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$(CuBr)_2P_8Se_3$: preparation, structural, and vibrational spectroscopic characterization of an adduct of P_8Se_3 cages to Cu_2Br_2 rhombs

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Dedicated to Prof. Dr H.D. Lutz on the occasion of his 70th birthday

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Abstract

Orange–red $(CuBr)_2P_8Se_3$ was obtained from stoichiometric amounts of CuBr, P and Se by melting and subsequent annealing at 380 °C for 1 month. The crystal structure was determined from single crystal X-ray data. $(CuBr)_2P_8Se_3$ crystallizes in the orthorhombic system, space group *Pbcm* (No. 57), with $a = 8.761(1)$ Å, $b = 11.957(1)$ Å, $c = 13.858(1)$ Å, $V = 1451.8(3)$ Å^3, and $Z = 4$. This compound consists of neutral P_8Se_3 cage molecules attached to Cu_2Br_2 rhombs. Vibrational spectroscopic data are reported for $(CuBr)_2P_8Se_3$ and for the homologous $(CuI)_2P_8Se_3$. The wavenumbers of the Cu–Br and Cu–I vibrational modes show an excellent correlation with the corresponding Cu–X bond lengths.

Keywords: Phosphorus chalcogenide; Copper; Halide; Vibrational spectroscopy; X-ray diffraction; Crystal structure

1. Introduction

Copper(I) halides have been established as an useful tool for the synthesis of hitherto unknown main group molecules and low charged polyanions [1]. These adduct compounds are of special interest because they show an enhanced ionic mobility due to only weak bonding interactions between copper and the neutral ligands [2]. Thus, a number of phosphorus polymers, chalcogen molecules and phosphorus chalcogenides could be obtained as their adducts to copper(I) halides. Recently, even an arsenic substituted phosphorus polymer embedded in CuI was reported [3]. In addition to their ion conducting properties, these compounds can be used as model compounds for the basic characterization of copper containing phosphorus chalcogenide glasses by solid state NMR spectroscopy [4]. Whereas the chalcogen polymers and chalcogen rings were obtained as adducts to CuCl, CuBr, and CuI the phosphorus containing compounds are usually based on CuI but never on CuCl and only in a few cases on CuBr, see Ref. [1]. Different compounds were observed, e.g. for CuX with phosphorus polyanions in dependence on X, namely $Cu_3P_{15}I_2$ [5] and $Cu_{12}P_{20}Br_{10}$ [6]. In case of the adducts of β-P_4Se_4 with CuX the resulting compounds have an analogous composition, i.e. $(CuX)_3P_4Se_4$ (X = Br, I) [7,8] but the crystal structures of these compounds differ significantly. When β-P_4S_4 is regarded instead of the β-P_4Se_4 cage $(CuI)_3P_4S_4$ results which is more or less isostructural with $(CuI)_3P_4Se_4$ [9]. Obviously different parameters as, e.g. the volume ratios of the constituent building groups, cf. [10], and the coordination modes of the phosphorus chalcogenide cages have to be taken into account when the crystal structures of these adduct compounds are discussed. Herein, we report on the synthesis and the structural and vibrational spectroscopic characterization of $(CuBr)_2P_8Se_3$ and discuss this compound in comparison with the iodine homologue $(CuI)_2P_8Se_3$ [11].

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2. Experimental

2.1. Preparation

$(CuBr)_2P_8Se_3$ was prepared from a 2:8:3 mixture of CuBr (Riedl de Haen, >99%), P (Hoechst, ultra high grade 99.9999%) and Se (Chempur, 99.999%). CuBr was purified by recrystallization from concentrated aqueous HBr (Fluka, purum p.a.) prior to use. The mixture was heated in an evacuated silica tube up to 873 K and kept at this temperature for several hours. Since the mixture was completely molten the temperature was reduced to 653 K. The compound was annealed at this temperature for 30 days. From DSC (SETARAM TG-DTA 92-16) measurements a peritectical decomposition temperature of 680 K was determined for $(CuBr)_2P_8Se_3$.

2.2. X-ray crystallography

The purity of $(CuBr)_2P_8Se_3$ was checked by X-ray powder diffraction using a STOE STADIP diffractometer (Cu Kα_1 radiation, Germanium monochromator) equipped with a linear 5° PSD. An orthorhombic unit cell with lattice constants of $a = 8.761(1)$ Å, $b = 11.957(1)$ Å, $c = 13.858(1)$ Å, and $V = 1451.8(3)$ Å^3 was calculated from powder diffraction data.

