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Synthesis and crystal structure of complexes of bipodal thiophosphorylated thioureas with divalent transition metals

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Abstract

New complexes of bipodal thiophosphorylated thioureas $\{[(i\mathrm{PrO})_2\mathrm{P(S)NC(S)NH}]_2\mathrm{Z}\}\mathrm{M}$, where Z = m-C_6H_4, p-C_6H_4, M = Co, Ni, Zn, Cd have been prepared and characterized. The crystal and molecular structures of Cd(II), Z = CH_2CH_2 and Pd(II), Z = $(CH_2CH_2)_2O$ complexes have been determined by single crystal X-ray diffraction analyses. Both complexes are binuclear in the solid state with a M_2L_2 stoichiometry. The cadmium and palladium atoms are four-coordinated and have the configuration of a slightly distorted tetrahedron for cadmium and a distorted square plane for palladium. Metal-containing macrocycles are formed as well as two spirocycles.

Keywords: *P*,*S*-metallocycles; Supramolecular chemistry; Bipodal ligands; Crystal structures; Macrocycles; Phosphorylated urea complexes

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1. Introduction

We have recently reported the syntheses and complexing properties of bipodal thiophosphorylated thioureas $[(i\mathrm{PrO})_2\mathrm{P(S)NHC(S)NH}]_2\mathrm{Z}$, where Z = $(CH_2)_2$, $(CH_2)_7$, $(CH_2)_2O(CH_2)_2$, $(CH_2)_2O(CH_2)_2O(CH_2)_2$, and some properties of the chelate complexes formed by these ligands with a series of metal ions [1,2].

In this paper, we report on the synthesis of the bis-urea $[(i\mathrm{PrO})_2\mathrm{P(S)NHC(S)NH}]_2\mathrm{Z}$ complexes with Co(II), Ni(II), Zn(II) and Cd(II) (Z = m-C_6H_4, p-C_6H_4), together with the X-ray study of the bis-urea $[(i\mathrm{PrO})_2\mathrm{P(S)NHC(S)NHCH_2}]_2$ and the complexes with the cadmium(II) ion (**1**) (Z = CH_2CH_2) and the palladium(II) ion (**2**) (Z = $(CH_2CH_2)_2O$).

2. Experimental

2.1. Synthesis of $[(i\mathrm{PrO})_2\mathrm{P(S)NHC(S)NH}]_2$-$m$-$C_6H_4$ (3)

A solution of m-phenylenediamine (2.163 g, 0.02 mol) in anhydrous benzene (50 ml) was added dropwise under stirring to a benzene solution (25 ml) of diisopropylthiophosphoryl isothiocyanate (9.572 g, 0.04 mol). The mixture was heated to 60 °C and stirred for 2 h. The solvent was removed in vacuum. A colourless precipitate was crystallized from benzene. Yield: 8.33 g (~71%), m.p. 122 °C. *Anal.* Calc. for $C_{20}H_{36}N_4O_4P_2S_4$: C, 40.95; H, 6.14; P, 10.58. Found: C, 41.58; H, 6.25; P, 10.30%. ^{1}H NMR (C_6D_6) 1.33 (d, 24H, CH_3, $^3J_{HH}$ 6.1 Hz), 4.78 (d, sept, 4H, OCH, $^3J_{HH}$ 6.3 Hz, $^3J_{POCH}$ 10.7 Hz), 6.86 (d, 2H, NHP(S), $^2J_{PH}$ 9.8 Hz), 7.24 (t, 1H, m-C_6H_4, $^3J_{HH}$ 8.2 Hz), 7.46 (d. d, 2H, m-C_6H_4, $^3J_{HH}$ 7.8 Hz, $^4J_{HH}$ 1.9 Hz), 8.14 (m, 1H, m-C_6H_4), 9.68 (s, 2H, C_6H_4*NH*). ^{31}P{^{1}H} NMR (ppm), 53.5. IR (cm^{-1}):

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3430(s) (NH), 3190(br, s) (NH), 1550(s) (S=C–N), 1315(m) (C=S), 1000(vs) (POC), 980(vs) (POC), 655(m) (P=S).

2.2. Synthesis of $[(iPrO)_2P(S)NHC(S)NH]_2$-p-C_6H_4 (**4**)

A solution of diisopropylthiophosphoryl isothiocyanate (9.572 g, 0.04 mol) in anhydrous benzene (25 ml) was added dropwise under stirring to a solution of *p*-phenylenediamine (2.163 g, 0.02 mol) in 50 ml of benzene heated to 60 °C. The mixture was refluxed with stirring for 3 h. *n*-Hexane (30 ml) was added, the mixture cooled down to 0 °C and then a white solid precipitated. The precipitate was crystallized twice from benzene. Yield: 8.8 g (∼75%), m.p. 139 °C. *Anal.* Calc. for $C_{20}H_{36}N_4O_4P_2S_4$: C, 40.95; H, 6.14; P, 10.58. Found: C, 41.09; H, 6.25; P, 10.18%. ^{1}H NMR (C_6D_6) 1.22 (d, 12H, CH_3, $^3J_{HH}$ 6.0 Hz), 1.25 (d, 12H, CH_3, $^3J_{HH}$ 6.4 Hz), 4.90 (d, sept, 4H, OCH, $^3J_{HH}$ 6.2 Hz, $^3J_{POCH}$ 10.6 Hz), 6.50 (d, 2H, NHP(S), $^2J_{PH}$ 8.4 Hz), 7.83 (s, 4H, C_6H_4), 10.19 (s, 2H, C_6H_4*NH*). $^{31}P\{^1H\}$ NMR (ppm), 53.28. IR (cm^{-1}): 3360(s) (NH), 3110(s) (NH), 1565(s) (S=C–N), 1335(m) (C=S), 980(vs) (POC), 655(m) (P=S).

