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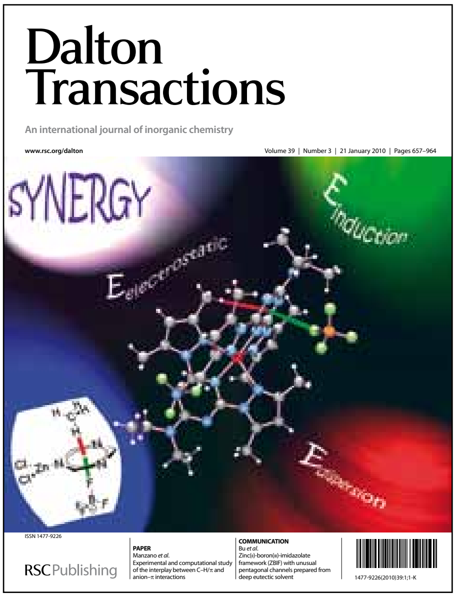

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COMMUNICATION

Structural and Magnetic Conformation of a Cerocene $[Ce(COT'')_2]^-$ Exhibiting a Uniconfigurational f^1 Ground State and Slow-Magnetic Relaxation

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Magnet-like behaviour, in the form of slow relaxation of the magnetization, was observed for a monometallic cerium (III) sandwich complex. The use of trimethylsilyl substituted COT ligands (COT") lead to the formation of a staggered COT" arrangement in the cerocene-type sandwich complex with a well-defined oxidation state +3 for the Ce ion.

Since its discovery in the mid 70's, cerocene has attracted much attention from experimentalists and theoreticians due to its unusual metal oxidation state assignment.[1] Although the analogous COT sandwich molecules in the actinide series provide a clear oxidation state assignment, in cerocene the oxidation state is understood to be an admixture of Ce^{III} ($4f^1$) and Ce^{IV} ($4f^0$) configurations.[2] This leads to a non-magnetic multiconfigurational ground state.[3] Several studies were conducted to understand this unusual electronic arrangement.[4] In addition, in order to further understand the origin of this admixing of states, substituted cerocenes were successfully synthesized.[5] Through this approach it was possible to isolate well defined oxidation states in these sandwich complexes. Although these molecules have now revealed some of the mystery surrounding their complex electronic structure, there is still much to discover particularly in regards to their magneto-chemistry.

For example, while Ce^{III} ion has only one unpaired electron, the spin-orbit coupling effect of this heavy element can lead to non-negligible magneto-anisotropy. When significant anisotropy is coupled with even a small spin state, a barrier to magnetization relaxation can be observed. Molecular complexes which exhibit such behaviour are termed Single-Molecule Magnets (SMMs). SMMs represent the smallest nanoscale magnetic particles with superparamagnetic behaviour thus they are predicted to be ideal candidates for applications in memory storage devices as well as quantum computation.[6] In recent years, lanthanide SMMs have clearly surpassed transition metal SMMs in terms of blocking temperature thanks to their inherent anisotropy. Among these SMMs, late lanthanides such as Tb^{III}, Dy^{III} and Er^{III} ions have been the most fruitful in terms of number of SMMs due to the large amount of unpaired electrons as well as high anisotropy.[7] There are very few examples of SMMs isolated with early lanthanide ions among which only one example of a Ce^{III} based SMM has been reported.[8] We have turned our attention to trimethylsilyl substituted COT (COT": bis(trimethylsilyl)cyclooctatetraenyl dianion) to isolate organolanthanide sandwich molecules and investigate their SMM behaviour. As such we have recently reported a Dy^{III} based COT" SMMs and its unique intrinsic magnetic properties.[9] Herein we present analogous $Li(DME)_3[Ce^{III}(COT'')_2]$ sandwich compound (**1**) which also exhibits SMM behaviour and represents the first example of a monometallic Ce^{III} based SMM.

