

Synthesis and Spectroscopic Study of Metal Complexes with New Schiff Base Derived from 2-acetylpyridine and Methionine Amino Acid

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ABSTRACT

In this research new tridentate Schiff base ligand (S)-4-(methylthio)-2-((1-(pyridin-2-yl)ethylidene)amino) butanoic acid (HL), have been prepared from condensation of (2-acetylpyridine) with methionine amino acid . A coordinated complexes of manganese (II), cobalt(II), nickel(II), copper(II) and zinc(II) have also been prepared. The prepared ligand and its complexes characterized depending upon (FTIR & Uv-Vis) spectroscopies, elemental microanalysis (C.H.N.S and M) , (^1H and ^{13}C) N.M.R spectroscopy, mass spectrum, flame atomic absorption, magnetic measurements and molar conductance. The results of different studies proved that new Schiff base ligand acts as a tridentate ONN donor in all the prepared complexes, as well as the results provided that the geometry of all prepared complexes was octahedral with (1:2) (M:L) ration , except Zn(II) complex which obtained tetrahedral geometry with (1:1) (M:L) ratio.

الخلاصة

في هذا البحث تم تحضير ليكاند قاعدة شف جديد ثلاثي السن 4-(مethyl ثايو)-2-((1-(بيريدين-2-يل)إثيليدين)امينو) حامض البيوتانوك (HL)، مشتق من تكثيف (2-أسيتيل بيريدين) والحامض الاميني (الميثيونين) في وسط الأيثانول المطلق. كما تم تحضير معقدات تناسقية لكل من المنغنيز (II)، الكوبلت (II)، النيكل (II)، النحاس (II) والزنك (II). شخص الليكاند المحضرومعقداته التناسقية بأعتماد مطيافيتي الأشعة تحت الحمراء والأشعة فوق البنفسجية-المرئية، التحاليل الدقيقة للعناصر (كربون، هيدروجين، نايتروجين، الكبريت و الفلز)، طيف الرنين النووي المغناطيسي للبروتون وللكاربون، طيف الكتلة، تقنية الامتصاص الذري اللهب، الحساسية المغناطيسية والتوصيل المولاري. أثبتت نتائج الدراسات المختلفة ان ليكاند قاعدة شف الجديد يسلك سلوك ليكاند ثلاثي السن ذا صيغة (NNO)، في جميع معقداته المحضرة، كما اثبتت الدراسات ان جميع المعقدات تتخذ الشكل ثماني السطوح ونسبة (فلز:ليكاند) هي (2:1)، عدا معقد الزنك الذي كان ذا بنية رباعي السطوح ونسبة (1:1) من (فلز:ليكاند).

INTRODUCTION

Amino acids are the principal building blocks of proteins and enzymes [1]. They exist naturally in a zwitter ionic state where the carboxylic acid moiety is ionized and the basic amino group is protonated [2]. Amino acid Schiff bases are an important class of ligands because, since their metal complexes have a variety of applications including biological, clinical, analytical and industrial interest, in addition to their important role in catalysis and organic synthesis [3, 4]. Condensation of L-amino acids with several aldehydes furnished various Schiff bases as reported in the literatures [5, 6]. Schiff base complexes of amino acids have gained importance not only from the inorganic point of view but also because of their physiological and pharmacological activities [7, 8]. Metal complexes of Schiff base phenolates with favorable cell membrane permeability have been exploited in cancer multidrug resistance [9] and tested as antimalarial agents [10].

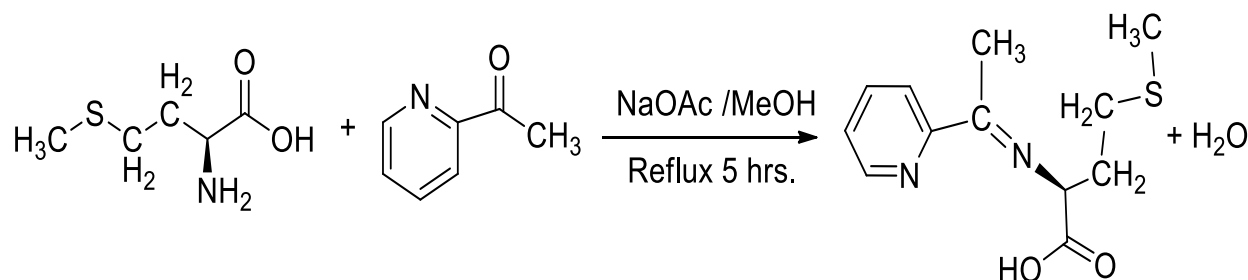
MATERIALS AND METHODS

All chemicals and solvents used in the syntheses were commercially available and used without further purification. The elemental microanalyses were carried out on a Perkin-Elmer 2400 elemental analyzer. The IR spectra were recorded (400 - 4000 cm^{-1}) on a FT-IR spectrometer Shimadzu IR-670 spectrometer. Metal