2.3. Synthesis of $[(iPrO)_2P(S)NHC(S)NHCH_2]_2$ (**5**)

The compound was prepared as described above for **3** from ethylenediamine (1.202 g, 0.02 mol, as an acetonitrile solution, 15 ml) and diisopropylthiophosphoryl isothiocyanate (9.572 g, 0.04 mol) in benzene (25 ml) to give 7.54 g (∼70%, after crystallization from benzene) of **5** as colourless crystals. M.p. 111 °C. *Anal.* Calc. for $C_{16}H_{36}N_4O_4P_2S_4$: C, 35.67; H, 6.74; P, 11.50. Found: C, 35.64; H, 6.67; P, 11.09%. ^{1}H NMR (C_6D_6) 1.404 (d, 12H, CH_3, $^3J_{HH}$ 6.2 Hz), 1.409 (d, 12H, CH_3, $^3J_{HH}$ 6.3 Hz), 3.97 (m, 4H, CH_2CH_2), 4.88 (d. sept, 4H, OCH, $^3J_{HH}$ 6.3 Hz, $^3J_{POCH}$ 10.4 Hz), 7.53 (d, 2H, NHP(S), $^2J_{PH}$ 8.3 Hz), 8.35 (br. s, 2H, CH_2*NH*). $^{31}P\{^1H\}$ NMR (ppm), 51.46. IR (cm^{-1}): 3440(s) (NH), 1560(s) (S=C–N), 1315(m) (C=S), 1010(vs) (POC), 640(m) (P=S).

2.4. Synthesis of $\{[(iPrO)_2P(S)NC(S)NH]_2$-m-$C_6H_4$ Co$\}$ (**6**)

A suspension of **3** (1.173 g, 2 mmol) in anhydrous ethanol (20 ml) was mixed with an ethanol solution of potassium hydroxide (0.224 g, 4 mmol). To the resulting potassium salt, a water (20 ml) solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.579 g, 2.2 mmol) was added dropwise with vigorous stirring. The mixture was stirred at room temperature for a further 3 h and left overnight. The resulting complex was extracted with methylene chloride, washed with water and dried over $MgSO_4$. Then the solvent was removed in vacuum. A green precipitate was precipitated from methylene chloride by *n*-hexane. Yield: ∼41%, m.p. 156 °C. *Anal.* Calc. for $C_{20}H_{34}CoN_4O_4P_2S_4$: C, 37.29; H, 5.28; P, 9.63; Co, 9.15. Found: C, 37.67; H, 5.72; P, 9.32; Co, 8.86%. $^{31}P\{^1H\}$ NMR (acetone; ppm; width at half height, Hz; integral intensity, %), 56.46 (58 Hz, 64.6%), 58.632 (79 Hz, 35.4%). IR (cm^{-1}): 3350(s) (NH), 1550(s) (SCN), 970(br, vs) (POC), 560, 580 (m) (P=S).

2.5. Synthesis of $\{[(iPrO)_2P(S)NC(S)NH]_2$-m-$C_6H_4$ Ni$\}$ (7)

This was prepared similarly to compound **6** by using $Ni(NO_3)_2 \cdot 6H_2O$. Yield: ∼45%, m.p. 140 °C. *Anal.* Calc. for $C_{20}H_{34}N_4NiO_4P_2S_4$: C, 37.30; H, 5.28; P, 9.63; Ni, 9.12. Found: C, 37.22; H, 5.68; P, 9.98; Ni, 9.95%. $^{31}P\{^1H\}$ NMR (CH_2Cl_2; ppm; width at half height, Hz; integral intensity, %), 51.20 (187 Hz, 51.3%), 53.05 (58 Hz, 36.6%), 54.40 (90 Hz, 12.1%). IR (cm^{-1}): 3345(s) (NH), 1545(s) (SCN), 975(br, vs) (POC), 573, 589(m) (P=S).

2.6. Synthesis of $\{[(iPrO)_2P(S)NC(S)NH]_2$-m-$C_6H_4$ Zn$\}$ (**8**)

This was prepared similarly to compound **6** by using $ZnCl_2$. Yield: ∼84%, m.p. 150 °C. *Anal.* Calc. for $C_{20}H_{34}N_4O_4P_2S_4Zn$: C, 36.94; H, 5.23; P, 9.53; Zn, 10.06. Found: C, 37.16; H, 5.17; P, 9.24; Zn, 9.76%. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$; ppm), 56.24. ^{1}H NMR ($(CD_3)_2CO$; ppm): 1.478 (d, 12H, $^3J_{HH}$ 5.5 Hz); 1.482 (d, 12H, $^3J_{HH}$ 6.0 Hz), 4.92 (d. sept, 4H, $^3J_{POCH}$ 9.9 Hz; $^3J_{HH}$ 6.1 Hz), 7.44 (m, 3H, Ph); 8.15 (m, 1H), 9.59 (br. d, 2H, $^4J_{PNCNH}$ 7.8 Hz). IR (cm^{-1}): 3340(br, s) (NH), 1520(s) (SCN), 1000(b, vs) (POC), 569, 595(m) (P=S).

2.7. Synthesis of $\{[(iPrO)_2P(S)NC(S)NH]_2$-m-$C_6H_4Cd\}$ (9)

This was prepared similarly to compound **6** by using $Cd(CH_3COO)_2 \cdot H_2O$. Yield: ∼69%, m.p. 146–147 °C. *Anal.* Calc. for $C_{20}H_{34}CdN_4O_4P_2S_4$: H, 4.88; P, 8.88. Found: H, 5.59; P, 8.20%. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$; ppm), 55.54. ^{1}H NMR ($(CD_3)_2CO$; ppm): 1.496 (d. 12H, $^3J_{HH}$ 6.5 Hz); 1.471 (d, 12H, $^3J_{HH}$ 6.5 Hz), 4.92 (d. sept, 4H, $^3J_{POCH}$ 10.2 Hz; $^3J_{HH}$ 6.1 Hz), 7.39 (m, 3H, Ph), 8.30 (m, 1H, Ph), 9.64 (br. d, 2H, NH, $^4J_{PNCNH}$ 8.2 Hz). IR (cm^{-1}): 3200(br, s) (NH), 1490(s) (SCN), 1005(br, vs) (POC), 573, 594(m) (P=S).

