Synthesis and spectral studies of new Schiff base pyrimidine-2-ylimino-acetic acid and its complexes with Cobalt(II), Nickel(II), Copper(II), Cadmium(II), Mercucry(II) and Lead(II) ions

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Abstract

Pyrimidine-2-ylamine condens with glyoxylic acid gave pyrimidine-2-ylimino-acetic acid (L) and characterized by elemental analysis (C.H.N), FT-IR and ^{1}H, ^{13}C-NMR. The ligand (L) reacted with metal ions (II); Co, Ni, Cu, Cd, Hg and Pb forming complexes. These complexes were identified by metal analysis (A.A.), FT-IR spectral, conductivity, magnetic susceptibility measurements and UV-visible spectral. The Co(II), Cd(II), Hg(II) and Pb(II) ions in each complexes are tetra coordinated in a tetrahedral geometry. The Ni(II), and Cu(II) ions are hexa coordinated in a octahedral geometry.

Keywords: Pyrimidine derivatives, spectral study, complexes.

الخلاصة

مفاعلة بريميدين-2-يل أمين مع حامض الكلايكوسيلك في وسط الايثانول معطياً ليكاند شيف جديد

بريميدين-2-يل ايمينو حامض الخليك (L) تم تشخيصه بتحليل الكاربون، النتروجين، الهيدروجين، طيف تحت

الحمراء، طيف بروتون– كاربون–13 الرنين النووي المغناطيسي مفاعلة الليكاند مع ايونات الفلزات الثنائية التكافؤ (الكوبلت، النيكل، النحاس، الكادميوم، الزئبق والرصاص) تنتج معقدات تلك الايونات، شخصت تلك المعقدات نسبة الفلز بوساطة طيف الامتصاص الذري، طيف تحت الحمراء، التوصيلية، الخاصية المغناطيسية والبنفسجية–المرئية.

تكون ايونات الكوبلت، الكادميوم، الزئبق والرصاص الثنائية التكافؤ في كل معقداتها رباعية التناسق في شكل هرم رباعي السطوح. أما ايونات النيكل والنحاس الثنائية التكافؤ في معقداتها فهي سداسية التناسق على شكل ثماني السطوح.

الكلمات المفتاحية: مشتقات البريميدين، دراسة طيفية، معقدات.

Introduction

Azomethines are generally known as Schiff bases to Honour Hugo, who synthesized such compounds. These compounds are containing characteristic (–\C=N–) group[1].

Kalpesh S. et.al., have reported some novel Schiff base derived from 4,6-dimethoxy pyrimidin-2-amine with various aromatic aldehyde[2]. Sawsan S. et.al. have reported physico chemical studies of some mercury pyrimidine complexes[3]. Jassim Sh. S. reported some metal ions of (2-aminophenylimino)-aceticacid[4] and [2-(carboxymethylene-amino)-phenyl imino] acetic acid[5]. In this paper, the synthesis of new Schiff base pyrimidine-2-ylimino-acetic acid (L) and its some complexes, with Co^{+2}, Ni^{+2}, Cu^{+2}, Cd^{+2}, Hg^{+2} and Pb^{+2} are reported.

Experimental

All chemicals were purchased from BDH, and used without further purifications.

Instrumentation

1. FTIR spectra were recorded in KBr on Shimadzu- 8300 Spectrophotometer in the range of (4000-400 cm^{-1}).
2. The electronic spectra in H_2O were recorded using the UV-Visible spectrophotometer type (spectra 190-900 nm) CECIL, England, with quartz cell of (1 cm) path length.

3. The melting point was recorded on "Gallen kamp Melting point Apparatus".
4. The Conductance Measurements were recorded on W. T. W. conductivity Meter.
5. Metal analysis. The metal contents of the complexes were determined by atomic absorption (A. A.) technique. Using a shimadzu PR-5. ORAPHIC PRINTER atomic obsorption spectrophotometer.
6. Balance Magnetic Susceptibility model MSB-MLI Al-Nahrain University
7. The characterize of new ligand (L) is achieved by:

A: ^{1}H and ^{13}C-NMR spectra were recorded by using a Bruker 300 MHZ (Switzerland). Chemical Shift of all ^{1}H and ^{13}C-NMR spectra were recorded in δ(ppm) unit downfield from internal reference tetramethylsilane (TMS), using D_2O as a solvent.

B: Elemental analysis for carbon, hydrogen and nitrogen was using a Euro Vector EA 3000 A Elemental Analysis (Italy), analysis (A and B) were done at AL-al-Bayt University, Al-Mafrag, Jordan.

Synthesis

1. Synthesis of pyrimidine-2ylimino-acetic acid (L)

To a hot solution of pyrimidine-2ylamine (0.95g. 1m mole) in (5ml) ethanol, a hot solution of glyoxylic acid (0.108 g. 1 m mole) in (5ml) ethanol was added. The solution was refluxed for 3.5 hrs. Upon cooling a pale brown precipitate formed, was filtered off and recrystallized from a hot mixture of (5:5:2) methanol, acetone and distilled water. A pale brown precipitate, yield 86%, melting point 170C°.

