$(CuBr)_3P_4Se_4$: A Low Symmetric Variant of the $(CuI)_3P_4Se_4$ Structure Type

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Dedicated to Professor Hartmut Bärnighausen on the Occasion of his 70th Birthday

Abstract. Bright orange $(CuBr)_3P_4Se_4$ is obtained from the reaction of CuBr, P, and Se in stoichiometric amounts (CuBr : P : Se = 3 : 4 : 4). The composition and the crystal structure of the compound were determined from single crystal X-ray diffraction data. Lattice constants are a = 33.627(2) Å, b = 6.402(1) Å, c = 19.059(1) Å, β = 90.19(3) °, V = 4103.2(3) Å^3, and Z = 12. The compound crystallizes in a structure that is related to $(CuI)_3P_4Se_4$. Cages of β-P_4Se_4 are stacked along the b-axis and are separated by columns of copper(I) bromide. However, the coordination of the β-P_4Se_4 cage molecules to the copper atoms in the CuBr columns in $(CuBr)_3P_4Se_4$ is quite different from $(CuI)_3P_4Se_4$. The monoclinic compound (space group: $P2_1$, no. 4) has an almost orthorhombic metric in combination with a threefold superstructure in [100]. Structural aspects of $(CuBr)_3P_4Se_4$ are discussed with respect to the heavier homologue $(CuI)_3P_4Se_4$.

Keywords: Copper; Phosphorus; Selenium

$(CuBr)_3P_4Se_4$: Eine niedersymmetrische Variante des $(CuI)_3P_4Se_4$-Strukturtyps

Inhaltsübersicht. Hell oranges $(CuBr)_3P_4Se_4$ wurde durch Umsetzung von CuBr, P und Se (CuBr : P : Se = 3 : 4 : 4) erhalten. Die Zusammensetzung und Kristallstruktur der Verbindung konnte aus Einkristalldaten bestimmt werden. Die Gitterkonstanten sind a = 33.627(2) Å, b = 6.402(1) Å, c = 19.059(1) Å, β = 90.19(3) °, V = 4103.2(3) Å^3 und Z = 12. Der strukturelle Aufbau von $(CuBr)_3P_4Se_4$ ähnelt dem von $(CuI)_3P_4Se_4$. Entlang der b-Achse gestapelte β-P_4Se_4-Käfige werden durch CuBr-Säulen getrennt. Strukturelle Unterschiede von $(CuBr)_3P_4Se_4$ im Vergleich zu $(CuI)_3P_4Se_4$ sind in der Koordination der β-P_4Se_4-Käfige an Kupfer in den CuX-Säulen zu finden. Das monokline $(CuBr)_3P_4Se_4$ hat eine nahezu orthorhombische Metrik und zeigt eine Überstruktur in [100]. Strukturelle Aspekte von $(CuBr)_3P_4Se_4$ und dem höheren Homologen $(CuI)_3P_4Se_4$ werden vergleichend diskutiert.

Introduction

The reactivity of binary mixtures of phosphorus and selenium is quite different from similar systems containing phosphorus and sulphur. Thus, mixtures of P and Se tend to form cage molecules at elevated temperatures which polymerize when the temperature is lowered [1, 2, 3]. As a consequence, numerous P-S cage molecules with compositions ranging from P_4S_3 to P_4S_{10} have been structurally characterized but only a very limited number of P-Se cages is well known. These known cages are P_4Se_3 [4, 5], P_4Se_5 [6], and P_2Se_5 [7]. Several controversial investigations concerning the most favourable molecular structure of P_4Se_4 are reported in references [8, 9]. In addition to the molecular cages the crystal structures of two P-Se polymers have been determined. These are $P_{14}Se$ and *catena*-$(P_4Se_4)_x$ [10, 11].

We have recently established a preparative access to neutral or low charged cage molecules or polymers of phosphorus and chalcogens. By using copper(I) halides, especially CuI, several adduct compounds with these cages have been obtained [12]. The comparison of the experimental conditions for the preparation of *catena*-$(P_4Se_4)_x$ from equimolar mixtures of P-Se [11] and for the preparation of $(CuI)P_4Se_4$ and $(CuI)_3P_4Se_4$ [13, 14] shows that the reactivity of P-Se mixtures does not vary when the reactions are performed in CuI. Obviously, the reactivity of P and Se remains unchanged when CuI is added as a solid solvent [12]. In addition, novel cage molecules as for example P_8Se_3 can be obtained as adducts to CuI [15]. The formation of $(CuI)_3P_4S_4$ indicates that Se in the P_4Se_4 cage molecules can be substituted by S without any significant structural alterations [16]. However, the CuX substructure changes insofar as copper is no longer disordered in the S containing compound. In order to elucidate the use of CuBr as solid solvent we started to explore mixtures of CuBr, P, and Se. Herein, we report on the preparation and the crystal structure of $(CuBr)_3P_4Se_4$, the lighter homologue of $(CuI)_3P_4Se_4$.

