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Synthesis and Spectroscopy Study of the New Amide Complexes of Platinum (II)

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Abstract

In this paper, the complexes of Pt (II) with N,N-bis (-3- carboxy -1- oxoprop-2-enyl)-1,2-ethylendiamine; N,N-bis (-3- carboxy -1- oxoprop-2-enyl)-1,2-hydrazine; N,N-bis (-3- carboxy -1- oxoprop-2-enyl)-1,2-phenyldiamine and N,N-bis (-3- carboxy -1- oxopropenyl)-1,2-ethylendiamine] have been synthesis and identified by elemental analysis, IR spectra and Uv –Vis. spectra. The FT-IR spectra by vibrational spectra studies indicated to combination and conjected o-phenylenediamine, hydrazine and ethylendiamine by Nitrogen of NH_2 group with carbonyl of carboxyl group COO- from dicarboxylic acid to formed amide bond to prepare quadra dentate ligands. The electronic spectra support square planner geometry around Pt (II) complex.

Key words: Complexes of platinum (II), complexes amide, spectroscopy studies.

Introduction

Transition metal complexes containing oxygen and nitrogen donor ligands have been of search interest for many years (1). The organometallic chemistry of platinum has been thoroughly studies it has great historical significance (2).The binding of metal ions to amide group has been the subject of research over the past three decades, precisely due to ambidentate nature of amide bond and many of these reactions provide simple models for much more complex metal–peptide systems and enzymes (3). There are numerous examples of the in vivo interactions of transition metal ions with the amide group, and these interactions can be of biological importance (3, 10-11). The chemistry of metal complexes containing amide ligands has been a subject of great interest. The reason for this interest stems from the fact that such complexes can be easily made and variation of the substituents is facile (4). This is due to partly to the stabilization of the M-amido bond by π-donation of the lone pair electrons of the amido N to empty d- orbitals in the early transition metals, which cannot occur in the late transition metals (5) .However, the number of reported amido complexes of the platinum group metals and some metals are growing (6-13). In this paper describes the synthesis ,characterization and spectroscopy studies of platinum (II) with N,N-bis (-3- carboxy -1- oxoprop-2-enyl)-1,2-ethylendiamine; N,N-bis (-3- carboxy -1- oxoprop-2-enyl)-1,2-hydrazine; N,N-bis (-3- carboxy -1- oxoprop-2-enyl)-1,2-phenyldiamine and N,N-bis (-3- carboxy -1- oxopropenyl)-1,2-ethylendiamine.

The Materials and Methods

All chemical materials were supplied from E. Merck and BDH; Analytical grade solvents were used and were purified as before by standard method (9). The chemical materials were used in the preparation are:- ethylene diamine $H_2NCH_2CH_2NH_2$ (6.001g, 0.1 mol.); Hydrazene $H_2NNH_2.XH_2O$ (3.2g, 0.1mol.); o-phenylene diamine $C_6H_4(NH_2)_2$ (10.8g, 0.1mol.); maleic anhydride $C_4H_2O_3$ (9.8g, 0.1mol.); succinic anhydride $C_4H_4O_3$ (10.4g, 0.1mol.); Barium hydroxide octahydrate $Ba(OH)_2.8H_2O$ (0.171g, 1mmol.); potassium iodide KI (0.66g, 1mmol.); silver sulphate Ag_2SO_4 (0.61g, 2mmol.); potassium tetrachloroplatinate (II) K_2PtCl_4 (0.41g, 1mmol.); ethanol CH_3CH_2OH; tetrahydro furane C_4H_8O; ether CH_3OCH_3; hexane C_6H_{14}.

