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Metal–selenium interactions: synthesis and crystal structure of an unusual coordination polymer [tetraiodo-bis{1,2-bis(diphenylselenophosphinyl)ethane}tetracopper(I)]$_n$ †

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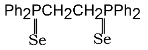
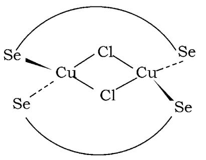
Copper(I) iodide reacts with 1,2-bis(diphenylselenophosphinyl)ethane, [$Ph_2P(Se)(CH_2)_2P(Se)Ph_2$, dppeSe$_2$] in a 2 : 1 molar ratio in acetonitrile–chloroform to form an infinite polymer, [$Cu_4I_4\{Ph_2P(Se)(CH_2)_2P(Se)Ph_2\}_2$]$_n$ (**1**), characterised using analytical data, infrared spectroscopy and X-ray crystallography. The polymer contains the centrosymmetric repeat unit $Cu_4I_4\{Ph_2P(Se)(CH_2)–\}_4$ (**A**), with four copper atoms forming a step-like (zig-zag) chain, Cu(2) ··· Cu(1) ··· Cu(1)* ··· Cu(2)*. While the Cu(1) ··· Cu(2) distance of 2.495(2) Å is shorter than the corresponding van der Waals separation (2.80 Å), the Cu(1) ··· Cu(1)* distance is longer at 2.820(4) Å. The Cu_4I_4 core has two doubly bridging and two triply bridging iodine atoms, with Cu–I bond lengths ranging from 2.514(2) to 2.910(2) Å. The terminal copper atoms, Cu(2), are bonded to two Se atoms from two $Ph_2P(Se)CH_2$– moieties [Cu(2)–Se(2) 2.359(2), Cu(2)–Se(1) 2.550(2) Å]. One of these Se atoms, Se(1), bridges Cu(1) and Cu(2) [Cu(1)–Se(1) 2.706(2) Å]. The four pendant $Ph_2P(Se)CH_2$– moieties of the repeat unit **A** link to four other Cu_4I_4 cores, leading to the formation of the polymer **1**, which is the first example in tertiary phosphine chalcogenide chemistry with a "tetradentate" mode of $Ph_2P(Se)(CH_2)_2P(Se)Ph_2$ coordination.

In the past decade, a large number of polymeric inorganic–organic coordination networks with fascinating topologies have been prepared using a diverse array of organic components. Such materials often exhibit interesting conduction, catalytic, magnetic, *etc*., properties.[1–7] The synthesis using organophosphorus ligands of tetranuclear and hexanuclear compounds, as well as nanoclusters, has been reported.[8] With analogous tertiary phosphine chalcogenides, which have been the focus of several investigations into their extraction, catalytic properties and structures, only monomeric, dimeric or, in a few cases, trimeric complexes are known.[9,10]

Since Cu^I has a strong tendency to form polynuclear complexes,[8] the reaction of copper(I) halides with mono- and di-tertiary phosphine selenides bearing polarisable Se donor atoms were carried out in the belief that the polarisable Se and halogen atoms might provide interesting coordination networks. There are a few reports describing the structures of tertiary phosphine selenide complexes which are monomeric (Zn, Au)[11,12] or halogen-bridged dimeric (Hg).[13,14] Reaction of copper(I) chloride with 1,2-bis(diphenylselenophosphinyl)ethane [$Ph_2P(Se)(CH_2)_2P(Se)Ph_2$, dppeSe$_2$; structure **I**] resulted in a dinuclear complex [$Cu_2(\mu\text{-}Cl)_2(dppeSe_2)_2$][15] (**2**; structure **II**), and that of copper(I) iodide with triphenylphosphine selenide (Ph_3PSe) gave [$Cu_2(\mu\text{-}I)_2(Ph_3PSe)_2(MeCN)_2$][16] (**3**; structure **III**). In contrast, the reaction of copper(I) iodide with $Ph_2P(Se)(CH_2)_2P(Se)Ph_2$, expected to result in a dinuclear complex similar to **2**, instead formed an unusual polymer, [$Cu_4I_4\{Ph_2P(Se)(CH_2)_2P(Se)Ph_2\}_2$]$_n$ (**1**), which is described in this paper. In this compound, the organophosphorus ligand shows two modes of ligating behaviour (structures **IV** and **V**).


