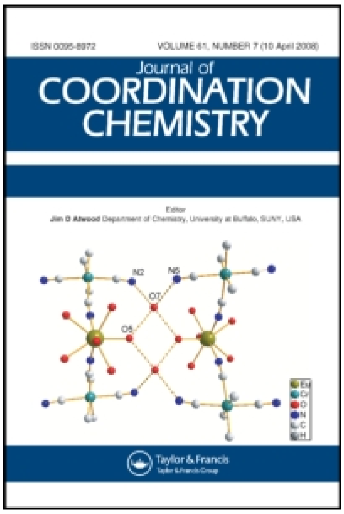

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Crystal structures of the selenium- and bromo-bridged copper(I) dimers $[Cu_2(\mu_2\text{-}Br)_2(SePPh_3)_2 \cdot (NCCH_3)_2]$ and $[Cu_2I_2(\mu_3\text{-}dppm\text{-}Se,Se)_2] \cdot 2CH_3CN$

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Crystal structures of the selenium- and bromo-bridged copper(I) dimers $[Cu_2(\mu_2\text{-}Br)_2(SePPh_3)_2 \cdot (NCCH_3)_2]$ and $[Cu_2I_2(\mu_3\text{-dppm-Se,Se})_2] \cdot 2CH_3CN$

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Reactions of copper(I) halides with Se-donor ligands, namely, triphenylphosphine selenide (Ph_3PSe) and *bis*(diphenylselenophosphinyl)methane (dppm-Se,Se) yielded bromo-bridged $[Cu_2(\mu_2\text{-}Br)_2(SePPh_3)_2(NCCH_3)_2]$ (**1**), and selenium-bridged, $[Cu_2I_2(\mu_3\text{-dppm-Se,Se})_2] \cdot 2CH_3CN$ (**2**) dimers, whose crystal structures are described. Acetonitrile stabilizes **1** by coordinating and helps to stabilize the packing in crystals of **2**.

Keywords: Triphenylphosphine selenides; Copper(I) bromide; Copper(I) iodide; *bis*(Diphenylselenophosphinyl)methane; Crystal structure

1. Introduction

Sulfur and selenium donor ligands derived from tertiary phosphine chalcogenides are important for their catalytic and extraction properties [1, 2], and for structural diversity of metal their metal complexes [1–11]. The structural chemistry of complexes of phosphine selenides has not been widely reported, even though these ligands have been known for some time [1, 2]. Triphenylphosphine selenide (Ph_3PSe) forms Se-bonded, mononuclear species like $(Ph_3PSe)AuCl_3$ as well as halogen-bridged dinuclear complexes $Cu_2(\mu_2\text{-}I)_2(Ph_3PSe)_2(CH_3CN)_2$ [4], and $Hg_2X_4(Ph_3PSe)_2$ ($X = Cl, I$) [5, 6]; structures have been characterized. *bis*(Diphenylselenophosphinyl)alkanes form mononuclear Zn(II)/Hg(II) chelate complexes [7, 8] as well as dinuclear and polynuclear Cu(I) complexes [9–11]. In this article, we report the crystal and molecular structures of bromo-bridged $Cu_2(\mu_2\text{-}Br)_2(Ph_3PSe)_2(CH_3CN)_2$ (**1**), and selenium bridged $[Cu_2I_2(\mu_3\text{-dppm-Se,Se})_2] \cdot 2CH_3CN$ (**2**) dinuclear complexes.

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2. Experimental

2.1. *Materials and techniques*

Copper(I) bromide and iodide were prepared by reduction of $CuSO_4 \cdot 5H_2O$ using SO_2 in the presence of NaBr/NaI in water [12]. Triphenylphosphine selenide (Ph_3PSe) and *bis*(diphenylselenophosphinyl)methane, $Ph_2P(Se)$-(CH_2)-$P(Se)PPh_2$ were prepared using a known method [11]. Evaporation of solvent after addition of ethanol gave crystalline compounds [1–4]. IR spectra were recorded using KBr pellets on a Schimadzu 8400 FT spectrophotometer in the range 4000–400 cm^{-1}.