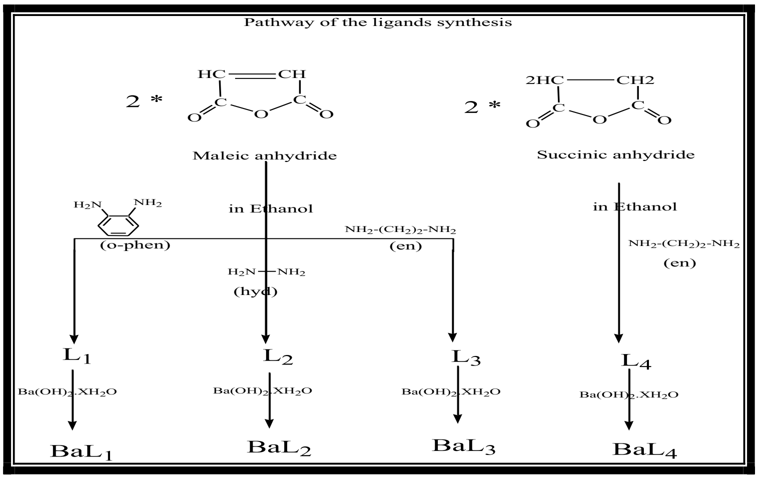
FT.IR spectra were recorder on a FTIR: 800SFOURIERTRANSFORMER INFRARED SPECTROPHOTOMETER/ SHIMADAZO in the region 400-4000 cm^{-1} by using KBr pellets. Elelmental analysis for C, H, and N were performed on a CHNS-Elements Analyzer in Iran polymer and petrochemical institute. The Uv-Vis. spectra were recorded in ethanol on a 80 D Uv-vis. spectroscopy with quartz cell of 1 cm path length. The electro thermal melting point model 9300 was used to measure the melting point of ligand and its complexes.

Synthesis of the ligands (L_1, L_2, L_3)

These ligands were prepared according to reported (6) by dissolve (0.1mole) ethylene diamine, hydrazine, o- phenyldiamine respectively with maleic anhydride in 100 ml absolute Ethanol with stirring the mixture for overnight at room temperature. Collect the product by filtration and wash it with ethanol, dried and recrystallization from THF or ethanol. The ligands were characterized by IR spectra, elemental analysis, electronic spectra and melting point.

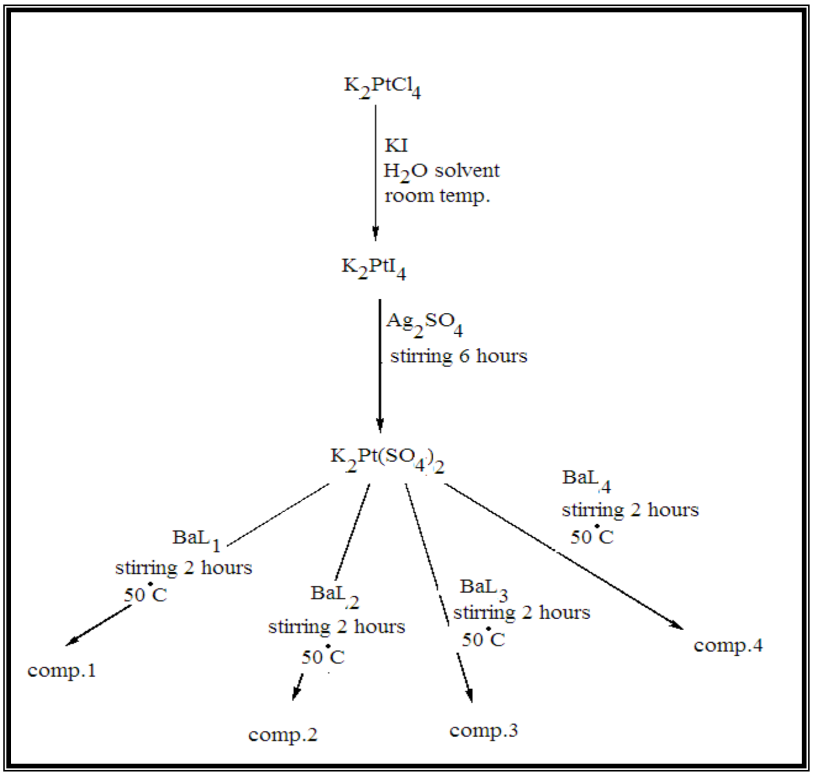
Synthesis of the ligand (L_4)

This ligand was prepared according to reported (6) by dissolve (0.1mole) ethylene diamine with succinic anhydride (0.1 moles) in 100 ml absolute Ethanol was then added with stirring the mixture for overnight at room temperature. The white solid product which precipitated was filtered, washed with ethanol, dried and recrystallization from THF or ethanol. The ligand was characterized by IR spectra, elemental analysis, electronic spectra and melting point.