contents were estimated using an Phoenix-986 AA spectrophotometer, at chemistry department, college of science university of Al-Mustansiriyah. The (^1H and ^{13}C) NMR spectra were recorded on a Bruker NMR spectrometer 300 MHz in DMSO-d_6 (Jordan). The electronic spectra of solutions were recorded on a Cary-2390 UV-Vis spectrophotometer. The magnetic susceptibilities were measured on Sherwood Auto Magnetic balance at room temperature using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as calibrate. The molar conductance measurements were recorded using 10^{-3} molar solutions in DMF. with a WWT. conductivity meter bridge (Model CM-180) and dip type cell calibrated with KCl solutions

Synthesis of (S)-4-(methylthio)-2-((1-(pyridin-2 yl) ethylidene) amino) butanoic acid (HL)

The new Schiff base ligand was prepared by mixing (0.01mole, 1.49 g) of methionine dissolved in 15 ml. of distilled water with (0.01mole, 1.21g) of 2-acetyl pyridine. A (0.30 g) of sodium acetate was added with stirring then refluxed the mixture on water bath for 3 hours. The mixture was left for three hours at room temperature to separate off yellow crude which was washed several times with cold ethanol and chloroform then recrystallized from hot methanol to afford pale yellow crystals, scheme 1.



Scheme 1: synthesis route of HL compound.

Table 1: physical properties and elemental microanalysis of some prepared compounds

Formula	Color	M.Wt g.mol ⁻¹	m.p °C	C% Calc. (found)	H% Calc. (found)	N% Calc. (found)	S% Calc. (found)	M% Calc. (found)
HL	Pale yellow	252.33	180-182	57.06 (56.99)	6.34 (6.20)	11.09 (11.091)	12.68 (11.95)	-
[MnL ₂].H ₂ O	Yellow	575.60	295 ^d					9.44 (13.90)
[CoL ₂].H ₂ O	Green	579.6	300 ^d	49.68 (50.40)	5.52 (4.07)	9.66 (10.11)	11.04 (9.73)	10.16 (10.00)
[NiL ₂].2H ₂ O	Brown	597.37	277 ^d	48.21 (50.70)	5.69 (4.99)	10.71 (10.00)	10.71 (9.68)	9.82 (10.82)
[CuL ₂]	Beige	566.20	278 ^d					11.22 (11.55)
[ZnLCl]	Off white	352.16	301 ^d	40.89 (50.70)	4.25 (4.99)	7.95 (10.00)	9.08 (9.68)	18.56 (18.00)

Synthesis of Mn(II),Co(II),Ni(II),Cu(II) and Zn(II) complexes with (HL) ligand:

The metal complexes were prepared by addition of hot ethanolic solution (1mmole) of the appropriate metal chloride to hot ethanolic solution (0.252 g, 2mmole) of the HL ligand. The resulting mixture was refluxed on water bath with constant stirring for 1-3 hours whereupon the colored precipitated. They were collected by filtration, washed several times with ethanol and chloroform for further purification and dried under vacuum.

RESULTS AND DISCUSSION

Table 1 represents physical properties and elemental microanalysis of some prepared compounds. **d=decomposition.**

Characterization of metal complexes

The complexes are colored and stable in air. They are insoluble in common organic solvents but soluble in CH₃CN, DMSO and DMF. They do not melt or decompose until 300 °C.

NMR spectra of HL

The ¹H NMR spectrum of the ligand LH, Figure 1 shows a singlet signal at δ (1.24) ppm corresponding to the –CH₃ protons attached to azomethine group. A second single signal was also appeared in the ligand spectrum at

δ (3.80) ppm represent the protons of –CH₃ group attached to sulphur atom of methionine moiety. The splitting of the pyridine aromatic protons, (4H,Py-H) (7.41-7.6) ppm. As well as the acidic –COOH proton of amino acid moiety was observed in the region 11.55 ppm which support remarkably the structure of the formed Schiff base HL [10,11]. Moreover, the ¹³C NMR spectrum of HL, figure(2), in DMSO- d₆ displays variable peaks at (41,48-49), (121-122) and (170) ppm [10,12] which are characteristic of two methyl groups, –C=N and –COOH carbon atoms,. The data correlated from NMR spectra indicates the proper suggested of free ligand.