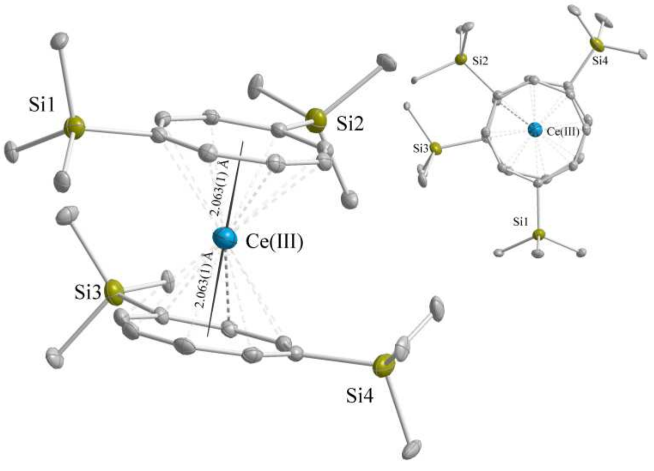

Fig. 1. Molecular X-ray structure of **1**, hydrogen atoms and $[Li(DME)_3]$ counter ion are omitted for clarity. Top view (right) illustrates staggered arrangement of C atoms in upper and lower COT" rings. Colour code: blue (Ce^{III}), green (Si), grey (C). Thermal ellipsoids are shown at 30% probability.

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† Electronic Supplementary Information (ESI) available: Details of crystallographic information of $LiDME_3[Ce(COT'')_2]$, experimental details, IR, NMR, Electrochemistry, SQUID magnetic measurements and supplementary figures. CCDC 944915. See DOI: 10.1039/b000000x/

Complex **1** was synthesised in an analogous manner to our recently reported dysprosium complex, Li(DME)$_3$ [Dy^{III}(COT”)$_2$], where CeCl$_3$ reacts with 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion (COT”) in a 3:2 molar ratio in THF to give **1** in 67% yield (Scheme S1). Due to the paramagnetic nature of the Ce^{III} ion, ^{1}H and ^{13}C NMR spectra show predominantly broadened singlet peaks (Fig. S1, S2). Therefore we turned towards solid state analysis where single crystals of **1**, suitable for single crystal X-ray diffraction, were grown from a concentrated mixture of 1:1 DME:hexanes (Fig. 1). Complex **1** crystallizes in the triclinic *P-1(2)* space group where the Ce^{III} ion is sandwiched between two COT” ligands in a η^8-fashion to form a distorted sandwich complex with a Li(DME)$_3$ counter cation. The Ce^{III}-C$_{\text{COT”}}$ bond distances range from 2.755(2)-2.781(2) Å reflecting an asymmetric η^8-COT” coordination. The near linear structure of **1** is reflected in the (COT”$_{\text{centroid}}$)-Ce^{III}-(COT”$_{\text{centroid}}$) angle which deviates from perfect linearity (180°) by 3.75°. The Ce^{III}-(COT”$_{\text{centroid}}$) distance of 2.063(1) Å for both COT” ligands suggests equivalent ligand donation by both ligands as seen in the Dy^{III} analogue.[9] In comparison, the original unsubstituted and recently published triphenylsilyl substituted cerocenes indicate smaller Ce^{III}-(COT$_{\text{centroid}}$) distance of 1.97 and 1.99 Å, respectively.[1, 5c] This shorter distance for the latter two molecules is consistent with the assigned predominant +IV oxidation state of the cerium ion. The lithium counter-ion adopts an octahedral coordination environment filled by three DME molecules (Fig. S3), the closest Li-C$_{\text{COT”}}$ distance is 5.651(5) Å confirming the Li ion is not bound to the ring. The closest intermolecular Ce^{III}-Ce^{III} distance is 11.58(5) Å, likely precluding any magnetic interaction between Ce^{III} ions considering the core orbital nature of 4*f* orbitals (Fig. S4-S6).

