Nearly Identical but Not Isotypic: Influence of Lanthanide Contraction on Cs\textsubscript{2}NaLn(PS\textsubscript{4})\textsubscript{2} (Ln = La–Nd, Sm, and Gd–Ho)

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ABSTRACT: The effect of lanthanide contraction often results in topological and symmetry changes in compounds with the same compositions as a function of lanthanide cation size. Here we report on the first example of a lanthanide thiophosphate exhibiting a change in the lanthanide cation environment without any topological or symmetry change. A series of new lanthanide thiophosphates with mixed alkali cations were obtained via a flux crystal growth technique using a CsI flux. The obtained compounds Cs\textsubscript{2}NaLn(PS\textsubscript{4})\textsubscript{2} (Ln = La–Nd, Sm, and Gd–Ho) were grown as large single crystals (~0.1–1 mm\textsuperscript{3}) and characterized using single-crystal X-ray diffraction and magnetic susceptibility measurements. As we moved across the series, the structural studies revealed a change in the lanthanide coordination environment depending on the identity of the lanthanide. Although all compounds in the Cs\textsubscript{2}NaLn(PS\textsubscript{4})\textsubscript{2} series crystallize in the same space group and have the same Wyckoff atom positions, a slight change in size between Sm\textsuperscript{3+} and Gd\textsuperscript{3+} causes a subtle change in coordination number from 9 (for Ln = La–Sm) to 8 (for Ln = Gd–Ho), resulting in two distinct but virtually identical structure types. Ab initio calculations were performed, and the observed experimental trend was corroborated computationally. Magnetic measurements performed on the Cs\textsubscript{2}NaLn(PS\textsubscript{4})\textsubscript{2} (Ln = Ce, Pr, Nd, Gd, and Tb) compounds revealed paramagnetic behavior.

INTRODUCTION

The stark difference between chalcogenide and oxide chemistry, which each require their own synthetic route due to their specific soft and hard acid base chemistry,\textsuperscript{1} has prompted researchers to seek out alternative synthesis methods in search of new chalcogenide materials that exhibit the desired properties, which cannot be readily achieved in oxide materials.\textsuperscript{2–5} Inorganic and inorganic/organic hybrid sulfides are therefore among the most rapidly expanding and developing classes of materials, which exhibit a host of potential applications due to their unique physical properties, such as their ionic conductivity,\textsuperscript{6–11} ion exchange,\textsuperscript{12–16} thermoelectric,\textsuperscript{17–21} ferroelectric,\textsuperscript{22} and magnetic properties.\textsuperscript{23} The sulfide affinity for certain elements, known as chalcophiles, allows for the formation of very stable complexes that can also be found in biological systems.\textsuperscript{24,25} Unlike chalcophiles, which are typically very stable, other chemical elements are usually less chemically stable and are therefore more sensitive to moisture and air, making their preparation and handling challenging; their syntheses require specific precautions and controlled reaction conditions. However, their potential use as functional materials significantly outweighs these difficulties, fueling interest and further advancement of sulfide chemistry.

While lanthanide oxo-salt compounds have been studied extensively with respect to their magnetic properties,\textsuperscript{26–28} there is less information available concerning the magnetic behavior of lanthanide thio-salt complexes. To date, a number of studies of ternary and quaternary chalcogenide systems have been reported, and a relatively small fraction of the discovered compounds were found to exhibit magnetic ordering at low temperatures.\textsuperscript{29} Also, lanthanide sulfides, as a result of their highly tunable optical properties, have been studied as potential luminescent materials, where fine-tuning of the emission spectra can be achieved by careful doping of a host matrix with lanthanides and 3d metals.\textsuperscript{30,31} Thiophosphates are particularly interesting as they show structural modularity, offering a certain degree of structural control over the target compositions and structures. For example, actinide and lanthanide cations were found to prefer a predetermined geometry when crystallized with chalcogenions, which resulted in a set of topologies ranging from isolated zero-dimensional (0D) species to three-dimensional (3D) moieties.\textsuperscript{32–35} A pronounced stability of [Ln(PS\textsubscript{4})\textsubscript{3}]\textsuperscript{3+} groups resulted in a number of lanthanide thiophosphates with the general formula A\textsubscript{3}Ln(PS\textsubscript{4})\textsubscript{3},\textsuperscript{36–39} where Ln is a trivalent lanthanide and A is either a single alkali metal cation or a mixture of alkali metal
Table 1. Crystallographic Data for Cs₂NaLn(PS₄)₂ (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, and Ho)