2. Synthesis of complexes

The complex $[LCo.2H_2O]Cl$ has been synthesized as follows:

To a hot solution of ligand (L) (0.151g. 1m mole) in (5ml) ethanol, a hot solution of cobalt(II) Chloride hexa hydrate (0.238g. 1m mole) in (5 ml) of ethanol was added.

The precipitate immediately formed, the mixture was boiled and stirred for 10-15min., filtered off and recrystallized from a hot methanol (10ml), a blue precipitate was obtained, yield 82%, decomposed at 200 D°. A similar method was used to prepare other complexes:

[$LNi.4H_2O$]Cl, L(0.151g 1m mole), $NiCl_2.6H_2O$ (0.238g, 1m mole), (10ml) ethanol, (10ml) methanol, yield 80% decomposed at 135 D°, [$LCu.4H_2O$]Cl, L(0.151g, lm mole), $CuCl_2.2H_2O$ (0.170g, 1m mole), (10ml) ethanol, (10ml) methanol, yield 78% melting point 220 C°, [$LCd.2H_2O$]Cl, L(0.151g, 1 m mole), $CdCl_2.H_2O$ (0.202g, 1m mole), (10ml) ethanol, (10ml) methanol, yield 92%, decomposed at 210 D°, [$LHg.2H_2O$]Cl, L(0.151g, lm mole), $HgCl_2$ (0.271g, 1m mole), (10ml) ethanol, (10ml) methanol, yield 88%, melting point 175 C°, [$LPb.2H_2O$]NO_3, L(0.151g, lm mole), $Pb(NO_3)_2$ (0.331g, 1m mole), (10ml) ethanol, (10ml) methanol, yield 85%, melting point 150 C°.

The physical properties for synthesized ligand (L) and its complexes are shown in Table (1).

Table (1): The physical properties for synthesized lignad (L) and its complexes

Empirical Formula	Yield %	M.P. C°	Colour	μ_{effect}	Found (Calc.) %				Solubility
					C	H	N	metal	
$L=C_6H_5N_3O_2$	86	170	Pale brown	-	48.00 (47.68)	3.61 (3.31)	28.29 (27.81)	-	Water, methanol, ethanol, acetone, ether, DMF, DMSO
[$LCo.2H_2O$]Cl	82	200 D°	Blue	4.80	-	-	-	21.28 (21.07)	Water, methanol, ethanol, acetone, DMF, DMSO
[$LNi.4H_2O$]Cl	80	135 D°	Pale green	3.10	-	-	-	19.10 (18.61)	=
[$LCu.4H_2O$]Cl	78	220	Green	1.85	-	-	-	20.01 (19.62)	=
[$LCd.2H_2O$]Cl	92	210 D°	Brown	-	-	-	-	33.80 (33.63)	=
[$LHg.2H_2O$]Cl	88	175	Brown	-	-	-	-	47.10 (47.50)	=
[$LPb.2H_2O$]NO_3	85	150	Pale brown	-	-	-	-	45.50 (45.39)	=

Results and Discussions

The characterization of the new ligand (L) has been achieved by:

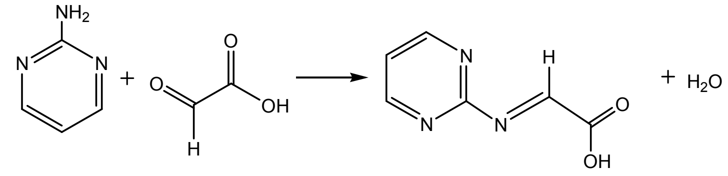
a) The ^{1}H-NMR is spectrum of the ligand (L) in D_2O Fig. (1) Table (2a) is characterized by the appearance of chemical shift related to; the (8.5) ppm. (S, 1H, N = CH)[6-7], (6.03- 7.88) ppm. (M, 3H) aromatic protons, (12.5) ppm. (b, OH) carboxylic acid.

b) The ^{13}C–NMR D_2O Fig. (2) Table (2b) showed the azomethine carbon peak at (160.28) ppm.[8]. The carboxylic C=O peak showed at (173) ppm., the aromatic carbon peak of pyrimidine are observed at (114.20) ppm.

c) IR spectrum of the ligand (L) Fig. (3) shows bands, υ(OH), υ(C=O) stretching vibration of the carboxylic group (3246- 3423 cm^{-1}, 1728 cm^{-1}) respectively[9-10]. Band appeared at 1581 cm^{-1} due to the azomethine υ(HC=N)[11-12]. Disappearace of υ(NH_2) (3329-3169) cm^{-1} (pyrimidine) and υ(C=O) (aldehyde) at 1745 cm^{-1} (glyoxal) (starting materials) suggested that the new Schif base was formed.

