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Copper–Selenium Interactions: Influence of Alkane Spacer and Halide Anion in the Synthesis of Unusual Polynuclear Copper(I) Complexes with Bis(diphenylselenophosphinyl)alkanes[†]

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The reactions of copper(I) halides with bis(diphenylselenophosphinyl)alkanes, namely $Ph_2P(Se)–(CH_2)_n–P(Se)Ph_2$ $\{n = 1–4\}$, in acetonitrile are described. The ligand 1,3-bis(diphenylselenophosphinyl)propane {dppp-Se,Se} with copper(I) bromide and copper(I) iodide formed two unusual infinite coordination polymers, namely $\{Cu_2Br_2(\mu_2$-dppp-Se–Se$)_2\}_n$, **1**, and $\{Cu_3I_3(\mu_2$-dppp-Se,Se$)_2\}_n$, **2**. Selenium bridged dinuclear complexes, $[Cu_2Br_2((\mu_3$-dppm-Se,Se$)_2]$, **3**, and $[Cu_2I_2$(dppm-Se,Se$)_2]$, **4**, were formed using 1,1-bis(diphenylselenophosphinyl)methane {dppm-Se,Se}. Similarly, 1,2-bis(diphenylselenophosphinyl)ethane {dppe-Se,Se} and 1,4-bis(diphenylselenophosphinyl)butane {dppb-Se,Se} formed complexes, Cu_2Br_2(dppe-Se,Se$)_2$, **5**, and Cu_2I_2(dppb-Se,Se), **6**. These have been characterized with the help of analytical data, infrared spectroscopy, and, for compounds **1**–**3**, X-ray crystallography. Compound **2**, $\{Cu_3I_{3(}$(dppp-Se,Se$)_2\}_n$, has two dppp-Se,Se molecules coordinating to two copper(I) atoms of the dinuclear $Cu(\mu$-I$)_2Cu$ core in unidentate fashion, with two pendant $Ph_2P(Se)$– moieties in *trans* orientation, and one of these groups is coordinated to another copper(I) iodide moiety, thus forming the repeat unit (A), –CuI(μ-dppp-Se,Se)-Cu(μ-I$)_2$Cu(μ-dppp-Se,Se)–. This repeat unit (A) combined with another unit, and this process continued and finally formed the infinite polymer **2**. In this polymer, the mononuclear $CuISe_2$ and dinuclear $Cu_2(\mu$-I$)_2Se_2$ cores have distorted trigonal planar geometries around Cu centers. The Cu(2)···Cu(2)* separation of 2.643(1) Å is less than twice the van der Waals radius of Cu, 2.80 Å. The structure of polymer **1** is similar to that of **2**, except that it has only mononuclear trigonal planar $CuBrSe_2$ units bridged by Se atoms of dppp-Se,Se ligand, and the repeat unit is –CuBr(μ_2-dppp-Se,Se)CuBr($\mu_{2–}$dppp-Se,Se)–. The formation of zigzag one-dimensional copper(I) coordination polymers (**1** and **2**), with trigonal planar copper(I) centers, provides the first examples of this type in tertiary phosphine chalcogenide chemistry. In contrast, the decrease in methylene chain length, from $–(CH_2)_3–$ to $–(CH_2\ )–$, resulted in chelation by the dppm-Se,Se ligand, forming CuBr(dppm-Se,Se), which dimerized via Se donor atoms and formed $[Cu_2Br_2(\mu_3$-dppm-Se,Se$)_2]$, **3**. It has a relatively less common central kernel, Cu(μ-Se$)_2$Cu, and each Cu atom is further bonded to one terminal Br and one Se atoms, and the geometry around each Cu center is distorted tetrahedral (bond angles, ca. 101–121°).

Introduction

Copper(I) is an important metal ion with soft Lewis acid character and has a strong tendency to form covalent bonds, with anionic or neutral ligands, and make close Cu···Cu contacts (less than twice the van der Waals radius of Cu, 2.80 Å).[1] These properties of Cu^I have led to the formation of oligomers, and polymers of diverse coordination networks.[2] The study of inorganic−organic coordination networks in the past decade has helped in developing new materials, which exhibit conducting, catalytic, and magnetic

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[†] Dedicated to my grandfather (late) Sardar Bhola Singh and grandmother (late) Sardarni Bishan Kaur of Village Gado Majra, P.O. Dhakansu Kalan, Rajpura, Patiala Punjab, India.

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(1) *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Huheey, J. E., Keiter, E. A., Keiter, R. L., Eds.; Harper Collins College Publishers: New York, 1993.

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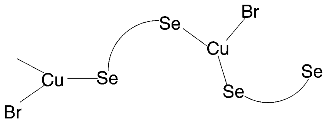
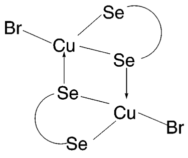
exchange properties.[3−10a] Further, metal−selenium interactions gain significance from the point of view of their potential to provide precursors for MOCVD materials.[10b,c]

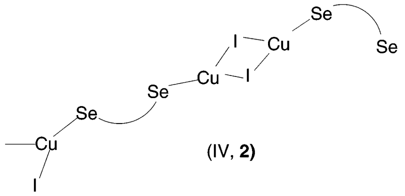
Tertiary phosphines are known to form tetranuclear and hexanuclear complexes, as well as nanoclusters,[11−13] while tertiary phosphine sulfides only formed monomeric, dimeric, or trimeric complexes.[14,15] While tertiary phosphine selenides have been known for a long time, the structural chemistry of their complexes has not been widely reported.[14,15] For instance, triphenylphosphine selenide (Ph_3PSe) formed Se-bonded mononuclear (Au),[16] and halogen-bridged dinuclear (Cu, Hg), complexes.[17−19] The 1,1-bis(diphenylselenophosphinyl)methane{dppm-Se,Se} formed the first examples of structurally characterized mononuclear chelate complexes in tertiary phosphine selenide chemistry (Zn, Hg).[20,21] The reaction of dppm-Se,Se with a copper(I) salt, namely, copper(I) bromide, has formed a selenium bridged dinuclear complex **3** (structure V), exhibiting behavior different from that of the mononuclear Zn, Hg complexes.[20,21]



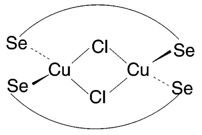
(III, **1**)



