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Synthesis, spectroscopic characterization and X-ray single crystal structures of trans-bis[4-methoxyphenyl (3-methylbutyl) dithiophosphinato] nickel(II) and bis [4-methoxyphenyl (3-methylbutyl) dithiophosphinato]cobalt(II) complexes

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Abstract Thionation of 3-methylbutylmagnesium bromide with Lawesson's Reagent (LR) gave 4-methoxyphenyl (3-methylbutyl)dithiophosphinic acid (DTPA), and the latter was converted to the ammonium salt (NH_4L = Ammonium 4-methoxyphenyl (3-methylbutyl) dithiophosphinate). The complex, trans–bis[4-methoxyphenyl(3–methylbutyl) dithiophosphinato] nickel(II) [NiL_2], was prepared by the reaction of NH_4L with $NiCl_2.6H_2O$ in EtOH. Bis [4-methoxyphenyl (3-methylbutyl) dithiophosphinato]cobalt(II) [$(CoL_2)_2$] was also prepared in the same way. The structures of the complexes have been characterized by elemental analysis, FTIR, ^1H, ^{13}C, ^{31}P NMR and X-ray diffraction. The single crystal X-ray structures of [NiL_2] and [$(CoL_2)_2$] show that the nickel complex is square planar while the cobalt counterpart has tetrahedral coordination with a dimeric structure. Bond lengths, angles, torsion angles and dihedral angles are correlated to the structures and also compared with the literature data on similar compounds.

Introduction

The dithiophosphinate (DTP) anions $[R_2PS_2]^-$ can act as bidentate ligands with many transition metals to form stable chelate complexes; consequently, these sulfur ligands are suitable for solvent extraction of metals [1–3]. An example of such dithiophosphinates, known as CYANEX 301, has found use in industry for metal extraction [4–6]. Some of these complexes have antitumor activity and are therefore the subject of chemotherapy studies [7]. Although there are several reports on the chemistry of symmetric dithiophosphinic acid complexes, studies on dithiophosphinic acids bearing different R groups are rather rare.

In this study, the reaction of Lawesson's Reagent (LR) with 3-methylbutylmagnesium bromide, subsequent salt formation of the product (NH_4L) with NH_3, and new Ni(II) and Co(II) complexes of the L^- anion have been investigated (Scheme 1). The compounds were characterized by elemental analyses, ^1H, ^{13}C, ^{31}P NMR and FTIR spectral data. The magnetic susceptibilities of the complexes were measured. The crystal structures of [NiL_2] and [$(CoL_2)_2$] were confirmed by X-ray crystallography.

Experimental

Analytical-grade LR and 1-bromo-3-methylbutane were purchased from Across and used without further purification. Benzene, diethyl ether, methanol, ethanol, $NiCl_2.6H_2O$ and $CoCl_2.6H_2O$ were purchased from Merck. All solvents were dried and distilled before use. Magnetic susceptibilities were determined 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. NMR spectra (^1H, ^{13}C and ^{31}P) were recorded at 400 MHz on a Bruker DPX FT-NMR spectrometer in D_2O and $CDCl_3$. $SiMe_4$ was used as the internal standard for ^1H and ^{13}C NMR; 85% H_3PO_4 was employed as

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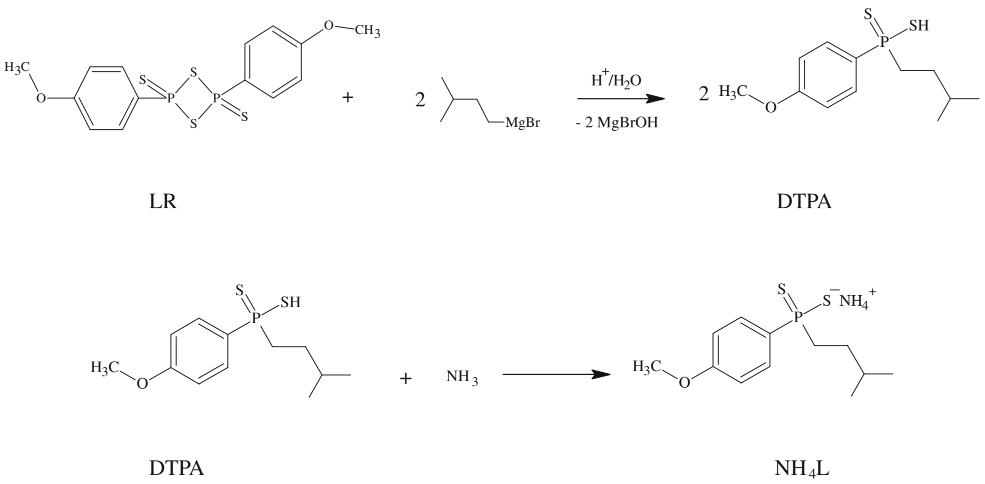
Scheme 1 Synthesis of NH_4L



