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Syntheses and structural characterizations of a new benzyl(4-methoxyphenyl)dithiophosphinic acid and its Ni(II), Co(II), Zn(II), Cd(II), and Ni–pyridine complexes

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ABSTRACT

Benzyl(4-methoxyphenyl)dithiophosphinic acid (HL) was obtained as solid and was treated with the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , and CdCl_2 to prepare its Ni(II), Co(II), Zn(II), and Cd(II) complexes. The nickel complex was further treated with pyridine which led to the formation of octahedral dipyridine derivative. HL was obtained through the addition reaction of the perthiophosphonic acid anhydride Lawesson reagent, (LR), [2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide], with the corresponding Grignard compound (benzylmagnesium bromide) in diethyl ether medium.

The complexes were all of the stoichiometry of $[\text{M}(\text{L})_2]_x$, with $x = 1$ for $\text{M} = \text{Ni}^{2+}$ and $x = 2$ for $\text{M} = \text{Co}^{2+}$, Cd^{2+} and Zn^{2+} . The coordination geometry was square planar in the nickel(II) complex and tetrahedral in the others. Similar to many other nickel(II) complexes, the $\text{Ni}(\text{L})_2$ reacts reversibly with pyridine to yield the octahedral complex $\{(\text{Py})_2\text{Ni}(\text{L})_2\}$.

The compounds were characterized by elemental analysis; MS, FTIR, and Raman spectroscopies. The magnetic susceptibilities of the complexes were measured to confirm the hybridization patterns and the geometries. Single-crystal X-ray analyses of $\text{Ni}(\text{L})_2$ and $[\text{Co}(\text{L})_2]_2$ complexes were also carried out to prove the molecular topologies.

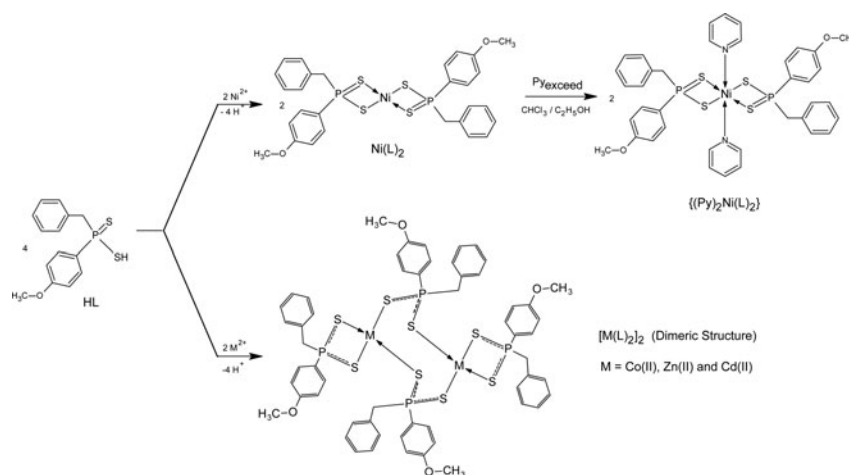
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Thio-Phosphorus complexes; phosphinodithioic acid; Lawesson reagent; Raman spectroscopy

GRAPHICAL ABSTRACT



Introduction

Dithiophosphinic acids $((\text{R}^1)(\text{R}^2)\text{P}(\text{S})\text{SH}$, $\text{R}^1 = \text{R}^2 = (\text{R})_2$ or $\text{R}^1 \neq \text{R}^2$) and their derivatives are known to find a wide range of industrial uses in, for example, lubricants as antioxidants,¹ rubber vulcanization as accelerators,² metal recycling as

sequestering agents,³ material development as flame retardants and antioxidants⁴ and in plastics as multi-purpose additives.⁵ The commercial insecticide anabasine was reported to become much more effective with the addition of dithiophosphinic acids.⁶ Nano-dimensional dithiophosphinic acid–metal chelate

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 Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. 1037078 (for $\text{Ni}(\text{L})_2$), and CCDC 1037079 (for $[\text{Co}(\text{L})_2]_2$). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44–1223–336033; E-mail: deposit@ccdc.cam.ac.uk).

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crystals were found to be effective semiconductors.⁷ Tin and antimony complexes of dithiophosphinic acid-type ligands were used in the treatment of cancer.⁸

In most cases, the use of the dithiophosphinic acids is based on the bidendate ligation nature of the dithiophosphinate ions. With this property, dithiophosphinic acids exhibit an interesting complexation behavior particularly against the soft acid-type cations.⁹ With differing ligation affinity toward various cations, (R)₂P(S)SH-type ligands find a wide use in the separation of metals by solvent extraction.¹⁰ As an example, the commercial extracting agent Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) is particularly valuable in the separation of lanthanides and actinides in the nuclear industry.¹¹

Compounds with the general formula of (R)₂P(S)SH are classified as symmetrical (sym-DTPA) if the two alkyl/aryl groups are identical and asymmetrical (asym-DTPA) otherwise. Sym-DTPAs can be prepared by different routes.¹² The characteristics of the DTPA (i.e., solubility, acidity power, affinity toward cations, etc.) depend on the nature of the alkyl-/aryl- groups attached to the phosphorus. For example, the metal complexes of long chain alkyl-DTPAs are expected to have a better potential to prefer organic solvents during extraction from aqueous media. DTPA derivatives bearing phenyl- and benzyl groups are particularly versatile due to the ease of attaching alkyls of different chain lengths.

