

RESEARCH ARTICLE

Synthesis, Structural Study, and Biological Activity Evaluation of VO(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) Complexes with New Schiff Base Ligand Derived from Pyrazine

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ABSTRACT

New Schiff base [3-(3-acetylthioureido)pyrazine-2-carboxylic acid][L] has been prepared through 2 stages, the chloro acetyl chloride has been reacting with the ammonium thiocyanate in the initial phase for producing precursor [A], after that [A] has been reacting with the 3-amino pyrazine-2-carboxylic acid to provide a novel bidentate ligand [L], such ligand [L] has been reacting with certain metal ions in the Mn(II), VO(II), Ni(II), Co(II), Zn(II), Cu(II), Hg(II), and Cd(II) for providing series of new metal complexes regarding general molecular formula $[M(L)_2XY]$, in which; VO(II); X=SO₄, Y=0, Co(II), Mn(II), Cu(II), Ni(II), Cd(II), Zn(II), and Hg(II); Y=Cl, X=Cl. Also, all the compounds were characterized through spectroscopic techniques [IR, UV-Vis, atomic absorption], conductivity measurements, chloride content, elemental micro analysis in addition to the ¹H, ¹³C-NMR for ligand [L] only. Based on the results taken from the methods mentioned above, the proposed geometrical structures with regard to each prepared complex have been in the agreement with octahedral formula.

Keywords: Pyrazine, Schiff bases, Thiocyanate.

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INTRODUCTION

The Schiff base compounds which are derivated from the pyrazine, have been majorly identified classes regarding the organic reagents from practical and theoretical perspectives.¹ The Schiff base complexes have been characterized through the existence of azomethine group (-CH=N-) due to the condensation between ketones or aldehydes with the aromatic amines.² The existence of azomethine linkage in the aromatic compounds makes such reagents act as chromogenic in specifying trace amounts of the transition metals, including Ni, in certain natural foods samples.³ Furthermore, the tendency as ligands towards coordinating with various ions of metals has been particularly indicated on such ligands with at least 2 donor atoms concentrated in the coordination chemistry; also, the coordination compounds have been defined as certain metal ions which are surrounded with ligands. The ligands might be molecules or anions; they might be donating the electrons to d-orbitals related to metal ion as well as forming a bond in such coordination's chemistry. The bio ligands are of high importance due to their possible activity in transition metal

complex.⁴ The Schiff bases are of high importance in various areas like in pharmacology as anti-cancer, anti-bacterial, and anti-fungal.⁵ In an industry with regard to the characteristics of the compounds as Thermal Initiation in the Radical Polymerization.⁶ In the presented study, a New Schiff base ligand in addition to its compounds for VO(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) have been made.

EXPERIMENTAL

Physical Measurements and Materials

Every utilized chemical has been of the maximum purity (merck, Fluka, and BDH) and also utilized with no more purification. The elemental analysis has been implemented via the micro-analytical unit of (EURO EA-3000 Single) CHN element analyzer/Ibn sina company. The spectra of the absorption have been recorded using Shimadzu UV-Vis1700 spectro-photometer, for a solution related to complexes in the DMSO at a temperature of 25 Celsius. With the use of quartz cell of (1cm), the IR spectra have been recorded with the use of FT-IR8000 Shimadzu, in range (400–4,000cm⁻¹) utilizing KBr

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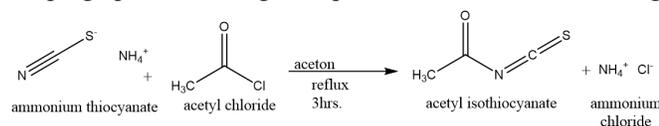
disc. The electrical molar conductivity measurements regarding complexes have been recorded at the room temperature for (10⁻³) M solutions related to samples in the ethanol using PW-9526 digital conductivity meter. ¹H, ¹³C nuclear magnetic resonance (NMR) spectra have been recorded with the use of DMSO-d-6 at Bruker 400 MHz spectrometer. Chloride content is specified with the use of potentiometric titration technique on 686-Titro Processor 665 Dosim A-Metrohm/Swiss. Also, melting points have been acquired by the use of electrothermal apparatus Stuart; the metals and melting point were specified with the use of Shimadzu (AA) 680 G atomic absorption spectrophotometer.

