تحضير ودراسة طيفية لمعقدات يورانيل أميد متعدد السن

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الخلاصة:

تم تحضير أربع معقدات يورانيل (VI) مع ليكاندات الاميد المتعددة السن لأول مرة بواسطة تفاعل محلول أيثانولي ساخن لليكاندات الاميد المتعددة السن مع محلول مائي لخلات اليورانيل. المعقدات الجديدة تمت دراستها بواسطة التحليل العنصري الدقيق , أطياف الأشعة الفوق بنفسجية والمرئية و أطياف الأشعة تحت الحمراء. استنادا إلى الدراسات الطيفية فقد تبين أن التناسق بين الليكاند واليورانيل قد حصل عبر أوكسجين مجموعة الاميد وأوكسجين مجموعة الكاربوكسيل مع دخول جزيئة ماء للمعقد لتعطي تناسق سباعي.

Synthesis and spectral study of Uranyl(VI) polydentate amide complexes

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Abstract

Four new complexes of polydentate amide ligands with Uranyl(VI) have been prepared by the reaction of the hot ethanolic solution of N,N′-bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-ethylenediamine (L_1), N,N′-bis-(3-carboxy-1-oxoprop-2-enyl) hydra zine (L_2), N,N′-bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-phenylenediamine (L_3) and N,N′-bis-(3-carboxy-1-oxopropanyl)hydrazine (L_4) with aqueous solution of Uranyl acetate. The four new complexes were studied by elemental analysis, ultra violet – visible spectra and infra red spectroscopy. Vibrational spectra indicate coordination of amide and carboxalate oxygen's of the ligands along with one water molecule giving a UO_2(VI) complexes with heptacoordination . Electronic spectra support the coordination of ligands with uranyl ions to form the UO_2(VI) complexes.

Introduction

The coordination chemistry of uranium has undergone significant expansion in the last few decades (1-5), and perhaps the most extensively studied unit in actinide chemistry, not only in the context of its chemical behavior under a variety of environmental conditions but also because of the unique structure and bonding of the linear O=U=O dioxo group and the photochemical and redox properties of this species (6). For these reasons the interest in the coordination chemistry of uranium has recently increased.

The general coordination motif of uranyl (VI) complexes involve the ligand bound in a tetradentate fashion along the equatorial axis of the uranyl ion and a solvent molecule occupying the fifth coordinate site in the equatorial position(7).

The coordination chemistry of the amide group has received much attention due to its diver's behavior and the role it plays in biological processes (8-11). Pannue et al.(12) have reported that salicylamide coordinates through the oxygen of the amide group, while Windle(13) have reported that accordination occurs through the nitrogen atom.

This paper describes the synthesis, spectral and properties study of uranyl complexes derived from N,N′-bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-ethylenediamine (L_1), N,N′-bis-(3-carboxy-1-oxoprop-2-enyl) hydra zine (L_2), N,N′-bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-phenylenediamine (L_3) and N,N′-bis-(3-carboxy-1-oxopropanyl)hydrazine (L_4).

Experimental

Material

All chemicals used were reagent grade and were used without further purification unless otherwise stated.

Physical measurements

The physical measurements, I.R. spectra was recorded on a 800S Fourier Transformer Infrared Spectrophotometer/ Shimadzo (FT-IR) in the region 400-4000 cm^{-1} by using KBr pellets. Elemental analysis for C, H, and N were performed on a CHNS-Elements Analyzer in Iran Polymer and petrochemical institute. The UV-Vis. Spectra were recorded in methanol on a spectroscan 80D UV-Vis. Spectrophotometer with quartz cell of a 1cm path length . The HANA instruments EC 214 Conductivity meter was used to measure the conductivity of ligands and their complexes.The electro thermal melting point model 9300 was used to measure the melting point of ligands and their complexes.

Synthesis of ligands

N,N̄-bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-ethylenediamine (L_1)

Maleic anhydride (9.8g, 0.1mol) was dissolved in absolute ethanol (20ml) with stirring until a clear solution was obtained. Ethyle ne diamine (2.7ml, 0.05mol) was then added drop wise with stirring, and the mixture was stirred for 3h at room temperature, giving a white precipitate. These were removed by filtration, recrystallized from ethanol, filtered off and dried in vacuum. The compound characterized as ($C_{10}H_{12}N_2O_6$) by FTIR, UV-Vis and elemental analysis; Yield 50%.