These types of compounds are generally oily liquids and require the conversion to the crystalline ammonium salt for purification. This purification step is particularly tedious, and so the solid DTPAs are easier to isolate.¹³ Asym-DTPAs, on the other hand, are prepared through the addition reaction of perthiophosphonic acid anhydrides and Grignard reagents.¹⁴ These types of DTPAs are typically oily liquids. As the compounds have a foul smell, it is desirable to handle them as promptly as possible. With this in mind, it is better to prepare metal-DTPA complexes from the unpurified DTPAs in their liquid form if possible.¹⁵

The nickel(II) complexes of DTPAs are generally square-planar with the sulfur atoms directly attached to nickel(II).^{16a,17a} On the other hand, four-coordinated complexes of cobalt(II), zinc(II), and cadmium(II) have tetrahedral coordination geometries. The nickel(II) complexes are invariably monomeric and, to the contrary cobalt(II), zinc(II), and cadmium(II) complexes are all dimeric. Sulfur atoms may bond to a single cation or act as a bridging ligand.^{17b} In the binuclear complexes, the central eight-membered ring is mostly in a chair conformation.¹⁸

In a similar way to the nickel(II) complexes, the binuclear cobalt(II) complexes of DTPAs are known to be capable of coordinating nitrogenous ligands like pyridine to form five- or six-coordinated new compounds.¹⁹

Result and discussion

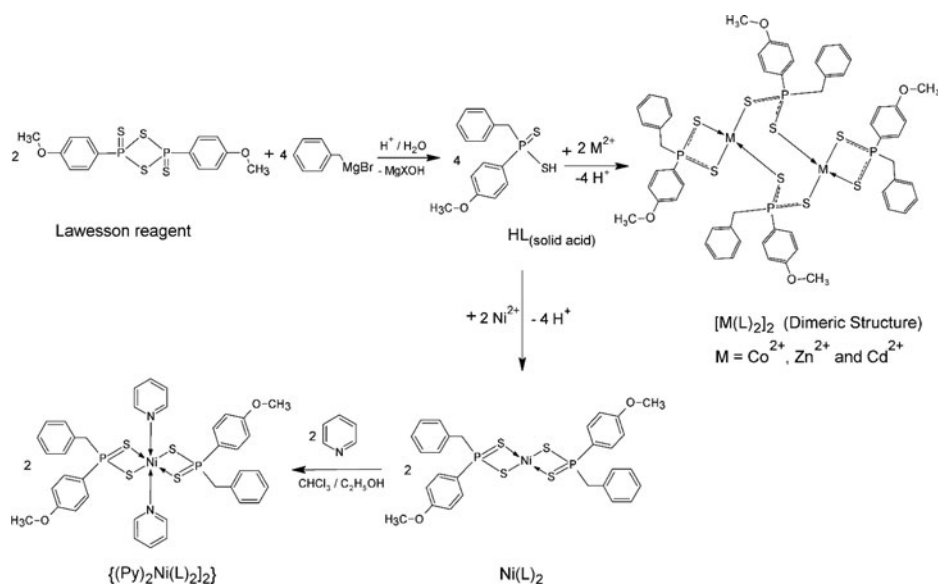
Six new compounds were synthesized. Of these benzyl(4-methoxyphenyl)dithiophosphinic acid proved to be a solid with a remarkably high melting point (88–89°C) as compared to similar structures reported to be liquids at room temperature.^{17a} The complex {(Py)₂Ni(L)₂} is thermally unstable and when exposed to air or heated gently, a loss of pyridine occurred and the color reverted to the original dark blue pyridine-free compound. In order to prevent decomposition, the green complex was kept under pyridine vapor in a desiccator.

The procedures starting with the LR and Grignard compound and ending up with the complex Ni(L)₂, {(Py)₂Ni(L)₂}, and [M(L)₂]₂ (M = Co(II), Zn(II), Cd(II)) are summarized in Scheme 1.

Spectroscopic studies

IR and raman spectra

The asymmetric and symmetric (PS) stretching signals (ν_{asym} and ν_{sym}) of the complexes appear in the regions of 571–695 cm⁻¹ and 568–464 cm⁻¹, respectively. In the Raman spectra,



Scheme 1. Syntheses reactions of HL and its complexes.

Table 1. Selected FTIR and Raman (R) data (cm^{-1}) assignment of significant bands.

Compound	$\nu_{(\text{asym})}$ (PS)		$\nu_{(\text{sym})}$ (PS)		$\nu_{(\text{M-S})}$		$\nu_{(\text{M-N})}$	
	IR	R	IR	R	IR	R	IR	R
HL	571;609	573;612	509;485	510;487	–	–	–	–
$\text{Ni}(\text{L})_2$	642;543	635;635	488;464	466	295	298	–	–
$\{(\text{Py})_2\text{Ni}(\text{L})_2\}$	695;638	698;637	540;521	546;521	343	345	284	284
$[\text{Co}(\text{L})_2]_2$	693;637	701;631	568;530	574;536	348	348	–	–
$[\text{Zn}(\text{L})_2]_2$	641;570	634;573	528;467	536;469	354	353	–	–
$[\text{Cd}(\text{L})_2]_2$	615;569	622;572	528;464	535;466	349	348	–	–

similar signals appear in the regions of $701\text{--}572\text{ cm}^{-1}$ and $546\text{--}466\text{ cm}^{-1}$, respectively.

The $200\text{--}400\text{ cm}^{-1}$ region of IR and Raman spectra of all the complexes displays peaks that are attributable to the metal–sulfur stretching vibrations ($295\text{--}354\text{ cm}^{-1}$ for IR; $298\text{--}353\text{ cm}^{-1}$ for Raman). The complex $\{(\text{Py})_2\text{Ni}(\text{L})_2\}$ also displays a metal–nitrogen stretching band at 284 cm^{-1} in IR and Raman spectra.

The wave numbers of the major signals in IR and the Raman spectra of all the compounds are all of expected values. All these values are in agreement with the literature.^{17b,20} The prominent peaks are given in Table 1.

NMR spectra

The benzyl(4-methoxyphenyl)dithiophosphinic acid complexes of $[\text{Co}(\text{L})_2]_2$, and $\{(\text{Py})_2\text{Ni}(\text{L})_2\}$ are paramagnetic and their ambient temperature NMR spectra are almost featureless to comment on. NMR spectral data (^1H -, ^{13}C - and ^{31}P -NMR) of the other compounds are given in the Experimental section.

^1H NMR spectra

The chemical shifts of all the signals in the spectrum of HL tend to have smaller (higher field) values compared to those of the complexes.

The aromatic protons, together with the phosphorus atom constitute an $\text{AA}'\text{MM}'\text{X}$ spin system. The $\text{AA}'\text{MM}'$ parts (proton signals) display essentially an AMX pattern, because $J_{\text{AM}'}$ and $J_{\text{A}'\text{M}}$ are close to zero. So the chemical shift assignments of the aromatic protons can be made on the basis of the magnitudes of the coupling constants to phosphorus. The aromatic protons *ortho*- to the phosphorus appear to have been split by $13.2\text{--}13.5\text{ Hz}$ due to the phosphorus (three-bond coupling) and further split by $8.7\text{--}8.9\text{ Hz}$ due to the geminal protons. The protons *meta*- to the phosphorus do interact with the phosphorus to the extend of $2.1\text{--}2.7\text{ Hz}$ (four-bond coupling). All these values are comparable to the literature data.²¹

The aromatic protons *ortho*- and *para*- to the benzyl $-\text{CH}_2$ on the benzyl group appear to have overlapped in the spectra of all the compounds. Indeed, the integral curve indicates the existence of three protons for HL, six for the nickel(II) complex, and twelve for the zinc(II) and cadmium(II) complexes reflecting the corresponding stoichiometries.

