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New Synthesis of Diselenophosphinates of Heavy Metals

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Abstract—The four-component reaction between secondary phosphines R_2PH (R = arylalkyl, hetarylalkyl), elemental selenium, diethylamine, and heavy metal acetates $M(OAc)_n$ (M = Ni, Zn, Cd, Sn, Hg, Pb, Bi) proceeds under mild conditions (22–55°C, 0.5 h, EtOH) with the formation of the corresponding diselenophosphinates $M(Se_2PR_2)_n$ in 55–90% yield.

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In recent years, diselenophosphinates of heavy metals are actively used as single-source precursors of nano-sized phosphides or selenides of Zn [1], Cd [2], Eu [3–5], Ni [6, 7], Co [8], and Ag [9] possessing unique semiconducting [10, 11], magneto-optical [3–5], and electric [7] properties. Besides, diselenophosphinates of heavy metals are convenient models for investigation of coordination chemistry of Se-donor ligands with the P–Se bonds [11, 12], potential intermediates in the synthesis of esters of diselenophosphine acids [13, 14], promising antioxidant additives to lubricant oils [15].

At the same time, the existing few methods of synthesis of diselenophosphinates of heavy metals are multistep, laborious, and, as a rule, low effective [11–14, 16]. For example, nickel diselenophosphinate $Ni(Se_2PPh_2)_2$ was synthesized by the reaction of elemental selenium with difficultly accessible $Ni(PPh_2)_2$ prepared by electrochemical oxidation of nickel metal in acetonitrile solution of diphenylphosphine [17]. More convenient method for preparation of diselenophosphinates of heavy metals is the reaction of their inorganic salts (for example, halides) with diselenophosphinates of sodium [18, 19], potassium [3–5, 20] or triethylammonium [1, 2, 6–9], which, however, until recently, were difficultly available compounds. Recently, a practical method of their synthesis was suggested by the three-component reaction of secondary phosphines with elemental selenium and diethylamine [21].

In this study, aiming at elaboration of a practical and original approach to the synthesis of diselenophosphinates of heavy metals we have performed for the first time a multicomponent reaction between the available [22, 23] secondary phosphines **I–III**, elemental selenium, diethylamine, and acetates of Ni, Zn, Cd, Sn, Hg, Pb, and Bi. The reaction proceeds under mild conditions (22–55°C, 0.5 h, EtOH) and leads to the formation of diselenophosphinates **IVa–IVi** in up to 90% yields (see the table).

$$\underset{\textbf{I–III}}{R_2PH} + 2n\,Se + n\,Et_2NH + M(OAc)_n \rightarrow \underset{\textbf{IVa–IVi}}{M(Se_2PR_2)_n}. \quad (1)$$

The formation of metal diselenophosphinates **IV** can be represented as follows. Diselenophosphinates of diethylammonium **A**, formed by the reaction of the secondary phosphines **I–III** with elemental selenium and diethylamine, reacts with metal acetates leading to metal salts **IV**.

$$\textbf{I–III} + 2Se + Et_2NH \longrightarrow \underset{\textbf{A}}{\left[R_2PSe_2^{-}\ {}^{+}NHEt_2\right]} \xrightarrow[-[Et_2NH_2]OAc]{M(OAc)_n} \textbf{IVa–IVi} \quad (2)$$

Synthesis of diselenophosphinates of Ni, Zn, Cd, Sn, Hg, Pb, and Bi

Phosphine	R	$M(OAc)_n$	Diselenophosphinate	Yield, %
I	$Ph(CH_2)_2$	$Ni(OAc)_2$	**IVa**	72
I	$Ph(CH_2)_2$	$Zn(OAc)_2$	**IVb**	76
I	$Ph(CH_2)_2$	$Cd(OAc)_2$	**IVc**	81
I	$Ph(CH_2)_2$	$Sn(OAc)_2$	**IVd**	74
I	$Ph(CH_2)_2$	$Hg(OAc)_2$	**IVe**	90
I	$Ph(CH_2)_2$	$Pb(OAc)_2$	**IVf**	89
I	$Ph(CH_2)_2$	$Bi(OAc)_3$	**IVg**	77
II	4-*t*-$BuC_6H_4(CH_2)_2$	$Ni(OAc)_2$	**IVh**	55
III	2-$Fur(CH_2)_2$	$Ni(OAc)_2$	**IVi**	66

Therefore, based on the four-component reaction with participation of easily available secondary phosphines, elemental selenium, diethylamine, and acetates of Ni, Zn, Cd, Sn, Hg, Pb, or Bi, we have developed a practical and effective one-pot synthesis of diselenophosphinates, promising single-source precursors of nano-sized phosphides or selenides possessing unique semiconducting, electric, and optical properties.

