(CuI)P_4Se_4: An Adduct of Polymeric P_4Se_4 with CuI

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Dedicated to Professor Gerhard Fritz on the Occasion of his 80th Birthday

Abstract. Pure yellow (CuI)P_4Se_4 was prepared by reaction of stoichiometric amounts of CuI, red P, and gray Se in evacuated silica ampoules. The crystal structure was determined from single crystals at room temperature. (CuI)P_4Se_4 crystallizes in the orthorhombic system, space group Cmca with a = 14.770 (1) Å, b = 12.029 (1) Å, c = 12.449 (1) Å, V = 2211.9(6) $Å^3$, and Z = 8. The structure refinement converged to $R = 0.0190$ ($wR = 0.0272$) for 1020 independent reflections and 51 parameters. A prominent feature of the crystal structure are neutral polymeric P_4Se_4 strands which are connected by copper iodide. These strands consist of norbornane analogous P_4Se_3 cages which are linked by selenium bridges. The polymers are achiral since a mirror plane exists perpendicular to the strands. The single polymers are connected by [Cu_2I_2] units to form layers. These layers are stacked along the *b* axis and are connected by van der Waals-interactions only. Raman spectra of (CuI)P_4Se_4 differ significantly from Raman spectra of $(CuI)_3P_4Se_4$ and *catena*-$(P_4Se_4)_x$.

Keywords: Copper iodide; phosphorus; selenium; cage molecules; crystal structure

(CuI)P_4Se_4: Ein Addukt von polymerem P_4Se_4 mit CuI

Inhaltsübersicht. Phasenreines, gelbes (CuI)P_4Se_4 wurde durch Reaktion stöchiometrischer Mengen von CuI, rotem Phosphor und grauem Selen in evakuierten Quarzglasampullen dargestellt. Die Kristallstruktur wurde an Einkristallen bei Raumtemperatur bestimmt. (CuI)P_4Se_4 kristallisiert orthorhombisch in der Raumgruppe Cmca mit a = 14,770 (1) Å, b = 12,029 (1) Å, c = 12.449 (1) Å, V = 2211.9(6) $Å^3$ und Z = 8. Die Verfeinerung konvergierte bei $R = 0.0190$ ($wR = 0.0272$) für 1020 Reflexe und 51 Parameter. Das wichtigste Strukturmerkmal sind polymere P_4Se_4-Einheiten, die durch Kupferiodid verbunden werden. Die Polymere bestehen aus norbornananalogen P_4Se_3-Einheiten, die durch Selenbrücken verknüpft sind. Sie sind achiral, da sie eine Spiegelebene senkrecht zur Polymerachse aufweisen. Zwischen den Polymeren befinden sich verbrückende [Cu_2I_2]-Gruppen. Es resultieren Schichten senkrecht zur kristallographischen *b*-Achse. Ramanspektren von (CuI)P_4Se_4 unterscheiden sich signifikant von Ramanspektren der Verbindungen $(CuI)_3P_4Se_4$ und *catena*-$(P_4Se_4)_x$.

1 Introduction

Copper(I) halides are known to be reaction media which readily incorporate neutral or low charged molecules of group 15 and group 16 elements. Several polymers of phosphorus and also of the heavier chalcogens could be obtained as copper halide adducts using this preparative approach. To date phosphorus compounds with the compositions $(CuI)_8P_{12}$, $(CuI)_3P_{12}$, $(CuI)_2P_{14}$, $(CuI)_2CuP_{15}$, and $(CuBr)_{10}Cu_2P_{20}$ [1–5] are known. Neutral selenium and tellurium species are found in compounds of the compositions CuXTe (X = Cl, Br, I) [6–8], $CuXQ_2$ (X = Cl, Br, I, Q = Se, Te) [9–12], and $(CuX)_2Se_6$ (X = Br, I) [13–14]. Recently also heteroatomic chalcogen polymers $^1_\infty$[SeTe] and $^1_\infty$[STe], respectively, and oligomers $(Se_{6-x}S_x)$ and $(Se_{6-x}Te_x)$ could be obtained as their copper halide adducts besides these homoatomic molecules [15–17]. Despite the fact that all of the neutral phosphorus polymers have a stability which is equal or only slightly smaller than that of Hittorf's phosphorus [18] none of them has yet been obtained as a pure crystalline material. This leads to the assumption that the copper halide may act stabilizing on the embedded neutral molecules. The idea of a certain stabilizing influence of the copper halides is especially supported by the existence of the stable compound (CuBr)S_4N_4 [19]. Therein, neutral S_4N_4 molecules are incorporated which are known to be highly reactive.

