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Synthesis and metal coordination chemistry of (phenyl)(pyridin-2-ylmethyl)phosphinodithioic acid, $[2\text{-}C_5H_4N]CH_2P(S)(SH)(Ph)$

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ABSTRACT

A three-step synthesis for the bifunctional ligand (phenyl)(pyridin-2-ylmethyl)phosphinodithioic acid, $[2\text{-}C_5H_4N]CH_2P(S)(SH)(Ph)$ (**3-H**), was developed. The molecule was characterized by spectroscopic methods, and single crystal X-ray diffraction analysis, and the molecule found to exist in a zwitterionic form (**3**′). Protonation constants for **3**′ were measured spectrophotometrically in 0.1 M $NaClO_4$ aqueous solution. The coordination chemistry of **3**′ toward $CdCl_2$ and $PtCl_2$ was explored, and the complexes $[Cd(\mathbf{3}')Cl_2]_2$ and $[Pt(\mathbf{3}^-)_2]\cdot CHCl_3$ were isolated and structurally characterized by single crystal X-ray diffraction methods. Complexation constants for **3**′ with Cd(II), Zn(II) and La(III), as a function of pH, were measured by titration techniques. An initial effort to prepare the [pyridin-bis(2,6-yl-methylphosphinodithioic acid)] analog of **3-H** led to the formation and isolation of (phenyl)(6-methylpyridin-2-ylmethyl)phosphinodithioic acid, $[2\text{-}C_5H_3N(6\text{-}CH_3)]CH_2P(S)(SH)(Ph)$ (**6-H**), that was characterized by spectroscopic methods and single crystal X-ray diffraction analysis. As found with **3-H**, **6-H**, adopts a zwitterionic structural form (**6**′).

1. Introduction

The syntheses and chemistry of mono-dithiophosphoric, $(RO)_2P(S)(SH)$, -dithiophosphonic, $(RO)(R)P(S)(SH)$, and -dithiophosphinic, $R_2P(S)(SH)$, acids have been widely studied, and numerous applications for the reagents have been developed [1–3]. The coordination chemistry of the respective anions has also attracted much attention as these species display a remarkable diversity in coordination modes with *s*-, *p*-, *d*- and *f*-block metal cations, and much of that activity has been reviewed [1–6]. Few bis-dithiophosphorus acids or their conjugate bases have been reported, but Kuchen and coworkers [7] have outlined a preparation for the bis(dithiophosphinic acids), $[R_2P(S)(SH)]_2(CH_2)_n$ ($n = 4–10$). Davies and coworkers [8] have also described a synthesis and coordination chemistry for a bis(dithiophosphinate), $Li_2[PhP(S)_2(CH_2)]_2$. In nearly all examples, the organyl groups, R, in the acids and their anionic conjugate bases are simple alkyl or aryl fragments that do not contain additional donor site functionality. In our own case, we are interested in attachment of dithiophosphorus acid fragments to organic platforms that also carry additional harder or softer donor sites such that unique asymmetric coordination fields may be produced. We report here the synthesis and selected coordination chemistry of one such target ligand type, $[2\text{-}C_5H_4N]CH_2P(S)(SH)(Ph)$ (**3-H**), that contains a pyridin-2-ylmethyl fragment and a dithiophosphinic acid group.

2. Experimental

2.1. Materials and general procedures

Organic reagents were purchased from Aldrich Chemical Co. and used as received. Organic solvents were rigorously dried according to standard procedures. The $CdCl_2$ and $PtCl_2$ for metal complex preparations were purchased from Ventron. The metal perchlorates for the titration analyses were purchased from VWR and Strem Chemicals. Titrations were performed with solutions prepared by using deionized water (Milli-Q, Waters Corp) of >18 M Ω cm^{-1} resistivity. Infrared spectra were recorded with a Tensor 200 FTIR spectrometer, and NMR spectra were recorded with Bruker FX-250, Avance 300 and Avance 500 NMR spectrometers. External chemical shift standards, Me_4Si (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P), were employed. Mass spectra were measured in the positive ion mode unless noted otherwise at the UNM Mass Spectrometry Facility, and elemental analyses were performed by Galbraith Laboratories.

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2.2. Experimental procedures

2.2.1. Ligand syntheses

*2.2.1.1. (Phenyl)(pyridin-2-ylmethyl)phosphinodithioic acid (**3-H**).* A sample of $PhP(OEt)_2$ (0.78 g, 3.9 mmol) was added to a solution of 2-bromomethylpyridine (0.68 g, 3.9 mmol) in dry CH_3CN (15 mL), and the mixture was heated under reflux (4 h). The CH_3CN was vacuum evaporated, the residue dissolved in CH_2Cl_2 (20 mL), and the resulting solution washed with water (2 × 10 mL). The organic phase was separated, vacuum evaporated, and the residue purified by column chromatography (SiO_2, 70–230 mesh, elution with CH_2Cl_2/MeOH, 80/20). (Phenyl)(pyridine-2-ylmethyl)phosphinic acid ethyl ester, 2-[(Ph)(EtO)P(O)CH_2]C_5H_4N (**1**), was obtained as a colorless liquid. Yield: 0.90 g, 87%. IR (KBr, cm^{-1}): v = 1226 (s, v_{PO}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 39.6. ^1H NMR ($CDCl_3$): δ = 1.27 (t, J_{HH} = 7.0 Hz, 3H, OCH_2CH_3), 3.57 (d, J_{PH} = 18.0 Hz, 2H, PCH_2), 3.88–3.98 (m, 1H, $OCH_AH_BCH_3$), 4.05–4.15 (m, 1H, $OCH_ACH_BCH_3$), 7.10 (t, J_{HH} = 6.0 Hz, 1H, *Ar-H*), 7.27–7.71 (m, 7H, *Ar-H*), 8.2 (d, J_{HH} = 4.7 Hz, 1H, *Ar-H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 16.3 (OCH_2CH_3), 40.8 (d, J_{PC} = 92.3 Hz, PCH_2), 61.0 (d, J_{PC} = 6.2 Hz, OCH_2CH_3), 121.6 (d, J_{PC} = 2.5 Hz, *Ar*), 124.4 (d, J_{PC} = 3.9 Hz, *Ar*), 128.3 (d, J_{PC} = 12.5 Hz, *Ar*), 130.2 (d, J_{PC} = 127.6 Hz, *Ar*), 131.6 (d, J_{PC} = 9.8 Hz, *Ar*), 132.2 (d, J_{PC} = 1.9 Hz, *Ar*), 136.2(*Ar*), 149.2(*Ar*), 152.4 (d, J_{PC} = 7.2 Hz, *Ar*). Mass spectrum (ESI): m/z = 262.09 [$M+H^+$], 284.07 [$M+Na^+$]. *Anal.* Calc. for $C_{14}H_{16}NO_2P$: C, 64.36; H, 6.17; N, 5.36. Found: C, 61.18; H, 6.04; N, 5.19%.

