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Complexes of *N*-thiophosphorylthiourea (EtO)₂P(O)CH₂C₆H₄-4-[NHC(S)NHP(S)(O*i*Pr)₂] with Zn(II), Cd(II), Co(II) and Cu(PPh₃)(I)

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1. Introduction

Imidodiphosphinates $R_2P(X)NHP(X)R'_2$ (X = S, Se) [1–5] and their complexes with divalent d-metal cations have been extensively investigated. Formation of chelate complexes of the ML_2 structure is characteristic for them. Ligands are coordinated bidentately in these compounds, through the atoms of X of the thio(seleno)carbonic and thio(seleno)phosphoric groups. Cobalt(II) chelates with oxygen-containing ligands RC(O)NHP(O)R'₂ show the expressed propensity to oligomerization in the solid phase and to the formation of complexes with the solvent molecules [6–8].

Heteroligand copper(I) complexes of triphenylphosphine and XCNPY or XPNPX (X, Y = O, S, Se) backbone ligands [8–11] have been earlier reported. It was established that PPh₃ was used as an additional donor ligand to prepare the non-cluster complex of Cu(I), where the copper atom is bound only to one molecule of chelating SPNPS ligand [10]. In this case, the filling of coordination sites of copper(I) is necessary to prevent cluster formation.

ABSTRACT

Reaction of 0,0'-diisopropylthiophosphoric acid isothiocyanate (iPrO)₂P(S)NCS with diethyl 4-aminobenzylphosphonate (EtO)₂P(0)CH₂C₆H₄-4-NH₂ leads to the new *N*-thiophosphorylated thiourea (EtO)₂-P(O)CH₂C₆H₄-4-[NHC(S)NHP(S)(*Oi*Pr)₂] (**HL**). Reaction of the potassium salt of **HL** with Zn(II), Cd(II) and Co(II) in aqueous EtOH leads to complexes of formula M(L-*S*,*S'*)₂ (**ML**₂). Heteroligand copper(I) complex of **HL** and triphenylphosphine was prepared by the reaction of the potassium salt **KL** and Cu(PPh₃)₃I. Copper in complex **Cu(PPh₃)L** is bound by one PPh₃ and one SCNPS fragment of the chelating ligand. Compounds obtained were investigated by IR, UV–Vis, ¹H and ³¹P{¹H} NMR spectroscopy, and microanalysis. The structures of **HL** and **Cu(PPh₃)L** were investigated by single crystal X-ray diffraction analysis.

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Published data reveal that structure and properties of triphenylphosphine containing complexes of XCNPY or XPNPX are strongly dependent on the nature of chelating ligand. To the best of our knowledge, there are no data explaining reasons of one or two PPh₃ molecules binding with Cu(I) metal centre. For this purpose we conceived to use thiophosphorylated thiourea, containing sterically demanding substituent capable to the hydrogen bonds formation.

Amidophosphates $RC(S)NHP(X)R_2$ have long attracted attention of researchers due to their ability to form stable chelates with IB, IIB, and VIIIB group transition metal cations. These compounds and their complexes exhibit antiviral activity [12]. They can be used as stationary phases for GLC [13], as well as components of ion-selective electrodes [14–17], extractants [18], and masking reagents in analytical chemistry [19].

These investigations are caused by the further utilizing of obtained Zn(II), Cd(II), Co(II) and Cu(I) compounds with dithiocontaining ligand as single source molecular precursors for the preparation of metal sulfide thin films and nanocrystals by chemical vapor deposition [20,21].

We report here the structure of the thiourea $(EtO)_2P(O)CH_2C_6H_4-4-[NHC(S)NHP(S)(OiPr)_2]$ (**HL**) and complex Cu(PPh₃-P){(EtO)_2-P(O)CH_2C_6H_4-4-[NHC(S)NP(S)(OiPr)_2]-*S*,*S*'} (**Cu(PPh_3)L**) determined by X-ray single crystal diffraction.





