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The crystal structure of Cu_3PSe_4 and other ternary normal tetrahedral structure compounds with composition 1_356_4.

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Cu_3PS_4 and Cu_3PSe_4 both have the enargite structure type, a wurtzite-related normal tetrahedral structure type. The space-group is $Pmn2_1$ (C^2_{7v}) and there are 2 formula units in the unit cell, which has the following dimensions: Cu_3PS_4: $a=7{\cdot}296$, $b=6{\cdot}319$ and $c=6{\cdot}072$ Å and Cu_3PSe_4: $a=7{\cdot}697$, $b=6{\cdot}661$ and $c=6{\cdot}381$ Å. Cu_3SbS_4 and Cu_3SbSe_4 both crystallize with the famatinite structure type, a zincblende-related normal tetrahedral structure type. The space group is $I\bar{4}2m$ (D^{11}_{2d}) and there are 2 formula units per unit cell. The cell constants are: Cu_3SbS_4: $a=5{\cdot}385$ and $c=10{\cdot}754$ Å and Cu_3SbSe_4: $a=5{\cdot}645$ and $c=11{\cdot}275$ Å.

The compositions and structural features of tetrahedral structure compounds are properly described by simple electron rules which have been adequately discussed in the literature (Parthé, 1967, 1971, 1972). To verify and corroborate these rules a series of structure determinations on tetrahedral structures had been performed (Parthé, Yvon & Deitch, 1969; Joubert-Bettan, Lachenal, Bertaut & Parthé, 1969; Parthé & Garin, 1971). This paper describes the results of some additional experimental studies on ternary normal tetrahedral structures which occur with normal valence compounds. Using the rules it can be shown that only five compositions are possible for two-cation compounds:

$$(13)6_2,\ (24)5_2,\ (1_24)6_3,\ (14_2)5_3 \text{ and } (1_35)6_4$$

where the large numerals indicate the valence electron contribution of the individual elements and the subscripts are the conventional chemical composition parameters. Compounds with these compositions should have wurtzite or zincblende superstructures.

The compounds of particular interest in this study are the 1_356_4 compounds for which we know the orthorhombic wurtzite-related enargite (Cu_3AsS_4) type, and the tetragonal zincblende-related famatinite (Cu_3SbS_4) type. For the compounds which contain copper there are data available for Cu_3PS_4 and Cu_3AsS_4 (enargite) both with enargite structure and for Cu_3AsS_4 (luzonite), Cu_3AsSe_4, Cu_3SbS_4 (famatinite) and Cu_3SbSe_4, all four with famatinite structure. A complete and exact structure determination has been made only for enargite, Cu_3AsS_4, by Adiwidjaja & Löhn (1970) and for luzonite, Cu_3AsS_4, by Marumo & Nowacki (1967). We decided to study the structures of the 1_356_4 compounds for the following reasons. The unit-cell dimensions reported for Cu_3PS_4 (Ferrari & Cavalca, 1948; Nitsche & Wild, 1970) are doubtful as they are virtually identical with those for enargite Cu_3AsS_4. The atom positions for the prototype famatinite Cu_3SbS_4 have not been listed in the original paper by Gaines (1957). The atomic positions may be however derived as idealized values, that is as simple unit-cell fractions from a figure given in Gaines's paper. Further, the electron rules suggest that the same structure types might be found with other related yet unknown compounds with the same valence electron concentration.

We have synthesized four compounds: Cu_3PS_4, Cu_3PSe_4, Cu_3SbS_4 and Cu_3SbSe_4. They were prepared in sealed quartz tubes by heating a mixture of the component elements. Cu_3PSe_4 was kept at 800°C for 10 days and then cooled slowly. In the case of Cu_3SbS_4 it was necessary to fill the tube partially with nitrogen to decrease the partial pressure of sulfur. Tubes with $\frac{2}{3}$ atm of nitrogen were heated very slowly to 600°C, kept there for 3 days and then slowly cooled to room temperature.

A complete structure determination using single-crystal intensity data measured on a computer-controlled Picker four-circle diffractometer was made with Cu_3PSe_4 and Cu_3SbS_4. The experimental procedure and the programs used are identical to those already described in our earlier publication on Cu_2GeSe_3 and Cu_2SiS_3 (Parthé & Garin, 1971). In the case of Cu_3PS_4 and Cu_3SbSe_4, powder intensity data were used to refine the unit-cell dimensions and to verify the structure type in general terms without making any effort to refine the atom positions.