The crystal structure of $(CuBr)_2P_8Se_3$ was determined by single crystal X-ray diffraction. Intensities of suitable crystals were recorded on a STOE IPDS (Mo Kα radiation, $\lambda = 0.71073$Å, graphite monochromator) at 298(1) K. A numerical absorption correction was applied after the optimization of the crystal shape based on symmetry equivalent reflections using the XRED and XSHAPE routines [12]. Intensities were averaged in the Laue group *mmm* and the space group *Pbcm* was derived from systematic extinctions. Due to the similarities in lattice parameters and the symmetry with the homologue $(CuI)_2P_8Se_3$ ($a = 9.1348(6)$ Å, $b = 12.351(1)$ Å and $c = 13.873(1)$ Å, $V = 1565.2(2)$ Å^3, space group *Pbcm* [11] an isotypic structure was assumed for $(CuBr)_2P_8Se_3$. Therefore, the atomic positions of $(CuI)_2P_8Se_3$ were used as a starting model for the structure refinement. The crystal structure was refined with the JANA2000 [13] program package. It converged at $R = 0.0404$ and $wR = 0.0902$ (for reflections with $I > 3\sigma_I$) after anisotropic treatment of all atoms. Crystallographic data, atomic coordinates and anisotropic displacement parameters are summarized in Tables 1–3.

2.3. Vibrational spectroscopy

Far infrared spectra were recorded on a Bruker 113v FT-IR spectrometer. Finely powdered samples were measured as nujol mulls on polyethylene plates with a resolution of 2 cm^{-1}.

Table 1
Crystallographic data of $(CuBr)_2P_8Se_3$

Compound	$(CuBr)_2P_8Se_3$
Formula weight (g/mol)	771.6
Crystal size (mm^3)	$0.08 \times 0.07 \times 0.06$
Temperature (K)	298
Crystal system	Orthorhombic
Space group	*Pbcm* (No. 57)
Lattice constants (Å) from powder data	$a = 8.761(1)$ $b = 11.957(1)$ $c = 13.858(1)$
Cell volume (Å^3), Z	1451.8(3), 4
ρ_{calc} (g/cm^3)	3.5290(6)
$\mu_{X\text{-ray}}$ (mm^{-1})	16.799
Diffractometer	STOE IPDS, Mo Kα, $\lambda = 0.71073$ Å, oriented graphite monochromator
θ-range (°)	2.94–26.64
hkl range	$-10 \le h \le 5$ $-14 \le k \le 15$ $-17 \le l \le 17$
No. of reflections, R_{int}	5192, 0.0609
No. of unique reflections	1477
Refinement	JANA [13], full matrix least squares on F^2
Number of parameters	75
Goodness of fit	1.03
Final R indices [$I > 3\sigma_I$]	$R = 0.0404$, $wR = 0.0902$
Final R indices [all data]	$R = 0.0873$, $wR = 0.0961$
Largest difference peaks $\Delta\rho_{min}$ and $\Delta\rho_{max}$ (e/Å^3)	−2.13, 1.91

Crystallographic data for $(CuBr)_2P_8Se_3$ have been deposited with the Fachinformationszentrum Karlsruhe, D-76334 Leopoldshafen, Germany, fax: +49-7247-808-666, e-mail: crysdata@fiz-karlsruhe.de. They are available on quoting the depository numbers CSD-413695, the name of the authors and the reference of the publication.

Raman spectra were recorded on a Bruker RFS100/S-Fourier transform spectrometer equipped with a Nd:YAG laser ($\lambda = 1064$ nm) and a liquid nitrogen cooled germanium detector. Samples were sealed in Duran glass capillaries of 1 mm outside diameter. The resolution was 2 cm^{-1}. Spectra were processed with the OPUS program package [14].

Table 2
Atomic coordinates and isotropic displacement parameters in Å^2 for $(CuBr)_2P_8Se_3$

Atom	Wyckhoff	x	y	z	U_{eq}[a]
Br1	4*d*	0.0837(3)	0.0753(1)	1/4	0.0315(6)
Br2	4*d*	−0.2701(3)	−0.1250(1)	1/4	0.0324(6)
Se1	4*c*	−0.0886(2)	−1/4	1/2	0.0265(6)
Se2	8*e*	0.4204(2)	−0.0767(1)	0.38919(9)	0.0385(5)
Cu1	4*d*	−0.2061(3)	0.0719(2)	1/4	0.0284(8)
Cu2	4*d*	0.0078(3)	−0.1250(2)	1/4	0.0258(7)
P1	8*e*	−0.2549(4)	0.1622(2)	0.3900(2)	0.021(1)
P2	8*e*	0.0887(4)	−0.1951(2)	0.3924(2)	0.0215(9)
P3	8*e*	0.4802(4)	−0.2579(2)	0.4188(2)	0.0181(9)
P4	8*e*	0.2020(4)	−0.0627(2)	0.4777(1)	0.0132(9)

All positions are fully occupied.

