

Lawrence Berkeley National Laboratory

Chemical Sciences

Title

Synthesis and magnetic properties of cerium macrocyclic complexes with tmtaaH₂, tetramethyldibenzotetraaza[14]-annulene

Permalink

<https://escholarship.org/uc/item/42c826pn>

Journal

Lawrence Berkeley National Laboratory

Authors

Walter, Marc D.

Fandos, Rosa

Andersen, Richard A.

Publication Date

2006-02-21

Peer reviewed

Synthesis and Magnetic Properties of Cerium Macrocyclic Complexes with tmtaaH₂, Tetramethyldibenzotetraaza[14]-annulene

Marc D. Walter,^a Rosa Fandos^{a,b} and Richard A. Andersen^{*a}

The complexes [Ce(tmtaa)₂], [Ce(tmtaa)(tmtaaH)] and [Ce₂(tmtaa)₃(thf)₂] are obtained from Ce[N(SiMe₃)₂]₃ and tmtaaH₂, 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 tmtaaH₂, 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 tmtaaH₂ to two related classes of ligands that have an extensive chemistry, viz., [8]-annulene, otherwise known as cyclooctatetraene, cot, and [16]-annulenes, the porphyrins, porphH₂, and phthalocyanines, pcH₂. Although all of these ligands form stable dianions, their electronic structure and therefore the electronic properties of their complexes are different. The tmtaa²⁻ is a 24 π -electron system ($4n\pi$, $n=6$) that is not Hückel aromatic. The negative charge is not delocalized over its 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 _{α} (Me)C _{β} (H)C _{α} (Me)N.^{6, 7} The tmtaa²⁻ is therefore not planar but is saddle shaped with idealized C_{2v} symmetry.⁸ The cot²⁻ ($4n\pi+2$, $n=2$) and porph²⁻ ($4n\pi+2$, $n=6$) 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)ZrX₂, (cot)ZrX₂, (porph)ZrX₂ have been studied as electronically altered analogues of Cp₂ZrX₂.^{9–14} In addition, the diamagnetic complexes Zr(cot)₂, Zr(porph)₂ and Zr(pc)₂ with a d⁰ electronic configuration are known.^{11, 15–20}

The binary f-transition metal complexes of cot²⁻, porph²⁻ and pc²⁻ 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, 4f¹(e_{2u}))(cot^{1.5-}, e_{2u}³)₂] and [Ce(IV, 4f⁰)(COT²⁻)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 tmtaaH₂ with Ce[N(SiMe₃)₂]₃ in various molar ratios. Proton transfer reactions of Ce[N(SiMe₃)₂]₃, the pK_a of (Me₃Si)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 reproducible when close attention to detail is observed, and shown schematically in Scheme 1. Solutions of complexes Ce(tmtaa)(tmtaaH) (**1**) and Ce₂tmtaa₃ (**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 tmtaaH₂ with Ce[N(SiMe₃)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 with the correct isotope pattern, although it does not melt 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

^a Department of Chemistry and Chemical Sciences Division of Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, USA. Tel: +1 510 642 4452; E-mail: raandersen@lbl.gov

^b Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha, 45071 Toledo, Spain.

† Electronic Supplementary Information (ESI) available: CCDC-reference number CCDC 298952. For crystallographic data in .cif or other electronic format see <http://dx.doi.org/10.1039/b000000/x/>

not when $\text{Ln} = \text{Ce}$. Crystals of $\text{Ce}(\text{tmtaa})(\text{tmtaaH})$ grown from toluene, were twinned, the tmtaa and tmtaaH fragments are disordered, and therefore the X-ray diffraction pattern could not be resolved. However, the 2:1 stoichiometry of the complex is confirmed.