We recently started to explore the system CuI–P–Se for new adduct compounds based on neutral phosphochalcogenide molecules. Especially the comparison of *catena*-$(P_4Se_4)_x$ [20] and a hypothetical adduct of these polymers with copper iodide should provide some more insight in the interactions of the neutral molecules and the surrounding copper halide. However, a first attempt to obtain *catena*-$(P_4Se_4)_x$ em-

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bedded in copper iodide failed and resulted in $(CuI)_3P_4Se_4$. This is the first example for a solid containing the so-called β-P_4Se_4 cage in a crystalline state [21]. Herein, we report the synthesis and the characterization of $(CuI)P_4Se_4$, a compound consisting of neutral polymeric P_4Se_4 and CuI.

2 Sample Characterization

Microcrystalline $(CuI)P_4Se_4$ was characterized by powder X-ray diffraction methods. The diffraction pattern is shown in Figure 1. All lines can be indexed with an orthorhombic *C*-centered cell with the dimensions a = 14.7286(5) Å, b = 11.9766(6) Å, and c = 12.4106(5) Å which corresponds to the single crystal X-ray data. However, a slight systematic difference between the powder data and the data derived from the single crystal measurements has to be noticed. It remains to be explained. No impurities can be detected in the powder pattern. Table 1 lists the refined *d*-spacings with $I_{obs} > 10\%$ extracted from this diffractogram. The strong anisotropy of the crystal structure results in a significant texture.

$(CuI)P_4Se_4$, $(CuI)_3P_4Se_4$, and *catena*-$(P_4Se_4)_x$ were also characterized by Raman spectroscopy. The spectra are displayed in Figure 2. They are dominated by the vibrational modes of the covalently bonded phosphoselenide molecules. Since the molecular structures of these molecules differ for the three compounds the spectra exhibit only a few similari-

Table 1 *d*-values (in Å) of $(CuI)P_4Se_4$ (reflections with $I_{obs} < 10\%$ are omitted, CuKα_1, $\lambda = 1.54051$ Å, flat sample in transmission geometry). The lattice constants determined from the powder are a = 14.7286(5) Å, b = 11.9766(6) Å, and c = 12.4106(5) Å

$2\theta_{obs}$	h	k	l	I_{obs}	I_{calc}	d_{obs}	d_{calc}
11.887	1	1	1	39	52	7.4394	7.4383
16.423	0	2	1	22	36	5.3931	5.3933
17.168	1	1	2	23	25	5.1608	5.1604
18.685	2	0	2	49	27	4.7452	4.7453
20.595	0	2	2	15	22	4.3091	4.3090
23.525	1	1	3	61	55	3.7787	3.7793
24.152	4	0	0	100	26	3.6820	3.6822
26.165	0	2	3	11	12	3.4031	3.4037
28.868	2	2	3	74	89	3.0903	3.0896
29.176	3	1	3	32	25	3.0584	3.0586
29.349	4	2	1	11	11	3.0407	3.0410
29.700	3	3	1	65	100	3.0056	3.0052
31.259	2	0	4	39	23	2.8591	2.8592
31.946	4	2	2	58	58	2.7992	2.7993
32.075	5	1	1	13	7	2.7883	2.7874
32.246	2	4	0	11	19	2.7738	2.7737
34.497	5	1	2	26	16	2.5978	2.5978
35.901	4	2	3	11	12	2.4994	2.4994
42.345	6	2	2	18	16	2.1328	2.1329
42.969	5	1	4	14	10	2.1032	2.1031
43.996	5	3	3	12	12	2.0565	2.0566
45.525	6	2	3	24	1	1.9909	1.9910
49.471	8	0	0	25	2	1.8409	1.8411
53.404	5	3	5	21	33	1.7142	1.7142
58.230	8	0	4	20	12	1.5832	1.5833
63.066	10	0	0	16	6	1.4729	1.4729