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properties of the obtained compounds were characterized. Cs were obtained as side products. All compounds with the starting materials, Ln (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, and Ho) along with 0.50 g of CsI, were loaded in a fused silica tube (0.33 mmol), in a 1:4:4 molar ratio along with 0.0832 mmol, NaS (0.333 mmol), and P2S5 (0.333 mmol), in a 1:4:4 molar ratio along with 0.50 g of CsI, were loaded in a fused silica tube (~120 mm long, 10 and 12 mm inner and outer diameters, respectively) inside a nitrogen bag. The tube was flame-sealed under vacuum and placed in a programmable furnace. The furnace was ramped up to 700 °C in 1 h, held at this temperature for 20 h, and then cooled to 500 °C at a cooling rate of 10 °C/h, followed by cooling to room temperature when the furnace was switched off. The flux was removed by dissolving it in ~50 mL of DMF over the course of several hours, and the resulting products were filtered. Large crystals (~0.25–1 mm³) of Cs2NaLn(PS4)2 (Ln = Ce, Pr, Nd, Gd, Tb, Dy) were picked manually for single-crystal X-ray diffraction and magnetic susceptibility measurements.

### Experimental Section

**Materials.** P5S5 (Sigma-Aldrich, 99%), CsI (Alfa Aesar, 99.9%), NaS (Alfa Aesar, 99.9%), Na2O (Alfa Aesar, 99.9%), CeO2 (Alfa Aesar, 99.99%), PrO1, (Alfa Aesar, 99.9%), Nd2O3 (Alfa Aesar, 99.9%), Sm2O3 (Alfa Aesar, 99.99%), Gd2O3 (Alfa Aesar, 99.99%), Tb2O3 (Alfa Aesar, 99.9%), Dy2O3 (Alfa Aesar, 99.9%), Ho2O3 (Alfa Aesar, 99.99%), and N,N-dimethylformamide (DMF, Sigma-Aldrich, ACS grade) were used as received. P2S5 and NaS were stored and handled in a nitrogen glovebag. Rare earth sulfides were obtained according to the procedure described in the literature.

**Synthesis.** Cs2NaLn(PS4)2 (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, and Ho) along with minor quantities of the side products Cs2Ln2(PS4)2 (Ln = La and Ce) and Cs2Ln4(PS4)2 (Ln = Sm and Dy) were obtained via flux growth using CsI flux. The starting materials, LnS3 (0.0832 mmol), Na2S (0.333 mmol), and P2S5 (0.333 mmol), in a 1:4:4 molar ratio along with 0.50 g of CsI, were loaded in a fused silica tube (~120 mm long, 10 and 12 mm inner and outer diameters, respectively) inside a nitrogen bag. The tube was flame-sealed under vacuum and placed in a programmable furnace. The furnace was ramped up to 700 °C in 1 h, held at this temperature for 20 h, and then cooled to 500 °C at a cooling rate of 10 °C/h, followed by cooling to room temperature when the furnace was switched off. The flux was removed by dissolving it in ~50 mL of DMF over the course of several hours, and the resulting products were filtered. Large crystals (~0.25–1 mm³) of Cs2NaLn(PS4)2 (Ln = Ce, Pr, Nd, Gd, Tb, Dy) were picked manually for single-crystal X-ray diffraction and magnetic susceptibility measurements.

**Single-Crystal X-ray Diffraction.** Single-crystal X-ray diffraction data were collected at 300(2) K on a Bruker D8 QUEST diffractometer equipped with an Incoatec μ³s 3.0 microfocus radiation source (Mo Kα, λ = 0.71073 Å) and a PHOTON II area detector. The crystals were mounted on a microloop using immersion oil. The raw data reduction and absorption corrections were performed using SAINT and SADABS programs. Initial structure solutions were obtained with SHELXS-2017 using direct methods and Olex2 GUL. Full-matrix least-squares refinements against F² were performed with SHELXL software. The presence of residual electron density peaks near the Cs sites in Cs2NaLn(PS4)2 was indicative of Cs site disorder. After disorder Cs sites had been introduced into the residual density peaks, with a total occupancy of the related sites constrained to unity, the model refined to provide a satisfactory R value and residual electron density map. The crystal structures of Cs5La2(PS4)4 and Cs5Ce5(PS4)4 are severely disordered with respect to Cs as well as some P and S atoms, which were refined in a manner similar to that for Cs disorder by constraining the total occupancy of the related sites to unity to provide a reasonable charge-balanced formula. All of the structures were checked for missing symmetry with the Addsym program implemented within the PLATON software, and no higher symmetry was found. The crystallographic data and results of the diffraction experiments are summarized in Tables 1 and 2.