$\text{Ce}(\text{tmtaa})(\text{tmtaaH})$ (**1**) decomposes slowly to $\text{Ce}(\text{tmtaa})_2$ (**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 $\text{Ce}_2(\text{tmtaa})_3$ (**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 the resonances due to tmtaaH_2 continue to increase until a steady state is reached. The decomposition does not eliminate hydrogen since the latter is not observed in the ^1H NMR spectrum and the addition of dehydroanthracene does not yield anthracene. It seems reasonable to suggest that the initial decomposition step of **1** is the formation of **2** and tmtaaH_2 , then **2** disproportionates to **3** and “ $\text{Ce}(\text{tmtaa})$ ”, which is not detected. This behaviour is different from the observations on $\text{Ce}(\text{oep})_2$ ($\text{oep} = \text{octaethylphorphyrinato}$), in which $\text{Ce}(\text{oep})_2$ is converted to $\text{Ce}_2(\text{oep})_3$ and oepH_2 .²²

A bulk synthesis of $\text{Ce}_2(\text{tmtaa})_3$ (**2**) is the reaction of tmtaaH_2 with $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$, 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. The complex **2** is insoluble in aliphatic 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, that is associated with formation of $\text{Ce}(\text{tmtaa})_2$ (**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 $\text{Gd}_2(\text{tmtaa})_3$ complex is known,³² and a schematic representation is shown in Figure 2. The molecule has idealized C_{2v} symmetry in solid state. The Gd-atoms are coordinated by slightly distorted cubes of the N-atoms of the tmtaa -ligand. The Gd-atoms have two different coordination environments. One Gd is displaced to the same side of the outer ligand, to which the benzoid rings are tipped, but coordinates to the middle deck in the opposite way. The bonding situation is different for the other Gd which is connected to each of the N-atoms of the two tmtaa -ligands on the same side of the ligand where the C_6H_4 -fragments are tipped to that is realized by a 90° rotation of the third tmtaa -ligand around the Gd-Gd axis. A similar structure is expected for **2** based upon the ^1H NMR evidence.

In the presence of O_2 , p -benzoquinone or $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ $\text{Ce}_2(\text{tmtaa})_3$ (**2**) gives $\text{Ce}(\text{tmtaa})_2$ (**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 $\text{Ce}(\text{tmtaa})_2$ (**3**) is the reaction of $[\text{Cp}_2\text{Fe}][\text{BF}_4]$ 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 ($m/e = 824$ amu) with the correct 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 identified as tmtaaH_2 , an unidentified green oil and an insoluble red-brown residue. $\text{Ce}_2(\text{tmtaa})_3$ 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 units consistent with a molecule of high symmetry.

The solid state structure of $\text{Ce}(\text{tmtaa})_2$ 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 $\text{Zr}(\text{tmtaa})_2$ is isostructural to the cerium analogue.⁹ An ORTEP diagram of **3** is shown in Figure 3 and selected bond distances and angles are given in Table 1. Most notably, the averaged Ce-N distance in compound **3** of 2.454(9) Å is identical to the value found for the averaged Ce-N distance (2.478(15) Å) for the $[\text{Ce}(\text{tmtaa})]$ fragment in $\text{Ce}(\text{tmtaa})[\text{tmtaaLi}(\text{thf})]$.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 ($\phi = 88.6^\circ$). 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 in the complexes which is shown by the dihedral angles α and β listed in Table 2 defined in the footnote to Table 2. The neutral free-base and the imidinate fragments in **3** and $\text{Zr}(\text{tmtaa})_2$ 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 $1.17(10)^\circ$, and the planes are separated by 3.02 Å. The eight Ce-N distances ranging from 2.428(3) to 2.462(4) Å.

Solid State Magnetic Susceptibility Studies (SQUID)

The magnetic susceptibility data of **1** and **2** are shown in Figures 4 and 5, together with the data of $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$. 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 $^2\text{F}_{5/2}$ ground state.^{33, 34}

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, $\mu_{\text{eff}}(300\text{K}) = 2.25\mu_{\text{B}}$,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 $\mu_{\text{eff}}(300\text{K}) = 3.23\mu_{\text{B}}$ (2.28 μ_{B} per Ce).

The experimentally determined magnetic susceptibility of **3** shows that it is not diamagnetic ($\chi_{\text{m}} < 0$). 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, but the molecular reason for the TIP behavior is unknown at this time.

