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

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ABSTRACT

Complexes of the type \([\text{Pt}(L\text{-Met})(L\text{orL})\text{Cl}]_2\) and \([\text{Pt}(\text{Met})(L\text{orL})\text{Cl}]\)Cl were prepared, \([L=\text{deprotonated amino acids: Glycine(Gly), Alanine(Ala), Valine(Val) or Methionine(Met);} L^- = \text{N-Methylcyclohexylthiocarbamate (N-MeCHdtc) or Benzylthiocarbamate (Bzdtc) anions and } L^- = O,O\text{-Dipropylthiophosphate (DiPrdtp) or O,O\text{-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 \((^1\text{H-nmr)}\) 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.

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معقدات ليكاندات مختلطة للبلاتين (IV) مع عدد من الأملاح الأمينية والثنائي ثايوكارباميت أو الثنائي ثايوفوسفيت

المعهد

يتضمن البحث تحضير معدات مختلطة للبلاتين (IV) ذات الصيغة [Pt(L-Met)(L’orL)Cl]2 حيث \([L=\text{الاملاح الأمينية منزوعة البروتون كلايسين و الالنين و فالينين و ميثيونين و} N\text{-ميثيل ايسوكسيكلوسيل ثنائي ثايوكارباميت و بنزيل ثنائي ثايوكارباميت و بنزيل ثنائي ثايوفوسفيت و藜}O,O\text{-دوبروبيل ثنائي ثايوفوسفيت و藜}O,O\text{-ثنائي بنزيل ثنائي ثايوفوسفيت). تم استخدام التوصيلية الكهروكيميائية واطيفات الإشعة تحت الحمراء الاتركترونيات لتحليل التحليل الدقيق للعناصر. تم تحليل التركيزات الإلكترونية في عينات وزيت النيتروجين النيوتروني المغناطيسي لعدد من هذه المعدات.

البحث والدراسة ان معدات البلاتين (IV) تمتلك اشكال سطحية ثلاثية الأبعاد للأحماض الأمينية بشكل ليكاندات ثنائية السطح (استنادًا إلى مثيونين المتكونات بشكل ثلاثية السطح) وكذلك ليكادات الثنائي ثايوكارباميت أو الثنائي ثايوفوسفيت تشكل بشكل ليكاندات ثلاثية السطح احادية الشحن السالبة.

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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 play 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-MeCHdte)(Gly)Cl₂].

A solution of potassium hexachloroplatinate (IV) (0.243 g, 0.0005 mol) in hot water (10cm³) was added with stirring to hot solution containing mixture of NaN-MeCHdte (0.105 g, 0.0005 mol) in (10cm³) of water and aqueous solution of sodium glycinate [prepared by dissolving (0.038 g, 0.0005 mol) glycine in (5cm³) 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-MeCHdte)(Ala)Cl₂], [Pt(N-MeCHdte)(Val)Cl₂], [Pt(N-MeCHdte)(Met)Cl₂], [Pt(Bzdtc)(Gly)Cl₂], [Pt(Bzdtc)(Ala)Cl₂], [Pt(Bzdtc)(Val)Cl₂], [Pt(Bzdtc)(Met)Cl₂], [Pt(DiPrdtc)(Gly)Cl₂], [Pt(DiPrdtc)(Ala)Cl₂], [Pt(DiPrdtc)(Val)Cl₂], [Pt(DiPrdtc)(Met)Cl₂], [Pt(DiBzdtp)(Gly)Cl₂], [Pt(DiBzdtp)(Ala)Cl₂], [Pt(DiBzdtp)(Val)Cl₂], [Pt(DiBzdtp)(Met)Cl₂] 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 NaDiPrdtc 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 Vector 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 (400-4000 cm⁻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 °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 (10⁻³M) 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 (¹H-nmr) for some of the dithiocarbamate complexes were measured using DMSO –d₆ as solvent at (25°C) with BRUKER 300 MHZ (Al al bait University, Jordan), melting points were done using Electrothermal 9300 Engineering LTD.
RESULT AND DISCUSSION

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

\[
\text{K}_2\text{PtCl}_6 + \text{Na}(\text{L-Met}) + \text{Na}(\text{L}^2\text{orL})^2 \rightarrow [\text{Pt}(\text{L-Met})(\text{L}^2\text{orL})\text{Cl}_2] + 2\text{KCl} + 2\text{NaCl}
\]

\[
\text{K}_2\text{PtCl}_6 + \text{Na}(\text{Met}) + \text{Na}(\text{L}^2\text{orL})^2 \rightarrow [\text{Pt}(\text{Met})(\text{L}^2\text{orL})\text{Cl}] + 2\text{KCl} + 2\text{NaCl}
\]

