Synthesis and magnetic properties of cerium macrocyclic complexes with tetramethyldibenzotetraaza[14]annulene, tmtaaH_2†

Marc D. Walter,[a] Rosa Fandos[ab] and Richard A. Andersen*[a]

Received (in Montpellier, France) 21st February 2006, Accepted 25th April 2006
First published as an Advance Article on the web 8th June 2006
DOI: 10.1039/b602644c

The complexes [Ce(tmtaa)$_2$], [Ce(tmtaa)(tmtaaH)] and [Ce_2(tmtaa)$_3$(thf)$_2$] are obtained from Ce[N($SiMe_3$)$_2$]$_3$ and tmtaaH_2, the macrocyclic ligand 6,8,15,17-tetramethyldibenzotetraaza[14]annulene, depending on the stoichiometry, solvent and temperature. The crystal structure of Ce(tmtaa)$_2$ is isostructural with Zr(tmtaa)$_2$, however magnetic susceptibility measurements in the range 5–300 K show that [Ce(tmtaa)$_2$] is not diamagnetic, but is a temperature-independent paramagnet (TIP), similar to Ce(cot)$_2$, cerocene.

Introduction

The d-transition metal complexes of 6,8,15,17-tetramethyldibenzotetraaza[14]annulene, abbreviated tmtaaH_2, whose systematic name is 7,16-dihydro-6,8,15,17-tetradecine, have been extensively developed since this ligand became available in synthetically useful amounts.[1–5] The [14]annulene nomenclature is informative since it connects tmtaaH_2 to two related classes of ligands that have an extensive chemistry, *viz*., [8]annulene, otherwise known as cyclooctatetraene, cot, and [16]annulenes, the porphyrins, porphH_2, and phthalacyanines, pcH_2. Although all of these ligands form dianions, their electronic structure and therefore the electronic properties of their complexes are different. The tmtaa^{2-} is a 24 π-electron system ($4n\pi$, $n = 6$) that is not Hückel aromatic. The negative charge is not delocalized over the entire framework, but is localized on the four nitrogen atoms, that carry a total negative charge of −0.98 *e*, and the two β-carbon atoms in the imidinate ring that carry a −0.24 *e* charge, $NC_\alpha(Me)C_\beta(H)C_\alpha(Me)N$.[6,7] The tmaa^{2-} is therefore not planar but is saddle shaped with idealized C_{2v} symmetry.[8] The cot^{2-} ($4n\pi + 2$, $n = 2$) and porph^{2-} ($4n\pi + 2$, $n = 6$) are aromatic and the negative charge is delocalized over the planar rings.[7] These three classes of ligands have been used to generate early d-transition metal compounds that are stoichiometric equivalents of the two Cp$^-$ ligands in metallocene fragments. For example, the zirconium derivatives of the type (tmtaa)ZrX_2, (cot)ZrX_2, (porph)ZrX_2 have been studied as electronically altered analogues of Cp_2ZrX_2.[9–14] In addition, the diamagnetic complexes Zr(cot)$_2$, Zr(porph)$_2$ and Zr(pc)$_2$ with a d^0 electronic configuration are known.[11,15–20]

The binary f-transition metal complexes of cot^{2-}, porph^{2-} and pc^{2-} are known only for cerium,[21–25] but Ce(tmtaa)$_2$ is unknown. These complexes are of considerable interest since deductions about their electronic structure implied by their stoichiometry have been questioned.[23,26] For example, the electronic structure of cerocene, Ce(cot)$_2$, is thought to be multiconfigurational, *viz*., the ground state wave function is an admixture of the two wave functions for [Ce(III, $4f^1(e_{2u})$)(cot$^{1.5-}$, $e_{2u}{}^3$)$_2$] and [Ce(IV, $4f^0$)(cot^{2-})$_2$],[26] a formulation that has recently been supported by experimental studies.[27] Complexes of the phthalocyanato ligand, Ce(pc)$_2$, have been suggested to be examples of this "valence ambiguity".[23,24] These long known and largely ignored complexes have therefore become the focus of intensive studies that are concerned with the question of exchange coupling between electrons in f-orbitals and therefore their role in covalent bonding.

With this brief introduction, the preparation and physical properties of Ce(tmtaa)$_2$ became a desirable goal. Only three papers have reported lanthanide complexes of this ligand, *viz*., [Li(thf)][Ce(tmtaa)$_2$],[28] M(tmtaa)(tmtaaH), where M is Y,[29] Pr, Nd, Sm, Gd, Tb, Er and Yb.[30] In this paper the synthesis and physical properties of Ce(tmtaa)$_2$ and related complexes are described.