d) The electronic spectrum of the ligand (L) Fig. (4) under study in water solution was characterized mainly by absorptions in the region (216) nm (46296) cm^{-1} (ε_{max}=2164 molar^{-1} cm^{-1}) assigned to π–π^* transition and (289) nm (34602) cm^{-1} (ε_{max}=1396 molar^{-1} cm^{-1}) due to the n–π^* transition[13].

e) The microanalysis (C.H.N) was performed and gave write formula $C_6H_5N_3O_2$, from above results the structure of prepared ligand (L) is shown in equation below;



Pyrimidin-2-ylamine glyoxylic acid (Pyrimidin-2-ylimino)-acetic acid

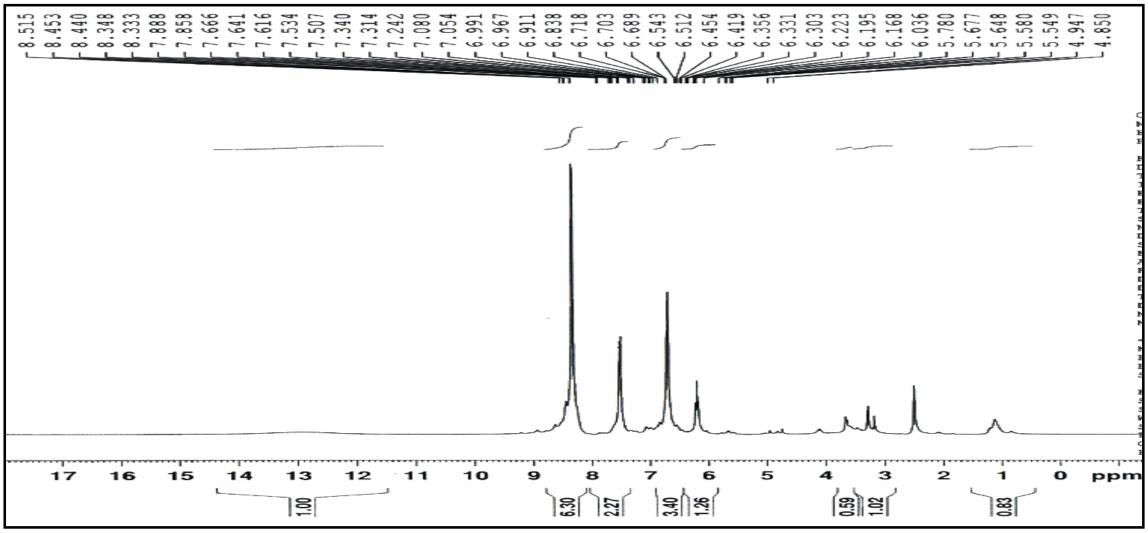


Fig. (1): The ^{1}H-NMR spectrum of ligand (L)

Table (2a): ^{1}H-NMR Chemical Shifts for Ligand (L) (ppm in D_2O)

H–C=N	3H Aromatic protons	COOH
(8.5) ppm.	(6.30 – 7.88) ppm.	12.5 ppm.

Table (2b): ^{13}C-NMR Chemical Shifts for Ligand (L) (ppm in D_2O)

H–C=N	COOH	Aromatic carbons of pyrimidine
(160.28) ppm.	(173) ppm.	114.20

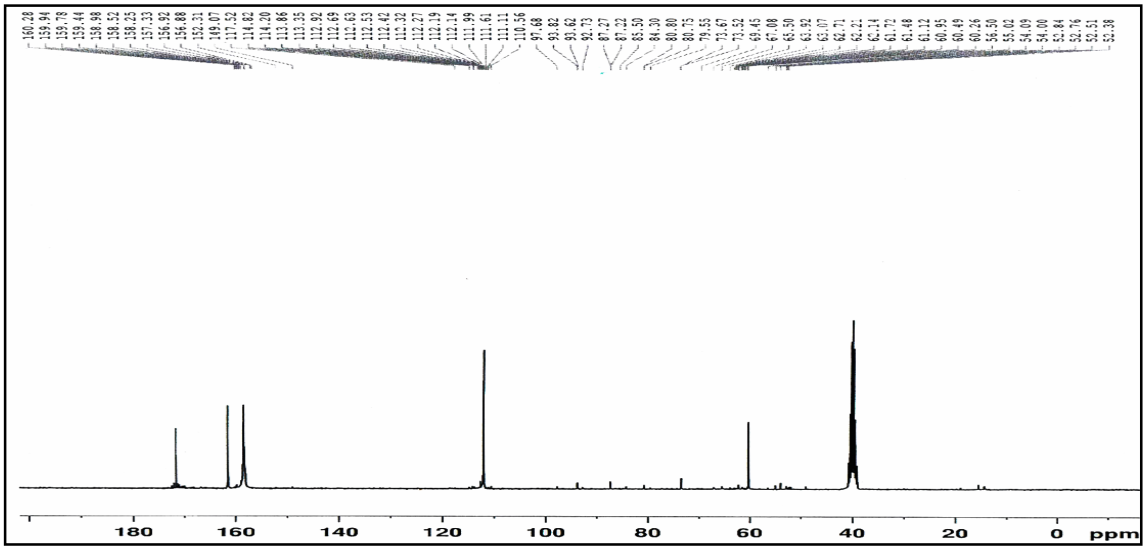


Fig. (2): The ^{13}C-NMR spectrum of ligand (L)

