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Cerium masquerading as a Group 4 element: synthesis, structure and computational characterisation of $[CeCl\{N(SiMe_3)_2\}_3]$†

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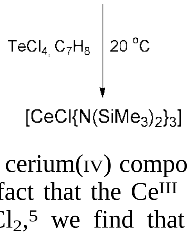
Oxidation of the three-coordinate cerium amide $[Ce\{N(SiMe_3)_2\}_3]$ with $TeCl_4$ in toluene solution yields purple, diamagnetic $[CeCl\{N(SiMe_3)_2\}_3]$, whose structure has been examined by X-ray crystallographic and computational methods.

Cerium occupies an unusual position in the periodic table, providing a bridge between Group 3 and the lanthanides, but rather than combining the useful characteristics of both families it often fails to fulfil expectations. Were it not for the fact that at atomic number 58 electrons begin to occupy the 4f shell,[1] cerium would behave more like a member of Group 4, and would presumably warrant study as intensive as that devoted to titanium, zirconium and hafnium.[2] Nature is, however, not that accommodating, and while cerium is abundant, cheap and readily available, it is very much a lanthanide element, is commonly encountered as Ce^{III}, and is thus often consigned to the backwaters of the Periodic Table.

When seen from the point of view of the other lanthanides, its standing is reversed, and it becomes potentially the most interesting of those elements as it is the only one so far proven to have chemically accessible (II),[3] (III) and (IV)[4] oxidation states. High-valent cerium chemistry (excluding *O*-donor complexes, where there is a more obvious convergence in behaviour between cerium and Group 4) is still very much under-developed, but an important contribution has been made in this area by Scott and co-workers,[5] who have reported the oxidation of the trisamidoamine complex $[Ce(NN'_3)]$ $[NN'_3 = N(CH_2CH_2NSiMe_2Bu^t)_3]$ with molecular halogens, which in the case of iodine produces the mononuclear Ce^{IV} amide $[CeI(NN'_3)]$.

We wish to report that it is possible to oxidise the prototypical cerium amide $[Ce(NR_2)_3]$ (R = $SiMe_3$)[6] **1** (eqn. 1), and to



$$[Ce\{N(SiMe_3)_2\}_3] \xrightarrow{TeCl_4,\ C_7H_8,\ 20\ °C} [CeCl\{N(SiMe_3)_2\}_3] \qquad (1)$$

isolate a well-defined cerium(IV) compound from the reaction. Notwithstanding the fact that the Ce^{III} amide is known to be unreactive towards Cl_2,[5] we find that the addition of 0.25 equivalents of $TeCl_4$[7] to a toluene solution of **1** results in an immediate change in colour from yellow to deep purple.‡ Very dark, almost black, needles, which are characterised as $[CeCl(NR_2)_3]$ **2** by ^1H NMR, EI-MS, microanalysis and an X-ray crystallographic study,§ are isolable in—admittedly low—yields of 24–30%. The diamagnetic nature of the complex (and by implication the cerium(IV) oxidation state) is apparent from the proton NMR spectrum in C_6D_6 which shows a sharp singlet at δ 0.42. The haloamide **2** has marginal stability in solvents other than thf, decomposing over a few hours into small amounts of $[Ce(NR_2)_3]$ **1**, and other, unidentified, products. This instability is reflected in the absence of a parent ion and the paucity of chlorine-containing fragments in its mass spectrum, the highest *m/z* peak being assigned as $[M - Me]^+$. A representation of the molecular structure is shown in Fig. 1.

The molecule is C_3 symmetric about the Ce–Cl axis, while the geometry at the metal is intermediate between tetrahedral and trigonal pyramidal (although closer to the latter) the angles Cl–Ce–N and N–Ce–N′ being 99.48(7) and 117.34(4)° respectively. The cerium ion protrudes 0.36 Å out of the plane formed by the three nitrogen atoms, which is around 0.05 Å further than is the case for the parent Ce^{III} species **1**.[8] These features may be contrasted with those of the superficially similar Group 4 complexes $[MCl(NR_2)_3]$ (M = Ti, Zr, Hf)[9] which are tetrahedral (despite their shorter M–N bonds) although distorted significantly from the ideal. The Ce–N and Ce–Cl bonds of 2.217(3) and 2.597(2) Å in **2** are all relatively short, as a consequence both of the presence of a contracted metal ion and the adoption of a lower coordination number than is normally found for Ce^{IV} species; we estimate from our data that Ce^{IV} has a radius of *ca.* 0.77 Å in four-coordination. There

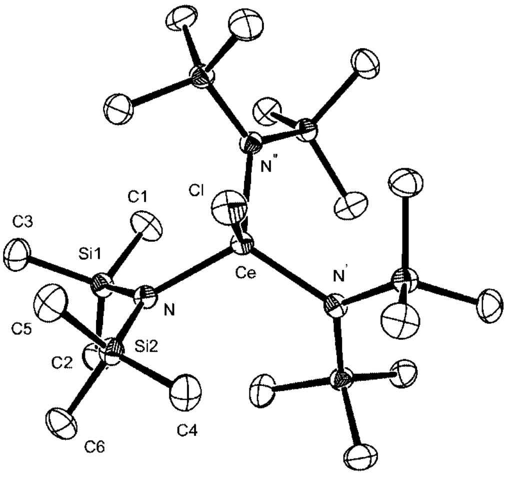


Fig. 1 Molecular structure of $[CeCl\{N(SiMe_3)_2\}_3]$ **2**. Ce–N 2.217(3), Ce–Cl 2.597(2), Si(1)–N 1.752(3), Si(2)–N 1.750(3) Å, N–Ce–N′ 117.34(4), Cl–Ce–N 99.48(7), Si(1)–N–Si(2) 120.13(16)°.

