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Synthesis, characterization and Nuclear Magnetic Resonance study of the stoichiometry and stability of several zwitterionic mercury(II) complexes in dimethylsulfoxide

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HIGHLIGHTS

• Synthesis and characterization of some Hg(II) complexes of the phosphorus ligands.

• IR, ¹H- and ¹³C-NMR data demonstrate P-coordination of the ligands to the metal.

• ³¹P chemical shifts were measured as a function of [HgX₂]/[ligand] mole ratio.

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ABSTRACT

The reaction of the non-symmetric phosphonium salts $[PPh_2CH_2PPh_2CH_2C(O)R]Br_2$ (R = 4'-biphenyl (L₁); OCH₂Ph (L₂); 4-methylphenyl (L₃); 2-naphtyl (L₄); 3-nitrophenyl (L₅) and [PPh₂CH₂PPh₂CH₂C(O)R]Cl₂ $(R = 2,4-dichlorophenyl (L_6))$, with mercury(II) halides in 1:1 (for chloride and bromide) and 1:2 (for iodide) mole ratio in methanol under mild conditions afford the monomeric P-coordinated complexes, 3-nitrophenyl (5)) and $[HgCl_3(Ph_2PCH_2PPh_2CH_2C(O)C_6H_4Cl_2)]$ (6), $[HgBr_3(Ph_2PCH_2PPh_2CH_2C(O)R)]$ $(R = 4'-biphenyl (7), OCH_2Ph (8), 4-methylphenyl (9), 2-naphtyl (10), 3-nitrophenyl (11) and [HgBr₂ (Cl)(Ph_2PCH_2PPh_2CH_2C(O)C_6H_4Cl_2)$] (12)), [HgBr₂(I)(Ph_2PCH_2PPh_2CH_2C(O)R)] (R = 4'-biphenyl (13), OCH₂Ph (14), 4-methylphenyl (15), 2-naphtyl (16), 3-nitrophenyl (17)) and [HgCl₂(I)(Ph₂PCH₂PPh₂CH₂- $C(O)C_6H_4Cl_2$] (18). These complexes were fully characterized by elemental analysis and IR, ¹H, ¹³C and ³¹P{¹H} NMR spectra. In addition, ³¹P{¹H} NMR spectroscopy was used to investigate the stoichiometry and stability of all complexes in pure dimethylsulfoxide solvent. The formation constants of the resulting 1:1 complexes were evaluated from computer fitting of the mole ratio data to an equation that relates the observed chemical shifts to the formation constant. It was found that, in pure dimethylsulfoxide, the stabilities of the resulting 1:1 complexes vary in the order $L_3 > L_4 > L_1 > L_5 > L_6 > L_2$ and HgCl₂ > HgBr₂ > HgI₂. Crown Copyright © 2013 Published by Elsevier B.V. All rights reserved.

1. Introduction

Phosphonium salts are useful intermediates in organic synthesis [1] and an important class of ligands that find wide-spread use in transition metal chemistry [2]. Different types of ylide complexes of transition metals such as Hg(II), Pd(II) and Au(I) were prepared using the corresponding phosphonium salts as precursors [3–7]. Phosphorus ylides are known to demonstrate rich coordination chemistry. The coordination chemistry of keto-stabilized phosphorus ylides, are interested to investigate because of the different bonding modes upon coordination of ylides to metal [8–16]: C-coordinated (through the C_{α} atom), O-bonded (through the carbonyl O), P-bonded (through the P of the phos-

Due to the resonance delocalisation of the ylide electron density, some ylides are also capable of chelating to the metals via two atoms in a bidentate manner [17–26]. Mono keto ylides with a methylenic spacer, $Ph_2PCH_2PPh_2 = C(H)C(O)PhR$ [R = H, Cl, Br, NO₂, OCH₃] affords P, C-coordinated complexes with mercury(II) halides [27–29]. On the other hand, $Ph_2PCH_2CH_2PPh_2 = C(H)C(O)Ph$ with a ethylenic spacer forms polymeric Hg(II) complexes with HgCl₂ via P, C-bridging mode while HgBr₂ and Hgl₂ react with the same ylide giving polymeric halogen bridged phosphine complexes with dangling ylide [18]. In this work, we report the formation of zwitterionic P-coordinated complexes of mercury(II) halides with phosphine–phosphonium salts. Among a variety of spectroscopic and electrochemical methods used for the study of

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phine group), or even situations in which the same ylide shows a combination of bonding modes. Different types of bonding are shown as depicted in Chart 1 for $Ph_2PCH_2PPh_2C(H)C(O)R$.

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Chart 1. The possible bonding modes of Ph₂PCH₂PPh₂C(H)C(O)R to metal M.

complexes [30–32] it has been found that nuclear magnetic resonance spectrometry offers a very sensitive technique for studies of changes in the immediate chemical environment of phosphine–phosphonium salts in solution. In recent years, we have used proton and alkali metal NMR techniques to study the thermodynamics [33,34] and kinetics [35,36] of metal ion complexation with some macroacyclic ligands in nonaqueous and mixed solvents. In this study, our interest in the physicochemical properties of the phosphorus ligands, encouraged us to determine the formation constants of mercury(II) complexes of phosphorus ligands and to gain some useful information about the properties of complex formation in the solvent.

2. Experimental

2.1. Materials

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Reactants and reagents were obtained from Merck Chemical Company and used without further purification. The solvents were dried and distilled using standard methods [37].

