

Syntheses and structural characterization of new *trans*-bis-[*n*-butyl-(*p*-methoxyphenyl) dithiophosphinato] nickel(II), the pyridine derivative thereof, and bis-{bis-[*n*-butyl-(*p*-methoxyphenyl) dithiophosphinato]cobalt(II)} complexes

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ABSTRACT

Three new metal complexes of ammonium *n*-butyl-(*p*-methoxyphenyl) dithiophosphinate (NH₄L) were synthesized. NH₄L was treated with NiCl₂·6H₂O and CoCl₂·6H₂O in ethanol to obtain a new *trans*-bis-[*n*-butyl-(*p*-methoxyphenyl) dithiophosphinato]nickel(II) and bis-{bis-[*n*-butyl-(*p*-methoxyphenyl) dithiophosphinato]cobalt(II)} complexes, ([Ni(L)₂] and [Co₂(μ-L)₂(L)₂], respectively). Square-planar nickel(II) complex was furthermore reacted with excess pyridine (Py) and the octahedral {bis-pyridine-bis-[*n*-butyl-(*p*-methoxyphenyl)]}nickel(II) complex, ([Ni(L)₂(Py)₂]), was obtained.

The structures of the complexes were analyzed by elemental analysis, ¹H-, ¹³C-, ³¹P- NMR; and also by MS-, FTIR- and Raman spectroscopies. The magnetic susceptibilities of the Co(II) and the pyridine-Ni(II) complexes were measured to throw further light on the hybridization patterns. The solid-state structures of the nickel complexes were also done by X-ray crystallography. The P–S bonds in the Ni(II) complexes are essentially of the same lengths; indicating an effective electron delocalization around the central PS₂ moiety.

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1. Introduction

There are many classes of ligands for coordination compounds [1–9]. Of these, organodithiophosphorus anions are not studied as extensively as other ligands. Organodithiophosphorus acids are grouped under three classes, namely dithiophosphoric (DTP), dithiophosphonic (DTPOA) and dithiophosphinic acids (DTPA) (Fig. 1).

All the organodithiophosphorus anions are known to be good ligands for soft-acid type metal cations [10]. It is this characteristic that makes them attractive for several industrial applications like metal extraction in the mining industry, radioactive nuclide separation in nuclear technology and environmental processes [11–17]. Other applications, for example as antibacterial and antifungal agents may or may not be to do with their metal-binding potential

[18,19]. Likewise, the mechanism of their synergistic contribution to the effectiveness of cephalosporin-type antibiotics is yet to be elucidated [20].

DTPAs are synthesized either by the reaction of phosphines with elemental sulfur (Scheme 1A) [21] or through an addition reaction of a thionophosphine sulfide (Lawesson reagent, LR) and a Grignard reagent (Scheme 1B) [22]. The latter route is relatively more practical and straightforward as compared to the former. Furthermore, the number of derivatives reachable by this route is so high as to make the technique preferable.

Studies on the DTPA-type compounds are fewer than their oxygen-analogs, DTPs and DTPOAs [22]. This is presumably due to their relatively more difficult synthesis procedure and the irritable odor almost always attached to them. The disagreeable smell can be mostly removed by converting the acids into its ammonium salts [23]. These salts offer further advantages of being easily crystallizable and much more stable than the acid. DTPA-Ni(II) complexes are known of always mononuclear square-planar coordination

