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

KEYWORDS: Thiosemicarbazone / Schiff bases/ Mo (V) and W (VI) / Biological Activity.

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 APTC), (Mo AATC)] and Tungsten [(W ATC), (W DMBTC), (W TATC), (W APTC), (W AATC)] 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. The chemistry of molybdenum has aroused considerable interest in view of its biological importance. The effect of Mo(V) and W(VI) metal compounds on biological systems has evoked considerable interest. 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 VI chloride (Fluka). Some New Schiff Base Complexes Derived From Thiosemicarbazone

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 continued for 10-15 min. The solid complex that separated was washed with aq. methanol and dried over P₂O₅ 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 [MoO₂(L)]. The molar conductance value of the complexes in DMF at 10⁻³ M dilution shows that the complexes were non-electrolyte.

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. The low intensity absorption peaks in the long wave length region were possibly due to first crystal field transition. The transition were observed at 12820 - 16000 cm⁻¹. The second crystal field transition were observed at 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, Melting Point and IR spectra.

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 Schiff bases were prepared by the condensation of respective aldehyde/ketone with thiosemicarbazide. The amino compound was dissolved in ethanol and refluxed for half an hour.
served at 18750 - 21000 cm\(^{-1}\) due to transition \(^2\)B\(_2\), \(^2\)B\(_1\) (dxy dx\(^2\)-y\(^2\)). The third peak appeared at 22000 - 30000 cm\(^{-1}\) and was due to transition \(^2\)B\(_3\), \(^2\)A\(_1\) (dxy dx\(^2\)-y\(^2\)). The spectral band at 15151 cm\(^{-1}\) indicates octahedral geometry for the complexes in agreement with Ballhausen Gray Scheme\(^{(15)}\).

**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 oxomolybdenum (V) complex showing the absence of any Mo-Mo interaction. Thus the complexes were found to be paramagnetic as expected for a d\(^5\) system\(^{(16)}\).

**I.R. Spectra :**

\[
\text{CH}_2
\]
\[
\text{H}_3\text{C} - \text{C} = \text{N} - \text{N} - \text{C} = \text{S}
\]
\[
\text{Cl} \quad \text{Cl}
\]

**Acetyl acetone thiosemicarbazone molybdenum (V) chloride**

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

**Table-1 CHARACTERIZATION OF OXOMOLYBDENUM (V) COMPLEXES**

| Sl. No. | Name and Molecular Formula of the complex | Colour | M.P./D.T. °C | Elemental Analyses | Molecular Conductance Ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) | Magnetic Moments in B.M. |
|---|---|---|---|---|---|---|
| 1. | Acetyl acetone thiosemicarbazone oxomolybdenum (V) chloride (MoO(C\(_2\)H\(_2\)N\(_2\)S)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) thiosemicarbazone oxomolybdenum (V) chloride (MoO(C\(_2\)H\(_2\)N\(_2\)O\(_2\)S)Cl\(_2\)) | Brown | 259 | 49.94 (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) thiosemicarbazone oxomolybdenum (V) chloride (MoO(C\(_2\)H\(_2\)N\(_2\)O\(_2\)S)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 oxomolybdenum (V) chloride (MoO(C\(_2\)H\(_2\)N\(_2\)S)Cl\(_2\)) | Pale Yellow | 255 | 36.53 (35.62) 3.19 (2.43) 12.09 (11.34) 26.33 (25.91) 26.92 (26.27) | 10 9 16 | 1.64 |
| 5. | Bis (2-acetyl pyridine) thiosemicarbazone oxomolybdenum (V) chloride (MoO(C\(_2\)H\(_2\)N\(_2\)S)Cl\(_2\)) | 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 |

Figures in parenthesis are calculated values.

**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 d\(^6\) system and the stabilization of higher oxidation through complex formation.

**I.R. Spectra :**

In the I.R. spectra of the ligands show two important bands which may be due to \(\text{n} (\text{C=N})\) group & \(\text{n} (\text{C=S})\) 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 I.R. 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-2
CHARACTERIZATION OF DIOXO TUNGSTEN (VI) COMPLEXES

