

Synthesis and structural characterization of novel zinc(II) and cadmium(II) complexes with pyridine–phosphine chalcogenide ligands

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ABSTRACT

New pyridine–phosphine chalcogenide ligands, tris[2-(2-pyridyl)ethyl]phosphine sulfide **1a** and tris[2-(2-pyridyl)ethyl]phosphine selenide **1b**, react with zinc(II) and cadmium(II) chlorides in EtOH at room temperature to afford complexes of compositions $2\text{ZnCl}_2 \cdot 2\text{L}$ (**2**, L = **1a**) and $3\text{CdCl}_2 \cdot 2\text{L}$ (**3a,b**, L = **1a,b**) in high yields. The solid-state structure of complexes **2**, **3** has been proved by X-ray analysis data. Complex **2** is a centrosymmetric dimer, where two atoms of zinc are bonded by two bridging pyridine–phosphine sulfide ligands through N atoms. Complexes **3a,b** exist as polymeric chains with each bridging ligand acting as a chelate N,S- or N,Se-donor to one cadmium(II) center and as a pyridine N-donor to the next cadmium(II) center.

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1. Introduction

Organophosphorus ligands such as tertiary phosphine oxides, sulfides, or selenides bearing O, S, or Se donor atoms have been the focus of investigations related to their coordination chemistry, extractive metallurgy, catalytic properties, and structural chemistry [1]. Besides, metal complexes with phosphine sulfides and selenides are important from the point of view of their application in chemical vapor deposition (CVD) processes [2] to give metal sulfide or selenide nanoparticles possessing unique magneto-optical, electrical and other properties [3].

Recent years have also seen a renaissance of interest in the study of multidentate nitrogen-donor ligands (in particular containing pyridine fragments) and their use in homogeneous catalysis [1b,c,e,f,4]. In addition, pyridyl ligands form often labile metal–ligand bonds that can be used in self-assembly of coordination polymers and network materials [5].

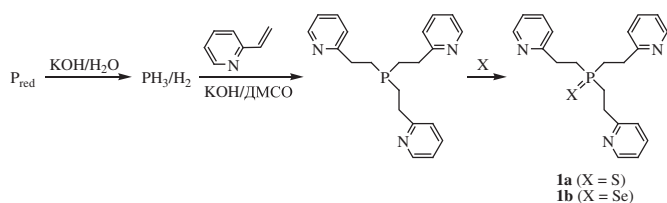
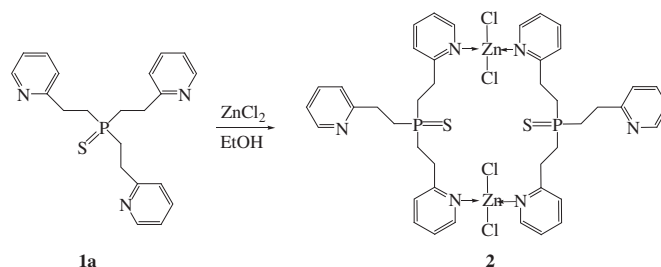
Currently, a particular emphasis is placed on phosphorus-based hemilabile ligands showing outstanding results in catalytic

processes [6], i.e. allylic substitution, hydrosilylation, hydroboration and hydrogen–transfer reactions [7]. Among these ligands are phosphine sulfides and selenides with pyridyl groups [2c,8]. Thus, in palladium(II) complex diphenyl(2-pyridyl)phosphine sulfide acts as S,N-chelating ligand whereas phenyl[di(2-pyridyl)]- and tri(2-pyridyl)phosphine sulfides behave both as S,N- and N,N-chelating ligands [8]. Diphenyl(2-pyridylmethyl)phosphine selenide participates in the formation of a calcium complex as hemilabile Se,N-ligand [2c]. The differential thermal analysis of the complex points to possible CVD applications to form CaSe from the gas phase [2c]. Zinc(II) and cadmium(II) complexes with ligands bearing N, P, S and Se donor atoms are also investigated intensively [9].

