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In memory of Prof. R. A. Andersen – a great mentor and friend

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Abstract: Divalent lanthanide organometallics are well-known highly reducing compounds usually used for single electron transfer reactivity and small molecule activation. Thus, their very reactive nature prevented for many years the study of their physical properties, such as magnetic studies on a reliable basis. In this article, the access to rare organometallic sandwich compounds of Tm^{II} with the cyclooctatetraenyl (Cot) ligand impacts on the use of divalent organolanthanide compounds as an additional strategy for the design of performing Single Molecule Magnets (SMM). Herein, the first divalent thulium sandwich complex with f^{13} configuration behaving as a Single Molecule Magnet in absence of DC field is highlighted.

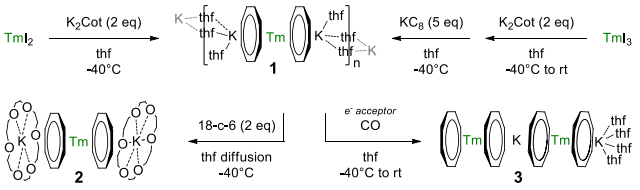
Introduction

In recent years, organolanthanide chemistry has been revitalized by the discovery of high blocking temperature lanthanide-based Single Molecule Magnets bearing typical organometallic ligands, such as the cyclopentadienyl (Cp)[1] and the cyclooctatetraenyl (Cot) ligand.[2] These ligands are indeed well adapted to access original and useful geometries that are more difficult to obtain with other coordination compounds.[1b] The use of a larger aromatic ligand, the cyclononatretraenyl (Cnt) ligand, recently led to the formation of perfectly linear neutral complexes of divalent lanthanides (Ln^{II})[3] and to heteroleptic complexes bearing both the Cot and Cnt ligands.[4] The synthetic description and structural analyses of such compounds remain very challenging in organometallic chemistry but the principal purpose of their reports has moved in the last years from reactivity, redox[5] or polymerization studies to attractive magnetic properties. As such, organolanthanide complexes with spectacular magnetic properties were until very recently[6] reserved for trivalent lanthanides but not divalent ones.

Yet, divalent lanthanide complexes have great advantages because they are powerful single-electron sources,[5] and have been used in reductive organic chemistry[7] and for small molecule activation.[8] The study of their electronic structures is also an important fundamental topic since the configuration of Ln^{II} ions is either $4f^n$,[9] or $4f^{n-1}5d^1$ if the empty 5d orbitals are close enough to become populated.[6, 10] Additionally, if ligand orbitals are involved in this picture, energy states with intermediate valence emerge.[11] More importantly, the modulation of the redox state of lanthanide compounds brings very interesting additional features such as higher magnetic moments[12] and larger magnetic anisotropy than those of the trivalent congeners.[13] However, there are also important drawbacks in the use of such compounds for SMMs because of their high reducing power, which reinforce the need for new accessible syntheses and stability studies.

Divalent lanthanide organometallic complexes containing the Cot ligand are underexplored for their magnetic properties because of their intricate syntheses.[14] For example, reactions of divalent lanthanide halide sources with aromatic molecules such as cyclooctatetraene led to trivalent thulium Cot compounds,[15] some of which behave as field-induced SMMs.[2c] Despite these difficulties, well-defined divalent lanthanide organometallics with inverted and multiple decker sandwiches of Cot ligands have been reported,[16] including divalent bis-Cot complexes.[16c, 17] In comparison with bulky substituted Cp ligands,[1b-d, 1f, 6] the access to highly symmetrical Cot- and Cnt-based compounds from a symmetry-adapted argument[3, 18] should simplify the bonding description.

We have been studying complexes containing divalent thulium[9, 19] for several years for the principal reason that Tm^{II} is very reactive and useful in single-electron transfer reaction but also because it is isoelectronic to Yb^{III},[9] with a $4f^{13}$ configuration. The resulting one-hole electronic structure may simplify the spectroscopic features as a first approximation. Recently, some of us reported the first divalent lanthanide coordination complex exhibiting a slow magnetic relaxation under a weak DC field.[19c] The need for this small DC field is typical in f^{13} compounds.[20] In this article, we extend this concept to the use of large typical organometallic ligands with rare occurrences in the divalent state. We report a highly reducing divalent thulium sandwich complex behaving as a Single Molecule Magnet in zero DC field.



Scheme 1. Synthetic scheme for the preparation of **1**, **2** and **3**.