Results and discussion

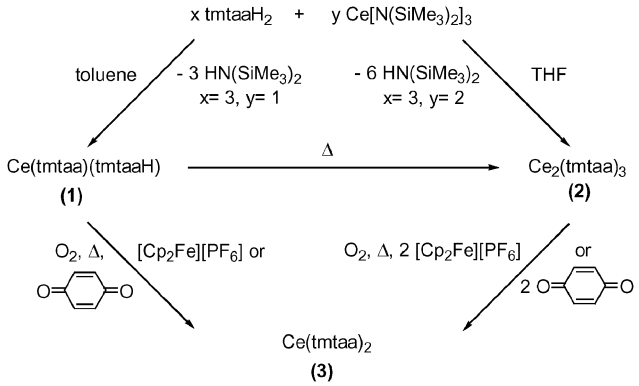
Synthesis and structure

The synthesis of the complexes involves the reaction of tmtaaH_2 with Ce[N($SiMe_3$)$_2$]$_3$ in various molar ratios. Proton transfer reactions of Ce[N($SiMe_3$)$_2$]$_3$ (the pK_a of (Me_3Si)NH in thf is 26[31]) depend critically on the solvent, concentration of the reactants, and temperature. These details are given in the Experimental section, which are reproduceable when close attention to detail is observed, and shown schematically in Scheme 1. Solutions of complexes Ce(tmtaa)(tmtaaH) (**1**) and Ce_2(tmtaa)$_3$ (**2**) are extremely sensitive to trace amounts of air, which result in formation of Ce(tmtaa)$_2$ (**3**), which is stable to air and moisture. Deliberate oxidation of either **1** or **2** is therefore an excellent synthetic route to **3**.

Ce(tmtaa)(tmtaaH) (**1**) is obtained from the reaction of tmtaaH_2 with Ce[N($SiMe_3$)$_2$]$_3$, when the ratio is 3.14 : 1, as red crystals that are sparingly soluble in tetrahydrofuran and aromatic hydrocarbons. The complex gives a molecular ion

[a] *Department of Chemistry and Chemical Sciences Division of Lawrence Berkeley National Laboratory, University of California, Berkeley, California, 94720, USA. E-mail: raandersen@lbl.gov; Tel: +1 510 642 4452*
[b] *Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha, 45071 Toledo, Spain*

† Electronic supplementary information (ESI) available: Crystallographic details. See DOI: 10.1039/b602644c



Scheme 1 Reactions of $tmtaaH_2$ with $Ce[N(SiMe_3)_2]_3$. The equations are not balanced, but the coefficients are the quantities used in the synthesis.

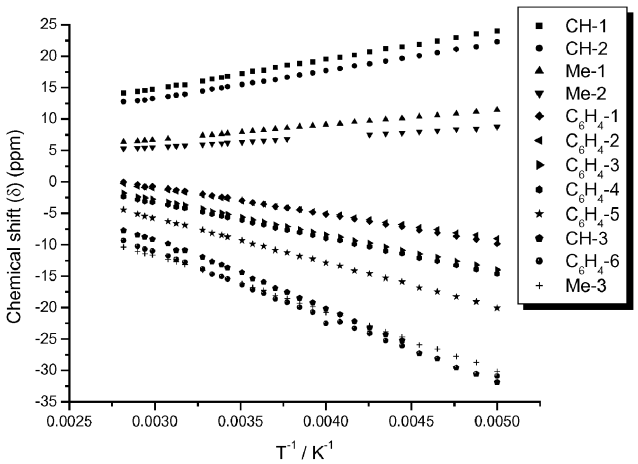


Fig. 1 Chemical shift (δ) *vs.* T^{-1} plot for $Ce_2(tmtaa)_3$.

with the correct isotope pattern, although it does not melt up to 330 °C. Compounds of the type Ln(tmtaa)(tmtaaH) have been prepared when Ln = Y,[29] Pr, Nd, Sm, Gd, Tb and Yb,[30] but not when Ln = Ce. Crystals of Ce(tmtaa)(tmtaaH) grown from toluene, were twinned and the tmtaa and tmtaaH fragments disordered, and therefore the X-ray diffraction pattern could not be resolved; details are available as ESI.† However, the 2 : 1 stoichiometry is confirmed.

Ce(tmtaa)(tmtaaH) (**1**) decomposes slowly to $Ce(tmtaa)_2$ (**3**) and $tmtaaH_2$ (ratio 1 : 1) in C_6D_6 at 65 °C over 14 days. Close inspection of the decomposition process reveals that after one day small amounts of $Ce_2(tmtaa)_3$ (**2**) and $tmtaaH_2$ are detected in the ^1H NMR spectrum. Over the time period of two weeks the resonances due to **2** increase then decrease as **3** is formed and resonances due to $tmtaaH_2$ continue to increase until a steady state is reached. The decomposition does not eliminate dihydrogen since the latter is not observed in the ^1H NMR spectrum and addition of dehydroanthracene does not yield anthracene. It seems reasonable to suggest that the initial decomposition step of **1** is formation of **2** and $tmtaaH_2$, then **2** disproportionates to **3** and "Ce(tmtaa)", which is not detected. This behaviour is different from the observations on $Ce(oep)_2$ (oep = octaethylphorphyrinato), in which $Ce(oep)_2$ is converted to $Ce_2(oep)_3$ and $oepH_2$.[22]

A bulk synthesis of $Ce_2(tmtaa)_3$ (**2**) is the reaction of $tmtaaH_2$ with $Ce[N(SiMe_3)_2]_3$, in the ratio 1.5 : 1, at room temperature in tetrahydrofuran. The dark red, air- and moisture-sensitive crystals incorporate two equivalents of tetrahydrofuran in the crystal lattice. On prolonged exposure to dynamic vacuum the crystals collapse to a red powder. Complex **2** is insoluble in aliphatic hydrocarbon solvents, but moderately soluble in aromatic hydrocarbons and tetrahydrofuran. However, the molecule cannot be purified by recrystallization which is most likely due to its high air sensitivity in solution associated with formation of $Ce(tmtaa)_2$ (**3**). Various attempts to obtain single crystals produced either amorphous or weakly diffracting crystals. However, the material is analytically pure and the ^1H NMR spectrum at 20 °C agrees with a molecule of C_{2v} symmetry, since twelve ^1H NMR signals for chemically inequivalent tmtaa ligands are observed in C_6D_6 solution. The chemical shifts of the resonances are temperature dependent and they obey the Curie–Weiss law as expected for paramagnetic compounds (Fig. 1). The crystal structure of the analogous $Gd_2(tmtaa)_3$ complex is known,[32] and a schematic representation is shown in Fig. 2. The molecule has idealized C_{2v} symmetry in the solid state and a similar structure is expected for **2** based upon the ^1H NMR evidence.