an external standard for ^{31}P NMR. IR spectra were recorded on a Mattson 1000 FTIR spectrophotometer (400–4,000 cm^{-1}) in KBr pellets (1%w/w) and are reported in cm^{-1} units. Microanalyses were performed using a LECO CHNS-932 C elemental analyzer.

X-ray studies

Suitable single crystals of sizes 0.25 × 0.20 × 0.15 mm for $[NiL_2]$ and 0.40 × 0.20 × 0.20 mm for $[(CoL_2)_2]$ were selected for X-ray diffraction. The intensity data were collected at room temperature on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å) [8]. Data were corrected for Lorenz and polarization effects, and an absorption correction was made using psi.scan after obtaining the complete structural model. The intensity data were collected by $\omega - 2\theta$ scan mode within $4.40° \leq 2\theta \leq 45.52°$ for $-17 \leq h \leq 0$, $0 \leq k \leq 12$, $-17 \leq l \leq 18$ in the monoclinic crystal system for $[NiL_2]$ and $4.60° \leq 2\theta \leq 52.58°$ for $-14 \leq h \leq 0$, $-15 \leq k \leq 13$, $-16 \leq l \leq 15$ in the triclinic crystal system for $[(CoL_2)_2]$. The structures were solved by direct methods using SHELXS 97 and refined by full-matrix least squares SHELXL 97 [9]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated by a riding model. ORTEP III plotting program was used for molecular graphics [10].

Preparation of NH_4L

NH_4L was prepared in accordance with the literature published for related compounds [11]. All the procedures that follow were performed under argon atmosphere. A suspension of LR (2 g, 4.9 mmol) in diethyl ether (200 mL) was stirred and cooled in ice while an etheral solution of isobutyl magnesium bromide (1.59 g, 9.9 mmol) was added. The mixture was heated under reflux for 1 h, then cooled and hydrolyzed with 5% H_2SO_4 (200 mL). The ether layer was separated, the aqueous phase was extracted several times with ether, and the combined ether layers were dried over Na_2SO_4 and evaporated under vacuum. The oily residue, dithiophosphinic acid, DTPA was taken into dry benzene, the solution was cooled with in an ice-salt bath, and dry ammonia was passed through the cooled solution. The precipitated white solid was filtered off and dried in a vacuum desiccator. Yield: 1,43 g (49%). M.P. 183–184 °C. Anal. Calcd. for $C_{12}H_{22}NOPS_2$ (291,4 g mol^{-1}): C, 49.5; H, 7.6; N, 4.8; S, 22.0; found: C, 49.7; H, 8.0; N, 4.8; S, 22.1. ^{1}H NMR (ppm in D_2O): $\delta = 0.60$ (d, $^{3}J_{HH} = 6$ Hz, 6H, CH–$(C\underline{H}_3)_2$), 1.30 (m, $^{3}J_{HH} = 7$ Hz, 1H, C–CH), 1.20 (m, 2H, CH_2–$C\underline{H}_2$), 2.06 (m, 2H, P–CH_2), 3.70 (s, 3H, Ar–OCH_3), 6.88 (dd, $^{4}J_{PH} = 1.7$ Hz, $^{3}J_{HH} = 8.6$ Hz, 2H, Ar–H_{meta}), 7.85 (dd, $^{3}J_{PH} = 12.6$ Hz, $^{3}J_{HH} = 8.6$ Hz, 2H, Ar–H_{orto}). ^{13}C NMR (ppm in D_2O): $\delta = 22.0$ (s, CH–$(\underline{C}H_3)_2$), 33.1 (d, $^{3}j_{P-C} = 4.1$ Hz, C–$\underline{C}H$), 28.5 (d, $^{2}j_{P-C} = 17.0$ Hz, CH_2–$\underline{C}H_2$), 42.6 (d, $j_{P-C} = 56.4$ Hz, P–$\underline{C}H_2$–CH_2), 56.1 (s, $\underline{C}H_3O$–Ar), 113.9 (d, $^{3}J_{P-C} = 13.2$ Hz, =$\underline{C}$H–CH=CH–P), 163.9 (s, CH_3O–$\underline{C}$), 132.4 (d, $^{2}J_{P-C} = 12.3$ Hz, –$\underline{C}$H=CH–P), 131.6 (d, $^{1}J_{P-C} = 74$ Hz, –CH=$\underline{C}$H–P). ^{31}P NMR (ppm in D_2O): $\delta = 66.37$.