Derivative Chloro acetyl Isothiocyanate[A] Preparation

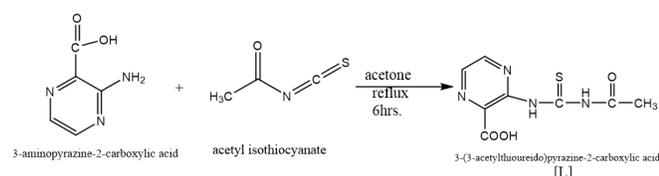
A mixture of chloro acetyl chloride (2.05 mL, 26 mmol.) and NH₄SCN (2.00 g., 26 mmol.) in 25 mL of (CH₃)₂CO and stirred under reflux for 3 hours, and then filtered,⁷ the preparation that is related to Schiff base can be seen in the Scheme 1.

New Schiff base ligand[L] preparation

3-amino pyrazine-2-carboxylic acid (3.61 g., 26 mmol.) in 20 mL of acetone has been added to the precursor A, also keeping up the refluxing for a period of 6 hours, the resulting



Scheme 1: Precursor's preparation [A]



Scheme 2: Ligand [L] Preparation

solid has been collected recrystallized from ethanol,⁸ yield (82%), mp (248-250)C. (Scheme 2).

Metal complexes preparation

The (1:2) chelate compounds that are related to ligand and metal have been prepared via dissolving (0.002 mol, 0.423 g) Schiff base [L] in 25 mL of the absolute ethanol. Also, the related hydrated metal chloride salts of (VOSO₄·H₂O, MnCl₂·4H₂O, CoCl₂·6H₂O, CuCl₂·2H₂O, NiCl₂·6H₂O, CdCl₂·H₂O, ZnCl₂, and HgCl₂) of (0.001 mol) is subjected to dissolving in absolute ethanol (25mL) and mixed with a solution of the hot ethanol which is related to ligand, also refluxed for a period of 3 hours on water bath, on cooling contents. Furthermore, the compounds have been separated out in every one of the cases. The product has been filtered, then washed by the ethanol, then left to dry under vacuum. Table 1 shows the collection of physical characteristics as well as analytical data for the compounds.

RESULTS AND DISCUSSIONS

Metal complexes have been insoluble in the water, also soluble in ethanol, acetone, DMSO, CHCl₃, DMF, and methanol.

Infra-red Spectra of Complexes and Ligand

Infra-red spectral data related to the Schiff base ligand (Figure 1) and their complexes have been provided in Table 2. Complexes' IR spectra compare with the ones of free ligand to determine the sites of the coordination that might be involved in the chelation.

The band in IR spectrum that is related to the free ligand at 1604 cm⁻¹, which is considered to be assignable to the stretching vibration ν (C=O) group of L that has been shifted to high frequency in complexes' Infra-Red spectra, indicating involvements of carbonyl oxygen atom in the coordination.⁹ Also, the appearance regarding the new non-ligand band

Table 1: Physical characteristics and the analytical data of ligand in addition to its complexes.

No.	Compound	Color	M wt.	MP C°	Found (Calc.)%						Cl content
					C	H	N	O	S	M	
1	C ₈ H ₈ N ₄ O ₃ S	yellow	240.24	240–242	38.00 (39.96)	2.95 (3.33)	22.51 (23.31)	19.00 (19.98)	12.52 (13.35)	—	—
2	[VO(C ₈ H ₈ N ₄ O ₃ S) ₂ SO ₄]	Deep green	627	290 dec.	29.50 (30.62)	2.00 (2.55)	17.11 (17.86)	27.00 (28.07)	25.00 (25.51)	7.33 (8.13)	---
3	[Mn(C ₈ H ₈ N ₄ O ₃ S) ₂ Cl ₂]	Deep yellow	605	248 dec.	31.00 (31.73)	2.11 (2.64)	17.30 (18.51)	15.00 (15.86)	9.21 (10.57)	9.00 (9.09)	11.05 (11.57)
4	[Co(C ₈ H ₈ N ₄ O ₃ S) ₂ Cl ₂]	blue	609	270–272	30.42 (31.52)	2.11 (2.62)	17.11 (18.39)	14.30 (15.76)	9.66 (10.50)	9.11 (9.68)	10.50 (11.49)
5	[Ni(C ₈ H ₈ N ₄ O ₃ S) ₂ Cl ₂]	Deep brown	609	278 dec.	30.40 (31.52)	2.13 (2.62)	17.13 (18.39)	14.33 (15.76)	9.69 (10.50)	9.15 (9.68)	10.55 (11.49)
6	[Cu(C ₈ H ₈ N ₄ O ₃ S) ₂ Cl ₂]	green	614	288–290	30.62 (31.27)	2.11 (2.60)	18.00 (18.24)	15.11 (15.63)	9.89 (10.42)	10.22 (10.42)	10.96 (11.40)
7	[Zn(C ₈ H ₈ N ₄ O ₃ S) ₂ Cl ₂]	yellow	615	300 dec.	30.55 (31.21)	2.00 (2.60)	18.14 (18.21)	15.20 (15.60)	10.01 (10.40)	10.00 (10.56)	10.50 (11.38)
8	[Cd(C ₈ H ₈ N ₄ O ₃ S) ₂ Cl ₂]	yellow	662	230 dec.	28.63 (29.00)	2.10 (2.41)	16.00 (16.91)	14.01 (14.50)	9.11 (9.66)	16.00 (16.91)	10.01 (10.57)
9	[Hg(C ₈ H ₈ N ₄ O ₃ S) ₂ Cl ₂]	yellow	751	210 dec.	25.32 (25.56)	2.11 (2.13)	14.21 (14.91)	12.55 (12.78)	8.11 (8.52)	14.54 (14.91)	9.00 (9.32)

