

Synthesis, Characterization, Theoretical studies and Biological activities of bimetallic Complexes of new Schiff base thiadiazole derivative with some trivalent metal ions

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Abstract:

Tetrachloro [5-(5⁻-phenyl-3⁻-N-ethyl-2⁻-thiazolene)imino-3-N-ethyl-2-thion-1,3,4-thiadiazole].titanium(IV), of a new Schiff base{TiL} derived from [tetra chloro (5- amino-3-N-ethyl – 2 -thione-1, 3, 4 – thiadiazole).titanium(IV)] and(3-N-ethyl- 2-one – 1, 3,4-thiadiazole) have been prepared.The product was characterized by (FT-IR) ,(UV-Vis) Spectroscopy and elemental analysis (C.H.N.S) . {TiL}has been used as a chelating ligand to prepare a number of metal complexes with[Cr(III), Fe(III) , Ru(III), Rh(III) and Au(III)] . The prepared complexes were isolated and characterized by using (FT-IR) and (UV-Vis) spectroscopy, elemental analysis (C.H.N.S), Flame atomic absorption technique, in addition to magnetic susceptibility and conductivity measurements. Molar ratio method measurement in solution gave comparable results with those obtained from solid state studies.

The work also include a theoretical treatment of the formed complex in the gas phase, this was done using the Hyperchem-6 program for the Molecular mechanics and Semi-empirical calculations. The heat of formation (ΔH_f°) , binding energy (ΔE_B) and bond length (ΔE_L) for [ASN] , [TiA]and {TiL} ligand and their metal complexes were calculated by (PM3 and AMBER) methods at 298 K°. Furthermore the electrostatic potential of the free ligand{TiL} was calculated to investigate the reactive sites of the molecules .PM3 were used to evaluate the vibrational spectra and electronic spectra of the ligand{TiL} and it's metal complexes(A1-A5) then compare the theoretically calculated wave numbers with the experimental values by using the [ASN] and [TiA]as authentic compounds .The theoretically obtained frequencies agreed with those found experimentally, in addition the calculation helped to assign unambiguously the most diagnostic bands.

The antibacterial activity for [ASN], [TiA] and free ligand {TiL} and their metal complexes(A1-A5) were studied against two selected micro - organisms [(Pseudomonas aeruginosa) as gram negative] and[(Bacillus Subtilis) as gram positive]. The minimal inhibitory concentrations (MIC) have been also studied to determine the low concentration for inhibition. The antibiotic (Ampicillin) has been chosen to compare their activity with those of the new compounds. Further more the antifungal activity against two micro-organism (Penicillium Spp.) and (Aspergillus flavus) were studied for all compounds. The results showed great enhancement of activity of the complexes relative to that of their respective [ASN], [TiA] and free ligand {TiL}.This was attributed to the synergetic effect between the metal ion and the ligand, in addition to the differences in the structural varieties.

الخلاصة:

يتضمن هذا البحث تحضير مشتق لقاعدة شف الجديدة:

Tetra chloro [5-(5⁻-phenyl-3⁻-N-ethyl-2⁻-thiazolene)imino-3-N-ethyl-2-thion-1,3,4-thiadiazole].titanium(IV).{TiL}

من عملية تكاثف [tetra chloro (5- amino - 3 - N- ethyl – 2 –thione – 1, 3) . titanium (IV)] مع thiadiazole - 4 , (5-phenyl-3-N-ethyl- 2-one – 1,3,4-thiadiazole). جرى تشخيص {TiL} بطرائق تحليل طيف الأشعة تحت الحمراء (FT-IR) وطيف الأشعة فوق البنفسجية-المرئية والتحليل الدقيق للعناصر (C.H.N.S). تم استخدام قاعدة شف {TiL} كليكاند في تحضير معقدات الايونات الفلزية الثلاثية (الكروم و الحديد و الروثينيوم و الروديوم و الذهب). تم عزل المعقدات الجديدة وتشخيصها باستخدام طيف الأشعة تحت الحمراء وطيف الأشعة فوق البنفسجية-المرئية وتقنية (C.H.N.S) وتقنية الامتصاص الذري للهبتي للعناصر اضافة الى قياسات الحساسية المغناطيسية والتوصيلية الكهربائية. تم قياس

النسبة المولية للفلز مع {TiL} في المحلول وقد اعطت هذه الدراسة نتائج مطابقة مع تلك التي تم الحصول عليها في الحالة الصلبة. تضمن العمل ايضا معالجة تكوين المعقدات نظريا في الطور الغازي، باستخدام برنامج (6-Hyperchem) وبتطبيق الميكانيك الجزيئي والشبه التجريبي في الحساب وباستخدام الدوال (PM3 و AMBER) لحساب حرارة تكوين (ΔH_f°) وطاقة التاصر (ΔE_b) و أطوال الأواصر (ΔE_L) وبدرجة حرارة 298 كلفن للمركبات [ASN] و [TiA] و لليكاند {TiL} و معقداته المحضرة، كذلك تم حساب الجهد الكهروستاتيكي لليكاند {TiL} لبيان المواقع الفعالة ضمن الجزيئة. جرى كذلك حساب التردد الاهتزازي والاطياف الالكترونية نظريا وباستخدام الدالة PM3 لليكاند {TiL} (ومقارنتها مع القيم المقاسة عمليا باستخدام [TiA و ASN] كمركبات قياسية) ومعقداتها (A1-A5) وجد بان هنالك توافقا كبيرا بين القيم العملية والمحسوبة نظريا مع إمكانية تشخيص الحزم بشكل أدق. تمّ تقويم الفعالية المضادة للبكتريا للمركبات [TiA و ASN] و لليكاند {TiL} ومعقداته وأختير نوعان من البكتريا (Pseudomonas aeruginosa) سالبة الصبغة و (Bacillus Subtilis) موجبة الصبغة لهذا الغرض ودراسة أقل تركيز يحدث عنده التثبيط (MIC). تمت مقارنة فعالية المركبات المحضرة مع المضاد الحيوي (Ampicillin). كما تم اجراء التقويم الحيوي للمركبات [TiA و ASN] و لليكاند {TiL} ومعقداته ضد نوعين من الفطريات Penicillium (Spp.) و Aspergillus flavus flavus) وقد أظهرت نتائج التقويم زيادة كبيرة في فعالية المعقدات المحضرة منها. تم تفسير الفعالية المضادة للبكتريا و الفطريات إلى التأثير المتداوب للفعالية بين الفلز و الليكاند فضلا عن الإختلاف في تراكيب المركبات المحضرة

Introduction:

Thiadiazoles and in particular, 1,3,4-thiadiazole derivatives, were among the various heterocyclic that have received a great deal of attention during the last years, especially as anti-microbial agents^(1, 2). Most of the substitution have been carried out at the 2- and 5- positions of the thiadiazole ring, these include amino derivatives, alkyl thio, disulfide and heterocyclic rings⁽³⁻⁶⁾. Since 2-thiol-5-amino-1,3,4-thiadiazole does contain the (-N-C=S) moiety, which have hard (N) besides soft (S) atoms and have a well established biological activity^(4, 6-8). The introduction of azomethine group on the thiadiazole ring is reported to have a strong of biological activities⁽⁹⁻¹⁴⁾.

