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New Homodinuclear Alkyl- and Aryl- Dithiophosphonato Cd(II) and Hg(II) complexes: Syntheses and Characterizations

Ertuğrul Gazi Sağlam[1*], Elif Bulat[1], Nurcan Acar[2] and İbrahim Demirel[1]

[1] University of Yozgat Bozok, Department of Chemistry, 66900, Yozgat, Turkey,
[2] University of Ankara, Department of Chemistry, 06100 Tandoğan, Ankara, Turkey

Abstract: New Cd(II) and Hg(II) complexes of five previously known dithiophosphonic acids ((p-MeO-C_6H_4)PS(SH)(OR), HL^n, (n= 1-5); R= 3-pentyl-, HL^1; R=1-phenyl-1-propyl-, HL^2; R= 4-*tert*-butylbenzyl-, HL^3; R= diphenylmethyl-, HL^4; R= 4-*tert*-butylcyclohexyl-, HL^5) were prepared and characterized. To do this, the dithiophosphonic acids involved were treated with stoichiometric amount of the corresponding metal salts in methyl alcohol. The complexes came of as powdery crystals and were recrystallized from chloroform. The pure complexes were characterized by using elemental analyses as well as mass-(ESI), FTIR-, Raman-, NMR- (^1H, ^{13}C, ^{31}P) spectroscopies.

Keywords: Dithiophosphonic Acid, Phosphonodithioic Acid, Dithiophosphonate Complexes, Lawesson's Reagent.

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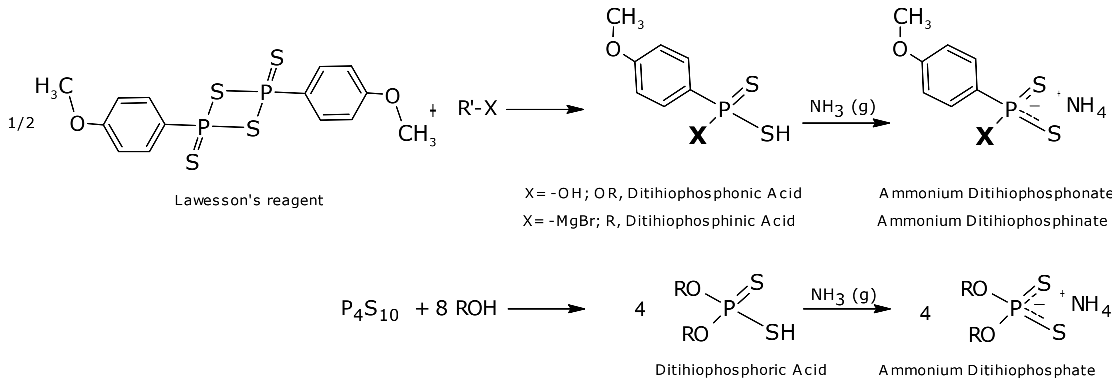
***Corresponding author. E-mail:** ertugrulgazi.saglam@bozok.edu.tr

INTRODUCTION

Dithiophosphate (phosphorodithioate, $(RO)_2PS_2^-$), dithiophosphonate (phosphonodithioate, (R)(R'O)PS_2^-) and dithiophosphinate (phosphinodithioate, (R)(R')PS_2^-) type ligands are an important class of phosphorus-sulfur compounds and collectively named as phosphoro-1,1-dithiolates (1). The three types of compounds are synthesized through the reactions of either the so-called Lawesson's reagent (2) (LR, 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide), or the Berzelius' reagent (P_4S_{10}, tetraphosphorus pentasulfide) (3). Dithiophosphates require the use of P_4S_{10} and the corresponding alcohol as starting material (4) while the dithiophosphonates and dithiophosphinates are obtained by the reaction of LR with a nucleophilic agent, an alcohol for dithiophosphonates (5) and a carbo-anion for dithiophosphinates (6). The dithiophosphoric (DTP), dithiophosphonic (DTPOA) and dithiophosphinic (DTPA) acids themselves are either liquids or else, difficult to crystallize as they are hygroscopic. Besides, all these compounds have disagreeable odors, and they have been found to be suitable to convert to their ammonium salts (7), which are easy to crystallize. As an example, the synthesis of dithiophosphonic acid ammonium salts is given in Scheme 1.



Scheme 1. Synthesis reaction of phosphor-1,1-dithiolates.

The dithiophosphonato groups are typical, soft base type ligands and naturally prone to be coordinated to transition metal cations of relatively lower charges (8,9). Generally, the reaction of the proper metal salts with the corresponding ammonium dithiophosphonate in an organic solvent (8) to obtained complexes. Alternatively, a one-pot reaction starting with the corresponding LR which is categorized perthiophosphonic acid (PTFA), nucleophile and metal salt sometimes proves to be preferable (10).

The dithiophosphonate anions act as bidentate ligands, because the negative charge is delocalized over the two sulfur atoms (11).

The coordination topology of the complexes formed is related to the nature of the metal cation. Group 10 metals tend to form monomeric complexes of the general formula $[M(DTPOA)]_2$ with square planar geometries (12), whereas Group 12 metals form dimeric complexes of the general formula $[M_2(\mu\text{-}DTPOA^n)_2(DTPOA^n)_2]$ and tetrahedral geometries. In these dimeric complexes, some of the sulfur atoms act as bridging ligands. As shown in Figure 1, the dimeric structure has an eight-membered ring comprising two metals, two phosphorus and four sulfur atoms (13).

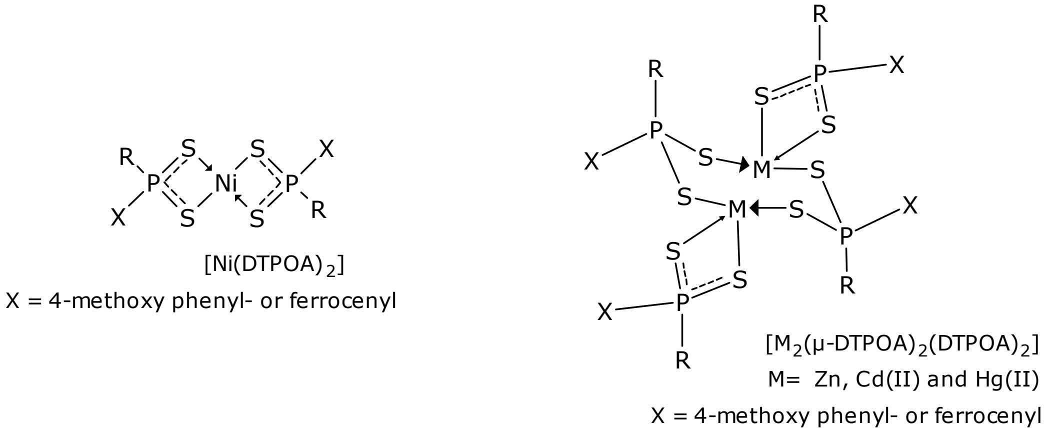
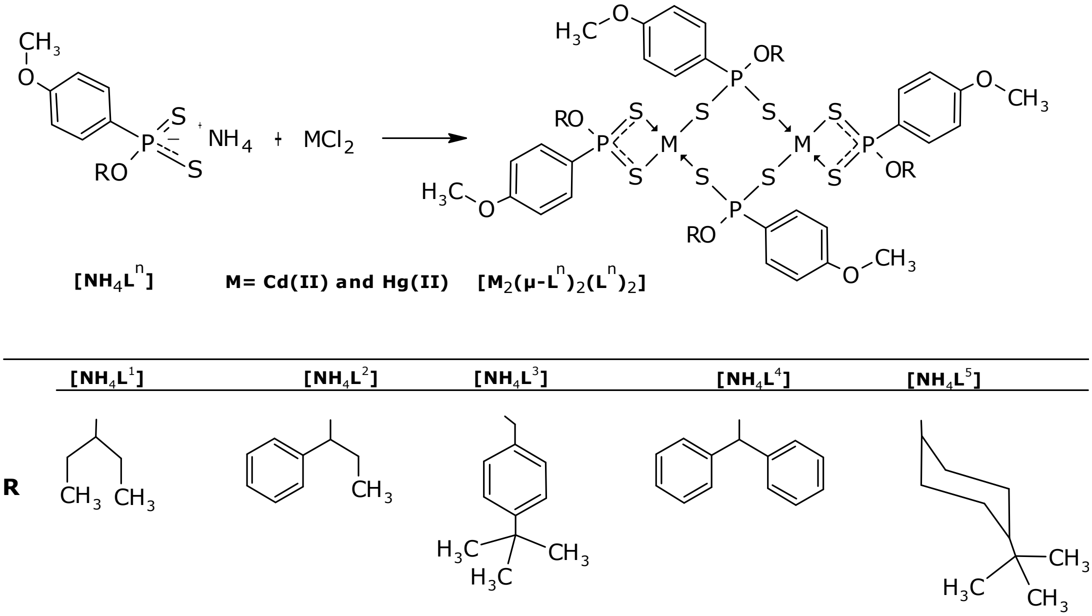


