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Syntheses and Spectroscopic Characterization on New [O–3-phenyl-1-propyl-(4-methoxyphenyl)dithiophosphonato] Ni(II), Cd(II) and Hg(II) Complexes

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Abstract : Four new [(R)(OR')dithiophosphonato] metal complexes (Metal= Ni(II), Cd(II) and Hg(II)) were synthesized (R= 4-methoxyphenyl-, R'= O–3-phenyl-1-propyl-). The complexes were of the general structure $[Ni((R)(OR'))_2]$, $[Cd\{\mu\text{-}(R)(OR')\}_2\{(R)(OR')\}_2]$ and $[Hg\{\mu\text{-}(R)(OR')\}_2\{(R)(OR')\}_2]$. $[Ni((R)(OR'))_2]$ was capable of coordinating two moles of pyridine per mole as many four-coordinated nickel(II) complex do leading to the six-coordinated complex, $[Ni((R)(OR'))_2(Py)_2]$. The structures of the complexes were investigated by elemental analysis along with mass spectra; FTIR and Raman spectroscopies. Further evidence for the structures of [Ni((R)(OR'))2], [Cd{μ-(R)(OR')}2{(R)(OR')}2] and [Hg{μ-(R)(OR')}2{(R)(OR')}2] were also obtained through 1H-, 13C- and 31P-NMR studies. The magnetic susceptibility of the pyridine nickel complex was measured to verify the hybridization patterns and the geometry.

Keywords: Dithiophosphonic acid, Dithiophosphonato metal complexes, Lawesson's Reagent, Spectroscopy.

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INTRODUCTION

2,4-bis-organo-1,3-dithia-2,4-diphosphetane 2,4-disulfides (DTDPA) react with nucleophilic reagents to produce organo-dithiophosphorus compounds. [2,4-bis (4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide] which is called Lawesson's reagent, (LR), a good example for DTDPAs, reacts with amines and bring about such as a dithiohosphonamido acid (1,2). LR also reacts with carbo anion such as Grignard compounds to produce dithiophosphinic acid (3). Moreover, the reaction of LR with aliphatic or aromatic alcohols ends up with the formation of dithiophosphonic acids (DTPOA) (4). DTPOA-type compounds are the best known organo-dithiophosphorus compounds (5). They are of several industrial applications; for example, some of them are used in the industry to serve as metal chelating agents (6), and antioxidants (in lubricating oils) (7, 8). They also have agricultural applications as herbicides (9) and insecticides (10). Some medicinal and pharmacological applications are of prospect (11-15).

The DTPOAs are also known to act as soft bases to react with metal cations, some of them being neutral, molecular species. Specifically Group 10 metal cations tend to form mononuclear molecules with square planar coordination environments (16). On the other hand, the cations Zn(II), Cd(II) and Hg(II) tend to form dinuclear DTPOA complexes that have tetrahedral cores (17-20). Square planar Ni(II)-DTPOA complexes can react with two moles of amine such as pyridine to produce a six-coordinated DTPOA complex (21). In these complexes, the sulfur atoms of -PS_2- group may serve as a singly bonded ligand or as a bridge-head (22-24).

EXPERIMENTAL

Materials and Instruments

The LR, 3-phenyl-1-propanol were purchased from Merck and used without any purification. $CHCl_3$, C_2H_5OH, C5H5N, $NiCl_2.6H_2O$, $CdCl_2$ and $HgCl_2$ were purchased from Sigma-Aldrich.

The LC/MS system was composed of a Waters Alliance HPLC with a C-18 column and a Waters Micromass ZQ combined to an ESI ionizer. ^{1}H-, ^{13}C-(proton decoupled) and ^{31}P-(proton decoupled) NMR spectra were recorded with a Varian Mercury (Agilent) 400 MHz FT instrument in $CDCl_3$. $SiMe_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P) were used as standards. IR spectra were done on a Perkin Elmer Spectrum 400 FTIR spectrometer (200–4000 cm^{-1}) and are reported in cm^{-1} units. Raman spectra were recorded in the range of 4000–100 cm^{-1}, at room temperature, using a Renishaw in-Via Raman microscope, equipped with a Peltier-cooled CCD detectors (−70°C). For Raman microscopy, a 50X objective was usually used and all the spectra were excited by the 785 line of a diode laser. Microanalyses were measured using a LECO CHNS-932 C elemental analyzer. Melting points were measured with a Gallenkamp apparatus using a capillary tube. Magnetic susceptibilities were performed measured on a Sherwood Scientific magnetic susceptibility balance (Model MK1) at room temperature (25°C).

