The First Cationic Complex of Tetravalent Cerium


Keywords: Cerium; Schiff bases; TRENDSAL ligand; Heptadentate ligands; Crystal structure

Abstract. The recently reported cerium(IV) tripodal Schiff-base complex (TRENDSAL)CeCl (TRENDSAL = N[CH₂CH₂N=CH(C₆H₂-tBu₂-3,5-O-2)]₃⁻) serves as excellent starting material for novel Ce⁴⁺ coordination compounds. The first cerium(IV) azide, (TRENDSAL)CeN₃, and the first cationic cerium(IV) complex, [(TRENDSAL)Ce][BPh₄] are both readily accessible from (TRENDSAL)CeCl via simple salt metathesis reaction.

Introduction

Due to their high oxidation potential (E = 1.70 V in 1 m HClO₄), cerium(IV) compounds are widely used in various areas of chemistry and technology. Important fields of application include organic synthesis,[1] bioinorganic chemistry,[2] materials science,[3] and industrial catalysis (automotive three-way catalysts, oxygen storage etc.).[4] More recently, soluble cerium(IV) compounds are increasingly employed for the production of ceria nanoparticles.[5] The long known cerium(IV) alkoxides form a well-investigated class of compounds which are useful precursors for the MOCVD production of thin CeO₂ layers.[6] Thus there is a constant demand for new, well-defined cerium(IV) species. Cerium is the only lanthanide with an extensive chemistry in the +4 oxidation state. Its coordination chemistry is dominated by oxygen and nitrogen donor ligands.[7] Well-investigated neutral complexes besides the alkoxides include e.g. the β-diketonates,[8] amides,[9] as well as bis(porphyrin) and bis(philhalocyanine) complexes.[10] Then there is a number of anionic complexes like the familiar orange-red ceric ammonium nitrate (= CAN), (NH₄)₂[Ce(NO₃)₆], as well as cerium(IV) halide complexes (e.g. (NH₄)₂[CeF₆], (NH₄)₃[CeF₇(H₂O)], and salts of [CeCl₆]²⁻ with bulky cations).[11] In sharp contrast, cationic cerium(IV) complexes are completely unknown. We report here the synthesis of the first cationic coordination compound of tetravalent cerium as well as the first cerium(IV) azide species.

Recently, several cerium(IV) complexes containing the very bulky tripodal Schiff-base ligand N[CH₂CH₂N=CH(C₆H₂-tBu₂-3,5-OH-2)]₃ (= H₃TRENDSAL) have been reported.[12] The dark purple compounds (TRENDSAL)CeCl (1) and (TRENDSAL)Ce(NO₃) (TRENDSAL)Ce(NO₃) were prepared in simple one-pot reactions via condensation of tris(2-aminoethyl)amine and 3,5-ditert-butylsalicylaldehyde and the appropriate starting material CeCl₃(H₂O)₆ (in air) or (NH₄)₂[Ce(NO₃)₆], respectively. In both cases, the anionic ligands are coordinated to the central cerium(4+) ion, resulting in eight- (Cl) or nine-coordinate (NO₃) species. In a continuation of this work, we now found that 1 can serve as excellent starting material for novel tetravalent cerium(IV) complexes, including the first cerium(IV) azide species and the first cationic cerium(IV) complex.

Results and Discussion

Treatment of blue-purple 1 with a large excess of NaN₃ afforded a dark red-purple solution, from which the cerium(IV)

Scheme 1. Synthesis of (TRENDSAL)Ce⁴⁺N₃ (2) and [(TRENDSAL)Ce][BPh₄] (3).
azide \((\text{TRENDSAL})\text{CeN}_3\) could be obtained in the form of black, block-like crystals in 53% isolated yield (Scheme 1).

The air- and moisture-stable azide derivative 2 is moderately soluble in THF and acetonitrile, little soluble in toluene and insoluble in \(n\)-pentane. A strong IR band at 2044 cm\(^{-1}\) can be assigned to the asymmetric stretching vibration of the azido ligand. A mass spectrum of 2 showed the molecular ion with very low intensity. The presence of the first cerium(IV) azide species was verified by a single-crystal X-ray analysis (Figure 1). Crystallographic data for 2 and 3 are summarized in Table 1, whereas selected bond lengths and angles for 2 and 3 are listed in Table 2 and Table 3.