A 100 mL three-necked flask, outfitted with an addition funnel, was charged with a sample of **1** (0.561 g, 2.15 mmol), frozen with liquid nitrogen, evacuated and backfilled with nitrogen. Dry toluene (10 mL) was added followed by dropwise addition (10 min, 23 °C) of DIBAL-H solution (Aldrich, 1 M in toluene, 8.6 mL). During the addition, the solution became light yellow in color. The mixture was then heated (50 °C) and stirred (12 h). The resulting mixture was cooled (−78 °C) and cautiously quenched with 4 M NaOH solution (4 mL). The phases were allowed to separate, and the organic phase was removed under nitrogen by syringe to another Schlenk vessel containing sulfur (0.137 g, 4.39 mmol). The remaining aqueous phase was extracted with fresh toluene (2 × 5 mL), and the organic layers were added to the vessel containing the first organic fraction and sulfur. The mixture was stirred (23 °C, 1 h) and then gently heated (70 °C, 4 h). A solid formed that was recovered by filtration and washed with toluene leaving a white solid (phenyl)(pyridin-2-ylmethyl)phosphinodithioic acid, (**3-H**), that was crystallized by slow evaporation from MeOH/CH_3CN (1/1)solution. Yield: 0.38 g (67%). Mp 238–240 °C. The compound is soluble in DMSO and DMF, slightly soluble in MeOH, EtOH, $CHCl_3$, CH_3CN and THF, and it has slight solubility in water. IR (KBr, cm^{-1}): v = 652 (vs, v_{PS}), 543 (s, v_{PS}). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ = 64.0. ^1H NMR (DMSO-d_6): δ = 3.69 (d, J_{PH} = 12.5 Hz, 2H, PCH_2), 7.36 (br, 3H, *Ph*), 7.48 (d, J_{HH} = 8.0 Hz, 1H, *Pyr-H*$_3$), 7.79 (dd, J_{HH} = 6.0 Hz, 1H, *Pyr-H*$_4$), 7.99–8.03 (m, 2H, *Ph*), 8.31 (dd, J_{HH} = 7 Hz, 1H, *Pyr-H*$_5$), 8.72 (d, J_{HH} = 5 Hz, 1H, *Pyr-H*$_6$). $^1H\{^{31}P\}$ NMR (DMSO-d_6): δ = 3.69 (s, 2H, PCH_2), 7.36 (br, 3H, *Ph*), 7.48 (d, J_{HH} = 7 Hz, 1H, *Pyr-H*$_3$), 7.79 (dd, J_{HH} = 6 Hz, 1H, *Pyr-H*$_4$), 8.02 (d, J_{HH} 3 Hz, 2H, *Ph*), 8.31 (dd, J_{HH} = 7 Hz, 1H, *Pyr-H*$_5$), 8.72, (br, 1H, *Pyr-H*$_6$), 15.34 (br, s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ = 52.1 (d, J_{PC} = 36.4 Hz, PCH_2), 124.0. 127.1 (d, J_{PC} = 11.9 Hz), 127.7, 129.4, 130.5 (d, J_{PC} = 10.7 Hz), 140.0, 142.5 (d, J_{PC} = 76 Hz), 143.9, 150.8 (d, J_{PC} = 6.8 Hz). Mass spectrum (HRESI): m/z = [$M+H^+$] 266.0223; $C_{12}H_{13}NP^{32}S_2$ requires 266.0227, [$M+Na^+$] 288.0045; $C_{12}H_{12}NNaP^{32}S_2$ requires 288.0047. *Anal.* Calc. For $C_{12}H_{12}NPS_2$: C, 54.32; H, 4.56; N, 5.28; S, 24.17. Found: C, 54.80, H, 4.65; N, 5.33; S, 23.95%.

*2.2.1.2. (Phenyl)(6-methyl-pyridin-2-ylmethyl)phosphinodithioic acid (**6-H**).* A sample of **4** (0.941 g, 2.21 mmol) [9] in dry THF (15 mL) was treated dropwise under nitrogen with DIBAL-H solution (Aldrich, 1 M in THF, 25.4 mL) over 10 min (23 °C). The mixture was stirred (23 °C, 24 h) and diethyl ether (15 mL) was added. This mixture was cooled (0 °C) and quenched cautiously with 6 M NaOH (40 mL). Following vigorous gas evolution, the layers were separated, and the organic layer was transferred via syringe to another flask, dried over Na_2SO_4 and then transferred to a flask containing sulfur (0.27 g, 8.4 mmol). The mixture was refluxed (12 h), filtered and the filtrate evaporated. The remaining residue was purified by column chromatography (SiO_2, $CHCl_3$/MeOH, 90/10). (Phenyl)(6-methylpyridin-2-ylmethyl)phosphinodithioic acid (**6-H**) was recovered as a colorless solid that was crystallized from MeOH/$CHCl_3$, 5/1. Yield: 0.12 g (20%). Mp 212–214 °C. IR (KBr, cm^{-1}): v = 646 (vs, v_{PS}), 549 (s, v_{PS}). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ = 63.8. ^1H NMR (DMSO-d_6): δ = 2.65 (s, 3H, CH_3), 3.71 (d, J_{PH} = 13.0 Hz, 2H, PCH_2), 7.22 (d, J_{HH} = 8.0 Hz, 1H, *Ar*), 7.39 (br, 3H, *Ar*), 7.66 (d, J_{HH} = 7.5 Hz, 1H, *Ar*), 7.99–8.07 (m, 2H, *Ar*), 8.20 (t, J_{HH} = 7.5 Hz, 1H, *Ar*), 14.89 (br, 1H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ = 19.1 (CH_3), 51.7 (d, J_{PC} = 35.7 Hz, PCH_2), 124.2, 124.6, 127.1 (d, J_{PC} = 11.6 Hz), 129.4, 130.6 (d, J_{PC} = 10.4 Hz), 142.8 (d, J_{PC} = 76.0 Hz), 143.8, 150.4, 151.4. Mass spectrum (ESI): m/z = [$M+H^+$] 280.03, [$M+Na^+$] 302.02. *Anal.* Calc. for $C_{13}H_{14}NPS_2$: C, 55.89; H, 5.05; N, 5.01; S, 22.95. Found: C, 55.46; H, 5.05; N, 4.92; S, 23.13%.

2.2.2. Coordination complex syntheses

2.2.2.1. Cadmium(II) complex. Compound **3′** (0.052 g, 0.19 mmol) and $CdCl_2$ (0.018 g, 0.1 mmol) were combined in a mixture of $CHCl_3$ (3 mL) and MeOH (3 mL), and the solution refluxed (12 h). A solid, [Cd(**3′**)Cl_2]$_2$, formed during heating. After cooling (23 °C), the solid was collected by filtration. Yield: 0.04 g (90%). IR (KBr, cm^{-1}): v = 629 (vs, v_{PS}), 534 (s, v_{PS}). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ = 66.9. ^1H NMR (DMSO-d_6): δ = 3.79 (d, J_{PH} = 13.0 Hz, 2H, PC*H*2), 4.45 (br, 1H, N*H*), 7.42 (br, 3H, *Ph*), 7.49 (br, 1H, *Pyr*), 7.79 (br, 1H, *Pyr*), 8.04–8.08 (m, 2H, *Ph*), 8.29 (br, 1H, *Pyr*), 8.75 (d, J_{HH} = 5 Hz, 1H, *Pyr*). Mass spectrum (HRMS-negative ion mode): m/z = [$M-H^-$] 447.8478; $C_{12}H_{11}{}^{114}Cd^{35}ClNP^{32}S$ requires 447.8481. *Anal.* Calc. for $C_{12}H_{12}CdCl_2NPS_2$: C, 32.13; H, 2.70; N, 3.12. Found: C, 34.18; H, 3.10, N, 2.91%.

