



SYNTHESIS AND CHARACTERIZATION OF SOME TRANSITION METAL COMPLEXES WITH TRIDENTATE N3 DONOR SCHIFF BASE DERIVED FROM 2-AMINOTHIAZOLE

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A 2,6-diacetylpyridine based novel acyclic tridentate compartmental ligand (E)-N-(1-(6-((E)-1-(thiazol-5-ylimino)ethyl)pyridin-2-yl)ethylidene)thiazol-2-amine was prepared by condensation of 2,6-diacetylpyridine and two equivalent of 2-thiazolamine in ethanol. The reaction of metal chlorides (Mn(II), Co(II), Ni(II), Cu(II), Zn(II)) and VOSO₄·5H₂O with the new ligand in methanol results the formation of deep colored metal complexes with the formula [MLCl]Cl (M=Mn, Ni, and Zn), [MLCl₂(H₂O)], M=Co, Cu(II), and [VOL(SO₄)], respectively. The free ligand and its metal complexes were characterized by elemental analyses, conductivity measurements, magnetic susceptibility data, IR, UV-Vis and NMR spectral data. The physical measurements and FTIR spectral data showed that most of the complexes contain tetrahedrally coordinated central ion(II) except the square-pyramidal vanadyl complex and octahedral geometry for Co(II) and Cu(II) complexes.

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Introduction

The presence of exocyclic nitrogen and sulphur atoms in the structure of Schiff bases gives mutative ability to coordination sites to link directly with the transition metal ions.¹⁻² Azomethine ligands involving thiazole ring have attracted the chemists to prepare novel metal chelate due to their importance in antimicrobial, anti-inflammatory, and anti-HIV applications.³⁻⁵ Aljibouri and co-workers⁶⁻⁹ have been synthesized and studied the biological effect of Cr(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) chelates with N5 donor Schiff bases derived from 2,6-diacetylpyridine.¹⁰⁻¹³ Due to the growing interest of metal chelates involving heterocyclic rings, here we report the synthesis and characterization of some first row transition metal complexes with new Schiff base derived from condensation of 2,6-diacetyl pyridine and 2-thiazolamine.

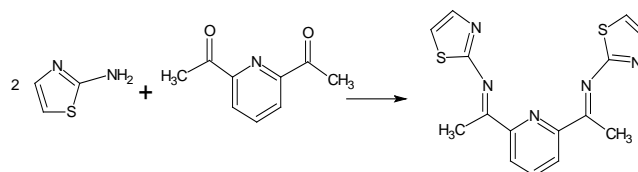
Experimental

All the organic chemicals and solvents used were analytical grade and procured from Sigma-Aldrich Co. The hydrated metal(II) chlorides of manganese, cobalt, nickel, copper(II), anhydrous zinc(II) chloride and vanadyl sulphate were purchases from Sigma-Aldrich company. As well as the 2,6-diacetylpyridine and 2-aminothiazole were used without any purification. The solvents used were ethanol, deuterated dimethyl sulfoxide (DMSO-d₆), methanol and DMF.

Electronic spectra were recorded in the region 800-200 nm on a Shimadzu 670 spectrophotometer. IR-spectra were recorded in the range of 200-4000 cm⁻¹ on a Shimadzu PC FT-IR spectrophotometer in KBr and CsI discs. The ¹H NMR spectra of the ligand were recorded in DMSO-d₆ on a 300 MHz Bruker spectrometer. The effective magnetic moment measurements of the solid complexes were carried out an MG Magnet Balance. The molar conductance of metal complexes in N,N-dimethylformamide (DMF) solution were measured with using a HPG G-3001 digital conductivity meter. The carbon, hydrogen, nitrogen and sulphur analysis were done on a Carlo Erba 1108 elemental analyzer. The metal content of complexes were measured with using a Shimadzu 670 spectrophotometer with standard addition method.¹⁴

Synthesis of the Ligand (L)

The ligand was prepared by the mixing of hot ethanolic solution (20 mL) of 2-aminothiazole (2 g, 0.02 mol) and an ethanolic solution (20 mL) of 2,6-diacetylpyridine (1.63 g, 0.01 mol) with constant stirring in the presence of few drops of 36 % HCl. This mixture was refluxed for 4 h then allowed to cool overnight at 20 °C. The isolated light yellow colored precipitate was filtered off, washed with cold EtOH and dried under *vacuum* over anhydrous MgSO₄. Yield (80 %), mp. 155-157 °C. Element chemical analysis data is shown in Table 1.