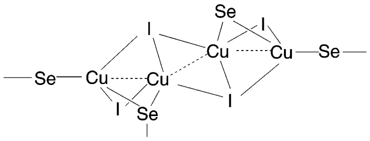
(V, **3**)



(IV, **2**)



(I, **7**)



(II, **8**)

Interestingly, the increase in chain length, from $-(CH_2)-$ to $-(CH_2)_2-$, involving reaction of 1,2-bis(diphenylselenophosphinyl)ethane (dppe-Se,Se), with copper(I) chloride, resulted in a chloro- and seleno-bridged dinuclear complex, **7**, $[Cu_2(\mu\text{-}Cl)_2(\mu\text{-dppe-Se,Se})_2]$ (structure I).[22] The change of anion from chloro to iodo formed an unusual coordination polymer, **8**, $[Cu_4I_4\{Ph_2P(Se)\text{-}CH_2\text{-}CH_2\text{-}PPh_2(Se)\}_2]_n$ (structure II, only repeat unit shown; each pendant $Ph_2P(Se)-$ group combined with other four Cu_4I_4 units, and the process continued, finally resulting in the formation of an infinite three-dimensional polymer).[23] Thus, in the case of copper(I) halides, the change of anion and alkane chain length has formed different products (**7** and **8**). A further increase in chain length from $-(CH_2)_2-$ to $-(CH_2)_3-$ has formed novel zigzag one-dimensional copper(I) coordination polymers, $[\{Cu_2Br_2(\text{dppp-Se,Se})_2]_n$, **1** (structure III), and $[\{Cu_3I_3(\text{dppp-Se,Se})_2]_n$, **2** (structure IV). In this paper, crystal structures of novel polymers **1** and **2** and selenium bridged dinuclear complex, $[Cu_2Br_2(\text{dppm-Se,Se})_2]$, **3** (structure V), are described. In addition, the complexes **4**−**6**, with stoichiometries similar to **3**, **7**, and **8**, respectively, are also discussed.

Experimental Section

General Materials and Techniques. The oxidation of bis(diphenylphosphino)alkanes, $\{Ph_2P-(CH_2)_n-PPh_2$, $n = 1$, dppm; $n = 2$, dppe; $n = 3$, dppp; and $n = 4$, dppb}, using Se metal in benzene, formed corresponding selenides, $Ph_2P(Se)\text{-}(CH_2)_n\text{-}P(Se)\text{-}Ph_2$.[14] Copper(I) bromide and copper(I) iodide were prepared by the reduction of $CuSO_4{\cdot}5H_2O$ using SO_2 in the presence of NaBr or NaI in water.[24] Bis(diphenylphosphino)methane and -propane were procured from Sigma-Aldrich Ltd., and bis(diphenylphosphino)ethane and -butane were prepared as reported.[14,15] The C, H elemental analyses were obtained with a Carlo-Erba 1108 microanalyzer. The melting points were determined with a Gallenkamp electrically heated apparatus. IR spectra were recorded using KBr pellets on a Pye Unicam SP 3-300 or FTIR-NICOLET 320 Fourier transform infrared spectrophotometers in the 4000−200 (400 cm^{-1} latter) range.

$[Cu_2Br_2\{\text{dppp-Se,Se}\}_2]_n$, 1. To a solution of copper(I) bromide (0.030 g, 0.210 mmol) in dry acetonitrile (20 mL) was added a

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(2) (a) Hanton, L. R.; Richardson, C.; Robinson, W. T.; Turnbull, J. M. *Chem. Commun.* **2000**, 2465. (b) Zhang, Q.-F.; Leung, W.-H.; Xin, X. Q.; Fun, H. K. *Inorg Chem.* **2000**, *39*, 417. (c) Ahlrichs, R.; Besinger, J.; Eichhoefer, A.; Fenske, D.; Gbureck, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3929. (d) Zhang, J.; Xiong, R. G.; Zuo, J. L.; You, X. Z. *Chem. Commun.* **2000**, 1495. (e) Zhang, J.; Xiong, R. G.; Zuo, J. L.; Che, C. M.; You, X. Z. *J. Chem. Soc., Dalton Trans.* **2000**, 2898. (f) Aakeroy, C. B.; Beatty, A. M.; Lorimer, K. R. *J. Chem. Soc., Dalton Trans.* **2000**, 3869. (g) Graham, P. M.; Pike, R. D.; Sabat, M.; Bailey, R. D.; Pennington, W. T. *Inorg Chem.* **2000**, *39*, 5121.

(3) Fortin, D.; Drouin, M.; Harvey, P. D. *Inorg. Chem.* **2000**, *39*, 2758 and references cited therein.

(4) Carlucci, L.; Ciani, G.; Moret, M.; Proserpio, D. M.; Rizzato, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1506.

(5) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. *Supramolecular Architecture*; American Chemical Society: Washington, DC, 1992; Chapter 19.

(6) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Adv. Inorg. Chem.* **1999**, *46*, 173.

(7) Janiak, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1431.

(8) Mitzi, D. B. *Prog. Inorg. Chem*. **1999**, *48*, 1.

(9) Clearfield. A. *Prog. Inorg. Chem.* **1998**, *47*, 371.

(10) (a) Kingsborough, R. P.; Swager, T. M. *Prog. Inorg. Chem.* **1999**, *48*, 123. (b) Cheng, Y.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1996**, *35*, 7339. (c) Cheng, Y.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1996**, *35*, 342.

(11) Marsich, M.; Nardin, G.; Randaccio, L. *J. Am. Chem. Soc.* **1973**, *95*, 4053.

(12) Benzman, S. A.; Churchill, M. R.; Osborn, J. A.; Wormold, J. *J. Am. Chem. Soc.* **1971**, *93*, 2063.

(13) Tran, D. T. T.; Taylor, N. J.; Corrigan, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 935 and references therein.

(14) Lobana, T. S. *Prog. Inorg. Chem.* **1989**, *37*, 495.

(15) Lobana, T. S. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley and Sons: Chichester, U.K., 1992; Vol. 2, Chapter 8.

(16) Hussain, M. S. *J. Crystallogr. Spectrosc. Res.* **1986**, *16*, 91.

