$CsXSi_{15}P_{21}$ (X = Sn or Pb): Polar Noncentrosymmetric Si−P Frameworks Stabilized by Covalent X−P Bonding

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ABSTRACT

Metal silicon phosphides composed of earth-abundant Si and P tend to exhibit semiconducting properties and adopt diverse crystal structures with relatively small additions of structure-directing elements. The potential of silicon phosphide materials in nonlinear optical applications has been hindered by the inability to systematically produce noncentrosymmetric structures with such a flexible framework. In this work, two isostructural compounds with a novel noncentrosymmetric structure were made possible by the inclusion of elements with stereochemically active lone pairs (Sn2+ and Pb2+). The structures were determined through single-crystal and synchrotron powder X-ray diffraction. Analysis of chemical bonding in real space through the electron localization function revealed stereochemically active Pb2+ and Sn2+ species in a trigonal pyramidal coordination with {Pb/Sn}−P bonds. Such covalent bonding between Pb and P is quite uncommon in extended solids and has been reported in a few rare instances. Band structure calculations and linear optical measurements confirm the semiconducting nature of CsXSi15P21 (X = Sn or Pb). The synthesis was optimized to yield high-purity polycrystalline samples. The nonlinear optical properties show promising second-harmonic generation (SHG) coefficients from the Kurtz−Perry method. First-principles calculations of the nonlinear optical properties support the experimentally determined SHG values and provide moderate values of birefringence, suggesting CsXSi15P21 could be phase-matchable and practical nonlinear optical materials in the mid-IR region.

1. INTRODUCTION

Materials composed mostly or entirely of Si and P are of interest to the scientific community given that both elements are earth-abundant and, when combined, primarily form semiconducting compounds. The binary Si−P compounds are semiconducting,1,2 and the possibility of synthesizing functional materials based on Si and P with additional structure-directing elements is a promising prospect.3 Recently, new Si−P-based materials have been discovered, demonstrating that Si−P bonding can leverage the huge structural space.4 From supertetrahedral SiP4 blocks,5−7 networks of SiP4 tetrahedra with massive pores,4,8 and layered compounds exhibiting Si2P6 ethane-like units9−11 to isolated SiP3 and SiP4 planar and tetrahedral units,11,12 there is much to learn about how different cations will template the flexible Si−P framework.

The flexibility of the Si−P framework to exhibit many bonding modes allows for the inclusion of different cation sizes and charges, which is important for directing the resulting bonding of the Si−P framework. For instance, Li5SiP3 and Na5SiP3 are isostructural and exhibit ethane-like [Si2P6]5− dimers, while the Rb and Cs analogues contain isolated [SiP3]5− anions instead.11 However, this flexibility of the Si−P framework can be a challenge for inspiring novel materials or making structural analogues, as small changes in composition can result in dramatic changes to the anionic framework. To continue with the previous example, K5SiP3 is not reported, and it is unclear which of these structures it would adopt or if neither or both structure types are stable. The synthesis of hypothetical K5SiP3 may depend on the impingement of discrete synthetic conditions that are not necessarily analogous to those for Na5SiP3 or Rb5SiP3. Additionally, the potential for polymorphism in silicon phosphides makes optimization of synthetic parameters extremely important, as was reported for the many structural transitions in KSi2P3 and LaSiP3.5,13

