



Synthesis and characterization of some transition metal (II) complexes with 1,2,4-triazole schiff base

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ABSTRACT

New five metal complexes of Cu(II), Cd(II), Sn(II), Zn(II) and Ni(II) with Schiff base ligand 4-(Benzyldene-amino)-5-pyridin-4-yl-4H-[1,2,4]triazole-3-thiol were synthesized in ethanol as a solvent. The new compounds were characterized by different physicochemical techniques such as melting point, flame atomic absorption, elemental analysis C.H.N.S, FT-IR, UV-visible spectrophotometry, ¹H NMR, conductivity and magnetic susceptibility measurements. The Schiff base ligand acted as bidentate and coordinated to the metal atoms via the azomethine-N and S atom of thiol group. From the spectral studies, square planar geometry was proposed for the copper complex. The other complexes were proposed to be tetrahedral.

Keywords: Schiff base; 1,2,4-triazole; Metal complexes; bidentate

INTRODUCTION

Workers interested in synthesizing and studying the structural aspects of metal complexes containing sulphur and nitrogen donor ligands because of their increasing physiological importance and the active role played by certain metal ions coordinated to them [1-4]. The chemistry of 1,2,4-triazole compounds has attracted widespread attention due to their diverse biological activities, especially as antimicrobial agents [5]. Triazole are heterocyclic compound featuring five member ring of two carbon atoms and three nitrogen atoms as part of the aromatic system [6]. There are two types of triazoles, the 1,2,3-triazoles and the 1,2,4-triazoles [7,8]. Tautomerism form could occur in triazole [9]. Several compounds containing 1,2,4-triazole ring are well known for drug synthesis [10]. 1,2,4-Triazole containing amino group is also important for obtaining various Schiff's bases with well-established antimicrobial properties [11]. The synthesis of high nitrogen containing heterocyclic systems has been attracting increasing interest over the past decade because of their utility in various applications[12].

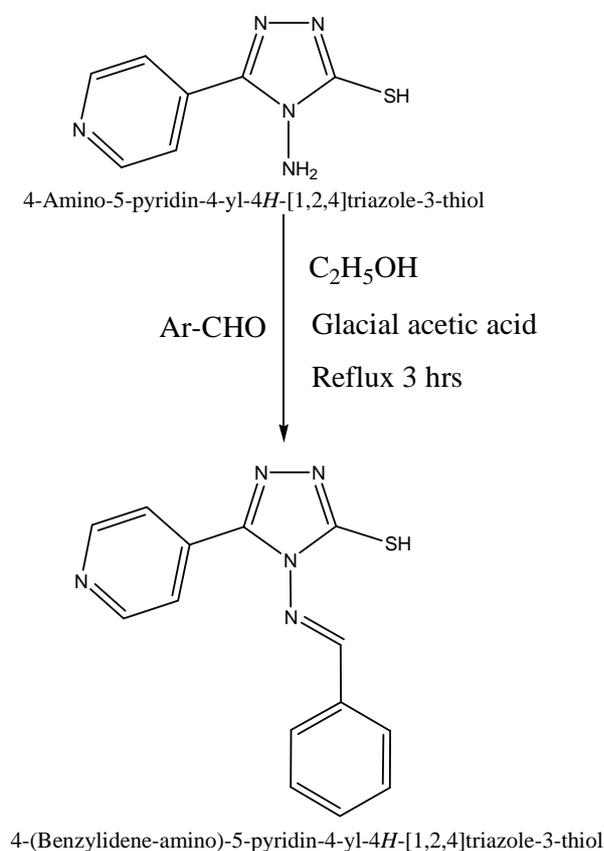
Schiff's bases are the compounds containing azimethine group (HC=N). They are condensation products of ketones or aldehydes with primary amines and were first reported by Hugo Schiff in 1864 [13]. Schiff's bases of aliphatic aldehydes are relatively unstable and are readily polymerized while those of aromatic aldehydes, having an effective conjugation system, are more stable. Schiff's bases derived from triazole were reported to possess antimicrobial, anti anxiety, anti depressant, plant growth regulatory activity [14]. As ligands, Schiff's bases have been extensively studied. The azomethine group (HC=N), supported by other electron donor groups form stable chelates with many metal ions. Schiff's bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules [15]. The attention Schiff base metal complexes have earned was because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [16,17,18]. In this work, we report the preparation of a new series of some of such metal complexes.