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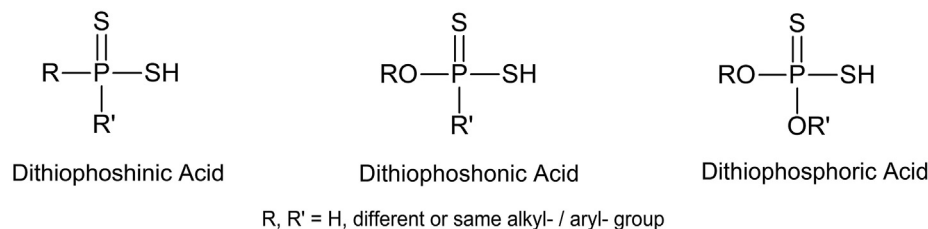
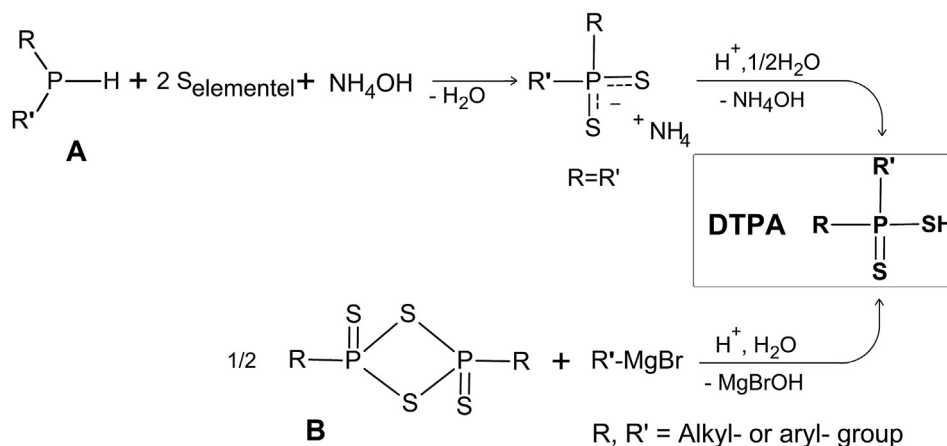


Fig. 1. Structures of organodithiophosphorus acids.



Scheme 1. Synthesis reactions of DTPAs.

geometry whereas Cd(II) and Co(II) analogs are dinuclear and have a slightly distorted bonding geometry around the metallic centers [24,25]. As is the case with the other square-planar Ni(II) complexes, DTPA-Ni(II) compounds can also bind to molecules of an amine (pyridine for example) to make up the coordination number to six [26].

Studies on dithiophosphinic acids and their complexes are relatively scarce and here we attempt to contribute to the existing endeavor related to the preparation and characterization of this group of compounds. Namely, *n*-butyl-(*p*-methoxyphenyl) dithiophosphinato-Ni(II), [Ni(L)₂], and butyl-(*p*-methoxyphenyl) dithiophosphinato-Co(II), [Co₂(μ-L)₂(L)₂], complexes and dipyr-ridine derivative of the former, [Ni(L)₂(Py)₂], were prepared. The complexes precipitated in the ethanolic medium as colored deep blue for nickel (Scheme 2A) and bright green for cobalt complex (Scheme 2B) fine crystals. The complex [Ni(L)₂] was treated with pyridine in chloroform-ethanol (1/1; v/v) medium (Scheme 2C). The octahedral complex so obtained is green colored, unstable in an open atmosphere, but stable in a desiccator under an inert atmosphere. The pyridine molecules attached leave under ambient situations; which is consistent with the similar structures [27].

2. Experimental section

2.1. Materials and equipment

NH₄L was prepared according to the literature [25]. Benzene, Chloroform, ethyl alcohol, pyridine, NiCl₂·6H₂O and CoCl₂·6H₂O were purchased from Merck.

The LC/MS system was provided by Waters with a C-18 HPLC column and a Waters Micromass ZQ connected with an ESI ionizer. A Sherwood Scientific magnetic susceptibility balance (Model MK1) apparatus was used to perform the magnetic properties of

[Co₂(μ-L)₂(L)₂] and [Ni(L)₂(Py)₂] at the room temperature. Melting points measurements were done with a Gallenkamp device. ¹H NMR, ¹³C NMR and ³¹P NMR spectra were measured with a Varian Mercury, Agilent, 400 MHz FT appliance in CDCl₃. SiMe₄ (¹H NMR, ¹³C NMR) and 85% H₃PO₄ (³¹P NMR) were used as standards for [Ni(L)₂]. IR spectra were done on a PerkinElmer Spectrum 400 FTIR spectrophotometer device ((200–4000) cm⁻¹). All of the Raman signals were recorded by using a Renishaw in-Via Raman microscope (4000–100 cm⁻¹), with Peltier-cooled CCD detectors. A 50X objective was applied in Raman spectroscopy. The Raman spectra were excited by the 785 lines of a diode laser. Elemental analyses were performed using a LECO CHNS-932 C.