Preparation of the compounds

Preparation of ammonium O–3-phenyl-1-propyl-(4-methoxyphenyl) dithiophosphonate, ([NH₄][(R)(OR′)])

This ligand was synthesized according to the literature (25).

Preparation of [Ni((R)(OR′))₂]

A solution of the $NiCl_2.6H_2O$, (0.17 g, 0.70 mmol) in ethanol (10 mL) was added to the solution of ammonium O–3-phenyl-1-propyl-(4-methoxyphenyl)dithiophosphonate (0.5g, 1.41 mmol) in ethanol (25 mL). After stirring for an hour, the mixture was left aside. The nickel(II) complex was violet. The crystalline solids were filtered off, and recrystallized from ethanol.

Preparation of [Cd{μ-(R)(OR′)}₂{(R)(OR′)}₂]

A solution of the $CdCl_2$ (0.13 g, 0.70 mmol) in ethanol (10 mL) was added to the solution of ammonium O–3-phenyl-1-propyl-(4-methoxyphenyl)dithiophosphonate (0.5g, 1.41 mmol) in ethanol (25 mL). After stirring for an hour, the mixture was left aside. Cd(II) complex was white-colorless and recrystallized from a mixture of chloroform/ethanol (2/1; v/v).

Preparation of [Hg{μ-(R)(OR′)}₂{(R)(OR′)}₂]

The same procedure as in [Cd{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] was applied for the [Hg{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] ($HgCl_2$, 0.13 g, 0.70 mmol in 10 mL ethanol for the of ammonium O–3-phenyl-1-propyl-(4-methoxyphenyl)dithiophosphonate, 0.5g, 1.41 mmol in 25 mL ethanol). Hg(II) complex was white-colorless and recrystallized from a mixture of chloroform/ethanol (2/1; v/v).

Preparation of [Ni((R)(OR′))₂(Py)₂]

To a chloroform solution of [Ni((R)(OR′))$_2$] (0.5 g, 0.73 mmol) complex in a beaker (50 mL) was added excess amount of pyridine. The color of the solution turned to from violet to light brown color. Green crystals formed were recrystallized from chloroform/ethanol (0.5/1 v/v). This powder is stable in the vacuum desiccator; but unstable at open atmosphere and returns to the violet colored complex.

[Ni((R)(OR′))$_2$] : Yield: 0.47 g (92%). Violet. M.P. 85-86 °C. LC/MS MS: m/z 733.15 ([Ni((R)(OR′))$_2$]$^+$, 5%), 395.08 ([Ni((R)(OR′))]$^+$, 100%), 339.20 ([(R)(OR′)+H]$^+$, 6%). Anal. Calcd. for $C_{32}H_{36}NiO_4P_2S_4$ (733.53 g.mol^{-1}): C, 52.40; H, 4.95; S, 17.49; found: C, 52.37; H, 4.89; S, 17.53 %.

[Ni((R)(OR′))$_2$(Py)$_2$] : Yield: 0.59 g (97%). Green. M.P. Decomposition upon heating. μ_{eff} = 2.99 B.M. LC/MS: MS m/z 916.1 [(Ni((R)(OR′))$_2$Py$_2$+Na]$^+$, 1%), 812.2 [(Ni((R)(OR′))$_2$Py$_2$-Py]$^+$, 2%), 553.2 [(Ni((R)(OR′))$_2$Py$_2$-(R)(OR′)]$^+$, 12%), 395.1 [(Ni((R)(OR′))]$^+$, 3%), 444.3 [(Ni((R)(OR′))Py-(OCH$_3$)]$^+$, 100%). Anal. Calcd. for $C_{42}H_{46}N_2Ni_2O_2P_2S_4$ (891.73 g.mol^{-1}): C, 56.57; H, 5.20; N, 3.14; S, 14.38; found: C, 56.53; H, 5.24; N, 3.08; S, 14.45 %.