Figure 1. Structures of Group 10 and Group 12 DTPOA complexes.

Due to their affinity to transition metals, lipophilic phosphorus-dithiolate ligands are designed to prepare stable metal chelates complexes that are extractable into nonpolar organic media. These ligands are used in the mining industry as flotation aids (14,15). Other applications that are DTPOA and their complexes including lubricants anti-wear additives (16,17) and agricultural pesticides (18) are also reported. Investigations are also underway to design molecular complexes of radioactive transition metal cations to introduce into the human body for medical imaging (19-21). Some of tin DTPOA complexes are effective in chemotherapy (22) while some cadmium DTPOA complexes show antibacterial effect (23).

Among the transition metal-DTPOA complexes, the Ni(II)-DTPOAs are the most extensively studied species (8,9) while studies on Cd(II)- and Hg(II)-DTPOAs are relatively scarce (13). Therefore, we have focused on the synthesis of Cd(II)- and Hg(II)-DTPOA complexes. In this study, we prepared the cadmium and mercury complexes of five, already known dithiophosphonate ligands (24) and characterized them by using elemental analyses, mass spectroscopic (ESI), Infrared spectroscopic (FT-IR), Raman spectroscopic, ^{1}H-NMR, ^{13}C-NMR ve ^{31}P-NMR data. The general reaction used for the synthesis is shown in Scheme 2.



Scheme 2. Synthesis reaction of cadmium(II) and mercury(II) dithiophosphonato complexes.

EXPERIMENTAL

Materials and instruments

Ethanol, $CdCl_2.H_2O$ and $HgCl_2$ were purchased from Sigma-Aldrich. Ammonium dithiophosphonates ([NH$_4$L^n], n= 1-5) were synthesized as described in the literature (24).

Microanalyses were carried out using a LECO CHNS-932 CHNS-O elemental analyzer.

Melting points were measured by an Electrothermal 9200 melting point apparatus.

Vibrational spectra were recorded on a Perkin Elmer Spectrum Two Model FT-IR Spectrometer using the ATR method (200–4000 cm^{-1}) and are presented in cm^{-1} units. Raman spectra were run in the range 4000–100 cm^{-1}, using a Renishaw in-Via Raman microscope, with a Peltier-cooled CCD detector (−70°C). The Raman microscope was equipped with a 50X objective. The excitation was carried out by the 785 lines of a diode laser.

The LC/MS spectra were obtained on a Waters Micromass ZQ connected to a Waters Alliance HPLC (C-18 column), using an ESI(+) ionizer.

^{1}H- (400 MHz), ^{13}C- (100 MHz) and ^{31}P-NMR (160 MHz) spectra were performed by using a Varian Mercury (Agilent) FT spectrometer in $CDCl_3$. $SiMe_4$ was used for ^{1}H-NMR and ^{13}C-NMR while 85% H_3PO_4 was used for ^{31}P- NMR as chemical shift standards. Chemical shifts (δ) are reported in ppm.

Syntheses of compounds

General Procedure of [Cd$_2$(μ-L^n)$_2$(L^n)$_2$] and [Hg$_2$(μ-L^n)$_2$(L^n)$_2$]

To an ethanolic solution of 4.70 mmoles of the [NH$_4$L^n] of interest (1.45 g of [NH$_4$L^1] and [NH$_4$L^2]; 1.68 g of [NH$_4$L^3]; 1.80 g of [NH$_4$L^4] and 1.80 g of [NH$_4$L^5]) were added 2.35 mmol of metal(II) chloride (0.48 g of $CdCl_2.H_2O$; 0.64 g of $HgCl_2$) dissolved in 50-60 mL of ethanol. The solution was stirred at room temperature for 15 min. The white complex participated is filtered through filter paper and dried in a vacuum desiccator.

Bis-{bis-[O-3-pentyl-(4-methoxyphenyl)dithiophosphonato]cadmium(II)}, [Cd$_2$(μ-L^1)$_2$(L^1)$_2$]

Yield: 0.25 g (71%). Yellow. m.p. 177-178°C, (decomposition). ^{1}H NMR (δ:ppm, $CDCl_3$): δ=

0.94 (t, $^3J_{HH}$= 7.5 Hz, 24H, C8-H), 1.77 (m, 16H, C7-H), 4.8 (m, 4H, C6-H), 3.83 (s, 12H, OCH$_3$), 6.93 (A-part of AA′MM′X, $^4J_{PH}$= 3.3 Hz (J_{AX}), *N*= 8.8 Hz, 8H, *m*-H), 8.01 (M-part of AA′MM′X, $^3J_{PH}$= 14.5 Hz (J_{MX}), *N*= 8.8 Hz, 8H, *o*-H). ^{13}C-NMR (CDCl$_3$): δ= 9.3 (s, C8), 27.1 (d, $^3J_{P-C}$= 4.0 Hz, C7), 81.1 (d, $^2J_{PC}$= 8.2 Hz, C6), 55.4 (s, $\underline{C}$H$_3$O-), 113.5 (d, $^3J_{P-C}$= 16.2 Hz, C3), 132.2 (d, $^2J_{P-C}$ = 14.2, C2) Hz, 132.2 (d, J_{P-C}= 123.9 Hz, C1) 162.3 (d, $^4J_{PC}$= 3.3, C4). ^{31}P-NMR (CDCl$_3$): δ= 103.42. LC/MS: m/z 1406.2 ([M+Na]$^+$, 2%), 1093.1 ([M-L^1]$^+$, 100%), 689.1 ([M/2]$^+$, 29%). Anal. Calcd. for: $C_{48}H_{72}Cd_2O_8P_4S_8$ (1382.32g.mol^{-1}): C, 41.71; H, 5.25; S, 18.56; found: C, 41.82; H, 5.29; S, 18.79 %.

