



A new convenient synthetic route to metal diselenophosphinates: Synthesis and characterization of $[M_2(Se_2PPh_2)_4]$ ($M = Zn, Cd$ and Hg) complexes

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ABSTRACT

An efficient synthesis for group 12 metal diselenophosphinates has been elaborated based on original reaction between easily available ammonium diselenophosphinates, $NH_4[Se_2PPh_2]$ or $Et_2NH_2[Se_2PPh_2]$ and corresponding metal(II) oxides (0–25 °C, acetone, 1–4 h). The Zn(II), Cd(II), and Hg(II) diselenophosphinates have been first fully characterized to reveal dimers $[M_2(Se_2PPh_2)_4]$ in the solid state. These dinuclear species contain an eight-membered chair-like ring, $(MSePSe)_2$, formed by two metal atoms connecting via Se–P–Se chains. The distorted tetrahedral environment of each metal center is defined by four Se atoms belonging to one chelating (η^2) and two bridging (μ^2 , η^2) diselenophosphinato ligands. A special feature for Cd(II) complex is the existence of a solvent- and temperature-dependent fluxional process (determined by VT ^{31}P NMR spectroscopy) which was tentatively assigned for the exchange between bridging and chelating “dsepi” (diselenophosphinato) ligands. The free energy of activation for this equilibrium calculated from the coalescence temperature being $\Delta G^\ddagger_{(233K)} = 41.9 \text{ kJ mol}^{-1}$.

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1. Introduction

Metal dithiophosph(in)ates find enormous applications as flotation collectors, reagents for extraction and analysis of noble metals, additives in lubricating oils, as well as reactive building blocks [1]. Their syntheses and structural chemistry are well established [2]. Less studied are their selenium congeners, i.e. metal diselenophosphinates and, respectively, their syntheses have been much less elaborated [3]. Meanwhile, the latter also attract a great interest, especially as single-source precursors [4], synthetic building blocks [5] and models for understanding of metal separation schemes [6]. For instance, Zn(II), Cd(II), Co(II), Ni(II), In(III), and Eu(III) diselenophosphinates were successfully employed as single-source precursors for the growth of metal selenide

nanoparticles and thin films [7]. Quite recently, preparation of CdSe semiconductor nanocrystals using Cd(II) diphenyldiselenophosphinate was published [7g].

In sharp contrast to dithiophosphinates [1], there are only limited examples of well characterized (either in the solid state or in the solution) diselenophosphinates [3], despite the regular reports on their applications [4,7]. Commonly, diselenophosphinate complexes have been synthesized *via* metathesis reaction of simple metal salts with sources of the free $[R_2PSe_2]$ anions, e.g. alkali metal or ammonium diselenophosphinates [3]. Nevertheless, this approach is not always predictable and sometimes the isolated yield is poor, because some metal salts can act as oxidizing agents towards $[R_2PSe_2]$ anions leading to by-products [3]. The diselenophosphinate complexes have also been prepared by oxidation of metal phosphides (e.g. Li, K, Ni, Ca and Ba) with elemental selenium [8] as well as *via* the reaction of metal halides or acetates with bis(selenophosphinyl)selenides, $(R_2P = Se)_2Se$ [9].

Herein, we report a new synthetic route to group 12 metal diselenophosphinates as well as their first characterization both in solid and solution states. This efficient approach is based on original

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reaction of metal oxides with ammonium diselenophosphinate, $\text{NH}_4[\text{Se}_2\text{PPh}_2]$, which now is easily available directly from commercial diphenylphosphine, elemental selenium and ammonia [10].

2. Results and discussion

2.1. Synthesis of complexes 2–4

We have found, that the salt $\text{NH}_4[\text{Se}_2\text{PPh}_2]$ (**1**) reacts with the corresponding metal(II) oxides in a 2:1 M ratio to afford Zn (**2**), Cd (**3**) and Hg (**4**) diselenophosphinates in 64–85% yields (non optimized), Scheme 1. The reaction readily proceeds in solution of acetonitrile, acetone or dichloromethane under mild conditions (0–25 °C, 1–4 h). Notably, salt **1** acts in this reaction as synthetic equivalent of the diselenophosphinic acid (HSe_2PPh_2), so far unknown in free form.

It should be noted, that the available diethylammonium salt [11], $\text{Et}_2\text{NH}_2[\text{Se}_2\text{PPh}_2]$, may also be successfully used for the synthesis of **2–4** instead of ammonium salt **1**.