In the presence of O_2, *p*-benzoquinone or $[Cp_2Fe][PF_6]$ $Ce_2(tmtaa)_3$ (**2**) gives $Ce(tmtaa)_2$ (**3**). Complex **2** does not melt nor decompose on heating to 300 °C in a melting point capillary, however as noted above, solutions of **2** in C_6D_6 at 65 °C slowly form **3** and $tmtaaH_2$.

The most convenient bulk scale preparation of $Ce(tmtaa)_2$ (**3**) is the reaction of $[Cp_2Fe][BF_4]$ or *p*-benzoquinone (1 equivalent per cerium) with **1** or **2** in tetrahydrofuran or toluene, respectively. Complex **3** may be crystallized by slow vapor diffusion of pentane into a concentrated toluene solution as deep green, air-stable shiny cubes which incorporate half a molecule of pentane per cerium. The stoichiometry was confirmed by X-ray crystallography, elemental analysis and ^1H NMR spectroscopy. It is sparingly soluble in aliphatic hydrocarbons, but more soluble in aromatic ones. The EI-MS spectra exhibit a molecular ion (*m*/*z* 824 amu) with the correct

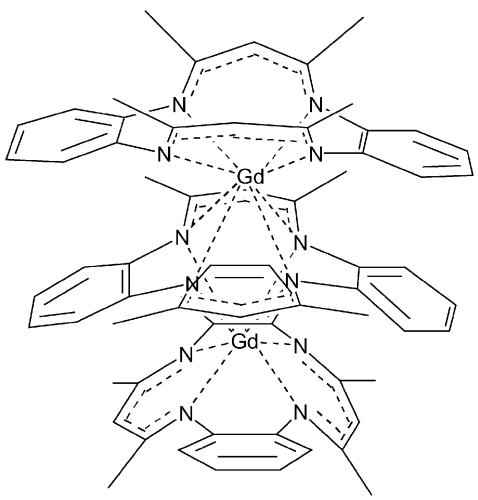


Fig. 2 Schematic representation of the $Gd_2(tmtaa)_3$ molecular structure.[32]

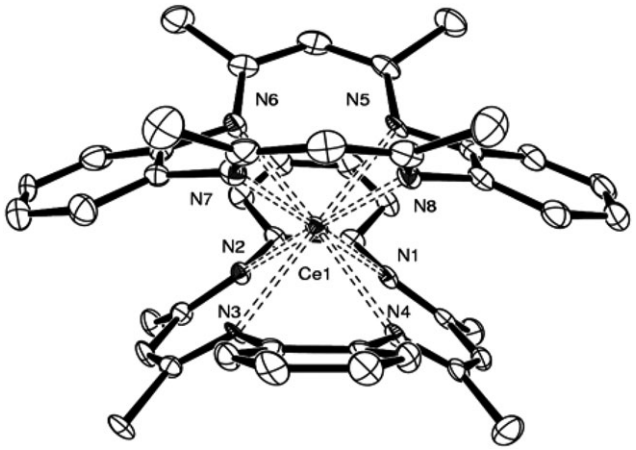


Fig. 3 ORTEP diagram of $Ce(tmtaa)_2$ (**3**) (50% probability ellipsoids). The disordered *n*-pentane molecule has been omitted for clarity.

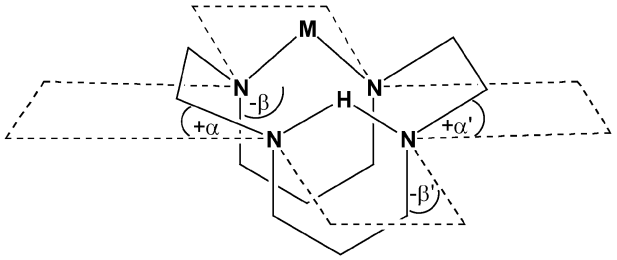
isotope pattern. However, the molecule does not melt to 310 °C nor sublime in an ampoule under static vacuum up to temperatures of 350 °C; instead it decomposes and the decomposition products are $tmtaaH_2$, an unidentified green oil, and an insoluble red–brown residue; $Ce_2(tmtaa)_3$ is not formed under these conditions as determined by ^1H NMR spectroscopy. The ^1H and ^{13}C NMR spectra of **3** show only one set of CH and CH_3 groups consistent with a molecule of high symmetry. The solid-state structure of $Ce(tmtaa)_2$ consists of discrete monomeric molecules with idealized D_{2d} symmetry, and with disordered pentane molecules in the unit cell. Analogous complexes of Ti, Zr and Hf have been reported and $Zr(tmtaa)_2$ is isostructural with the cerium analogue.[9] An ORTEP diagram of **3** is shown in Fig. 3 and selected bond distances and angles are given in Table 1. The averaged Ce–N distance in compound **3** of 2.454(9) Å is identical to the averaged Ce–N distance (2.478(15) Å) for the [Ce(tmtaa)] fragment in Ce(tmtaa)[tmtaaLi(thf)].[28] In **3** the cerium atom is sandwiched between two tmtaa molecules, each of which adopt a saddle-shape, and the tmtaa ligands have a staggered orientation (φ = 88.6°). This results in an eight-coordinate molecule in which the eight nitrogen atoms are located on the corners of a cube. An interesting feature of the molecular structure of tmtaa complexes is the distortion of the ligand that is shown by the dihedral angles α and β listed in Table 2 and defined in the footnote to Table 2. The neutral free-base and the imidinate fragments in **3** and $Zr(tmtaa)_2$ have similar β-angles. The angles referred to as α decrease slightly (5–8°) on going from the free-ligand to **3** making the saddle shape more open. The two planes defined by the N_4 cores are parallel, the dihedral angle between them is 1.2(1)°, and the planes are separated by 3.02 Å. The eight Ce–N distances range from 2.428(3) to 2.462(4) Å.