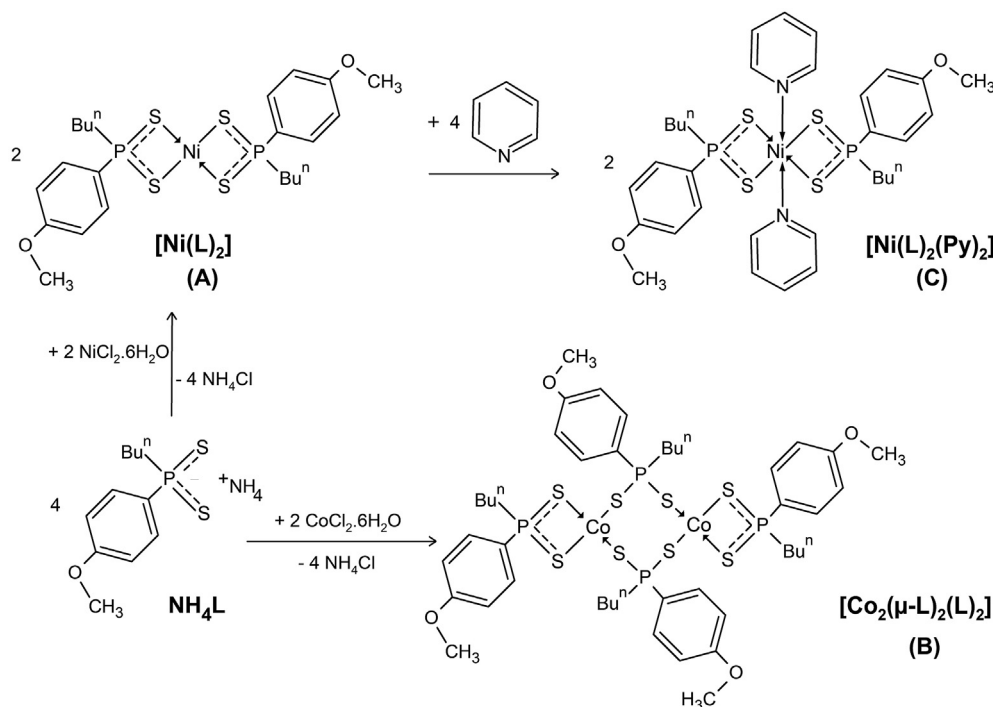
2.2. Syntheses of complexes

2.2.1. Syntheses of [Ni(L)₂] and [Co₂(μ-L)₂(L)₂]

An ethanolic solution of NiCl₂·6H₂O or CoCl₂·6H₂O (0.29 g, 1.24 mmol) in ethanol (10 mL) was added to NH₄L (0.69 g, 2.48 mmol) same solvent (25 mL). The mixture was stirred and left to stand 4 h and crystals formed at room temperature. Nickel(II) complex was navy blue while the cobalt(II) complex was bright green. The solid crystals were filtered off and recrystallized from ethanol.

The synthesis data for the complexes were as follows:

2.2.1.1. [Ni(L)₂]. Yield: 0.62 g (86%). M.P. 127–128 °C. Anal. Calcd. for C₂₂H₃₂NiO₂P₂S₄ (577.4 g mol⁻¹): C, 45.8; H, 5.6; S, 22.2; found: C, 45.7; H, 5.6; S, 22.4%. ¹H NMR (ppm in CDCl₃): δ = 0.93 (t, ³J_{HH} = 7.4 Hz, 3H, -CH₃), 1.40 (m, 2H, -CH₂-CH₃), 1.70 (m, 2H, -CH₂-CH₂-CH₃), 2.22 (m, 2H, -CH₂-CH₂-CH₂-CH₃), 3.85 (s, 3H, OCH₃), 6.98 (A-moiety of AA'MM'X, ⁴J_{PH} = 2.2 Hz (J_{AX}), N = J_{AM} + J_{AM'} = 8.8 Hz, 2H, *m*-H), 7.56 (M-moiety of AA'MM'X, ³J_{PH} = 13.0 Hz (J_{MX}), N = 8.8 Hz, 2H, *o*-H). ¹³C{¹H} NMR (ppm in CDCl₃): δ = 13.9 (s, -CH₃),



Scheme 2. Synthesis reactions of the complexes.

23.6 (d, $^2J_{\text{P-C}} = 18.4$ Hz, $\text{P}-\text{CH}_2-\text{CH}_2-$), 24.3 (s, $-\text{CH}_2-\text{CH}_3$), 41.6 (d, $J_{\text{P-C}} = 43.7$ Hz, $\text{P}-\text{CH}_2-$), 55.7 (s, CH_3O), 114.3 (d, $^3J_{\text{P-C}} = 14.6$ Hz, $\text{Ar-C}_{\text{meta}}$), 127.4 (d, $J_{\text{P-C}} = 69.7$ Hz, P-C_{Ar}), 130.9 (d, $^2J_{\text{P-C}} = 13.9$ Hz, $\text{Ar-C}_{\text{orto}}$), 162.7 (s, $\text{CH}_3\text{O}-\text{C}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (ppm in CDCl_3): $\delta = 88.0$. LC/MS MS: m/z 1177.0 ($[\text{M}_2+\text{Na}]^+$, 3%); 894.9 ($[\text{M}_2-\text{L}]^+$, 100%); 576.0 ($[\text{M}]^+$, 26%).