Results and Discussion

The bis-cyclooctatetraenyl sandwich complex $(Cot)_2TmK_2(thf)_4$, **1**, was prepared in good yield by salt metathesis from thulium bis-iodide and freshly prepared K_2Cot at low temperature (-40 °C) in thf (Scheme 1). This procedure is similar to that used for the synthesis of $Tm(OTf)_2$.[9] After filtration of the KI formed during the reaction, the concentrated deep green solution is kept cold to yield large X-ray suitable dark green blocks of **1**. Alternatively, **1** can be synthesized in better yield by reduction with KC_8 of the trivalent $(Cot)_2TmK$ complex made in situ from TmI_3 and freshly prepared K_2Cot. **1** is well soluble in thf and addition of 18-crown-6 (18-c-6) to tentatively trap the potassium cations led to dark green insoluble material. Thus, a solution of 18-c-6 in cold thf was slowly diffused into a cold solution of **1** and X-ray suitable green crystals of $(Cot)_2Tm\{K(18\text{-c-}6)\}_2$, **2**, appeared at the interface in good yield.

One broad signal at -5.23 ppm appears in the room temperature (293 K) ^{1}H NMR spectrum of **1** (Figure S1) in thf-d_8. A relative small shift of the chemical shift compared to the diamagnetic analogues is typical of divalent Tm complexes in opposition to highly paramagnetic trivalent Tm complexes.[21] Variable temperature ^{1}H NMR studies (Figure S2-S3) only reveal a broadening of the signal upon decreasing the temperature and show a linear plot for δ *vs* 1/*T*, which is indicative of a Curie behavior of the magnetic susceptibility in the 223 – 363 K temperature regime. Complex **2** is not soluble in thf-d_8 or in any of the hydrocarbon solvents commonly used for this sensitive chemistry and no NMR spectrum could be obtained.

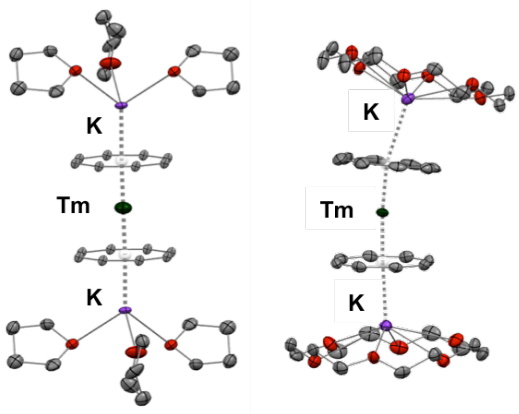


Figure 1. ORTEP of **1** (left) and **2** (right). Hydrogen atoms and Cot carbon disorder have been removed for clarity.

Complex **1** crystalizes in *P*-1 while **2** in the monoclinic $P2_1/n$ space group (Figure 1). Both **1** and **2** are sandwich complexes made of Cot ligands located above and below the thulium ion. The C-C distances in Cot are ranging from 1.384(17) to 1.445(17) Å in **1** and from 1.387(7) to 1.420(7) Å in **2**, indicative of a delocalized aromatic π system. The Tm-C distance is 2.74(2) Å in average, ranging from 2.703(14) to 2.764(14) Å, and 2.73(3) Å in average, ranging from 2.679(5) to 2.772(4) Å, in **1** and **2**, respectively, while the average Tm-Ctr (Ctr is for centroid) distances are identical in both **1** and **2** (2.02(2) Å) (Table S3). These distances are significantly longer than the Tm^{III}-Ctr distances reported in the literature ranging from 1.7017(3) Å to 1.861 Å,[2c, 15, 22] to one exception corresponding to a triple decker arrangement reported by Edelmann, in which the Cot ligand is sandwiched between two trivalent Tm (Tm^{III}-Ctr distance of 2.043 Å).[22f] The relatively long Tm-Ctr distances are therefore indicative of the divalent nature of the thulium center in **1** and **2**.