EXPERIMENTAL SECTION

All used chemicals were of analytical analar grade. Metal salts used in this study are Copper acetate $\text{Cu}(\text{CH}_3\text{CO}_2)_2$, Cadmium acetate dihydrate $\text{Cd}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, Tin chloride SnCl_2 , Zinc acetate dihydrate $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ and Nickel nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The metal analyses were performed by using GBS-933 Flame Plus Atomic Absorption Spectrophotometer. The elemental Analysis (C.H.N.S) of compounds was carried out with EM-1108. The electronic spectra were recorded on a Shimadzu UV-160 Spectrophotometer. FTIR spectra were recorded using FTIR.8300 Shimadzu spectrophotometer as CsI disc. Magnetic susceptibility measurements were determined using Magnetic Susceptibility Balance Johnson Matthey at room temperature. The molar conductance was measured in ethanol as a solvent at room temperature using WTW conductometer. Melting point apparatus of Gallen Kamp M.F.B-60 was used for the determination of melting points. The spectra of ^1H NMR were recorded on a Bruker Ultrasheid 300 MHZ, using deuterated DMSO- d_6 as the solvent and tetramethylsilane, TMS as the internal standard.

2.1. Synthesis of 4-(Benzylidene-amino)-5-pyridin-4-yl-4H-[1,2,4]triazole-3-thiol (L)

The Schiff base ligand was prepared by the condensation of respective aldehyde & amino compound. A mixture of 4-Amino-5-pyridin-4-yl-4H-[1,2,4]triazole-3-thiol (1g, 0.005mol), benzaldehyde (0.005mol) and 4-5 drops of glacial acetic acid in ethanol medium was refluxed for 3 hrs [19]. The resulting solution was cooled to room temperature and the precipitated solid, was filtered, washed with cold ethanol and recrystallized from hot ethanol, Scheme 1.



Scheme 1. General step of preparation of the ligand (L)

2.2. Synthesis of metal complexes:

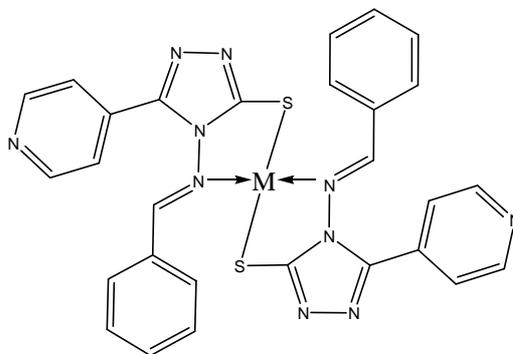
A solution of the suitable metal salt [Copper (II) acetate, Cadmium (II) acetate dihydrate, Tin (II) chloride, Zinc (II) acetate dihydrate, Nickel (II) nitrate hexahydrate], a hot solution of the ligand were mixed in 2:1 (ligand : metal) molar ratios. The resulting mixture was stirred under reflux for 1h whereupon the crystalline colored complexes precipitated. Thereafter, crystalline complexes slowly separated. The complexes were filtered and washed with hot alcohol. The products were dried at room temperature [20].

RESULTS AND DISCUSSION

The physical analytical data, melting point and elemental analysis of ligand (L) and its complexes are given in Table 1. The percent's of Cu(II), Cd(II), Sn(II), Zn(II) and Ni(II) in metal chelates were estimated by flame atomic absorption spectroscopy (F.A.A.S) using GBS-933 Flame Plus Atomic Absorption Spectrophotometer. The calculated values were in good agreement with the experimental values and the melting points were sharp, indicating the purity of the prepared compounds.

