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Mixed Ligand Complexes of Platinum (IV) with some Amino acids and Dithiocarbamates or Dithiophosphates

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ABSTRACT

Complexes of the type $[Pt(L\text{-}Met)(L^{-}orL^{=})Cl_2]$ and $[Pt(Met)(L^{-}orL^{=})Cl]Cl$ were prepared, [L= deprotonated amino acids: Glycine(Gly), Alanine(Ala), Valine(Val) or Methionine(Met); L^{-} = N-Methylcyclohexyldithiocarbamate (N-MeCHdtc) or Benzyldithiocarbamate (Bzdtc) anions and $L^{=}$ =O,O -Dipropyldithiophosphate (DiPrdtp) or O,O - Dibenzyldithiophosphate (DiBzdtp) anions. The prepared complexes were characterized by IR , UV-Vis spectra, magnetic susceptibility and molar conductivity. Some complexes were characterized by CHNS analysis and (^{1}H-nmr) spectra. All the Pt(IV) complexes showed octahedral structure with the dithiocarbamates or dithiophosphates acting as uninegative bidentate ligands coordinated through the two sulfur atoms and the amino acid anions coordinate through N and O except for the methionine which coordinate through S,N and O atoms.

Keywords: Platinum(IV), amino acids, Dithiocarbamates.

معقدات ليكاندات مختلطة للبلاتين (IV) مع عدد من الأحماض الامينية والثنائي ثايوكارباميت او الثنائي ثايوفوسفيت

الملخص

يتضمن البحث تحضير معقدات مختلطة للبلاتين (IV) ذات الصيغة $[Pt(L\text{-}Met)(L^{-}orL^{=})Cl_2]$ $[Pt(Met)(L^{-})Cl]Cl$ حيث (L= الاحماض الامينية منزوعة البروتون كلايسين و الالنين وفالين و مثيونين و L^{-}= N−مثيل سايكلوهكسيل ثنائي ثايوكارباميت و بنزيل ثنائي ثايوكارباميت و $L^{=}$=O,O− ثنائي بروبيل ثنائي ثايوفوسفيت او O,O − ثنائي بنزيل ثنائي ثايوفوسفيت). شخصت المعقدات المحضرة باستخدام التوصيلية الكهربائية و اطياف الاشعة تحت الحمراء والاطياف الالكترونية والقياسات المغناطيسية اضافة الى التحليل الدقيق للعناصر وبروتون الرنين النووي المغناطيسي لعدد من هذه المعقدات. اثبتت الدراسة ان معقدات البلاتين (IV) تمتلك اشكال ثماني السطوح إذ تسلك الايونات السالبة للأحماض الامينية بشكل ليكاندات ثنائية السن (باستثناء المثيونين المتناسقة بشكل ثلاثية السن) وكذلك ليكاندات الثنائي ثايوكارباميت او الثنائي ثايوفوسفيت تسلك بشكل ليكندات ثنائية السن احادية الشحنة السالبة.

INTRODUCTION

Octahedral platinum (IV) complexes have attracted increasing interest in antitumor chemotherapy, which comes in efforts to decrease toxic side effects caused by platinum (II) complexes. (Vtku *et al.*, 2008; Farrell, 2000 ; Iakovidis and Hadjiliadis, 1994).

Mixed ligand complexes plays a recognized role in biological process and their stabilities are important in biological systems as many metabolic functions are dependent upon this stability(Reddy *et al.*, 2000; Rajaseker *et al.*, 2012). Amino acids, dithiocarbamates and dithiophosphates are all important from both the biological and industrial aspects (Mariana, 2012; Freeman,1973; Manav *et al*., 2006 ; Hogrth, 2012).

Complexes of amino acids, dithiocarbamates or dithiophosphates alone are well known to possess biological activities. Ternary complexes of platinum(IV) with amino acids and dithiocarbamates or dithiophosphates are not known. It is thought that the combination of both amino acids with the dithiocarbamates or dithiophosphates in mixed ligand complexes with the biologically important platinum (IV) metal ion might enhance these activities. The present work deals with the preparation and characterization of such complexes.