Comparatively, the divalent ytterbium half sandwich $(Cot)Yb(C_5H_4N)_3$ has Yb-Ctr distances between 1.91 and 1.92 Å,[14] while the isomorphous complex of Eu^{II} has a distance of 2.153 Å,[16c] in agreement with a smaller ionic radius for Tm compared to Eu.[23] In **1**, each potassium is coordinated with three molecules of thf, two of them bridging between two potassium ions, resulting in a zig-zag polymeric chain (Figure S13), while the 18-c-6 coordination of the potassium prevents the formation of a polymer in **2**. The Ctr(Cot)-K average distance is 2.37(2) Å in **1** and 2.69(10) Å **2**. The significant difference is due to the coordination of the six oxygen donor atoms reducing the interaction of the potassium ion with the Cot ligand. Finally, the Cot-Tm-Cot angle of 173.9° is more bent in **2** compared to that nearly linear of 179.8° in **1.** The K-Tm-K angle bends from 180.0° to 164.5° in **1** and **2**, respectively (Figure 1, Figure S14). This bending shows that the primarily electrostatic nature of the bonding in these compounds influences much the structural features.[24]

Both complexes **1** and **2** are extremely sensitive to air, moisture and temperature, especially **2**. It is plausible that the polymeric nature of **1** makes it more stable, comparatively. Reactions with typical reactants used in divalent lanthanide chemistry, such as pyridine,[25] bipyridine, or carbon monoxide, and with transition metal precursors used in the formation of heterobimetallic complexes[11b, 26] were performed but all these led to one same product, the tetra-decker $[(Cot)_2Tm]_2(\mu\text{-}K)(K(thf)_4)$, **3**, that was crystalized very easily from all reaction mixtures. The formation of this trivalent compound, which is isomorphous of the known $[(Cot)_2Ln]_2(\mu\text{-}K)(K(thf)_4)$ Ln = Er, Gd,[27] is indicative of a fast electron transfer and not likely a coordination induced electron transfer. An ORTEP of **3** and crystal structure description can be found in SI (Figure S15).

The useful qualitative static model reported by Rinehart and Long predicts that f^{13} elements have a prolate shape[28] of the electron density and therefore require equatorial coordination to stabilize Ising ground states. The ground state multiplet $^2F_{7/2}$ splits in four terms. A close analysis of the above electrostatic model[28] shows that a sandwich geometry with large π aromatic ligands best leads to m_J = ±5/2 rather than the m_J = ±7/2 obtained with a strong equatorial ligand field.

Ab-initio theoretical calculations were performed at the CASSCF and CASPT2 level (see computational methods). All methods confirmed the pure m_J = ±5/2 ground state for both **1** and **2** (See Tables S11-S20), followed by the m_J = ±3/2, the m_J = ±7/2 and the m_J = ±1/2 but the energy gaps between the excited states

differ slightly depending upon the method used. The presence of the potassium and of the thf and 18-crown-6 molecules in the computation does not influence the ground-state composition and only marginally the energy splitting of the crystal field states. The variable temperature magnetic data were recorded both in DC and in AC. All our efforts to reproduce the magnetic data on various samples and batches of **1** have demonstrated that the THF molecules are not maintained depending on how the samples were prepared. Thus, the use of a macrocyclic 18-c-6 ligand to replace them is really advantageous and only the magnetic data of **2** are reported. Figure 2 shows the DC magnetic data recorded for **2** over the 2-250 K temperature range (in order to avoid any decomposition). With **2**, we faced orientation problems despite our efforts to immobilize the powder without degrading the compound. Magnetization curves on **2** are not easily reproducible and thus not represented. The magnetic susceptibility curve of **2** was compared to the one obtained from the computations at various levels of theory and confirmed that the f^{13} configuration imposes the use of methods that include dynamic correlation (CASPT2) to get an almost perfect agreement with the experiment. The excited states are found at 400 cm^{-1}, 448 cm^{-1} and 757 cm^{-1} above the ground state Kramers doublet of the $^2F_{7/2}$ multiplet, which explains the monotone increase of the magnetic curve over the 2-250 K temperature range (Tables S16-S20, S23).

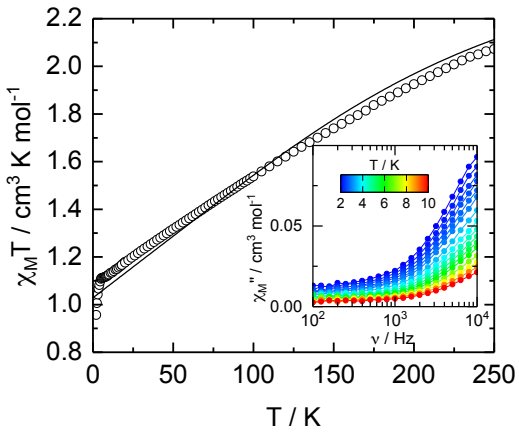


Figure 2. Temperature variations of $\chi_M T$ for compound **2** with the equivalent calculated curve in full line from quantum chemical calculations. In inset the frequency dependence of the out-of-phase component of ac susceptibility at various temperatures and in zero external dc field.

