



Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis and characterization of organic, ligands of 3-(2-thiazolylazo)-2,4-pentandione with aliphatic diamines and their metal complexes

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ABSTRACT

Reaction of 1, 2-diaminoethane with 3-(2-thiazolylazo)-2,4-pentanedione yielded polydentate Schiff base ligand. The existence of this ligand in intra-molecularly bonded keto-imine form has been established with its analytical I.R., ¹H&NMR data. Dibasic tetradentate coordination of the ligand with metals (Ti⁺³, Mn⁺³, V⁺³, Co⁺³, Fe⁺³, MoO(v), Ru⁺³, Ru⁺², & MoO₂(VI) has been established on the basis of analytical, conductometric, magnetic & spectral data.

Key words: 3-(2-Thiazolylazo)-2,4-pentanedione, Schiff base, Keto imine & ¹H NMR spectra.

INTRODUCTION

The polydentate Schiff bases are well known to coordinate with various metal ions to form metallic complexes with theoretical and practical applications of different types (1). A large number of ligands having imine linkages can be synthesized by the reaction between dicarbonyl compound and diamines (2). These ligand systems have gained considerable importance because of their utility as model compounds in bio-inorganic studies as well as their potential as catalyst in many reactions (3). They find application in the determination of transition metal ions (4-6), in the study of acid-base equilibrium (7) and for analytical purposes (8), we report herein the synthesis and characterization of Schiff base derived from 3-(2-thiazolylazo)-2,4-pentanedione with 1,2-diaminoethane.

EXPERIMENTAL SECTION

Carbon, hydrogen and nitrogen percentages were determined by microanalyses (Heraeus Elemental analyzer) and metal contents of complexes by AAS (Perkin-Elmer 2380). The electronic spectra of the compounds were recorded in methanol solution (10⁻⁴M) on a 1601 Shimadzu UV-Vis spectrophotometer, IR spectra (KBr discs) on an 8101 Shimadzu FTIR spectrophotometer, ¹H NMR spectra (CDCl₃ or DMSO-*d*₆) on a Varian 300 NMR spectrometer and mass spectra on a jeol/SX-102 mass spectrometer (FAB using Argon and meta-nitrobenzyl alcohol as the matrix). Molar conductance of the complexes was determined in DMF at 28± 1°C using solution of about 10⁻³M concentration. Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance.

Synthesis of the ligand :

3-(2-thiazolylazo)-2,4-pentanedione was prepared as re-period (22). An ethanolic solution of the diamine (0.01 mol in 20 mL) was added to an ethanolic solution of 3-(2-thiazolylazo)-2,4-pentanedione (0.02 mol, 20 mL) and stirred for -5 h in a closed vessel maintaining the temperature at 60-65 °C, evaporated at reduced pressure and the crystalline compound formed was filtered and recrystallized from hot methanol to get chromatographically (tlc) pure compound.

Synthesis of complex :

An ethanolic solution of metal (II) acetate (0.01 mol, 20ml) was added to an ethanolic solution of the ligand (0.01 mol, 20 ml) and the mixture refluxed on a water bath for -2 h. The solution was kept overnight at room temperature and added to crushed ice, containing -1 g sodium acetate to maintain the pH around 6. The precipitated complex was filtered, washed with excess of water, recrystallized from hot ethanol and dried in vacuum.

RESULTS AND DISCUSSION

The Schiff bases H₂bte, H₂btp, and H₂bth are formed in good yield by the condensation of 3-(2-thiazolylazo)-2,4-pentanedione with 1,2-diaminoethane, 1,3-diaminopropane and 1,6-diaminohexane. Elemental analysis data (Table 1) of the compounds suggest that the condensation of 3-(2-thiazolylazo)-2,4-pentanedione with diamine occurred in the 2:1 ratio as in structure 1 (Scheme 1). The compound is crystalline in nature and is insoluble in water but soluble in organic solvents like benzene CCl₄, petroleum, ether, chloroform and acetone. It formed well defined and crystalline complexes with metal ions. The analytical data (Table 1) together with electrolytic/non-electrolytic nature in DMF (specific conductance <10 Ω⁻¹ cm⁻¹; 10⁻³ M solution) suggest 1:2 M-L (ML) stoichiometry of the complexes.

All the complexes are paramagnetic in nature except those of Co(III), MoO₂ (VI), UO₂ (VI) and Ru (II) complexes, which are diamagnetic in nature.