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2. Experimental

2.1. Synthesis of HL

A solution of diethyl 4-aminobenzylphosphonate (0.243 g, 1 mmol) in CH₂Cl₂ (15 mL) was added dropwise to a solution of SCNP(S)(OiPr)₂ (0.263 g, 1.1 mmol) in the same solvent (15 mL). The mixture was stirred at room temperature for 3 h. The solvent was then removed in vacuum. The residue was recrystallized from a dichloromethane-*n*-hexane mixture 1:5 (v/v). The product was obtained as colorless crystals. Yield: 0.429 g (89%). M.p. 73 °C. ¹H NMR (CDCl₃): $\delta = 1.26$ (t, ${}^{3}J_{H,H} = 7.1$ Hz, 6H, CH₃, EtO), 1.38 (d, ${}^{3}J_{H,H}$ = 6.2 Hz, 12H, CH₃, *i*PrO), 3.14 (d, ${}^{2}J_{P,H}$ = 21.5 Hz, 2H, CH₂, P(O)CH₂), 4.04 (d. quart, ${}^{3}J_{H,H}$ = 7.1 Hz, ${}^{3}J_{POCH}$ = 8.8 Hz, 4H, OCH₂, EtO), 4.86 (d. sept, ${}^{3}J_{H,H}$ = 6.2 Hz, ${}^{3}J_{POCH}$ = 10.5 Hz, 2H, OCH, *i*PrO), 7.19 (d, ${}^{2}J_{PNH}$ = 10.4 Hz, 1H, NH, P(S)NH), 7.27–7.53 (m, 4H, C₆H₄), 9.66 (s, 1H, NH). ${}^{31}P{}^{1}H$ NMR (CDCl₃): $\delta = 26.7$ (1P, P=O), 53.4 (1P, P=S). IR: v = 622 (P=S), 968, 992, 1026 (POC), 1207 (P=O), 1559 (S=C-N), 3126, 3272 (NH) cm⁻¹. Anal. Calc. for C₁₈H₃₂N₂O₅P₂S₂ (482.53): C, 44.80; H, 6.68; N, 5.81. Found: C, 44.68; H, 6.79; N, 5.74.

2.2. Synthesis of ML₂

A suspension of **HL** (0.241 g, 0.5 mmol) in aqueous ethanol (20 mL) was mixed with an ethanol solution of potassium hydroxide (0.031 g 0.55 mmol). An aqueous (20 mL) solution of ZnCl₂, $Cd(CH_3COO)_2 \cdot 2H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ (0.041, 0.080 or 0.087 g, respectively; 0.3 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further 3 h and left overnight. The resulting complex was extracted with dichloromethane, washed with water and dried with anhydrous MgSO₄. The solvent was then removed in vacuo. The residue was recrystallized from a dichloromethane/*n*-hexane mixture.

ZnL₂. Complex was obtained as colorless crystals. Yield: 0.157 g (61%). M.p. 163 °C. ¹H NMR (CDCl₃): δ = 1.08–1.47 (m, 36H, CH₃, EtO + *i*PrO), 3.13 (d, ²J_{P,H} = 21.1 Hz, 4H, CH₂, P(O)CH₂), 3.93–4.10 (m, 8H, OCH₂, EtO), 4.79 (d. sept, ³J_{H,H} = 6.2 Hz, ³J_{POCH} = 10.1 Hz, 4H, OCH, *i*PrO), 7.25–7.79 (m, 8H, C₆H₄), 6.53 (s, 2H, NH). ³¹P{¹H} NMR (CDCl₃): δ = 24.9 (2P, P=O), 56.0 (2P, P=S). IR: v = 603 (P=S), 1008, 1012 (POC), 1263 (P=O), 1547 (S=C-N), 3305 (NH) cm⁻¹. *Anal.* Calc. for C₃₆H₆₂N₄O₁₀P₄S₄Zn (1028.44): C, 42.04; H, 6.08; N, 5.45. Found: C, 42.13; H, 5.91; N, 5.52.