EXPERIMENTAL

IR spectra were recorded on a Bruker IFS-25 spectrometer in KBr pellets. ^1H, ^{13}C and ^{31}P NMR spectra were obtained on a Bruker DPX-400 spectrometer (400.13, 101.61, and 161.98 MHz, respectively) for solutions in $CDCl_3$, internal standard (^1H) HMDS, external standard (^{31}P) 85% H_3PO_4. Acetates of Ni, Zn, Cd, and Pb were used as crystal hydrates $Ni(OAc)_2 \cdot 4H_2O$, $Zn(OAc)_2 \cdot 2H_2O$, $Cd(OAc)_2 \cdot 2H_2O$, and $Pb(OAc)_2 \cdot 3H_2O$. $Sn(OAc)_2$, $Hg(OAc)_2$, and $Bi(OAc)_3$ were used as anhydrous salts. Secondary phosphines **I–III** were prepared from red phosphorus, styrene [22], 4-*tert*-butylstyrene [23] or 2-vinylfuran [22], respectively. 96% commercial ethanol was used as a solvent. All syntheses were carried out in an inert atmosphere (argon).

Synthesis of diselenophosphinates (IV) *(general procedure).* To the solution of secondary phosphine **I–III** (1.0 mmol) and diethylamine (0.08 g, 1.1 mmol) in 10 ml of ethanol, amorphous selenium (0.158 g, 2.0 mmol) was added at room temperature (22–25°C, argon). The suspension was stirred at 50–55°C till dissolution of selenium was complete (30 min), diluted with 10 ml of ethanol, and cooled to 22–25°C. To the obtained solution the solution of metal acetate [0.50 mmol, in the case of $Bi(OAc)_3$ 0.34 mol] in 10 ml of ethanol was added at stirring (22–25°C). The precipitate formed was centrifuged, washed with ethanol (2×10 ml), dried in a vacuum (1 mm Hg, 45°C).

Nickel bis(2-phenylethyl)diselenophosphinate (IVa). Yield 0.31 g (72%), green powder, mp 163–165°C (decomp.). IR spectrum, ν, cm^{-1}: 3083, 3064, 3022, 3001, 2928, 2879, 2855, 1637, 1602, 1496, 1452, 1433, 1388, 1352, 1333, 1317, 1260, 1211, 1184, 1155, 1132, 1124, 1077, 1031, 1020, 994, 963, 949, 935, 910, 893, 829, 816, 805, 774, 760, 752, 728, 708, 697, 577, 564, 506, 479, 427. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.18–2.55 m (4H, CH_2P), 3.00–3.37 m (4H, CH_2Ph), 6.91–7.52 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 29.31 (CH_2Ph), 39.50 d (CH_2P, $^1J_{CP}$ 19.6 Hz), 126.69 (C_p), 128.47 (C_o), 128.83 (C_m), 140.60 d (C_{ipso}, $^3J_{CP}$ 18.0 Hz). ^{31}P NMR spectrum: δ_P 42.56 ppm (+ d of satellites, $^1J_{PSe}$ 458 Hz). Found, %: C 44.80; H 4.38; P 7.11; Se 36.64. $C_{32}H_{36}NiP_2Se_4$. Calculated, %: C 44.84; H 4.23; P 7.23; Se 36.85.

Zinc bis(2-phenylethyl)diselenophosphinate (IVb). Yield 0.33 g (76%), white powder, mp 151–152°C. IR spectrum, ν, cm^{-1}: 3083, 3060, 3000, 2925, 2858, 1686, 1656, 1639, 1601, 1583, 1495, 1452, 1392, 1333, 1264, 1209, 1199, 1180, 1129, 1071, 1029, 1007, 944, 906, 855, 831, 745, 696, 575, 504, 474. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.50–2.76 m (4H, CH_2P), 2.95–3.22 m (4H, CH_2Ph), 6.90–7.31 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 30.47 (CH_2Ph), 40.39 d (CH_2P, $^1J_{CP}$ 32.5 Hz), 125.55 (C_p), 128.32

(C_o), 128.42 (C_m), 139.95 d (C_{ipso}, $^3J_{CP}$ 14.4 Hz). ^{31}P NMR spectrum: δ_P 27.97 ppm. Found, %: C 44.60; H 4.29; P 7.08; Se 36.23. $C_{32}H_{36}P_2Se_4Zn$. Calculated, %: C 44.49; H 4.20; P 7.17; Se 36.46.