Bis-{bis-[O-1-phenyl-1-propyl-(4-methoxyphenyl)dithiophosphonato]cadmium(II)}, [Cd$_2$(μ-L^2)$_2$(L^2)$_2$]
Yield: 0.29 g (74%). White. m.p. 137-138°C, (decomposition). ^{1}H NMR (δ:ppm, CDCl$_3$): δ= 0.87 (t, $^3J_{HH}$= 7.4 Hz, 12H, C8-H), 2.01 (m, 8H, diastereotopic protons, C7-H), 5.70 (m, 4H, C6-H), 3.80 (s, 12H, OCH$_3$), 6.93 (A-part of AA′MM′X, $^4J_{PH}$= 3.2 Hz (J_{AX}), *N*= 8.8 Hz, 8H, *m*-H), 7.28 (m, 20H, Ar-CH), 7.93 (M-part of AA′MM′X, $^3J_{PH}$= 14.6 Hz (J_{MX}), *N*= 8.8 Hz, 8H, *o*-H). ^{13}C-NMR (CDCl$_3$): δ= 9.8 (s, C8), 31.4 (d, $^3J_{P-C}$= 5.4 Hz, C7), 80.8 (d, $^2J_{PC}$= 7.3 Hz, C6), 55.4 (s, $\underline{C}$H$_3$O-), 113.5 (d, $^3J_{P-C}$= 16.3 Hz, C3), 126.9 (s, C12), 127.5 (s, C11), 128.1 (s, C10), 129.0 (d, J_{P-C}= 122.7 Hz, C1), 132.4, 140.9 (d, $^2J_{PC}$= 3.1 Hz, C9), (d, $^2J_{P-C}$ = 14.4 Hz, C2), 162.4 (d, $^4J_{PC}$= 3.3, C4). ^{31}P-NMR (CDCl$_3$): δ= 104.58. LC/MS: m/z 1597.3 ([M+Na]$^+$, 29%), 1237.3 ([M-L^2]$^+$, 100%), 810.2 ([M/2]$^+$, 36%). Anal. Calcd. for: $C_{64}H_{72}Cd_2O_8P_4S_8$ (1574.49 g.mol^{-1}): C, 48.82; H, 4.61; S, 16.29; found: C, 49.01; H, 4.67; S, 16.56 %.

Bis-{bis-[O-4-*tert*-butylbenzyl-(4-methoxyphenyl)dithiophosphonato]cadmium(II)}, [Cd$_2$(μ-L^3)$_2$(L^3)$_2$]
Yield: 0.32 g (80%). White. m.p. 189-200°C, (decomposition). ^{1}H NMR (δ:ppm, CDCl$_3$): δ= 1.32 (s, 36H, C12), 5.34 (m, 8H, C6-H), 3.83 (s, 12H, OCH$_3$), 6.94 (A-part of AA′MM′X, $^4J_{PH}$= 3.3 Hz (J_{AX}), *N*= 8.7 Hz, 8H, *m*-H), 7.35 (m, 16H, Ar-CH), 8.00 (M-part of AA′MM′X, $^3J_{PH}$= 14.5 Hz (J_{MX}), *N*= 8.7 Hz, 8H, *o*-H). ^{13}C-NMR (CDCl$_3$): δ= 31.3 (s, C12), 34.6 (s, C11), 55.4 (s, $\underline{C}$H$_3$O-), 67.6 (d, $^2J_{P-C}$ = 6.7 Hz, C6), 113.7 (d, $^3J_{P-C}$= 16.3 Hz, C3), 125.3 (s, C9), 130.7 (s, C8), 132.5 (d, $^2J_{PC}$= 14.5 Hz, C2), 128.4 (d, J_{P-C}= 121.7 Hz, C1), 133.1 (d, $^3J_{P-C}$ = 9.9 Hz, C7), 151.2 (s, C10), 162.6 (d, $^4J_{PC}$= 3.2, C4). ^{31}P-NMR (CDCl$_3$): δ= 106.20. LC/MS: m/z 1687.90 ([M]$^+$, 17%), 1321.4 ([M-L^3]$^+$, 100%), 843.4 ([M/2]$^+$, 55%), 479.3 ([CdL^3]$^+$, 36%). Anal. Calcd. for: $C_{72}H_{88}Cd_2O_8P_4S_8$ (1686.70 g.mol^{-1}): C, 51.27; H, 5.26; S, 15.21; found: C, 51.33; H, 5.29; S, 15.39 %.

Bis-{bis-[O-di-phenylmethyl-(4-methoxyphenyl)dithiophosphonato]cadmium(II)}, [Cd$_2$(μ-L^4)$_2$(L^4)$_2$]
Yield: 0.28 g (68%). White. m.p. 101-102°C, (decomposition). ^{1}H NMR (δ:ppm, CDCl$_3$): 7.28 (s, 40H, Ar-CH), 7.93 (A-part of AA′MM′X, $^4J_{PH}$= 14.7 Hz (J_{AX}), *N*= 8.8 Hz, 8H, *m*-H), 7.28 (m, 16H, Ar-CH), 6.93 (d, $^3J_{PH}$= 16.4 Hz 4H, C6H), 6.79 (M-part of AA′MM′X, $^3J_{PH}$= 3.3 Hz (J_{MX}), *N*= 8.8 Hz, 8H, *o*-H), 3.78 (s, 12H, OCH$_3$). ^{13}C-NMR (CDCl$_3$): δ= 55.4 (s, $\underline{C}$H$_3$O-), 79.6 (d, $^2J_{P-C}$ = 6.9, C6) Hz, 113.6 (d, $^3J_{P-C}$= 16.1 Hz, C3), 127.5 (s, C9), 127.6 (s, C10), 128.2 (s, C8), 129.6 (d, J_{P-C}= 121.5 Hz, C1), 132.3 (d, $^2J_{PC}$= 14.3 Hz, C2), 141.0 (d, $^3J_{P-C}$ = 4.6 Hz, C7), 162.4 (d, $^4J_{PC}$= 3.3 Hz, C4). ^{31}P-NMR (CDCl$_3$): δ= 106.25. LC/MS: m/z 1787.80 ([M+Na]$^+$, 31%), 907.9 ([M/2+Na]$^+$, 32%), 575.9 ([Cd$_2$P$_3$S$_8$]$^+$, 100%). Anal. Calcd. for: $C_{80}H_{72}Cd_2O_8P_4S_8$ (1766.66 g.mol^{-1}): C, 54.39; H, 4.11; S, 14.52; found: C, 54.47; H, 4.14; S, 14.77 %.

Bis-{bis-[O-4 *tert*-butylcyclohexyl-(4-methoxyphenyl)dithiophosphonato]cadmium(II)}, [Cd$_2$(μ-L^5)$_2$(L^5)$_2$]
Yield: 0.32 g (78%). White. m.p. 115-116°C, (decomposition). ^{1}H NMR (δ:ppm, CDCl$_3$): δ= 0.82 (m, 36H, C11-H), 0.96 (m, 4H, C9-H), 1.11 (m, 8H, C8′-H), 1.43 (m, 8H, C8-H), 1.74 (m, 8H, C7′-H), 2.25 (m, 8H, C7-H), 3.83 (m, 16H, C6-H overlapped with OCH$_3$), 6.92 (A-part of AA′MM′X, $^4J_{PH}$= 3.3 Hz (J_{AX}), *N*= 8.8 Hz, 8H, *m*-H), 7.99 (M-part of AA′MM′X, $^3J_{PH}$= 14.5 Hz (J_{MX}), *N*= 8.8 Hz, 8H, *o*-H). ^{13}C-NMR (CDCl$_3$): δ= 25.7 (s, C8), 27.6 (s, C11), 32.3 (s, C10), 46.9 (s, C9), 34.2 (s, C7), 78.1 (d, $^2J_{PC}$= 7.9 Hz, C6), 55.4 (s, $\underline{C}$H$_3$O-), 113.6 (d, $^3J_{P-C}$= 16.1 Hz, C3), 129.6 (d, J_{P-C}= 121.5 Hz, C1), 132.3 (d, $^2J_{P-C}$ = 14.3 Hz, C2), 162.4 (d, $^4J_{PC}$= 3.3, C4). ^{31}P-NMR (CDCl$_3$): δ= 102.65. LC/MS: m/z 1679.1 ([M+Na]$^+$, 28%), 1297.1 ([M-L^5]$^+$, 35%), 827.9 ([M/2]$^+$, 32%), 512.8 ([Cd$_2$PS$_8$]$^+$, 100%). Anal. Calcd. for: $C_{68}H_{104}Cd_2O_8P_4S_8$ (1654.79 g.mol^{-1}): C, 49.36; H, 6.33; S, 15.50; found: C, 49.52; H, 6.39; S, 15.71 %.