Synthesis of complexes

1 mmole from ligand dissolved in 20 ml ethanol was added to the solution of barium hydroxide octahydrate (1 mmole , 0.171 g) in the same solvent, the mixture was stirred for 3 h . Excess ether/hexane was added to precipitate, the barium salt (L') which was filtered and vacuum dried (17). An aqueous solution of the (L') (1 mmole) was add to aqueous solution of platinum sulphate salt which prepared according to reported (8) {by dissolving K_2PtCl_4 (0.415 g, 1 mmole) in 25 ml distillation water then add with stirring KI (0.66 g, 4 mmole), Silver sulphate (2 mmole, 0.626 g) was add to the aqueous solution of K_2PtI_4, mixture was stirred for 6 h with isolated light(18), the product was filtered}. The aqueous solution mixture of the (L') and platinum sulphate salt are stirred for 2 h at (50 °c) .The color precipitate was filtered, washed with ethanol/acetone and dried in desiccator.



The Results and discussion

The complexes varied from yellow to violet, they were crystalline and stable under normal laboratory condition. All complexes were insoluble in common non polar solvent. The physical properties and analytical data of complexes are presented in Table(1).

Table 1: physicochemical and analytical data of the ligand and complexes

Formula	Sympol	Colour	Yield (%)	M.p. ˚C	Elemental analysis		
					C	H	N
$C_{14}H_{12}O_6N_2$	L1	white	82	199	Fou. 55.0 Cal. 55.26	3.6 3.94	9.3 9.21
$C_8H_8O_6N_2$	L2	white	89	145	Fou. 42.3 Cal. 42.1	3.4 3.5	12.1 12.2
$C_{10}H_{12}O_6N_2$	L3	white	74	201	Fou. 46.6 Cal. 46.8	4.6 4.68	10.8 10.9
$C_{10}H_{16}O_6N_2$	L4	white	91	167	Fou. 46.1 Cal. 42.15	6.2 6.15	10.9 10.76
$C_{14}H_{10}O_6N_2Pt$	Comp1	yellow	75	222(d.)	Fou. 33.6 Cal. 33.8	2.2 2.01	5.7 5.63
$C_8H_8O_6N_2Pt$	Comp2	Brown	77	202(d.)	Fou. 22.6 Cal. 22.8	1.43 1.42	6.8 6.6
$C_{10}H_{10}O_6N_2Pt$	Comp3	Brown	69	243(d.)	Fou. 26.8 Cal 26.72	2.1 2.22	6.1 6.23
$C_{10}H_{14}O_6N_2Pt$	Comp4	yellow	82	231(d.)	Fou. 26.3 Cal. 26.49	3.2 3.09	6.3 6.18

IR. Spectra

The important infrared spectral bands for the synthesized ligands and complexes are given in table (2) and shown in figure (1) and (2). The ligands contain four potential donor sites which the oxygen atom of carbonyl oxygen in amide groups and carboxyl oxygen in carboxyl groups due (C-O). .

The bands due to the amide υ(N-H) mode at (3118-3184)cm^{-1} for the free ligands is shifted toward higher frequency while the band of υ(C=O) is shift towards lower frequency in the complexes , this indicating non involvement of the amide nitrogen and involvement of the carboxyl oxygen atom of amide group in coordination with the metal ion(19). , The υ(C=O) and υ(C-O) stretching frequency in the 1600 cm^{-1} and 1433 cm^{-1} region have been assigned to υ(COO^-) asym and υ(COO^-) sym modes respectively in the free ligand , the positive and negative shift in complexes indicate a Δυ enhancement upon complexation and suggest coordinated of carboxylate groups in all the complexes of the ligand in monodentate fashion (20). Here υ implies the difference between $(COO^-)_{asym}$ and υ $(COO^-)_{sym}$.

The υ(O-H) due to the carboxylic groups appearing at 3497 cm^{-1} in the free ligand , disappear in the spectra of their complexes , indicated that both the carboxylic groups are involved in complexation .