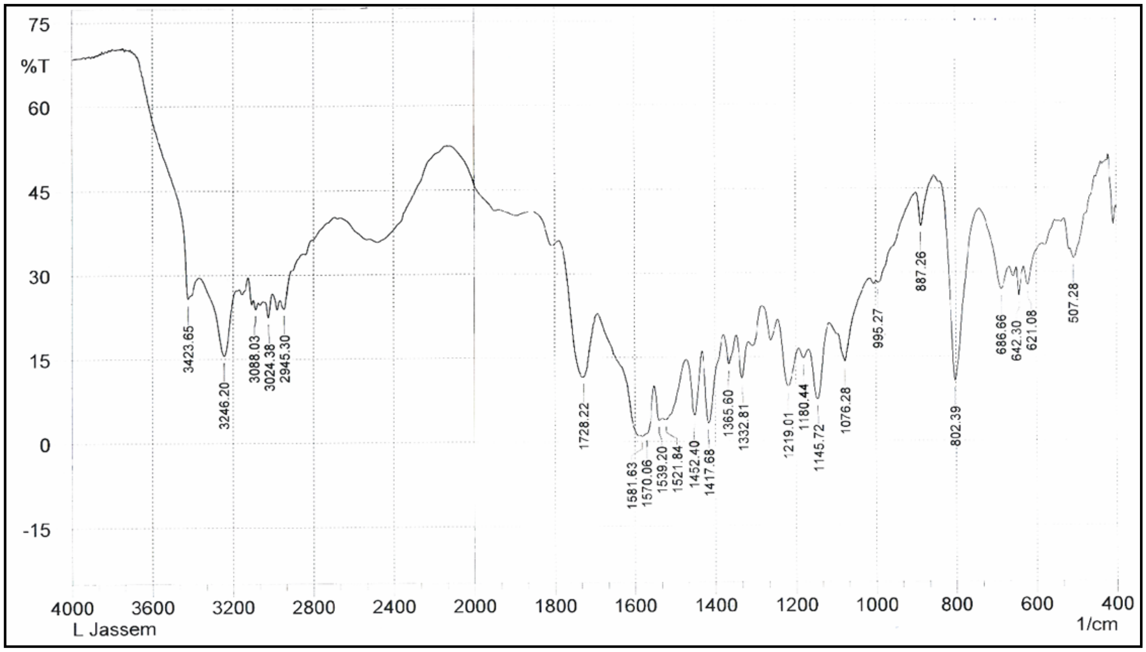


Fig. (3): The IR spectrum of ligand (L)

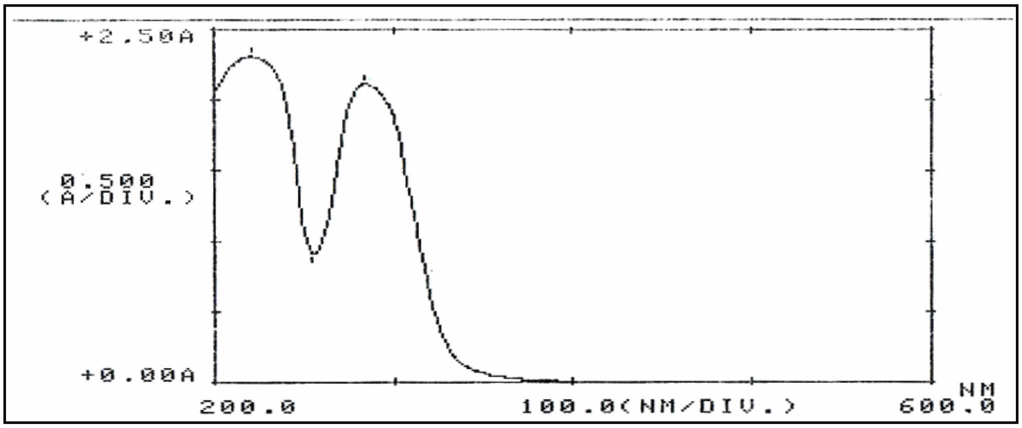


Fig. (4): Electronic spectrum of the ligand (L)

The IR, UV spectral and magnetic moments of complexes

The isolated ligand was subjected to elemental analysis (C,H,N). The metal analysis in the isolated complexes were done by A.A., giving L.Mx.nH_2O.

The data of the IR spectra of the ligand (L) and its complexes are listed in Table (3).