Bis-{bis-[O-3-pentyl-(4-methoxyphenyl)dithiophosphonato]mercury(II)},
[Hg$_2$(μ-L^1)$_2$(L^1)$_2$]
Yield: 0.27 g (69%). White. m.p. 125-126°C, (decomposition). ^{1}H NMR (δ:ppm, CDCl$_3$): δ= 0.99 (t, $^3J_{HH}$= 7.5 Hz, 24H, C8-H), 1.83 (m, 16H, C7-H), 4.8 (m, 4H, C6-H), 3.85 (s, 12H,

OCH$_3$), 6.96 (A-part of AA′MM′X, $^4J_{PH}$= 3.4 Hz (J_{AX}), *N*= 8.6 Hz, 8H, *m*-H), 8.6 (M-part of AA′MM′X, $^3J_{PH}$= 14.5 Hz (J_{MX}), *N*= 8.6 Hz, 8H, *o*-H). ^{13}C-NMR (CDCl$_3$): δ= 9.4 (s, C8), 27.1 (s, C7), 81.4 (d, $^2J_{PC}$= 8.0 Hz, C6), 58.4 (s, $\underline{C}H_3O$-), 113.7 (d, $^3J_{P\text{-}C}$= 16.3 Hz, C3), 131.9 (d, $^2J_{P\text{-}C}$ = 14.0 Hz, C2) Hz, 130.1 (d, $J_{P\text{-}C}$= 126.6 Hz, C1) 162.4 (d, $^4J_{PC}$= 3.3, C4). ^{31}P-NMR (CDCl$_3$): δ= 100.63. LC/MS: m/z 1581.8 ([M+Na]$^+$, 100%), 1268.8 ([M-L^1]$^+$, 35%), 803.0 ([M/2]$^+$, 47%). Anal. Calcd. for: $C_{48}H_{72}Hg_2O_8P_4S_8$ (1558.68g.mol^{-1}): C, 39.99; H, 4.66; S, 16.46; found: C, 40.13; H, 4.70; S, 16.59 %.

Bis-{bis-[O-1-phenyl-1-propyl-(4-methoxyphenyl)dithiophosphonato]mercury(II)},
$[Hg_2(\mu\text{-}L^2)_2(L^2)_2]$
Yield: 0.21 g (48%). White. m.p. 90-91°C, (decomposition). ^{1}H NMR (δ:ppm, CDCl$_3$): δ= 0.94 (t, $^3J_{HH}$= 7.4 Hz, 12H, C8-H), 2.03 (m, 8H, diastereotopic protons, C7-H), 5.84 (m, 4H, C6-H), 3.85 (s, 12H, OCH$_3$), 6.93 (A-part of AA′MM′X, $^4J_{PH}$= 3.4 Hz (J_{AX}), *N*= 8.9 Hz, 8H, *m*-H), 7.31 (m, 20H, Ar-CH), 7.93 (M-part of AA′MM′X, $^3J_{PH}$= 14.4 Hz (J_{MX}), *N*= 8.9 Hz, 8H, *o*-H). ^{13}C-NMR (CDCl$_3$): δ= 9.8 (s, C8), 31.2 (s, C7), 55.4 (s, $\underline{C}H_3O$-), 81.2 (s, C6), 113.7 (d, $^3J_{P\text{-}C}$= 16.3 Hz, C3), 127.1 (s, C12), 127.9 (s, C11), 128.4 (s, C10), 129.5 (d, $J_{P\text{-}C}$= 125.3 Hz, C1), 132.0, (d, $^2J_{P\text{-}C}$ = 14.2 Hz, C2), 140.6 (d, $^2J_{PC}$= 3.0 Hz, C9), 162.5 (d, $^4J_{PC}$= 3.4, C4). ^{31}P-NMR (CDCl$_3$): δ= 106.20. LC/MS: m/z 1413.3 ([M-L^2]$^+$, 32%), 339.2 ([L^2]$^+$, 28%), 233.0 ([HgS]$^+$, 100%). Anal. Calcd. for: $C_{64}H_{72}Hg_2O_8P_4S_8$ (1750.85 g.mol^{-1}): C, 43.90; H, 4.14; S, 14.65; found: C, 43.97; H, 4.16; S, 14.77 %.

Bis-{bis-[O-4-*tert*-butylbenzyl-(4-methoxyphenyl)dithiophosphonato]mercury(II)}, $[Hg_2(\mu\text{-}L^3)_2(L^3)_2]$
Yield: 0.36 g (78%). White. m.p. 138-139°C, (decomposition). ^{1}H NMR (δ:ppm, CDCl$_3$): δ= 1.32 (s, 36H, C12), 5.4 (m, 8H, C6-H), 3.83 (s, 12H, OCH$_3$), 6.94 (A-part of AA′MM′X, $^4J_{PH}$= 3.3 Hz (J_{AX}), *N*= 8.7 Hz, 8H, *m*-H), 7.35 (m, 16H, Ar-CH), 8.00 (M-part of AA′MM′X, $^3J_{PH}$= 14.5 Hz (J_{MX}), *N*= 8.7 Hz, 8H, *o*-H). ^{13}C-NMR (CDCl$_3$): δ= 30.9 (s, C12), 34.6 (s, C11), 55.4 (s, $\underline{C}H_3O$-), 67.6 (d, $^2J_{P\text{-}C}$ = 6.5 Hz, C6), 113.8 (d, $^3J_{P\text{-}C}$= 16.3 Hz, C3), 125.5 (s, C9), 128.1 (s, C8), 132.3 (d, $^2J_{PC}$= 14.3 Hz, C2), 129.3 (d, $J_{P\text{-}C}$= 124.2 Hz, C1), 133.0 (d, $^3J_{P\text{-}C}$ = 9.8 Hz, C7), 151.4 (s, C10), 162.7 (d, $^4J_{PC}$= 3.3, C4). ^{31}P-NMR (CDCl$_3$): δ= 103.94. LC/MS: m/z 1498.6 ([M-L^3]$^+$, 100%), 932.6 ([M/2]$^+$, 20%). Anal. Calcd. for: $C_{72}H_{88}Hg_2O_8P_4S_8$ (1683.01 g.mol^{-1}): C, 46.42; H, 4.76; S, 13.77; found: C, 46.57; H, 4.83; S, 13.97 %.

