl pyridine) thiosemicarbazone oxo- molybdenum (V) chloride	Complex	3310(vw) 1470 (w) 920 (s) 645 (m)	3079 (w) 1285 (m) 832 (w) 519 (w)	2940 (w) 1154 (m) 752 (vs) 340 (vs)	1602 (vs) 1080 (w) 711 (s)

Table-4 SPECTRA FOR TUNGSTEN (VI) COMPLEXES

S.No.	Name of the complexes	Bands (Cm ⁻¹))			
1	Acetyl acetone thiosemicarbazone	Ligand	3410 (s) 2071 (m) 1157(w) 665 (m)	3290 (w) 1069 (vs) 1056 (s) 583 (w)	3018 (vw) 1475 (w) 946 (m) 418 (w)	2876 (m) 1286 (m) 824 (vs)
1.	Acetyl acetone thiosemicarbazone dioxotung- sten (VI) chloride	Complex	3419 (m) 2079 (m) 1105 (m) 638 (w)	3291 (vw) 1585 (vs) 913 (m) 476 (m)	3083 (w) 1414 (w) 850 (s) 365 (s)	2993 (w) 1292 (m) 745 (s)
2	Bis (anisaldehyde) thiosemicarbazone	Ligand	3400 (s) 2018 (m) 1357 (s) 721 (s)	3286 (w) 1604 (vs) 1081 (w) 597 (m)	3146 (m) 1530 (w) 1013 (s) 512 (s)	2886 (m) 1525 (sh) 820 (vs)
2	Bis (anisaldehyde) thiosemicarbazone dioxo- tungsten (VI) cholride	Complex	3357 (w) 2091 (m) 1187 (m) 766 (s)	3218 (m) 1587 (vs) 1004 (w) 590 (m)	3139 (vw) 1467 (w) 935 (m) 360 (w)	2958 (m) 1383 (m) 880 (vs)
	Bis (3,4-didmethoxy bezaldehyde) thiosemicar- bazone	Ligand	3350 (m) 1809(vw) 1238 (m) 683 (m)	3272 (w) 1630 (vs) 1173 (s) 547 (w)	3049 (m) 1558 (w) 951 (m) 458 (w)	2825 (w) 1337 (w) 835 (vs)
3	Bis (3,4-didmethoxy bezaldehyde) thiosemicar- bazone dioxotungsten (VI) chloride	Complex	3405 (w) 2014 (w) 1020 (w) 539 (m)	3290 (m) 1596 (vs) 915 (m) 417 (w)	3110 (m) 1487 (w) 875 (s) 340 (s)	2924 (m) 1256 (m) 790 (vs)
	Bis (thiophene-2-aldehyde) thiosemicarbazone	Ligand	3486 (m) 2829 (w) 1257 (w) 840 (vs)	3216 (w) 2027 (m) 1138 (s) 698 (m)	3105 (m) 1622 (vs) 1048 (m) 487 (w)	2990 (w) 1418 (m) 942 (vw)
4.	Bis (thiophene-2-aldehyde) thiosemicarbazone dioxotungsten (VI) chloride	Complex	3350 (w) 2062 (w) 1129 (m) 686 (m)	3269 (w) 1597 (vs) 989 (w) 543 (w)	3017 (m) 1455 (w) 905 (s) 325 (s)	2923 (m) 1357 (m) 953 (s)
F	Bis (2-acetyl pyridine) thiosemicarbazone	Ligand	3515 (m) 2092 (w) 1264 (w) 815 (vs)	3458 (w) 1635 (vs) 1174 (w) 720 (s)	3305 (m) 1546 (w) 1026 (s) 510 (m)	2947 (w) 1320 (m) 949 (w)
5.	Bis (2-acetyl pyridine) thiosemicarbazone dioxotungsten (VI) chloride	Complex	3475 (m) 2064 (m) 1147 (m) 567 (m)	3343 (w) 1645 (vs) 923 (m) 413 (w)	3112 (w) 1477 (m) 860 (s) 315 (s)	2904 (w) 1238 (w) 739 (s)

Antimicrobial Screening :

The antifungal activity was evaluated by the radial growth method using Czapek's agar medium having the composition, glucose 20g, starch 20g, agar-agar 20g and distilled water 10000 ml. To this medium was added requisite amount of the compound after being dissolved in DMF so as to obtain certain final concentrations (25, 50, 100 & 200 ppm) the organism use in these investigations included alternaria alternate, Rhizoctina bataticola. The fungicidal activity of the ligands and their metal complexes against pathogenic fungi is recorded in Table-5.

