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Ionothermal Synthesis of Four New Nickel Thiophosphate Anions: $[Ni(P_2S_8)_2]^{2-}$, $[Ni(P_3S_9)(P_2S_8)]^{3-}$, $[Ni(P_3S_9)_2]^{4-}$, and $[(NiP_3S_8)_4(PS_4)]^{7-}$

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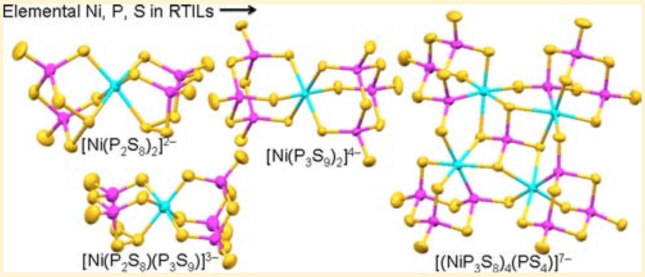
Ⓢ *Supporting Information*

ABSTRACT: Four new nickel thiophosphate anions have been isolated as 1-ethyl-3-methylimidazolium (EMIM) salts: $[EMIM]_2[Ni(P_2S_8)_2]$ (**1**), $[EMIM]_3[Ni(P_3S_9)(P_2S_8)]$ (**2**), $[EMIM]_4[Ni(P_3S_9)_2]$ (**3**), and $[EMIM]_7[(NiP_3S_8)_4(PS_4)]$ (**4**). Single crystals of each were prepared by ionothermal reaction of the elements in $[EMIM][BF_4]$. **1** can also be obtained from $[EMIM][CF_3SO_3]$. In all four anions, Ni atoms are octahedrally coordinated and P atoms are tetrahedrally coordinated. In the anion found in **1**, two tridentate 1,3-$P_2S_8^{2-}$ ligands are cis to each other. The anion in **2** contains two different tridentate thiophosphate ligands, 1,3-$P_2S_8^{2-}$ and $P_3S_9^{3-}$, whereas the anion in **3** consists of two $P_3S_9^{3-}$ ligands coordinated to the central Ni atom. The anion in **4** is complex, consisting of four $NiP_3S_8^-$ clusters surrounding a central PS_4 tetrahedron; within the $NiP_3S_8^-$ groups, one P atom is directly bound to Ni. The discovery of these four new compounds demonstrates the versatility of ionothermal methods for the synthesis of novel thiophosphates.



■ INTRODUCTION

The unique properties of ionic liquids (ILs), including high thermal stability, wide liquidus ranges, negligible vapor pressure, and their ability to dissolve a variety of materials, make them favorable media for both organic and inorganic reactions.[1−4] Recently, ILs have been successfully used as media for the preparation of zeolites,[5] metal-containing nanoparticles,[1] metal−organic frameworks,[6,7] polyoxometalates,[8] as well as coordination polymers.[9,10] Thus, ILs, specifically room-temperature ILs (RTILs),[11−13] have been studied in detail in order to replace more hazardous or environmentally harmful solvents. However, while ILs themselves have been known for decades, inorganic synthesis using ionothermal methods is a developing field of study.[14,15]

Among research on inorganic compounds using ILs, chalcogenide synthesis has been of particular interest because of the potential thermoelectric[16,17] and solar energy conversion[18] properties of the resulting products. However, of the handful of reports on chalcogenide syntheses in ILs found in the literature,[16,19−21] many result in simple binary structures.[22,23] More specifically, thiophosphates have shown important properties such as luminescence[24] but have yet to be explored with ILs.[15]

Because access to new properties often comes through the preparation of new materials, ionothermal synthesis provides an important avenue for exploration because most thiophosphates prepared via more traditional molten flux routes tend to contain smaller P/S groups such as isolated tetrahedral PS_4^{3-} or ethane-like $[P_2S_6]^{4-}$ anions.[25] For example, the compounds $A_3Nd[PS_4]_2$ (A = K, Cs)[26] and $Ba_3Ln_2[P_4S_{16}]$ (Ln = Gd−Er)[27] contain isolated PS_4^{3-} tetrahedra, whereas $A_3Zr_2P_5S_{18}$ (A = Rb, Cs)[28] and $Cs_2Ti_2(P_2S_8)(PS_4)_2$[29] have only slightly larger $[P_2S_7]^{4-}$ and $[P_2S_8]^{4-}$ anions, respectively.