Bis-{bis-[O-di-phenylmethyl-(4-methoxyphenyl)dithiophosphonato]mercury(II)}, $[Hg_2(\mu\text{-}L^4)_2(L^4)_2]$
Yield: 0.24 g (49%). White. m.p. 89-90°C, (decomposition). ^{1}H NMR (δ:ppm, CDCl$_3$): δ= 7.36 (s, 40H, Ar-CH), 7.92 (A-part of AA′MM′X, $^4J_{PH}$= 14.6 Hz (J_{AX}), *N*= 8.7 Hz, 8H, *m*-H), 7.28 (m, 16H, Ar-CH), 6.98 (d, 4H, C6 adjacent with Ar$_{meta}$), 6.92 (M-part of AA′MM′X, $^3J_{PH}$= 3.4 Hz (J_{MX}), *N*= 8.7 Hz, 8H, *o*-H adjacent with C6), 3.84 (s, 12H, OCH$_3$). ^{13}C-NMR (CDCl$_3$): δ= 55.4 (s, $\underline{C}H_3O$-), 80.1 (d, $^2J_{P\text{-}C}$ = 6.4, C6) Hz, 113.7 (d, $^3J_{P\text{-}C}$= 16.4 Hz, C3), 127.6 (s, C9), 128.0 (s, C10), 128.5 (s, C8), 129.5 (d, $J_{P\text{-}C}$= 125.0 Hz, C1), 132.0 (d, $^2J_{PC}$= 14.3 Hz, C2), 140.6 (s, C7), 162.6 (d, $^4J_{PC}$= 3.3, C4). ^{31}P-NMR (CDCl$_3$): δ= 102.22. LC/MS: m/z 1381.6 ([(M-HgL^4)+Na]$^+$, 29%), 996.1 ([M/2+Na]$^+$, 47%), 575.9 ([HgP_2S_4-O-$CH_2(C_6H_4)_2$]$^+$, 100%). Anal. Calcd. for: $C_{80}H_{72}Hg_2O_8P_4S_8$ (1943.02 g.mol^{-1}): C, 49.45; H, 3.73; S, 13.20; found: C, 49.63; H, 3.78; S, 13.41 %.

Bis-{bis-[O-4-*tert*-butylcyclohexyl-(4-methoxyphenyl)dithiophosphonato]mercury(II)}, $[Hg_2(\mu\text{-}L^5)_2(L^5)_2]$
Yield: 0.18 g (39%). White. m.p. 84-85°C, (decomposition). ^{1}H NMR (δ:ppm, CDCl$_3$): δ= 0.85 (m, 36H, C11-H), 1.01 (m, 4H, C9-H), 1.24 (m, 8H, C8′-H), 1.50 (m, 8H, C8-H), 1.82 (m, 8H, C7′-H), 2.34 (m, 8H, C7-H), 3.85 (m, 16H, C6-H overlapped with OCH$_3$), 7.00 (A-part of AA′MM′X, $^4J_{PH}$= 3.4 Hz (J_{AX}), *N*= 8.8 Hz, 8H, *m*-H), 8.04 (M-part of AA′MM′X, $^3J_{PH}$= 14.4 Hz (J_{MX}), *N*= 8.8 Hz, 8H, *o*-H). ^{13}C-NMR (CDCl$_3$): δ= 25.7 (s, C8), 25.7 (s, C11), 32.3 (s, C10), 46.4 (s, C9), 34.2 (s, C7), 78.2 (s, C6), 55.4 (s, $\underline{C}H_3O$-), 113.7 (d, $^3J_{P\text{-}C}$= 16.2 Hz, C3), 129.7 (d, $J_{P\text{-}C}$= 124.6 Hz, C1), 132.1 (d, $^2J_{P\text{-}C}$ = 14.1 Hz, C2), 162.8 (s, C4). ^{31}P-NMR (CDCl$_3$): δ= 101.05. LC/MS: m/z 1854.3 ([M+Na]$^+$, 23%), 1268.8 ([M-L^5]$^+$, 31%), 350.9 ([HgS_4+Na]$^+$, 100%). Anal. Calcd. for: $C_{68}H_{104}Hg_2O_8P_4S_8$ (1831.14 g.mol^{-1}): C, 44.60; H, 5.72; S, 14.01; found: C, 44.67; H, 5.74; S, 14.15 %.

RESULTS AND DISCUSSION

Spectroscopic studies

IR and Raman spectra

IR and Raman spectra are expected to bear evidence about the existence of PS and M-S bonds in the structures of the complexes. Indeed, $\nu(PS)_{asym}$ and $\nu(PS)_{sym}$ bands as well as a couple of bands another relating to the coordination, namely, $\nu(M\text{-}S)_{asym}$) and $\nu(M\text{-}S)_{sym}$ are clearly visible in both the spectra as listed in Table 1.

Table 1: Selected IR and Raman (R) data (cm^{-1}) assignment of vibrational bands for the complexes.

Complex	**$\nu(Cd\text{-}S)_{sym}$**		**$\nu(Cd\text{-}S)_{asym}$**		**$\nu(PS)_{sym}$**		**$\nu(PS)_{asym}$**	
	IR	**R**	**IR**	**R**	**IR**	**R**	**IR**	**R**
$[Cd_2(\mu\text{-}L^1)_2(L^1)_2]$	286	288	340	341	539	552	660;647	664;635
$[Cd_2(\mu\text{-}L^2)_2(L^2)_2]$	283	285	362	366	536	542	676;648	680;635
$[Cd_2(\mu\text{-}L^3)_2(L^3)_2]$	293;308	292;307	393	393	543	550	661;646	666;635
$[Cd_2(\mu\text{-}L^4)_2(L^4)_2]$	295	292	347	347	555;517	564;523	620	618
$[Cd_2(\mu\text{-}L^5)_2(L^5)_2]$	267	289	294	414	582	540;524	663	664

Complex	**$\nu(Hg\text{-}S)_{sym}$**		**$\nu(Hg\text{-}S)_{asym}$**		**$\nu(PS)_{sym}$**		**$\nu(PS)_{asym}$**	
	IR	**R**	**IR**	**R**	**IR**	**R**	**IR**	**R**
$[Hg_2(\mu\text{-}L^1)_2(L^1)_2]$	389	311	386	310	555	541	629	633
$[Hg_2(\mu\text{-}L^2)_2(L^2)_2]$	335	330	363	350	563	569	637	619
$[Hg_2(\mu\text{-}L^3)_2(L^3)_2]$	363	363	394	389	544	547	645	641
$[Hg_2(\mu\text{-}L^4)_2(L^4)_2]$	382	378	417	407	547	547	622	619
$[Hg_2(\mu\text{-}L^5)_2(L^5)_2]$	356	357	389	389	579	582	627	629

Meanwhile, the N-H stretching signal does not exist in the vibrational spectra of the complexes, indicating that the ammonium salt is no longer present (24).

IR and Raman data reported for similar compounds agree well with the signals (24-29).

Mass Spectra

The main features of the mass spectra for the complexes are given in Table 2.

The natural abundance of cadmium and mercury, as well as sulfur isotopes, are reflected in the appearance of the peaks. Some mass peaks have the mass to charge values that are 23 units higher than the molecular mass, related to the leaving group. This discrepancy is suggested to have come from the Na^+ ions that may have detached from the buffer solution used in the ionizer. The compounds $[Cd_2(\mu\text{-}L^1)_2(L^1)_2]$, $[Cd_2(\mu\text{-}L^2)_2(L^2)_2]$, $[Cd_2(\mu\text{-}L^3)_2(L^3)_2]$ and $[Hg_2(\mu\text{-}L^3)_2(L^3)_2]$ display mass signals corresponding to the molecule minus a single ligand but the disintegration patterns of the other six complexes do not appear to show any commentable feature. For these complexes, the molecular ion peaks are the sole usable information.

The molecular ion peaks corresponding to the dimeric $[Cd_2(\mu\text{-}L^n)_2(L^n)_2]$ complexes are relatively weak but visible anyway. On the other hand, Hg(II) complexes, except for $[Hg_2(\mu\text{-}L^1)_2(L^1)_2]$ and $[Hg_2(\mu\text{-}L^5)_2(L^5)_2]$ do not display any molecular ion peak at all. The molecular peak of $[Hg_2(\mu\text{-}L^1)_2(L^1)_2]$ is extraordinarily intense (the main peak actually). Mass spectral data reported for similar compounds agree well (30-33) with the signals we observed.