$\mathrm{Ph_2\underset{\overset{\|}{Se}}{P}CH_2CH_2\underset{\overset{\|}{Se}}{P}Ph_2}$

I



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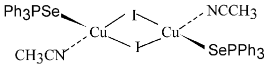

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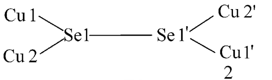
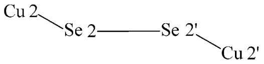


IV



V

Experimental

General materials and techniques

The oxidation of 1,2-bis(diphenylphosphino)ethane (dppe) using Se metal in benzene formed 1,2-bis(diphenylselenophosphinyl)ethane.[9] Copper(I) iodide was prepared by reduction of $CuSO_4{\cdot}5H_2O$ using SO_2 in presence of NaI in water.[17] 1,2-Bis(diphenylphosphino)ethane was prepared by the lithiation of Ph_3P in THF, followed by reaction with 1,2-dichloroethane.[9] The C, H elemental analyses were obtained with a Carlo-Erba 1108 microanalyser. The melting point was determined with a Gallenkamp electrically heated apparatus. IR

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† Dedicated to the memory of the father of T. S. L., the late Sardar Harnam Singh Lobana of Vill. Gado Majra, Rajpura, Patiala, Punjab, India.

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Table 1 Summary of crystal data for compound **1**

Parameters	
Empirical formula	$C_{26}H_{24}Cu_2I_2P_2Se_2$
M	937.19
T/K	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a/Å	10.617(2)
b/Å	10.753(2)
c/Å	13.466(3)
α/°	94.62(3)
β/°	95.43(3)
γ/°	107.88(3)
U/Å^3	1446.7(5)
Z	2
D_{calcd}/Mg m^{-3}	2.151
μ(Mo-Kα)/mm^{-1}	6.245
No. reflections collected	4110
No. unique reflections	3809
R_{int}	0.0271
Final R indices	
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0382, 0.1021
$R1$, $wR2$ (all data)	0.0596, 0.1413

spectra were recorded using KBr pellets on a Pye-Unicam SP3-300 infrared spectrophotometer in the range 4000–400 cm^{-1}. The ^{1}H NMR spectrum was recorded in CD_3CN using a Bruker AMX 300. The probe frequency was 300.13 MHz, and TMS was used as the internal reference.

Preparation of $[Cu_4I_4\{Ph_2P(Se)(CH_2)_2P(Se)Ph_2\}_2]_n$ (1)

To a solution of copper(I) iodide (0.050 g, 0.262 mmol) in dry acetonitrile (15 cm^3) was added a solution of $Ph_2P(Se)(CH_2)_2P(Se)Ph_2$ (0.150 g, 0.269 mmol) in chloroform (20 cm^3) and the mixture was stirred for 5 h. The product was obtained on slow evaporation of the solution at room temperature. Yield: 75%; m.p.: 208–210 °C. Found: C, 32.87; H, 2.83; calcd. for $C_{52}H_{48}Cu_4I_4P_4Se_4$: C, 33.30, H, 2.56%. The solid was recrystallised from hot acetonitrile after addition of dry ethanol. Crystals suitable for X-ray crystallography were then obtained.

X-Ray data collection and reduction

The data were collected at room temperature, 293(2) K, on a Siemens P4 diffractometer. The θ–2θ scan technique was used to measure the intensities, up to a maximum of $2\theta = 50°$, with graphite monochromatised Mo-Kα radiation (λ = 0.71073 Å). Cell parameters were refined using 25 reflections in the θ range 8–20° with XSCANS.[18] No detectable decomposition of the crystal occurred during data collection. The data were corrected for Lorentz and polarisation factors. An empirical psi absorption correction was applied. The structure was solved by direct methods and refined by full matrix least squares methods based on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed geometrically and were not refined. Refinements of 307 parameters converged to a final $R = 0.0382$, $wR = 0.1021$. No extinction correction was applied. Scattering factors from the *International Tables for X-ray Crystallography* were used.[19] Data reduction, structure solution, refinement and molecular graphics were performed using SHELXTL-PC.[20] A summary of the crystal data, experimental details and refinement results are listed in Table 1.

CCDC reference number 157345.

See http://www.rsc.org/suppdata/dt/b2/b201871n/ for crystallographic data in CIF or other electronic format.

