Heteroatom Chemistry
Volume 4, Number 4, 1993

Crystal Structure and Vibrational Spectrum of Copper Mercury ortho-Thiophosphate $CuHgPS_4$

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Received 11 May 1992

ABSTRACT

The compound $CuHgPS_4$ crystallizes in the orthorhombic system, space group $Pna2_1$ (No. 33), $Z = 4$, with lattice parameters $a = 12.660(3)$, $b = 7.3498(7)$, $c = 6.0943(4)$ Å, and $\delta_{calc} = 4.96$ g/cm^3. The title compound is stable in air and moisture and behaves as a semiconductor. The crystal structure consists of discrete tetrahedral PS_4^{3-} anions joined together by Cu^+ and Hg^{2+} cations. The arrangement of the sulfur atoms is approximately hexagonal close-packed in which P, Cu, and Hg occupy tetrahedral sites. The PS_4, HgS_4, and CuS_4 tetrahedra are slightly distorted with mean distances $d(P–S) = 2.055$, $d(Hg–S) = 2.524$, and $d(Cu–S) = 2.320$ Å, and 8% of the Hg atoms were found to be disordered, occupying interstitial tetrahedral sites. The title compound is isotypic to $AgZnPS_4$ and can be considered to be a defect structure of Enargite (Cu_3AsS_4), which is a substitution derivative of the Wurtzite (ZnS) structure. The $CuHgPS_4$ vibrational spectrum has been recorded. The internal modes experimentally observed are in accord with the factor group prediction. A tentative assignment of the vibrational frequencies is proposed.

INTRODUCTION

In previous articles, it was shown that the kind of thiophosphate species formed in high-temperature syntheses is not only dependent on the stoichiometry of the element mixtures but also on the cation and its preferred oxidation state with sulfur [1–3]. So, trivalent cations yield mostly ortho-thiophosphates of the type $Me(III)PS_4$; however, ternary $Me(I)Me(II)PS_4$ ortho-thiophosphates could also be obtained under certain conditions, e.g., $AgZnPS_4$ [4], $TlSnPS_4$ [5], and $TlEuPS_4$ [2], respectively. The title compound [6] is isostructural to $AgZnPS_4$, and the vibrational spectrum of $CuHgPS_4$ is reported as the first example of this structure type.

EXPERIMENTAL

Sample Preparation

The title compound was obtained using high-temperature element synthesis (900°C, 4d) of stoichiometric amounts in evacuated and sealed quartz glass tubes (cf. Ref. [2]). The synthesis proceeds completely to a homogeneous product, which consists of dark red prismatic crystals of $CuHgPS_4$, stable in air and moisture.

A band gap of 1.84 eV, typical for semiconductors, has been derived from diffuse reflection spectra. Differential thermal analysis measurements have shown no phase transition, but decomposition takes place above 930°C.

Structure Determination

The preliminary data obtained from oscillation photographs indicated a primitive orthorhombic

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TABLE 1 Parameters Used for the X-ray Data Collection

Diffractometer type	Stoe-Stadi4
Wavelength	MoK_α radiation (0.7107 Å)
Crystal characteristics	Red prism, δ_{calc} = 4.96 g/cm^3
Temperature	293 K
$2\vartheta_{max}$	80°
Unique reflections	3262
Criterion for unobserved reflections	$F_0 < 3\sigma\ (F_o)$
Refined parameters	69
Scan mode	2ϑ-ω
μ	305.4 cm^{-1}
Structure solution program	SHELX

cell. The conditions for $(0kl)$ reflections were $k + l = 2n$ and for $(h\ 0\ l)$ reflections $h = 2n$, which are consistent with the space group $Pna2_1$ or Pnam (=Pnma). Consideration of these features together with the magnitude of the unit cell dimensions and the composition suggested that $CuHgPS_4$ might be isotypic with $AgZnPS_4$ [4]. Thus, the noncentrosymmetric space group $Pna2_1$ was chosen and finally confirmed in the refinement.

