

**Synthesis and Characterization of Phthalimide-benzothiazole
Mercury(II) Complexes with Diphosphine and Diamines**

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Abstract

Phthalimide-benzothiazole ligand (L) and their complexes of Hg(II) with diphosphine and diamines have been prepared. Conductivity measurements show the 2:1 (ion- complex ion) behavior of the complexes except for [Hg(L)Cl₂] (1) complex which was non-conductive. The Phthalimide-benzothiazole ligand has been observed to be bonded to the Hg(II) ion through the nitrogen and oxygen atoms as a bidentate chelating ligand, whereas the diphosphine and diamine ligands have been bonded as bidentate chelating ligands to give a tetrahedral geometry around the Hg(II) ion.

Keywords: Phthalimide, Mercury, phosphine, complexes

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**تحضير وتشخيص معقدات فثالاميد-بنزو ثيازول الزئبق (II) مع ليكاندات الفوسفينات والامينات
الثنائية**

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الخلاصة

تم تحضير ليكاند فثالاميد-بنزو ثيازول (L) مع عدد من معقدات الزئبق (II) والفوسفينات والامينات الثنائية. ووجد من خلال قياسات التوصيلية المولارية ان المعقدات المحضرة موصلة ونسبة 2 : 1 (ايون : ايون معقد) فيما عدى المعقد [Hg(L)Cl₂] (1) الذي يكون غير موصل. وجد في المعقدات المحضرة ان ليكاند فثالاميد-بنزو ثيازول يسلك سلوك ليكاند ثنائي السن المخلي يرتبط من خلال ذرتي النتروجين والاكسجين، في حين ترتبط ليكاندات الفوسفينات والامينات الثنائية بشكل ثنائي السن المخلي ايضاً لتعطي ترتيب رباعي السطوح حول ايون الزئبق (II).
كلمات مفتاحية: فثالاميد، الزئبق، الفوسفين، المعقدات.

Introduction

The phthalimide compounds possess a structural features –CO-N(R)-CO- and a heterocyclic ring help the phthalimide to be pharmaceutically useful and biologically active[1]. Phthalimides and benzothiazoles have received attention due to their antitumour [2,3], anxiolytic [4] antifungal, antibacterial, analgesic [5], and anti HIV-1 activities. Several metal complexes of Mannich bases are known to have antimalarial, anti-inflammatory and antimicrobial drugs [6-13]. Recently, we reported several new mixed ligand complexes of Hg(II) with Phthalimide-benzothiazole as primary ligand and diphosphine and diamines as co-ligands.

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Experimental

1. General and instrumental

All the reagents, starting materials as well as solvents were purchased commercially and used without any further purification. The melting points were recorded on SMP40 supplied by Stuart Company. Elemental C, H, and N analysis were carried out on Eurovector, EA 3000A, Italy. Infrared spectra (with KBr disc) were recorded in the 4000 – 400 cm^{-1} range on Shimadzu 8400S FTIR Spectrophotometer. Conductivity measurements were carried out using a WTW conductivity meter. The ^1H - NMR spectra were recorded on Bruker, Ultra Shield 300 MHz, Switzerland spectrometer using DMSO- d_6 as a solvent and TMS as an internal reference.

2. Synthesis of Phthalimide-benzothiazoles (L)

A suspension of phthalic anhydride (1.481 g, 0.010 mmole) in glacial acetic acid (10 ml) was added to a suspension of 2-aminobenzothiazole (1.502 g, 0.010 mmol) in glacial acetic acid (10 ml). The mixture was refluxed for 3 hours. The clear solution formed was left for solvent to evaporate at room temperature to give white crystals. The crystals were collected by filtration and dried under vacuum. This compound had been prepared by a rather different method [14]. **(L)**: white crystals (2.00 g, 71%). Anal. Calc. for $\text{C}_{15}\text{H}_8\text{N}_2\text{O}_2\text{S}$: C, 64.27; H, 2.88; N, 9.99. Found: C, 64.22; H, 2.92; N, 10.03%. IR (KBr): 3091w(CH aromatic), 1785m, 1730s(C=O), 1591s (C=N), 1456m (C=C), 748m(C-S-C) cm^{-1} . ^1H NMR (DMSO- d_6): δ 7.33(td, 1H) $^3\text{J}(\text{HH})= 7.32\text{Hz}$, $^4\text{J}(\text{HH})= 1.24\text{Hz}$; 7.41(td, 1H) $^3\text{J}(\text{HH})= 7.22\text{Hz}$, $^4\text{J}(\text{HH})= 1.35\text{Hz}$; 7.82-7.84(m, 2H); 7.89(d, 1H); 7.91-7.93(m, 2H); 8.01(d, 1H) ppm. Melting point: 258°C decomposes.