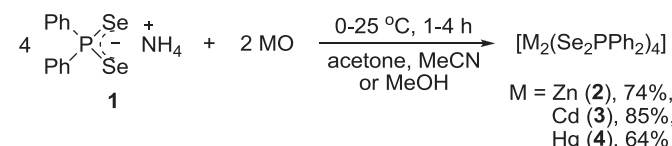
The main advantage of the developed synthetic protocol is accessibility of the starting materials; the oxides used represent cheapest sources of Zn, Cd, and Hg. The high-yields, mild conditions, and relatively short reaction time also demonstrate the synthetic efficacy of the disclosed protocol. Noteworthy, the isolation procedure is so simple that the expected reaction by-products, i.e. ammonia and water, are easily separated from the target compounds. Therefore, this innovative protocol is a comfortable both for laboratories and further scaling up.

Noted, that the above reaction proceeds chemoselectively such that the complexes of $[\text{M}_2(\text{Se}_2\text{PPh}_2)_4]$ type are only formed. Interestingly, using of the habitual zinc sources, e.g. ZnCl_2 , instead of ZnO leads to self-assembly of four-nuclear Se-centered cluster $\{\text{Zn}_4(\text{Se})[\text{Se}_2\text{PR}_2]_6\}$ ($\text{R} = \text{CH}_2\text{CH}_2\text{Ph}$) in good yield (the formation of expected product **2** does not take place). The detailed results of this reaction will be published elsewhere.

Complexes obtained **2–4** were fully characterized by X-ray crystallography, ESI-MS, and solution ^1H , ^{31}P , ^{77}Se NMR (including VT ^{31}P NMR) techniques. The elemental analysis data of the compounds support their compositions. The ESI-MS spectra of **2–4** exhibit peaks at m/z 1162.6, 1254.6, and 1430.6, respectively, assigned to species $[\text{M}_2(\text{Se}_2\text{PPh}_2)_3]^+$ formed by elimination of one the “dsepi” ligands from initial complexes.

2.2. Crystal structures of complexes 2–4

According to X-ray diffraction study, the compounds **2–4** are isostructural and crystallize in the triclinic space group $P(-1)$ with one molecule per unit cell. These complexes reveal a dimeric structure, $[\text{M}_2(\text{Se}_2\text{PPh}_2)_4]$ (Figs. 1–3), containing an 8-membered ring $(\text{MSePSe})_2$, which adopts a chair-like conformation *[cf. saddle-shape geometry of such ring in $\text{Zn}_2[\text{Se}_2\text{P}(\text{O}i\text{-Pr})_2]_4$ [12], $\text{Cd}_2[\text{Se}_2\text{P}(\text{O}i\text{-Pr})_2]_4$ [13] and $\text{Cd}_2[\text{Se}_2\text{P}(\text{OMe})\text{Ph}]_4$ [14]]*. Within the ring, the metal atoms are connected by two bridging (μ^2, η^2) “dsepi” ligands. Two other ligands are chelated (η^2) to each metal atom so that the latter has a distorted tetrahedral geometry. As expected, the P atoms have a distorted tetrahedral environment. A specific



Scheme 1. Synthesis of complexes 2–4.

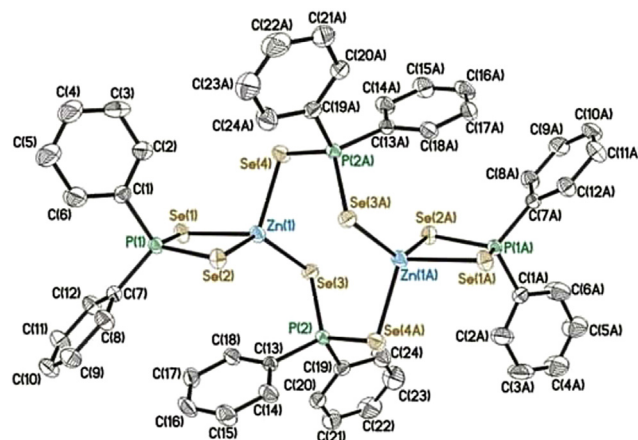


Fig. 1. The thermal ellipsoid drawing (50% probability) of the structure of **2**. Selected bond distances (Å) and angles (°): P(1)–Se(1), 2.1655(12); P(1)–Se(2), 2.1847(13); P(2)–Se(3), 2.1745(12); P(2)–Se(4), 2.1705(12); Se(1)–Zn(1), 2.5519(7); Se(2)–Zn(1), 2.4491(7); Se(3)–Zn(1), 2.4322(7); Se(4)–Zn(1), 2.4756(7); Se(1)–P(1)–Se(2), 107.89(5); Se(4)–P(2)–Se(3), 115.12(5); Se(3)–Zn(1)–Se(4), 102.59(3); Se(2)–Zn(1)–Se(1), 89.35(2).

