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

Ertuğrul Gazi Sağlam, Nurcan Aca, Berline Mougang-Soumé, Hakan Dal, and Tuncer Hökelek

aDepartment of Chemistry, Bozok University, Yozgat, Turkey; bDepartment of Chemistry, Ankara University, Tandoğan, Ankara, Turkey; cDepartment of Chemistry, Université de Montréal, Montréal, Québec, Canada; dDepartment of Chemistry, Anadolu University, Yenibağlar, Eskişehir, Turkey; eDepartment of Physics, Hacettepe University, Beytepe, Ankara, Turkey

ABSTRACT

Benzyl(4-methoxyphenyl)dithiophosphinic acid (HL) was obtained as solid and was treated with the NiCl₂·6H₂O, CoCl₂·6H₂O, ZnCl₂, and CdCl₂ 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 [M(L)₂]ₓ with x = 1 for M = Ni²⁺ and x = 2 for M = Co²⁺, Cd²⁺ and Zn²⁺. The coordination geometry was square planar in the nickel(II) complex and tetrahedral in the others. Similar to many other nickel(II) complexes, the Ni(L)₂ reacts reversibly with pyridine to yield the octahedral complex ([Py]₂Ni(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 Ni(L)₂ and [Co(L)₂]₂ complexes were also carried out to prove the molecular topologies.

GRAPHICAL ABSTRACT

Introduction

Dithiophosphinic acids ((R¹)(R²)P(S)SH, R¹ = R² = (R)₂ or R¹≠R²) and their derivatives are known to find a wide range of industrial uses in, for example, lubricants as antioxidants, rubber vulcanization as accelerators, metal recycling as sequestering agents, material development as flame retardants and antioxidants and in plastics as multi-purpose additives. The commercial insecticide anabasine was reported to become much more effective with the addition of dithiophosphinic acids. Nano-dimensional dithiophosphinic acid–metal chelate...
Crystals were found to be effective semiconductors. Tin and antimony complexes of dithiophosphinic acid-type ligands were used in the treatment of cancer.

In most cases, the use of the dithiophosphinic acids is based on the bidentate ligation nature of the dithiophosphinite ions. With this property, dithiophosphinic acids exhibit an interesting complexation behavior particularly against the soft acid-type cations. 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. As an example, the commercial extracting agent Cyanex 301 (bus(2,4,4-trimethylpentyl)dithiophosphinic acid) is particularly valuable in the separation of lanthanides and actinides in the nuclear industry.

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. 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. Asym-DTPAs, on the other hand, are prepared through the addition reaction of perthiophosphonic acid anhydrides and Grignard reagents. 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.

The nickel(II) complexes of DTPAs are generally square-planar with the sulfur atoms directly attached to nickel(II). 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. In the binuclear complexes, the central eight-membered ring is mostly in a chair conformation.

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.

**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. 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,
similar signals appear in the regions of 701–572 cm\(^{-1}\) and 546–466 cm\(^{-1}\), respectively.

The 200–400 cm\(^{-1}\) region of IR and Raman spectra of all the complexes displays peaks that are attributable to the metal–sulfur stretching vibrations (295–354 cm\(^{-1}\) for IR; 298–353 cm\(^{-1}\) for Raman). The complex \{\((\text{Py})\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.

| Compound | \(v_\text{(asym)}\) (PS) | \(v_\text{(sym)}\) (PS) | \(v_\text{(M-S)}\) | \(v_\text{(M-N)}\) |
|---------|-----------------|-----------------|-----------------|-----------------|
| HL      | 351.25           | 349.75           | 347.5            | 345.25          |
| Ni(L)\(_2\) | 352.75           | 351.25           | 349.75           | 347.5            |
| (IP$_2$)Ni(L)$_2$ | 353.25           | 351.75           | 349.25           | 346.75          |
| (Co(L)$_2$)$_2$ | 354.75           | 352.75           | 350.25           | 347.75          |
| (Zn(L)$_2$)$_2$ | 355.25           | 353.75           | 351.25           | 348.75          |
| [Cd(L)$_2$]$_2$ | 356.75           | 354.75           | 352.25           | 349.75          |

**NMR spectra**

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

**\(^{1}H\) 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 AA’ MM’ X spin system. The AA’ MM’ parts (proton signals) display essentially an AMX pattern, because \(J_{AA’}\) and \(J_{MM’}\) 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 meta- to the benzyl -CH$_2$ appears is more shielded (85.6–70.9 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 3.3–4.6 Hz to phosphorus. The aromatic carbons ortho- to the benzyl -CH$_2$ on the benzyl group show up at 130 ppm with a three-bond \(^{31}P–^{1}C\) coupling of 5.5–6.0 Hz. The signal at 128 ppm is assigned to the carbons meta- to the benzyl -CH$_2$. This signal is coupled to the phosphorus by 3.9–4.0 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, (Ni(L)$_2$), [Zn(L)$_2$]$_2$, and [Cd(L)$_2$]$_2$ show singlets at 64.7, 84.0, 67.4, and 70.2 ppm, respectively.