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Results

Structure determination

Single crystals suitable for a structure determination were obtained from a stoichiometric reaction mixture after four

weeks. X-ray intensities were collected on a STOE IPDS using MoKα radiation. First attempts to index the resulting data led to an orthorhombic cell with lattice constants of a = 11.203(1) Å, b = 19.054(1) Å, c = 6.409(1) Å, V = 1368.2(3) Å^3, and Z = 4. The only possible space group seemed to be $P222_1$ (no. 17). Unfortunately, no proper structure solution could be obtained. After a detailed analysis of the extinctions and taking into account the results of a profile fitted high quality powder diffraction pattern a monoclinic metric with β very close to 90° was detected. A structure solution using the space group $P2_1$ (no. 4) resulted in a promising structure model. The refinement in this space group with lattice constants of a = 11.209(1) Å, b = 6.402(1) Å, c = 19.057(1) Å, β = 90.21(3) °, V = 1367.5(2) Å^3, and Z = 4 converged at R = 0.0566 and wR = 0.1083 (all reflections), respectively. However, unusual displacement parameters and split positions for the selenium atoms could not satisfy at this stage of the structure determination. Some weak and unindexed reflections in powder diffraction measurements as well as in the single crystal dataset remained. They could all be indexed by using a threefold a-axis. The structure model was modified to give a threefold superstructure. This improved the refinement significantly. It converged at R = 0.0362 and wR = 0.0701 (I>3σ_I). According to the last stage of the refinement $(CuBr)_3P_4Se_4$ crystallizes monoclinic, space group $P2_1$, with lattice constants of a = 33.627(2) Å, b = 6.402(1) Å, c = 19.059(1) Å, β = 90.19(3) °, V = 4103.2(3) Å^3, and Z = 12. Inversion twinning was not observed in $(CuBr)_3P_4Se_4$. Further crystallographic details are summarized in Table 1. Atomic positions and isotropic displacement parameters are collected in Table 2.

Table 1 Selected crystallographic data of $(CuBr)_3P_4Se_4$.

Compound	$(CuBr)_3P_4Se_4$
Formula weight/(g mol^{-1})	870.10
Crystal size/(mm^3)	0.05 x 0.2 x 0.04
Colour	orange
Crystal shape	needle
Crystal system	monoclinic
Space group	$P2_1$ (no. 4)
Lattice constants/Å	a = 33.627(2) b = 6.402(3) c = 19.059(1) β = 90.19(1) °
Cell volume/Å^3, Z	4103.2(3), 12
$\rho_{X\text{-ray}}$/(g cm^{-3})	4.225
μ/mm^{-1}	24.455
Diffractometer	STOE IPDS, MoK_α, λ = 0.71073 Å, oriented graphite monochromator
Image plate distance/mm	65
φ-range/°, Δφ/°	0 ≤ φ ≤ 235.2, 0.7
Temperature/K	298
θ-range/°	2.10 < θ < 26.65
hkl-range	−42 ≤ h ≤ 42 −8 ≤ k ≤ 8 −24 ≤ l ≤ 24
No. of reflections, $R_{int.}$	41564; 0.0806
No. of independent reflections	17174
No. of parameters	756
Refinement program	Jana2000 [19]
R (I>3$\sigma(I)$), R (all reflections)	0.0362, 0.0769
wR (I>3$\sigma(I)$), wR (all reflections)	0.0701, 0.0786
GooF	1.03
Largest difference peaks $\Delta\rho_{min}$, $\Delta\rho_{max}$/e Å^{-3}	−1.37, +2.70

Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), Fax: 0049 7247 808 666, E-mail: crysdata@fiz-karlsruhe.de, on quoting the depository number CSD-412886, the name of the authors, and the reference of the publication.

Structure description and discussion

$(CuBr)_3P_4Se_4$ can be described as an adduct compound of copper(I) bromide and β-P_4Se_4 cage molecules. The molecular structure of the P_4Se_4 cages is the same as already observed in $(CuI)_3P_4Se_4$ [14] and in $(CuI)_3P_4S_4$ [16]. Thus, only one of the four different cages under discussion for P_4Se_4 [1, 8] has yet been obtained as an adduct compound with copper halides.