Results and discussion

General comments

Reaction of copper(I) chloride with 1,2-bis(diphenylselenophosphinyl)ethane in a 1 : 1 molar ratio in acetonitrile yielded a product of stoichiometry $CuCl(dppeSe_2)$. X-Ray crystallography showed that it exists as the chloro-bridged centrosymmetric dimer **2**, with a long Cu ··· Cu distance of 3.249(2) Å. The $dppeSe_2$ ligands bridge two Cu centers (structure **II**).[15] Monodentate Ph_3PSe with copper(I) iodide in an acetonitrile–acetone mixture formed the dinuclear compound **3** (structure **III**), and the same product was formed even when the metal to ligand ratio was changed from 1 : 1 to 1 : 2.[16] The reaction of copper(I) iodide with $dppeSe_2$ was expected to form a dinuclear compound similar to **2**, however, the reaction led to the formation of an unusual polymer (**1**), the subject of discussion in this paper. The polymer **1**, as expected, shows poor solubility in acetonitrile, chloroform and other organic solvents, and thus the only solution phase study carried out was the recording of proton NMR spectrum in CD_3CN (*vide infra*).

The IR spectrum of free $dppeSe_2$ shows one νP=Se peak at 540 cm^{-1}, which generally undergoes a low-energy shift upon complexation.[9,10] Interestingly, while compound **2** showed one νP=Se signal at 520 cm^{-1}, the polymer **1** showed two types of P=Se groups, with νP=Se peaks at 515 and 525 cm^{-1}, in agreement with the two types of P=Se groups revealed in the X-ray crystallographic study (*vide infra*).

^{1}H NMR study

The ^{1}H NMR spectrum of the poorly soluble polymer **1** in CD_3CN (the polymer is nearly insoluble in most organic solvents) shows the *ortho*- and *para*-protons of the Ph groups of the $Ph_2P(Se)$– moiety as multiplets at 7.70 and 7.40 ppm, respectively. The –CH_2– protons resonate at 2.76 ppm. The NMR study on the polymer clearly suggests that in the solution phase there is depolymerisation to some extent, resulting in single molecules or oligomers of unknown structure with the same stoichiometry.

Crystal and molecular structure

The atomic numbering scheme of the repeat unit, $Cu_4I_4\{Ph_2P(Se)–(CH_2)–\}_4$ (**A**), of the polymer **1** is shown in the Fig. 1, while Fig. 2 shows a view of the three-dimensional network of the polymer. The bond lengths and angles are listed in Table 2.

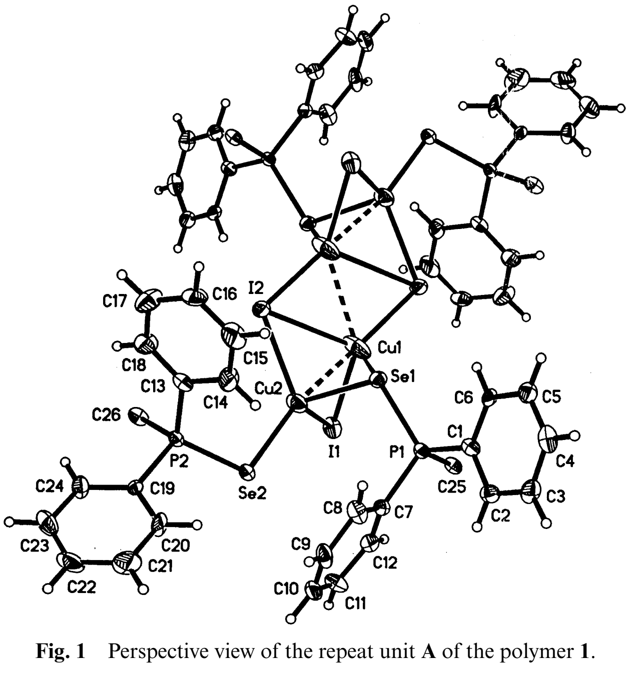

Fig. 1 Perspective view of the repeat unit **A** of the polymer **1**.

