Complexeation Behavior of Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II} Ions Toward Schiff Base Derived From 2, 4 -Dihydroxy Benzaldehyde and O-Phenylene Diamine

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Abstract

The aim of this work covers the synthesis and characterization of the new tertra dentate ligand (H_4L) containing (N and O) as donor set atoms kind (N_2O_2) where: H_4L=Bis-1,2 (2,4-dihydroxybenzylediene phylinediamine . The preparation of ligand contains reaction 2, 4 - Dihydroxy benzaldehyde and o-phenylene diamine . Schiff base was reacted with some metal ions in the presence of methanol to give the complexes in the general formula
[M (H_2L)] where: M^{II} = Co, Ni, Cu, Zn, Cd. All compounds were characterized by spectroscopic methods I.R , U.V.-Vis, metal content and molar conductivity measurements, showed that the complexes are non-electrolyte. The proposed geometry for all of the proposed complexes was a tetrahedral while Ni complex was square planar.

Introduction

Metal complexes of Schiff base are extensively studied due to synthetic flexibility and sensitivity toward a variety of metal atoms (1). They are found useful in catalysis, in medicine as antibiotics and anti-inflammatory agent and in the industry as anti-corrosion
(2-8). salicylaldehyde compound is a bidentate ligand and has several applications in chemistry and medicine .In 2005 Halabiand and co-workers (9) prepared a Schiff base ligand (N_2O_2) kind derived from amino -1,2,3,6-oxatrizain and salicylaldehyde and its transition metal complexes with (Ni^{II}, Cu^{II} ,and Pd^{II}). In this paper the synthesis and characterization of Schiff base [Bis-1,2 (2,4-dihydroxybenzylediene phylinediamine] ligand derived from the reaction of 2,4 -Dihydroxy benzaldehyde and o-phenylene diamine ,and some of its complexes with (Co, Ni, Cu, Zn and Cd) are reported.

Experimental

Reagents were purchased from Fluka and Redial-Dehenge chemical Co. I.R spectra were recorded as (KBr) dicsic a shimadzu 8300 FTIR Spectrophotometer in the range (4000-400) cm^{-1} . Electronic spectra of prepared compounds were measured in the region (200-1100) nm for 10^{-3}M solutions in (DMF) as a solvent at 25 C° by using a shimadz, 160 spectrophotometer with 1.000 + 0.001cm^{-1} matched quartz cell. While metal contents of the complexes were determined by atomic absorption (A.A) technique using a shimadz AA .680G atomic absorption spectrophotometer .Electrical conductivity measurements of the complexes were recorded at 25 C° for 10^{-3} M solutions of the samples in (DMF)by using a PW 9526 digital conductivity meter .

Synthesis of the ligand (H_4L)

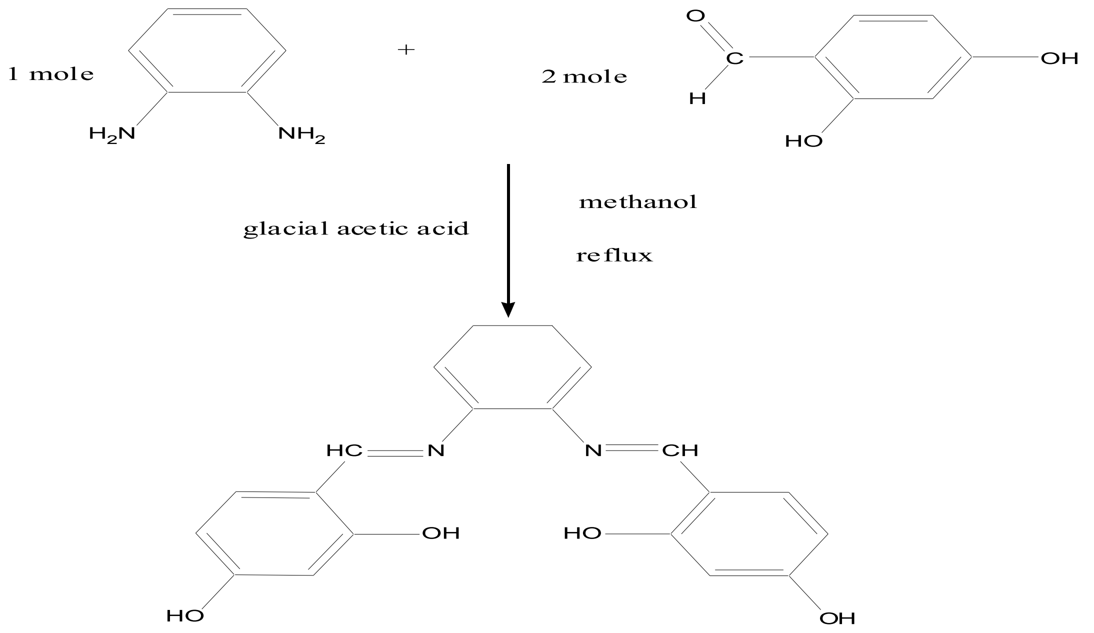
A solution of (o-phenylene diamine), (0.59g, 4.6 mmole) in methanol (5ml) was added slowly to 2,4-Dihydroxy benzaldehyde (1.27 g, 9.2 mmole) dissolved in methanol (5ml) . Then added drops from glacial acetic acid to them. The mixture was refluxed for (4hrs) and then stirred at room temperature for (1 hr). A pale yellow precipitate was collected by filtration, dried under vacuum for (24 hr), to give (H_4L), Yield (84%), m.p. (198) dec.