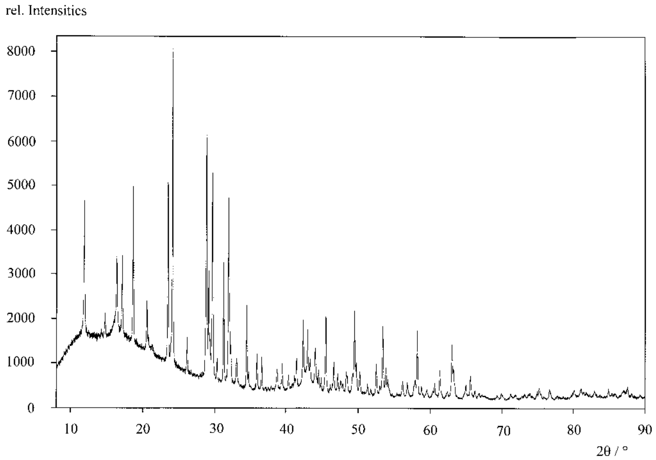

Fig. 1 X-ray powder pattern of $(CuI)P_4Se_4$. There are no impurities to be detected in this diffractogram and all lines can be indexed with an orthorhombic *C*-centered cell, see Table 1.

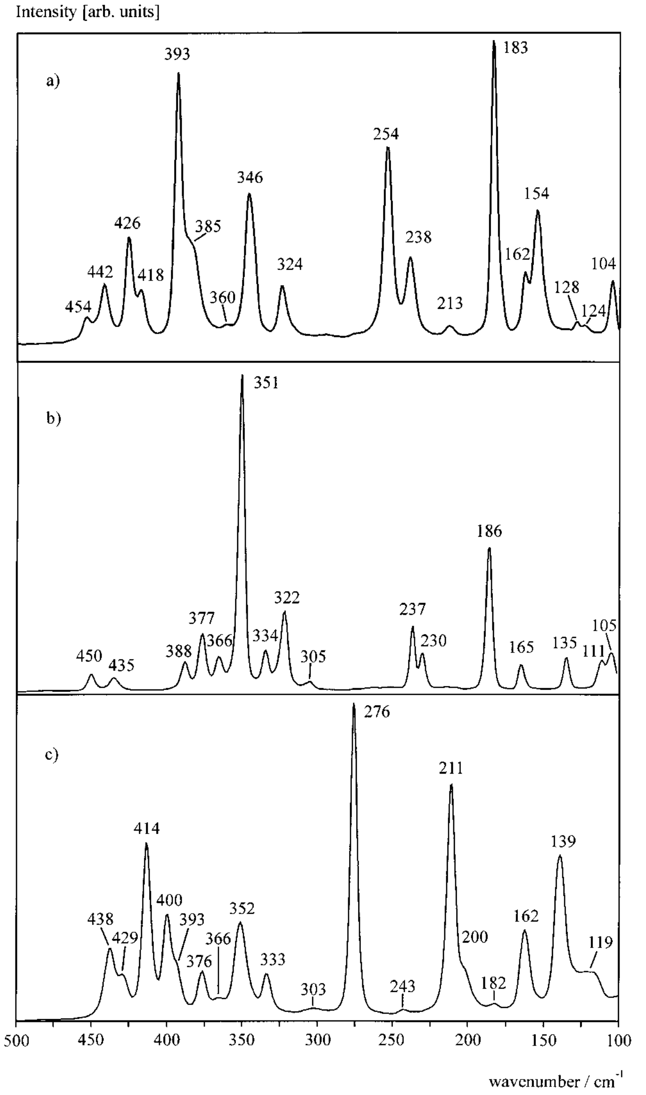

Fig. 2 Raman spectra of a) $(CuI)P_4Se_4$, b) of *catena*-$(P_4Se_4)_x$, and c) of $(CuI)_3P_4Se_4$. Note that the spectra of $(CuI)P_4Se_4$ and of *catena*-$(P_4Se_4)_x$ look quite different, even if some additional Cu–I and Cu–P modes are kept in mind in a).

ties. It has to be noted that the Raman spectrum of *catena*-$(P_4Se_4)_x$ has been reported earlier [22] for a phase which was called microcristalline P_4Se_4. This phase is the low temperature form of P_4Se_4 as reported by *Monteil* and *Vincent* [23]. However, the Raman spectra of $(CuI)_3P_4Se_4$ (containing the discrete β-P_4Se_4 cage) and especially of $(CuI)P_4Se_4$ (containing polymeric P_4Se_4) are quite different from the Raman spectrum of *catena*-$(P_4Se_4)_x$. An assignment of the observed vibrational modes on the basis of ab-initio calculations is in progress.