(17) Lobana, T. S. ; Verma, R.; Mahajan, R.; Tiekink, E. R. T. *Z. Kristallogr.*−*New. Cryst. Struct.* **1999**, *214*, 513.

(18) Lobana, T. S.; Singh, A.; Kaur, M.; Castineiras, A. *Proc. Indian Acad. Sci., Chem. Sci.* **2001**, *113*, 89.

(19) Glasser, L. S. D.; Ingram, L.; King, M. G.; McQuillan, G. P. *J. Chem. Soc.* **1969**, 2501.

(20) Lobana, T. S.; Hundal, R.; Turner, P. *J. Coord. Chem.* **2001**, *53*, 301.

(21) Lobana, T. S.; Hundal, R.; Singh, A.; Sehdev, A.; Turner, P.; Castineiras, A. *J. Coord. Chem.* **2002**, *55*, 353.

(22) Lobana, T. S.; Mahajan, R.; Castineiras, A. *Transition Met. Chem.* **2001**, *26*, 440.

(23) Lobana, T. S.; Hundal, G. *J. Chem Soc., Dalton Trans.* **2002**, 2203.

(24) Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic Press: New York, 1965; Vol. 2.

solution of dppp-Se,Se (0.060 g, 0.105 mmol) in acetonitrile (30 mL), and the mixture was stirred for 6 h and filtered. The product was obtained on slow evaporation of the solution at room temperature (brown, 0.090 g, 60%; mp 168−170 °C). Anal. Calcd for $C_{54}H_{52}Cu_2Br_2P_4Se_4$: C, 45.4; H, 3.64. Found: C, 45.1; H, 3.70. Crystals were grown from acetonitrile at room temperature. Main IR peaks (cm^{-1}): ν(P−Se), 520 (m); ν(P−C) , 1101 (m).

[Cu_3I_3{dppp-Se,Se}$_2$]$_n$, 2. To a solution of copper(I) iodide (0.040 g, 0.210 mmol) in dry acetonitrile (15 mL) was added a solution of dppp-Se,Se (0.060 g, 0.105 mmol) in acetonitrile (30 mL), and the mixture was stirred for 6 h and filtered. The product was obtained on slow evaporation of the solution at room temperature (white, 0.070 g, 65%; mp 144−146°C). Anal. Calcd for $C_{54}H_{52}Cu_3I_3P_4Se_4$: C, 37.9; H, 3.04. Found: C, 38.1; H, 3.11. Crystals were grown from acetonitrile at room temperature. Main IR peaks (cm^{-1}): ν(P−Se), 532 (m), 525 (m); ν(P−C), 1104 (m).

[Cu_2Br_2(dppm-Se,Se)$_2$]·2CH_3CN, 3. To a solution of copper(I) bromide (0.014 g, 0.098 mmol) in dry acetonitrile (10 mL) was added a solution of dppm-Se,Se (0.053 g, 0.099 mmol) in acetonitrile (20 mL), and the mixture was stirred for 6 h and filtered. The product was obtained on slow evaporation of the solution at room temperature (yellow, 0.047 g, 71%; mp 190−195 °C). Anal. Calcd for $C_{54}H_{50}Br_2Cu_2N_2P_4Se_4$: C, 44.6; H, 3.44. Found: C, 44.8; H, 3.41. Crystals were grown from acetonitrile at room temperature. Main IR peaks (cm^{-1}): ν(P−Se), 500 (sb); ν(P−C), 1102 (s).

[Cu_2I_2(dppm-Se,Se)$_2$], 4. To a solution of copper(I) iodide (0.018 g, 0.094 mmol) in dry acetonitrile (10 mL) was added a solution of dppm-Se,Se (0.025, 0.046 mmol) in acetonitrile (20 mL), and the mixture was stirred for 4 h and filtered. The product was obtained on slow evaporation of the solution at room temperature (white, 0.048 g, 70%; mp 136−138 °C). Anal. Calcd for $C_{50}H_{44}I_2Cu_2P_4Se_4$: C, 41.0; H, 3.01. Found: C, 40.5; H, 2.99. Main IR peaks (cm^{-1}): ν(P−Se), 500 (sb); ν(P−C), 1105 (s).

[Cu_2Br_2(dppe-Se,Se)$_2$], 5. To a solution of copper(I) bromide (0.014 g, 0.098 mmol) in dry acetonitrile (10 mL) was added a solution of dppe-Se,Se (0.050, 0.092 mmol) in acetonitrile (20 mL), and the mixture was stirred for 4 h and filtered. The product was obtained on slow evaporation of the solution at room temperature (yellow, 0.050 g, 74%; mp 98−100 °C). Anal. Calcd for $C_{52}H_{48}Br_2Cu_2P_4Se_4$: C, 44.62; H, 3.43. Found: C, 44.64; H, 3.25. Main IR peaks (cm^{-1}): ν(P−Se), 535 (m); ν(P−C), 1140 (s).

[Cu_2I_2(dppb-Se,Se)], 6. To a solution of copper(I) iodide (0.026 g, 0.136 mmol) in dry acetonitrile (10 mL) was added a solution of dppb-Se,Se (0.076 g, 0.13 mmol) in acetonitrile (20 mL), and the mixture was stirred for 4 h and filtered. The product was obtained on slow evaporation of the solution at room temperature (white, 0.046 g, 70%; mp 142−145 °C). Anal. Calcd for $C_{28}H_{28}I_2Cu_2P_2Se_2$: C, 34.8; H, 2.90. Found: C, 35.4; H, 2.91. Main IR peaks (cm^{-1}): ν(P−Se), 526 (s), 503 (s); ν(P−C), 1070 (s).

Ligand Main IR Peaks (cm^{-1}). ν(P−Se), L: dppm-Se,Se, 512 (s); dppe-Se,Se, 548 (s); dppp-Se,Se, 531 (s); dppb-Se,Se, 537 (s).