N,N̄-bis-(3-carboxy-1-oxoprop-2-enyl) hydrazine (L_2)

This ligand was prepared by the same method described before for (L_1) to obtain a white precipitate which were characterized as ($C_8H_8N_2O_6$) by FTIR, UV-Vis and elemental analysis; Yield 55%.

N,N̄-bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-phenylenediamine (L_3)

This ligand was prepared in the similar method described before for (L_1) to obtain apale yellow precipitate which were characterized as ($C_{14}H_{12}N_2O_6$) by FTIR, UV-Vis and elemental analysis; Yield 58%.

N,N̄-bis-(3-carboxy-1-oxopropanyl)hydrazine (L_4)

This ligand was prepared by the same method described before for (L_1) to obtain a white precipitate which were characterized as ($C_8H_{12}N_2O_6$) by FTIR, UV-Vis and elemental analysis; Yield 60%.

Synthesis of complexes

[$UO_2(L_1)$ H_2O]

Solution of $UO_2(OAC)_2.2H_2O$ (0.06gm, 0.16 mmol) in water (2oml) was added to a hot ethanolic solution of N,N̄-bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-ethylenediamine (L_1) (0.04gm, 0.16 mmol). The mixture was stirred for 4hours then left in the solution for 2-days, giving a yellow precipitate. This was removed by filtration, recrystilized

from aqueous ethanolic solution, filtered off and dried in vacuum and characterized as ($C_{10}H_{12}N_2O_9U$) by FTIR, UV-Vis and elemental analysis; Yield 75%.

[$UO_2(L_2)$ H_2O]

This complex was prepared by the same method described before for [UO_2(L_1) H_2O]

to obtain a yellowish-orange precipitate which were characterized as ($C_8H_8N_2O_9U$) by FTIR, UV-Vis and elemental analysis; Yield 73%.

[UO_2(L_3) H_2O]

This complex was prepared by a similar method described before for [UO_2(L_1) H_2O] to obtain an orange precipitate which were characterized as ($C_{14}H_{12}N_2O_9U$) by FTIR, UV-Vis and elemental analysis; Yield 77%.

[UO_2(L_4) H_2O]

This complex was prepared by a similar method described before for [UO_2(L_1) H_2O] to obtain a yellow precipitate which were characterized as ($C_8H_{12}N_2O_9U$) by FTIR, UV-Vis and elemental analysis; Yield 77%.

Result and discussion

The ligands L_1, L_2, L_4 colors were white while L_3 yellow. The complexes varied from yellow to orang. They were stable under normal laboratory conditions, and were insoluble in common non-polar solvents, hexan, diethyl ether, benzene, and toluene. The ligands and their complexes were appreciable solubility in common polar organic solvents methanol, ethanol and acetone. The physical and analytical data of ligands and their complexes are presented in Table 1.

Table 1. Analytical data, Physical properties and conductivity measurements of the ligands and their complexes.

Compounds	m.p °C	Conductivity ×199.9µs at 19°C in Methanol Con.1×10^{-3} M	Color	Elemental analysis		
				C	H	N
N,N -bis-(3-carboxy -1-oxoprop-2-enyl)-1,2-ethylenediamine (L_1)	234	26	white	Fou. 46.2 Cal. 46.87	4.51 4.68	10.8 10.9
N,N -bis-(3-carboxy-1-oxoprop-2-enyl) hydrazine (L_2)	180	6.4	white	Fou. 42.3 Cal. 42.1	3.42 3.5	12.1 12.2
N,N -bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-phenylenediamine (L_3)	165	9.6	Pale yellow	Fou. 55.1 Cal. 55.26	4.21 3.947	9.0 9.2
N,N -bis-(3-carboxy-1-oxopropanyl) hydrazine (L_4)	218	1.8	white	Fou. 41.55 Cal. 41.37	4.987 5.172	11.9 12
[UO_2(L_1) H_2O]	317	25.7	yellow	Fou. 1.88 Cal. 22.14	2.211 2.214	5.0 5.1
[UO_2(L_2) H_2O]	290	8.8	Yellowish - Orange	Fou. 18.5 Cal. 18.67	1.455 1.556	5.7 5.4
[UO_2(L_3) H_2O]	254	8	Orange	Fou. 28.1 Cal. 28.47	2.11 2.033	4.6 4.7
[UO_2(L_4) H_2O]	270	10.6	Yellow	Fou. 19.1 Cal. 18.53	2.22 2.31	5.6 5.4