Table 2: MS spectral data for the complexes.

			Removing groups from $[M]^+$	
	$[M]^+$	**m/z 100 % Intensity**	**$[M-L^n]^+$**	**$[M/2]^+$**
$[Cd_2(\mu-L^1)_2(L^1)_2]$	1406.2, $[M+Na]^+$; 2%	1093.1, $[M-L^1]^+$; 100%		689.1, $[M/2]^+$; 29%
$[Cd_2(\mu-L^2)_2(L^2)_2]$	1597.3, $[M+Na]^+$; 29%	1237.3, $[M-L^2]^+$; 100%		810.2, $[M/2]^+$; 36%
$[Cd_2(\mu-L^3)_2(L^3)_2]$	1687.90, $[M]^+$; 17%	1321.4, $[M-L^3]^+$; 100%		843.4, $[M/2]^+$; 55%
$[Cd_2(\mu-L^4)_2(L^4)_2]$	1787.80, $[M+Na]^+$; 31%	575.9, $[Cd_2P_3S_8]^+$; 100%	-	907.9, $[M/2+Na]^+$; 32%
$[Cd_2(\mu-L^5)_2(L^5)_2]$	1679.1, $[M+Na]^+$; 28%	512.8, $[Cd_2PS_8]^+$; 100%	1297.1, $[M-L^5]^+$; 35%	827.9, $[M/2]^+$; 32%
$[Hg_2(\mu-L^1)_2(L^1)_2]$	1581.8, $[M+Na]^+$; 100%		1268.8, $[M-L^1]^+$; 35%	803.0, $[M/2]^+$; 47%
$[Hg_2(\mu-L^2)_2(L^2)_2]$	-	233.0, $[HgS]^+$; 100%	1413.3, $[M-L^2]^+$; 32%	-
$[Hg_2(\mu-L^3)_2(L^3)_2]$	-	1498.6, $[M-L^3]^+$, 100%		932.6, $[M/2]^+$; 20%
$[Hg_2(\mu-L^4)_2(L^4)_2]$	-	575.9, $[HgP_2S_4\text{-}O\text{-}CH_2(C_6H_4)_2]^+$; 100%	-	996.1, $[M/2+Na]^+$; 47%
$[Hg_2(\mu-L^5)_2(L^5)_2]$	1854.3, $[M+Na]^+$; 23%	350.9, $[HgS_4+Na]^+$; 100%	1268.8, $[M-L^5]^+$; 31%	-

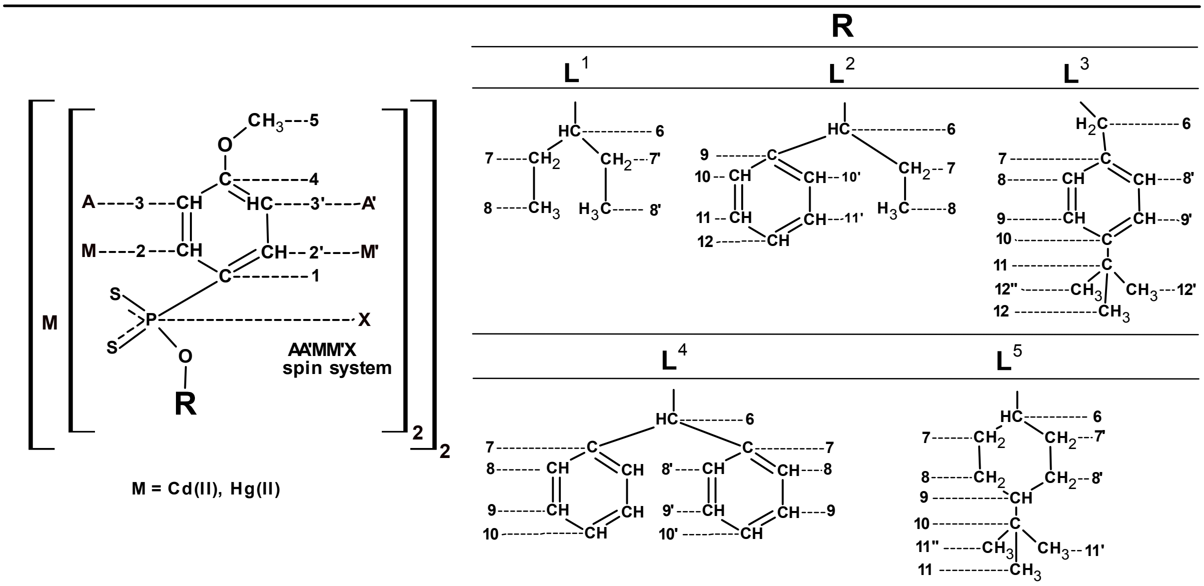


Figure 2. Numbering scheme for $[Cd_2(\mu\text{-}L^n)_2(L^n)_2]$ and $[Hg_2(L^n)_2(L^n)_2]$ complexes.

NMR Spectra

The numbering scheme for carbon atoms is given in Figure **2**.

^{1}H-NMR spectra

The ^{1}H-NMR spectra of all the compounds display a signal corresponding to the anisole group protons, a doublet of two doublets; therefore these four protons constitute an AA'MM'X spin system in each compound.

In all the complexes the *ortho*-protons on the anisole ring are all split by ~14.5 Hz by the phosphorus atom. The four bond P-H splitting of the *meta*-protons on the same ring is ~3.3 Hz in the Cd(II)-DTPOAs (δ= 6.93 ppm) and ~3.4 Hz in the Hg(II)-DTPOAs (δ= 6.93 ppm) species.

On the ^{1}H-NMR spectra of the complexes containing L^2, the methylene protons on C7 show up as a diastereotopic couple as expected spectra.

The signals of some of the alkyl protons on the cyclohexyl group of L^5 overlapped with each other in the spectra of $[Cd_2(\mu\text{-}L^5)_2(L^5)_2]$ and $[Hg_2(\mu\text{-}L^5)_2(L^5)_2]$. There are also overlaps between C6 protons and the phenyl protons of diphenylmethyl group of the complexes $[Cd_2(\mu\text{-}L^4)_2(L^4)_2]$ and $[Hg_2(\mu\text{-}L^4)_2(L^4)_2]$. The overall ^{1}H-NMR spectral data are given in Table 3.

Table 3: ^{1}H NMR spectral data for the complexes.