EXPERIMENTAL

Materials and methods

Sodium salt of the dithiocarbamates (N-methylcyclohexyl) and (benzyl) or dithiophosphates (O,O -Dipropyl) and (O,O -Dibenzyl) were prepared as cited in the literature (Vogel, 1968 ; Jian *et al*., 2000) potassium hexa chloro palatinate, glycine, alanine, valine, methionine, N-methylcyclohexyl amine, benzylamine, carbon disulfide, propyl alcohol, benzyl alcohol, phosphorus pentasulfide and sodium hydroxide were either Aldrich, or Fluka products. Organic solvents (dimethylformamide and diethylether) were reagent grade chemicals and were used without further purification.

Preparation of the platinum complexes:

Preparation of $[Pt(N\text{-}MeCHdtc)(Gly)Cl_2]$.

A solution of potassium hexachloropalatinate (IV) (0.243 g, 0.0005 mol) in hot water (10cm^3) was added with stirring to hot solution containing mixture of NaN-MeCHdtc (0.105 g, 0.0005 mol) in (10cm^3) of water and aqueous solution of sodium glycinate [prepared by dissolving (0.038 g, 0.0005 mol) glycine in (5cm^3) water followed by adding aqueous solution of sodium hydroxide to pH~7.5]. The resulting precipitate was allowed to cool, filtered and washed several times with water and dried in air.

The following complexes:

$[Pt(N\text{-}MeCHdtc)(Ala)Cl_2]$,$[Pt(N\text{-}MeCHdtc)(Val)Cl_2]$,$[Pt(N\text{-}MeCHdtc)(Met)Cl]Cl$,$[Pt(Bzdtc)(Gly)Cl_2]$,$[Pt(Bzdtc)(Ala)Cl_2]$,$[Pt(Bzdtc)(Val)Cl_2]$,$[Pt(Bzdtc)(Met)Cl]Cl$,$[Pt(DiPrdtp)(Gly)Cl_2]$,$[Pt(DiPrdtp)(Ala)Cl_2]$,$[Pt(DiPrdtp)(Val)Cl_2]$, $[Pt(DiPrdtp)(Met)Cl]Cl$,$[Pt(DiBzdtp)(Gly)Cl_2]$,$[Pt(DiBzdtp)(Ala)Cl_2]$,$[Pt(DiBzdtp)(Val)Cl_2]$,$[Pt(DiBzdtp)(Met)Cl]Cl$ were prepare following the same method using (0.0005 mol) of each component of the reactant and (0.045 g) of alanine, (0.117 g) of valine, (0.149 g) of methionine, (0.102 g) of NaBzdtc, (0.118 g) of NaDiPrdtp and (0.116 g) of Na DiBzdtp.

Physical Measurements

Elemental analysis of carbon, hydrogen, nitrogen, and sulfur for some of the complexes were done using Euro Vactor Model EA 3000 A (Italy) at (Al al bait University, Jordan), IR spectra were recorded on FT.IR spectrophotometer, Tensor 27 Co. Brucker 2003 at the range (400-4000cm^{-1}) using KBr discs. Electronic spectra were recorded on a UV-Vis. spectrophotometer (Shimadzu, UV-1650PC-Spectrophotometer using DMF as solvent at room temperature for the dithiocarbamate complexes (no.1-8) and at ~40 ^{0}C for the dithiophosphate complexes (no. 9-16) with partial dissolution. Magnetic susceptibility of the complexes have been measured by Bruker BM6. using Faraday method, conductivity measurements for the dithiocarbamate complexes (no.1-8) have been carried out using DMF as solvent (10^{-3}M) at room temperature with conductivity meter model PCM3 Jenway and conductivity of the dithiophosphate complexes(no. 9-16) were measured in the solid state using 3 prope cell. Proton nuclear magnetic resonance (^{1}H-nmr) for some of the dithiocarbamate complexes were measured using DMSO –d$_6$ as solvent at (25^{o}C) with BRUKER 300 MHZ (Al al bait University, Jordan), melting points were done using Electriothermal 9300 Engineering LTD.