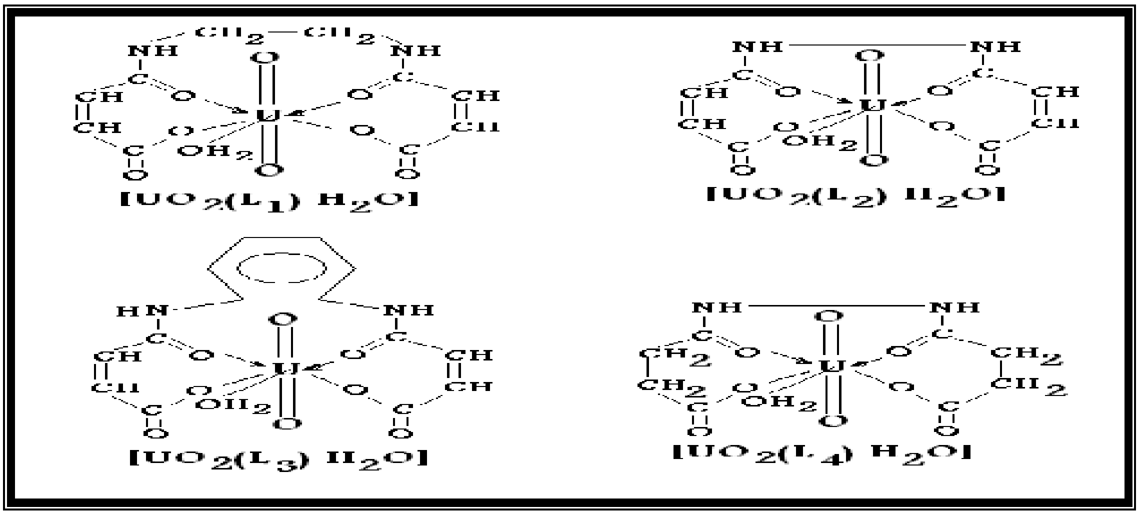


Figure1. The structure of the prepared complexes.

Electronic UV-vis spectra analysis

The electronic spectra of the ligands L_1, L_2, L_3 and L_4 are shown in Figure 2, while the electronic spectra of their complexes are shown in figure 3.

From figure 2 it can be observed that the UV electronic spectra of the four ligands exhibit three bands:

For L_1 at 206, 232 and 284nm; for L_2 at 207, 230 and 286nm; for L_3 at 210, 236 and 288nm and for L_4 at 203, 232 and 281nm. λ_{max} for L_1, L_2, L_3 and L_4 at 206, 207, 210 and 203nm respectively, these bands may be attribute to internal ligand charg transfer while the second band may be assigned to $\pi\rightarrow\pi^*$ and the third weak band in all ligands may be due to $n\rightarrow\pi^*$.

Small bathochromic shift was observed for $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ in the corresponding uranyl complexes due to the coordination of the carbonyl oxygen to the uranyl.

The spectrum of diamegnatic uranyl complexes showed approximately two bands, in addition to the ligand bands, the first band observed approximately at 600nm corresponding to charge transfer from equatorial donor atoms of the ligands to the uranyl ion which impairing the complexes their colors. The second band observed at about 520-530nm due to electronic transition from apical oxygen atom to the f-orbitals of the uranyl atom characteristic the uranyl moiety (14,15).