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† Electronic supplementary information (ESI) available: further details of calculations relating to **3**. See http://www.rsc.org/suppdata/cc/b1/b103634n/

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is a notable elongation of the N–Si bonds to around 1.751 Å, 0.05 Å longer than those found in **1** (see below).

In order to investigate the factors which determine the overall geometry of **2**, we have undertaken a computational study, using methods previously described,[10] on the hypothetical complex $[CeCl\{N(SiH_3)_2\}_3]$ **3**. The optimised model has C_3 symmetry, with the Ce–Cl bond coincident with the C_3 axis, and in general its geometrical features are very close to those of the experimental complex **2**, although the Ce–L separations are slightly longer (Ce–Cl 2.589; Ce–N 2.246 Å) than those determined by X-ray methods, all L–Ce–L′ bond angles are around 109°, and the dihedral angle Cl–Ce–N–Si is smaller in **2** (40°) than it is in **3** (55°). These latter, more substantial, angular differences may be ascribed to imperfect modelling of steric bulk in the periphery of the amide ligands; however, even in their absence the lengthening of the N–Si bond is reproduced very well (1.762 Å *vs*. 1.75 Å experimental) indicating that the effect is electronic in origin.

The calculated structure **3** may in turn be compared to that of the model cation $[Ce\{N(SiH_3)_2\}_3]^+$ **4**.[11] It is apparent that the N–Si bonds are significantly elongated in those complexes containing an additional chloride ligand, apparently irrespective of the metal oxidation state,¶ unperturbed bonds being 1.70 Å by our initial calculations on the Ce^{IV} centre **4** and 1.702(2) Å by X-ray analysis on the parent Ce^{III} amide **1**,[8] both of which are nominally three-coordinate. It is surprising to find that the presence of an additional ligand appears to exert a greater influence on the geometry within the amido ligand than on the Ce–N distances themselves (Ce–N in **4** is calculated to be 2.22 Å, similar to equivalent bonds in **2** and **3**).

In summary, we have accomplished the isolation of $[CeCl(NR_2)_3]$ **2**, a cerium analogue of the familiar [M(anion)(amido)$_3$] family of complexes perhaps best known for M = Ti, Zr and Hf. Its structural characterisation has revealed an elongation of the N–Si bonds in the hexamethyldisilylamido ligands, which, when the continued uncertainty over the existence or otherwise of $N(p_\pi)–Si(d_\pi)$ bonding is considered, invites further study of its origin. Preliminary steps towards this end have been taken in the computational characterisation of $[CeCl\{N(SiH_3)_2\}_3]$ **3**, which reproduces the effect very well even in the absence of significant steric crowding.

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Notes and references

‡ *Synthesis of* $[CeCl(NR_2)_3]$ **2**: $[Ce(NR_2)_3]$[6] **1** (1.0 g, 1.6 mmol) was dissolved in toluene (25 mL) at room temperature and $TeCl_4$ (0.11 g, 0.25 eq.) was added in one portion with vigorous stirring. The solution immediately turned purple, although stirring was continued for 2 h; its volume was reduced under vacuum to *ca*. 2 mL, hexane (*ca*. 15 mL) was added, and the resulting mixture was filtered and stored overnight at −25 °C to produce well-formed purple–black needles of **2**, which were isolated by filtration (0.25 g, 24%). Found: C, 32.4; H, 8.2; N, 6.5. $C_{18}H_{54}CeClN_3Si_6$ requires C, 32.92; H, 8.29; N, 6.40%. Mp, 119–121 °C (decomp.). ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C): δ 0.42. EI-MS: *m/z* (%) 640 (4) $[M - Me]^+$, 620 (54) $[Ce(NR_2)_3]^+$, 605 (14) $[Ce(NR_2)_3 - Me]^+$, 459 (78) $[Ce(NR_2)_2]^+$, 444 (24) $[Ce(NR_2)_2 - Me]^+$, 299 (73) $[Ce(NR_2)]^+$, 284 (57) $[Ce(NR_2)-Me]^+$.

§ Crystals from thf–hexane at −25 °C; $C_{18}H_{54}CeClN_3Si_6$, M = 656.75, rhombohedral (on hexagonal axes), $a = b = 18.4508(7)$ Å, $c = 16.8934(7)$ Å, $V = 4980.6(3)$ Å^3, space group $R3c$, $Z = 6$, μ(Mo-Kα) = 1.68 mm^{-1}, 173(2) K, 1781 independent reflections, 1693 reflections with $I > 2\sigma I$, refined using SHELXL-97[12] with 88 parameters, $R1 = 0.023$ and $wR2$ (all data) = 0.057, max./min. residual electron density = 0.62 and 0.41 e Å^{-3}.

CCDC reference number 162978. See http://www.rsc.org/suppdata/cc/b1/b103634n/ for crystallographic data in CIF or other electronic format.

¶ We have been unable to synthesise the $[CeCl(NR_2)_3]^-$ anion to test this hypothesis further.

1 It should be noted that like Ti^{4+} and Zr^{4+}, but in contrast to Hf^{4+}, the Ce^{4+} ion has no 4f electrons, and so in one way deserves to be associated with Group 4. While a re-ordering of the Periodic Table is clearly not appropriate in this case, see W. B. Jensen, *J. Chem. Educ.*, 1982, **59**, 634 for an interesting and persuasive discussion of the relative positioning of La and Lu.

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