Glenn T. Seaborg Center Seminar

Recent Advances in the Chemistry of $[(C_5H_4SiMe_3)_3M]^{1-}$, $\{[C_5H_3(SiMe_3)_2]_3M\}^{1-}$, and Related Complexes of the Rare Earth and Actinide Metals

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Bldg. 70A, Room 3377

Recent studies of dinitrogen reduction chemistry with the rare earth elements have led to the synthesis of a series of complexes, $(Cp'_3M)^{1-}$ ($Cp' = C_5H_4SiMe_3$), which represent the first examples of molecular species of Y^{2+}, Ho^{2+}, Er^{2+}, Pr^{2+}, Gd^{2+}, Tb^{2+}, Lu^{2+}, and U^{2+}. These complexes along with the $(Cp''_3Ln)^{1-}$ ($Cp'' = C_5H_3(SiMe_3)_2$-1,3) complexes of La^{2+} and Ce^{2+} reported earlier by Lappert et al., demonstrate that the +2 oxidation state is available for all the rare earths and uranium. These complexes are unusual compared to complexes of the traditional six +2 rare earth ions, Eu^{2+}, Yb^{2+}, Sm^{2+}, Tm^{2+}, Dy^{2+}, and Nd^{2+}, in that the bond distances are only slightly larger (ca. 0.03 Å) than those of their +3 analogs. This small change is more characteristic of d orbital transition metal complexes than f orbital species that often have 0.1-0.2 Å differences in bond lengths for analogous +2 and +3 species. Although extensive structural information is available on complexes of the traditional six Ln^{2+} ions, data on the direct analogs of the new complexes were not available. To make direct comparisons, the $(Cp'_3M)^{1-}$ versions of La and Ce and the traditional six rare earths have now been made so the structural features and UV-vis spectra of the traditional six can be compared with those of the new nine Ln^{2+} ions in a single homologous set of complexes. The surprising results of this study and the implications in f element chemistry will be discussed along with the latest results from reactivity and physical characterization studies and density functional analysis. The precedents for these results that have gone unnoticed in the literature will also be discussed.

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