RAPID COMMUNICATION

Cs$_2$CuP$_3$S$_9$: A Chiral Compound with Screw Helices

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The reaction of Cu with a molten mixture of Cs$_2$S/P$_2$S$_5$ produced the quaternary compound Cs$_2$CuP$_3$S$_9$. The bright yellow crystals of Cs$_2$CuP$_3$S$_9$ are stable in air and water for several weeks. The compound crystallizes in the chiral, hexagonal space group $P6_5$ (No. 170) and at 23°C: $a = 15.874(2)$ Å; $c = 35.100(7)$ Å; $V = 7660(3)$ Å$^3$; $Z = 18$. The [CuP$_3$S$_9$]$^{2-}$ chains are composed of an alternating arrangement of tetrahedral Cu$^+$ ions and cyclic [P$_3$S$_9$]$^{-}$ units. The structure contains parallel helical [CuP$_3$S$_9$]$^{2-}$ chains that run along the c-axis. The cyclic [P$_3$S$_9$]$^{-}$ unit derives from the molecular adamantane [P$_4$S$_{10}$] unit with one [PS]$_3$ vertex removed. The title compound was characterized by differential thermal analysis, far-IR, Raman, and single-crystal optical transmission UV/vis spectroscopy. Positive nonlinear optical response and second harmonic generation response was observed.

INTRODUCTION

The use of chalcophosphate fluxes has enabled the discovery of many new chalcophosphate compounds (1). These fluxes are commonly formed by the in situ fusion of $A_2Q/P_2Q_5$ (Q = alkali metal; Q = S, Se), forming a variety of [P$_n$Q$_7$]$^{n-}$ units in a molten polychalcogenide solvent. In these “solutions” metals are oxidized and then “captured” by the various [P$_n$Q$_7$]$^{n-}$ units, building up extended frameworks which, if anionic, are stabilized by alkali cations. This approach has produced several unusual compounds; examples include Cs$_3$M$_2$P$_3$Se$_6$ (M = Cu, Ag) (2), K$_3$M$_3$P$_3$Se$_9$ (M = Cu (3), Ag (4)), ALa$_4$(P$_2$Se$_6$) (5), the mixed-valent $A_4$Au$_{11/2}$Al$_{11/2}$(P$_2$Se$_6$)$_3$ ($A =$ K, Rb) (6), $A_4$Au$_3$P$_2$Se$_8$ ($A =$ K, Rb, Cs) (7), $A_2$Au$_2$P$_2$Se$_5$ ($A =$ K, Rb) (7), $A_2$AuPS$_4$ ($A =$ K, Rb, Cs) (7), $AAuP$_2$S$_7$ ($A =$ K, Rb) (7), K$_3$Cu$_2$P$_2$S$_7$ (8), $A_2$Cu$_3$P$_3$S$_9$ ($A =$ K, Rb) (8), Cs$_2$Cu$_2$P$_2$S$_6$ (8), Rb$_4$Sn$_2$Ag$_4$(P$_2$Se$_6$)$_3$ (9), K$_2$Cu$_2$P$_2$Se$_10$ (10), [Cr$_2$(PS$_4$)$_4$] (6–11), and CsTa$_4$S$_5$(S$_2$)$_2$(PS$_4$)$_3$ (12). One of the lessons learned from these studies, for example, is that increasing the concentration of P$_2$S$_5$ in the flux favors the formation of higher order species such as [P$_2$S$_7$]$^{4-}$ and the cyclic

FIG. 1. ORTEP representation of Cs$_2$CuP$_3$S$_9$ as viewed perpendicular to the c-axis (50% probability ellipsoids). Ellipsoids with octant shading are Cu atoms, boundary and axis ellipsoids are P atoms, boundary ellipsoids are S, and principal and axis ellipsoids are Cs atoms.
[PS₃S₉]⁴⁻ units, whereas increasing the concentration of \( A_2S \) tends to break down those species and stabilize the discrete and fundamental [PS₄]³⁻ unit. In the context of these investigations we have discovered Cs₂CuP₃S₉ (I), a hexagonal chiral compound with helical screw chains of \([CuP₃S₉]₂^{2⁻}\) conforming to a \(6_5\) screw axis (13). Discrete

