Inorg. Chem. **2003**, *42*, 658–660

Inorganic Chemistry
Communication

Toward an Arsenic Analogue of Hittorf's Phosphorus: Mixed Pnicogen Chains in $Cu_2P_{1.8}As_{1.2}I_2$

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Received July 22, 2002

The new compound $Cu_2P_{1.8}As_{1.2}I_2$, with neutral, mixed pnicogen chains, has been synthesized from a stoichiometric combination of CuI, P, and As heated in vacuo at 550 °C. $Cu_2P_{1.8}As_{1.2}I_2$ represents substitution of 40% of P in $Cu_2P_3I_2$ by As, with the As predominantly occupying "roof" positions in the tubular chains. The mixed pnicogen modification demonstrates increased stability (T_d = 330 °C) relative to $Cu_2P_3I_2$ (T_d = 290 °C) but a similar optical band gap ($E_g \sim 1.2$ eV). Crystallographic data: $Cu_2P_{1.8}As_{1.2}I_2$, monoclinic $P2_1/c$, $a = 15.477(3)$ Å, $b = 13.200(3)$ Å, $c = 15.421(3)$ Å, $\beta = 115.406(4)°$, $Z = 16$ ($T = 293$ K).

The copper(I) phosphorus halides are a small but unique class of compounds that feature either neutral or anionic tubular chains of phosphorus. Representative compounds include $Cu_2P_3I_2$,[1] CuP_7I,[2] CuP_4I[3] (neutral); $Cu_3P_{15}I_2$,[4] and $Cu_{12}P_{20}Br_{10}$ (anionic).[5] Compounds with neutral chains are known to demonstrate moderate copper ion conductivity, in contrast to their anionic congeners. $Cu_2P_3I_2$ is the best conductor of those studied to date;[6] however, the conductivity is still several orders of magnitude less than that of the best copper ion based solid electrolytes.[7] It is reasonable to expect that the ionic conductivity can be enhanced in these materials if phosphorus can be substituted by a more polarizable atom while maintaining charge neutrality.[8] Accordingly, we have set out to explore substitution of P in $Cu_2P_3I_2$ by the more polarizable pnicogens, As and Sb.

The parent compound, $Cu_2P_3I_2$, contains neutral, linear tubes of phosphorus, similar to those found in Hittorf's Phosphorus: the only crystallographically characterized modification of red phosphorus.[9] The polymeric chains within $Cu_2P_3I_2$ consist of eight-membered units (themselves produced from fused five-membered rings) linked together via four-membered square rings in an alternating arrangement. The chain can be formulated as $^1_\infty([P8]P4(4)[])^0$ according to nomenclature rules set forth by Böcker et al.[10] These tubes are surrounded by Cu^+ and I^-, with the copper ions distributed over multiple partially occupied sites, contributing to the relatively high copper ion conductivity in $Cu_2P_3I_2$.

Initially, heavier pnicogen analogues of stoichiometries "$Cu_2As_3I_2$" and "$Cu_2Sb_3I_2$" were targeted. Despite an extensive range of heating conditions, no ternary materials were found in the Cu−Pn−I phase diagrams (Pn = As, Sb).[11] This is perhaps not a surprise because elemental As and Sb are not known to form tubular structures, as does P. However, As *is* reported to substitute for up to 5% of P in Hittorf's Phosphorus, occupying only the "roof" positions in the strained 5-fold P8 units.[9] We have begun to investigate the ability to substitute As into the related chains in $Cu_2P_3I_2$ and find that it is possible to incorporate surprisingly large quantities of As (up to ca. 50%). Herein, we report the synthesis, structure, and physicochemical properties of one such phase, $Cu_2P_{1.8}As_{1.2}I_2$ (40% As), which represents, to date, the best case for an arsenic analogue of Hittorf's Phosphorus.