**Magnetism.** Magnetic property measurements were performed using a Quantum Design MPMS 3 SQUID magnetometer. Zero-field-cooled (ZFC) magnetic susceptibility measurements were taken from 2 to 300 K in an applied field of 0.1 T. The raw data were corrected for radial offset and sample shape effects according to the method described in the literature.

**Crystal Chemical Calculations.** Crystal structure analysis was performed using the TOPOS 4.0 software package. The method of intersecting spheres was employed for coordination number determination using the AutoCN program. Dirichlet and ADS
programs were employed for the construction of Voronoi–Dirichlet polyhedra and topological analysis, respectively. The standard structure simplification procedure was employed to obtain the underlying nets of the compounds.56

First-Principles Calculations. First-principles calculations were performed via density functional theory (DFT), using the Vienna Ab-initio Package (VASP) plane-wave code,57,58 generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE),59 and projector-augmented wave (PAW) method.60,61 The Na, Cs, P, and S valence electron configurations considered for construction of the PAW potentials were 2p^3s^1, 5s^2p^6s^1, 3s^2p^3s, and 3s^2p^4, respectively. For the rare earth elements, the Ce_3, Pr_3, Nd_3, Sm_3, Gd_3, Tb_3, Dy_3, and Ho_3 pseudopotentials from the VASP distribution were used. These potentials were chosen because of energy convergence issues with the other rare earth pseudopotentials from the VASP distribution. To model the partial occupancy of the Cs atoms, superquasirandom structures (SQSs) were generated by ensuring an equidistant distribution of the Cs atoms. Spin-polarized calculations were performed with a 410 eV cutoff energy for the plane wave basis set, a 10^{-6} eV energy convergence criterion, and a 4 x 4 x 4 k-point mesh. The ground state geometries at 0 K were optimized by relaxing the cell volume, atomic positions, and cell symmetry until the maximum force on each atom was <0.001 eV/Å. During the geometry optimization, each of the studied SQSs relaxed to a state with a 0 μB net magnetic moment.

Results and Discussion

Synthesis. All reactions were carried out using the identical reaction conditions with different lanthanide sulfides as starting materials. Despite the similarity, the products of the reactions were affected by lanthanide contraction, which manifests itself as a tendency of early lanthanides to adopt structural types with a coordination number (CN) higher than that of the later lanthanides.62 The previously reported NaLnP_2S_4 series is a good illustration of this phenomenon, favoring a CN of 9 for early lanthanides from La to Sm, while the rest of the series adopts a structure with a CN of 6 + 2 for the lanthanide sites.35 In this report, single crystals of Cs_2NaLn(P_2S_4) were obtained for the elements from La to Ho (except for Prm and Eu, the latter of which tends to reduce to Eu(II) in a sulfide environment). The series was completed up to Ln = Ho, as ErS_3 starting material yielded only poorly crystalline products that could not be characterized due to their rapid crystal decomposition upon exposure to air. Although Cs_2NaLn(P_2S_4) remains the major reaction product across the La–Ho series, the nature of the side products changes. For the early lanthanides La and Ce, the Cs_2Ln(P_2S_4) phase formed as a side product. When we moved further across the series, the quantity of the side products decreases, and their crystal quality deteriorates. A side product having the composition Cs_2Ln(P_2S_4) which forms as block-like crystals, was observed for Ln = Sm and Dy and was a very small fraction of the resulting product. Therefore, while the nature of the major product, Cs_2NaLn(P_2S_4), remains the same, the structure, quantity, and crystal quality of the side products vary across the series due to the lanthanide cation size difference.

Crystal Structure Description. There are three structure types reported in this study, Cs_2NaLn(P_2S_4) (Ln = La–Nd and Sm–Ho), Cs_2Ln(P_2S_4) (Ln = Sm and Dy), and Cs_2Ln(P_2S_4) (Ln = La and Ce), that are isotypic with K_2Ln(P_2S_4) (Ln = La, Ce, and Nd),63–65 Rb_2Er(P_2S_4)66 and Cs_2Ln(P_2S_4) (Ln = Pr and Er),64,66 respectively.