CdL₂. Complex was obtained as colorless crystals. Yield: 0.231 g (86%). M.p. 109 °C. ¹H NMR (CDCl₃): δ = 1.17–1.51 (m, 36H, CH₃, EtO + *i*PrO), 3.03 (d, ²*J*_{P,H} = 21.8 Hz, 4H, CH₂, P(O)CH₂), 3.85–4.02 (m, 8H, OCH₂, EtO), 4.82 (d. sept, ³*J*_{H,H} = 6.2 Hz, ³*J*_{POCH} = 10.3 Hz, 4H, OCH, *i*PrO), 7.27–7.72 (m, 8H, C₆H₄), 6.71 (s, 2H, NH). ³¹P{¹H} NMR (CDCl₃): δ = 25.2 (2P, P=O), 56.2 (2P, P=S). IR: v = 607 (P=S), 1007 (POC), 1259 (P=O), 1539 (S=C–N), 3296 (NH) cm⁻¹. *Anal.* Calc. for C₃₆H₆₂CdN₄O₁₀P₄S₄ (1075.46): C, 40.20; H, 5.81; N, 5.21. Found: C, 40.39; H, 5.73; N, 5.30.

CoL₂. Complex was obtained as green crystals. Yield: 0.233 g (91%). M.p. 94 °C. IR: v = 600 (P=S), 1012 (POC), 1260 (P=O), 1551 (S=C-N), 3311 (NH) cm⁻¹. UV-Vis spectra, [λ_{max} , nm (ε , 1 mol⁻¹ dm³cm⁻¹)]: 558 (263), 607 (286), 668 (157). *Anal.* Calc. for C₃₆H₆₂CoN₄O₁₀P₄S₄ (1021.99): C, 42.31; H, 6.11; N, 5.48. Found: C, 42.47; H, 6.25; N, 5.41.

2.3. Synthesis of Cu(PPh₃)L

A suspension of **HL** (0.241 g, 0.5 mmol) in aqueous ethanol (15 mL) was mixed with an ethanol solution of KOH (0.031 g 0.55 mmol). A dichloromethane (15 mL) solution of $Cu(PPh_3)_3I$

(0.489 g, 0.5 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further hour and a precipitate was filtered off. The filtrate was concentrated until the crystallization began. The residue was recrystallized from a dichloromethane–*n*-hexane mixture 1:5 (v/v). Complex was obtained as colorless crystals. Yield: 0.295 g (73%). M.p. 127 °C. ¹H NMR (CDCl₃): δ = 1.12–1.44 (m, 18H, CH₃, EtO + *i*PrO), 3.10 (d, ²J_{P,H} = 21.3 Hz, 2H, CH₂, P(O)CH₂), 3.89–4.08 (m, 4H, OCH, EtO), 4.73 (d. sept, ³J_{H,H} = 6.1 Hz, ³J_{POCH} = 10.4 Hz, 2H, OCH, *i*PrO), 7.13–7.23, 7.28–7.77 (m, 19H, C₆H₄ + C₆H₅), 8.47 (s, 1H, NH). ³¹P{¹H} NMR (CDCl₃): δ = -0.9 (1P, PPh₃), 27.1 (1P, P=O), 55.3 (1P, P=S). IR: v = 606 (P=S), 962, 974, 998, 1017 (POC), 1252 (P=O), 1530 (S=C-N), 3263 (NH) cm⁻¹. *Anal.* Calc. for C₃₆H₄₆CuN₂O₅P₃S₂ (807.36): C, 53.56; H, 5.74; N, 3.47. Found: C, 53.43; H, 5.85; N, 3.34.

2.4. Physical measurements

Infrared spectra (Nujol) were recorded with a Specord M-80 spectrometer in the range 400–3600 cm⁻¹. NMR spectra were obtained on a Varian Unity-300 NMR spectrometer at 25 °C. ¹H and ³¹P{¹H} spectra were recorded at 299.948 and 75.429 MHz, respectively. Chemical shifts are reported with reference to SiMe₄ (¹H) and H₃PO₄ (³¹P{¹H}). Electronic spectra of absorption in 0.001 M solution of CH₂Cl₂ were measured on a Perkin–Elmer Lambda-35 spectrometer in the range 200–1000 nm. Elemental analyses were performed on a Perkin–Elmer 2400 CHN microanalyser.

