Synthesis, structures and magnetic properties of \[(\eta^9\text{-}C_9H_9)\text{Ln}(\eta^8\text{-}C_8H_8)]\) super sandwich complexes

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Sandwich complexes are an indispensable part of organometallic chemistry, which is becoming increasingly important in the field of lanthanide-based single molecule magnets. Herein, a fundamental class of pure sandwich complexes, \[(\eta^9\text{-}C_9H_9)\text{Ln}(\eta^8\text{-}C_8H_8)]\) (\(\text{Ln} = \text{Nd, Sm, Dy, Er}\)), is reported. These neutral and sandwiched lanthanide compounds exclusively contain fully \(\pi\)-coordinated coplanar eight and nine membered CH rings. The magnetic properties of these compounds are investigated, leading to the observation of slow relaxation of the magnetization, including open hysteresis loops up to 10 K for the Er(III) analogue. Fast relaxation of the magnetization is likewise observed near zero field, a highly important characteristic for quantum information processing schemes. Our synthetic strategy is straightforward and utilizes the reaction of \[(\eta^8\text{-}C_8H_8)\text{LnI}(\text{thf})_n\] complexes with [K(C\(_9\text{H}_9\)]. Although all compounds are fully characterized, structural details of the title compounds can also be deduced by Raman spectroscopy only.
Sandwich complexes, that is, compounds bearing exclusively two planar, cyclic and π-bonded ligands, are a fundamental class of compounds in organometallic chemistry. In fact, the discovery of ferrocene \([\eta^5-C_5H_5]Fe\) by Kealy and Pauson\(^1\) and the subsequent structural analysis by Fischer and Wilkinson paved the way to modern organometallic chemistry\(^2\). Ever since, the quest for new sandwich complexes has been a central part of modern organometallic chemistry. In the last decades, sandwich complexes, and particularly ferrocene, have become widely used compounds, which found a variety of applications, e.g. in synthesis, catalysis, electrochemistry, medicine and even as fuel additive\(^3\). In a classical homoleptic sandwich or metallocene complex, two identical aromatic ring systems equally bind with all carbon atoms to a metal center\(^4\). Well established examples of this structural motif are the above-mentioned ferrocene, bis(benzene) chromium and uranocene\(^5,6\). Besides these homoleptic complexes, there are also examples of heteroleptic sandwich complexes ligated by two different aromatic ring systems. As aromatic moieties, rings ranging from three to nine-membered systems have been established in organometallic chemistry. Despite the large variety of possible ligand permutations, considering these seven different ring sizes, only a limited number of structurally characterized ligand combinations has been reported in terms of homoleptic and heteroleptic complexes. These are the four non-substituted homoleptic metallocene archetypes with five to nine-membered rings: \([\eta^5-C_5H_5]M\)\(^7\), \([\eta^6-C_6H_6]M\)\(^8,9\), and \([\eta^8-C_8H_8]M\) (Fig. 1)\(^9-11\). Considering heteroleptic sandwich complexes, only four non-substituted types were structurally characterized, which are: \([\eta^5-C_5H_5]M(\eta^1-C_6H_6)\)\(^12\), \([\eta^6-C_6H_6]M(\eta^5-C_5H_5)\)\(^13,14\), \([\eta^7-C_7H_7]M(\eta^5-C_5H_5)\)\(^15-18\), and \([\eta^8-C_8H_8]M(\eta^5-C_5H_5)\) (Fig. 1)\(^18-20\). All of these are cyclopentadienyl derivatives combined with four to eight-membered rings.

Obviously, the vast majority of sandwich complexes is ligated by cyclopentadienyl derived moieties. In contrast, complexes ligated by larger aromatic monoycyles are scarce. Therefore, we define the class of sandwich complexes having more than 16 carbon atoms coordinated to the central metal atom as super sandwich compounds, to distinguish them from classical sandwich complexes.