**Magnetic susceptibilities**

The magnetic susceptibility \(\mu_{\text{eff}}\) 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 \{(Py)$_2$Ni(L)$_2\}\) complex displays \(\mu_{\text{eff}}\) value as 2.93 BM which corresponds to a high spin, d$^6$ species.

**Descriptions of the crystal structures**

The X-ray structural determinations of Ni(L)$_2$ and [Co(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 Ni(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 Ni(L)$_2$ complex along with those of similar structures are given in Table 3. The average P–S bond length (2.0101 Å) is remarkably longer compared to the P=S bonds of phosphine–sulfides (1.95–1.96 Å) and dithiophosphato nickel complexes (1.97–1.98 Å), whereas the average Ni–S bond (2.2413 Å) is shorter than those in octahedral dithiophosphato nickel complexes. The angle S-Ni-S is perfectly rect-angled (90.00)° in the square–planar nickel complexes compared to narrower counterparts in octahedral dithiophosphato nickel compounds (81.33–82.66)°. In contrast, the angle S–P–S (102.84)° is narrower in Ni(L)$_2$, than in dithiophosphato nickel compounds (111.81–113.20)°.

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)° indicating 7.16(3)° buckling and A ring has a total wrinkle of 0.3038(13) Å.\(^{23}\) 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)°.

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respectively (Table 2). The Co–S and P–S bond lengths, and S–

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 109.963(6)°, 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 intramolecu-
lar Co1 ... Co1' [3.777(2) Å], S3 ... S3' [3.716(2) Å], S4 ...
S4' [5.771(3) Å], and P2 ... P2' [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)
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) com-
plex was further treated with pyridine to obtain a mixed, octa-
hedrally 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+ and [Cd(L)2]2+ and the free DTPA were also investigat-
ed 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-
well as NMR-spectra, and elemental analyses of zinc(II) and ca-
dium(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 mea-
sured on a Gallenkamp apparatus using a capillary tube. 1H,
13C[1H], and 31P[31P] NMR spectra were recorded with a Var-
ian 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 com-
pounds were estimated by difference. The Supplemental Mate-
rials contain sample 1H, 13C, and 31P NMR spectra for HL and
metal complexes (Figures S1–S12).

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

|    | Ni(L)2 | [Co(L)2]2 |
|----|--------|----------|
| Ni-P1 | 2.846(7) | 2.238(6) |
| Ni-Si | 2.237(8) | 2.449(3) |
| Ni-S1’ | 2.244(7) | 2.362(5) |
| P1–S1 | 2.006(10) | 2.345(5) |
| P1–S2 | 2.012(10) | 2.256(6) |
| P1–C1 | 1.800(3) | 2.003(6) |
| P1–C8 | 1.823(3) | 2.026(6) |
| S1–Ni–P1 | 44.55(2) | 2.082(6) |
| S1–Ni–P1’ | 135.45(2) | 1.8026(19) |
| S2–Ni–P1 | 44.66(2) | 1.8304(19) |
| S1–Ni–P1 | 135.34(2) | 85.730(7) |
| S1–Ni–S2 | 89.03(3) | 129.23(2) |
| S1–Ni–S2 | 90.97(3) | 130.32(2) |
| S1–Ni–S2 | 102.84(4) | 107.60(19) |
| C1–P1–S1 | 111.91(10) | 99.035(18) |
| C1–P1–S2 | 112.40(10) | 96.588(19) |
| C1–P1–C8 | 106.77(13) | 84.52(2) |
| C8–P1–S1 | 111.20(11) | 81.93(2) |
| C8–P1–S2 | 111.82(11) | 108.29(2) |
| P1–S1–P1 | 84.01(3) | 90.64(2) |
| P1–S2–Ni | 83.71(3) | 107.73(3) |
| C1–P1–S1 | 113.05(6) | 111.71(6) |
| C1–P1–S2 | 115.09(9) | 105.72(6) |
| C8–P1–S1 | 111.97(7) | 108.26(2) |
| C8–P1–S2 | 112.18(3) | 112.87(6) |
| C15–P2–S3 | 112.33(6) | 105.07(8) |
| C22–P2–S3 | 115.10(6) | 108.70(6) |