To generate nonlinear optical (NLO) materials, the flexibility of silicon phosphides presents an opportunity for highly selective material design. However, 88% of reported ternary silicon phosphides with alkali (A) and alkaline earth (Ae) metals are centrosymmetric structures, excluding their usefulness for NLO applications.4 Clearly, exploratory work in the Si−P space will yield few useful NLO materials, and more targeted approaches for generating noncentrosymmetric (NCS) structures must be used. Ye and co-workers used large ionic units such as Sr4Br to direct the SiP4 tetrahedral backbone to coalign and form NCS structures.4 Realization of materials containing fac-MSi3P3 units, such as those found in CoSi3P3, may be another avenue to form NCS structures.14 The inclusion of cations that have stereochemically active lone pairs is an underexplored avenue of generating NCS structures within Si−P frameworks. Stereochemically active lone pairs create polar local bonding environments that lack local inversion centers. If combined with a framework that allows for the alignment of the lone pairs, then an NCS structure should form. Given that many Si−P frameworks are built upon tetrahedral SiP4 units, which are also locally noncentrosymmetric, it is plausible that NCS structures will form. So far, only one ternary silicon phosphide with an atom containing stereochemically active lone pairs has been reported, Sn4.2Si9P16, and it has a NCS structure.15 This provides motivation for synthesizing NCS compounds containing Si−P and stereochemically active lone pairs. More examples of such compounds will inevitably lead to a better understanding of the interplay between the Si−P framework and the generation of NCS structures. Harnessing predictability and control over the Si−P framework is immensely desirable to leverage structure−property relationships and inspire new materials. For now, with all of the advancements made in structure prediction, the discovery of new structures in the M−Si−P and M−M′−Si−P systems has largely relied on rigorous synthetic efforts and the serendipitous crystallization of novel phases. In this work, we report two new examples of quaternary silicon phosphides, CsXSi15P21 (X = Sn or Pb), with stereochemically active lone pairs (Sn2+ or Pb2+) that direct the formation of a new polar NCS structure.

2. EXPERIMENTAL SECTION

Warning! *Elemental Cs and P react violently and immediately if placed in contact with each other, while Cs is molten. Small quantities of materials should be used, and care should be taken when flame sealing to not heat or melt the unreacted Cs. At relatively high synthetic temperatures, the vapor pressure of P or reaction of Cs with silica may be sufficient to cause the sealed ampule to shatter or explode! Enclosing ampules into secondary containment, such as a ceramic beaker filled with sand or silica wool cocoon, and placing furnaces into well-ventilated space, such as a fume hood, are highly recommended.*

Samples were prepared from elements in carbonized silica ampules that were evacuated and flame-sealed. Cs and P were prereacted first, and the "CsP3" sample was further reacted with extra P, Si, and Sn or Pb. Samples were characterized by powder X-ray diffraction (PXRD), synchrotron high-resolution powder X-ray diffraction (HR-PXRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), single-crystal X-ray diffraction, solid-state diffuse reflectance spectroscopy, differential scanning calorimetry, and second-harmonic generation (SHG) and laser damage threshold (LDT) nonlinear optical spectroscopy. The band structure and optical properties of the compounds were determined through first-principles calculations. The details of the synthesis and methods are available in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1 Synthesis

Note the warning regarding working with elemental Cs and P above. CsPbSi15P21 was discovered serendipitously in an attempt to incorporate Pb2+ in place of Ba2+ into the CsBa6Si12P20Cl family of compounds.8 Initially, a reaction mixture of Pb, Si, and P in a 6:12:20 ratio with excess CsCl was loaded into a carbonized fused silica ampule, flame-sealed, heated to 1000 °C over 10 h, and annealed for 120 h. The product was analyzed via powder X-ray diffraction (PXRD) and revealed a multiphase mixture with many diffraction peaks that could not be indexed. From this reaction, a single crystal was selected from the solidified part of the sample. The crystal structure was determined via SXRD. To confirm the composition determined by SXRD, elemental analysis (energy-dispersive X-ray spectroscopy) was performed on the sample (Table S1), and among other phases, CsPbSi15P21 was found, confirming the composition determined by SXRD.

Subsequent experiments were performed, targeting the stoichiometric ratio of elements. To achieve high-purity samples, Cs and P were first prereacted in a 1:3 ratio in an alumina crucible inside an evacuated and sealed silica ampule at 300 °C for 12 h in a muffle furnace. The product was an air-sensitive reddish-orange powder. This product will be termed "CsP3", although we do not claim that this is a single-phase material. The primary importance of this prereaction step is to avoid difficulties of working with elemental Cs. In the next step, "CsP3", Pb, Si, and P were measured in stoichiometric amounts in a 1:1:15:18 ratio, placed in a fused silica ampule, flame-sealed, heated to 850 °C over 10 h, and annealed for 120 h. The product was ground in a mortar and pestle inside a glovebox and reannealed. This time, the product was heated to 1000 °C over 10 h and annealed for 120 h. An identical method was used for CsSnSi15P21 with the replacement of Pb powder with Sn powder, resulting in a high-purity product.