Conclusions

Cerium tris(bis(trimethylsilyl)amide), Ce[N(SiMe₃)₂]₃, is a convenient starting material for the tmtaa coordination compounds, Ce(tmtaa)(tmtaaH), Ce₂(tmtaa)₃ and Ce(tmtaa)₂. The magnetic susceptibility of Ce(tmtaa)(tmtaaH) and Ce₂(tmtaa)₃ show that these macrocyclic complexes behave as simple f¹-paramagnets. The magnetic susceptibility behaviour of Ce(tmtaa)₂ is not simple. The stoichiometry of **3** implies that the electronic structure is Ce(IV), 4f⁰ 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 microscopic or molecular reason is not necessarily the same. Studies, using the tools of physicists, have been initiated to answer this fascinating question.²⁷

Experimental Section

The experiments were carried out and characterized as previously described.^{41, 42} The magnetic susceptibility was obtained as previously reported.⁴¹ Ce[N(SiMe₃)₂]₃ was prepared according to a published method and sublimed and crystallized prior to use.⁴³

[Ce(tmtaa)(tmtaaH)] (1). A hot, light yellow solution of Ce[N(SiMe₃)₂]₃ (0.18 g, 0.29 mmol), dissolved in ca. 10 mL of toluene was added slowly to a hot, yellow solution of tmtaaH₂ (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. M.p. > 330 °C. Anal. Calcd for C₄₄H₄₅N₈Ce: C, 63.98; H, 5.49; N, 13.59. Found: C, 63.83; H, 5.47; N, 13.49. The E.I. mass spectrum showed a molecular ion at m/e = 825 amu. The parent ion isotopic cluster was simulated: (calcd. %, obsv'd. %): 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-d₈ and the air-sensitivity the ¹H NMR spectra were not reproducible and uninformative.

[Ce₂(tmtaa)₃] (2). A solution of tmtaaH₂ (0.15 g, 0.43 mmol) dissolved in ca. 15 mL of tetrahydrofuran was added to a solution of Ce[N(SiMe₃)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. M.p. > 330 °C. Anal. Calcd for C₇₄H₈₂N₁₂O₂Ce₂: C, 61.22; H, 5.69; N, 11.57. Found: C, 60.75; H, 5.81; N, 11.31. ¹H NMR (C₆D₆, 20°C): δ 16.75 (2H, $\nu_{1/2} = 50$ Hz, CH), 15.10 (2H, $\nu_{1/2} = 50$ Hz, CH), 7.68 (12H, $\nu_{1/2} = 21$ Hz, CH₃), 6.21 (12H, $\nu_{1/2} = 36$ Hz, CH₃), -2.53 (4H, $\nu_{1/2} = 15$ Hz, C₆H₄), -2.64 (4H, $\nu_{1/2} = 13$ Hz, C₆H₄), -5.08 (4H, $\nu_{1/2} = 13$ Hz, C₆H₄), -5.51 (4H, $\nu_{1/2} = 35$ Hz, C₆H₄), -8.59 (4H, $\nu_{1/2} = 52$ Hz, C₆H₄), -13.20 (2H, $\nu_{1/2} = 60$ Hz, CH), -15.26 (16H, $\nu_{1/2} = 45$ Hz, overlapping CH₃ + C₆H₄). 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). Ce₂(tmtaa)₃ or Ce(tmtaa)(tmtaaH) were converted to Ce(tmtaa)₂, thermally or chemically by addition of 1,4-benzoquinone, [Cp₂Fe][PF₆] or traces of O₂. The most convenient way employed the reaction of [Cp₂Fe][PF₆] 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 tmtaaH₂. 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 over night.