feature of the compounds **2–4** is the lack of selenophilic Se···Se interactions, typical for many metal diselenophosph(in)ates [3,15].

In complex **2**, the two adjacent Zn–Se pairs within $(\text{ZnSePSe})_2$ cycle form an essentially planar Zn_2Se_2 core, wherein the average bond angle is 90.0°. Due to the long Zn(1)–Se(3A) and Zn(1A)–Se(3) distances (3.447 Å), there are no transannular interactions between the non-bonded Zn(1) and Se(3) atoms, *cf.* sum of their van der Waals radii = 3.29 Å [16]. The intramolecular $\text{Zn}\ddot{\text{A}}\text{Zn}$ distance is 4.247 Å which is almost the same as observed length, 4.316 Å, in diselenophosphate analog, $\text{Zn}_2[\text{Se}_2\text{P}(\text{O}i\text{-Pr})_2]_4$ [12]. In a series of related Zn complexes, $[\text{Zn}_2(\text{S}_2\text{PETe}_2)_4]$, $\text{Zn}_2[\text{S}_2\text{P}(\text{OEt})\text{An}]_4$, $\text{Zn}_2[\text{S}_2\text{P}(\text{OMe})\text{Fc}]_4$, $\text{Zn}_2[\text{S}_2\text{P}(\text{O}i\text{-Pr})_2]_4$ and $\text{Zn}_2[\text{S}_2\text{P}(\text{OCy})_2]_4$ also possess a dimeric structure [1,17].

Unlike **2**, within 8-membered cycle of **3** there are weak transannular Cd(1)···Se(3) interactions (interatomic distance 3.256 Å vs. sum of the van der Waals radii 3.48 Å [16]), making the $(\text{CdSePSe})_2$ core to be quasi tricyclic. Noteworthy, $\text{Cd}_2[\text{Se}_2\text{P}(\text{O}i\text{-Pr})_2]_4$ does not exhibit transannular Cd···Se contacts in the $(\text{CdSePSe})_2$ cycle, while

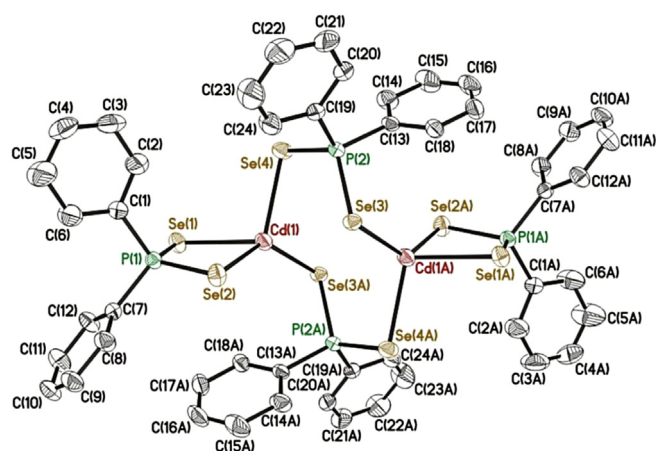


Fig. 2. The thermal ellipsoid drawing (50% probability) of the structure of **3**. Selected bond distances (Å) and angles (°): P(1)–Se(1), 2.1610(10); P(1)–Se(2), 2.1845(11); P(2)–Se(3), 2.1832(10); P(2)–Se(4), 2.1607(10); Cd(1)–Se(1), 2.7566(5); Cd(1)–Se(2), 2.6205(5); Cd(1)–Se(3), 2.6212(5); Cd(1)–Se(4), 2.6705(5); Se(1)–P(1)–Se(2), 110.43(5); Se(4)–P(2)–Se(3), 113.82(4); Se(2)–Cd(1)–Se(1), 83.131(15); Se(3)–Cd(1)–Se(4), 101.093(16).

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