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

Table 3
Anisotropic displacement parameters in Å^2 of $(CuBr)_2P_8Se_3$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br1	0.040(1)	0.0194(8)	0.0345(8)	−0.001(1)	0	0
Br2	0.026(1)	0.0211(9)	0.050(1)	−0.0023(9)	0	0
Se1	0.025(1)	0.0288(9)	0.0256(7)	0	0	0.0015(6)
Se2	0.045(1)	0.0344(7)	0.0357(6)	−0.0080(8)	0.0051(7)	0.0039(6)
Cu1	0.047(2)	0.021(1)	0.0170(9)	−0.001(1)	0	0
Cu2	0.031(2)	0.028(1)	0.0178(8)	0.004(1)	0	0
P1	0.030(2)	0.021(1)	0.013(1)	−0.002(1)	−0.000(1)	0.001(1)
P2	0.028(2)	0.022(1)	0.015(1)	0.002(1)	−0.003(1)	0.003(1)
P3	0.019(2)	0.018(1)	0.017(1)	0.001(1)	0.005(1)	0.001(1)
P4	0.026(2)	0.005(1)	0.008(1)	0.000(1)	−0.002(1)	0.0012(9)

3. Results and discussion

3.1. The crystal structure of $(CuBr)_2P_8Se_3$

$(CuBr)_2P_8Se_3$ can be regarded as an adduct compound of neutral cage molecules P_8Se_3 and rhombs of Cu_2Br_2. The P_8Se_3 cages are the neutral equivalents of the well known so-called 'ufosane' polyphosphide $[P_{11}]^{3-}$, e.g. [15]. By a formal substitution of the three P^- atoms of the $[P_{11}]^{3-}$ anion one can easily derive the neutral P_8Se_3 molecule, see Fig. 1. The symmetry of an undistorted P_8Se_3 is D_3, namely one C_3 axis and three C_2 axes perpendicular to the C_3 axis. However, to date no crystalline compound is known where the 'ideal' D_3 symmetry is observed for the $[P_{11}]^{3-}$ anion or the P_8Se_3 cage molecule. This is due to the asymmetrical coordination of the cages in the solid state. A comparison of the structural parameters of the two different cages shows their close relation. Thus, the average distances d(P–P) and d(P–Se) are almost equivalent, i.e. $d \approx 2.23$ Å, which is a typical P–P bond length, see Table 4. A 'height' of d(P1–P1′) = 3.70 Å results for P_8Se_3 and $d = 3.78$ Å for the corresponding P atoms in $[P_{11}]^{3-}$. The distances for the atoms defining the 'tail' of the molecules, i.e. the Se atoms in P_8Se_3 and the P^- atoms in $[P_{11}]^{3-}$, are also within a very narrow range. Thus, d(Se–Se) ≈ 5.15 Å and $d(P^- – P^-) \approx 5.11$ Å differ only slightly above the experimental error. These differences become even less meaningful taking into account the different temperatures of 123 K for the structure determination of $Cs_3P_{11}\cdot 3NH_3$ vs. 298 K for $(CuBr)_2P_8Se_3$. The most prominent difference between the molecular parameters of the two cages is the bond angle of the two-bonded atoms. It varies from 92.9° < ∠(P–Se–P) < 99.5°, and from 95.6° < ∠(P–P^-–P) < 96.7°.

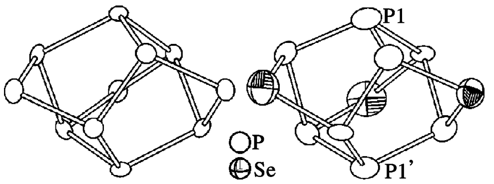

Fig. 1. Molecular structures of $[P_{11}]^{3-}$ and $[P_8Se_3]$. View parallel to a C_2 axis of the D_3 symmetrical molecules. The symmetry of the cages is reduced in the crystalline compounds. Data for $[P_{11}]^{3-}$ are taken from Ref. [15].

