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Rare-Earth Cyclobutadienyl Sandwich Complexes: Synthesis, Structure and Dynamic Magnetic Properties

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Abstract: The potassium cyclobutadienyl $[K_2\{\eta^4\text{-C}_4(\text{SiMe}_3)_4\}]$ (**1**) reacts with $MCl_3(\text{THF})_{3.5}$ ($M = \text{Y, Dy}$) to give the first rare-earth cyclobutadienyl complexes, i.e. the complex anions $[M\{\eta^4\text{-C}_4(\text{SiMe}_3)_4\}\{\eta^4\text{-C}_4(\text{SiMe}_3)_3\text{-}\kappa\text{-(CH}_2\text{SiMe}_2)\}]^{2-}$, (**2_M**), as their dipotassium salts. The tuck-in alkyl ligand in **2_M** is thought to form through deprotonation of the 'squares' complexes $[M\{\eta^4\text{-C}_4(\text{SiMe}_3)_4\}]^{2-}$ by **1**. Complex **2_{Dy}** is a single-molecule magnet, but with prominent quantum tunnelling. An anisotropy barrier of 323(22) cm^{-1} was determined for **2_{Dy}** in an applied field of 1 kOe, and S-shaped magnetic hysteresis loops were observed up to 7 K.

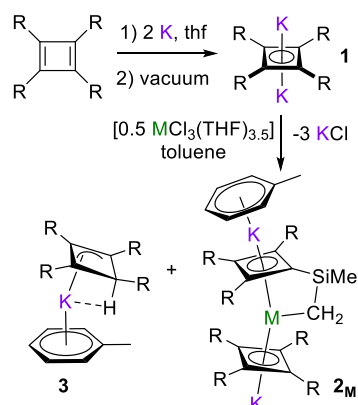
The use of η -bonded carbocyclic ligands has enabled many significant advances in the chemistry of the rare-earth elements, with a strong focus on applications in catalysis and small-molecule activation,^[1,2] and on the study of fundamental aspects such as novel oxidation states and electronic structure.^[3] Cyclopentadienyl ligands have underpinned most of the key developments,^[4] however rare-earth complexes of other anionic organometallic ligands such as cycloheptatriene^[5] and cyclooctatetraene (COT),^[6] reduced arenes^[7] and dianionic pentalene^[8] have also enabled important advances. In contrast, rare-earth complexes of cyclobutadienyl (Cb) ligands, $[\eta^4\text{-C}_4\text{R}_4]^{2-}$, are conspicuous by their absence, and only one actinide cyclobutadienyl complex is known.^[9] The paucity of f-block cyclobutadienyl compounds is presumably due to the rarity of cyclobutadiene pro-ligands, and the fact that rare-earth elements have not yet been shown to mediate cyclobutadiene formation via alkyne cyclo-dimerization.^[10]

With the aim of isolating the first rare-earth cyclobutadienyl complexes, we reasoned that a salt metathesis reaction between an alkali metal salt of 1,2,3,4-*tetrakis*(trimethylsilyl)cyclobuta-1,3-diene^[11] and a rare-earth halide could furnish a compound containing the 'squares' complex $[M\{\eta^4\text{-C}_4(\text{SiMe}_3)_4\}]^{2-}$. Thus, the reaction of 1,2,3,4-*tetrakis*(trimethylsilyl)cyclobuta-1,3-diene with potassium metal in THF produced $[K_2\{\eta^4\text{-C}_4(\text{SiMe}_3)_4\}]$ (**1**) as a yellow powder in 72% yield. The ¹H NMR spectrum of **1** showed a peak at $\delta = 0.45$ ppm for the SiMe₃ substituents (Figures S1-S3), and in the ¹³C{¹H} NMR spectrum the cyclobutadienyl carbons occur at $\delta = 109.1$ ppm and the SiMe₃ carbons at 5.6 ppm. The ²⁹Si NMR displays a single resonance at $\delta = -31.6$ ppm. The molecular structure of **1** was determined by X-ray diffraction (Table S1) and found to consist of a planar Cb ring η^4 -bound to two potassium ions, one on each side of the ring. The cyclobutadienyl C–C distances are 1.473(3)-1.487(3) Å, with K1–C distances of 2.828(2)-2.867(2) Å and K2–C distances of 2.857(2)-2.874(2) Å. The K–Cb_{cent} distances are 2.6465(15) Å and 2.6640(15) Å for K1 and K2, respectively, with a K1–Cb_{cent}–K2 angle of 178.23(5)° (Figure 1). The extended structure of **1** is coordination polymer *via* short contacts between the potassium centers and methyl groups of neighboring molecules, with K...C distances of 3.369(2)-3.518(3) Å.