In the crystal structure CuBr forms columns and the β-P_4Se_4 cages are forming stacks which are both oriented along [010]. Each CuBr column is surrounded by six stacks of P_4Se_4 molecules, and each stack of P_4Se_4 molecules has three columns of CuBr and three further stacks of P_4Se_4 cages as neighbours (see Figure 1).

The CuBr columns are formed by six membered rings Cu_3Br_3 in chair conformation. The arrangement of CuBr can be regarded as a section of the wurtzite structure type. Copper is tetrahedrally coordinated by three bromine and one phosphorus atom of a P_4Se_4 molecule. Insofar $(CuBr)_3$-P_4Se_4 closely resembles $(CuI)_3P_4S_4$ and $(CuI)_3P_4Se_4$. However, there exist a number of differences when the details of the crystal structures are analysed. First of all it becomes obvious that the copper atoms are no longer disordered as they are in $(CuI)_3P_4Se_4$. The second point is more important since it concerns the coordination behaviour of the β-P_4Se_4 cages. As described earlier $(CuI)_3P_4Q_4$ (Q = Se, S) crystallize in the space group $P6_3cm$ [14, 16]. When iodine is substituted by bromine the symmetry of the resulting compound is drastically reduced to $P2_1$ accompanied by a doubling of the unit cell volume. The resulting crystal structure is shown in Figure 1. It becomes obvious that six different stacks of β-P_4Se_4 cages result. Focusing on these stacks each two of them seem to be related by a mirror plane (001) but this mirror plane is not present in the crystal structure, see Figure 1. From the data given in Table 4 the close relationship between stacks ***1*** and ***4***, stacks ***2*** and ***5***, and stacks ***3*** and ***6***, respectively, can be realized. The corresponding atoms are labelled as Pn1-Pn4, and Sen1-Sen4 (n = 1, 2, ... 6). A similar labelling scheme is used for copper and bromine, i.e., the two different copper bromide columns in $(CuI)_3P_4Q_4$ are split into three different columns in $(CuBr)_3P_4Se_4$. Each column consists of six different bromine and copper atoms, respectively.

The arrangement of the cages in the stacks is shown in Figure 2. Thus, Sen1 of one cage is embedded in a six membered ring of the next P_4Se_4 molecule. These rings consist of Pn1, Pn3, and Pn4, and of Sen2, Sen3, and Sen4. This is supposed to be the optimised way of stacking the β-P_4Se_4

Table 2 Atomic coordinates and isotropic displacement parameters in Å^2 of $(CuBr)_3P_4Se_4$. All positions are fully occupied.

