

Preparation and Structural Studies of new Metal Complexes with 2-N(4- N,N- dimethyl benzyliden) 5 - (p-methoxy phenyl)- 1,3,4- thiodiazole

S. K. Abraheim , Sh. R. Bakir , M. F. Alias

Department of Chemistry , College of Science for Women , University of Baghdad

Abstract

A new Schiff base, 2-N(4- N,N – dimethyl benzyliden)5 – (p- methoxy phenyl) – 1,3,4-thiodiazol ,and their metal complexes Cu (II) ,Ni (II), Fe (III) , Pd (II) , Pt (IV) , Zn(II) ,V(IV) and Co (II) , were synthesized. The prepared complexes were identified and their structural geometries were suggested by using flame atomic absorption technique , FT-IR and Uv-Vis spectroscopy, in addition to magnetic susceptibility and conductivity measurements. The study of the nature of the complexes formed in ethanol solution , following the mole ratio method , gave results which were compared successfully with those obtained from the isolated solid state studied.

Structural geometries of compounds were also suggested in gas phase by using theoretical treatments , using HyperChem-6 program for the molecular mechanics and semi- empirical calculations. The heat of formation (ΔH_f°) and binding energy (ΔE_b) for the free ligand and their metal complexes were calculated by PM3 and AMBER methods, PM3 was used to evaluate the vibration spectra of schiff base and to compare the theoretically calculated wave numbers with experimental values by using 2- amino- 5 (p- methoxy phenyl)-1,3,4- thiodiazole as authentic compound. The theoretically obtained frequencies agreed calculation helped to assign unambiguously the most diagnostic bands.

Introduction

During the past two decades, a considerable attention has been paid to the chemistry of the metal complexes of schiff bases (**SB**) containing nitrogen and other donors, this may be attributed to their stability , biological activity and potential application in many fields such as oxidation catalysis, electro chemistry, etc (1-3). **SB** derived from sulfa drugs were successfully used for the bacteriostatic activities (4), and on the other side **SB** have been a great importance in the visual process (5), in addition to the reaction that involves removing the amino group by enzymic effect (enzymatic transition reaction), and some- B6. Catalysed reaction , as well as used as reversible oxygen carriers (4).

Another, path way of **SB** is involved in the metabolism of Aflatoxin , produced by the fungi *Aspergillus flavus*, which grows on peanuts, is an extremely potent carcinogen capable of inducing liver cancer. It inhibits both replication and transcript of DNA (6). **SB** are well known to have pronounced biological activities(7). The biological activity of SB is attributed to the formation of stable chelates with transition metals present in cell (8) Their ready synthesis and myriad properties have contributed greatly to their popularity and to the study of many biological systems. Many of the physiologically active compounds of SB find applications in the treatment of several diseases (9,10).

Bidentate and tridentate **SB** were among ligands that are extensively used for preparing metal complexes. These ligands are described according to their donor set NN, NO, NNO, NNS, NOO and NSO donors sets (11,12) The complexes of SB ligands have received a great deal of attention during the last years to prepare new sets of these bases and their complexes , these complexes have proven to be antitumor and have carcinostatic activity (13,14).

Experimental

A- Materials , Physical Measurements and Analysis

All chemicals were of the highest purity and were used as received. Melting points were recorded on Gallen Kamp melting point apparatus and were uncorrected. FT-IR spectra were recorded by using FT-IR 8400 Shimadzu in the range of $(4000-200)\text{cm}^{-1}$ and samples were measured as KBr disc. Electronic spectra were obtained by using (UV - 160) Shimadzu spectrophotometer at room temperature, using ethanol as a solvent. The metal content was estimated spectrometrically by using atomic absorption Shimadzu AA670 spectrophotometer. Conductivity measurements were obtained by using (WTW) conductometer, these measurements were obtained in DMF solvent by using concentration 10^{-3}M at 25°C . Magnetic susceptibility measurements were obtained at 25°C on the solid state applying Faraday's method using Bruker BM6 instrument.

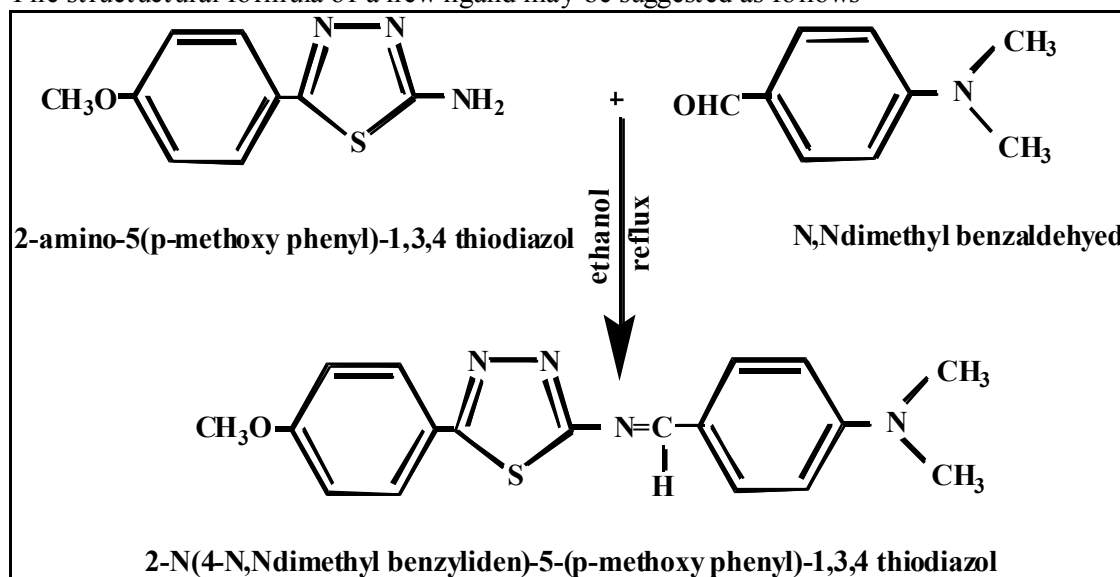
B- Preparation the Compounds

1- Preparation of the Ligand

The method that was used to prepare the 2-amino-5-(p-methoxy phenyl)-1,3,4-thiazol (AM) was reported elsewhere (15). The Schiff base (L) was prepared according to the following:-

(AM) (0.05 mmol, 5.17g) was dissolved in 15 ml of Absolute ethanol and N,N-dimethyl benzyldehyde (3.7g, 0.05 mole) in 10 ml of the same solvent was added, with drop of glacial acetic acid, the reaction mixture was refluxed for (4) hours, after that, the mixture was cooling at room temperature, then, left over night in a refrigerator, the separated solid was filtered and crystallized from ethanol. The physical properties of the (L) was listed in table (1)

The structural formula of a new ligand may be suggested as follows



2- Preparation of Complexes

One general procedure was adopted, as follows: The salts of $(\text{VO})\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{PdCl}_2(\text{PhCN})_2$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were dissolved in ethanol and added to an ethanol solution of schiff base in (1 : 2) or (1 : 1) mole ratio respectively with stirring. The mixture was heated under reflux for (4) hours. During this period the precipitation was completed. The precipitation was then collected by filtration, washed with ethanol and dried under vacuum. All these complexes were analyzed by using different available techniques, the physical properties of these compounds are listed in table(1).