Method 2: A suspension of Ce(tmtaa)(tmtaaH) (0.15 g, 0.18 mmol) and [Cp₂Fe][PF₆] (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 Cp₂Fe and tmtaaH₂. 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 (0.086g, 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 Ce₂(tmtaa)₃ were identical to those with Ce(tmtaa)(tmtaaH) with the exception that one equivalent of *p*-benzoquinone or [Cp₂Fe][PF₆] was used per cerium. M.p.: > 310 °C. Anal. Calcd for C_{46.5}H₅₀N₈Ce: C, 64.86; H, 5.85; N, 13.01. Found: C, 64.81; H, 5.89; N, 12.69. ¹H NMR (C₆D₆, 20°C): δ 7.29 (8H, m, C₆H₄), 7.21 (8H, m, C₆H₄), 3.85 (4H, s, CH), 1.77 (24H, s, CH₃), the pentane resonances appeared at 1.23 (3H, m, CH₂) and 0.87 (3H, t, CH₃) ppm. ¹³C{¹H} NMR (C₆D₆, 20°C): δ 156.5 (s, CMe), 136.6 (s, *ipso*-Ar), 126.0 (s, C₆H₄), 125.2 (s, C₆H₄), 106.1 (s, CH), 24.3 (s, CH₃). The E.I. mass spectrum showed a molecular ion at m/e = 824 amu. The parent ion isotopic cluster was simulated: (calcd. %, observd. %): 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

Crystallographic Studies. 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 σ 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

Acknowledgement

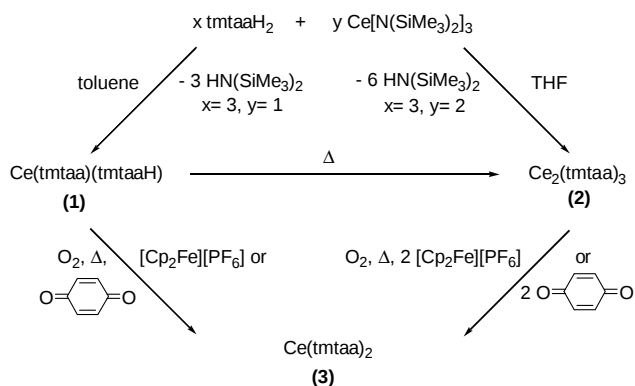
This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under

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

- V. L. Goedken, J. Molin-Case and Y. Whang, *J. Chem. Soc., Chem. Commun.*, 1973, 337.
- V. L. Goedken, M. C. Weiss, D. Place and J. Dabrowiak, *Inorg. Synth.*, 1980, **20**, 115.
- F. A. Cotton and J. Czuchajowska, *Polyhedron*, 1990, **9**, 2553.
- G. Parkin, *Prog. Inorg. Chem.*, 1998, **47**, 1.
- P. Mountford, *Chem. Soc. Rev.*, 1998, **27**, 105.
- 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.
- K. Tatsumi and R. Hoffmann, *Inorg. Chem.*, 1981, **20**, 3771.
- V. L. Goedken, J. J. Pluth, S.-M. Peng and B. E. Bursten, *J. Am. Chem. Soc.*, 1976, **98**, 8014.
- S. De Angelis, E. Solari, E. Gallo, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1992, **31**, 2520.
- A. Martin, R. Uhrhammer, T. G. Gardner, R. F. Jordan and R. D. Rogers, *Organometallics*, 1998, **17**, 382.
- H.-J. Kablitz and G. Wilke, *J. Organomet. Chem.*, 1973, **51**, 241.
- H.-J. Kim, D. Whang, K. Kim and Y. Do, *Inorg. Chem.*, 1993, **32**, 360.
- H. Brand and J. Arnold, *J. Am. Chem. Soc.*, 1992, **114**, 2266.
- D. G. Black, D. C. Swenson, R. F. Jordan and R. D. Rogers, *Organometallics*, 1995, **14**, 3539.
- D. M. Rogers, S. R. Wilson and G. S. Girolami, *Organometallics*, 1991, **10**, 2419.
- 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.
- J. W. Buchler, A. De Cian, S. Elschner, J. Fischer, P. Hammerschmitt and R. Weiss, *Chem. Ber.*, 1992, **125**, 107.
- J. P. Collman, J. L. Kendall, J. L. Chen, T. A. Eberspacher and C. R. Moylan, *Inorg. Chem.*, 1997, **36**, 5603.
- J. Silver, J. P. Lukes, P. K. Hey and C. M. O'Connor, *Polyhedron*, 1989, **8**, 1631.
- J. Silver, J. P. Lukes, S. D. Howe and B. Howlin, *J. Mater. Chem.*, 1991, **1**, 29.
- A. Greco, S. Cesca and G. Bertolini, *J. Am. Chem. Soc.*, 1976, **119**, 321.
- J. W. Buchler, A. De Cian, J. Fischer, M. Khin-Botulinski, H. Paulus and R. Weiss, *J. Am. Chem. Soc.*, 1986, **108**, 3652.
- 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.
- H. Isago and M. Shimoda, *Chem. Lett.*, 1992, 147.
- M. Safarpour Haghighi, C. L. Teske and H. Homborg, *Z. Anorg. Allg. Chem.*, 1992, **608**, 73.
- M. Dolg, P. Fulde, H. Stoll, H. Preuss, A. Chang and R. M. Pitzer, *Chem. Phys.*, 1995, **195**, 71.
- C. H. Booth, M. D. Walter, M. Daniel, W. W. Lukens and R. A. Andersen, *Phys. Rev. Lett.*, 2005, **95**, 267202.
- J. Magull and A. Simon, *Z. Anorg. Allg. Chem.*, 1992, **615**, 77.
- Z. Wang, K. Sakata and M. Hashimoto, *Polyhedron*, 1998, **17**, 4451.
- Z. Wang, N. Hu, K. Sakata and M. Hashimoto, *J. Chem. Soc., Dalton Trans.*, 1999, **1999**, 1695.
- R. R. Fraser, T. S. Mansour and S. Savard, *J. Org. Chem.*, 1985, **50**, 3232.
- A ball-stick representation of Gd₂(tmtaa)₃ was found on the website of the Max-Planck-Institute in Stuttgart, <http://www.fkf.mpg.de/simon/publications/jb91/magull.html>.
- J. H. van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Clarendon Press, Oxford, 1932.
- E. A. Boudreaux and L. N. Mulay, *Theory and Applications of Molecular Paramagnetism*, Wiley-Interscience, New York, 1976.