Atom	*x*	*y*	*z*	U_{eq}*
Br11	0.26378(4)	0.6376(3)	0.12025(9)	0.0310(4)
Br12	0.31496(5)	0.6290(3)	0.32474(8)	0.0322(4)
Br13	0.19656(5)	0.6585(3)	0.29415(8)	0.0306(4)
Br14	0.20337(5)	0.1588(3)	0.18315(8)	0.0309(4)
Br15	0.32128(5)	0.1288(3)	0.19744(8)	0.0311(4)
Br16	0.24976(4)	0.1339(3)	0.37793(8)	0.0309(4)
Br21	0.59557(4)	0.6308(3)	0.12212(8)	0.0287(4)
Br22	0.64740(5)	0.6225(3)	0.32486(8)	0.0297(4)
Br23	0.52633(5)	0.6445(3)	0.29687(8)	0.0295(4)
Br24	0.53342(5)	0.1442(3)	0.18066(8)	0.0295(4)
Br25	0.65350(4)	0.1202(3)	0.19851(8)	0.0286(4)
Br26	0.58208(4)	0.1267(3)	0.37653(8)	0.0287(4)
Br31	0.92739(4)	0.6548(3)	0.12311(9)	0.0297(4)
Br32	0.98124(5)	0.6463(3)	0.32220(8)	0.0301(4)
Br33	0.85966(5)	0.6603(3)	0.30019(8)	0.0300(4)
Br34	0.86567(5)	0.1626(3)	0.18101(8)	0.0294(4)
Br35	0.98663(5)	0.1448(3)	0.19587(8)	0.0293(4)
Br36	0.91616(4)	0.1495(3)	0.37633(8)	0.0294(5)
Cu11	0.19895(5)	0.5478(4)	0.16965(9)	0.0353(5)
Cu12	0.31851(5)	0.5307(4)	0.20232(9)	0.0392(5)
Cu13	0.24865(5)	0.5331(4)	0.37077(8)	0.0390(6)
Cu14	0.19158(5)	0.0480(4)	0.30369(9)	0.0364(5)
Cu15	0.26472(5)	0.0354(4)	0.12502(8)	0.0374(5)
Cu16	0.31157(5)	0.0298(4)	0.32142(9)	0.0390(5)
Cu21	0.53310(5)	0.7515(4)	0.17244(9)	0.0336(5)
Cu22	0.65139(5)	0.7232(4)	0.20245(9)	0.0358(6)
Cu23	0.58195(6)	0.7305(4)	0.37259(9)	0.0364(6)
Cu24	0.52606(5)	0.2504(4)	0.30202(9)	0.0341(6)
Cu25	0.59793(5)	0.2365(4)	0.12565(9)	0.0342(6)
Cu26	0.64514(5)	0.2273(4)	0.32305(9)	0.0347(6)
Cu31	0.86522(5)	0.7686(3)	0.17601(9)	0.0332(5)
Cu32	0.98485(5)	0.7476(4)	0.19953(9)	0.0366(6)
Cu33	0.91641(5)	0.7547(4)	0.37264(9)	0.0349(6)
Cu34	0.85915(5)	0.2654(4)	0.30302(9)	0.0337(6)
Cu35	0.92973(5)	0.2612(3)	0.12621(9)	0.0338(6)
Cu36	0.97871(5)	0.2515(3)	0.3201(1)	0.0346(6)
Se11	0.11955(4)	0.9706(3)	0.11317(7)	0.0344(4)
Se12	0.13238(4)	0.5180(3)	0.01254(7)	0.0323(4)
Se13	0.09173(4)	0.4981(3)	0.18918(7)	0.0340(4)
Se14	0.02544(4)	0.4590(3)	0.03805(7)	0.0356(4)
Se21	0.44076(3)	0.9991(3)	0.10743(7)	0.0282(4)
Se22	0.46989(4)	0.5593(3)	0.01262(7)	0.0296(4)
Se23	0.43256(4)	0.5172(3)	0.19147(6)	0.0276(4)
Se24	0.36790(4)	0.3923(3)	0.04048(7)	0.0300(4)
Se31	0.77495(4)	1.0070(3)	0.09900(7)	0.0292(4)
Se32	0.80287(4)	0.5369(3)	0.02082(7)	0.0298(4)
Se33	0.76348(4)	0.5499(3)	0.19768(7)	0.0290(4)
Se34	0.69792(4)	0.3946(3)	0.05249(7)	0.0299(4)
Se41	0.11787(4)	0.4701(3)	0.38034(7)	0.0319(4)
Se42	0.08011(4)	0.0088(3)	0.30772(7)	0.0305(4)
Se43	0.13895(4)	0.0053(3)	0.46845(7)	0.0329(4)
Se44	0.03117(4)	-0.0446(3)	0.47783(7)	0.0339(4)
Se51	0.43948(4)	0.5002(3)	0.38761(7)	0.0290(4)
Se52	0.41852(4)	0.0257(3)	0.30500(6)	0.0300(4)
Se53	0.47840(4)	0.0461(3)	0.46393(7)	0.0303(4)
Se54	0.37408(4)	-0.1060(3)	0.47670(7)	0.0300(4)
Se61	0.77562(4)	0.5023(3)	0.39834(7)	0.0290(4)
Se62	0.75016(4)	0.0581(3)	0.30160(7)	0.0303(4)
Se63	0.81096(3)	0.0208(3)	0.45921(7)	0.0283(4)
Se64	0.70416(4)	-0.1095(3)	0.46556(7)	0.0299(4)
P11	0.1409(1)	0.6309(6)	0.1228(2)	0.028(1)
P12	0.0606(1)	0.8963(6)	0.0684(2)	0.029(1)
P13	0.0727(1)	0.6589(6)	-0.0146(2)	0.026(1)
P14	0.0377(1)	0.6433(5)	0.1382(2)	0.026(1)
P21	0.4744(1)	0.6940(6)	0.1212(2)	0.025(1)
P22	0.3849(1)	0.8566(6)	0.0677(2)	0.0260(9)
P23	0.4061(1)	0.6362(5)	-0.0145(2)	0.024(1)
P24	0.37355(9)	0.5886(6)	0.1397(2)	0.0235(9)
P31	0.8069(1)	0.7031(6)	0.1248(2)	0.0243(9)
P32	0.7196(1)	0.8608(6)	0.0604(2)	0.0262(9)
P33	0.7394(1)	0.6043(5)	-0.0110(2)	0.024(1)
P34	0.7052(1)	0.6249(6)	0.1429(2)	0.026(1)
P41	0.1358(1)	0.1329(6)	0.3583(2)	0.028(1)
P42	0.06382(9)	0.3958(6)	0.4410(2)	0.0264(9)
P43	0.0332(1)	0.1499(6)	0.3777(2)	0.026(1)
P44	0.0839(1)	0.1477(6)	0.5163(2)	0.026(1)
P51	0.4693(1)	0.1926(6)	0.3582(2)	0.024(1)
P52	0.3898(1)	0.3587(6)	0.4466(2)	0.0250(9)
P53	0.3681(1)	0.0968(6)	0.3792(2)	0.025(1)
P54	0.4199(1)	0.1290(6)	0.5162(2)	0.027(1)
P61	0.8024(1)	0.1996(6)	0.3583(2)	0.025(1)
P62	0.7258(1)	0.3561(5)	0.4557(2)	0.027(1)
P63	0.7010(1)	0.1301(5)	0.3780(2)	0.025(1)
P64	0.7530(1)	0.0917(6)	0.5145(2)	0.0243(9)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Selected interatomic distances of $(CuBr)_3P_4Se_4$.