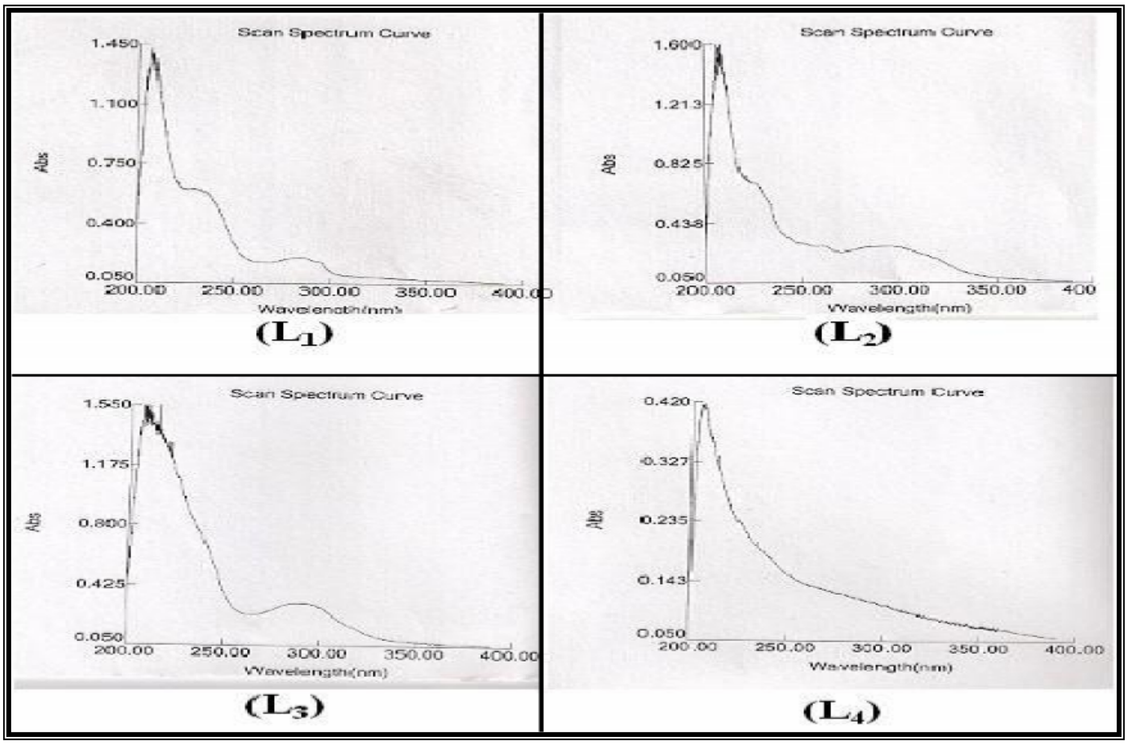
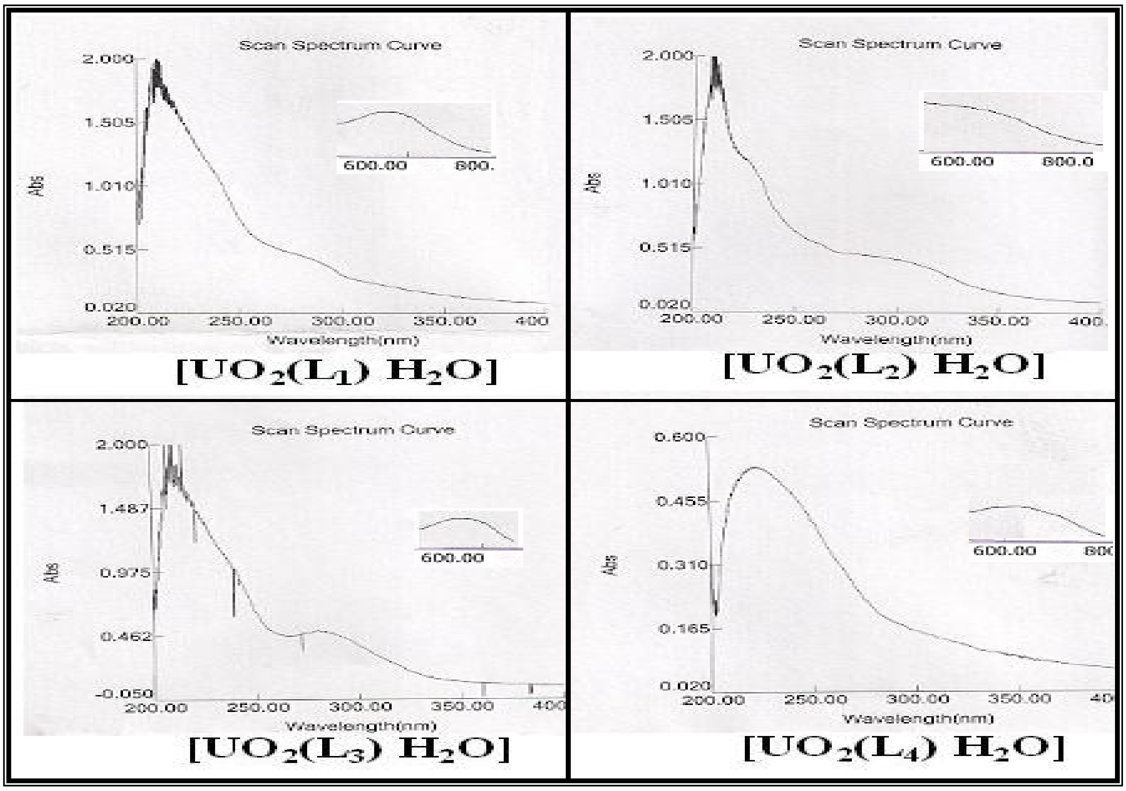