RESULT AND DISCUSSION

The reaction of potassium hexachloropalatinate(IV) with sodium salt of amino acid and sodium salt of dithiocarbamate or dithiophosphate ligands in1:1:1 molar ratio may be represented by the following equations:

K_2PtCl_6+Na(L-Met)+Na(L^-or$L^=$) $\longrightarrow$ [Pt(L-Met)(L^-or$L^=$)Cl_2] + 2KCl + 2NaCl
K_2PtCl_6 + Na(Met) + Na(L^-or$L^=$) $\longrightarrow$ [Pt(Met)(L^-or$L^=$)Cl]Cl + 2KCl + 2NaCl

Elemental analyses (Table 1) for the prepared dithiocarbamate complexes and two of the dithiophosphate complexes revealed that the complexes have the proposed compositions. The molar conductivity of the dithiocarbamate complexes (no.1-8) were determined in (10^{-3}M) dimethylformamide solution and the values given in (Table 2) are those expected for non electrolyte (Geary, 1971) with the exception of the methionine complexes (no.4 and 8) which are 1:1 electrolyte. The insolubility of the dithiophosphate complexes (no. 9-16) in many polar and none polar solvents such as THF, DMF, diochloromethane, ethanol, DMSO, methyl cyanide ,mixture of DMF +DMSO, chloroform and benzene and their partial solubility in warm DMF (~40^0C) makes the usual measurement in solution at 25^0C with (10^{-3}M) not possible. Accordingly the conductivity of the dithiophosphates were measured in the solid state and the result indicate similar behavior to their dithiocarbamate counter part i.e , non electrolyte with the exception of methionine complex (no.12 and 16) which are 1: 1 electrolyte (Mitsubayashi *et al*., 1988).

The magnetic moments of the complexes calculated from the corrected magnetic susceptibilities determined at room temperature revealed the expected diamagnetic nature of the Pt (IV) complexes with octahedral geometries.

The electronic spectra for the prepared complexes are listed in (Table 3).The spectra exhibited four absorption bands appeared at the range 20669-21528 cm^{-1}, 22624 – 24606 cm^{-1}, 25380 - 26954 cm^{-1} and 27677-29940 cm^{-1} with the assignment $^1A_1g \longrightarrow {}^3T_1g$,$^1A_1g \longrightarrow {}^3T_2g$, $^1A_1g \longrightarrow {}^1T_1g$ and $^1A_1g \longrightarrow {}^1T_2g$ transitions, respectively. These are the d-d transitions of the first excited state [$t_2g(xy,xz,yz)^5$][$eg(z^2,x^2-y^2)^1$]. Other transition such as[$t_2g(xy,xz,yz,)^4$][$eg(z^2,x^2-y^2)^2$] or higher states, that are theoretically possible need very high energy in addition to being very weak .the observed bands support the expected low spin d^6 of platinum (IV) octahedral complexes (Swihart and Mason, 1970). Other bands at higher than 30000 cm^{-1} were considered as charge transfer and ligand transition bands.

The significant IR spectral data of the ligands and their complexes with the corresponding assignment are listed in (Table 4). The ν(C-S) band in the IR spectra of the two dithiocarbamates appeared at 990 and 957 cm^{-1} . The positions of the two bands were shifted to lower frequencies upon complex formation and appeared in the IR spectra of the complexes at (966-979 cm^{-1}) and (938-949cm^{-1}) respectively. The blue shift together with the appearance of a single band indicate the coordination of the dithiocarbamate as bidentate ligands (Manav *et al*., 2006). The other supported evidence are the shift in ν(C-N) (thioureide) values to higher wave numbers on complexes formation from 1454 and 1469cm^{-1} to 1479-1489cm^{-1} and 1488-1500cm^{-1} respectively (Geetha and Thirumaran, 2008). The two dithiophosphate ligands exhibit ν_s(P-S) and ν_{as}(P-S) bands in the IR spectra of the ligands at (538, 563cm^{-1}) and (617, 619cm^{-1}) respectively. On complex formation the ν_s(P-S) bands shifted two lower frequencies (519-555cm^{-1}) and the ν_{as}(P-S) bands shifted to higher frequencies (628-637cm^{-1}) indicating the coordination of the dithiophosphate as bidentate ligand(Bolundut *et al*., 2010). The other supported evidence are the appearance of ν(P-O) bands at 985 and 993cm^{-1} in the IR spectra of the dithiophosphate ligands which were shifted to lower frequencies on complex formation (958-977 cm^{-1}). The ν(C-SMe) in the IR spectra of the methionine observed at (1316 cm^{-1}) were shifted to higher frequencies (1331-1334cm^{-1}) in the platinum complexes containing methionine ligand, suggesting that sulfur atom of the methionine is involved in bonding (Caubet *et al*., 1992). The N-H vibration observed at (2956-3164 cm^{-1}) in the