$(CuBr)_3P_4Se_4$				
average distance (Å)		min. dist. (Å)	max. dist. (Å)	number of data
P−Se	2.259(5)	2.208(5)	2.297(4)	48
Cu−P	2.2258(7)	2.210(6)	2.237(7)	18
P−P	2.233(6)	2.223(6)	2.243(6)	12
Cu−Br	2.456(7)	2.414(7)	2.490(7)	36
$(CuI)_3P_4Se_4$ (data taken from [14])				
average distance (Å)		min. dist. (Å)	max. dist. (Å)	number of data
P−Se	2.254(3)	2.210(3)	2.278(3)	6
Cu−P	2.267(4)	2.239(3)	2.281(4)	3
P−P	2.241(5)			1
Cu−I	2.636(3)	2.594(2)	2.740(4)	9

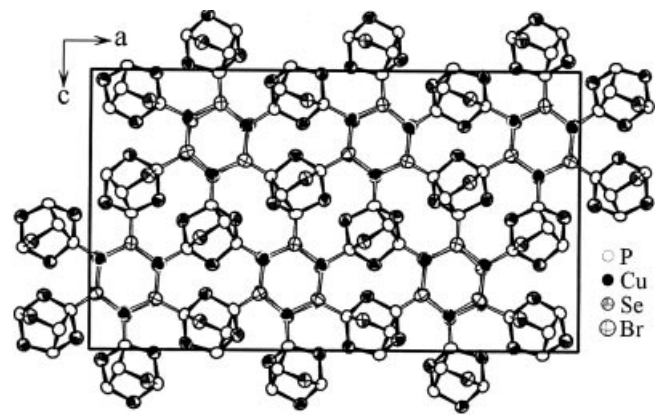


Figure 1 Section of the crystal structure of $(CuBr)_3P_4Se_4$. Anisotropic displacement parameters represent a probability of 90 %. CuBr and P_4Se_4 molecules are stacked along [010].

molecules. The average intermolecular distance in this direction calculated from the shortest intermolecular distances d(Se*n*1−Se*n*2$^{\#}$,3$^{\#}$,4$^{\#}$) = 3.69 Å is in the range of the corresponding van der Waals distance (3.8 Å). Compared to the shortest intermolecular distance d(Se−Se) = 3.49 Å in $(CuI)_3P_4Se_4$ this distance is significantly increased in $(CuBr)_3P_4Se_4$. This finding is quite surprising because the lattice constants along the stacking directions and the molar volumes of both compounds are showing the opposite tendency. The lattice constant increases from b = 6.402(3) Å ($(CuBr)_3P_4Se_4$) to c = 6.720(1) Å ($(CuI)_3P_4Se_4$) and the molar volume increases from 341.9 Å^3 ($(CuBr)_3P_4Se_4$) to 372.6 Å^3 ($(CuI)_3P_4Se_4$). Shortest intermolecular distances of Se perpendicular to the stacking direction vary around the van der Waals distance (3.75 Å to 3.88 Å). Obviously, the lower symmetry of $(CuBr)_3P_4Se_4$ as compared to $(CuI)_3P_4Se_4$ increases the structural flexibility and thus allows an optimisation of the intermolecular distances. The differences between the different stacks of molecules can be quantified for example by the angle of Se*n*1 embedded in the P_3Se_3 ring of a neighboured molecule and the Se*n*1$^{\#}$−P*n*1$^{\#}$ bond, see Figure 2. This angle is in the range