Cadmium bis(2-phenylethyl)diselenophosphinate (IVc). Yield 0.37 g (81%), white powder, mp 202–204°C (decomp). IR spectrum, ν, cm^{-1}: 3084, 3060, 3024, 3001, 2924, 2892, 2855, 1637, 1631, 1602, 1584, 1496, 1453, 1392, 1324, 1266, 1211, 1199, 1178, 1156, 1129, 1071, 1029, 1010, 945, 931, 909, 833, 743, 577, 569, 504, 477, 415, 407. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.62–2.69 m (4H, CH_2P), 3.07–3.14 m (4H, CH_2Ph), 7.16–7.26 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 31.05 (CH_2Ph), 41.05 d (CH_2P, $^1J_{CP}$ 31.1 Hz), 126.61 (C_p), 128.62 (C_o), 128.79 (C_m), 140.12 d (C_{ipso}, $^3J_{CP}$ 16.1 Hz). ^{31}P NMR spectrum: δ_P 28.26 ppm (+ d of satellites, $^1J_{PSe}$ 486.2 Hz). Found, %: C 42.31; H 3.88; P 6.71; Se 34.79. $C_{32}H_{36}CdP_2Se_4$. Calculated, %: C 42.20; H 3.98; P 6.80; Se 34.68.

Tin bis(2-phenylethyl)diselenophosphinate (IVd). Yield 0.34 g (74%), beige powder, mp 191–194°C (decomp.). IR spectrum, ν, cm^{-1}: 3083, 3060, 2999, 2925, 2858, 1638, 1601, 1583, 1495, 1453, 1441, 1395, 1264, 1210, 1128, 1068, 1029, 1004, 944, 909, 863, 835, 743, 697, 662, 574, 495, 566, 421, 401, 376. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.62–2.69 m (4H, CH_2P), 3.07–3.14 m (4H, CH_2Ph), 7.16–7.26 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 31.05 (CH_2Ph), 41.05 d (CH_2P, $^1J_{CP}$ 31.1 Hz), 126.61 (C_p), 128.62 (C_o), 128.79 (C_m), 140.12 d (C_{ipso}, $^3J_{CP}$ 16.1 Hz). ^{31}P NMR spectrum: δ_P 28.26 ppm (+ d of satellites, $^1J_{PSe}$ 486.2 Hz). Found, %: C 41.86; H 4.01; P 6.67; Se 34.28. $C_{32}H_{36}P_2Se_4Sn$. Calculated, %: C 41.91; H 3.96; P 6.75; Se 34.44.

Mercury bis(2-phenylethyl)diselenophosphinate (IVe). Yield 0.45 g (90%), white powder, mp 102–105°C (decomp.). IR spectrum, ν, cm^{-1}: 3083, 3058, 3023, 2999, 2927, 2858, 1642, 1601, 1583, 1514, 1495, 1452, 1390, 1319, 1265, 1208, 1198, 1155, 1129, 1070, 1029, 1004, 941, 908, 861, 829, 744, 733, 696, 574, 498, 461. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.74–2.81 m (4H, CH_2P), 2.96–3.03 m (4H, CH_2Ph), 7.18–7.28 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 30.96 (CH_2Ph), 40.03 d (CH_2P, $^1J_{CP}$ 29.2 Hz), 126.52 (C_p), 128.52 (C_o), 128.63 (C_m), 139.50 d (C_{ipso}, $^3J_{CP}$ 16.4 Hz). ^{31}P NMR spectrum: δ_P 39.02 ppm. Found, %: C 38.55; H 3.45; P 6.08; Se 31.43. $C_{32}H_{36}HgP_2Se_4$. Calculated, %: C 38.47; H 3.63; P 6.20; Se 31.62.

Lead bis(2-phenylethyl)diselenophosphinate (IVf). Yield 0.45 g (89%), yellowish-white powder, mp 144–145°C (decomp.). IR spectrum, ν, cm^{-1}: 3103, 3082, 3061, 3022, 2999, 2940, 2921, 2892, 2857, 1645, 1601, 1582, 1495, 1453, 1440, 1392, 1324, 1264, 1206, 1193, 1157, 1127, 1067, 1027, 1007, 953, 943, 920, 908, 836, 762, 732, 707, 695, 665, 566, 494, 488, 475, 463, 414, 388. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.62–2.69 m (4H, CH_2P), 3.07–3.14 m (4H, CH_2Ph), 7.16–7.26 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 31.05 (CH_2Ph), 41.05 d (CH_2P, $^1J_{CP}$ 31.1 Hz), 126.61 (C_p), 128.62 (C_o), 128.79 (C_m), 140.12 d (C_{ipso}, $^3J_{CP}$ 16.1 Hz). ^{31}P NMR spectrum: δ_P 28.26 ppm (+ d of satellites, $^1J_{PSe}$ 480 Hz). Found, %: C 44.60; H 4.29; P 7.08; Se 36.23. $C_{32}H_{36}P_2PbSe_4$. Calculated, %: C 44.32; H 4.25; P 6.98; Se 36.11.

