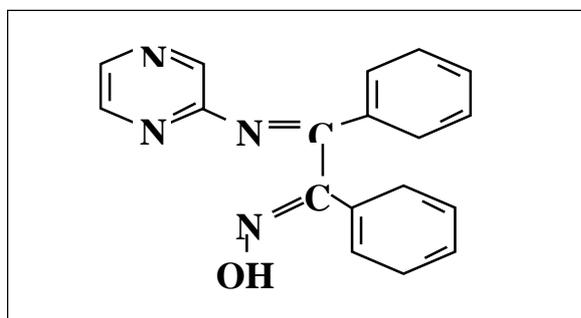


Synthesis and Identification of Complexes of [1, 2-diphenyl -2-(pyrazin -2- ylimino)- ethanone oxime] with Some Metal Salts

A.N.Al-Jeboori, T.H .AL-Noor and R.L.Sadawi
Chemistry Department.Ibn-AI-Haithem College of Education,
University of Baghdad-IRAQ

الخلاصة

يتضمن البحث تحضير وتشخيص اللكند الجديد (HL) اوكزيم ثنائي السن- [1, 2-diphenyl -2-(pyrazin -2- ylimino)- ethanone oxime]. (HL) اذ حضر هذا الليكاند من خلال تفاعل 2-aminopyrimidine (A) مع benzylmono oxime (B) تحت التصعيد الارجاعي في الميثانول وقطرات من حامض CH_3COOH واذا اعطى التفاعل الليكاند (HL). شخص الليكاند بواسطة طيف الاشعة تحت الحمراء (I.R), طيف الاشعة فوق البنفسجية (U.V-vis). هذا الليكاند تم مفاعله مع مجموعة من العناصر الفلزية تحت التصعيد الارجاعي في الميثانول بنسبة مولية (1:1) واذا اعطى التفاعل المعقدات ذوات الصيغه $[M(HL)]$ $M= Mn^{II}, Fe^{II}, Co^{II}, Cu^{II}, Zn^{II}, Cd^{II}, Ni^{II},$ and Hg^{II} . هذه المعقدات قد شخصت بواسطة المطيافية الذرية (A.A) وقياسات التوصيلة المولارية ومحتوى الكلور وقياس درجات الانصهار واطياف الاشعة تحت الحمراء (I.R) وفوق البنفسجية (U.V-vis). اظهرت قياسات التوصيلية المولارية ان جميع المعقدات المذكورة اعلاه غير مشحونة (متعادلة). واستنادا الى كل القياسات اعلاه ومن قياس اطوال الاواصر والزوايا رسمت الاشكال الفراغية المتوقعة لهذه المعقدات باستعمال البرنامج الجاهز.



Fig(1)Ligand HL

Abstract

Aim of this work is synthesis and characterization of bidentate Oxime ligand (HL) [1,2-diphenyl-2-(pyrazin-2-ylimino)-ethanoneoxime]. This ligand was prepared by reacting of 2-aminopyrimidine (A) with benzylmonooxime (B) under reflux in methanol and drops of CH_3COOH gave the ligand (HL).fig(1). The prepared ligand were characterized by I.R, U.V-vis spectra and melting point. The ligand were reacted with some metal ions under reflux in methanol with (1:1) ratio gave complexes of the general formula: $[\text{M}(\text{HL})]$, Where: $\text{M} = \text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Co}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}, \text{Ni}^{\text{II}},$ and Hg^{II} . These complexes were characterized by (A.A), chloride content I.R, U.V-vis spectra, molar conductivity and melting point. The molar conductance showed that, all complexe are non-electrolyte.

Introduction

Oximes:

The name of oxime concerns the compounds having the functional group($\text{C} = \text{N-OH}$). The oxime group is amphiprotic with a slightly basic nitrogen atom and a mildly acidic hydroxyl group ⁽¹⁾. The chemistry of oxime/oximato metal complexes has been investigated actively since the time of the first synthesis, of nickel(II) dimethylglyoximate, and the recognition of the chelate five-membered character of this complex by chugaev⁽²⁾, and has been reviewed twice ⁽³⁻⁵⁾. The different coordination modes of oxime and oximato species, depicted in fig. (2) indicate a versatile electronic distribution within the ligands. This in turn, suggests that the chemistry of metal- bonded oximes should be rich ⁽⁶⁾.