The single-crystal X-ray measurements were accomplished with a computer controlled Stoe-Stadi4 (MoK_α radiation) automatic diffractometer. In the range $3° < 2\vartheta < 80°$, a total of 5055 intensities of reflections, which follow the space group conditions, were measured. After averaging symmetry related reflections, the original data set was reduced to 3262 independent reflections of which 2673 reflections with F_0 values larger than $3\sigma(F_0)$ were used. The structure was refined using the full matrix least-squares SHELX program [7]. Complex neutral scattering factors were taken from Ref. [8]. Relevant experimental data are summarized in Table 1.

For initial values of the positional parameters, the atomic coordinates of $AgZnPS_4$ were used, but the z coordinates for the atoms in $CuHgPS_4$ were shifted by 1/6 in order to show that those of the sulfur atoms have values near $z = 0$ or $1/2$. With 64 refined parameters, the R value dropped to 0.0824. Inspection of the electron density difference maps reveals the existence of a significant peak (equivalent to 8% of the Hg peak or 22% of the Cu peak) at the interstitial position (0.342, 0.503, 0.165). Furthermore, a preliminary refinement of the occupancy factor of Hg and Cu indicated a significant amount of vacancies only in the Hg site. Taking into account the principle of charge neutrality, a partial disordering of the mercury atoms was then considered and the other possibility that the interstitial site would be occupied by copper was rejected. So, in the final refinement, the positional parameters of the extra peak (denoted Hg12), its occupancy factor, and its isotropic temperature factor together with the occupancy factor of mercury (denoted Hg11) were introduced, and the reliability factor dropped to R = 0.0573. This result substantiated the model of partial disordered Hg. The final refinement on F (2673 reflections and 69 refined parameters) gave the following reliability factors:

$$R(F) = 0.0573 \text{ and } R_w(F) = 0.0518$$

The results from the final refinement are presented in Tables 2 and 3.[*]

STRUCTURE DESCRIPTION

The most relevant building elements in the structure of $CuHgPS_4$ are discrete tetrahedral PS_4^{3-} units, which are linked by the Cu^+ and Hg^{2+} cations (Figure 1). The PS_4^{3-} units are slightly distorted, as the bond angles vary between 104^0 and 117^0, and the P–S bond lengths are in the range of 2.048 to 2.062 Å (Table 3). The $CuHgPS_4$ structure can also be described as a hexagonal close-packing arrangement

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[*] The observed and calculated structure factors have been deposited as Collection No. 300223 in the database of Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen, Federal Republic of Germany.

TABLE 2 Final Structure Data for $CuHgPS_4$, Including Anisotropic (or Isotropic) Thermal Parameters ($\times 10^4$ pm^2)[a]

Atom	x	y	z	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	0.33918(8)	−0.0035(1)	0.1649(4)	163(4)	241(4)	227(4)	−14(3)	−2(8)	18(6)
Hg(11)[b]	0.57245(3)	0.26895(5)	0.166667[c]	195(1)	306(2)	230(1)	−25(1)	−14(2)	25(4)
Hg(12)[b]	0.3412(4)	0.5018(6)	0.163(2)	297(12)	—	—	—	—	—
P(1)	0.4087(1)	0.2419(2)	0.6564(5)	42(5)	115(5)	131(6)	2(4)	3(7)	−6(8)
S(1)	0.3287(2)	0.0185(3)	0.5421(4)	118(8)	150(6)	170(8)	−30(5)	−5(6)	−17(6)
S(2)	0.5652(2)	0.2623(3)	0.5751(4)	57(6)	214(7)	241(8)	4(6)	13(6)	56(7)
S(3)	0.3313(2)	0.4591(3)	0.5163(4)	84(7)	211(7)	222(9)	48(6)	15(6)	82(7)
S(4)	0.3919(2)	0.2591(3)	0.9924(3)	167(8)	194(7)	140(7)	−36(6)	11(6)	4(6)

[a] Standard deviations are given in parentheses. Space group $Pna2_1$ (No. 33), $Z = 4$; unit cell data: $a = 12.660(3)$, $b = 7.3498(7)$, $c = 6.0943(4)$ Å, $V = 567.1$ Å^3. The anisotropic temperature factor is of the following form: $\exp\ [-2\pi^2\ (U_{11}h^2a^{*2} + \ldots + 2U_{13}hla^*c^*)]$.
[b] Defect positions, see text; site occupancies: Hg11, 0.920(2): Hg12, 0.080 (reset).
[c] Arbitrary fixed.