In the present paper a new type of bimetallic compounds involving [tetrachloro [5-(5⁻-phenyl-3⁻-N-ethyl-2⁻-thiazolene) imino-3-N-ethyl-2-thion-1,3,4-thiadiazole].titanium(IV)] {TiL} derivative of Schiff base have been reported and evaluation the biological activities of {TiL} and their metal complexes.

Experimental:

(A) Physical measurements and analysis:

Melting points were recorded on gallenkamp Melting point apparatus and were uncorrected. FT-IR spectra were recorded using FT-IR8300 Shimadzu in the range of (4000-300) cm^{-1} , samples were measured as (CsI disc). Electronic spectra were obtained using UV-1650PC Shimadzu Spectrophotometer at room temperature, the measurements were recorded using a concentration of ($1 \times 10^{-3} \text{M}$) of the complex in chloroform as a solvent. The metal content was estimated using atomic absorption Shimadzu AA670 Spectrophotometer. The elemental analyses (C.H.N.S) were obtained using EA-034.mth. Conductivity measurements were obtained using Corning conductivity meter 220, these measurements were obtained in DMF solvent using concentration of (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) Material and Methods:

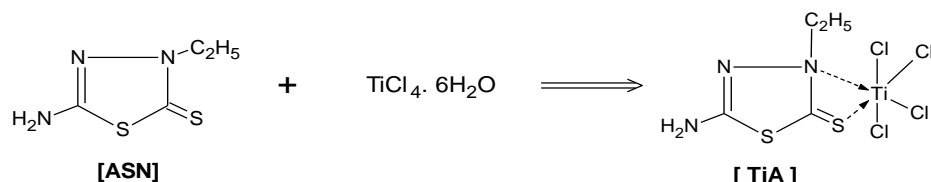
All chemicals were of highest purity and were used as received.

Preparation of the ligand {TiL}:-

(1)- Preparation tetrachloro [5-amino-3-N-ethyl-2-thion-1, 3, 4- thiadiazole].titanium(IV), [(TiA)] .

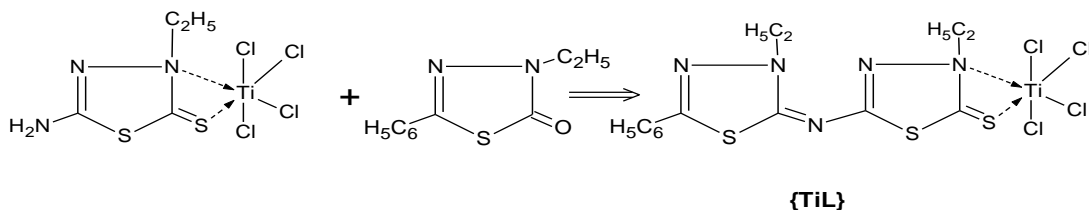
5-amino -3-N-ethyl-2-thion-1,3,4- thiadiazole (ASN) was prepared as described in literature method^(6,15). Ethanolic solution of titanium chloride ($\text{TiCl}_4 \cdot 6\text{H}_2\text{O}$) (0.01 mole, 2.26gm) was added to an ethanolic solution (0.01mole, 2.26gm) of (ASN) with stirring. The mixture was heated under reflux for one hour during this time a white precipitate was formed.

The residue was filtered off, dried and recrystallized from ethanol, to give compound (TiA). The physical data are given in Table (1).



(2)-Preparation tetrachloro [5-(5-phenyl-3--N-ethyl-2--thiazolene) imino-3-N-ethyl-2-thion-1, 3, 4- thiadiazole].titanium(IV), [{TiL}].

The Schiff base {TiL} was prepared by condensing the (TiA) (0.01 mole, 3.51gm) and (5-phenyl-3-N-ethyl- 2-one – 1,3,4-thiadiazole) (0.01 mole,2.06gm) in ethanol ,the reaction mixture was refluxed for (3) hours. On cooling the separated solid was filtered off, dried and recrystallized from ethanol, the physical data are given in Table (1).



Preparation of Schiff base complexes (A1-A5):

Hot ethanolic solution of metal chloride (0.01M) [CrCl₃.6H₂O,FeCl₃.9H₂O ,RuCl₃. H₂O,RhCl₃. H₂Oand HAuCl₄. H₂O] and (0.01M)of{TiL},were mixed in stoichiometric ratio with continuous stirring and heated under reflux for one hour. The reaction mixture was then concentrated to half of its original volume when complexes precipitated. The complexes thus obtained were filtered and washed with hot water and finally washed well with hot ethanol. The complexes were dried under vacuum. The physical data of the prepared complexes are shown in Table (1).

Study of complex formation in solution:-

Complexes of {TiL} with metal ions were studied in solution using ethanol as a solvent, in order to determined [M: TiL] ratio in the complex following molar ratio method⁽¹⁶⁾.A series of solutions were prepared having a constant concentration[1×10⁻⁴M]of the metal ion and{TiL}.The[M/TiL] ratio was determined from the relation ship between the absorption of the absorbed light and the mole ratio of [M: TiL].The results of complexes formation in solution were listed in Table(1).

Theoretical treatment:-

Hyperchem is a sophisticated molecular modeler, editor and powerful computational package, that is known for its' quality, flexibility and ease of use^(17,18). It can plot orbital wave functions resulting from semi-empirical quantum mechanical calculations,as well as the electrostatic potential, the total charge density or the total spin density can also be determined during semi-empirical calculation, this information is useful in determining reactivity and correlating calculation results with experimental data.

Computational methods:

- a) Semi -empirical quantum mechanical
- b) Molecular mechanics
- c) Mopac 2000

Types of calculations:

The types^(19,20) of prediction possible of Molecules are:

- a) Geometry optimization calculations employ energy minimization algorithms to locate stable structures.
- b) Bond distances
- c) Molecular dynamics witch provide the thermodymemic calculations and dynamic behavior of molecules
- d) Plot the electrostatic potential field (HOMO and LUMO).
- e) Vibrational spectrum (I.R and Raman spectra).
- f)Electronic spectrum (U.V- Visible spectra).