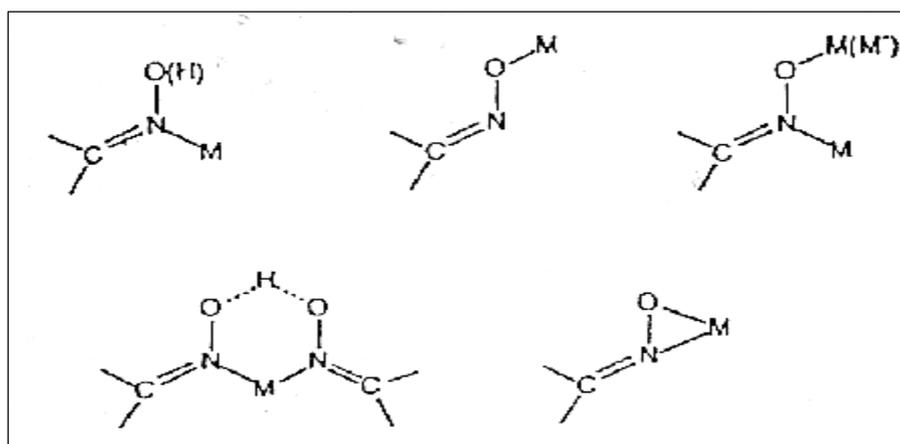


Figure 2: Coordination modes of oxime and oximato moieties with metal ions

Oxime compounds and their complexes with transition metals play a great importance in medicine, industry, chemistry and biochemistry ⁽⁷⁾ For example, 2-

pyridine aldoxime methiodide (PAM – 2) and diacetymonoxime (DAM) have used as antidotes for organophosphorus poisoning⁽⁸⁾. Organic chelating ligands containing the

oxime functional group have been used extensively in analytical chemistry for the detection and separation of metals^(2, -9). One of the analytical applications of oxime compounds is their use as organic precipitants for transition metals. In this paper we present the synthesis and study of some transition metal complexes with [1, 2-diphenyl -2- (pyrazin -2- ylimino)- ethanone oxime]

Material and Methods

A - All the chemicals were reagent grad (fluka & BDH) and were used without further purification. FT. IR spectra were recorded as KBr discs using Fourier Transformed rotatorphSpec Inframeter Shimadzu 24FT-IR8300. Electronic spectrum of the prepared complex were measured in the in DMF at 25°C using shimadzu-U.V-160 A Ultra Violet Visible - Spectrophotometer with 1.000 ± 0.001 cm matched quartz cell. metal contents of the complex es were determined by Atomic Absorption (A.A)Technique using a Shimadzu (A.A 620) atomic absorption spectrophotometer. The chloride contents of complexes were determined by potentiometer titration method using (686- Titro Processor- 665. Domsimat Metrohn Swiss).. Electrical conductivity measurements of the complex were recorded at 25°C for 10^{-3} M solutions of the samples in DMF using pw 9527 Digital conductivity meter (Philips) . The modeling package chem 3Dprog (ver 3,5,2)Cambride soft (1997) . Melting points were recorded by using Stuart melting point apparatus .

B - Synthesis of the ligand (HL): A solution of 2-amino pyrmidine (A) (0.1 gm, 1.0526 m mole) in methanol (5 ml) was added drop wise to a solution of (0.25 gm, 1.11 m mole) benzylmono oxime (B) in (5ml) methanol, then (2-3) drops of (CH₃COOH) was added slowly to the reaction mixture.The mixture was refluxed for (13 hours) with stirring, then allowed to cool at room temperature.A light brown solid was obtained after evaporation of methanol during(24 hours),0.954 gm, yield84%melting point 78°C).

C - Synthesis of (HL) complexes with some metal ions:

1 - Synthesis of [Cu(HL)] complex: A solution of (HL) (0.2 gm, 0.6619 m mole) in methanol(5 ml)was added to a stirred solution ofCuCl₂.2H₂O (0.11gm, 0.66mmole) in methanol 5 ml.The resulting mixture was heated under reflux for (3 hours), then the mixture was filtered and the precipitation was washed with an excess of methanol and dried at room temperature during 24 hours. A dark green solid was obtained, weight (0.16 gm), yield (55%) m.p (250° C.).