-
35. μ_{eff} values expressed in Bohr magnetons (μ_B) are related to those values expressed as χT by the expression $\mu_{\text{eff}}=2.828 (\chi T)^{0.5}$ in units of μ_B .
445
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 Organof-Element Chemistry*, eds. T. J. Marks and I. L. Fragala, D. Reidel, Dordrecht, The Netherlands, Editon edn., 1985, p. 277.
450
39. H. Reddmann, H. Schultze, H.-D. Amberger, C. Apostolidis and B. Kanellakopulos, *Spectrochim. Acta*, 1990, **46A**, 1223.
40. H.-D. Amberger, H. Reddmann, H. Schultze, S. Jank, B. Kanellakopulos and C. Apostolidis, *Spectrochim. Acta*, 2003, **59A**, 2527.
455
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.
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*, (2003) Bruker Analytical X-ray Systems, Inc., Madison, WI.
45. Saint, *SAINT SAX Area-Dectector Integration Program*, (2003) Siemens Industrial Automation, Inc, Madison, WI.
465
46. G. M. Sheldrick, *XPREP*, (2001) Siemens Industrial Automation, Inc, Madison, WI.
47. G. M. Sheldrick, *SADABS*, (2003) Bruker Analytical X-ray Systems, Inc., Madison, WI.
470
48. G. M. Sheldrick, *SHELXS-97*, (1997), University of Göttingen, Germany.
49. G. M. Sheldrick, *SHELXL-97*, (1997), University of Göttingen, Germany.
- 475 50. E. L. Mutterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1974, **96**, 1748.



Scheme 1 Reactions of tmtaaH₂ with Ce[N(SiMe₃)₂]₃. The equations are not balanced, but the coefficients are the quantities used in the synthesis.