X-ray Crystallography. A brown prismatic crystal of compound **1** (or white compound **2**; yellow compound **3**) was mounted on a glass fiber and used for data collection. Crystal data were collected at 293(2) K using a Bruker SMART CCD 1000 diffractometer. Graphite monochromated Mo Kα radiation (λ = 0.71073 Å) was used throughout. The data were processed with SAINT[25] and corrected for absorption using SADABS (transmission factors: 1.000−0.669, **1**; 0.512−0.352, **2**; 1.000−0.289, **3**).[26] The structure was solved by direct methods using the program SHELXS-97,[27] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97.[28] Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed geometrically, and positional parameters were refined using a riding model. Isotropic atomic displacement parameters for hydrogen atoms were constrained to be 1.2 times those of the respective C atoms. Criteria of a satisfactory complete analysis were the ratios of rms shift to standard deviation less than 0.01 and no significant features in final difference maps. Atomic scattering factors were taken from “International Tables for X-ray Crystallography”,[29] while molecular graphics were taken from ZORTEP[30a] (compound **2**)/PLATON/SCHAKAL[30bc] (compounds **1** and **3**).[30] A summary of crystal data, experimental details, and refinement results is listed in Table 1.

Table 1. Crystallographic Data for Compounds **1**−**3**

params	**1**	**2**	**3**
empirical formula	$C_{54}H_{52}Cu_2Br_2P_4Se_4$	$C_{54}H_{52}Cu_3I_3P_4Se_4$	$C_{54}H_{50}Cu_2Br_2N_2P_4Se_4$
molecular mass	1427.58	1712.00	1453.58
temp, K	293(2)	293(1)	293(2)
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No.2)	$C2/c$ (No. 15)	$P2_1/n$ (No.14)
a, Å	9.759(1)	37.352(5)	12.221(2)
b, Å	13.728(1)	9.638(1)	15.965(2)
c, Å	22.118(2)	17.729(2)	14.204(2)
α, deg	97.40(1)	90	90
β, deg	93.68(1)	111.98(1)	94.52(1)
γ, deg	110.57(1)	90	90
V, Å^3	2732.1(4)	5918.3(13)	2762.7(7)
Z	2	4	2
D_{calcd}, Mg/m^3)	1.735	1.921	1.747
μ(Mo Kα)/mm^{-1}	5.058	5.236	5.005
no. unique reflns, R_{int}	10422, 0.0596	6033, 0.0336	4708, 0.0902
final R indices [$I > 2\sigma(I)$]	R1 = 0.0544 wR2 = 0.0770	R1 = 0. 0295 wR2 = 0.0759	R1 = 0.0516 wR2 = 0.0891
final indices (all data)	R1 = 0.0969 wR2 = 0.1676	R1 = 0.0653 wR2 = 0.0866	R1 = 0.1174 wR2 = 0.1365

Results and Discussion

Synthesis and IR Spectroscopy. Scheme 1 shows the formation of complexes of copper(I) halides. Copper(I) bromide and copper(I) iodide reacted with 1,3-bis(diphenylselenophosphinyl)propane (dppp-Se,Se) in 2:2 (bromide) and 3:2 (iodide) mole ratios and yielded complexes of stoichiometry Cu_2Br_2(dppp-Se,Se)$_2$, **1**, and Cu_3I_3(dppp-Se,Se)$_2$, **2**, even though their mixing ratios were 2:1 (metal to ligand). The dppm-Se,Se, however, reacted in 1:1 mole ratio {and a 2:1 Cu/L ratio also formed the same product} forming Cu_2X_2(dppm-Se,Se)$_2$ (X = Br, **3**, and X = I, **4**). It may be noted that copper(I) iodide reacted with 1,2-bis-

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(25) *SMART and SAINT. Area Detector Control and Integration Software*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1997.

(26) Sheldrick, G. M. *SADABS. Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1997.

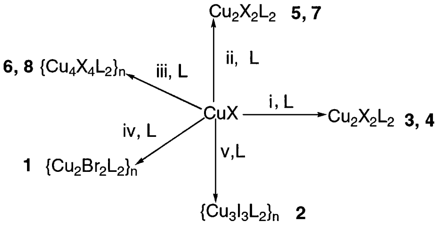
(27) Sheldrick, G. M. *Acta Crystallgr.* **1990**, *A46*, 467.

(28) Sheldrick, G. M. *SHELXL-97. Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(29) *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; Vol. C.

(30) (a) Zsolnai, L. *ZORTEP. A Program for the Presentation of Thermal Ellipsoids*; University of Heidelberg: Heidelberg, Germany, 1997. (b) Spek, A. L. *PLATON. A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2002. (c) Keller, E. *SCHAKAL-97. A Computer Program for the Graphic Representation of Molecular and Crystallographic Models*; University of Freiburg: Freiburg, Germany, 1997.

Scheme 1[a]



[a] The following synthetic conditions apply: (i) L = dppm-Se,Se, X = Br (**3**), I(**4**); (ii) L = dppe-Se,Se, X = Br(**5**), Cl (**7**); (iii) L = dppb-Se,Se, X = I (**6**), L = dppe-Se,Se, X = I (**8**); (iv) L = dppp-Se,Se, X = Br (**1**); (v) L = dppp-Se,Se, X = I (**2**).

(diphenylselenophosphinyl)ethane in a 2:1 ratio forming infinite polymer **8**, $\{Cu_4I_4(\text{dppe-Se,Se})_2\}_n$,[23] even though their mixing ratio was 1:1. However, dppe-Se,Se reacted with copper(I) chloride in a 1:1 ratio forming dimer **7**,[22] and also, it reacted in the same ratio with copper(I) bromide (compound **5**) in conformity with their 1:1 mixing ratios. The ligand 1,4-bis(diphenylselenophosphinyl)butane with copper(I) iodide also reacted in 2:1 mole ratio, irrespective of their mixing ratios, and this behavior is similar to that of dppe-Se,Se (compound **8**). Thus, the formation of dinuclear or polynuclear complexes is being governed not by the mixing ratios of the reactants, but rather by the type of the anion, and the alkane chain length connecting $-Ph_2P(Se)-$ groups. Recently, dppm-Se,Se was observed to form only monomeric compounds, e.g., with Zn and Hg.[20,21]

The IR spectrum of dppp-Se,Se showed a strong peak due to ν(P−Se) at 531 cm^{-1}; in polymer **1**, this peak shifted to 520 (m), and in **2**, it splits into a closely lying pair of peaks at 532 (m), 525 (m) cm^{-1}. Compound **3** showed a broad unresolved ν(P−Se) peak at 500 cm^{-1}, and the same behavior was shown by compound **4**. Compound **5** showed only one ν(P−Se) peak at 535 cm^{-1} with a shift of 13 cm^{-1}. Finally, compound **6** showed two peaks at 526 (s), 503 (s) cm^{-1}. The IR spectral trends of diagnostic ν(P−Se) peaks are supported by the crystal structures of compounds **1**−**3** (vide infra). X-ray crystallography has confirmed two types of PSe groups for compounds **2** and **3** and only one type for compound **1**. The IR spectrum of **4** is similar to that of **3**; of **5**, it is similar to that of **7**,[22] and of **6**, it is similar to that of compound **8**.[23] Due to poor solubility of **1**−**6**, solution phase studies such as recording of NMR spectrum could not be pursued.