Recent reports of new chalcogenide complexes prepared in ILs are the cationic species such as $[Bi_2TeBr](AlCl_4)$[16] and $[Sb_7S_8Br_2](AlCl_4)_3$.[20] These complex cations, the former crystallized as two-dimensional sheets and the latter as a double-cubane molecular cation, were isolated from an acidic IL, $[EMIM]Br/AlCl_3$.

Among known thiophosphate compounds, $KNiPS_4$ piqued our interest because of its unusual combination of solid-state and solution-phase reactivity.[30] When the $^1_\infty[NiPS_4^-]$ chains of the solid-state reaction product are dissolved in *N*,*N*-dimethylformamide (DMF), a liquid-crystalline phase is observed that, in turn, ultimately forms discrete $[Ni_3P_3S_{12}]^{3-}$ rings.[31,32] These crownlike rings exhibit pseudo-C_{3v} symmetry, and each contains three square-planar Ni^{II} d^8 atoms and three tetrahedrally coordinated P^V atoms; the counterions in the solid salts can be cryptand-encased alkali metals, alkaline-earth ions, or even other transition-metal coordination complexes.[33] This chemistry is quite different from that of the simpler solid-state $NiPS_3$ compound that contains ethane-like $P_2S_6^{2-}$ anions that coordinate octahedral Ni atoms.[34]

Here, we report the discovery of four new nickel thiophosphate anions using two different 1-ethyl-3-methylimi-

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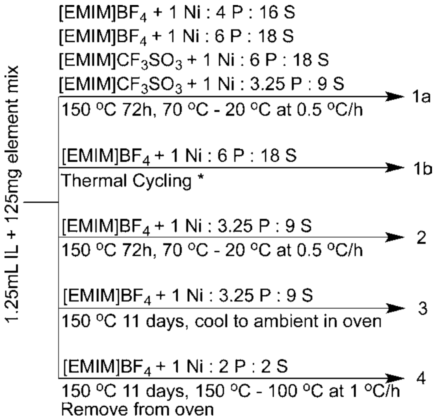
dazolium RTILs as the solvent (with tetrafluoroborate, BF_4^-, and triflate, $CF_3SO_3^-$, anions) for reactions of elemental Ni, P, and S. We also present the structures and spectroscopy of the novel anions.

■ EXPERIMENTAL SECTION

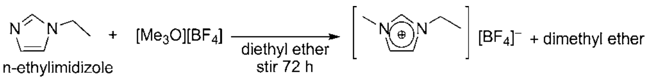
General Procedures. Elemental Ni, P, and S were combined in a nitrogen-filled MBraun Lab Master 130 glovebox. According to the ratios given in Scheme 1, the mass sums for 6−10 reactions were combined, ground together, and distributed by mass into the corresponding number of reaction tubes, and then 1.25 mL of the appropriate IL was added to each tube in a nitrogen-filled glovebag. The ILs [EMIM][BF_4] and [EMIM][CF_3SO_3] (EMIM = 1-ethyl-3-methylimidazolium) were synthesized according to the literature procedure shown in Schemes 2[35] and 3.[36] The tubes were evacuated, sealed, and heated in a temperature-controller-equipped drying oven according to the heating profiles discussed in the respective synthesis sections. Once heating and cooling were completed, the reaction tubes were opened, the ILs were decanted, and the solids were vacuum-filtered and washed with dry acetone prior to characterization.

Scheme 1. Summary of the Synthetic Routes Used for Nickel Thiophosphate Anions 1−4[a]

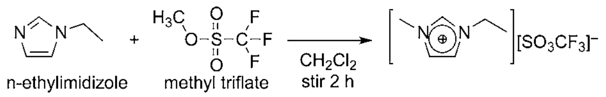


[a] Thermal cycling involved heating at 150 °C for 5 days. A power outage allowed the oven to cool to ambient temperature, and then when the power was restored, the oven returned to 150 °C before slowly cooling from 70 °C at 0.5 °C/h.