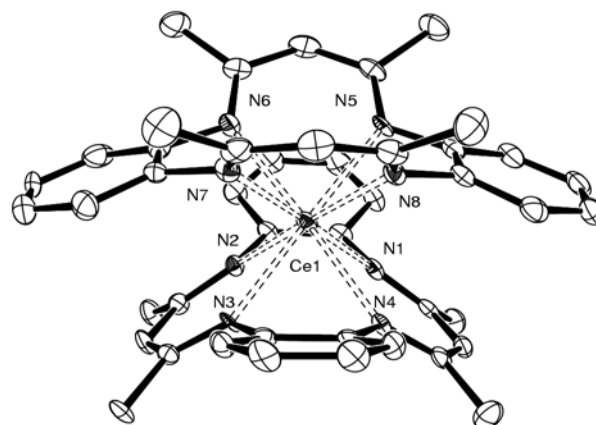


Fig. 3 ORTEP diagram of Ce(tmtaa)₂ (50 % probability ellipsoids). The disordered n-pentane molecule has been omitted for clarity.

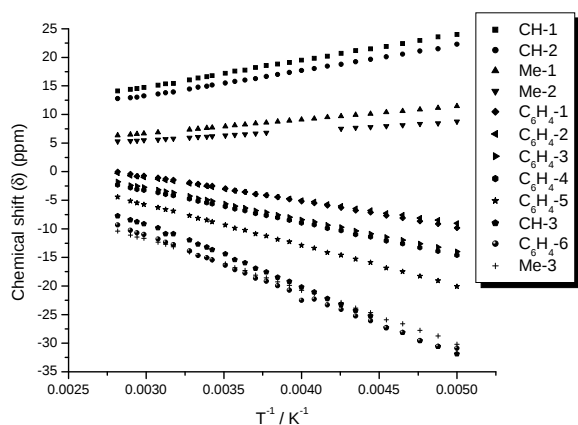


Fig. 1 Chemical shift (δ) vs T^{-1} plot for Ce₂(tmtaa)₃.

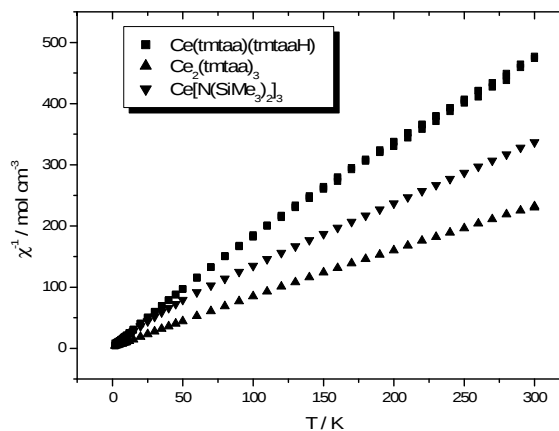


Fig. 4 Solid state magnetic susceptibility, χ^{-1} vs. T plot for Ce[N(SiMe₃)₂]₃, Ce(tmtaa)(tmtaaH) and Ce₂(tmtaa)₃.

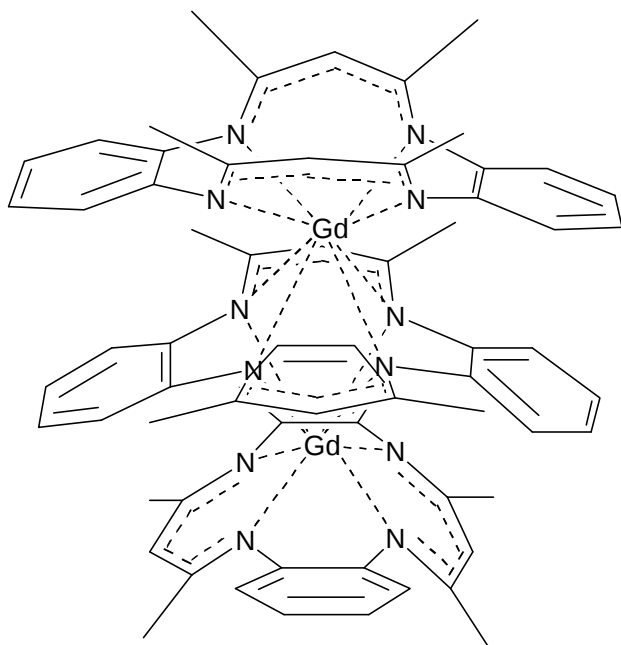


Fig. 2 Schematic representation of the Gd₂(tmtaa)₃ molecular structure.