The 2:1 stoichiometric reaction of **1** with $MCl_3(\text{THF})_{3.5}$ ($M = \text{Y, Dy}$) was undertaken with the aim of synthesizing $[K][M\{\eta^4\text{-C}_4(\text{SiMe}_3)_4\}_2]$. Heating the reaction mixtures to 70°C in toluene for 16 hours produced, after work-up, red/orange crystals, which X-ray crystallography (Table S1) revealed to be the *bis*(cyclobutadienyl) sandwich complexes $M\{\eta^4\text{-C}_4(\text{SiMe}_3)_4\}\{\eta^4\text{-C}_4(\text{SiMe}_3)_3\text{-}\kappa\text{-(CH}_2\text{SiMe}_2)\}^{2-}$ (**2_M**), complete with a tuck-in methyl ligand arising from deprotonation of an SiMe₃ substituent. The complexes form as their dipotassium salts $[[K_2(\text{toluene})]_2\text{2}_M]$. Complexes **2_Y** and **2_{Dy}** are isostructural, with the tuck-in Cb ligand also engaging in an η^4 -bridging interaction to a toluene-ligated potassium cation. The two Cb rings are square-shaped,

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Scheme 1. Synthesis of **1-3** ($M = \text{Y, Dy}$; $R = \text{SiMe}_3$).

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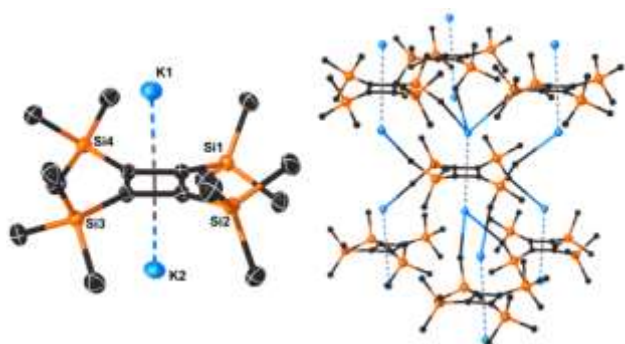


Figure 1 Molecular structure (left) and the extended structure (right) of **1**. Thermal ellipsoids at 50% probability.

with C–C distances of 1.473(4)–1.505(4) Å and 1.476(7)–1.515(7) Å for **2_y** and **2_{Dy}**, respectively. The M–C bond lengths are in the range 2.518(3)–2.620(3) Å for **2_y** and 2.524(6)–2.621(5) Å for **2_{Dy}**. The M–C_{D_{cent}} distances are 2.3479(13) Å and 2.3716(14) Å for **2_y** and 2.354(3) Å and 2.376(3) Å for **2_{Dy}**, with the centroid–Ln–centroid angles being 156.00(5)° and 156.42(9)°, respectively. The extended structure of **2_M** is also a coordination polymer by virtue of K1 linking a μ : η^4 -C₄(SiMe₃)₄ ligand to a μ : η^1 -CH₂ ligand, with K–C distances of 3.193(3) Å and 3.184(6) Å, respectively. The solution-phase structure of [K₂(toluene)][**2_y**] is consistent with the solid-state structure, with the ¹H NMR spectrum showing a singlet at δ = 0.37 ppm for the cyclobutadienyl SiMe₃ substituents on the intact Cb ligand, and resonances at δ = 0.61, 0.46, 0.24 and –0.54 ppm for the SiMe₃ and SiMe₂CH₂ substituents on the tuck-in Cb ligand. The two-proton doublet at δ = –0.54 ppm is consistent with the [CH₂SiMe₂][–] ligand, with ²J_{H_Y} = 2.0 Hz (Figures S5–S8).

An explanation for the deprotonation of a cyclobutadienyl SiMe₃ substituent was obtained by concentrating the nascent hexane solution resulting from washing crude [K₂(toluene)][**2_M**], which yielded yellow crystals. The ¹H NMR spectrum of this material in toluene-*D*₈ displayed resonances at δ = 2.41, 0.35,