Scheme 2. Preparation of [EMIM]BF_4 from Reference 35



Scheme 3. Preparation of [EMIM]CF_3SO_3 from Reference 36



Energy-Dispersive X-ray (EDX). The chemical compositions of all samples were analyzed using an EDX-equipped scanning electron microscope (Hitachi S-3400N-II). These analyses were performed on single crystals mounted with double-sided conducting tape on aluminum stubs. The average percent compositions for all compounds agree very well with the expected molar ratios from the single-crystal diffraction studies.

Elemental Analysis. The carbon, nitrogen, and hydrogen compositions of compounds **1** and **2** were analyzed by ALS Environmental, formerly Columbia Analytical Services.

X-ray Crystallography. The structures of all compounds were determined by single-crystal X-ray diffraction studies. Data collections were carried out using an IPDS-1 or IPDS-2 Imaging Plate Diffraction System from STOE & CIE using graphite-monochromated Mo Kα radiation. For all compounds, a face-indexed absorption correction was performed using *X-red* and *X-Shape* from STOE & CIE. All structures were solved with *SHELXS-97*, and refinement was done against F^2 using *SHELXL-97*.[37] All non-H atoms, except some of the disordered C atoms of lower occupancy as well as the C and N atoms in compound **2**, were refined anisotropically. The H atoms were positioned with idealized geometry and refined isotropically with $U_{iso}(H) = 1.2U_{eq}(C)$ (1.5 for methyl H atoms). In compound **1a**, the ethyl and methyl orientations of one EMIM cation are disordered and were refined using a split model (occupancies 0.6 and 0.4, respectively). In compound **2**, all organic cations were refined using restraints. In compound **3**, one organic cation is disordered in two orientations and was refined using a split model. This cation is additionally disordered around a crystallographic mirror plane. Therefore, the structure was additionally refined in space groups *C*2 and *Cc*, but the disordering remains constant. In compound **4**, one organic cation has a disordered ethyl group that was refined using a split model, and another organic cation is disordered over two overlapping positions with refined occupancies of 0.7 and 0.3 for the two orientations. Selected crystal data and details on the structure refinements are given in Table 1.

^{31}P NMR Spectroscopy. The ^{31}P resonances of compound **1** were recorded on Varian Inova 400 MHz Fourier transform (FT)-NMR equipped with a multinuclear variable-temperature probe. Dimethyl sulfoxide (DMSO)-d_6 was used as the solvent for all scans; the samples decompose in DMSO, as evidenced by the gradual decrease in the intensity of the characteristic peaks of the anions and the concurrent appearance of additional peaks in less than 1 h.

IR Spectroscopy. The IR stretches of all compounds were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrometer in pressed KBr disks.