Figure 2, UV-Vis spectra of the ligands



$[UO_2(L_1)\ H_2O]$ $[UO_2(L_2)\ H_2O]$

$[UO_2(L_3)\ H_2O]$ $[UO_2(L_4)\ H_2O]$

Figure 3, UV-Vis spectra of the complexes

Vibrational spectra

All investigated complexes showed additional characteristic strong bands in comparison with spectrum of free ligands at 920,916, 923 and 931 cm^{-1} for the complexes of L_1, L_2, L_3 and L_4 ligands respectively, due to the asymmetric UO_2 stretching are characteristic of linear uranyl ion in the complexes(16,17) , indicates the coordination of uranium with the ligands. The vibrational bands due to rocking and wagging modes due to water and uranyl ion-oxygen stretching modes are observed in the 600-800 cm^{-1} region also the broad bands in the 3000-3650 cm^{-1} region for all the complexes of all the ligands may be attributed to coordinated water in all the complexes (18)

The bands belong to the amide υ(N-H) mode at 3200-3415 cm^{-1} for the free ligands L_1, L_2, L_3 and L_4 are shifted towards higher frequencies while the carbonyl υ(C=O) (amide) frequency undergoes shift towards lower frequency in the uranyl complexes, indicating non involvement of the amide nitrogen and involvement of the carbonyl oxygen atom of amide group in coordination with uranyl ion(19). This result is explained by the decrease in the double bond character of C=O and subsequent increase of C-N double bond character (20,21). In other words, it is the lengthening of the C=O bond and shortening of the C-N bond which cause the decrease and increase of the frequencies respectively, in the IR spectra[22].

The υ(C=O) and υ(C-O) stretching frequencies in the 1543-1600 cm^{-1} and 1419-1494cm^{-1} region have been assigned to υ(COO^-)$_{asym}$ and υ(COO^-)$_{sym}$ modes respectively in the uncomplexed ligands. A positive and negative shift in complexes indicates a Δυ enhancement upon complexation and suggests coordination of carboxylate groups in all the complexes of the four ligands in a monodentate fashion[23-25]. Here Δυ implies the difference between υ(COO^-)$_{asym}$ and υ(COO^-)$_{sym}$.