2.8. Synthesis of $\{[(iPrO)_2P(S)NC(S)NH]_2$-p-$C_6H_4Co\}$ (**10**)

A suspension of 1.173 g (2 mmol) of $[(i\text{PrO})_2P(S)NHC(S)NH]_2$-*p*-$C_6H_4$ in anhydrous ethanol (20 ml) was mixed with an ethanol solution of potassium hydroxide (0.224 g, 4 mmol). To the resulting potassium salt, a water (20 ml) solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.579 g, 2.2 mmol) was added dropwise with vigorous stirring. The resulting complex was extracted with methylene chloride as a suspension and then the organic phase was washed with water (20 ml). The solvent was removed in vacuum. The residue was dried over $MgSO_4$ as an acetone solution and the solvent was removed in vacuum. A green solid was precipitated from acetone by *n*-hexane and dried in vacuum at 50 °C. Yield: 66%, m.p. 190–200 °C, decomposes. *Anal.* Calc. for $C_{20}H_{34}CoN_4O_4P_2S_4$: C, 37.29; H, 5.28; P, 9.63; Co, 9.15. Found: C, 36.60; H, 5.38; P, 11.94; Co, 11.37%. $^{31}P\{^1H\}$ NMR (CH_2Cl_2; ppm; width at half height, Hz); 169.54 (341 Hz). IR (cm^{-1}): 3360(br, s) (NH), 1504(s) (SCN), 1000(br, vs) (POC), 568(m) (P=S).

*2.9. Synthesis of {[(iPrO)$_2$P(S)NC(S)NH]$_2$-p-C$_6$H$_4$Zn} (**11**)*

This was prepared similarly to compound **10** by using $ZnCl_2$. Yield: ~65%, m.p. 305 °C, decomposes. *Anal.* Calc. for $C_{20}H_{34}N_4O_4P_2S_4Zn$: C, 36.94; H, 5.23; P, 9.53; Zn, 10.06. Found: C, 36.60; H, 5.22; P, 9.89; Zn, 10.04%. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$; ppm), 56.39. ^1H NMR ($(CD_3)_2CO$; ppm): 1.475 (d, 24H, $^3J_{HH}$ 6.2 Hz), 4.90 (d. sept, 4H, $^3J_{POCH}$ 10.2 Hz; $^3J_{HH}$ 6.1 Hz), 7.79 (s, 4H, Ph), 9.577 (d, 2H, NH, $^4J_{PNCNH}$ 8.2 Hz). IR (cm^{-1}): 3280(br, s) (NH), 1500(s) (SCN), 980(br, vs) (POC), 575(m) (P=S).

*2.10. Synthesis of {[(iPrO)$_2$P(S)NC(S)NH]$_2$-p-C$_6$H$_4$Cd} (**12**)*

This was prepared similarly to compound **10** by using $Cd(CH_3COO)_2 \cdot H_2O$. Yield: ~20%, m.p. 175 °C. *Anal.* Calc. for $C_{20}H_{34}CdN_4O_4P_2S_4$: C, 34.46; H, 4.88; P, 8.88; Cd, 16.12. Found: C, 34.71; H, 4.56; P, 9.06; Cd, 16.71%. $^{31}P\{^1H\}$ NMR ($(CH_3)_2CO$; ppm), 55.29. IR (cm^{-1}): 3220(br, s) (NH), 1510(s) (SCN), 980–1000 (POC), 568(m) (P=S).

2.11. Physical measurements

Infrared spectra (Nujol) were recorded on 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 ^{31}P spectra were recorded

Table 1
Crystal data, data collection and refinement parameters for **1**, **2** and **5**

	1	**2**	**5**
Empirical formula	$C_{32}H_{68}N_8O_8P_4S_8Cd_2$	$C_{36}H_{76}N_8O_{10}P_4S_8Pd_2 \cdot 2CH_2Cl_2$	$C_{16}H_{36}N_4O_4P_2S_4$
Formula weight	1298.1	772.03	538.69
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions			
a (Å)	15.297(2)	9.883(4)	10.556(2)
b (Å)	12.938(5)	12.368(2)	12.521(1)
c (Å)	30.089(5)	14.481(4)	10.723(2)
α (°)	90	73.75(2)	90
β (°)	103.55(1)	82.74(3)	103.41(1)
γ (°)	90	72.12(2)	90
V (Å^3)	5787(2)	1616(1)	1378.5(4)
Z	4	1	2
D_{calc} (g cm^{-3})	1.49	1.59	1.30
F(000)	664	792	572
Crystal colour	colourless	orange	colourless
Crystal form	prismatic	prismatic	prismatic
Crystal size (mm)	0.4 × 0.3 × 0.2	0.4 × 0.3 × 0.4	0.4 × 0.3 × 0.4
Radiation (Å)	0.71073	0.71073	0.71073
Temperature (K)	294	143	294
Scan mode	$\omega/2\theta$	$\omega/2\theta$	ω
Recording range θ_{max} (°)	33.76	26.28	32.28
Absorption correction	ψ-scans	none	none
μ (cm^{-1})	11.81	11.3	4.9
Scan speed (° min^{-1})	Variable, 1-16.4	Variable, 1-16.4	Variable, 1-16.4
Index ranges	$0 \leqslant h \leqslant 16, -16 \leqslant k \leqslant 0, -36 \leqslant l \leqslant 37$	$-11 \leqslant h \leqslant 0, -15 \leqslant k \leqslant 13, -16 \leqslant l \leqslant 16$	$0 \leqslant h \leqslant 12, 0 \leqslant k \leqslant 12, -13 \leqslant l \leqslant 13$
No. of recorded reflections	11091	5944	1895
Observed reflections $F^2 \geqslant 4\sigma(F^o)$	6704	3693	784
R (%)	0.038	0.058	0.057
R_w (%)	0.087	0.138	0.149
S	1.000	0.997	0.991

at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P).