^{13}C NMR data

The two-bond $^{31}\text{P}\text{--}^{13}\text{C}$ coupling for the aromatic carbon atoms *ortho*- to the phosphorus are observed to be in the narrow range of $12.7\text{--}13.8\text{ Hz}$ in the anisol groups. The single bond $^{31}\text{P}\text{--}^{13}\text{C}$

coupling of the *ipso* carbon for all the compounds lie in the range of $85.6\text{--}70.9\text{ Hz}$.

The aromatic carbons *para*- to the CH_2 - group of the benzyl moiety gave rise to the peak at 127 ppm . This signal displays a remarkable five-bond coupling of $3.3\text{--}4.6\text{ Hz}$ to phosphorus. The aromatic carbons *ortho*- to the benzyl $-\text{CH}_2$ on the benzyl group show up at 130 ppm with a three-bond $^{31}\text{P}\text{--}^{13}\text{C}$ coupling of $5.5\text{--}6.0\text{ Hz}$. The signal at 128 ppm is assigned to the carbons *meta*- to the benzyl $-\text{CH}_2$. This signal is coupled to the phosphorus by $3.9\text{--}4.0\text{ Hz}$. These values compare well with those given in the literature.²²

^{31}P -NMR spectra

The proton-decoupled ^{31}P -NMR spectra of HL, $[\text{Ni}(\text{L})_2]$, $[\text{Zn}(\text{L})_2]_2$, and $[\text{Cd}(\text{L})_2]_2$ show singlets at 64.7 , 84.0 , 67.4 , and 70.2 ppm , respectively.

Magnetic susceptibilities

The magnetic susceptibility μ_{eff} value of the cobalt complex is 4.08 BM . This is in agreement with a d^7 -configuration. Therefore, we conclude that the cobalt(II) complex is of the so-called high spin species. The $\{(\text{Py})_2\text{Ni}(\text{L})_2\}$ complex displays μ_{eff} value as 2.93 BM which corresponds to a high spin, d^8 species.

Descriptions of the crystal structures

The X-ray structural determinations of $\text{Ni}(\text{L})_2$ and $[\text{Co}(\text{L})_2]_2$ confirm the assignments of their structures from spectroscopic data. Selected atom distances and bond angles are listed in Table 2.

The molecular structures along with the atom-numbering schemes are depicted in Figures 1 and 2, while the packing diagrams are given in Figures 3 and 4, respectively. In the $\text{Ni}(\text{L})_2$, the Ni1 atom is located on an inversion centre and coordinated by four symmetry-related S atoms having a slightly distorted square-planar geometry (Figure 1).

The prominent bond lengths and bond angles of the square-planar $\text{Ni}(\text{L})_2$ complex along with those of similar structures are given in Table 3. The average P–S bond length ($2.0101\text{ \AA}$) is remarkably longer compared to the $\text{P}=\text{S}$ bonds of phosphine-sulfides ($1.95\text{--}1.96\text{ \AA}$)^{16b} and dithiophosphato nickel complexes^{17c,d} ($1.97\text{--}1.98\text{ \AA}$), whereas the average Ni–S bond ($2.2413\text{ \AA}$) is shorter than those in octahedral dithiophosphato nickel complexes. The angle S–Ni–S is perfectly rectangular (90.00°) in the square-planar nickel complexes compared to narrower counterparts in octahedral dithiophosphato nickel compounds ($81.33\text{--}82.66^\circ$). In contrast, the angle S–P–S (102.84°) is narrower in $\text{Ni}(\text{L})_2$ than in dithiophosphato nickel compounds ($111.81\text{--}113.20^\circ$).

In the four-membered ring A (Ni1/S1/S2/P1), the angle between the (Ni1/S1/S2) and (S1/S2/P1) planes is $172.84(3)^\circ$ indicating $7.16(3)^\circ$ buckling and A ring has a total wrinkle of $0.3038(13)\text{ \AA}$.²³ So, A ring conveniently be called to have twisted-chair conformation. The two phenyl rings B (C1–C6) and C (C9–C14) are oriented at a dihedral angle of $32.89(11)^\circ$. In $[\text{Co}(\text{L})_2]_2$, the asymmetric unit contains one-half molecule, where the Co atom is coordinated by four S atoms, while the P atom is coordinated by two symmetry related S atoms and two

Table 2. Selected bond lengths (Å) and angles (°) for Ni(L)₂ and [Co(L)₂]₂.

Ni(L) ₂		[Co(L) ₂] ₂	
Ni1-P1 ⁱ	2.8461(7)	Co1-S1	2.3286(5)
Ni1-S1 ⁱ	2.2378(7)	Co1-S2	2.4493(5)
Ni1-S2 ⁱ	2.2448(7)	Co1-S3	2.3623(5)
P1-S1	2.0076(10)	Co1-S4	2.3451(5)
P1-S2	2.0126(10)	S1-P1	2.0256(6)
P1-C1	1.800(3)	S2-P1	2.0003(6)
P1-C8	1.823(3)	S3-P2	2.0256(6)
S1-Ni1-P1	44.55(2)	S4-P2 ⁱ	2.0082(6)
S1-Ni1-P1 ⁱ	135.45(2)	P1-C1	1.8026(19)
S2-Ni1-P1	44.66(2)	P1-C8	1.8304(19)
S2-Ni1-P1 ⁱ	135.34(2)	S1-Co1-S2	85.730(17)
S1-Ni1-S2	89.03(3)	S1-Co1-S3	129.22(2)
S1-Ni1-S2 ⁱ	90.97(3)	S1-Co1-S4	130.32(2)
S1-P1-S2	102.84(4)	S3-Co1-S2	107.600(19)
C1-P1-S1	111.91(10)	S4-Co1-S2	99.035(18)
C1-P1-S2	112.40(10)	S4-Co1-S3	96.588(19)
C1-P1-C8	106.77(13)	P1-S1-Co1	84.52(2)
C8-P1-S1	111.20(11)	P1-S2-Co1	81.93(2)
C8-P1-S2	111.82(11)	P2-S3-Co1	108.20(2)
P1-S1-Ni1	84.01(3)	P2-S4-Co1 ⁱ	90.64(2)
P1-S2-Ni1	83.71(3)	S2-P1-S1	107.73(3)
		C1-P1-S1	113.05(6)
		C1-P1-S2	111.71(6)
		C1-P1-C8	105.09(9)
		C8-P1-S1	107.25(6)
		C8-P1-S2	111.97(7)
		S4-P2-S3 ⁱ	112.18(3)
		C15-P2-S3	112.87(6)
		C15-P2-S4 ⁱ	112.33(6)
		C15-P2-C22	105.07(8)
		C22-P2-S3	105.10(6)
		C22-P2-S4 ⁱ	108.70(6)