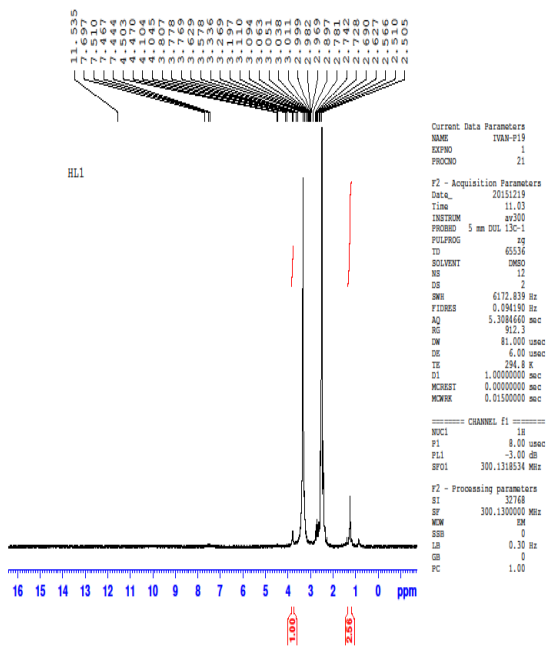


Figure 1: ¹H NMR spectrum of HL in DMSO- d₆

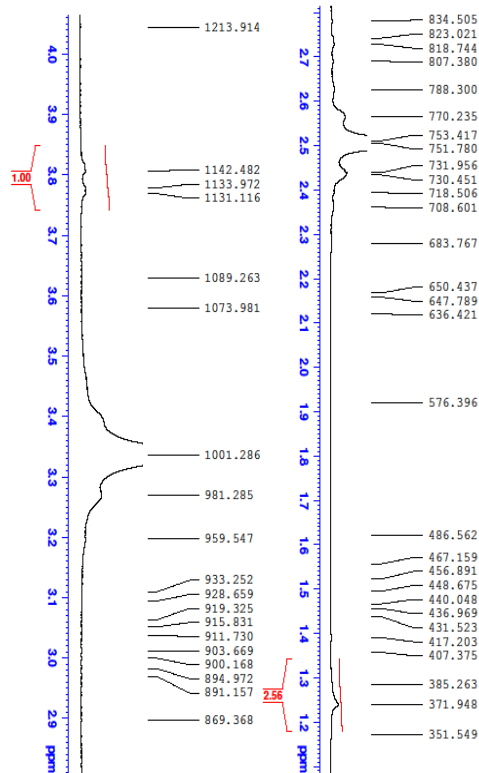


Figure 1: ¹H NMR spectrum of HL in DMSO- d₆

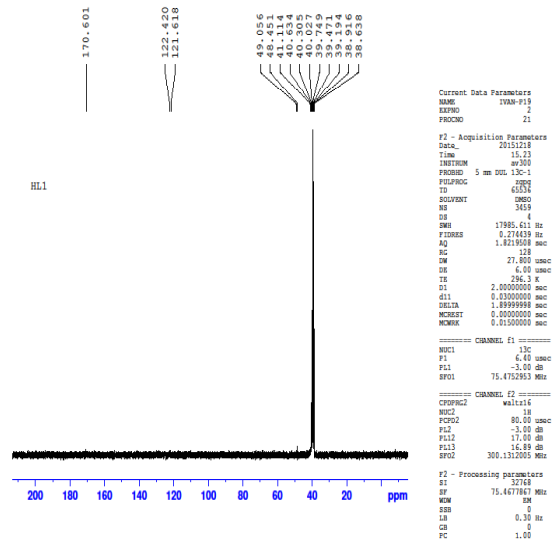


Figure 2: ¹³C NMR spectrum of HL in DMSO-d₆

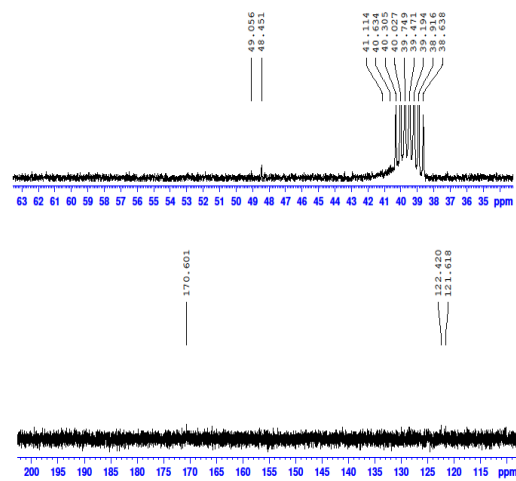


Figure 2: ¹³C NMR spectrum of HL in DMSO-d₆

Mass spectrum

Figure 3 exhibits the molecular ion M¹⁺ for the Schiff base of m/e=252 which supports the suggested formula of the prepared ligand. As well as the other peaks at 243 (base peak), 213, 187, and 102 might be attributed to cleavage of methyl, amino groups and other fragments of methylene moiety of methionine amino acid [12.13].

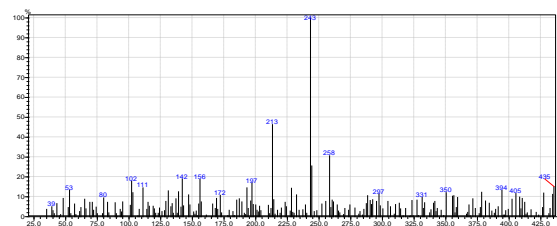


Figure 3: GC-Mass spectrum of HL Schiff base.

IR spectra

The free ligand showed a broad band at (3500-2800) cm^{-1} due to carboxylic $\nu(\text{COOH})$ in case of ligand has disappeared in all the complexes indicating its involvement in the coordination with the metal ions via deprotonation [17]. The free ligand showed a strong intensity band at (1680) cm^{-1} assigned to $\nu(\text{C=O})$ of carboxylate moiety [15,18] which has been observed in the (1650-1660) cm^{-1} region in the case of the complexes. It can be observed that there is clear considerable shift in the $\nu(\text{C=N})$ vibrations in the case of the complexes compared to the ligand from depression it's wave numbers from (1544-1609) cm^{-1} region indicating the involvement of imine (C=N-) function of Schiff base and pyridine ring in the