C-Study of Complex Formation in Solution

Complexes of the schiff base with metal ions were studied in solution by using ethanol as a solvent, in order to determine [M:L] ratio in the complex following molar ratio method(16). A series of solutions were prepared by having a constant concentration 10^{-3}M of metal ion and the ligand. The [M:L] ratio was determined from the relationship between the absorption of the absorbed light and the mole ratio of [M:L]. The results of complexes formation in a solution were listed in table (1).

D- Programs Used in Theoretical Calculation

1- HyperChem-6

It is a sophisticated molecular modeler, editor and powerful computational package, that is known for its quality, flexibility and ease of use, uniting 3D visualization and animation with quantum chemical calculations, mechanics and dynamics.

HyperChem-6 can plot orbital wave functions resulting from semi-empirical quantum mechanical calculation, as well as the electrostatic potential, the total charge density or the total spin density can also be determined during a semi-empirical calculation. This information is useful in determining reactivity and correlating calculation results with the experimental data.

2- Types of Calculation

- Single point calculation that determines the molecular energy and properties for a given fixed geometry.
- Geometry optimization calculations employ energy minimization algorithms to locate stable structures.
- Vibrational frequency calculations to find the normal vibrational modes of an optimized structure. The vibrational spectrum can be displayed and the vibrational motions associated with specific transitions can be animated (17).

3- Computational Methods

a-Semi-empirical Quantum Mechanics

HyperChem offers ten semi-empirical molecular orbital methods, with options for organic and main group compounds, for transition metal complexes and spectral simulation (18). PM3 was used for the calculation of heat of formation and binding energy for all metal complexes except platinum (IV) and vanadium (IV) complexes.

b-Molecular Mechanics

It has three important concepts. Functional form, atom types and parameter sets. Each molecular mechanics method has its own functional form (Assisted Model Building and Energy Refinement) (AMBER) is based on a force field (19). AMBER was used for the calculation of the binding energy and heat of formation of platinum(IV) and vanadium(IV) complexes.

Result and Discussion

A- Elemental Analyses

The importance of preparing a new Schiff base arises from their versatility as starting materials for the synthesis of many complexes especially with transition metal ions. The physical and analytical data of the ligand and metal complexes are given in table (1). The results obtained from metal analysis are in a satisfactory agreement with the calculated values. The suggested molecular formula was also supported by spectral measurement as well as magnetic moments.

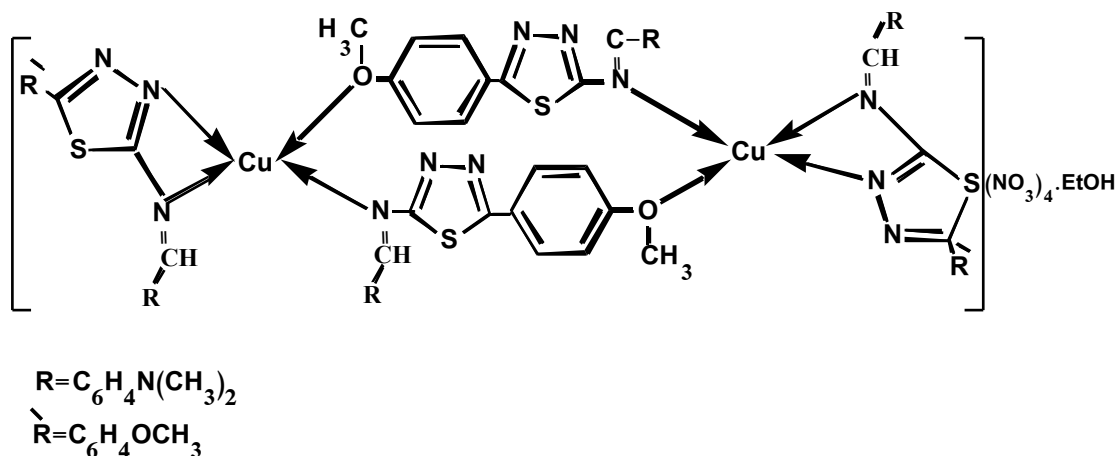
B- Infrared Spectroscopic Study

- 1- There is no appreciable change that took place in the absorption of $\nu_s(\text{COC})$ and $\nu_{as}(\text{COC})$ modes in the monomeric zinc, palladium and cobalt complexes, which exclude the possibility of oxygen atom of methoxy group participation in coordination. Furthermore, there is a change in frequency and intensity of $\nu_{\text{C}=\text{N}}$ and $\nu_{\text{N}-\text{N}}$ bands, this behaviour refers to coordinate modes of the ligand through nitrogen of isomethane group and nitrogen of the thiodiazole ring (20), table (2).
- 2- The ligand behaviour is a different coordinate, i.e. through oxygen of methoxy group and nitrogen of isomethane as a bridge for the dimeric iron, platinum, copper and vanadium complexes or through sulfur atom of thiodiazole for the nickel complex. The other behaviour of the ligand took place as bidentate through N,N or N,S atoms for the complexes copper, vanadium, platinum and nickel ion, while the ligand behaves as a monodentate coordinate through nitrogen of isomethane only in iron complex (20).
- 3- $\nu_{\text{V}=\text{O}}$ stretching mode in vanadium complex was observed at 979 cm^{-1} as a strong band. Coordination of sulfate ion to this complex was observed as a bidentate behaviour (21).
- 4- These absorptions were further supported by the appearance frequencies of $\nu_{\text{M}-\text{S}}$, $\nu_{\text{M}-\text{O}}$, $\nu_{\text{M}-\text{N}}$ and $\nu_{\text{M}-\text{Cl}}$ respectively (20, 22).
- 5- A broad band was observed around $(3450-3510)\text{ cm}^{-1}$ in the spectra of the complexes, assigned to $\nu_{\text{O}-\text{H}}$ and suggested the presence of water or ethanol molecules in the crystal lattice of the complexes (23).

C-Electronic Spectroscopy Study

1-CuL Complex

The electronic spectra of copper complex showed one broad absorption band in the region around 12987 cm^{-1} which was attributed to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition table (3). The position of this band is in an agreement with what is reported for highly distortion octahedral geometry (24,25). The electronic spectra coupled with magnetic moment (1.03 BM) studies indicate square planar geometry around Cu(II) complex (26), conductivity measurement showed that the complex was ionic. The structure of this complex can be suggested as below.



