Metal clusters as ligands. Substitution of Fe atoms in Fe/Mo/S clusters by thiophilic Cu(I) ions. The synthesis and structures of clusters with unique Fe/Mo/Cu/S cores.

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Core rearrangements of the $[(Cl_4\text{-cat})_2Mo_2Fe_6S_8(PR_3)_6]$ clusters in the presence of thiophilic metals such as Cu leads to the formation of unique and unprecedented trimetalic-sulfur (Mo/Fe/Cu/S) clusters. The reactivity of Fe/S and Fe/Mo/S clusters, similar or analogous to those occurring in biological systems, with thiophilic metal ions has not been explored. Such reactivity may have implications in metal ion toxicity but may also be important for the synthesis of new materials.

These clusters contain Fe(III), Mo(V) or Mo(III), and Cu(I) and display pseudo-tetrahedral, square pyramidal or pseudo-octahedral and pseudo-trigonal geometries respectively. Different metal sites, characterized by different terminal ligands and ligand substitution kinetics, may offer the complexity needed for site specific activation of substrates in catalysis.

The synthesis of heteropolynuclear clusters with different coordination geometries at different sites is possible in what we believe are metal substitution reactions. The use of metal clusters as ligands is not commonly practiced, but it could be an approach to the designed synthesis of new materials with very interesting structural, electronic and magnetic characteristics.