TABLE 3 Main Interatomic Distances (Å) and Angles (°) in $CuHgPS_4$ (Standard Deviations in Parentheses)

Cu(1)-S(4)	2.296(2)	Hg(11)-S(2)	2.491(2)
-S(1)	2.308(3)	-S(3)	2.514(2)
-S(2)	2.320(2)	-S(4)	2.522(2)
-S(3)	2.356(3)	-S(1)	2.570(2)
Hg(12)-S(4)	2.161(7)	P(1)-S(2)	2.048(3)
-S(2)	2.167(6)	-S(1)	2.051(3)
-S(3)	2.18(1)	-S(3)	2.059(3)
-S(1)	2.277(6)	-S(4)	2.062(4)
S(1)-P(1)-S(2)	117.0(1)	S(2)-P(1)-S(3)	107.7(1)
S(1)-P(1)-S(3)	104.2(1)	S(2)-P(1)-S(4)	109.6(1)
S(1)-P(1)-S(4)	109.6(1)	S(3)-P(1)-S(4)	108.4(1)

of puckered sulfur layers (located near $z = 0$ and $z = 1/2$ planes) stacked in the c direction. A fraction of the tetragonal sites in this arrangement is occupied by P, Cu, and Hg, as shown in Figure 2.

The main difference between $CuHgPS_4$ and $AgZnPS_4$ [4] is the presence of mercury Frenkel defects in the structure of the former compound. More specifically, 8% of the mercury atoms are partially disordered, occupying interstitial positions (Figure 2). Otherwise, the average P–S distance is similar in both structures with 2.052 and 2.055 Å for $AgZnPS_4$ and $CuHgPS_4$, respectively. Mean Hg11-S and Cu-S distances with 2.52 and 2.32 Å (Table 3) are very similar to those in the $Cu_6Hg_3As_4S_{12}$ structure (2.53 and 2.33 Å, respectively), where Cu and Hg also occupy tetrahedral environments [9]. The average Hg12-S distance (2.196 Å) is much shorter than the average Hg11-S distance (2.524 Å). This feature is a consequence of the presence of 92% vacancies in the Hg12 sites and signifies the interstitial nature of the Hg12 atoms.

The $AgZnPS_4$ structure type ($a'' = 12.502$, $b'' = 7.599$, $c'' = 6.070$ Å, $V'' = 576.7$ Å^3) can also be considered as an ordered defect superstructure ($a'' = 2a'$) of that of Enargite (Cu_3AsS_4, $Pnm2_1$, $a' = 6.436$, $b' = 7.407$, $c' = 6.154$ Å, $V' = 293.4$ Å^3) [10], which is an ordered substitution superstructure ($a' = \sqrt{3}a$, $b' = 2a$) of that of the Wurtzite (ZnS, $a = 3.84$, $c = 6.28$ Å) hexagonal structure [11].

VIBRATIONAL STECTRUM

The Raman spectrum was recorded with a CODERG PH 1 spectrometer and laser light excitation (Polytec HeNe-Laser, 632.8 nm). The infrared spectrum was obtained from $CuHgPS_4$-PE pellets with a BRUKER IFS 113FT spectrometer. The room-temperature Raman and infrared spectra are shown in Figure 3. The vibrational frequencies are summarized in Table 4 along with their intensities and assignment, and a comparison to those of the PS_4^{3-} ion [12] is also given.