The molar conductance measurement suggested 1:1 electrolytic nature for Ti(III), Fe(III), Ru(III), Mn (III), Mo (III), V(III) complexes while the complexes of Ru (II), MoO₂(VI) & UO₂(VI) were non-electrolytes.

Magnetic Moment and Electronic Spectra :

The Ti (III) complex shows magnetic moment of 1.96 B.M for one unpaired electron. The higher value may be due to the orbital contribution. The electronic spectra of the chelate shows a single broad band has been observed in 19230 cm⁻¹, for Ti(III) complex derived from the transition ²T_{2g} → ²E_g for an octahedral symmetry (9). This band is unsymmetrical in shape and is indeed made up to two closely shaped bands. The second band appears as a hump and which is due to the presence of Jahn Teller distortion in the complex.

The Co (III) complex shows three absorption bands at 15110, 21095 and 23370 cm⁻¹ which may be assigned to ¹A_{1g} → ³T_{2g}, ¹A_{1g} → ¹T_{1g} and ¹A_{1g} → ¹T_{2g} respectively. These are similar to those reported for six-coordinated Co (III) complexes.

The electronic spectrum of V (III) complexes was recorded in pyridine solution which showed bands at 16000 cm⁻¹ with a shoulder at 21,000 cm⁻¹. The low energy band has been assigned to the ³T_{1g} → ³T_{2g} where as the high-energy band to ³T_{1g} → ³T_{1g}(p) transitions, respectively. These are characteristic of octahedral geometry around V(III) ion, which is further confirmed by the μ_{eff} value in the range of 2.88 - 2.93 B.M. for all V(III) complexes. The electronic spectrum of Mn (III) complexes exhibited an intense charge-transfer band at 27,000 cm⁻¹ and two d-d transitions at 19,000 and 13,000 cm⁻¹. Since, Mn (III) ion is easily reducible, the charge transfer will be from ligands to the metal corresponding to π → t₂ transition. The other two bands may be assigned to ⁵B₁ → ⁵B₂ and ⁵B₁ → ⁵E, respectively. All these are characteristic of square pyramidal geometry (10) around Mn (III) ion and which is further confirmed by the μ_{eff} value in the range of 4.70 - 4.90 B.M. for all Mn (III) complexes.

The electronic spectrum of oxomolybdenum (V) complex suggested that the complex may be considered as octahedral with a strong tetragonal distortion resulting from Mo=O bond. The spectrum exhibited three distinct absorption bands in the ligand field region. The low intensity band at 13,000 cm⁻¹ in the long wavelength region is possibly due to first crystal field transition ²B₂ → E (d_{zy}, d_{yz}, d_{xy}). The second crystal field transition at 19,000 cm⁻¹ is assignable to ²B₂ → B₁(d_{xy} → d_{x² - y²}). The third peak was observed at 30000 assignable to ²B₂ → ²A₁ (d_{xy} - d_{z²}).}}

The electronic spectrum of MoO₂ (VI) complex has a single band due to charge transfer transition.

The magnetic moment for the complex is 2.10 B.M. which is nearly the same as reported for other Ru (III) complexes 19. Three transitions are observed, the first two bands are assigned to ²T_{2g} → ⁴T_{1g}, and ²T_{2g} → ⁴T_{2g} transitions and the third one to ²T_{2g} → ²A_{2g}, ²T_{1g} levels respectively. These are characteristic of octahedral symmetry

The Ru (II) complex is diamagnetic in nature. The electronic spectrum of the complex in CH₂Cl₂ shows a band assigned to the charge transfer transition arising from the excitation of an electron from the metal t_{2g} level to the unfilled molecular orbitals derived from the π* level of the ligand in accordance with the assignments made for other similar octahedral ruthenium (II) complexes (11-13).

The Fe (III) complex shows exhibits three bands at 12,700, 19,600 and 25,000 cm^{-1} due to ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}$ (G) transitions respectively is an octahedral symmetry.