For CsSnSi15P21, single-crystal growth was attempted by employing a molten salt flux and metal fluxes. Slow cooling of the flux-free samples did not result in single crystals either. Thus, to determine the structure of CsSnSi15P21, high-resolution synchrotron PXRD was recorded at beamline 11-BM at the Advanced Photon Source at Argonne National Laboratory (APS ANL) (Figure 1). The high-resolution diffraction pattern was refined by using the structural model generated from the SXRD results for CsPbSi15P21 by replacing Pb with Sn. The lattice parameters, atomic coordinates, and displacement parameters were refined, leading to an exceptional fit of the powder diffraction pattern. The atoms in CsSnSi15P21 moved only slightly to accommodate the shorter Sn−P bonding distances; thus, we conclude that CsSnSi15P21 and CsPbSi15P21 are isostructural.

3.2 Crystal Structure

CsXSi15P21 (X = Sn or Pb) crystallizes in noncentrosymmetric rhombohedral space group R3m (No. 160) with the Pearson symbol hR-114 and Wyckoff sequence c4b4a2. Lattice parameters and other pertinent crystallographic information can be found in Table 1. Atomic coordinates and selected interatomic distances are listed in Tables S2 and S3. CsXSi15P21 exhibits a novel and complex crystal structure composed of a 3D network of condensed SiP4 tetrahedra, templated by large Cs and Pb (or Sn) cations alternating in columns along the c-axis (Figure 2). Cs is coordinated by 12 phosphorus atoms that form a truncated tetrahedron with a polyhedral volume of 114 Å^3. Cs−P distances range from 3.7 to 4.3 Å (Table S3). This coordination environment is similar to that of Cs in CsP7 where Cs is coordinated by 12 phosphorus atoms with a polyhedral volume of 117 Å^3.16 In CsP7 and CsPbSi15P21, Cs occupies a relatively low-symmetry coordination environment, which points to the high polarizability of the Cs cation.17

CsPbSi15P21 exhibits Pb−P bonding, which is a rather uncommon occurrence. In fact, until 2014, no binary compound of Pb and P had been reported until the excellent work of Pöttgen et al., who reported PbP7.18 In this compound, the P atoms form a polyphosphide unit, [P7]2∞1, which is described as chair-conformed P6 hexagons bridged with two coordinate P atoms forming a 3D network. The Pb in PbP7 exhibits trigonal planar coordination with Pb−P distances of 2.83−2.97 Å. The ternary compounds MIIPbP14 (where MII = Zn, Cd, or Hg), exhibiting Pb−P interactions (2.62−2.88 Å), were reported earlier as the first examples of Pb−P bonding in extended solids.19 Although the formulas of PbP7 and MIIPbP14 appear as if these compounds are closely related, the polyanionic phosphorus structures are totally different. In MIIPbP14, polyanion P is better described as infinite 1D pillars of [P14]4∞1 where the ratio of two- to three-coordinate P is 4:10.

The same Pb−P bonding and [P14]4∞1 polyanion can be found in Pb5P28I2, which incorporates a unique [Pb3I2]2+ unit causing rearrangement of the packing of the [P14]∞14 pillars.20

The striking dissimilarities of the P polyanion in PbP7 and HgPbP14-type compounds articulate the difficulty of predicting and controlling the nature of P−P bonding when changing compositions in phosphides. Pb−P bonding can also be seen in a few coordination compounds. Pb2+ has been shown to coordinate to diphosphine ligands with a Pb−P distance of 2.79 Å and bridging disilylphosphido ligands with distances of 2.70−2.79 Å.21,22 Additionally, a heterocubane structure with Pb−P distances of 2.72−2.74 Å was reported.23 Besides these covalent or coordination Pb−P interactions, substantially weaker Pb−P interactions (the shortest being 3.81 Å) are demonstrated in Au2PbP2.24,25 The Pb atoms in CsPbSi15P21 are coordinated by three P atoms in a trigonal pyramidal coordination at 2.746(2) Å, indicating a covalent bond in line with previously reported instances. The Pb−P distance is slightly shorter than that found in HgPbP14 and PbP7, but this is expected since a formally neutral P will have a smaller covalent radius than P−. In the opposite direction of the phosphorus atoms, the nearest atom to Pb is Cs with a Cs−Pb distance of 3.831(1) Å. In binary Cs−Pb Zintl phases, most of the Cs−Pb distances are longer than 4.0 Å, yet the shortest Cs−Pb separations of 3.77 and 3.84 Å were reported in Cs3NaPb4 and Cs4Pb9, respectively.26−28 The geometry of the Pb atom suggests Pb has a 2+ oxidation state, which is further supported by the formula of CsPbSi15P21 being electron-precise assuming Cs+, Pb2+, Si4+, and P3−. The electron-precise composition is further justified as the sample was dark red/brown in color, suggesting its semiconducting nature. Unlike previously reported compounds with Pb−P bonding, CsPbSi15P21 does not exhibit P−P bonding.