IR spectra of the free amino acids were shifted to higher wave numbers (2990-3236 cm^{-1}) in the complexes suggesting coordination of the amino group (Nakamoto, 1978). The values of ν_{as}(COO) and ν_{s}(COO) for the amino acids are given in (Table 4). The corresponding values for the prepared complexes indicate that the ν_{s}(COO) were shifted to lower wave numbers while the ν_{as}(COO) frequencies were shifted to higher wave numbers. The values of $\Delta[\nu_{as}$(COO)- ν_{s}(COO)] for the prepared complexes (Table 4) are (230-274cm^{-1}) indicate the involvement of the carboxylate anion in bonding to the platinum(IV) ion as monodentate ligand (Reddy and Reddy, 2000). The IR spectra of the complexes showed the appearance of non ligand bands observed at (543-575 cm^{-1}) and (467-495 cm^{-1}), and were assigned to ν(M-O) and ν(M-N) respectively. Proton nuclear magnetic resonance (^{1}H-nmr) were recorded for five of the platinum(IV) complexes using DMSO-d_6 as a solvents. The chemical shift signals and assignments (Table 5) confirm the formation of the prepared complexes. (Manav *et al*., 2006).

CONCLUSION

Mixed ligand complexes of platinum(IV) with four amino acids (Gly, Ala, Val and Met) and two dithiocarbamates (N-MeCHdtc and Bzdtc) or two dithiophosphates (DiPrdtp or DiBzdtp) were successfully prepared by simple mixing of aqueous solution of the three components. The results were diamagnetic octahedral complexes of platinum(IV) with the dithiocarbamates and dithiophosphates behaved as bidentate ligands coordinated through the two sulfur atoms. The amino acid anions coordinated through the nitrogen atom of the amino group and the oxygen atom of the carboxylate group in addition to the coordination of sulfur atom in the case of methionine. The dithiophosphate complexes are insoluble in common polar and nonpolar solvents. This fact inforce some limitation such as conductivity measurements in solution and ^{1}H-nmr measurements, yet it was possible to deduce the proposed structure in a similar way to the dithiocarbamate complexes.

Complex	**Complex formula**	**Colour**	**m.p.(°C**	**Yield**	**Chemical formula**	**Elemental analysis, found/(calc)**