The complexes show vibrational modes due to the presence of water , The υ(O-H) due to H_2O is observed in the (3400-3460) cm^{-1} region in the complexes(19-20). The vibration bands due to rocking and wagging modes due to water and (M-O) stretching mode are observed in the (850-400) cm^{-1} region for all the complexes and may be attributed to coordinated water in the complexes.

Table2: IR spectra frequencies for the ligand and its metal complexes in cm^{-1}unit

compound	υ(N-H)	$υ(C=O)_{amide}$	$υ(COO^-)_{asym}$	$υ(COO^-)_{sym}$	$Δυ(COO^-)$	υ (M-O)
L1	3118m	1674_m	COMP1	1456s	119	-
L2	3137m	1647s	1548s	1444s	104	-
L3	3184m	1712s	1537s	1433s	104	-
L4	3165m	1660s	1600s	1452s	108	-
Comp.1	3211s	1695s	1602s	1419s	183	545_w
Comp.2	3182s	1667s	1602m	1382m	220	530_w
Comp.3	3215br	1697s	1602s	1408m	206	547_w
Comp.4	**3251m**	**1710s**	**1639s**	**1452s**	**187**	**555_w**

S= strong, w= weak, m= medium, br= broad

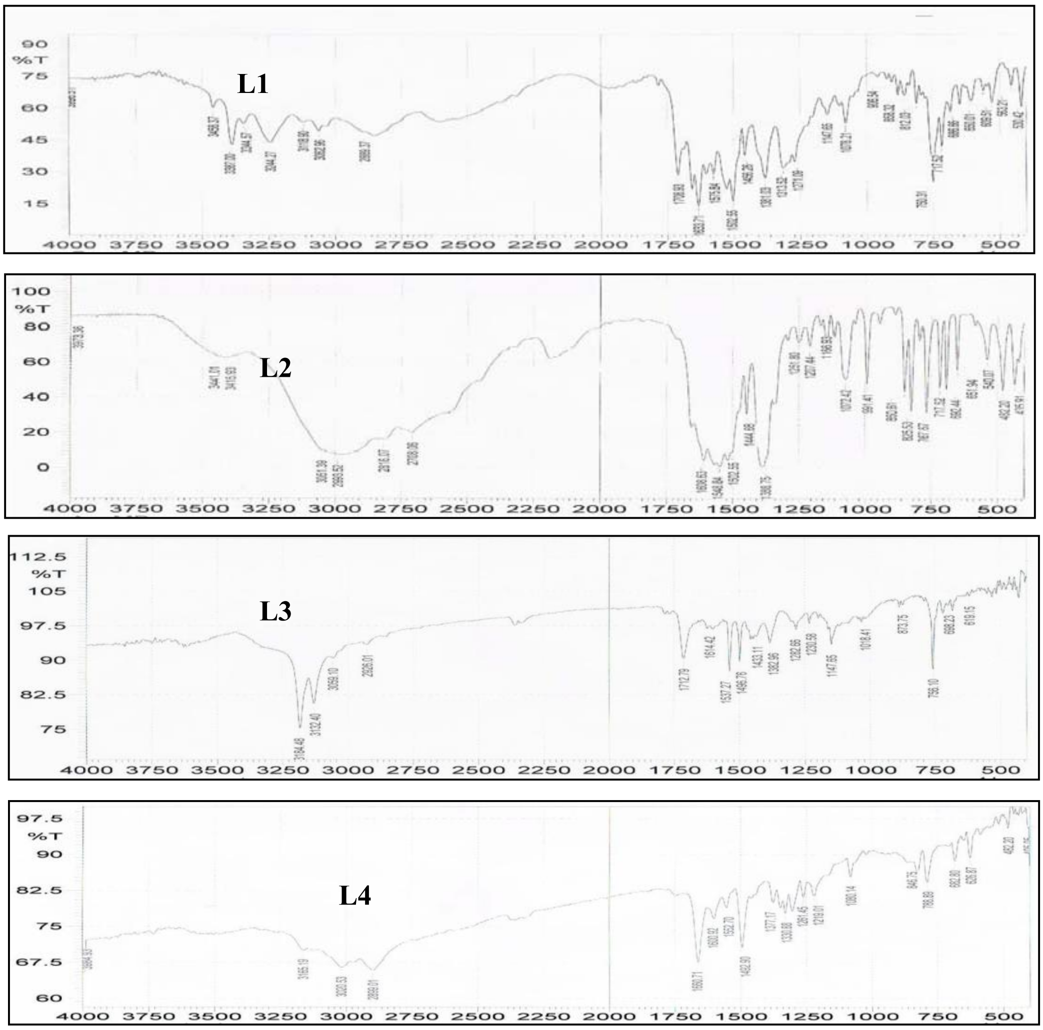


Figure 1: IR spectra of the ligands

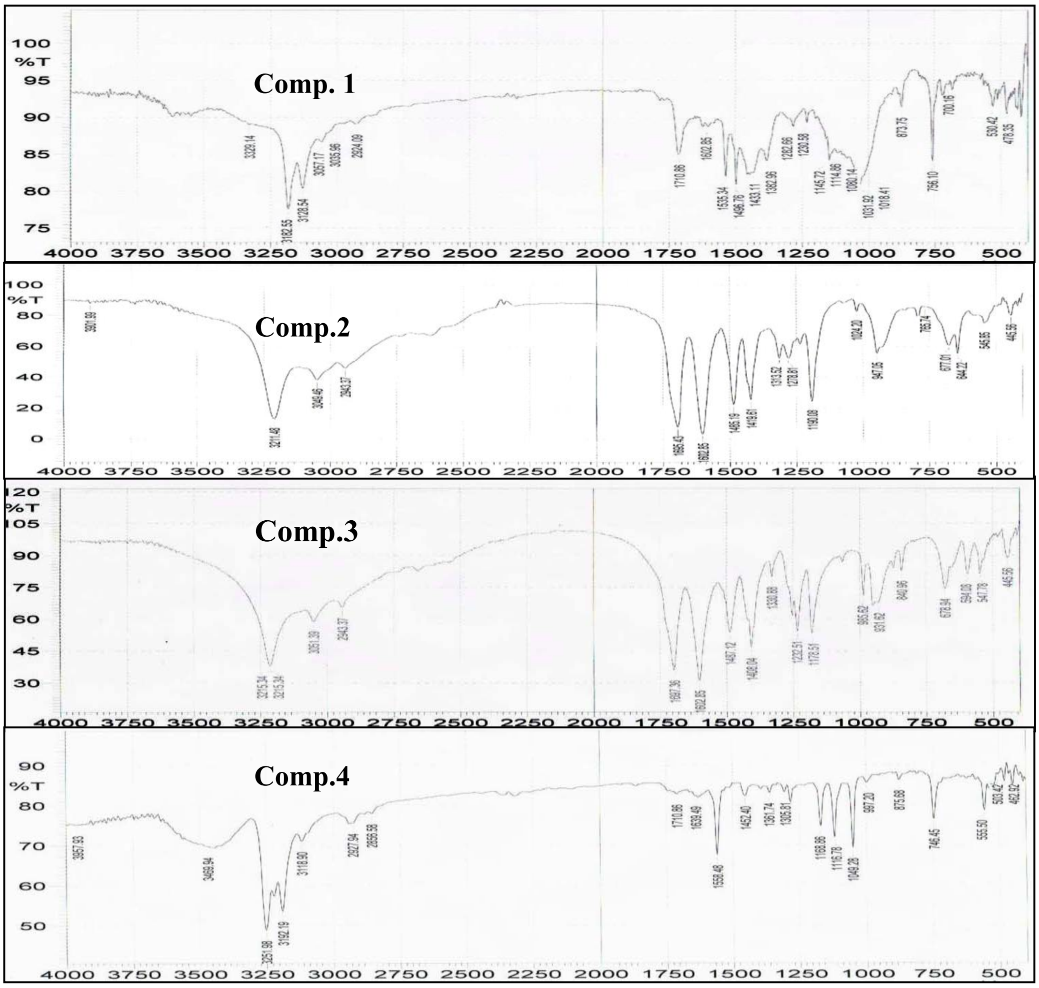


Figure (2): IR spectra for complexes

Electronic spectra

The solution spectral data of all the complexes are presented in the table (3) and shown in figure (3).