The IR spectra of the complexes for example Fig. (5) are compared with those of the free ligand

(L) in order to determine the coordination sites that may involved in chelation. The spectrum of the ligand (L) contained a band at 1581 cm^{-1}, υ(HC=N), which shifted to lower values by (6-42) cm^{-1} in the complexes suggesting that the ligand (L) coordinate to the metal ion through azomethine[14-16]. The spectra of these complexes exhibited a broad band around (3442- 3200) cm^{-1} assigned to water, υ(OH), associated with the complexes in addition to these modes, coordinated water exhibited (H_2O) rocking at (790-777) cm^{-1}[17]. The free ligand (L) exhibits strong absorption band at 1219 cm^{-1} is due to the stretching vibration of carboxyl group. This band is disappeared and two new bands appeared in all complexes, in the range (1494–1450), (1363- 1354) cm^{-1} with Δυ = (134- 91) cm^{-1} are due to the $\upsilon_{asymm.}$ (COO^-) and υ_{symm} (COO^-) and the value of Δ υ indicates the carboxylate group is coordinated to metal ions as a monodentate fashion[14-15].

New absorption bands υ(M–N), υ(M–O) appeared at (520- 505), (472-418) cm^{-1} in the spectra of the complexes[13,6], which support the coordination of the ligand (L) through the nitrogen of azometheine and the oxygen of carboxylato ion. In case of Pb(II) nitrato complex, the presence of band at 1270 cm^{-1} is due to the monodentate-ONO_2-group[18].

Table (3): Infrared spectral data (wave number υ¯) cm^{-1} for the ligand, precursors and its complexes

Compound	υ(OH)	υ(NH_2)	υ(C=N)	υ(C-H) Aromatic	υ(C=O)	$\upsilon_{assmm.}$ COO^-	$\upsilon_{symm.}$ COO^-	Δυ cm^{-1}	Coordinate water	M-N	M-O
Glyoxylic acid	(3361)b	-	-	-	(1745)s	-	-	-	-	-	-
Pyrimidine-2-ylamine	-	(3329)s (3169)s	-	(3050)w	-		-	-	-	-	-
L=$C_6H_5N_3O_2$	(3246)s 3423	-	(1581)m	(3088)w	1728	1219	-	-	-	-	-
[$LCo.2H_2O$]Cl	(3323)b	-	1539	3097	-	1458	1354	104	777	505	418
[$LNi.4H_2O$]Cl	(3332)b	-	1541	3093	-	1462	1357	105	788	516	439
[$LCu.4H_2O$]Cl	3300	-	1540	3060	-	(1494) w	(1360) w	134	750	510	420
[$LCd.2H_2O$]Cl	3396	-	1564	3097	-	1450	1359	91	790	513	472
[$LHg.2H_2O$]Cl	3342	-	1568	3093	-	1456	1355	101	790	520	455
[$LPb.2H_2O$]NO_3	(3320)m	-	1575	3097	-	1466	1363	103	779	505	457

Where: w = weak, b = broad, s = strong, m = medium,.