2.2.2.2. Platinum(II) complex. Compound **3′** (0.099 g, 0.37 mmol) and $PtCl_2$ (0.050 g, 0.19 mmol) were initially combined in CH_3CN (10 mL), and the solution refluxed (12 h). The resulting yellow solution was evaporated, the residue was dissolved in $CHCl_3$/MeOH (1:5), and the resulting solution refluxed (12 h). A clear reddish brown solution was obtained that was allowed to slowly evaporate leaving yellow crystals, [Pt(**3**$^-$)$_2$]. IR spectra (KBr, cm^{-1}): v = 653 (vs, v_{PS}), 523 (s, v_{PS}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 55.5. Mass spectrum (HRMS): m/z = [$M+H^+$] 723.9883; $C_{24}H_{23}N_2P_2{}^{32}S_4{}^{195}Pt$ requires 723.9867.

2.2.3. Ligand pK_a and metal stability constant determinations

The spectrophotometric titration experiments were carried out with a 1.0 cm quartz flow cell (VWR) placed in a Varian 300 Cary 1E UV–Vis spectrophotometer controlled by Cary Win UV Scan Application version 02.00(5) software. This was connected to an external, temperature controlled titration cell maintained at 25.0 ± 0.1 °C. The solution was continually circulated from the external cell to the flow cell in the spectrophotometer using a peristaltic pump. A VWR sympHony™ SR60IC pH meter with a VWR sympHony™ gel epoxy semi-micro combination pH electrode was used for all pH readings, which were recorded in the external cell. Equilibration and mixing were allowed for by circulating the solution for 15 min before each new spectrum was recorded. Fitting of theoretical absorbance versus pH or log[*M*] curves was accomplished using the SOLVER module of EXCEL [10]. For a set

Table 1
Crystallographic data.

	3′	**6**′	[Cd(**3**′)Cl_2]$_2$	[Pt(**3**$^-$)$_2$]·$CHCl_3$
Empirical formula	$C_{12}H_{12}NPS_2$	$C_{13}H_{14}NPS_2$	$C_{12}H_{12}CdCl_2NPS_2$	$C_{13}H_{12}Cl_3NPPt_{0.5}S_2$
Formula weight	265.32	279.34	448.62	481.22
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$C2/c$	$P2_1/c$	$P\bar{1}$	$C2/c$
Unit cell dimensions				
a (Å)	12.1486(4)	8.0467(2)	8.2646(3)	19.6310 (3)
b (Å)	24.3471(9)	10.6324(3)	8.6321(3)	12.9702(2)
c (Å)	8.7351(3)	15.9585(4)	12.8299(4)	16.4569(4)
α (°)	90	90	106.785(2)	90
β (°)	101.726(1)	101.249(2)	90.200(2)	125.164(1)
γ (°)	90	90	112.724(2)	90
Volume	2529.8(2)	1339.11(6)	801.39(5)	3425.5(1)
Z	8	4	2	8
T (K)	188(2)	183(2)	202(2)	223(2)
D_{calc} (g cm^{-3})	1.393	1.386	1.859	1.866
Absorption coefficient (mm^{-1})	0.518	0.493	2.040	4.924
Minimum/maximum transmission	0.8800/0.9003	0.8804/0.9777	0.7468/0.8996	0.9162/0.8052
Reflection collected	32488	37396	16884	60338
Independent reflections [R_{int}]	5486[0.0236]	5602[0.0315]	5215[0.0296]	8316[0.0293]
Final R indices [$I > 2\sigma(I)$] R_1 (wR_2)	0.0282(0.0686)	0.0308(0.0796)	0.0278(0.0518)	0.0205(0.0479)
Final R indices (all data) R_1(wR_2)	0.0345(0.0724)	0.0433(0.0862)	0.0451(0.0561)	0.0342(0.0537)

of spectra of any one metal ion with **3**′, SOLVER was used to fit formation constants and molar absorbances for the species in solution. The standard deviations given for log$K$ values in Table 1 were calculated using the SOLVSTAT macro [10].

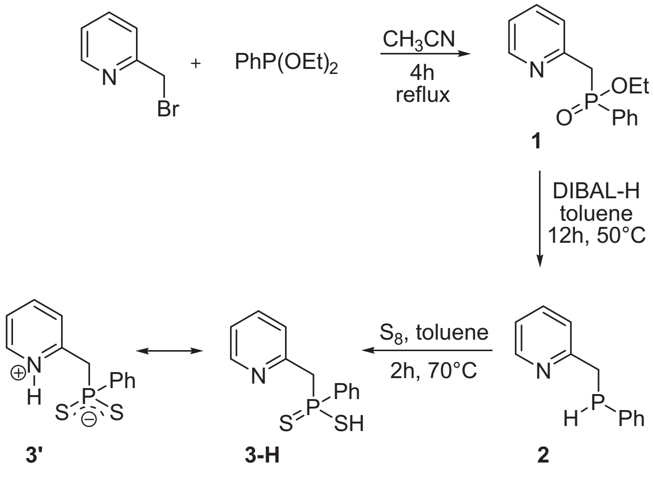
2.2.4. Single crystal X-ray diffraction analyses

Single crystals of **3**′ (colorless prism, 0.25 × 0.21 × 0.21 mm) and **6**′ (pale yellow thin platelet, 0.05 × 0.07 × 0.27 mm) were selected from preparative samples described above. Single crystals of [Cd(**3**′)Cl_2]$_2$ (colorless prism, 0.15 × 0.11 × 0.05 mm) were obtained by slow cooling of a hot $CHCl_3$/MeOH (1:1) solution of the crude complex. Single crystals of [Pt(**3**$^-$)$_2$]·$CHCl_3$ (pale yellow needle, 0.046 × 0.069 × 0.437 mm) were grown by slow evaporation of a solution of [Pt(**3**$^-$)$_2$] in $CHCl_3$/MeOH (1:5). The X-ray diffraction data were collected with a BRUKER X8 Apex II CCD system equipped with a graphite monochromator, Mo Kα sealed X-ray tube (λ = 0.71073 Å) and Oxford Cryostream 700 low temperature device. Full spheres of diffraction data were collected and integrated with SAINT [11] using a narrow frame algorithm. Data were corrected for adsorption (SADABS) [12], and the structures solved by direct methods and refined with full-matrix least-squares on F^2 using SHELXTL [13]. Selected crystal data are summarized in Table 1. All structure solutions and refinements were well behaved. The H-atoms on C-atoms were included in idealized positions, and they were allowed to vary in position with U_{iso} = 1.2 U_{eq} of the parent atom. For compounds **3**′ and **6**′, the H atom on the N-atom was located in difference maps, and it was allowed to vary in position and U_{iso}. For [Pt(**3**$^-$)$_2$]·2$CHCl_3$, the $CHCl_3$ solvent molecule in the asymmetric unit was disordered over two positions with occupancies 58.5% (C13H13ACl1Cl2Cl3) and 41.5% (C13H13BCl1Cl4Cl5). Atoms C13 and Cl1 are common to both positions.