2.5. Crystal structure determination and refinement

Crystals of HL were obtained by slow evaporation of the solvent from dichloromethane/n-hexane solution. C₁₈H₃₂N₂O₅P₂S₂, M_r = 482.54 g mol⁻¹, crystal system: monoclinic, space group: $P2_1/c$, a = 7.6294(1), b = 9.3135(2), c = 35.2519(6) Å, $\beta = 94.964$ (1)°, $V = 2495.48(8) \text{ Å}^3$, $\rho = 1.284 \text{ g cm}^{-3}$. Cell parameters and intensities of 5931 independent reflections, from which 3689 with $I \ge 2\sigma$, were measured (ω -scan, $\theta \le 27.00^{\circ}$) at 296 K on a Bruker Smart Apex II diffractometer and graphite-monochromatied Mo Kα radiation generated by fine-focus X-ray tube operated at 50 kV and 30 mA. The images were indexed, integrated and scaled using the Apex2 data reduction package [22]. Data were corrected for absorption using sadabs [23] program (μ Mo 3.71 cm⁻¹). The structure was solved by direct method using siR-97 [24] program and refined first isotropically and then anisotropically using SHELxL97 [25] and WINGX programs [26]. Hydrogen atoms were revealed from $\Delta \rho$ maps and refined isotropically. The final residuals were $R_{ob} = 0.0492$, $R_{wob} = 0.0903$ based on 3689 independent reflections with $F^2 \ge 2\sigma$. All figures were made using the program PLA-TON [27].

Crystals of Cu(PPh₃)L were obtained by slow evaporation of the solvent from dichloromethane/n-hexane solution. C₃₆H₄₆Cu- $N_2O_5P_3S_2$, $M_r = 807.32$ g mol⁻¹, crystal system: triclinic, space group: $P\overline{1}$, a = 8.9510(8), b = 11.5966(9), c = 20.0844(16) Å, $\alpha =$ 77.572(6)°, $\beta = 77.538(6)^\circ$, $\gamma = 79.331(7)^\circ$, $V = 1966.8(3) \text{ Å}^3$, ρ = 1.363 g cm⁻³. Cell parameters and intensities of 18274 reflections (7710 unique, R_{int} = 0.0822), from which 4594 had $I \ge 2\sigma$, were measured (ω -scan, $\theta \leq 25.12^{\circ}$) at 173 K on a STOE IPDS-II diffractometer and graphite-monochromatied Mo Ka radiation generated by fine-focus X-ray tube operated at 50 kV and 40 mA. The images were indexed, integrated and scaled using the X-Area package [28]. Data were corrected for absorption using PLATON [27] program (μ Mo 0.826 mm⁻¹). The structure was solved by direct method using SHELXS [29] program and refined first isotropically and then anisotropically using SHELXL97 [25]. Hydrogen atoms were revealed from $\Delta \rho$ maps and refined using a riding model. The final residuals were $R_{ob} = 0.0466$, $R_{wob} = 0.0801$ based on

4594 independent reflections with $F^2 \ge 2\sigma$. All figures were made using the program PLATON [27].

3. Results and discussion

3.1. Synthesis

N-Thiophosphorylated thiourea **HL** was prepared by the addition of diethyl 4-aminobenzylphosphonate $(EtO)_2P(O)CH_2C_6H_4-4-NH_2$ to 0,0'-diisopropylthiophosphoric acid isothiocyanate (*i*PrO)_2P(S)NCS (Scheme 1).

Complexes of **HL** with the Zn(II) (**ZnL**₂), Cd(II) (**CdL**₂) and Co(II) (**CoL**₂) cations were prepared by the following procedure: ligand was converted into potassium salt **KL** and followed by reaction with ZnCl₂, Cd(CH₃COO)₂ · 2H₂O or Co(NO₃)₂ · 6H₂O in aqueous EtOH (Scheme 2).

Reaction of the potassium salt of **HL** with $Cu(PPh_3)_3I$ in aqueous EtOH/CH₂Cl₂ leads to mononuclear **Cu(PPh_3)L** complex (Scheme 2).

The compounds obtained are colorless (**HL**, **ZnL**₂ and **CdL**₂) or green (**CoL**₂) crystalline powders, soluble in acetone, benzene, dichloromethane and insoluble in water and *n*-hexane. UV–Vis, ¹H, ³¹P{¹H} NMR in solution and IR data indicated that the thiourea **HL** is a 1,5-*S*,*S*'-ligand.



Scheme 1. Preparation of HL.



 $M = Zn(II) (ZnL_2); Cd(II) (CdL_2); Co(II) (CoL_2)$



Scheme 2. Preparation of ZnL₂, CdL₂, CoL₂ and Cu(PPh₃)L.