Scheme 1. Preparation of the ligand

Preparation of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and VO(IV) complexes

Methanolic (25 ml) solution of metal chlorides or $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (1 mmol) was added to methanolic solution of the ligand (0.327g, 1 mmol) with keeping the pH to be neutral. The resulting mixture was refluxed on a water bath for 2-3 h then cooled to room temperature to afford deep colored precipitates of metal complexes.

Result and Discussion

The new acyclic Schiff base L ligand derived from condensation of 2,6-diacetylpyridine and two equivalents of 2-aminothiazole behaves as a tridentate chelating agent toward the studied metal ions. The stoichiometry of the ligand and its complexes were confirmed by their elemental analysis (Table 2). The Mn(II), Zn(II) and Ni(II) complexes showed 54-78 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ molar conductivity in DMF while the vanadyl(IV), cobalt(II) and copper(II) complexes gave 18-24 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ values, thus these later complexes proved to be non-electrolytes.¹⁵

The proton NMR spectrum of the ligand, figure(1), can be classified into two distinct classes, the methyl ($\text{C}=\text{N}-\text{CH}_3$), and aromatic protons appear as singlet peaks and resonate in the ranges 3.6-3.88 ppm and 7.5-8.4 ppm respectively.^{12,16} Deshielding and splitting of signals in the ^1H NMR spectrum of $\text{Zn}[\text{LCl}]\text{Cl}$ complex in $\text{DMSO}-d_6$ show the changes in electron density due to coordination of the nitrogen atoms of $-\text{C}=\text{N}-$ to Zn(II) ion causing the shift of proton resonance toward deshielded field¹⁶ (Figure 2.).

Electronic spectra and Magnetic moments

The free ligand in abs. EtOH shows high intensity peaks at 255 and 388 nm that related to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of $\text{C}=\text{N}$ -, $\text{C}=\text{O}$ and $\text{C}=\text{C}$ - groups.¹⁷ (Table 2). The electronic spectra of the metal(II) complexes were recorded in DMF. The pale olive solution of VO(IV) complex exhibits two weak spin allowed peaks in the region 610-510 nm that are consistent with d-d transitions of square pyramidal oxovanadium(IV) complexes.

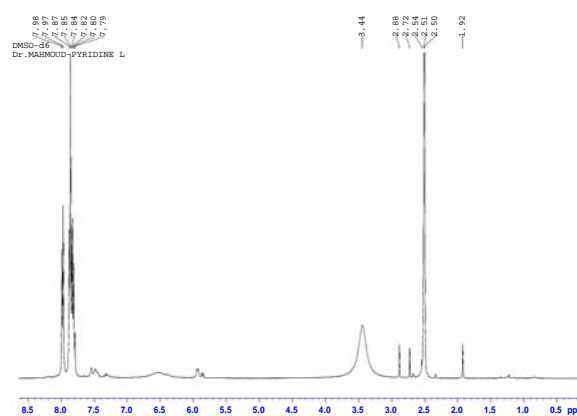


Figure 1. ^1H NMR spectrum of Schiff base ligand in $\text{DMSO}-d_6$

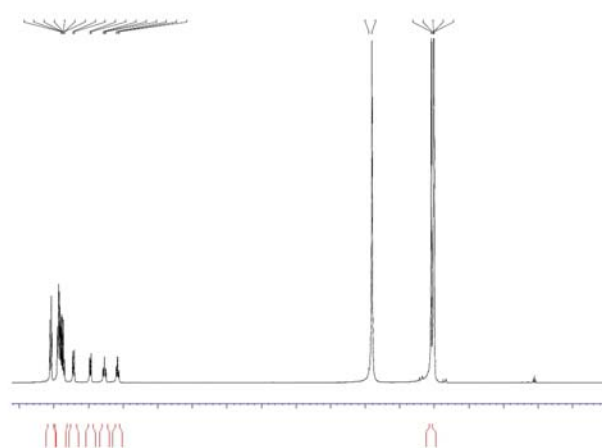


Figure 2. ^1H NMR spectrum of $[\text{ZnLCl}]\text{Cl}$ in $\text{DMSO}-d_6$

The spectrum of the Mn(II) complex exhibits bands at 440 nm and 388 nm belong to d-d and charge transfer, respectively confirming the high spin octahedral symmetry around manganese(II) ion.¹⁸ The magnetic moments for Mn, Co and Ni(II) complexes were 5.64, 3.66. and 3.96 *B.M.* which revealed the magnetic properties of well agreement with their electronic spectra.¹⁹⁻²⁰