2-CoL Complex

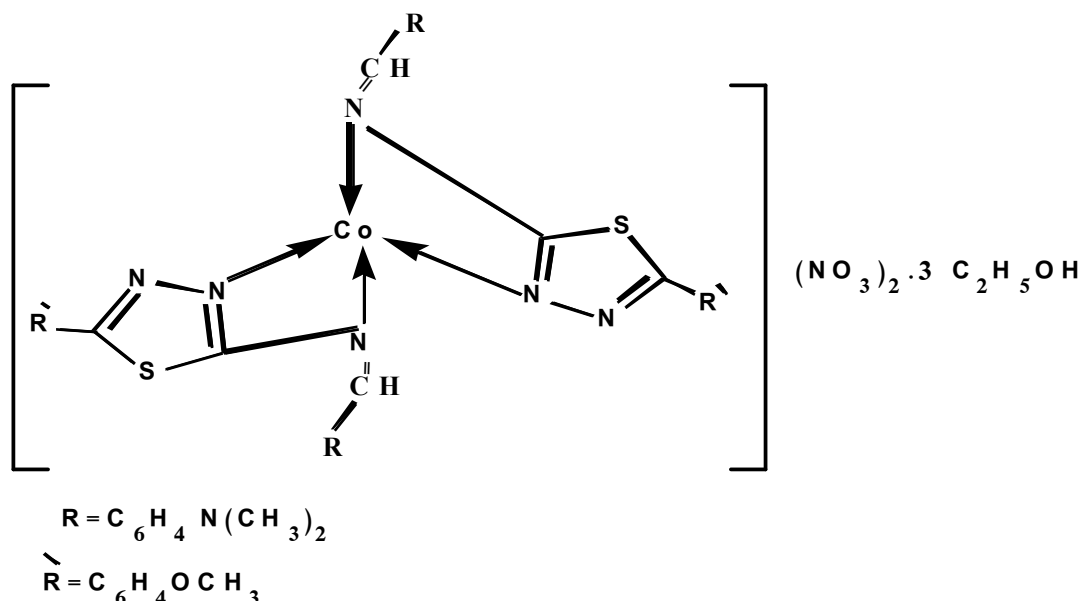
The blue – greenish cobalt(II) complex with ligand showed a magnetic moment of (4.8 BM), which indicates a high – spin type complex. Electronic spectrum in ethanol solution exhibited a split band in the range of $(17000\text{--}14000)\text{ cm}^{-1}$, the split band is a typical tetrahedral spectral type and can be assigned as ${}^4A_2 \rightarrow {}^4T_{1(p)}(v_3)$, and in addition there is a band at 3409 cm^{-1} which was taken from IR and can be assigned to ${}^4A_2 \rightarrow {}^4T_{2(F)}(v_2)$ transition (27, 28). The colour as well as the magnetic moment further indicated tetrahedral geometry. The (v_2) and various ligand field parameters were calculated by reference to Tanabe-Sugano diagram for d^7 configuration table (3). The calculation of the spin-orbit coupling constant (λ) was

$$\mu_{\text{obs}} = \mu_{\text{s.o}} - 15.59 \lambda / 10 Dq$$

where μ_{obs} = The observed effective magnetic

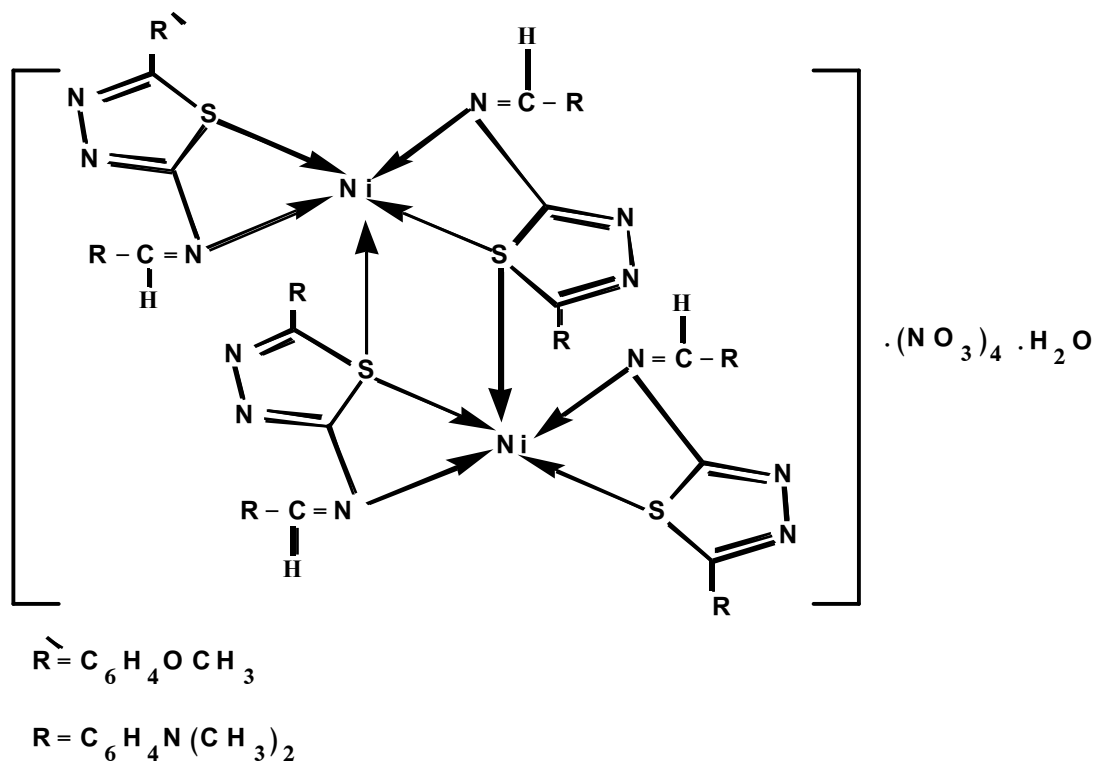
$\mu_{\text{s.o}}$ = The electronic spin only magnetic moment

The resulting value ($\lambda = -218.5\text{ cm}^{-1}$), this value shows the present complex to be distorted tetrahedral (29). The nephelauxetic factor β was calculated and found to be (0.63) indicating high degree of covalence in the bonding of ligand-donor atoms with cobalt (II) ion. The molar conductance showed that the complex is electrolyte, and the following structural may be proposed.



3-NiL Complex

The electronic spectral data, and their assignment as well as the calculated ligand field parameters for nickel thiodiazal benzyliden, are shown in table (3). Considering these data and comparison with a large number of published works (30- 32), led to the proposal of the following dimeric structure.