3. Results and discussion

3.1. Ligand synthesis and characterization

A variety of methods have been reported for the synthesis of dithiophosphinic acids [1–3,14]. In particular, the reaction of sulfur with secondary phosphines is known to provide good access to both alkyl and aryl substituted dithiophosphinic acids [15–17]. Given that [2-C_5H_4N]CH_2P(S)(SH)(Ph), **3-H**, is the target ligand molecule, its formation by this approach requires the preparation of the intermediate secondary phosphine, [2-C_5H_4N]CH_2P(H)(Ph), **2**. A synthesis for **2**, from the combination of 2-(chloromethyl)pyridine and NaP(H)Ph, has been described in the literature [18,19]; however, the yield was found to vary. Therefore, an alternative approach, that does not involve isolation of the intermediate phosphine, was employed as summarized in Scheme 1. Initially, a solvent free Arbusov synthesis for the starting reagent (phenyl)(pyridin-2-ylmethyl)phosphine acid ethyl ester, **1**, was explored. Mixtures of 2-(bromomethyl)pyridine and PhP(OEt)$_2$, were heated without solvent, in a fashion similar to that described by Horner and coworkers [20]. This synthesis proved to be unsatisfactory as the formation of **1** was accompanied by several unidentified products resulting from thermal decomposition of 2-(bromomethyl)pyridine. Use of 2-(chloromethyl)pyridine also gave poor results. However, when the Arbusov reaction of 2-(bromomethyl)pyridine and PhP(OEt)$_2$ was performed in refluxing CH_3CN solution, the conversion was efficient, and [2-C_5H_4N]CH_2P(O)(OEt)(Ph), **1**, was isolated in good yield (87%) as a colorless liquid. The compound displays a parent ion, [M+H$^+$], in its ESI mass spectrum and a very strong absorption in the IR spectrum, 1226 cm^{-1}, that is assigned to the ν_{PO} terminal phosphoryl stretching frequency. The band position is intermediate between

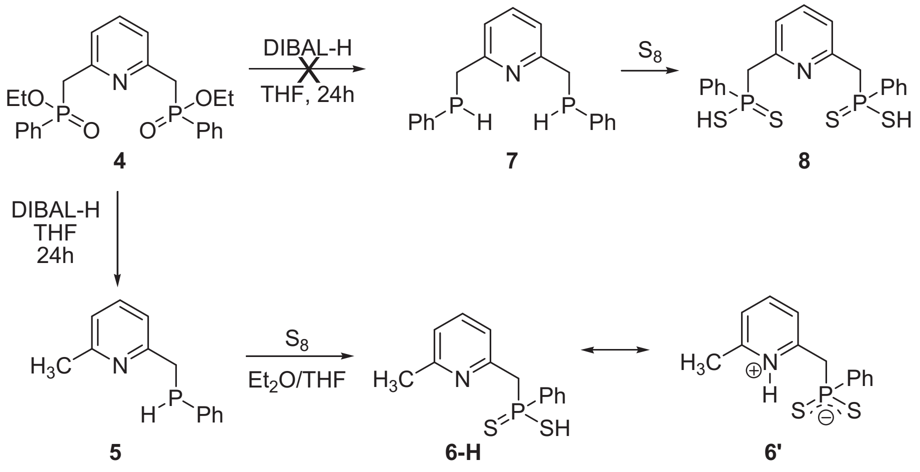


Scheme 1. Synthesis of compound **3-H** and **3**′.

values of ν_{PO} for $[2\text{-}C_5H_4N]CH_2P(O)Ph_2$, 1190 cm^{-1} [21] and $[2\text{-}C_5H_4N]CH_2P(O)(OEt)_2$, 1248 cm^{-1}. A similar shift with substituent group modifications occurs in the series $Ph_2P(O)CH_2COOH$, 1168 cm^{-1}, $Ph(EtO)P(O)CH_2COOH$, 1177 cm^{-1} and $(EtO)_2P(O)CH_2COOH$, 1257 cm^{-1} [22,23]. These trends reflect the greater electron withdrawing effect exerted by the ethoxy group relative to the phenyl group. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a single resonance, δ 39.6, that is typical for phosphonate esters [24], and the ^1H and $^{13}C\{^1H\}$ NMR spectra are consistent with the assumed structure. As evidenced by the CHN microanalytical data and a low intensity ^1H NMR signal (δ 3.09), a minor organic impurity is present in samples of **1**, but it does not complicate the subsequent reduction chemistry.

Several reagents have been described in the literature as effective reducing agents for organyl phosphinates, and much of that chemistry has been summarized by Busacca and coworkers [25–27]. In the present work, DIBAL-H is found to be most effective for reduction of **1**, although slightly different reagent stoichiometry and reaction time conditions are employed compared to typical literature descriptions. For example, Busacca reported that phenylmethylmethyl phosphinate, (Ph)(Me)P(O)(OMe), is reduced by 2.2 equivalents of DIBAL-H in toluene at 50 °C over 2 h [27]. Applications of these conditions to the reduction of **1** leads to only 50% conversion to **2** based upon ^{31}P NMR analysis of the aqueous NaOH quenched reaction mixture. However, increasing the amount of DIBAL-H reductant to 4.5 equivalents and the reaction time to 12 h give **2** in 80–90% yield. The synthesis outlined in the Experimental section calls for use of 4 eq. of DIBAL-H and a 4 h reaction time. The formation of **2** is supported by ^{31}P NMR analysis that shows a doublet resonance, δ −45.3, J_{PH} = 208.9 Hz, in toluene solution, and this shift and coupling constant compare favorably with reported data for **2** recorded from Et_2O solution: δ −48.0, J_{PH} = 209 Hz [18]. Without isolation, the toluene solution of **2** was combined with sulfur flowers, and the combination was gently heated at 70 °C for 4 h. The product, 3-**H**, is obtained as a white solid. Multiple CHN analyses show small variances between theoretical and observed values that may result either from a minor impurity or difficulties with the combustion analyses for the molecule. Spectroscopic data do not show evidence for impurities although they may exist below the detection limits of the data. The compound displays a parent ion, [M+H$^+$], in its high resolution ESI mass spectrum, and a IR spectrum shows strong absorptions at 652 and 582 cm^{-1} that are tentatively assigned to $\nu_{PS\ asym}$ and $\nu_{PS\ sym}$ stretching modes based upon prior literature assignments [17,28–30]. It is noted that no band is observed in the region 2600–2200 cm^{-1} that could be attributed to a free or associated ν_{SH} mode [17,29,31]. The $^{31}P\{^1H\}$ NMR spectrum for **3-H** contains a single sharp, symmetrical resonance, δ 64.1, that is typical of shifts reported for other secondary dithiophosphinates and phosphin odithioic acids [17,24]. The proton coupled ^{31}P NMR spectrum displays a nearly symmetrical 1, 4, 6, 4, 1 pentet-like pattern that simulation suggests arises from nearly equivalent coupling of the phosphorus with the two methylene protons (J_{HP} = 12.5 Hz) and two *ortho*-phenyl protons (J_{HP} = 13.0 Hz). The ^1H and $^{13}C\{^1H\}$ NMR spectra are consistent with the proposed structure except that a ^1H resonance that might be assigned to a S–H proton is not detected. However, a broad resonance, with relative intensity of one, is observed at δ 15.34 that is assigned to a pyridinium proton. It is also noted that the proton resonances for the H_4 and H_5 protons of the pyridyl ring appear as pseudo-triplets (overlapping doublet of doublets) due to nearly equivalent neighboring H–H couplings. Therefore, the IR and ^1H NMR data suggest that **3-H** exists in a zwitterionic form, **3′** as illustrated in Scheme 1. If correct, the molecule in this form should display a N–H stretching frequency. Unfortunately, this vibration was not confidently assigned since it can appear over a large frequency range depending upon the strength of the N–H$^+$ bond which is impacted by hydrogen bonding interactions [32,33]. Alternative evidence for the zwitterionic form, as well as an estimate of the strength of the N–H interaction, could be provided by resolution of the ^{15}N–H coupling constant. Limbach and coworkers [34–36], in a series of elegant studies, have assessed the strength of N–H$^+$ interactions in a number of pyridine–acid complexes by measuring J_{NH} for ^{15}N enriched samples, at low temperature, in fluorocarbon solvent systems. Parallel studies with **3′** would be very informative, but the synthesis of the ^{15}N enriched molecule would be time consuming, and it has not been undertaken.