Table 1. Physical properties and elemental analyses of prepared compounds

Compound	Color	M.P., °C	C% Calc. (found)	H% Calc. (found)	N% Calc. (found)	S% Calc. (found)	M% Calc. (found)
L	Yellow	155-157	55.02 (54.98)	4.01 (3.60)	21.39 (20.83)	19.59 (18.88)	-
$[\text{VOL}]\text{SO}_4$	Olive	177-179	39.37 (38.81)	3.49 (3.11)	13.47 (14.07)	18.53 (18.00)	9.82 (8.696)
$[\text{MnLCl}]\text{Cl}$	Dark yellow	222 ^d	43.66 (42.78)	4.59 (4.21)	13.88 (14.00)	13.22 (12.88)	11.76 (10.80)
$[\text{CoL}(\text{H}_2\text{O})\text{Cl}_2]$	Dark green	212 ^d	40.24 (39.71)	4.19 (3.92)	13.86 (14.99)	12.69 (12.00)	11.66 (10.99)
$[\text{NiL}]\text{Cl}$	Brown	225 ^d	42.03 (41.09)	3.74 (3.66)	11.97 (12.11)	10.77 (9.66)	10.54 (10.11)
$[\text{CuL}(\text{H}_2\text{O})\text{Cl}_2]$	Pale brown	231 ^d	40.06 (39.51)	4.15 (3.81)	13.76 (14.10)	12.44 (11.61)	11.35 (10.88)
$[\text{ZnLCl}]\text{Cl}$	White off	241	38.88 (37.87)	3.65 (3.11)	10.28 (11.11)	8.56 (8.03)	10.36 (9.32)

Table 2. Electronic spectral, magnetic moment and molar conductance data of the metal(II) complexes

Compound	λ_{\max} , nm	Band assignment	Λ , S mol ⁻¹ cm ⁻²	μ , B.M.	Geometry
L	255 338	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	10		—
[VOLSO ₄]	610 510 355	${}^2B_{1g} \rightarrow {}^2B_{2g}(D)$ ${}^2B_{1g} \rightarrow {}^2E_{2g}(D)$ ${}^2B_{1g} \rightarrow {}^2A_{1g}(F)$	22	1.55	Square pyramidal
[MnLCl]Cl	440 366	${}^6A_1 \rightarrow {}^4T_1(F)$ ${}^6A_1 \rightarrow {}^4E_1(F)$	60	5.64	Tetrahedral
[CoL(H ₂ O)Cl ₂]	780 660 398	${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$ ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$ LMCT	24	3.66	Octahedral
[NiLCl]Cl	699 612 388	${}^3T_1 \rightarrow {}^3T_2$ ${}^3T_1 \rightarrow {}^3A_2$ LMCT	78	3.96	Tetrahedral
[CuL(H ₂ O)Cl ₂]	710 404 311	${}^2B_{1g} \rightarrow {}^2A_{1g}$ ${}^2B_{1g} \rightarrow {}^2B_{1g}$ MLCT	18	1.72	Octahedral
[ZnLCl]Cl	390 255	CT $\pi \rightarrow \pi^*$	54	0	Tetrahedral

C.T=Charge transfer,m=molar conductivity in DMF solutions(ohm⁻¹.cm².mol.⁻¹)

The vanadyl complex recorded paramagnetic properties with 1.55 *B.M.* value suggesting the square pyramidal geometry around V(IV) ion. The cobalt(II) complex in its DMF solution showed two weak bands in the visible region at 660-780 nm, respectively, these absorptions support the octahedral structure of Co(II) complex.^{19,21} The electronic spectra of Cu(II) complex displays two prominent bands. A low intensity broad band around 404-710 nm is assignable to ${}^2T_{2g} \rightarrow {}^2E_g$ transition. The other high intensity band at 300 nm belongs to a symmetry forbidden ligand to metal charge transfer. On the basis of electronic spectrum, a distorted octahedral geometry of Cu(II) ion can be suggested.²²⁻²³ The Cu(II) complex showed magnetic moment 1.72 BM, is slightly higher than the spin-only value 1.73 BM expected for one unpaired electron, which offers possibility of an octahedral geometry.