about (415–450 cm^{-1}) in Infra-Red spectra of all the complexes because of ν (M-O) substantiates.¹⁰ Furthermore, the band at (1234 cm^{-1}) in the IR spectrum regarding the free ligand might be due to the ν (C=S) stretching vibration, filled with low frequency in complexes' IR spectra. Such shifting specified the coordination regarding ligand with the metal ion through sulfur atoms.^{11,12} This has been more substantiated with the existence of new band about (499–590 cm^{-1}) which is considered to be assignable to ν (M-S).¹³ It has been indicated that the ligand behaves as a bidentate ligand that is coordinated to the ions of the metal through the oxygen atom of the carbonyl group of L and sulfur atoms every complex.

Electronic Spectra

Ligand's electronic spectra (Figure 3), as well as its Hg (II), Zn (II), Ni (II), Mn (II), VO(II), Co(II), Cu(II), and Cd(II) complexes, were examined; also the spectral data were provided in the Table 3. UV-vis spectrum that is related to

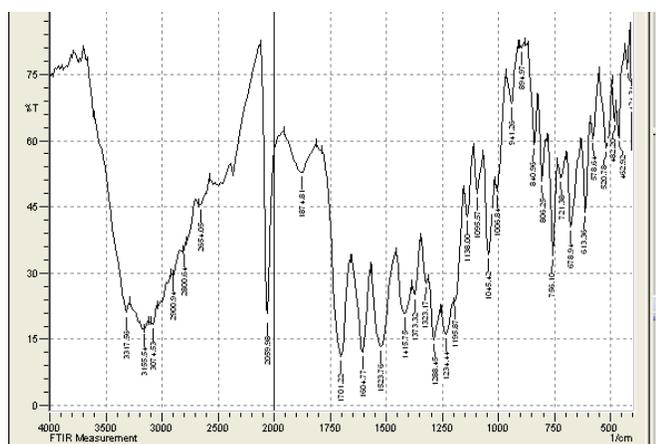


Figure 1: Ligand's infrared spectrum

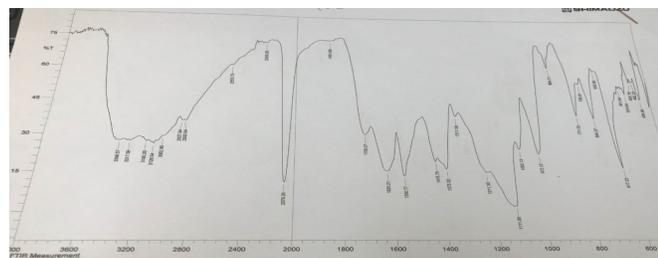


Figure 2: Infra-Red spectrum of ion complex of VO(II) with ligand

Schiff base ligand was mainly characterized via 2 absorption peaks at (295 nm) allocated to ($\pi \pi^*$), also at (563 nm) allocated to ($n \pi^*$).¹⁴ Such electronic transition has been shifting toward high or low frequency in electronic spectra regarding every prepared complex, indicating the ligand's coordination with metal ions. Also, electronic spectrum regarding VO (II) complex (Figure 4) showed 2 new peaks of absorption, the first one is at (275 nm) and allocated to intra – ligand, while the other is at (569 nm) and allocated to (d-d) electronic transition type ($2B_{2g} \rightarrow 2B_{1g}$), specifying octahedral geometry around VO(II) ion.¹⁵ The electronic spectrum regarding the Mn (II) complex indicated 2 new peaks of absorption, the first peak is at (276 nm) might be allocated to intra-ligand, while the other peak is at (567 nm) has been allocated to (d-d) electronic transition type ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$. The