The AC analysis of **2** was performed only on freshly filtered dark green crystals without a further drying step under reduced pressure. **2** shows zero-field SMM behavior at 10 kHz (Figures 2 and S7). The low frequency limit (100 Hz) of the AC susceptibility provides $\chi_M T$ equal to 1.06 cm^3 K mol^{-1}, which is in fairly good agreement with DC measurements. There is no maximum in the χ_M'' vs. frequency curve at 0 Oe in the 10^2 to 10^4 frequency window, which prevents fitting the data with the extended Debye model, but the slow relaxation persists (visible) up to 10 K (Figure 2). The application of a moderate field completely shifts the maximum to lower frequency, which falls below 0.1 Hz for higher fields than 500 Oe (Figure S8). It is noticeable that the isoelectronic anionic $(Cot)_2Yb^-$ complex is not reported to show any signal under zero field.

In zero-field, Ln-SMM relaxation is often dominated by quantum tunneling of the magnetization (QTM),[29] and also hyperfine interactions in this particular case because of a single I=1/2 isotope for thulium. Dipolar contributions can be easily tested by dilution experiments of the Tm^{II} compound **2** into an isomorphous diamagnetic matrix. In this case, the nearest right neighbor in the periodic table, Yb, which is diamagnetic in its divalent state and presents a comparable ionic radius, is an ideal candidate. The synthesis of a diluted sample of **1** can thus be achieved by the salt metathesis reaction of K_2Cot with a mixture of YbI_2 (90%) and TmI_2 (10%). This reaction led to the formation of compound **4** (See NMR, Figures S4-S6) whose X-ray diffraction structure as well as bonding distances are very similar to those in **1**. Similarly, substitution of the thf ligands in **4** by 18-c-6 ligands led to **5**, the diluted analogue of **2** (Table S3 and Figures S16-S17). The proportion of Yb and Tm could not be determined by XRD since the ratio is too small, but the elemental analysis results indicate a ratio of Yb:Tm being 98:2. Dynamic AC susceptibility measurements on the diluted sample of **2** (**5**) show out-of-phase component emerging at relative low frequency in zero external DC field and at 2 K (Figure 3). This component disappears into the noise background at temperatures higher than 10 K. Between 2 and 10 K, the AC data can be analyzed in the framework of the extended Debye model (see SI, Table S1).

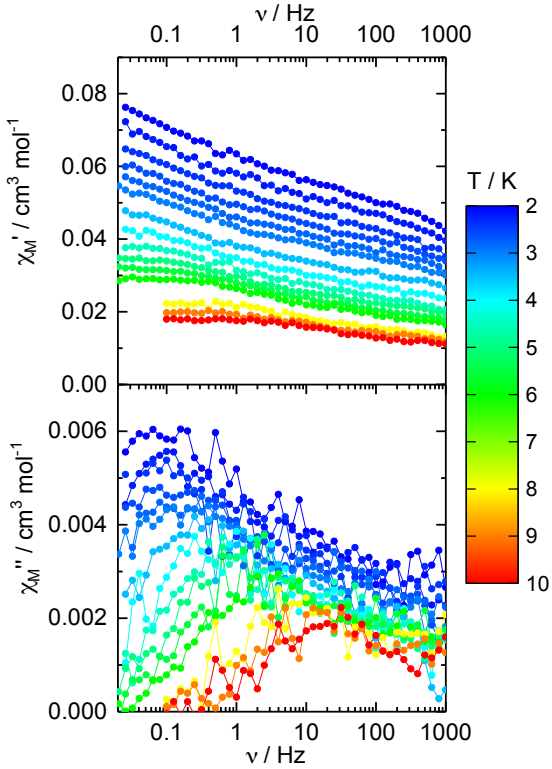


Figure 3. Frequency dependences of both in-phase, χ_M', and out-of-phase, χM'', components of the ac susceptibility for **5** at zero external dc field between 2 and 10 K.

