**Ionothermal Synthesis of New Cobalt and Chromium Thiophosphate Anions
[Co{Co(P₃S₈)₂]₂}⁴⁻ and [Cr(P₃S₉)₂]³⁻**

Authors:

***Jason A. Cody¹**

Lauren M. Dalecky¹

Christian A. Juillerat¹

Grant C. B. Alexander¹

Luke C. Shylanski¹

**¹Department of Chemistry, Lake Forest College, 555 N. Sheridan Rd. Lake Forest, IL
60044, United States**

***Corresponding Author: cody@lakeforest.edu**

Abstract

Two new metal thiophosphate anions, $[\text{Co}(\text{Co}(\text{P}_3\text{S}_8)_2)_2]^{4-}$ and $[\text{Cr}(\text{P}_3\text{S}_9)_2]^{3-}$, have been isolated as single crystals of EMIM (1-ethyl-3-methylimidazolium) salts from ionothermal reaction of the elements in $[\text{EMIM}][\text{CF}_3\text{SO}_3]$. The former compound is structurally unique from known thiophosphate anions, contains three cobalt ions in two different coordination environments and oxidation states, and has bridging, polydentate $\text{P}_3\text{S}_8^{3-}$ groups that coordinate to the cobalt ions through both S and P ions. The chromium thiophosphate anion contains octahedrally-coordinated Cr ions and is structurally similar to the known ion $[\text{Ni}(\text{P}_3\text{S}_9)_2]^{4-}$. The structures of both salts were determined by single-crystal X-ray diffraction. Both compounds were characterized by EDX and IR spectroscopies.

KEYWORDS: ionothermal, ionic liquid, thiophosphate

Introduction

Ionic Liquids (ILs) have been extensively studied because of their high thermal stability, negligible vapor pressure, ability to dissolve a variety of materials, reusability, and wide liquid-phase range.¹ Renewed interest has been spurred by their unique properties that enable them to be employed in a wide-range of applications including environmental air and soil purifiers,² electrolytes in photovoltaic cells and batteries,^{3,4} and synthesis of useful materials including electrodes,⁵ aluminophosphates, organic-inorganic hybrids, metal organic frameworks, and zeolites^{6,7}. The low vapor pressure and ability to dissolve a variety of materials have made ILs ideal for replacing environmentally harmful conventional organic solvents.⁸ Ionothermal synthesis methods use ILs as the solvent that can often double as a structure directing agent, in high temperature synthesis.⁹ Ionothermal methods have employed ILs to synthesize zeolites,¹⁰ metal-organic frameworks,¹¹ and polyoxometalates.¹²

The unique properties of ILs and the nearly endless cation/anion combinations provide a wide variety of experimental conditions to produce novel inorganic compounds.¹ The combination of the cation and anion changes the solvent properties. In the recent example of four nickel thiophosphate anions that precipitated as EMIM salts using ILs, the non-precipitating anion of the solvent determined the nature of the isolated salts.¹³ All four were isolated from $[\text{EMIM}][\text{BF}_4]$, but all reactions in $[\text{EMIM}][\text{CF}_3\text{SO}_3]$, regardless of widely ranging reagent proportions, heating schemes, etc. yielded only the $[\text{Ni}(\text{P}_2\text{S}_8)_2]^{2-}$ anion.¹³ Recently, we expanded the technique to include chromium and cobalt. For a more lengthy introduction to the process and importance of this approach, please see this earlier article.

There are few known ternary cobalt thiophosphate compounds: CoPS_3 ¹⁴ and CoPS .¹⁵ The CoPS_3 structure has staggered ethane-like P_2S_6 units that bridge two six-coordinate, octahedral cobalt ions making two-dimensional sheets. The cubic CoPS structure is highly condensed with octahedrally coordinated cobalt ions and disordered, tetrahedrally coordinated phosphorus and sulfur ions.

