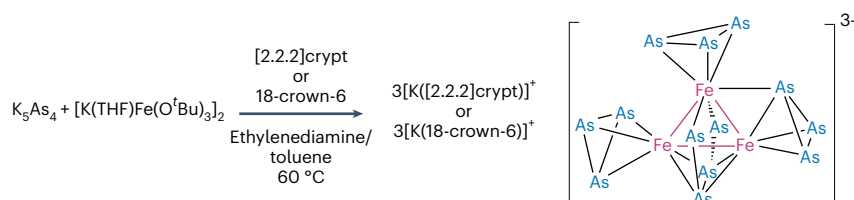


Iron arsenide clusters



Molecular clusters comprising transition metals and pnictogens are noteworthy because of the isolobal relationship between the group 5 elements and a C–H fragment. $CpFe(\eta^5-P_3)$ (where Cp is a cyclopentadienyl ligand) is a good illustration of the isolobality of the Cp^- and P_3^- fragments. However, the all-phosphorous analogue ($Fe(\eta^5-P_3)$) remains elusive. Arsenic is also known to catenate to form long chains and rings. $Cp^*Fe(\eta^5-As_3)$ was first synthesized in 1990, and a family of similar compounds has since been synthesized. Exploration of their chemistry indicates that the valence levels of Fe and As are delicately balanced, and changes in oxidation state, steric bulk or electron donating power can generate structural changes, reflecting the redistribution of electron density between Fe and As.

Now, writing in *Angewandte Chemie International Edition*, John Ewart McGrady, Zhong-Ming Sun and co-workers have investigated the reactivity of the Zintl phase K_5As_4 , with $[K(THF)Fe(O^tBu)_3]_2$. The absence of a Cp ligand in the precursors allows the isolation of the first reported binary iron arsenide cluster anion, $[Fe_3(As_3)_3As_4]^{3-}$ (pictured).

The reaction between K_5As_4 and a low valent Fe^{II} complex, $[K(THF)Fe(O^tBu)_3]_2$ (where THF is tetrahydrofuran), in the presence of a cryptand ([2.2.2]crypt) or 18-crown-6, occurs at 60 °C. Two compounds are generated, $[K([2.2.2]\text{crypt})]_3[Fe_3(As_3)_3As_4]$ (**1**) and $[K(18\text{-crown-6})]_3[Fe_3(As_3)_3As_4]$ -en (**2**). Single-crystal X-ray

diffraction confirmed that both compounds crystallize in the $P2_1/n$ space group, that both compounds contain the binary cluster, $[Fe_3(As_3)_3As_4]^{3-}$, and that both clusters contain a triangular Fe_3 core.

The different cations in clusters **1** ($[K([2.2.2]\text{crypt})]^+$) and **2** ($[K(18\text{-crown-6})]^+$) cause changes in packing which primarily impacts the orientation of the single As_3 ring. In **1**, the $[K([2.2.2]\text{crypt})]^+$ cations are fully encapsulated, but in **2**, the macrocyclic structure of the 18-crown-6 ligand results in vacant coordination sites on the three K^+ cations. One of these sites is filled by a coordinating ethylenediamine ligand, but the other two sites form K^+-As contacts, distorting one of the three As_3 rings.

In contrast to the As_3 ring, the single crystal X-ray diffraction data suggest that the structure of the Fe_3 core remains largely unaffected by the different cations. Experimental and theoretical observations indicate the presence of Fe–Fe covalent bonds, and the cluster is described as a diamagnetic Fe_2 dimer unit which is bridged by an As_3Fe unit carrying two unpaired electrons.

McGrady, Sun and co-workers hope that these results will offer useful comparisons to the work on Fe/As clusters with Cp capping ligands.

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