Structures of Polymers 1 and 2. Figures 1 and 2 show parts of polymers **1** and **2** along with numbering scheme. The selected bond lengths and bond angles for all three complexes (**1**−**3**) are listed in Table 2. The moiety $Cu_3I_3(\text{dppp-Se,Se})_2$ of polymer **2** has two dppp-Se,Se molecules coordinating to two Cu^I centers of the dinuclear $Cu(\mu\text{-}I)_2Cu$ core, in unidentate fashion with two pendant $Ph_2P(Se)-$ groups in *trans* orientations, and one of these two groups is coordinated to another Cu^I center, thus forming the repeat unit (A), $-CuI(\mu\text{-dppp-Se,Se})Cu(\mu\text{-}I)_2Cu(\mu\text{-dppp-Se,Se})-$ (structure IV). This repeat unit (A) with one $Ph_2P(Se)-$ pendant group combined with another unit, and the process continued and finally resulted in the formation of the infinite polymer, **2**. Interestingly, the increase in chain length from $-(CH_2)_2-$ to $-(CH_2)_3-$ has formed a new zigzag polymer **2** instead of three-dimensional polymer of type **8**.[23] This

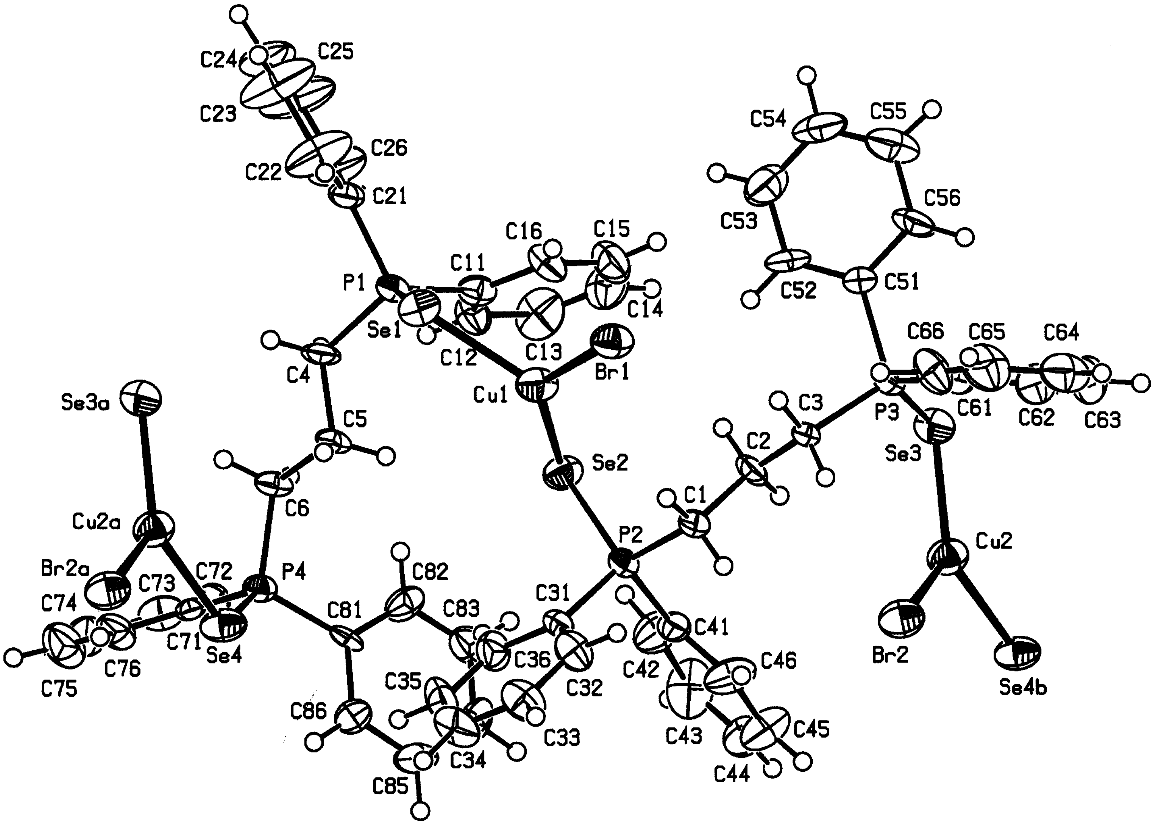


Figure 1. Part of the polymer $[Cu_2Br_2\{Ph_2P(Se)-(CH_2)_3-P(Se)Ph_2\}_2]_n$ (**1**) along with numbering scheme.

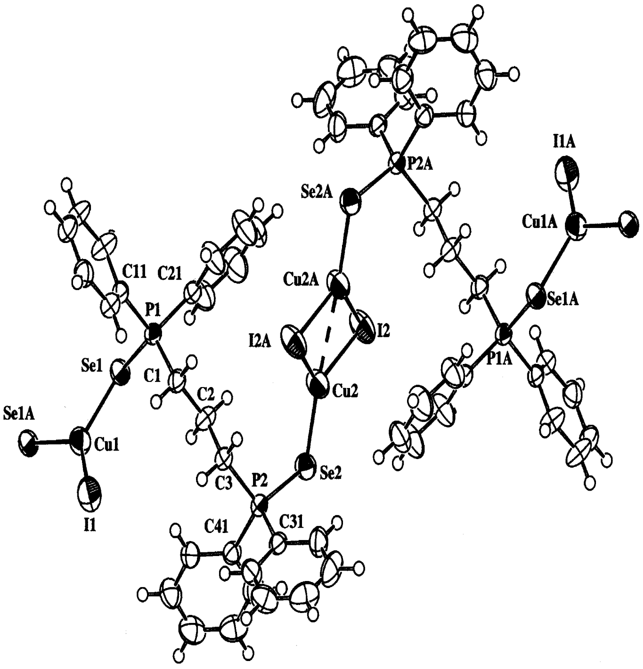


Figure 2. Part of the polymer [Cu$_3$I$_3${Ph$_2$P(Se)−(CH$_2$)$_3$−P(Se)Ph$_2$}$_2$]$_n$ (**2**) along with numbering scheme.