There are few cobalt structures that contain cobalt ions with both 2+ and 3+ oxidation states, and all of the known compounds contain cobalt ions that are octahedrally coordinated to nitrogen or oxygen ions.^{16,17,18} The most interesting of these, $\text{Co}_3(\mu\text{-Hdartz})_6(\text{H}_2\text{O})_6 \cdot (\text{NO}_3)_8 \cdot 4\text{H}_2\text{O}$ (Hdartz = 3,5-diamino-1,2,4-triazole),¹⁹ contains three cobalt ions, two of which are 3+ and one that is 2+, similar to the title compound.

In all three of the known simple chromium thiophosphates, CrPS_4 ,²⁰ $\text{K}_3\text{Cr}_2(\text{PS}_4)_3$,²¹ and $\text{CrP}_3\text{S}_{9,24}$,²² the chromium ion is octahedrally coordinated to sulfur ions. The two-dimensional sheets found in CrPS_4 comprise one-dimensional chains of CrS_6 octahedra linked by PS_4 groups. The $\text{CrP}_3\text{S}_{9,24}$ structure contains chromium ions octahedrally coordinated to PS_4 groups bridged by disulfur linkages and single sulfur ions. All of the phosphorus ions are tetrahedrally coordinated to sulfur ions in the $\text{CrP}_3\text{S}_{9,24}$ compound.

Herein we present the structures of the new metal thiophosphates $[\text{EMIM}]_4[\text{Co}(\text{Co}(\text{P}_3\text{S}_8)_2)_2]$ and $[\text{EMIM}]_3[\text{Cr}(\text{P}_3\text{S}_9)_2]$.

Material and Methods

A total mass of 1.25 g of elemental transition metal, phosphorus, and sulfur were combined and ground together in a nitrogen-filled MBraun Lab Master 130 glovebox. Pyrex tubes were charged with 125 mg of the elemental mixture and then transferred to a nitrogen-filled glovebag wherein a 1.25 mL aliquot of $[\text{EMIM}][\text{CF}_3\text{SO}_3]$ was added. The IL was synthesized according to the procedure shown in Figure 1.²³ The tubes were vacuum-sealed and heated in a temperature-controller-equipped drying oven. After the heating profile was complete, the solids in the reaction tubes were filtered in the glovebag and kept under nitrogen before analysis. The IL filtered off was stored under nitrogen and reused for reactions with similar conditions.

Synthesis of $[\text{EMIM}]_4[\text{Co}(\text{Co}(\text{P}_3\text{S}_8)_2)_2]$

In an attempt to make a 1:6:18 ratio, an undergraduate research student inadvertently prepared a 1:22:4 molar ratio (8.5 mg: 98.1 mg: 18.5 mg) of cobalt, phosphorus and sulfur that was loaded as described above and heated in an oven at 150 °C for 72 hours. This error was fortuitous; based on the compounds previously isolated with nickel,¹³ such a large phosphorous loading might never have been attempted. The tube was then quickly cooled to 70 °C and slowly cooled at a rate of 0.5 °C/h from 70 °C to 30 °C. After completion of the heating profile, the tube was opened, filtered, and the crystals were separated by hand. The few isolated crystals were red needles surrounded by gray powder (EDX indicates a 1:2.2 ratio of phosphorus to sulfur). The red needles slowly decompose in air with no visible change in appearance.

Synthesis of [EMIM]₃[Cr(P₃S₉)₂]

A 1:6:18 molar ratio (8.0 mg: 28.7 mg: 90.6 mg), of chromium, phosphorus, and sulfur was used in an attempt to prepare an analog of nickel thiophosphate anion with the same ratios.¹³ The mix was prepared as described above and heated in an oven at 150 °C for 72 hours. The tube was then cooled to 30 °C at 0.5 °C/h, opened, filtered, and contents sorted by hand. The isolated solids were orange plates of the product surrounded by a byproduct of black powder. The color of the plates varies from yellow to red as the thickness increases. The orange plates are also air sensitive.