Synthesis of $[\text{Hg}(\text{L})\text{Cl}_2]$ (1)

A suspension of HgCl_2 (0.271 g, 1.000 mmole) in CHCl_3 (10 ml) was added to a solution of Phthalimide - benzothiazole **(L)** (0.280 g, 1.000 mmole) in CHCl_3 (10 ml). The final mixture was refluxed for two hours, the white precipitate was formed, which was filtered off, dried under vacuum.

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Synthesis of [Hg(L)(Bipy)]Cl₂ (2)

A suspension of HgCl₂ (0.271 g, 1.000 mmole) in CHCl₃ (10 ml) was added to a solution of Phthalimide-benzothiazole (**L**) (0.280 g, 1.000 mmole) in CHCl₃ (10 ml). The mixture was refluxed for three hours. The white suspension formed was added to a solution of Bipy (0.172 g, 1.000 mmole) in CHCl₃ (10 ml). The final mixture was refluxed for three hours; the yellow solution was formed, which was filtered off, then left for solvent to evaporate at room temperature to give pale yellow solid which filtered off, dried under vacuum.

The related complexes [Hg(L)(Phen)]Cl₂(**3**), [Hg(L)(dppe)]Cl₂(**4**), [Hg(L)(dppp)]Cl₂ (**5**) and [Hg(L)(dppb)]Cl₂ (**6**) were prepared and isolated by similar method.

(1) White precipitate, (0.472 g, 85%). Anal. Calc. for C₁₅H₈Cl₂HgN₂O₂S: C, 32.65; H, 1.46; N, 5.08. Found: C, 32.92; H, 1.64; N, 5.44 %. IR (KBr): 3052w(CH aromatic), 1722m, 1652s(C=O), 1542m(C=N), 1468m (C=C), 748m (C-S-C) cm⁻¹. ¹H NMR (DMSO-d⁶): δ 7.33(t,2H) ³J(HH)= 7.41Hz; 7.42(t,2H) ³J(HH)= 7.51Hz; 7.80-7.94(m,4H) ppm. Melting point: 231°C decomposes.

(2) Pale yellow precipitate, (0.613 g, 86%). Anal. Calc. for C₂₅H₁₆Cl₂HgN₄O₂S: C, 42.41; H, 2.28; N, 7.91. Found: C, 42.12; H, 2.11; N, 7.53%. IR (KBr):3068w(CH aromatic), 1755m, 1690s(C=O), 1563s (C=N),1454m (C=C),746m(C-S-C) cm⁻¹. ¹H NMR (DMSO-d⁶): δ 6.93(td,2H) ³J(HH)= 5.10Hz, ⁴J(HH)= 1.09Hz; 6.85(td,1H) ³J(HH)= 7.40Hz, ⁴J(HH)= 1.56Hz; 7.17(td,1H) ³J(HH)= 7.50Hz, ⁴J(HH)= 1.56Hz; 7.48(td,2H) ³J(HH)= 7.87Hz, ⁴J(HH)= 1.27Hz; 7.81-7.83(m,2H); 7.88(dd,1H); 7.92(dd,1H); 7.97-7.99(m,2H); 8.52(dd,2H) ³J(HH)= 4.99Hz ; 8.81(d,2H) ³J(HH)= 8.03Hz ppm. Melting point: 289°C decomposes.