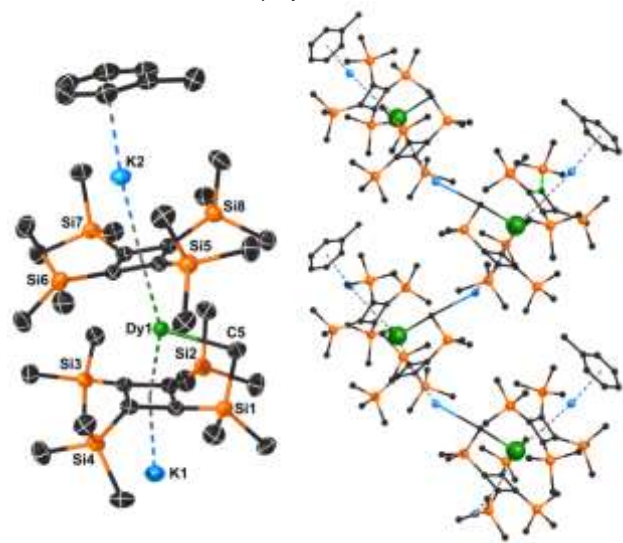


Figure 2 Molecular structure (left) and the extended polymeric structure (right) of **2_{by}**. Thermal ellipsoids at 30% probability.

0.34 and 0.22 ppm in a 1:9:9:18 ratio, implying partial protonation of a Cb ligand (Figures S9–S11). Analysis by X-ray crystallography confirmed that the by-product is the potassium cyclobutenyl complex **3** (Scheme 1, Figure 3, Table S1). The structure of **3** consists of a potassium center coordinated to a planar η^3 -cyclobutenyl ligand, with additional coordination by a molecule of toluene. The cyclobutenyl C–C bond lengths are 1.553(3) Å for C1–C2/C2' and 1.431(3) Å for C2/C2'–C3, with K–C distances in the range 2.907(2)–3.001(3) Å. The SiMe₃ substituent on C1 is disposed at an angle of 115.32(15)° relative to the cyclobutenyl ring, with the hydrogen on C1 engaging in an agostic interaction with potassium. The extended structure of **3** is a zigzag-type coordination polymer by virtue of CH...K interactions with the SiMe₃ groups of neighbouring molecules (Figure 3). The isolation of **3** supports the notion that a 'squarescene' complex of the type [M{ η^4 -C₄(SiMe₃)₄}₂][–] does indeed form, but also that it is subsequently deprotonated by **1**, leading to the formation of **2_M**. Repeating the reaction of **1** with MCl₃ using the 3:1 stoichiometry found in the products increased the yields of [K₂(toluene)][**2_M**] and **3** to 53% (**2_{Dy}**), 51% (**2_y**) and 26%, respectively.

The dynamic magnetic properties of lanthanide coordination compounds have attracted considerable interest in recent years owing to their potential single-molecule magnet (SMM) properties.^[12–14] In circumstances where the oblate ion Dy³⁺ resides in a strong axial crystal field, magnetic blocking can be prominent, and here π -bonded organic ligands such as cyclopentadienyl are of particular interest.^[12a,13d] The magnetic properties of materials containing the {Dy(η^4 -C₄R₄)_n} building block should therefore be very interesting, and hence [K₂(toluene)][**2_{Dy}**] was studied in this context. In a static (D.C.) field of 5 kOe, the temperature dependence of $\chi_M T$, where χ_M is the molar magnetic susceptibility, is typical of a monometallic Dy³⁺ complex. The value of $\chi_M T$ at 300 K is 13.54 cm³ K mol^{–1}, which gradually decreases to 11.90 cm³ K mol^{–1} at 25 K, before rapidly decreasing to a value of 1.95 cm³ K mol^{–1} at 2 K (Figure S14). The field dependence of the magnetization, $M(H)$, of [K₂(toluene)][**2_{Dy}**] at 1.8 and 5 K both show a rapid increase in M as the field is increased to 2 T before slowly increasing to saturation values of

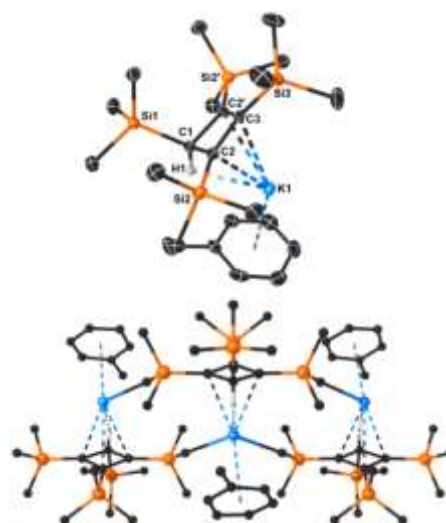


Figure 3 Molecular structure (top) and the extended polymeric structure (bottom) of **3**. Thermal ellipsoids at 30% probability.

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5.01 and 4.96 μ_B for 1.8 K and 5 K respectively (Figure S15).