In the centrosymmetric repeat unit **A**, the four copper atoms form a step-like (zig-zag) chain, Cu(2) ··· Cu(1) ··· Cu(1)* ··· Cu(2)*, where the Cu(1) ··· Cu(2) distance of

Table 2 Selected bond lengths (Å) and angles (°)[a]

Cu(1) $\cdots$ Cu(2)	2.495(2)	Cu(1)–I(1)	2.585(2)
Cu(1) $\cdots$ Cu(1)$^{\#1}$	2.820(4)	Cu(2)–I(1)	2.671(2)
Cu(1)–Se(1)	2.706(2)	Cu(1)–I(2)	2.910(2)
Cu(2)–Se(1)	2.550(2)	Cu(2)–I(2)	2.684(2)
Cu(2)–Se(2)	2.359(2)	Cu(1)–I(2)$^{\#1}$	2.514(2)
P(1)–Se(1)	2.155(3)	P(2)–Se(2)	2.129(3)
P(1)–C(1)	1.809(10)	P(2)–C(13)	1.808(10)
P(1)–C(7)	1.806(9)	P(2)–C(19)	1.822(8)
Cu(2)–Cu(1)–Cu(1)$^{\#1}$	110.04(10)	Se(2)–Cu(2)–I(1)	108.33(6)
Se(2)–Cu(2)–Cu(1)	167.10(8)	Se(2)–Cu(2)–Se(1)	116.42(7)
Cu(2)–Cu(1)–I(2)$^{\#1}$	168.86(8)	I(1)–Cu(2)–I(2)	107.23(6)
Cu(1)–I(2)–Cu(1)$^{\#1}$	62.16(7)	Se(1)–Cu(2)–I(2)	96.20(6)
Cu(2)–I(2)–Cu(1)	52.78(5)	I(1)–Cu(2)–Se(1)	103.57(6)
Cu(2)–I(1)–Cu(1)	56.63(5)	I(2)–Cu(1)–I(2)$^{\#1}$	117.84(7)
Cu(2)–Se(1)–Cu(1)	56.57(5)	I(2)–Cu(1)–Se(1)	87.80(6)
P(1)–Se(1)–Cu(1)	115.15(8)	I(2)–Cu(1)–I(1)	103.21(6)
P(1)–Se(1)–Cu(2)	104.39(8)	I(1)–Cu(1)–Se(1)	101.65(7)
P(2)–Se(2)–Cu(2)	104.99(9)	I(1)–Cu(1)–I(2)$^{\#1}$	126.71(7)
Se(2)–Cu(2)–I(2)	123.07(7)	Se(1)–Cu(1)–I(2)$^{\#1}$	111.84(8)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, -y-1, -z$; $^{\#2}$ $-x+1, -y-1, -z$; $^{\#3}$ $-x, -y-1, -z+1$.

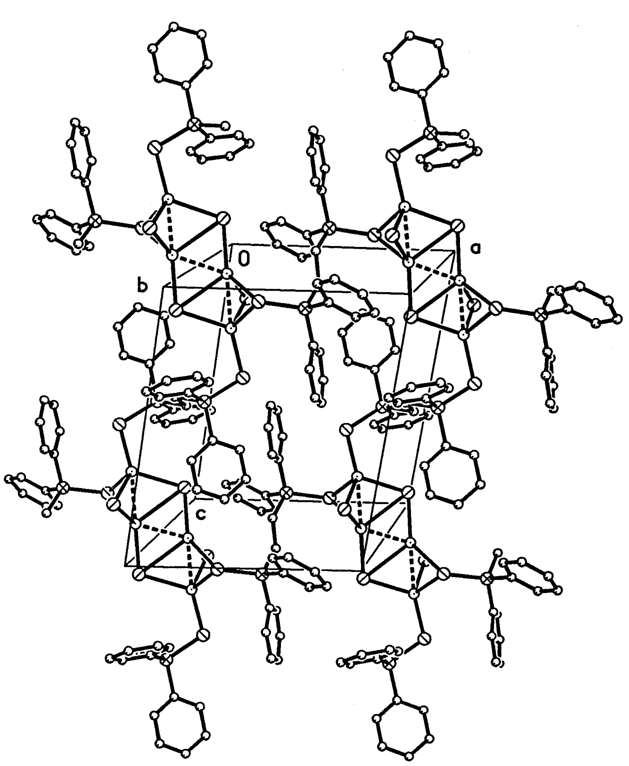

Fig. 2 A view of three-dimensional network of copper coordination polymer **1**.