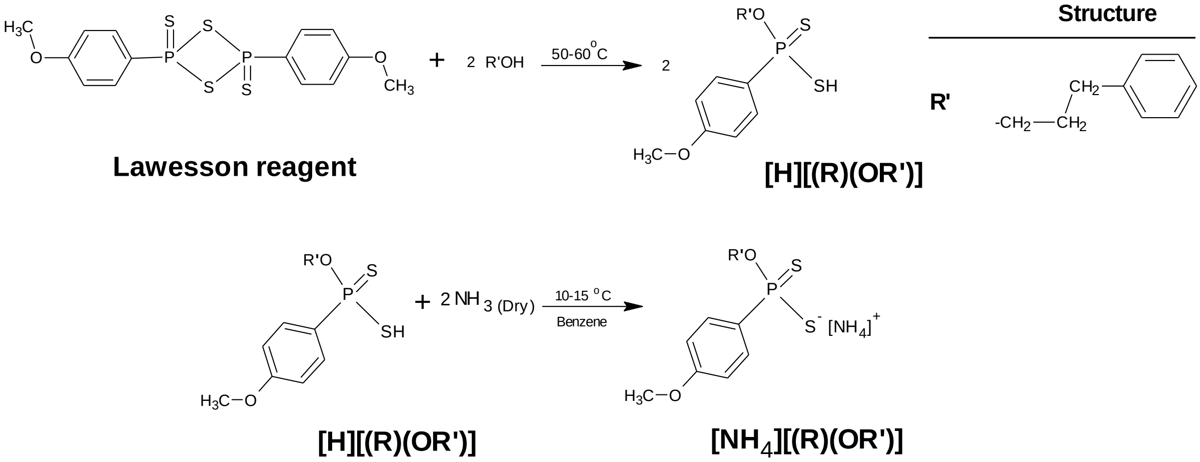
[Cd{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] : Yield: 0.44 g (80%). White-colorless. M.P. 120°C. LC/MS: MS m/z 1240.2 [(Cd$_2$((R)(OR′))$_3$]$^+$, 1%), 806.7 [(Cd((R)(OR′))$_2$]$^+$, 15%), 451.0

[(Cd((R)(OR′))+H]$^+$, 15%), 413.3 [(O-C_6H_4-PS_2)$_2$O+Na]$^+$, 100%) 391,4 [(O-C_6H_4-PS_2)$_2$O+H]$^+$, 77%). 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, 48.76; H, 4.58; S, 16.23 %.

[Hg{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] : Yield: 0.52 g (85%). White-colorless. M.P. 94-95°C. LC/MS MS: m/z 1412.4 [(Hg$_2$((R)(OR′))$_3$]$^+$, 3%), 877.2 [(Hg$_2$((R)(OR′))$_2$+H]$^+$, 4%), 391.4 [(O-C_6H_4-PS_2)$_2$O]$^+$, 64%), 189.3 [(S_2P-C_6H_4-O)+H]$^+$, 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, 43.86; H, 4.11; S, 14.59 %.