Symmetry codes: (i) 1 - x, 1 - y, - z (for Ni(L)₂), 1 - x, - y, - z (for [Co(L)₂]₂).

phenyl C atoms (Figure 2). The average Co-S bond length and S-Co-S bond angle are 2.3713(5) Å and 93.784(13)°, while the average P-S bond length and S-P-S bond angle are 2.0149(6) Å and 109.96(3)°, and the average P-S-Co bond angle is 91.32(2)°, respectively (Table 2). The Co-S and P-S bond lengths, and S-Co-S and S-P-S bond angles are in good agreement with the corresponding average values [2.477(1) Å and 2.075(2) Å, and 87.29(5)° and 108.68(8)°, respectively] in [Co(4-NH₂Py)(iso-Bu₂PS₂)₂].²⁴ The ligand cavity may play an important role in the complexation and metal-ion selectivity. The intramolecular Co1 ... Co1ⁱ [3.777(2) Å], S3 ... S3ⁱ [3.716(2) Å], S4 ... S4ⁱ [5.771(3) Å], and P2 ... P2ⁱ [5.509(3) Å] [symmetry code (i): 1 - x, - y, - z] distances may indicate the hole size of the ring. In the four-membered ring A (Co1/S1/S2/P1), the angle between the (Co1/S1/S2) and (S1/S2/P1) planes is 176.51(3)°, indicating a 3.49(3)° buckling with a total wrinkle of 0.1238(14)

Table 3. Comparison of prominent bond lengths and bond angles of the square-planer Ni(L)₂ complex with those of similar structures.

Ni-S (Å)	P-S (Å)	S-Ni-S (°)	S-P-S (°)	Reference
2.2413(7)	2.0101(10)	90.00(3)	102.84(4)	Present Study 17c
2.229(11)	1.984(13)	91.96(4)	102.65(5)	
2.2305(6)	1.9778(8)	88.79(2)	104.43(4)	17d
2.2396(5)	1.9723(7)	89.142(18)	105.61(3)	
2.4881(3)	1.9765(5)	81.303(12)	111.81(2)	
2.4775(5)	1.9708(7)	82.666(16)	113.15(3)	
2.5213(5)	1.9709(6)	81.333(15)	112.61(3)	

Å, respectively.²³ Thus, A ring may be called to have a twisted-chair conformation. The phenyl rings B (C1-C6), C (C9-C14), D (C15-C20), and E (C23-C28) are oriented at dihedral angles of B/C = 48.29(7)°, B/D = 23.61(7)°, B/E = 58.39(7)°, C/D = 26.86(7)°, C/E = 26.10(7)°, and D/E = 45.39(7)°.

In the crystal array, the Ni(L)₂ molecules are elongated along the diagonal of the plane (101) and stacked along the *b*-axis (Figure 3). [Co(L)₂]₂ molecules are elongated along the *a*-axis and stacked along the *c*-axis (Figure 4).

Conclusions

A new DTPA and its complexes with nickel(II), cobalt(II), zinc(II), and cadmium(II) were prepared. The nickel(II) complex was further treated with pyridine to obtain a mixed, octahedrally coordinated derivative. The six new compounds were characterized by MS, FTIR and RAMAN spectroscopies and also by elemental analysis. The diamagnetic complexes Ni(L)₂, [Zn(L)₂]₂, [Cd(L)₂]₂ and the free DTPA were also investigated by ¹H-, ¹³C- and ³¹P-NMR. The single crystal X-ray analyses of the complexes Ni(L)₂ and [Co(L)₂]₂ were done. The mass- as well as NMR-spectra, and elemental analyses of zinc(II) and cadmium(II) complexes also indicate that they are dimeric structures.

Experimental

Materials and instruments

Analytical-grade LR and benzylbromide were purchased from Merck and used directly without further purification. Chloroform, diethyl ether, ethanol, pyridine, NiCl₂·6H₂O, CoCl₂·6H₂O, ZnCl₂ and CdCl₂ were purchased from Merck. Diethyl ether was distilled and dried over metallic sodium before use.

The LC/MS system was composed of a Waters Alliance HPLC with a C-18 column and a Waters Micromass ZQ connected to an ESI ionizer. Magnetic susceptibilities were measured on a Sherwood Scientific magnetic susceptibility balance (Model MK1) at room temperature (25°C). Melting points were measured on a Gallenkamp apparatus using a capillary tube. ¹H-, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded with a Varian Mercury (Agilent) 400 MHz FT spectrometer in CDCl₃. SiMe₄ (¹H, ¹³C, and 85% H₃PO₄ (³¹P)) were used as standards. IR spectra were recorded on a Perkin-Elmer Spectrum 400 FTIR spectrophotometer (200–4000 cm⁻¹) and are reported in cm⁻¹ units. All Raman spectra were measured 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 50× objective was usually used and all the spectra were excited by the 785 line of a diode laser. Microanalyses were performed using a LECO CHNS-932 C elemental analyzer. Metal content of the compounds were estimated by difference. The Supplemental Materials contain sample ¹H, ¹³C, and ³¹P NMR spectra for HL and metal complexes (Figures S1–S12).