One of the most recent application of sandwich compounds in rare earth chemistry is their use as single molecule magnets (SMMs)\(^21-30\). Such lanthanide-based SMMs have been shown to act as quantum computing units, so-called qubits, for the implementation of Grover’s quantum search algorithm\(^31\), and more recently have displayed magnetic hysteresis at liquid nitrogen temperatures\(^32-34\). Herein, we present a long sought for class of sandwich complexes \([\eta^8-C_8H_8]Ln(\eta^8-C_8H_8)\], which exclusively contain fully π-coordinated eight and nine-membered rings. Synthesizing these compounds was already attempted by Streitwieser et al.\(^43,44\) in 1973, shortly after the first successful synthesis of \(\text{KC}_{8}\text{H}_{8}\) was reported by Katz and coworkers\(^43,44\). Their strategy was based on a one-pot reaction between \(\text{LnCl}_3\) (\(\text{Ln} = \text{Ce(III)},\text{Pr(III)},\text{Nd(III)},\text{Sm(III)},\text{K}_{8}\text{C}_{8}\text{H}_{8},\text{and KC}_{8}\text{H}_{8}\). However, they could only isolate complexes of the type \([\eta^8-C_8H_8]\text{LnCl(thf)}_2\) thereby highlighting, that the \(\text{C}_8\text{H}_8\) anion does not form sandwich complexes analogous to \(\text{C}_8\text{H}_8\)\(^2-\). After a 45 years quest for \([\eta^9-C_9H_9]\text{Ln(\eta^8-C_8H_8)}\), we now report a synthetic protocol based on two distinct steps.

Results

Synthesis and crystallographic characterization of \([\eta^9-C_9H_9]\text{Ln(\eta^8-C_8H_8)}\]. First, we synthesized the starting material \(\text{KC}_{9}\text{H}_{9}\), following the procedure of Katz et al.\(^44\) The \(^{1}H\)-NMR spectrum shows only one sharp resonance at \(\delta 7.05\) ppm, which is attributed to the nine ring protons and consistent with the regular \(1\)-\(all\)-cis-configuration being present in solution. Additionally, the molecular structure of the dimethoxyethane solvate \([\eta^9-C_9H_9]K(\text{DME})_2\] (1) was established by X-ray diffraction experiments. A flat and aromatic nine-membered carbon ring is observed with C–C bond lengths ranging from 1.389(3) Å to 1.394(3) Å, which is in the expected region for aromatic sp\(^2\)-hybridized carbon atoms (Fig. 2). Only the perfectly nonagonal all cis-isomer was found in the solid state and no positional disorder, indicating the presence of the cis,cis,cis,trans-cyclononatetraenyl isomer, was observed. This is in contrast to very recent findings from Nocton et al.\(^11\), who also reported on the solid-state structure of \([\eta^9,11-\text{C}_{9}\text{H}_{9}]\text{K(\text{OEt})}_2\)]. They obtained \(\text{KC}_{9}\text{H}_{9}\) from diethyl ether as a Kryptofix 222 complex. The 1H-NMR spectrum shows only one sharp resonance at \(\delta 3.154(2)\) ppm. These two examples highlight the local symmetry generated around the central lanthanide ion, determined by the ligand field and the rigidity of the complex, plays a crucial role in the design of SMMs\(^32,34-42\).

With \(\text{KC}_{9}\text{H}_{9}\) in hand, we next aimed to synthesize defined \([\eta^8-C_8H_8]\text{LnI(\eta^8-C_8H_8)}\) complexes, in which the residual iodide ligand can be replaced by \(\text{C}_8\text{H}_8\)\(^2-\) in a salt metathesis approach. Therefore, we synthesized \([\eta^8-C_8H_8]\text{LnI(thf)}_2\] (\(\text{Ln} = \text{Nd(III)}\)}.
Compounds 2a and 2b, which have been reported earlier by Mashima et al., were obtained within two days. Complex 2c and 2d could only be obtained on this route after activation of the metal by in situ amalgamation. Nevertheless, significantly longer reactions times (3–4 weeks) were needed to obtain crystalline yields of 57% (2c) and 43% (2d). Ultimately, we were able to react the \[\text{Ln}[\text{η}^8-\text{C}_8\text{H}_8]\text{I}(\text{thf})_2\] complexes with 1 in refluxing toluene, which gave the title compounds \([\text{Ln}[\text{η}^8-\text{C}_8\text{H}_8]\text{I}(\text{thf})_2]\) in moderate crystalline yields of 36% (Nd, 3a), 32% (Sm, 3b), 31% (Dy, 3c) and 32% (Er, 3d) (Fig. 4).