linking with the central metal ion. However the bands in the regions (680-685) and (3100-2963) cm^{-1} in all complexes proved the stretching vibration modes of (C-S) and aliphatic (C-H) bonds [19]. However the weak intensity vibrations in the regions (400-448) and (527-566) cm^{-1} ascribing the coordination bonds (M-N) and (M-O) respectively [20]. Unfortunately the identification of M-Cl were not possible due to processing the FTIR spectra in the range (4000-400) cm^{-1} . It is obviously that the data of FTIR suggested the tridentate behavior of Schiff base via loss of acidic proton -COOH and involving -C=N- moiety in coordination with central metal ions in addition the broad bands of -OH in the region 3290-3600 cm^{-1} related to lattice water molecules in the outer sphere of complexes structures [18]. The important characteristic bands related to the (HL) and its chelation complexes and their assignments are described in Table 2.

Table 2: Vibration absorptions of Ligand and its metal complexes.

compound	$\nu(\text{C=O})$ $\nu(\text{COOH})$	$\nu(\text{C=N})$	$\nu(\text{M-N})$ $\nu(\text{M-O})$	$\nu(\text{C-H})$ $\nu(\text{C-S})$
HL	1680(s), 3500- 2800(br)	1622 (s)	-	2960(m) 680
[MnL ₂].H ₂ O	1650(s) 3600(br.)	1580 (m.)	540 433	3020(w) 688
[CoL ₂].H ₂ O	1662(s) 3450(br.)	1570 (s.)	566 400	3016(w) 678
[NiL ₂].2H ₂ O	1655 (s) 3300(br.)	1544 (s.)	540 437	3100(w) 683
[CuL ₂]	1660(s) 3290(br.)	1599 (s.)	527 406	2960- 3040(w) 679
[ZnLCl]	1656(s) 3460(br.)	1609 (m.)	528 448	2988- 3000(w) 681

s=strong, m=medium, br.=broad, w=weak.