Table 1 Important bond distances (Å) and angles (°) and shape parameters (°)[a] of $Ce(tmtaa)_2$ (**3**)

Ce1–N1	2.460(3)	Ce1–N5	2.450(3)
Ce1–N2	2.427(4)	Ce1–N6	2.449(3)
Ce1–N3	2.461(3)	Ce1–N7	2.456(5)
Ce1–N4	2.462(3)	Ce1–N8	2.448(4)
N1–Ce1–N2	65.42(12)	N5–Ce1–N6	69.89(11)
N1–Ce1–N3	104.03(11)	N5–Ce1–N7	103.34(13)
N1–Ce1–N4	70.06(11)	N5–Ce1–N8	65.22(12)
N2–Ce1–N3	70.49(11)	N6–Ce1–N7	69.94(14)
N2–Ce1–N4	104.35(11)	N6–Ce1–N8	104.60(11)
N3–Ce1–N4	65.26(11)	N7–Ce1–N8	70.70(14)
δ_1	0.9	δ_4	89.2
δ_2	1.0	δ_3	92.4
ϕ	0.1		

[a] As defined in ref. 50.

Table 2 Dihedral angles (°) in selected TMTAA structures



	$[Ce(tmtaa)_2]$ (**3**)[a]	[(thf)Li(tmtaa) Ce(tmtaa)][b]	$[Zr(tmtaa)_2]$[c]	$tmtaaH_2$[d]
α/°	12	13	15	20
	12	16[e]	16	21
β/°	34	37	38	37
	36	30[e]	39	37

Angles α and β are defined in the schematic drawing.[a] This work. [b] Ref. 28. [c] Ref. 9. [d] Ref. 8.

Solid-state magnetic susceptibility studies (SQUID)

The magnetic susceptibility data of **1** and **2** are shown in Fig. 4 and 5, together with the data of $Ce[N(SiMe_3)_2]_3$. The χ^{-1} *vs.* *T* plots of these compounds are non-linear, *i.e.*, they deviate from Curie–Weiss behaviour as expected for a cerium(III) ion with a $^2F_{5/2}$ ground state.[33,34]

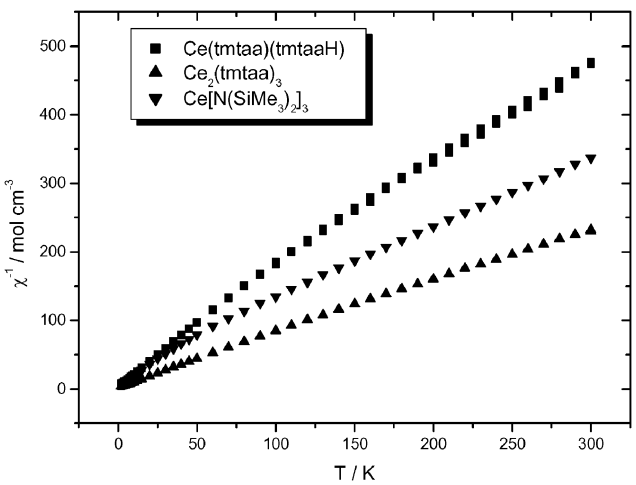


Fig. 4 Solid-state magnetic susceptibility, χ^{-1} *vs.* *T* plot for $Ce[N(SiMe_3)_2]_3$, Ce(tmtaa)(tmtaaH) and $Ce_2(tmtaa)_3$.

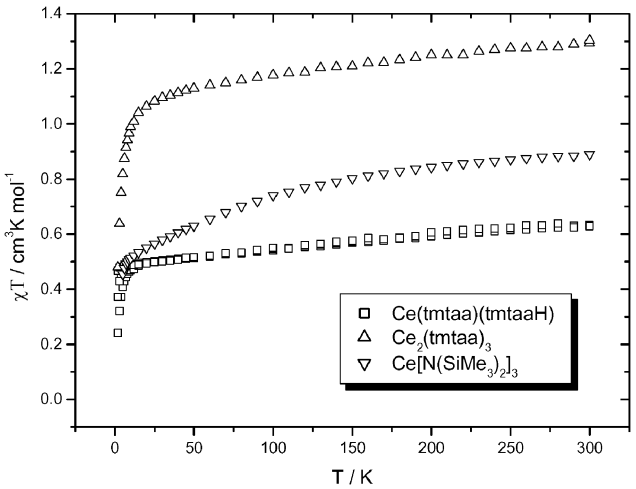


Fig. 5 Solid-state magnetic susceptibility, (χT) *vs.* T plot for Ce[N$(SiMe_3)_2]_3$, Ce(tmtaa)(tmtaaH) and Ce_2(tmtaa)$_3$.