Cs_2NaLn(P_2S_4) (Ln = La–Nd and Sm–Ho). All compounds crystallize in monoclinic space group P2_1/c and feature lanthanide thiophosphate chains extending along the a axis that are held in a framework by electrostatic interactions with Cs^+ and Na^+ cations. Having a similar set of unit cell parameters, all of the structures seemingly belong to the same structure type. However, the coordination number of the lanthanide atoms varies from 9 for the early lanthanides (La–Sm) to 8 for the rest of the series (Gd–Ho). In the first group, the single unique lanthanide atom forms a LnS_6 coordination polyhedron in the shape of a monocapped tetragonal antiprism (Figure 1a), while in the second group, the LnS_8 coordination polyhedra adopt a bicapped trigonal prismatic environment (Figure 1b). The Ln–S bond lengths decrease monotonically in the series from 2.9291(5)–3.2549(6) Å for La to 2.7639(9)–3.2574(11) Å for Ho. The phosphorus atoms form almost regular Ps tetrahedra with P–S bond distances and S–P–S angles in the ranges of 1.9897(7)–2.0734(12) Å and 100.04(3)–115.75(3)°, respectively. In Cs_2NaLa(P_2S_4) and the related compounds, both phosphorus groups connect to two lanthanide coordination polyhedra so that P(1)S_4 shares two edges and P(2)S_4 shares one edge and one face with two lanthanum atoms, resulting in a chain of successively edge- and face-sharing lanthanum atoms (Figure 1c). In Cs_2NaGd(P_2S_4), both unique phosphorus tetrahedra share two edges with gadolinium atoms, forming a chain of edge-sharing GdS_4 polyhedra (Figure 1d). The sodium and cesium atoms are located between the negatively charged [Ln(P_2S_4)]^3− chains, maintaining the charge balance and connecting the chains into a framework via electrostatic interactions (Figure 1e).

To date, 13 compounds with the A_2Ln(P_2S_4)_2 composition have been identified, where A is an alkali metal cation.60–63 Although all compositions exhibit [Ln(P_2S_4)]^3− chains in their structures, there are two distinct structural motifs of the chains. Similar to K_2La(P_2S_4)_2, K_2Ce(P_2S_4)_2, and K_2Nd(P_2S_4)_260–62 the Cs_2NaLn(P_2S_4)_2 structures exhibit almost linear chains, as is shown in Figure 2. The chain topology observed in Rb_2Sm(P_2S_4)_2, Cs_2Sm(P_2S_4)_2, and Cs_2Nd(P_2S_4)_263,64 has a zigzag arrangement of the lanthanide atoms in their structures (Figure 2). From the reports to date, it appears that the linear chains
Experiments were performed using dilutions of periodic structures with respect to quantitative investigations of computational geometry optimizations of Rb can form only if smaller alkali cations, Na⁺ or K⁺, are present in the structure, whereas the larger cations, Rb⁺ and Cs⁺, favor the formation of the zigzag chains. It is interesting that the presence of even a small fraction of a smaller cation promotes the formation of the linear chains, as observed in the structures of Rb₂₄Na₉₃La(PS₄)₂ and Rb₂₄Na₉₃Nd(PS₄)₂. This indicates a structure-directing role of the alkali cations in the stabilization of the lanthanide thiophosphate chains.

The change in the lanthanide coordination number in the series from 9 to 8 when moving across the series is a commonly observed feature. The transition is typically accompanied by a change in the structure type, with a possibility that some intermediate compounds crystallize in both structure types. A unique feature of this reported series is that the transition can be directly observed in virtually the same structure type, enabling its crystallochemical analysis. To characterize the transition, bond distances, solid angles (Ω), and the lanthanide atom Voronoi polyhedron volumes (Vᵥp) were calculated and plotted against the lanthanide atomic number in Figure 3. The solid angles are expressed as percentages, showing the contribution of a selected contact to the total lanthanide atom solid angle (4π steradian), i.e., representing the strength of the bonding between lanthanide and sulfur atoms. As one can see in Figure 3, Vᵥp values, which correspond to the size of the lanthanide atoms in the crystal structure, show a monotonic decrease in accordance with lanthanide contraction. At the same time, the Ln−S(8) bond distance exhibits a sharp difference between Sm and Gd, increasing from 3.36 to 3.58 Å. The second longest bond in the lanthanide atom environments is ∼3.23 Å and remains almost unchanged across the series. Depending on the Ln−S(8) bond distance, the lanthanide CN changes from 9 for Ln = La−Sm to 8 for Ln = Gd−Ho, illustrating well lanthanide contraction within the same, virtually isotypic series.