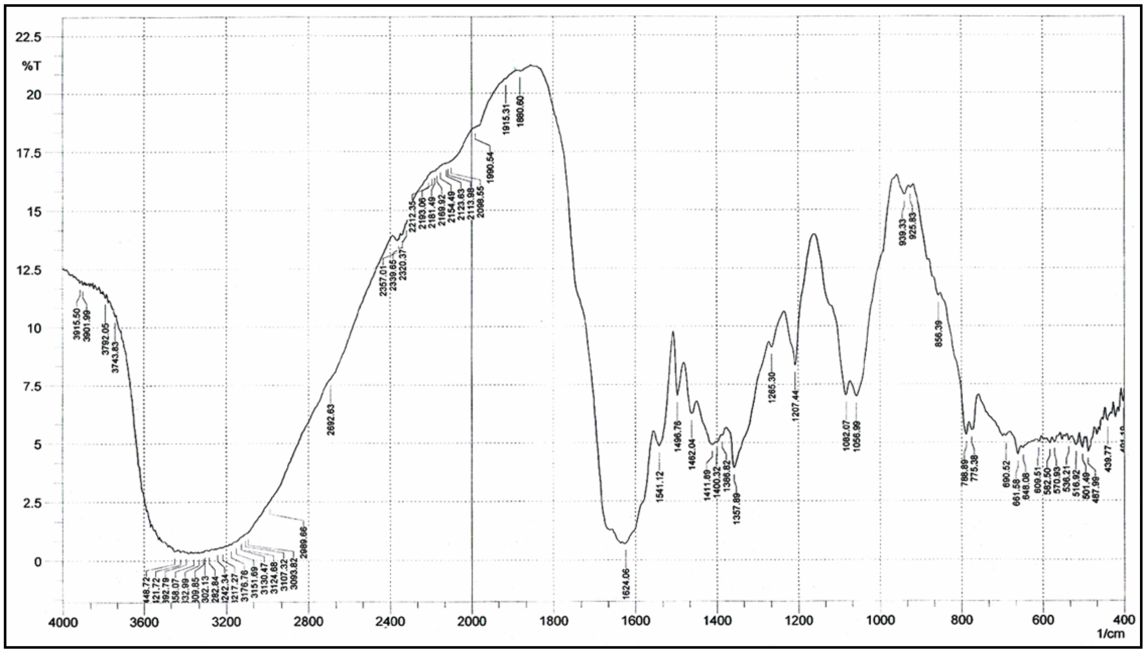


Fig. (5): The IR spectrum of [LNi.4H_2O]Cl complex

The electronic absorption of Co(II) complex (blue colour) in DMSO solution Table (4), resolved multiple bands at (614) nm and (680) nm centered at (647) nm (15455) cm^{-1} (ε_{max}=800 $molar^{-1}$ cm^{-1}) which assigned to $^4T_{1(P)} \leftarrow {}^4A_2$ (υ_3) for tetrahedral geometry.

Table (4): Electronic spectral data of the Ligand (L) and its complexes

Compound	λnm	υ^- wave number cm^{-1}	(ε_{max} $molar^{-1}$ cm^{-1})	Assignments	Proposed structure
L=$C_6H_5N_3O_2$	216 289	46296 34602	2164 1396	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-
[LCo.2H_2O]Cl	647	15455	800	$^4T_{1(P)} \leftarrow {}^4A_2$	Tetrahedral
[LNi.4H_2O]Cl	416 747	24038 13386	1300 200	$^3T_1g_{(P)} \leftarrow {}^3A_2g$ $^3T_1g \leftarrow {}^3A_2g$	Octahedral
[LCu.4H_2O]Cl	884	11312	2700	$^2Eg \leftarrow {}^2T_2g$	Octahedral
[LCd.2H_2O]Cl	300	33333	1396	C. T.	Tetrahedral
[LHg.2H_2O]Cl	320	31250	1121	C. T.	=
[LPb.2H_2O]NO_3	350	28571	564	C. T.	=

Where C.T. = Charge Transfer

The υ_2 ($^4T_{1(F)} \leftarrow ^4A_2$) is usually appeared in the near infrared. The blue colour and magnetic susceptibility measurement (4.80) BM for the solid Co(II) complex is also indicative of three unpaired electrons per Co(II) ions consistent with its tetrahedral environment[19].

The electronic absorption of Ni(II) complex (pale green) in DMSO is shown in Fig. (6) gave one peak at (416) nm (24038) cm^{-1} (ε_{max}=1300 molar^{-1} cm^{-1}) is assigned to $^3T_1g_{(P)} \leftarrow ^3A_2g$, ($\upsilon_3$) and doublet peaks at (707 and 786) nm centered at (747) nm (13386) cm^{-1} (ε_{max}=200 molar^{-1} cm^{-1}) is assigned to the $^3T_1g \leftarrow ^3A_2g$ (υ_2) for octahedral geometry.

The value of (υ_1), B complex and β can calculated as below:

$$\frac{\upsilon_3}{\upsilon_2} = \frac{24038}{13386} = 1.79$$

Form appendix Fig. (7).

$$E = \frac{\upsilon_3}{B_{\text{complex}}} = 25 \qquad \text{and} \qquad \frac{\Delta_0}{B_{complex}} = 10$$

$$\therefore \frac{24038}{B} = 25$$

$$B_{complex} = \frac{24038}{25} = 961$$

$$\beta = \frac{B_{\text{comp.}}}{B_{\text{free metal}}} = \frac{961}{1030} = 0.93$$