Infra Red Spectra :

The IR spectra of the Schiff base showed four strong bands at ~ 1680 , 1630, 1620 and 1615 cm^{-1} . The band at ~ 1680 cm^{-1} is due to conjugated free acetyl carbonyl. The remaining three bands are due to C=N of hydrazone, imine and thiazole groups (14). A prominent band appeared at ~ 1540 cm^{-1} is due to NH deformation vibration. Several medium intensity bands appeared in the 1580-1600 cm^{-1} region of the spectra are due to the stretching of various C=C vibrations. That the compounds exist in the intramolecularly hydrogen bonded form (15) is clearly evident from the broad band appeared at 2810 cm^{-1} . In the IR spectra of all the complexes the strong band at ~ 1680 cm^{-1} due to conjugated free acetyl carbonyl group of the ligand remain unaffected indicating its non-involvement in complexation. The strong band at ~ 1620 cm^{-1} of the free ligand due to $\nu\text{C}=\text{N}$ (imine) shifted to low wave number and appeared as a prominent band in the 1550-1600 cm^{-1} region. The hydrazone and thiazole $\nu\text{C}=\text{N}$ are only marginally affected in the spectra of all the complexes. These indicate that the imine and one of the hydrazone nitrogens are involved in bonding with the metal ion (16). The replacement of the NH proton by metal ion is clearly indicated from the disappearance of the NH deformation band of the free ligand at 1540 cm^{-1} in the spectra of all the complexes. The broad band in the region 810 cm^{-1} cleared up in the spectra of all the complexes confirming the replacement of the hydrogen bonded NH proton by metal ion. The presence of new medium intensity bands appeared in the 500-550 cm^{-1} region assignable to $\nu\text{M}-\text{N}$ in the spectra of all the complexes (17) also support round structure.

The IR spectra of all the complexes excepted of MoO_2 (V), CuO_2 (VI) show some additional bands in the range of 3450 - 3510 cm^{-1} , 835-859 cm^{-1} and 740-750 cm^{-1} which may be due to the presence of coordinated water molecules.

The IR spectrum of MoO_2 (VI) complex shows a bands at 945 and 905 cm^{-1} assignable to $\nu_{\text{sy}}(\text{O}=\text{Mo}=\text{O})$ and $\text{Mo}=\text{O}$, which indicated the presence of cis MoO_2 moiety. The IR spectrum of UO_2 (VI) complex shows bands at $\nu_{\text{asy}}(\text{O}=\text{U}=\text{O})$ at 905 cm^{-1} which suggested the presence of trans $\text{O}=\text{U}=\text{O}$ moiety. The $\text{MoO}(\text{V})$ complex shows a band at 955 cm^{-1} due to the presence of $\text{Mo}=\text{O}$ moiety.

${}^1\text{H}$ NMR Spectra :

In the ${}^1\text{H}$ NMR spectra of the Schiff bases, no signals were observed above δ 10 ppm assignable to intramolecularly hydrogen bonded N-H...O=C/O-H...N groups of the keto-hydrazone/azo-enol forms typical of arylazo derivatives of acetylacetone (18-20). The spectra of all the compounds show a two proton signal at $-\delta$ 9.50 ppm due to the intramolecularly hydrogen bonded N-H...N protons (21). The methylene and thiazolyl protons show signals at positions as expected. The spectra showed two six proton singlets at δ 2.20 - 2.60 ppm due to methyl groups. The integrated intensities of all the signals agree well with the structure of the compounds. In the ${}^1\text{H}$ NMR spectra of the complexes, signal due to the NH protons of the free ligand disappeared indicating the replacement of these protons by metal ions. Integrated intensities of all other protons agree well with the 1:1 metal ligand stoichiometry of the complexes.

