

Ionothermal Synthesis and Characterization of Transition-Metal Thiophosphates: Ideas vs. Reality

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Extending the reactive flux concept into lower-temperature regimes in unusual solvents led us to explore ionic liquids as reaction medium. Because of the array of possible structural motifs available from thiophosphate units, we employed elemental sulfur and phosphorus when we set out to explore ionothermal reactions of transition metals in room-temperature ionic liquids, [EMIM][CF₃SO₃] (EMIM = 1-ethyl-3-methylimidazolium) and [EMIM][BF₄]. To date, we've isolated simple and complex molecular anions that have been structurally characterized by single crystal diffraction and further characterized by IR and NMR spectroscopies as well as DSC. As an example, the recurrent structure, [M(P₂S₈)₂]²⁻, has been isolated for M = Ni²⁺, Mn²⁺, and Fe²⁺ (shown), with coordination to three S atoms of each P₂S₈²⁻ ligand that includes an S₃ group. However, the similar anion [M(P₃S₉)₂]ⁿ⁻, has been isolated for M = Ni²⁺ (n = 4), Cr³⁺ (n = 3), and Fe³⁺ (n = 3), with coordination to three S atoms of each P₃S₉³⁻ ligand. Simple extensions aren't obvious as phosphorus can also directly coordinate to the metal atoms in the isolated anions [FeP₇S₁₇]⁻ (shown), [(NiP₃S₈)₄(PS₄)]⁷⁻, and [Co(Co(P₃S₈)₂)]⁴⁻.

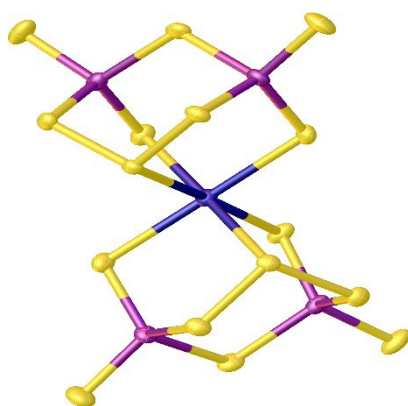


Figure 1

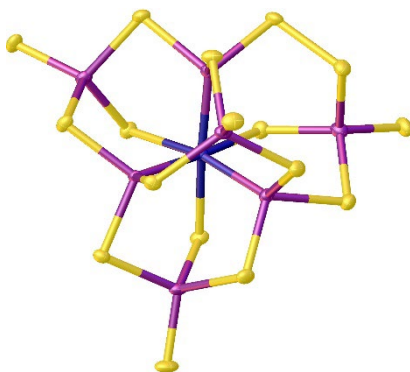


Figure 2