$Cu_2P_{1.8}As_{1.2}I_2$ was synthesized by heating a pressed pellet containing stoichiometric amounts of CuI, red phosphorus, and elemental arsenic in an evacuated fused-silica tube at 550 °C for 2 weeks. The product is obtained as dark, shiny, needlelike crystals[12] in conjunction with a black, polycrystalline pellet residue. Single-crystal X-ray diffraction data were collected in order to verify the structure, determine if

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(9) (a) von Schnering, H. G.; Hönle, W. *Chem. Rev.* **1988**, *88* (1), 242−269. (b) The chains can be formulated[10] as $^2_\infty([P8]P2[P9]P2[])^0$.

(10) Böcker, S.; Häser, M. *Z. Anorg. Allg. Chem.* **1995**, *621*, 258−286.

(11) A literature search suggests no existing phases in the Cu−Pn−I phase diagram (Pn = As, Sb). In our studies, reaction temperatures of 400−1000 °C and periods of 1−3 weeks were explored; CuI and As(Sb) were obtained as products.

(12) Samples of $Cu_2P_{1.8}As_{1.2}I_2$ were prepared for ICP-MS from a sample of ground crystals dissolved in concentrated HNO_3. Analytical data: Cu (43(4) ppm), P (19(2) ppm), and As (32(3) ppm); formula $Cu_{1.95}P_{1.77}As_{1.23}$, assuming total pnicogen (P + As) equal to 3.0.

10.1021/ic0258936 CCC: $25.00

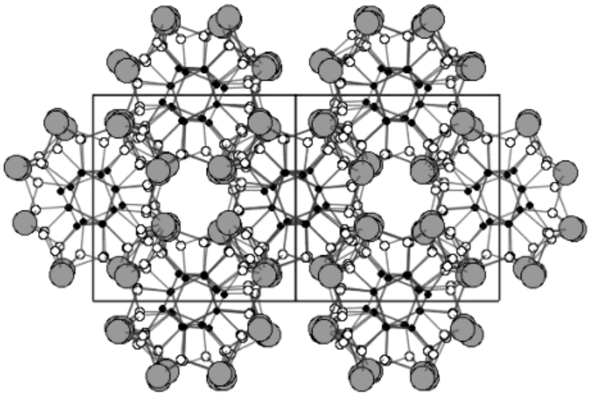

Figure 1. Structure of $Cu_2P_{1.8}As_{1.2}I_2$ viewed down the [101] direction. Phosphorus, copper, and iodine atoms are shown as black, open, and gray spheres, respectively.

there is any site preference for As within the polymeric chain, and evaluate the influence of pnicogen substitution on the degree of copper disorder.[13]

$Cu_2P_{1.8}As_{1.2}I_2$ (Figure 1) is fundamentally isostructural to $Cu_2P_3I_2$;[14] however, the structure is more complex because of shared occupancy of the pnicogen positions by P and As, and an increased number of partially occupied copper sites. As indicated in Table 1, the distribution of As over the pnicogen sites is not random. Rather, there is a preference of, on average, 2:1 for As to occupy the "roof" positions of the P8 units, P/As(7) and P/As(10) (Figure 2a, Table 1), relative to the other positions. These positions are the most strained within the polymer.[9a,15] Incorporation of the larger, more polarizable As at these sites presumably decreases the strain, analogous to the case of Hittorf's Phosphorus.[9a] In keeping with this observation, the mixed pnicogen phase demonstrates increased stability with respect to thermal decomposition relative to the pure phosphorus phase. Thermal gravimetric analyses of the two phases show a clear difference in initial weight loss (Figure 3), with the onset of decomposition for $Cu_2P_{1.8}As_{1.2}I_2$ occurring at a temperature substantially higher than that for $Cu_2P_3I_2$ (330 °C vs 290 °C).[16]