3.1. FTIR spectra

The structure of the prepared ligand (L) and the metal (II) complexes were confirmed by infrared spectroscopy. The characteristic bands in the IR spectra of ligand (L) and its metal (II) complexes are reported in Table 2. The disappearance of original bands at 3250, 3213 and 1699 cm^{-1} due to amino (NH_2) and aldehyde (CHO) groups and, in turn, the appearance of a new band at 1656 cm^{-1} assigned to the azomethine ($-\text{C}=\text{N}$) linkage provided a clue to the condensation of amine with aldehyde resulting in the formation of the desired Schiff base [21]. The IR spectra of the Schiff base ligand exhibited bands at 2660, 1629, 1656, 1570, 3032 and 682 cm^{-1} respectively assigned to the vibrations (S-H), (C=N) triazole ring, (C=N) azomethine, (C=C), (C-H) aromatic and the last one is for stretching of (C-S) bond [22,23]. The tautomerism form could occur in triazole. As a result, the band at 1286 cm^{-1} assigned to the (C=S) vibrations could be observed in the spectra of the ligand [24]. It is reasonable to expect deprotonation of the ligand molecules before complexation; the complete disappearance of the band due to ν (S-H) in the spectra of the complexes unambiguously supports this view [20]. The Schiff base ligand possessed potential donor sites such as the azomethine linkage ($-\text{C}=\text{N}$), and the S atom of thiol group, which have a tendency to coordinate with the metal ions [23]. The azomethine group, appearing at 1656 cm^{-1} in the free ligand, is shifted to lower frequency by 3-12 cm^{-1} in the complexes, and a new band appearing at 528-539 cm^{-1} due to $\nu(\text{M}-\text{N})$ vibrations indicating the involvement of azomethine nitrogen atom in coordination [25]. However, the band appearing at 682 cm^{-1} due to (C-S) vibration in the spectra of the ligand shifted to a higher frequency by 2-16 cm^{-1} due to increasing of the bond order of carbon-sulphate bond, indicating the participation of the S atom in complexation. This coordination was supported by the appearance of a new band at 427-454 cm^{-1} assigned to (M-S) [26]. All other bands such as C=C, C-H aromatic remain unchanged in the spectra of the ligand and their corresponding metal complexes because they are not participating in the complexation [27]. Thus, these results establish that the ligand chelates with metal ions through the deprotonated sulphur of the (thiol) group and the nitrogen of the Azomethine group as bidentate ligand, Fig. 1.



Where M = Cu (II), Cd(II), Sn(II), Zn(II) or Ni(II)

Figure 1. structure of the complexes

Table 1 Physical data of new ligand (L) and its metal complexes

Compound	Colour	M.P.(°C)	Yield (%)	Molar ratio M:L	M. Wt.	Elemental analysis theoretical (Experimental) %				Metal percentage	
						C %	H %	N %	S %	Found	Calc.
L	Yellow	215-217	67	----	281.34	59.78 (59.75)	3.91 (3.80)	24.91 (24.38)	11.38 (10.20)	----	----
CuL ₂	Dark green	241-243	88.2	1:2	626.22	53.71 (52.85)	3.51 (3.33)	22.38 (21.74)	10.23 (9.65)	10.15	10.05
CdL ₂	Off white	252-254	58.7	1:2	675.08	49.82 (50.55)	3.26 (2.93)	20.75 (21.06)	9.48 (8.65)	16.66	15.95
SnL ₂	Yellow	226-228	74.41	1:2	681.38	49.36 (49.18)	3.23 (3.65)	20.56 (19.74)	9.40 (8.68)	17.43	17.48
ZnL ₂	Pale yellow	192-194	61.58	1:2	628.06	53.55 (53.19)	3.50 (3.64)	22.31 (21.62)	10.20 (10.51)	10.42	10.36
NiL ₂	Green	237-239	72.8	1:2	621.36	54.13 (54.66)	3.54 (3.01)	22.55 (22.05)	10.31 (10.78)	9.45	9.83

Table 2. Diagnostic FTIR bands of the ligand and complexes (cm⁻¹)

Comp.	Triazole ν C=N	Azomethine ν C=N	ν C-S	ν S-H	ν M-N	ν M-S
L	1629	1656	682	2660	-	-
CuL ₂	1610	1653	694	-	528	436
CdL ₂	1612	1650	693	-	530	454
SnL ₂	1618	1642	682	-	531	430
ZnL ₂	1614	1649	696	-	534	427
NiL ₂	1614	1647	698	-	539	451

3.2. Nuclear Magnetic Resonance

The ¹H NMR spectra of free ligand was recorded in DMSO-d₆. The formation of imine group is established by the loss of signal due to the aldehyde group of benzaldehyde at 9.7 in the ¹H NMR spectra [28]. ¹H NMR spectrum of ligand shows the signals (ppm) at 7.311 (m, 5H, Ar-H), 8.018, 7.788 (d,d, 4H, Ar-H), 2.522 (s, 1H, SH), 8.518 (s, 1H, N=CH).