Table 1: Some physical properties and elemental analysis of the complexes

No.			)	(%)		C%	H%	N%	S%
1	[Pt (N-MeCHdtc) (Gly) Cl_2]	Light -brown	196*	77	$C_{10}H_{18}N_2S_2O_2PtCl_2$	21.98 (22.73)	3.98 (3.43)	5.74 (5.30)	12.73 (12.13)
2	[Pt (N-MeCHdtc) (Ala) Cl_2]	Brown	208*	79	$C_{11}H_{20}N_2S_2O_2 PtCl_2$	24.92 (24.35)	2.94 (3.71)	4.92 (5.16)	11.00 (11.82)
3	[Pt (N-MeCHdtc) (Val) Cl_2]	Brown	202*	71	$C_{13}H_{24}N_2S_2O_2 PtCl_2$	26.82 (27.37)	5.77 (4.24)	4.37 (4.91)	11.81 (11.24)
4	[Pt (N-MeCHdtc) (Met)Cl]Cl	Yellowish-brown	200*	88	$C_{13}H_{24}N_2S_3O_2 PtCl_2$	25.21 (25.91)	4.61 (4.01)	4.91 (4.64)	16.32 (15.96)
5	[Pt (Bzdtc)(Gly) Cl_2]	Deep-brown	156*	74	$C_{10}H_{12}N_2S_2O_2 PtCl_2$	21.73 (22.99)	2.72 (2.31)	4.86 (5.36)	13.02 (12.27)
6	[Pt (Bzdtc)(Ala) Cl_2]	Mustard	160*	68	$C_{11}H_{14}N_2S_2O_2 PtCl_2$	23.92 (24.63)	3.37 (2.63)	5.01 (5.22)	12.45 (11.95)
7	[Pt (Bzdtc)(Val) Cl_2]	Yellowish brown	167*	76	$C_{13}H_{18}N_2S_2O_2 PtCl_2$	26.81 (27.66)	3.73 (3.21)	4.23 (4.96)	11.01 (11.36)
8	[Pt (Bzdtc)(Met) Cl]Cl	Yellow	174*	78	$C_{13}H_{18}N_2S_3O_2 PtCl_2$	25.42 (26.17)	3.65 (3.04)	3.82 (4.69)	16.92 (16.12)
9	[Pt (DiPrdtp) (Gly) Cl_2]	Yellow	288*	73	$C_8H_{18}NS_2O_4P PtCl_2$	--------	-------	-------	-------
10	[Pt (DiPrdtp) (Ala) Cl_2]	Light-yellow	267*	69	$C_9H_{20}NS_2O_4P PtCl_2$	-------	-------	-------	-------
11	[Pt (DiPrdtp) (Val) Cl_2]	Light-yellow	272*	78	$C_{11}H_{24}NS_2O_4PPtCl_2$	-------	-------	-------	-------
12	[Pt(DiPrdtp)(Met) Cl]Cl	Light-yellow	256*	87	$C_{11}H_{24}NS_3O_4PPtCl_2$	21.09 (21.05)	4.44 (3.85)	2.54 (2.23)	16.89 (15.32)
13	[Pt (DiBzdtp) (Gly) Cl_2]	Brown	282*	73	$C_{16}H_{18}NS_2O_4PPtCl_2$	-------	-------	-------	-------
14	[Pt (DiBzdtp) (Ala) Cl_2]	Light-yellow	240*	76	$C_{17}H_{20}NS_2O_4PPtCl_2$	-------	-------	-------	-------
15	[Pt (DiBzdtp) (Val) Cl_2]	Light-yellow	258*	71	$C_{19}H_{24}NS_2O_4PPtCl_2$	-------	-------	-------	-------
16	[Pt (DiBzdtp) (Met) Cl]Cl	Light-yellow	270*	86	$C_{19}H_{24}NS_3O_4PPtCl_2$	29.71 (31.54)	2.62 (3.34)	2.09 (1.93)	13.09 (13.29)

*decomposition

Complex no.	μeff (B.M.)	Molar Conductance ($cm^2 ohm^{-1} mol^{-1}$)	Complex no.	μeff (B.M)	Conductance ($ohm^{-1} cm^{-1}$)
1	Dia	13.4	9	Dia	3.46 $x10^{-13}$
2	Dia	7.9	10	Dia	7.32 $x10^{-14}$
3	Dia	6.7	11	Dia	3.59 $x10^{-13}$
4	Dia	79.5	12	dia	4.23 $x10^{-7}$
5	Dia	3.5	13	dia	2.01 $x10^{-14}$
6	Dia	7.7	14	dia	3.51 $x10^{-13}$
7	Dia	4.5	15	dia	6.89 $x10^{-14}$
8	Dia	47.43	16	dia	2.12 $x10^{-7}$

Table 2: Magnetic properties (μeff (B.M)) and Molar Conductance of the platinum(IV) complexes

Table 3: Electronic transition of the platinum(IV) complexes (cm^{-1})