Table 1. Site Occupancy Factors (SOFs)[a] for P/As and Cu Atoms of $Cu_2P_{1.8}As_{1.2}I_2$

atom	occupancy	atom	occupancy
P/As (1)	0.65/0.347(10)	P/As (7)	0.26/0.736(11)
P/As (2)	0.70/0.300(11)	P/As (8)	0.58/0.424(11)
P/As (3)	0.76/0.241(11)	P/As (9)	0.64/0.355(11)
P/As (4)	0.58/0.423(11)	P/As (10)	0.35/0.647(11)
P/As (5)	0.64/0.357(11)	P/As (11)	0.53/0.467(11)
P/As (6)	0.65/0.349(11)	P/As (12)	0.53/0.473(11)
Cu(1)	0.471(13)	Cu(13)	0.316(16)
Cu(2)	0.776(14)	Cu(14)	0.137(14)
Cu(3)	0.778(13)	Cu(15)	0.605(13)
Cu(4)	0.59(2)	Cu(16)	0.11(2)
Cu(5)	0.620(13)	Cu(17)	0.19(6)
Cu(6)	0.194(15)	Cu(18)	0.176(19)
Cu(7)	0.192(18)	Cu(19)	0.088(18)
Cu(8)	0.247(15)	Cu(20)	0.100(18)
Cu(9)	0.426(13)	Cu(21)	0.057(14)
Cu(10)	0.617(14)	Cu(22)	0.090(16)
Cu(11)	0.656(13)	Cu(23)	0.09(2)
Cu(12)	0.47(6)		

[a] The SOF is equal to 1 for a fully occupied position. The SOFs for Cu(1)−Cu(23) were constrained to sum up to 8. A sum of 7.43 was obtained when the occupancies were refined freely. The difference in the *R* values before and after the constraint was added to the instruction file was negligible. Iodine sites were fully occupied.

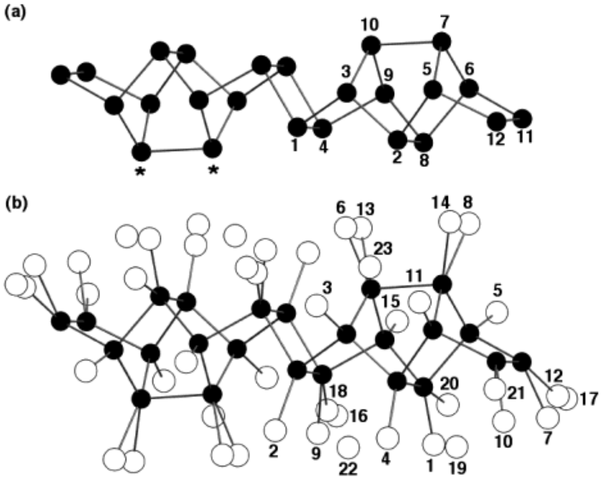

Figure 2. (a) Fragment of the ${}^{1}_{\infty}([\mathrm{Pn8}]\mathrm{Pn4}(4)[\,])^{0}$ chain found in $Cu_2P_{1.8}As_{1.2}I_2$ (Pn = P/As). Asterisks represent the "roof" positions, which contain the largest amounts of As. (b) ${}^{1}_{\infty}([\mathrm{Pn8}]\mathrm{Pn4}(4)[\,])^{0}$ chain shown with neighboring Cu atoms.

In $Cu_2P_{1.8}As_{1.2}I_2$, each P/As atom is bound to three other P/As atoms to form the ${}^{1}_{\infty}([\mathrm{Pn8}]\mathrm{Pn4}(4)[\,])^{0}$ polymer (Pn = P/As), and one or two copper atoms, completely analogous to the parent compound. However, because of arsenic incorporation, all P/As−P/As bond distances in $Cu_2P_{1.8}As_{1.2}I_2$ are considerably longer than the P−P bond distances found in $Cu_2P_3I_2$ (average distances: 2.38(5) vs 2.23(3) Å, respectively). Furthermore, the P/As−P/As bond lengths in $Cu_2P_{1.8}As_{1.2}I_2$ correlate well with the quantity of As incorporation: P/As(7)−(10) = 2.524(4) Å (average As occupancy: 0.69), P/As(2)−(3) = 2.285(6) Å (average As occupancy: 0.27).

