Stabilization of Cerium(IV) in the Presence of an Iodide Ligand: Remarkable Effects of Lewis Acidity on Valence State

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Received June 17, 1999

The stability of the trivalent state in the lanthanides is exploited in the use of Sm³⁺ as a reducing agent, and also in the use of unknown reactions of Sm II I₂ as a reducing agent, and also in the use of Sm₃⁺ oxidation states in the metal are stabilized. Here we report that the potential of this ion is the only lanthanide for which the tetravalent state is readily in the use of Sm II I₂ as a reducing agent, 2 and also in the use of Sm III I₂ as a reducing agent, 2 and also in the use of Sm IV I₂ as a reducing agent, 2 and also in the use of Sm V I₂ as a reducing agent, 2 and also in the use of Sm VI I₂ as a reducing agent.

The presence of a crystallographic inversion center that coincides with the apparent position of the halogen atoms in the structures of Sm I and Sm II does not require that the two 3-fold symmetric (triamidoamine)-cerium fragments are crystallographically equivalent. The anisotropic displacement ellipsoid for the Sm atom in Sm I has its greatest amplitude along the Ce—Cl—Ce vector, i.e. at right angles to the expected maximum thermal libration. This is consistent with the presence in Sm I of unsymmetric Ce—X → Ce bridges with the halogen atom disordered between two positions on the intermetallic axis.

Although the molecular structure of the triamidoamine complex in Sm II is unexceptional, 9,10 the Ce IV—III unit [3.1284(6) Å] is without precedent. Known Ce IV—I distances range from 3.517(1) Å in Ce₄[Ce(N(O)₃)₃]⁺ to 3.299(1) Å in Ce₄[Ce(III)₂(THF)₄]⁺. 11

Scheme 1

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We propose that this, rather than any unusual electrochemical properties of the system, is the most important factor in stabilizing the tetravalent centers in 2–4. The unfavorable electrochemical potential for the oxidation of CeIV with molecular halogens is overcome by the favorable bond enthalpies in the products. It is noteworthy that the conformationally less restricted complexes [CeIII(N(SiMe3)2)], [CeIII(η-C3H5)], and analogous compounds are not oxidized in a similar manner, even by Cl2.

We would expect the disproportionation reaction in Scheme 2 to be favorable for all three halides. From our results, however, it is clear that this process is spontaneous for X = Cl and Br but not for X = I. Chloride and bromide, as relatively hard bases, may form strong dative bonds with the CeIV ion, and so the loss of the CeIV–X bond enthalpy in Scheme 2 is sufficiently offset by the formation of a dative CeIV–Cl → CeIII for the equilibrium position to be controlled by the balance of electrochemical potentials. In contrast, the softer base iodide would form a relatively weak dative bond with CeIII, and the uncompensated loss of the CeIV–I bond enthalpy means that 4 is relatively stable with respect to reduction by this mechanism.

The strongly electron-donating nature of amide R3N– and its resistance to oxidation mean that this ligand has great synthetic utility in high-valent metal coordination chemistry.18 In the case of the triamidoamines, this characteristic is enhanced by the rigorously “facial” coordination behavior of the ligand and the consequent high Lewis acidity of the cerium center. We propose that this, rather than any unusual electrochemical potentials, is the most important factor in stabilizing the mixed-valence species. 17 The pseudo-trigonal monopyramidal complex I does not have to rearrange its ligands to accommodate an incoming group, and this greatly enhances the Lewis acidity of the cerium center. We propose that this, rather than any unusual electrochemical properties of the system, is the most important factor in stabilizing the tetravalent centers in 2–4. The unfavorable electrochemical potential for the oxidation of CeIV with molecular halogens is overcome by the favorable bond enthalpies in the products. It is noteworthy that the conformationally less restricted complexes [CeIII(N(SiMe3)2)], [CeIII(η-C3H5)], and analogous compounds are not oxidized in a similar manner, even by Cl2.

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Acknowledgment. P.S. wishes to thank EPSRC for Project Studentships (to C.M. and C.J.S.), SmithKline Beecham for a CASE award (to C.J.S.), and Pfizer (UK) Ltd for a CASE award (to I.J.M.). We thank EPSRC, Siemens Analytical Instruments, Elliot Scientific Ltd., and Quantum Design for grants in support of the diffractometer and SQUID magnetometer.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, and bond lengths and angles for 2, 3 and 4 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

J19920563