2.12. Crystal structure determination and refinement

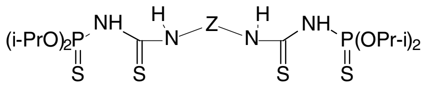
The crystals of **1** were obtained from the mixture of dichloromethane and *n*-hexane (1:13) and the crystals of **2** via the slow evaporation of solvent from a dichloromethane solution. At room temperature the crystals of **2**, taken from the saturated solution, lose solvents molecules and destroy themselves.

The X-Ray diffraction data for the crystals of **1** and **2** were collected on a CAD4 Enraf-Nonius automatic diffractometer using graphite monochromated Mo Kα (0.71073 Å) radiation. Molecules of **2** and **5** in the crystals are in special positions. The details of crystal data, data collection and the refinement are given in Table 1. The stability of the crystals and the experimental conditions were checked every 2 h using three control reflections, while the orientation was monitored every 200 reflections by centreing two standards. No significant decay was observed. An empirical absorption correction based on ψ-scans was applied. The structures were solved by direct methods using the SIR 92 [3] program and refined using the SHELXL-97 program [4]. For the crystals (**1**, **2**, **5**) all non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealised. All figures were made using the program PLATON [5].

3. Results and discussion

3.1. Synthesis

Ligands were prepared by the addition reaction of bis-amines $H_2N–Z–NH_2$ to diisopropoxythiophosphoryisothiocyanate $(iPrO)_2P(S)NCS$.



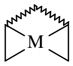
3–5

Complexes of $[(iPrO)_2P(S)NHC(S)NH]_2(m\text{-}C_6H_4)$ and $[(iPrO)_2P(S)NHC(S)NH]_2(p\text{-}C_6H_4)$ with Co(II), Ni(II), Zn(II) and Cd(II) **6–12** were prepared by the following procedure: the ligands were converted to their potassium salts, followed by interaction with inorganic salts of the corresponding metals. The obtained compounds are crystalline solids, soluble in most polar solvents. According to elemental analyses, they have a ratio M/L = 1:1. Complexes of bis-urea $[(iPrO)_2P(S)NHC(S)NH]_2(p\text{-}C_6H_4)$ are unstable in solution, in the presence of moisture, alcohols and air oxygen.

3.2. IR and NMR spectroscopy

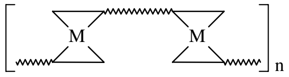
The IR spectra of **1**, **2**, **6–12** exhibit absorptions at 450–300 cm^{-1}, which correspond to the stretching vibration of M–S bonds. The absorption band of the P=S group is shifted from 630–655 cm^{-1} in the parent ligands to 560–595 cm^{-1} in the complexes. The strong infrared absorption observed for all complexes in the region 1490–1570 cm^{-1} was assigned to the group vibrations of the SCN fragment. The signal of the C(S)NHP(S) group proton is absent in NMR ^{1}H spectra. The signal of the ZNH proton is shifted upfield with respect to the same signal of free ligands. High $^{4}J_{PNCNH}$ coupling constants, about 8 Hz, were noted previously for the complexes of *N*-diisopropoxyphosphoryl-*N′*-phenyl thiourea [6]. Such a high constant can be explained by the almost planar bond arrangement in the PNCNH backbone and by the accordance of this fragment configuration to the so-called *W*-criterion [7]. ^{31}P NMR spectra of complexes **1**, **2**, **6–9**, **11** and **12** each show a resonance in the region 51–59 ppm. As a rule the signals are shifted downfield with respect to the parent ligands. Obtained IR and NMR spectral data are evidence of the chelate knot formation with participation of C=S and P=S groups and the metal cation. Due to the presence of the paramagnetic centres, the signals for the ^{1}H NMR spectrum of cobalt and nickel complexes **6**, **7** and **10** are broadened and their number increased, this makes assignment of the signals much more complicated.

Divalent metals can form complexes of 1:1 ML **A** and 2:2 M_2L_2 **B** compositions with such a kind of bipodal ligands. Formation of oligomeric or polymeric compositions M_nL_n (**C**) is also possible.



A

B



C

Thus, there is the possibility of an equilibrium in solution between all described types of complexes. We suppose that the equilibrium state depends first of all on the bridging chain Z length and secondly on the nature of the metal.

The ^{31}P NMR spectra of cobalt and nickel complexes **6**, **7** and **10** show several (up to three) signals of different intensities and widths at half height, which correspond to the different metal cation environments in the complexes. Such behaviour is common of the other complexes of bipodal thiophosphorylated thiourea [1]. The nickel cation has a *cis*-square-planar coordination environment in a dimer **B** and a *trans*-square-planar in an oligomer **C**. Nickel can also stay tetrahedral. Moreover, Ni(II) cations can be coordinated by lone pair donors, such as nitrogen or oxygen, which are present in the ligand molecules. Different signals in the phosphorus spectrum of **7** can be due to any of proposed forms. Cobalt(II) cations are usually tetrahedral, but they can also form adducts with donor molecules.