2.2. *Syntheses*

To a solution of copper(I) bromide (0.025 g, 0.174 mmol) in acetonitrile (10 cm^3) was added a solution of Ph_3PSe (0.059 g, 0.174 mmol) in acetonitrile (10 cm^3). The mixture was stirred for 10 min and the clear solution kept for crystallization at room temperature (25 ± 2°C), to give crystals of $Cu_2Br_2(Ph_3PSe)_2(CH_3CN)_2$ (**1**). $[Cu_2I_2(\mu_3\text{-dppm-Se,Se})_2] \cdot 2CH_3CN$ (**2**) was prepared by reported method [11] and crystals were grown from acetonitrile. Neither complex is stable in the solid state. Samples thus were stored in acetonitrile for X-ray study.

2.3. *X-ray crystallography*

Suitable crystals of **1** and **2** were mounted on diffractometers (Siemens P4 for **1** and Enfra-Nonius CAD-4 for **2**). Data for **1** and **2** were collected at room temperature, 293(2) K, by using the θ–2θ technique to $2\theta = 50°$ for **1** and 56° for **2**. Cell parameters were refined using 25 reflections in the θ range 10–12.5° using XSCANS [13]. Data were corrected for Lorentz and polarization factors. An empirical absorption correction using psi scans was applied. The structures were solved by direct methods using SHELX-97 [14], and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on F^2 using SHELXTL-PC [15] and Wingx [16]. Scattering factors from the International tables for X-ray crystallography were used [17]. H-atoms were included in structure factor calculations in idealised positions. A summary of crystal data, experimental and refinement details is given in table 1.

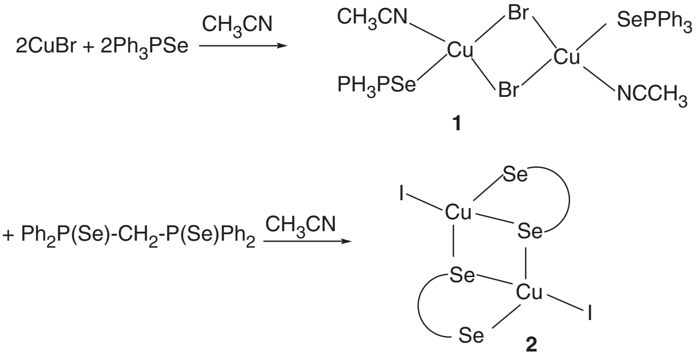
3. Results and discussion

3.1. *General comments*

Scheme 1 depicts the formation of **1** and **2** from copper(I) halides and Se-donor ligands in acetonitrile. Reaction of copper(I) bromide with Ph_3PSe in a 1 : 1 mol ratio in acetonitrile gave the bromo-bridged dimer **1**, similar to $Cu_2(\mu_2\text{-I})_2(Ph_3PSe)_2(CH_3CN)_2$ (**3**) [4]. Addition of double the amount of Ph_3PSe resulted in the same product. Thus coordination of acetonitrile to copper(I) is not affected by change of mol ratio or change of anion from more polarizable iodide to less polarizable bromide. There was no

Table 1. Crystallographic data for complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{40}H_{36}Br_2Cu_2N_2P_2Se_2$	$C_{54}H_{50}Cu_2I_2N_2P_4Se_4$
M	1051.46	1547.56
T (K)	293(2)	103(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	11.994(5)	12.038(2)
b (Å)	9.440(5)	16.150(3)
c (Å)	17.994(5)	13.879(2)
α (°)	90	90
β (°)	108.360(5)	96.094(4)
γ (°)	90	90
V (Å^3)	1933.6(14)	2683.0(7)
Z	4	2
D_{Calcd} (g cm^{-3})	1.806	1.916
μ (mm^{-1})	5.164	4.815
Reflections collected	3580	20082
Unique reflections	3404 ($R_{int} = 0.0386$)	6512 ($R_{int} = 0.0715$)
Reflns with $[I > 2\sigma(I)]$	3404	4787
R indices	$R_1 = 0.0582$, $wR_2 = 0.1289$	$R_1 = 0.0359$, $wR_2 = 0.0833$



Scheme 1. Formation of **1** and **2**.

evidence for formation of complexes of the type $Cu_2(\mu_2\text{-}I)_2(Ph_3PSe)_4$ or $CuI(Ph_3PSe)_3$ and dimers appear to be most stable involving halogen-bridging in **1** and **3** [4].