Which satisfies the EAN configuration for Ni. The ligand field parameters B/β and $10Dq$ were calculated by fitting the ratio of the observed two bands, i.e v_2 and v_3 to T-S. diagram as shown in d^8 configuration. The calculation of spin- orbit coupling constant λ was

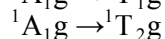
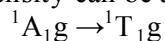
$$\mu_{obs} = \mu_{s.o} \left(1 - \frac{4\lambda}{10Dq} \right)$$

$$3.35 = 2.83 \left(1 - \frac{4\lambda}{10767} \right)$$

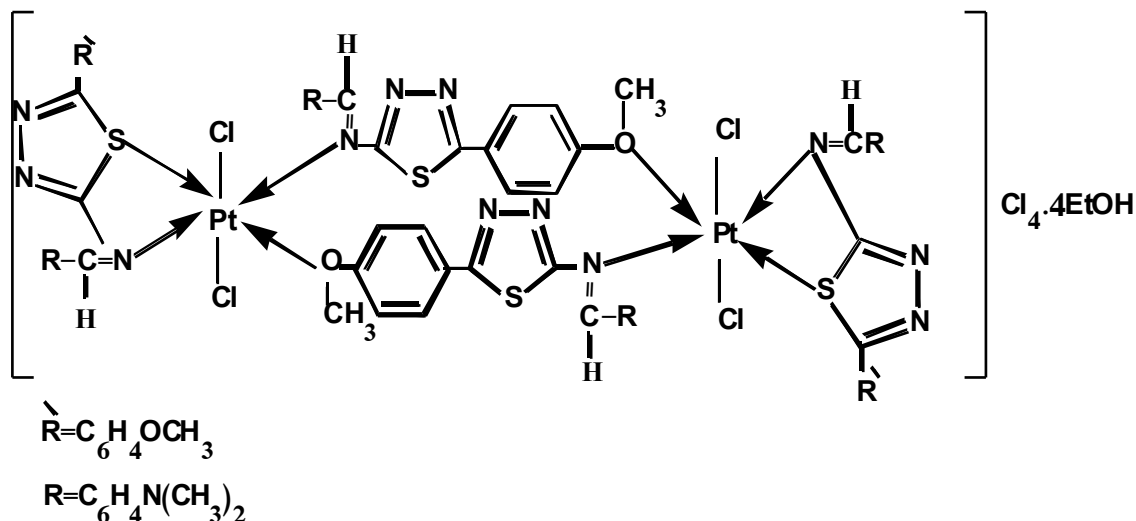
The resulting value $= -3186.3 \text{ cm}^{-1}$, shows the present nickel complex to be tetragonal distortion (33) or this value is well showing tetragonal distortion. The magnetic measurement is (3.35BM), which shows the complex to be paramagnetic and conductivity studied show that the complex is electrolyte.

4-PtL Complex

The electronic spectrum of the platinum (IV) shows three bands, the first weak one appeared at 13315 cm^{-1} can be assigned to the forbidden transition $^1A_{1g} \rightarrow ^3T_{1g}$ and other two bands with higher intensity can be assigned to the following transition in octahedral environment (34).

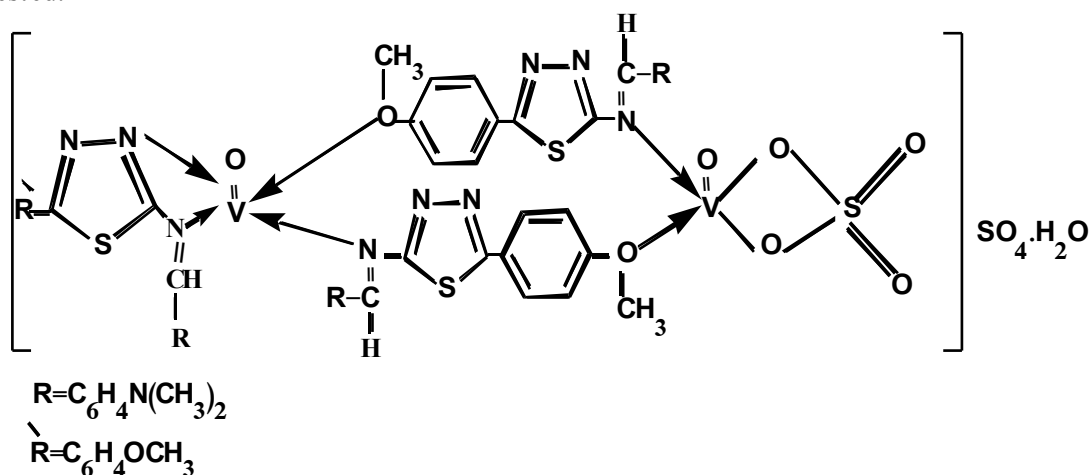


This coordination type is common for Pt(IV) complexes (33,34), the study of conductivity behaviour in DMF shows the complex to be ionic. The magnetic measurement data is (0.82 BM) which shows the complex to be diamagnetic, table (3), therefore, the following structure can be suggested:



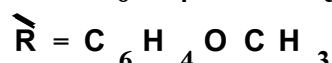
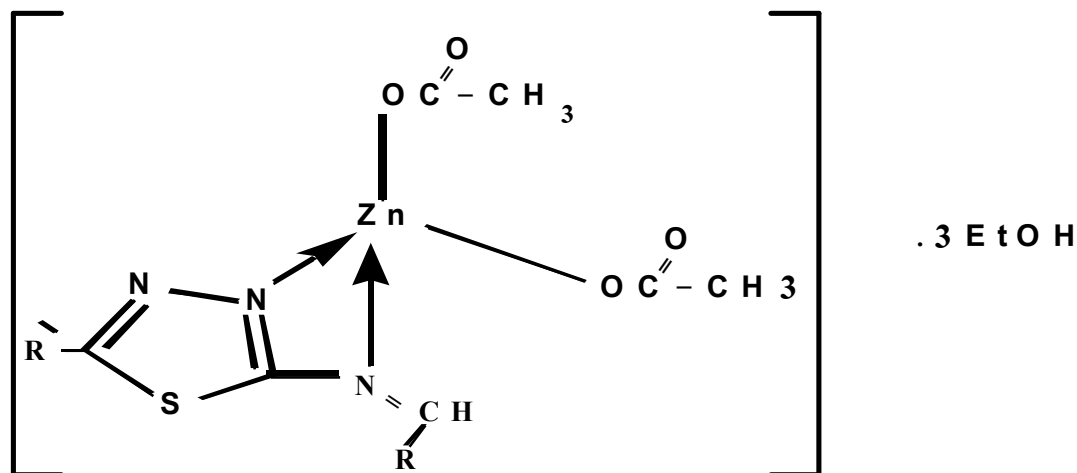
5-VL Complex

Vanadium complex showed two bands related to square pyramidal vanadium complex (34,35). They were observed at $12755, 17699\text{ cm}^{-1}$ table (3) for the first and second transition and were assigned to $^2B_{2g} \rightarrow ^2E_g$ and $^2B_{2g} \rightarrow ^2B_{1g}$ transition respectively (27,29,26,34). The magnetic moment (1.3 BM) is lower than spin only value, this is due to spin-coupling (29, 36). Conductivity in DMF showed that the complex was ionic, According to this, the following structural formula can be suggested.