Synthesis of 1a and 1b, $[EMIM]_2[Ni(P_2S_8)_2]$. A total mass of 1.25 g of elemental Ni, P, and S was assembled and ground in a glovebox in the molar ratios of 1:6:18 and 1:4:16, as shown in Scheme 1. Then, 125 mg portions of the mixture were weighed into reaction tubes, and 1.25 mL of the IL, either [EMIM][BF_4] or [EMIM][CF_3SO_3], was added. The original molar ratio of 1:6:18 was used in an attempt to remake **3**; however, after characterization of **1a** and **1b**, the direct elemental ratio of 1:4:16 was used and resulted in higher yield. The tubes were heated for 4 days at 150 °C, followed by rapid cooling to 70 °C, and then were further cooled at 0.5 °C/h to 20 °C. **1b** was isolated from a single set of reaction tubes that underwent uncontrolled thermal cycling due to a power outage. Yields based on Ni were 37.6% (62.0 mg) from [EMIM][BF_4] and 55.8% (92.1 mg) from [EMIM][CF_3SO_3]. Elem anal. Calcd for **1** ($C_{12}H_{22}N_4NiP_4S_{16}$): C, 15.7; H, 2.42; N, 6.10. Found: C, 15.3; H, 2.91; N, 5.89. ^{31}P NMR (400 MHz, DMSO-d_6, 20 °C): δ 82.0. FT-IR from [EMIM][BF_4]: ν($EMIM^+$) 960 (w), 916 (w), 798 (w), 772.98 (vw), 699 (w), 667 (sh), 642 (s), 618 (m), 592 (vw), 522 (w), ν($[Ni(P_2S_8)_2]^{2-}$) 824 (m), 751 (w), 741 (w), 691 (m), 675 (s), 574 (m), 548 (m), 500 (m), 467 (m), 461 (m), 457 (w) cm^{-1}. FT-IR from [EMIM][CF_3SO_3]: ν($EMIM^+$) 953 (w), 916 (w), 798 (w), 700 (w), 667 (sh), 644 (s), 618 (s), 596 (vw), ν($[Ni(P_2S_8)_2]^{2-}$) 825 (m), 751 (w), 741 (w), 690 (m), 676 (s), 575 (s), 548 (m), 502 (m), 468 (m), 463 (m), 457 (w) cm^{-1}.

Synthesis of 2, $[EMIM]_3[Ni(P_3S_9)(P_2S_8)]$. **2** was prepared in the same manner as **1**; however, it was only isolated from [EMIM][BF_4] from the molar ratio 1:3.25:9 Ni/P/S (see Scheme 1). Large, dark-orange crystals formed in long, hollow hexagonal tubes, encasing the IL within. The yield was found to be 38% (115.9 mg) based on Ni. Elem anal. Calcd for **2** ($C_{18}H_{33}N_6NiP_5S_{17}$): C, 19.8; H, 3.05; N, 7.69. Found: C, 21.5; H, 2.88; N, 7.89. FT-IR: ν($EMIM^+$) 956 (br), 798 (w), 699 (w), 668 (sh), 646 (s), 617 (s), ν($[Ni(P_3S_9)(P_2S_8)]^{3-}$) 983

Table 1. Crystallographic Data for 1–4

	1a	1b	2	3	4
chemical formula	$[Ni(P_2S_8)_2]^{2-}$	β-$[Ni(P_2S_8)_2]^{2-}$	$[Ni(P_3S_9)(P_2S_8)]^{3-}$	$[Ni(P_3S_9)_2]^{4-}$	$[(NiP_3S_8)_4(PS_4)]^{7-}$
a, Å	22.5477(9)	7.2317(5)	11.8394(2)	22.0276(14)	10.5512(7)
b, Å	7.2491(2)	17.7138(9)	20.0693(3)	12.2186(7)	16.0948(10)
c, Å	24.0143(9)	13.4488(9)	56.7194(13)	22.3472(12)	32.066(2)
α, deg	90	90	90	90	100.936(8)
β, deg	116.410(3)	93.637(8)	90	119.397(6)	91.108(8)
γ, deg	90	90	90	90	105.420(7)
V, Å^3	2515.9(2)	1719.33(19)	13476.8(4)	5240.2(5)	5140.0(6)
Z	4	2	12	4	2
fw, g mol^{-1}	917.89	917.89	1092.08	1266.28	2569.79
space group	$P\,2_1/n$	$P\,2_1$	$P\,2_1\,2_1\,2_1$	$C\,2/c$	$P\,\bar{1}$
T, °C	20	−73	20	−100	20
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
D_{calcd}	1.734	1.773	1.615	1.605	1.661
μ, mm^{-1}	1.701	1.739	1.425	1.303	1.695
R1(F_o)^a	0.0356	0.0478	0.0444	0.0380	0.0554
wR2(F_o^2)	0.0838	0.1194	0.1222	0.0916	0.1309