Preparation of $[NiL_2]$

A solution of $NiCl_2.6H_2O$ (0.08 g, 0.3 mmol) in methanol (10 mL) was added to a solution of NH_4L (0.2 g, 0.6 mmol) in the same solvent (25 mL). The mixture was heated gently. The resulting solution was left to stand overnight to obtain needle-like crystals. The dark blue crystalline solid was filtered off and recrystallized from ethanol. Yield: 0.17 g (% 85). M.P. 133–134 °C. μ_{eff} = Diamagnetic. Anal. Calcd. for $C_{24}H_{36}NiO_2P_2S_4$ (605,4 g mol^{-1}): C, 47.6; H, 6.0; S, 21.2; found: C, 47.5; H, 5.7; S, 21.5. ^{1}H NMR (ppm in $CDCl_3$): $\delta = 0.60$ (d, $^{3}J_{HH} = 6$ Hz, 6H, CH–$(C\underline{H}_3)_2$), 1.63 (m, ^{3} 2H, C–CH), 1.60 (m, 2H, $CH_2–\underline{CH_2}$), 2.20 (m, 2H, $P–CH_2$), 3.78 (s, 3H, Ar–OCH_3), 7.00 (d, $^3J_{PH} = 7.5$ Hz, 2H, Ar–H_{meta}), 7.70 (dd, $^3J_{PH} = 12.7$ Hz, $^3J_{HH} = 8.7$ Hz, 2H, Ar–H_{orto}). ^{13}C NMR (ppm in $CDCl_3$): $\delta = 22.0$ (s, CH–($\underline{C}H_3)_2$), 31.0 (s, C–$\underline{C}$H), 29.2 (d, $^2j_{P–C} = 15.7$ Hz, $CH_2–\underline{C}H_2$), 40.1 (d, $j_{P–C} = 43.7$ Hz, P–$\underline{C}H_2–CH_2$–), 161.9 (s, $CH_3O–\underline{C}$), 56.2 (s, $\underline{C}H_3O$–Ar), 115.2 (d, $^3J_{P–C} = 15.0$ Hz, =$\underline{C}$H–CH=CH–P), 131.9 (d, $^2J_{P–C} = 14.0$ Hz, –$\underline{C}$H=CH–P), 131.1 (d, $^1J_{P–C} = 70.1$ Hz, –CH=$\underline{C}$H–P). ^{31}P NMR (ppm in $CDCl_3$): $\delta = 90.00$.

Preparation of [($CoL_2)_2$]

A solution of $CoCl_2.6H_2O$ (0.08 g, 0.3 mmol) in ethanol (10 mL) was added to a solution of NH_4L (0.2 g, 0.6 mmol) in the same solvent (25 mL). The mixture was heated gently. The solution was kept overnight 21 °C, whereupon the complex precipitated as a green crystalline solid, which was filtered off and recrystallized from ethanol. Yield: 0.18 g (% 90). M.P. 188–190 °C. $\mu_{eff} = 4.11$ B.M. Anal. Calcd. for $C_{48}H_{72}Co_2O_4P_4S_8$ (1,211,4 g mol^{-1}): C, 47.6; H, 6.0; S, 21.2; found: C, 47.6; H, 5.4; S, 22.0.

Single crystals of both complexes suitable for X-ray analysis were obtained by recrystallization from ethanol.

Results and discussion

Spectroscopic data

Selected IR data for the compounds NH_4L, [NiL_2] and [($CoL_2)_2$] are listed in Table 1. The characteristic asymmetric and symmetric $\nu_{P=S}$ bands are observed at 596–619 and 518–546, respectively. Characteristic $\nu_{N–H}$ bands are observed at 3,171 and 3,111 cm^{-1} for NH_4L; these bands are absent in the spectra of the two complexes, confirming the exclusion of the NH_4^+ ion.