The electronic spectra of the Mn(II) complex display weak absorption bands in the region 440-3660 nm supporting the electronic transitions of high spin Mn(II) tetrahedral.²² In contrast, the red solution of Ni-complex in DMF shows two low energy bands in the region 612-699 nm that are related to tetrahedral geometry around nickel(II) ion.²⁰

IR spectra

The infrared spectral data of the ligand and its metal complexes are presented in Table 3. The IR spectra of the Schiff base exhibited characteristic band of C=N- and C-S groups at 1640 cm⁻¹ and 1000-1070 cm⁻¹, respectively.²³

The strong band at 1614 cm⁻¹ and a characteristic weak intensity band at 3090 cm⁻¹ in the IR spectra of the Schiff base are assigned to C-H stretching of pyridine moiety. The disappearance of strong absorptions in the region 1730-1690 cm⁻¹ of carbonyl groups related to 2,6-diacetylpyridine gives good indication to condensation with the -NH₂ group of 2-aminothiazole to form the new Schiff base L that is involving-C=N-moiety.²⁴ All the metal complexes showed a downshift in the wavenumbers of C=N- stretching in the region 1522-1633 cm⁻¹ which reveals the coordination of nitrogen atoms to the central metal ions. The weak bands appeared in the region 490-533 cm⁻¹ belongs to M-N bonds²⁵ support this conclusion. The bands in the region 250-389 cm⁻¹ can be ascribed to (M-Cl) bond formation.²³

The FTIR spectra of all complexes in CsI disc showed downshift in the wavenumbers of imine group of range 1522-1633 cm⁻¹ that support remarkably the bonding of nitrogen atoms of -C=N- to metal ions. The IR spectral results provide strong evidence for the interaction of the Schiff base with metal ions in a supposed tridentate N₃ mode. The vanadyl complex in CsI disc showed strong and medium absorptions at 989 and 412 cm⁻¹ that were assignable to vibrational modes of V=O and M-O bonds, respectively.²⁵

The cobalt(II) and copper(II) complexes display broad bands in the region 3550-3600 cm⁻¹ which indicate the presence of coordinated water molecules in the structure of the two mentioned complexes. The spectra of metal complexes do not show changes in intensity and position of C-S²⁶⁻²⁷ bonds, thus it confirms the lack of S-metal coordination.

Table 3. Selected vibrational FTIR absorptions for the free ligand and its metal(II) complexes

Compound	$\nu\text{C=N}$	$\nu\text{C-S}$	$\nu\text{M-N}$, $\nu\text{M-Cl}$	Other bands
L	1640(s)	1070-1000(s)	—	
[VOL]SO ₄	1630-1590(s)	1067-1005	490-533.	988 ^b , 412 ^c
[MnLCl]Cl	1600-1588	1068-1010 (s)	460-488, 389	3022
[CoL(H ₂ O)Cl ₂]	1610-1577	1072-1000 (s)	517(w), 300	3600 ^a
[NiLCl]Cl	1590-1533	1065-1007	510(w), 250-322	2965
[CuL(H ₂ O)Cl ₂]	1543-1522	1062-1000	568, 278-344	466 ^c , 3550 ^a
[ZnLCl]Cl	1633-1559	1066-1009	422, 370(w)	3070, 2964

s=strong, m=medium, br=broud, w=weak, a=broad band of H₂O molecules coordinated to Co(II) and Cu(II) b - V=O and c - M-O bonds.

Conclusions

The complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and vanadyl(IV) with Schiff base derived from 2,6-diacetylpyridine and 2-aminothiazole were synthesized and characterized. The Schiff base act as versatile tridentate ligand. The Co(II) and Cu(II)-complexes have octahedral geometry, Mn(II), Ni(II) and Zn(II) complexes are tetrahedral and vanadyl complex has square-pyramidal structure with monocoordinated sulphate ion.

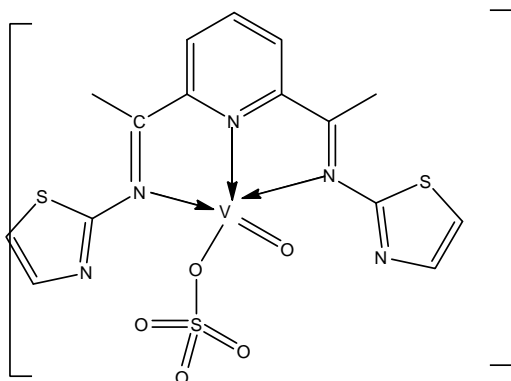


Figure 3. The proposed structure of vanadyl-complex.

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