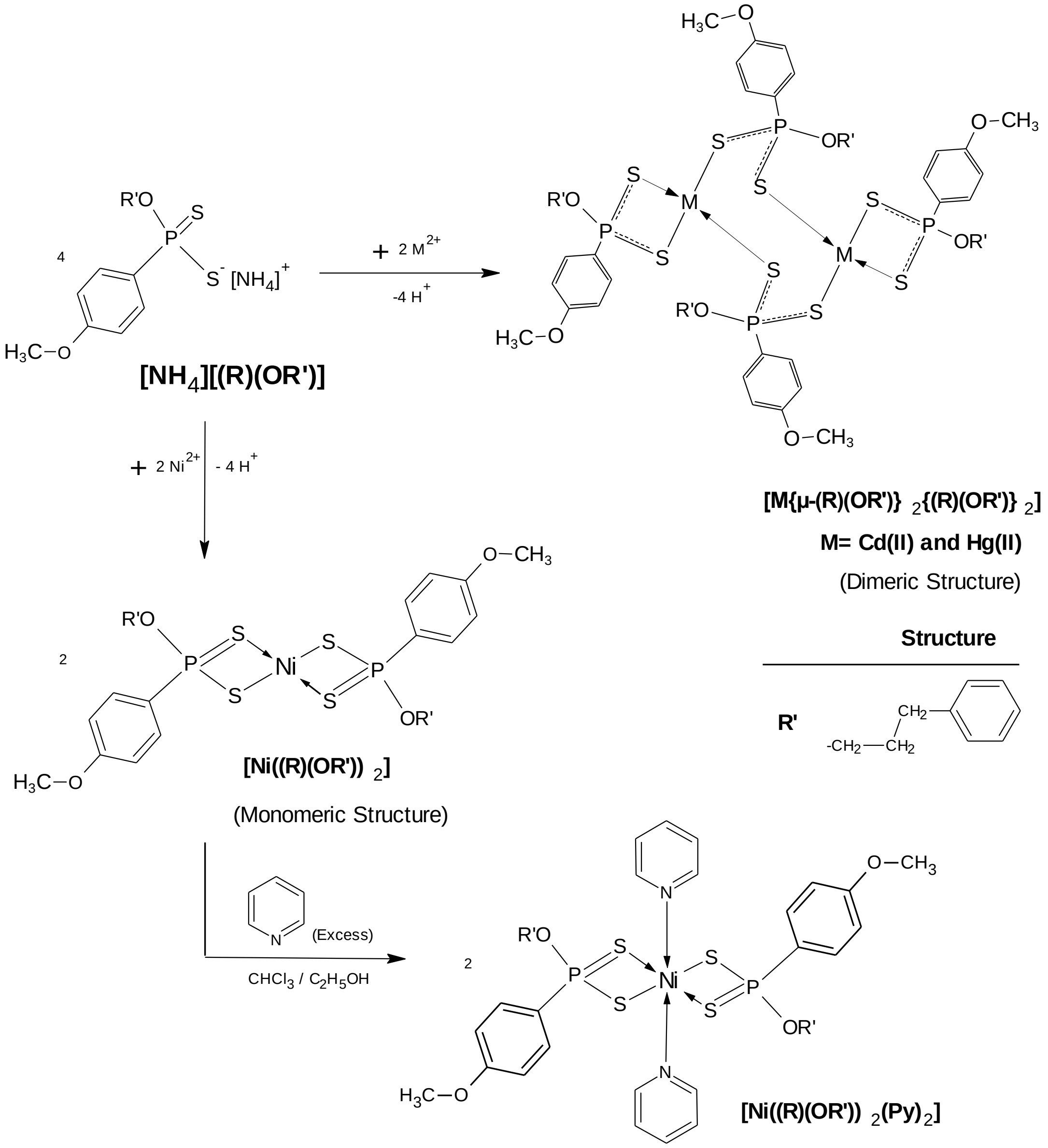
RESULT AND DISCUSSION

LR and O–3–phenylpropanol were reacted to yield a crude dithiophosphonic acid. The DTPOA obtained is a viscous liquid with a disagreeable odor. To get rid of the impurities and the bad odor, it was converted to the corresponding ammonium derivative, that is, the ammonium dithiophosphonate (Scheme 1).



Scheme 1. Synthesis reaction for the ligand.

[NH_4][(R)(OR′)] was reacted with nickel(II), cadmium(II) and mercury(II) to give the corresponding complexes. The complex [Ni((R)(OR′))$_2$] was further treated with pyridine to convert it to [Ni((R)(OR′))$_2$(Py)$_2$], a six-coordinated structure (Scheme 2).



Scheme 2. Syntheses of the complexes.

The magnetic susceptibility measured for the octahedrally coordinated complex [Ni((R)(OR′))$_2$(Py)$_2$] indicates a two-electron paramagnetism which agrees with the literature findings for similar structures (26).

Spectroscopic Studies

Mass spectra

The m/z values of the mass signals agree well with the theoretical isotopic abundance of the elements, nickel, cadmium, mercury as well as sulfur. The molecular ion and some fragments display m/z values that are 23 units higher than that of the calculated counterparts. Na^+ ions known to be presented in the buffer solution of the LC/ES system, are assumed to be responsible for this observation. Similar observations were reported in the literature (27).