The principle features of the ^1H NMR spectra assignments being made on the bases of the numbering scheme given in Fig. 1 are as follows: The doublet at 0.6 ppm is assigned to the CH_3 protons at 9 and 9'. The multiplet at around 1.2 ppm is attributed to the CH_2 protons of the position 7. The general appearance of the multiplet reflects a partly superimposed doublet of triplets, as expected. The neighboring multiplet at 1.3 ppm belongs to the methine proton of the isopropyl group, while the multiplet at 2.06 ppm is assigned to the CH_2 protons at position 6. This multiplet does not give any indication that the phosphorus center is chiral, which implies that the two sulfur atoms are chemically equivalent in solution. The signal at 3.7 ppm reflects the presence of the OCH_3 group, while the signals at 6.88 and 7.85 ppm, both of which are doublets of doublets, belong to the phenolic protons. The signal of the NH_4^+ protons appears to be been overlapped with the H_2O signals, as expected.

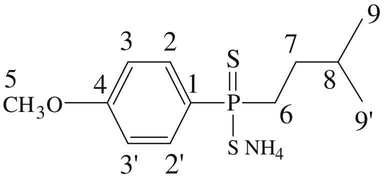


Fig. 1 Numbering scheme for NH_4L

The ^1H NMR features of the complex [NiL_2] are essentially the same as those of free NH_4L, except that the resonances are shifted downfield, which may be the result of solvent change (from D_2O to $CDCl_3$) as well as the bonding to Ni^{2+}.

The complex [($CoL_2)_2$] is paramagnetic, and the ambient temperature NMR spectrum is so complicated as to make it awkward to comment on.

The ^{13}C NMR spectrum of NH_4L displays nine distinct signals, as expected from the structure. The signal at 22 ppm is due to the CH_3 carbons at positions 9 and 9′ (Fig. 1) and the one at 28.5 ppm to the CH_2 carbon at position 7. This signal is split by 17 Hz through two-bond coupling to P. The doublet at 33.1 ppm is assigned to the carbon at position 8. A three-bond ^{31}P-coupling of 4.1 Hz is observable here. The doublet at 42.6 ppm belongs to the CH_2 carbon at positions 6. The splitting here is 56.4 Hz, reflecting an interaction of normal order for one-bond coupling.

The singlet at 56.1 ppm is due to the OCH_3 carbon, and the doublet at 113.9 ppm to the aromatic carbons at position 3. The three-bond splitting of 13.2 Hz conforms with the literature values for similar structures [12–15]. The ipso-carbon at position 1 gives rise to a doublet signal at around 131.6 ppm. The downfield member of the doublet appears to be overlapped with the doublet signal of C2. The C2 signal at 132.4 ppm is a doublet with coupling of 12.3 Hz, which is comparable with similar structures

Table 1 Selected FTIR data (cm^{-1}) for the compounds

Compound	$\nu_{(as,s)}$ (P S)	ν(N–H)	ν(C=C)	$\nu(C–H)_{aliph}$	$\nu(C–H)_{arom}$
NH_4L	619; 544	3,171; 3,111	1,592; 1,496	2,955; 2,868; 2,839	3,010
[NiL_2]	596; 546	–	1,592; 1,498	2,955; 2,926; 2,839	3,008
[($CoL_2)_2$]	610; 518	–	1,591; 1,498; 1,459	2,955; 2,895; 2,868	3,026

[16–18]. The signal at 160.0 ppm belongs to the C4 ipso-carbon and is unsplit as expected.

The ^{13}C NMR spectrum of [NiL$_2$] displays essentially the same features as NH$_4$L. [(CoL$_2$)$_2$] is paramagnetic, and its ^{13}C NMR spectrum is not commented on.

The proton de-coupled ^{31}P NMR spectra of NH$_4$L and [NiL$_2$] show singlets at 66.37 and 90.00 ppm, respectively.

X-ray crystal structures

Crystal and experimental data are given in Table 2 for the compounds [NiL$_2$] and [(CoL$_2$)$_2$].