Measuring the in-phase (χ') and the out-of-phase (χ'') susceptibility of $[\text{K}_2(\text{toluene})][\mathbf{2Dy}]$ using a small A.C. field of 1.55 Oe and zero D.C. field, as a function of frequency (ν) and temperature, revealed slow magnetic relaxation properties, but with strong quantum tunneling of the magnetization (QTM). Maxima in the $\chi''(\nu)$ data were only found at very high frequencies (997 Hz) (Figure S17), making it difficult to extract an effective energy barrier to reversal of the magnetization (U_{eff}). However, measuring $\chi'(\nu)$ and $\chi''(\nu)$ at 25 K in several DC fields in the range 200-1800 Oe (Figure S18) allowed the relaxation time (τ) to be determined for each field by fitting of the associated Cole-Cole plots of $\chi'(\chi'')$ (Figures S19-S27). These measurements allowed an optimum field of 1000 Oe to be determined (Figure S28, Table S2) and, hence, used to suppress the QTM for the in-field A.C. susceptibility measurements. Under the optimum conditions, clear maxima in $\chi'(\nu)$ were observed in the temperature range 8-40 K (Figures 4, S29). The plot of $\chi'(\chi'')$ (Figure S30, Table S3) was then fitted using a generalized Debye model and α parameters of 0.013-0.042, which indicate a very narrow distribution of relaxation times. A plot of the relaxation times as $\ln(\tau)$ vs. T^{-1} (Figure S31) is linear at $T = 36-40$ K, whilst at lower temperatures the data adopt a curved appearance. Since the application of a DC field mitigates the effects of QTM, the relaxation in $[\text{K}_2(\text{toluene})][\mathbf{2Dy}]$ can therefore be assigned to Orbach processes at higher temperatures and Raman processes at lower temperatures. Fitting the $\ln(\tau)$ vs. T^{-1} data to the high-temperature linear region using $\tau^{-1} = \tau_0^{-1} e^{-U_{\text{eff}}/k_B T}$ yielded $U_{\text{eff}} = 323(22) \text{ cm}^{-1}$ and $\tau_0 = 1.83 \times 10^{-9} \text{ s}$.

Detailed insight into the magnetic relaxation in $\mathbf{2Dy}$ was obtained using multireference *ab-initio* calculations (see SI for details).^[15] The calculations incorporated three potassium ions involved in $\mu-\eta^4$ -bridging interactions with the Cb ligand, an η^6 -toluene ligand, and two nearest neighbour complexes of $\mathbf{2Dy}$ (Figure S32). The principal magnetic axis of the ground Kramers doublet within the ${}^6\text{H}_{15/2}$ ground multiplet is oriented towards the centres of the $[\text{Cb}]^{2-}$ ligands (Figure 5), thus establishing an important magneto-structural property reminiscent of related dysprosium metallocene SMMs.^[12] The calculated g-tensors (Table S4) and crystal field parameters (Table S5)^[16] show that the ground doublet is highly axial, with the projection on the $M_J = \pm 15/2$ state being 0.949 (Table S5). However, the g-tensors consist of a small-but-significant transverse component, i.e. $g_x = 0.0076$, $g_y = 0.0130$, $g_z = 19.7338$, which is sufficient to induce QTM in the absence of an external magnetic field, consistent with experimental observations.

The excited doublets in $\mathbf{2Dy}$ do not correspond to any definite projection, with the first-excited doublet consisting only of 0.591 $M_J = \pm 13/2$ character, indicating strong mixing by the non-axial components of the crystal field. Indeed, the off-diagonal crystal field parameters for this system are substantial, with, e.g., B_2^2 being much larger than B_2^0 (Table S5), which is most likely due to the influence of the equatorial tuck-in ligand. The first-excited doublet lies at 284 cm^{-1} , which agrees qualitatively with the experimental barrier, taking into account experimental error and the omission from the calculations of electron correlation effects outside the 4f active space. Overall, the calculations point to the most probable relaxation mechanism occurring via the first-excited doublet, with prominent QTM in the ground doublet, which