There are three unique crystallographic sites for Si in the SiP4 network. Si(1) and Si(2) occupy separate 18c sites, while Si(3) occupies the 9b site. All SiP4 units are connected exclusively through corner sharing. Each P atom is coordinated by three Si/Pb atoms. While P(1)−P(4) are bonded to three Si atoms, P(5) has two bonds with Si and one bond with Pb. The unit cell of CsPbSi15P21 contains three layers of SiP4 tetrahedra stacked along the [0001] direction (Figure 2C−E). Each layer is identical and translationally related by (1/3 1/3 1/3). Each layer contains 15 SiP4 tetrahedral units, where the smallest repeating subunit is five corner-sharing SiP4 tetrahedra composed: 2 × Si(1) + 2 × Si(2) + Si(3).

Table 1. Crystallographic Data from Single-Crystal (Pb) Structure Solution and Rietveld Refinement (Sn)

	$CsPbSi_{15}P_{21}$	**$CsSnSi_{15}P_{21}$**
CSD number	2484765	2484764
Temperature (K)	100	293
Radiation (Å)	0.71073	0.45896
Diffraction experiment	single crystal	powder
Crystal system	trigonal	trigonal
Space group	R3m (No. 160)	R3m (No. 160)

a (Å)	17.9494(8)	17.92731(4)
c (Å)	8.7747(4)	8.77148(2)
Volume (Å^3)	2448.3(2)	2441.371(7)
Z	3	3
Data/parameters	2244/67	—
Density (g/cm^3)	2.87	—
μ	7.86	—
Flack parameter	0.033(6)	—
Rint	0.079	—
Goodness of fit	1.02	—
R1 [I > 2σ(I)]	0.030	—
wR2 [I > 2σ(I)]	0.056	—
R1 (all data)	0.033	—
wR2 (all data)	0.057	—
Difference peaks (e Å^{-3})	2.37/−2.25	—

3.3 Electronic Structure and Electron Localization Function (ELF)

Band structures and the corresponding density of states (DOS) were calculated through first-principles calculations using the open-source software ABINIT (Figure 3A,B). The Pb analogue is a semiconductor with direct and indirect band gaps of ~1.5 and ~1.4 eV, respectively. The valence band is relatively flat, leading to nearly degenerate energy maxima at Z, Γ, and F high-symmetry points. The valence and conduction bands are both dominated by silicon and phosphorus states, in accordance with related materials.29,30 The substitution of Sn for Pb does not substantially impact the band gap (Figure S3).

To analyze chemical bonding via the electron localization function (ELF) approach, the electronic structures of CsXSi15P21 were computed through the linear muffin tin orbital atomic sphere approximation (LMTO-ASA) method (Figure 3C). Analysis of ELF reveals clear covalent Si−P bonding, common for this class of materials. The X−P bonding is strongly polarized with electron density shifted toward P atoms. No drastic differences between Sn−P and Pb−P bonding were observed. When considering the ⋯Cs⋯X⋯Cs⋯X⋯ tunnels, one can clearly see an electron lone pair located on the X atoms, which points toward neighboring Cs atoms. Thus, the Cs−X interactions are not completely ionic.

3.4 Optical Properties

Studies of the linear optical properties confirm the semiconducting nature of the CsXSi15P21 materials with an observed direct band gap of 1.9 eV and indirect band gaps of 1.3−1.4 eV (Figure 4) from diffuse reflectance spectroscopy measurements. Since both materials have NCS structures and appropriate band gaps for the mid-infrared (mid-IR) range, the nonlinear properties were studied both theoretically and experimentally.