X-ray Crystallography

The structure of the cobalt compound was determined by single-crystal X-ray diffraction data collected on a Bruker KAPPA APEX-II single crystal X-ray diffractometer with a molybdenum source. The structure was solved and refined using *SHELXL-14*²⁴ in the Olex 2 GUI.^{25,26} The inorganic anion was refined anisotropically and the EMIM cations were refined isotropically. One of the EMIM⁺ cations is disordered over two overlapping positions with refined occupancies of 0.6 and 0.4 for the two orientations. All of the EMIM cations in the Co structure were refined using restraints.

The structure of the chromium compound was obtained using Nonius CCD diffractometer with a molybdenum source. A set of 200 frames was collected with a rotation of 2.000° per frame and an exposure time of 600s; the crystal to detector distance was 29.60 mm. Refinements were done with the *SHELXTL-97*²⁷ software package; absorption correction was made with the program *Jana2006*²⁸ using the program *X-SHAPE*.²⁹

Refinement of the inorganic portion of the structure [Cr(P₃S₉)₂]³⁻ was straightforward whereas the refinement of the organic EMIM⁺ cations was not. Both unique cations are disordered; the first is disordered over two overlapping, planar locations, sharing two common carbon ions. The occupancy of the two positions was refined to a value of 0.673(10) for the major part and 0.327(10) for the minor part. The second unique EMIM cation is disordered over a center of inversion and therefore was refined as 50% occupied for the original and 50% occupied for the symmetry-generated version of the molecule. Both cations were refined anisotropically and hydrogen ions were fixed in a riding model.

EDX

Energy dispersive x-ray analysis (EDX) provides semi-quantitative micro-elemental analysis from the use of a scanning electron microscope (SEM) that analyses characteristic x-rays emitted from atoms when stimulated with a beam of electrons.³⁰ The chemical composition of needles of both compounds were analyzed by an EDX-equipped SEM (Hitachi S-3400N-II). This was preformed with the crystal mounted on double-sided conducting tape on an aluminum stub.

The observed molar ratio of cobalt, phosphorus, sulfur averaged over several spot and area analyses of several crystals was 1 : 4.66 : 11.4, in good agreement with the molar ratio determined from the crystal structure solution (1 : 4 : 10.7). Synthesis from this molar ratio was attempted, but the lack of success implies the excess phosphorous is needed to produce the Co crystals.

The observed molar ratios of chromium, phosphorus, sulfur averaged 1:7.1:22.1, in an acceptable agreement with the ratio determined from the crystal structure solution (1:6:18). The ratio of sulfur to phosphorus averaged 3.1:1.

FT-IR

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

The observed stretches for [EMIM]₄[Co(Co(P₃S₈)₂)₂] were $\nu(\text{EMIM}^+)$ 668 (vw) and 623 (w) cm⁻¹, $\nu[\text{Co}(\text{Co}(\text{P}_3\text{S}_8)_2)_2^{4-}]$ 824 (w), 813 (sh), 746 (sh), 735 (w), 720 (sh), 618 (sh), 558 (sh), 493 (m), 473 (sh), 458 (sh), and 449 (m) cm⁻¹, $\nu(\text{CF}_3\text{SO}_3^-)$ 758 (w), 640 (s), 571 (m), 520 (w) cm⁻¹.

The observed stretches for [EMIM]₃[Cr(P₃S₉)₂] were FT-IR: $\nu(\text{EMIM}^+)$ 846 (vw), 701 (vw), 668 (vw), and 616 (w) cm⁻¹, $\nu[(\text{Cr}(\text{P}_3\text{S}_9)_2)^{3-}]$ 965 (vw), 818 (w), 807 (w), 734 (w), 706 (sh), 673 (sh), 658 (s), 590 (sh), 580 (m), 522 (sh), 494 (s), 459 (sh), 419 (vw), and 402 (w) cm⁻¹. The IR spectrum of the nickel analog shares similar stretches to those at 658 (s) and 494 (s) cm⁻¹.¹³