2 - Synthesis of [Mn(H L)], [Fe(H L)], [Co(H L)], [Ni(H L)], [Zn(H L)], [Cd(H L)] and [Hg(H L)] complexes: A similar method to that mentioned in (c-1) for the preparation of [Cu(HL)] complex was used to

prepare the complexes of (HL) with Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) ions, by using (0.2 gm, 0.661 m mole) of the ligand, other quantities of reagents were adjusted accordingly. Table (1).

Compound	m.pC°	Co lour	Weight of metal		Wight of product (gm)	Yield (%)
			gm	m mole		
[Mn(H L)]	101	Pale brown	0.1310	0.6618	0.17	60.1
[Fe(H L)]	170	Deep brown	0.083	0.654	0.18	73.91
[Co(H L)]	177	Violet	0.157	0.6616	0.13	70.2
[Ni(H L)]	174	Orange	0.08	0.3366	0.08	57.1
[Zn(H L)]	182	Pale brown	0.1	0.7304	0.15	51.72
[Cd(H L)]	360 dec	White	0.145	0.6618	0.19	59.19
[Hg(H L)]	360 dec	White	0.18	0.6652	0.25	65.96

Dec= decomposition, m.p= melting point, gm= gram

Table 1: Quantities of Materials, reaction conditions and some physical properties of the prepared complexes

Results & Discussion

I.R spectrum of the (HL):

The (I.R)spectrum of the starting material (2- amino pyrimidine) (A) exhibited bands at $(3500) \text{ cm}^{-1}$, $(3100) \text{ cm}^{-1}$ and $(1650) \text{ cm}^{-1}$ attributed to the ν_{as} (N—H), ν_{s} (N—H), and δ (N—H) bending respectively^[10,11]. On the other hand, the band at $(1667) \text{ cm}^{-1}$ for the diphenyl mono oxime (B) was assigned to the ν (C=O) stretching^[10] vibration. These bands have been disappeared in the free ligand (HL).The (I.R)spectrum of(HL),displayed two bands at $(1568) \text{ cm}^{-1}$ and at $(1631) \text{ cm}^{-1}$ due to the ν (C=N) stretching for the oxime and imine groups respectively^[12].The band at $(3390) \text{ cm}^{-1}$ is attributed to the ν (O — H) stretching of the oxime group, which is shifted by $(240) \text{ cm}^{-1}$ to higher frequency in comparison with that for the diphenylmono oxime at $\sim(3150) \text{ cm}^{-1}$. The band at $(1413) \text{ cm}^{-1}$ was due to the (C=N) stretching for the N- pyridyl group which is shifted by $(111) \text{ cm}^{-1}$ to lower frequency in comparison with that for 2 – amine pyrimidine at $(1524) \text{ cm}^{-1}$. The band at $(919) \text{ cm}^{-1}$ is attributed to ν (N — O) stretching. The assignment of the characteristic bands are listed in table (3).

(U.V-vis) spectrum of (HL):

The (U.V-vis) spectrum of (HL), figure (3-9) exhibits a high intense absorption peak at $(300\text{nm}) (33333.33 \text{ cm}^{-1})$ ($\epsilon_{\text{max}} = 2035 \text{ molar}^{-1} \cdot \text{cm}^{-1}$) which is assigned to $(n \rightarrow \pi^*)$ or $(\pi \rightarrow \pi^*)$ transition respectively^[13], table (3).

EL-Mass spectra of (HL)

The mass spectra of compounds (HL) shown in figure (3-16).The molecular ion peaks ($M/Z = 302.12$) and

(M/Z = 252) for (HL) are prominent which correspond to the molecular weights of the structure suggested to these compounds. The fragmentation pattern for (HL) are shown in schemes (1).