(3) Yellow precipitate, (0.604 g, 82%). Anal. Calc. for C₂₇H₁₆Cl₂HgN₄O₂S: C, 44.30; H, 2.20; N, 7.65. Found: C, 44.21; H, 2.56; N, 7.51 %. IR (KBr): 3068w(CH aromatic), 1753m, 1695s(C=O), 1566m(C=N), 1456m (C=C), 747m (C-S-C) cm⁻¹. ¹H NMR (DMSO-d⁶): δ 6.99(td,1H) ³J(HH)= 7.41Hz, ⁴J(HH)= 1.57Hz; 7.19(td,1H) ³J(HH)= 7.48Hz, ⁴J(HH)= 1.47Hz; 7.68(t,2H) ³J(HH)= 7.46Hz; 7.81-7.83(m,2H); 7.87(dd,1H); 7.91(dd,1H); 7.97-7.99(m,2H); 8.01(s,2H); 8.51(d,2H) ³J(HH)= 7.47Hz ; 9.13(dd,2H) ppm ³J(HH)= 7.50Hz, ⁴J(HH)= 1.45Hz. Melting point: 273°C decomposes.

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(4) Pale orange precipitate, (0.768 g, 80%). Anal. Calc. for $C_{41}H_{32}Cl_2HgN_2O_2P_2S$: C, 51.82; H, 3.39; N, 2.95. Found: C, 51.73; H, 3.43; N, 2.84 %. IR (KBr): 3055w(CH aromatic), 1750m, 1682s(C=O), 1567m(C=N), 1455m (C=C), 1434s, 690s (C-P), 748m (C-S-C) cm^{-1} . 1H NMR (DMSO- d_6): δ 1.40(*vq,4H); 6.99(t,1H) $^3J(HH)= 7.41Hz$; 7.19(t,1H) $^3J(HH)= 7.50Hz$; 7.27-7.38(m,20H); 7.80-7.84(m,2H); 7.88(d,1H); 7.91(d,1H); 7.96-7.99(m,2H) ppm. Melting point: 196°C decomposes.

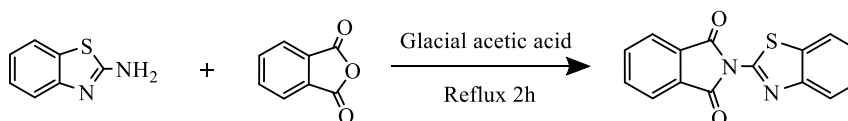
*vq: virtual quartet

(5) Pale orange precipitate, (0.758 g, 78%). Anal. Calc. for $C_{42}H_{34}Cl_2HgN_2O_2P_2S$: C, 52.32; H, 3.55; N, 2.91. Found: C, 51.96; H, 3.41; N, 2.64 %. IR (KBr): 3054w(CH aromatic), 1751m, 1681s(C=O), 1567m(C=N), 1454m (C=C), 1433m, 694s (C-P), 747m (C-S-C) cm^{-1} . 1H NMR (DMSO- d_6): δ 1.28-1.33(m,4H); 1.37-1.45(m,2H); 6.99(t,1H) $^3J(HH)= 7.40Hz$; 7.19(t,1H) $^3J(HH)= 7.51Hz$; 7.28-7.38(m,20H); 7.81-7.83(m,2H); 7.88(d,1H); 7.92(d,1H); 7.97-7.99(m,2H); ppm. Melting point: 224°C decomposes.

(6) pale orange precipitate, (0.758 g, 77%). Anal. Calc. for $C_{43}H_{36}Cl_2HgN_2O_2P_2S$: C, 52.79; H, 3.71; N, 2.86. Found: C, 52.96; H, 3.63; N, 3.04 %. IR (KBr): 3052w(CH aromatic), 1753m, 1680s(C=O), 1566m(C=N), 1465m (C=C), 1434m, 693s (C-P), 748m (C-S-C) cm^{-1} . 1H NMR (DMSO- d_6): δ 1.26-1.33(m,4H); 1.36-1.39(m,4H); 6.98(t,1H) $^3J(HH)= 7.41Hz$; 7.19(t,1H) $^3J(HH)= 7.51Hz$; 7.28-7.39(m,20H); 7.80-7.84(m,2H); 7.88(d,1H); 7.92(d,1H); 7.96-7.99(m,2H) ppm. Melting point: 256°C decomposes.