2.2.1.2. $[\text{Co}_2(\mu\text{-L})_2(\text{L})_2]$. Yield: 0.55 g (83%). M.P. 109–111 °C. $\mu_{\text{eff}} = 4.01$ B.M. Anal. Calcd. for $\text{C}_{44}\text{H}_{64}\text{Co}_2\text{O}_4\text{P}_4\text{S}_8$ ($1155.3 \text{ g mol}^{-1}$): C, 45.7; H, 5.6; S, 22.2; found: C, 45.6; H, 5.5; S, 22.1%. LC/MS MS: m/z 1177.0 ($[\text{M}+\text{Na}]^+$, 1%); 894.9 ($[\text{M}(\text{L})]^+$, 100%); 576.1 ($[(\text{M}/2)]^+$, 5%).

2.2.2. Synthesis of $[\text{Ni}(\text{L})_2(\text{Py})_2]$ complexes

$[\text{Ni}(\text{L})_2]$ complex (0.5 g, 0.09 mmol) was dissolved in 25 mL of boiling chloroform. While stirring, a mixture of pyridine (5 mL) and ethanol (25 mL) was added dropwise. The colour changes from navy blue to a brown colour. The solution is kept at room temperature for two days. The pyridine complex was precipitated as a green colour solid and recrystallized from ethanol.

A loss of pyridine occurred and the colour changed back to the navy blue that is the primary colour of the complex, pyridine-free complex when exposed to air or heated gently. However, the pyridine complex was durable when kept under an inert atmosphere in a desiccator indicating that the dissociation was reversible.

The following data apply to the product:

2.2.2.1. $[\text{Ni}(\text{L})_2(\text{Py})_2]$. Yield: 0.61 g (95%). M.P. decomposition upon heating. $\mu_{\text{eff}} = 2.85$ B.M. $\text{C}_{32}\text{H}_{42}\text{N}_2\text{NiO}_2\text{P}_2\text{S}_4$ (735.6 g mol^{-1}): C, 52.3; H, 5.8; N, 3.8; S, 17.4; found: C, 52.4; H, 5.4; N, 3.9; S, 17.2%. LC/MS MS: m/z 1177.0 ($[(\text{M}_2-4\text{py})+\text{Na}]^+$, 2%); 894.9 ($[\text{M}_2-(\text{L}+4\text{Py})]^+$, 100%); 599.3 ($[(\text{M}-2\text{Py})+\text{Na}]^+$, 1%), 396.0 ($[\text{M}(\text{L})\text{Py}]^+$, 82%).

2.3. X-ray diffraction

Single-crystal X-ray diffraction studies of $[\text{Ni}(\text{L})_2]$ and

$[\text{Ni}(\text{L})_2(\text{Py})_2]$ were done on a Bruker Kappa APEXII CCD area-detector diffractometer operating MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at temperatures of 100 K (296 K (for $[\text{Ni}(\text{L})_2]$ and $[\text{Ni}(\text{L})_2(\text{Py})_2]$). Structures were solved by direct methods [28] and refined by full-matrix least squares against F^2 using all data [28]. All non-H atoms were refined anisotropically. H atoms were positioned geometrically at distances of 0.93 Å (aromatic CH), 0.97 Å (CH_2) and 0.96 Å (CH_3) from the parent C atoms; a riding model was used during the refinement process and the U_{iso} (H) values were constrained to be xU_{eq} (carrier atom), where $x = 1.2$ for CH and CH_2 , and $x = 1.5$ for CH_3 . Experimental data of $[\text{Ni}(\text{L})_2]$ and $[\text{Ni}(\text{L})_2(\text{Py})_2]$ are given in Table 1.