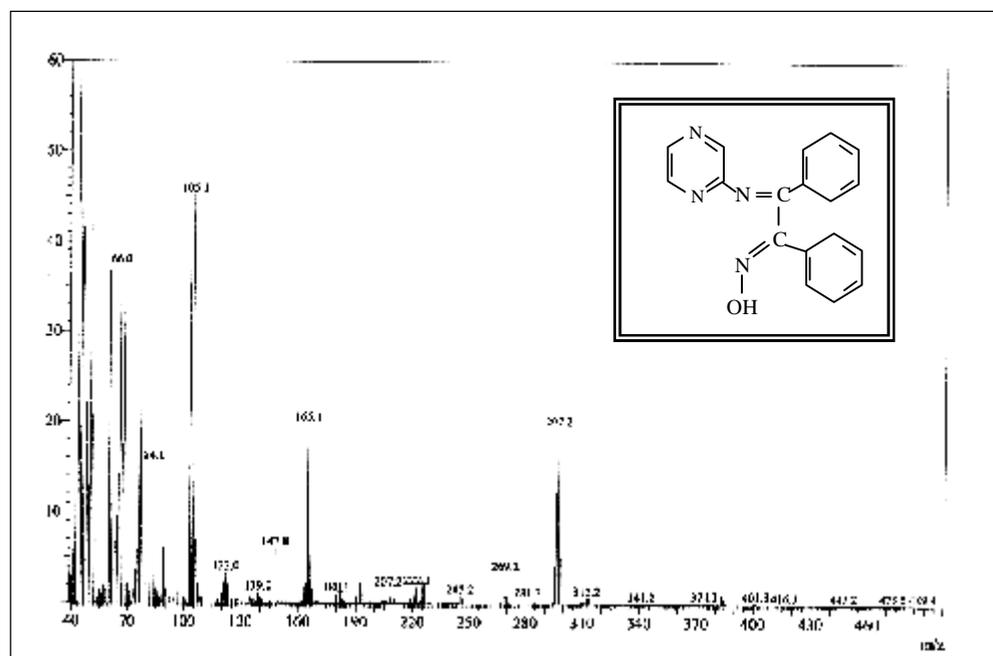


Fig (3) The mass spectrum of (HL)

Scheme1: The fragmentation sequence of (HL)

Synthesis and characterization of (HL) Complex:

All complexes of ligands (HL)), were prepared by a similar method, The complexes were characterized by spectroscopic methods [FT. IR, (U.V- Vis)] along with molar conductivity, chloride contents and atomic absorption (A.A), they were in good agreement with the calculated values. Table (2)

(I.R) Spectral data of the (HL) complexes [Mn(HL)](1), [Fe(HL)](2), [Co(HL)](3), [Cu(HL)](4), [Zn(HL)](5), [Cd(HL)](6) and [Hg(HL)](7):

The assignment of the characteristic bands are summarized in table (3). The band of $\nu(\text{O} - \text{H})$ stretching band of the oxime group in the free ligand (HL) at $(3390) \text{ cm}^{-1}$ was shifted to higher frequency and appeared at (3448) , (3340) , (3400) , (3332) , (3449) , (3405) and $(3441) \text{ cm}^{-1}$ for the compounds (1-6) and (7) respectively^[16]. The strong $\nu(\text{C} = \text{N})$ stretching bands in the free ligand at $(1631) \text{ cm}^{-1}$ and $(1568) \text{ cm}^{-1}$ for the imine and oxime groups were shifted to $(1672, 1573)$, $(1672, 1618)$, $(1598, 1577)$, $(11650, 1633)$, $(1676, 1627)$, $(1847, 1600)$, and $(1659, 1605) \text{ cm}^{-1}$ for the compounds (1-6) and (7). The strong $\nu(\text{C} = \text{N})$ stretching band in the free ligand

at (1413) cm^{-1} for the (n-pridyl) group was shifted to (1450), (1496), (1494), (1487), (1487), (1496) and (1490) cm^{-1} for the compounds (1-6) and (7) respectively. The strong $\nu(\text{N} - \text{O})$ stretching band at (919) cm^{-1} for the free ligand is shifted to higher frequency and appeared at (946), (993), (1000), (998), (1000), (1199) and (1201) cm^{-1} for the compounds (1-6) and (7) respectively. The increase of the $\nu(\text{N} - \text{O})$ was presumably due to the complexation^[14-17] and The bands at rang (433-592) cm^{-1} were assigned to $\nu(\text{M} - \text{N})$ indicating that the imine and oxime nitrogens were involved in coordination with metal ion^[18, 19, 20, 21].