Synthesis of [(Co (H_2L)] complex

A (0.226g, 0.82 mmole) of $CoCl_2.6H_2O$ was dissolved in (5 ml) methanol. A solution of (0.2g, 0.95 mmole) of the ligand (H_4L) in (15 ml) methanol was added to the above mixture, then (0.106 g, 0.89 m mole) of KOH was dissolved in methanol and added to them. The reaction was allowed to reflux for (3 hrs), a dark violet the precipitate which were collected ,and washed with (2ml) benzene ,then let it to dry to give (0.25g), yield (80%), mp (280^0C) dec. The method that was used to prepare the other complexes [Ni (H_2L)] (2), [Cu (H_2L)] (3), [Zn (H_2L)] (4) and [Cd (H_2L)](5) was similar to that mentioned in the preparation of [Co (H_2L)] complex. Table (1) Shows some physical properties of the prepared complexes:

Results and Discussion

The new ligand type (N_2O_2) was prepared according to the general method shown in Scheme (1).



Bis-1,2 (2,4-dihydroxybenzylediene phylinediamine

Scheme (1) Synthesis route of the Schiff base

The (1.R) spectrum for (H_4L) ligand Fig (1) displayed two bands at (1610) and (1587) cm^{-1} due to the υ (C=N) stretching for the imine groups respectively $_{(10)}$ .The band at (3355) cm^{-1} is attributed to υ (O-H) stretching, the strong bands at (1342) and (1217) cm^{-1} are attributed to υ (C-N) and υ (C-O) stretching respectively.

The (I.R) spectral data of the complexes are presented in Table (2) .In general the (I.R) spectra of the complexes show two bands at the range (1600-1541) cm^{-1} which assigned to the υ

(C=N) stretches frequency for the imine groups which are shifted to alower frequency by (10-46) cm^{-1} in comparison to that for the free ligand fig (1a, 1b and 1c), these shiftings could be attributed to the reduced bond order of the imine group . This can be attributed to delocalization of metal electrons density at (t_2g) in the π system of the ligand (HOMO → LUMO)(12-14).
Where:

HOMO = highest occupied molecular orbital.
LUMO = lowest unoccupied molecular orbital.

The υ (O-H) stretching band in the free ligand at (3355) cm^{-1} is still present at the (3550-3450) cm^{-1}range for these complexes (15). The new bands at the range (447-541) $cm-^{1}$were assigned to υ (M-O) and υ (M-N) stretching respectively, indicating that the imine nitrogen and oxygen of hydroxyl group were involved in coordination with metal ion Table(2) (16-22).

(U.V-Vis) spectrum for the ligand Fig (2) exhibits a high intense absorption peak at (301) nm ($33222cm^{-1}$) εmax = 417 molar $^{-1}$.cm^{-1} which is assigned to overlap of (π → π*) and (π→ π^{*}) transitions (11) Table (3).The reaction of (H_4L) ligand with [$MCl_2.H_2O$] (where M=Co, Ni, Cu, Zn, and Cd) was carried out in MeOH under reflux.. The analytical and physical data Table (1) and spectral data Table (2) and Table (3).

The electronic spectral data of the complexes are summarized in Table (3) .The (U.V-Vis) spectra ofthe complexes displayed absorption at the range (314-342) nm which were assigned to the ligand filed (23).