The compounds [Cd{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] and [Hg{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] appear to display no molecular ions but [Ni((R)(OR′))$_2$] does display one. The masses of the fragments observed in the mass spectra of [Cd{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] and [Hg{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] agree well with the structures suggested. The MS spectra of the octahedral compounds [Ni((R)(OR′))$_2$(Py)$_2$] displays $[M+Na]^+$ peaks of measurable intensity. In the mass spectrum of [Ni((R)(OR′))$_2$], the m/z value of the molecular ion peak matches perfectly with the theoretically calculated figure for the complex itself. The mass spectra of [Cd{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] and [Hg{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] complexes display peaks corresponding to a species formed by the removal of a ligand from the whole molecule, that is, $[M_2\{(R)(OR')\}_3]^+$. In the mass spectra of the dimeric complexes of Cd(II) and Hg(II), ion peaks attributable to the moieties $[Cd\{\mu\text{-}(R)(OR')\}_2\{(R)(OR')\}_2]$ and $[Hg\{\mu\text{-}(R)(OR')\}_2\{(R)(OR')\}_2]$ are obvious, respectively. Experimental m/z data for the mass spectral peaks of the complexes are listed in the Experimental section relating to the individual complexes. The patterns of disintegration given in the literature for similar structures (28-30) are compatible with the ones we obtained here.

IR and Raman Spectra

The specific $\nu_{N\text{-}H}$ vibration band is visible at 3198 cm^{-1} in the ligand disappears in the complexes (25).

IR spectral symmetric and asymmetric PS stretching bands ($\nu(PS)_{sym}$ and $\nu(PS)_{asym}$) of the compounds are located at 547–552 cm^{-1} and 646–664 cm^{-1}, respectively. In the vibrational spectra of the Raman, similar bands are located at 541–555 cm^{-1} and 634–668 cm^{-1}, respectively.

M-S stretching vibrations appear at 306–308 cm^{-1} on IR and 280–306 cm^{-1} on Raman spectra. In the complex $[Ni((R)(OR'))_2(Py)_2]$, the metal-nitrogen stretching signals appear at the expected frequency region of the IR and Raman spectra (31). All the IR and Raman data are in good agreement with the previous observations (5,21,32–34). The significant peaks are given in Table 1.

Table 1: The selected vibrational spectral data ((FTIR and Raman, R, cm^{-1}) assignments of the important bands

Compound	$\nu_{(M\text{-}N)}$		$\nu_{(M\text{-}S)}$		$\nu(PS)_{sym}$		$\nu(PS)_{asym}$		$\nu_{(P\text{-}O\text{-}C)}$	
	IR	**R**	**IR**	**R**	**IR**	**R**	**IR**	**R**	**IR**	**R**
$[Ni((R)(OR'))_2]$	-	-	306	307	548	555	664	668	1011	1003
$[Ni((R)(OR'))_2(Py)_2]$	232	236	304	305	547	547	655	659	1004	1012
$[Cd\{\mu\text{-}(R)(OR')\}_2\{(R)(OR')\}_2]$	-	-	279	280	550-538	541-555	650	659	999	1005
$[Cd\{\mu\text{-}(R)(OR')\}_2\{(R)(OR')\}_2]$	-	-	308	306	552-533	552-537	646	634	999	1004

NMR Spectra

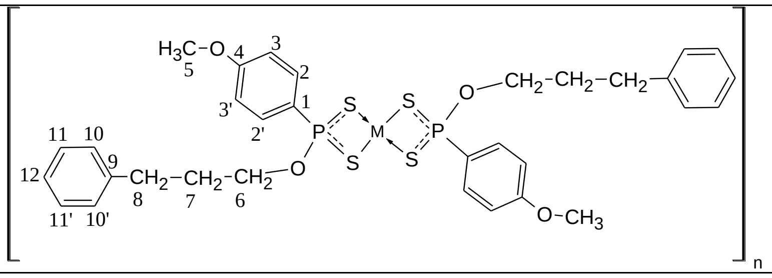
The complex $[Ni((R)(OR'))_2(Py)_2]$ is paramagnetic and its ambient temperature NMR spectra is nearly unidentified to comment on.

^{1}H–NMR Spectra

^{1}H-NMR spectral data of the three complexes are presented in Table 2. The chemical shifts of the signals in the ^{1}H-NMR spectrum of the ligand (25) are somewhat higher than those of the corresponding signals for the complexes. The phenyl ring protons in the anisole moiety that are *ortho-* to the phosphorus are split in the frequency range of 14.0–14.5 Hz. This is explained on account of the phosphorus ($^3J_{PH}$) and a further splitting of 8.9 Hz due to the geminal protons. The *meta* protons (in relation to phosphorus) do interact with the phosphorus by 3.3–3.4 Hz ($^4J_{PH}$).