An ORTEP III diagram and numbering scheme for [NiL$_2$] is shown in Fig. 2. The crystal structure reveals that the central Ni atom is four-coordinate, with the two crystallographically independent L$^-$ anions acting as S,S′-bidentate ligands. The alkyl substituents of the two phosphinate anions are in trans-configuration with respect to the central coordination plane. The central coordination geometry is slightly distorted square planar, with the distances S1–S2 and S3–S4 being 3.125 Å and 3.218 Å, respectively. The torsion angle S1–S2–S3–S4 is 0.1°, supporting the nearly perfect planar coordination. Other torsion angles, namely Ni–S2–P1–S1 (0.6°) and Ni–S3–P2–S4 (0.0°), are also strong indications of the near co-planarity of the two four-membered chelate rings. The dihedral angle between the two ring-planes is measured to be 0.55(6)°. The deviation from coplanarity can be attributed to packing effects. P1 shows a slight deviation of 0.0134 Å from the coordination plane. The angle between the two phenyl planes is 69.6(3)°. The bond lengths, Ni–S1, Ni–S2, Ni–S3 and Ni–S4, are 2.238(3), 2.244(2), 2.224(2) and 2.225(3) Å, respectively. These values are comparable to the literature values reported for similar structures as shown in Table 3 [19–22]. The phosphorus atoms have an essentially tetrahedral geometry.

Table 2 Crystal and experimental data for [NiL$_2$] and [(CoL$_2$)$_2$]

Compound	[NiL$_2$]	[(CoL$_2$)$_2$]
Formula	$C_{24}H_{36}NiO_2P_2S_4$	$C_{48}H_{72}Co_2O_4P_4S_8$
Formula weight	605.44	1,211.36
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/a$ (14)	$P-1$
Unit cell dimensions		
a (Å)	15.8616(12)	11.3566(13)
b (Å)	11.5704(18)	12.487(3)
c (Å)	17.110(2)	12.9779(12)
α (°)	90.000	74.349(9)
β (°)	107.700(9)	68.082(8)
γ (°)	90.000	63.545(10)
V (Å^3)	2,991.5(7)	1,516.7(4)
Z	4	2
Calculated density (g cm^{-1})	1.34	1.33
Absorption coefficient (mm^{-1})	1.054	0.965
Crystal size (mm)	0.25 × 0.20 × 0.15	0.40 × 0.20 × 0.20
θ(max) (°)	22.76	26.29
Reflexions measured	4,003	6,010
Unique reflexions	3,838	5,723
R_{int}	0.0505	0.0203
Reflexions with $F^2 > 2\sigma(F^2)$	1,767	3,634
Number of parameters	298	271
R_1 [$F^2 > 2\sigma(F^2)$]	0.052	0.051
R_1 (all data)	0.198	0.111
wR_2 (all data)	0.147	0.153
GOOF, S	0.973	1.000
Difference peak and hole (e Å^{-3})	0.401 and −0.322	0.870 and −0.527

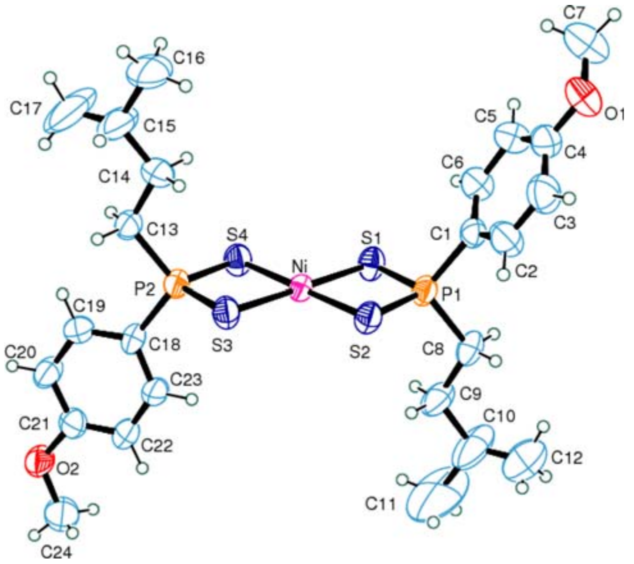


Fig. 2 ORTEP III diagram of [NiL$_2$] with thermal ellipsoids at 50% probability level

The average P–S and P–C bond lengths are 2.011(3) and 1.802(3) Å, respectively. Apparently, the molecular geometry is affected by the C6–H1···S1 intramolecular hydrogen bond, the bond lengths being 0.930 Å (D···H) and 2.858(3) Å (H–A). The angle A–H···D is 115.3(7)°, and the distance A···D is 3.362(12) Å .