Results and Discussion

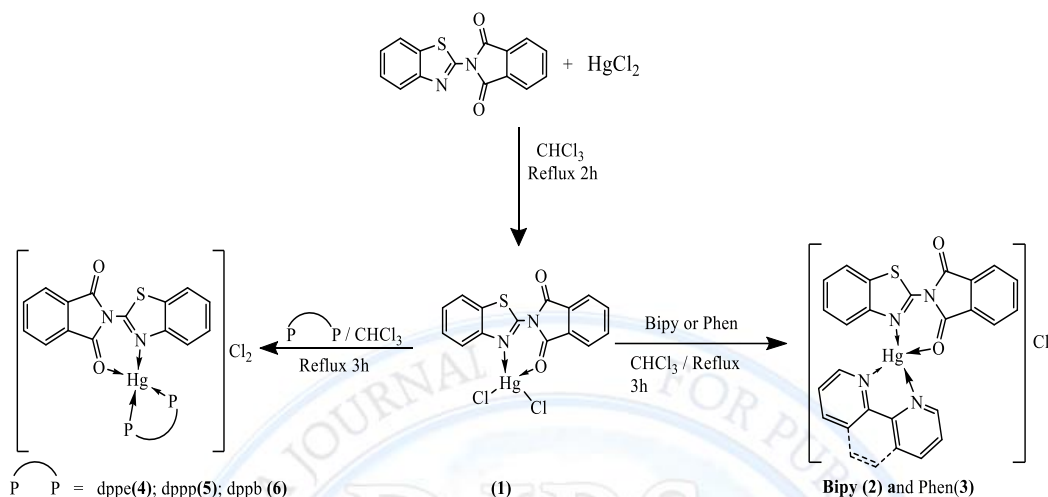
Preparation of the ligand and its new complexes are represented in Scheme 1 and 2.



Scheme 1: Preparation of phthalimide-benzothiazole ligand (L)

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Scheme 2: Preparation of complexes (1-6)

The prepared complexes are air-stable, insoluble in EtOH, MeOH, acetone and water, but soluble in CHCl₃, DMSO and DMF. Molar conductance values of Hg(II) complexes in DMSO solution correspond to 1:2 electrolytic nature [15], as shown in table (1).

Table (1) Shows Molar Conductivity of the Prepared Complexes at 1x10⁻³ concentration in DMSO.

| No. | Complexes | Λ _m (Cm ² .ohm ⁻¹ .mol ⁻¹) |
|-----|------------------------------|--|
| 1 | [Hg(L)Cl ₂] | 20 |
| 2 | [Hg(L)(Bipy)]Cl ₂ | 73 |
| 3 | [Hg(L)(Phen)]Cl ₂ | 71.5 |
| 4 | [Hg(L)(dppe)]Cl ₂ | 78 |
| 5 | [Hg(L)(dppp)]Cl ₂ | 76 |
| 6 | [Hg(L)(dppb)]Cl ₂ | 76 |

The coordination of the Hg(II) ion to the ligand (L) affected the ν(C=O)_{asy/sy} and ν(C=N) stretching vibrations. The ν(C=O)_{asy/sy} and ν(C=N) that show at (1785/1730) cm⁻¹

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and $(1591)\text{cm}^{-1}$ in the free ligand, shifted to lower frequencies in all prepared complexes indicating that the Hg(II) ion is coordinated through to the oxygen / nitrogen atoms of the L ligand[6-9] a new bands were observed in the IR spectra of the $[\text{HgL}(\text{diphos})]$ (diphos = dppe, dppp and dppb) which didn't found in the spectrum of the $[\text{HgCl}_2\text{L}]$ are the $\nu(\text{P-Ph})$ and $\nu(\text{P-C})$, observed within the $1434, 1433, 1434\text{ cm}^{-1}$ and $690, 694, 694\text{cm}^{-1}$, respectively [16-18]. It is thought [18] that this vibration arises from the deformation of the planarity of the phenyl ring bonded to the phosphorus atom.

The ^1H NMR spectra of phthalimide-benzothiazole ligand (L) and its Hg(II) complexes were recorded in DMSO- d_6 and are given with the experimental data.