In the [Co (H_2L)] complex the band at (430) nm was attributed to (d-d) electronic transition type ($^4T_{1(p)} \leftarrow {}^4A_2$) (24), suggesting tetrahedral structure about Co ion.

The band at (455) nm in the spectrum of [Ni (H_2L)] complex was attributed to (d-d) electronic transition type ($^1B_1g \leftarrow {}^1A_1g$) (Fig-2a), suggesting a square planar structure about Ni ion(25-27), (Fig-2b), while the band at (449) nm in the spectrum of [Cu (H_2L)] complex which was assigned to (d-d) electronic transition type ($^2E \leftarrow {}^2B_2$), suggesting tetrahedral structure about Cu ion.

The absence of (d-d) electronic transition in the complexes [Zn (H_2L)] and [Cd (H_2L)] are due to the configuration (d^{10}) structure for the metal ions, suggesting tetrahedral structure for sp^3 hyperdization of (Zn and Cd) (28).

The molar conductance values determined in (DMF) solution (10^{-3} M) (Table-3) lie in the range (23.5-3.19 $s.cm^{-1}mole^{-1}$) indicates that the complexes are non electrolytes (23) and confirm the suggested formula [M (H_2L)]

The experimental data of metal content is obtained by the atomic absorption method and the chloride content for all of the prepared complexes, Table (1) are in a good agreement with the calculated values.

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Table (1) Some physical properties of the complexes and their reactants quantities.

Compound	decomposition temperature 0C	Color	Weight of metal		Weight of product g	Yield %	M.Wt g.mol^{-1}	Chloride content	Metal Content
			g	mmole					Found (calc)
(H_4L)	198 dec	pale yellow	-	-	1.02	80	210.12	Nil	-
[(Co(H_2L)]	280 dec	dark violet	0.2.0	0.82	0.25	80	266	Nil	14.06 (13.63)
[Ni(H_2L)]	270 dec	red	0.226	0.82	0.28	67	266	Nil	14.46 (13.33)
[Cu(H_2L)]	210 dec	brown	0.16	0.84	0,2	66	271	Nil	15.01 (14.67)
[Zn(H_2L)]	200 dec	Yellow	0.129	0.82	0.25	81	273	Nil	16.54 (15.85)
[Cd(H_2L)]	255 dec	Yellow	0.2	0.86	0.42	92	322	Nil	24.21 (22.54)

dec: decomposition

Table (2): I.R spectral data of the ligand and its complexes (cm^{-1})

No.	Formula	υ (O-H)	υ (N=C)	υ (C-H)	υ (C-N)	υ (C-O)	υ (M-N)	υ (M-O)	Additional peaks
1	[H_4L]	3355	1610 1587	3060 2752	1342	1217	-	-	-
2	[Co(H_2L)]	3550	1600 1541	-	1373	1265	503	447	1438(C=C) ring
3	[Ni(H_2L)]	3527	1602 1552	3078 2921	1371	1242	541	507	1448(C=C) ring
4	[Cu(H_2L)]	3539	1602 1554	3178 3066	1369	1236	532	495	1477(C=C) ring
5	[Zn(H_2L)]	3450	1604 1558	3209 3072	1355	1240	524	487	1541(C=C) ring
6	[Cd(H_2L)]	-----	1606 1558	2786	1350	1276	526	482	1446(C=C) ring

Table (3): Electronic spectral data and conductance measurement in DMF as asolvant

Compound	nm λ	ε max molar^{-1} cm^{-1}	Λ_m s.cm^2.mole^{-1}	Assignment
(H_4L)	301	1121	–	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$
$[Co(H_2L)]$	342 430	403 505	23.5	$^4T_{1(p)}\leftarrow{}^4A_{2(f)}$
$[Ni(H_2L)]$	342 455	414 448	3.19	$^1B_1g\leftarrow{}^1A_1g$
$[Cu(H_2L)]$	314 449	547 3952	3.65	$^2E\leftarrow{}^2B_2$
$[Zn(H_2L)]$	321	423	4.33	C.T
$[Cd(H_2L)]$	341	414	5.40	C.T