The Cs₂NaLn(PS₄)₂ series offers a unique opportunity to investigate the precision of computational geometry optimizations of periodic structures with respect to quantitative structural changes. Several sets of geometry optimization experiments were performed using different approaches for selecting the starting model. (i) The experimental crystal structures were selected as starting models, and their geometries optimized. (ii) The experimental Cs₂NaCe(PS₄)₂ structure was optimized and then introduced as a starting model for the Pr analogue, scaling the volume of the Pr analogue by the experimental volume ratios of Pr and Ce analogues, V(Pr)/V(Ce). The optimized Cs₂NaPr(PS₄)₂ structure was used as a starting model for the Nd analogue, with the volume scaled by the V(Nd)/V(Pr) ratio, and so forth (optimization with an increasing atomic number). (iii) The experimental Cs₂NaHo(PS₄)₂ structure was optimized and then introduced as a starting model for the Dy analogue, with the volume scaled by the V(Dy)/V(Ho) ratio. The optimized Cs₂NaDy(PS₄)₂ structure was used as a starting model for the Tb analogue, with the volume scaled by the V(Tb)/V(Dy) ratio, and so forth (optimization with a decreasing atomic number).

Ideally, all three approaches should have resulted in the same outcome; however, this was not the case (Figure 4). The geometry optimization using approach (i) resulted in a CN of 9 for the structures of Cs₂NaCe(PS₄)₂ and Cs₂NaPr(PS₄)₂, while Cs₂NaNd(PS₄)₂ and other heavier analogues adopt a structure with a CN of 8 for the lanthanide sites. These changes qualitatively agree with the experimental data, although quantitively the transition between high- and low-CN structures is observed between Sm and Gd, which is further toward the heavier elements in the lanthanide series than the calculation predicted. A similar trend was observed when we employed approach (ii), in which the Cs₂NaCe(PS₄)₂ model was used as a starting point for geometry optimization. Surprisingly, the opposite result was obtained when we started the geometry optimization from the other end of the series.
starting with the structure of Cs$_2$NaHo(PS$_4$)$_2$ as the initial input following approach (iii). In this case, the high-CN structure was never obtained even for the Ce and Pr analogues. Energy calculations show similar yet different energies for the modifications. There is a distinct energetic difference in the case of Cs$_2$NaCe(PS$_4$)$_2$, with the higher-CN modification clearly more energetically favorable than the lower-CN analogue. The difference is not as apparent for the Pr analogue, showing almost identical energies for both CNs. This indicates that the low-CN modifications create a local energy minimum that can be overcome using a different starting geometry. It may be thus concluded that the computed geometries are highly dependent on the starting geometry, which can promote relaxation to a local minimum, and that having a good starting model is crucial for finding an accurate lowest-energy geometry. Note that an SQS with fixed locations for Cs atoms was used, whereas allowing the position of Cs to vary might influence the Ln−S(8) distances, and hence the CN.

Cs$_5$Ln$_2$(PS$_4$)$_6$ (Ln = La and Ce). Cs$_5$La$_5$(PS$_4$)$_6$ and Cs$_5$Ce$_5$(PS$_4$)$_6$ crystallize in monoclinic space group C2/c and are characterized by a three-dimensional framework. The structure consists of [LnS$_8$]$_{13-}$ distorted square antiprisms, where corrugated chains running along the b axis are composed of 8-coordinate rare earth polyhedra surrounded by [PS$_4$]$^{3-}$ tetrahedra (Figure 5). The framework is formed by corner- and edge-sharing rare earth polyhedra that link the chains. Ln−S bond lengths are shorter than expected due to the presence of disordered sulfur atoms, and bond distances range from 2.46(2)−3.244(13) Å for La to 2.527(15)−3.237(11) Å for Ce. There are three unique Ln$^{3+}$ sites, where edge-sharing Ln(2) and Ln(3) polyhedra make up the aforementioned chains and are connected to a framework by a Ln(1) polyhedron. The Ln(1) polyhedron is coordinated on opposing sides by two edge-sharing Ln(3) polyhedra and two corner-sharing Ln(2) polyhedra, as well as four edge-sharing o-thiophosphate tetrahedra.

There are three unique phosphorus sites, where P(3) is split as a result of the disordered sulfur atoms in the [LnS$_8$]$^{13-}$ polyhedra. Consequently, the [PS$_4$]$^{3-}$ tetrahedra are highly distorted, where P−S bond lengths are shorter than expected and range from 1.859(17)−2.08(2) Å for La to 1.802(15)−2.08(2) Å for Ce, and S−P−S bond angles range from 102.1(6)−123.1(6)$^\circ$ for La to 102.8(6)−123.2(6)$^\circ$ for Ce. Due to the disordered P(3) site, significantly shortened Ln(1)−S(9B) bond lengths of 2.606(19) Å for La and 2.531(16) Å for Ce are observed. Cesium atoms are disordered throughout the structure extending down the c axis (Figure 5). The considerable disorder exhibited in this structure initially resulted in some ambiguity in the structural similarities of Cs$_5$La$_5$(PS$_4$)$_6$ (Ln = La and Ce) and Cs$_5$Ln$_2$(PS$_4$)$_6$ (Ln = Pr and Er), however, a comparison of the coordination sequences for the respective structures confirmed that they are indeed isotypic to the previously reported phases of this composition.