Electronic spectra, Molar conductivity and Magnetic moments

The free ligand (HL) in ethanol displayed two distinct absorptions in the range (35735) and (30200) cm^{-1} which

are assigned to $\pi-\pi^*$ transitions of benzenoid and $n-\pi^*$ transitions of C=N, and C=O chromospheres [15]. The paramagnetic property of Ni(II) reveals the octahedral symmetry of high spin d^8 , and thus agrees well with the high energy of absorption in the range (18500) and (21000) cm^{-1} are assigned to ${}^3A_{2g}^{(F)} \rightarrow {}^3T_{1g}^{(F)}$ (ν_2) and ${}^3A_{2g}^{(F)} \rightarrow {}^3T_{1g}^{(F)}$ (ν_3) respectively [16]. As well as the paramagnetic properties of mononuclear Cu(II) complex indicate the orbital contribution [17], the absorption spectra of copper complex exhibits shoulder peak at (~ 24600) cm^{-1} which assigned to (CT) transition, and another peak at low energy side (~ 19000) cm^{-1} , attributed to ${}^2E_g \rightarrow {}^2T_{2g}$, assuming tetragonal distortion in the molecule the dz^2 orbital [18]. In contrast the Mn(II) complex exhibited one weak band at (19400) cm^{-1} which is assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G) (ν_1), and a high energy transitions at (28900) cm^{-1} of CT, supporting high spin octahedral environment around Mn(II) ion. The magnetic moment of Mn(II) complex was (5.45 B.M), it less than expected than theoretical value assuming the effect of ligand field donor atoms like N₂O with no orbital contribution of d^5 configuration. However, the measurements of molar conductivity in DMF solution and the data obtained assigned no electrolytic properties for all complexes then support the expected formula [20]. The (U.V- Vis) spectra data of (HL) and its complexes are described in Table 3.

Table 3: UV-Visible spectra, magnetic susceptibility, molar conductance data and geometry of prepared complexes.

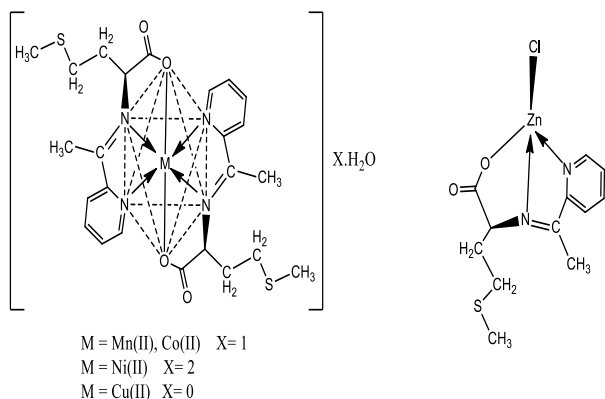
Compound	cm^{-1}	Band assignment	μ_{eff} (BM)	$^{\circ}\Omega$	geometry
HL	30200 35735	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	12	---
[MnL ₂].H ₂ O	19400 28900	${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G) (ν_1) CT	5.45	30	Octahedral
[CoL ₂].H ₂ O	16600 19000 32000	${}^4T_{1g} \rightarrow {}^4T_{2g}$ (F) ${}^4T_{1g} \rightarrow {}^4T_{1g}$ (P) $\pi \rightarrow \pi^*$	3.87	23	Octahedral
[NiL ₂].2H ₂ O	18500 21000	${}^3A_{2g}^{(F)} \rightarrow {}^3T_{1g}^{(F)}$ (ν_3) ${}^3A_{2g}^{(F)} \rightarrow {}^3T_{1g}^{(F)}$ (ν_2)	2.77	20	Octahedral
[CuL ₂]	24600 19000	CT ${}^2E_g \rightarrow {}^2T_{2g}$	1.67	22	Octahedral
[ZnLCl]	34000 31000	$\pi \rightarrow \pi^*$ CT	0.00	16	Tetrahedral

$^{\circ}\Omega$ = molar conductance ($\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) in DMF solvent, C.T=charge transfer bands

CONCLUSIONS

According to the results obtained from elemental microanalysis, (IR and UV-Vis.) spectroscopies, NMR spectrum, Mass spectrum and magnetic susceptibility the octahedral geometry around Mn(II), Co(II), Ni(II) and Cu(II) ions were approved whereas the tetrahedral

symmetry was suggested for [ZnLCl] complex. As well as the absorptions of IR spectra revealed that the prepared Schiff base HL from condensation of L-methionine and 2-acetylpyridine behaved as monobasic tri dentate ligand toward all metal ions via two nitrogen atoms of two imine groups with participation of carboxylato group up on deprotonation. Scheme 2, represents proposed geometries of the prepared complexes.



Scheme 2: Proposed geometries of the prepared complexes.

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