Single crystals of the heteroleptic sandwich complexes \([\text{[(η}^9-\text{C}_9\text{H}_9)]\text{Ln}([\text{η}^8-\text{C}_8\text{H}_8])\] (Ln = Nd (3a), Sm (3b), Dy (3c), Er (3d)) were obtained from toluene. The solid-state structures of 3c and 3d show a disorder of the eight and the nine-membered rings (see Supplementary Information for details). Especially the molecular solid-state structure of 3d exhibits a complicated disorder with split positions of the Er(III) ion, showing slight indications of ring slipping and tilting in both ligands. The Er-C distances in the eight-membered ring vary between 2.406(11) Å and 2.670(10) Å with 5 carbon atoms closer located to the Er(III) ion than the others. Similarly, the Er-C distances in the nine-membered ring vary between 2.468(12) Å and 2.733(10) Å with four carbon atoms in closer proximity to the Er(III) ion (see Supplementary Table 10 for detailed bond lengths). However, this might also be caused by the unusual split Er(III) positions and thus, do not reflect the actual binding mode of the two aromatic moieties. We, therefore, performed a DFT geometry optimization and found the energetic minimum for 3d to be a perfect sandwich-type configured \([\text{[(η}^9-\text{C}_9\text{H}_9)]\text{Er}([\text{η}^8-\text{C}_8\text{H}_8])\] molecule (see Fig. 5). As a result, we propose 3d to comprise two fully π-coordinated and

\[
\begin{align*}
\text{Ln}^3 + \frac{1}{2} \text{I}_2 + \text{THF, reflux} & \quad \text{For } 2a, 2b: 48 \text{ h} \\
& \quad \text{For } 2c, 2d: + \text{Hg, } >48 \text{ h}
\end{align*}
\]

\[
\begin{align*}
\text{K}^+ & \quad \text{Toluene, reflux, 30 min} \\
& \quad -\text{KI}
\end{align*}
\]
Table 1 Ln-Cg distances in the solid state of compounds 3a–d

| Compound | Ln-Cg(C8H8) [Å] | Ln-Cg(C9H9) [Å] |
|----------|-----------------|-----------------|
| 3a       | 1.8925 (3)      | 2.0441 (3)      |
| 3b       | 1.8687 (5)      | 1.9908 (6)      |
| 3c       | 1.8869 (4)      | 1.8752 (3)      |
| 3d       | 1.6725 (4)      | 1.7248 (4)      |

Fig. 6 Raman-spectroscopic analysis. FT-Raman spectrum of [(η⁶-C₆H₆)Sm(η⁶-C₆H₆)] 3b. The motion vectors of four prominent bands are inserted. Hydrogen atoms and their motion vectors are omitted for clarity.

Magnetic properties of [(η⁹-C₉H₉)Er(η⁸-C₈H₈)] (3d). Although the single-crystal X-ray structures of 3c and 3d show some disorder, we conclude an almost coplanar η⁹-C₉H₉ and η⁸-C₈H₈ arrangement of the ligands as observed in 3a and 3b, based on the Raman-spectroscopic analysis. This arrangement is known to exert an equatorial ligand field, which drastically stabilizes prolate shaped mI states of lanthanide ions. The prime example for this family of trivalent lanthanide ions in terms of single molecule magnetic behavior is without doubt erbium (vide supra), where the equatorial ligand field exerted by a η⁹-C₉H₉ ligand, can yield SMMs with not just large energy barriers to the relaxation of the magnetization, but also leading to open hysteresis loops at temperatures as high as 10 K due to possible coupling with lattice vibrations (see Table 4b in the SI).

