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

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

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The stability of the trivalent state in the lanthanides[1] is exploited in the use of $Sm^{II}I_2$ as a reducing agent,[2] and also in the use of $[(NH_4)_2][Ce^{IV}(NO_3)_6]$ (CAN) as an oxidizing agent.[3] Cerium is the only lanthanide for which the tetravalent state is readily attained in solution, although in view of the high oxidizing potential of this ion [$E°(Ce^{IV/III})$: 1.7 V (1 M $HClO_4$)] its stability in water must be due to kinetic factors.[4] The organometallic chemistry of cerium(IV) is correspondingly sparse[5] and it has recently been confirmed experimentally[6] that cerocene [$Ce(\eta^8\text{-}C_8H_8)_2$] and its analogues[7] are best described as [$Ce^{3+}\{(\eta^8\text{-}C_8H_8)_2\}^{3-}$], i.e. containing cerium(III). We note that in the actinide complexes of the triamidoamines[8] [$N(CH_2CH_2NR)_3$]$^{3-}$ (particularly the ligand with R = $SiMe_2Bu^t$, henceforth NN′$_3$) the higher oxidation states in the metal are stabilized.[9] Here we report that as a consequence of exceptionally high Lewis acidity at the metal, cerium(IV) triamidoamines are unusually stable to reduction, even in the presence of an iodide ligand.

The solvent-base free trivalent complex [$Ce(NN′_3)$] (**1**) was readily synthesized (Scheme 1) by a method similar to that which we have used to prepare the group 3 complexes,[10] *i.e.* treatment of [$CeCl_3(THF)_4$] with [$Li_3(THF)_3(NN′_3)$][11] in dry THF followed by sublimation in vacuo. This bright yellow−orange complex decomposes rapidly in air but is otherwise quite stable.[12]

The reaction of **1** as a solution in pentane with 0.5−1.5 equiv of chlorine led to an immediate color change to purple and deposition of large purple crystals of the fascinating mixed valence $Ce^{III/IV}$ complex [$\{Ce(NN′_3)\}_2(\mu\text{-}Cl)$] (**2**). Similarly, reaction of **1** with bromine gave purple [$\{Ce(NN′_3)\}_2(\mu\text{-}Br)$] (**3**). Most unexpectedly, however, the weakest oxidizing agent iodine gave the purple cerium(IV) iodide complex, [$Ce(NN′_3)I$] (**4**).

The molecular structures of **2** (Figure 1) and **3**[13] are analogous to those of the uranium complex [$\{U(NN′_3)\}_2(\mu\text{-}Cl)$] which we have synthesized by reduction of [$U(NN′_3)Cl$] with potassium.[9d] The presence of a crystallographic inversion center that coincides

## Scheme 1



R = SiBu$^t$Me$_2$

**2** X = Cl
**3** X = Br
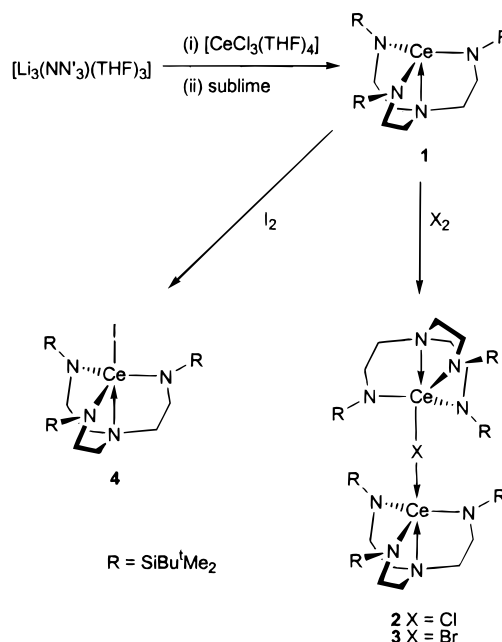
with the apparent position of the halogen atoms in the structures of **2** and **3** requires that the two 3-fold symmetric (triamidoamine)-cerium fragments are crystallographically equivalent. The anisotropic displacement ellipsoid for the Cl atom in **2** has its greatest amplitude along the Ce−Cl−Ce vector, i.e. at right angles to the expected maximum thermal libration. This is consistent with the presence in **2** and **3** 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 fragment in **4** (Figure 2) is unexceptional,[9,10] the $Ce^{IV}$−I unit [3.1284(6) Å] is without precedent. Known $Ce^{III}$−I distances range from 3.157(1) Å in [$CeI_3(HOPr^i)_3$][14] to 3.299(1) Å in [$Ce(\eta\text{-}C_8H_8)I(THF)_3$].[15]