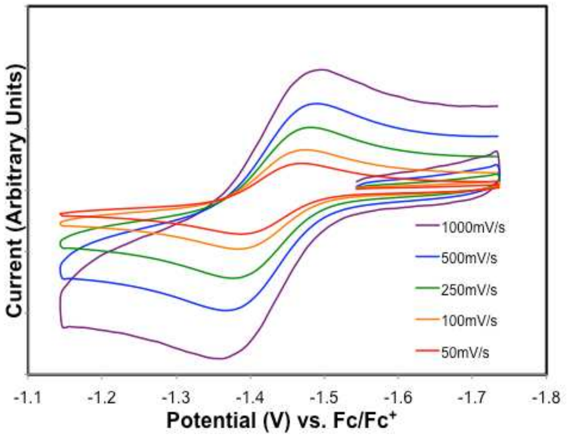

Fig. 2. Cyclic voltammograms for **1** displaying the scan rate dependence of the formally Ce$^{III/IV}$ reversible redox couple recorded in THF. Potentials were referenced to a Fc/Fc$^+$ internal standard with 0.1 M [^{n}Pr$_4$N][BAr$^F{}_4$] supporting electrolyte and ~1 mM analyte concentration.

Electrochemical measurements performed on **1** revealed a one-electron oxidation at –1.43 V *versus* Fc/Fc$^+$ with a peak-to-peak separation of 80 mV (Fig. 2); the scan rate dependent behaviour of the wave indicated a reversible electrochemical process as judged by a Randels–Sevcik analysis (Fig. S7). This result is consistent with the reported electrochemical behaviour of K[Ce(C$_8$H$_8$)$_2$], which exhibited a single electron oxidation at –1.4 V *versus* Fc/Fc$^+$.[10] A wider potential scan between +0.6 and –3.0 V revealed an irreversible oxidation at $E_{p,a}$ = +0.1 V and an irreversible reduction at $E_{p,c}$ = –2.4 V (Fig. S8). As with K[Ce(C$_8$H$_8$)$_2$], the result for **1** indicates a strongly reducing Ce^{III} complex.

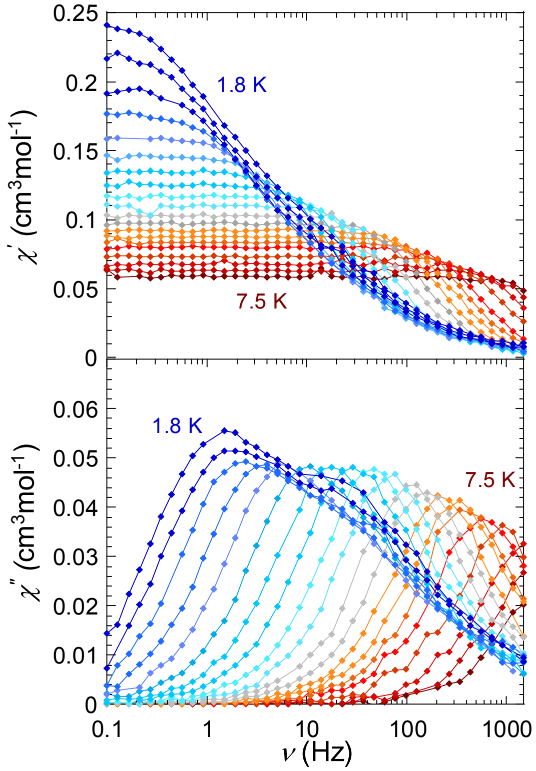

Fig. 3. Frequency dependence of the in-phase (χ’) (top) and out-of-phase (χ”) (bottom) magnetic susceptibility of **1** between 1.8-7.5 K under a 400 Oe dc field.

A detailed magnetic analysis was conducted to confirm the oxidation state of **1** and to investigate possible Single-Ion Magnet (SIM) behaviour. Hino *et al.* recently reported the first Ce^{III} coordination complex exhibiting SMM behaviour.[8] This linear Zn^{II}–Ce^{III}–Zn^{II} complex exhibits an effective energy barrier against magnetization reversal (U_{eff}) of 21.2(6) K under zero applied dc field. The SMM properties were surprising due to the (4f^1) spin source; the authors stipulated the large barrier was due to the predominant axial ligand field provided by four phenoxo oxygen bridging atoms. The ground state of Ce^{III} contains a single unpaired electron in the 4$f_{x(x^2-3y^2)}$ orbital.[8] Recently, Rinehart *et al.* predicted a strictly axial ligand field environment would be ideal to prevent quenching of orbital angular momentum for this configuration.[11] The use of planar COT” ligands in **1** provides an axial symmetry (C_8 axis) with strictly axial coordination environment around the spin carrier, therefore axial anisotropy with SMM behaviour is plausible.[9]