In the spectra of all the complexes, the $C_{10,10'}$-**H** and C_{12}**H** protons on the O–3-phenylpropyl- accidentally superimpose. The integral curve of the multiplet corresponds to six (for the $[Ni((R)(OR'))_2]$) and twelve (for $[Cd\{\mu\text{-}(R)(OR')\}_2\{(R)(OR')\}_2]$ and $[Hg\{\mu\text{-}(R)(OR')\}_2\{(R)(OR')\}_2]$) protons; which supports the idea of superimposition. All the ^{1}H-NMR chemical data are in agreement with the literature (35,36).

Table 2: ^{1}H NMR spectral data for [Ni((R)(OR′))$_2$], [Cd{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] and [Hg{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$].



	n=1, M=Ni(II)	n=2, M=Cd(II)	n=2, M=Hg(II)
Ar-**H**$_{ortho}$	δ= 8.02 (dd, 4H) $^{3}J_{PH}$= 14.03; $^{3}J_{HH}$ = 8.8	δ= 8.02 (dd, 8H) $^{3}J_{PH}$= 14.52;$^{3}J_{HH}$ = 8.9	δ= 8.01 (dd, 8H) $^{3}J_{PH}$= 14.44; $^{3}J_{HH}$ = 8.8
C11-**H**	δ= 7.32 (t, 4H) $^{3}J_{HH}$ = 7.5	δ= 7.27 (t, 8H) $^{3}J_{HH}$ = 7.5	δ= 7.31 (t, 8H) $^{3}J_{HH}$ = 7.4
C12-**H**	δ= 7.20-7.26 (m, 6H)	δ= 7.18-7.20 (m, 12H)	δ= 7.25-7.21 (m, 12H)
C10-**H**	C-10 and C-12 superimposed	C-10 and C-12 superimposed	C-10 and C-12 superimposed
Ar-**H**$_{meta}$	δ= 7.04 (dd, 4H) $^{4}J_{PH}$= 3.13; $^{3}J_{HH}$ = 8.9	δ= 6.95 (dd, 8H) $^{4}J_{PH}$= 3.25; $^{3}J_{HH}$ = 8.9	δ= 7.00 (dd, 8H) $^{4}J_{PH}$= 3.4; $^{3}J_{HH}$ = 8.9
C6-**H**	δ= 4.42(m, 4H) $^{4}J_{PH}$= 12.62; $^{3}J_{HH}$ = 9.0	δ= 4.25 (m, 8H) $^{4}J_{PH}$= 12.6; $^{3}J_{HH}$ = 9.1	δ= 4.42(m, 8H) $^{4}J_{PH}$= 12.6; $^{3}J_{HH}$ = 9.0
OC**H$_3$**	δ= 3.91 (s, 6H)	δ= 3.85 (s, 12H)	δ= 3.89 (s, 12H)
C8-**H**	δ= 2.79 (t, 4H) $^{3}J_{HH}$ = 7.7	δ= 2.73 (t, 8H) $^{3}J_{HH}$ = 7.8	δ= 2.80 (t, 8H) $^{3}J_{HH}$ = 7.7
C7-**H**	δ= 2.140 (m, 4H) $^{3}J_{HH}$ = 7.0	δ= 2.05 (m, 8H) $^{3}J_{HH}$ = 7.0	δ= 2.15 (m, 8H) $^{3}J_{HH}$ = 7.0

(Chemical shifts (δ) are reported in ppm. *J* values are reported in Hz. s: singlet; d:doublet; t:triplet dd:doublet of doublets; m:multiplet. The atom responsible for the signal is boldfaced.)

^{13}C-NMR Spectra

The ^{13}C-NMR data for the complexes are summarized in Table 3. The two-bond coupling, $^{2}J_{P\text{-}C}$, for the phenyl carbon atoms in the anisole group (*ortho*- to the phosphorus) are situated within the frequency range 14.2–14.7 Hz. The anisole group *meta*-phenyl carbon atoms (with reference to phosphorus) display a three-bond ^{31}P-^{13}C coupling of 16.2 Hz.