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(12) Characterizing data for **1**: Anal. Calcd for $C_{24}H_{57}N_4Si_3Ce$: C, 46.04; H, 9.18; N, 8.95. Found: C, 45.42; H, 9.04; N, 8.83. $^1H$ NMR (298 K $d_8$-toluene) δ 6.00 (s, 27H, Bu$^t$), 4.89 (s, 6H, CH$_2$), 1.51 (s, 18H, Me$_2$Si), −17.41 (s, 6H, CH$_2$). MS (EI) *m/z* 625 (26%, M$^+$), 568 (18%, M$^+$ − Bu$^t$). $\tilde{\nu}_{max}$ cm$^{-1}$ ($\epsilon$ M$^{-1}$ cm$^{-1}$) 24630 (440). For **2**: Anal. Calcd for $C_{48}H_{114}N_8Si_6Ce_2Cl$: C, 44.77; H, 8.92; N, 8.70. Found: C, 44.13; H, 8.76; N, 8.36. $^1H$ NMR (298 K $d_8$-toluene) δ 4.59 (s, 12H, CH$_2$), 3.50 (s, 12H, CH$_2$), 3.32 (s, 54H, Bu$^t$), −0.50 (s, 36H, Me$_2$Si). MS (EI) *m/z* 625 (63%, M$^+$ − Ce(NN′$_3$)Cl), 568 (66%, M$^+$ − Ce(NN′$_3$)Cl − Bu$^t$). $\tilde{\nu}_{max}$ cm$^{-1}$ ($\epsilon$ M$^{-1}$cm$^{-1}$) 20325 (3450), 29412 (2290). For **3**: Anal. Calcd for $C_{48}H_{114}N_8Si_6Ce_2Br$: C, 43.28; H, 8.63; N, 8.41. Found: C, 43.51; H, 8.21; N, 8.31. $^1H$ NMR (298 K $d_8$-toluene) δ 4.63 (s, 12H, CH$_2$), 3.52 (s, 54H, Bu$^t$), −0.55 (s, 36H, Me$_2$Si). MS (EI) *m/z* 625 (72%, M$^+$ − Ce(NN′$_3$)Br), 568 (14%, M$^+$ − Ce(NN′$_3$)Br − Bu$^t$). $\tilde{\nu}_{max}$ cm$^{-1}$ ($\epsilon$ M$^{-1}$ cm$^{-1}$) 20000 (2840), 29586 (2430). For **4**: Anal. Calcd for $C_{24}H_{57}N_4Si_3CeI$: C, 38.28; H, 7.63; N, 7.44. Found: C, 36.59; H, 7.26; N, 7.16. $^1H$ NMR (298 K $d_6$-benzene) δ 4.62 (t, 6H, CH$_2$), 2.88 (t, 6H, CH$_2$), 1.05 (s, 18H, Me$_2$Si). $^{13}C\{^1H\}$ NMR (298 K $d_6$-benzene) δ 67.72 (s, CH$_2$), 50.82 (s, CH$_2$), 27.38 (s, CMe$_3$), 21.64 (s, CMe$_3$), −4.55 (s, Me$_2$Si). MS (EI) 625 (6%, M$^+$ − I), 568 (2%, M$^+$ − I − Bu$^t$). $\tilde{\nu}_{max}$ cm$^{-1}$ ($\epsilon$ M$^{-1}$ cm$^{-1}$) 19920 (3180), 24272 (2260), 28571 (1740).