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

Table 3. Comparison of prominent bond lengths and bond angles of the square-

plane Ni(L)2 complex with those of similar structures.

|    | Ni(L)2 | S–Ni–P (°) | S–P–S (°) |
|----|--------|------------|----------|
| P1–S1 | 2.010(10) | 90.00(3) | 102.84(4) | Present Study |
| 2.229(11) | 1.984(13) | 91.96(4) | 102.65(5) | 17c |
| 2.230(5) | 1.977(8) | 88.79(2) | 104.43(4) | 17d |
| 2.239(5) | 1.972(3) | 89.14(18) | 105.61(3) | 17d |
| 2.488(13) | 1.976(5) | 81.30(12) | 111.81(12) | 17d |
| 2.677(5) | 1.970(8) | 82.66(16) | 113.15(3) | 17d |
| 2.5213(5) | 1.970(9) | 81.33(15) | 112.61(3) | 17d |
X-ray crystallography

Single-crystal X-ray diffraction analyses of Ni(L)₂, and [Co(L)₂]₂ were performed on a Bruker Kappa APEXII CCD area-detector diffractometer using Mo Kα (λ = 0.71073 Å) radiation at a temperature of 296 K (for Ni(L)₂) and Cu Kα (λ = 1.54178 Å) radiation at a temperature of 150 K (for [Co(L)₂]₂). Structures were solved by direct methods and refined by full-matrix least squares against F² using all data. All non-H atoms were refined anisotropically. H atoms were positioned geometrically at distances of 0.93 Å (aromatic CH), 0.97 Å (CH₂), and 0.96 Å (CH₃) (for Ni(L)₂) and 0.95 Å (aromatic CH), 0.99 Å (CH₂), and 0.98 Å (CH₃) (for [Co(L)₂]₂) from the parent C atoms; a riding model was used during the refinement process and the U₁iso (H) values were constrained to be xUeq(carrier atom), where x = 1.2 for CH and CH₂, and x = 1.5 for CH₃. Experimental data are given in Table 4.

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Figure 1. An ORTEP-3 view of Ni(L)₂. The thermal ellipsoids are drawn at the 50% probability level.

Figure 2. An ORTEP-3 view of [Co(L)₂]₂. The thermal ellipsoids are drawn at the 50% probability level.
**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% H₂SO₄ (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 Na₂SO₄. The dried liquid mixture was filtered through a black band filter-paper into an erlenmeyer and the filtrate was
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.

**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 | C₆H₁₂NiO₂P₂S₄ | C₆H₁₂CoO₂P₂S₄ |
| Formula Weight | 645.39 | 1292.28 |
| Crystal System / Space Group | Monoclinic / P 2₁/c | Triclinic / P ₁ |
| α (Å) | 11.6362(7) | 11.2050(6) |
| β (Å) | 9.7252(7) | 11.9760(6) |
| γ (Å) | 13.1043(8) | 12.3397(6) |
| α (°) | 90 | 112.205(6) |
| β (°) | 90 | 112.205(6) |
| γ (°) | 90 | 112.205(6) |
| V (Å³) | 1470.48(16) | 1459.91(13) |

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

**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, JPH = 13.70 Hz, 4H, C6H), 3.83 (s, 6H, C5H), 6.87 (8H, C7H overlapped with C10H).

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

Yield: 0.43 g (78%). Green color. M.P. 180–181°C. μeff = 4.08 B.M. Paramagnetic. LC/MS, MS: m/z 997.2 ([Co₂L₄]⁺, 6.0%); 393.0 ([CoL]+, 100.0%); 351.9 ([CoL]⁺, 14.2%); Anal. Calcd. for C₆H₁₂NiO₂P₂S₄ (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-[benzyl(4-methoxyphenyl)dithiophosphinato] zinc(II), Zn(L)₂**

Yield: 0.49 g (89%). Colorless M.P. 200–201°C. Diamagnetic. ¹H NMR (ppm): δ = 3.64 (d, JPH = 14.00 Hz, 8H, C6H), 3.82 (s, C6H), 3.95 (s, 8H, C7H overlapped with C10H).
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