Cu_3PSe_4: Weissenberg and precession photographs indicate an orthorhombic unit cell with the refined lattice par ameters

$$a=7{\cdot}697\pm0{\cdot}002,\ b=6{\cdot}661\pm0{\cdot}002,\ c=6{\cdot}381\pm0{\cdot}002\ \text{Å}.$$

The systematic extinctions $h+l=2n+1$ for $h0l$ reflections lead to the possible space groups $Pmnm$ (D^{13}_{2h}) and $Pmn2_1$(C^7_{2v}). Since the powder pattern intensities show acceptable agreement with those calculated for the enargite type we assumed space group $Pmn2_1$ (C^7_{2v}) and refined the point positions starting from an idealized enargite structure

Table 1. Cu_3PSe_4 *with enargite structure* [*space group* $Pmn2_1$ (C^7_{2v})]. *Point positions, their standard deviations and isotropic temperature factors*

	x	*y*	*z*	*B*
2 Cu in 2(*a*)	0	0·167 (0·0009)	0·500 (0·0001)	1·38
4 Cu in 4(*b*)	0·249 (0·0004)	0·331 (0·001)	0·000 (0·0001)	1·32
2 P in 2(*a*)	0	0·834 (0·002)	0*	2·58
2 Se in 2(*a*)	0	0·832 (0·001)	0·374 (0·0007)	1·56
2 Se in 2(*a*)	0	0·167 (0·001)	0·874 (0·0007)	1·46
4 Se in 4(*b*)	0·249 (0·0004)	0·332 (0·001)	0·376 (0·0006)	1·46

* Value was arbitrarily assumed to be zero.

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but using the single-crystal intensities. 311 independent reflections were measured with the c axis of the crystal mounted parallel to the φ axis of the automatic diffractometer. A graphite monochromator was used to obtain Cu $K\alpha$ radiation. The intensities were corrected for background, Lorentz–polarization and absorption effects. For the refinement the weights of all the reflections were assumed to be constant. The final results with a R value of 0·10 are given in Table 1. The tetrahedral angles vary only between 108·4 and 110·2°. The average observed Cu–Se and P–Se distances both have the value of 2·37 Å (Table 2). We did not find any of the structure transitions reported for Li_3PO_4 (West & Glasser, 1972).

Table 2. *Interatomic distances and angles in* Cu_3PSe_4

Interatomic distances (in Å ± 0·005)	
$Cu(2a)-Se_1(2a)$	2·372
$Cu(2a)-Se_2(2a)$	2·386
$Cu(2a)-Se(4b)$	2·347
$Cu(4b)-Se_1(2a)$	2·357
$Cu(4b)-Se_2(2a)$	2·350
$Cu(4b)-Se(4b)$	2·380
$Se_1(2a)-P(2a)$	2·387
$Se_2(2a)-P(2a)$	2·359
$Se\cdot(4b)-P(2a)$	2·362
Tetrahedral angles (in degrees ± 0·3)	
$Se_1(2a)-P(2a)-Se_2(2a)$	110·2
$Se_1(2a)-P(2a)-Se(4b)$	109·4
$Se_2(2a)-P(2a)-Se(4b)$	109·0
$Se(4b)-P(2a)-Se(4b)$	109·7
$Se_1(2a)-Cu(2a)-Se_2(2a)$	109·8
$Se_1(2a)-Cu(2a)-Se(4b)$	109·0
$Se_2(2a)-Cu(2a)-Se(4b)$	109·7
$Se(4b)-Cu(2a)-Se(4b)$	109·5
$Se_1(2a)-Cu(4b)-Se_2(2a)$	109·7
$Se_1(2a)-Cu(4b)-Se(4b)$	108·4
$Se_2(2a)-Cu(4b)-Se(4b)$	109·3
$Se(4b)-Cu(4b)-Se(4b)$	109·3
$P(2a)-Se_1(2a)-Cu(2a)$	109·5
$P(2a)-Se_1(2a)-Cu(4b)$	110·1
$Cu(2a)-Se_1(2a)-Cu(4b)$	108·5
$Cu(4b)-Se_1(2a)-Cu(4b)$	110·1
$P(2a)-Se_2(2a)-Cu(2a)$	109·9
$P(2a)-Se_2(2a)-Cu(4b)$	108·7
$Cu(2a)-Se_2(2a)-Cu(4b)$	109·9
$Cu(4b)-Se_2(2a)-Cu(4b)$	109·6
$P(2a)-Se(4b)-Cu(2a)$	109·6
$P(2a)-Se(4b)-Cu(4b)$	109·5
$Cu(2a)-Se(4b)-Cu(4b)$	109·6
$Cu(4b)-Se(4b)-Cu(4b)$	109·6

Cu_3PS_4: A powder pattern showed that this compound is isotypic with enargite or Cu_3PSe_4. The refined lattice parameters are:

$$a = 7{\cdot}296 \pm 0{\cdot}002,\ b = 6{\cdot}319 \pm 0{\cdot}002,\ c = 6{\cdot}072 \pm 0{\cdot}002\ \text{Å}.$$

These parameter values are smaller than those for $CuAsS_4$, in agreement with the smaller size of the P atoms as compared with As atoms.

Cu_3SbS_4: Single-crystal film techniques indicated a tetragonal unit cell with the refined parameters

$$a = 5{\cdot}385 \pm 0{\cdot}001,\ c = 10{\cdot}754 \pm 0{\cdot}002\ \text{Å and } c/a = 1{\cdot}997.$$

We can corroborate the space group given for famatinite which is $I\bar{4}2m$ (D_{2d}^{11}). 166 intensities were collected with the crystal mounted with the [110] direction parallel to the φ axis of the machine. Because of the small size of the crystal the intensities were only corrected for background and Lorentz–polarization effects. Using the positions given by Gaines (1957) as starting value, the refinement leads to a weighted R value of 0·09 and the parameters given in Table 3 (weighting scheme: $w = 1/\sigma$ with $\sigma = (F_0^2 + \sigma_o)^{1/2} - F_o$). The interatomic distances and tetrahedral angles are given in Table 4.