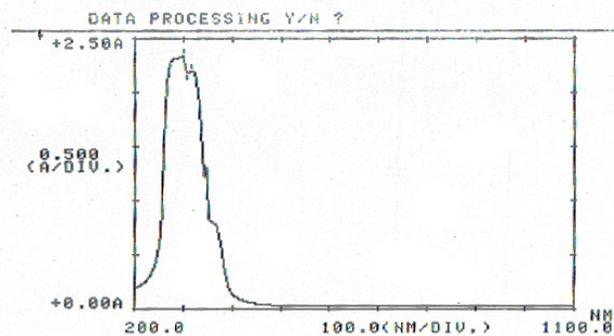


Figure 3: Ligand's absorbance spectrum

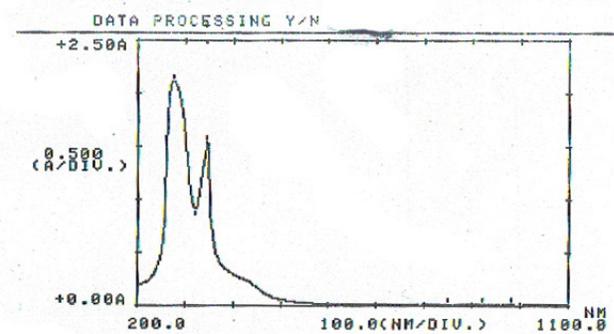


Figure 4: The ligand's absorbance spectrum with Ni (II) ion complex

Table 2: Characteristic Infra-Red absorption bands of ligand (L) as well as its complexes in cm^{-1}

Compounds	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{S})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{S})$
L = $\text{C}_8\text{H}_8\text{N}_4\text{O}_3\text{S}$	1604(s)	1234(s)	–	–
[VO ($\text{C}_8\text{H}_8\text{N}_4\text{O}_3\text{S}$) ₂ SO ₄]	1620(s)	1211(w)	524(m)	459(w)
[Mn ($\text{C}_8\text{H}_8\text{N}_4\text{O}_3\text{S}$) ₂ Cl ₂]	1627(s)	1215(s)	528(m)	420(m)
[Co ($\text{C}_8\text{H}_8\text{N}_4\text{O}_3\text{S}$) ₂ Cl ₂]	1612(m)	1230(m)	536(m)	443(m)
[Ni ($\text{C}_8\text{H}_8\text{N}_4\text{O}_3\text{S}$) ₂ Cl ₂]	1612(s)	1226(s)	547(w)	435(w)
[Cu ($\text{C}_8\text{H}_8\text{N}_4\text{O}_3\text{S}$) ₂ Cl ₂]	1627(m)	1226(m)	528(m)	439(m)
[Zn ($\text{C}_8\text{H}_8\text{N}_4\text{O}_3\text{S}$) ₂ Cl ₂]	1616(s)	1215(s)	528(m)	424(m)
[Cd ($\text{C}_8\text{H}_8\text{N}_4\text{O}_3\text{S}$) ₂ Cl ₂]	1627(s)	1211(s)	528(m)	420(m)
[Hg ($\text{C}_8\text{H}_8\text{N}_4\text{O}_3\text{S}$) ₂ Cl ₂]	1616(s)	1215(s)	543(w)	420(w)

Table 3: The electronic spectra of ligand and its chelate complexes

Compound	λ_{Max} nm	Transition	Suggested structure	$L_m S.cm^2.mole^{-1}$
$C_8H_8N_4O_3S$	295 563	$\pi \pi^*$ $n \pi^*$	—	—
$[VO(C_8H_8N_4O_3S)_2SO_4]$	275 569	Intra - ligand $2B_2g \rightarrow 2B_1g$	Oh.	18.82
$[Mn(C_8H_8N_4O_3S)_2Cl_2]$	276 567	Intra - ligand ${}^6A_1g \rightarrow {}^4T_2g(G)$	Oh.	13.41
$[Co(C_8H_8N_4O_3S)_2Cl_2]$	230 565 990	Intra - ligand $(4 T_1g \rightarrow 4 T_1g(P))$ $({}^4T_1g \rightarrow {}^4T_2g)$	Oh.	9.32
$[Ni(C_8H_8N_4O_3S)_2Cl_2]$	303 324 720 822	Intra - ligand Intra - ligand $({}^3A_2g \rightarrow {}^3T_1g)$ $({}^3A_2g \rightarrow {}^3T_2g)$	Oh.	19.15
$[Cu(C_8H_8N_4O_3S)_2Cl_2]$	307 325 729 822	Intra - ligand Intra - ligand $({}^2B_1g \rightarrow {}^2Eg)$ $({}^2B_1g \rightarrow {}^2A_2g)$	Oh.	9.87
$[Zn(C_8H_8N_4O_3S)_2Cl_2]$	277 325	Intra - ligand Intra - ligand	Oh.	8.92
$[Cd(C_8H_8N_4O_3S)_2Cl_2]$	277 321	Intra - ligand Intra - ligand	Oh.	15.91
$[Hg(C_8H_8N_4O_3S)_2Cl_2]$	271 323	Intra - ligand Intra - ligand	Oh.	17.10