Reaction of copper(I) iodide with *bis*(diphenylselenophosphinyl)methane formed dimer **2**, similar to $[Cu_2Br_2(\mu_3\text{-dppm-Se,Se})_2] \cdot 2CH_3CN$ (**4**) [11]. Unlike halogen-bridging and CH_3CN coordination in compounds **1** and **3**, there is Se-bridging in **2** and **4** with non-coordinated acetonitrile sited in the lattice. In the formation of **2** and and **4** [11], dppm-Se,Se chelates to Cu forming a three-coordinate X-Cu(η^2-dppm-Se,Se) species ($X = Br, I$) which dimerize via coordinated Se atoms. Dimers **1** and **3** involve coordination of CH_3CN to Cu(I); dimers **2** and **4** need CH_3CN in the lattice for crystal stability.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
Cu–Se	2.459(2)	Cu–N	2.016(9)
Cu–Br(1)	2.492(2)	Cu–Cu*	3.171
Cu–Br(1)*	2.543(2)	P–Se	2.145(2)
C(1)–N(1)	1.133(11)	C(1)–C(2)	1.423(14)
Cu–Br(1)–Cu*	78.06(5)	Br(1)*–Cu–N	102.9(2)
Br(1)–Cu–Br(1)*	101.94(5)	Se–Cu–Br(1)*	105.80(5)
Se–Cu–N	110.2(2)	Cu–N–C(1)	164.8(8)
Br(1)–Cu–N	115.3(2)	N–C(1)–C(2)	177.1(11)
Se–Cu–Br(1)	118.57(6)		
2			
Cu–Se(1)	2.3968(7)	Se(1)–P(1)	2.1160(11)
Cu–Se(2)*	2.4549(7)	Se(2)–P(2)	2.1411(11)
Cu–Se(2)	2.4748(7)	Se(2)–Cu*	2.4549(7)
Cu–I	2.5423(7)	C(1A)–C(2A)	1.460(7)
Cu(1)···Cu(1)	3.063(1)		
N(1A)–C(1A)	1.122(6)	Se(2)–Cu–I	107.66(2)
Se(1)–Cu–Se(2)*	111.28(2)	Cu*–Se(2)–Cu	76.82(2)
Se(1)–Cu–Se(2)	110.84(3)	P(1)–Se(1)–Cu	103.17(3)
Se(1)–Cu–I	101.94(2)	P(2)–Se(2)–Cu*	103.93(4)
Se(2)*–Cu–Se(2)	103.18(2)	P(2)–Se(2)–Cu	99.81(3)
Se(2)*–Cu–I	121.88(3)	N(1A)–C(1A)–C(2A)	178.9(5)
Cu(1)···Cu(1)*^{5}	3.063(1)		

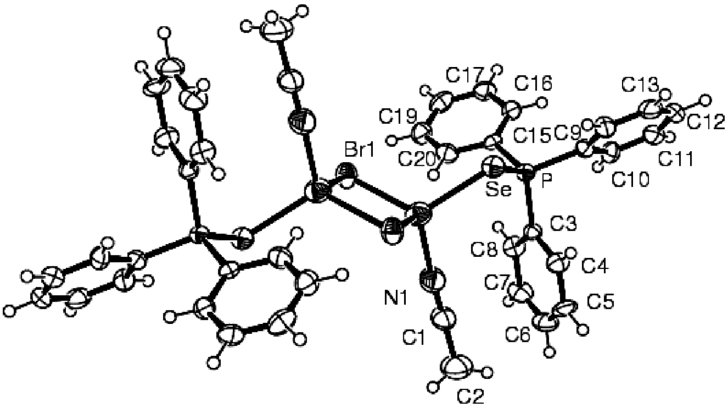


Figure 1. The structure of **1** showing the atom numbering scheme.

3.2. *Crystal structures of 1 and 2*

Figures 1 and 2 depict the structures of **1** and **2**, respectively, with the atom numbering schemes. There are no close dimer–dimer contacts in **1** and **2**. Crystal data and bond parameters are listed in tables 1 and 2, respectively. The bridging bromine atoms of **1** (figure 1) form a parallelogram (Cu–Br = 2.492(2), 2.543(2) Å) with a Cu···Cu separation of 3.171 Å, more than twice the sum of the van der Waals' radius of the Cu atom (2.80 Å) [18], but less than the same distance of 3.414 Å in the iodide-bridged dimer (**3**) [4]. Cu–Se distances in two cases are identical (2.459(2) Å). Acetonitrile is bonded to Cu with a Cu–N distance of 2.016(9) Å, similar to that of 2.02(1) Å in **3**.