Compound 2 crystallizes in the triclinic space group \(P\bar{1}\) with two independent molecules in the unit cell. The coordination geometry around the eight-coordinate cerium can be described as distorted bicapped octahedral. Bond lengths and angles within the tripod alligand do not differ significantly from those in 1. With 2.437(3) and 2.423(2) Å the Ce–N(N3) distance is significantly longer than typical Ce(IV)–N(amide) bond lengths (e.g. 2.217(3) in [(Me3Si)2N]3CeCl).\(^{[9b]}\)

Of even greater importance was the finding at the chlorido complex 1 can also serve as starting material in the preparation of the first cationic cerium(IV) complex. Chloride abstraction from 1 seemed feasible as the TRENDSAL is known to effectively encapsulate even the large lighter lanthanide ions.\(^{[12]}\) A reaction of equimolar amounts of 1 and Na[BPh4] in THF (Scheme 1) led to formation of a red-purple solution, from which the salt-like product 3 could be isolated. Crystallization from acetonitrile afforded large black, block-like crystals of...
Table 2. Selected bond lengths /Å and angles ° for (TRENDSAL)Ce<sup>IV</sup>N<sub>3</sub> (2). Compound 2 crystallizes with two molecules in the asymmetric unit.

| Bond Length/Angle | 2.159(2) | 2.1542(19) | 2.1888(19) | 2.1870(19) | 2.193(2) | 2.197(2) | 2.762(2) | 2.773(2) | 2.661(3) | 2.630(2) | 2.587(2) | 2.603(2) | 2.4373 | 2.423(2) | 96.17(7) | 94.90(8) | 80.28(3) | 79.23(8) |
|-------------------|----------|-------------|-------------|-------------|----------|----------|-------|---------|-------|---------|-------|---------|---------|---------|---------|
|                  | Ce(1)–O(1) | Ce(2)–O(2)  | Ce(1)–O(3)  | Ce(1)–N(1)  | Ce(1)–N(2) | Ce(1)–N(3) | O(1)–Ce(1)–O(2) | O(2)–Ce(2)–N(10) | O(3)–Ce(3)–N(11) | O(4)–Ce(4)–O(6) | O(5)–Ce(5)–O(12) | O(6)–Ce(6)–N(8) |
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Table 3. Selected bond lengths /Å and angles ° for [(TRENDSAL)Ce][BPh<sub>4</sub>] (3).

| Bond Length/Angle | 2.1438(16) | 2.1427(16) | 2.1376(15) | 2.1249(8) | 77.30(8) | 2.472(2) | 2.4857(19) | 94.64(6) | 66.80(8) | 66.40(7) | 79.23(8) | 127.71(8) | 120.37(6) | 121.08(6) | 117.30(6) | 94.64(6) | 66.80(8) | 79.23(8) |
|-------------------|-------------|-------------|-------------|----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|                  | Ce–O(1)     | Ce–O(2)     | Ce–O(3)     | Ce–N(1)  | Ce–N(2) | Ce–N(3) | Ce–N(4) | N(2)–Ce(N–3) | N(9)–Ce(N–10) | N(8)–Ce(N–11) | O(4)–Ce(2)–O(6) | O(5)–Ce(2)–O(12) | O(6)–Ce(2)–N(8) |
| Ce–O(1)          | 2.1438(16) | 2.1427(16) | 2.1376(15) | 2.1249(8) | 77.30(8) | 2.472(2) | 2.4857(19) | 94.64(6) | 66.80(8) | 66.40(7) | 79.23(8) | 127.71(8) | 120.37(6) | 121.08(6) | 117.30(6) | 94.64(6) | 66.80(8) | 79.23(8) |
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In summary, the results reported here, we established the readily accessible cerium(IV) tripodal Schiff-base complex.