Biological activities:-

The in vitro biological screening effects of the investigated compounds were tested against selected types of bacteria which include (*Pseudomonas aeruginosa*) as gram negative and (*Bacillus Subtilis*) as gram positive and the fungus, (*Penicillium Spp.*) and (*Aspergillus niger*) by the Well Diffusion Method^(21, 22) using agar nutrient as the medium. Stock solutions ($10^{-3}M$) were prepared by dissolving the compounds in DMSO solution. In a typical procedure, a well was made on the agar medium inoculated with microorganisms. The well was filled with the test solution using a micropipette and the plate was incubated at 35°C for 72 hours. During this period, the test solution diffused and the growth of the inoculated microorganisms was affected. The second technique was to get the sensitivity of each microorganism toward the new compounds by determining the minimal inhibitory concentration (MIC) which was achieved by using Tube Dilution Method^(21, 22). The (MIC) of the new compounds for each micro-organism was measured at the lowest concentration of the compound required to inhibit the growth of this micro-organism, these tubes containing different concentrations of the new compounds were incubated at 37 °C for 45 hours and the antibiotic (Ampicillin) has been chosen to compare their activity with those of the new compounds.

Result and discussion:

Part (I):- Synthesis and characterization of the isolated Schiff base derivatives and its metal complexes

(A)Elemental analysis:

The interaction of Schiff base {TiL} with appropriate metal salt under study in ethanol gave a crystalline products with different colors depending on the metal ion. All complexes were readily soluble in chloroform, dimethyleformamide and dimethylsulfoxide and were found to be stable toward air and moisture, as well as they were decomposed before melting. The physical and analytical data of [ASN], [TiA] and free ligand {TiL} and their metal complexes (A1-A5) are given in Table (1). Results obtained from elemental analyses (C.H.N.S) and flame atomic absorption are in a satisfactory agreement with the calculated values. The suggested molecular formulas also supported by spectra(FT-IR) and (UV-Vis.) analyses, furthermore magnetic susceptibility and conductivity measurements.

Table (1) Physical data for ([ASN], [TiA]) and free ligand{TiL} and its metal complexes(A1-A5)

Comp. No.	Color	Melting point	Yield %	Metal analyses found (calc.)					Mole ratio [M:TiL] Ratio	Suggested formula for precipitate isolated
				C%	H%	N%	S%	M%		
[ASN]	Bright Yellow	132-135	95	29.26 (29.81)	3.92 (4.35)	26.16 (26.09)	39.03 (39.75)	–	–	C ₄ H ₇ N ₈ S ₂
[TiA]	White	150-153	90	13.08 (13.67)	2.03 (1.99)	11.47 (11.96)	28.11 (27.35)	13.82 (13.65)	1:1	C ₄ H ₇ N ₈ S ₂ TiCl ₄
{TiL}	Pale Yellow	187-190	82	30.79 (31.16)	2.46 (2.78)	11.99 (12.98)	17.69 (17.81)	8.14 (8.89)	1:1	C ₁₄ H ₁₅ N ₅ S ₃ TiCl ₄
(A1)	Dark Green	212	75	23.11 (23.48)	3.16 (2.38)	10.09 (9.78)	12.90 (13.42)	6.18 (7.27)	1:1	[Cr {TiL} Cl ₃]. H ₂ O
(A2)	Dark Brown	290	73	22.86 (22.24)	2.33 (2.78)	8.59 (9.27)	13.43 (12.71)	7.27 (7.39)	1:1	[Fe {TiL} Cl ₃]. 3H ₂ O
(A3)	Brownish-Yellow	278	80	21.68 (22.42)	2.34 (2.00)	10.21 (9.34)	13.67 (12.81)	13.61 (13.86)	1:1	[Rh {TiL} Cl ₃]
(A4)	Brown	285	77	20.68 (21.56)	1.48 (2.36)	6.99 (7.86)	10.54 (10.78)	22.53 (22.12)	1:1	[Au{TiL}Cl ₃]. C ₂ H ₅ OH
(A5)	Black red	298	75	21.73 (22.50)	2.43 (2.01)	10.24 (9.38)	12.69 (12.86)	14.42 (13.54)	1:1	[Ru{TiL}Cl ₃]

Infrared Spectra:-

All the recorded spectra were in the solid state using CsI .As expected, FT-IR gave a good information about the complexation behavior of the ligand with various metal ions. The characteristic frequencies of free ligand{TiL} and its metal complexes (A1-A5) were readily assigned based on comparison with literature values⁽²³⁻²⁵⁾.

The FT-IR of [5-amino -3-N-ethyl-2-thion-1,3,4- thiadiazole] (ASN) was characterized by bands at the regions [1274,(3250 and 3531),(2960 and 2871) and (975)] cm⁻¹,these can be assigned to [νC=S, νNH₂, νN-C₂H₅ and νN-N] respectively ⁽²⁴⁾ ,a negative shift with reduced intensity were observed for[νC=S, νN-C₂H₅ and νN-N] when react with titanium tetrachloride, table(2),while no significant change in the position of νNH₂,these clearly indicate that the [5-amino -3-N-ethyl-2-thion-1,3,4- thiadiazole] act as a bidentate chelating agent by coordinating to the titanium ion (Ti⁺⁴) through sulpher atom of the thione and nitrogen of the thiadiazole ring to form [5-amino-3-N-ethyl-2-thion-1, 3, 4- thiadiazole].tetanium(IV), (TiA) octahedralgeometry around (Ti⁺⁴) complex. An analysis the spectrum of free ligand{TiL} to their respective (TiA) complex show absence of the absorption band at (3250 and 3531) cm⁻¹ for νNH₂,the appearance of the (C=N) stretching mode of azomethine group at(1649) cm⁻¹ ,are utilized to confirm the structure of {TiL} , as well as a strong high intensity bands appeared at (975) and (2871 and 2954) cm⁻¹,were assigned to the stretching mode of [N-N and N-C₂H₅] respectively ⁽²⁴⁾ , table(2).In the all complexes(A1-A5) the Schiff base {TiL} ligand behave as a tridentate coordinating to the [Cr(III) , Fe(III) , Rh(III), Au(III) and Ru(III)]ions throw the nitrogen of azomethine and nitrogen of the thiadiazole rings, therefore the bands due to[νC=N, νN-C₂H₅ and νN-N] were shifted to lower frequencies side on complexation, table(2).The behavior of {TiL} was further indicated by appearance of (M-N and M-Cl) bands stretching frequencies respectively ⁽²⁵⁾ , table (2) . Abroad band was observed in the spectra of [A1, A2 and A4] complexes assigned as (νO-H) suggested the presence of a water or ethanol molecule ⁽²³⁻²⁶⁾.