2.495(2) Å is shorter than the corresponding van der Waals separation (2.80 Å),[21] although the Cu(1) $\cdots$ Cu(1)* distance is longer at 2.820(4) Å. The Cu(1) $\cdots$ Cu(2) distance is shorter than those observed in the dinuclear compounds **2** [3.4141(16) Å][15] and **3** (3.320 Å),[16] and is comparable with that in the nanocluster $Hg_{15}Cu_{20}S_{25}(nPr_3P)_{18}$ (av. 2.54 Å).[8c] The central Cu_4I_4 core has two doubly bridging [Cu(1)–I(1) 2.585(2), Cu(2)–I(1) 2.671(2) Å] and two triply bridging [Cu(1)–I(2) 2.910(2), Cu(2)–I(2) 2.684(2), Cu(1)*–I(2), 2.514(2) Å] iodine atoms. These Cu–I bonds have lengths less than the sum of the radii of the Cu^+ and I^- ions (2.97 Å),[21] but comparable to those observed in **3** [2.646(2) and 2.700(2) Å].[16]

The terminal copper atoms [Cu(2), Cu(2)*] of the repeat unit are bonded to one Se atom each from two $Ph_2P(Se)CH_2$– moieties [Cu(2)–Se(2), 2.359(2) Å] and two Se atoms from two other $Ph_2P(Se)CH_2$– moieties bridge Cu(1) $\cdots$ Cu(2) and Cu(1)* $\cdots$ Cu(2)* in a *trans* orientation [Cu(1)–Se(1) 2.706(2), Cu(2)–Se(1) 2.550(2) Å] (Fig. 1). The terminal Cu–Se bond distances are smaller than those in **2** [2.4042(11), 2.4060(11) Å][15] and **3** [2.459(2) Å];[16] however, as expected, the second type of Se donor atoms bridging Cu(1) $\cdots$ Cu(2) form long bonds, as shown above. As expected, the P(1)–Se(1) bond distance (involving doubly bridging Se) is longer [2.155(3) Å] than the P(2)–Se(2) bond distance [2.129(3) Å] and both are shorter than the sum of the covalent radii of the P and Se atoms (2.27 Å).[21] Similar P–Se bond distances [average 2.1374(15) Å] were observed in compound **2**, indicating a weakening of the P–Se bonds upon complex formation.[15,16] The angles about each Cu(2) vary from 96.20(6) to 123.07(7)° while those about Cu(1) vary from 87.80(6) to 126.71(7)°. The angles Cu(2)–Se(1)–Cu(1), Cu(2)–I(1)–Cu(1), Cu(2)–I(2)–Cu(1) and Cu(1)–I(2)–Cu(1)* subtended at Se(1), I(1) and I(2) are acute and lie in the range 52.78(5) to 62.16(7)° (Table 2). Ignoring Cu $\cdots$ Cu contacts, the geometry about each Cu center can be formally regarded as distorted tetrahedral, and a similar geometry was observed for compound **2**.[15]

Fig. 2 shows the three-dimensional network of polymer **1**. Half the $dppeSe_2$ ligands run parallel to the *ac*-plane, bridging the Cu(2)/Cu(2)* atoms of the Cu_4I_4 moieties in a *trans*-orientation, with short Cu(2)–Se(2) and P(2)–Se(2) bond distances. The other $dppeSe_2$ ligands run parallel to the *bc*-plane, forming bridges at each step beween the Cu(2) $\cdots$ Cu(1) and Cu(1)* $\cdots$ Cu(2)* atoms in a *trans*-orientation *via* Se donor atoms with relatively long Cu(1)–Se(1), Cu(2)–Se(1) and P(1)–Se(1) bonds (Fig. 2). The repeat unit **A** contains four half-$dppeSe_2$ ligands which connect to four other Cu_4I_4 species *via* the other halves of the ligands and the process continues, resulting in the formation of a three-dimensional infinite polymer (Fig. 2). The lack of formation of a dimer of type **2** may be attributed to the higher steric crowding caused by the bulky iodine atoms as compared to the smaller Cl atoms in **2**. Compound **1** represents the first example of an infinite polymer reported in organophosphorus chemistry.[8–10] The bonding mode of the $Ph_2P(Se)–CH_2–CH_2–P(Se)Ph_2$ ligand bridging four metal centres is also the first observation of such behaviour in phosphine chalcogenide chemistry.[9,10] The analogous ligand $Ph_2P(S)(CH_2)_2P(S)Ph_2$ shows the expected bridging behaviour, forming one M–S bond at each end in dimeric {Cu(I)[9a] or Te(IV)[9b]} or chelating monomeric (Hg) complexes.[10]

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