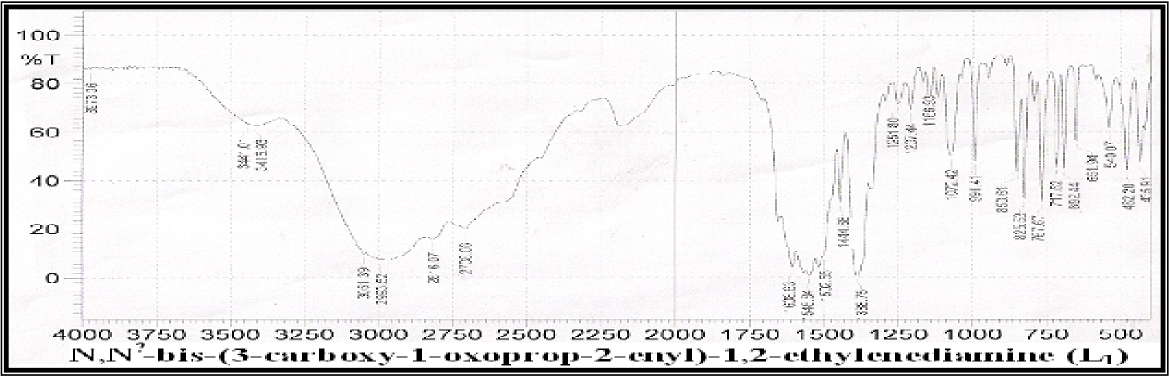
The solution vibrational data of all the ligands and their complexes are presented in the table 2 and shown in figure 3.

Table2, Infrared spectra (cm^{-1}) for the ligands and their complexes.

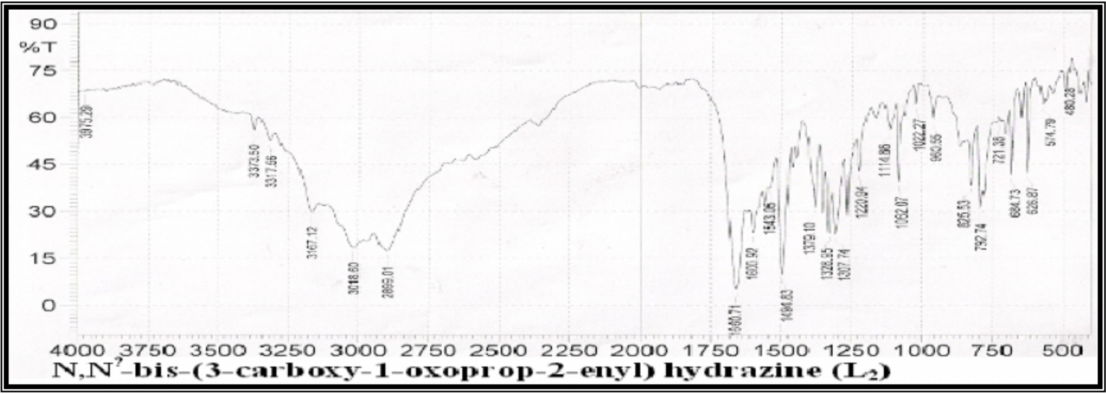
compound	υ(C=O)$_{amide}$	υ(COO^-)$_{asym}$	υ(COO^-)$_{sym}$	Δυ(COO^-)	υ (U=O)
L_1	1608s	1548s	1444m	104	-
L_2	1660s	1600m	1494s	106	-
L_3	1708m	1575m	1456w	119	-
L_4	1695s	1602s	1485m	107	-
$[UO_2(L_1)\ H_2O]$	1602s	1539s	1450m	89	920m
$[UO_2(L_2)\ H_2O]$	1631m	1570s	1446s	124	916s
$[UO_2(L_3)\ H_2O]$	1718w	1521s	1411s	110	923s

[$UO_2(L_4)$ H_2O]	1697s	1539s	1419s	120	931s

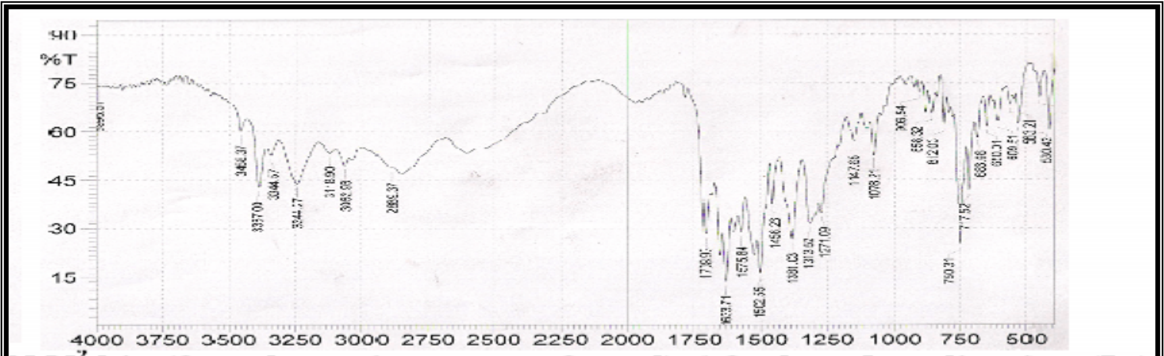
Where s=strong; m=medium; w=weak;