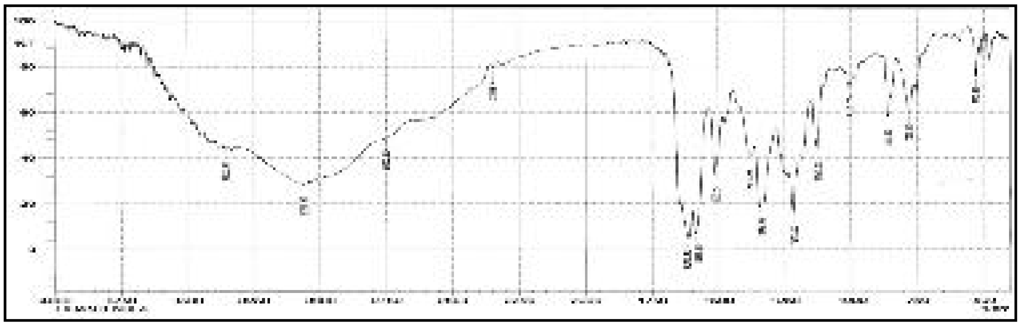


Fig. (1): The (I.R) Spectrum of the ligand

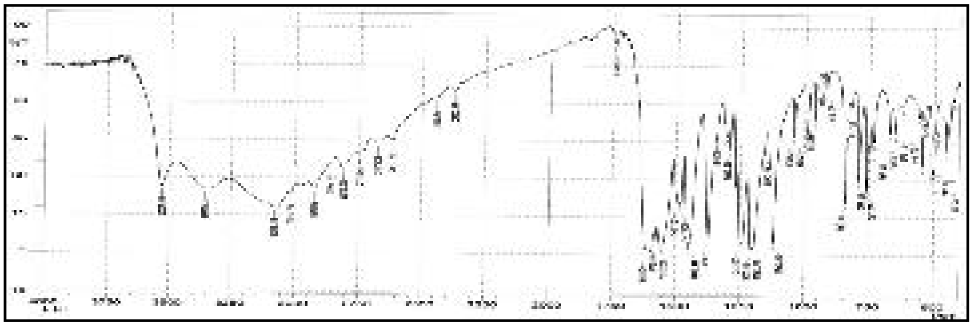


Fig. (1a): The(I.R) Spectrum of $[(Ni\ (H_2L)]$ complex

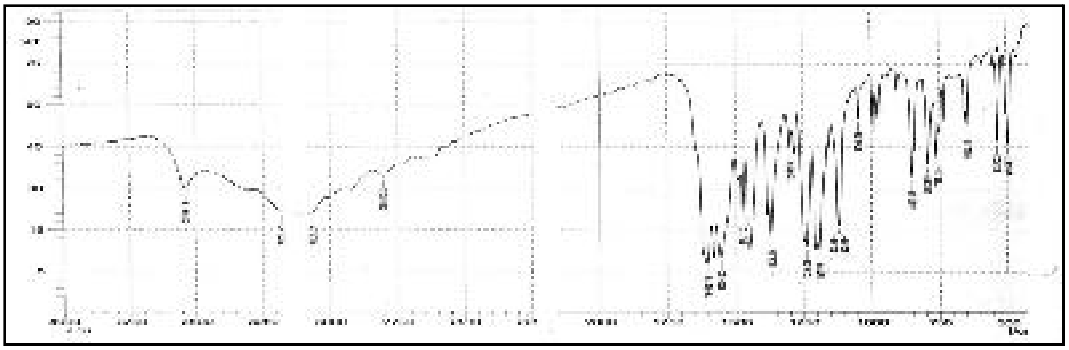


Fig. (1b):The(I.R) Spectrum of [(Cu (H_2L)] complex

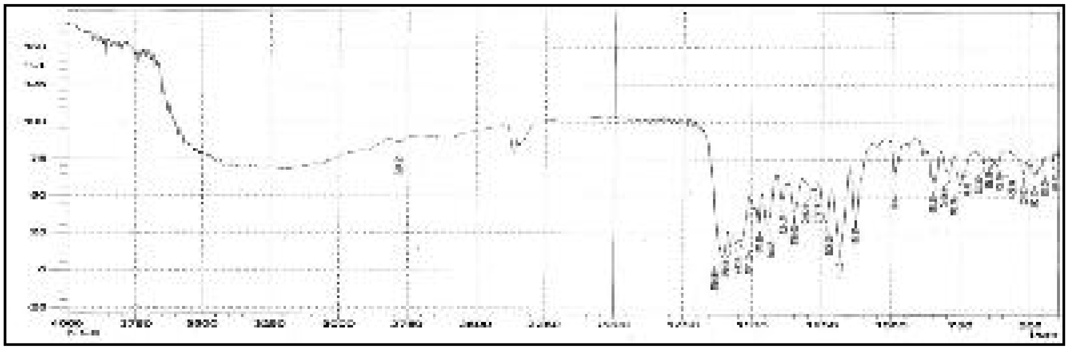