2.2. Physical measurements

Melting points were measured on a Stuart SMP3 apparatus. Elemental analysis for C, H and N were performed using a Perkin–Elmer 2400 series analyzer. The IR spectra in the interval of 4000–400 cm⁻¹ were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. ¹H and ³¹P{¹H} NMR spectra were recorded on 90 MHz Jeol and ¹³C NMR spectra on 300 MHz Bruker spectrometers in DMSO-d₆ as solvent at 25 °C. Chemical shifts (ppm) are reported according to internal TMS and external 85% H₃PO₄.

2.3. Sample preparation

The ligands $[PPh_2CH_2PPh_2CH_2C(O)R]Br_2$ [R = 4'-biphenyl (**L**₁); OCH₂Ph (**L**₂); 4-methylphenyl (**L**₃); 2-naphtyl (**L**₄); 3-nitrophenyl (**L**₅) and $[PPh_2CH_2PPh_2CH_2C(O)C_6H_3Cl_2]Cl_2$ (**L**₆)] were prepared by our group previously [38].

2.3.1. Synthesis of Hg(II) halide complexes

General procedure: To a solution of HgX_2 , X = Cl and Br (0.30 mmol) or HgI_2 (0.15 mmol) in methanol (10 mL), a solution of L (L = L_1-L_6) (0.30 mmol) in the same solvent (5 mL) was added dropwise at 25 °C and the reaction allowed to proceed under stirring for 5 h. The resulting solid was isolated, washed twice with

10 mL methanol and 10 mL diethylether and dried under reduced pressure.

2.3.1.1. Data for [HgCl₂(Br)(Ph₂PCH₂PPh₂CH₂C()C₆H₄Ph)] (**1**). Yield: 0.22 g, 81%. M.p. 155–157 °C. Anal. Calc. for $C_{39}H_{33}BrCl_2HgOP_2$: C, 50.32; H, 3.57. Found: C, 50.79; H, 3.52. IR (KBr, cm⁻¹): 1670 (vC=O). ¹H NMR (DMSO-d₆): δ 4.24 (t, 2H, PCH₂P_. ²J_{PH} = 13.50); 5.65 (d, 2H, PCH₂CO, ²J_{PH} = 11.07); 7.30–8.00 (m, 29H, Ph). ³¹P NMR (DMSO-d₆): δ –26.24 (d, PPh₂, ²J_{PP} = 68.71); 23.88 (d, PCH₂CO, ²J_{PP} = 66.72). ¹³C NMR (DMSO-d₆): δ 19.45 (br, PCH₂P); 34.24 (d, PCH₂); 119.17–145.53 (Ph); 192.41 (s, CO).

2.3.1.2. Data for $[HgCl_2(Br)(Ph_2PCH_2PPh_2CH_2CO_2CH_2Ph)]$ (2). Yield: 0.19 g, 72. M.p. 143–145 °C. Anal. Calc. for $C_{34}H_{31}BrCl_2HgO_2P_2$: C, 46.15; H, 3.53. Found: C, 45.84; H, 3.47. IR (KBr, cm⁻¹): 1718 (vC=O). ¹H NMR (DMSO-d_6): δ 4.53 (d, PCH₂P, CH₂. ²J_{PH} = 15.93); 5.11 (d, 2H, PCH₂CO, ²J_{PH} = 13.76); 4.97 (s, 2H, CH₂O); 7.13–8.05 (m, 25H, Ph). ³¹P NMR (DMSO-d_6): δ –14.73 (d, PPh₂, ²J_{PP} = 49.32); 22.66 (d, PCH₂CO, ²J_{PP} = 48.84). ¹³C NMR (DMSO-d_6): δ 19.65 (br, PCH₂P); 29.82 (br, PCH₂); 68.20 (s, CH₂O); 117.22–135.39 (Ph); 164.58 (s, CO).

2.3.1.3. *Data for* [*HgCl*₂(*Br*)(*Ph*₂*PCH*₂*PPh*₂*C*(*D*)*C*₆*H*₄*Me*)] (**3**). Yield: 0.22 g, 85%. M.p. 147–149 °C. Anal. Calc. for C₃₄H₃₁BrCl₂HgOP₂: C, 46.99; H, 3.59. Found: C, 47.17; H, 3.64. IR (KBr, cm⁻¹): 1669 (vC=O). ¹H NMR (DMSO-d₆): δ 4.52 (d, 2H, PCH₂P_.²*J*_{PH} = 12.78); 5.74 (d, 2H, PCH₂CO, ²*J*_{PH} = 12.60); 2.38 (s, 3H, CH₃); 7.33–8.05 (m, 24H, Ph). ³¹P NMR (DMSO-d₆): δ –17.11 (d, PPh₂, ²*J*_{PP} = 54.53); 23.35 (d, PCH₂CO, ²*J*_{PP} = 54.03). ¹³C NMR (DMSOd₆): δ 22.64 (br, PCH₂P); 34.33 (br, PCH₂); 21.90 (s, CH₃); 118.65– 145.17 (Ph); 191.71 (s, CO).

2.3.1.4. Data for [HgCl₂(Br)(Ph₂PCH₂PPh₂CH₂C(O)C₁₀H₇)] (**4**). Yield: 0.21 g, 78%. M.p. 148–150 °C. Anal. Calcd. for C₃₇H₃₁BrCl₂HgOP₂: C, 49.11; H, 3.45. Found: C, 48.97; H, 3.48. Selected IR absorption in KBr (cm⁻¹): 1667 (v_{C=0}). ¹H NMR (DMSO-d₆): δ 4.60 (d, 2H, PCH₂P, ²J_{PH} = 13.95); 5.89 (d, 2H, PCH₂CO, ²J_{PH} = 12.15); 7.32–8.89 (m, 27H, Ph and 2-naphtyl). ³¹P NMR (DMSO-d₆): δ-13.20 (d, PPh₂, ²J_{PP} = 40.83); 22.97 (d, PCH₂CO, ²J_{PP} = 28.53). ¹³C NMR (DMSO-d₆): δ 19.80 (br, PCH₂P); 37.75 (br, PCH₂); 124.20–138.50 (Ph and 2-naphtyl); 196.42 (s, CO).