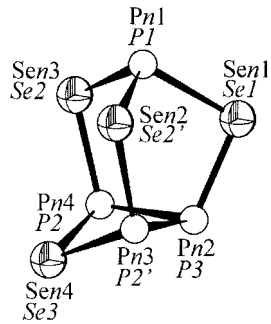
Table 4 Selected inter- and intramolecular angles of β-P_4Se_4 in $(CuBr)_3P_4Se_4$ and $(CuI)_3P_4Se_4$ (data taken from [14]).

$(CuBr)_3P_4Se_4$

intermolecular angles (°)

Se11···P12#−Se11#	82.5(1)
Se21···P22#−Se21#	94.0(1)
Se31···P32#−Se31#	95.0(1)
Se41···P42#−Se41#	82.4(1)
Se51···P52#−Se51#	94.0(1)
Se61···P62#−Se61#	94.9(1)
average angle	**90.5 (1)**

coordinates: x, 1+y, z



$(CuBr)_3P_4Se_4$, β-P_4Se_4 molecules $n = 1-6$
$(CuI)_3P_4Se_4$, labelling in italics

intramolecular angles (°)

molecule	Pn1−Sen1−Pn2	Sen1−Pn2−Pn3	Sen1−Pn2−Pn4	Sen2−Pn1−Sen1
$n = 1$	96.1(2)	104.8(2)	103.7(2)	101.1(2)
$n = 2$	96.1(1)	103.2(2)	104.6(2)	101.0(2)
$n = 3$	96.1(1)	105.1(2)	103.6(2)	100.8(2)
$n = 4$	96.4(2)	104.3(2)	104.0(2)	101.1(2)
$n = 5$	96.0(1)	105.2(2)	103.3(2)	100.8(2)
$n = 6$	96.1(1)	103.3(2)	105.1(2)	101.3(2)
average	**96.1(1)**	**104.3(2)**	**104.1(2)**	**101.0(2)**

$(CuI)_3P_4Se_4$ (data taken from [14])

angle (°)		
Se1···P3−Se1		100.9(1) (intermolecular)
P1−Se1−P3		96.33(9)
Se1−P3−P2	2x	104.33(9)
Se2−P1−Se1	2x	100.19(7)

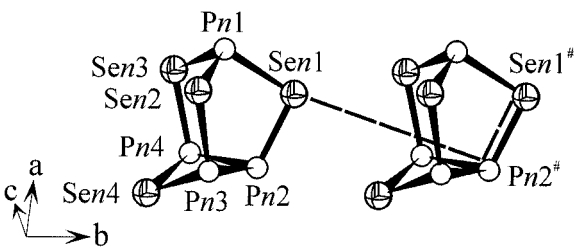


Figure 2 Stacking of β-P_4Se_4 along [010]. Se*n*1 is tending towards a P_3Se_3 ring of a neighboured molecule. P (white circles), Se (octands). The angle Se*n*1···P*n*2#-Se*n*1# is marked by a dashed line. # coordinates: x, 1+y, z.

from 82.4−95.0° (average angle 90.5°) in $(CuBr)_3P_4Se_4$ as compared to 100.9° in $(CuI)_3P_4Se_4$, see Table 4. However, the intramolecular bonding distances and angles of β-P_4Se_4 of $(CuBr)_3P_4Se_4$ are in accordance with the corresponding values of $(CuI)_3P_4Se_4$ (see Tables 3 and 4). This can be realized only because of the different coordination mode of the cage molecules to the columns of CuBr.