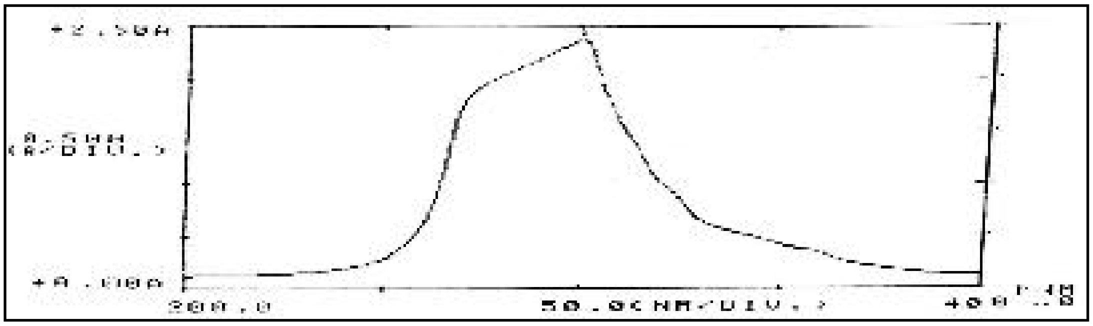


Fig. (1c): The(I.R) Spectrum of [Cd(H_2L)] complex



Fig(2) The (UV-Vis)Spectrum of The ligand (H_2L)] complex

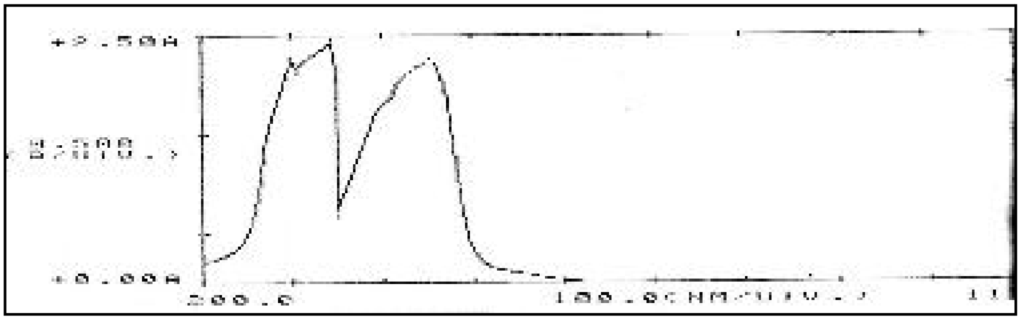


Fig. (2a): The (UV-Vis) Spectrum of complex [(Ni (H_2L)]

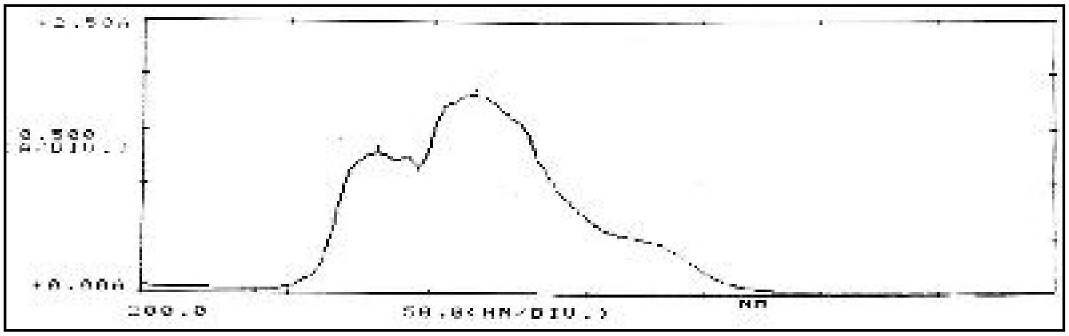


Fig. (2b): The (UV-Vis) Spectrum of complex [(Cu (H_2L)]