^{31}P NMR spectra of complexes **1**, **8**, **9**, **11** and **12** exhibit only one signal. Cd(II) and Zn(II) cations are diamagnetic and their signals in ^{31}P NMR spectra are less sensitive to the environment of the metal cation. That is why both forms can have the same chemical shift.

In contrast to nickel, palladium(II) does not give a tetrahedral form or adducts and *cis*- and *trans*-isomers have different signals in spectra, as shown for the complex of *N*-diisopropoxythiophosphoryl-*N*′-phenylthiourea with Pd(II) [6]. Nonetheless, the ^{31}P spectrum of compound **2** shows a single resonance, which could correspond to the binuclear complex as the only form present in solution.

3.3. Crystal structure of 5

Ligand **5** has been studied by X-ray analysis in order to compare its structure with the structures of **1** and **2**. The crystal structure of **5** is shown in Fig. 1, selected values of bond lengths, bond and torsion angles are given in Table 2. The NC(S)N fragment is almost planar, which is evidence of the resonance between the nitrogen lone pair and the double C=S bond. The conformation of the P–N–C–N fragment is almost shielded, torsion ∠P(1)–N(1)–C(1)–N(2) = 8.5(1)°. The NH group protons stay in an anti-disposition. The molecule has an inversion centre (see Table 3).

In the crystals of bisthiourea intra- and inter-molecular H-bonds of the NH···S type were found. Their parameters are presented in Table 3. Intermolecular H-bonds form endless chains. In the crystal these chains are oriented parallel to each other, along the *OY* axis.

3.4. Crystal structures of 1 and 2

Figs. 2 and 3 show the structures of **1** and **2**, respectively, selected values of bond lengths, bond and torsion angles are given in Tables 4 and 5. For compound **1** only the data concerning one chelate knot are presented. The second one has a very similar geometry. According to the X-ray data these complexes are of M_2L_2 structure.

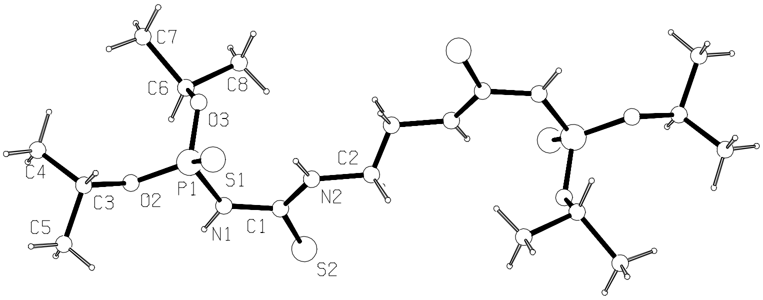


Fig. 1. Molecular structure of **5**.

Table 2
Selected bond distances (Å), bond and torsion angles (°) for the ligand **5**

Bond distances			
P(1)–S(1)	1.921(4)	P(1)–N(1)	1.684(5)
S(2)–C(1)	1.683(6)	N(1)–C(1)	1.382(7)
P(1)–O(2)	1.546(5)	N(2)–C(1)	1.306(8)
P(1)–O(3)	1.522(6)	N(2)–H(2)	0.8597
N(1)–H(1)	0.8597		
Bond angles			
S(1)–P(1)–N(1)	117.0(2)	N(1)–C(1)–N(2)	117.5(5)
P(1)–N(1)–C(1)	127.5(4)	S(2)–C(1)–N(2)	124.0(5)
S(2)–C(1)–N(1)	118.5(5)	C(1)–N(2)–C(2)	125.3(5)
P(1)–N(1)–H(1)	116.22	C(1)–N(1)–H(1)	116.23
Torsion angles			
P(1)–N(1)–C(1)–N(2)	8.5(1)	S(1)–P(1)–N(1)–C(1)	–52.7(7)
P(1)–N(1)–C(1)–S(2)	–170.9(4)		

Table 3
Parameters of H-bonds in the bisthiourea **5**

Bond	Symmetry operation	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N1–H1···S2	$-x$, $1-y$, $1-z$	0.86	2.62	3.467(4)	170.0
N2–H2···S1	intramolecular	0.86	2.59	3.332(6)	145.0

Bond lengths in Å and bond angles in degrees.

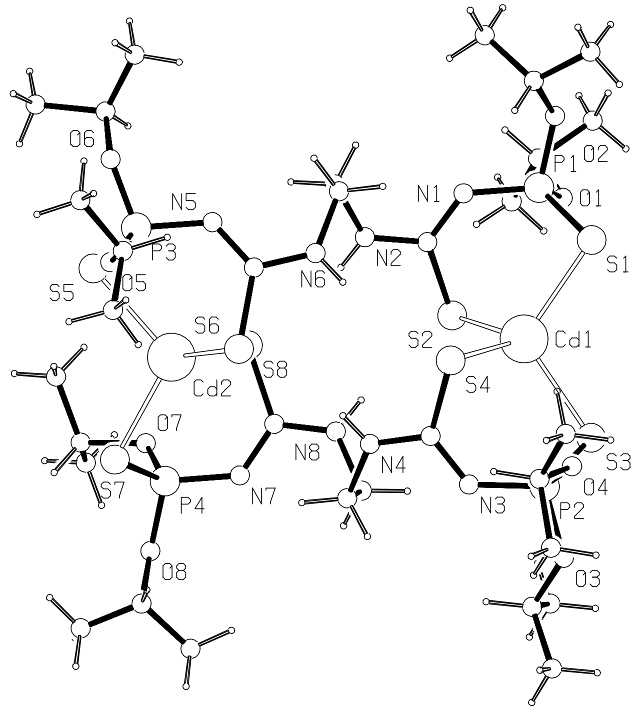


Fig. 2. Molecular structure of complex **1**.