Table 4
Selected average distances $\bar{d}$ in Å of $(CuBr)_2P_8Se_3$ and $(CuI)_2P_8Se_3$

	$\bar{d}$(P–P)	$\bar{d}$(P–Se)	$\bar{d}$(Cu–P)
$(CuBr)_2P_8Se_3$	2.233	2.266	2.259
$(CuI)_2P_8Se_3$	2.230	2.265	2.266

Data taken from Ref. [11].

In $(CuBr)_2P_8Se_3$ each P_8Se_3 molecule is surrounded by four Cu_2Br_2 rhombs, i.e. four of the eight P atoms are coordinated to one copper atom of each Cu_2Br_2 rhomb. Vice versa each copper atom coordinates to two different P_8Se_3 cages and $[Cu_2Br_2P_4]$ double tetrahedra result. Fig. 2 shows the layered arrangement of P_8Se_3 cages and Cu_2Br_2 rhombs in the crystal structure of $(CuBr)_2P_8Se_3$.

When the crystal structures of $(CuX)_2P_8Se_3$ are compared it becomes immediately obvious why only the a and b lattice parameters differ for X = Br and X = I, respectively. Thus, the different radii of Br^- and I^- do not affect the crystal structure along c since there are no bonds for the halide ions parallel to this direction. A similar effect

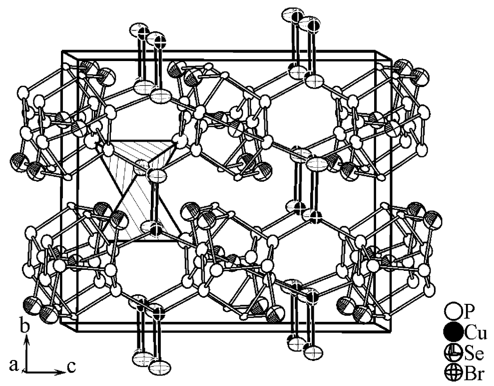

Fig. 2. Section of the crystal structure of $(CuBr)_2P_8Se_3$. View along layers of P_8Se_3 molecules and Cu_2Br_2 rhombs. Four P_8Se_3 molecules are coordinated by one Cu_2Br_2 rhomb to form edge sharing $[Cu_2Br_2P_4]$ double tetrahedra. Ellipsoids are drawn at an 80% probability level.

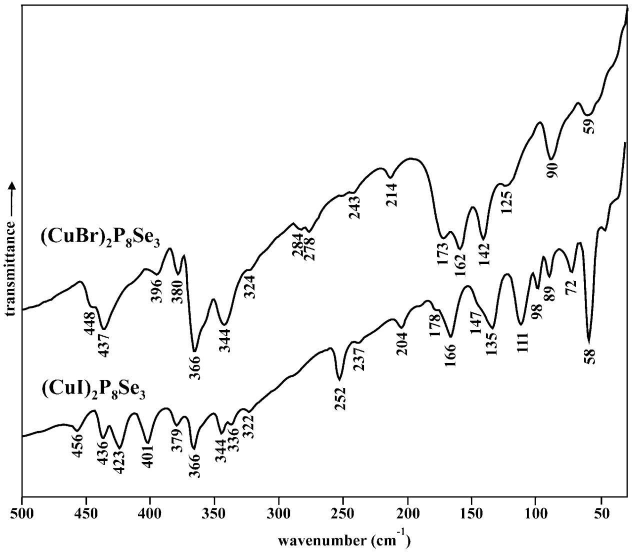

Fig. 3. Far infrared spectra of $(CuBr)_2P_8Se_3$ and $(CuI)_2P_8Se_3$. Resolution $2\ cm^{-1}$.

was observed for the homologous pair $(CuI)_3P_4Se_4$ and $(CuI)_3P_4S_4$ [8,9]. This behavior underlines the adduct character of the compounds under discussion.

3.2. IR and Raman spectroscopic investigations

Due to the isotypic structures of $(CuBr)_2P_8Se_3$ and $(CuI)_2P_8Se_3$ coming along with almost identical molecular parameters of the P_8Se_3 molecule one can also expect similar vibrational modes for the molecular parts of the compounds.