3.2. IR, UV-Vis and NMR spectroscopic data

The IR spectrum of **HL** contains a weak band at 622 cm^{-1} assigned to the P=S group. It is shifted to low frequencies $(600-607 \text{ cm}^{-1})$ in the spectra of complexes **ML**₂ and **Cu(PPh₃)L** due to the coordination with the cation. Occurrence of the new broad and strong absorption peak at $1530-1551 \text{ cm}^{-1}$, related to the conjugated SCN group [30], also proves the formation of 1,5-*S*,*S*'-chelate. Presence of the substituted POC groups in **HL** and its complexes are seen in the IR spectra by their absorption bands at $962-1026 \text{ cm}^{-1}$.

There are two bands for the ArNH and P(S)NH groups at 3126 and 3272 cm⁻¹ in the IR spectrum of **HL**, whereas a unique band at 3296–3311 and 3263 cm⁻¹ related to the ArNH group was observed in the spectra of complexes ML₂ and Cu(PPh₃)L, respectively. It should be noted that the band for the ArNH group in the IR spectra of ML₂ is shifted to high frequencies whereas in **Cu(PPh₃)L** this band is practically at the same frequencies relative to the band of the parent ligand HL. The similar is observed for the P=O absorption band in the IR spectra. The band at $1259-1263 \text{ cm}^{-1}$ in the spectra of **ML**₂ corresponds to the P=O group and shifted to high frequencies relative to that in **HL**. The P=0 band at 1257 cm⁻¹ in the IR spectrum of complex Cu(PPh₃)L is practically at the same area as it was observed in the parent thiourea (1252 cm⁻¹) due to the intermolecular N–H \dots O=P hydrogen bonds in a crystal (Figs. 1 and 2). This confirms the preservation of the hydrogen bonding in the structure of **Cu(PPh₃)L** and absence of it in complexes ML₂.

The ³¹P{¹H} NMR spectrum of **HL** in a CDCl₃ solution shows two single resonances at 26.7 and 53.4 ppm, corresponding to the phosphorus atoms of the P=O and P=S groups, respectively. In the ³¹P{¹H} NMR spectra of complexes **ZnL₂**, **CdL₂** and **Cu(PPh₃)L**, the resonance for the phosphoryl and thiophosphoryl groups are shown at 24.9–27.1 and 55.3–56.2 ppm, respectively. The signal corresponding to the P=S group is low-field shifted, whereas the singlet for the P=O group is practically at the same region relative to those in the parent ligand for **Cu(PPh₃)L** and low-field shifted in the ³¹P{¹H} NMR spectra of complexes **ZnL₂** and **CdL₂**. The signal of the triphenylphosphine group in copper(I) complex is shifted downfield relative to the free PPh₃ and exhibit ³¹P{¹H} NMR



Fig. 1. Molecular structure and hydrogen bonding dimer in crystal of **HL**. Selected bond distances (Å) and angles (°): S(1)-P(1) 1.9166(11), S(2)-C(1) 1.657(3), P(1)-O(1) 1.583(2), P(1)-O(2) 1.551(2), P(1)-N(1) 1.666(2), P(2)-O(3) 1.556(2), P(2)-O(4) 1.570(2), P(2)-O(5) 1.469(2), N(1)-C(1) 1.376(3), N(2)-C(1) 1.346(3); S(1)-P(1)-O(1) 115.73(8), S(1)-P(1)-O(2) 115.57(8), S(1)-P(1)-N(1) 118.90(8), O(1)-P(1)-O(2) 102.92(9), O(1)-P(1)-N(1) 94.11(10), O(2)-P(1)-N(1) 106.58(11), O(3)-P(2)-O(4) 105.24(10), O(3)-P(2)-O(5) 113.44(10), O(4)-P(2)-O(5) 113.67(11), P(1)-N(1) -C(1) 126.8(2), S(2)-C(1)-N(1) 120.3(2), S(2)-C(1)-N(2) 127.1(2), N(1)-C(1)-N(2) 112.6(2). The intermolecular hydrogen bond parameters in the molecule are as follows: $N(1)-H(1)\cdots O(5)'(1-x, 1-y, -2)$: d(N-H) 0.81(3), $d(H\cdots O') 2.26(3)$, $d(N\cdots O') 2.997(3)$, $\angle(NHO') 153(3)$; $N(2)-H(2)\cdots O(5)'$ (1-x, 1-y, -2): d(N-H) 0.79(3), $d(H\cdots O') 2.11(3)$, $d(M\cdots O') 2.88(3)$, $\angle(NHO') 167(3)$.