DISCUSSION

The title compound crystallizes in the orthorhombic space group $Pna2_1$ (C_{2v}^9) with four formula units in the unit cell [6]. According to the X-ray structure determination, the spectroscopic relevant unit should be the tetrahedral PS_4^{3-} anion with T_d symmetry. Therefore, the vibrational spectrum should show four fundamentals [13]:

$$\Gamma_{vib}(T_d) = A_1\,(R) + E\,(R) + 2\,F_2\,(R, IR)$$

Compared to the "free" PS_4^{3-} anion in K_3PS_4 [14], the covalent PS_4^{3-} unit in the title compound does not deviate in the P–S distances but varies slightly from T_d symmetry in the two bond angles 104° and 117°, respectively (Table 3). Nevertheless, the spectrum of crystalline $CuHgPS_4$ (Figure 3) cannot be interpreted only by the PS_4^{3-} vibrations, so a factor group analysis was performed. Using the space group $Pna2_1$ with four formula units and the formalism of Ref. [15], the unit cell group analysis ($\vec{k} = 0$) results in a total of 81 optical vibrations

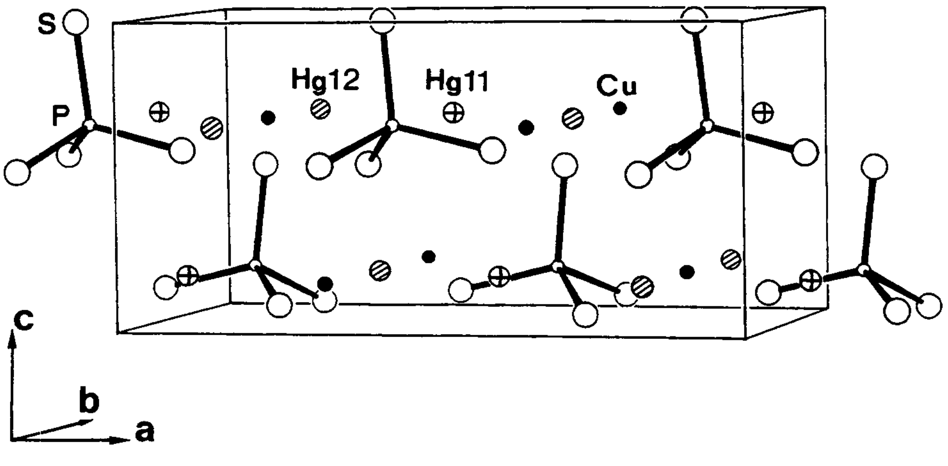

FIGURE 1 Perspective view of $CuHgPS_4$ structure.

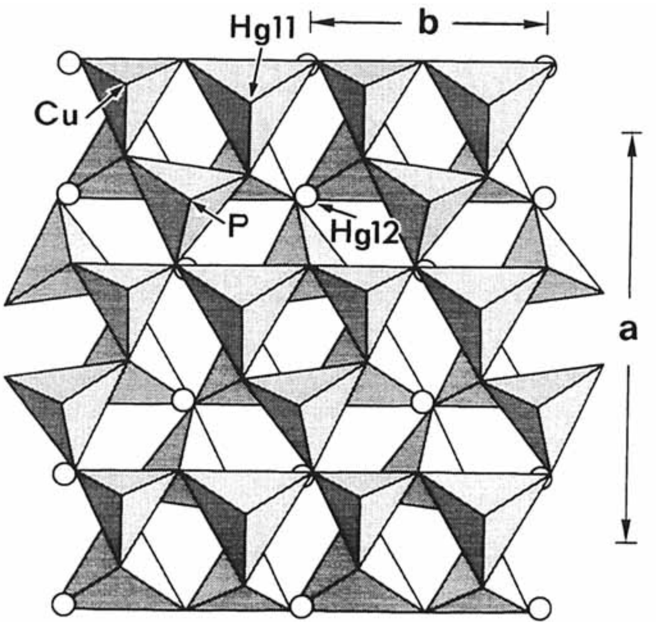

FIGURE 2 Connection of the PS_4, CuS_4, and HgS_4 tetrahedra in the $CuHgPS_4$ structure as viewed along the *c*-axis. The sites of the interstitial Hg12 atoms are indicated as empty circles.