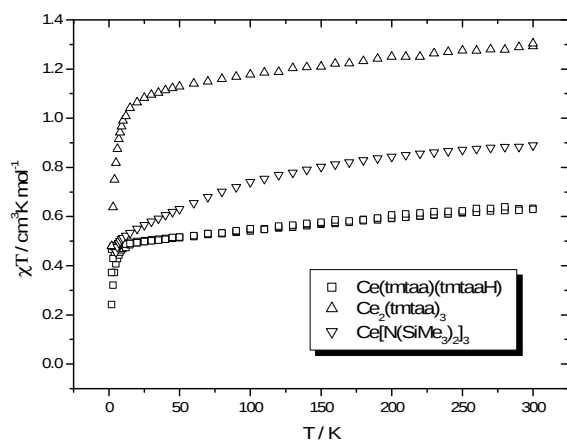


Fig.. 5 Solid state magnetic susceptibility, χT vs. T plot for $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$, $\text{Ce}(\text{tmtaa})(\text{tmtaaH})$ and $\text{Ce}_2(\text{tmtaa})_3$.

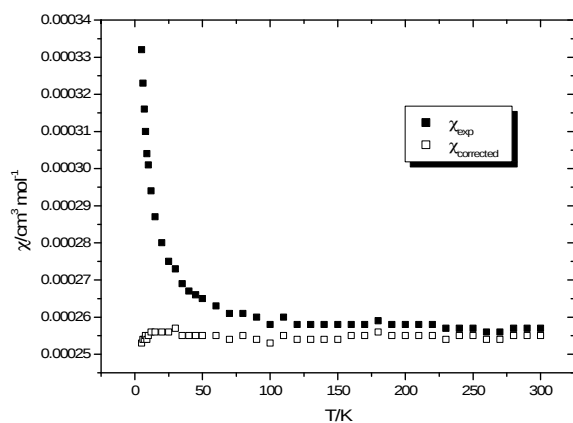


Fig. 6 Solid state magnetic susceptibility (χ) vs. T plot for $\text{Ce}(\text{tmtaa})_2$ at 40kG. The experimental values χ_{exp} include a small magnetic impurity ($\sim 0.1\%$ of a $J = 5/2$ impurity), which is removed in $\chi_{\text{corrected}}$. The data clearly show TIP behaviour with $\chi_0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

Table 1 Some Important Bond Distances (Å) and Angles (°) of Ce(tmtaa)₂ (**3**)

Bond Distances			
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)
Bond Angles			
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)
Shape Parameters (deg) ^a			
δ ₁	0.9	δ ₄	89.2
δ ₂	1.0	δ ₃	92.4
φ	0.1		

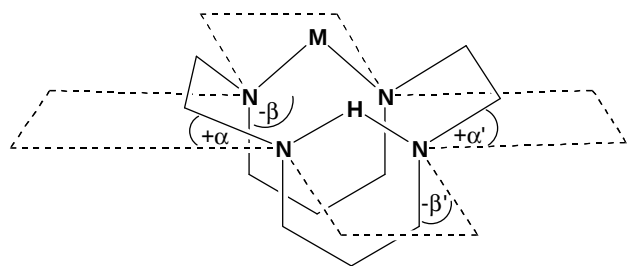
^a As defined in ref. 50

Table 2 Dihedral Angles in Selected TMTAA Structures

Compound	[Ce(tmtaa) ₂] (3) ^(a)	[(thf)Li(tmtaa)Ce(tmtaa)] ^(b)	[Zr(tmtaa) ₂] ^(c)	tmtaaH ₂ ^(d)
α (deg)	12	13	15	20
	12	16 ^c	16	21
β (deg)	34	37	38	37
	36	30 ^c	39	37

α and β are defined in the schematic drawing. ^(a) this work. ^(b) ref. 28. ^(c) ref. 9. ^(d) ref. 8

Figure for Table 2:



515

520