Here we report on the synthesis of zinc(II) and cadmium(II) complexes based on hemilabile pyridine–phosphine chalcogenide ligands, tris[2-(2-pyridyl)ethyl]phosphine sulfide **1a** and tris[2-(2-pyridyl)ethyl]phosphine selenide **1b**. The latter are easily prepared by the procedure [10] involving generation of phosphine–hydrogen mixture from red phosphorus and potassium hydroxide in the system water – toluene, addition of phosphine to 2-vinylpyridine in the presence of strong base (KOH – DMSO) and oxidation of intermediate tris[2-(2-pyridyl)ethyl]phosphine by elemental sulfur or selenium in benzene (Scheme 1).

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Scheme 1. Synthesis of ligands **1a,b**.Scheme 2. Synthesis of zinc(II) complex **2**.

2. Results and discussion

The reaction of tris[2-(2-pyridyl)ethyl]phosphine sulfide **1a** with ZnCl_2 (molar ratio 1:1) proceeded under mild conditions (r. t., 2.5 h, EtOH) to form complex **2** of composition $2\text{ZnCl}_2 \cdot 2\text{L}$ ($\text{L} = \mathbf{1a}$) in 70% yield (Scheme 2).

Complex **2** crystallizes in the monoclinic space group $P2_1/n$ (Table 1) and exists as a centrosymmetric dimer (Scheme 2), where two atoms of zinc are bonded by two bridging pyridine-phosphine sulfide **1b** ligands through N atoms.

The molecular structure of **2** is shown in Fig. 1 and the selected bond lengths and angles are given in Table 2. The Zn(1) atom's coordination polyhedron is a distorted tetrahedron with coordination sites occupied by Cl(1), Cl(2), N(17) and N(18) atoms. The bond distances [Zn(1)–Cl(1) 2.236(1) Å, Zn(1)–Cl(2) 2.236(1) Å, Zn(1)–N(17) 2.067(3) Å, Zn(1)–N(18) 2.040(3) Å] in the tetrahedron are normal and comparable in particular with the related distances reported for the complex of ZnCl_2 with phosphine sulfide-imidazole ligand [11]. The coordination polyhedron of phosphorus atom P(1) is a distorted tetrahedron. The P(1)–S(1) bond distance [1.937(2) Å] is comparable with uncoordinated double P=S bond distances described in the literature [12]. The P–C bond distances [1.801(4) ÷ 1.852(5) Å] are slightly longer than those in analogous compounds [13].

Under conditions of complex **2** synthesis (r. t., 3 h, EtOH, molar ratio 1:1) phosphine sulfide **1a** and phosphine selenide **1b** reacted with CdCl_2 to give compounds **3a,b** of composition $3\text{CdCl}_2 \cdot 2\text{L}$ ($\text{L} = \mathbf{1a}$ in **3a**, $\text{L} = \mathbf{1b}$ in **3b**) in 65% and 64% yields, respectively (Scheme 3). Slightly higher yield (71%) of **3a** was gained using CdCl_2 and ligand **1a** in 3:2 ratio.

Compounds **3a,b** crystallize in the triclinic space group $P\bar{1}$ (Table 1) and exist as polymeric chains, formed along the a -axis, with each bridging ligand **1a,b** acting as a chelate N,S- or N,Se-donor to one cadmium(II) center and as a pyridine N-donor to the next cadmium(II) center (Figs. 2–4). The coordination by ligands **1a,b** can be rationalized by the fact that Cd(II) as a soft Lewis acid [1a] is involved in assembling of complexes **3a,b** not only through N atom but also through softer S or Se atoms. There are two crystallographically unequal cadmium atoms (hexacoordinated and pentacoordinated), bridged by two chlorine ligands in the crystals of **3**. The selected bond lengths and angles for compounds **3a,b** are given in Tables 3 and 4, respectively.