2.3.1.5. Data for $[HgCl_2(Br)(Ph_2PCH_2PPh_2CH_2C(O)C_6H_4NO_2)]$ (5). Yield: 0.23 g, 85%. M.p. 142–144 °C. Anal. Calcd. for C₃₃H₂₈-BrCl_2HgNO_3P_2: C, 44.04; H, 3.13; N, 1.55. Found: C, 43.82; H, 3.06; N, 1.64. Selected IR absorption in KBr (cm⁻¹): 1685 (v_{C=0}). ¹H NMR (DMSO-d₆): δ 4.31 (d, 2H, PCH₂P, ²*J*_{PH} = 15.57); 5.77 (t, 2H, PCH₂CO, ²*J*_{PH} = 13.23); 7.26–8.73 (m, 24H, Ph). ³¹P NMR (DMSO-d₆) δ_{P} : –26.75 (d, PPh₂, ²*J*_{PP} = 65.65); 23.70 (d, PCH₂CO, ${}^{2}J_{PP}$ = 73.28). ¹³C NMR (DMSO-d₆): δ 21.71 (br, PCH₂P); 34.84 (br, PCH₂); 118.71–151.15 (Ph); 191.64 (s, CO).

2.3.1.6. Data for [HgCl₃(Ph₂PCH₂PPh₂CH₂C(O)C₆H₃Cl₂)] (**6**). Yield: 0.19 g, 75%. M.p. 169–171 °C. Anal. Calcd. for C₃₃H₂₇Cl₅HgOP₂: C, 45.1; H, 3.09. Found: C, 45.17; H, 3.14. Selected IR absorption in KBr (cm⁻¹): 1689 (v_{C=0}). ¹H NMR (DMSO-d₆): δ 4.56 (bd, 2H, PCH₂-P, ²J_{PH} = 13.5); 5.79 (d, 2H, PCH₂CO, ²J_{PH} = 12.6); 7.37–8.15 (m, 23H, Ph). ³¹P NMR (DMSO-d₆): δ –14.05 (d, PPh₂, ²J_{PP} = 48.30); 22.93 (d, PCH₂CO, ²J_{PP} = 51.11). ¹³C NMR (DMSO-d₆): δ 22.35 (br, PCH₂P); 38.21 (br, PCH₂); 115.27–139.97 (Ph); 191.14 (d, CO, ²J_{PC} = 4.01).

2.3.1.7. Data for [HgBr₃(Ph₂PCH₂PPh₂CH₂C(O)C₆H₄Ph)] (7). Yield: 0.27 g, 88%. M.p. 130–132 °C. Anal. Calc. for C₃₉H₃₃Br₃HgOP₂: C, 45.93; H, 3.26. Found: C, 45.97; H, 3.20. IR (KBr, cm⁻¹): 1669 (vC=O). ¹H NMR (DMSO-d₆): δ 4.40 (d, PCH₂P, CH₂. ²J_{PH} = 6.12); 5.72 (d, 2H, PCH₂CO, ²J_{PH} = 5.00); 7.31–8.03 (m, 29H, Ph). ³¹P NMR (DMSO-d₆): δ –22.80 (d, PPh₂, ²J_{PP} = 60.16); 23.40 (d, PCH₂CO, ²J_{PP} = 58.38). ¹³C NMR (DMSO-d₆): δ 19.69 (br, PCH₂P); 33.36 (br, PCH₂); 119.21–145.50 (Ph); 192.12 (s, CO).

2.3.1.8. *Data* for $[HgBr_3(Ph_2PCH_2PPh_2CH_2CO_2CH_2Ph)]$ (**8**). Yield: 0.24 g, 83%. M.p. 134–136 °C. Anal. Calc. for $C_{34}H_{31}Br_3HgO_2P_2$: C, 41.97; H, 3.21. Found: C, 41.86; H, 3.14. IR (KBr, cm⁻¹): 1718 (vC=O). ¹H NMR (DMSO-d₆): δ 4.34 (d, PCH₂P, CH₂. ²J_{PH} = 14.85); 4.84 (d, 2H, PCH₂CO, ²J_{PH} = 13.56); 4.98 (s, 2H, CH₂O); 7.12–7.94 (m, 25H, Ph). ³¹P NMR (DMSO-d₆): δ –23.00 (d, PPh₂, ²J_{PP} = 58.46); 23.15 (d, PCH₂CO, ²J_{PP} = 58.60). ¹³C NMR (DMSOd₆): δ 19.95 (d, PCH₂P, ¹J_{PC} = 53.55); 29.40 (d, PCH₂, ¹J_{PC} = 38.4); 68.16 (s, CH₂O); 117.48–135.34 (Ph); 164.65 (s, CO).

2.3.1.9. Data for $[HgBr_3(Ph_2PCH_2PPh_2CH_2C(O)C_6H_4Me)]$ (**9**). Yield: 0.25 g, 89%. M.p. 139–141 °C. Anal. Calc. for $C_{34}H_{31}Br_3HgOP_2$: C, 42.68; H, 3.26. Found: C, 42.72; H, 3.31. IR (KBr, cm⁻¹): 1669 (vC=O). ¹H NMR (DMSO-d₆): δ 4.38 (d, 2H, PCH₂P_. ²J_{PH} = 16.20); 5.62(d, 2H, PCH₂CO, ²J_{PH} = 11.61); 2.38 (s, 3H, CH₃); 7.30–7.96 (m, 24H, Ph). ³¹P NMR (DMSO-d₆): δ –15.00 (d, PPh₂, ²J_{PP} = 61.93); 19.10 (d, PCH₂CO, ²J_{PP} = 57.72). ¹³C NMR (DMSOd₆): δ 22.86 (br, PCH₂P); 34.02 (br, PCH₂); 21.82 (s, CH₃); 119.16– 146.16 (Ph); 191.95 (s, CO).