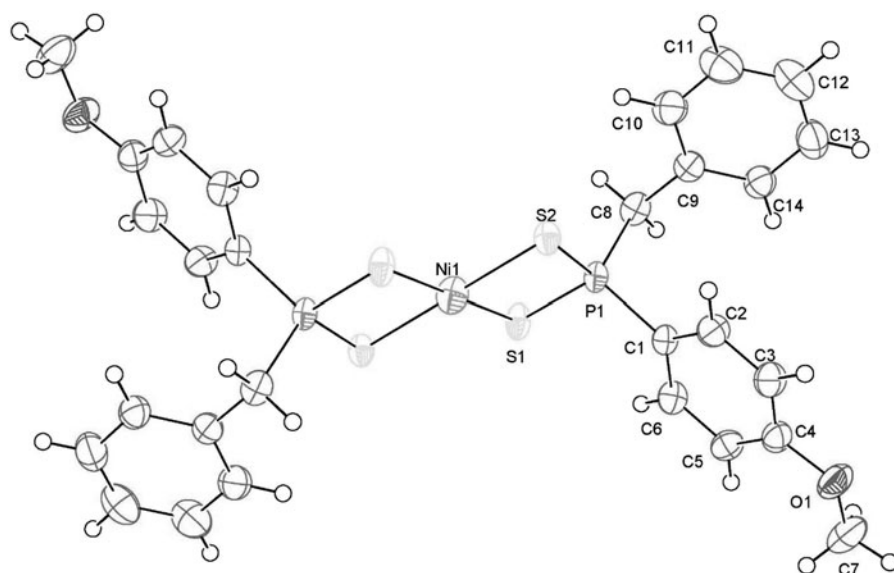


Figure 1. An ORTEP-3 view of $\text{Ni}(\text{L})_2$. The thermal ellipsoids are drawn at the 50% probability level.

X-ray crystallography

Single-crystal X-ray diffraction analyses of $\text{Ni}(\text{L})_2$, and $[\text{Co}(\text{L})_2]_2$ were performed on a Bruker Kappa APEXII CCD area-detector diffractometer using $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation at a temperature of 296 K (for $\text{Ni}(\text{L})_2$) and $\text{Cu K}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) radiation at a temperature of 150 K (for $[\text{Co}(\text{L})_2]_2$). Structures were solved by direct methods²⁵ and refined by full-matrix least squares against F^2 using all data.²⁵ All non-H atoms were refined anisotropically. H atoms were positioned geometrically at distances of 0.93 $\text{\AA}$ (aromatic CH), 0.97 $\text{\AA}$ (CH_2), and 0.96 $\text{\AA}$ (CH_3) (for $\text{Ni}(\text{L})_2$) and 0.95 $\text{\AA}$ (aromatic CH), 0.99 $\text{\AA}$ (CH_2), and 0.98 $\text{\AA}$ (CH_3) (for $[\text{Co}(\text{L})_2]_2$) 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 are given in Table 4.

Single-crystal X-ray diffraction analyses of $\text{Ni}(\text{L})_2$, and $[\text{Co}(\text{L})_2]_2$ were performed on a Bruker Kappa APEXII CCD area-detector diffractometer using $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation at a temperature of 296 K (for $\text{Ni}(\text{L})_2$) and $\text{Cu K}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) radiation at a temperature of 150 K (for $[\text{Co}(\text{L})_2]_2$). Structures were solved by direct methods (SHELXS-97²⁵) and refined by full-matrix least squares against F^2 using all data (SHELXL-97²⁵, where the source of the scattering factors used is International Table for X-Ray Crystallography²⁶). The figures are drawn using ORTEP-3²⁷. All non-H atoms were refined anisotropically. H atoms were positioned geometrically at distances of 0.93 $\text{\AA}$ (aromatic CH), 0.97 $\text{\AA}$ (CH_2), and 0.96 $\text{\AA}$ (CH_3)

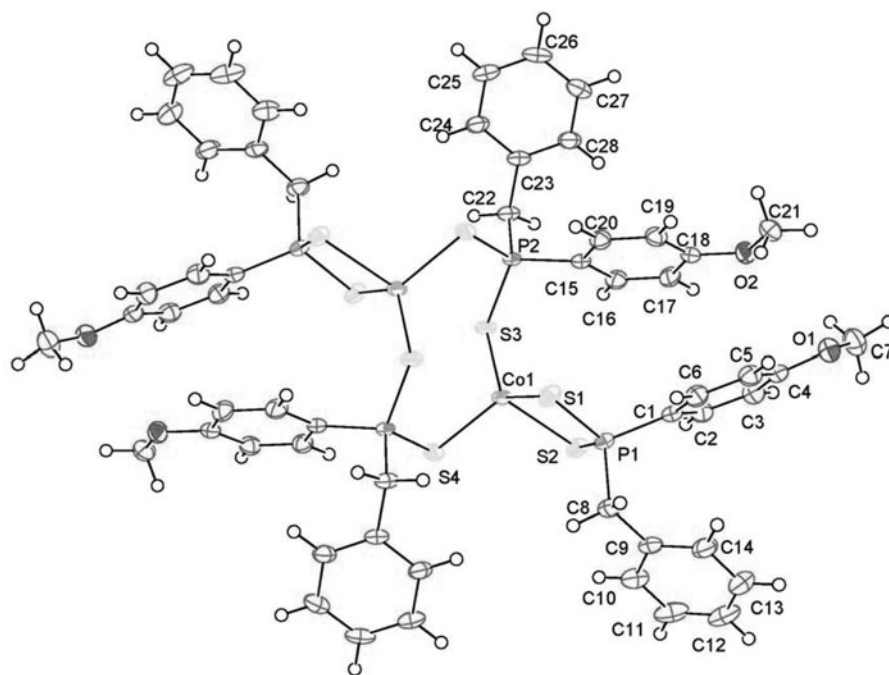


Figure 2. An ORTEP-3 view of $[\text{Co}(\text{L})_2]_2$. The thermal ellipsoids are drawn at the 50% probability level.