Table (2) Characteristic stretching vibrational frequencies (cm⁻¹) located in the FT-IR spectra of [ASN], [TiA] and free ligand {TiL} and its metal complexes (A1-A5)

Comp. No.	νC=N	νN-C ₂ H ₅	ν NH ₂	νC=S	νN-N	ν M-N	ν M-Cl	Others
[ASN]	-	2871,2960(s)	3250,3531(sb)	1274(ms)	975(s)	-	-	-
[TiA]	-	2863,2925(m)	3251,3531 (sb)	1263(m)	945(m s)	506 (mw)	380(w)	ν M-S= (449)
{TiL}	1649(ms)	2871, 2738, 2954(ms)	-	1264 (m)	975,945 (s,ms)	506 (mw)	382(w)	ν M-S= (449)
(A1)	1596(m)	2863,2926(m)	-	1262(m)	921(m)	512(mw)	391(w)	ν(O-H) 3504(b)
(A2)	1598(m)	2856, 2923 (m)	-	1264 (m)	923(m)	510(mw)	389(w)	ν(O-H) 3508(b)
(A3)	1596(m)	2858, 2925 (m)	-	1262(m)	920(m)	515(mw)	387(w)	-
(A4)	1596 (m)	2856, 2925 (m)	-	1262(m)	923 (m)	512(mw)	390(w)	3510(b)
(A5)	1598 (m)	2858,2925(m)	-	1263(m)	921(m)	510(mw)	391(w)	-

Where :- (s=strong, m=medium, sb=strong broad, ms=medium strong, mw=medium weak, w=week, b=broad)

Electronic absorption Spectra, Magnetic susceptibility and Conductivity measurement:-

The ultra violet spectra of [ASN] ,showed three absorption peaks in the regions(25641-27027),(29412-33898)and (36496-43478) cm^{-1} ,assignable to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions respectively^(27,28) .However these bands were shifted to high wave length when titanium tetrachloride coordinating with[ASN]through the sulfur of carbonyl and nitrogen atom of thiadiazole ring.

The [TiA] complex was diamagnetic as expected for $[d^0]$ ion; therefore the UV-Vis. Spectra of the complex show relative change in the band position compared to that of [ASN] alon, table (3). The conductivity measurements indicate a non conductive behavior of the complex table (3).

The UV.spectrum of Schiff base{TiL}ligand showed an intense band at $(40820)\text{cm}^{-1}$ with a weak shoulder at (36680) followed by a strong intense bands at $(32260)\text{cm}^{-1}$ and $(26954)\text{cm}^{-1}$.The former two above bands may be due to $\pi \rightarrow \pi^*$ transition⁽²⁸⁾ in a heterocyclic thiadiazole moiety, whereas the latter two bands indicates a $n \rightarrow \pi^*$ transitions in an extended conjugated system which arises due to greater delocalization (azomethiane group and thiadiazole ring)of the π -electron resulting in a bath chromic shift⁽²⁷⁾ .

As further structural tools, electronic spectral (were recorded for their solution in chloroform in the range [200-900]nm),magnetic susceptibility (at room temperature) and conductivity (in DMF as a solvent)studied have been used to confirm the geometry of the (A1-A5) complexes .

(A1) :- Electronic spectrum of the dark green Cr(III) complex in chloroform solution, showed tree absorption band , the first at $(16393)\text{cm}^{-1}$ a second band at $(26953)\text{cm}^{-1}$ and the absorption band at $(35875)\text{cm}^{-1}$,which came in accordance with the published data for octahedral Cr(III) complexes⁽²⁹⁻³¹⁾ ,as well as the ratio (ν_2/ν_1) (1.6) lies close to that required for octahedral geometry^(32,33) .The values of $(10Dq, Dq/ B-, B-$ and $\beta)$ have been calculated to be $(16120,1.65,977$ and $1.06)$ respectively. The measured magnetic moment (3.86 B.M) . Conductivity in (DMF) showed that the complex non ionic, table (3).

(A2) :-The solution spectrum of the dark brown Fe(III) complex shows three absorption bands at $(16530,21200$ and $25920)\text{cm}^{-1}$ which are assigned to the transitions:- ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and $\{\text{TiL}\} \rightarrow \text{Fe}_{(\text{C.T})}$ ⁽³³⁾ ,The values of $(10 Dq, Dq/ B-, B-$ and $\beta)$ come out to be $(14760,1.7,868$ and $0.67)$ respectively. The magnetic moment of the present complex is (5.69 B.M) with five unpaired electrons and octahedral configuration⁽³²⁻³⁴⁾ . Conductivity measurement showed the complex was non ionic, table (3).

(A3) :- The solution spectrum of the brownish-Yellow Rh(III) complex gave weak bands at $(18068)\text{cm}^{-1}$ and a shoulder at $(22934)\text{cm}^{-1}$,these two bands correspond to those of octahedral Rh(III) complex⁽³⁵⁻³⁷⁾ ,and were assigned to ${}^1A_{1g} \rightarrow {}^3T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition respectively^(23,34) . The values of $(10 Dq, Dq/ B-, B-$ and $\beta)$ came out to $(22171,2.03,410$ and $0.57)$ respectively. The observed magnetic value (1.95 B.M) of the present Rh(III) complex (d^6) configuration agree with octahedral geometry around metal ion, this result indicates higher orbital contribution⁽³⁸⁾ . Conductivity measurement in (DMF) showed that the complex to be non ionic, table (3).

(A4) :- The UV-Vis spectrum of the prepared Au(III) complex is largely dominated by charge transfer band at $(38682)\text{cm}^{-1}$,the other bands at $(33642)\text{cm}^{-1}$,which is a shoulder on the previous one , as well as the weak band at $(27855)\text{cm}^{-1}$, are assigned as ligand field bands due to the transitions:- ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}$,these assignments when compared to those published for octahedral low spin Au(III) complexes^(30,35,36,39) ,it show good compatibility ,so octahedral stereochemistry is suggested for the named complex. The observed high magnetic value (1.82 B.M) of the present Au(III) complex(d^8) configuration agree with octahedral geometry around metal ion, this result indicates a higher orbital contribution around Au(III)⁽³⁰⁾ .conduct metric measurement in (DMF) showed a non conductive behavior of the complex, table (3).

(A5) :-The electronic spectrum of Ru(III) complex in chloroform gave four absorption bands appeared at $(16889,19610,27722$ and $34053)\text{cm}^{-1}$,following octahedral field

with(d⁵)configuration^(37,40-42). The effective magnetic moment at room temperature was found to be (1.89 B.M) revealing inner-orbital low spin octahedral stereochemistry of the{TiL}ligand around Ru(III) metal ion^(38,41). Conductivity measurement showed that the complex wasn't ionic, table (3).