| Sl. No. | Name and Molecular Formula of the complex | Colour | M.P./ D.T. °C | Elemental Analyses | Molar Conductance Ohm⁻¹ Cm² Mol⁻¹ DMF | Magnetic Moments in B.M. |
|---------|------------------------------------------|--------|---------------|-------------------|----------------------------------------|-------------------------|
| 1.      | Acetyl acetone thiosemicarbazone dioxoxotungsten (VI) chloride [WO₄(C₅H₅N₂)_2Cl₂] | Orange | 252 | 23.38 (22.74), 3.11 (2.84), 14.68 (13.27), 11.88 (10.11), 30.56 (29.06) | 2.2 | dia magnetic |
| 2.      | Bis (anisaldehyde) thiosemicarbazone dioxoxotungsten (VI) chloride [WO₄(C₅H₅N₂)_2Cl₂] | Dark Yellow | 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 benzaldehyde) thiosemicarbazone dioxoxotungsten (VI) chloride [WO₄(C₅H₅N₂O₂)_2Cl₂] | 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 dioxoxotungsten (VI) chloride [WO₄(C₅H₅N₂S)_2Cl₂] | 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) thiosemicarbazone dioxoxotungsten (VI) chloride [WO₄(C₅H₅N₂S)_2Cl₂] | 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) |
|-------|----------------------|--------------|
| 1.    | Acetyl acetone thiosemicarbazone | 3410 (s), 2071 (m), 1157 (w), 665 (m), 736 (vs), 3290 (w), 1069 (vs), 1056 (s), 583 (w), 3018 (vw), 1475 (w), 946 (m), 418 (w), 2876 (m), 1286 (m), 824 (vs) |
| 2.    | Bis (anisaldehyde) thiosemicarbazone | 3481 (w), 2071 (m), 1353 (s), 736 (vs), 3316 (w), 1596 (vs), 1229 (m), 574 (m), 3111 (w), 1528 (w), 1068 (m), 335 (w), 2943 (w), 1408 (vw), 915 (m) |
| 3.    | Bis (3,4-dimethoxy benzaldehyde) thiosemicarbazone | 3481 (w), 2018 (m), 1357 (s), 721 (s), 3286 (w), 1604 (vs), 1081 (w), 597 (m), 3146 (w), 1530 (w), 1013 (s), 512 (s), 2886 (m), 1525 (sh), 820 (vs) |
| 4.    | Bis (thiophene-2-aldehyde) thiosemicarbazone | 3304 (w), 1583 (s), 1038 (w), 556 (w), 3081 (w), 1448 (m), 910 (s), 409 (m), 2850 (m), 1363 (w), 868 (w), 345 (w), 2078 (w), 1246 (m), 759 (w) |
| 5.    | Bis (3,4-dimethoxy benzaldehyde) thiosemicarbazone | 3350 (m), 1809 (w), 1238 (m), 683 (m), 3272 (w), 1630 (w), 1173 (s), 547 (m), 2966 (w), 1558 (w), 951 (m), 458 (m), 2825 (w), 1337 (w), 835 (vs) |
| 6.    | Bis (thiophene-2-aldehyde) thiosemicarbazone | 3381 (w), 1601 (s), 1032 (vs), 670 (w), 3312 (w), 1463 (w), 620 (m), 529 (s), 1259 (m), 840 (s), 340 (w), 2226 (vw), 1157 (w), 778 (w) |
| 7.    | Bis (thiophene-2-aldehyde) thiosemicarbazone | 3486 (m), 2829 (w), 1257 (w), 840 (vs), 3216 (w), 2027 (m), 1138 (s), 698 (m), 3105 (w), 1622 (w), 1048 (m), 487 (vs), 2990 (w), 1418 (m), 942 (ww) |
| 8.    | Bis (2-acetyl pyridine) thiosemicarbazone | 3320 (w), 1603 (vs), 1249 (s), 756 (vs), 3200 (m), 1532 (m), 1043 (m), 550 (m), 3020 (w), 1444 (w), 915 (m), 320 (w), 2976 (w), 1358 (m), 848 (m) |
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 alternata, Rhizoctonia 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 campestris. The compound were dissolved in DMF in 500 and 1000 ppm concentrations. The compound 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 complexes arises due to the chelation nature of these complexes arising due to the increased lipophilic nature of the complexes arising due to the chelation 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 of the ligands and their metal complexes.
### Table-5 Fungicidal screening data for the ligands and their metal complexes

| Compound | Inhibition after 96 h(%) (conc. in ppm) | Diameter of Inhibition Zone (mm) (conc. in ppm) |
|----------|----------------------------------------|----------------------------------------------|
| Alternaria alternata | Rhizoctonia batacticola | Staphylococcus aureus | Xanthomonas campestris |
| AATC | 50 100 200 | 50 100 200 | 500 1000 | 500 1000 |
| ATC | 30 42 48 | 34 38 45 | 6 9 | 8 10 |
| DMBTC | 44 55 65 | 40 52 59 | 9 11 | 12 10 |
| TATC | 41 55 60 | 41 62 60 | 6 10 | 8 12 |
| APTC | 36 43 52 | 37 41 52 | 9 12 | 10 13 |
| [MoO (AATC)₂ Cl₂] | 40 55 63 | 45 57 62 | 10 15 | 9 12 |
| [MoO (ATC)₂ Cl₂] | 38 43 53 | 37 48 52 | 7 11 | 10 10 |
| [MoO(DMBTC)₂ Cl₂] | 46 50 65 | 42 55 62 | 10 12 | 11 13 |
| [MoO(TATC)₂ Cl₂] | 46 62 66 | 45 63 65 | 8 12 | 11 13 |
| [MoO (APTC)₂ Cl₂] | 40 45 53 | 40 41 55 | 10 11 | 12 14 |
| [WO₂ (AATC)₂ Cl₂] | 41 53 62 | 42 55 59 | 12 14 | 9 12 |
| [WO₂ (ATC)₂ Cl₂] | 36 43 52 | 36 40 51 | 8 12 | 12 14 |
| [WO₂(DMBTC)₂ Cl₂] | 46 55 61 | 45 56 63 | 12 15 | 12 10 |
| [WO₂ (TATC)₂ Cl₂] | 49 63 68 | 46 62 67 | 9 12 | 10 12 |
| [WO₂ (APTC)₂ Cl₂] | 41 46 55 | 42 44 53 | 10 13 | 11 16 |
| Bavistin | 33 94 100 | 85 96 100 | Streptomycin | 15 19 16 |

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

| Compound | Diameter of Inhibition Zone (mm) (conc. in ppm) |
|----------|-----------------------------------------------|
| Alternaria alternata | Rhizoctonia batacticola | Staphylococcus aureus | Xanthomonas campestris |
| Bavistin | 33 94 100 | 85 96 100 | Streptomycin | 15 19 16 |

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