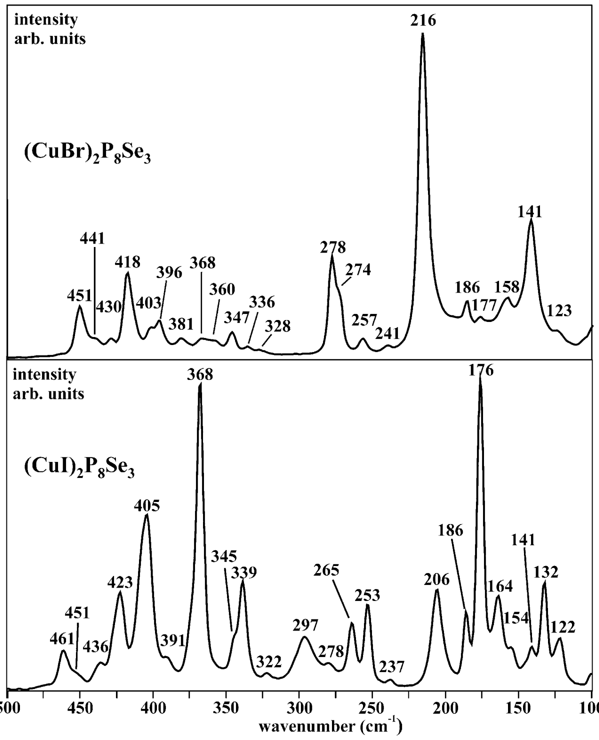

Fig. 4. Raman spectra of $(CuBr)_2P_8Se_3$ and $(CuI)_2P_8Se_3$. Resolution $2\ cm^{-1}$.

From ab initio calculations for numerous phosphorus-selenium molecules [16] and IR and Raman spectroscopic investigations of cage molecules like P_4Q_3 (Q = S, Se) [17,18] the ranges for the wavenumbers of the P–Se and P–P modes have been determined. Vibrational bands can be expected in the range from 530 to $20\ cm^{-1}$. A gap of about $100\ cm^{-1}$ was observed between the bending modes of P_4Se_3 below $220\ cm^{-1}$ and the stretching modes above $315\ cm^{-1}$. This gap was also derived from theoretical calculations for phosphorus rich molecules [16]. Transferring these findings to the phosphorus rich P_8Se_3 molecule one should observe a similar separation of bending and stretching modes in $(CuBr)_2P_8Se_3$ and $(CuI)_2P_8Se_3$.

No bands could be detected above $500\ cm^{-1}$ neither in Raman nor in IR-experiments, see Figs. 3 and 4. The observed frequencies are summarized in Table 5. Focusing on the range between 500 and $300\ cm^{-1}$ the IR spectra of $(CuBr)_2P_8Se_3$ and $(CuI)_2P_8Se_3$ are almost identical in their relative intensities and positions of

Table 5
Observed Raman and IR modes of $(CuBr)_2P_8Se_3$ and $(CuI)_2P_8Se_3$

Raman $(CuBr)_2P_8Se_3$	$(CuI)_2P_8Se_3$	IR $(CuBr)_2P_8Se_3$	$(CuI)_2P_8Se_3$	
		59(w)	58(m)	
			72(w)	
		90(m)	89(w)	
			98(w)	
			111(m)	
123 (vw)[a]	122(w)	125(m)[a]		P_8Se_3 bending mode region
	132(m)[a]		135(m)[a]	
141(s)[a]	141(w)	142(s)[a]		
158(m)[a]	154(w)[a]		147(w)[a]	
	164(m)[a]	162(s)[a]	166(m)[a]	
177(m)[a]	176(vs)[a]	173(s)[a]	178(w)[a]	
186(m)	186(m)			
216(vs)	206(s,b)	214(w)	204(m)	
241(vw)	237(vw)	243(vw)	237(w)	
257(w)	253(m)		252(s)	
274(m,sh)	265(m)			
278(s)	278(w)	284(w)		
	297(m,b)	287(w)		
328(vw)	322(vw)	324(w)	322(w)	
336(vw)	339(s)		336(w)	
347(m)	345(m,sh)	344(s)	344(m)	
360(w)				
368(w)	368(vs)	366(vs)	366(s)	
381(w)		380(m)	379(m)	P_8Se_3 stretching mode region
396(w)	391(w)			
403(w)	405(s)	396(m)	401(s)	
418(m)	423(m)		423(s)	
430(vw)	436(w)	437(s)	436(m)	
441(vw)	451(vw)	448(m)	456(m)	
451(w)	461(w)			

Intensities: vw, very weak; w, weak; m, middle; s, strong; vs, very strong.
[a] Marked frequencies are used for the correlation curve shown in Fig. 5.

