Synthesis and Magnetic Properties of Cerium Macrocyclic Complexes with tmtaaH$_2$, Tetramethyldibenzotetraaza[14]-annulene

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5 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 10 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-6,8,15,17-15 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 20 cyclooctatetraene, cot, and [16]-annulenes, the porphyrins, porphH$_2$, and phthalacyanines, pcH$_2$. Although all of these ligands form stable dianions, their electronic structure and therefore the electronic properties of their complexes are different. The tmtaa^{2-} is a 24 π-electron system (4nπ, n= 6) 25 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$_\alpha$(Me)C$_\beta$(H)C$_\alpha$(Me)N.[6, 7] The tmaa^{2-} is 30 therefore not planar but is saddle shaped with idealized C$_{2v}$ symmetry.[8] The cot^{2-} (4nπ+2, n=2) and porph^{2-} (4nπ+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 35 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$_2$ZrX$_2$.[9-14] In addition, the diamagnetic complexes Zr(cot)$_2$, 40 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 45 deductions about their electronic structure implied by their

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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 50 [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 55 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 60 properties of Ce(tmtaa)$_2$ became a desireable 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 65 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 70 transfer reactions of Ce[N(SiMe$_3$)$_2$]$_3$, the pK$_a$ of (Me$_3$Si)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 reproducable when close attention to detail is observed, and shown schematically in 75 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**.

80

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 85 with the correct isotope pattern, although is 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

not when Ln = Ce. Crystals of Ce(tmtaa)(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.

Ce(tmtaa)(tmtaaH) (**1**) decomposes slowly to Ce(tmtaa)$_2$ (**3**) and tmtaaH$_2$ (ratio 1:1) in C$_6$D$_6$ at 65 °C over 14 days. Close inspection of the decomposition process reveales that after one day small amounts of Ce$_2$(tmtaa)$_3$ (**2**) and tmtaaH$_2$ are detected in the ^{1}H NMR spectrum. Over the time priod 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 ^{1}H 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** disproportinates 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. 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 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 ^{1}H NMR spectrum at 20 °C agrees with a molecule of C$_{2v}$ symmetry, since twelve ^{1}H NMR signals for chemically inequivalent tmtaa ligands are observed in C$_6$D$_6$ 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 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$_6$H$_4$-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 ^{1}H NMR evidence.

In the presence of O$_2$, *p*-benzoquinone or [Cp$_2$Fe][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$_6$D$_6$ 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$_2$Fe][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 ^{1}H 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. Ce$_2$(tmtaa)$_3$ is not formed under these conditions as determined by ^{1}H NMR spectroscopy. The ^{1}H 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 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 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 [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 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 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 1.17(10)°, 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 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 ^{2}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, $\mu_{eff}(300K) = 2.25\mu_B$,[35] is in agreement with data from other mononuclear Ce(III) compounds (1.8-2.5μ_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 $\mu_{eff}(300K) = 3.23\mu_B$ (2.28μ_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)$_2$, but the molecular reason for the TIP behavior is unknow at this time.

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 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(SiMe$_3$)$_2$]$_3$ 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(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. M.p. > 330 °C. Anal. Calcd for C$_{44}$H$_{45}$N$_8$Ce: 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. %, observd. %): 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 the air-sensitivity the ^{1}H NMR spectra were not reproducible and uninformative.

[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)$_2$. M.p. > 330 °C. Anal. Calcd for C$_{74}$H$_{82}$N$_{12}$O$_2$Ce$_2$: C, 61.22; H, 5.69; N, 11.57. Found: C, 60.75; H, 5.81; N, 11.31. ^{1}H NMR (C$_6$D$_6$, 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, 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, CH), −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 way 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 handeled 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 over night.