As anticipated, none of the copper positions in the structure of $Cu_2P_{1.8}As_{1.2}I_2$ are fully occupied (Table 1). Indeed, the degree of disorder is quite high: 32 copper atoms are distributed over 92 atomic positions in the unit cell of the mixed pnicogen phase (occupancy range: 0.06−0.78), relative to 60 atomic positions reported for $Cu_2P_3I_2$ (occupancy range: 0.15−0.97). Furthermore, unlike the parent compound, there are a number of copper atoms residing at locations that are well outside Cu−As/P bonding distances.

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(13) (a) Crystal data at 293(2) K: Bruker P4/CCD single-crystal diffractometer, Mo Kα radiation ($\lambda = 0.71073$ Å), monoclinic, $P2_1/c$, $a = 15.477(3)$ Å, $b = 13.200(3)$ Å, $c = 15.421(3)$ Å, $\beta = 115.406(4)°$, $V = 2845.9(9)$ Å^3, $Z = 16$, $D_c = 4.948$ mg/m^3, crystal dimensions 0.04 × 0.16 × 0.04 mm^3, $\mu = 20.825$ mm^{-1}, $2\theta = 1.46-28.37°$, 20385 total reflections, 6856 unique reflections with $R(\mathrm{int}) = 0.054$, refinement on F^2, GOF = 1.045, 384 parameters, R1[13b] = 7.43%, wR2 = 19.99% for $I > 2\sigma(I)$. An empirical absorption correction was done using SADABS,[13c] and all atoms except for Cu(16) through Cu(23) were refined anisotropically. Structure solution and refinement was performed using the SHELXTL[13c] package of crystallographic programs. (b) *R*-values are slightly high because of crystal twinning that was prevalent in our samples, as well as in $Cu_2P_3I_2$ (ref 1). (c) Bruker Analytical X-ray Instruments, Inc., Madison, WI.

(14) Lattice parameters for $Cu_2P_3I_2$: $P2_1/c$, $a = 15.343(2)$ Å, $b = 12.925(2)$ Å, $c = 15.260(2)$ Å, $\beta = 116.38(1)°$.[1]

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(16) Thermogravimetric analyses were performed on a Pyris 1 TGA instrument. Samples were analyzed in ceramic pans at a heating rate of 2 °C/min to 500 °C and 10 °C/min from 500 to 800 °C in N_2.

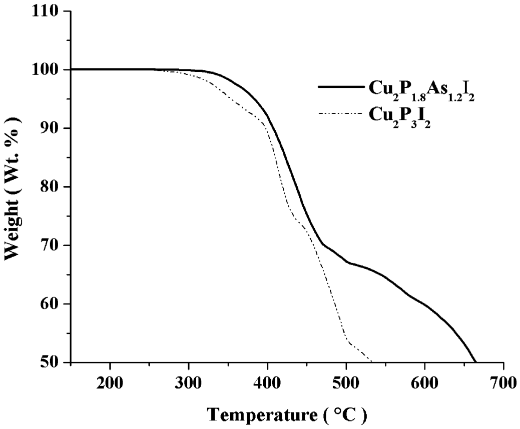

Figure 3. Thermal gravimetric analysis weight loss curves for $Cu_2P_{1.8}As_{1.2}I_2$ and $Cu_2P_3I_2$.

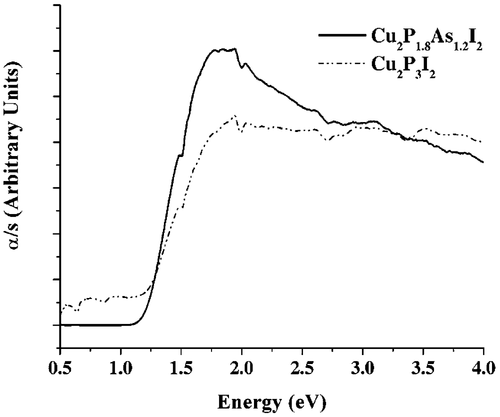

Figure 4. Optical diffuse reflectance spectra (converted to absorption) for $Cu_2P_{1.8}As_{1.2}I_2$ and $Cu_2P_3I_2$. The discontinuity at 1.5 eV is due to a change in detector.