The ^1H -NMR spectrum that of phthalimide-benzothiazole ligand (L) (Fig 1), display the (a) and (d) protons as a doublet at $\delta 8.01\text{ppm}$, $\delta 7.87\text{ppm}$. whereas the protons in position (e) and (f) showed as unresolved multiplets peaks within $\delta(7.91-7.93)$ and $\delta(7.82-7.84)$ ppm range respectively. Each of these signals represent two protons, as indicated the integration values under each signal. And triplet of doublets at $\delta 7.41$ and $\delta 7.33$ ppm for the protons in position (b) and (c) respectively.

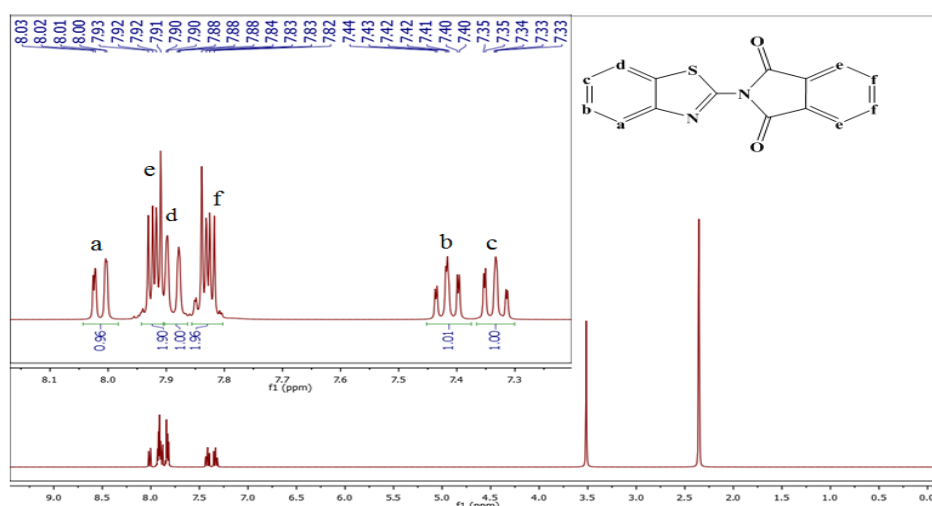


Fig 1: ^1H -NMR Spectrum of Phthalimide-benzothiazole (L) in DMSO- d_6

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The $^1\text{H-NMR}$ spectrum of complex (1) shown three signals two as a triplet peak at $\delta 7.33\text{ppm}$, and $\delta 7.42\text{ppm}$ due to the protons in position (c) and (b) respectively. whereas the other peak showed as unresolved multiplets peaks within $\delta(7.80-7.98)\text{ppm}$.

The $^1\text{H-NMR}$ spectra of each displayed the expected signals for the phthalimide-benzothiazole ligand as well as diamines and phosphine ligands (see Figs. 2 to 4).

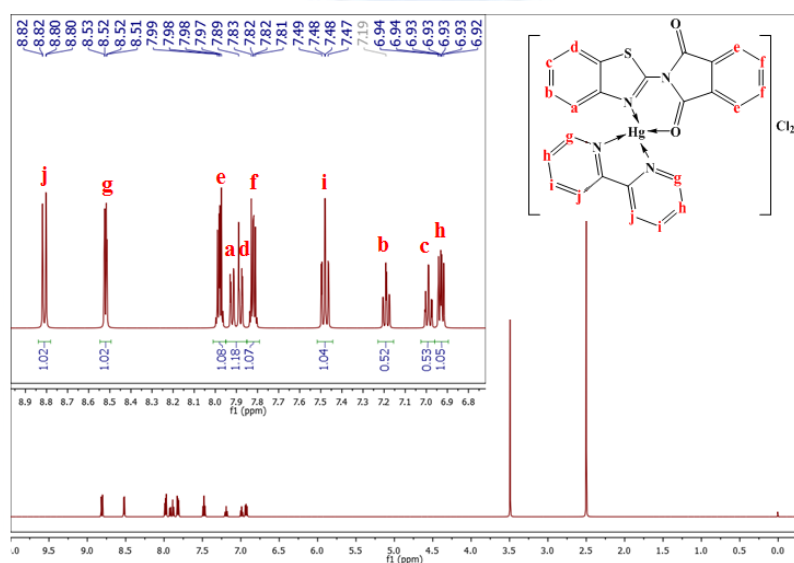


Fig 2. $^1\text{H-NMR}$ Spectrum of $[\text{Hg}(\text{L})(\text{Bipy})]\text{Cl}_2$ in DMSO-d_6