(U.V-vis) Spectral data for ligand (HL) and its complexes [Mn(HL)](1), [Fe(HL)](2), [Co(HL)](3), [Ni(HL)](4), [Cu(HL)](5):

The absorption data for complexes are given in table (3). In general, the (U.V-vis) spectra showed intense peaks in the (U.V) region [(295 nm) (33898.33 cm^{-1}) ($\epsilon_{\text{max}}=1893 \text{ molar}^{-1} \cdot \text{cm}^{-1}$)], [(306 nm) (32679.73 cm^{-1}) ($\epsilon_{\text{max}}=2072 \text{ molar}^{-1} \cdot \text{cm}^{-1}$)], [(308 nm) (32467.53 cm^{-1}) ($\epsilon_{\text{max}}=1867 \text{ molar}^{-1} \cdot \text{cm}^{-1}$)], [(279 nm) (35842.29 cm^{-1}) ($\epsilon_{\text{max}}=1549 \text{ molar}^{-1} \cdot \text{cm}^{-1}$)], and [(307 nm) (32573.28 cm^{-1}) ($\epsilon_{\text{max}}=2103 \text{ molar}^{-1} \cdot \text{cm}^{-1}$)] for compound (1-4) and (5), these peaks were assigned to ligand field^[16]

Molar conductivity measurement for the ligand (HL) complexes:

The molar conductivity (Λ_m) of the all complexes in DMF, table (2), lie in (1-37) range, indicating their non-electrolytic behavior^[22]

Magnetic moment measurements:

The magnetic moment has been determined in the solid state by Faraday's method. Table(6).

Complexes	$X_g \times 10^{-6}$ gram susceptibility	$X_m \times 10^{-6}$ molar susceptibility	$X_A \times 10^{-6}$ atom susceptibility	M_{eff} B.M. expt.	M_{eff} B.M. ^a calc	Suggested structure
[Co(HL)]	10.2	4.4	4.2	3.071	3.182	Tetrahedral
[Cu(HL)]	3.53	1.541	1.390	1.61	1.82	Tetrahedral
[Mn(H ₃ L ²)]	17.485	6.608	6.457	3.722	3.922	Tetrahedral
[Co(H ₃ L ²)]	21.675	8.278	8.127	4.2	4.40	Tetrahedral
[Cu(H ₃ L ²)]	3.825	1.453	1.3029	1.551	1.762	Tetrahedral

^aspin only value^[19], expt: experimental, calc.: calculated

Table 6: Data of magnetic moment ($\mu_{\text{eff}}=\text{B.M.}$) of solid at 298 k and suggested astrochemical structure of complexes

Determination the mole – ratio for the ligand (HL) complex [Ni (HL)]

The mole ratio curves to these complexes in (DMF) are painted in figures(5).

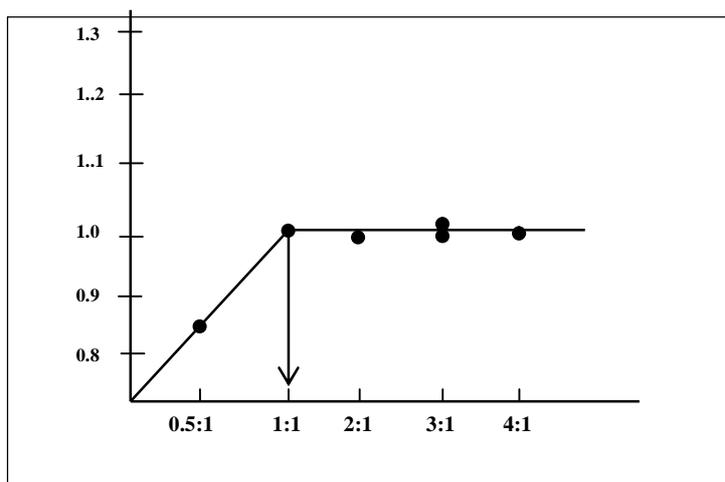
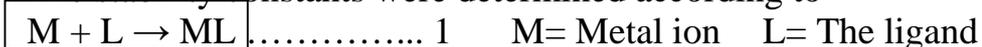