Results and Discussion

Table 1. Crystallographic Data

	Co	Cr
Formula	[EMIM] ₄ [Co(Co(P ₃ S ₈) ₂) ₂]	[EMIM] ₃ [Cr(P ₃ S ₉) ₂]
M	2019.02	1148.40
Crystal system	orthorhombic	monoclinic
Space group	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	17.6238(11)	12.735(3)
<i>b</i> (Å)	19.2860(12)	10.150(2)
<i>c</i> (Å)	21.2766(14)	18.316(4)
α (°)	90	90
β (°)	90	100.80(3)
γ (°)	90	90
<i>V</i> (Å ³)	7231.8(8)	2325.6(9)
<i>Z</i>	4	2
<i>D</i> _{calc} (g cm ⁻³)	1.854	1.640
μ (mm ⁻¹)	1.90	1.287
F(000)	4068.0	1170

R_{int}	0.1206	0.0672
Total reflections	141596	28259
Unique reflections	21128	5084
$I > 2\sigma(I)$	11209	3455
$R_1, wR_2 \text{ } I > 2\sigma(I)$	0.055, 0.1216	0.0689, 0.1779
T (K)	100	293
Maximum, minimum electron density ($\text{e}/\text{\AA}^3$)	1.33, -1.29	2.006, -0.669

[EMIM]₄[Co(Co(P₃S₈)₂)₂]

Crystal Structure

The compound, [EMIM]₄[Co(Co(P₃S₈)₂)₂] contains three cobalt ions in two different coordination environments (octahedral and tetrahedral) and two different oxidation states, +3 and +2 (See Fig 2).

The central, tetrahedrally-coordinated Co ion bridges two Co(P₃S₈)₂ units through four S atoms; each of the S atoms belongs to one of the four P₃S₈³⁻ ligands. In turn, each of these P₃S₈³⁻ groups coordinates to their respective Co ions through one P(III) ion and two S ions, creating an octahedral coordination environment for the Co ions. The presence of both phosphorus- and sulfur-ion bonding modes for thiophosphates is rare and has only been reported previously in Ni₄P₁₃S₃₂⁷⁻.¹³ The P₃S₈³⁻ ligands also contain two P(V) ions tetrahedrally-coordinated to S ions. All P-S, Co-P, and Co-S distances are consistent with previous structural studies.

These coordination geometries for Co(II) and Co(III) are not new, but the combination of both in the same structure with only one type of ligand is unique. In the literature there are several examples of tetrahedral CoS₄ groups including those containing two bidentate sulfur-containing ligands such as in [Co(C₃S₅)₂]²⁻,³¹ or four monodentate sulfur-containing ligands as in [Co(C₅H₁₂N₂S)₄](ClO₄)₂.³² In all of these examples, when the oxidation state was assigned to the central, tetrahedrally coordinated cobalt ion it is 2+.³²

There are seven reported structures of a cobalt ion octahedrally coordinated to two phosphorus ions and four sulfur ions, all of which contain two bidentate sulfur ligands and one bidentate phosphate ligand; none have S and P coordinating from the same ligand. In the following compounds the cobalt ion is octahedrally coordinated to three organic bidentate ligands attached to the metal by the sulfur or phosphorus ions: [Co(C₂H₅OCS₂)₂(C₆H₁₆P₂)] [B(C₆H₅)₄],³³ [Co(dppe)(EtOCS₂)(COS₂)] (dppe = 1,2-bis(diphenylphosphino)ethane),³⁴ [Co(dtc)₂{(Ph₂PO)₂BF₂}] (dtc = N,N-dimethyldithiocarbamate)³⁵, and [Co(S₂PMe₂)₂(Me₂PCH₂CH₂PMe₂)]BF₄.³⁶ The other three examples contain two bidentate organic ligands attached to the metal by a sulfur

and two phosphines: trans- and cis-[Co(dtc)₂(PMe_{3-n}Ph_n)₂]⁺ (n = 0, 1, 2 or 3),³⁷ [Co(dtc)₂(PPh₂)₂]BF₄,³⁸ and [Co(dtc)₂{P(OMe)_{3-n}Ph_n}₂]⁺ (n = 0-2) complexes.³⁹