Table 2. Bond Lengths (Å) and Angles (deg) for Compounds **1−3**

Compound **1**			
Cu(1)−Se(2)	2. 361(1)	Cu(2)−Se(4)*^{1a}	2. 370(1)
Cu(1)−Se(1)	2. 429(1)	Se(4)−Cu(2)*^{2}	2. 370(1)
Cu(1)−Br(1)	2. 380(2)	Se(1)−P(1)	2. 133(3)
Cu(1)···Cu(2)	7.773(2)	Se(2)−P(2)	2. 165(3)
Cu(2)−Se(3)	2. 341(2)	Se(3)−P(3)	2. 144(2)
Cu(2)−Br(2)	2. 369(2)	Se(4)−P(4)	2. 142(3)
Se(2)−Cu(1)−Br(1)	132.35(6)	Br(2)−Cu(2)−Se(4)*^{1}	105.52(6)
Se(2)−Cu(1)−Se(1)	123.57(6)	P(1)−Se(1)−Cu(1)	102.16(8)
Br(1)−Cu(1)−Se(1)	103.92(5)	P(2)−Se(2)−Cu(1)	100.76(8)
Se(3)−Cu(2)−Br(2)	127.53(6)	P(3)−Se(3)−Cu(2)	99.95(8)
Se(3)−Cu(2)−Se(4)*^{1}	126.86(6)	P(4)−Se(4)−Cu(2)*^{2}	113.33(8)
Compound **2**			
Cu(1)−Se(1)	2. 398(1)	Cu(2)−I(2)	2. 615(1)
Cu(1)−Se(1)*^{3}	2. 398(1)	Cu(2)*^{4}−I(2)	2. 540(1)
Cu(1)−I(1)	2. 502(1)	I(2)···I(2)*^{4}	4. 426(1)
Cu(2)−Se(2)	2. 351(1)	Se(2)−P(2)	2.149(1)
Cu(2)−I(2)*^{4}	2. 540(1)	Se(1)−P(1)	2.147(1)
Cu(2)···Cu(2)*^{4}	2. 643(1)		
Se(1)−Cu(1)−Se(1)*^{3}	96. 96(4)	Se(2)−Cu(2)−I(2)	107.70(3)
Se(1)−Cu(1)−I(1)	131. 52(2)	I(2)−Cu(2)−I(2)*^{4}	118.33(3)
Se(1)*^{3}−Cu(1)−I(1)	131. 52(2)	Se(2)−Cu(2)−Cu(2)*^{4}	165. 08(3)
Se(2)−Cu(2)−I(2)*^{4}	133. 83(3)	Cu(2)*^{4}−I(2)−Cu(2)	61.67(3)
P(2)−Se(2)−Cu(2)	106.16(4)	P(1)−Se(1)−Cu(1)	107. 04(4)
Compound **3**			
Cu(1)−Br(1)	2. 397(2)	Se(1)···Se(1)*^{5}	3.907(2)
Cu(1)−Se(2)	2. 416(2)	Se(1)−P(1)	2.150(3)
Cu(1)−Se(1)*^{5}	2. 507(2)	Se(2)−P(2)	2.130(3)
Cu(1)−Se(1)	2.532(2)	Se(1)−Cu(1)*^{5}	2.507(2)
Cu(1)···Cu(1)*^{5}	3.182(3)		
Se(2)−Cu(1)−Br(1)	105.98(6)	Br(1)−Cu(1)−Se(1)	120.35(7)
Se(2)−Cu(1)−Se(1)*^{5}	111.64(6)	Cu(1)*^{5}−Se(1)−Cu(1)	78.32(6)
Br(1)−Cu(1)−Se(1)*^{5}	107.72(6)	P(1)−Se(1)−Cu(1)*^{5}	100.00(8)
Se(2)−Cu(1)−Se(1)	109.46(6)	P(1)−Se(1)−Cu(1)	103.58(8)
Se(1)*^{5}−Cu(1)−Se(1)	101.68(6)	P(2)−Se(2)−Cu(1)	103.78(8)

[a] Symmetry transformations used to generate equivalent atoms: $*1 = x + 1, y + 1, z$; $*2 = x - 1, y - 1, z$; $*3 = -x, y, -z + {}^{1}/_{2}$; $*4 = -x + {}^{1}/_{2}, -y + {}^{3}/_{2}, -z + 1$; $*5 = -x + 1, -y, -z + 1$.

polymer **2** contains mononuclear (CuISe$_2$) and dinuclear {Cu$_2$(μ-I)$_2$Se$_2$} cores. The geometry around each Cu center is distorted trigonal planar {Se(1)−Cu(1)−Se(1), 96.96°, Se(1)−Cu(1)−I(1), 131.52°, Se(1)−Cu(1)−I(1), 131.52°; Se(2)−Cu(2)−I(2), 133.83°, Se(2)−Cu(2)−I(2), 107.70°, and I(2)−Cu(2)−I(2), 118.33°} (Table 2). The plane defined by Cu(1), Se(1), Se(1), and I(1) atoms formed an angle of 63.86° with the plane defined by Cu(2), Se(2), I(2), and I(2) atoms. The angles subtended at I(2) and I(2) atoms are acute {Cu(2)−I(2)−Cu(2), 61.67°}.