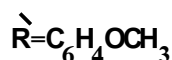
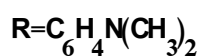
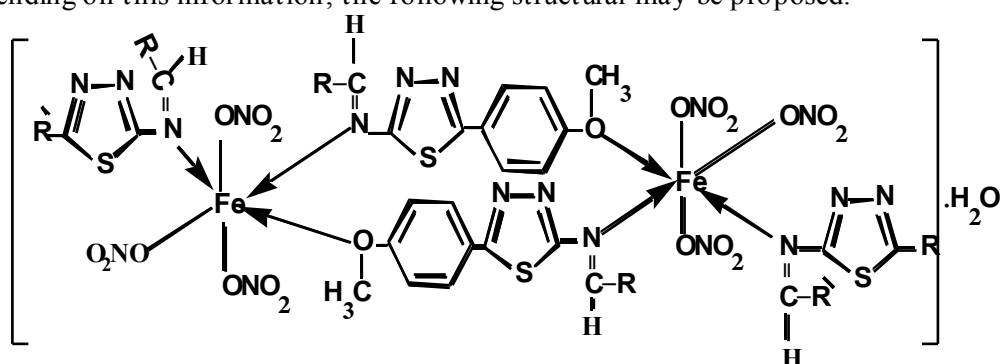
6-ZnL Complex

The prepared complex is colourless and diamagnetic which is expected for d^{10} ion. The UV-Vis spectrum of the compound shows a relative change in the band position compared to that of the free. The conductivity measurement for this complex in DMF at 25°C showed to be nonconducting ($22\mu\text{S}\cdot\text{cm}^{-1}$). The most probable structure of this complex is tetrahedral as shown below.



7-FeL Complex

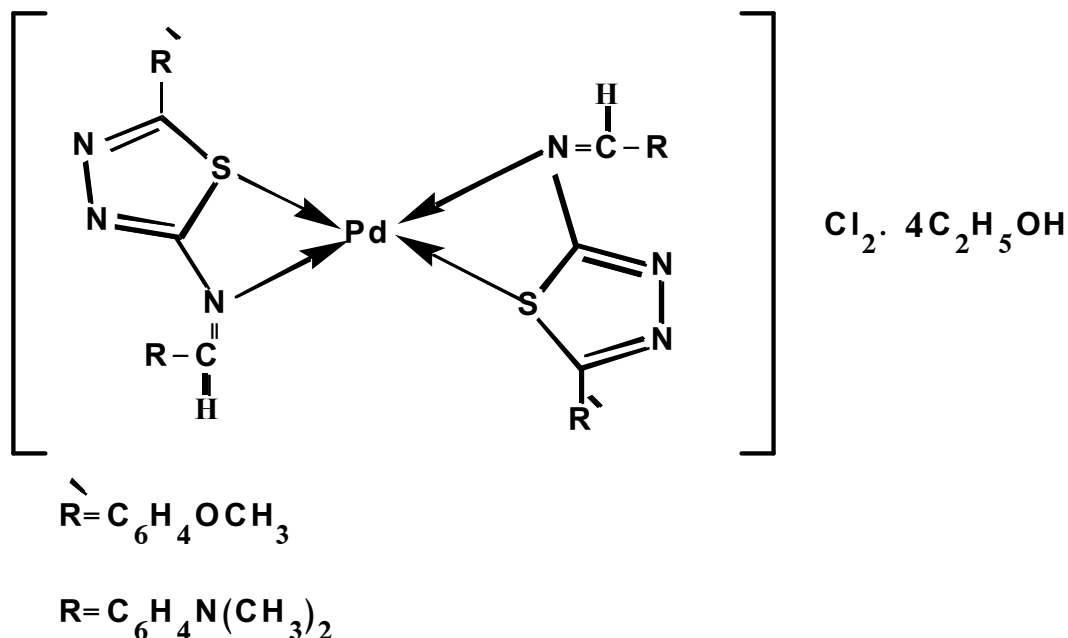
The magnetic measurement shows the iron ion in its orange complex to be a high spin paramagnetic (5.32 BM), of d^5 configuration. This suggestion was supported by the number of maxima observed in the electronic spectrum of the complex, which show two maxima bands which may be assigned to transition ${}^6A_1g \rightarrow {}^4T_{2g(g)}$, ${}^6A_1g \rightarrow {}^4A_1g + {}^4E_{g(g)}$ as shown in table (3) (33,37). The v_1 and Racah parameter β , and the value of $10Dq$, which were calculated by reference to Tanabe-Sugano for d^5 configuration. The conductivity measurement in DMF shows the complex to be non-electrolyte. Depending on this information, the following structural may be proposed.



8-PdL Complex

The brown palladium complex shows strong charge transfer bands which was extended to the visible region, so the ligand field bands could not be established easily. Nevertheless two weak bands at 22471 and 28169 cm^{-1} (table 3) may be assigned to the transition

${}^1A_1g \rightarrow {}^1B_1g$ (${}^2a_1g \rightarrow {}^1a_1g$, 1b_1g) and ${}^1A_1g \rightarrow {}^1E_g$ (4eg , ${}^2a_1g \rightarrow {}^3eg$, ${}^2a_1g \rightarrow {}^3eg$, 2a_1g , 1b_1g) respectively, for spin-paired d^8 square planar configuration with magnetic moment value of (0.00 BM). This assignment was made by reference to known palladium complex with square planar stereochemistry, and came in a good agreement with published data (34,33). Conductivity value confirmed the ionic structure. Depending on this finding the following structural formula of this complex may be proposed.



D- Solution Study

Molar ratio method was followed to determine the M : L ratio. The results of complexes in ethanol solution suggest that the metal to ligand ratio was (1 : 2), which are dimeric in nature for copper, platinum, nickel, and monomer for palladium and cobalt complexes, and (1 : 1.7) for vanadium complex, while (1 : 1) for the zinc and iron metal complexes, which were comparable to those obtained from isolated solid study, table (1).

E- Theoretical Studies

(i) The program HyperChem-6 was used for the semi-empirical and molecular mechanics calculations, at optimized geometries energies, the results on PM3 and AMBER methods of calculation in gas phase for the heat of formation (ΔH_f°) and binding energy (ΔE_b) for the ligands and their complexes were calculated and tabulated in table (4). Also PM3 was used for the evaluation of the vibrational spectra of the AM and Schiff base to compare the theoretically calculated wave numbers with the experimental values. Theoretically calculated wave numbers for these ligands showed that some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations and are described in table (2) and (5) and the figures (1) (2).

(ii) **Electrostatic Potential (E.P.):** Electron distribution governs the electrostatic potential of molecules and describes the interaction of energy of the molecular system with a positive point charge, so it is useful for finding sites of reaction in a molecule. Positive charged species tend to attack a molecule where the E.P. is strongly negative. Electrophilic attack (38,39). (E.P.) of free ligand was calculated and plotted as 2D contour to investigate the reactive sites of the molecules Fig(3), and one can interpret the stereochemistry and rates of many reactions involving soft electrophiles and nucleophiles in terms of the properties of frontier orbitals (HOMO and LUMO). Overlap between the HOMO and LUMO is a governing factor in many reactions. The HOMO and LUMO values were plotted as 2D contour to get more information about these molecules. The results of calculation showed that the LUMO of transition metal ion prefer to react with the HOMO of sulfur and nitrogen atoms of Schiff base ligand.