In addition, the magnetic susceptibility data for **1** provide independent support for the supposition derived from X-ray diffraction, that **1** contains a cerium(III) center, and the magnetic moment, μ_{eff}(300 K) = 2.25 μ_B,[35] is in agreement with data from other mononuclear Ce(III) compounds (1.8–2.5 μ_B).[36–40] The magnetic susceptibility of the triple-decker complex **2** is unexceptional, and spins on the Ce(III) ions are uncorrelated as shown by the χ^{-1} *vs.* T plot and the magnetic moment μ_{eff}(300 K) = 3.23 μ_B (2.28 μ_B per Ce).

The experimentally determined magnetic susceptibility of **3** shows that it is not diamagnetic ($\chi_m < 0$). The plot of χ, when corrected for a small amount of a $J = 5/2$ impurity, Ce(III), as outlined in ref. 41, shows that in the solid state **3** behaves as a temperature independent paramagnet (TIP) (Fig. 6). This behaviour is analogous to that of Ce(cot)$_2$.

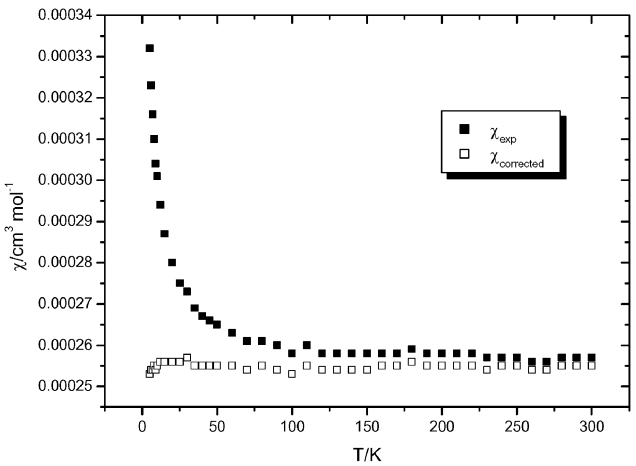


Fig. 6 Solid-state magnetic susceptibility (χ) *vs.* T plot for Ce(tmtaa)$_2$ at 40 kG. The experimental values χ_{exp} include a small magnetic impurity (~0.1% of a $J = 5/2$ impurity), which is removed in $\chi_{corrected}$. The data clearly show TIP behaviour with $\chi_0 = (2.55 \pm 0.02) \times 10^{-4}$ cm^3 mol^{-1}.

Conclusions

Cerium tris(bistrimethylsilylamide), Ce[N$(SiMe_3)_2]_3$, is a convenient starting material for the tmtaa coordination compounds, Ce(tmtaa)(tmtaaH), Ce_2(tmtaa)$_3$ and Ce(tmtaa)$_2$. The magnetic susceptibility of Ce(tmtaa)(tmtaaH) and Ce_2(tmtaa)$_3$ show that these macrocyclic complexes behave as simple f^1-paramagnets. The magnetic susceptibility behaviour of Ce(tmtaa)$_2$ is not simple. The stoichiometry of **3** implies that the electronic structure is Ce(IV) ($4f^0$) and diamagnetic. However, **3** is a TIP, as found for Ce(cot)$_2$. Although the temperature dependence of the magnetic susceptibility of these two compounds is similar, the underlying microscopic or molecular reason is not necessarily the same. Studies, using the tools of physicists, have been initiated to provide more detailed molecular explanations for this behavior.[27]

Experimental

The experiments were carried out and characterized as previously described.[41,42] The magnetic susceptibility was obtained as previously reported.[41] Ce[N$(SiMe_3)_2$] was made by a published method and sublimed then crystallized from pentane prior to use.[43]

Syntheses

[Ce(tmtaa)(tmtaaH)] (1). A hot, light yellow solution of Ce[N$(SiMe_3)_2]_3$ (0.18 g, 0.29 mmol), dissolved in *ca.* 10 mL of toluene was added slowly to a hot, yellow solution of tmtaaH_2 (0.314 g, 0.91 mmol) dissolved in *ca.* 10 mL of toluene without stirring. During the addition, the color changed to red and the solution was allowed to reach room temperature without stirring. Red crystals (0.148 g, 0.18 mmol, 59%) formed over 24 h. The product was very sparingly soluble in tetrahydrofuran and aromatic hydrocarbons, and insoluble in aliphatic solvents and it could not be recrystallized. Mp > 330 °C. Anal. Calc. for $C_{44}H_{45}N_8Ce$: C, 63.98; H, 5.49; N, 13.59. Found: C, 63.83; H, 5.47; N, 13.49%. The EI mass spectrum showed a molecular ion at m/z 825 amu. The parent ion isotopic cluster was simulated: (calc., found %): 825 (100, 100), 826 (51, 51), 827 (25, 26), 828 (8, 8), 829 (2, 2). IR (Nujol mull; CsI windows; cm^{-1}): 3050 (w), 1675 (s), 1650 (w), 1560 (s), 1530 (m), 1420 (vs), 1395 (vs), 1380 (vs), 1270 (s), 1265 (s), 1221 (w), 1180 (vs), 1155 (m), 1110 (m), 1100 (m), 1100 (m), 1042 (m), 1020 (s), 932 (w), 935 (w), 795 (s), 788 (vs), 740 (vs), 700 (w), 658 (w), 620 (w), 550 (w), 480 (w), 382 (m). Due to the low solubility in thf-d_8 and air-sensitivity the ^{1}H NMR spectra were not reproducible.