Cu(16), Cu(17), Cu(19), Cu(22), and Cu(23) range from 2.83(7) to 2.99(8) Å to the nearest P/As atom (Figure 2b). In contrast, the rest of the Cu positions are, on average, 2.20(8) Å from P/As positions, similar to distances found in $Cu_2P_3I_2$ (2.25(4) Å), and form, as expected, a distorted tetrahedral geometry (one pnicogen, three iodine atoms). A closer look at the structure reveals that these five "non-bonded" Cu positions are located between two P/As chains along the edges of the square array of pnicogen chains (Figures 1 and 2b). Therefore, these copper atoms are bonded only to iodine atoms. The iodine atoms, in turn, have only copper atoms as nearest neighbors (Figure 1), and throughout the structure, each iodine atom is bound to 8−10 copper atoms.

The powder X-ray diffraction (PXRD) pattern of the ground crystals of $Cu_2P_{1.8}As_{1.2}I_2$ is fully consistent with the single crystal data. Over 30 intense reflections were refined using least-squares methods to yield room temperature lattice parameters: $a = 15.466(7)$ Å, $b = 13.206(2)$ Å, $c = 15.420(7)$ Å, $\beta = 115.39(3)°$,[17] virtually identical to those obtained from the single crystal refinement. Therefore, it appears that the bulk product of the reaction is quite uniform with respect to arsenic concentration. In harmony with this conclusion, the PXRD peaks are all quite narrow (FWHM $\sim$ 0.1°), suggesting only a very limited range of lattice parameters present in the samples.

Optical diffuse reflectance measurements[18] of the new compound and that of $Cu_2P_3I_2$ show that the band gaps for both compounds are surprisingly similar: $\sim$1.2 eV (Figure 4). Because a significant change in the local density of states (DOS) for the polymer would be expected upon arsenic substitution, the implication is that the local bands for the polymer are well outside of the band gap region for these materials. This is consistent with data obtained from other neutral phosphorus tubular polymers, which typically show a much larger band gap (2.0−2.25 eV).[9a] Accordingly, the semiconducting properties of $Cu_2P_3I_2$ and its derivatives would appear to be largely attributed to the highly defective CuI sublattice.

Despite minimal influence on the electronic properties, the arsenic substitution is expected to have a profound influence on the dielectric properties. The presence of a significant fraction of copper ions ($\sim$7%) that are *not* bonded to the pnicogen atoms, is expected to result in enhanced Cu ion conductivity in $Cu_2P_{1.8}As_{1.2}I_2$ relative to $Cu_2P_3I_2$. Accordingly, impedance measurements on a series of arsenic incorporated samples will be undertaken in the near future.

Acknowledgment. Financial support for this work was provided by Research Corporation (Research Innovation Award, R10617), Wayne State University-Institute of Manufacturing Research, and NSF-CAREER (DMR-0094273). We thank Mercouri Kanatzidis at Michigan State University for use of band gap measurement facilities.

Supporting Information Available: X-ray crystallographic file for $Cu_2P_{1.8}As_{1.2}I_2$ in CIF format, a description of how the structure was modeled, an ortep diagram illustrating thermal ellipsoids, and results of least squares refinement of the powder X-ray diffraction data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Peaks were refined using the program CELREF V3 with silicon as an internal standard. Only peaks of <3% relative intensity were discarded from the refinement. The powder XRD pattern of the crystals does not show any peaks due to starting materials, although the residual polycrystalline pellet contains small amounts of unreacted CuI.

(18) (a) Optical diffuse reflectance measurements were performed at room temperature using a UV−vis/near-IR scanning spectrophotometer. The reflectance versus wavelength data generated were used to estimate the band gap of the material by converting reflectance to absorption data.[18b] E_g calculated from electrical conductivity measurements of $Cu_2P_3I_2$ suggested a value of 0.72 eV.[1] (b) Wendlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966.