(iii) Optimized Geometries Energy of Metal Complexes for Schiff Base

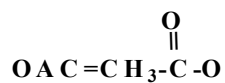
All theoretically probable structures of metal complexes with Schiff base were calculated to search for the most probable model building stable structure, these shapes Fig(4), show the calculated optimal geometries for (L) and their metal complexes. The results of PM3 method of calculation in gas phase for the binding energies and heat of formation of Co(II), Cu(II), Pd(II), Zn(II), Ni(II) and Fe(III), while AMBER method was used to calculate the binding energies which is equal to heat formation for both Pt(IV) and V(IV) complexes, and are described in table (4).

References

1. Tai,X.; Yin, X.; Chen, Q. and Tan,M. (2003). *Molecules*, 8, 439 .
2. .Miliani, F.; Casellato, U.; Vigato, P. A. and Vidali, M. (1985). *Inorg. Chem. , Acta.* 103, 15.
3. Shady,H.; Ragab, F. A. and Aly,E. I. (1988). *Kimphrmzh*, 16 (12), 1466, (1989). *Chem Alost*, 110, 173068W
4. Echhor,G.L. (1993). "Inorganic Biochemistry" Elsevier Scientific Puplishing Company, Amsterdam.
5. Mohomed,A.Z.; (1992). M. SC. Thesis, university of mosul .
6. Massey,T.E.; Stewart, R. K.; Dainels, (1995) J. M. and L. Liv, pro. Soc. Exp. Biol. Med, 205-213.
7. Sahai,R. K.; Kushwaha, S.S.and Chaudhary, A. K. (1989). *J. Indian chem*, 19:13,844 .
8. Banerjea ,O. (1980)."Coordination Chemistry, 20" , Pergaman Press. IUPAC, Oxford, New York.
9. Lai, Keemti; Shukla,P.K. (1981). *J. Indian Chem.* 58:115 .
10. Tren,Mats. T. M. (1953)."Antibiotics of chemotherapy" , 3,941.
11. Freyberg, D. P. and Mockler,G. M. (1976). *J. Chem. Soc. Daltontrans*, 5, 445 .
12. Goodiwn,J.A. and Wilson,L. (1989).*J. Inorg. Chem. ,* 28, 42.
13. Davar Boghaei,M. and Sajjed,M. (2000).*J. Molecular Catalysis A: Chemical*, 179, 41 .
14. Shrivastava ,V. S.; Bhasin ,C. P. and Saxena,G. C. (1989).*J. Indian Chem. Soc. ,* 63, 865 .
15. Shafiee,A. ; Nami, E.; Amnsobi, P.; Forommav,A. and Shekar, M. (1995).*J. Hetro Cyclic Chem.,* 32,p.1235 .
16. . Skooge ,D. A. , (1988)."Fundemental of Analytical Chemistry", 5th Ed. New York.
17. Foresman, J. and . Frish. ,C., (1996). "Exploring Chemistry with Electronic Structure Methods" 2nd Ed.,Gaussian Inc., Pittsburgh, P.A.
18. Fried, Howard L.; and Souers,P.; (1999).CHEETAH 2-Ovsers Mannal, Lawrence Livermore National Laboratory.
19. Atkins P. and Friedman , R. (1997)."Molecular Quantum Mechainics"; 3rd Ed. ; New York; Oxford University press Inc ; NY .
20. Nakamoto ,N. (1997). " Infrared Spectra of Inorganic and Coordination Compounds". 6th ed , Wiley Intrescience, New York.
21. . Kumari ,U. N. and Singh ,C. P. (1990). "Oxovanadium (IV) Complexes with thiohydrazide derivatives" *J. Ind. Chem. Soc. Lvu* (8).
22. Singh ,B. and Thakup ,K. P. (1973). *J. Inorg. Nud. Chem.,* 36, 1735.
23. Silvertistein,R. M.; Bassler ,G. C. and Morrill,T. C. (1981). "Spectrometric Ident ification of Organic Compounds", 4th ed., John Wiley and Sons.
24. Hiremath, A. C. ; Halli, M. B. and Huggi, N. V. ; (1986). *J Ind. Chem. Soc. ; Lx III* ; 374.
25. Nawar, N. E. ; Khattab,M. A. and El Kaddan, A. H. ; (1996). *J. Ind. Chem., LXV*, 308.
26. Burger , K. ; (1956) ; "Magneto Chemistry" 2nd. Ed. ; Ins.; Publishers; Ltd. ; Londo.
27. Carlin, R. L. ; ; (1965). "Transition Metal chemistry"; 1, Marcel Dekker N.
28. Hedwy, S. ; (1978).*Inorg. Chem.*; 29;155 .
29. Lever,A.B.P.(1986)."Inorganic Electronic Spectroscopy", Ansterdam London .
30. Aggarwal ,R.C. and Yadava,R. B. S. *Trans. (1979) Met. Chem.,* 1, 139.
31. Wu, Y. M. and Peng,S. M. (1980) *J. , Inorg. Nucl. Chem.* 42,205.
32. Deshmuke ,K. and Bhobe, R. A. (1979)*J. Inorg. Nucl. Chem.* ,40, 134.
33. Jorgeuson, C. K. (1968)."Absorption Spectra and Chemical bonding in Complexes"; pergaman press.
34. Figgis, B., N.,(1966). "Introduction to Ligand Field"; Interscience; New York .
35. ao ,P. V. and Rao,N. R. (1988).*Ind. J. of Chem. ;* 27A,73.
36. Mahta,P. K. ; Gahlot,A. (1986). *J. Ind. Chem. Soc. , LXIII* (2).
37. Bailer,J. C.; Emeleus, H. J. and Nypholm, R. (1973). "Comprehensive Inorganic Chemistry", Perganmon Press.
38. Steward,J .J .P.; MOPAC 2000 VIO for windows (Singie), MO20-AS-W, Fujitsu STEM EUROPE.
39. Anderson,W .P .; Behm, P. and Glennon,T .M. , (1997).*J. Phys. Chem.,vol.* (101)

Table (1): Physical data for the ligand (L) and their metal complexes						
Co mp.	Colour	m.p C°	Yield %	Atomic Abs. Found (Cal.)	Metal to ligand ratio	Suggest Molecular formula
L	Pale Orang	114	84.0	—		C ₁₈ H ₁₈ N ₄ SO
Cu L	Pale Brown	84	50.0	5.58 (6.70)	1 : 2	[Cu ₂ (L) ₄](NO ₃) ₄ . C ₂ H ₅ OH
Co L	Bluish-Green	63 d	75.8	5.29 (4.51)	1 : 2	[Co(L) ₂](NO ₃) ₂ .3 C ₂ H ₅ OH
Ni L	Dark Orang	160	51.7	6.78 (7.39)	1 : 2	[Ni ₂ (L) ₂](NO ₃) ₄ . H ₂ O
Pt L	Dark Orang	204	40.0	17.61 (17.88)	1:2	[Pt(L) ₂ Cl ₂] ₂ Cl ₄ .4 C ₂ H ₅ OH
V L	Olive	> 360	44.4	—	1:1.7	[(VO) ₂ (L) ₃ SO ₄] ₂ SO ₄ .H ₂ O
Zn L	Orang	122 -23	42.8	4.49 (5.33)	1 : 1	[Zn(L)(OAC) ₂] ₂ .3 C ₂ H ₅ OH
Fe L	Reddish-orange	65	64.0	.96 (5.90)	1:1	[Fe(L) ₂ (NO ₃) ₃] ₂ .2 H ₂ O
Pd L	Dark Brown	201	84.0	10.2 (9.8)	1 : 2	[Pd(L) ₂] ₂ Cl ₂ .4C ₂ H ₅ OH

d : decomposed poin



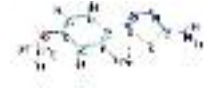
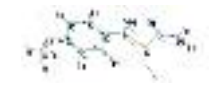
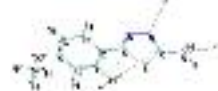
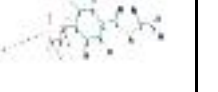
		