[Ce_2(tmtaa)$_3$] (2). A solution of tmtaaH_2 (0.15 g, 0.43 mmol) dissolved in *ca.* 15 mL of tetrahydrofuran was added to a solution of Ce[N$(SiMe_3)_2]_3$ (0.18 g, 0.29 mmol) dissolved in 5 mL of tetrahydrofuran and the mixture was allowed to stand at room temperature, without stirring, for 48 h. During this time the color of the mixture slowly changed from orange to red and dark red crystals deposited on the walls of the Schlenk tube. The crystals, which co-crystallized with one molecule of tetrahydrofuran per cerium, were isolated by filtration and

washed with pentane (5 mL) to yield 0.12 g (0.083 mmol, 57%) of **2**(thf)$_2$. Mp >330 °C. Anal. Calc. for $C_{74}H_{82}N_{12}O_2Ce_2$: C, 61.22; H, 5.69; N, 11.57. Found: C, 60.75; H, 5.81; N, 11.31%. ^{1}H NMR (C_6D_6, 20 °C): δ 16.75 (2H, $\nu_{1/2}$ = 50 Hz, C*H*), 15.10 (2H, $\nu_{1/2}$ = 50 Hz, C*H*), 7.68 (12H, $\nu_{1/2}$ = 21 Hz, CH_3), 6.21 (12H, $\nu_{1/2}$ = 36 Hz, CH_3), −2.53 (4H, $\nu_{1/2}$ = 15 Hz, C$_6H_4$), −2.64 (4H, $\nu_{1/2}$ = 13 Hz, C$_6H_4$), −5.08 (4H, $\nu_{1/2}$ = 13 Hz, C$_6H_4$), −5.51 (4H, $\nu_{1/2}$ = 35 Hz, C$_6H_4$), −8.59 (4H, $\nu_{1/2}$ = 52 Hz, C$_6H_4$), −13.20 (2H, $\nu_{1/2}$ = 60 Hz, C*H*), −15.26 (16H, $\nu_{1/2}$ = 45 Hz, overlapping CH_3 + C$_6H_4$). IR (Nujol mull; CsI windows; cm^{-1}): 3050 (m), 1675 (vw), 1620 (w), 1560 (sh), 1550 (vs), 1535 (vs), 1415 (vs), 1380 (vs), 1270 (s), 1221 (m), 1185 (s), 1115 (m), 1070 (m), 1022 (s), 922 (m), 848 (w), 795 (vs), 770 (sh), 738 (vs), 700 (m), 625 (w), 615 (w), 390 (m), 362 (w), 329 (m).

[Ce(tmtaa)$_2$] (3). Ce$_2$(tmtaa)$_3$ or Ce(tmtaa)(tmtaaH) were converted to Ce(tmtaa)$_2$, thermally or chemically by addition of 1,4-benzoquinone, [Cp$_2$Fe][PF$_6$] or traces of O$_2$. The most convenient synthesis employed the reaction of [Cp$_2$Fe][PF$_6$] or 1,4-benzoquinone as outlined below.

Method 1: Ce(tmtaa)(tmtaaH) (0.15 g, 0.18 mmol) was suspended in toluene (*ca.* 10 mL) and a yellow solution of freshly sublimed 1,4-benzoquinone (0.020 g, 0.18 mmol) in toluene (10 mL) was added. The suspension turned dark green and an insoluble colorless precipitate was formed. The reaction mixture was filtered and the solvent removed under dynamic vacuum. At this point the residue was handled in air and washed with hot heptane to remove trace amounts of tmtaaH$_2$. The residue was dissolved in toluene, the solution concentrated and the compound was crystallized at −20 °C or by vapour diffusion of pentane into the concentrated toluene solution overnight.

Method 2: A suspension of Ce(tmtaa)(tmtaaH) (0.15 g, 0.18 mmol) and [Cp$_2$Fe][PF$_6$] (0.06 g, 0.18 mmol) in tetrahydrofuran (10 mL) yielded a dark green solution and an insoluble colorless precipitate. The reaction mixture was filtered and the solvent was removed from the filtrate under dynamic vacuum. At this point the residue was handled in air and washed with hot heptane to remove trace amounts of Cp$_2$Fe and tmtaaH$_2$. The residue was dissolved in toluene, the solution concentrated and the compound was crystallized by vapour diffusion of pentane into the concentrated toluene solution over night or at −20 °C. The product was obtained as deep green, shiny cubes (0.086 g, 0.10 mmol, 56%), which co-crystallized with half a molecule of pentane per cerium, as established by X-ray crystallography, elemental analysis and NMR spectroscopy.