In a parallel synthetic effort, the chemistry summarized in Scheme 2 was explored in an attempt to convert **4** into the bis(phosphinodithioic acid), **8-H$_2$**. However, under the conditions examined, DIBAL-H addition to **4** results in partial reductive dephosphorylation with formation of **5**. The intermediate diphosphine, **7**, also forms as indicated by a ^{31}P NMR resonance, δ −45.5, J_{PH} = 206 Hz. Addition of sulfur to the crude reaction mixture gives **6-H** as a pale yellow solid with modest, unoptimized yield (20%). The compound displays a parent ion [M+H$^+$] in its high resolution ESI mass spectrum, and the IR spectrum is very similar to that for **3-H** with strong bands at 646 and 548 cm^{-1} that are tentatively assigned to ν_{PS} modes. As found with **3-H**, there are no absorptions in the region 2600–2200 cm^{-1} that can be ascribed to a ν_{SH} mode in a monomeric –P(S)(SH) containing molecule or to associated, hydrogen bonded species [17,29,31]. The



Scheme 2. Synthesis of **6-H** and **6′**.

$^{31}P\{^1H\}$ NMR spectrum displays a symmetrical singlet, δ 64.5, that is split into a pentet-like pattern in the ^{31}P proton coupled spectrum. The ^1H and $^{13}C\{^1H\}$ NMR spectra are similar to those of **3-H** except a resonance for the *o*-Me group also appears: ^1H δ 2.54; $^{13}C\{^1H\}$ δ 19.1. In addition, a broad, low field ^1H NMR resonance, assigned to a pyridinium proton, is found at δ 14.89. As noted, the synthesis of **6-H**, described in Scheme 2, is not optimized, and it is likely that the compound would be more efficiently prepared by reduction of $[C_5H_3(o\text{-}CH_3)N]CH_2P(O)(Ph)(OEt)$ with DIBAL-H followed by reaction of the intermediate phosphine with sulfur. Given reports in the literature [37,38], it is not surprising that the conditions described here for the reduction of **4** lead to partial dephosphorylation of **7**. A modified procedure that produces the bis(phosphinodithioic acid), **8-H$_2$**, will be reported separately along with its coordination chemistry.

3.2. Ligand pK_a and metal stability constant determinations

The solubility of **3-H** in water is quite low (~10^{-4} M); however, the molecule displays intense electronic absorption bands in the region 200–350 nm due to π–π^* transitions involving the pyridine fragment. Therefore, it is possible to determine the ligand protonation constants and to assess metal ion complexation equilibria in 0.1 M $NaClO_4$ solutions as described previously for other heterocyclic ligands [39–45]. The spectra for acid titrations of **3-H(3′)** between pH 2.42 and 8.17 are shown in Fig. 1, and the variation in absorbance at five wavelengths for **3-H(3′)** as a function of pH is shown in Fig. 2. Analysis of these spectra provides the protonation constants summarized in Table 2. The value for $pK_1 = 5.40(3)$ is assigned to protonation of the pyridyl N-atom based upon known constants for pyridine ($pK = 5.24$ at ionic strength 0.1) and substituted pyridines [46]. Protonation constants for dithiophosphinic acids are sparse in the literature, but they are known to be relatively strong acids and not strongly influenced by the nature of substituent groups [17]. For example, Kabachnik and coworkers [47] have reported values between 1.74 and 2.64 for a series of dithiophosphinic acids, RR′P(S)(SH), in water/alcohol mixtures, and Zucal and coworkers [48] list values of 0.08 to 0.2 for several dialkyldithiophosphinic acids in CCl_4/H_2O mixtures. Therefore, the measured second protonation constant, $pK_2 = 1.2(1)$, is assigned with confidence to the dithiophosphinic acid fragment. A reviewer quite correctly questioned how a $pK_2 = 1.2$ could be determined if the titration went down to only pH 2.42, as suggested by Fig. 1. In fact, as seen in Fig. 2, the titration went down to pH 2.27 although the spectra at lower pH are not included in Fig. 1, as they obscure the isosbestic points. One sees the change in absorbance produced by the small amount of diprotonated ligand present near pH 2 in Fig. 2. Because the diprotonated form of the ligand is only of the order of 10% at the lowest pH values attained, the pK_2 is reported with a relatively large standard deviation in Table 2.

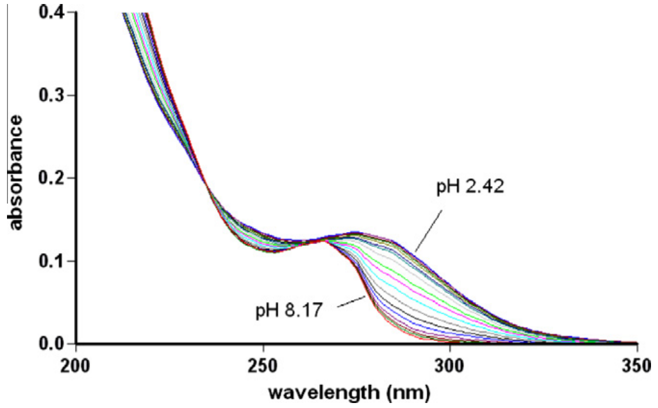


Fig. 1. Variation of the spectra of 10^{-4} M **3-H(3′)** in aqueous 0.1 M $NaClO_4$ solution as a function of pH between pH 2.42 and 8.17.

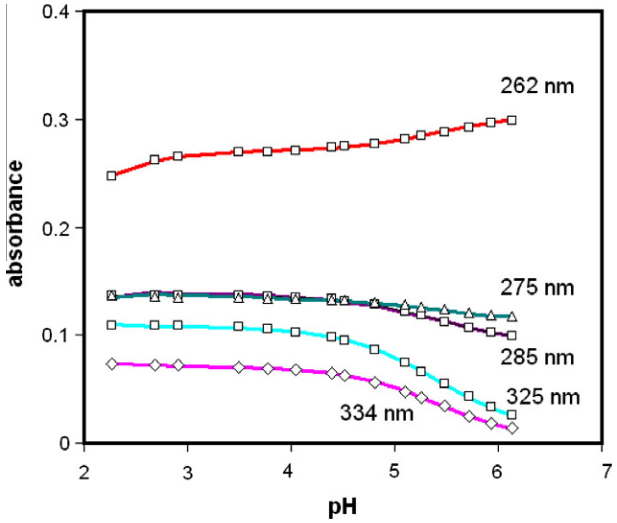


Fig. 2. Absorbance as a function of pH for 10^{-4} M **3-H(3′)** in aqueous 0.1 M $NaClO_4$ solution as a function of pH between pH 2.27 and 6.13. Points are experimental points, solid lines are theoretical curves of absorbance versus pH calculated as described in the text.