2.3.1.10. Data for [HgBr₃(Ph₂PCH₂PPh₂CH₂C(O)C₁₀H₇)] (**10**). Yield: 0.26 g, 89%. M.p. 141–143 °C. Anal. Calcd. for C₃₇H₃₁Br₃HgOP₂: C, 44.76; H, 3.14. Found: C, 44.87; H, 3.11. Selected IR absorption in KBr (cm⁻¹): 1668 (v_{C=O}). ¹H NMR (DMSO-d₆): δ 4.47 (d, 2H, PCH₂P, ²J_{PH} = 15.39); 5.84 (d, 2H, PCH₂CO, ²J_{PH} = 12.06); 7.30–8.88 (m, 27H, Ph and 2-naphtyl). ³¹P NMR (DMSO-d₆): δ –19.11 (d, PPh₂, ²J_{PP} = 56.53); 24.48 (d, PCH₂CO, ²J_{PP} = 43.98). ¹³C NMR (DMSOd₆): δ 19.51 (br, PCH₂P); 37.19 (br, PCH₂); 123.86–137.92 (Ph and 2-naphtyl); 195.78 (s, CO).

2.3.1.11. Data for [HgBr₃(Ph₂PCH₂PPh₂CH₂C(*O*)C₆H₄NO₂)] (**11**). Yield: 0.27 g, 92%. M.p. 128–130 °C. Anal. Calcd. for C₃₃H₂₈Br₃HgNO₃P₂: C, 40.12; H, 2.85; N, 1.42. Found: C, 39.56; H, 2.80; N, 1.45. Selected IR absorption in KBr (cm⁻¹): 1685 (ν _{C=O}). ¹H NMR (DMSO-d₆): δ 4.47 (d, 2H, PCH₂P, ²J_{PH} = 15.30); 5.83 (d, 2H, PCH₂CO, ²J_{PH} = 11.97); 7.29–8.72 (m, 24H, Ph). ³¹P NMR (DMSO-d₆): δ –22.98 (d, PPh₂, ²J_{PP} = 58.99); 22.49 (d, PCH₂CO, ²J_{PP} = 62.84). ¹³C NMR (DMSOd₆): δ 21.13 (br, PCH₂P); 34.11 (br, PCH₂); 122.7–150.44 (Ph); 190.52 (s, CO).

2.3.1.12. Data for $[HgBr_2(Cl)(Ph_2PCH_2PPh_2CH_2C(O)C_6H_3Cl_2)]$ (**12**). Yield: 0.23 g, 79%. M.p. 153–155 °C. Anal. Calcd. for C₃₃H₂₇. Br₂Cl₃HgOP₂: C, 40.99; H, 2.81. Found: C, 41.13; H, 2.82. Selected IR absorption in KBr (cm⁻¹): 1685 ($\nu_{C=O}$). ¹H NMR (DMSO-d₆): δ 4.35 (d, 2H, PCH₂P, ²J_{PH} = 15.39); 5.63 (d, 2H, PCH₂CO, ²*J*_{PH} = 12.59); 7.35–8.02 (m, 23H, Ph). ³¹P NMR (DMSO-d₆): δ –24.08 (d, PPh₂, ²*J*_{PP} = 61.79); 23.48 (d, PCH₂CO, ²*J*_{PP} = 61.72). ¹³C NMR (DMSO-d₆): δ 22.57 (d, PCH₂P, ¹*J*_{PC} = 61.54); 38.73 (d, PCH₂, ¹*J*_{PC} = 58.14); 114.85–139.64 (Ph); 190.73 (d, CO, ²*J*_{PC} = 4.57).

2.3.1.13. Data for $[HgBr_2(I)(Ph_2PCH_2PPh_2CH_2C(O)C_6H_4Ph)]$ (**13**). Yield: 0.091 g, 57%. M.p. 109–111 °C. Anal. Calc. for $C_{39}H_{33}$. Br₂HgIOP₂: C, 43.90; H, 3.12. Found: C, 43.97; H, 3.08. IR (KBr, cm⁻¹): 1672 (ν C=O). ¹H NMR (DMSO-d₆): δ 4.27 (d, PCH₂P, CH₂. ²J_{PH} = 15.66); 5.62 (d, 2H, PCH₂CO, ²J_{PH} = 12.42); 7.29–8.11 (m, 29H, Ph). ³¹P NMR (DMSO-d₆): δ –28.24 (d, PPh₂, ²J_{PP} = 67.73); 23.68 (d, PCH₂CO, ²J_{PP} = 67.99). ¹³C NMR (DMSO-d₆): δ 20.17 (br, PCH₂P); 34.87 (br, CH₂); 119.42–146.52 (Ph); 192.17 (s, CO).

