Abstract
Reactive oxygen species, including both terminal and bridging oxo, superoxo, and peroxo moieties, are among the most widely studied units in transition metal chemistry and are featured prominently in biology and the solid state. The work presented in this seminar will highlight the use of both bi-metallic cryptands and metal-organic frameworks containing coordinatively-unsaturated transition metal cations to stabilize these reactive species. In the case of the former, the cofacial arrangement of metal cations enforced by this hexacarboxamide cryptand system has allowed the isolation of reactive single-oxygen-atom-bridged bimetallic complexes of iron, cobalt, and nickel. The synthesis, characterization, and reactivity of these products, and a metal-organic framework supported high-spin iron(IV)-oxo, will be discussed. The metal-organic frameworks presented here, in addition to their utility in stabilizing reactive species, remain among the best materials for a variety of challenging gas separation applications, including oxygen/nitrogen and paraffin/olefin separations. Spectroscopic and crystallographic characterization of the metal-adsorbate interactions responsible for the high adsorption selectivities displayed by these materials will be highlighted.