Bismuth bis(2-phenylethyl)diselenophosphinate (IVg). Yield 0.36 g (77%), bright-orange powder, mp 167–170°C (decomp.). IR spectrum, ν, cm^{-1}: 3104, 3082, 3023, 2924, 2899, 2859, 1601, 1582, 1495, 1452, 1392, 1324, 1263, 1209, 1198, 1155, 1129, 1069, 1029, 1019, 1004, 965, 940, 907, 864, 836, 737, 697, 621, 576, 567, 488, 462, 451, 412, 397, 385. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.62–2.69 m (4H, CH_2P), 3.07–3.14 m (4H, CH_2Ph), 7.16–7.26 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 31.05 (CH_2Ph), 41.05 d (CH_2P, $^1J_{CP}$ 31.1 Hz), 126.61 (C_p), 128.62 (C_o), 128.79 (C_m), 140.12 d (C_{ipso}, $^3J_{CP}$ 16.1 Hz). ^{31}P NMR spectrum: δ_P 28.26 ppm (+ d of satellites, $^1J_{PSe}$ 490 Hz). Found, %: C 40.78; H 4.04; P 6.28; Se 33.60. $C_{48}H_{54}BiP_3Se_6$. Calculated, %: C 40.99; H 3.87; P 6.61; Se 33.68.

Nickel bis[(4-tertbutyl)phenylethyl]diselenophosphinate (IVh). Yield 0.3 g (55%), light-green powder, mp 165–170°C (decomp.). IR spectrum, ν, cm^{-1}: 3135, 3092, 3055, 3023, 2961, 2903, 2866, 1905, 1791, 1645, 1517, 1474, 1463, 1440, 1413, 1393, 1363, 1269, 1202, 1134, 1109, 1017, 997, 942, 876, 852, 838, 815, 772, 759, 738, 726, 667, 563, 550, 524, 483, 445. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.28 s (18H, Me), 2.33–2.40 m (4H, CH_2P), 3.08–3.15 m (4H, $CH_2C_6H_4$), 7.10–7.12 and 7.29–7.31 m (8H, C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 28.71 ($CH_2C_6H_4$), 31.41 (Me_3C), 34.47 (CMe_3), 39.50 d (CH_2P, $^1J_{CP}$ 21.3 Hz), 125.66 ($C^{2,6}$, C_6H_4), 128.10 ($C^{3,5}$, C_6H_4), 136.65 d (C^1, C_6H_4, $^3J_{CP}$ 16.1 Hz), 149.56 (C^4, C_6H_4). ^{31}P NMR spectrum: δ_P 43.00 ppm (+ d of satellites, $^1J_{PSe}$ 452 Hz). Found, %: C 53.29; H 6.21; P 5.60; Se 29.48. $C_{48}H_{68}NiP_2Se_4$. Calculated, %: C 53.31; H 6.34; P 5.73; Se 29.20.

Nickel bis[2-(2-furyl)ethyl]diselenophosphinate (IVi). Yield 0.66 g (66%), bright-green fine-crystalline powder, mp 171–175°C (decomp.). IR spectrum, cm^{-1}: 3134, 3113, 2905, 2891, 2851, 1595, 1505, 1439, 1396, 1382, 1334, 1271, 1231, 1218, 1170, 1143, 1135, 1074, 1038, 1025, 1002, 957, 935, 922, 883, 800, 773, 733, 697, 682, 638, 596, 489, 447. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.35–2.41 m (4H, CH_2P), 3.23–3.30 m (4H, CH_2Fur), 6.09–6.10, 6.27–6.29 and 7.30–7.31 m (6H, Fur). ^{13}C NMR spectrum, δ_C, ppm: 22.27 (CH_2Fur), 35.90 d (CH_2P, $^1J_{CP}$ 23.2 Hz), 106.30 (C^3, furan), 110.45 (C^4, furan), 141.60 (C^5, furan), 152.75 d (C^2, furan, $^3J_{PC}$ 18.0 Hz). ^{31}P NMR spectrum: δ_P 41.43 ppm (+ d of satellites, $^1J_{PSe}$ 456 Hz). Found, %: C 35.32; H 3.37; P 7.18; Se 39.04. $C_{24}H_{28}NiO_4P_2Se_4$. Calculated, %: C 35.28; H 3.45; P 7.58; Se 38.66.

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