FIG. 2. (A) View of a long filament of the infinite \([CuP₃S₉]₂^{2⁻}\) chain to show the helical conformation. (B) View down the helical axis of a \([CuP₃S₉]₂^{2⁻}\) chain containing Cu(1). (C) View down the helical axis of a \([CuP₃S₉]₂^{2⁻}\) chain containing Cu(2) and Cu(3). (D) Fragments from each chain showing the adamantane clusters and the atomic labeling scheme.
chiral inorganic helices crystallizing in polar space groups are rare with HgS and elemental Se and Te being examples.

The unit cell of Cs₂CuP₃S₃ (14) is shown in Fig. 1. A careful look reveals three independent helices running down the c-axis. They are composed of alternating cyclic [P₃S₉]³⁻ units chelating in a tridentate fashion to Cu⁺ ions; see Fig. 2. The binding to Cu ions leads to recognizable adamantane [CuP₃S₉] clusters which propagate to form a helix by sharing two sulfur atoms. In all [CuP₃S₉]ₙ⁻ helices in the crystal, all dipoles point in the same direction, giving rise to the P6₃ space group. The three parallel [CuP₃S₉]ₙ⁻ chains in the cell are separated crystallographically into two different kinds: one which consists of a single chain containing Cu(1) propagates and coils around the c-axis itself, and another which consists of two identical helices with their axes located at 1/3, 1/3 and 2/3, 2/3, respectively. The latter contains the atoms Cu(2) and Cu(3). A view of the two types of [CuP₃S₉]ₙ⁻ screw helix is shown in Figs. 2B and 2C. Using a threaded bolt analogy, we can describe the overall side-by-side packing of the helical chains such that the ridges of one fit in the grooves of its nearest neighbors. The average Cu–S distance of the three [CuS₄] tetrahedra is 2.306(9), 2.307(9), and 2.316(7) Å for Cu(1), Cu(2), and Cu(3), respectively. The S–Cu–S angles display a slight distortion from the tetrahedral geometry, with an average S–Cu–S angle of 109(2)°, 109(1)°, and 109(2)° for Cu(1), Cu(2), and Cu(3), respectively.

The two [CuP₃S₉]ₙ⁻ chains in (I) contain three crystallographically different [P₃S₉]³⁻ units, with normal P–S bond distances in the range from 1.954(4) to 2.139(3) Å with an average P–S distance of 2.05(3) Å. The S–P–S angles reveal only slight distortions from the ideal tetrahedral coordination geometry, with an average angle of 109(2)°. The [P₃S₉]³⁻ unit contains a cyclic [P₃S₃] ring (chair conformation) with a mean P–P distance of 3.483(3) Å. There are two types of P–S distances in the three different cyclic [P₃S₉]³⁻ units: the longer P–S distances within the P₃S₃ ring at 2.11(5) Å, and the shorter P–S distances for the terminal sulfide atoms at 1.97(1) Å.

The [CuP₃S₉]ₙ⁻ chains are separated by Cs⁺ ions that are located in six different sites. The coordination of the Cs⁺ counterions is made of sulfur atoms and varies from 8 to 10. The helical screw-like, polar [CuP₃S₉]ₙ⁻ chains in (I) differ dramatically from the straight chains of A₂Cu₂P₃S₉ (A = K, Rb) (8), which also pack in a centrosymmetric fashion. The optical absorption properties of Cs₂CuP₃S₉ were assessed by measuring the optical transmission spectrum of single crystal samples; see Fig. 3A. The sharp optical gap observed in the spectrum indicates that the compound is a wide band-gap semiconductor with a gap Ɛ₈ ~ 2.4 eV. Below the band-gap the material shows good optical transparency down to the infrared region up to 0.2 eV.