3. Results and discussion

3.1. Spectroscopic studies

3.1.1. IR and Raman spectra

Some of the critical IR and Raman bands of the complexes are listed in Table 2. FTIR and Raman signals of $[\text{Ni}(\text{L})_2]$, $[\text{Ni}(\text{L})_2(\text{Py})_2]$ and $[\text{Co}_2(\mu\text{-L})_2(\text{L})_2]$ display bands comparable in wavenumbers with the literature reports for similar structures [31–33].

The $\nu_{\text{N-H}}$ stretching band at 3180 cm^{-1} reported for the ligand [25] disappears on the IR vibrational spectra of the compounds, supporting the attachment of the ligand to the metal cation. The FTIR spectra for the three complexes display asymmetric and symmetric PS stretching bands (ν_{asym} and ν_{sym}) in the ranges of $(652\text{--}617) \text{ cm}^{-1}$ and $(534\text{--}544) \text{ cm}^{-1}$, respectively. On the Raman vibrational spectra, these bands show up in the ranges of $(650\text{--}605) \text{ cm}^{-1}$ and $(550\text{--}524) \text{ cm}^{-1}$.

The metal-sulfur vibrational bands are located between 200 cm^{-1} and 400 cm^{-1} , which is consistent with the literature [27]. In the IR and Raman spectra, the metal-nitrogen stretching vibrations in the complex $[\text{Ni}(\text{L})_2(\text{Py})_2]$, were assigned to the bands at 259 cm^{-1} and 260 cm^{-1} , respectively.

Table 1X-ray experimental data for the [Ni(L)₂] and [Ni(L)₂(Py)₂] complexes.

Complex	[Ni(L) ₂]	[Ni(L) ₂ (Py) ₂]
Empirical Formula	C ₂₂ H ₃₂ NiO ₂ P ₂ S ₄	C ₃₂ H ₄₂ N ₂ NiO ₂ P ₂ S ₄
Colour/shape	purple/block	yellow/plate
Formula weight	577.40	735.57
Temperature (K)	296(2)	296(2)
Radiation, graphite monochr.	Mo K _α (λ = 0.71073)	
Crystal system	monoclinic	monoclinic
Space group	P 2 ₁ /c	P 2 ₁ /n
a (Å)	11.6069(5)	11.9170(2)
b (Å)	10.1284(4)	9.2936(2)
c (Å)	11.8279(5)	16.3578(3)
α (°)	90	90
β (°)	106.646(2)	101.204(1)
γ (°)	90	90
Volume (Å ³)	1332.21(10)	1777.13(6)
Z	2	2
Abs. coefficients (mm ⁻¹)	1.179	0.902
D _{calc} (mg m ⁻³)	1.439	1.375
Max. crystal dim. (mm)	0.10X0.13X0.21	0.03X0.10X0.10
Θ(max) (°)	25.56	25.84
Reflections measured	2476	3430
Range of h, k, l	−12 < h < 14, −12 < k < 12, −14 < l < 14	−14 < h < 14, −11 < k < 11, −20 < l < 19
Diffractionmeter/scan	Bruker Kappa APEX II/phi and w	
No of reflections with I > 2 σ(I)	2463	3283
Corrections applied	Lorentz polarization	
Computer programs	SHELXS-9, SHELXL-97 [28], ORTEP-3 [29]	
Source of scatter. Factors	International Table for X-Ray Crystallography [30]	
Structure solution	Direct methods	
Treatment of hydrogen atoms	Geometric calculation	
No of parameters varied	142	196
GOF	1.092	1.053
R = F _o − F _c / F _o	0.0447	0.0424
R _w	0.1383	0.1287
(Δρ) _{max} (e Å ⁻³)	0.551	0.686
(Δρ) _{min} (e Å ⁻³)	−1.491	−1.418

Table 2The selected important IR and Raman (R) bands (cm⁻¹) of the complexes.

Complex	ν(asy) (PS)		ν(sym) (PS)		ν(M-S)		ν(M-N)	
	IR	R	IR	R	IR	R	IR	R
[Ni(L) ₂]	652; 626	634; 605	542	549	255	255	—	—
[Co ₂ (μ-L) ₂ (L) ₂]	648; 636	650; 634	534; 518	534; 524	308	301	—	—
[Ni(L) ₂ (Py) ₂]	643; 617	648; 611	544	550	301	300	259	260

3.2. NMR analysis

The dithiophosphinato complexes, [Ni(L)₂(Py)₂] and [Co₂(μ-L)₂(L)₂] are paramagnetic, and their ambient temperature NMR signals do not have assignable features.