The log*K* values derived from metal ion titrations of **3-H(3′)** with Cd(II), Zn(II) and La(III) in 0.1 M $NaClO_4$ aqueous solutions at 25 °C are also listed in Table 2. As would be expected for sulfur-donors that are soft in the HSAB sense of Pearson [49,50], the hard La(III) ion in aqueous solution appears to have little affinity for **3-H** as indicated by no change in the spectrum of the ligand in the presence of even 10^{-3} M La(III). Zinc(II) is intermediate in the HSAB classification [49,50], and this ion also displays only a very low affinity for **3-H(3′)** in aqueous solution. The weak interaction indicated by $\log K = 2.1(1)$ probably results from Zn(II) binding to the pyridyl donor fragment. Only the soft Cd(II) shows a reasonable affinity for **3-H(3′)** in water ($\log K = 4.33(5)$), and this might be expected to result from Cd(II) binding to both the pyridyl N-atom, and the S-atom(s) of the ligand.

3.3. Selected nonaqueous metal ion coordination chemistry

Given the results of the metal/ligand titration analyses, the coordination chemistry of **3-H(3′)** was initially examined with the soft cations Cd(II) and Pt(II). Combinations of **3-H** with $CdCl_2$ in a 2:1 ratio in $CHCl_3$/MeOH mixtures gives a colorless, crystalline complex, and the same complex is obtained from a 1:1 reactant combination. The CHN analytical data for the complex are most consistent with a 1:1 metal:ligand composition, Cd(**3′**)Cl_2, although the agreement with the theoretical composition is not acceptable indicating that either the sample is impure or there are difficulties

Table 2
Protonation and formation constants for **3-H** (L) determined in 0.1 M $NaClO_4$ at 25 °C.

Lewis acid	Equilibrium	log*K*	Reference
H^+	$H^+ + OH^- \leftrightarrows H_2O$	13.78	[46]
H^+	$L^- + H^+ \leftrightarrows LH$	5.40(3)	this work
H^+	$LH + H^+ \leftrightarrows LH_2^+$	1.2(1)	this work
Cd^{2+}	$Cd^{2+} + L^- \leftrightarrows CdL^+$	4.33(5)	this work
Zn^{2+}	$Zn^{2+} + L^- \leftrightarrows ZnL^{2+}$	2.1(1)	this work
La^{3+}	$La^{3+} + L^- \leftrightarrows LaL^{2+}$	<2	this work

with the combustion analysis. A high resolution, electrospray ionization mass spectrum (negative ion mode) of the complex, on the other hand, displays an intense negative ion envelop with the maximum intensity ion at $m/z = 447.8478$; a negative ion composition $C_{12}H_{11}NP^{32}S_2{}^{35}Cl_2{}^{112}Cd$ requires $m/z = 447.8481$. This is consistent with the proposed Cd(**3′**)Cl_2 composition. An IR spectrum for the complex shows two strong absorptions at 629 cm^{-1} ($\nu_{PS\ asym}$) and 533 ($\nu_{PS\ sym}$) cm^{-1}, both strongly shifted from the respective bands (652 and 582 cm^{-1}) in **3-H(3′)**. The ^{31}P NMR spectrum for the complex shows a single resonance at δ 66.9. These data suggest that the ligand is present in its zwitterionic form, and, based on the magnitudes of the IR shifts, it appears to be bound to Cd(II) as a bidentate S,S′ phosphinate in the solid state.

Very little relevant formation constant data are available for Pt(II) [46], but an estimate of how strong a Lewis acid Pt(II) is can be obtained by comparison with its more labile and more easily studied congener Pd(II). The $\log K_1$ for Pd(II) with pyridine is 8.5 [46], indicating that Pd(II) is a stronger Lewis acid than the proton (pK_a for pyridine is 5.24), Cd(II) or Zn(II). Further, Pt(II) should be at least equally as strong a Lewis acid as Pd(II). Indeed, a 2:1 combination of **3-H(3′)** with $PtCl_2$, first in CH_3CN solution and then in $CHCl_3$/MeOH solution, produces a reddish brown solution that, upon standing, deposits yellow crystals. Elemental analyses were not collected, but a high resolution mass spectrum for this complex shows an intense parent ion envelop with a maximum intensity ion, $m/z = 723.9883$ consistent with a 2:1 ligand: metal composition $C_{24}H_{23}N_2P_2{}^{32}S_4{}^{195}Pt$, $m/z = 723.9867$. An IR spectrum of the crystals contains two strong absorptions at 653 and 523 cm^{-1}. The absence of a significant shift in the higher frequency band suggests a monodentate coordination mode for the dithiophosphinate ligand [29,30]. The ^{31}P NMR spectrum displays a single resonance at δ 55.5. While Cd(II) is a fairly weak Lewis acid, and thus not as readily able to drive the proton off the pyridine N-atom in **3-H(3′)** at the acidity levels present in the synthesis of the Cd(II)/**3-H(3′)** complex, the more powerful Lewis acid Pt(II) apparently is able to displace the proton from the pyridinium fragment. Further, the spectroscopic data, suggest that the anion $\mathbf{3}^-$ acts as a monodentate ligand toward Pt(II). Single crystal X-ray analyses were undertaken in order to reveal the details of the ligand–metal interactions in these complexes.

3.4. X-ray crystal structure analyses for ligands and complexes

The molecular structures for **3**-**H**(**3′**) and **6**-**H**(**6′**) have been determined by single crystal X-ray diffraction analyses, and views of the molecules are shown in Figs. 3 and 4, respectively. Selected bond lengths are summarized in Table 3. The structure determinations confirm that both molecules exist in the respective zwitterionic forms, **3′** and **6′**, wherein the dithioic acid proton has migrated to the pyridinyl N-atom. The P atom in both molecules has a distorted tetrahedral geometry in which the C–P–C and the S–P–S bond angles are the smallest and largest, respectively, of the set of angles about the P-atom: **3′**, C6–P–C7 102.06(4), S1–P–S2 118.15(2); **6′**, C7–P–C8 103.10(4), S1–P–S2 118.74(2). The P–S bond lengths are expected to be equivalent in an anionic dithiolate structure and intermediate in length between a typical P═S double bond (1.91 Å) and a P–S single bond (2.1 Å) [51]. The measured bond lengths in **3′** and **6′** are found to be intermediate in length, but they are slightly different within each molecule: **3′**, P1–S1 1.9763(3) Å and P1–S2 1.9955(3) Å; **6′**, P1–S1 1.9863 Å and P1–S2 1.9785(3) Å. The differences may result from weak intermolecular hydrogen bonding (**3′**) or a combination of intramolecular and intermolecular hydrogen bonding (**6′**) interactions that occur between the pyridinium N–H$^+$ proton and the $PS_2{}^-$ unit: **3′** for N1–H1···S2A, H1···S2A 2.39(2) Å, N···S2A 3.2447(8) Å, angle 168(1)°; **6′** for N1–H1···S2, H1···S2 2.85(2) Å, N1···S2 3.2194(9) Å, angle 109(1)° and for N1–H1···S1A, H1–S1A 2.69(2) Å, N1···S1A 3.465(1), angle 153(1)°. van Zyl and coworkers [52] have reported a similar but more symmetric bifurcated N–H···(S,S′) hydrogen bonding interaction in a dithiophosphonate decorated cholesteryl fragment, and a similar structure has been proposed by Swan and coworkers [53,54] for an *o*-aminobenzylphenyldithiophosphinic acid.