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 handeled 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 (0.086g, 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 $Ce_2(tmtaa)_3$ were identical to those with Ce(tmtaa)(tmtaaH) with the exception that one equivalent of *p*-benzoquinone or $[Cp_2Fe][PF_6]$ was used per cerium. M.p.: > 310 °C. Anal. Calcd 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. ^1H 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, C*H_3*), the pentane resonances appeared at 1.23 (3H, m, C*H_2*) and 0.87 (3H, t, C*H_3*) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 20°C): δ 156.5 (s, *C*Me), 136.6 (s, *ipso*-Ar), 126.0 (s, C_6H_4), 125.2 (s, C_6H_4), 106.1 (s, *C*H), 24.3 (s, *C*H_3). 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]

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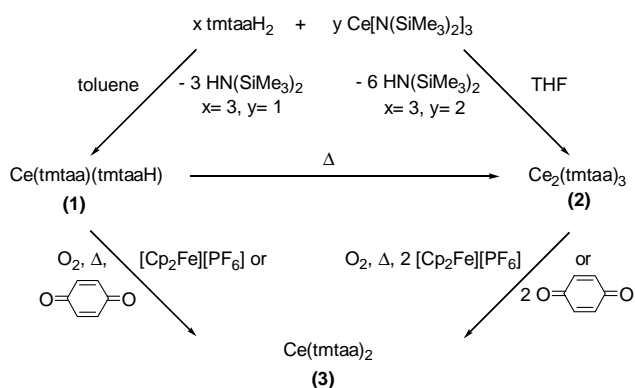
Scheme 1 Reactions of tmtaaH$_2$ with Ce[N(SiMe$_3$)$_2$]$_3$. The equations are not balanced, but the coefficients are the quantities used in the synthesis.
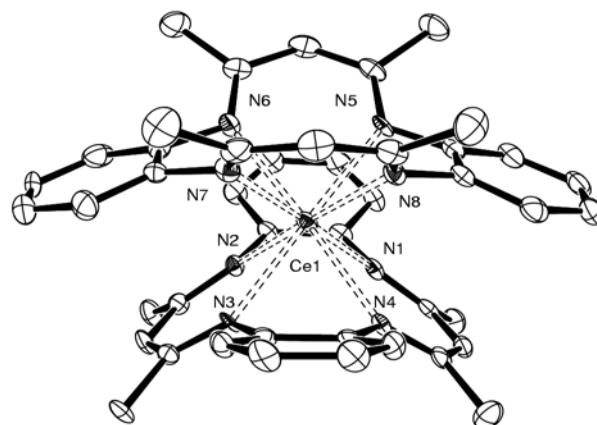

Fig. 3 ORTEP diagram of Ce(tmtaa)$_2$ (50 % probability ellipsoids). The disordered n-pentane molecule has been omitted for clarity.
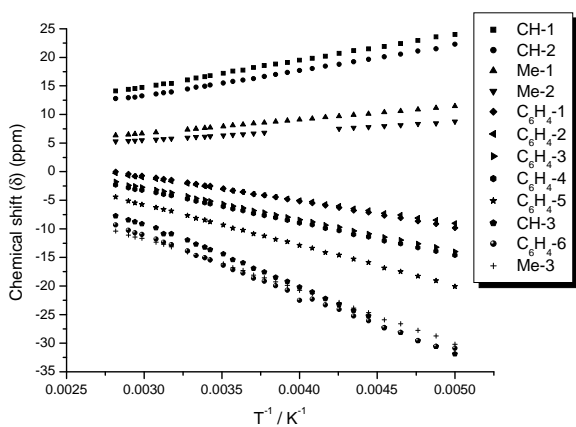

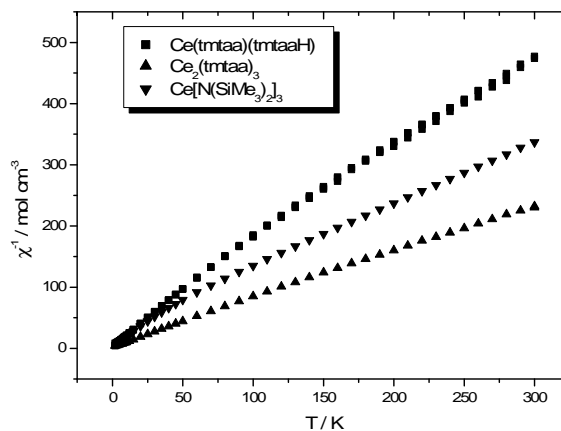**Fig. 1** Chemical shift (δ) vs T^{-1} plot for Ce$_2$(tmtaa)$_3$.