	[$Cd_2(\mu\text{-}L^1)_2(L^1)_2$]	**[$Cd_2(\mu\text{-}L^2)_2(L^2)_2$]**	**[$Cd_2(\mu\text{-}L^3)_2(L^3)_2$]**	**[$Cd_2(\mu\text{-}L^4)_2(L4)_2$]**	**[$Cd_2(\mu\text{-}L^5)_2(L^5)_2$]**
Ar_{ortho} M part of AA′MM′X N= J_{AM} + $J_{AM'}$	δ= 8.01 (8H) $^{3}J_{PH}$= 14.5 (J_{MX}); N= 8.8	δ= 7.93 (8H) $^{3}J_{PH}$= 14.6 (J_{MX}); N= 8.8	δ= 8.03 (8H) $^{3}J_{PH}$= 14.6 (J_{MX}); N= 8.7	δ= 7.93 (8H) $^{3}J_{PH}$= 14.7 (J_{MX}); N= 8.8	δ= 7.99 (8H) $^{3}J_{PH}$= 14.5 (J_{MX}); N= 8.8
Ar_{meta} A part of AA′MM′X	δ= 6.93 (8H) $^{4}J_{PH}$= 3.3 (J_{AX}); N= 8.8	δ= 6.93 (8H) $^{4}J_{PH}$= 3.2 (J_{AX}); N= 8.8	δ= 6.91 (8H) $^{4}J_{PH}$= 3.2 (J_{AX}); N= 8.7	δ= 6.79 (8H) $^{4}J_{PH}$= 3.3 (J_{AX}); N= 8.8	δ= 6.92 (8H) $^{4}J_{PH}$= 3.3 (J_{AX}); N= 8.8
OCH_3	δ= 3.83 (s, 12H)	δ= 3.80 (s, 12H)	δ= 3.81 (s, 12H)	δ= 3.78 (s, 12H)	δ= 3.83 (s, 16H) overlapped with C6-H
C6-H	δ= 4.8 (m, 4H)	δ= 5.70 (m, 4H)	δ= 5.3 (d, 4H) $^{3}J_{PH}$= 8.7	δ= 6.93 (d, 4H) $^{3}J_{PH}$= 16.4	
C7-H	δ= 1.77 (m, 16H)	δ= 2.01 (m, 8H) diastereotopic protons	-	-	C7-H, δ= 2.25 ; (m, 8H) C7′-H, δ= 1.74 ; (m, 8H)
C8-H	δ= 0.94 (t, 24H) $^{3}J_{HH}$= 7.5	δ= 0.87 (t, 12H) $^{3}J_{HH}$= 7.4	-	-	C8-H, δ= 1.43 ; (m, 8H) C8′-H, δ= 1.11 ; (m, 8H)
C9-H	-	-	-	-	δ= 0.96 (m, 4H)
C11-H	-	-	-	-	δ= 0.82 ; (m, 36H)
C12H	-	-	δ= 1.31 ; (s, 36H)	-	-
Ar-CH	-	δ= 7.28 ; (m, 20H)	δ= 7.32 ; (m, 16H)	δ= 7.28 ; (m, 40H)	-

	$[Hg_2(\mu\text{-}L^1)_2(L^1)_2]$	**$[Hg_2(\mu\text{-}L^2)_2(L^2)_2]$**	**$[Hg_2(\mu\text{-}L^3)_2(L^3)_2]$**	**$[Hg_2(\mu\text{-}L^4)_2(L^4)_2]$**	**$[Hg_2(\mu\text{-}L^5)_2(L^5)_2]$**
Ar$_{ortho}$ M part of AA′MM′X N= J_{AM} + $J_{AM'}$	δ= 8.6 (4H) $^3J_{PH}$= 14.5 (J_{MX}); N= 8.6	δ= 7.95 (4H) $^3J_{PH}$= 14.5 (J_{MX}); N= 8.9	δ= 8.00 (8H) $^3J_{PH}$= 14.5 (J_{MX}); N= 8.7	δ= 7.92 (8H) $^3J_{PH}$= 14.6 (J_{MX}); N= 8.7	δ= 8.04 (8H) $^3J_{PH}$= 14.4 (J_{MX}); N= 8.8
Ar$_{meta}$ A part of AA′MM′X	δ= 6.96 (4H) $^4J_{PH}$= 3.4 (J_{AX}); N= 8.6	δ= 6.93 (4H) $^4J_{PH}$= 3.4 (J_{AX}); N= 8.9	δ= 6.94 (8H) $^4J_{PH}$= 3.3 (J_{AX}); N= 8.7	δ= 6.92 (8H) $^4J_{PH}$= 3.4 (J_{AX}); N= 8.8, Ar-H$_{ort}$. (adjacent C-6H)	δ= 7.00 (8H) $^4J_{PH}$= 3.4 (J_{AX}); N= 8.8
OCH_3	δ= 3.85 (s, 12H)	δ= 3.85 (s, 12H)	δ= 3.83 (s, 12H)	δ= 3.84 (s, 12H)	
C6-H	δ= 4.8 (m, 4H)	δ= 5.84 (m, 8H)	δ= 5.4 (d, 8H) $^3J_{PH}$= 9.2	δ= 6.98 (d, 4H) $^3J_{PH}$= 16.4 (Ar$_{meta}$ adjacent)	δ= 3.85 (s, 16H) overlapped with C6-H
C7-H	δ= 1.83 (m, 16H)	δ= 2.03 (m, 8H) diastereotopic protons	-	-	C7-H, δ= 2.34 ; (m, 4H) C7′-H, δ= 1.82 ; (m, 4H)
C8-H	δ= 0.99 (t, 24H) $^3J_{HH}$= 7.5	δ= 0.94 (t, 12H) $^3J_{HH}$= 7.4	-	-	C8-H, δ= 1.50 ; (m, 4H) C8′-H, δ= 1.24 ; (m, 4H)
C9-H	-	-	-	-	δ= 1.01 (m, 4H)
C11-H	-	-	-	-	δ= 0.85 ; (m, 36H)
C12H	-	-	δ= 1.32 ; (s, 36H)	-	-
Ar-CH	-	δ= 7.31 ; (m, 20H)	δ= 7.35 ; (m, 16H)	δ= 7.36 ; (m, 40H)	-

(Chemical shifts (d) are reported in ppm. *J* values are reported in Hz. s: singlet; d:doublet; t:triplet dd:doublet of doublets; m:multiplet).

^{13}C-NMR spectra

The proton-decoupled ^{13}C-NMR spectra display a one-bond P-C coupling of about the same order of magnitude (114.2-123.9 Hz) in all the Cd(II) complexes. The same couplings are within even a narrower range (124.2-126.6 Hz) in the Hg(II) species. The C1 and C2 carbons appear at further downfield (by about ~7 ppm and ~2 ppm, respectively) in all the complexes compared to their position in the spectra of the corresponding ligands (2). The NMR signals of C8 on the spectra of $[Cd_2(\mu\text{-}L^3)_2(L^3)_2]$ and $[Hg_2(\mu\text{-}L^3)_2(L^3)_2]$ are situated between the two hands of the doublet corresponding to C1 (split into two by phosphorus). Similar overlap is observed between the signals C8, C9 and C10 of $[Cd_2(\mu\text{-}L^4)_2(L^4)_2]$ all of which falling between C1 signals.

^{13}C-NMR data of all the complexes are presented in Table 4.

^{31}P-NMR spectra

The chemical shift data for the proton-decoupled ^{31}P-NMR spectra of the ten complexes are presented in Table 5.

For comparison, ^{31}P-NMR chemical shift values are also given. All the compounds display a single ^{31}P-NMR signal indicating that the compounds are somehow symmetrical in solution. This is also evident from the formula given in Scheme 2.

Table 5 indicates that there is no parallel relation between the chemical shifts of the ligands and of the complexes, but all lay within the narrow range, 100.63-107.17 ppm. This indicates that the chemical environment of the phosphorus atom those not undergo either geometrically or electronically to a drastic change during the complexation.

Other features of the NMR spectra (^{1}H-, ^{13}C- and ^{31}P-) are in a good agreement with the literature (24,31, 34-36).

Table 4: ^{13}C-NMR data for the complexes.