Fig 3: The mole-ratio curve to complex [Ni (HL)] in solution

Determination of the stability constant and ΔG for the ligands complexes:-

The stability constants were determined according to



$K = [ML] / [M] [L]$ 2

K= Stability constant (or formation constant) [] = Concentration

$\alpha = (A_m - A_s) / A_m$ 3

α = Decomposition degree

A_s = The absorption at the mole ratio (1:1) (L:M).

A_m = The absorption at the mole ratio (2:1) (L:M).

The equation (2) is written to mole ratio (1:1) as the following:

$K = (1 - \alpha) / \alpha^2 C$ 4

C= The complex concentration. (mole. L^{-1})

The ΔG Gibbs free energy, it is a function determine the direction (way) of the chemical reaction thermodynamically, since the chemical reaction is direct toward the side which ΔG is less than zero ($\Delta G < 0$).

The ΔG were determined according to ^[23,24]:

$\Delta G = -2.303 RT \text{ Log } K$

Compound	m.p°C	Colour	Λ_m (S. cm ² . mol ⁻¹)	M. wt	Found (calc.)%	
					Cl%	Metal
(HL)	89	Pale brown	10	302.12	—	—
[Mn(HL)]	101	Pale brown	30	427.96	(16.56) 15.12	(12.82) 11.29
[Fe(HL)]	170	Deep brown	5.3	428.87	(16.52) 16.22	(13.01) 12.15
[(HL)]	177	Violet	37	431.96	(16.41) 15.89	(13.64) 12.41
[Ni(HL)]	174	Orange	5.3	431.76	(16.42) 15.79	(13.59) 12.8
[Cu(HL)]	250	Green	37	436.57	(14.55) 14.81	(14.54) 13.32
[Zn(HL)]	182	Pale brown	15	438.39	(14.91) 14.99	(14.89) 13.21
[Cd(HL)]	360 dec	White	15	485.4	(14.60) 15.23	(23.15) 24.30
[Hg(HL)]	360 dec	White	14	573.62	(12.36) 13.45	— —

Dec.= decomposition, Calc. = calculated, ()= theoretical

Table 2: Element analysis results and some physical properties of the ligand (HL) and its metal complexes

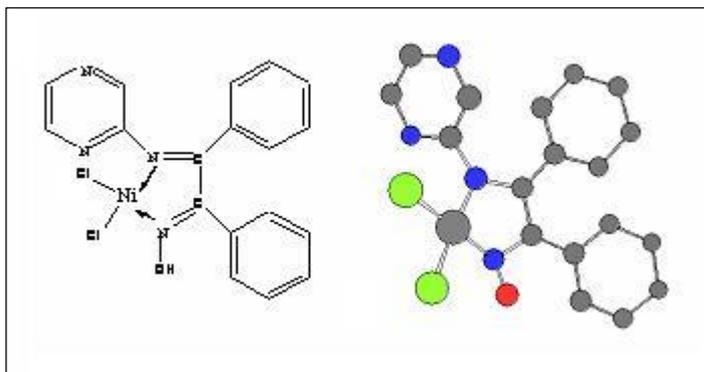
Stability constant and ΔG for the ligand (HL) complexes [Ni(HL)], Cu(HL)] and [Zn (HL)]:

Compound	A_s	A_m	α	k	Log k	1/k	ΔG
[Ni (HL)]	1.54	1.73	0.1098	7.357025×10^3	4.868 2	1.3543×10^{-5}	- 273.963
[Cu (HL)]	0.1	0.101	0.0099	1.0102030×10^5	7.004 4	0.9899×10^{-9}	-394.18
[Zn (HL)]	0.7	0.722	0.022	2.0206611×10^5	5.305 4	0.4988×10^{-7}	-298.56

[Zn (HL)] > [Cu(HL)] > [Ni(HL)]

Table 7: Is containing accounts of A_s , A_m , K, Log K, 1/K, ΔG , to these complexes with its concentration (1×10^{-3} mol. L⁻¹)

The result which we have seen in the above table (7), its seems that the reaction is spontaneous and stable.