Table 2 Crystallographic data (e. s. d. s) for the structure analysis of $(CuI)P_4Se_4$

Compound	$(CuI)P_4Se_4$
Formula weight (g mol^{-1})	630.19
Crystal size (mm^3) and colour	$0.34 \times 0.12 \times 0.02$, yellow
Crystal system	orthorhombic
Space group	Cmca (No. 64)
Lattice constants (Å) from single crystal	a = 14.770(1) Å b = 12.029(1) Å c = 12.449(1) Å
Cell volume, Z	2211.8(3), 8
$\varphi_{\text{X-ray}}$ (g cm^{-1})	3.784
Diffractometer	STOE IPDS, MoKα, $\lambda = 0.71073$ Å, oriented graphite monochromator
φ-range (°), $\Delta\varphi$(°)	$-1.0 \le \varphi \le 360.0$, 1.0
Absorption correction	numerical, crystal description with ten faces, shape optimized with X-SHAPE [24]
No. of measured images	361
Irradiation time/image (min)	3
Temperature (°C)	25
2θ-range (°)	$3.76 < 2\theta < 50.0$
hkl-range	$-17 \le h \le 17$ $-14 \le k \le 14$ $-14 \le l \le 14$
No. of reflections, R_{int}	28275, 0.0451
No. of independent reflections	1020
No. of parameters	51
Program	JANA98 [25]
$R^{a)}(I > 3\sigma_I)$, $R^{a)}$ (all reflections)	0.0149, 0.0190
$wR^{a)}$ $(I > 3_I)$, $wR^{a)}$ (all reflections)	0.0270, 0.0272
$GooF^{a)}$	2.11
Largest difference peak $\Delta\rho_{max}$ and hole $\Delta\rho_{min}$ (e $Å^3$)	0.45 –0.68

a) $R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$, $Rw = \sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{\Sigma[w(F_o^2)^2]}}$, $GooF = \sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{n - p}}$

$w = 1/(\sigma^2(F_o^2))$

Table 3 Atomic coordinates and equivalent isotropic displacement parameters U_{eq} a) (in $Å^2$) for $(CuI)P_4Se_4$

Atom	x	y	z	U_{eq}
I	0	0.18415(2)	0.52138(2)	0.02339(7)
Cu	0.09509(3)	0	$^1/_2$	0.0193(1)
Se1	0.29776(2)	0.15043(2)	0.40482(2)	0.02085(7)
Se2	$^1/_2$	0.02532(3)	0.30859(3)	0.0216(1)
Se3	$^1/_4$	–0.09102(3)	$^1/_4$	0.0227(1)
P1	0.18251(4)	0.03865(6)	0.35348(5)	0.0153(2)
P2	0.39142(4)	0.15023(5)	0.25794(5)	0.0168(2)

a) U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 4 Anisotropic displacement parameters U^{ij} (in $Å^2$) for $(CuI)P_4Se_4$

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I	0.0195(1)	0.0207(1)	0.0299(1)	0	0	–0.0064(1)
Cu	0.0148(2)	0.0275(3)	0.0155(2)	0	0	0.0042(2)
Se1	0.0143(1)	0.0317(1)	0.0166(1)	–0.0017(1)	0.0018(1)	–0.0081(1)
Se2	0.0122(2)	0.0249(2)	0.0276(2)	0	0	0.0021(2)
Se3	0.0258(2)	0.0163(2)	0.0259(2)	0	0.0061(2)	0
P1	0.0112(3)	0.0223(3)	0.0124(2)	–0.0007(2)	0.0023(3)	0.0019(3)
P2	0.0107(3)	0.0213(3)	0.0184(3)	–0.0012(2)	0.0015(3)	–0.0011(3)

Thermal analyses (DTA, heating rate 10 °C min^{-1}) reveal that $(CuI)P_4Se_4$ decomposes upon heating. In the first DTA run there is only one endothermic effect at 421 °C (onset temperature) to be detected, the cooling curve shows no effects. The second heating curve shows a broad exothermic effect at 292 ºC and once more an endothermic effect at 421 °C.