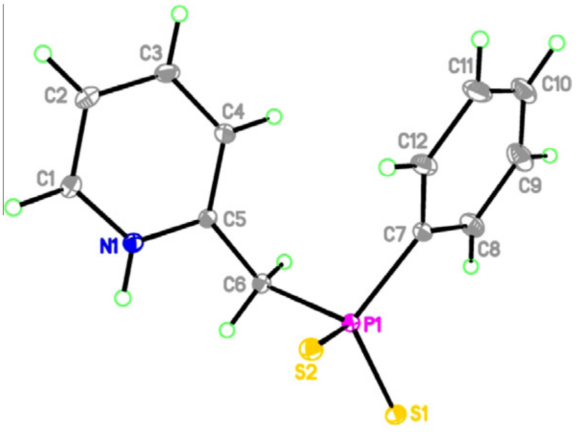


Fig. 3. Molecular structure and atom labeling scheme for **3′**. Thermal ellipsoids are shown at the 20% level.

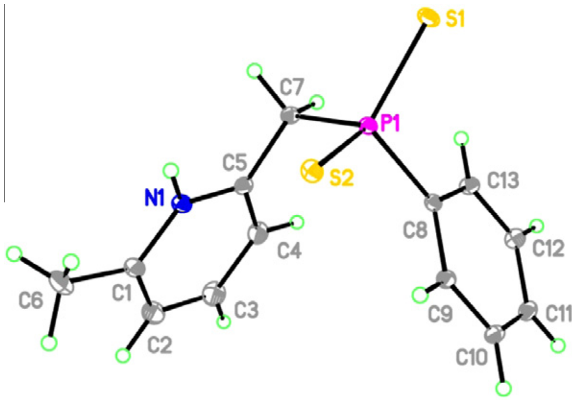


Fig. 4. Molecular structure and atom labeling scheme for **6′**. Thermal ellipsoids are shown at the 20% level.

The molecular structure for the complex formed between **3-H(3′)** and $CdCl_2$ is shown in Fig. 5 and selected bond lengths are presented in Table 3. In the solid state, the proposed 1:1 metal:ligand composition is confirmed, but the complex is clearly dimeric, $[Cd(\mathbf{3'})Cl_2]_2$. The structure is centrosymmetric, and the ligands are in the neutral zwitterionic form, **3′**. Each Cd(II) is five coordinate with coordination positions occupied by a terminal Cl atom, two bridging Cl atoms and two sulfur atoms from one S,S′ chelating bidentate dithiophosphinate fragment. This results in a highly distorted square pyramidal-like coordination geometry about the Cd(II) ion. The terminal Cd1–Cl2 bond length, 2.4599(5) Å is shorter than the bridging interactions, Cd1–Cl1 2.5004(5) Å and Cd–Cl1A 2.6714(5) Å, and the Cd–S distances, Cd1–S1 2.5004(5) Å and Cd1–S2 2.8670(5) Å are quite different. As expected, the shorter Cd–S interaction involves the S-atom with a longer P–S bond length, 2.0160(7) Å, and the longer Cd–S interaction is associated with a shorter P–S distance, P1–S2, 1.9836(7) Å. The dimeric molecular units are weakly associated in the unit cell along the *b*-axis via intermolecular N–H···Cl hydrogen bond interactions: H1···Cl2D 2.26(2) Å, N1···Cl2D, 3.107(2) Å, angle 176(2)°. For comparison, structures for numer-

Table 3
Selected bond lengths (Å).

Bond type	**3**′	**6**′	[Cd(**3**′)$_2$Cl$_2$]$_2$	[Pt(**3**$^-$)2]·CHCl$_3$
P–S	P1–S1 1.9763(3) P1–S2 1.9955(3)	P1–S1 1.9863(3) P1–S2 1.9785(3)	P1–S1 2.0160(8) P1–S2 1.9836(7)	P1–S1 2.0476(6) P1–S2 1.9615(7)
P–C	P1–C6 1.8571(9) P1–C7 1.8200(9)	P1–C8 1.8239(9) P1–C9 1.857(1)	P1–C7 1.846(2) P1–C1 1.809(2)	P1–C6 1.837(2) P1–C7 1.816(2)
C–N	C1–N1 1.345(1) C5–N1 1.347(1)	C1–N1 1.351(1) C5–N1 1.351(1)	C8–N1 1.331(3) C12–N1 1.339(3)	C1–N1 1.354(2) C5–N1 1.356(2)
C–C	C5–C6 1.483(1)	C5–C7 1.481(1)	C7–C8 1.491(3)	C5–C6 1.489(2)
M–S			Cd1–S1 2.5519(5) Cd1–S2 2.8670(5)	Pt1–S1 2.3249(4) Pt1–S1A 2.3249(4)
M–Cl			Cd1–Cl1 2.5004(5) Cd1–Cl2 2.4599(5) Cd1–Cl1A 2.6714(5) Cd1A–Cl1 2.6713(5)	
M–N				Pt1–N1 2.026(1) Pt1–N1A 2.026(1)

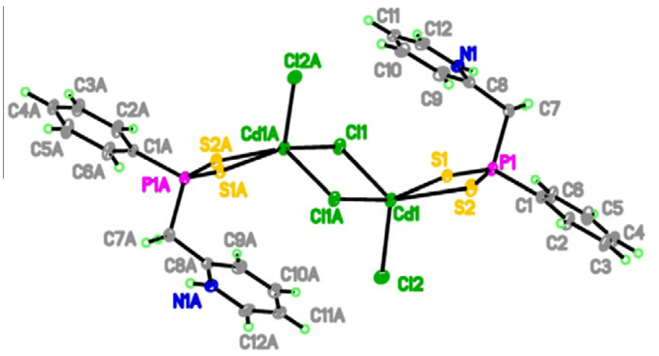


Fig. 5. Molecular structure and atom labeling scheme for [Cd(**3**′)Cl$_2$]$_2$. Thermal ellipsoids are shown at the 20% level.

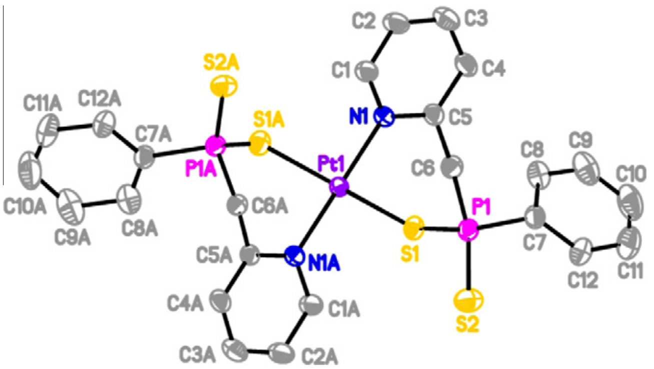


Fig. 6. Molecular structure and atom labeling scheme for [Pt(**3**$^-$)$_2$]·2CHCl$_3$ with the outer sphere CHCl$_3$ molecules omitted for clarity. Thermal ellipsoids are shown at the 20% level.