The activity against bacteria was evaluated by the inhibition zone technique (paper-disc plate method), 15 ml nutrient agar medium having the composition peptone 5g, beef extract 5 g, Nacl 5gm, agar-agar 20 g and distilled water 1000 ml., was pipetted into the petri dish. The organisms used in the present investigations included Staphylococcus aureus and Xanthomonas compestris. The compound were dissolved in DMF in 500 and 1000 ppm concentrations. The bactericidal activity of the ligands and their metal complexes against pathogenic bacteria is recorded in Table-6.

The free ligands and their respective metal chelates were screened against selected fungi and bacteria to assess their potential as antimicrobial agents. The results are quite promising. The antimicrobial data reveal that the complexes are superior to the free ligands. The enhanced activity of the metal chelates may be ascribed to the increased lipophilic nature of these complexes arising due to the chelation^(21,22). The toxicity increased as the concentration was increased.

Volume : 4 | Issue : 2 | Feb 2014 | ISSN - 2249-555X

Table-5 Fungicidal screening data for the ligands and their metal complexes

Table-6 Antibacterial screening data for the ligands and their metal complexes

Compound	Inhibition after 96 h(%) (conc. in ppm)						Compound Diameter of Inhibition Zone (mm) (conc. in ppm)				
	Alternaria alter- nate Rhizoctonia bata- ticola			Staphyloc aureus	occus	Xanthomonas compestris					
	50	100	200	50	100	200		500	1000	500	1000
AATC	41	53	60	40	52	56	AATC	8	11	7	9
ATC	30	42	48	34	38	45	ATC	6	9	8	10
DMBTC	44	55	65	40	52	59	DMBTC	9	11	12	10
TATC	41	55	60	41	62	60	TATC	6	10	8	12
APTC	36	43	52	37	41	52	APTC	9	12	10	13
[MoO (AATC) ₂ Cl ₂]	40	55	63	45	57	62	[MoO (AATC) ₂ Cl ₂]	10	15	9	12
[MoO (ATC) ₂ Cl ₂]	38	43	53	37	48	52	[MoO (ATC) ₂ Cl ₂]	7	11	10	10
[MoO(DMBTC) ₂ Cl ₂]	46	50	65	42	55	62	[MoO(DMBTC) ₂ Cl ₂]	10	12	11	13
[MoO (TATC), Cl,]	46	62	66	45	63	65	[MoO (TATC) ₂ Cl ₂]	8	12	11	13
[MoO (APTC) ₂ Cl ₂]	40	45	53	40	41	55	[MoO (APTC) ₂ Cl ₂]	10	11	12	14
[WO ₂ (AATC) ₂ Cl ₂]	41	53	62	42	55	59	$[WO_2 (AATC)_2 Cl_2]$	12	14	9	12
$[WO_2 (ATC)_2 Cl_2]$	36	43	52	36	40	51	$[WO_2 (ATC)_2 Cl_2]$	8	12	12	14
[WO ₂ (DMBTC) ₂ Cl ₂]	46	55	61	45	56	63	[WO ₂ (DMBTC) ₂ Cl ₂]	12	15	12	10
[WO ₂ (TATC) ₂ Cl ₂]	49	63	68	46	62	67	[WO ₂ (TATC) ₂ Cl ₂]	9	12	10	12
[WO ₂ (APTC) ₂ Cl ₂]	41	46	55	42	44	53	[WO ₂ (APTC) ₂ Cl ₂]	10	13	11	16
Bavistin	33	94	100	85	96	100	Streptomycin	15	19	16	19

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