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^-3M) 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, dichloromethane, ethanol, DMSO, methyl cyanide ,mixture of DMF +DMSO, chloroform and benzene and their partial solubility in warm DMF (~40°C) makes the usual measurement in solution at 25°C with (10^-3M) 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 \(1\text{A}_1\text{g} \rightarrow 3\text{T}_1\text{g} \), \(1\text{A}_1\text{g} \rightarrow 1\text{T}_2\text{g} \), \(1\text{A}_1\text{g} \rightarrow 1\text{T}_1\text{g} \), and \(1\text{A}_1\text{g} \rightarrow 1\text{T}_2\text{g} \) transitions, respectively. These are the d-d transitions of the first excited state \(\text{t}_2\text{g}(\text{xy},\text{xz},\text{yz})^3 \text{[eg}(z^2,-x^2-y^2)^3)\) Other transition such as\(\text{t}_2\text{g}(\text{xy},\text{xz},\text{yz})^4\text{[eg}(z^2,-x^2-y^2)^3)\) 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 (938-949 cm\(^{-1}\)) 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 νs(P-S) and νas(P-S) bands in the IR spectra of the ligands at (538, 563cm\(^{-1}\)) and (617, 619cm\(^{-1}\)) respectively. On complex formation the νs(P-S) bands shifted two lower frequencies (519-555cm\(^{-1}\)) and the νas(P-S) bands shifted to higher frequencies (628-637cm\(^{-1}\)) indicating the coordination of the dithiophosphatate 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 \(\nu_{\text{as}}(\text{COO})\) and \(\nu_{\text{s}}(\text{COO})\) for the amino acids are given in (Table 4). The corresponding values for the prepared complexes indicate that the \(\nu_{\text{s}}(\text{COO})\) were shifted to lower wave numbers while the \(\nu_{\text{as}}(\text{COO})\) frequencies were shifted to higher wave numbers. The values of \(\Delta[\nu_{\text{as}}(\text{COO})-\nu_{\text{s}}(\text{COO})]\) for the prepared complexes (Table 4) are (230-274 cm\(^{-1}\)) 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 \(\nu(\text{M-O})\) and \(\nu(\text{M-N})\) 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 enforce 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.(\(^\circ\)C) | Yield | Chemical formula | Elemental analysis, found/(calc) |
|---------|----------------|--------|----------------|-------|-----------------|-----------------------------|

Table 1: Some physical properties and elemental analysis of the complexes
### Table 3: Electronical transition of the platinum(IV) complexes (cm⁻¹)

| No. | Complex | λmax (nm) | Conductance (ohm⁻¹ cm⁻¹) | μeff (B.M.) | Molar Conductance |
|-----|---------|------------|---------------------------|-------------|-------------------|
| 1   | [Pt (N-MeCHdtc) (Gly) Cl₂] | Light-brown | 298* | 77 | C₃H₁₂N₂S₂O₂PtCl₂ | 21.98 (22.73) | 3.98 (3.43) | 5.74 (5.30) | 12.73 (12.13) |
| 2   | [Pt (N-MeCHdtc) (Ala) Cl₂] | Brown | 208* | 79 | C₃H₁₂N₂S₂O₂PtCl₂ | 24.92 (24.35) | 2.94 (3.71) | 4.92 (5.16) | 11.00 (11.82) |
| 3   | [Pt (N-MeCHdtc) (Val) Cl₂] | Brown | 202* | 71 | C₃H₁₂N₂S₂O₂PtCl₂ | 26.82 | 5.77 | 4.37 | 11.81 |
| 4   | [Pt (N-MeCHdtc) (Met) Cl₂] | Light-brown | 167* | 11 | C₃H₁₂N₂S₂O₂PtCl₂ | 25.21 (25.91) | 4.69 (4.01) | 4.57 (4.44) | 16.32 (5.96) |
| 5   | [Pt (Bzdtc) (Ala) Cl₂] | Deep-brown | 13.4 | 11 | C₃H₁₂N₂S₂O₂PtCl₂ | 21.98 (22.73) | 3.98 (3.43) | 5.74 (5.30) | 12.73 (12.13) |
| 6   | [Pt (Bzdtc) (Val) Cl₂] | Deep-brown | 167* | 79.5 | C₃H₁₂N₂S₂O₂PtCl₂ | 24.92 (24.35) | 2.94 (3.71) | 4.92 (5.16) | 11.00 (11.82) |
| 7   | [Pt (Bzdtc) (Met) Cl₂] | Light-brown | 174* | 14 | C₃H₁₂N₂S₂O₂PtCl₂ | 26.82 | 5.77 | 4.37 | 11.81 |
| 8   | [Pt (Bzdtc) (Ala) Cl₂] | Light-brown | 288* | 73 | C₃H₁₂N₂S₂O₂PtCl₂ | 26.82 | 5.77 | 4.37 | 11.81 |
| 9   | [Pt (Bzdtc) (Val) Cl₂] | Light-brown | 270* | 86 | C₃H₁₂N₂S₂O₂PtCl₂ | 29.71 (31.54) | 2.62 (3.34) | 2.09 (1.93) | 13.09 (13.29) |