Figure 3 shows the ORTEP III diagram of the complete complex molecule, [(CoL$_2$)$_2$] with 50% probability level ellipsoids. The most important bond lengths, angles and torsion angles are listed in Table 4. In Fig. 4, are given three planes around the central coordination sphere. The molecule is a discrete dimer. The catenation is mediated by two dithiophosphinato groups as monodentate ligands to one Co atom with the remaining sulfur atoms being

Table 3 Selected geometric parameters for [NiL$_2$] and similar structures

Compound	Ni–S (Å)	S–Ni (°)	P–S (Å)	S–P–S (°)	P–C (Å)	Literature
I	2.232(2)	88.17(9)	2.011(3)	101.07(14)	1.802(3)	Present study
II	2.170(2)	87.64(6)	2.015(2)	99.66(7)	1.784(4)	[19]
III	2.226(9)	88.34(3)	2.006(1)	No data	1,787(3)	[20]
IV	2.222(8)	88.14(3)	1.994(1)	100.57(4)	1.782(3)	[21]
V	2.241(5)	87.7(2)	2.004(6)	101.6(3)	1.828(19)	[22]

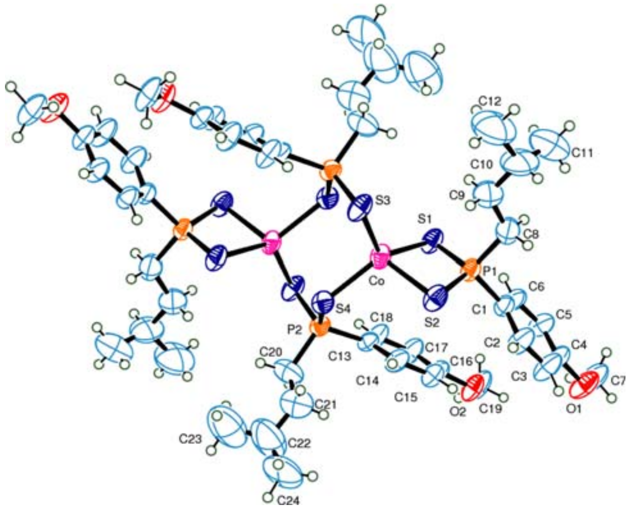


Fig. 3 ORTEP III drawing of the complete molecule and atom-labeling scheme for [(CoL$_2$)$_2$] with thermal ellipsoids at 50% probability level

Table 4 Selected bond lengths (Å), bond and torsion angles (°) for complexes [NiL$_2$] and [(CoL$_2$)$_2$]