First-principles calculations confirmed the potential of these compounds for nonlinear optical applications. Table 2 shows the independent components of their second-harmonic generation (SHG) tensors, dij, along with the effective powder coefficients, deff.31 Corroborating the experimental signals in Figure 5, CsPbSi15P21 indeed displays a stronger effective nonlinear optical response than CsSnSi15P21, despite their similar band gap. The SHG intensity is usually compared to that of reference sample R, here chosen to be AgGaS2 (AGS), by computing their ratio. The latter is related to the ratio of their effective powder coefficients. Following this equation, the density functional perturbation theory (DFPT) effective coefficient yields ratios of 49.1 and 58.7 for CsSnSi15P21 and CsPbSi15P21, respectively. However, the experimental SHG component of AGS reported in the literature spans a wide range of values (see Table S6), and the DFPT one is in the low end of that range (Table S5). Therefore, we also compare the DFPT effective coefficients for CsSnSi15P21 and CsPbSi15P21 to the largest experimental value (d36AGS = 34.8 pm/V) to afford values of 3.5 and 4.1, respectively. This emphasizes the limitations when comparing results from different sources, in a manner independent of their experimental or computational nature.

Both compounds boast a static birefringence in the required range to achieve phase matching (0.03−0.1) when computed within DFPT (Table 2 and Figure S4). This is in line with the observed linear increase in the SHG response in the powder measurements, in contrast with the very low birefringence computed with the sum-over-states (SOS) approach in the independent particle approximation (IPA). This discrepancy illustrates the limitation of the widely used SOS-IPA method and deserves further investigation, which falls outside the scope of the present work. Other studies have also encountered such a large discrepancy and observed that the DFPT approach yields birefringence values that better agree with the experimental data.32,33 The full dispersion curves and the corresponding computational details can be found in the Supporting Information.

The Kurtz−Perry method was utilized for SHG powder measurements using a Q-switch 2.09 μm laser source (3 Hz, 50 ns). The SHG response may be weakened due to their narrow optical band gap, so reflectance SHG signals were collected. CsPbSi15P21 and CsSnSi15P21 exhibit SHG activity exceeding that of the home-grown high-quality AGS state-of-the-art standard in the whole measured crystallite size range (Figure 5A). Their performance in the 54−88 μm particle size range is comparable to that of most ternary silicon pnictides. Given that measured relative SHG versus AGS can be influenced by sample quality and AGS quality, we will compare the calculated static SHG tensors as well as experimental SHG versus AGS to achieve a better understanding of the relative NLO properties for the silicon phosphide family of compounds.

The typical inverse correlation between SHG efficiency and band gap is shown in Figure 5D, with Mg2In3Si2P7 appearing as a notable outlier. When comparing relative SHG values, CsXSi15P21 compounds are less competitive but on par with structurally similar compounds like BaSi7P10, despite having larger maximum |dij| values.34 A larger maximum |dij| is ideal for applications in which a large crystal would be cut and oriented, but in the first stages of material discovery, the Kurtz−Perry method for determining SHG is often used and is considered to be an average of the SHG coefficients because of the average orientation of powders.35−37

The relationship between the maximum |dij| and SHG intensity does not give a good correlation (Figure 5C). Different laser powers, frequencies, pulse durations, experimental setups, and quality of AGS standards may affect the reported experimental SHG intensity.37 On the other hand, the choice of computational method can greatly affect the individual components of the SHG tensor and hence the maximum |dij|, as illustrated in Table 2 and Table S5. The SOS-IPA framework is commonly employed due to its ability to evaluate the SHG response at finite frequencies. In contrast, the DFPT remains limited to the static regime but incorporates local-field effects. While the latter are generally observed to reduce the SHG response,38,39 this is not consistently reflected in the individual components of Table 2 such that this observation appears to hold primarily when considering deff.40

Since materials with higher maximum |dij| values may not have higher deff coefficients (for instance, that is the case in Table 2 for the DFPT values), it may be best to consider the maximum |dij| as the optimizable parameter. SHG intensity on powders is a poor proxy for the maximum |dij| (Figure 5C). Therefore, deff as shown in Table 2 is a more realistic comparison of the SHG intensity determined by the Kurtz−Perry method. However, due to the lack of reported deff values (from calculations) in the literature, we will use the maximum |dij| as reported in recent reviews.41,42 The maximum |dij| values of CsXSi15P21 indicate it is among the most promising NLO materials based on tetrahedral Si−P frameworks.43−45 The higher |dij| values of CsXSi15P21 compared to those of (Sr,Ba)Si7P10 reinforce the idea that the addition of polarized units and further distortion of SiP4 tetrahedra can lead to an overall higher SHG coefficient.