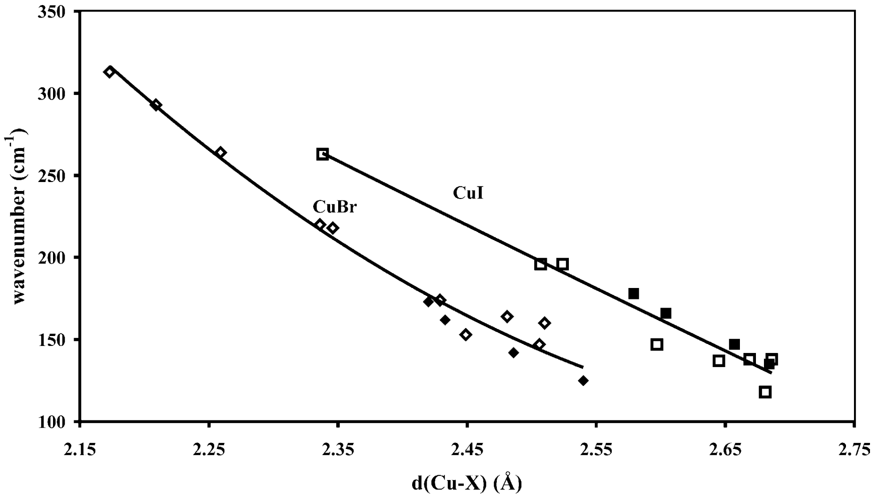

Fig. 5. Plot of the wavenumbers of Cu–X modes vs. Cu–X bond lengths for CuX complexes (data from Ref. [19]) and $CuXSe_3$ (X = Br, I) [22] (white marks) and $(CuX)_2P_8Se_3$ (X = Br, I) (black marks).

the bands, see Fig. 3. This region is supposed to be the stretching mode area of the P_8Se_3 molecule in analogy to the results from other cage molecules like P_4Q_3 (Q = S, Se). Comparing the IR spectra of $(CuBr)_2P_8Se_3$ and of $(CuI)_2$ P_8Se_3 a more pronounced splitting of the bands becomes obvious for $(CuI)_2P_8Se_3$. For example, the broad band at 437 cm^{-1} in $(CuBr)_2P_8Se_3$ splits into a double band at 436 and 423 cm^{-1} in $(CuI)_2P_8Se_3$. The same is found for the bands at 344 and 142 cm^{-1}. However, this effect might be due to a better crystalline sample of $(CuI)_2P_8Se_3$ resulting in bands with smaller half-widths since no reduction of symmetry is present.

Contrary to the IR spectra, the relative intensities of the Raman spectra of the two homologous compounds differ quite drastically, see Fig. 4. However, at the present stage we cannot comment on this finding. The pronounced tendency of the splitting of the bands can also be observed in the Raman spectra, e.g. at 418 and 347 cm^{-1} ($(CuBr)_2P_8Se_3$).

The bending mode region of the P_8Se_3 molecule as well as the Cu–X stretching mode region can be expected at wavenumbers below 220 cm^{-1} and superimposition cannot be excluded. A separation of bending and stretching mode regions comparable to other phosphorus chalcogenide molecules does not become obvious from the spectra of the compounds under discussion.

A helpful correlation was found to identify the Cu–X modes beside the P_8Se_3 bending modes. The Cu–X stretching modes depend on the bond distances d(Cu–X) in copper(I) halide phosphine complexes [19–21]. The Cu–X stretching modes of 34 complexes containing terminal Cu–X bonds were correlated with the respective Cu–X distances. It was shown that the vibrational frequencies of the Cu–X modes are independent of the nature of the phosphine ligands. Based on this correlation the Cu–X modes of $CuBrSe_3$ and $CuISe_3$ reported by Sarfati and Burns [22], i.e. $(CuX)_2Se_6$ with molecular neutral selenium rings Se_6, were clearly identified and the vibrational frequencies were fitted to the distances observed in the crystal structures. These materials show some structural similarities with the compounds under discussion as they also exhibit some kind of copper halide matrix and neutral molecules embedded therein, cf. [1]. Fig. 5 shows the correlation of the data reported in Refs. [19,22] extended by the corresponding data for the compounds under discussion in this work. Due to the excellent fit, the bands at 125–173 cm^{-1} are assigned to Cu–Br stretching modes and the bands at 135–178 cm^{-1} to Cu–I stretching modes.

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[21] ($\nu = b(r)^{-m}$ with $\nu =$ wavenumber (cm^{-1}), $r =$ bond distance (Å), $b = 18{,}000$ (Br) 32,300 (I) and $m = 5.2$ (Br) 5.6 (I)).
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