3.3. Electronic spectra

The electronic spectra of the Schiff base ligand and all complexes in 10⁻³ M DMSO solution at room temperature and resulting data are listed in Table 3. The UV-Visible spectrum of ligand showed three bands at 263, 307 and 331 nm. The former two bands are due to the π - π^* transitions within the aromatic ring and remain almost unchanged in the spectra of metal complexes while the third band is due to the n - π^* transitions of azomethine group and also observed in the spectra of metal complexes with a slight shift to lower wavelength, indicating coordination of the ligand to metal centre [29].

Table 3. Electronic spectra in DMSO solvent for the prepared ligand and its metal complexes

Comp.	Absorption Bands(nm)	Assignment
L	263, 307, 331	π - π^* , π - π^* , n - π^*
CuL ₂	263, 307, 326, 494	π - π^* , π - π^* , n - π^* , ${}^2T_2 \rightarrow {}^2E$
CdL ₂	265, 306, 320	π - π^* , π - π^* , n - π^*
SnL ₂	263, 307, 329	π - π^* , π - π^* , n - π^*
ZnL ₂	266, 307, 319	π - π^* , π - π^* , n - π^*
NiL ₂	263, 307, 323, 591	π - π^* , π - π^* , n - π^* , ${}^3T_{1(F)} \rightarrow {}^3T_{1(P)}$

In the electronic spectra of copper and nickel complexes, one new band appears which may be assigned to d-d transition. The Cu(II) complex exhibits d-d transition band centred at 494 nm, attributable to the ${}^2T_2 \rightarrow {}^2E$ transition suggesting square geometry [30]. The Ni(II) complex shows a band at 591 nm, which may be assigned to the ${}^3T_{1(F)} \rightarrow {}^3T_{1(P)}$ and ${}^3T_{1(F)} \rightarrow {}^3A_{2(F)}$ transition, respectively in a tetrahedral environment [31]. Other complexes were diamagnetic as expected for d¹⁰ ions, so that no (d-d) transition can be expected in the visible region [32].

3.4. Magnetic measurements and molar conductivity

The magnetic moment measurements of compounds were carried out at 25 °C. Magnetic susceptibility measurements provide sufficient data to characterize the structure of the complexes. The magnetic moment for Cu(II) complex was approximately 1.62 B.M. This value refers to square planar structure while the value of Ni(II) complex is approximately 2.74 B.M. leading to suggest a high spin tetrahedral structure [33]. Cd(II), Sn(II) and Zn(II) complexes are diamagnetic and there were no magnetic moment recorded in this study [32]. The molar conductivity value of all complexes has been measured in ethanol as a solvent at concentration of 10⁻³ M at room temperature. This measurement was carried out to determine whether the solution was an electrolyte. Table 4 shows the molar conductivity measurements of complexes, it shows that all the prepared complexes were found to be non-electrolyte [34]. Based on the results obtained from spectral study, magnetic moment and conductivity measurements, all complexes exhibited distorted tetrahedral geometry except Cu(II) complex (distorted square planar) [35].

Table 4. Conductivity measurement and magnetic moment of L and its complexes

Comp.	Conductivity (μ S/cm)	Magnetic moment (BM)
L	---	---
CuL ₂	11.4	1.62
CdL ₂	21	0
SnL ₂	14.78	0
ZnL ₂	18.4	0
NiL ₂	22.8	2.74

CONCLUSION

This paper describes the synthesis and characterization of a Schiff base derived from 1,2,4-triazol and its five complexes. The ligand acts as a bidentate and coordinates through azomethine-N, and thiol-S leading to the formation of five member ring chelate. General structures of the complexes are shown in Fig. 1. The Cd(II), Sn(II), Zn(II) and Ni(II) complexes probability show tetrahedral geometry, while Cu(II) complex probability shows square planar geometry.