[NiL$_2$]		[(CoL$_2$)$_2$]	
Ni–S1	2.238(3)	Co–S1	2.321(1)
Ni–S2	2.244(2)	Co–S2	2.449(1)
Ni–S4	2.224(2)	Co–S3	2.328(1)
Ni–S3	2.225(3)	Co–S4	2.357(1)
S1–S2	3.125	P1–S1	2.018(2)
S2–S3	3.218	P1–S2	1.998(2)
S1–P1	2.007(3)	P2–S4	2.018(2)
S2–P1	2.014(3)	P1–C1	1.791(4)
P1–C8	1.801(8)	P1–C8	1.834(5)
P1–C1	1.812(10)	P2–C13	1.789(4)
P2–C18	1.788(10)	P2–C20	1.826(5)
P2–C13	1.804(8)	O2–C16	1.363(5)
P2–S3	2.012(3)	O2–C19	1.431(6)
P2–S4	2.016(3)	O1–C4	1.355(5)
O2–C21	1.370(11)	O1–C7	1.447(6)
O2–C24	1.436(10)		
O1–C4	1.368(12)		
O1–C7	1.424(11)		
S4–Ni–S3	87.93(9)	S1–Co–S3	122.09(5)
S4–Ni–S1	91.57(9)	S1–Co–S4	130.73(5)
S3–Ni–S1	179.40(10)	S3–Co–S4	103.34(4)
S4–Ni–S2	179.87(12)	S1–Co–S2	85.99(4)
S3–Ni–S2	92.10(9)	S3–Co–S2	100.86(4)
S1–Ni–S2	88.40(9)	S4–Co–S2	104.43(5)
P1–S2–Ni	84.63(11)	P1–S2–Co	80.86(5)
P1–S1–Ni	84.96(11)	P2–S4–Co	111.46(5)
C8–P1–C1	105.9(4)	C1–P1–C8	103.1(2)
C8–P1–S1	113.1(3)	C1–P1–S2	113.00(1)
C1–P1–S1	111.9(3)	C8–P1–S2	111.6(2)
C8–P1–S2	111.5(3)	C1–P1–S1	111.59(1)
C1–P1–S2	112.6(3)	C8–P1–S1	109.22(2)
S1–P1–S2	102.01(14)	S2–P1–S1	108.28(7)
C18–P2–C13	106.5(4)	P1–S1–Co	83.72(5)
S3–P2–S4	100.12(14)	C4–O1–C7	116.7(4)
P2–S3–Ni	86.00(11)	C13–P2–C20	106.8(3)
P2–S4–Ni	85.95(11)	C13–P2–S4	113.12(1)
		C20–P2–S4	105.8(2)
S4–Ni–S2–P1	−76(51)	S1–Co–S2–P1	7.38(5)
S3–Ni–S2–P1	−179.2(1)	S3–Co–S2–P1	−114.54(6)
S1–Ni–S2–P1	0.50(13)	S4–Co–S2–P1	138.48(5)
S4–Ni–S1–P1	179.4(1)	S1–Co–S4–P2	−4.75(9)
S3–Ni–S1–P1	145(1)	S3–Co–S4–P2	152.87(6)
S2–Ni–S1–P1	−0.5(1)	S2–Co–S4–P2	−102.00(6)
Ni–S1–P1–C8	120.4(4)	Co–S2–P1–C1	−133.06(2)
Ni–S1–P1–C1	−120.0(3)	Co–S2–P1–C8	111.30(2)
Ni–S1–P1–S2	0.58(14)	Co–S2–P1–S1	−8.93(6)
Ni–S2–P1–C8	−121.6(4)	C1–P1–S1–Co	134.33(2)
Ni–S2–P1–S1	−0.6(1)	C8–P1–S1–Co	−112.3(2)
S4–Ni–S3–P2	0.04(1)	S2–P1–S1–Co	9.36(7)
S1–Ni–S3–P2	34(11)	S3–Co–S1–P1	93.06(6)
S2–Ni–S3–P2	179.9(1)	S4–Co–S1–P1	−112.88(6)
C18–P2–S4–Ni	−119.2(3)	S2–Co–S1–P1	−7.25(5)
C13–P2–S4–Ni	121.1(3)	Co–S4–P2–C13	43.46(2)
S3–P2–S4–Ni	0.04(1)	Co–S4–P2–C20	160.0(2)
S1–Ni–S4–P2	−179.7(1)		
S1–S2–S3–S4	0.1(1)		