Magnetic susceptibility measurements were performed using a SQUID magnetometer on a freshly prepared ground polycrystalline sample of **1** sealed under N$_2$. Direct current (DC) magnetic susceptibility measurements were conducted in the temperature range of 1.8-300 K under a 0.1 T applied DC field. The room temperature χT value of 0.66 cm^3·K·mol^{-1} is in good agreement with the theoretical value of 0.80 $cm^3 \cdot K \cdot mol^{-1}$ for a Ce^{III} ($^2F_{5/2}$, $S = 1/2$; $L = 3$, $g = 0.857$) monomer (Fig. S9), thus confirming +III oxidation state. The χT product remains nearly linear with a slight decrease below 50 K reaching a minimum value of 0.60 $cm^3 \cdot K \cdot mol^{-1}$ at 1.8 K. The low temperature decrease could indicate either large magnetic anisotropy due to ligand field splitting and/or the depopulation of low lying excited states. Field dependent magnetization measurements were carried out to confirm magnetic anisotropy in **1**. The non-saturation as well as the non-superimposition of iso-temperature lines in the M versus H/T data also suggests magnetic anisotropy in **1** (Fig. S10).

The magnetic relaxation dynamics of **1** were probed using alternating current (AC) magnetic susceptibility measurements. Under zero applied dc field, no AC signal was observed. Under an optimal 400 Oe applied DC field and 3 Oe ac field, a strong temperature and frequency dependent out-of phase (χ") signal was observed. Frequency dependent χ" data revealed full frequency dependent peaks with peak maxima shifting towards lower frequency consistent with field-induced slow relaxation of the magnetisation (Fig. 3). Interestingly, at temperatures below 3.5 K the peaks gradually broaden and below 2.5 K a secondary higher frequency peak is apparent. Multiple peak maxima in χ" versus frequency data suggests multiple magnetic relaxation processes are occurring at the spin centre. Such intricate magnetic behaviour for single ion complexes has only previously been observed in Dy^{III} and U^{III} including our $[Dy^{III}(COT")_2]^-$ analog.[7b, 9,12] To confirm this low temperature phenomena is a result of two relaxation modes, we utilized the Cole-Cole (χ" *vs.* χ') plot and generalized Debye model, $\chi(\omega) = \chi S + (\chi T + \chi S)/(1 + i\omega\tau)^{1-\alpha}$, where $\alpha = 0$ corresponds to a single relaxation process (Fig. S11).[13, 14] Cole-Cole plots between 6-4 K show good agreement with the Debye model with alpha values between 0.02 and 0.06, consistent with one relaxation time. From 3.75 K to 2.5 K the Debye model for a single relaxation cannot be fit to the experimental data. Below 2.5 K two clear peaks are observed which can each be fit to the Debye model, with α values ranging from 1.2 to 3.7. The clear multiple peak maxima observed in the Cole-Cole plot at 1.8 K confirms at least two relaxation processes are occurring from the Ce^{III} ($4f^1$) ion. The poor separation of peaks is expected if a narrow distribution in relaxation time is occurring.

An effective energy barrier of 30 K with a pre-exponential factor (τ_0) of 1.2×10^{-6} s was extracted from the ac data above 3.5 K (Fig. S12). This obtained value is comparable with $[Dy^{III}(COT")_2]^-$ SIM ($U_{eff} = 25$ K, 0 Oe; $U_{eff} = 28$ K, 100 Oe), which is surprising due to the significant difference in ($4f^1$) versus ($4f^9$) electronic configurations.[9] In both complexes small U_{eff} values are likely the result of competing multiple relaxation processes.

Conclusions

In summary, we have successfully synthesized and investigated a Ce^{III} sandwich compound with substituted COT" ligands. Through single crystal X-ray diffraction, electrochemistry and SQUID magnetic measurements, the +III oxidation state was assigned to the Ce ion. Interestingly, dynamic magnetic relaxation studies revealed slow relaxation of the magnetization below 8 K. It is remarkable to observe superparamagnet behaviour for an early lanthanide ion with only one unpaired electron. These results incite the use of early lanthanide ions in the future preparation of molecular magnetic materials.

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