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REFERENCES

- [1] M. Al-Sabti; A. Al-Amiery; Y. Al- Majedy; A. Hussain. *Biotechnology Research Center (special edition)*, **2009**, 3(2), 1-12.
- [2] V. Reddy; N. Patil; S. Angadi. *E-Journal of Chemistry*, **2008**, 5(3), 577-583.
- [3] S. Chandra; U. Kumar. *Spectrochimica. Acta. Part A: Molecular and Bimolecular Spectroscopy*, **2005**, 61, 219-224.
- [4] D.Shukla; L. Gupta; S. Chandra. *Spectrochimica. Acta. Part A: Molecular and Bimolecular Spectroscopy*, **2008**, 71(3), 746-750.
- [5] A. Kulkarni; S. Patil; P. Badami. *J. Sulfur. Chem.*, **2009**, 30, 145-159.
- [6] A. Wahi; A. Singh. *Asian J. Biochemical and Pharmaceutical Research*, **2011**,1, 193-205.
- [7] J. Clayden; N. Greeves; S. Warren; P. Wothers. *New York, Oxford university*, **2001**, 798-799.
- [8] D. Bele; I. Singhvi. *Asian J. of Biochem. and Pharmaceutical Res.*, **2011**, 1, 88-100.
- [9] M. Davari; H. Bahrami; Z. Haghighi; M. Zahedi. *J. Mol. Model*, **2010**, 16(5), 841-855.
- [10] O. Bekirkan; H. Bectas. *Molecules*, **2006**,11(6), 469-477.
- [11] A. Singh; O. Pandey; S. Sengupta. *Spectrochimica. Acta. Part A*, **2012**, 85, 1-6.
- [12] H. Bektaş; N. Karaali; D. Şahin; A. Demirbaş; Ş. Karaoglu; N. Demirbaş. *Molecules*, **2010**, 15, 2427-2438.
- [13] T. Mahmud. *school of chemistry, the university of Manchester, UK*, **2010**.
- [14] A. Wahi; A. Singh. *Der. Pharma. Chemica.*, **2011**, 3(5), 146-154.
- [15] K. Singh; M. Barwa; P. Tyagi. *Eur. J. Med. Chem.*, **2007**, 42, 394-402.
- [16] P. Cozzi. *Chem. Soc. Rev.*, **2004**, 33, 410-421.
- [17] S. Chandra; J. Sangeetika. *J. Indian Chem. Soc.*, **2004**, 81, 203-206.
- [18] A. Majeed. *Journal of Al-Nahrain University (Science)*, **2008**, 11(1), 44-49.
- [19] S. Jubie; P. Sikdar; S. Antony; R. Kalirajan; B. Gowramma; S. Gomathy; K. Elango. *Pak. J. Pharm. Sci.*, **2011**, 24(2), 109-112.
- [20] B. Narayana; M. Gajendragad. *Tur. J. Chem.*, **1997**, 21: 71-76.
- [21] M. Hanif; Z. Chohan. *Appl. Organometal. Chem.*, **2013**, 27, 36-44.
- [22] S. Patai. *John Wiley and Sons Inc., New York*, **1970**.
- [23] L. Saghatforoush; A. Aminkhani; S. Ershad; G. Karimnezhad; S. Ghammamy; R. Kabiri. *Molecules*, **2008**, 13, 804-811.
- [24] J. Gowda; A. Khader; B. Kalluraya; P. Shree; A. Shabaraya. *European Journal of Medicinal Chemistry*, **2011**, 46, 4100-4106.
- [25] N. Raman; J. Joseph; S. Kumar; S. Sujatha; K. Sahayaraj. *Journal of Biopesticides*, **2008**, 1(2), 206-209.
- [26] R. Haddad; E. Yousif; A. Ahmed. *Springer Plus*, **2013**, 2, 510-516.
- [27] I. Flifel; S. Kadhim. *J. of Kerbala Uni.*, **2012**, 10(3), 197-209.
- [28] Z. Shaghghi. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2014**, 131, 67-71.
- [29] J. Anaconda; J. Rodriguez; J. Camus. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2014**, 129, 96-102.
- [30] N. Greenwood; A. Earnshaw. *Elsevier Science Ltd, New York*, **2002**.
- [31] Y. Win; E. Yousif; A. Majeed; S. Ha. *Asian J. Chem.*, **2011**, 23(11), 5009-5012.
- [32] Z. Chohan; *Trans. Met. Chem.*, **2009**, 34, 153-161.
- [33] H. Ibraheem; H. Adel; A. Ahmed; N. Salih; J. Salimon; A. Graisa; Y. Farina; E. Yousif. *Journal of Al-Nahrain University*, **2010**, 13 (1), 43-47.
- [34] A. Majeed; *Al Mustansiriya J. Sci.*, **2010**, 21(5), 195-204.
- [35] Y. Foo; E. Yousif; S. Tiong; A. Majeed. *Asian J. Chem.*, **2013**, 25(8), 4203-4206.