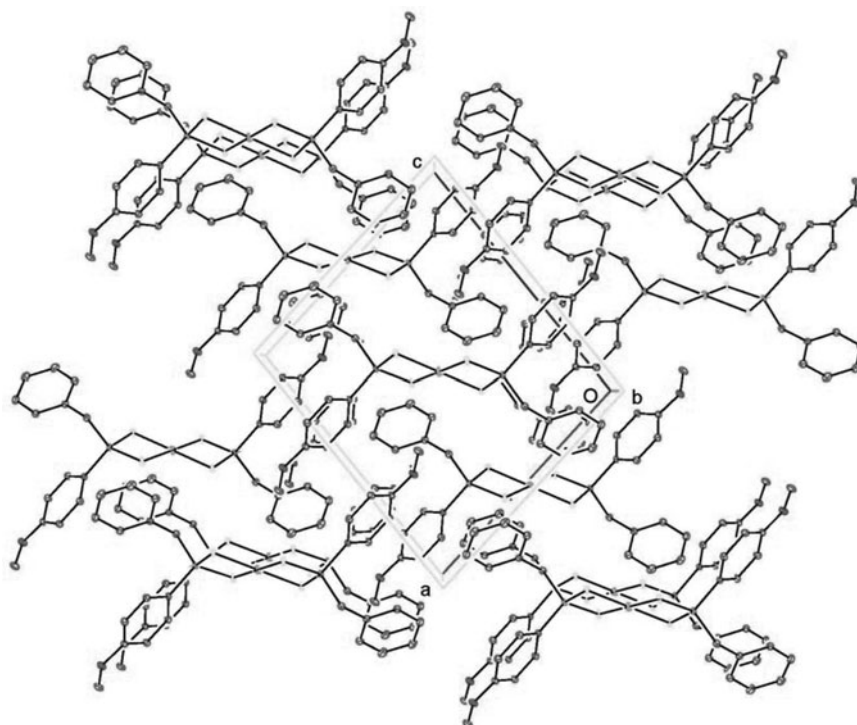


Figure 3. A packing diagram along the *b*-axis of $\text{Ni}(\text{L})_2$.

(for $\text{Ni}(\text{L})_2$) and 0.95 Å (aromatic CH), 0.99 Å (CH_2), and 0.98 Å (CH_3) (for $[\text{Co}(\text{L})_2]_2$) from the parent C atoms; a riding model was used during the refinement process and the Uiso (H) values were constrained to be $x\text{Ueq}$ (carrier atom), where $x = 1.2$ for CH and CH_2 , and $x = 1.5$ for CH_3 . Crystal structure and data refinement parameters are given in Table 4.

Preparation of compounds

Preparation of solid benzyl(4-methoxyphenyl) dithiophosphinic acid (HL)

The title compound was prepared in accordance with the literature [14]. The difference in detail is described as follows. HL

precipitated as cream-colored needle-like crystals. In the process of preparing this compound, all the procedures were performed under argon atmosphere. A suspension of LR (2.00 g, 4.94 mmol) in ether (250 mL) was stirred and cooled in an ice bath and an ethereal solution of benzylmagnesium bromide (1.93 g, 9.88 mmol) was added dropwise. The mixture was heated under reflux for 2 h, and then cooled in an ice bath. The mixture was then treated with 5% H_2SO_4 (100 mL) for hydrolysis to the free acid form. The ether layer was separated, the aqueous phase was extracted several times with small portions (10 mL) of ether, and the combined ether layers were dried over Na_2SO_4 . The dried liquid mixture was filtered through a black band filter-paper into an erlenmeyer and the filtrate was

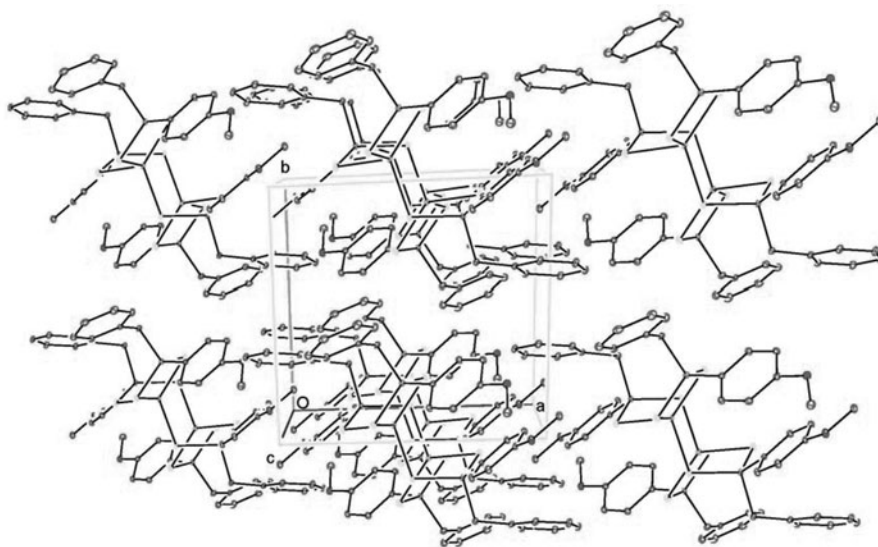


Figure 4. A packing diagram along the *c*-axis of $[\text{Co}(\text{L})_2]_2$.

Table 4. X-ray experimental data for Ni(L)₂ and [Co(L)₂]₂.

Compound	Ni(L) ₂	[Co(L) ₂] ₂
Empirical Formula	C ₂₈ H ₂₈ Ni O ₂ P ₂ S ₄	C ₅₆ H ₅₆ Co ₂ O ₄ P ₄ S ₈
Formula Weight	645.39	1291.23
Crystal System / Space Group	Monoclinic / P 2 ₁ /c	Triclinic / P -1
<i>a</i> (Å)	11.6362(7)	11.2205(6)
<i>b</i> (Å)	9.7525(7)	11.9760(6)
<i>c</i> (Å)	13.1043(8)	12.3397(6)
α (°)	90	11.2205(6)
β (°)	98.608(2)	11.9760(6)
γ (°)	90	12.3397(6)
<i>V</i> (Å ³)	1470.48(16)	1459.91(13)
<i>Z</i>	2	1
<i>D</i> _{calc} (g/cm ³)	1.458	1.469
μ (mm ⁻¹)	1.078 (Mo K α)	8.519 (Cu K α)
Crystal size (mm)	0.20 × 0.21 × 0.39	0.16 × 0.18 × 0.21
Color / Shape	Blue/block	Green/plate
Temp (K)	296(2)	150(2)
Theta range for collection	1.77–25.64	4.03–69.29
Reflections collected	43273	58591
Independent reflections	2759	5396
Data/restraints/parameters	2737 / 0 / 169	5355 / 0 / 336
Goodness of fit on <i>R</i> ²	1.101	1.068
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0478	0.0332
<i>R</i> indices (all data)	0.0479	0.0334
Largest difference peak/hole	0.546 / -1.271	0.486 / -0.384

protected against air moisture by mounting a tube of anhydrous CaCl₂. The needle-like crystals formed in a few days were filtered and dried in a vacuum desiccator.