Fig. 2. Molecular structure and hydrogen bonding dimer in crystal of **Cu(PPh₃)L**. Selected bond distances (Å) and angles (°): Cu(1)–S(1) 2.2485(11), Cu(1)–S(2) 2.2163(11), Cu(1)–P(3) 2.2142(11), S(1)–P(1) 1.9950(13), S(2)–C(1) 1.754(4), P(1)–O(1) 1.583(3), P(1)–O(2) 1.588(3), P(1)–N(1) 1.600(3), P(2)–O(3) 1.579(4), P(2)–O(4) 1.579(3), P(2)–O(5) 1.474(3), N(1)–C(1) 1.326(5), N(2)–C(1) 1.335(5); S(1)–Cu(1)–S(2) 115.77(4), S(1)–Cu(1)–P(3) 118.63(4), S(2)–Cu(1)–P(3) 124.78(4), Cu(1)–S(1)–P(1) 94.83(5), Cu(1)–S(2)–C(1) 104.63(13), S(1)–P(1)–O(1) 113.38(10), S(1)–P(1)–O(2) 109.24(11), S(1)–P(1)–N(1) 118.28(13), O(1)–P(1)–O(2) 102.08(14), O(1)–P(1)–N(1) 106.69(15), O(2)–P(1)–N(1) 105.71(15), O(3)–P(2)–O(4) 104.27(18), O(3)–P(2)–O(5) 115.38(19), O(4)–P(2)–O(5) 113.47(17), P(1)–N(1)–C(1) 129.1(3), S(2)–C(1)–N(1) 128.4(3), S(2)–C(1)–N(2) 113.9(3), N(1)–C(1)–N(2) 117.6(3). The intermolecular hydrogen bond parameters in the molecule are as follows: N(2)–H(2)···O(5) (1–x, 2–y, 1–z): d(N–H) 0.84(4), d(H···O') 2.10(4), d(N···O') 2.922(4), ∠(NHO') 164(4).

chemical shift at -0.9 ppm. In solution, the exchange between free and bound triphenylphosphine group of complex **Cu(PPh₃)L** results in a signal broadening of the ³¹P{¹H} NMR spectrum, as it was previously observed for the Cu(I) complexes with *N*-thiophosphorylated thioureas and thioamides [31,32].

The ¹H NMR spectra of HL, ZnL₂, CdL₂ and Cu(PPh₃)L contain a set of signals, corresponding to the resulting products. The signals for the CH₃ protons of the $(iPrO)_2P(S)$ and $(EtO)_2P(O)$ groups are observed as a doublet, triplet or multiplet at 1.08-1.51 ppm and a doublet of septets, doublet of quartets or multiplet at 3.85-4.86 ppm, corresponding to the OCH and OCH₂ protons. The signals for the C₆H₄ protons in the spectra of HL, ZnL₂, CdL₂ and Cu(PPh₃)L are shown as a multiplet at 7.25–7.79 ppm. The signals for the C_6H_5 protons in the ¹H NMR spectrum of **Cu(PPh₃)L** are observed as a multiplet at 7.13–7.23 ppm. The CH₂ protons doublet signals are at 3.03-3.14 ppm. There is a doublet and singlet for the P(S)NH and ArNH protons at 7.19 and 9.66 ppm, respectively, in the spectrum of HL, whereas only one singlet signal for the ArNH proton at 6.53–6.71 (ZnL₂ and CdL₂) and 8.47 [Cu(PPh₃)L] ppm is observed in the ¹H NMR spectra of complexes. This confirms the anionic forms L in the structure of complex.

Investigation of complex **CoL**₂ by NMR spectroscopy was not successful, because of the paramagnetic Co(II) cation presence.