Each ligand "tail" covers only its own metal atom. The coordination sphere of the metal includes a second ligand molecule. The structures of the described complexes are similar to the structures of the complexes of *para*-phenylene bis(imines) and *para*-phenylene methylpyridines [8,9]. In the crystal of compound **1** there is only the independent molecule in the asymmetric part of the lattice. In compound **2** the molecule is in a special position respective to the centre of symmetry. The cadmium and palladium atoms are four-coordinated and have the configuration of a slightly distorted tetrahedron for cadmium and a distorted square plane for palladium. The tetrahedral configuration of the cadmium atoms in compound **1** resembles those previously found in imidobis-seleno-[$Ph_2P(Se)NP(Se)Ph_2]_2Cd$ [10] and -thiophosphinyl [$iPr_2P(S)NP(S)iPr_2]_2Cd$ [11] cadmium complexes. They have a bis-chelate structure with a tetrahedral configuration of the central atom.

In compound **1** the Cd–S(C) bond lengths range from 2.527(1) to 2.536(1) Å, and Cd–S(P) bond lengths range from 2.503(2) to 2.523(1) Å. This reveals the equalization of the metal bond lengths with either the thiophosphoryl or the thiocarbonyl sulfur atoms. The values of the P–S (1.990 Å mean) and C–S (1.760 Å mean) bond

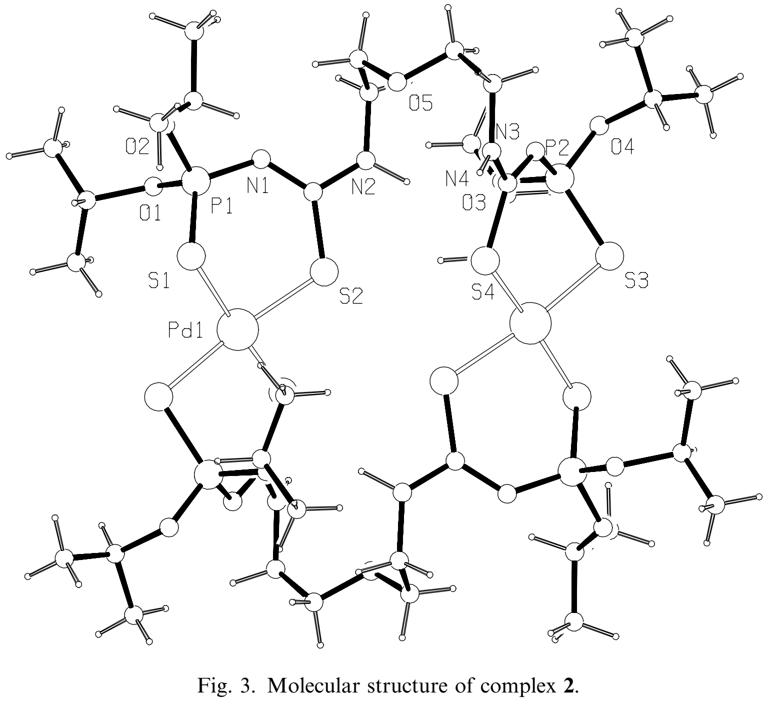


Fig. 3. Molecular structure of complex **2**.

Table 4
Selected bond distances (Å), bond and torsion angles (°) for complex **1**

Bond distances			
Cd(1)–S(1)	2.522(1)	Cd(1)–S(2)	2.536(1)
Cd(1)–S(3)	2.522(1)	Cd(1)–S(4)	2.532(1)
S(1)–P(1)	1.989(2)	S(3)–P(2)	1.986(2)
S(2)–C(1)	1.764(4)	S(4)–C(2)	1.758(4)
P(1)–N(1)	1.603(4)	P(2)–N(3)	1.595(4)
N(1)–C(1)	1.310(5)	N(3)–C(2)	1.317(6)
Bond angles			
S(1)–Cd(1)–S(2)	100.62(4)	S(2)–Cd(1)–S(4)	105.68(4)
S(3)–Cd(1)–S(4)	103.49(4)	S(1)–Cd(1)–S(4)	118.96(4)
S(1)–Cd(1)–S(3)	111.47(5)	S(2)–Cd(1)–S(3)	117.22(4)
Cd(1)–S(1)–P(1)	97.84(5)	Cd(1)–S(2)–(1)	92.9(1)
Cd(1)–S(3)–P(2)	96.49(7)	Cd(1)–S(4)–(2)	92.2(1)
P(1)–N(1)–C(1)	127.9(3)	P(2)–N(3)–C(2)	128.7(3)
S(1)–P(1)–N(1)	116.4(1)	S(3)–P(2)–N(3)	115.7(1)
S(2)–C(1)–N(1)	126.4(3)	S(4)–C(2)–N(3)	127.0(3)
Torsion angles			
P(1)–N(1)–C(1)–S(2)	−1.1(5)	P(2)–N(3)–C(2)–S(4)	−8.5(6)
S(1)–P(1)–N(1)–C(1)	−68.9(4)	S(3)–P(2)–N(3)–C(2)	−67.3(4)

Table 5
Selected bond distances (Å), bond and torsion angles (°) for complex **2**