The electronic spectra of the complexes are consistent with the d^8 square-planar platinum (II) complex of the ligand is expected to exhibit three spin-allowed d–d bands in their electronic spectra, corresponding to the ${}^1A_1g \rightarrow {}^1A_2g$, ${}^1A_1g \rightarrow {}^1B_1g$ and ${}^1A_1g \longrightarrow {}^1Eg$ transitions respectively (21-24). The electronic spectra of all the complexes showed one to two bands in the (204-287) nm region. The bands in the (204-287) nm region have been assigned to charge transfer transitions.

Table 3: Electronic spectra for the complexes in cm^{-1}unit:

The complex	λ max of Charge transfer nm (cm^{-1})	λ max of d-d transition nm (cm^{-1}) (electronic transfer)
Comp. 1	226 (44247) 237 (42194)	261 (38197) ($^1A_1g \rightarrow {}^1Eg$) 272 (36764) ($^1A_1g \rightarrow {}^1A_2g$) 287 (34843) ($^1A_1g \rightarrow {}^1B_1g$)
Comp.2	210(47619)	267(37453) 314(31847)
Comp.3	204(49019)	237(42194) 271(36900) 294(34013)
Comp.4	207(48309)	307(32573)

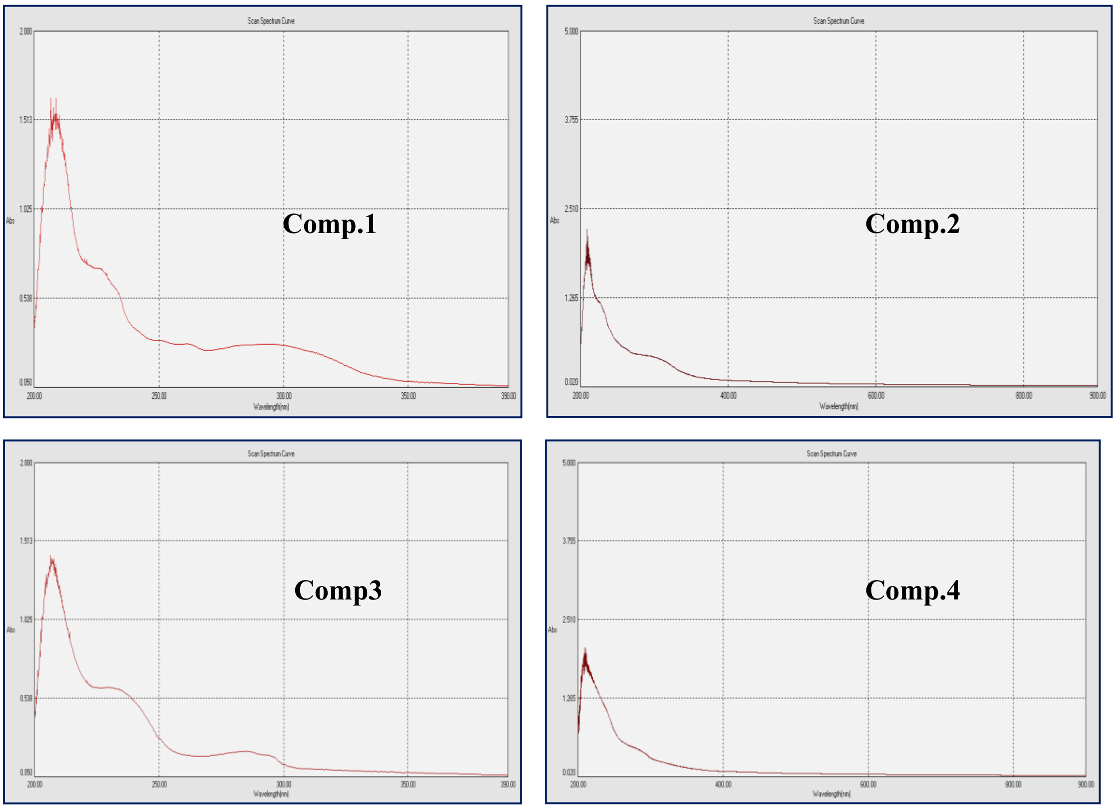


Figure (3): Uv –Vis. spectra of complexes

Conclusion

The ligands N,N-bis (-3- carboxy -1- oxoprop-2-enyl)-1,2-ethylendiamine; N,N-bis (-3- carboxy -1- oxoprop-2-enyl)-1,2-hydrazine; N,N-bis (-3- carboxy -1- oxoprop-2-enyl)-1,2-phenyldiamine and N,N-bis (-3- carboxy -1- oxopropenyl)-1,2-ethylendiamine are coordinated