Raman-spectroscopic analysis. We further investigated the bonding situation and ligand aromaticity using Raman spectroscopy and vibrational analysis. Fourier transform Raman (FT-Raman) spectra of 3a–3d were recorded powdered samples (Fig. 6). The band assignments were validated by quantum chemical calculations. The Raman spectra can be divided in two sections: (i) above 300 cm⁻¹ the spectra of all molecules are almost identical as the signals are solely attributable to both sandwich ligands. Vibrational coupling to the lanthanide cations is not expected due to the orthogonality of the in-plane vibrations of the ligands with respect to that of the lanthanide-ring centroid. Therefore, the signals at 3042 (η⁶-C₆H₆) and 3006 cm⁻¹ (η⁷-C₆H₆) are attributed to the fully symmetric C-H valence motions, those at 1495 (η⁶-C₆H₆) and 1517 cm⁻¹ (η⁷-C₆H₆) to the antisymmetric C-C-stretching vibrations of the ligands. A third group of bands belongs to the (local) symmetric ring breathing modes at 749 cm⁻¹ (υₐs(η⁷-C₆H₆)) and at 681 cm⁻¹ (υₐs(η⁹-C₉H₉)). Analyzing these modes is an unambiguous proof of the ring size and the bond strength within these aromatic ligand systems. According to normal coordinate analyses on C₈H₈⁻, C₉H₉ and C₉H₉⁺ the stretching force constant values of the C–H and C–C bonds are each of comparable size. Assuming this is furthermore true for larger aromatic C₈H₈ monocyclic ligand systems, the approximate wavenumber of the fully symmetric ring breathing mode is easily calculated using a mathematical expression deduced in the Supplemental Information (see Supplementary Equation 1). This formula nicely reproduces the observed ring breathing mode energies of the two ligands (υ(C₈H₈)²–574 cm⁻¹ (calc. 761 cm⁻¹) and υ(C₉H₉)–680 cm⁻¹ (calc. 680 cm⁻¹)) and therefore, confirms the comparable bonding situation in these ligand systems with those of aromatic ligands like C₈H₈⁻, C₉H₉ and C₉H₉⁺ (see SI for details). (ii) At vibrational energies lower than 300 cm⁻¹ lanthanide-ring-stretching modes are expected in the Raman spectra of [(η⁹-C₉H₉)Ln(η⁶-C₆H₆)]. Due to the larger (η⁹-C₉H₉)-Ln bond lengths their vibrations are found between 100 and 166 cm⁻¹, whereas those of the shorter Ln-(η⁸-C₈H₈) bonds are observed between 236 and 247 cm⁻¹ (Nd, 3a: 137.0 (s), 242.1 (s); Sm, 3b: 126.8 (s), 236.0 (vs); Dy, 3c: 100 (s), 237.2 (s) and Er, 3d: 165.9 (m), 207.4 (m)). Both vibrations remind of the symmetric and antisymmetric modes of trivalent linear molecules like CO₂. For these bands, the agreement with the results of the quantum chemical calculations is only of limited accordance due to possible coupling with lattice vibrations (see Table 4b in the SI). However, 3a–d are rare cases in modern organometallic chemistry, in which the coordination mode of the ligands can be determined by Raman spectroscopy as sole method.
where pinning of the magnetic moment in the immobilized crystalline material occurs.

The dynamic behavior of 3d was probed via magnetic susceptibility AC studies under zero applied DC field. A single peak is observed in the temperature and field dependent out-of-phase magnetic susceptibility, i.e. $\chi_{\text{m}}^{\prime\prime}(T)$ and $\chi_{\text{m}}^{\prime\prime}(\nu)$, respectively. This result is in agreement with the dynamic studies for [(η⁸-C₅H₅)Er(η⁸-C₅H₅)]⁻⁻28, where they differ from the asymmetric [(η⁵-C₅H₅)Er(η⁸-C₅H₅)]⁻ counterparts24, where two maxima were observed. The $\chi_{\text{m}}^{\prime\prime}(T, \nu)$ reveals a temperature dependent maximum at temperatures between 16–26 K, whilst below 15 K the parameter $\chi_{\text{m}}^{\prime\prime}(T)$ remains practically constant (Fig. 7a). Between 18 and 26 K, the Arrhenius analysis of $\tau$ at different temperatures show a relaxation dominated thermally activated Orbach process, whereas below 9 K temperature independent processes dominate. The curvature between 10 and 15 K suggests that other relaxations pathways, such as Raman, are also active. The distribution of the relaxation parameter ($\alpha$) likewise indicates a narrow distribution of relaxation times between 20 K and 26 K ($\alpha \leq 0.18(1)$), while for temperatures below 15 K the parameter is greater ($\alpha \geq 0.18(1)$). The energy barrier $U_{\text{eff}}$ of 251(1) cm⁻¹ and $r_0 = 1.3(2) \times 10^{-10}$ s (Fig. 7b) are very similar to the ones observed for homoletic and heteroleptic erbium complexes24,27,28,36. The plateau at temperatures between 2 and 5 K marks the quantum tunneling of the magnetization regime, with a $\tau_{\text{QTM}} = 0.18(1)$ s. Application of an optimal field of 2 kG (at which relaxation is slower), efficiently suppressed QTM, leading to an almost purely temperature dependent relaxation (green symbols in Fig. 7b and SI (see Supplementary Fig. 14)), with a slightly enhanced $U_{\text{eff}} = 261(1)$ cm⁻¹.