Each P_4Se_4 cage is coordinated to three copper atoms with distances *d*(Cu-P) of about 2.23 Å, which is in the

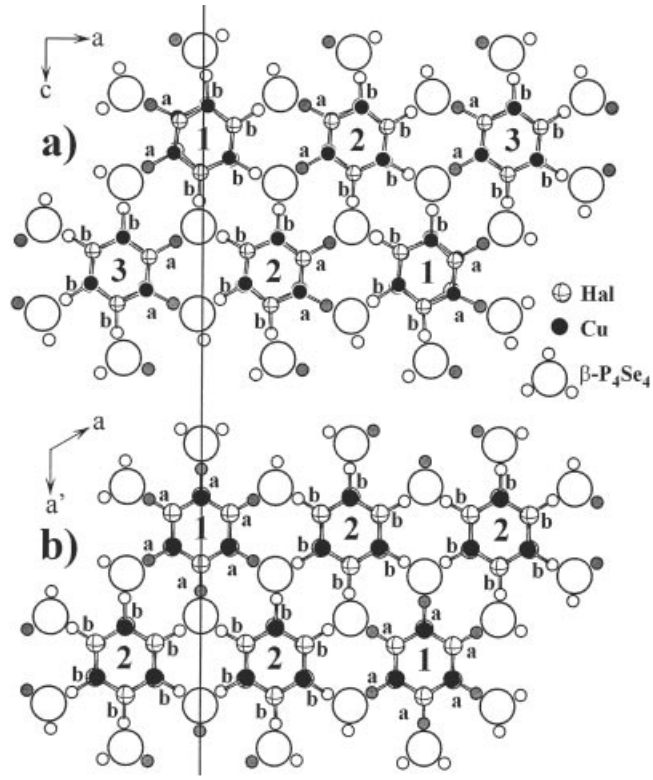


Figure 3 Arrangement of CuX columns and β-P_4Se_4 molecules in a) $(CuBr)_3P_4Se_4$ and b) $(CuI)_3P_4Se_4$ (data taken from [14]). β-P_4Se_4 is represented by large circles. Apical and basal P atoms coordinating the Cu atoms are drawn as grey and white circles. The coordination modes of the CuX columns change from 2*a*4*b* (a) to 6*a* or 6*b* (b). A slight opposite rotation of the columns and of the β-P_4Se_4 molecules in $(CuBr)_3P_4Se_4$ as compared to the arrangement in $(CuI)_3P_4Se_4$ can be observed.

typical range for Cu-P bonds. All cage molecules have in common that P*n*1, P*n*3, and P*n*4 are attached to copper. In $(CuBr)_3P_4Se_4$ all columns of CuBr are coordinated by six P_4Se_4 cages in the same way, i.e., two apical P atoms (P*n*1) and four P atoms (P*n*3, P*n*4) of the basal P_3Se rings are bonded to copper. This is quite different from the way how the homologous iodine compounds are built. Therein, two types of CuI columns are observed. One of them is exclusively coordinated by apical P atoms whereas the other one is surrounded only by basal P atoms. Thus, the difference between the CuX columns in these compounds is induced by the orientation of the three-dentate β-P_4Se_4 ligands, see Figure 3. The coordination mode of the P_4Se_4 cages to copper in the CuBr columns can be described as 2*a*4*b* with *a* = apical P atom and *b* = basal P atom, see Figure 3. As mentioned above six crystallographically different stacks of β-P_4Se_4 are found around each CuBr column in $(CuBr)_3$-P_4Se_4. However, the columns are all coordinated in the same way, and only small distortions are observed. In the case of $(CuI)_3P_4Se_4$ the columns are either coordinated in a 6*a* or in a 6*b* mode. Obviously the change of the anion in