Table (3) Electronic spectra (in CHCl₃), Magnetic moment (B.M) and Conductance in (DMF) for[TiA] and free ligand{TiL} and its metal complexes

Comp. No.	Bands cm ⁻¹	Assignment	10Dq	Molar cond. μs. Cm ⁻¹	μ _{eff} . B.M	Suggested structure
[TiA]	40675 33557 26831	π → π* π → π* n → π*	-	13.54	0.33	Octahedral
{TiL}	40820 36680 32260 26954	π → π* π → π* π → π* n → π*	-	13.89	0.33	Octahedral
(A1)	16393 26953 35875	⁴ A _{2g} → ⁴ T _{2g} (F) ⁴ A _{2g} → ⁴ T _{1g} (F) ⁴ A _{2g} → ⁴ T _{1g} (P)	16120	15.04	3.86	Octahedral
(A2)	16530 21200 25920	⁶ A _{1g} → ⁴ T _{1g} ⁶ A _{1g} → ⁴ T _{2g} {TiL} → Fe _(C.T)	14760	11.97	5.69	Octahedral
(A3)	18068 22934	¹ A _{1g} → ³ T _{1g} ¹ A _{1g} → ¹ T _{1g}	22171	14.43	1.95	Octahedral
(A4)	27855 33642 38682	³ A _{2g} → ³ T _{2g} ³ A _{2g} → ³ T _{1g} {TiL} → Au _(C.T))	27855	17.39	1.82	Octahedral
(A5)	16889 19610 27722 34053	² T _{2g} → ⁴ T _{1g} ² T _{2g} → ⁴ T _{2g} ² T _{1g} → ² E _g ² T _{1g} → ² A _{1g}	27722	13.68	1.89	Octahedral

Part (II):- Spectrophotometer study of Schiff base complexes formation in organic solvent Molar ratio method:

The compositions of the (A1-A5) complexes have been studied by the molar ratio method. The results of complexes in ethanol as a solvent, suggest that the metal to ligand ratio was [1:1] for all complexes, which were comparable to those obtained from solid state study, as is shown in Table (1).

Part (III):- Theoretical study of Schiff base and their metal complexes in gas phase

A) Electrostatic Potentials:

Electron distribution governs the electrostatic potential of the molecules. The electrostatic potential (E.P) describes the interaction of energy of the molecular system with a positive point charge. (E.P) is useful for finding sites of reaction in a molecule; positively charged species tend to attack a molecule where the electro static potential is strongly negative (electrophonic attack)⁽¹⁷⁾.

The (E.P) of the free ligand {TiL} was calculated and plotted as 2D contour to investigate the reactive sites of the molecules, Fig (1). Also one can interpret the stereochemistry and rates of many reactions involving “soft” electrophiles and nucleophiles in terms of the properties of frontier orbital (HOMO, highest occupied molecular orbital) and (LUMO, lowest unoccupied molecules). The results of calculations show that the LUMO of transition metal ions prefer to react with the HOMO of(N-N) , (C=N) and (-N-C₂H₅) for {TiL} ligand.

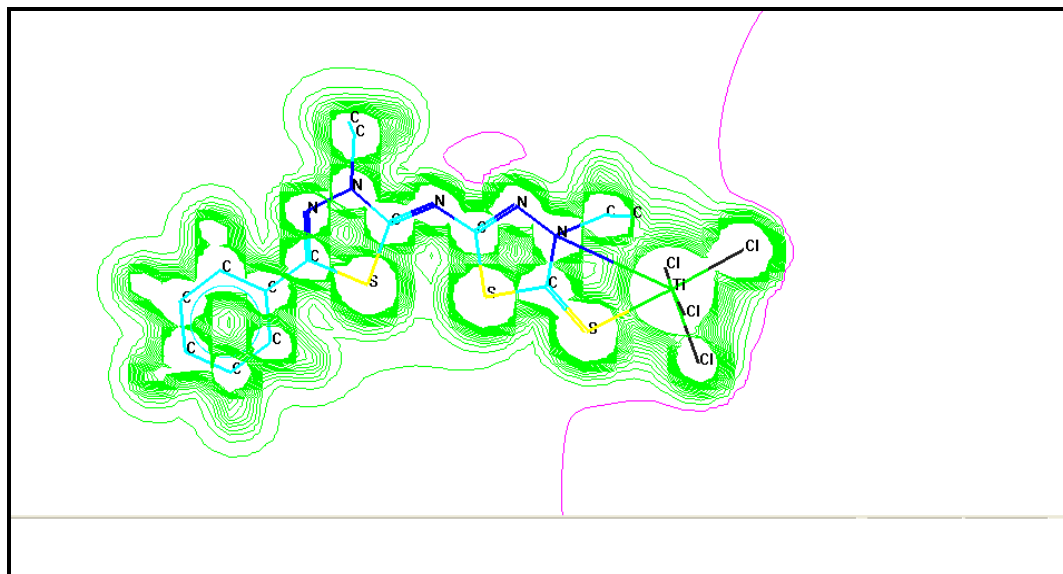


Fig. (1):- Electrostatic potential (HOMO and LUMO) as 2D contours for Schiff base {TiL}

A) Optimized geometries and energies:

The conformations of the ligand and complexes obtained from molecular mechanics calculation were fully re-optimized to estimate the binding energy and the enthalpies of formation for the free ligand{TiL} and their metal complexes by using the (PM3 and AMBER) semi-empirical methods at a value of Geometry Optimization constant (0.01Kj/mol) for the ligand and their metal complexes, as is shown in Table (4) .

Table (4) Conformation energetic in (Kj. mol⁻¹) for Schiff base and their metal complexes

Conformation	ΔH_f°	ΔE_b
{TiL}	172.33	- 4021.25
(A1)	-107.29	-3575.32
(A2)	-97.03	-3399.18
(A3)	-89.68	-3061.77
(A4)	-69.78	-2999.79
(A5)	-62.59	-2972.84

B) Optimized vibrational spectra for {TiL} and their metal complexes (A1-A5):

The vibrational spectra of the free ligand {TiL} and their metal complexes (A1-A5) have been calculated, Table (5). The theoretically calculated wave numbers for {TiL} and (A1-A5) compounds showed that some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations⁽¹⁸⁾. The most diagnostic calculated vibrational frequencies were chosen for the assignment of {TiL}ligand and (A1-A5) metal complexes which are included in Table (5), Fig(2) and their respective experimental vibrational modes are shown in Table(2).

The results obtained from the theoretical calculated wave numbers for the ligand were compared successfully with the calculated frequencies of [5-amino-3-N-ethyl-2-thion-1, 3, 4-thiadiazole].titanium(IV) , [(TiA)] as authentic sample to predict the deviation or error caused

from the difference between the experimental measurements and theoretically calculated results of the vibrational spectra, Table (5).

The results obtained for the theoretical calculations of the frequencies of $\nu(\text{C}=\text{N})$, $\nu(-\text{N}-\text{C}_2\text{H}_5)$, $\nu(\text{C}=\text{S})$, $\nu(\text{NH}_2)$ and $\nu(\text{N}-\text{N})$ for (TiA), {TiL} ligand and (A1-A5) complexes as well as $\nu(\text{M}-\text{N})$, $\nu(\text{M}-\text{Cl})$ and $\nu(\text{O}-\text{H})$ which agreed well with those obtained with the experimental values in Table(2).