^{a}R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1–4

	1a	1b	2	3	4
Ni–S	2.354(1) −2.5821(8)	2.369(2) −2.554(2)	2.369(3) −2.563(3)	2.4337(7) −2.4580(6)	2.381(2) −2.602(2)
P–S	1.931(2) −2.137(1)	1.945(3) −2.130(2)	1.936(5)− 2.128(3)	1.953(1) −2.1266(9)	1.941(3) −2.195(2)
S–S	2.056(1) −2.064(1)	2.060(2) −2.068(3)	2.056(4) −2.063(4)		
cis-S–Ni–S	78.01(2) −95.34(3)	80.44(6) −95.90(6)	78.9(1) −101.5(1)	82.96(2) −97.04(2)	80.99(6) −98.55(7)
trans-S–Ni–S	172.82(3) −177.78(3)	175.94(7) −176.81(7)	169.4(1) −179.4(2)	180.00(2)	167.41(8) −175.99(8)
cis-P–Ni–S					79.48(7) −98.55(7)
trans-P–Ni–S					170.17(8) −175.48(8)
S–P–S	102.94(5) −118.08(5)	103.5(1) −119.8(1)	102.7(2) −120.1(2)	102.37(4) −116.79(5)	100.4(1) −117.9(2)
P–S–P	109.89(4) −110.81(5)	110.0(1) −110.2(1)	109.1(2) −110.4(2)	109.18(4) −110.08(4)	97.6(1) −110.9(1)
P–S–S	99.64(5) −101.60(5)	99.8(1) −101.63(9)	99.7(1) −100.9(2)		
S–S–S	106.20(5) −106.75(5)	105.2(1) −106.1(1)	106.1(2) −106.7(2)		
Ni–P–S					109.9(1) −127.8(1)
Ni–S–Ni					120.09(8) −123.18(8)

(br), 924 (br), 818 (m), 741 (w), 730 (w), 686 (m), 666 (s), 656 (s), 607 (m), 590 (m), 579 (m), 556 (m), 544 (w), 493 (s), 464 (m), 460 (m), 458 (m) cm^{-1}.

Synthesis of 3, $[EMIM]_4[Ni(P_3S_9)_2]$. **3** was prepared in the same fashion as **2** except for the heating profile (see Scheme 1). The tubes were heated at 150 °C for 11 days and then removed from the oven without slow cooling. After no initial crystal formation, the tubes were left for 1 month without disturbance; opaque orange crystals formed. The yield was not calculated. FT-IR: $\nu(EMIM^+)$ 958(br), 840 (m), 773 (w), 757 (m), 703 (vw), 669 (sh), 641 (s), 620 (s), 519 (w) cm^{-1}, $\nu([Ni(P_3S_9)_2]^{4-})$ 983 (br), 923 (br), 790 (vw), 658 (s), 647 (s), 607 (w), 586 (s), 576 (vw), 559 (m), 549 (w), 509 (w), 500 (s), 497 (s), 494 (s), 485 (m) cm^{-1}.

Synthesis of 4, $[EMIM]_7[(NiP_3S_8)_4(PS_4)]$. **4** was prepared in the same manner as **1** using the molar ratio described in Scheme 1. The tubes were heated for 11 days at 150 °C and then slowly cooled to 100 °C at 1 °C/h, at which point the tubes were removed from the oven to cool rapidly to room temperature. A few black needles were produced in sufficient amounts to perform EDX (see the Supporting Information) and single-crystal X-ray diffraction studies (Table 1). The yield was not calculated. FT-IR: $\nu(EMIM^+)$ 959 (w), 798 (w), 618 (m), 597 (w), 523 (w), $\nu([(NiP_3S_8)_4(PS_4)]^{7-})$ 983 (vw), 874 (vw), 875 (vw), 819 (br), 747 (w), 732 (w), 670 (s), 667 (s), 655 (s), 618 (m), 574 (s), 559 (s), 515 (m), 506 (w), 501 (w), 483 (s), 472 (w), 458 (w), 438 (s), 433 (m), 424 (w), 419 (w) cm^{-1}.