A single crystal of suitable size for the X-ray structure determination was isolated from a stoichiometric reaction mixture. The crystal was fixed on top of a glass capillary and mounted on a STOE IPDS diffractometer. Experimental details are summarized in Table 2.[1] The crystal structure was solved by direct methods and refined against F^2 using the JANA98 [25] program package. The refinement converged to a final $R = 0.0190$ using all reflections and 51 refined parameters including a parameter for isotropic extinction. Table 3 contains the positional parameters, anisotropic displacement parameters are gathered in Table 4.

3 Discussion

$(CuI)P_4Se_4$ is an adduct compound of neutral polymeric P_4Se_4 molecules which are coordinated by copper iodide. Figure 3 shows the polymer which consists of norbonane analogous P_4Se_3 units and bridging Se atoms. These units are built up by two P_2 dumbbells and three Se atoms which are bonded to one P atom of each P_2 group, see Figure 4. With respect to this basic setup the polymer is closely related to *catena*-$(P_4Se_4)_x$. However, from Figure 3 it becomes obvious that these polymeric P_4Se_4 molecules differ in an important point. The P_4Se_4 polymers in $(CuI)P_4Se_4$ are achiral since a crystallographic mirror plane perpendicular to the polymer axis is observed. By contrast, crystalline *catena*-$(P_4Se_4)_x$ contains a racemic mixture of two chiral polymers. Nevertheless, $(CuI)P_4Se_4$ can be regarded as the first example for an adduct compound of a neutral polymer of main group elements with a copper halide which is also known as a pure material. Hence, the influence of the coordination to copper on the molecular parameters can readily be derived from the structural data. Table 5 summarizes selected interatomic distances and angles. The distance $d(P1\text{–}P2) = 2.218$ Å is typical for a covalent single bond between phosphorus atoms, and it is only slightly larger than in *catena*-$(P_4Se_4)_x$. The same holds for the bond lengths d(P-Se) which vary in the range $2.25 < d(P\text{–}Se) < 2.30$ Å. No influence of the coordination of copper to the phosphorus atom P1 can be

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[1] Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany),
E-mail: crysdata@fiz-karlsruhe.de, on quoting the depository number CSD-410913.

found. Comparing the data for (CuI)P_4Se_4 and for *catena*-$(P_4Se_4)_x$ shows that there is a small variation in bond lengths without a systematic trend. Whereas the interatomic distances lie in a narrow range the bond angles in the covalently bonded polymer are very flexible. That is, the bond angles of the phosphorus atoms vary from about 97° to 106°, those of the selenium atoms range from 89° to 103°. The smallest bond angles are found for Se2 which links two P_4Se_3 cages. This does not depend on whether the free polymer or the adduct with copper iodide is considered.

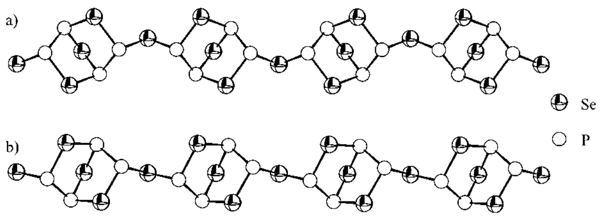

Fig. 3 The molecular structures of polymeric P_4Se_4 units in a) (CuI)P_4Se_4 and in b) *catena*-$(P_4Se_4)_x$ (data taken from ref. [20]). Both polymers consist of norbornane analogous P_4Se_3 units which are linked by Se atoms. Due to a crystallographic mirror plane in the structure of (CuI)P_4Se_4 this polymer is achiral, whereas two chiral species are observed in *catena*-$(P_4Se_4)_x$.

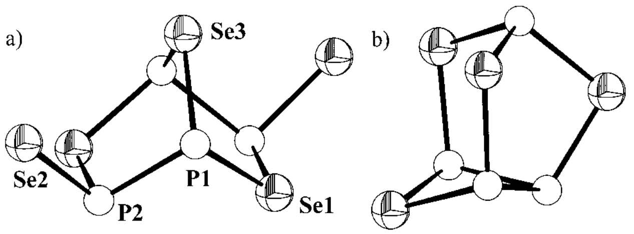

Fig. 4 a) Norbornane analogous P_4Se_3 cages are the basic building units of the P_4Se_4 polymers in (CuI)P_4Se_4. These units are bridged by Se atoms. b) The *β*-P_4Se_4 cage molecule is formed in mixtures of CuI, P, and Se at higher temperatures [21].