peaks have been in the excellent agreement of the octahedral geometry which is related to the complex of the Mn (II).¹⁶ The electronic spectrum regarding the complex of Co (II) specified 3 new peaks of absorption, the first one is at (230 nm) allocated to intra – ligand, the other ones are at 565 nm and 990 nm have been allocated to (d-d) electronic transition type ($4 T_1g \rightarrow 4 T_1g(P)$ and $({}^4T_1g \rightarrow {}^4T_2g)$). The peaks have been in excellent agreement with the octahedral geometry related to Co (II).¹⁶ Also, the electronic spectrum regarding Ni (II) complex specified 4 new peaks of absorption; they have been at (303 nm and 324 nm) might be allocated to intra–ligand. The rest of the peaks have been at 720 nm and 822 nm and allocated to (d-d) electronic type of transition ($({}^3A_2g \rightarrow {}^3T_1g)$ as well as $({}^3A_2g \rightarrow {}^3T_2g)$), such peaks have been in excellent agreement regarding the octahedral geometry for Ni (II) complex.¹⁶ The electronic spectrum related to the Cu (II) complex indicated 4 new absorption peaks; the peaks at (307 and 325 nm) might be allocated to intra – ligand. The other peaks have been at 729 nm and 822 nm allocated to (d-d) electronic type of transition ($({}^2B_1g \rightarrow {}^2Eg)$ as well as $({}^2B_1g \rightarrow {}^2A_2g)$). Such peaks have been in excellent agreement regarding the octahedral geometry for the complex of Cu (II).¹⁶ The electronic spectrum of the complexes of Cd(II), Hg(II), and Zn(II) specified absorption peaks at (277, 277 and 271 nm) referring to ($\pi \pi^*$), whereas at (325, 321 and 323 nm) might be allocated to ($n \pi^*$),¹³ the metal ion regarding such complexes belong to d^{10} system, also such metals are not showing (d-d) electronic transition.¹⁶

Molar Conductivity

Molar conductance regarding all the ethanol complexes lies

in the range of (8.92-19.15) $S.cm^{-1}.mole^{-1}$, specifying their non-electrolytic behaviors.^{17,18}

Nuclear Magnetic Resonance Spectra for Ligand

The 1H , as well as ${}^{13}C$ correlating to NMR analysis, have been utilized for characterizing ligand. Also, the spectra have been recorded in the solution of the DMSO- d_6 .

Spectrum of the 1H NMR for the Ligand

In the solution, like in solid-state, such phenomenon was verified via IR as well as the spectra of the NMR. 1H NMR spectrum for ligand, Figure 5 in the DMSO- d_6 specified signal at chemical shift ($\delta_H = 3.67$ ppm) have been allocated to (3H, CH_3) protons,²³ also at (8.26–8.60 ppm) with regard to aromatic protons. The appearances of such protons as multi are because of mutual coupling. The sharp singlet signal at ($\delta_H = 10.15$ ppm) has been allocated to protons of (1H, NH-CS), peak at ($\delta_H = 12.30$ ppm) for 1H, COOH.²⁴