Table 4. *Interatomic distances and angles in* Cu_3SbS_4

Interatomic distances (in Å ± 0·004)	
S–Sb	2·405
S–Cu(2*b*)	2·344
S–Cu(4*d*)	2·288
Tetrahedral angles (in degrees ± 0·2)	
S———Sb———S	107·7
S′———Sb———S	110·4
S———Cu(2*b*)-S	105·5
S———Cu(2*b*)-S″	112·0
S———Cu(4*d*)-S	107·9
Cu(4*d*)-S———Cu(4*d*)	110·4
Cu(2*b*)-S———Cu(4*d*)	110·4
Sb——S———Cu(4*d*)	108·3
Sb——S———Cu(2*b*)	106·6

Cu_3SbSe_4: A powder pattern indicates isotypism with famatinite. The refined lattice parameters

$$a = 5{\cdot}645 \pm 0{\cdot}001,\ c = 11{\cdot}275 \pm 0{\cdot}002\ \text{Å and } c/a = 1{\cdot}997$$

are not too different from the values given by Busch & Hulliger (1960) and Johan, Picot, Pierrot & Kvaček (1971).

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Table 3. Cu_3SbS_4 *with famatinite structure* [*space group* $I\bar{4}2m$ (D_{2d}^{11})]. *Point positions, their standard deviations and isotropic temperature factors*

	x	*y*	*z*	*B*
2 Cu in 2(*b*)	0	0	½	3·62
4 Cu in 4(*d*)	0	½	¼	3·59
2 Sb in 2(*a*)	0	0	0	0·59
8 S in 8(*i*)	0·255 (0·001)	0·255 (0·001)	0·132 (0·0007)	2·54

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A rapid method of assessing the number of molecules in the unit cell of an organic crystal.

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A rough relationship is empirically derived between the volume of the unit cell of an organic crystal and the number of atoms it contains.

When the unit cell of a crystal has been derived, one needs to know the number of atoms that it contains before deciding whether the determination of its structure is practicable. The determination of the density can be time-consuming, and it is the purpose of the present note to point out that for organic crystals the result can be derived accurately enough from the volume of the unit cell alone.

Organic molecules normally crystallize in a space group which permits fairly close packing with a minimum of empty space between molecules (see, for example, Kitaigorodsky, 1957). This behaviour presumably arises from the non-directional nature of van der Waals forces, and is not seriously affected by a small proportion of hydrogen bonds between molecules or by a few 'foreign' atoms. Since carbon, oxygen and nitrogen atoms are about the same size, there should be a roughly linear relation between the volume and the number of atoms (excluding hydrogen). We have made the calculations for forty crystals, arbitrarily chosen, and the result is shown in Fig. 1. It will be seen that for most crystals $N \simeq V/18$. The individual points are shown in order to indicate the spread of the relationship.

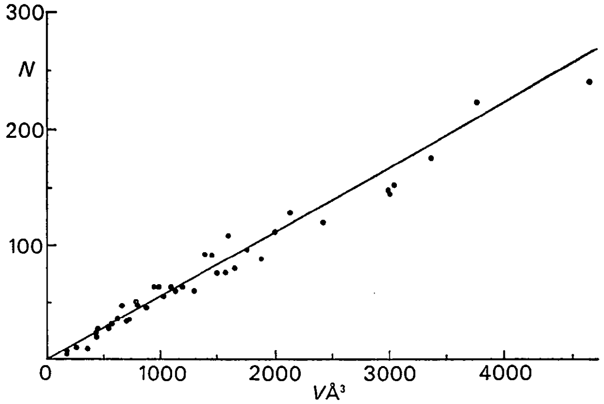

Fig. 1. Relation between the number of C, N, O atoms in the unit cell and the volume of the unit cell for 40 arbitrarily chosen crystals. A few crystals contain other atoms, which are also included.

The graph can be used to estimate the number of C, N and O atoms in a given unit cell to an accuracy of about 10%. This should be adequate for determining the number of molecules. We must emphasize that it should be used only for a first estimate; the final figure should always be checked by an accurate determination of the density.

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Structural relationships in compounds with $R\bar{3}c$ symmetry: erratum.

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The values of c/a and α_r for $LaAlO_3$ in Table 1 of Michel, Moreau & James [*Acta Cryst.* (1971), B**27**, 501] should be 2·443 and 60·10.

Dr Helen Megaw has pointed out to us an error in Table 1 of our paper (Michel, Moreau & James, 1971). The values of c/a and α_r for $LaAlO_3$ should read 2·443 and 60·10 rather than 2·462 and 59·90 respectively. The corrected values are taken from Geller & Bala (1956).

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