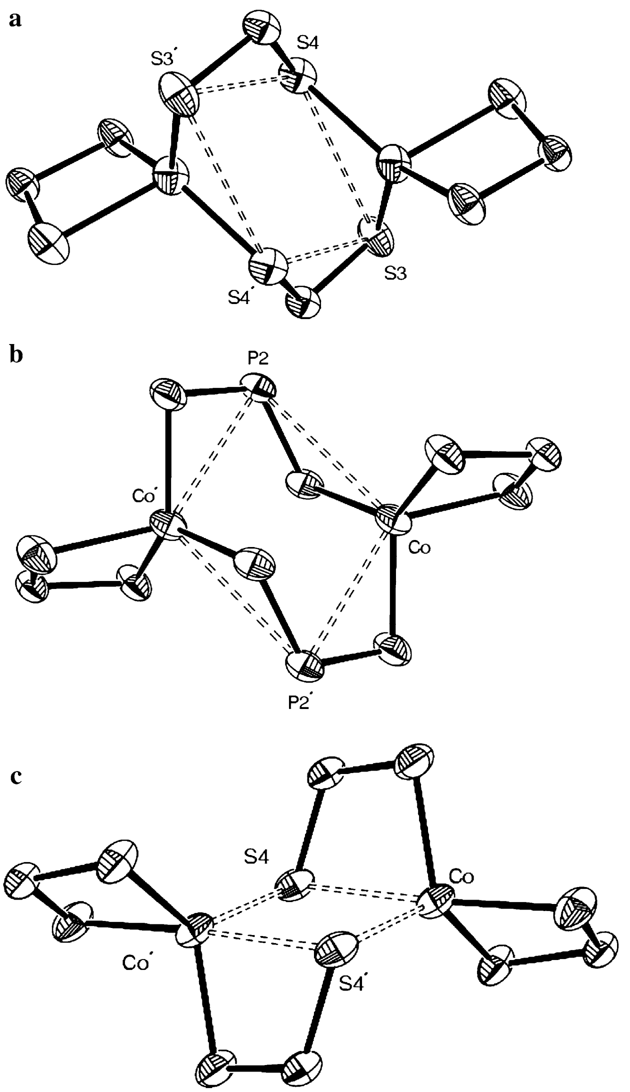


Fig. 4 ORTEP III drawing of some planes of the chelate geometry for $[(CoL_2)_2]$ with thermal ellipsoids at 50% probability

attached to the second Co atom, and vice versa. By the dimerization via a crystallographic center of symmetry, a puckered eight-membered ring is formed that has a chair conformation [formed by the atoms Co, S3, S4, P2, Co′, S3′, S4′, P2′]. The cobalt atoms are coordinated by four sulfur atoms to give a slightly distorted tetrahedral arrangement. The inter-ion chelate bite is certainly responsible for the rather short Co–Co distance of 3.952 Å. The Co–S1, Co–S2, Co–S3 and Co–S4 bond lengths are 2.321(1), 2.449(1), 2.328(1) and 2.357(1) Å, respectively. In the Co chelate geometry, each S3–S4′–S3′–S4, P2–Co–P2′–Co′ and Co–S4–Co′–S4′ atom group forms planes, as shown in Fig. 4a–c. The two sulfur and two carbon atoms around the phosphorus atoms are of essentially tetrahedral configuration. The P1–S1, P1–S2 and P2–S4 bond lengths are 2.018(2), 1.998(2) and 2.018(2) Å, respectively, and P1–C1, P1–C8, P2–C13 and P2–C20 are 1.791(4), 1.834(5), 1.789(4) and 1.826(5) Å, respectively. Remarkably, the P–C bonds attaching the methoxyphenyl moiety are shorter than the P–C bonds attaching the aliphatic moiety. This may—at least partly—be due to the electron delocalization on the phenyl rings. The dihedral angle between the Co–S1–S2 and P1–S1–S2 planes is 12.44(6)°. In addition, the dihedral angle between the two phenyl rings (with C1 and C13) is 27.84(15)°. Other compounds of similar structures, namely, chelates of Cd, Zn, Hg and Au with dithiophosphinates, compare well with these findings [23–25].

The hydrogen bond molecular geometry data for the complexes are given in Table 5. The molecular geometry is obviously affected by the four C–H···S intramolecular, as well as two C–H···O intermolecular hydrogen bond interactions.

Conclusion

Three new compounds, NH_4L, $[NiL_2]$ and $[(CoL_2)_2]$, have been synthesized. The ammonium salt has been characterized by elemental analysis and spectroscopy. The complexes were investigated by X-ray single crystal methods as well as elemental analysis and spectroscopy. The structure of $[(CoL_2)_2]$ comprises a dimer with an eight-membered metallocyclic ring formed by chelating and bridging of ligands and has a ‘chair’ conformation. Both complexes are stable at room temperature for at least a period of 11 months.

Table 5 Hydrogen bonding geometry (Å, °) for $[NiL_2]$ and $[(CoL_2)_2]$

Compound	*D*–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
$[NiL_2]$	C6–H1···S1^{i}	0.930	2.858(3)	3.362(12)	115.3(7)
$[(CoL_2)_2]$	C6–H6···S1^{i}	0.930	2.954(2)	3.417(6)	112.3(3)
	C2–H2···S2^{i}	0.930	2.982(2)	3.426(7)	110.9(4)
	C21–H21A···S4^{i}	0.970	2.893(1)	3.451(9)	117.6(4)
	C7–H7A···O2^{iib}	0.960	2.651(3)	3.428(8)	138.3(4)
	C19–H19A··· O1^{iib}	0.960	2.707(4)	3.409(8)	130.4(4)
	C18–H18··· S3^{iiib}	0.930	2.819(2)	3.329(6)	115.6(3)

Symmetry codes: (i) x, y, z; (iib) $-x + 2, -y + 1, -z + 1$; (iiib) $-x + 1, -y, -z + 1$

Supplementary material

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC) under the deposition numbers 743998 for $[NiL_2]$ and 743997 for $[(CoL_2)_2]$.

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