with the Pt(II) metal ion by oxygen atom of carbonyl in amide groups and oxygen atom of carbonyl carboxyl groups. The ligands are tetradentate. The complexes crystalline and stable under normal laboratory condition .The complexes structures are shown in figure (4) .

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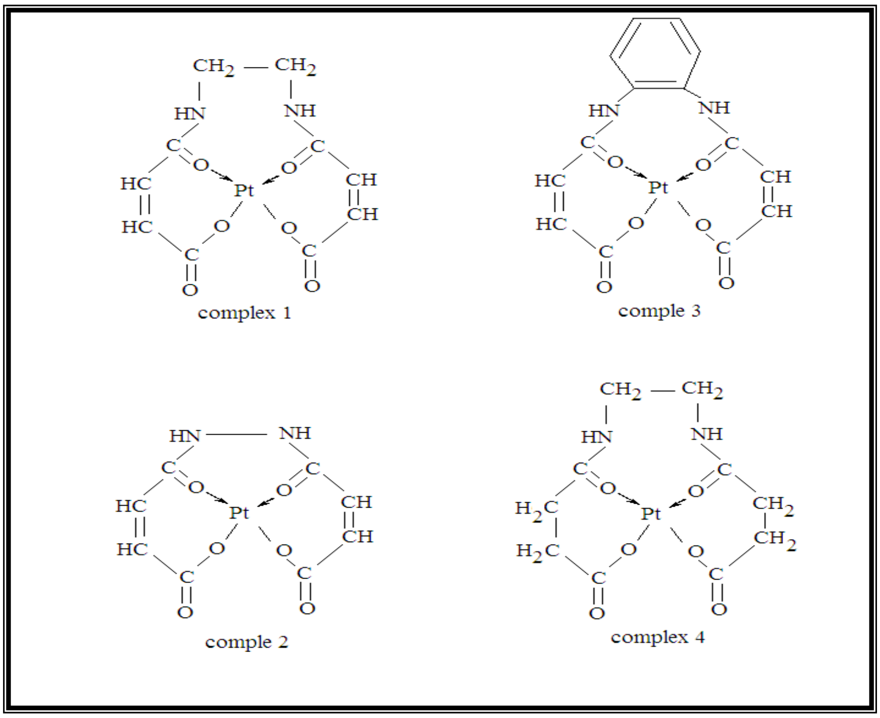

Figure (4): The structure of the prepared complexes

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تحضير ودراسة طيفية لمعقدات الاميد الجديدة للبلاتين الثنائي

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الخلاصـــــة

في هذا البحث تم تحضير ودراسة معقدات البلاتين الثنائي مع
N,N-bis (-3- carboxy -1- oxoprop-2-enyl) -1,2-ethylendiamine; N,N-bis (-3- carboxy -1 oxoprop-2-enyl)-1,2-hydrazine; N,N-bis (-3- carboxy -1- oxoprop-2-enyl)-1,2 phenyldi amine and N,N-bis (-3- carboxy -1- oxopropenyl)-1,2-ethylendiamine.
المعقدات المحضرة تم دراستها بواسطة أطياف الاشعة المرئية والفوق بنفسجية واطياف الاشعة تحت الحمراء والطيف العنصري الدقيق. من أطياف الاشعة تحت الحمراء تم الاستدلال على أن أرتباط الاثلين ثنائي الامين والاورثوفنلين ثنائي الامين والهيدرازين يحصل عبر ذرة النايتروجين لمجموعة الامين مع كاربونيل مجموعة الكاربوكسيل للحامض الثنائي الكاربوكسيل لتكوين مجموعة الاميد لتحضير ليكاندات رباعية السن. الاطياف الالكترونية أثبتت تكون التركيب المربع المستوي لمعقدات البلاتين الثنائي.