2.3.1.14. Data for [HgBr₂(I)(Ph₂PCH₂PPh₂CH₂CO₂CH₂Ph)] (**14**). Yield: 0.078 g, 51%. M.p. 117–119 °C. Anal. Calc. for $C_{34}H_{31}Br_2HglO_2P_2$: C, 40.00; H, 3.06. Found: C, 39.85; H, 3.02. IR (KBr, cm⁻¹): 1718 (vC=O). ¹H NMR (DMSO-d₆): δ 4.31 (d, PCH₂P, CH₂. ²J_{PH} = 15.82); 4.74 (d, 2H, PCH₂CO, ²J_{PH} = 14.06); 5.05 (s, 2H, CH₂O); 7.06–8.11 (m, 25H, Ph). ³¹P NMR (DMSO-d₆): δ –27.64 (d, PPh₂, ²J_{PP} = 64.29); 23.48 (d, PCH₂CO, ²J_{PP} = 65.82). ¹³C NMR (DMSOd₆): δ 19.92 (br, PCH₂P); 29.31 (d, PCH₂, ¹J_{PC} = 55.05); 68.12 (s, CH₂O); 117.75–135.28 (Ph); 164.74 (s, CO).

2.3.1.15. Data for $[HgBr_2(I)(Ph_2PCH_2PPh_2CH_2C(O)C_6H_4Me)]$ (**15**). Yield: 0.088 g, 59%. M.p. 111–113 °C. Anal. Calc. for C₃₄H₃₁. Br₂HgIOP₂: C, 40.64; H, 3.11. Found: C, 41.02; H, 3.06. IR (KBr, cm⁻¹): 1667 (vC=O). ¹H NMR (DMSO-d₆): δ 4.23 (d, 2H, PCH₂P_. ²J_{PH} = 14.85); 5.52(d, 2H, PCH₂CO, ²J_{PH} = 13.23); 2.41 (s, 3H, CH₃); 7.29–7.90 (m, 24H, Ph). ³¹P NMR (DMSO-d₆): δ –27.80 (d, PPh₂, ²J_{PP} = 66.32); 23.68 (d, PCH₂CO, ²J_{PP} = 67.44). ¹³C NMR (DMSO-d₆): δ 22.05 (br, PCH₂P); 33.88 (br, PCH₂); 21.12 (s, CH₃); 119.24– 146.28 (Ph); 191.57 (s, CO).

2.3.1.16. Data for [HgBr₂(I)(Ph₂PCH₂PPh₂CH₂C(O)C₁₀H₇)] (**16**). Yield: 0.081 g, 52%. M.p. 105–107 °C. Anal. Calcd. for C₃₇H₃₁Br₂HgIOP₂: C, 42.69; H, 3.00. Found: C, 42.58; H, 2.95. Selected IR absorption in KBr (cm⁻¹): 1668 (v_{C=0}). ¹H NMR (DMSO-d₆): δ 3.43 (br, 2H, PCH₂P); 5.65 (bd, 2H, PCH₂CO, ²J_{PH} = 20.16); 7.06–7.95 (m, 27H, Ph and 2-naphtyl). ³¹P NMR (DMSO-d₆): δ –28.20 (d, PPh₂, ²J_{PP} = 51.12); 23.89 (d, PCH₂CO, ²J_{PP} = 45.32). ¹³C NMR (DMSOd₆): δ 19.67 (br, PCH₂P); 36.89 (br, PCH₂); 123.66–138.74 (Ph and 2-naphtyl); 195.32 (s, CO).

2.3.1.17. Data for $[HgBr_2(1)(Ph_2PCH_2PPh_2CH_2C(O)C_6H_4NO_2)]$ (17). Yield: 0.094 g, 61%. M.p. 98–100 °C. Anal. Calcd. for $C_{33}H_{28}$. Br_2HgINO_3P_2: C, 38.26; H, 2.72; N, 1.35. Found: C, 37.97; H, 2.66; N, 1.41. Selected IR absorption in KBr (cm⁻¹): 1684 (v_{C=0}). ¹H NMR (DMSO-d_6): δ 4.26 (d, 2H, PCH₂P, ²J_{PH} = 15.93); 5.66 (d, 2H, PCH₂CO, ²J_{PH} = 12.87); 7.25–8.74 (m, 24H, Ph). ³¹P NMR (DMSO-d_6): δ –27.98 (d, PPh₂, ²J_{PP} = 69.27); 23.70 (d, PCH₂CO, ²J_{PP} = 70.89). ¹³C NMR (DMSO-d_6): δ 21.51 (br, PCH₂P); 33.94 (br, PCH₂); 124.3–151.16 (Ph); 191.72 (s, CO).

2.3.1.18. Data for $[HgCl_2(I)(Ph_2PCH_2PPh_2CH_2C(O)C_6H_3Cl_2)]$ (**18**). Yield: 0.069 g, 48%. M.p. 134–136 °C. Anal. Calcd. for C₃₃H₂₇. Cl₄HgIOP₂: C, 40.82; H, 2.80. Found: C, 40.92; H, 2.84. Selected IR absorption in KBr (cm⁻¹): 1684 (v_{C=O}). ¹H NMR (DMSO-d₆): δ 4.23 (d, 2H, PCH₂P, ²*J*_{PH} = 14.22); 5.52 (d, 2H, PCH₂CO, ²*J*_{PH} = 12.59); 7.34–7.91 (m, 23H, Ph). ³¹P NMR (DMSO-d₆): δ –25.95 (d, PPh₂, ²*J*_{PP} = 63.85); 23.59 (d, PCH₂CO, ²*J*_{PP} = 65.45). ¹³C NMR (DMSO-d₆): δ 22.11 (br, PCH₂P); 38.41 (d, PCH₂); 115.57–141.28 (Ph); 189.91 (s, CO).