Fig(6) The proposed molecular structure of [Ni(HL)]

Type of bond	Bond length(A ^o)	Type of bond	Bond angle (°)
Ni – N ₁	1.822	N ₁ – Ni – N ₂	83.894
Ni – N ₂	1.826	N ₁ – Ni – Cl ₁	90.00
Ni – Cl ₁	2.14	N ₁ – Ni – Cl ₂	180.00
Ni – Cl ₂	2.14	N ₂ – Ni – Cl ₁	173.868

Table 8: The proposed bond length and bond angles of [Ni(HL)]

Compound	$\nu(\text{C}=\text{N})$ imine	$\nu(\text{C}=\text{N})$ ring	$\nu(\text{C}=\text{C})$ arom.	$\nu(\text{C}-\text{H})$ arom.	$\nu(\text{O}-\text{H})$ oxime	$\nu(\text{O}-\text{H}-\text{O})$	$\nu(\text{N}-\text{O})$	$\nu(\text{M}-\text{N})$ imine	$\nu(\text{M}-\text{Cl})$	Other bands
(HL)	1631 1568	1413	1483	3188	3390	3315	919	—	—	$\delta(\text{C}-\text{H})=869$
2- amino Pyrimidine (A)	$\nu_{as}(3500)$ $\nu_s(3100)$	—	—	—	1050	1400	1524	3340	—	—
Benzyl- mono oxime (B)	—	1667	1000	— 1650	—	—	—	3070	1480	3150
[Mn (HL)]	1672 1573	1450	1498	3031	3448	3220	946	522 476	630	$\delta(\text{C}-\text{H})=867$
[Fe (HL)]	1672 1618	1496	1539	3145	3340	3200	993	507 433	632	$\delta(\text{C}-\text{H})=865$
[Co (HL)]	1598 1577	1494	1514	3058	3400	3160	1000	505 484	653	$\delta(\text{C}-\text{H})=808$
[Cu (HL)]	1650 1633	1487	1568	3178	3332	3178	998	518 487	671	$\delta(\text{C}-\text{H})=808$
[Zn (HL)]	1676 1627	1487	1571	3062	3449	3317	1000	510 488	692	$\delta(\text{C}-\text{H})=875$
[Cd (HL)]	1647 1600	1496	1581	3097	3405	3100	1199	520 472	691	$\delta(\text{C}-\text{H})=871$
[Hg (HL)]	1659 1605	1490	1570	3021	3441	3220	1201	532 455	651	$\delta(\text{C}-\text{H})=869$

rom. = aromatic δ = Bending ν = stretching

Table 3: Infrared spectral data (wave number ν) cm^{-1} of the (HL) and its complexes

Compound	λ nm	ϵ cm ⁻¹	ϵ_{\max} =(molar ⁻¹ . cm ⁻¹)	assignments	coordination
(HL)	300	33333.33	2035	$\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$	_____
[Mn(HL)]	295 350	33898.33 28571.42	1893 590	Ligand field C.T	Tetrahedral
[Fe(HL)]	306 344 369	32679.73 29069.76 27100.27	2072 1559 1067	Ligand field C.T ${}^5E \rightarrow {}^5T_2$	Tetrahedral
[Co(HL)]	308 357 667	32467.35 28011.204 14992.503	1867 662 92	Ligand field C.T ${}^4T_1P \leftarrow {}^4A_2$	Tetrahedral
[Ni(HL)]	279 344 406	35842.29 29069.76 24630.54	1549 956 91	Ligand field C.T $b_2g \rightarrow b_1g$	Square-planar
[Cu(HL)]	307 883	32573.28 11325.028	2103 95	Ligand field ${}^2E \rightarrow {}^2T_2$	Tetrahedral
[Zn(HL)]	281	35587.18	1552	C.T	Tetrahedral
[Cd(HL)]	294	34013.6	1959	C.T	Tetrahedral
[Hg(HL)]	306	32679.73	1874	C.T	Tetrahedral