■ RESULTS AND DISCUSSION

Syntheses. All title compounds were obtained as single crystals using the reactions shown in Scheme 1. All preparations of the title thiophosphate anions were carried out in ILs synthesized according to literature procedures as shown in Schemes 2 and 3. Because of the preparation routes chosen, we avoided the two largest challenges of using ILs in synthesis: the high purchase price by preparing the ILs ourselves and the difficulty in purification of prepared ILs because the only byproducts of the syntheses were solvents that were easily removed via vacuum. In addition to the crystals of the new anions, all reactions in $[EMIM][BF_4]$ yielded various amounts of amorphous black powder; all reactions carried out in $[EMIM][CF_3SO_3]$ yielded only orange needles of **1**. Despite its role as our initial impetus for the exploration, $[Ni_3P_3S_{12}]^{3-}$ was not observed in any crystalline products.

Crystal Structures. In **1**–**4**, there are several structural similarities: all Ni^{II} atoms are octahedrally coordinated, all P atoms are tetrahedrally coordinated, and S atoms are found in several different bonding modes ranging from terminal to μ_3. In addition, the only cations observed in the crystalline products were $EMIM^+$ cations, regardless of whether $[EMIM][BF_4]$ or $[EMIM][CF_3SO_3]$ was used as the IL for the synthesis. The Ni–S distances of 2.354(1)–2.602(2) Å, P–S distances of

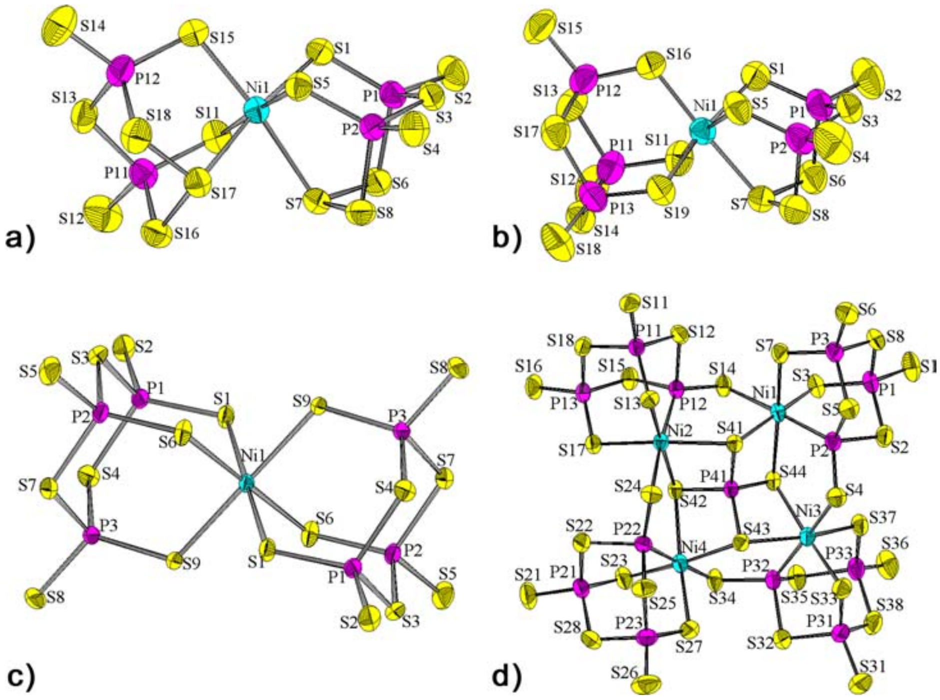


Figure 1. Thermal ellipsoid plots (50%) of the structures of nickel thiophosphate anions: (a) **1a**, $[Ni(P_2S_8)_2]^{2-}$ identical with that found in **1b**; (b) **2**, $[Ni(P_3S_9)(P_2S_8)]^{3-}$; (c) **3**, $[Ni(P_3S_9)_2]^{4-}$, (d) **4**, $[(NiP_3S_8)_4(PS_4)]^{7-}$. Ni atoms are teal, P atoms are magenta, and S atoms are yellow.