Preparation of Ni(L)₂, [Co(L)₂]₂, [Zn(L)₂]₂ and [Cd(L)₂]₂

A solution of the metal salt (NiCl₂·6H₂O, 0.20 g, 0.84 mmol; CoCl₂·6H₂O, 0.20 g, 0.84 mmol; ZnCl₂, 0.12 g, 0.84 mmol and CdCl₂, 0.16 g, 0.84 mmol) in ethanol (10 mL) was added to the solution of benzyl(4-methoxyphenyl)dithiophosphinic acid (0.5 g, 1.70 mmol) in ethanol (25 mL). The mixture was stirred overnight at room temperature. The resulting solution was left to stand overnight, and needle-like crystals of different colors formed. The nickel(II) complex was of a deep blue color; cobalt(II) complex was green, and the other two were white-colorless. The crystalline solids were filtered off and recrystallized from ethanol. The crystals of nickel(II) and cobalt(II) proved to be suitable for single crystal X-ray analyses, but repeated recrystallization of the zinc(II) and cadmium(II) complexes turned out to be fruitless.

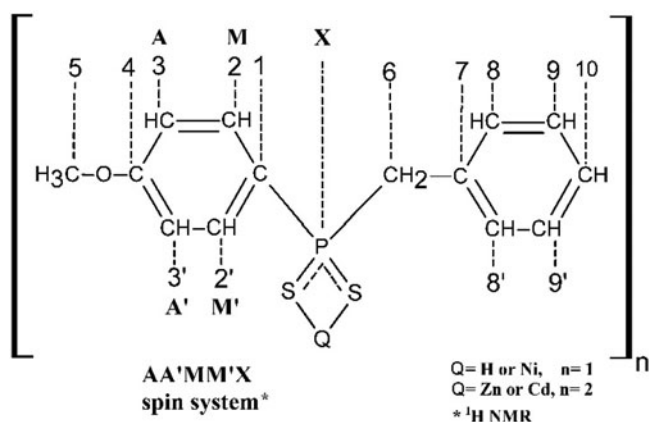
Preparation of {Ni(L)₂(Py)₂}

A solution of Ni(L)₂ (0.5 g, 0.78 mmol) was dissolved in 25 mL of CHCl₃ while boiling. To this solution, a mixture of excess pyridine and ethanol (1:1, v/v) was added dropwise with constant stirring. The color of the mixture changed immediately from deep blue to light brown. The mixture was left aside for a few days and a green solid formed. This solid was filtered and recrystallized from ethanol.

The numbering scheme for compounds is given in Figure 5. The identification data for the compounds were as follows:

Benzyl(4-methoxyphenyl)dithiophosphinic acid, HL

Yield: 2.11 g (71%). Cream-colored. M.P. 88–89°C. ¹H NMR (ppm): δ = 2.40 (bs, 1H, -SH), 3.65 (d, ²J_{PH} = 13.40 Hz, 2H,

**Figure 5.** Numbering scheme for compounds.

C6H), 3.85 (s, 3H, C5H), 6.95 (A-part of AA'MM'X, ⁴J_{PH} = 2.70 Hz (*J*_{AX}), N = *J*_{AM} + *J*_{AM'} = 8.80 Hz, 2H, *m*-H), 7.81 (M-part of AA'MM'X, ³J_{PH} = 13.40 Hz (*J*_{MX}), N = 8.80 Hz, 2H, *o*-H), 7.11 (m, 2H, C9H), 7.26 (m, 3H, C7H overlapped with C10H). ¹³C NMR (ppm): δ = 49.7 (d, *J*_{P-C} = 50.0 Hz, C6), 55.5 (s, C5), 113.9 (d, ³J_{P-C} = 14.5 Hz, C3), 124.4 (d, *J*_{P-C} = 85.4 Hz, C1), 127.6 (d, ⁵J_{P-C} = 4.6 Hz, C10), 128.3 (d, ⁴J_{P-C} = 4.0 Hz, C9), 130.4 (d, ³J_{P-C} = 6.0 Hz, C8), 131.2 (d, ²J_{P-C} = 9.2 Hz, C7), 133.3 (d, ²J_{P-C} = 12.7 Hz, C2), 162.7 (d, ⁴J_{P-C} = 3.1 Hz, C4). ³¹P NMR (ppm): δ = 64.7. LC/MS, MS: *m/z* 293.1 ([HL]⁻, 100.0%); Anal. Calcd. for C₁₄H₁₅OPS₂ (294.37 g mol⁻¹): C, 57.12; H, 5.14; S, 21.79; found: C, 57.27; H, 5.15; S, 22.01%.

Trans-bis-[benzyl(4-methoxyphenyl)dithiophosphinato]nickel(II), Ni(L)₂

Yield: 0.48 g (87%). Deep blue. M.P. 173–174°C. Diamagnetic. ¹H NMR (ppm): δ = 3.65 (d, ²J_{PH} = 13.70 Hz, 4H, C6H), 3.83 (s, 6H, C5H), 6.87 (A-part of AA'MM'X, ⁴J_{PH} = 2.10 Hz (*J*_{AX}), N = *J*_{AM} + *J*_{AM'} = 8.80 Hz, 4H, *m*-H), 7.32 (M-part of AA'MM'X, ³J_{PH} = 13.20 Hz (*J*_{MX}), N = 8.80 Hz, 4H, *o*-H), 6.93 (m, 4H, C9H), 7.17 (m, 6H, C8H overlapped with C10H). ¹³C NMR (ppm): δ = 50.8 (d, *J*_{P-C} = 36.7 Hz, C6), 55.5 (s, C5), 113.6 (d, ³J_{P-C} = 14.9 Hz, C3), 126.1 (d, *J*_{P-C} = 70.9 Hz, C1), 127.3 (d, ⁵J_{P-C} = 3.3 Hz, C10), 128.1 (s, C9), 130.4 (d, ³J_{P-C} = 5.5 Hz, C8), 129.7 (d, ²J_{P-C} = 9.6 Hz, C7), 131.0 (d, ²J_{P-C} = 13.8 Hz, C2), 162.5 (s, C4). ³¹P NMR (ppm): δ = 84.0. LC/MS, MS: *m/z* 645.0 ([Ni(L)₂]⁺, 5.0%); 432.9 ([Ni(L)₂-(CH₃O-C₆H₄)₂]⁺, 49.5%); 391.8 ([Ni(L)+CH₃CN]⁺, 100.0%); 350.8 ([Ni(L)]⁺, 2.0%). Anal. Calcd. for C₂₈H₂₈NiO₂P₂S₄ (645.42 g mol⁻¹): C, 52.11; H, 4.37; S, 19.87; found: C, 52.20; H, 4.41; S, 19.94%.