Complex no.	$^{1}A_{1}g \longrightarrow {}^{3}T_{1}g$	$^{1}A_{1}g \longrightarrow {}^{3}T_{2}g$	$^{1}A_{1}g \longrightarrow {}^{1}T_{1}g$	$^{1}A_{1}g \longrightarrow {}^{1}T_{2}g$	**C.T**
1	21498	22869	26041	29940	32679
2	20909	23850	25641	29761	49504
3	21378	23310	25641	27677	33112
4	21807	22876	26954	28571	32894
5	20946	23041	26178	28409	32258
6	21528	23474	25679	29850	31645
7	20669	22624	----	29069	31545
8	----	24038	25380	27777	34013
9	20887	22897	25499	----	34563
10	20765	23487	----	28675	36759
11	21487	24606	26178	29440	37654
12	20763	----	25659	28705	35971
13	20698	23647	26765	29510	43678
14	----	22717	26452	28710	34232
15	20784	22943	----	29450	31055
16	----	32675	25499	28665	32894

Table 4: Selected IR bands of the ligands and complexes(cm^{-1})

compound	**ν(NH$_2$)**	**ν(COO$^-$)**		**Δ ν(COO)**	**ν(C–N)**	**ν(C–S)**	**ν(C-SMe)**	**ν(P–S)**		**ν(P–O)**	**ν(M–O)**	**ν(M–N)**
		ν$_{as}$ (COO$^-$)	**ν$_s$(COO)**					**ν$_{as}$(P–S)**	**ν$_s$(P–S)**			
NaN-Me CHdtc	----	----	----	----	1469	990	----	----	----	----	----	----
NaBzdtc	----	----	----	----	1454	957	----	----	----	----	----	----
NaDiPrdtp	----	----	----	----	----		----	619	538	993	----	----
NadiBzdtp	----	----	----	----	----		----	617	563	985	----	----
Gly	3164	1615	1457	----	----		----	----	----	----	----	----
L-Ala	3082	1597	1413	----	----		----	----	----	----	----	----
L-Val	3080	1590	1410	----	----		----	----	----	----	----	----
L-Met	2956	1616	1408	----	----		1316	----	----	----	----	----
1	3238	1634	1396	238	1496	978	----	----	----	----	547	490
2	3100	1628	1373	251	1500	970	----	----	----	----	543	478
3	3095	1635	1377	258	1498	966	----	----	----	----	570	483
4	2998	1638	1396	242	1488	979	1331	----	----	----	554	492
5	3225	1628	1398	230	1479	948	----	----	----	----	550	488
6	3130	1637	1394	243	1480	938	----	----	----	----	554	468
7	3090	1629	1373	256	1489	949	----	----	----	----	540	488
8	3120	1638	1388	250	1484	945	1334	----	----	----	549	484
9	3225	1625	1392	233	----	----	----	634	522	970	552	492
10	3099	1635	1384	251	----	----	----	637	519	968	563	484
11	3098	1645	1388	257	----	----	----	629	530	977	575	488
12	3112	1640	1392	248	----	----	1332	637	526	973	569	490
13	3235	1630	1399	231	----	----	----	632	548	958	565	487
14	3111	1638	1388	250	----	----	----	628	552	968	575	495
15	3095	1642	1375	267	----	----	----	630	555	972	578	467
16	2990	1639	1379	260	----	----	1331	635	549	975	567	478