However, [Ni(L)₂] complex is diamagnetic as expected and ¹H-, ¹³C and ³¹P NMR data related to this compound are presented in the section, Experimental.

3.2.1. ¹H NMR spectra

The phenyl-ring protons and the phosphorus atom can be regarded as an AA'MM'X spin system. The AA'MM' moiety gives rise to an AMX type appearance. This is probably because J_{AM'} and J_{A'M} are close to zero. Therefore, the assignments of the anisole group aromatic protons were utilized on the basis of the magnitudes of the coupling constants to the phosphorus atom. Namely, the protons in *ortho*-position to phosphorus display a ³J_{PH} of ~9 Hz and those *meta*-position to phosphorus a ⁴J_{PH} of ~2.2 Hz.

The chemical shift difference between the NMR signals of the inner methylene protons of the −CH₂−CH₂−CH₂−CH₃ group (at 1.40 ppm and 1.70 ppm) is more than twice as much as that in the

ligand [25].

In general, ¹H NMR data are consistent with the findings reported for analogous compounds [34,35].

3.2.2. ¹³C NMR spectra

For the complex [Ni(L)₂], the ¹³C chemical shift assignments of the phenyl carbons that are *ortho*- and *meta*-to phosphorus, Ar_{ortho} and Ar_{meta} were done as described in the literature [16]. The ¹³C chemical shifts and coupling constants are given in the Section, Experimental. The data are generally in good agreement with the literature [35].

3.2.3. ³¹P NMR spectra

[Ni(L)₂] complex is composed of a singlet at 88.04 ppm as expected [34] in the proton-decoupled ³¹P NMR spectra. Comparing with the ³¹P NMR singlet reported for the ligand [25], there appears to be an important deshielding effect exerted by the Ni(II) cation.

3.3. Mass spectra

The prominent peaks of the mass spectra of the three complexes are presented in the section, Experimental. The complexes, $[\text{Ni}(\text{L})_2]$ and $[\text{Ni}(\text{L})_2(\text{Py})_2]$ display some of the fragment peaks indicating the attachment of a Na^+ cation. These fragment peaks probably came from the buffer solution used in the ionization procedure in the LC/MS method. The disintegration patterns compare well with similar structures reported in the literature [36–39].

Peculiarly, the heaviest ion peak for the $[\text{Ni}(\text{L})_2]$ complex (weak, 3%) corresponds to the dimer of the molecule plus Na^+ ion. The molecular ion peak of the monomeric complex is also present and much more intense (26%). Presumably, under the ionization conditions, some complex molecules rearrange and form a dimeric species, and that species binds to a Na^+ ion. The molecular peak does not contain Na^+ ions. The principal peak has a mass corresponding to the ion formed by the removal of one of the ligands from the heaviest ion peak.

The molecular ion peak of $[\text{Ni}(\text{L})_2(\text{Py})_2]$ was not observed at all. This complex displays a principle peak corresponding to $[\text{Ni}_2(\text{L})_3]^+$ indicating that the pyridine molecules are not attached as firmly as to endure the ionization condition.

$[\text{Co}_2(\mu\text{-L})_2(\text{L})_2]$ complex displays a weak (1%) molecular ion peak $[\text{M} + \text{Na}^+]$. The principal mass peak corresponds to $[\text{Co}_2(\text{L})_3]$ which indicates that the dimeric structure easily loses a ligand.

3.4. Magnetic susceptibility, μ_{eff}

As with other paramagnetic complexes reported in the literature [40–42], cobalt(II) and pyridine nickel(II) complexes are of susceptibility values corresponding to three and two single electrons, respectively (4.01 BM for $[\text{Co}_2(\mu\text{-L})_2(\text{L})_2]$ and 2.85 BM for $[\text{Ni}(\text{L})_2(\text{Py})_2]$). So, it is concluded that the complexes are of the so-called high spin species. These values agree well with the theoretical counterparts computed for three (3.87 BM) and two single electrons (2.82 BM) respectively. Comparable μ_{eff} values have been for similar structures [43].

3.5. X-ray crystal structures of $[\text{Ni}(\text{L})_2]$ and $[\text{Ni}(\text{L})_2(\text{Py})_2]$

The X-ray structural studies of $[\text{Ni}(\text{L})_2]$ and $[\text{Ni}(\text{L})_2(\text{Py})_2]$ support

Table 3

Selected bond lengths (Å) and angles (°) of nickel(II) complexes.