The reaction conditions for the conversion of Ce$_2$(tmtaa)$_3$ were identical to those with Ce(tmtaa)(tmtaaH) with the exception that one equivalent of *p*-benzoquinone or [Cp$_2$Fe][PF$_6$] was used per cerium. Mp >310 °C. Anal. Calc. for $C_{46.5}H_{50}N_8Ce$: C, 64.86; H, 5.85; N, 13.01. Found: C, 64.81; H, 5.89; N, 12.69%. ^{1}H NMR (C_6D_6, 20 °C): δ 7.29 (8H, m, C$_6H_4$), 7.21 (8H, m, C$_6H_4$), 3.85 (4H, s, C*H*), 1.77 (24H, s, CH_3), the pentane resonances appeared at 1.23 (3H, m, CH_2) and 0.87 (3H, t, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 20 °C): δ 156.5 (s, *C*Me), 136.6 (s, *ipso*-Ar), 126.0 (s, C$_6$H$_4$), 125.2 (s, C$_6$H$_4$), 106.1 (s, *C*H), 24.3 (s, *C*H$_3$). The EI mass spectrum showed a molecular ion at *m*/*z* 824 amu. The parent ion isotopic cluster was simulated: (calc., found %): 824 (100, 100), 825 (51, 51), 826 (25, 26), 827 (8, 8), 828 (2, 2). IR (Nujol mull; CsI windows; cm^{-1}): 3095 (vw), 3060 (m), 1565 (sh. vs), 1558 (vs), 1532 (s), 1438 (s), 1410 (br. vs), 1198 (m-s), 1280 (vs), 1228 (m), 1195 (vs), 1122 (m), 1050 (m), 1028 (s), 930 (m), 862 (vw), 853 (w), 800 (vs), 772 (m), 742 (vs), 702 (m), 620 (w), 570 (vw), 510 (vw), 398 (m), 380 (m), 228 (vs).

Crystallographic study of 3

X-Ray quality crystals were grown by vapour diffusion of pentane into a concentrated toluene solution overnight. A crystal of appropriate dimensions was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on a Bruker SMART 1K CCD diffractometer.[44] Cell constants and an orientation matrix were obtained of the measured positions of reflections with $I > 10\sigma$ to give the unit cell. The systematic absences uniquely determined the space group in each case. An arbitrary hemisphere of data was collected at low temperature using the ω scan technique with 0.3° scans counted for 10 s per frame. Data were integrated using SAINT.[45] and corrected for Lorentz and polarization effects. The data were analyzed for agreement and absorption using XPREP,[46] and an empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.[47] The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in calculated positions, but not refined. No hydrogen atoms for the disordered pentane were included in the refinement. The structure was solved and refined using the software packages SHELXS-97 (structure solution)[48] and SHELXL-97 (refinement).[49]

Crystal data. $C_{46.50}H_{44}CeN_8$, M_r = 855.02, 0.32 × 0.24 × 0.16 mm, triclinic, space group $P\bar{1}$, a = 11.417(1), b = 11.543(1), c = 16.419(2) Å, α = 7.720(2), β = 261(2), γ = 107.884(2)°, V = 1950.1(4) Å^3, Z = 2, D_c = 1.456 g cm^{-3}, F(000) = 874, μ(Mo-Kα) = 1.21 cm^{-1}, λ(Mo-Kα) = 0.71073 Å, no. of reflections measured: total: 9863, unique: 6189 (R_{int} = 0.0425). Residuals: R; $wR2$ ($I > 2\sigma(I)$) 0.0468, 0.1238; R_{all} = 0.0524; $\Delta\rho_{max,min}$ = 2.009, −2.059 e Å^{-3}.

CCDC reference number 298952.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602644c

Acknowledgements

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. We thank Dr F. J. Hollander and Dr A. Oliver at the CHEXRAY facility for assistance with the X-ray crystallography, the Spanish Ministry of Educación, Cultura y Deporte for a Sabbatical Fellowship (R. F.), and Wayne W. Lukens and Corwin H. Booth for discussions.