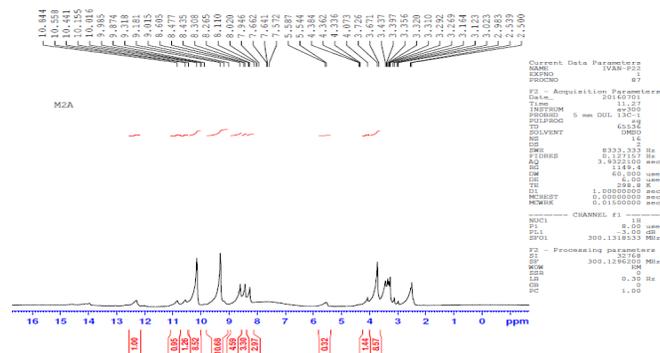


Figure 5: Spectrum of the 1H NMR for ligand in DMSO- d_6

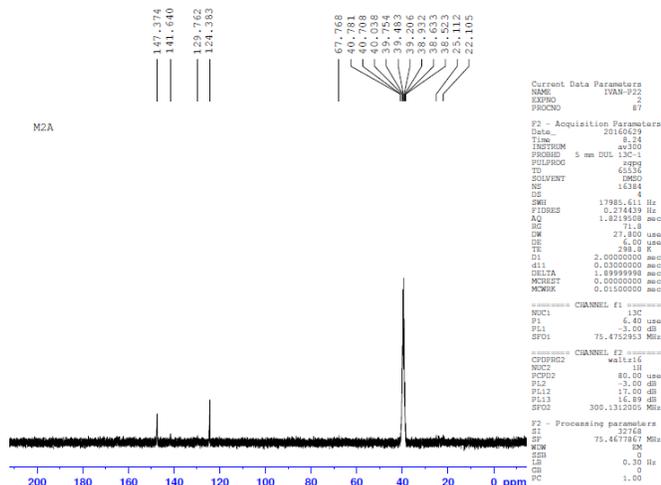
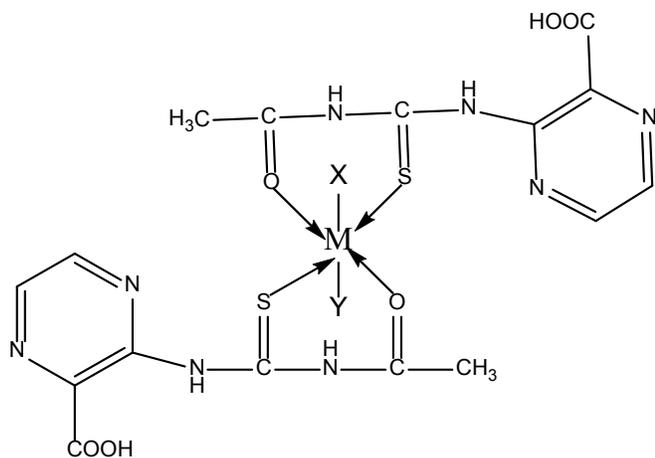


Figure 6: ¹³C NMR spectrum of ligand in DMSO-d⁶



M= VO (II), X=SO₄, Y=O; Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II); X=Cl, Y=Cl

Figure 7: The proposed structure of the complexes with the Schiff base ligand [L]

¹³C NMR Spectrum for Ligand.

¹³CNMR spectrum of free ligand in (DMSO-d₆), Figure 6, has shown the following signals: signal at δ (38.68–40.67 ppm) for DMSO and CH₂Cl, signal at δ (114.92–149.32 ppm) for the aromatic carbons, signals at δ (164.92 ppm) for COOH, signal at δ (171.84 ppm) (C=O sec. amid), signal at δ (180 ppm) for (C=S).²⁴⁻²⁶

Suggested Structure

Based on the elemental microanalysis as well as the spectroscopic studies related to ligand [L], and all the complexes, the present work suggesting that ligand behaving like bidentate on the complexation with the ions of the metal through oxygen atom of carbonyl group in addition to the sulfur atom, also it has been indicated that the M:L ratio has been 1:2. On the basis of such results, the complexes have octahedral geometry (Figure 7).

Biological Activity

We studied the effects of biological screening for the compounds by testing in vitro against the bacteria: *Staphylococcus aureus*,