Complex	$[\text{Ni}(\text{L})_2]$	$[\text{Ni}(\text{L})_2(\text{Py})_2]$
Ni1–N1	—	2.130(2)
Ni1–S1	2.2350(7)	2.5097(6)
Ni1–S2	2.2331(7)	2.4880(6)
P1–S1	2.0245(10)	2.0094(9)
P1–S2	2.0195(10)	2.0080(9)
P1–C1	1.799(3)	1.812(3)
P1–C8	1.809(3)	1.812(3)
S1–Ni1–N1	—	89.12(6)
S1–Ni1–N1 ⁱ	—	90.88(6)
S2–Ni1–N1	—	91.14(6)
S2–Ni1–N1 ⁱ	—	88.86(6)
S1–Ni1–S2	88.17(2)	97.40(2)
S1–Ni1–S2 ⁱ	91.83(3)	82.60(2)
S1–P1–S2	100.47(4)	110.38(4)
C1–P1–S1	114.93(10)	110.75(9)
C1–P1–S2	112.57(10)	109.13(9)
C1–P1–C8	105.08(13)	105.84(13)
C8–P1–S1	111.96(10)	111.74(10)
C8–P1–S2	112.09(10)	108.87(10)
P1–S1–Ni1	84.79(3)	81.61(3)
P1–S2–Ni1	84.96(3)	82.19(3)

Symmetry codes: (i) $-x, 2 - y, 1 - z$ (for $[\text{Ni}(\text{L})_2]$) and $1 - x, 1 - y, 1 - z$ (for $[\text{Ni}(\text{L})_2(\text{Py})_2]$).

the structures inferred from the spectroscopic data. The bond lengths and bond angles of the nickel(II) complexes are summarized in Table 3. The molecular structures of the $[\text{Ni}(\text{L})_2]$ and $[\text{Ni}(\text{L})_2(\text{Py})_2]$ along with the atom-numbering schemes are depicted in Figs. 2 and 3, respectively.

The Ni atoms are situated on inversion centers and coordinated by four symmetry-related S atoms. The average Ni–S bond lengths and S–Ni–S bond angles are 2.4989(6) Å and 90.00(2)°; 2.2341(7) Å and 90.00(3)°, while the average P–S bond lengths and S–P–S bond angles are 2.022(1) Å and 100.47(4)°; 2.0087(9) Å and 110.38(4) and the average P–S–Ni bond angles are 84.88(3)° and 81.90(3)° for $[\text{Ni}(\text{L})_2]$ and $[\text{Ni}(\text{L})_2(\text{Py})_2]$, respectively (Table 3). The Ni–S and P–S bond lengths, and S–Ni–S and S–P–S bond angles are in good agreement with the corresponding average values [2.224(2) Å and 2.002(3) Å, and 88.18(8)° and 101.38(12)°] in *trans*-bis-[O-(2-butoxyethyl)-(p-methoxyphenyl)-dithiophosphonato]nickel(II) [44], [2.2448(7) Å and 2.0076(9) Å, and 89.03(3)° and 102.84(4)°] in *trans*-bis-[benzyl-(p-methoxyphenyl)-dithiophosphinato]nickel(II) complex [45] and [2.2328(5) Å and 2.0035(7) Å, and 88.32(2)° and 101.93(3)°] in *trans*-bis-[O-propyl-(4-

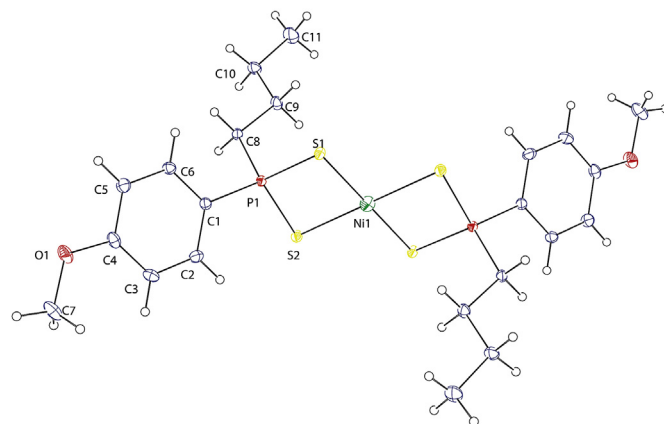


Fig. 2. An ORTEP-3 [20] view of $[\text{Ni}(\text{L})_2]$. The thermal ellipsoids are drawn at the 50% probability level.