Table-1 : Physical Data of Ligand and its Complexes

Sl No	Molecular Formula of Ligand/Complex	M.P. $^{\circ}\text{C}$	Colour	Elemental analyses				Magnetic Moments in (B.M.)	Molar Conductance $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in DMF	
				% of C	% of H	% of N	% of M			
1	$[\text{C}_{18}\text{H}_{22}\text{N}_8\text{O}_2\text{S}_2]$ ligand	85	Yellow	48.43 (48.88)	4.74 (4.93)	24.98 (25.11)	-	-	-	
2	$[\text{Ti}(\text{C}_{18}\text{H}_{20}\text{N}_8\text{O}_2\text{S}_2)_2 \cdot 2\text{H}_2\text{O}] \text{Cl}$	135	Dark Yellow	42.78 (42.81)	4.51 (4.55)	12.62 (12.68)	4.71 (4.75)	1.71	65	1:1 elect.
3	$[\text{V}(\text{C}_{18}\text{H}_{20}\text{N}_8\text{O}_2\text{S}_2)_2 \cdot 2\text{H}_2\text{O}] \text{Cl}$	137	Light Yellow	42.61 (42.68)	4.50 (4.54)	12.60 (12.64)	4.98 (5.03)	2.80	70	1:1 elect.
4	$[\text{Mn}(\text{C}_{18}\text{H}_{20}\text{N}_8\text{O}_2\text{S}_2)_2 \cdot 2\text{H}_2\text{O}] \text{Cl}$	139	Brown	42.49 (42.51)	4.51 (4.52)	12.54 (12.59)	5.03 (5.41)	5.40	75	1:1 elect.
5	$[\text{Co}(\text{C}_{18}\text{H}_{20}\text{N}_8\text{O}_2\text{S}_2)_2 \cdot 2\text{H}_2\text{O}] \text{Cl}$	140	Reddish Brown	42.18 (42.35)	4.49 (4.50)	12.51 (12.54)	5.72 (5.78)	Dia magnetic	65	1:1 elect.
6	$[\text{Fe}(\text{C}_{18}\text{H}_{20}\text{N}_8\text{O}_2\text{S}_2)_2 \cdot 2\text{H}_2\text{O}] \text{Cl}$	138	Dark brown	42.40 (42.47)	4.51 (4.52)	12.53 (12.58)	5.48 (5.50)	4.68	70	1:1 elect.
7	$[\text{Ru}(\text{C}_{18}\text{H}_{20}\text{N}_8\text{O}_2\text{S}_2)_2 \cdot 2\text{H}_2\text{O}] \text{Cl}$	178	Green	40.62 (40.67)	4.29 (4.33)	11.99 (12.05)	9.49 (9.51)	1.96	70	1:1 elect.
8	$[\text{Ru}(\text{C}_{18}\text{H}_{20}\text{N}_8\text{O}_2\text{S}_2)_2 \cdot 2\text{H}_2\text{O}]$	169	White	42.00 (42.06)	4.45 (4.47)	12.42 (12.46)	9.79 (9.83)	Dia magnetic	Non electrolyte	
9	$[\text{MoO}(\text{C}_{18}\text{H}_{20}\text{N}_8\text{O}_2\text{S}_2)_2 \cdot \text{H}_2\text{O}] \text{Cl}$	180	Yellow	41.49 (41.53)	4.19 (4.23)	12.28 (12.30)	9.18 (9.23)	1.84	70	1:1 elect.
10	$[\text{MoO}_2(\text{C}_{18}\text{H}_{20}\text{N}_8\text{O}_2\text{S}_2)_2]$	176	White	41.28 (41.41)	4.20 (4.21)	12.20 (12.27)	9.19 (9.20)	Dia magnetic	Non-Electrolyte	

Calcld. values are given in brackets.

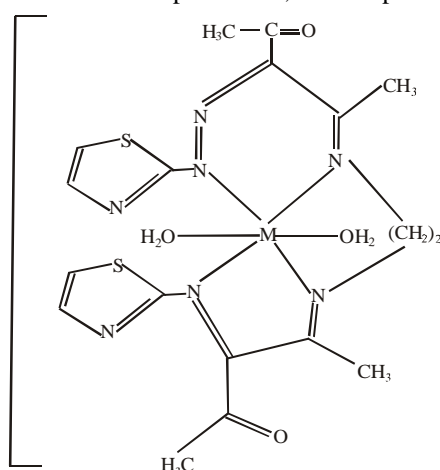
Fungicidal activity:

To evaluate fungicidal activity of the ligand and its corresponding metal complexes, their effect on the growth of *Aspergillus flavus*, *Curvularia lunata* and *Penicillium notatum* was studied. The ligand and its corresponding metal chelates in DMF were screened by mycelia dry weight method in vitro for their fungicidal activity in glucose nitrate media. The ligand exhibited 20-25 and 30-35% inhibition for 125 and 250 ppm concentration respectively, it is observed that the metal complexes show enhanced antifungal activity as compared to the ligand. This is because of chelation, which reduces the polarity of metal ion due to partial sharing of its positive charge with donor groups and also due to delocalization of p-1 electrons over whole chelate ring. Thus chelation increase lipophilic character in the complexes and results in the enhancement of activity. The inhibition by metal complexes has been increased by 30-65% and 40-70% for 12 and 250ppm concentration respectively. The order of inhibition with respect to metal ions $\text{Mo(V)} > \text{V} > \text{Ti} > \text{Ru}$.