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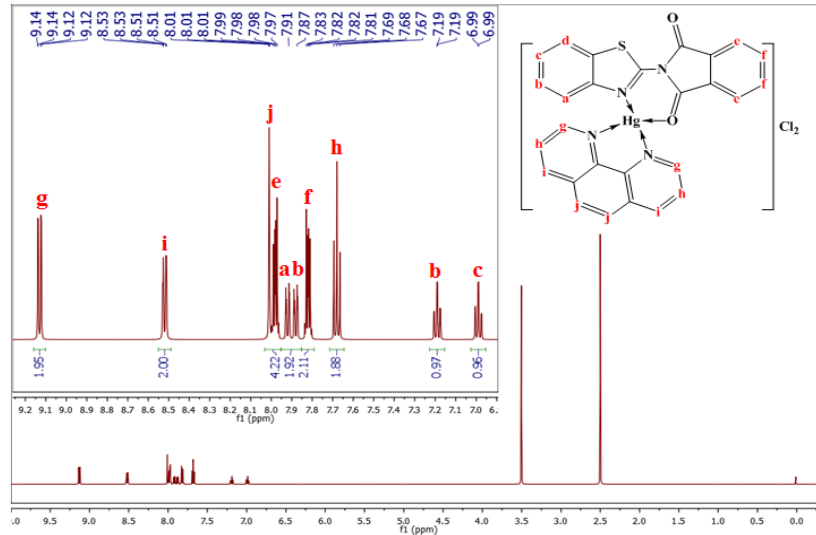


Fig 3. 1H -NMR Spectrum of $[Hg(L)(Phen)]Cl_2$ in $DMSO-d_6$

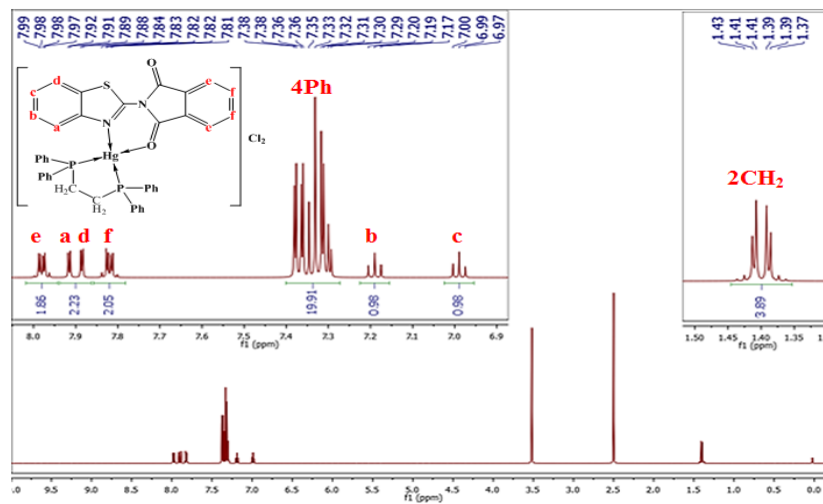


Fig 4. 1H -NMR Spectrum of $[Hg(L)(dppe)]Cl_2$ in $DMSO-d_6$

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Conclusions

- 1- Reaction of phthalic anhydride with 2-aminobenzothiazole took place through dehydration of the H₂O in glacial acetic acid to give the phthalimide-benzothiazoles (L).
- 2- Reaction of phthalimide-benzothiazole ligand (L) with HgCl₂ afford [Hg(L)Cl₂] complex which was non-conductive, (L) ligand behave as a bidentate chelate ligand bonds through N/O to Hg(II) ion.
- 3- The [Hg(L)(diamine)]Cl₂ and [Hg(L)(diphosphine)]Cl₂ complexes have been prepared, the (L) ligand behave as a bidentate chelate ligand bonds through N/O to Hg(II) ion, whereas the diphosphine and diamine ligands have been bonded as bidentate chelating ligands to give a tetrahedral geometry around the Hg(II) ion.

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