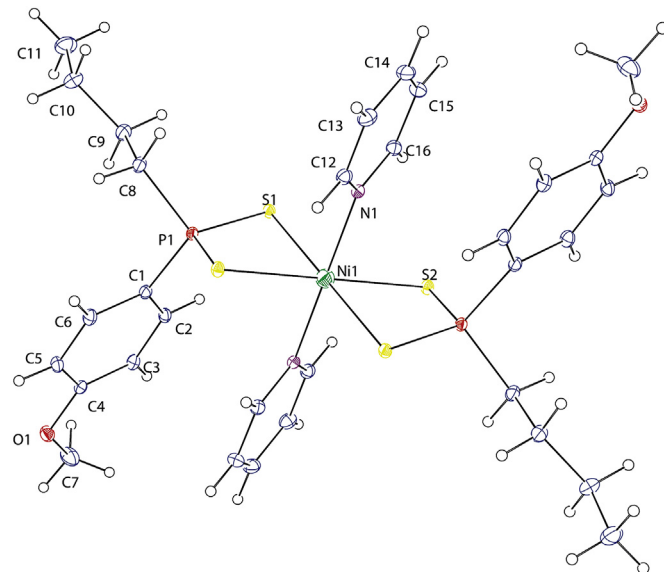


Fig. 3. An ORTEP-3 [20] view of $[\text{Ni}(\text{L})_2(\text{Py})_2]$. The thermal ellipsoids are drawn at the 50% probability level.

ethoxyphenyl)-dithiophosphonato]nickel(II) complex [46]). In the four-membered rings A (Ni1/S1/S2/P1), the angles between the (Ni1/S1/S2) and (S1/S2/P1) planes are $165.81(3)^\circ$ and $166.24(3)^\circ$, indicating $14.19(3)^\circ$ and $13.76(3)^\circ$ bucklings and A rings have total wrinkles of $0.1768(7)$ Å and $0.2564(8)$ Å for $[\text{Ni}(\text{L})_2]$ and $[\text{Ni}(\text{L})_2(\text{Py})_2]$, respectively [47]. Thus, rings conveniently be named to have twisted-chair conformations. In $[\text{Ni}(\text{L})_2]$, the Ni1 atom is of a lightly distorted square-planar geometry, but in $[\text{Ni}(\text{L})_2(\text{Py})_2]$, the Ni1 atom has a vaguely distorted octahedral coordination with the symmetry-related 4-S atoms at the corners of a slightly distorted square and two symmetry-related pyridine donor N atoms at distances of $2.130(2)$ Å. In $[\text{Ni}(\text{L})_2(\text{Py})_2]$; the phenyl and pyridine rings are oriented at a dihedral angle of $20.12(9)^\circ$, a $\pi \cdots \pi$ interaction of $3.604(4)$ Å [$\text{Cg}2 \cdots \text{Cg}3^i = 3.604(4)$ Å, where Cg2 and Cg3 are the centroids of B (C1–C6) and C (N1/C12–C16) rings, symmetry code (i): $1 - x, 1 - y, 1 - z$] and a C–H $\cdots \pi$ interaction [C11–H11A $\cdots$ Cg2ⁱⁱ, where H11A $\cdots$ Cg2ⁱⁱ = 2.85 Å, C11 $\cdots$ Cg2ⁱⁱ = $3.604(4)$ Å and C11–H11A $\cdots$ Cg2ⁱⁱ = 136° , symmetry code (ii): $-x, -y, 1 - z$] are also observed.

4. Conclusions

Three new DTPA nickel(II) and cobalt(II) complexes were synthesized and characterized by different spectroscopic methods. The magnetic susceptibility measurements show that $[\text{Co}_2(\mu\text{-L})_2(\text{L})_2]$ and $[\text{Ni}(\text{L})_2(\text{Py})_2]$ complexes are of high spins. X-ray diffraction studies were also done on $[\text{Ni}(\text{L})_2]$ and $[\text{Ni}(\text{L})_2(\text{Py})_2]$. Four-coordinated nickel complex, $[\text{Ni}(\text{L})_2]$, was found to have a square-planar coordination environment whereas the six coordinated species, $[\text{Ni}(\text{L})_2(\text{Py})_2]$, was of an octahedral geometry. The PS bond lengths on the PS_2 moiety is found to be virtually equal confirming that electron delocalization prevails in the coordination neighbourhood.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molstruc.2019.127222>.

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