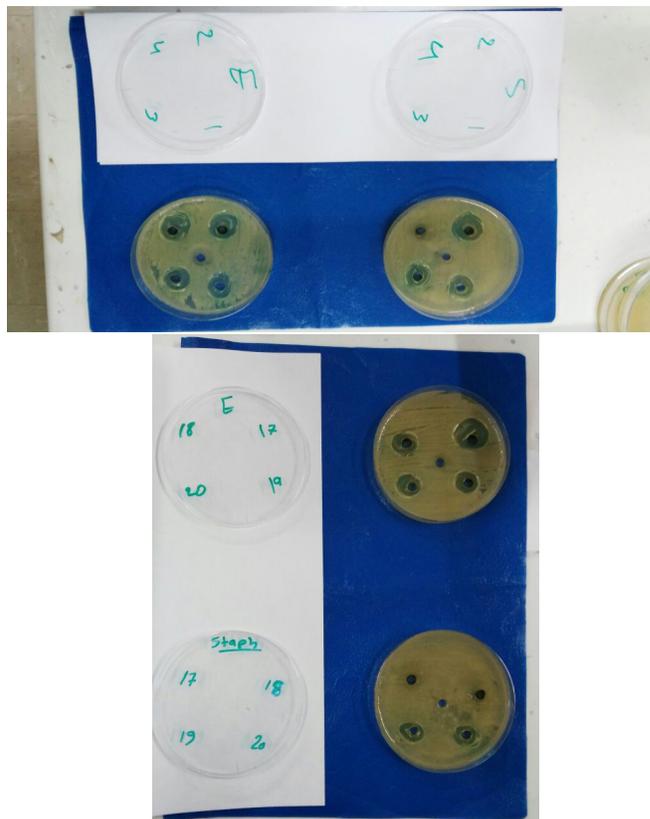


Figure 8: The biological activity of complexes

Escherichia coli, *Pseudomonas aeruginosa*, and (*Bacillus subtilis*) by the well diffusion method at 25°C.²⁷⁻³⁰ The well is filled with the test solution 10–3 M is prepared by dissolving the compounds in DMSO using a micropipette, and the plate is incubated for 24 hours. Using agar nutrient as the medium inoculated with microorganisms. During this time, the test solution spreads and the evolution of inoculated bacteria are affected as in Figure 8.

REFERENCES

1. Jaafar WA. Journal of Global Pharma Technology Synthesis , Structural Study and Biological Activity Evaluation of Cr (III), Mn (II), Zn (II), Cd (II) and Hg (II) Complexes with New Schiff Base Ligand Derived from Isatin. 2018;(November): 513–521.
2. Al-Jeboori MJ, Hasan HA, Jaafer Al-Sa'idy WA. Formation of polymeric chain assemblies of transition metal complexes with a multidentate Schiff-base. Transit Met Chem [Internet]. 2009 Sep;34(6):593–598. Available from: <http://link.springer.com/10.1007/s11243-009-9235-7>
3. Ali Jaafar W, Fezea SM, Al-Shemary RKR. Employing the physicochemical, spectroscopy, antimicrobial and antifungal efficacy studies of p-hydroxy acetophenone based azo schiff base complexes. J Glob Pharma Technol. 2018;10(6):503–512.
4. Lateef SM, Sarhan BM, Al-saedi WAJ. Synthesis, Characterization and Biological Activity for Complexes VO (II), Mn (II), Co (II) and Ni (II) with new multidentate ligand. 2016;2(1):10–27.
5. Al-Saidi, Wurud Ali Jafar. Synthesis, characterisation and biological activity for binuclear complexes with Co (II), Cu (II) and Zn (II) with new ligand m-phenylendi (azo-2-naphthol)