(13) Crystal data for **2**: $C_{24}H_{57}CeCl_{0.5}N_4Si_3$, trigonal, $P\bar{3}1c$, *a* = 12.5843-(5) Å, *c* = 25.433(2) Å, *U* = 3488.1(3) Å$^3$, *Z* = 4, $D_c$ = 1.226 g cm$^{-3}$, *T* = 210(2) K, $\lambda$(Mo Kα) = 0.71073 Å. Final *R* indices [for 2337 reflections with *I* > 2σ(*I*)]: $R_1$ = 0.0296, $wR_2$ = 0.0621. GOOF on $F^2$ = 1.080. Crystal data for **3**: $C_{24}H_{57}Br_{0.5}CeN_4Si_3$, trigonal, space group $P\bar{3}1c$, *a* = 12.6070(19) Å, *c* = 25.557(3) Å, *U* = 3517.8(8) Å$^3$, *Z* = 4, $D_c$ = 1.333 g cm$^{-3}$, *T* = 200(2) K, $\lambda$(Mo Kα) = 0.71073 Å. Final *R* indices [for 2879 reflections with *I* > 2σ(*I*)]: $R_1$ = 0.0444, $wR_2$ = 0.0765. GOOF on $F^2$ = 1.584. Crystal data for **4**: $C_{24}H_{57}CeIN_4Si_3$, monoclinic, space group $P2_1/n$, *a* = 9.7738(10) Å, *b* = 22.570(3) Å, *c* = 16.122(2) Å, $\beta$ = 97.680(5)°, *U* = 3524.5(7) Å$^3$, *Z* = 4, $D_c$ = 1.419 g cm$^{-3}$, *T* = 200(2) K, $\lambda$(Mo Kα) = 0.71073 Å. Final *R* indices [for 8219 reflections with *I* > 2σ(*I*)]: $R_1$ = 0.0539, $wR_2$ = 0.0934. GOOF on $F^2$ = 0.858. Data were collected on a Siemens SMART CCD. The structures were solved by direct methods with additional light atoms found by Fourier methods.
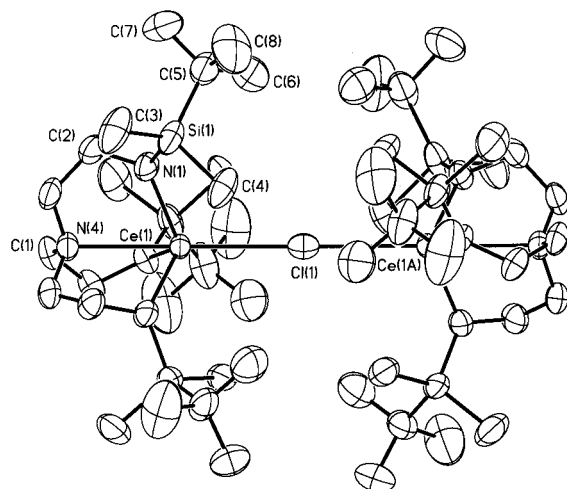
**Figure 1.** Molecular structure of **2** (non-hydrogen atoms). The structure of **3** is analogous. Selected distances (Å) and angles (deg) for **2**: Ce(1)−N(1) 2.255(2), Ce(1)−N(4) 2.730(3), Ce(1)−Cl(1) 3.0080(3), N(1)−Ce(1)−N1′ 107.36(6), N(1)−Ce(1)−N(4) 68.49(5), N(1)−Ce(1)−Cl(1) 111.51(5), N(4)−Ce(1)−N(1)−Si(1) 132.10(15). For **3**: Ce(1)−N(1) 2.263(3), Ce(1)−N(4) 2.700(4), Ce(1)−Br(1) 3.1150(5), N(1)−Ce(1)−N1′ 107.83(7), N(1)−Ce(1)−N(4) 68.93(7), N(1)−Ce(1)−Br(1) 111.07-(7).
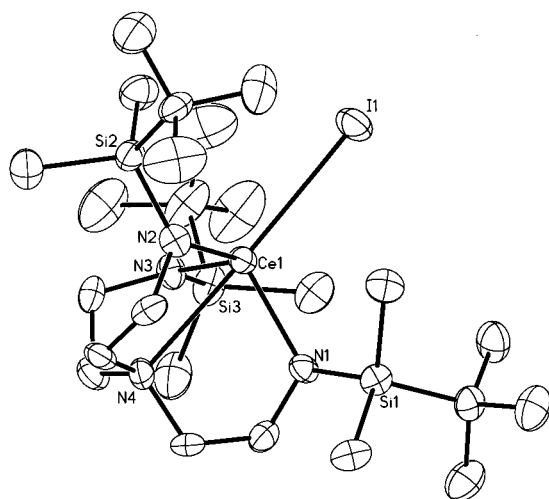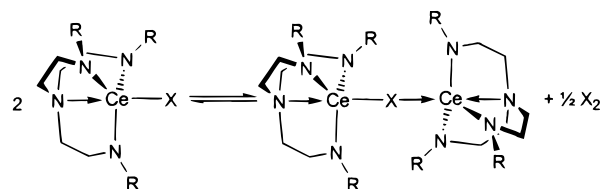