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Preparation of \([\text{TRENDSAL} \text{Ce}]_{2} \text{[BPh}_4]\) (3): In a 250 mL round-bottom flask, \([\text{TRENDSAL}]_{2} \text{[Ce]}\) (1, 0.18 g, 0.81 mmol) was dissolved in THF (70 mL), solid Na[BPh] (0.28 g, 0.81 mmol) was added, and the mixture was stirred at room temp. for 30 min. The resulting red-purple solution was filtered and the solvents were evaporated to dryness (50 °C/350 mbar). The residue was redissolved in hot acetonitrile (120 mL). Cooling to 5 °C for 24 h afforded the mono-acetonitrile solvate of 3 as black, block-like single-crystals that were suitable for X-ray diffraction. Thorough drying under vacuum (oil pump) afforded the unsolvated material, which was subsequently analyzed. Yield: 0.90 g (89%), m.p. > 260 °C. \(\text{C}_7\text{H}_3\text{NO}_3\text{Ce}_2 \text{[BPh}_4]\) (Mr = 1250.66 g mol\(^{-1}\)): C, 71.98; H, 7.65; N, 4.48. Found: C, 71.60; H, 7.71; N, 5.33 %. \(^{1}H\) NMR (400 MHz, D\(_2\) [acetone, 25 °C]): \(\delta = 8.63\) (s, 3 H, –N=CH–Ar), 7.43 (t, 8 H, Ar–H), 7.13 (br, 3 H, Ar–H), 4.24 (s, 6 H, –CH\(_2–\text{CH}_2–\text{CH}_2–\text{CH}\)): 3.07 (s, 48 H, –N=CH–Ar), 1.27 (s, 54 H, –CH\(_2–\text{CH}_2–\text{CH}_2–\text{CH}\)). \(^{13}C\) NMR (100.6 MHz, D\(_2\) [THF, 25 °C]): \(\delta = 168.2 \text{(–CH}_2–\text{N=CH–Ar)}, 139.9 \text{(–Bu–C\(_9\)}, 137.9 \text{(–Bu–C\(_9\)}, 129.9 \text{(–H–C\(_5\)}, 126.8 \text{(–H–C\(_5\)}, 65.8 \text{(–CH}_2–\text{C\(_9\)}, 64.2 \text{(–CH}_2–\text{C\(_9\)}, 35.3 \text{(–Ar–CMe\(_5\)}, 32.8 \text{(–C\(_9\)}, 31.8 \text{(–CH\(_2\))}}). IR (KBr): \(\nu_{\text{max}} = 3437\) (m), 2956 (v, \(\nu\text{as, CH}\)), 2907 (m, \(\nu\text{as, CH}\)), 2868 (m, \(\nu\text{as, CH}\)), 2044 (vs, \(\nu\text{as, N–H}\)), 1618 (vs, C–C ring), 1544 (mm), 1478 (m), 1459 (m), 1435 (m), 1412 (m), 1391 (m), 1362 (m), 1333 (m), 1270 (st), 1252 (v), 1200 (m), 1177 (m), 1135 (w), 1062 (w), 1033 (w), 979 (w), 908 (w), 879 (w), 837 (st, CH ring), 811 (w), 776 (w), 745 (st), 734 (m), 706 (m), 613 (w), 531 (m), 453 (v), 416 (w) cm\(^{-1}\)). MS (EI, 140eV): m/z (%) 931.7 (100) [M – BPh\(_4\)]\(^+\).

Supporting Information (see footnote on the first page of this article): ORTEP drawings and X-ray structural data as well as complete CIF files for 2 and 3. Crystallographic data for the crystal structures reported in this paper can be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-366-033; E-Mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/) by referring to the CIF deposition codes CCDC-793139 (2) and 793138 (3).

Acknowledgement

P. D. thanks the Government of Sachsen-Anhalt for a Ph.D. scholarship (Graduiertenförderung). Financial support by the Otto-von-Guericke-Universität Magdeburg is also gratefully acknowledged.

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Received: October 26, 2010
Published Online: January 10, 2011