The Cu(2)···Cu(2) separation of 2.643(1) Å is less than twice the van der Waals radius of Cu, 2.80 Å.[1] This distance is longer than that observed in polymer **8** [Cu···Cu, 2.495 Å],[23] comparable with that in the nanocluster Hg$_{15}$Cu$_{20}$S$_{25}$(n-Pr$_3$P)$_{18}$ (Cu···Cu, 2.54 Å)[13] but shorter than that observed in the dinuclear compound **7** (Cu···Cu, 3.320 Å).[18] In the dinuclear Cu$_2$(μ-I)$_2$Se$_2$ core, the Cu(2)−I(2) and Cu(2)−I(2) distances {2.615(1) and 2.540(1) Å, respectively} reveal that the central Cu(μ-I)$_2$Cu core forms a parallelogram. The terminal Cu(1)−I(1) bond distance of 2.502(1) Å observed in the mononuclear CuISe$_2$ core is shorter than the bridging Cu−I distances. These Cu−I bonds have lengths less than the sum of the radii of the Cu$^+$and I$^-$ (2.97 Å).[1]

In polymer **2**, the Cu−Se distances of the mononuclear CuSe$_2$I core are equal to {2.340(1) Å} but longer than the Cu(2)−Se(2) distance (2.351(1) Å) of the dinuclear Cu(μ-I)$_2$Cu core. Thus, the binding of two iodine atoms to one Cu atom shortens the Cu−Se bond distance and lengthens Cu−I distances while the reverse is true when two Se atoms bind to one Cu center. These Cu−Se bonds have lengths less than the sum of the radii of Cu$^+$ and Se^{2-} ions (2.75 Å)[1] but are comparable to similar Cu−Se bonds.[17,18,23] As expected, the P(1)−Se(1) bond distance is shorter {2.147(1) Å} than the P(2)−Se(2) bond distance {2.149(1) Å} but comparable with the literature values,[17,18,23] and both of these are shorter than the sum of the covalent radii of P and Se atoms (2.27 Å).[1] These distances indicate a weakening of P−Se bonds upon complex formation, a fact not established by IR spectroscopy.

In polymer **1**, dppp-Se,Se also acts as a bridging bidentate ligand forming the repeat unit (B), −CuBr(μ-dppp-Se,Se)-CuBr(μ-dppp-Se,Se)− (structure III), with one pendant P(Se)Ph$_2$ moiety. This repeat unit (B) combined with another repeat unit via the Se donor atom of the pendant P(Se)Ph$_2$ moiety, and this process continued and finally formed the infinite polymer **1**. There is only one type of mononuclear CuBrSe$_2$ core, and the geometry around each Cu^{I} center is distorted trigonal planar {Se(2)−Cu(1)−Br(1), 132.35°, Se(2)−Cu(1)−Se(1), 123.57°, Br(1)−Cu(1)−Se(1) 103.92°}. The planes defined by Se(1), Se(2), Br(1), Cu(1) and Se(3), Se(4), Br(2), Cu(2) make an angle of 76.09°. In this polymer, there is no close Cu···Cu distance {Cu(1)···Cu(2), 7.773(2) Å} unlike that in **2** (vide supra). The Cu(1)−Br(1) bond distance, 2.380(2) Å, which is much less than the sum of the radii of Cu$^+$ and Br$^-$ (2.73 Å),[1] shows the formation of a strong bond.

As noted, polymer **1** has only one mononuclear repeating core while polymer **2** has both mono- and dinuclear repeating

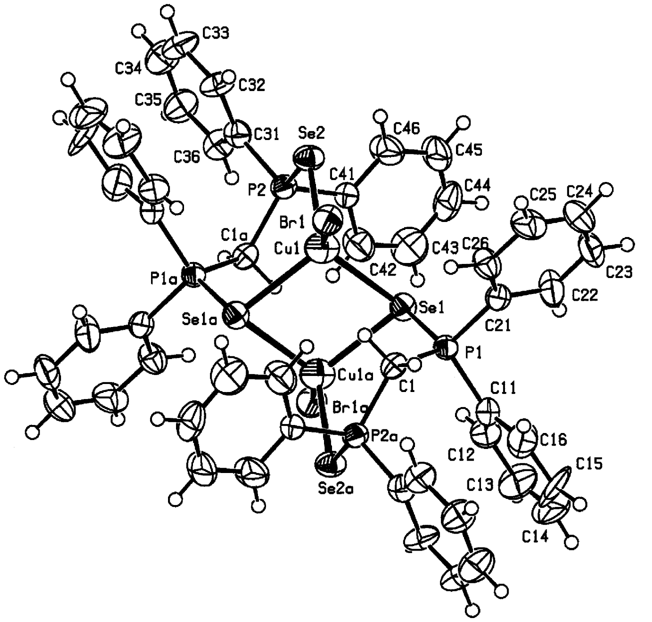


Figure 3. Dinuclear $[Cu_2Br_2\{Ph_2P(Se){-}CH_2{-}P(Se)Ph_2\}_2]_n$ (**3**) along with numbering scheme.

cores. The behavior of mononuclear cores of both in respect to bond distances is not the same. While the Cu−Se bond distances of the $CuSe_2I$ core of **2** are equal, the same is not true of the $CuSe_2Br$ core of **1** which shows different bond distances {Cu(1)−Se(1), 2.429(1) Å, Cu(1)−Se(2), 2.360(1) Å}. Further analysis of Cu−Se and Cu−Br bond distances reveals interesting information that the two adjacent $CuSe_2Br$ cores of **1** have unequal bond lengths, and the alternate units have equal bond lengths. The Cu−Se bond distances of the adjacent $Cu(2)Se_2Br$ core {Cu(2)−Se(3), 2.341(2) Å, Cu(2)−Se(4)*, 2.370(1) Å} are shorter than those of $Cu(1)Se_2Br$ core, as listed. In addition, the Cu−Br bond distances are also different for the two adjacent cores {Cu(1)−Br(1), 2.380(2) Å, Cu(2)−Br(2), 2.369(2) Å}. In short, the $Cu(1)Se_2Br$ core has long bond distances while the other core $Cu(2)Se_2Br$ has short distances. These Cu−Se bond distances are comparable to those of polymer **2** and other similar Cu−Se bonds.[17,18,23]

The P(1)−Se(1) bond distance of 2.133(3) Å is the shortest among the four P−Se distances listed in Table 2 for polymer **1**, and it is in line with the longest Cu(1)−Se(1) bond distance. The trends in other P−Se distances are in near conformity with the Cu−Se distances. The Cu−Se−P angles at Se are not same in both the polymers. In **2**, these angles are nearly same {ca. 106−107°} while there is large variation in Cu−Se−P angles in polymer **1** {ca. 99−113°} (Table 2). The variations of bond angles and bond distances as discussed might be the consequence of the electronic and steric requirements of **1** which are different in the two cases.