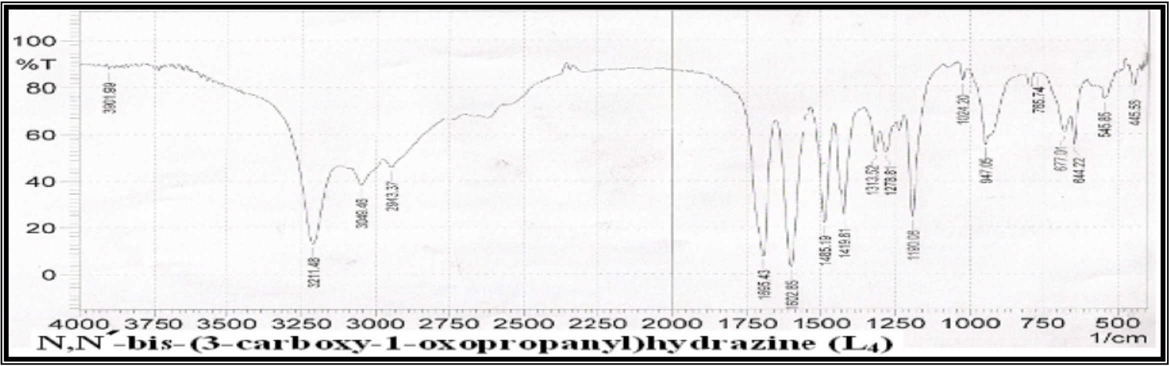
N,N$^{?}$-bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-ethylenediamine (L_1)



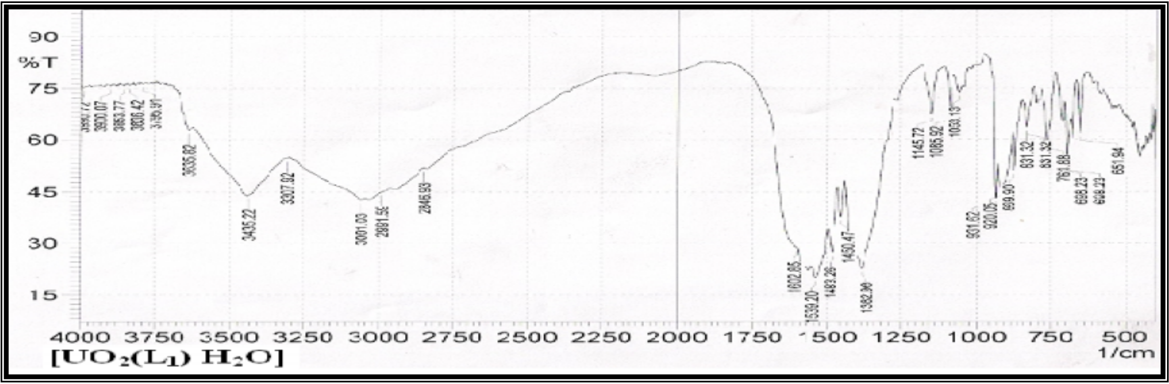
N,N$^{?}$-bis-(3-carboxy-1-oxoprop-2-enyl) hydrazine (L_2)