The angles around each Cu atom vary in the range 102–119° suggesting distorted tetrahedral geometry. The central Cu_2Br_2 core has angles of 78.06(5) and 101.94(5)° at Br and Cu atoms, respectively, similar to the values of 78.94(3) and 101.06(3)° at iodine and Cu atoms in **3**. The Cu–N–C bond angle of 164.8(8)° is similar to others reported in the literature [5, 9].

In **2**, dppm-Se,Se chelates to form CuI(μ_2-dppm-Se,Se), which dimerizes to yield [$Cu_2I_2(\mu_3$-dppm-Se,Se$)_2$] (figure 2). The formation of **2** is similar to **4**, and shows

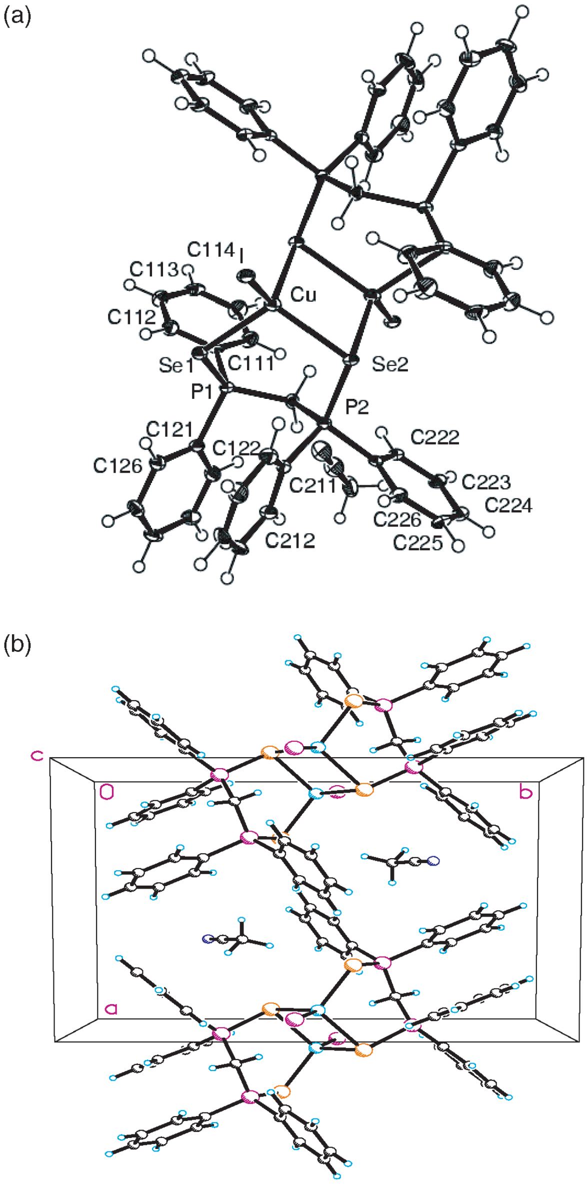


Figure 2. (a) Structure of complex **2** with the atom numbering scheme; (b) packing diagram for **2**.

that despite iodide being more polarizable than Se, bridging is still via Se atoms. This implies a higher stability of the Cu_2Se_2 core *versus* Cu_2X_2 ($X = Br$, I), but it is characteristic of only a-$(CH_2)_m$– alkane spacer with $m = 1$. Each copper of the dimer in **2** is bonded to one iodine, one terminal Se and two bridging Se donor atoms. The geometry around each Cu centre is distorted tetrahedral with bond angles in the range 102–122°. The $Cu \cdots Cu$ distance is 3.063(1) Å, which is more than twice the van der Waals radius of Cu, but less than in **1**, indicating lack of metal–metal interaction. The Cu–Se–Cu* and Se–Cu–Se* bond angles of 76.82(2) and 103.18(2)° in the Cu_2Se_2 core respectively are similar to the values 78.32(6) and 101.68(6)° observed in **4** [11]. The terminal Cu–Se bond distance of 2.397(1) Å is less than the bridging Cu–Se distances (2.455(1), 2.475(1) Å), and these are shorter than in **4** (2.416(2), 2.532(2), 2.507(2) Å, respectively). Packing in **2** is shown in figure 2(b) with CH_3CN lying in the lattice and there is no dimer–dimer contact.

Supplementary material

Full details have been deposited with the Cambridge Crystallographic Data Centre, CCDC 604853 for **1** and 604854 for **2**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-1223-336-033; Email: deposit@ccdc.cam.ac.uk; or http://www.ccdc.cam.ac.uk).

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