Cs$_5$Ln$_2$(PS$_4$)$_6$ (Ln = Sm and Dy). Crystallizing in monoclinic space group $P2_1/n$, the two-dimensional structure of Cs$_5$Sm$_5$(PS$_4$)$_6$ and Cs$_5$Dy$_5$(PS$_4$)$_6$ consists of [M$_8$(PS$_4$)$_6$]$^{3-}$ layers separated by cesium cations and is isotypic to Rb$_2$Er$_2$(PS$_4$)$_6$.$^{63}$ The three unique M$^{3+}$ sites are each 8-coordinate and surrounded by sulfur atoms, where M(1) exhibits a square antiprismatic geometry while M(2) and M(3) adopt a bicapped trigonal prismatic geometry. [PS$_4$]$^{3-}$ tetrahedra share three edges with [MS$_8$]$^{13-}$ polyhedra and

Figure 4. Energies and Ln−S(8) bond distances for Ln = Ce−Ho. The experimental values of the Ln−S(8) distance change rapidly between Sm and Gd, while ab initio calculations predict a change between Pr and Nd.

Figure 5. View of the framework structure of Cs$_5$Ce$_5$(PS$_4$)$_6$ along the b axis (left) and the c axis (right). The cerium and phosphorus polyhedra and cesium atoms are colored yellow, orange, and magenta, respectively.
are arranged on opposing edges of M(2) and M(3) polyhedra. Chains formed by edge-sharing M(2) and M(3) polyhedra run along the a axis (Figure 6a) and are connected to neighboring chains to form sheets by edge-sharing M(1) polyhedra (Figure 6b). As expected, M−S bond lengths decrease from 2.7520(8)–3.3053(9) Å for Sm to 2.6972(7)–3.2410(7) Å for Dy. P−S bond lengths range from 2.0109(11)–2.0871(11) Å for Sm to 2.0107(9)–2.0827(9) Å for Dy, while S−P−S bond angles are slightly distorted and range from 103.52(5)–115.31(5)° for Sm to 102.88(4)–115.49(4)° for Dy.

**Structural Modularity in Lanthanide Thiophosphates.** To determine how the title compounds fit into the larger family of lanthanide thiophosphates, we decided to explore the topology of thiophosphates reported in the literature. This approach is based on one that we have used in the past where, for example, we recently revisited framework formation in uranium thiophosphates using a topological approach. A similar approach that allows systematization and prediction of possible topologies can be applied to lanthanide thiophosphates. To demonstrate this, we determined the topologies of all alkali-containing lanthanide thiophosphates contained in the ICSD and found in the literature, comprising 81 compounds in total (Table 3). The structures of the compounds were simplified to reveal their underlying nets by excluding alkali cations and constricting thiophosphate units to their center of gravity without changing the overall connectivity in the structure. We found that in all of these compounds the lanthanide centers are surrounded by four thiophosphate groups (either PS$^{3−}$, P$_2$S$_6^{4−}$, or P$_3$S$_9^{5−}$) in an irregular tetrahedral arrangement, giving rise to topologies based on 4-connected nodes (Figure 7). It is noteworthy that there is only one identified exception to this observation, K$_2$Yb$_2$(PS$_4$)$_4$ in which both 3- and 4-connected Yb nodes are present, likely due to steric factors and the smaller size of the Yb$^{3+}$ cation as compared to the early lanthanides. As a result, this compound forms interwoven frameworks based on a self-dual 3,4-connected tfa net. There are a number of other self-dual 3,4-coordinated nets, such as sto and tfe, that can be employed for the formation of interwoven frameworks, which are possible to achieve using the late lanthanide cations.

Depending on their connectivity, the thiophosphate groups play the role of 2, 3, or 4-connected nodes. In a series of mixed thiophosphate/halide lanthanide compounds, a halide anion in the coordination sphere of the lanthanide atom can take the role of a terminal node to decrease overall connectivity in the structure. A combination of 4-connected lanthanide nodes with thiophosphate and halide units gives rise to a large variety of topologies ranging from 0-periodic to 3-periodic nets (Table 3).