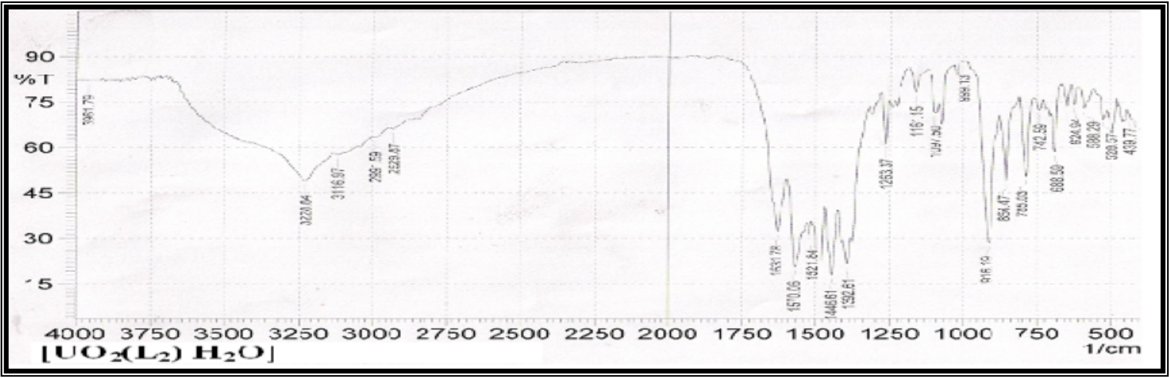
N,N$^{?}$-bis-(3-carboxy-1-oxoprop-2-enyl)-1,2-phenylenediamine (L_3)



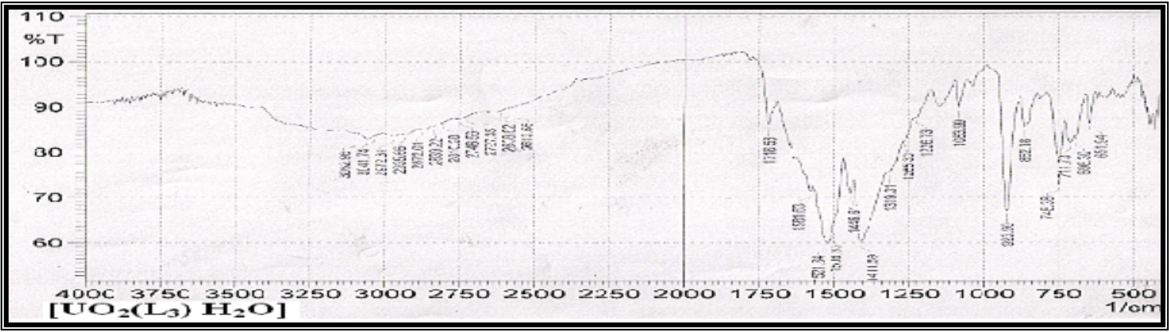
N,N´-bis-(3-carboxy-1-oxopropanyl)hydrazine (L_4)



[$UO_2(L_1)$ H_2O]



[$UO_2(L_2)$ H_2O]



[$UO_2(L_3)$ H_2O]

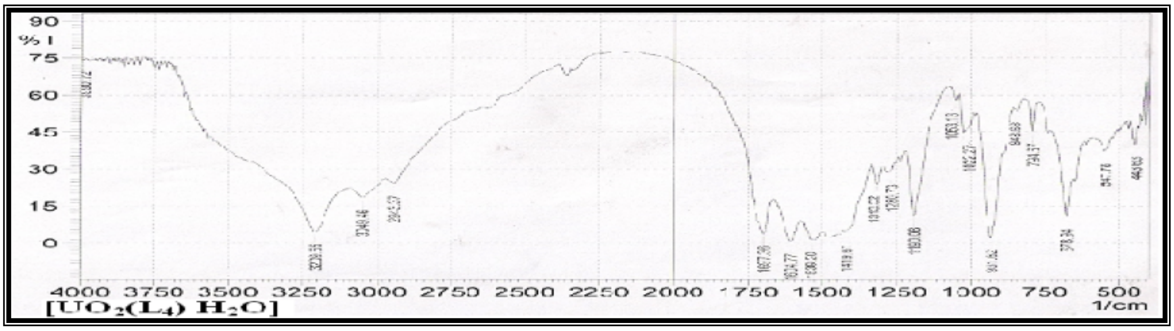


Figure 4, I.R. spectra of the compounds

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