^{31}P–^{13}C couplings (single bond) of the *ipso*-carbon for all the complexes are found to be in the range, 116.5–124.3 Hz. The $^{2}J_{P\text{-}C}$ coupling for C6 is 5.7 Hz in [Ni((R)(OR′))$_2$] while the $^{2}J_{P\text{-}C}$ coupling for C6 is 7.4 and 7.2 Hz in [Cd{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] and [Hg{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$], respectively. The $^{3}J_{P\text{-}C}$ for C7 atom is 7.3 Hz, although the $^{3}J_{P\text{-}C}$ coupling for C7 is 7.4 and 7.2 Hz in [Cd{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] and [Hg{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$], respectively. All the ^{13}C-NMR chemical shift data compare well with those given in the literature (3, 37, 38).

Table 3: ^{13}C-NMR spectral data for [Ni((R)(OR′))$_2$], [Cd{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] and [Hg{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$]

	M=Ni(II)	**M=Cd(II)**	**M=Hg(II)**
C4	δ= 162.98 (s)	δ= 162.62 (d) $^{4}J_{P\text{-}C}$ = 3.1	δ= 162.75 (d) $^{4}J_{P\text{-}C}$ = 3.3
C9	δ= 141.10 (s)	δ= 141.36 (s)	δ= 141.23 (s)
C1	δ= 129.03 and 128.11 (d) $^{3}J_{P\text{-}C}$ = 116.5	δ=129.10 and 128.14 (d) $^{3}J_{P\text{-}C}$ =121.2	δ= 129.27 and 128.28 (d) $^{3}J_{P\text{-}C}$ = 124.3
Ar-**C**$_{ortho}$	δ= 131.64 (d) $^{3}J_{P\text{-}C}$ = 14.7	δ= 132.39 (d) $^{3}J_{P\text{-}C}$ =14.4	δ= 132.16 (d) $^{2}J_{P\text{-}C}$ = 14.2
C10	δ= 128.52 (s)	δ= 128.53 (s)	δ= 128. 56 (s)
C11	δ= 128.49 (s)	δ= 128.38 (s)	δ= 128. 45 (s)
C12	δ= 126.05 (s)	δ= 125.89 (s)	δ= 126 (s)
Ar-**C**$_{meta}$	δ=114.00 (d) $^{3}J_{P\text{-}C}$ = 16.2	δ=113.72 (d) $^{3}J_{P\text{-}C}$ = 16.2	δ=113.87 (d) $^{3}J_{P\text{-}C}$ = 16.2
C6	δ= 65.74 (d) $^{2}J_{P\text{-}C}$ = 5.7	δ= 65.9 (d) $^{2}J_{P\text{-}C}$ = 7.4	δ= 65.77 (d) $^{2}J_{P\text{-}C}$ = 7.2
C5	δ= 55.52 (s)	δ= 55.44 (s)	δ= 55.48 (s)
C8	δ= 32.02 (s)	δ= 32.06 (s)	δ= 32.07 (s)
C7	δ= 31.83 (d) $^{3}J_{P\text{-}C}$= 7.3	δ= 31.81 (d) $^{2}J_{P\text{-}C}$ = 8.6	δ= 31.79 (d) $^{3}J_{P\text{-}C}$ = 8.6

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

^{31}P–NMR Spectra

^{31}P–NMR spectra of all the complexes is composed of a single ^{31}P peak except for the paramagnetic [Ni((R)(OR′))$_2$(Py)$_2$]. This finding indicates that all the phosphorus atoms in one compound are of the same environment. The ^{31}P chemical shifts for [Ni((R)(OR′))$_2$], [Cd{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] and [Hg{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] are 101,3, 105,7 and 103,5 ppm, respectively. These findings agree well with the literature (3,37,38).

CONCLUSIONS

A dithiophosphonato ligand (([NH$_4$][(R)(OR′)]) and four complexes thereof, namely, [Ni((R)(OR′))$_2$], [Cd{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] and [Hg{μ-(R)(OR′)}$_2${(R)(OR′)}$_2$] were prepared. All the complexes are stable and soluble in organic solvents. The octahedral pyridino complex is relatively unstable and tends to reversibly lose pyridine at high temperatures (and even at room temperature in the long run). The singlet peak in the ^{31}P-NMR spectrum confirms that the phosphorus atoms are of identical environments in the complex. The structural details of the compounds were elucidated by elemental analysis, MS, FTIR and Raman spectroscopies, ^{1}H-, ^{13}C- and ^{31}P-NMR.

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