Bond distances			
Pd(1)–S(1)	2.342(2)	Pd(1)–S(3)	2.354(2)
Pd(1)–S(2)	2.289(2)	Pd(1)–S(4)	2.296(2)
S(1)–P(1)	2.004(3)	S(3)–P(2)	1.993(3)
S(2)–(1)	1.733(8)	S(4)–(2)	1.739(8)
P(1)–N(1)	1.580(6)	P(2)–N(3)	1.579(6)
N(1)–C(1)	1.333(9)	N(3)–C(2)	1.319(9)
Bond angles			
S(1)–Pd(1)–S(2)	96.05(7)	S(2)–Pd(1)–S(4)	80.31(7)
S(1)–Pd(1)–S(3)	85.26(7)	S(3)–Pd(1)–S(4)	99.32(7)
Pd(1)–S(1)–P(1)	99.48(9)	Pd(1)–S(3)–P(2)	97.57(9)
Pd(1)–S(2)–C(1)	115.0(2)	Pd(1)–S(4)–C(2)	115.4(3)
P(1)–N(1)–C(1)	128.9(5)	P(2)–N(3)–C(2)	126.5(5)
S(1)–P(1)–N(1)	119.0(2)	S(3)–P(2)–N(3)	117.1(2)
S(2)–C(1)–N(1)	129.9(6)	S(4)–C(2)–N(3)	129.7(6)
Torsion angles			
P(1)–N(1)–C(1)–S(2)	15(1)	P(2)–N(3)–C(2)–S(4)	−2(1)
S(1)–P(1)–N(1)–C(1)	23.2(8)	S(3)–P(2)–N(3)–C(2)	−48.4(7)

lengths also correspond to the values intermediate between double (P=S 1.91–1.92 Å, C=S 1.68 Å in the thioureas) and the single (P–S 2.05–2.11 Å, C–S 1.751 Å) bonds [12]. The P=S bonds order stays in agreement with IR spectroscopy observations. Meanwhile, the C–N and P–N bonds are shorter on comparison with those in the free ligand **5** (C–N 1.382(7), P–N 1.684(5) Å). This picture is characteristic for the complexes discussed.

The metal-containing heterocycles CdSPNCS have the conformation of a non-symmetric boat, with the most deviation of P and S(C) atoms from the mean square planes of these fragments (Table 6).

In complex **2** the palladium atom has a distorted square-planar configuration. The deviations of the S(1) and S(4a) atoms from the plane S(1)S(2)S(3a)S(4a) are −0.147(2) and −0.154(2) Å, respectively, S(2) and S(3a) atoms are 0.158(2) and 0.154(2) Å, respectively. The palladium atom deviates from the plane S(1)S(2)S(3a)S(4a) by 0.0305(6) Å. The Pd–S(C) and Pd–S(P) bond lengths are within the usual limits for bonds of these kinds. For example, in the complex [PhC(S)NP(S)(O*i*Pr)$_2$]$_2$Pd (**13**) Pd–S(C) is 2.310 Å and Pd–S(P) is 2.341 Å [13]. The Pd–S(P) bond lengths in the compounds Pd[(EtO)$_2$P(S)NP(S)Ph$_2$]$_2$ (**14**) [14], Pd[{(PhO)$_2$P(S)}$_2$N]$_2$ [15], Pd[{*i*Pr$_2$P(S)}$_2$N]$_2$ [16] are in the range 2.325–2.351 Å. The Pd–S(C) bond lengths in the complex Pd[Et$_2$NC(S)NC(O)Ph]$_2$ (**15**) are 2.310–2.315 Å [17]. The values of the bond lengths also show the equalization of the bond lengths, but in contrast to complex **1**, there is an evident difference between the bonds M–S(P) and M–S(C) in complex **2**.

The metal-containing six-membered heterocycle Pd(1)S(1)P(1)N(1)C(1)S(2) is in a "sofa" conformation. The conformation of the second metal-containing heterocycle Pd(1)($-x$, $-y$, $1-z$)S(3)P(2)N(3)C(2)S(4) is a non-symmetric boat, see Table 7. The conformation of the SCNPS backbone in **1** and **2** is similar: the NC(S)NP fragment is almost planar and the phosphoryl sulfur is deviated from its least-square plane. Torsion S–P–N–C angles range from 67.3(4)° to 72.3(5)° for **1** and 23.2(8)° to 48.4(7)° for **2**. The values of torsion angles in compounds **1** and **2** show that these deviations are higher in the cadmium complex **1**.

Table 6
Deviations (Å) from the mean-square planes CdSPNCS in **1**

Atoms in plane	Deviation	Atoms in plane	Deviation	Atoms in plane	Deviation	Atoms in plane	Deviation
Cd(1)	−0.4825	Cd(1)	−0.3911	Cd(2)	−0.4419	Cd(2)	−0.3636
S(1)	0.0958	S(3)	−0.1801	S(5)	−0.1369	S(7)	−0.2061
P(1)	0.4879	P(2)	0.5063	P(3)	0.5083	P(4)	0.5205
N(1)	−0.3018	N(3)	−0.2614	N(5)	−0.3009	N(7)	−0.2652
C(1)	−0.2765	C(2)	−0.3098	C(3)	−0.2779	C(4)	−0.3045
S(2)	0.6687	S(4)	0.6360	S(6)	0.6493	S(8)	0.6189

Table 7
Deviations (Å) from the mean-square planes PdSPNCS in **2**

Atoms in plane	Deviation	Atoms in plane	Deviation
Pd(1)	−0.4537	Pd(1)	0.2818
S(1)	0.5521	S(3) (−*x*, −*y*, 1 − *z*)	0.5275
P(1)	−0.2806	P(2) (−*x*, −*y*, 1 − *z*)	−0.4083
N(1)	−0.0894	N(3) (−*x*, −*y*, 1 − *z*)	0.0435
C(1)	0.1879	C(2) (−*x*, −*y*, 1 − *z*)	0.2021
S(2)	0.0837	S(4) (−*x*, −*y*, 1 − *z*)	−0.0829

Table 8
Parameters of intramolecular H-bonds of the complex **1**

Bond	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N2–H2···S8	0.86	2.66	3.504(3)	168.0
N4–H4···S6	0.86	2.69	3.529(4)	167.0
N6–H6···S4	0.86	2.82	3.662(4)	167.0
N8–H8···S2	0.86	2.63	3.477(3)	170.0

Bond lengths in Å and bond angles in degrees.