Table 4: Element data for the ligand (HL) and its metal complexes

References:

- 1 - G. B. Kanffman & J. chem. (1966). Educ., **43**, 155.
- 2 - L.A. chugaev & Zh. Russ. (1909). Physicochem. Soc. **41**, 184.
- 3 - S.G. Sakharov ; Yu, A. Buslaev & Koord. Khim. (1994). **20**, 3.
- 4 - (a) y. Watanabe ; M. Akazome ; T. Kondo & Yuki Gosei Kagaku Kenkyusho Koenshu. (1994). 8, 50.
(b) Y. Watanabe ; M. Akazome ; T. Kondo ; Yuki Gosei Kagaku Kenkyusho Koenshu. (1994). chem.. Abs. **121**:59644V.
- 5 - A. P. Kriven Ko (Ed.). (1997). "**The chemistry of Five- and Six – membered N-, O-Containing Hetero cycles [in Russian]**", Sarator University Saratov, P. 154.
- 6 - A. Singh ; V.D. Gupta ; G. Srivastava ; R.C. Mehrotra & J. Organomet. (1974). Chem, **64**, 145.
- 7 - K. Burger. (1973). "**Organic Reagents in metal Anaysis**" Pergamon, Oxford.
- 8 - S.E.R.B. Laboratories. (2001). "**Handbook of Cyainde, Lesd and organo phosphate intoxications**", Biological Trials and Research company Department of Toxicology, Paris, France.

- 9 - K. Burger. (1973). "**Organic Reagents in metal Analysis**" Pergamon, Oxford.
- 10 - M. Bhavna ; P. Krishna ; A. Pralhad & J. Molecular Catalysis.(1992). **75**, 109.
- 11 - R.M. Silverstein ; G.C. Bassler & T.C. Morrill. (1981). "**Spectrometric Identification of Organic Compounds**". 4th. Ed., J. Wiley and Sons .
- 12 - M. Bhavna ; P. Krishna ; A. Pralhad & J. Molecular Catalysis. (1992). **75**, 109.
- 13 - A. A. El- Bindary ; A.S. AL-Shihri ; A.Z. El- Sonbati. (2003)."**Designed Monomers and Polymers**", **6**, 3, 283-298.
- 14 - William Kemp. (1987). "**Organic Spectroscopy**" 2nd Edition.
- 15 - V.M. Parikh. (1985). "**Absorption Spectroscopy of Organic Molecules**" Translated by Abdul Hussain Khuthier, Jasim M.A. Al-Rawi, and Mahammed A. Al-Iraqi.
- 16 - Robert, M. ; Silver Schtein ; Bassler and Morrill (1981). "**Spectorphotometer Identification of Organic Ccompound**" Translated by Dr. Hadi Khazem Awad, Dr. Fahad Ali Hussain and Subhi Al-Azawi, 5^{yh} ed .
- 17 - A.B.P. Lever (1968). "**Inorganic Electornic Spectroscopy**", New York, **6**. 121.
- 18 - I. K. Biernacka and K. Kurzak & Polish, J. (2002). chem., **77**, 13.
- 19 - R. M. Silverstein ; G. C. Bassler and T.C. Morrill (1981). "**Spectrometric Identification of Organic Compounds**". 4th. Ed., J. Wiley and Sons .
- 20 - N.N. Green wood and A. Earnshaw (1998)."**Chemistry of the Elements**" J. Wiely and Sons Inc. New York .
- 21 - A. Z.El- Sonbati and A.A. El-Bindary (2000). "**Stereochemistry of New Nitrogen Containing Aldehydes. V. Novel Synthesis and Spectroscopic studies of Some Quinoline Schiff Bases Complexes**", Polish J. chem., **74**, (621-630) .
- 22 - A.M. Al-Haidary (1992). "**Instrumental chemical Analysis**" for 4 Stage Students, Collage of education, Baghdad .
- 23 - AL-Chapsha and M.Q. AL-Ach (1986). "**Fundamental of Analytical chemistry**", university of Mousel.
- 24 - Farrington Daniels and A. Robert Al berty (1975). "**Physical Chemistry**" 4th ed .