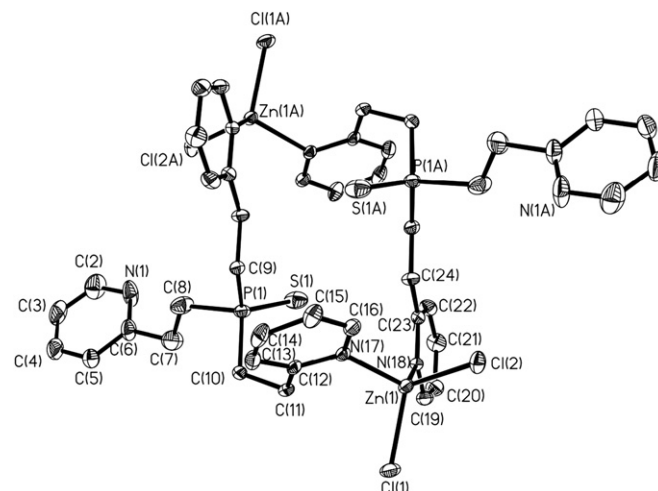
Centrosymmetric coordination polyhedron of the hexacoordinated cadmium atom Cd(2A) in **3a** is a square bipyramid with N(20B) and N(20C) atoms occupying apical positions. Atoms Cl(1A), Cl(2A), Cl(1D) and Cl(2D) are located on the equatorial plane positions. The pentacoordinated cadmium atom Cd(1D) has a distorted trigonal bipyramidal bonds configuration with N(1D) and Cl(1D) atoms occupying apical positions and N(1D)–Cd(1D)–Cl(1D) angle being $178.77(6)^\circ$. Atoms S(1D), Cl(2D) and Cl(3D) are located on the equatorial plane positions. The phosphorus atom P(1) has a distorted tetrahedral bonds configuration. The P(1)–S(1) bond distance [1.998(1) Å] is much longer than uncoordinated P=S distance in compound **2** and comparable with the lengths of coordinated double P=S bonds reported in the literature [1h,i,14].

The P–C bond distances [1.809(3) ÷ 1.814(3) Å] are comparable with the related distances [1i,12,14a].

Centrosymmetric coordination polyhedron of the hexacoordinated cadmium atom Cd(2B) in **3b** has a square bipyramidal geometry with N(20A) and N(20F) atoms occupying apical positions. Atoms Cl(1C), Cl(2C), Cl(1D) and Cl(2D) are located on the equatorial plane positions. The pentacoordinated cadmium atom Cd(1C) has a distorted trigonal bipyramidal geometry of bonds with N(1B) and Cl(1C) atoms occupying apical positions and angle N(1B)–Cd(1C)–Cl(1C) being $178.77(6)^\circ$. Atoms Se(1C) and Cl(3C) are located on the equatorial plane positions. The P(1) atom's bonds configuration is a distorted tetrahedron. The P(1)–Se(1) bond distance [2.158(1) Å] is longer than uncoordinated P=Se bond distances (2.09 ÷ 2.13 Å) [1g,h,15] and comparable with the lengths of coordinated double P=Se bonds reported in the literature [1g,h,15a]. The P–C bond distances [1.814(5) ÷ 1.827(5) Å] are comparable with the related distances [15].

The elongation of P–S(Se) distances in compounds **3a,b** compared to uncoordinated phosphine sulfide or phosphine selenide bonds shows that the double bond character of P–S and P–Se bonds is reduced after coordination to the Cd center through S(Se) atom.

Expectedly, the absorption band at 560 cm^{-1} [$\nu(\text{P}=\text{S})$] in the IR spectrum of compound **2** is not shifted to compare with this absorption band of ligand **1a** [10]. The IR spectra of the ligands **1a,b** and complexes **3a,b** are different and the diagnostic $\nu(\text{P}=\text{S})$ absorption band at 560 cm^{-1} in ligand **1a** appears at 539 cm^{-1} in complex **3a**. Similarly, the $\nu(\text{P}=\text{Se})$ absorption band at 447 cm^{-1} in ligand **1b** is shifted to 415 cm^{-1} in complex **3b** supporting the coordination by the ligands through S and Se atoms in the corresponding complexes.

Fig. 1. An ORTEP drawing and atom-numbering scheme for complex **2**.

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