Table (5) Comparison between the experimental and theoretical vibrational frequencies (cm^{-1}) For [TiA], free ligand {TiL} and their metal complexes (A1-A5) (cm^{-1})

Com p. No.	$\nu\text{C}=\text{N}$	$\nu\text{N}-\text{C}_2\text{H}_5$	νNH_2	$\nu\text{C}=\text{S}$	$\nu\text{N}-\text{N}$	$\nu \text{M}-\text{N}$	$\nu \text{M}-\text{Cl}$	Others
[TiA]	-	(2843,2924)*	(3498)*	(1288)*	(946)*	(508)*	(379)*	(451)*
	-	(2863,2925)**	(3530)**	(1263)**	(945)**	(506)**	(380)**	M-S= (449) **
	-	[0.70,0.03] ***	[0.91] ***	[1.94] ***	[0.11] ***	[0.39] ***	[0.26] ***	[0.44] ***
{TiL }	(1647)*	(2869,2729,2950)*	-	(1260)*	(969,940)*	(510)*	(380)*	(453)*
	(1649)**	(2871,2738,2954)**	-	(1264)**	(975,945)**	(506)**	(382)**	M-S= (449) **
	[0.12] ***	[0.07,0.33,0.14] **	-	[0.32] ***	[0.62,0.53] ***	[0.78] ***	[0.53] ***	[0.88] ***
(A1)	(1589)*	(2868,2946)*	-	(1260)*	(918)*	(515)*	(395)*	(3510) *
	(1596)**	(2863,2926)**	-	(1262)**	(921)**	(512)**	(391)**	$\nu(\text{O}-\text{H})$ (3504) **
	[0.44] ***	[0.17,0.68] ***	-	[0.16] ***	[0.33] ***	[0.58] ***	[1.01] ***	[0.17] ***
(A2)	(1598)*	(2867,2940)*	-	(1268)*	(916)*	(508)*	(390)*	(3512)*
	(1588)**	(2856, 2923)**	-	(1264)**	(923)**	(510)**	(389)**	$\nu(\text{O}-\text{H})$ (3508) **
	[0.63] **	[0.38,0.58] ***	-	[0.32] ***	[0.76] ***	[0.39] ***	[0.26] ***	[0.11] ***
(A3)	(1596)*	(2866,2931)*	-	(1268)*	(929)*	(517)*	(390)*	-
	(1589)**	(2858,2925)**	-	(1263)**	(920)**	(515)**	(387)**	-
	[0.44] ***	[0.28,0.20] ***	-	[0.39] ***	[0.97] ***	[0.38] ***	[0.77] ***	-
(A4)	(1587)*	(2858, 2946)*	-	(1266)*	(929)*	(510)*	(389)*	(3512)*
	(1596)**	(2856, 2925)**	-	(1262)**	(923)**	(512)**	(390)**	$\nu(\text{O}-\text{H})$ (3510)**
	[0.57] **	[0.07 ,0.71] ***	-	[0.32] ***	[0.65] ***	[0.39] ***	[0.26] ***	[0.06] ***
(A5)	(1590)*	(2853,2922)*	-	(1268)*	(920)*	(508)*	(390)*	-
	(1598)**	(2858, 2925)**	-	(1263)*	(921)**	(510)**	(391)**	-
	[0.50] **	[0.18 ,0.10] ***	-	[0.39] ***	[0.11] ***	[0.39] ***	[0.26] ***	-

Where:-

*Theoretical frequency.

**Experimental frequency.

***Error% due to main difference in the experimental measurements and theoretical treatment of vibration spectrum

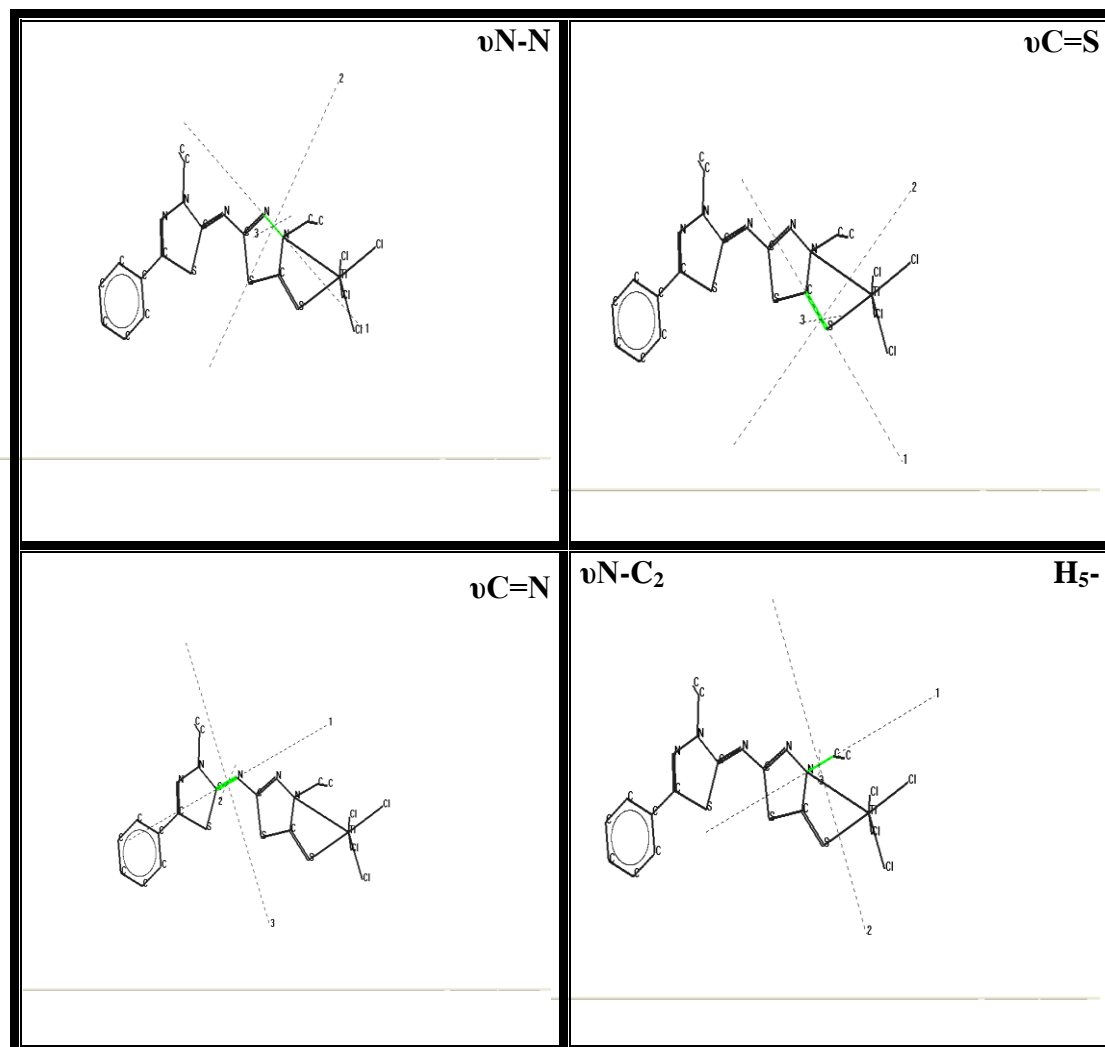


Fig. (2):- Virational frequencies for Schiff base {TiL}

C) Theoretical electronic spectra for the free ligand {TiL} and its metal complexes (A1-A5):

The electronic spectra of the free ligand and its metal complexes have been calculated and the wave numbered for these compounds showed some deviations from the experimental values as shown in Table(6).These deviations in theoretical calculation are generally acceptable due to couplings between the electronic spectra modes and the approximation that each normal mode of the electronic spectra inter acts independently electronic spectra beam ⁽¹⁹⁾. The most diagnostic calculated electronic spectra were chosen for the assignment of the free ligand {TiL} and their metal complexes (A1-A5) which their respective experimental electronic modes as shown in Table (3). All the theoretical electronic spectra of [{TiL} and (A1-A5)] compounds were calculated by using the semi- empirical (PM3) and (AMBER) methods at Geometry Optimization (0.01K.Cal. mol⁻¹) was used, and the comparison between of the experimental data and theoretical data of the electronic spectra for {TiL}free ligand and (A1-A5) their metal complexes showed that the percentage of error was with in the range of (0.33-1.71), as is shown in Table (6).