$\nu_{\text{asy}}\text{NH}_2$ (3534.00)	$\nu_{\text{sym}}\text{NH}_2$ (3426.39)	$\nu\text{N-N}$ (1441.58)
		
08). $\nu\text{C-S}$ (839	$\nu_{\text{asy}}\text{C-H}$ (3041.60)	$\nu_{\text{sym}}\text{C-H}$ (3029.29)
		
νNCS (1014.63)	νNCS (1238.01)	$\nu\text{N-C-N}$ (1330.84)
		
$\nu\text{C-S-C}$ (1166.09)	$\nu_{\text{asy}}\text{OCH}_3$ (1281.19)	$\nu_{\text{sym}}\text{OCH}_3$ (1003.63)
		
	δNH_2 (1652.39)	$\nu\text{C-N}$ (879.42)

Fig. (1) The Calculated Vibrational Frequencies of AM

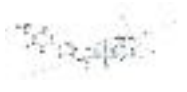
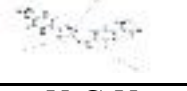
		
$\nu\text{C=Nis}$ (1628.62)	$\nu\text{N-N}$ (1439.56)	$\nu\text{C-S}$ (717.39)
		
$\nu\text{Ar-N}$ (1328.25)	$\nu\text{C=Nring}$ (1568.45)	$\nu\text{C=Nring}$ (1576.88)
		
$\nu\text{OCH}_3\text{asy}$ (1293.73)	$\nu\text{OCH}_3\text{sy}$ (1099.09)	$\nu\text{C-S-C}$ (1155.76)
		
$\nu\text{N-C-N}$ (1325.22)	νNCS (1073.69)	νNCS (1166.13)

Fig. (2) The Calculated Vibrational Frequencies of Schiff Base L

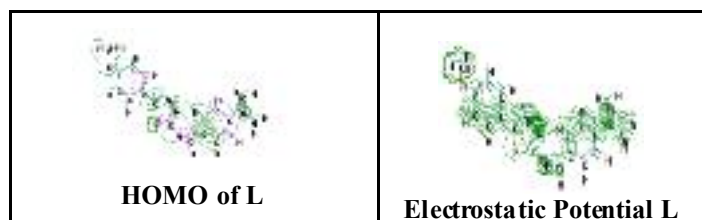


Fig. (3): HOMO and Electrostatic Potential as 2D Contours for L

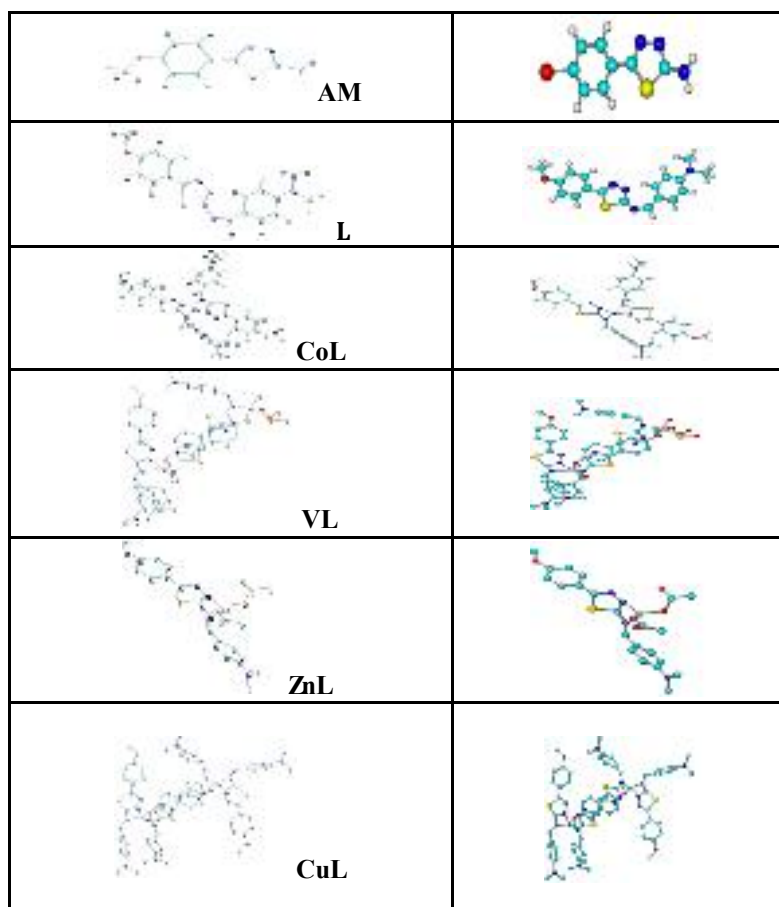


Fig. (4): Conformational Structure of AM, L and their Complexes

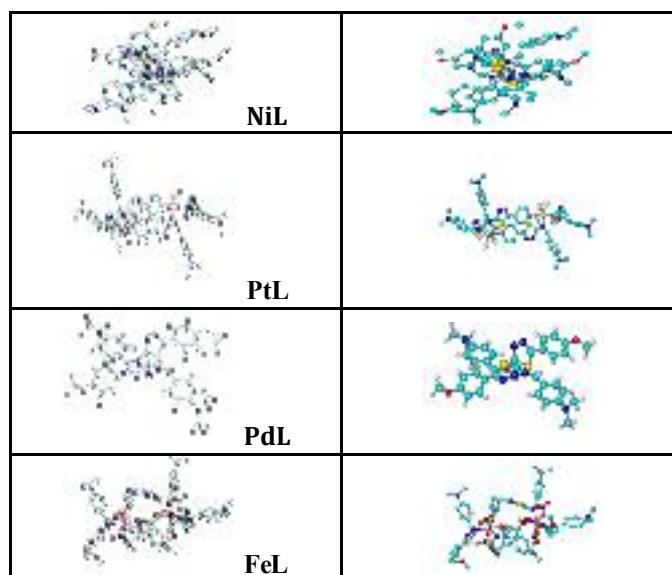


Table (3) : Electronic spectra, conductance and magnetic moment, for metal complexes of L										
Co mp.	Bands cm ⁻¹	Assignm ent	B	B [\]	Dq /B [\]	β	10D q	15B [\]	μ _{eff}	μ _s c m ⁻¹
Co L	3409 (5541) cal. 15460 av	⁴ A ₂ → ⁴ T _{2(F)} ⁴ A ₂ → ⁴ T _{1(F)} ⁴ A ₂ → ⁴ T _{1(P)}	11 28	718 .3	0.5	0. 63	3663 .3	107 74.5	4. 8	18 2
Cu L	12987	² B _{1g} → ² A _{1g}							1. 03	21
V L	12755 17699	² B _{2g} → ² E _g ² B _{2g} → ² B _{1g}							1. 3	18 2
Pt L	13315 23148 27397	¹ A _{1g} → ³ T _{1g} ¹ A _{1g} → ¹ T _{1g} ¹ A _{1g} → ¹ T _{1g}							0. 82	20 5