2.4. General experimental procedure for nuclear magnetic resonance studies

In a typical experiment, 0.5 mL of the solutions containing 0.06 M of ligand in dimethylsulfoxide (DMSO) was placed in the NMR tube, thermostated to the desired temperature and the ${}^{31}P{}^{1}H$ NMR spectra of the resulting solutions were recorded and chemical shift of the NMR signals were measured. Then, a known amount of a concentrated mercury(II) halide solution (0.12 M) in the same solvent was added up to the [HgX₂]/[ligand] mole ratio of 4, in a stepwise manner using a microsyringe. After the mixture was stirred under ultrasonic agitation for 5 min, ${}^{31}P$ NMR spectra of the resulting solutions were recorded. According to molar ratio data and KINFIT program, which acts based on Eq. (1.7), the stoichiometry of complexation between the ligands and mercury(II) salts was 1:1. Formation constants of these complexes were derived using ${}^{31}P{}^{1}H$ NMR data.

All NMR measurements for complex formation constants were made on a JEOL(FX90Q)-NMR spectrometer with a field strength of 2.35T equipped with a temperature controller (\pm 0.1 °C). At this field, ³¹P resonates at 36.262 MHz. Typical acquisition parameters were 20,000 Hz sweep width, 700 scans, 1s relaxation delay, 1s acquisition time, 15 µs pulse width (30° pulse) with proton decoupling in 90.0 MHz and 64 k = 65,536 words. In ³¹P{¹H} NMR experiments, the standard was 85% H₃PO₄. All chemical shift measurements were carried out at a temperature of 25.0 ± 0.1 °C.

3. Results and discussion

3.1. Synthesis

The reaction of mercury(II) halides with non-symmetrical phosphonium salts (L_1-L_6), in 1:1 (for chloride and bromide) and 1:2 (for iodide) mole ratio yield two different types of zwitterionic mercury(II) complexes (Schemes 1 and 2). The mercury(II) chloride and bromide produce simple complexation products while the formation of iodide complexes involve a halogen exchange [2]:

 $2[Ph_2PCH_2PPh_2CH_2C(O)R]Br + HgI_2$ $\rightarrow [Br_2(I)HgPh_2PCH_2PPhCH_2C(O)R] + [Ph_2PCH_2PPh_2CH_2C(O)R]I$

 $[R = 4'-biphenyl, OCH_2Ph, 4-methylphenyl, 2-naphtyl, 2-naphtyl,$

3-nitophenyl, 2,4-dichlorophenyl

 $2[Ph_2PCH_2PPh_2CH_2C(0)C_6H_3CI_2]CI + HgI_2 \\$

 $\rightarrow [Cl(I)HgPh_2PCH_2PPh_2CH_2C(O)C_6H_3Cl_2]$

 $+ [Ph_2PCH_2PPh_2CH_2C(O)C_6H_3CI_2]I \\$

3.2. Spectroscopy

The IR spectra of complexes 1-18 show single sharp and intense absorption band in the range $1667-1718 \text{ cm}^{-1}$, due to the carbonyl stretch which is close to the same frequency in free phosphonium salts (1661–1729 cm⁻¹) indicates the non-involvement of the PCH₂C(O)R group in the reactions [2]. The IR data for all complexes and free phosphonium salts reported in Table 1. The chemical nature of the all complexes were checked by means of ³¹P. ¹H and ¹³C NMR spectroscopy. The ³¹P NMR spectra result more informative which show in all cases the presence of two doublets signals in ca. 1:1 ratio. These signals indicate the presence of the PCH₂CO and PPh₂ groups in the complexes. In contrast to the ³¹P NMR spectrum of Hg(II)-phosphine complexes [39], the coordination of phosphorous atom to mercury in these complexes did not cause significant downfield shifts. All complexes show downfield shifts compared to that of phosphine of the related phosphonium salts. The chemical shifts show a slight downfield shifts for mercury(II) iodide complexes (1.01-3.08 ppm) whereas the coordination of phosphine to mercury(II) bromide and chloride cause significant downfield shifts (4.95-14.3 and 2.89-14.82 ppm, respectively) to that of phosphine of the related phosphonium salts. These data indicate that the presence of a formal negative charge on the metal may effectively reduce the deshielding experienced by the phosphorus due to complexation [2]. The ¹H NMR spectra (ratio of signal intensities for PCH₂P and PCH₂CO protons) of all compounds confirm the presence of two sets of signals in agreement with the other spectroscopic data. Two sets of signals are observed in the ¹H NMR specta of all complexes at around 3.43–4.60 ppm



Scheme 1. Synthetic route for the preparation of complexes 1-5, 7-11 and 13-17.



Scheme 2. Synthetic route for the preparation of complexes 6, 12 and 18.

Table 1 Relevant ¹H, ³¹P NMR (δ , ppm) and IR (cm⁻¹) data for compounds 1–18 and free phosphorus ligands.

Compound	$\delta \left(PCH_2 C(O) R \right)^b$	$\delta (PPh_2)^b$	\varDelta^{a}	υ(CO)
L ₁	5.83(d)	-30.71(d)	-	1669
L ₂	4.87(d)	-30.83(d)	-	1729
L ₃	5.73(d)	-30.68(d)	-	1661
L ₄	5.78(d)	-30.77(d)	-	1666
L ₅	5.88(d)	-31.11(d)	-	1682
L ₆	5.96(d)	-30.54(d)	-	1683
1	5.65(d)	-26.24(d)	4.47	1670
2	5.11(d)	-14.73(d)	16.10	1718
3	5.74(d)	-17.11(d)	13.57	1669
4	5.89(d)	-13.20(d)	17.57	1667
5	5.77(d)	-26.75(d)	4.36	1685
6	5.79(d)	-14.05(d)	16.49	1689
7	5.72(d)	-22.80(d)	7.91	1669
8	4.84(d)	-23.00(d)	7.83	1718
9	5.62(d)	-15.00(d)	15.68	1669
10	5.84(d)	-19.11(d)	11.66	1668
11	5.83(d)	-22.98(d)	8.13	1685
12	5.63(d)	-24.08(d)	6.46	1685
13	5.62(d)	-28.24(d)	2.47	1672
14	4.74(d)	-27.64(d)	3.19	1718
15	5.52(d)	-27.80(d)	2.88	1667
16	5.65(d)	-28.20(d)	2.57	1668
17	5.66(d)	-27.98(d)	3.13	1684
18	5.52(d)	-25.95(d)	4.59	1684