In the UV-spectrum of complex **CoL**₂ there is an absorption band with peaks at 558 (ε_{max} , 263 mol⁻¹ dm³ cm⁻¹), 607 (ε_{max} , 286 mol⁻¹ dm³ cm⁻¹) and 668 (ε_{max} , 157 mol⁻¹ dm³ cm⁻¹) nm. The specified absorption band corresponds to a transition from the basic state ⁴A₂ to a ⁴T₁(P) state. The thin structure is caused by spin–orbital interaction as a result of which, first, there is a splitting of the state ⁴T₁(P) and, secondly, there are resolved transitions in the next doublet states with the same intensity. Other possible transitions: ⁴A₂ \rightarrow ⁴T₂ and ⁴A₂ \rightarrow ⁴T₁(F) are outside of the visible area. Data of UV-spectroscopy unequivocally confirm the tetrahedral environment of the Co(II) cation in complex **CoL**₂.

3.3. Crystal structures

According to the X-ray data, the molecule of **HL** in a crystal is located in a special position at the symmetry centre (Fig. 1).

X-ray analysis of the product **HL** showed that the NC(S)N fragmnet is almost planar, which is evidence of the resonance between the nitrogen lone pair and the double C=S bond. The phosphorus atoms have a distorted tetrahedral configuration typical of phosphates. The conformation of the N–C–N–P fragmnet is almost shielded, torsion angle N(2)–C(1)–N(1)–P(1) is $-173.8(2)^{\circ}$. The bonds C(1)–S(2) and P(1)–S(1) are in *anti*-orientation. The molecule of **HL** in the crystal has a *syn*-orientation of the bonds N(1)– H(1) and N(2)–H(2) and an *anti*-orientation of the P(1)–N(1) and N(2)–C(1) bonds. Such arrangement, apparently, is caused by the formation of the intermolecular hydrogen bonds N(1)–H(1)…O(5)' (1 - x, 1 - y, -z), N(2)–H(2)…O(5)' (1 - x, 1 - y, -z) and N(1)'–H(1)'…O(5), N(2)'–H'…O(5) (Fig. 1). As a result of the intermolecular interactions, a centosymmetric dimer is formed.

The molecular structure of complex **Cu(PPh₃)L** is shown in Fig. 2. The geometry around the Cu atom is trigonal formed by two sulfurs and one PPh₃. S–P and S–C bonds are longer while P–N and N–C are shorter in comparison to those for the free ligand **HL** and have intermediate bond order values between the double and single. The six-membered CuSPNCS metallocyle has the conformation of a distorted boat with the P(1) an S(1) atoms showing the greatest deviation from the least square plane of the CuSPNCS cycle, 0.4260(13) and -0.3256(13) Å, respectively. The fragment NC(S)NP is almost planar, the sulfur of the thiophosphoryl group is significantly deviated from the average plane of this fragment, torsion angle S(1)–P(1)–N(1)–(1) is $-57.5(4)^{\circ}$. The phosphorus atoms have a distorted tetrahedral configuration.

In a crystal two molecules of complex **Cu(PPh₃)L** also form a centrosymmetric dimer, which is caused by the formation of the intermolecular hydrogen bonds $N(2)-H(2)\cdots O(5)'$ (1 - x, 2 - y, 1 - z) (Fig. 2). As a result of the intermolecular interactions and steric demanding, only one molecule of PPh₃ is coordinated with the Cu atom. Complex **Cu(PPh₃)L** is the first example of copper(I) complexes of *N*-thiophosphorylated thioureas and thioamides of common formula RC(S)NHP(S)R'₂ and one molecule of PPh₃.

4. Conclusions

In summary, novel Zn(II), Cd(II), Co(II) and Cu(PPh₃)(I) complexes with *N*-thiophosphorylated thiourea **HL** have been successfully synthesized. Copper(I) complex dissociates in a solution of CDCl₃, splitting off a molecule of triphenylphosphine. This process has reversible character.

NMR and UV–Vis experiments in solution and IR have shown that **HL** is a 1,5-*S*,5'-ligand in all complexes obtained.

Crystal structures of **HL** and **Cu(PPh₃)L** were determined by single crystal X-ray diffraction. According to the X-ray data, both ligand and complex in a crystal form dimer structures by intermolecular hydrogen bonds.

5. Appendix A. Supplementary data

CCDC 680113 and 682359 contain the supplementary crystallographic data for (**HL**) and [**Cu(PPh₃)L**]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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