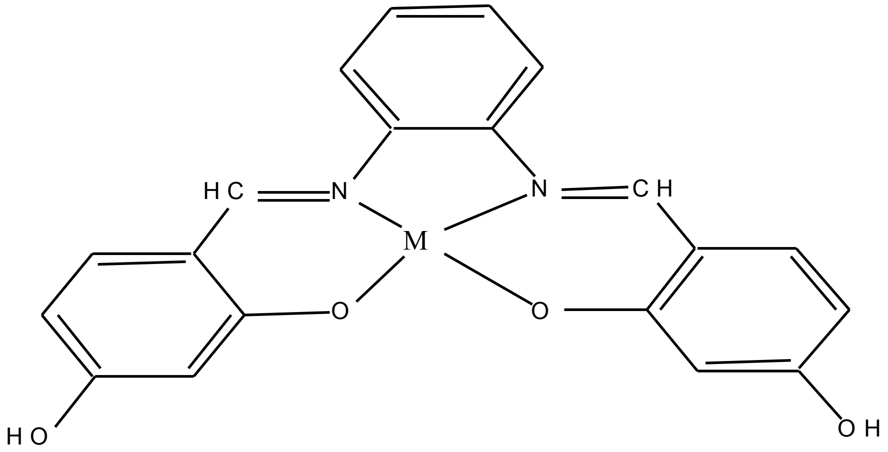


figure (3) the suggested structure for the M(H_2L)complexes

M =Co,Zn,Cd

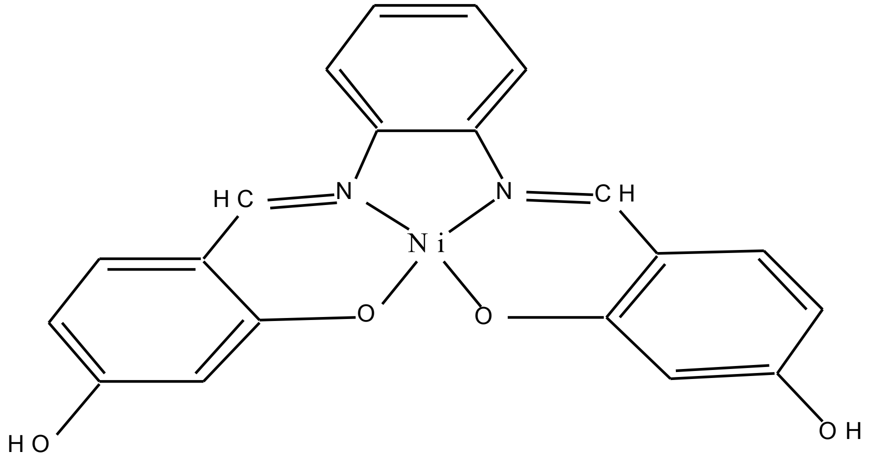


figure (4) the suggested structure of the Ni(H_2L) complex

سلوك التخلب الايوني للكوبلت الثنائي ،والنيكل الثنائي، والنحاس الثنائي ،و الزنك الثنائي، والكادميوم الثنائي اتجاه قاعدة شيف المشتقة من اورثو فنيلين داي امين و4,2- داي هايدروكسي بنزلديهايد

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الخلاصة

تضمن البحث تحضير الليكند الجديد الرباعي السن نوع N_2O_2
Bis-1,2-(2,4-dihydroxybenzylediene phylinediamine =(H_4L)
وذلك من مفاعلة
(o-phenylene diamine) مع (2,4- Dihydroxy benzaldehyd ثم مفاعلة الليكند مع بعض ايونات العناصر
(Co^{II}, Ni^{II} ,Cu^{II}, Zn^{II}, Cd^{II}) باستعمال الميثانول وسطا للتفاعل وبوجود هيدروكسيد البوتاسيوم قاعدة، اذ تكونت سلسلة من المعقدات ذي الصيغة العامة [M(H_2L)].

شخصت جميع المركبات بالطرائق الطيفية ، الأشعة تحت الحمراء ، والأشعة فوق البنفسجية – المرئية ،مطيافية الامتصاص الذري للعناصر وعين محتوى الكلور ودرجات الانصهار ، مع قياس التوصيلية المولارية الكهربائية.

من نتائج البحث كان الشكل الفراغي المقترح لمعقدات الكوبلت والنحاس والزنك والكادميوم هي رباعي السطوح مشوه، بينما للنيكل فكان شكل معقده مربعا مستويا.