References

1 V. L. Goedken, J. Molin-Case and Y. Whang, *J. Chem. Soc., Chem. Commun.*, 1973, 337.

2 V. L. Goedken, M. C. Weiss, D. Place and J. Dabrowiak, *Inorg. Synth.*, 1980, **20**, 115.
3 F. A. Cotton and J. Czuchajowska, *Polyhedron*, 1990, **9**, 2553.
4 G. Parkin, *Prog. Inorg. Chem.*, 1998, **47**, 1.
5 P. Mountford, *Chem. Soc. Rev.*, 1998, **27**, 105.
6 L. Giannini, E. Solari, S. De Angelis, T. R. Ward, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1995, **117**, 5801.
7 K. Tatsumi and R. Hoffmann, *Inorg. Chem.*, 1981, **20**, 3771.
8 V. L. Goedken, J. J. Pluth, S.-M. Peng and B. E. Bursten, *J. Am. Chem. Soc.*, 1976, **98**, 8014.
9 S. De Angelis, E. Solari, E. Gallo, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1992, **31**, 2520.
10 A. Martin, R. Uhrhammer, T. G. Gardner, R. F. Jordan and R. D. Rogers, *Organometallics*, 1998, **17**, 382.
11 H.-J. Kablitz and G. Wilke, *J. Organomet. Chem.*, 1973, **51**, 241.
12 H.-J. Kim, D. Whang, K. Kim and Y. Do, *Inorg. Chem.*, 1993, **32**, 360.
13 H. Brand and J. Arnold, *J. Am. Chem. Soc.*, 1992, **114**, 2266.
14 D. G. Black, D. C. Swenson, R. F. Jordan and R. D. Rogers, *Organometallics*, 1995, **14**, 3539.
15 D. M. Rogers, S. R. Wilson and G. S. Girolami, *Organometallics*, 1991, **10**, 2419.
16 K. Kim, W. S. Lee, H.-J. Kim, S.-H. Cho, G. S. Girolami, P. A. Gorlin and K. S. Suslick, *Inorg. Chem.*, 1991, **30**, 2652.
17 J. W. Buchler, A. De Cian, S. Elschner, J. Fischer, P. Hammerschmitt and R. Weiss, *Chem. Ber.*, 1992, **125**, 107.
18 J. P. Collman, J. L. Kendall, J. L. Chen, T. A. Eberspacher and C. R. Moylan, *Inorg. Chem.*, 1997, **36**, 5603.
19 J. Silver, J. P. Lukes, P. K. Hey and C. M. O'Connor, *Polyhedron*, 1989, **8**, 1631.
20 J. Silver, J. P. Lukes, S. D. Howe and B. Howlin, *J. Mater. Chem.*, 1991, **1**, 29.
21 A. Greco, S. Cesca and G. Bertolini, *J. Am. Chem. Soc.*, 1976, **119**, 321.
22 J. W. Buchler, A. De Cian, J. Fischer, M. Khin-Botulinski, H. Paulus and R. Weiss, *J. Am. Chem. Soc.*, 1986, **108**, 3652.
23 Y. Bian, J. Jiang, Y. Tao, M. T. M. Choi, R. Li, A. C. H. Ng, P. Zhu, N. Pan, X. Sun, D. P. Arnold, Z.-Y. Zhou, H.-W. Li, T. C. W. Mak and D. K. P. Ng, *J. Am. Chem. Soc.*, 2003, **125**, 12257.
24 H. Isago and M. Shimoda, *Chem. Lett.*, 1992, 147.
25 M. Safarpour Haghighi, C. L. Teske and H. Homborg, *Z. Anorg. Allg. Chem.*, 1992, **608**, 73.
26 M. Dolg, P. Fulde, H. Stoll, H. Preuss, A. Chang and R. M. Pitzer, *Chem. Phys.*, 1995, **195**, 71.
27 C. H. Booth, M. D. Walter, M. Daniel, W. W. Lukens and R. A. Andersen, *Phys. Rev. Lett.*, 2005, **95**, 267202.
28 J. Magull and A. Simon, *Z. Anorg. Allg. Chem.*, 1992, **615**, 77.
29 Z. Wang, K. Sakata and M. Hashimato, *Polyhedron*, 1998, **17**, 4451.
30 Z. Wang, N. Hu, K. Sakata and M. Hashimato, *J. Chem. Soc., Dalton Trans.*, 1999, 1695.
31 R. R. Fraser, T. S. Mansour and S. Savard, *J. Org. Chem.*, 1985, **50**, 3232.
32 A ball-and-stick representation of $Gd_2(tmtaa)_3$ was found on the website of the Max-Planck-Institute in Stuttgart, http://www.fkf.mpg.de/simon/publications/jb91/magull.html.
33 J. H. van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Clarendon Press, Oxford, 1932.
34 E. A. Boudreaux and L. N. Mulay, *Theory and Applications of Molecular Paramagnetism*, Wiley-Interscience, New York, 1976.
35 Values of μ_{eff} values expressed in Bohr magnetons (μ_B) are related to those values expressed as χT by the expression $\mu_{eff} = 2.828(\chi T)^{0.5}$ in units of μ_B.
36 S. D. Stults and R. A. Andersen, *Organometallics*, 1990, **9**, 115.
37 W. J. Evans and M. A. Hozbor, *J. Organomet. Chem.*, 1987, **326**, 299.
38 R. D. Fischer, in *Fundamental and Technological Aspects of Organo-f-Element Chemistry*, ed. T. J. Marks and I. L. Fragala, D. Reidel, Dordrecht, The Netherlands, 1985, p. 277.
39 H. Reddmann, H. Schultze, H.-D. Amberger, C. Apostolidis and B. Kanellakopulos, *Spectrochim. Acta, Part A*, 1990, **46**, 1223.
40 H.-D. Amberger, H. Reddmann, H. Schultze, S. Jank, B. Kanellakopulos and C. Apostolidis, *Spectrochim. Acta, Part A*, 2003, **59**, 2527.
41 M. D. Walter, M. Schultz and R. A. Andersen, *New J. Chem.*, 2006, **30**, 238.
42 M. Schultz, J. M. Boncella, D. J. Berg, T. D. Tilley and R. A. Andersen, *Organometallics*, 2002, **21**, 460.
43 D. C. Bradley, J. S. Gohtra and F. A. Hart, *J. Chem. Soc., Dalton Trans.*, 1973, 1021.
44 Smart, *SMART Area-Detection Software Package*, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2003.
45 Saint, *SAINT SAX Area-Dectector Integration Program*, Siemens Industrial Automation, Inc., Madison, WI, 2003.
46 G. M. Sheldrick, *XPREP*, Siemens Industrial Automation, Inc., Madison, WI, 2001.
47 G. M. Sheldrick, *SADABS*, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2003.
48 G. M. Sheldrick, *SHELXS-97*, University of Göttingen, Germany, 1997.
49 G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, 1997.
50 E. L. Mutterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1974, **96**, 1748.