 $^a~\Delta$ = $\delta(coordinated~ligands)$ – $\delta(free~ligands). ^{31}P$ NMR shifts, d, doublet. $^b~$ Record in DMSO-d_6.

attributed to PCH₂P, and in the region of 4.74–5.89 ppm attributed to PCH₂CO group. The former peaks remain unaffected, while the latter peaks show a slight upfield shift to that of PCH₂CO group of the related phosphonium salts due to complexation. In the ¹H NMR spectra of complexes **2**, **8** and **14** a singlet signal around 5.0 ppm attributed to methinic hydrogens of CH₂O group. Signals appeared around 2.4 ppm in the ¹H NMR spectra of complexes **3**, **9** and **15** attributed to methyl group. Rest of the chemical shifts are more or less the same in the ligands and their complexes. These observations support the assigned structure to the complexes. In the ¹³C NMR spectra, signals observed in the complexes due to the various carbons have either remained unaffected or shifted slightly with reference to those of the parent ligands. NMR data for compounds **1–18** and free phosphorus ligands are given in Table 1.

3.3. nuclear magnetic resonance study

³¹P chemical shifts were measured as a function of the mole ratio of complexant some phosphine–phosphonium ligands to mercury(II) halides in dimethylsulfoxide solution. The resulting mole data are shown in Fig. 1. As can be seen in it, in all cases, addition of HgX₂ to the L₅ ligand solution causes an almost linear paramagnetic shift that begins to level off at mole ratio greater than unity. The slope of the corresponding mole ratio plots changes significantly at the point where the cation-to-phosphorus ligand cation mole ratio is equal to one, showing the formation of a relatively stable complex. In general, the behavior of the ³¹P chemical shift as a function of [HgX₂]/[ligand] mole ratio can be approximately divided into two groups:

- 12A gradual paramagnetic shift of the ³¹P resonance with an increase in the mercury(II) halide concentration which does not seem to reach a limiting value even at a mole ratio of 4. Such behavior, which is observed for HgI₂ in all phosphine–phosphonium salt cases (Fig. 1), is indicative of the formation of a weak 1:1 complex.
- The paramagnetic chemical shift varies linearly with the [HgX₂]/[ligand] mole ratio until a mole ratio of about 1 is reached; further increase of the mercury(II) halide does not change the resonance frequency. Such behavior, observed for all HgCl₂ and HgBr₂ complexes except L₂ ligand in solvent, emphasizes the formation of a rather stable 1:1 complex in solution (Fig. 1).

The formation constant of 1:1 complexes are calculated from the variation of ligand chemical shift with the $[HgX_2]/[L]$ mole ratio [40]. The observed chemical shift of the ligand (δ_{obs}) is a mass average of the characteristic chemical shifts of L at each site (i.e. L in the bulk solution and L in the complex). Assuming that a fast exchange occurs between these two sites with respect to the NMR time scale.

 $\delta_{\rm obs} = P_{\rm L} \delta_{\rm L} + P_{\rm (ML)} \delta_{\rm (ML)}$

where δ_L and $\delta_{(ML)}$ are the characteristic chemical shifts for L in the bulk solution and in the complex, respectively and P_L and $P_{(ML)}$ are the respective mole fractions of these species.

Knowing that $P_L + P_{(ML)} = 1$ and $P_L = [L]/C_L$ then:

$$\delta_{\text{obs}} = P_{\text{L}}\delta_{\text{L}} + (1 - P_{\text{L}})\delta_{(\text{ML})} \tag{1.1}$$



Fig. 1. ³¹P chemical shifts as a function of the (a) [HgCl₂]/[L] (b) [HgBr₂]/[L] (c) [HgI₂]/[L] (L = phosphorus ligand), mole ratio in dimethylsulfoxide solvent at 25.0 ± 0.1 °C.

 $\delta_{obs} = P_{L}(\delta_{L} - \delta_{(ML)}) + \delta_{(ML)}$ $\delta_{obs} = \frac{[L]}{C_{L}}(\delta_{M} - \delta_{(ML)}) + \delta_{(ML)}$ (1.2)
(1.3)

$$C_{\rm M} = [\rm M] + [\rm ML] \tag{1.4}$$

$$C_{\rm L} = [\rm L] + [\rm ML] \tag{1.5}$$

$$K_{\rm f} = \frac{[\rm ML]}{[\rm M][\rm L]} \tag{1.6}$$

By substitution of Eqs. (1.4), (1.5) and (1.6) in Eq. (1.3) one obtains the following equation:

$$\begin{split} \delta_{obs} &= \Big\{ [(K_{\rm f}C_{\rm HgX_2} - K_{\rm f}C_L - 1) + (K_{\rm f}^2C_L^2 + K_{\rm f}^2C_{\rm HgX_2}^2 - 2K_{\rm f}^2C_LC_{\rm HgX_2} \\ &+ 2K_{\rm f}C_L + 2K_{\rm f}C_{\rm HgX_2} + 1)^{1/2}](\delta_{\rm L} - \delta_{\rm HgX_2-L})/2K_{\rm f}C_{\rm HgX_2} \Big\} \\ &+ \delta_{\rm HgX_2-L} \end{split}$$
(1.7)