The thermal variation of the relaxation time is plotted in Figure 4. It can be reproduced with the combination of Raman and Quantum tunnelling of Magnetization processes ($\tau^{-1}=CT^n+1/\tau_{QTM}$)[30] with C=0.0137(5) s^{-1} K^{-n}, n=4.1(2) and τ_{QTM}=4(2) s (Figure 4). For a dilute sample, the presence of QTM

might be surprising since dipolar interactions between magnetic moments is suppressed, but hyperfine coupling is still operating. For **5**, this slow relaxation process disappears with the application of an external DC field probably at the expense of a growing process at much lower frequency (out of the investigation time window) (Figure S9). However, at 1 kOe, this main relaxation process returns into the available frequency window with increasing temperature (Figure S10). Interestingly, the same temperature-frequency scan on **2** at 1 kOe resembles the zero field scan of **5** (Figure S11, Table S2). This is perfectly logical since the effect of the magnetic field in the condensed phase is known to overcome dipolar interactions between magnetic centers. This can be performed in another way by diluting those moments in an isomorphous diamagnetic matrix. The only difference resides in the occurrence of the direct process in field. The hysteresis loop at 2 K measured at 16 Oe s^{-1} reveals magnetic memory effect (slight opening of the loop) at moderate field with a butterfly shape, while for **5**, the hysteresis loop at 2 K reveals in-field memory effect with a butterfly shape (Figure S12).

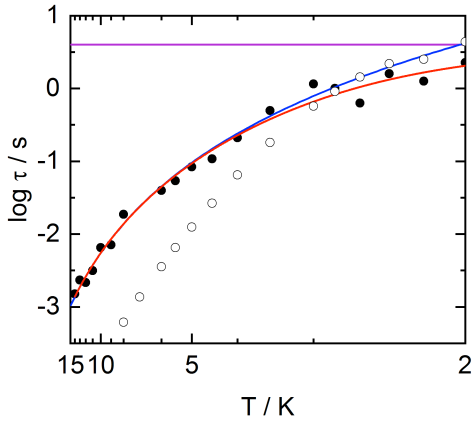


Figure 4. Temperature dependence of the relaxation time of **2** (white circles) and **5** (black dots) in the 2-15 K temperature range with the best fitted curves (see text) in red line. Blue and purple lines are Raman and QTM contributions to the relaxation processes, respectively.

The calculation of dipolar contributions in both complexes was performed, showing only small contributions and similar ones between **1** and **2** (Table S21-S22). This finding, added to the difficulties in reproducing the magnetic data with labile THF molecules in the second sphere of coordination in **1**, tends to indicate that small structural modifications drastically influence the magnetic relaxation in organolanthanides. It nicely shows that the reasons for stability of the divalent thulium complex (rigidity of the bulk, kinetic inertness) are somehow related to what enhances slow relaxation properties in these compounds (dipolar, vibronic contributions). This shall serve us as a guide in further design of divalent organolanthanide complexes.

Conclusion

In conclusion, this work presents the first f^{13} compound, with only one hole in the f-shell, behaving as a Single Molecule Magnet in absence of DC field. The out-of-phase signal persists up to 10 K at high frequencies in the condensed phase and up to 30 K in the diluted phase. The findings of this work contribute to show that the rational geometric design of lanthanide SMM, which is based on a simple electrostatic model, remains perfectly valid and, as other groups showed earlier,[1b-f, 6] organometallic lanthanide compounds are highly suitable for the design of performing SMMs. However, yet pathways for the magnetic relaxation still remain to be investigated because it seems that very small changes cause large consequences on the SMM properties. The reasons for relative stability - or high reactivity - of divalent lanthanides may help to dig deeper in this direction.

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Keywords: Lanthanides • Organometallics • Single Molecule Magnets • Electron transfer • Divalent thulium

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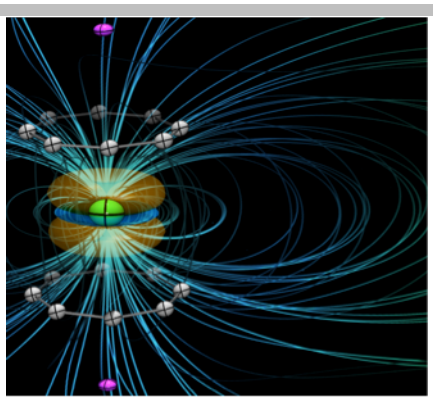
The highly reactive divalent sandwich $(Cot)_2Tm\{K(18\text{-}c\text{-}6)\}_2$ exhibits slow magnetic relaxation in absence of a DC field, an unprecedented report for f^{13} configuration. The variation of the counter-cation influences the magnetic relaxation in line with the overall stability of the organometallic sandwich complex.



Jules Moutet, Jules Schleinitz, Leo La Droitte, Maxime Tricoire, Fabrice Pointillart, Frédéric Gendron, Thomas Simler, Carine Clavaguéra, Boris Le Guennic, Olivier Cador and Grégory Nocton**

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Bis-cyclooctatetraenyl Thulium(II): Highly Reducing Lanthanide Sandwich Single Molecule Magnets

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