The charge of the [Co(Co(P₃S₈)₂)₂]⁴⁻ anion was determined from the number of [EMIM]⁺ cations observed in the crystal structure. This overall charge of 4-, combined with all S ions (2- each for a total -64), the reasonably-assigned +3 and +5 for the phosphine and sulfur-surrounded phosphorus ions (sum = +52), balances all but eight positive charges for the three Co ions. Thus, they are reasonably assigned +2 for the central Co ion and +3 for the two octahedrally-coordinated Co ions. The observed Co-S distances are consistent with this assignment; the Co(II)-S distances of 2.326(3)-2.332(4) are slightly longer than those of Co(III)-S 2.272(4)-2.319(3).

[EMIM]₃[Cr(P₃S₉)₂]

Crystal Structure

The first instance of the P₃S₉³⁻ appearing as a tridentate ligand in a mono-metal complex was in [EMIM]₂[Ni(P₃S₉)₂].¹³ The prior to this, the anion appeared as a multi-metal bidentate ligand, coordinating to three Ga ions in (t-Bu)₆Ga₃P₃S₉,⁴⁰ and as coordination polymer with Cu in K₂CuP₃S₉.⁴¹ In neither case does P₃S₉³⁻ act as a tridentate ligand.

Within crystallographic databases when chromium is found coordinated to sulfur it is most often found with three bidentate ligands, such as S₂CC₆H₆⁴² or S₂COC₂H₅,⁴³ or within highly coordinated metallocubane structures such as [Cp₆Cr₈S₈{C(S)NEt₂}₂]. Although sulfur and phosphorus have both been used as coordination method of many organic ligands, strictly triphosphates have not been found coordinated to Cr(III).⁴⁴

The chromium ion is octahedrally coordinated to the sulfur ions in the P₃S₉³⁻ tridentate ligand. The coordination complex is analogous to that found in the [EMIM]₂[Ni(P₃S₉)₂]¹³ compound, but the crystal structure varies since an additional [EMIM]⁺ cation is needed to balance the charge, thus resulting in a new structure.

Conclusions

The new cobalt and chromium thiophosphate compounds presented herein demonstrate the applicability of ionothermal synthesis to two new metals in the thiophosphate system. The structurally unique anion [Co(Co(P₃S₈)₂)₂]⁴⁻ has rare coordination of P ions to a metal ion from a thiophosphate ligand and contains Co ions in both tetrahedral and octahedral coordination. The synthesis of the chromium analog of the original nickel thiophosphate anion, [Ni(P₃S₉)₂]²⁻ demonstrates the reactivity of another transition metal with thiophosphate ligands. Both syntheses demonstrate the versatility of ionothermal synthesis for preparing new thiophosphate compounds.

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Appendices

CCDC 1428601 contains the supplementary crystallographic data for [EMIM]₄[Co(Co(P₃S₈)₂)₂] and CCDC 1428305 for [EMIM]₃[Cr(P₃S₉)₂]. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

Figure Captions

Figure 1: Synthesis of [EMIM][CF₃SO₃].

Figure 2: Thermal ellipsoid plot of the cobalt thiophosphate anion from the salt [EMIM]₄[CoS₄(Co(P₃S₇)₂)₂]. Cobalt ions are indigo, phosphorus magenta, and sulfurs yellow. Bond distance ranges: [CoS₄(Co(P₃S₇)₂)₂]⁴⁻, Co1-S 2.326(3)-2.332(4), Co2,3-S 2.272(4)-2.319(3), Co2,3-P 2.224(4)-2.248(3) Å.

Figure 3: Thermal ellipsoid plot of the chromium thiophosphate anion from the salt [EMIM]₃[Cr(P₃S₉)₂]. The chromium ion is indigo, phosphorus magenta, and sulfur yellow. Bond distance ranges: Cr-S 2.4082(15)-2.4108(17) Å.

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Figure 1

Figure 2

Figure 3

Graphical Abstract