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

| Complex no. | \(^1A_{1g} \rightarrow ^3T_{1g}\) | \(^1A_{1g} \rightarrow ^3T_{2g}\) | \(^1A_{1g} \rightarrow ^1T_{1g}\) | \(^1A_{1g} \rightarrow ^1T_{2g}\) | 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          | ---- |
| 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 |
| compound | ν(NH₂) | ν(CO₂⁻) | Δ | ν(C-N) | ν(C-S) | ν(C-SM) | ν(P-S) | ν(P-O) | ν(M-O) | ν(M-N) |
|----------|--------|---------|---|--------|--------|---------|--------|--------|--------|--------|
| NaN-MeCHdtc | ---- | ---- | ---- | 1469 | 990 | ---- | ---- | ---- | ---- | ---- |
| NaN-MeBzdtc | ---- | ---- | ---- | 1454 | 957 | ---- | ---- | ---- | ---- | ---- |
| NaN-MeNddip | ---- | ---- | ---- | ---- | ---- | 619 | 538 | 993 | ---- | ---- |
| Gly | 3164 | 1615 | 1457 | ---- | ---- | ---- | ---- | ---- | 547 | 490 |
| L-Ala | 3082 | 1597 | 1413 | ---- | ---- | ---- | ---- | ---- | 550 | 488 |
| L-Val | 3080 | 1590 | 1410 | ---- | ---- | ---- | ---- | ---- | 554 | 468 |
| L-Met | 2956 | 1616 | 1408 | ---- | ---- | ---- | ---- | ---- | 570 | 483 |
| 1 | 3238 | 1634 | 1396 | 238 | 1496 | 978 | ---- | ---- | 1316 | ---- |
| 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 | ---- | ---- | ---- | 632 | 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

| Complex no. | NMR |
|-------------|-----|
| 1 | ^1^H-nmr (DMSO-d₆): δ 4.03(2H,br,NH(Gly)), δ 2.54(2H, S, CH₂(Gly)), δ 2.27-1.68(10H,m, Chexy and Me), δ 1.23-1.17(4H,m,Chexy)ppm |
| 2 | 1H-nmr (DMSO-d₆): δ 4.03(2H,br,NH(Ala)), δ 3.12 (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(DMSOd₆):δ 4.03(2H,br,NHVal),δ 3.18(3H,Medtc),δ 2.73(1H,CHVal), δ 1.79-1.64(12H,m,5Chexy+7Val),1.33-1.11(6H,m,C-H Chexy)ppm |
| 5 | ^1^H-nmr (DMSO-d₆): δ 7.39-7.30(5H,m,C-H Bzdtc), 6.84 (1H,S,Bzdtc), δ4.65,(2H, NHGly),4.22 (2H,S,CH Gly) δ2.73 (2H,S,N-CH₂Bzdtc)ppm |
| 6 | ^1^H-nmr(DMSO-d₆):δ 8.14-7.32(5H,m,C₄H₆ inBzdtc),δ 94.9-4.85(3H,br,NH-NH₂-Ala+NH Bzdtc), δ 4.66 (1H,S ,CH-Ala), δ 2.31(2H,S ,CH-N-CH₂ in Bzdtc), δ 1.25 (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 \([\text{Pt}(\text{L-Met})(\text{L}^\prime)\text{Cl}_2]\)

\(R^\prime = \text{H}(\text{Gly}), \text{CH}_3(\text{Ala}), \text{CH}(\text{CH}_3)_2(\text{Val})\)

\((R = \text{H} \text{ when } R^\prime = \text{benzyl}, R = \text{CH}_3 \text{ when } R^\prime = \text{cyclohexyl})\)

Complexes 1-3,5-7

Fig. 2: Proposed structure for the complexes \([\text{Pt}(\text{Met})(\text{L}^\prime)\text{Cl}\text{Cl}]\)

\(R,R^\prime, \text{as defined in Fig. (1) Complex 4,8}\)

Fig. 3: Proposed structure for the complexes \([\text{Pt}(\text{L-Met})(\text{L}^\prime)\text{Cl}_2]\)

\(R=\text{propyl or benzyl}\)

\(R^\prime =\text{as defined in Fig. (1)}\)

Complex 9-11,13-15

Fig. 4: Proposed structure for the complexes \([\text{Pt}(\text{Met})(\text{L}^\prime)\text{Cl}\text{Cl}]\)

\(R=\text{propyl or benzyl}\)

Complex 12, 16

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