Ni L	13850 1067.2 18148 23529 (26250).cal.	$^3A_{2g} \rightarrow$ 1E_g $^3A_{2g}$ $\rightarrow ^3T_{2g(F)}$ $^3A_{2g}$ $\rightarrow ^3T_{1g(F)}$ $^3A_{2g}$ $\rightarrow ^3T_{1g(P)}$	10 80	102 5.5	1.0 5	0. 94	1076 7	153 82	3. 35	30 6
Fe L	99300 cal. (88268) 14814 21834	$^6A_{1g} \rightarrow$ $^4T_{1g(G)}$ $^6A_{1g} \rightarrow$ $^4T_{2g(G)}$ $^6A_{1g} \rightarrow$ $^4T_{1g} + ^4E_g$	13 00	677 .8	1.7	0. 52	1152 0	101 67	5. 32	21
Pd L	22471 28169	$^1A_{1g} \rightarrow$ $^1B_{1g}$ $^1A_{1g} \rightarrow$ $^1E_{1g}$							0. 00	69

Table (2) The most diagnostic FT- IR bands for the L and its metal complexes											
Comp.	$\nu_{(C=N)}$	(NCS)	(CSC)	(CS)	$\nu_{(C=N)}$ ring	$\nu_{(NCN)}$	$\nu_{(N-N)}$	Ar-N	M-N	M-S	M-O
L	558.6	1051 1120	164. 9	732	589.2 527.5	373.2	4426	311. 5			
Co L	1647	1064 18.6	172. 6	5.1	604.6 535.2	137 3.2	1442	311. 5	563	478	
Ni L	1649	1070 10.9	174	5.1	596.9 527.5	137 3.2	144 2	311	505	486	
Zn L	1647	1058 18.6	168	729	604.6 535.2	137 3.2	148 1.2	311. 5	516		47.4
Cu L	1647	1049.2 10.0 2	168	72.9	596.9 535.2	1369	1485		6.8		78.3
Pt L	597.2	1063 26.3	0.3 118	750	604.6 542.9	373.2	1460	311. 5	78.0	70.6	32.3
V L	1646	1057 41.7	167	733	1604 504.3	1373	1485	311	540		
Pd L	1650	1033 1126	172. 6	5.1	1596 1520	1373	1442	310	516	486	
Fe L	1627	1050 1125	166	733	1590 1530	1373		310	520		416

Table (4): Conformation Energetic (in KJ.Mol⁻¹) for L and their metal complexes

Conform ation	PM3		AMBER
	ΔH_f°	ΔE_b	$\Delta H_f^\circ = \Delta E_b$
AM	54.01773	-2417.8692	
L	-100.3836365	- 4491.4313635	
CoL	-109.3332	-9447.4652	
NiL	-180.8655578	-9328.1735578	
CuL	-315.9996320	-18212.6603680	
PtL			469.320923
VL			-377002.125000
ZnL	-27.446653	-5884.83965	
PdL	151.5953	-9122.034	

IBN AL- HAITHAM J. FOR PURE & APPL. SCI VOL.22 (3) 2009

Table (5): Comparison of experimental and

ν N-N	ν CSC	ν C=S	ν NCN	ν OCH	ν AF-N
(1441) **)	(1166) **)	(839) **)	(1330) **)	(1281, ** 1003.6)	-
(1439) ** 5)	(1155. ** 7)	(717. ** 3)	(1325 ** 2)	(2970,28 ** 94)	(13282 **)

Where :
 * : Experimental frequency
 ** : Theoretical frequency
 *** : Error % due to main difference in the experimental measurements and theoretical treatment of vibrational spectrum

Sy mb.	ν NH ₂	C=N _{is}	ν NCS
A	(3534, 3426) ^{**}	-	(1238.01, 1014.6) ^{**}
M			
L ₁	-	(1628. _{**} 6)	(1073.6, _{**} 1166.1)

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية المجلد 22 (3) 2009

تحضير ودراسة تراكيب معقدات فلزية جديدة مع $N-2$ (N ، N ، 4)

ثنائي مثيل بنزيلدين (5 - P) - ميثوكسي فينيل (1 ، 3 ، 4 -

ثايوديازول

سرى خليل ابراهيم ، شيماء رجب باقر ، محاسن فيصل الياس
قسم الكيمياء، كلية العلوم للبنات ، جامعة بغداد

الخلاصة

تم تحضير الليكاند N-2 (N ، N ، 4 ، - ثنائي مثيل بنزيلدين) 5 - بارا ميثوكسي فينيل) - 1 ، 3 ، 4 - ثايوديازول ومعداته مع الايونات النحاس (II)، والنيكل (II)، والبلاديوم (II)، والبلاتين (IV)، والزنك (II)، والحديد (III)، والكوبلت (II)، والفناديوم (IV) 0 شخص وعين الشكل الهندسي للمركبات المحضرة باستخدام الأجهزة الطيفية ، الأشعة تحت الحمراء والأشعة فوق البنفسجية - المرئية فضلا عن قياس الحساسية المغناطيسية والتوصيل الكهربائي لها 0 درس طبيعة المعقد المتكون في المحاليل باتباع طريقة النسب المولية، اذ اعطت نتائج مقارنة مع النتائج التي تم الحصول عليها بالحالة الصلبة المعزولة.

اجريت معالجة تكوين المعقدات نظرياً في الطور الغازي باستخدام برنامج (HyperChem-6) بتطبيق الميكانيك الجزيئي والشبه التجريبي في الحساب وذلك باستخدام الدوال PM3 ، AMBER لحساب حرارة التكوين (ΔH_f°) وطاقة الترابط (ΔE_b) وبدرجة حرارة 298 كلفن لليكاند ومعداته المحضرة. كذلك حسب الجهد الألكتروستاتيكي لبيان المواقع الفعالة لقاعدة شف وجرى حساب التردد الاهتزازي نظرياً وباستخدام الدالة PM3 لقاعدة شف ومقارنتها مع القيم المقاسه عملياً باستخدام 2-امينو - 5 (بارا ميثوكسي فينيل) - 1 ، 3 ، 4 - ثايوديازول مركبا قياسيا ووجد أن هناك توافقاً كبيراً بين القيم العملية والمحسوبة نظرياً مع زيادة امكانية تشخيص الحزم بشكل ادق 0