**Figure 2.** Molecular structure of **4** (non-hydrogen atoms). Selected distances (Å) and angles (deg): Ce(1)−N(3) 2.192(6), Ce(1)−N(1) 2.206-(6), Ce(1)−N(2) 2.208(5), Ce(1)−N(4) 2.699(5), Ce(1)−I(1) 3.1284(6), N(3)−Ce(1)−N(1) 106.3(2), N(3)−Ce(1)−N(2) 112.2(2), N(1)−Ce(1)−N(2) 108.3(2), N(3)−Ce(1)−N(4) 70.06(18), N(1)−Ce(1)−N(4) 70.35-(18), N(2)−Ce(1)−N(4) 69.67(19), N(3)−Ce(1)−I(1) 107.88(14), N(1)−Ce(1)−I(1) 111.62(13), N(2)−Ce(1)−I(1) 110.50(14), N(4)−Ce(1)−I(1) 177.63(13).

In mixed-valence **2** and **3**, the presence of only one set of $^1$H NMR resonances for the triamidoamine ligands between 220 and 300 K indicates that equilibration of the magnetic environments of the two metal centers (presumably by axial exchange of the halogen atom) is rapid on this time scale. Diamagnetic **4** (vide infra) gives NMR spectra similar to those observed for triamidoamines such as [Zr(NN′$_3$)(NMe$_2$)].[16]

Trivalent **1** is a paramagnet between 340 and 5 K showing Curie−Weiss behavior [$\chi = C/(T + \theta)$] with 2.32 ± 0.01 $\mu_B$/Ce

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**Scheme 2**



and $\theta = 3.2 \pm 0.1$ K, while tetravalent **4** is diamagnetic. The bimetallic complexes **2** and **3** have magnetic susceptibilities which can be modeled accurately by assuming that they are simple 1:1 adducts of a diamagnetic tetravalent species [Ce(NN′$_3$)X] and **1**. We therefore propose that **2** and **3** are best described as Class II mixed-valence species.[17]

The *pseudo*-trigonal monopyramidal complex **1** 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 Ce$^{III}$ with molecular halogens is overcome by the favorable bond enthalpies in the products. It is noteworthy that the conformationally less restricted complexes [Ce$^{III}$\{N(SiMe$_3$)$_2$\}$_3$], [Ce$^{III}$($\eta$-C$_5$H$_5$)$_3$], and analogous compounds are not oxidized in a similar manner, even by Cl$_2$.

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 Ce$^{III}$ ion, and so the loss of the Ce$^{IV}$−X bond enthalpy in Scheme 2 is sufficiently offset by the formation of a dative Ce$^{IV}$−Cl → Ce$^{III}$ 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 Ce$^{III}$, and the uncompensated loss of the Ce$^{IV}$−I bond enthalpy means that **4** is relatively stable with respect to reduction by this mechanism.

The strongly electron-donating nature of amide R$_2$N$^-$ 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 metal. More generally, conformationally restricted chelate ligand systems will tend to stabilize high formal oxidation states in the metal. Our findings also suggest that the matching of hard and soft acids and bases should be considered during the design of metal/ligand combinations for the stabilization of particular oxidation states.

**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.

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