$$\frac{\Delta_0}{B_{complex}} = 10;$$

$$\frac{\Delta_0}{961} = 10$$

$$\Delta_0\ (\upsilon_1) = 9610\ \text{cm}^{-1}$$

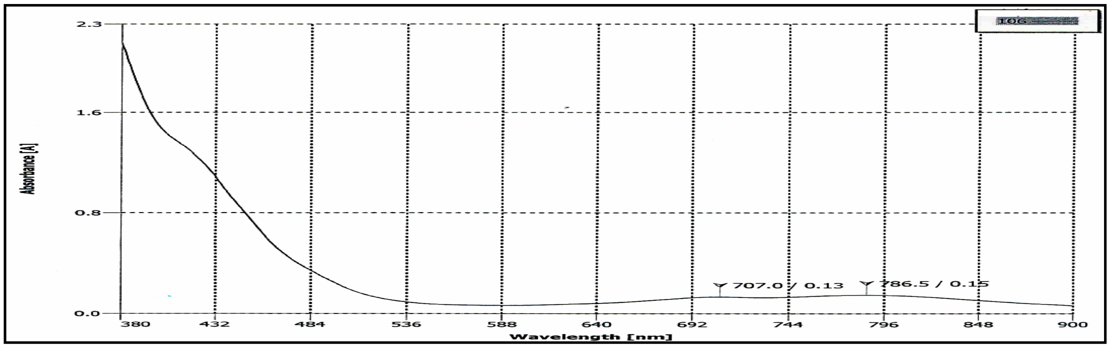


Fig. (6): Electronic spectrum of [LNi.$4H_2O$]Cl complex

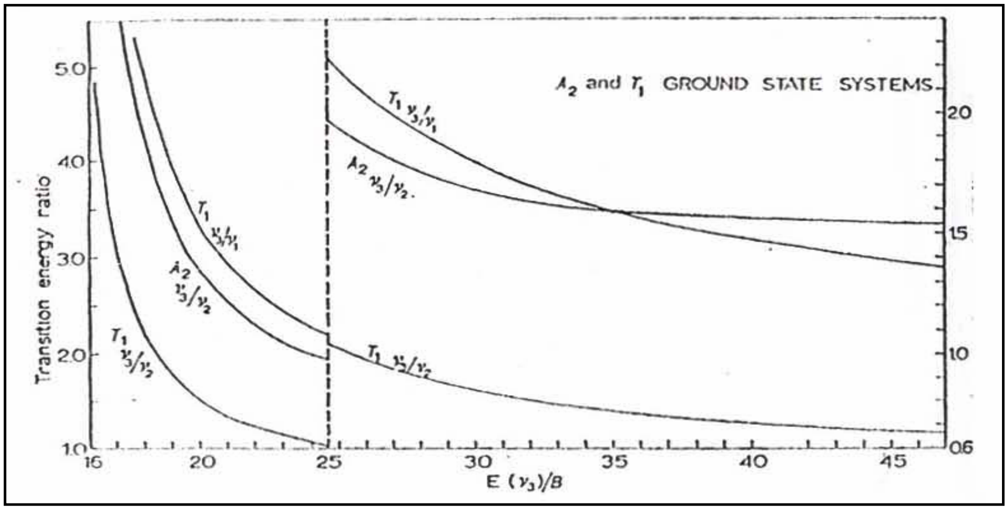


Fig. (7): A_2 and T1 ground states, transition energy ratios versus E(v3)/B (range 16-47). Note that the left-hand ordinate refers to E(v3)/B (16-24.6) and the right-hand ordinate to E(v3)/B (24.6-47) Co and Ni complexes

The value of μ_{eff} for the solid Ni(II) complex is (3.10) B.M. is also indicative of two unpaired electrons per Ni(II) ion consistent with its octahedral geometry[20]. The electronic absorption of Cu(II) complex (green colour) gave broad band centered at (884) nm (11312) cm^{-1} (ε_{max}=2700 $molar^{-1}$ cm^{-1}) the ion in fact, is tetragonaly distorted, presumably of the operation of the Jan Taller effect which assigned to $^2Eg \rightarrow {}^2T_2g$ transition. The magnetic susceptibility measurement is (1.85) BM is supported of one unipair electron of per Cu(II) ion is quite fit with octahedral geometry[21]. The electronic spectra of the metal complexes M^{II}= Cd, Pb, Hg Table (4) showed shift in $n\text{–}\pi^*$ absorption and tail (300-350) nm consistent metal ions with coordination ligand from their elemental analysis

Table (1) and UV- visible spectral tetrahedral structures were proposed for them[22-23].

Solutions chemistry

Molar ratio

The complexes of the ligand (L) with selected ions (Co^{+2}, Cd^{+2}) were studied in solution using water as solvents, in order to determine (M:L) ratio in the prepared complexes, following molar ratio method[24].

A series of solutions were prepared having a constant concentration (C) 10^{-3} M of the hydrated metal salts and the ligand (L). The (M:L) ratio was determined from the relationship between the absorption of the observed light and mole ratio (M:L) found to be (1:1). The result of complexes formation in solution are show in Table (5–6), Fig. (8).

To determined ΔG[25]:

$k = ML/[M][L]$

(1)

$\alpha = (Am - As)/ Am$

(2)

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

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

(3)

$\Lambda = \varepsilon_{max}.b.c.$

(4)

k_f = stability constant

α = decomposition Degree

M = metal ion

L = The ligand

[ ] = concentration

As = The absorption of the equivalent point of mole ratio

Am = The maximum absorption of the mole ratio

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

$\Delta G = - 2.303 RT Log K.$

R = 8.303

T = 273 + 25 = 298

The values of As, Am, α, k, log k and ΔG are presented in Table (6).

Molar conductivity for the complexes

The molar conductance of the complexes in (water), Table (7) lie in the (135-162) S. cm^2 $molar^{-1}$ range, indicating their electrolytic nature with (1:1) ratio[26].