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)$_3$.
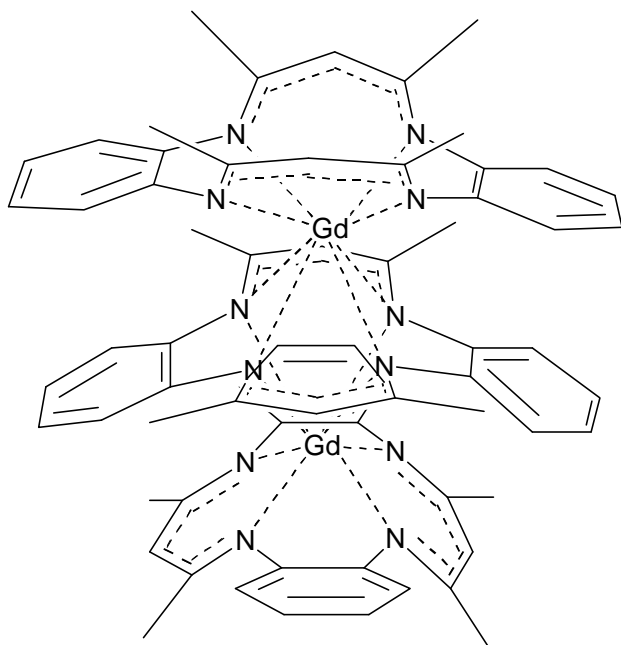
480

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Fig. 2 Schematic representation of the Gd$_2$(tmtaa)$_3$ molecular structure.
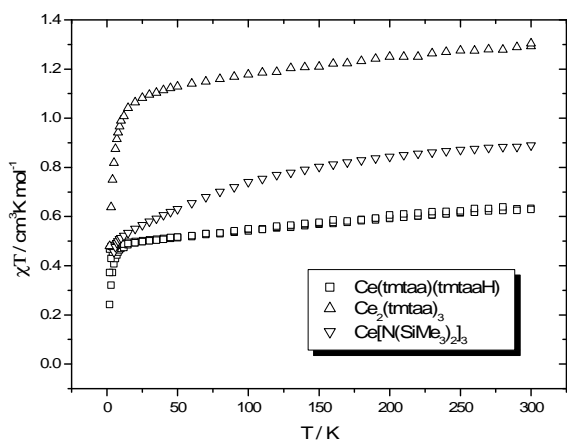
Fig.. 5 Solid state magnetic susceptibility, χT vs. T plot for Ce[N(SiMe$_3$)$_2$]$_3$, Ce(tmtaa)(tmtaaH) and Ce$_2$(tmtaa)$_3$.
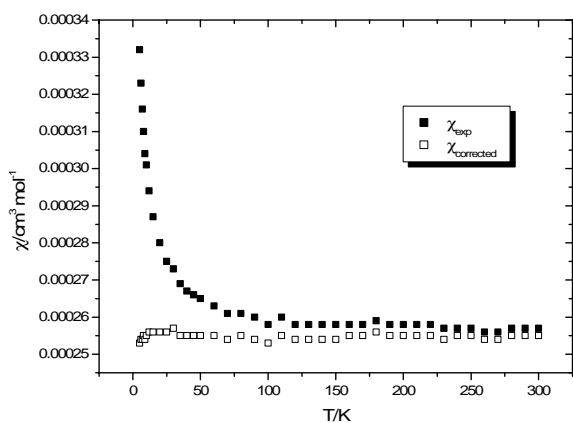

Fig. 6 Solid state magnetic susceptibility (χ) vs. T plot for Ce(tmtaa)$_2$ at 40kG. The experimental values χ_{exp} include a small magnetic impurity (~ 0.1 % of a $J = 5/2$ impurity), which is removed in $\chi_{corrected}$. The data clearly show TIP behaviour with $\chi_0 = (2.55\pm0.02)\text{x}10^{-4}$ cm^3 mol^{-1}.

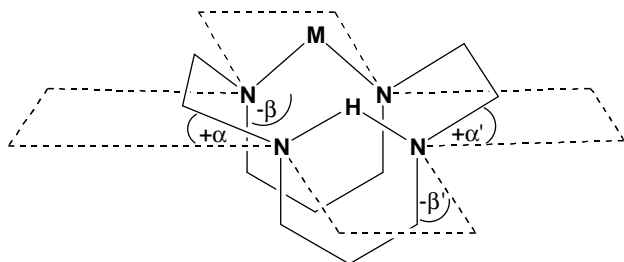**Table 1** Some Important Bond Distances (Å) and Angles (°) of Ce(tmtaa)$_2$ (**3**)

	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:

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