The far-IR (15) spectrum of Cs₂CuP₃S₉ displays several absorptions in the 620–400 cm⁻¹ range. The sharp absorption at 400 and 463 cm⁻¹ are characteristic of the P–S–P stretching vibrations in the cyclic [P₃S₉]³⁻ unit. The remaining absorptions are tentatively assigned to the −PS₂ stretching vibrations by analogy to AAuPS₄, AAu₂P₇S₁₇ (A = K, Rb) (7). Absorptions below 400 cm⁻¹ are assigned to Cu–S stretching vibrations. The Raman spectrum (15) of Cs₂CuP₃S₉, shown in Fig. 3B, displays shifts in the 675–to 250-cm⁻¹ range that are tentatively assigned to P–S and shifts below 250 cm⁻¹ are assigned to Cu–S stretching vibrations. The shifts at ca. 386 and 294 cm⁻¹ are assigned to the [PS₄]³⁻ by analogy to AAuPS₄, AAu₂P₇S₁₇ (A = K, Rb) (7), and A₃P₃S₉ (A = K, Cs) (16). The Raman spectrum of Cs₂CuP₃S₉ is shown in Fig. 3B. Differential thermal analysis followed by careful XRD analysis of the residues revealed that the title compound melts incongruently at ~477°C, forming a mixture of Cs₂CuP₃S₉ and Cs₂P₂S₆ (17) and a ternary Cu/P/S phase.

The unique chiral structure of Cs₂CuP₃S₉ is evidently stabilized by the Cs cation. The polar character makes the
compound a potential candidate for nonlinear optical applications. Preliminary qualitative tests for nonlinear optical properties of powder samples of Cs$_2$CuP$_3$S$_9$ using a frequency-doubled green light exiting the sample. Further work should be carried out to explore this property.

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REFERENCES

13. (a) Cs$_2$CuP$_3$S$_9$ was synthesized from a mixture of 0.032 g (0.50 mmol) Cu, 0.220 g (1 mol) P$_2$S$_4$, and 0.149 g (0.50 mmol) Cs$_2$S which was sealed under vacuum in a Pyrex tube and heated to 500°C for 4 days followed by cooling to 100°C at 4°C h$^{-1}$. The excess Cs$_2$[P$_2$S$_4$] flux was removed by washing with degassed methanol under inert atmosphere to reveal irregular bright yellow crystals (75% yield based on Cu). Microprobe energy dispersive (EDS) analysis, on several (>10) single crystals, gave an average composition of Cs$_{2.22}$CuP$_3$S$_9$.
14. A Siemens SMART Platform CCD diffractometer from a crystal of 0.200 × 0.200 × 0.120 mm dimensions and MoKα (λ = 0.71073 Å) radiation. An empirical absorption correction was applied to the data during data processing. Crystal data at 23°C: a = 15.874(2) Å; b = 15.874(2) Å; c = 35.100(7) Å; γ = 120.00; V = 7660(3) Å$^3$; Z = 18; D$_{calc}$ = 2.767 g/cm$^3$; space group P6$_3$; μ = 6.804 cm$^{-1}$ index ranges −19 ≤ h ≤ 21, −20 ≤ k ≤ 21, −22 ≤ l ≤ 47; total data 48681; unique data 9745; (R$_int$ = 0.0944); data with $F^2 > 2σ(F^2)$ 4056; No. of variables, 406; final R/R$_w$ = 0.030/0.069; GOF 0.335; largest diff. peak and hole 0.882/−0.767 e Å$^{-3}$; (b) G. M. Sheldrick, “SHELXL: Version 5.03,” Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.
15. (a) Far-IR (CsI matrix) gave absorptions at 619(w), 519(w), 400(S), 355(w), 3040 (1998).