- ligand type N2O2. *Ibn al-Haitham Journal for Pure and Applied Science*. 2012. Vol. 25, no. 1.
- Hasan HA, Samir AH, Al-saedi WAJ. Spectroscopic and Biological Activity Studies of Thiadiazole Ligand Type N2O and its Complexes with Fe (II), Co (II) and Ni (II). 2011;22(4):222–32.
 - Wurood A.J. Al-Saedi Sajid. M. Lateef BMS. Synthesis , Characterisation And Biological Activity For. *Int J Eng Sci Res*. 2015;4(2):606–620.
 - Raman N, Kulandaisamy A, Jeyasubramanian K. Synthesis , spectral , redox and biological studies of some Schiff base copper (II),. *Indian J Chem*. 2002;41A(May):942–949
 - Dipanwita D., Biprajit S., Tapan KM, Shaikh MM, Jan F, Wolfgang K, and Goutam KL . Oxidation State Analysis of a Four-Component Redox Series [Os(pap)2(Q)]n Involving Two Different Non-Innocent Ligands on a Redox-Active Transition Metal. *Inorganic Chemistry* 2011, 50 (15) , 7090-7098. <https://doi.org/10.1021/ic200615s>
 - Socrates, G. (George). *Infrared characteristic group frequencies*. Chichester ; New York : Wiley, 1980
 - Tümer M, Çelik C, Köksal H, Serin S. Transition metal complexes of bidentate Schiff base ligands. *Transit Met Chem*. 1999;24(5):525–532.
 - Abd M, Mahmoud E, Ibrahim OB. Nano Sized Schiff Base Complexes with Mn(II), Co(II), Cu(II), Ni(II) and Zn(II) Metals : Synthesis, Spectroscopic and Medicinal Studies. *Can Chem Trans* [Internet]. 2014 Apr 6;(January):108–21. Available from: <http://canchemtrans.ca/uploads/journals/CCT-2013-0077.pdf>
 - El-Sonbati AZ, Diab MA, El-Bindary AA, Abou-Dobara MI, Seyam HA. Supramolecular coordination and antimicrobial activities of constructed mixed ligand complexes. *Spectrochim Acta - Part A Mol Biomol Spectrosc* [Internet]. 2013;104:213–221. Available from: <http://dx.doi.org/10.1016/j.saa.2012.11.024>
 - A. B. P. Lever, “Inorganic Electronic Spectroscopy,” 2nd Edition, Elsevier, New York, 1984.
 - Singh D, Malik V, Kumar R, Kumar K. Template synthesis of macrocyclic complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II): Spectroscopic, antibacterial and antifungal studies. *J Serbian Chem Soc* [Internet]. 2010;75(6):763–772. Available from: <http://www.doiserbia.nb.rs/Article.aspx?ID=0352-51391000049S>
 - El-Asmy AA, Al-Ansi TY, Shaibi YM. Chelated complexes of cadmium(II), cobalt(II), copper(II), mercury(II), nickel(II), uranyl(II) and zinc(II) with benzil bis(4-phenylthiosemicarbazone). *Transit Met Chem*. 1989;14(6):446–448.
 - Geary WJ. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coord Chem Rev*. 1971 Oct;7(1):81–122.
 - Prabir G, Ritwika R, Ankita D, and Goutam KL . Revelation of Varying Coordination Modes and Noninnocence of Deprotonated 2,2'-Bipyridine-3,3'-diol in {Os(bpy)2} Frameworks. *Inorganic Chemistry* 2014, 53 (19) , 10695-10707. <https://doi.org/10.1021/ic501852a>
 - Pandeya SN, Smitha S, Jyoti M, Sridhar SK. Biological activities of isatin and its derivatives. *Acta Pharm*. 2005 Mar;55(1):27–46
 - Carlin ,R and Van, A. a magnetic properties of Transition Metal Compounds. Verlage, New York Springer 1977.
 - Mulay,L. a magnetic Susceptibility. John Wiley and sons, New York . 1963 part 1,Vol(4).
 - R.C. Shank, J.P. Duguid, B.P. Marmion, R.A. Swain, 1975, “The practical of medical microbiology 12th ed.”, 2.
 - Suresh MS, Prakash V. Preparation Characterization and Antibacterial Studies of Chelates of Schiff Base Derived from 4-Aminoantipyrine, Furfural and o -phenylenediamine. *E-Journal Chem* [Internet]. 2011;8(3):1408–1416. Available from: <http://www.hindawi.com/journals/jchem/2011/254018/>
 - Suresh MS, Prakash V. Preparation, characterization and antibacterial studies of chelates of Schiff base derived from 4-aminoantipyrinevanillin and o-phen-Ylene diamine. *Int. J. Current*. 2011:268-275.
 - Lever ABP, Lewis J, Nyholm RS. Pyrazine-Metal Halide Complexes : New Types of Metal-Ligand Polymers. *Nature* [Internet]. 1961 Jan;189(4758):58–59. Available from: <https://doi.org/10.1038/189058a0>
 - Kavitha T, Kulandaisamy A. Synthesis, Spectroscopic Characterization, Electrochemical and Antimicrobial Studies of Copper(II), Nickel(II), Cobalt(II) and Zinc(II) Complexes Derived from 1-Phenyl-2,3-dimethyl-4(2-iminomethylbenzylidene)-pyroazol-5-(α -imino)-indole-3-propionic Acid. *Chem Sci Trans* [Internet]. 2013 May 1;2(S1):25–32. Available from: <http://www.e-journals.in/abstract.asp?Totarticle=3>
 - Mishra AP, Mishra R, Jain R, Gupta S. Synthesis of new VO(II), Co(II), Ni(II) and Cu(II) complexes with Isatin-3-chloro-4-floroaniline and 2-pyridinecarboxylidene-4-aminoantipyrine and their antimicrobial studies. *Mycobiology*. 2012;
 - Patel, A., & Bari, S., & Talele, G., & Patel, J., & Sarangapani, M. Synthesis And Antimicrobial Activity Of Some New Isatin Derivatives. *Iranian Journal Of Pharmaceutical Research (IJPR)*. 2006 [cited 2021 March 10];5(4):249-254. Available from: <https://www.sid.ir/en/journal/ViewPaper.aspx?id=79776>
 - Jaafar WA, Saeed RS. Synthesis, characterization and corrosion inhibition study of new heterocyclic compounds and schiff base with [Co (II), Ni (II), Cu (II) and Hg (II)] complexes. *Syst Rev Pharm*. 2020;11(10):134–143.
 - Ayati A, Emami S, Moghimi S, Foroumadi A. Thiazole in the targeted anticancer drug discovery. *Future Med Chem* [Internet]. 2019 Aug;11(15):1929–1952. Available from: <https://www.future-science.com/doi/10.4155/fmc-2018-0416>