Table (6)

Comparison between the experimental and theoretical of the electronic spectra for {TiL} free ligand and (A1-A5) complexes

Comp. No.	Bands	Assignment
[TiA]	(244)*, (246)**, [0.82] ^{***} (300)*, (298)**, [0.67] ^{***} (378)*, (373)**, [1.32] ^{***}	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
{TiL}	(246)*, (245)**, [0.41] ^{***} (275)*, (273)**, [0.73] ^{***} (308)*, (310)**, [0.65] ^{***} (368)*, (371)**, [0.82] ^{***}	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
(A1)	(612)*, (610)**, [0.33] ^{***} (375)*, (371)**, [1.07] ^{***} (281)*, (279)**, [0.71] ^{***}	${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$ ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$
(A2)	(608)*, (605)**, [0.49] ^{***} (469)*, (472)** [0.64] ^{***} (351)*, (349)** [0.57] ^{***}	${}^6A_{1g} \rightarrow {}^4T_{1g}$ ${}^6A_{1g} \rightarrow {}^4T_{2g}$ {TiL} \rightarrow Fe _(C.T)
(A3)	(550)*, (553)**, [0.55] ^{***} (438)*, (436)**, [0.46] ^{***}	${}^1A_{1g} \rightarrow {}^3T_{1g}$ ${}^1A_{1g} \rightarrow {}^1T_{1g}$
(A4)	(362)*, (359)**, [0.83] ^{***} (292)*, (297)**, [1.71] ^{***} (257)*, (259)**, [0.78] ^{***}	${}^3A_{2g} \rightarrow {}^3T_{2g}$ ${}^3A_{2g} \rightarrow {}^3T_{1g}$ {TiL} \rightarrow Au _(C.T)
(A5)	(594)*, (592)**, [0.34] ^{***} (513)*, (510)**, [0.58] ^{***} (360)*, (361)**, [0.28] ^{***} (290)*, (294)**, [1.38] ^{***}	${}^2T_{2g} \rightarrow {}^4T_{1g}$ ${}^2T_{2g} \rightarrow {}^4T_{2g}$ ${}^2T_{1g} \rightarrow {}^2E_g$ ${}^2T_{1g} \rightarrow {}^2A_{1g}$

*Theoretical transitions band of electronic spectra, **Experimental transitions band of electronic spectra,

***Error% due to main difference in the experimental measurements and theoretical treatment of electronic spectra.

D) Bond lengths measurements for {TiL} and their metal complexes (A1-A5):

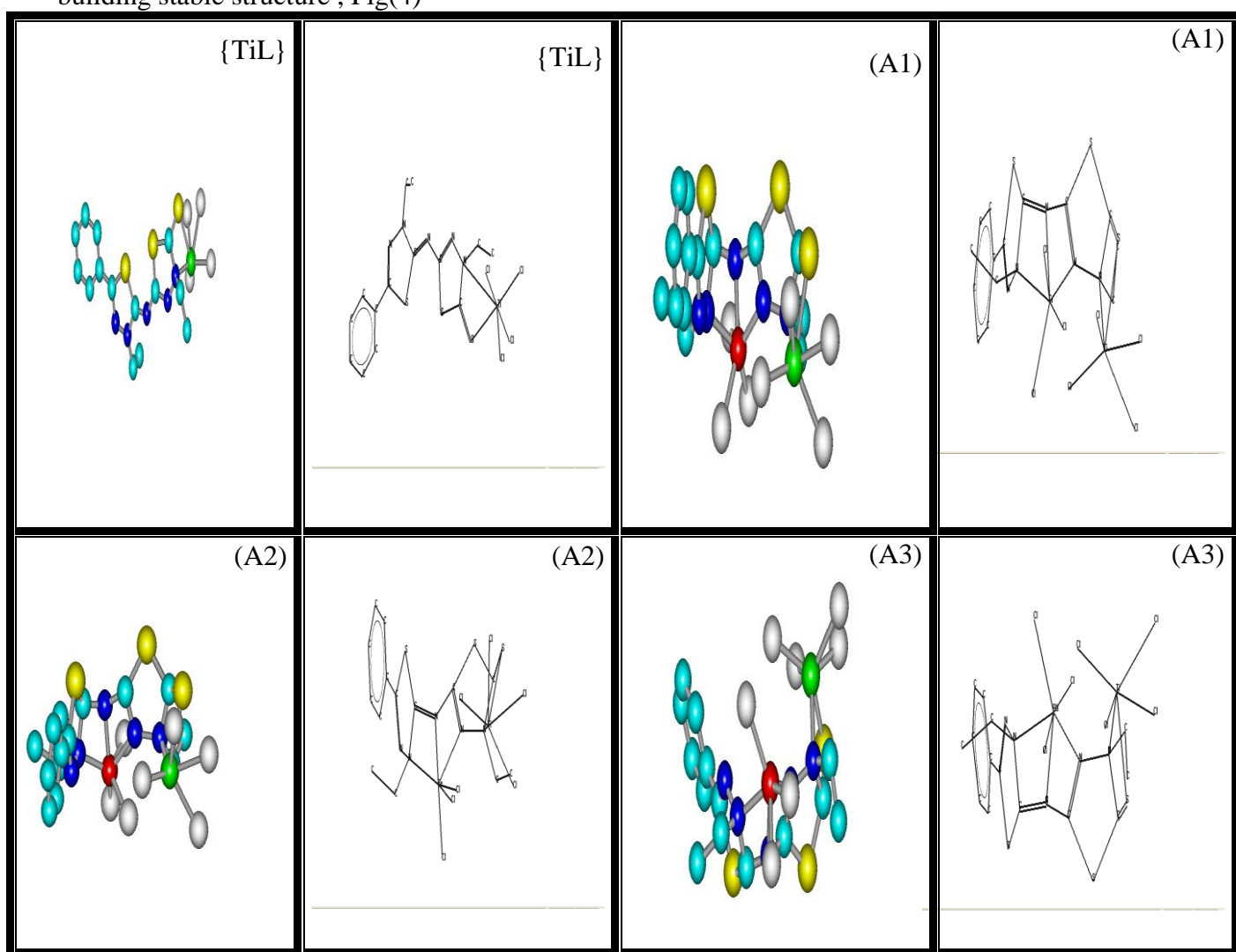
The Gaussian suite of software was employed throughout this study optimizations were carried out for the model systems represented in fig.(3). The initial state for structure didn't give bond lengths naturally so that the geometry optimization was used for correct bond lengths, calculation parameters were optimized of bond lengths for the free ligands and its metal complexes by using the semi-empirical (PM3) method at geometry optimization (0.001 Kcal / mol), to give excellent agreement with the experimental data^(18,20), as it shown in Table (7), fig.(3).