Bis-[bis-[benzyl(4-methoxyphenyl)dithiophosphinato]cobalt(II)], [Co(L)₂]₂

Yield: 0.43 g (78%). Green color. M.P. 180–181°C. μ_{eff} = 4.08 B.M. Paramagnetic. LC/MS, MS: *m/z* 997.2 ([Co₂(L)₃]⁺, 6.0%); 393.0 ([Co(L)+CH₃CN]⁺, 100.0%); 351.9 ([Co(L)]⁺, 14.2%); Anal. Calcd. for C₅₆H₅₆Co₂O₄P₄S₈ (1291.31 g mol⁻¹): C, 52.09; H, 4.37; S, 19.86; found: C, 52.15; H, 4.37; S, 20.05%.

Bis-[bis-[benzyl(4-methoxyphenyl)dithiophosphinato]zinc(II)], [Zn(L)₂]₂

Yield: 0.49 g (89%). Colorless M.P. 200–201°C. Diamagnetic. ¹H NMR (ppm): δ = 3.64 (d, ²J_{PH} = 14.00 Hz, 8H, C6H), 3.82 (s,

12H, C5H), 6.85 (A-part of AA'MM'X, $^4J_{PH} = 2.40$ Hz (J_{AX}), N = $J_{AM} + J_{AM'} = 8.80$ Hz, 8H, *m*-H), 7.62 (M-part of AA'MM'X, $^3J_{PH} = 13.50$ Hz (J_{MX}), N = 8.80 Hz, 8H, *o*-H), 6.90 (m, 8H, C9H), 7.15 (m, 12H, C8H overlapped with C10H). ^{13}C NMR (ppm): $\delta = 50.6$ (d, $J_{P-C} = 45.6$ Hz, C6), 55.4 (s, C5), 113.4 (d, $^3J_{P-C} = 14.4$ Hz, C3), 125.2 (d, $J_{P-C} = 73.9$ Hz, C1), 127.1 (d, $^5J_{P-C} = 4.5$ Hz, C10), 127.8 (d, $^4J_{P-C} = 3.9$ Hz, C9), 130.5 (d, $^3J_{P-C} = 5.9$ Hz, C8), 131.6 (d, $^2J_{P-C} = 9.1$ Hz, C7), 132.9 (d, $^2J_{P-C} = 12.7$ Hz, C2), 162.2 (d, $^4J_{P-C} = 3.0$ Hz, C4). ^{31}P NMR (ppm): $\delta = 67.4$. LC/MS, MS: m/z 1303.1 ($[Zn_2(L)_4]^-$, 2.0%); 293.3 ($[L]^-$, 100.0%). Anal. Calcd. for $C_{56}H_{56}Zn_2O_4P_4S_8$ (1304.28 g mol $^{-1}$): C, 51.57; H, 4.33; S, 19.67; found: C, 51.72; H, 4.48; S, 19.78%.

Bis-[bis-[benzyl(4-methoxyphenyl)dithiophosphinato]cadmium(II)], $[Cd(L)_2]_2$

Yield: 0.54 g (91%). Colorless. M.P. 231–232°C. Diamagnetic. ^1H NMR (ppm): $\delta = 3.64$ (d, $^2J_{PH} = 14.10$ Hz, 8H, C6H), 3.79 (s, 12H, C5H), 6.82 (A-part of AA'MM'X, $^4J_{PH} = 2.60$ Hz (J_{AX}), N = $J_{AM} + J_{AM'} = 8.90$ Hz, 8H, *m*-H), 7.63 (M-part of AA'MM'X, $^3J_{PH} = 13.40$ Hz (J_{MX}), N = 8.90 Hz, 8H, *o*-H), 6.86 (m, 8H, C9H), 7.12 (m, 12H, C8H overlapped with C10H). ^{13}C NMR (ppm): $\delta = 51.2$ (d, $J_{P-C} = 45.6$ Hz, C6), 55.3 (s, C5), 113.4 (d, $^3J_{P-C} = 14.3$ Hz, C3), 125.5 (d, $J_{P-C} = 81.4$ Hz, C1), 126.9 (d, $^5J_{P-C} = 4.5$ Hz, C10), 127.8 (d, $^4J_{P-C} = 3.9$ Hz, C9), 130.4 (d, $^3J_{P-C} = 5.9$ Hz, C8), 132.2 (d, $^2J_{P-C} = 9.1$ Hz, C7), 133.3 (d, $^2J_{P-C} = 12.8$ Hz, C2), 162.1 (d, $^4J_{P-C} = 3.1$ Hz, C4). ^{31}P NMR (ppm): $\delta = 70.2$. LC/MS, MS: m/z 293.3 ($[L]^-$, 100.0%). Anal. Calcd. for $C_{56}H_{56}Cd_2O_4P_4S_8$ (1398.28 g mol $^{-1}$): C, 48.10; H, 4.04; S, 18.35; found: C, 48.21; H, 4.11; S, 18.44%.

[bis-pyridino-bis-[benzyl(4-methoxyphenyl)dithiophosphinato]nickel(II)], $\{(Py)_2Ni(L)_2\}$

Yield: 0.58 g (93%). M.P., decomposition upon heating. $\mu_{eff} = 2.93$ B.M. Paramagnetic. LC/MS, MS: m/z 825.9 ($[(Py)_2Ni(L)_2+Na]^+$, 8.2%); 508.9 ($[(Py)_2Ni(L)]^+$, 83.3%); 429.9 ($[(Py)Ni(L)]^+$, 100.0%); Anal. Calcd. for $C_{38}H_{38}N_2Ni_2O_4P_4S_8$ (803.62 g mol $^{-1}$): C, 56.79; H, 4.77; N, 3.49; S, 15.96; found: C, 56.87; H, 4.78; N, 3.51; S, 16.15%.

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