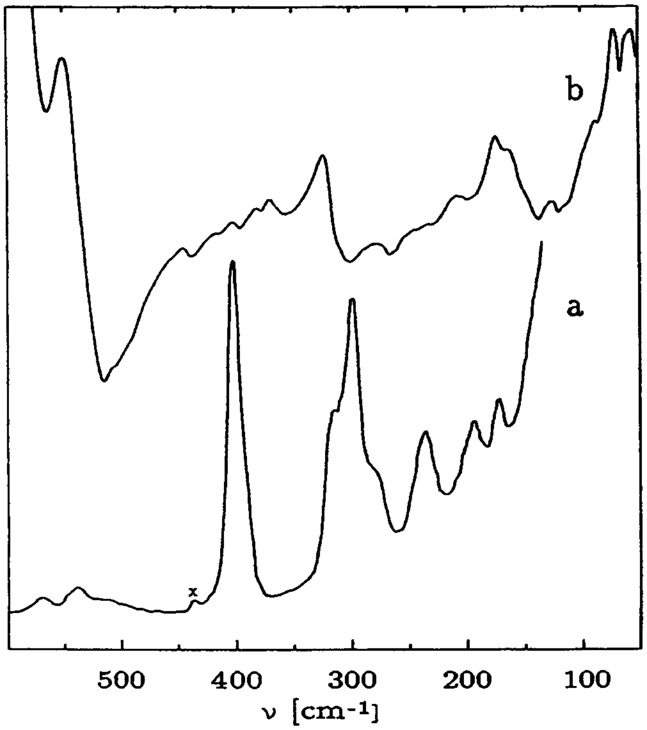

FIGURE 3 Room-temperature (**a**) Raman and (**b**) FIR spectra of $CuHgPS_4$ x = laser line.

(Table 5) which leaves 36 internal vibrations for assignment. Although the reduction of the primitive cell is forbidden, in general [15,16], we carried out a factor group analysis with two and one formula units where 18 (C_2; 9 A (R, IR) + 9 B (R, IR)) and 9 (C_1; 9 A (R, IR)) internal modes remained. Since the symmetry elements and operations of the crystallographic unit cell generate new $CuHgPS_4$ units, the attempt of a factor group analysis was made with one unit and with C_{2v} symmetry of the whole cell. This yielded a distinct basis for the assignment of the $CuHgPS_4$ fundamentals (Table 5) resulting in nine internal vibrations

$$\Gamma_{\text{int}}(C_{2V}) = 2\,A_1\,(R, IR) + A_2\,(R) + 3\,B_1\,(R, IR) + 3\,B_2\,(R, IR)$$

It should be noted that the factor group predictions of $CuHgPS_4$ (orthorhombic system) prevent degenerate vibrations, and so there must be at least nine internal vibrations observed in the spectrum.

The sulfur metal distances cannot be considered as covalent bonds, as the relevant distances (Table 3) are similar to those of related metal chalcogenides (cf. d(Hg–S) in HgS = 2.53 Å [17], d(CuS) in Cu_2S = 2.33 Å [17]) which show, for example, "second-order" Raman spectra [18], thus showing the absence of pure covalent metal sulfur bonds.

Nevertheless, the symmetrical stretching, typical for PS_4^{3-} at 416 cm^{-1} [12], decreases significantly to 402 cm^{-1}. Also, changes of the other fundamentals are seen, and no degeneration of the vibrational modes can be observed. Thus, the splitting of the degenerate vibrations is so pronounced that an interaction between the metal ions and the PS_4^{3-} unit must be considered.