1.931(2)−2.195(2) Å, and S−S distances of 2.056(1)−2.068(3) Å (see Table 2) all agree with other published thiophosphate compounds in the literature.[38−40] Structures **1a**, **3**, and **4** contain disordered cations, but simple modeling of the two major orientations was sufficient for reasonable accounting of the available electron density. Despite the low value for sin θ/λ of the data collected for **3**, owing to the very large unit cell dimension of 56.7194(13) Å, the single-crystal structure solution clearly resolves the inorganic portions of the structure that were refined anisotropically; the lighter atoms were refined only isotropically. In all other structure solutions, all atoms were refined anisotropically.

The same nickel thiophosphate anion is found in both **1a** and **1b**. It contains a central Ni atom with two tridentate 1,3-$P_2S_8^{2-}$ ligands (see Figure 1a). On each, only S atoms coordinate with the Ni; two of these are coordinated to the P atoms of the 1,3-$P_2S_8^{2-}$ moiety, and the third is the central S atom of the trisulfide group of the P_2S_4 ring of the 1,3-$P_2S_8^{2-}$ group. The trisulfide bridges of the two 1,3-$P_2S_8^{2-}$ ligands are arranged cis rather than trans relative to one another, giving the anion pseudo-C_2 symmetry. The structural differences between uncoordinated and coordinated 1,3-$P_2S_8^{2-}$ ligands are small enough to be attributed to the difference in temperature between X-ray data collection experiments.

The 1,3-$P_2S_8^{2-}$ ligand found in **1a** and **1b** is not new, but the tridentate coordination mode has never been observed. The first appearance of 1,3-$P_2S_8^{2-}$ is as an isolated anion prepared as a PPh_4^+ salt from the reaction of PPh_4S_5 and white phosphorus in acetonitrile.[38] The only report of this anion as a ligand to transition-metal centers is $[(TiCl_2)(P_2S_8)]_2$ prepared from $TiCl_4$ and P_4S_{10} in CS_2.[41] In this ring-shaped neutral molecule, the P_2S_8 groups bridge two octahedrally coordinated Ti atoms; the four terminal S atoms of each P_2S_8 group coordinate to the Ti atoms, and two Cl atoms complete the coordination sphere. The trisulfide group of the P_2S_4 ring of the 1,3-$P_2S_8^{2-}$ group does not coordinate to the Ti atoms.

The bond angles and distances found in **1a** and **1b** are essentially the same (Table 2). Apparently, unintentional thermal cycling due to a thunderstorm power outage caused dissolution of the $[Ni(P_2S_8)_2]^{2-}$ anion and precipitation in the different monoclinic crystalline form. However, only the morphology of the crystals is different: **1a** grows as long, orange, rectangular needles, and **1b** appears as cubes of the same orange color.

The new anion in **2** contains two different tridentate thiophosphate ligands: the same 1,3-$P_2S_8^{2-}$ unit found in **1** and a nonathiocyclotriphosphate, $P_3S_9^{3-}$, moiety (see Figure 1b). Upon coordination to the Ni atom, the geometrical features of the $P_3S_9^{3-}$ group change very little; differences observed in the P−S distances of the coordinating S atoms are sufficiently small as to arise from the temperature difference in data acquisition: from an average of 1.963 Å (120 K)[39] to an average of 1.988 Å (173 K) in **2**.

Similar to the $P_2S_8^{2-}$ group, the $P_3S_9^{3-}$ moiety is not new, but it has never been observed in the coordination mode exhibited in **2**. This anion, first reported in 1982,[42] was prepared from P_4S_{10} in liquid ammonia at −33 °C, and the structure was first reported in 1992 from a crystal prepared from the direct reaction of the elements with amines in various traditional solvents (i.e., chloroform and DMF).[39] More recently, it was prepared from the reaction of P_4S_{10} and *N*,*N*′-diphenylurea and isolated as the pyridinium salt $[pyH]_3[P_3S_9]$.[40]

There are only two reports of $P_3S_9^{3-}$ serving as a ligand, one compound with Ga atoms and the other with Cu atoms. In (*t*-Bu)$_6$Ga$_3$P$_3$S$_9$,[43] one central P_3S_9 group participates in bidentate bonding through terminal S atoms to three Ga atoms, forming a large trimetallic ring. This compound was prepared from *t*-Bu$_3$Ga and P_4S_{10} in pentane at ambient temperature. The P_3S_9 groups found in $K_2CuP_3S_9$[44] were prepared from K_2S, P_2S_5, and Cu under reactive flux conditions. In this case, the thiophosphate ligands bridge Cu atoms to form a coordination polymer, binding in a tridentate mode to one Cu atom on one side and in a monodentate mode to a Cu atom on the other.