Table (7) Selected bond lengths (A°) for {TiL}ligand and their metal complexes [A1 – A5]

Comp. No.	C=N	N-C ₂ H ₅	N-N	M-N	M-Cl
{TiL}	1.3286	1.4885	1.3828	-	-
(A1)	1.2753	1.4061	1.3233	1.8912	2.1839
(A2)	1.2798	1.4346	1.4061	1.8823	2.1625
(A3)	1.2760	1.4841	1.4021	1.9725	2.2489
(A4)	1.2783	1.4038	1.4033	2.0857	2.3331
(A5)	1.2638	1.4621	1.4317	1.9889	2.2682

C) Optimized geometries of {TiL} and their metal complexes (A1-A5):

All theoretically probable structures of {TiL}schiff base and their metal complexes have been calculated by (PM3) and (AMBER) methods in gas phase to search for the most probable model building stable structure , Fig(4)



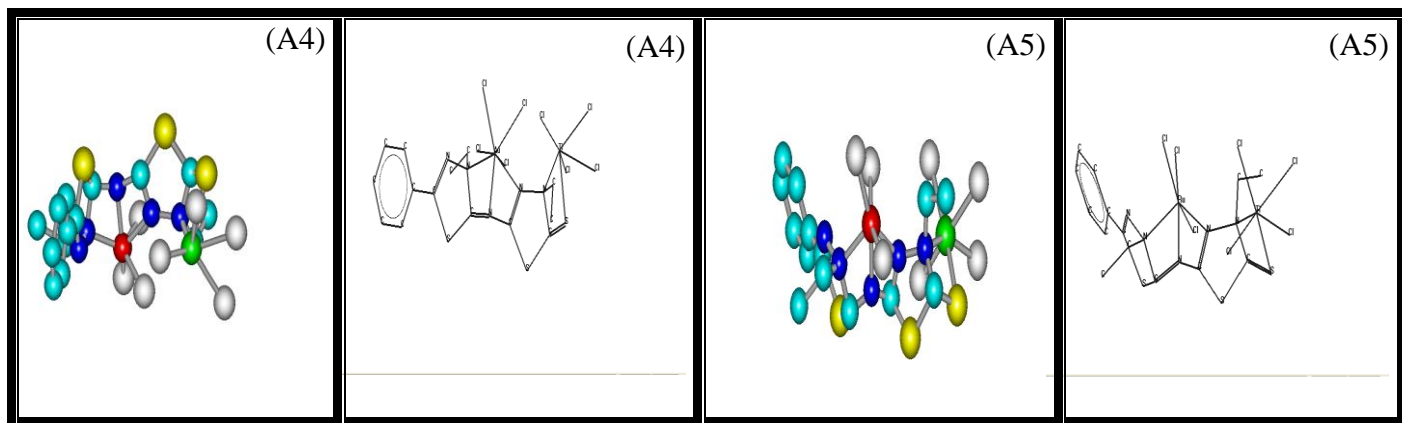


Fig :-(4) Conformational Structure of {TiL} and their metal complexes (A1-A5)

Biological Studies:-

The new synthetic compounds were screened in vitro for their ability to inhibit the growth of representative [(Pseudomonas aeruginosa) as gram negative] and [(Bacillus Subtilis) as gram positive]. Also the study was done against (Candida albicans and Aspergillus flavus) fungus, in DMSO as a solvent at two different concentrations. The results showed that the (ASN and TiA) compounds are moderate activities against the studied bacteria and fungus as compared with their Schiff base ligand {TiL} against the same microorganisms and under the identical experimental conditions, Table(8), this difference attributed to effect of introducing the pharmacologically important Schiff base moiety in the structure of the prepared free ligand.

The [A1-A5] complexes were found to be more toxic than the corresponding parent ligand {TiL} against all the types of the microorganisms Table(8), this was attributed to the synergetic effect^(21,22) between the metal ion and the ligand. Furthermore the results of the (MIC) study for the (ASN and TiA) and {TiL} and their metal complexes [A1-A5] are shown in table (9), these results indicate that some of the new compounds exhibited antibacterial activity against the studied bacteria at lower concentration, while they don't show such activity at higher concentration. As well as the all compounds were more active at lower concentration on comparison of these values with the antibiotic.

Table (8) Antibacterial and antifungal activities for (ASN) [TiA] and free ligand{TiL} and their Metal Complexes (A1-A5) (mgm.ml⁻¹)

Compo.	Pseudomonous aerugionosa		Bacillus Subtilis		Penicillum Spp.		Aspergillus flavus	
	100 ppm	200 ppm	100 ppm	200 ppm	100 ppm	200 ppm	100 ppm	200 ppm
Control (DMSO)	-	-	-	-	-	-	-	-
(ASN)	33	44	30	38	6	2	8	4
[TiA]	19	29	22	32	8	6	10	8
{TiL}	23	27	24	22	12	8	10	10
(A1)	11	23	15	20	10	12	8	10
(A2)	14	14	10	17	10	16	10	12
(A3)	13	16	18	14	12	16	18	14
(A4)	12	10	20	12	14	23	18	18
(A5)	25	12	10	13	12	18	8	16
Where :[6-8: (+),8-10: (++) , >10: (+++)]					30-40: (+++) , 20-30 :(++++) , 10-20: (+++++)			

Table (9) Minimal Inhibitory Concentration (MIC) for (ASN) [TiA] and free ligand{TiL} and their Metal Complexes (A1-A5) ($\mu\text{gm. ml}^{-1}$)

Compo.	Pseudonomous aerugionosa				Bacillus Subtili			
	0.05	0.5	1.5	2	0.05	0.5	1.5	2
(ASN)	+	+	MIC	-	+	+	+	MIC
(TIA)	+	+	MIC	-	+	+	MIC	-
{TiL}	+	MIC	-	-	+	+	MIC	-
(A1)	MIC	-	-	-	+	MIC	-	-
(A2)	MIC	-	-	-	MIC	-	-	-
(A3)	MIC	-	-	-	MIC	-	-	-
(A4)	MIC	-	-	-	MIC	-	-	-
(A5)	+	MIC	-	-	MIC	-	-	-
Ampicillin	+	+	MIC	-	+	+	+	MIC

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