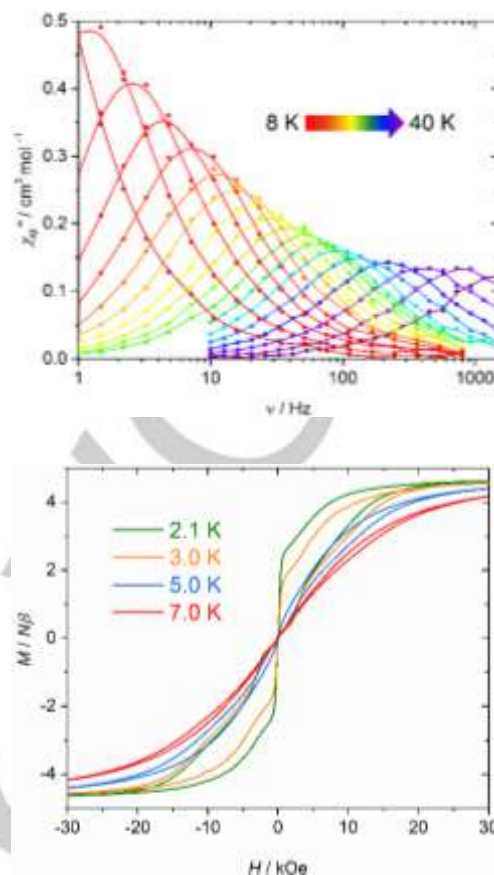
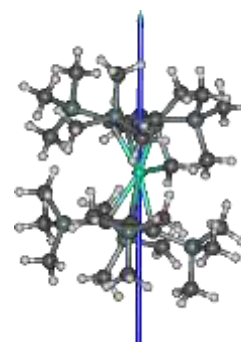


Figure 4 Upper: frequency dependence of $\chi''(\nu)$ in an applied field of 1 kOe for $[\text{K}_2(\text{toluene})][\mathbf{2Dy}]$. Lower: $M(H)$ hysteresis at $T = 2.1-7.0$ K using an average sweep rate of 50 Oe s^{-1} (5 mT s^{-1}).

is fully consistent with the experimental observations.

Since the magnetic memory properties of SMMs have been used a basis for proposing nanoscale devices,^[13a] the magnetization (M) vs. field (H) hysteresis properties of $[\text{K}_2(\text{toluene})][\mathbf{2Dy}]$ are also of interest. The $M(H)$ data (Figure 4) show S-shaped loops which remain open up to 7 K (scan rate of 50 Oe s^{-1}), but without any appreciable coercivity. In light of the prominent QTM in $\mathbf{2Dy}$, this observation is somewhat surprising, but can be attributed to the large Dy...Dy separation of 10.45 Å, which is sufficiently large to mitigate against the effects of dipolar exchange. This hysteresis properties are broadly consistent with the divergence in the field-cooled and zero-field-cooled magnetic



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Figure 5 Principal axis of the g -tensor in the ground KD of $2D_y$ -susceptibility, which occurs at 3.6 K (Figure S16).

In summary, we have described the synthesis and structures of the first rare-earth cyclobutadienyl complexes, 2_M , which were obtained from the reaction of $[K_2\{\eta^4-C_4(SiMe_3)_4\}]$ (**1**) with MCl_3 ($M = Y, Dy$). The 'squares' complexes 2_M consist of a *bis*(η^4 -cyclobutadienyl) coordination environment with the metal centers additionally bound to a tuck-in $[CH_2SiMe_2]^-$ ligand, the formation of which can be accounted for by deprotonation of the postulated sandwich complex $[M\{\eta^4-C_4(SiMe_3)_4\}_2]^-$ by **1**. Whilst 2_{Dy} is an SMM but with prominent QTM, the large anisotropy barrier of $323(22) \text{ cm}^{-1}$ and the open hysteresis loops observed for a system with a strong equatorial crystal field provide an enticement for pursuing a *bis*(cyclobutadienyl)dysprosium complex as a potentially outstanding SMM, which we are actively pursuing. Introducing the cyclobutadienyl ligand into rare-earth chemistry also furnishes new opportunities for studying the chemistry of these elements in a broader context, potentially including catalysis and small-molecule activation.

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Keywords: rare-earth elements • cyclobutadienyl ligands • organometallics • dysprosium • single-molecule magnets

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Rare-Earth Cyclobutadienyl Sandwich Complexes: Synthesis, Structure and Dynamic Magnetic Properties

Squarocene complexes: The potassium cyclobutadienyl [$K_2\{\eta^4-C_4(SiMe_3)_4\}$] reacts with $MCl_3(THF)_{3.5}$ ($M = Y, Dy$) to give the first rare-earth cyclobutadienyl complexes, i.e. the anions $[M\{\eta^4-C_4(SiMe_3)_4\}\{\eta^4-C_4(SiMe_3)_3-\kappa^-(CH_2SiMe_2)\}^{2-}$ (**2_M**) as their dipotassium salts. The dysprosium complex **2_{Dy}** shows single-molecule magnet behaviour, with an anisotropy barrier of 323 cm^{-1} and magnetization versus field hysteresis loops up to 7 K.