ous Cd(II) complexes with anionic dithiophosphorus ligands have been reported. In most cases the Cd(II) is six coordinate, and the ligand is bonded in a symmetrical S,S′ bidentate manner [1–6,55]. Two structures are particularly relevant to [Cd(**3**′)Cl$_2$]$_2$. Shimoi and coworkers [56] reported the structure for Cd[(EtO)$_2$P(S)$_2$]$_2$(hexamethylenetetramine)$_2$, and Jian and coworkers [57] described the structure of Cd[(iPrO)$_2$P (S)$_2$]$_2$(pyridine)$_2$. In both cases, the Cd(II) ion has a six coordinate, octahedral geometry with the monodentate amine N-atoms in *trans* positions, and the dithiophosphates bonded in a much more symmetrical bidentate fashion: Cd[(EtO)$_2$P(S)$_2$]$_2$(hexamethylenetetramine)$_2$, Cd–S1 2.704(1) Å, Cd–S2 2.682(1) Å, Cd–N1 2.595(2) Å, P–S1 1.982(1) Å, P–S2 1.979(1) Å and Cd[(iPrO)$_2$P(S)$_2$]$_2$(pyridine)$_2$, Cd–S1 2.704(1) Å, Cd–S2 2.694(1) Å, Cd–N1 2.399(3) Å, P–S1 1.993(1) Å, P–S2 1.996 Å. It is interesting that the MS and IR data and the X-ray crystal structure determination for [Cd(**3**′)Cl$_2$]$_2$ indicate that the Cd(II) does not displace the proton from the pyridine N-atom. However, in aqueous solution there is considerable change in the electronic spectra that involve π–π^* transitions within the pyridine fragment upon formation of the complex as the pH is increased. This suggests that the Cd(II) may displace the pyridinium proton, and coordinate to the N-atom as well as to a S-donor center of **3**$^-$ in aqueous solution. Similarly, the changes in the π–π^* transitions within the pyridine upon formation of the Zn(II) complex suggest that the Zn(II) may coordinate via an N,S interaction. Supporting the conclusion that the ligand binds in a N,S mode is the fact that the logK_1 values for the Cd(II) and Zn(II) with **3-H**(**3**′) are greater than for pyridine itself (logK_1 (pyridine) for Cd(II) = 1.37 and for Zn(II) = 1.05 [46]). This would not be the case if the S-donor of **3-H**(**3**′) was not also involved in coordination.

The molecular structure for the complex formed between **3-H**(**3**′) and PtCl$_2$ is shown in Fig. 6 and selected bond lengths are summarized in Table 3. The structure contains monomeric [Pt(**3**$^-$)$_2$] units in which the ligands are deprotonated and bind as anionic dithiophosphinates, RR′P(S)(S)$^-$, **3**$^-$. The Pt(II) ion has a square planar geometry, and each ligand interacts with the Pt(II) via a bidentate N,S chelate interaction: Pt1–N1 2.026(1) Å and Pt–S1 2.3249(4) Å. The coordinated sulfur has a significantly longer phosphorus–sulfur bond length, P1–S1 2.0476(6) Å, compared to the terminal uncoordinated sulfur, P1–S2 1.9615(7) Å. The composition and N,S chelate mode are, therefore, consistent with the MS and IR data. There are few structural reports for Pt(II) complexes of anionic dithiophosphorus ligands available for comparison, but in most cases the ligand acts as a symmetrical S,S′ bidentate chelate. For example, the structures of Pt[(EtO)$_2$P(S)$_2$]$_2$ [58]and Pt[(EtO)(Ph)P(S)$_2$]$_2$ [59] have square planar geometries with symmetrical bidentate Pt(S,S′) interactions: Pt[(EtO)$_2$P(S)$_2$]$_2$ Pt–S1 2.332(4) Å, Pt–S2 2.325(3) Å, P–S1 2.007(4) Å, P–S2 1.998(4) Å and Pt[(EtO)(Ph)P(S)$_2$]$_2$ Pt–S1 2.333(3) Å, Pt–S2 2.343(3) Å. Examples also exist with mixed bis (bidentate)(monodentate) coordination as in [Pt(Cy$_2$PS$_2$)$_2$(Cy$_2$PH)] [29] that contains two anionic dithiophospinate ligands, one of which is symmetrical S,S′ bidentate, Pt–S1 2.342(2) Å, Pt–S2 2.413(2) Å, and the second is monodentate, Pt–S3 2.302(2) Å. The P–S bond lengths involving the Pt-bonded S-atoms are longer, P1–S1 2.024(2) Å, P1–S2 2.017(2) Å, P2–S3 2.062(2) Å, than the terminal P–S bond length, 1.964(2) Å. Apparently the neutral phosphine, Cy_2PH, out-competes with the second bidentate chelate interaction for the fourth coordination position on Pt(II). In another interesting example, $Pt[(EtO)_2P(S)_2](ppy)$ (ppy = 2-phenylpyridine), the dithiophosphonate binds in a symmetrical bidentate S,S′ mode with Pt–S1 2.402(2) Å and Pt–S2 2.311(2) Å, and the ppy^- is orto-metalated with Pt–N1 2.018(5) Å [60].

4. Conclusion

A convenient, high yield synthesis for a bifunctional pyridin-2-ylmethylphosphinodithioic acid, **3-H**(**3**′), has been developed. The ^1H NMR spectra and X-ray crystal structure determination reveal that the strongly acidic phosphinodithioic acid proton migrates from a sulfur atom to the basic pyridinyl N-atom resulting in a zwitterionic structure, **3**′. Selected metal binding affinities for **3-H**(**3**′) as a function of pH have been accessed spectrophotometrically with La(III), Zn(II) and Cd(II) in water solution. Not surprisingly, harder cations such as La(III) and Zn(II), under these conditions, show low affinity for the neutral ligand. However, the ligand shows modest coordination strength with the softer cation Cd(II), and in water the ligand may be coordinated in its anionic form as a bidentate N,S-chelator. On the other hand, the X-ray crystal structure determination for the complex $[Cd(\mathbf{3}')Cl]_2$, formed in $CHCl_3$/MeOH solution, indicates that, under this condition, the ligand binds in its neutral **3**′ form utilizing an asymmetric bidentate S,S′ chelate interaction. In contrast, the crystal structure for $[Pt(\mathbf{3}^-)_2]$, shows that Pt(II) displaces the proton from **3-H**(**3**′), and the resulting anionic ligand acts as a bidentate N,S-chelator.

Given the interesting acid–base and complexation properties of the neutral dithioic acid, **3-H**, its zwitterionic isomer, **3**′, and the monoanion form, $\mathbf{3}^-$, it is anticipated that a rich variety of coordination complex structures will evolve depending on the HSAB character of the coordinated metal, metal coordination geometry preferences, steric effects introduced by ligand substituent groups and solvent. Further coordination chemistry with soft *d*-block metal cations as well as with *f*-block cations in the absence of strongly bonded water will be forthcoming. The latter will provide some interesting experimental results to consider in light of the revealing computational studies reported by Boehme and Wipff [61,62] regarding the formation of thiophosphoryl ligand complexes with lanthanide ions.

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Appendix A. Supplementary data

CCDC 832336, 832337, 832338 and 832339 contains the supplementary crystallographic data for compounds (**3**′), (**6**′), $[Cd(\mathbf{3}')Cl_2]_2$ and $[Pt(\mathbf{3}^-)_2]\cdot CHCl_3$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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