	[$Cd_2(\mu-L^1)_2(L^1)_2$]	**[$Cd_2(\mu-L^2)_2(L^2)_2$]**	**[$Cd_2(\mu-L^3)_2(L^3)_2$]**	**[$Cd_2(\mu-L^4)_2(L^4)_2$]**	**[$Cd_2(\mu-L^5)_2(L^5)_2$]**
C1	δ= 130.0 (d) J_{PC}= 123.9	δ= 129.0 (d) J_{PC}= 122.7	δ= 128.4 (d) J_{PC}= 121.7	δ= 127.3 (d) J_{PC}= 114.2	δ= 129.6 (d) J_{PC}= 121.5
C2	δ= 132.2 (d) $^2J_{PC}$= 14.2	δ= 132.4 (d) $^2J_{PC}$= 14.4	δ= 132.5 (d) $^2J_{PC}$= 14.5	δ= 132.4 (d) $^2J_{PC}$= 14.3	δ= 132.3 (d) $^2J_{PC}$= 14.3
C3	δ= 113.5 (d) $^3J_{PC}$= 16.2	δ= 113.5 (d) $^3J_{PC}$= 16.3	δ= 113.7 (d) $^3J_{PC}$= 16.3	δ= 113.6 (d) $^3J_{PC}$= 16.4	δ= 113.6 (d) $^3J_{PC}$= 16.1
C4	δ= 162.3 (d) $^4J_{PC}$= 3.3	δ= 162.4 (d) $^4J_{PC}$= 3.3	δ= 162.6 (d) $^4J_{PC}$= 3.2	δ= 162.4 (d) $^4J_{PC}$= 3.0	δ= 162.4 (d) $^4J_{PC}$= 3.3
C5	δ= 55.4 (s)	δ= 55.4 (s)	δ= 55.4 (s)	δ= 55.4 (s)	δ= 54.4 (s)
C6	δ= 81.1 (d), $^2J_{PC}$= 8.2	δ= 80.8 (d) $^2J_{PC}$= 7.3	δ= 67.6 (d) $^2J_{PC}$= 6.7	δ= 79.6 (d) $^2J_{PC}$= 6.9	δ= 78.1 (d) $^2J_{PC}$= 7.9
C7	δ= 27.1 (d) $^3J_{PC}$= 4.0	δ= 31.4 (d) $^3J_{PC}$= 5.4	δ= 133.1 (d) $^3J_{PC}$= 9.9	δ= 141.0 (d) $^3J_{PC}$= 4.6	δ= 34.2 (d) $^3J_{PC}$= 3.8
C8	δ= 9.3 (s)	δ= 9.8 (s)	δ= 130.7 (s)	δ= 128.2 (s)	δ= 25.7 (s)
C9	-	δ= 140.9 (d) $^3J_{PC}$= 3.1	δ= 125.3 (s)	δ= 127.5 (s)	δ= 46.9 (s)
C10	-	δ=128.1 (s)	δ= 151.2 (s)	δ= 127.6 (s)	δ= 32.3 (s)
C11	-	δ=127.5 (s)	δ= 34.6 (s)	-	δ= 27.6 (s)
C12	-	δ= 126.9 (s)	δ= 31.3 (s)	-	-

	$[Hg_2(\mu\text{-}L^1)_2(L^1)_2]$	**$[Hg_2(\mu\text{-}L^2)_2(L^2)_2]$**	**$[Hg_2(\mu\text{-}L^3)_2(L^3)_2]$**	**$[Hg_2(\mu\text{-}L^4)_2(L^4)_2]$**	**$[Hg_2(\mu\text{-}L^5)_2(L^5)_2]$**
C1	δ= 130.1 (d) J_{PC}= 126.6	δ= 129.5 (d) J_{PC}= 125.3	δ= 129.3 (d) J_{PC}= 124.2	δ= 129.5 (d) J_{PC}= 125.0	δ= 129.7 (d) J_{PC}= 124.6
C2	δ= 131.9 (d) $^{2}J_{PC}$= 14.0	δ= 132.0 (d) $^{2}J_{PC}$= 14.2	δ= 132.3 (d) $^{2}J_{PC}$= 14.3	δ= 132.0 (d) $^{2}J_{PC}$= 14.3	δ= 132.1 (d) $^{2}J_{PC}$= 14.1
C3	δ= 113.7 (d) $^{3}J_{PC}$= 16.3	δ= 113.7 (d) $^{3}J_{PC}$= 16.3	δ= 113.8 (d) $^{3}J_{PC}$= 16.3	δ= 113.7 (d) $^{3}J_{PC}$= 16.4	δ= 113.7 (d) $^{3}J_{PC}$= 16.2
C4	δ= 162.4 (d) $^{4}J_{PC}$= 3.3	δ= 162.5 (d) $^{4}J_{PC}$= 3.4	δ= 162.7 (s) $^{4}J_{PC}$= 3.3	δ= 162.6 (s) $^{4}J_{PC}$= 3.3	δ= 162.8 (s)
C5	δ= 58.4 (s)	δ= 55.4 (s)	δ= 55.4 (s)	δ= 55.4 (s)	δ= 54.4 (s)
C6	δ= 81.4 (d) $^{2}J_{PC}$= 8.0	δ= 81.2 (s)	δ= 67.6 (s) $^{2}J_{PC}$= 6.5	δ= 80.1 (s) $^{2}J_{PC}$= 6.4	δ= 78.2 (s)
C7	δ= 27.1 (s)	δ= 31.2 (s)	δ= 133.0 (d) $^{3}J_{PC}$= 9.8	δ= 140.6 (s)	δ= 34.2 (s)
C8	δ= 9.4 (s)	δ= 9.8 (s)	δ= 128.1 (s)	δ= 128.5 (s)	δ= 25.7 (s)
C9	-	δ= 140.6 (s) $^{3}J_{PC}$= 3.0	δ= 125.5 (s)	δ= 127.6 (s)	δ= 46.4 (s)
C10	-	δ= 128.4 (s)	δ= 151.4 (s)	δ= 128.0 (s)	δ= 32.3 (s)
C11	-	δ=127.9 (s)	δ= 34.6 (s)	-	δ= 27.6 (s)
C12	-	δ= 127.1 (s)	δ= 30.9 (s)	-	-

(Chemical shifts (d) are reported in ppm. *J* values are reported in Hz. s: singlet; d:doublet; m:multiplet)

Table 5: ^{31}P-NMR data relating to the complexes and the corresponding ligands.

	$[NH_4L^1]$	**$[NH_4L^2]$**	**$[NH_4L^3]$**	**$[NH_4L^4]$**	**$[NH_4L^5]$**
δ, **ppm**	101.62	105.56	106.82	103.41	107.17
	$[Cd_2(\mu\text{-}L^1)_2(L^1)_2]$	**$[Cd_2(\mu\text{-}L^2)_2(L^2)_2]$**	**$[Cd_2(\mu\text{-}L^3)_2(L^3)_2]$**	**$[Cd_2(\mu\text{-}L^4)_2(L^4)_2]$**	**$[Cd_2(\mu\text{-}L^5)_2(L^5)_2]$**
δ, **ppm**	103.42	104.58	106.20	106.25	102.65
	$[Hg_2(\mu\text{-}L^1)_2(L^1)_2]$	**$[Hg_2(\mu\text{-}L^2)_2(L^2)_2]$**	**$[Hg_2(\mu\text{-}L^3)_2(L^3)_2]$**	**$[Hg_2(\mu\text{-}L^4)_2(L^4)_2]$**	**$[Hg_2(\mu\text{-}L^5)_2(L^5)_2]$**
δ, **ppm**	100.63	106.20	103.94	102.22	101.05

CONCLUSIONS

Five different dithiophosphonato ligands were synthesized and purified according to the procedure reported elsewhere (22). New Cd(II) and Hg(II) complexes were synthesized and characterized by elemental analyses and ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR and MS.

Based on the MS data, all the complexes were found to be of dimeric structure. ^{31}P-NMR data indicate that the complex molecules are symmetrical in solution. A comparative examination of the ^{31}P-NMR data of the ligands and of the complexes show that the process of coordination has some influence on the electron delocalization within the aromatic ring attached the P atom, but also that the same process has of little strain on the environment of the phosphorus atom.

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