Table 5 Selected interatomic distances (in Å), and angles (in degrees), e. s. d. s are given in parentheses

Cu–I	2.6363(3)	2×	Cu–I–Cu	64.38(1)	
Se1–P1	2.2614(7)		P1–Se1–P2	103.19(2)	
–P2	2.2929(7)		P2–Se2–P2	89.08(3)	
Se2–P2	2.2864(6)	2×	P1–Se3–P1	92.48(3)	
Se3–P1	2.2552(7)	2×	Se1–P1–Cu	108.72(3)	
P1–Cu1	2.2827(6)		Se3–P1–Cu	124.44(3)	
–P2	2.2176(9)		P2–P1–Cu	110.15(3)	
			Se1–P1–Se3	103.89(2)	
Cu–Cu	2.8090(5)		Se3–P1–P2	106.20(3)	
			Se1–P1–P2	100.81(3)	
			Se1–P2–Se2	101.77(3)	
			Se1–P2–P1	101.67(3)	
			Se2–P2–P1	96.90(3)	
			I–Cu–I	115.62(1)	
			I–Cu–P1	102.17(2)	2×
			I–Cu–P1	113.07(2)	2×
			P1–Cu–P1	111.10(3)	

The P_4Se_4 polymers are attached to copper in the crystal structure of (CuI)P_4Se_4. It has to be stated that the copper atoms are exclusively linked to the bridgehead phosphorus atoms. Neither a coordination to the other phosphorus atoms nor to the selenium atoms occurs. The bond angles at P1 show that the cooper atom is located at the position where one can assume the lone electron pair of P1 to be. The distance $d(\text{Cu–P}) = 2.283$ Å is in the typical range found for this type of compounds and the bond angles are relatively close to the ideal tetrahedral angle. Only the angle Se3–P1–Cu = 124° shows a larger deviation.

The three-dimensional crystal structure of (CuI)P_4Se_4 consists of layers formed by the P_4Se_4 strands which are connected by bridging copper atoms, see Figure 5. These layers are oriented parallel

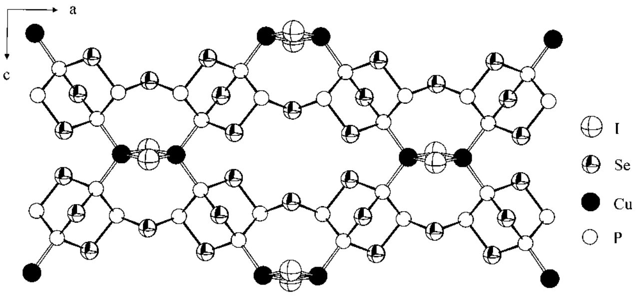

Fig. 5 P_4Se_4 strands are linked by copper atoms and thus, layers parallel to (010) result. The copper atoms complete their distorted tetrahedral environment by iodine.

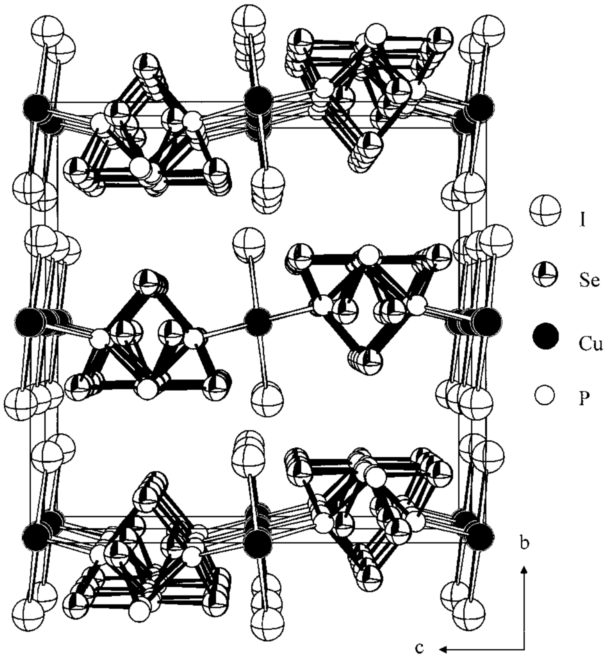

Fig. 6 The three-dimensional crystal structure of (CuI)P_4Se_4 is built by layers perpendicular to [010] which are connected by van der Waals-interactions only.