A series of compounds with a K$_{9-x}$La$_{14+x/3}$(PS$_4$)$_4$ (Ln = La, Ce, Nd, and Gd) composition exhibit nets with the lowest, 0D, periodicity due to Ln/K disorder on the lanthanide sites, which breaks the chains in the structure into isolated fragments. There are 26 compounds containing 1-periodic nets, which comprises three topological types shown in Figure 7a–c. Two of them, panels a and b, are topological isomers of [Ln(PS$_4$)$_2$]$_n^−$ chains, while Cs$_5$Ce$_2$Br$_3$(P$_2$S$_6$)$_2$(PS$_4$)$_4$ represents a distinct topology with terminal bromide anions. Of 34 lanthanide thiophosphates with a 2-periodic underlying net, 15 and 8 compounds are based on sqa and (6,3)Ia (the symbols are listed as assigned during the topology classification using the TOPOS software package) topologies shown in panels e and f of Figure 7, respectively. The sqa topological type plays an important role for lanthanide thiophosphates as most of the other underlying topologies can be derived from it by removing edges and nodes as can be seen in Figure 7g–i. The 16 remaining compounds are based on 3-periodic nets as exemplified in panels j and k of Figure 7.

The known lanthanide thiophosphates offer a convenient example of studying cation size effects on the composition and topology, symmetry, and local environment of the resulting phases. Previously, a size difference was shown to cause a change in the topology of a family of ALaP$_2$S$_6$ (A = Na, K, Rb, and Cs; Ln = lanthanide) compounds. As one can see from Table 3, this composition encompasses a broad range of topologies, which includes 2-periodic sqa and (6,3)Ia and 3-periodic pts nets. Other good illustrations of such an influence are the Cs$_5$La$_2$Br$_3$(P$_2$S$_6$)$_2$(PS$_4$)$_4$ and Cs$_5$Ce$_2$Br$_3$(P$_2$S$_6$)$_2$(PS$_4$)$_4$ compositions, in which a change from a 2D to a 1D lanthanide thiophosphate building unit that is based solely on the replacement of Ce with La is observed. K$_2$Ce[PS$_4$]$_4$ and K$_2$Gd[PS$_4$]$_4$ compositions can serve as good illustrations of a symmetry change from C2/c to C2 due to a subtle difference in the size of the lanthanide cations. While both topological and symmetric changes are well-known, a change in the local environment of the lanthanide cation without changes in topology or symmetry
has never been reported before. The Cs$_3$NaLn(PS$_4_2$) (Ln = La–Nd, Sm, and Gd–Ho) series is the first example in which the symmetry of the compound and the atomic coordinates show no significant difference, while the coordination polyhedron of the lanthanide cations changes from 9-coordinated to 8-coordinated. Despite the same composition and topology, along with close atomic coordinates and unit cell parameters (Table 1 and Table S2), the difference in the coordination environment of the lanthanide cations breaks this series into two groups of compounds with distinct structure types. In the Cs$_3$NaLn(PS$_4_2$) (Ln = Gd–Ho) series, although the lanthanide cations with a CN of 8 are “missing” a bond as compared to their analogues with Ln = La–Sm, which exhibit a CN of 9, the connectivity between the units (and therefore the topology of the underlying net) of the system stays the same, exemplifying a new type of size-driven effect on the structures on lanthanide thiophosphate compounds.

**Magnetism.** Magnetic susceptibility measurements were performed on Cs$_3$NaLn(PS$_4_2$) samples (Ln = Ce, Pr, Nd, Gd, and Tb). Both the magnetic susceptibility and the inverse magnetic susceptibility versus temperature plots can be found in Figure 8 and Figure S18, respectively. All compounds follow the Curie–Weiss law allowing for the effective magnetic moment and Weiss constant to be derived from the fit of the inverse magnetic susceptibility versus temperature. In the low-temperature region, the Pr analogue displayed some curvature that could possibly be due to crystal field splitting effects of the $^3H_4$ ground state. The derived effective magnetic moments agree with the calculated moments of the free lanthanide cations in the literature (Table 4). The Cs$_3$NaGd(PS$_4_2$) analogue showed ideal paramagnetic behavior with a Weiss constant of 0 K. The remaining analogues with Ln = Ce, Pr, Nd, and Tb exhibit negative Weiss constants, which could suggest antiferromagnetic interactions, although no magnetic ordering was observed down to 2 K. The non-zero Weiss constants for the Ce, Pr, Nd, and Tb analogues can be attributed to crystal field splitting effects, which is typical for most lanthanides excluding gadolinium. The 0 K Weiss constant for the Gd analogue supports the hypothesis that crystal field splitting effects also occur in the other analogues. The absence of magnetic interactions or ordering in the compounds can be expected as the shortest Ln–Ln distance in the series was 4.163 Å, found in the Nd and Pr analogues, which is much larger than the distance at which magnetic interactions for highly localized 4f orbitals would be expected.

