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, \([\text{EMIM}][\text{CF}_3\text{SO}_3]\) (EMIM = 1-ethyl-3-methylimidazolium) and \([\text{EMIM}][\text{BF}_4]\). 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, \([\text{M}(\text{P}_2\text{S}_8)_2]^{2-}\), has been isolated for M = Ni$^{2+}$, Mn$^{2+}$, and Fe$^{2+}$ (shown), with coordination to three S atoms of each P$_2$S$_8$$^{2-}$ ligand that includes an S$_3$ group. However, the similar anion \([\text{M}(\text{P}_3\text{S}_9)_2]^n-\), has been isolated for M = Ni$^{2+}$ (n = 4), Cr$^{3+}$ (n = 3), and Fe$^{3+}$ (n = 3), with coordination to three S atoms of each P$_3$S$_9$$^{3-}$ ligand. Simple extensions aren’t obvious as phosphorus can also directly coordinate to the metal atoms in the isolated anions [FeP$_7$S$_{17}$]$^-$ (shown), [[Ni(P$_3$S$_8$)$_4$(PS$_4$)]$^7-$, and [Co(Co(P$_3$S$_8$)$_2$]$^{4-}$. 

**Figure 1**

**Figure 2**