where $K_{\rm f}$ is the formation constant for the 1:1 complex, $C_{\rm L}$ and $C_{\rm Hgx_2}$ are the total concentrations of the phosphine–phosphonium salt and mercury(II) halide, respectively, $\delta_{\rm L}$ is the chemical shift of the uncomplexed ligand and $\delta_{\rm Hgx_2-L}$ is the chemical shift of the complexed ligand. For most complexes $\delta_{\rm Hgx_2-L}$ cannot be obtained directly. In Eq. (1.7) values of $C_{\rm Hgx_2}$, $C_{\rm L}$ and $\delta_{\rm L}$ are known. $\delta_{\rm Hgx_2-L}$ and $K_{\rm f}$ are the two unknowns. These parameters are initially estimated and used to calculate $\delta_{\rm cal}$ for different values of $[\rm HgX_2]/[L]$ mole ratio with the aid of Eq. (1.7). The calculated chemical shifts are iteratively fitted to the observed chemical shifts and values of $\delta_{\rm Hgx_2-L}$



Fig. 2. Computer fit of ³¹P chemical shift vs. $[HgBr_2]/[L_2]$ mole ratio in DMSO. (×) Experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

and K_f are varied to obtain the best fit. A non-linear least-squares program KINFIT [41] was used in the calculations. A sample computer fit of the ³¹P chemical shift-mole ratio data is shown in Fig. 2 and the calculated log K_f values are given in Table 2. A fair agreement between the observed and calculated chemical shifts further supports the formation of a complex with 1:1 stoichiometry between ligand and mercury(II) salts.

The complex stability results from the superposition of several factors including the extent of interaction of phosphorus atom of the ligand with the cation, the consonance between metal ion and ligand, the extent of ligand conformational changes as a consequence of complex formation, desolvation of the ligand and cation and solvation of the resulting complex. The two later factors being Table 2

Cation	Log K _f	Log <i>K</i> _f						
_	L ₁	L ₂	L ₃	L ₄	L ₅	L ₆		
HgCl ₂	2.40 ± 0.04	1.94 ± 0.07	2.51 ± 0.04	2.45 ± 0.05	2.28 ± 0.05	2.17 ± 0.07		
HgBr ₂	1.75 ± 0.02	1.25 ± 0.02	2.25 ± 0.06	1.88 ± 0.03	1.53 ± 0.03	1.41 ± 0.03		
HgI_2	1.62 ± 0.04	1.15 ± 0.03	1.82 ± 0.06	1.73 ± 0.05	1.47 ± 0.04	1.31 ± 0.04		

Formation constants for metal ion complexes with L1, L2, L3, L4, L5 and L6 phosphorus ligands in dimethylsolfuxide at 25 °C.

strongly dependent on the nature of solvent used [42], so that the nature of solvent is expected to affect the overall energy balances involved in the metal ion complexation in solution [30,31,36,43]. It has been well documented that the solvating ability of the solvent, as expressed by the Gutmann donor number [42], plays a key role in different complexation reactions [44–48]. DMSO is a solvent of relatively high solvating ability (DN = 29.8) which can compete with the ligand and counter ion for metal. Thus, it is not surprising to observe the low stability for the all complexes.

The data given in Table 2 clearly indicate that, the stability of all complexes decreases in the order $HgCl_2 > HgBr_2 > Hgl_2$, as it shown in the theoretical studies [49,50]. Thus, there is an important role on complex stability constant for halides. In DMSO solution, the stabilities of 1:1 complexes of mercury(II) salts with different phosphine-phosphonium salts decrease in the order $L_3 > L_4 > L_1 > L_5 > L_6 > L_2$. In all cases, the presence of different groups in ligands can inductively enhance the electron density of the phosphinephosphonium salts and thus increases the basicity of the donate atom of ligands, while the flexibility of phosphorus moiety is the same as the others. It has been shown that, the complexation ability of HgX₂ to ligand can be considerably increased by attaching different endgroups to the ligand backbone. In fact, the stability of their complexes arises from the two type centers: the phosphorus moiety and the aromatic residue which controls the strength of complexation by donor-electron interactions, steric influences and supplying two phosphorus atoms [32]. Subsequently, the metal ion is surrounded by the flexible phosphorus chain, which can easily adapt to mercury(II) cation sizes, and is better shielded from the solvent and the counter ions by terminal different aromatic groups [51,52].

4. Conclusion

The present study describes the synthesis and characterization of a series of mercury(II) complexes derived from mercury halides and non-symmetric phosphorus ligands. On the basis of the physicochemical and spectroscopic data we propose that ligands herein exhibit a P-coordination behavior to the metal center affording a zwitterionic complexes. The complexation reaction between the Hg(II) ion, with different counter ions, with some posphoruse ligands in DMSO solvent was studied by ³¹PNMR spectroscopy. In all studied cases, the variation of ³¹P chemical shift with the [M]/ [L] mole ratio indicated the formation of 1:1 complexes. The data given in Table 2 shows that, the stability of all complexes decreases in the order $HgCl_2 > HgBr_2 > HgI_2$ in DMSO as a solvent of higher solvating ability can compare with L for the metal as a poor solvating solvent. These results clearly illustrate the fundamental role of the various counter ions on complex stability constant. In all cases, the stabilities of the resulting 1:1 complexes varied in the order $L_3 > L_4 > L_1 > L_5 > L_6 > L_2$.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013. 02.042.

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