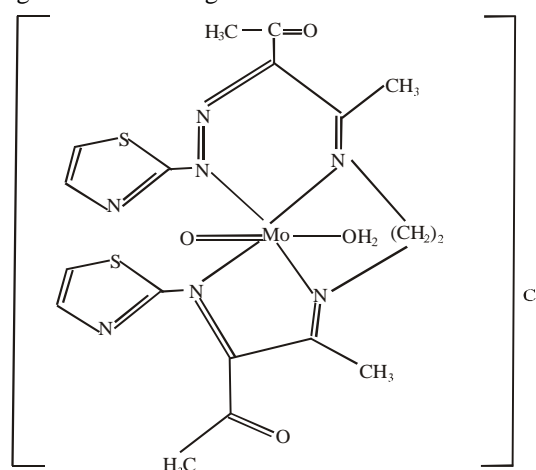
CONCLUSION

Three new Schiff base ligands have been prepared by the condensation of 3-(2-thiazolylazo)-2,4-pentanedione with 1,2-diaminoethane. Analytical, IR & ^1H NMR data revealed a 2:1 product in which one of the carbonyl group of the diketone is involved in Schiff base formation. Analytical, physical and spectral data of the [ML] complexes showed the dibasic tetradentate N_4 coordination involving, the imino and hydrazone nitrogens while the carbonyl groups are excluded from coordination.

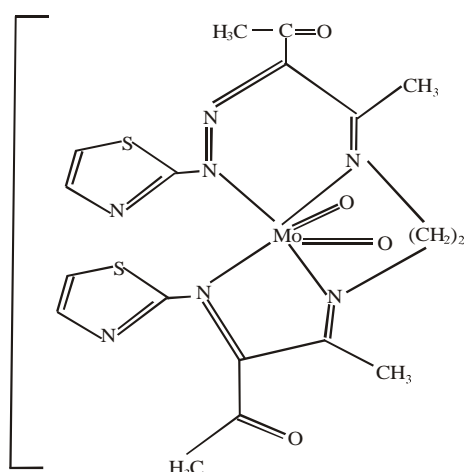
On the basis of studies performed, the complexes may be assigned the following octahedral structures.



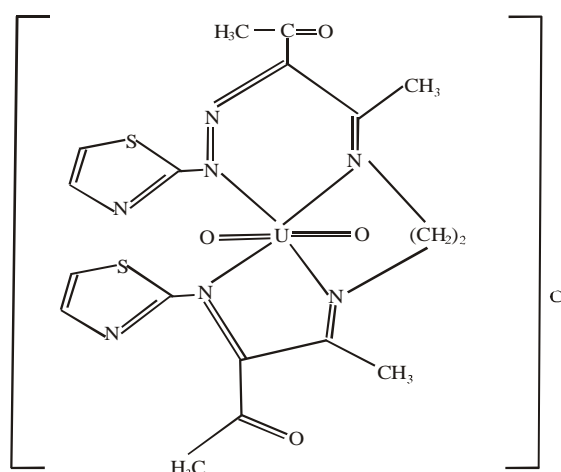
M= Ti(III), Fe(III), V(III), Ru(III), Co(III) or Mn(III)



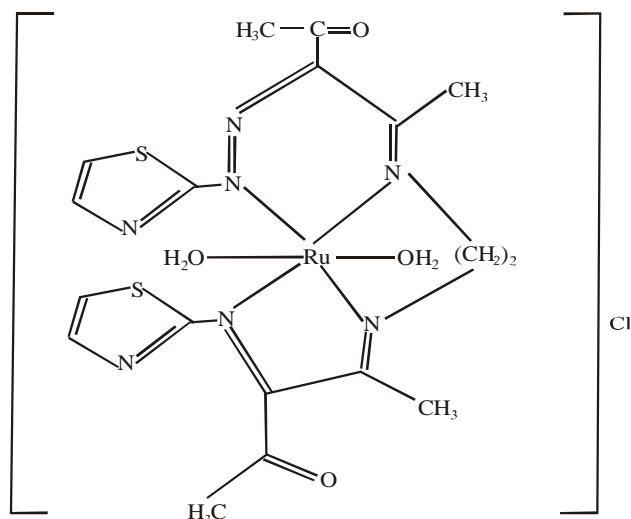
MoO (V) Complex



MoO₂(VI) Complex



UO₂(VI) Complex



Ru (II) Complex

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