(010) with the polymer axis tending along [100]. They are stacked along [010] and only van der Waals-interactions occur between them, see Figure 6. Copper has a distorted tetrahedral coordination of two phosphorus atoms and two iodine atoms. Each two of these tetrahedra share a common edge formed by iodine atoms. The distance *d*(Cu–Cu) between the copper atoms in these pairs of tetrahedra is 2.809 Å. This is significantly shorter than the distance in compounds of the $(CuI)_2Se_6$ structure type [14, 17] which exhibit a similar $[Cu_2I_2]$ fragment with $d(Cu–Cu) \geq 3$ Å. This rhomboid arrangement can be squeezed both along the I–I axis and the Cu–Cu axis due to the flexibility of the Cu–I–Cu and the I–Cu–I bond angles. Thus, it can adapt the actual coordination necessities of a given ligand molecule.

It becomes obvious from the hitherto characterized adducts of a copper halide and a neutral ligand consisting both of group 15 and group 16 elements that copper prefers the coordination of a group 15 element to the coordination of a group 16 element. This holds at least for the combination of P and Se or S, or the combination of N and S. Obviously the chalcophily of copper is not as strong pronounced as one might assume in these materials.

Another point of interest is the question of a stabilizing influence of the copper halide "matrix" on incorporated molecules. As already derived from the interatomic distances, *vide supra*, there is no significant bond lengthening observed for the atoms which are coordinated directly to cooper as compared to those atoms which have no copper atom as a bonding partner. When *catena*-$(P_4Se_4)_x$ is incorporated in copper iodide the symmetry of the neutral strand changes. However, the basic building units, that is, P_4Se_3 cages and bridging Se atoms, are not changed. A much more important fact is the finding that the behavior of P–Se mixtures in the ratio 1 : 1 is not principally changed when copper iodide is added. Thus, the β-P_4Se_4 cage molecule is stable in the high temperature regime and a polymerization of these cage molecules is observed only when the reaction temperature is lowered. From these considerations it can be concluded that the most important role of the copper halide is not the stabilization of incorporated molecules but it is a medium which just helps to arrange these molecules in a three-dimensional crystal structure. Therefore, the change of the chiral free P_4Se_4 polymer to an achiral polymer in $(CuI)P_4Se_4$ can be regarded as a packing effect.

4 Experimental

$(CuI)P_4Se_4$ was first obtained when a powder of $(CuI)_3P_4Se_4$ [21] was subject of a chemical transport reaction. $(CuI)_3P_4Se_4$ was transported with iodine in an evacuated silica ampoule from 400 to 295 °C. A number of yellow crystals resulted at the cold end and the crystal structure could be determined from these crystals. Pure $(CuI)P_4Se_4$ was then synthesized by the reaction of stoichiometric amounts of CuI (>98%, Merck), red phosphorus (99.999%, Hoechst), and gray selenium Se (99.999%, Chempur) (CuI : P : Se = 1 : 4 : 4). CuI was purified by recrystallization from aqueous HI prior to use. The resulting white powder was separated from the solution under an atmosphere of argon, washed with demineralized water and ethanol, and then dried in a vacuum for several days. The reaction mixture of CuI, P, and Se was heated slowly to 600 °C and then cooled to 270 °C. A pure microcrystalline product containing numerous single crystals was obtained after an annealing period of 9 days at 270 °C. X-ray powder diffraction data at room temperature were collected from a flat sample in transmission geometry on a Siemens D5000 diffractometer ($CuK\alpha_1$, $\lambda = 1.54051$ Å, Si as an external standard). Raman spectra were recorded on a RFS100/S (Bruker) Raman spectrometer in a backscattering mode using a Nd:YAG laser with an excitation wavelength of 1064 nm. Thermal analyses were performed with a DTA L62 (Linseis) with Al_2O_3 as reference material. Single crystal X-ray diffraction data were collected on a Stoe IPDS, *vide supra.*

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