In the crystal of complex **1** intramolecular H-bonds of the NH···S type were found (Fig. 4). In contrast to complex **1**, in the crystal of complex **2** both inter- and intramolecular H-bonds take place (Fig. 5). The H-bonds parameters of complexes **1** and **2** are presented in Tables 8 and 9. As a result of hydrogen bonding in **2** centrosymmetric dimers are formed. Since the first molecule of the dimer lies in the local symmetry centre, the second molecule is linked to another dimer's molecule. Finally, due to this interaction the dimers are linked into endless chains.

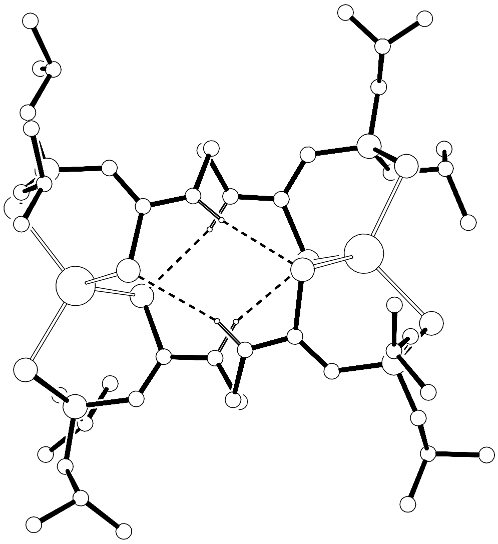


Fig. 4. H-bonds in complex **1**.

The nature of the close chemical environment of the central atom imposes a major impact on the chelate knot structure. If these atoms are the same then the square-planar complexes of "soft" metals with anionic ligands of the [A(X)NB(Y)] type have, as a rule, a *trans*-structure: **13** [13], **14** [14], [PhNHC(S)NP(S)(O*i*Pr)$_2$]$_2$Ni [18], [Pr$_2$NC(S)NP(S)(OPh)$_2$]$_2$Ni [19], [MeNHC(S)NP(S)Ph$_2$]$_2$Ni [20], [(EtO)$_2$P(S)NP(S)Ph$_2$]$_2$Pt [14], [Me$_2$P(S)NP(S)Ph$_2$]$_2$Ni [21], [Et$_2$NC(S)NC(S)Ph]$_2$Ni [22]. The only exception is the complex {[H$_2$NC(S)NP(S)Ph$_2$]$_2$Pt}(Et$_2$O) [23]. If $X \neq Y$ the *cis*-structure is preferable due to the *trans*-influence: **15** [17], [Et$_2$NC(S)NC(O)Ph]$_2$Cu [24], [Ph$_2$P(Se)NP(O)Ph$_2$]$_2$Pd [25], [(*i*PrO)$_2$P(O)NC(S)Ph]$_2$Cu [26], [(*i*PrO)$_2$P(O)NC(S)NEt$_2$]$_2$Cu [27]. The central atom's surroundings affects in turn the structure of the macrocyclic complexes with bipodal ligands. For example the dimer

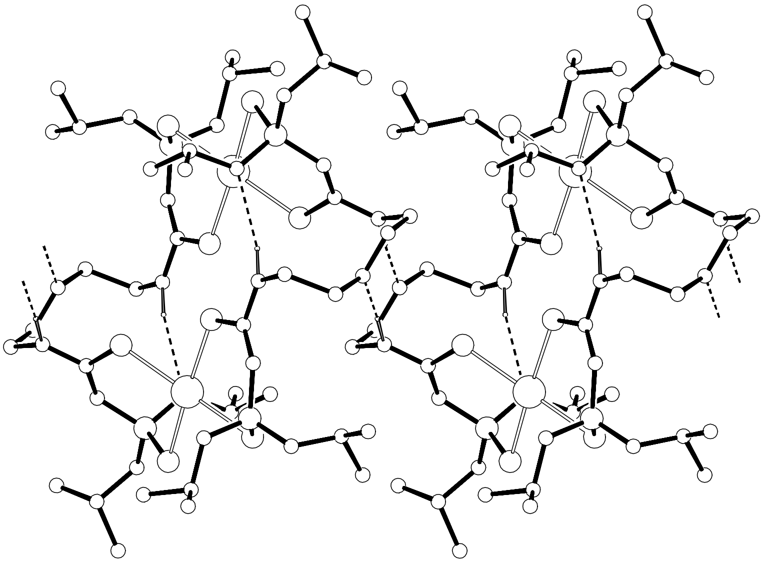


Fig. 5. H-bonds in complex **2**.

Table 9
Parameters of H-bonds of the complex **2**

Bond	Symmetry operation	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N2–H2···O3	Intramolecular	1.00	2.34	3.177(7)	141.0
N4–H4···O5	$-x, 1-y, -z$	0.86	1.99	2.823(8)	164.0

Bond lengths in Å and bond angles in degrees.

and trimer complexes with bipodal *O*,*S*-acylthioureas have the *cis*-structure only [28,29].

Ligands having coordinating atoms with similar donor abilities can form both *cis*- and *trans*-isomers depending on slight peculiarities like the entropy of an isomer, steric preferences, polarity of media. Hence, it is evident, why the complexes with *S*,*S*-bipodal ligands form both polymers [1,2] and dimers as in this case. When there is a tendency to form chelate molecules with a *trans*-structure, the minimal accepted size for the cyclic molecule $(ML)_n$ should be $n = 4$.

The results of the presented work are in a good agreement with the data published by Kluiber and Lewis [30], Kobuke and Satoh [31], – both the dimeric complexes **1** and **2** are formed with ligands that contain less than 7 atoms in the bridging chain Z.

Acknowledgements

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC Nos. 189278, 189279 and 218902. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-(1223)-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2004.07.005.

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