Table (5): VM, VL and absorption of ligand (L). VM= volume of metal in ml, vl= Volume of ligand in ml

[LCo.2H_2O]Cl at (291)nm			**[LCd.2H_2O]Cl at (291)nm**		
VM	VL	Abs	VM	VL	Abs
1ml	0.25	0.500	1ml	0.25	0.507
1	0.50	0.804	1	0.50	0.801
1	0.75	1.102	1	0.75	1.102
1	1.00	1.301	1	1.00	1.405
1	1.25	1.402	1	1.25	1.431
1	1.50	1.502	1	1.50	1.526
1	1.75	1.604	1	1.75	1.602
1	2.00	1.701	1	2.00	1.701
1	2.25	1.803	1	2.25	1.780
1	2.50	1.902	1	2.50	1.830

Table (6): stability constant and ΔG for the Ligand (L) complexes

Compounds	**As**	**Am**	**α**	**K**	**Log K**	**ΔG**
[LCo.2H_2O]Cl	1.301	1.701	0.235	13×10^{8}	9.11	–51.9
[LCd.2H_2O]Cl	1.405	1.701	0.296	8×10^{8}	8.90	–50.7

[LCo.2H_2O]Cl > [LCd.2H_2O]Cl

Table (7): The molar conductance of the complexes

Compound fragmentations	**Λm S.cm^2 molar^{-1}**	**ratio**
[LCo.2H_2O]Cl	150	1:1
[LNi.4H_2O]Cl	162	1:1
[LCu.4H_2O]Cl	140	1:1
[LCd.2H_2O]Cl	155	1:1
[LHg.2H_2O]Cl	140	1:1
[LPb.2H_2O]NO_3	135	1:1

Recorded in (water) solvent, where L= $C_6H_5N_3O_2$

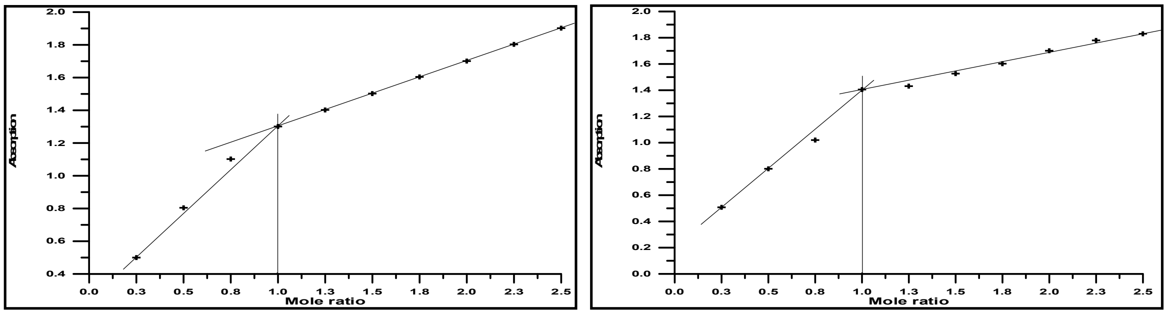
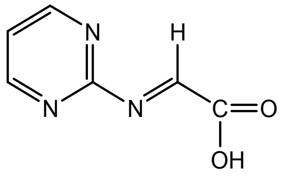


Fig. (8): The mole ratio curves of complexes [LCo.2H_2O]Cl and [LCd.2H_2O]Cl in solution (1×10^{-3} mole. l^{-1}) at (λ=291 nm)

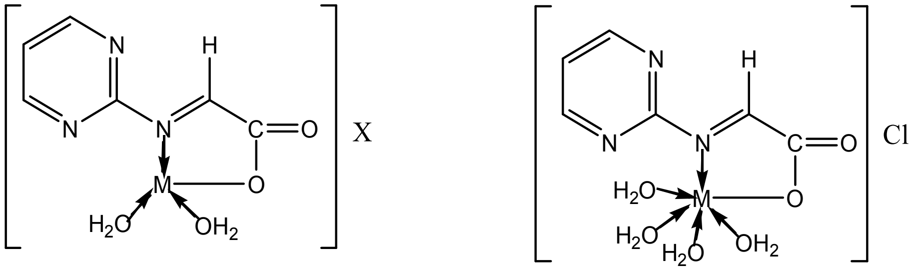
Conclusion

In conclusion, we have prepared new Schiff base ligand (L). The elemental analysis (C,H,N) gave formula $C_6H_5N_3O_2$. Spectroscpic (FT-IR, ^1H, ^{13}C-NMR) data showed the structure of the ligand contain azomethine and carboxylic groups. The metal complexes $[ML.nH_2O]Cl$ $[M^{II}$=Co, Ni, Cu, Cd, Hg and Pb$]$ are confirmed by elemental analysis (C,H,N) and metal content (A.A.). Spectroscopic, structural, conductivity and magnetic data show the metal ions are coordinated by azomethine–N and mono carboxylate–O.

The $[ML.nH_2O]Cl$, $[M^{II}$= Co, Cd, Hg and Pb$]$ have tetrahedral structure, while $[ML.nH_2O]Cl$, $[M^{II}$=Ni or Cu$]$ are octahedral structural as below:



Structure of the ligand ($C_6H_5N_3O_2$)



M^{II}=Co, Cd, Hg and Pb
X=Cl^- for all metal ions except Pb
where X = NO^-_3
(Tetrahedral)

M^{II}=Cu or Ni
(Octahedral)

Structures of the complexes

References

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