Structure of Selenuim-Bridged Dinuclear Complex 3. Figure 3 shows the structure of compound **3** along with a numbering scheme. In this compound, the dppm-Se,Se acted as a chelating ligand forming a monomeric species, CuBr(μ_2-dppm-Se,Se), which dimerized via the Se atom of each unit to yield $[Cu_2Br_2(\mu_3\text{-dppm-Se,Se})_2]$. Interestingly, the sulfur analogue dppm-S,S also formed a similar sulfur-bridged dinuclear complex, $[Cu_2Cl_2(\mu_3\text{-dppm-S,S})_2]$.[31] However, in the unit cell two molecules of monomeric $[CuCl(\mu_3\text{-dppm-S,S})]$ and one molecule of dimeric $[Cu_2Cl_2(\mu_3\text{-dppm-S,S})_2]$ were present unlike only dimeric units in the present case. The large size of Br and Se might be responsible for this apparent difference.

Each copper of dimer **3** is bonded to one Br, one terminal Se, and two bridging Se donor atoms. The geometry around each Cu center is distorted tetrahedral with bond angles in the range ca. 101−120° {Se(1)−Cu−Se(1)* being shortest and Br(1)−Cu(1)−Se(1) being the largest bond angles}. The terminal Cu(1)−Se(2) bond distance of 2.416(2) Å is less than the bridging Cu(1)−Se(1) and Cu(1)−Se(1)* distances {2.532(2), 2.507(2) Å}. This shows that the Cu−Se bonds are somewhat weak when Se is acting as a bridging atom. The terminal Cu−Se bond length is similar to that observed in **1** and **2**, while the bridging Cu−Se bond length is similar to that observed in **8** {2.550(2), 2.706(2) Å}.[23] The Cu−Br bond distance is 2.397(2) Å which shows the formation of a strong bond similar to that observed in polymer **1**. The bridging Se leads to a long P(1)−Se(1) bond length {2.150(3) Å} versus the terminally bonded Se atom {2.130(3) Å}. These P−Se distances are comparable with **1** and **2** and with similar distances observed in the literature.[17,18,23]

In the central Cu_2Se_2 kernel, the Cu(1)···Cu(1)* distance is 3.182(3) Å which is more than twice the van der Waals radius of Cu, 2.80 Å, indicating a lack of metal−metal interaction.[1] This Cu(1)···Cu(1)* separation is more than that observed in polymer **2** but less than that observed in the chloro-bridged dimer **7** {Cu···Cu, 3.20 Å}.[22] The Se(1)···Se(1)* bond distance of 3.907(2) Å is more than twice the van der Waals radius of Se, 3.80 Å, which rules out any Se···Se interaction. The Cu−Se−Cu* bond angle of 78.32(6)° and Se(1)−Cu−Se(1)* angle of 101.68° are similar to those observed in analogous $Cu(\mu\text{-S})_2Cu$ bridges.[36] The $Cu(\mu\text{-Se})_2Cu$ core is the first kernel reported in metal−tertiary phosphine selenide chemistry,[14,15,17−23] though $Cu(\mu\text{-Se})Cu$ with one Se bridging the two Cu atoms was reported recently.[23]

A further comparison with tertiary phosphine sulfide analogues may be appropriate. The ligand $Ph_2P(S){-}CH_2{-}P(S)Ph_2$ (dppm-S,S) having one $-CH_2-$ group connecting $Ph_2P(S)-$ groups essentially acts as a chelating ligand forming six-membered rings,[31] and in this respect, dppm-Se,Se behaved in a similar way (**3**). In contrast, $Ph_2P(S){-}(CH_2)_2{-}P(S)Ph_2$ (dppe-S,S) acts both as a chelating (Hg, Pd)[32,33] ligand with seven-membered metallacyclic rings and as a bridging ligand in the case of Cu[34] and Te(IV).[35] As noted, dppm-Se,Se has formed monomeric chelate complexes (e.g., Zn, Hg),[20,21] and in **3**, it dimerized as already discussed.

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(31) Ainscough, E. W.; Bergen, H. A.; Brodie, A. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1649.

(32) Lobana, T. S.; Sandhu, M. K.; Liddell, M. J.; Tiekink, E. R. T. *J. Chem. Soc., Dalton Trans.* **1990**, 691.

(33) Lobana, T. S.; Verma, R.; Singh, A.; Shikha, M.; Castineiras, A. *Polyhedron* **2002**, *21*, 205.

(34) Brown, K. L. *Acta Crystallogr.* **1979**, *B35*, 462.

(35) Novosad, J.; Tornroos, K. W.; Necas, M.; Slawin, A. M. Z.; Woollins, J. D.; Husebye, S. *Polyhedron* **1999**, *18*, 2861.

(36) Lobana, T. S.; Castineiras, A. *Polyhedron* **2002**, *21*, 1603.

Also, $Ph_2P(Se)-(CH_2)_2-P(Se)Ph_2$ (dppe-Se,Se) has formed complexes with only the bridging mode of the ligand (Cu).[22,23] Polymers **1** and **2** formed with $Ph_2P(Se)-(CH_2)_3-P(Se)Ph_2$ (dppp-Se,Se) are the only complexes structurally characterized having an alkane spacer, $-(CH_2)_3-$. There is no complex of $Ph_2P(S)-(CH_2)_3-P(S)Ph_2$ (dppp-S,S) with any metal which is structurally characterized, and thus, no comparison could be made.[14,15]

In summary, it is concluded here that both the chain length connecting $-P(Se)Ph_2$ groups and anion play an important role in determining the type of the compound formation. The formation of the zigzag one-dimensional copper(I) coordination polymers **1** and **2** with trigonal planar copper(I) centers are the first examples in tertiary phosphine chalcogenide chemistry.[14,15,17−23] Also, **3** shows the first Se-bridging Cu(μ-Se)$_2$Cu kernel ever reported in metal−phosphine chalcogenide chemistry.[14,15,17−23] The poor quality of crystals of **4**−**6** prevented their structure determination by X-ray crystallography, and structures similar to those of **3**, **7**, and **8**, respectively, are sugessted.

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Supporting Information Available: X-ray crystal data in CIF format {CCDC numbers 200946−200948}. This material is available free of charge via the Internet at http://pubs.acs.org.

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