The molecular anion found in **3** comprises a central Ni atom coordinated to two tridentate $P_3S_9^{3-}$ ligands, assuming pseudo-D_{3h} symmetry (see Figure 1c). The geometrical parameters for the ligand are essentially the same as those found in **2**.

The structure of the nickel thiophosphate anion found in **4** is complex (see Figure 1d). It can be described as a central PS_4^{3-} group surrounded by four interconnecting $NiP_3S_8^-$ groups, thus forming a disk-shaped 7− polyatomic anion. In fact, there is a distorted square of Ni_4S_4 circumscribed around the central PS_4^{3-} group. The Ni-atom coordination sphere is thus comprised of two S atoms from the central square, two S and one P atom from the P_3S_8 groups, and one S atom from a neighboring $NiP_3S_8^-$ moiety.

The coordination within the $NiP_3S_8^-$ groups is unusual because one P atom is directly bound to Ni; we know of no other thiophosphate compounds that exhibit P atoms that coordinate to metal atoms in *two modes*: directly, acting as a phosphine ligand, and through bridging S atoms. The four $NiP_3S_8^-$ groups resemble β-P_4S_8, wherein one P−P bond is found in the midst of many P−S−P linkages.[45] The P atoms coordinated to the Ni atoms must be formally P^{III} atoms, whereas the P atoms surrounded by four S atoms are formally P^{V}. This is consistent with the overall charge on the molecular anion; the empirical formula for the anion can be written as $Ni^{II}_4P^{III}_4P^{V}_9S^{II-}_{36}$ for an overall ionic charge of 7−. Moreover, the P^{III}−S distances are longer, on average, than those observed for P^{V}−S.

Of the four anions presented herein, **4** exhibits the most distortion from idealized tetrahedral coordination for P atoms and octahedral coordination for Ni atoms. In particular, the 100.38(11)° S34−P32−S35 angle from the phosphine-coordinated P atom is the smallest observed. Moreover, the Ni atoms have S−Ni−S angles that range from 80.99(6)° S41−Ni1−S44 to 98.55(7)° S33−Ni3−S43 (Table 2).

^{31}P NMR Spectroscopy. Finding a suitable solvent for NMR spectroscopy was a challenge because the thiophosphate anions were soluble in few non-oxygen-containing solvents. Compounds **1**−**3** are insoluble in chloroform, acetone, and acetonitrile. DMSO-d_6 was used for all scans, but slow decomposition of all products was observed, beginning after only ~30 min. The observed chemical shift of δ 81.98 for **1** is consistent with the shift (δ 83) observed for the isolated $P_3S_9^{3-}$ anion.[42]

IR Spectroscopy. Most features of the IR spectra of **1**−**4** are observed below 800 cm^{-1}. After removal of the many peaks from the EMIM cations present in all salts, distinctive patterns for the 1,3-$P_2S_8^{2-}$ and $P_3S_9^{3-}$ ligands are observed (see the Supporting Information). Several of the peaks from the homoleptic anions found in **1** and **3** are observed in the mixed-anion **2**. The IR spectrum of **4** has many peaks in the same low-energy range, but these do not match peaks from **1**−**3** (see Table S1 in the Supporting Information). Uniquely identified absorbances are observed for all four compounds: **1**, 825 and 675 cm^{-1}; **2**, 818 cm^{-1}; **3**, 647 and 497 cm^{-1}; **4**, 670, 618, and 438 cm^{-1}.

■ CONCLUSION

This work demonstrates the versatility of ionothermal synthesis for preparing new thiophosphate compounds directly from the elements. We are currently exploring the reactivity of other metals with thiophosphate ligands under ionothermal conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

IR spectra, CIF files, and EDX analysis for compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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