The laser damage threshold (LDT) of the title compounds was measured by adjusting the laser output energy and observing color changes by using an optical microscope. The validity of this method was verified on the state-of-the-art AgGaS2 standard, which shows LDT close to 30 MW/cm2 in agreement with multiple literature reports.46,47 The LDT of CsSnSi15P21 is comparable to that of the standard, while the LDT of CsPbSi15P21 is almost doubled (Table 3). Unlike the majority of the NCS metal−silicon phosphides, CsPbSi15P21 and CsSnSi15P21 are phase-matchable because they show a linear increase in their SHG signal with crystallite size. Other phase-matchable silicon phosphides that were recently reported include BaSi7P10, SrSi7P10, FeSi4P4, and CoSi3P3.14,34

Table 2. Static SHG Coefficients and Refractive Indices and Birefringence Values of $CsPbSi_{15}P_{21}$ and $CsSnSi_{15}P_{21}$ Computed from First Principles

Compound	Method	d_{16} (pm/V)	d_{31} (pm/V)	d_{33} (pm/V)	d_e^{ff} (pm/V)	n_x	n_r
$CsSnSi_{15}P_{21}$	DFPT (0 eV)	−54.728	−38.268	65.218	54.650	3.106	3.153
	SOS-IPA (0 eV)	−53.062	−43.223	54.586	54.359	3.313	3.326
	SOS-IPA (0.6 eV)	−73.464	−64.828	69.903	75.675	3.350	3.362

CsPbSi$_{15}$P$_{21}$	DFPT (0 eV)	−62.829	−40.543	64.784	59.749	3.138	3.173
	SOS-IPA (0 eV)	−61.693	−50.767	46.905	62.237	3.349	3.352
	SOS-IPA (0.6 eV)	−85.419	−74.744	59.154	86.982	3.387	3.391

Table 3. LDTs and Measured SHG of CsXSi$_{15}$P$_{21}$ Normalized to That of Reference AgGaS$_2$

Compound	SHG (×AGS)	LDT (×AGS)
AgGaS$_2$	1	1
CsSnSi$_{15}$P$_{21}$	1.77	1.06
CsPbSi$_{15}$P$_{21}$	1.92	1.85

4. CONCLUSIONS

Two novel semiconductors, CsPbSi15P21 and CsSnSi15P21, were synthesized, and their structures were characterized through single-crystal and high-resolution synchrotron powder XRD. The compounds are polar and noncentrosymmetric and exhibit direct band gaps of ~1.9 eV, making them potential infrared nonlinear optical materials. The introduction of stereochemically active lone pair elements, Sn and Pb, is responsible for the NCS structure and contributes to the high static SHG tensors as calculated by DFT. SHG and LDT values were measured at 2.09 µm and were observed to be greater than those of standard AgGaS2. Both materials are phase-matchable at 2.09 µm (Kurtz−Perry powder method), and the DFPT-calculated refractive indices point to promising phase-matchable behavior. In addition to NLO properties, the stereochemically active lone pairs make these compounds interesting for future studies of other lone pair-induced properties. Lone pairs have been implicated in low thermal conductivity48−50 and suppressed nonradiative carrier recombination in photovoltaics.51 Furthermore, the possibility of substituting the anion sublattice may unlock the tunability of the band gap and other electronic effects that can be the subject of future studies. The discovery of these structures highlights the growing number of NCS silicon phosphide materials, the rich structural diversity of this group of materials, and the ability of stereochemically active lone pairs to induce NCS structures.

ASSOCIATED CONTENT

Supporting Information. Detailed description of synthesis and experimental and computational methods used, including figures and tables for SEM/EDS, DSC, atomic coordinates and interatomic distances, band structure and DOS, optical properties, and calculated birefringence and dij coefficients.

Accession Codes. Deposition Numbers 2484764−2484765 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

The authors declare no competing financial interest.

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