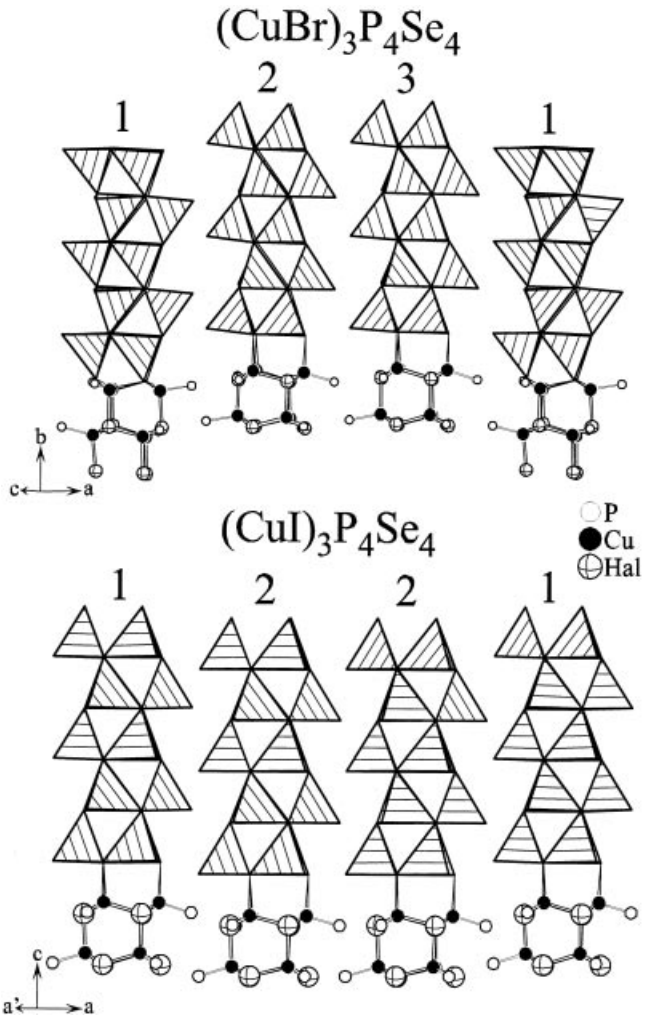


Figure 4 Wurtzite like CuX columns (X = Br, I) in $(CuBr)_3P_4Se_4$ and in $(CuI)_3P_4Se_4$. Cu (black circles), X (white circles & cross), P (white circles). [CuX_3P] tetrahedra are drawn to underline the different arrangement in $(CuBr)_3P_4Se_4$ and $(CuI)_3P_4Se_4$.

the $(CuX)_3P_4Se_4$ compounds is very important for the crystal structure and different possibilities are observed how to optimize competing necessities.

In addition to this different coordination mode a slight rotation of the columns of CuBr and of the stacks of the cage molecules is observed. The CuBr columns are rotated in the opposite direction as the coordinating P-Se cages. This becomes obvious from the vertical line drawn in Figure 3. Figure 4 shows that the number of different CuX columns is increased from two in $(CuI)_3P_4Se_4$ to three in $(CuBr)_3P_4Se_4$.

Focusing on the tetrahedra [$CuBr_3P$] of $(CuBr)_3P_4Se_4$ one can distinguish between two different orientations along the stacking direction [010]. [$CuBr_3P$] tetrahedra of column 1 are oriented in the opposite direction than those in columns 2 and 3. As a consequence the copper atoms of column 1 are shifted for approximately 1.28 Å as compared to the corresponding copper atoms in columns 2 and 3. The difference between the copper positions of column 2 and 3 is comparably small, i.e., 0.096 Å. Contrary to the Cu positions only a small variation is observed for the bromine atoms in the different columns, see Figure 4. However, the orientation of the tetrahedra in $(CuI)_3P_4Se_4$ is not as clear as the one in $(CuBr)_3P_4Se_4$ since the copper atoms of column 2 are disordered in the case of the iodine compound.

$(CuBr)_3P_4Se_4$ differs from $(CuI)_3P_4Se_4$ in a) the 2*a*4*b* coordination mode of the β-P_4Se_4 cages to the columns CuX and b) a clockwise rotation of the CuX columns combined with an anti-clockwise rotation of the β-P_4Se_4 stacks (see Figure 3). The combination of these effects results in a threefold superstructure along [100].

Experimental

CuBr (Fluka, 98%) was purified prior to use by solving it in concentrated aqueous HBr (Fluka, p.a.) and recrystallising it by adding distilled water. The crude product was washed with ethanol and acetone, and dried in a vacuum for several days. $(CuBr)_3P_4Se_4$ was synthesized from a 3 : 4 : 4 mixture of CuBr, P (Hoechst, 99.9999 %) and Se (Chempur, 99.999 %) in evacuated silica ampoules. After heating to 600 °C the homogenised starting material was annealed at 350 °C for four weeks. Purity was checked by X-ray powder diffraction using a Stoe STADI-P powder diffractometer, Cu $K\alpha_1$ radiation (λ = 1.54051 Å, germanium monochromator, transmission geometry). A linear PSD was used for collecting X-ray intensities. Single crystal data were collected on a Stoe IPDS (Mo $K\alpha$, λ = 0.71073 Å) and corrected for Lorentz and polarization effects. A numerical absorption correction based on an optimized crystal shape (STOE XRED, XSHAPE [17]) was applied. The structure of $(CuBr)_3P_4Se_4$ was solved by direct methods (SHELXS97 [18]) and refined with the JANA2000 [19] program package. Differential thermal analysis measurements were performed on a SETARAM TG-DTA 92-16. $(CuBr)_3P_4Se_4$ decomposes at 374 ± 2 °C and forms an amorphous solid upon cooling.

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