Table 5: ^{1}H-NMR spectral data for some of the Pt(IV) complexes

Cmplex no.	**NMR**
1	^{1}H-nmr (DMSO-d$_6$): δ 4.03(2H,br,NH(Gly)), δ 2.54(2H, S, CH$_2$(Gly)), δ 2.27-1.68(10H,m, Chexy and Me), δ 1.23-1.17(4H,m,Chexy)ppm
2	1H-nmr (DMSO-d$_6$): δ 4.03(2H,br,NH(Ala)), δ3.12 (3H, S, Me-Ala), δ 2.72(3H,S,Me.dtc) 1.79-1.64 (8H,d,Chexy) + 1H CH-Ala), δ 1.34-1.12(4H,m,Chexy)ppm
3	^{1}H-nmr(DMSOd$_6$):δ4.03(2H,br,NHVal.),δ3.18(3H,S,Medtc),δ2.73(1H,S,CHVal), , δ1.79-1.64(12H,m,5Chexy+7Val),1.33-1.11)(6H,m,C-H Chexy)ppm
5	^{1}H-nmr (DMSO-d$_6$): δ 7.39-7.30(5H,m,C-H Bzdtc), δ4.84 (1H,S,Bzdtc), δ4.65,(2H, NHGly),4.22 (2H,S,CH Gly) δ2.73 (2H,S ,N-CH$_2$Bzdtc)ppm
6	^{1}H-nmr(DMSO-d$_6$):δ8.14-7.32(5H,m,C$_6$H$_5$ inBzdtc),δ4.94-4.85(3H,br,NH-NH$_2$-Ala+NH Bzdtc), δ 4.66 (1H,S ,CH-Ala), δ2.31(2H,S ,CH-N-CH$_2$in Bzdtc), δ1.25 (3H,S,Me-Ala)ppm.

The following Figs. (1-4) give possible structure representation for the prepared complexes.

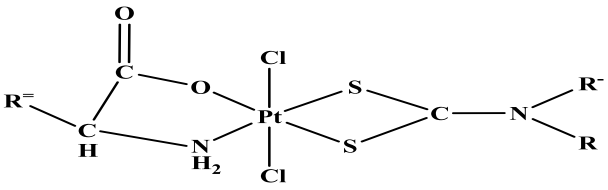

Fig. 1: Proposed structure for the complexes$[Pt(L\text{-}Met)(L^{-})Cl_2]$
$R^{=}$ = H(Gly), CH_3(Ala), $CH(CH_3)_2$(Val)
(R =H when R^{-} =benzyl, R =CH_3 when R^{-} =cyclohexyl)
Complexes 1-3,5-7

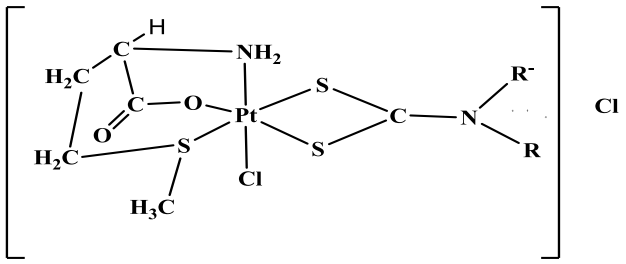

Fig. 2: Proposed structure for the complexes$[Pt(Met)(L^{-})Cl]Cl$
R,R^{-}, as defined in Fig. (1) Complex 4,8

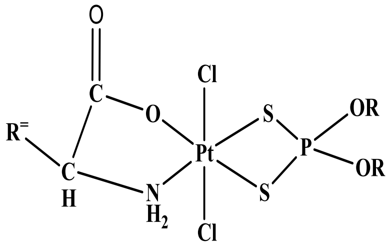

Fig. 3: Proposed structure for the complexes$[Pt(L\text{-}Met)(L^{=})Cl_2]$
R=propyl or benzyl
$R^{=}$=as defined in Fig. (1)
Complex 9-11,13-15

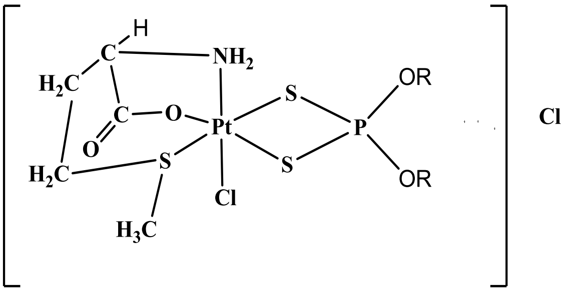

Fig. 4: Proposed structure for the complexes$[Pt(Met)(L^{=})Cl]Cl$
R=propyl or benzyl
Complex 12, 16

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