### CONCLUSION

Using identical reaction conditions, a series of Cs$_3$NaLn(PS$_4_2$) (Ln = La–Nd, Sm, and Gd–Ho) compounds were obtained
and characterized, along with CsLa$_3$(PS$_4$)$_2$, CsCe$_4$(PS$_4$)$_6$, CsSm$_3$(PS$_4$)$_4$, and CsDy$_3$(PS$_4$)$_4$ side products. The CsNaLn(PS$_4$)$_2$ compounds crystallize in virtually the same structure with the only difference being in the length of one of the Ln–S bonds, which elongates as the atomic number of the lanthanide increases. This results in a transition occurring between Sm and Gd that involves a change in the lanthanide coordination number from 9 to 8, representing the first example of a size-driven effect on the structure of lanthanide thiophosphate without any topological or symmetry changes. The experimentally observed transition was corroborated with theoretical calculations, which offered a qualitative prediction of the observed trend. It was observed in the calculations that the nature the starting model used for geometry optimization affects the results as there is a local minimum in energy preventing geometry optimization when the lower-CN structure is selected as the starting point for geometry optimization.

The magnetic properties of Cs$_2$NaLn(PS$_4$)$_2$ (Ln = Ce, Pr, Nd, Gd, and Tb) were characterized by magnetic susceptibility measurements. In accordance with the large interatomic distances between the lanthanide atoms within the [Ln(PS$_4$)$_3$]$^+$ chains, all five compounds were found to be paramagnetic, with crystal electric field effects resulting in non-zero Weiss temperatures in all compounds except Cs$_2$NaGd(PS$_4$)$_2$ compounds. The ideal paramagnetic behavior observed in the case of the Gd analogue is a good indication of the absence of any magnetic interaction between the lanthanide centers.

Table 4. Derived Effective Moments and Weiss Constants for Each Analogue Along with the Calculated Literature Effective Moments for the Free Cations

<table>
<thead>
<tr>
<th></th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Gd</th>
<th>Tb</th>
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<tr>
<td>$\mu_{cd}$ ($\mu_B$)</td>
<td>2.42</td>
<td>3.63</td>
<td>3.91</td>
<td>8.05</td>
<td>9.79</td>
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<td>−40.18</td>
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<td>3.58</td>
<td>3.62</td>
<td>7.94</td>
<td>9.72</td>
</tr>
</tbody>
</table>

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03200.

PXRD patterns, EDS results, and magnetic susceptibility versus temperature plots (PDF)

Accession Codes

CCDC 1962585–1962596 and 1962605 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Figure 7. Topologies in lanthanide thiophosphates. (a–c) Topologies of the chains in Cs$_2$NaLn(PS$_4$)$_2$, Cs$_2$Nd(PS$_4$)$_2$, and Cs$_3$Ce$_4$(PS$_4$)$_6$, respectively. (d and f) hcb and (6,3)Ia topologies in Li$_2$Nd$_4$(PS$_4$)$_4$ and NaLn(PS$_4$)$_2$ (Ln = Pr and Sm), respectively. (g–i) How the ideal sqf net found in CsNdP$_2$S$_6$ relates to the topologies of K$_2$Ln$_3$(PS$_4$)$_4$ (Ln = La, Nd, and Sm), Cs$_4$Ln$_5$(PS$_4$)$_4$ (Ln = Sm and Dy), and Cs$_3$LaX$_5$(PS$_4$)$_4$ (X = Cl and Br), respectively. (j and k) Three periodic topologies found in NaLnP$_2$S$_6$ (Ln = Tb, Er, Yb, and Lu) and K$_2$Ln$_3$(PS$_4$)$_4$ (Ln = Nd and Gd), respectively. See Table 3 and the text for more details. The terminal halide anions that do not alter the topology are represented as an edge without a node.

Figure 8. Molar magnetic susceptibility vs temperature plots of Cs$_2$NaPr(PS$_4$)$_2$, Cs$_2$NaNd(PS$_4$)$_2$, and Cs$_2$NaGd(PS$_4$)$_2$. 

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Notes
The authors declare no competing financial interest.

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