In the vibrational spectrum of the title compound, PS_4^{3-} fundamentals are observed, but they vary somewhat from the vibrational modes of the "free" PS_4^{3-}, and an additional vibrational frequency appears. In HgS, the most intensive Raman band is observed at 256 cm^{-1} [18], and also in Cu_3NbS_4 and Cu_3TaS_4 the metal sulfur vibration is found at 267 cm^{-1} [19]; therefore, the 236 cm^{-1} Raman frequency of $CuHgPS_4$ is assigned to a metal sulfur vibration. Alternatively, the 171 cm^{-1} Raman band could be assigned to this metal sulfur vibration, and then the rest of the assignment would shift down by one line.

Furthermore, startling effects on vibrational frequencies of thiometallates of transition metals, especially for Tl, Ag, Cu, Pb, and Hg, are reported by Müller *et al.* [19]. Additionally, the influence of these cations on the internal vibrations is supported by considering the most intensive Raman bands of the series $CuZnPS_4$, $CuCdPS_4$ [20], and the title compound (410, 405, and 402 cm^{-1}) with similar effects in the thiostannate series (Cu_2ZnSnS_4, Cu_2CdSnS_4, and Cu_2HgSnS_4) [21] or with the spectral features of Ag_3PS_4 and Cu_3PS_4 [22].

In related semiconducting thiophosphate sys-

TABLE 4 Vibrational Frequencies (cm^{-1}) of Crystalline $CuHgPS_4$ and Tentative Assignment in Comparison to the PS_4^{3-} Vibrations

PS_4^{3-} *[12]*	*Assignment* *(T_d)*	*$CuHgPS_4$*		*Tentative Assignment*
		Raman	*FIR/IR*	
			51 m	Lattice modes
			67 m	
			120 m	
			138 m	
215	ν_2 (E)	171 m	168 w	PS_4^{3-} bending modes
		194 m	199 m	
		236 m	228 w	Metal sulfur vibration
		280 m, sh	266 m	PS_4^{3-} bending modes
270	ν_4 (F_2)	298 vs	300 m	
		314 m, sh	320 sh	
			356 m	Combination modes (?)
			378 w	
416	ν_1 (A_1)	402 vs	396 w	ν_s (PS_4^{3-})
		509 br, w	504 sh	PS_4^{3-} stretching modes
548	ν_3 (F_2)	540 m	515 vs	
		570 m	564 m	

s = strong; m = medium; w = weak; v = very; sh = shoulder; br = broad.

TABLE 5 Factor Group Analysis of Crystalline $CuHgPS_4$[a]

Z	*Symmetry*	*Species*	*N*	*T*	*T'*	*R'*	*n_i*	*R*	*IR*
4	C_{2v}	A_1	21	1	11	0	9	+	+
		A_2	21	0	0	4	17	+	−
		B_1	21	1	11	4	5	+	+
		B_2	21	1	11	4	5	+	+
2	C_2	A	21	1	8	3	9	+	+
		B	21	2	7	3	9	+	+
1	C_1	A	21	3	6	3	9	+	+
1	C_{2v}	A_1	5	1	2	0	2	+	+
		A_2	2	0	0	1	1	+	−
		B_1	7	1	2	1	3	+	+
		B_2	7	1	2	1	3	+	+

[a] *Z*-number of formula units; *N*-total number of degrees of freedom; *T*-acoustic modes; *T'*-translatory lattice modes; *R'*-rotary lattice modes; n_i-internal modes of the PS_4^{3-} ion; *R*-Raman activity; and IR-infrared activity.

tems, the nature of the conduction bands is still unclear [23]. Their magnetic measurements indicate little change in the d-electron configuration of the transition metal ions. It is concluded that the conduction band is made of sulfur wave functions and possibly metal wave functions [23]. For $CuHgPS_4$, we assume similar conditions in order to understand the drop of the mentioned frequencies.

ACKNOWLEDGMENTS

The authors wish to thank Prof. Dr. H. G. von Schnering for the kind welcome to his laboratory, Dr. L. Walz for collecting the X-ray data, and D. Grünewald for recording the Raman spectrum.

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