An open magnetic hysteresis is the ultimate proof of the strong anisotropic behavior in SMMs and their bistable magnetic behavior. Extrapolation of the Arrhenius data to low temperature indicates that the observation of magnetic hysteresis below 12 K is feasible, where the relaxation time is 100 s. To confirm the SMM behavior and the slow relaxation observed through AC studies, magnetization hysteresis loops were collected between 1.8–10 K. Figure 7c shows butterfly-like hysteresis loops between 2 and 10 K and a field ranging from ±2 T, leading to a blocking temperature ($T_{\text{B}}$) of 10 K. Note that, albeit the energy barrier being rather large, the hysteresis loops are practically close at zero field, strongly indicating that QTM is rather efficient, as commonly observed in lanthanide-based SMMs.

To gain deeper insight into the relaxation mechanism and the anisotropic magnetic properties of 3d, CASSCF/SO-RASSI/SINGLE_ANISO calculations were performed49–54. Due to the highly disordered character of the crystal structure of 3d, CASSCF calculation were carried out employing an optimized crystal structure (see SI for details). The electronic calculation predicts a highly axial ground state with $g_z = 17.95$ and $g_{x,y} \approx 10^{-3}$. As observed in Fig. 7d, the anisotropy axis is perpendicular to the η⁸-C₅H₅ and η⁸-C₅H₅ planes. Employing the ligand field parameters from electronic calculations, we find that the ground, first and second excited states are almost colinear and highly pure...
m_I = ±1/2 and ±3/2 and ±1/2 states, respectively. The relative energies for the first and second excited state are 140 and 268 cm⁻¹. The succeeding excited states are highly pure and huddled over 330–490 cm⁻¹. As it can be observed in Fig. 7c, ab-initio results reproduce rather well the χ_M(T) and M(H) (see Supplementary Fig. 11) with only small differences. The discrepancies might arise by structural distortions not reflected in the geometry optimization. Using the average matrix elements of magnetic moment between the electronic states, it is predicted that the most efficient magnetic relaxation pathway is to occur via thermally assisted QTM through the second excited state at 268 cm⁻¹. As observed, this state is very close to the U_eff obtained from dynamic studies (cf. ~260 cm⁻¹ (Fig. 7c)). Interestingly, the energy barrier is also very similar to the antisymmetric vibration of the Cp/Cp' rings observed in the Raman spectrum (240 cm⁻¹). As molecular vibrations have been predicted to facilitate spin-phonon coupling, these could be relevant for the relaxation in 3d53.

Note that the strongly equatorial ligand field exerted by the η⁵-C₅H₅ and η⁶-C₆H₆ ligands is optimal at stabilizing the largest m_I state for Er(III), characterized by a prolate electron density, as demonstrated by the magnetic studies and supported by CASSCF calculations. In contrast, for the Dy(III) ions an axial ligand field is more suitable to stabilize the largest m_I = ±1/2 state, thus the anisotropic magnetic properties in [(η⁶-C₆H₆)Dy(η⁶-C₆H₆)]²⁺ are expectedly worse, as confirmed by AC tests and other reports.7,55

Discussion

By synthesizing [(η⁶-C₆H₆)Ln(η⁶-C₆H₆)] (Ln=Nd, Sm, Dy, Er), we unveiled a fundamental class of pure sandwich complexes. The title compounds represent a long sought asymmetric organometallic motif, leading to the observation of hysteresis loops up to 10 K. In addition, we observe fast quantum tunneling of the magnetization near zero field, which opens the possibility of nuclear spin read-out with the 162Er(III) analog of [(η⁶-C₆H₆)Er(η⁶-C₆H₆)]¹⁵⁶. Our results clearly highlight the significance of not just a long desired and extremely elusive organometallic complex class, but are also of relevance to future quantum spintronic applications.

Methods

Synthetic methods. Experiments were carried out under a dry, oxygen-free argon atmosphere using Schlenk-line and glovebox techniques. All solvents and reagents were rigorously dried and deoxygenated before use. All compounds were characterized by single-crystal X-ray diffraction studies. Further details are available in the Supplementary Information (see section Supplementary Methods).

Data availability

All data is available from the authors on reasonable request. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 1894445-1894450. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Author contributions
L.M. synthesized and analyzed all compounds with support from C.S. and S.B. L.M. and C.S. conducted X-ray experiments. E.M.P. and M.R. conducted and interpreted magnetic measurements and carried out the ab-initio CASSCF calculations and interpreted the results. R.K. performed and analyzed quantum chemical calculations. PWR originated the idea, supervised the work, and interpreted the results. All authors contributed to the preparation of the manuscript.

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