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First structural evidence for multiple alkali metals between sandwich decks in a metallocene†

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A tetralithio salt (1) derived by treating 1,4-bis(trimethylsilyl)-cyclooctatriene with “BuLi serves as the first structural evidence for a multi-alkali metallocene. Single-crystal XRD confirms two Li⁺ each asymmetrically bind to η³ and η⁴ between two COT” rings and two Li⁺ terminally bind to η³. Solid-state NMR studies confirm the presence of two distinct lithium ion sites while the solution NMR studies suggest the formation of an (COT” dianion) ion-pair in solution. Further treating of the tetralithio salt with NaCl leads to linear sodium polymeric chains. Therefore, simply changing the ionic radius changes the molecular structure.

1. Introduction

Alkali metals arrange in fascinating metallic assemblies, including rings, cages, and other aggregates.† Olbrich and co-workers even demonstrated that lithium and sodium cyclopentadienide (Cp) form linear polymeric chains.‡ The amount of organo-alkali chemistry encompassing dianionic ligands, such as cyclooctatetraene (COT), pales in comparison to monoanionic ligands such as Cp, alkyls, etc. Organolanthanide chemistry often employs dianionic COT ligands, and start from 1,3,5,7-COT or M₂COT precursors (M = Li, K).§ Bellama, Cloke and co-workers introduced COT rings modified with silyl groups to increase solubility of COT complexes.¶ Since then, Li₂(COT)₂ (COT” = 1,4-bis(trimethylsilyl)cyclooctatetraene) has become one of the most important precursors in Ln–COT chemistry,‖ and has become increasingly popular.¶ Surprisingly the molecular structure of this well utilised precursor has never been reported. In recent years only a few examples of the use of this important starting material have been reported.‖ This trend is understandable as the stoichiometry plays a critical role in successfully generating multi-decker lanthanide sandwich complexes (particularly with COT rings), and therefore starting from well-defined precursors is important.

Sandwich complexes containing transition, lanthanide, and actinide metals are ubiquitous in organometallic chemistry, with ferrocene as the prime example. By comparison, metallocenes with group 1 and 2 metals are less abundant,§ despite pre-dating ferrocene. In addition, these complexes are mainly limited to Cp ligands or other monoanionic rings. However, there are a couple of examples of triple decker sandwich metallocenes that incorporate a dianionic COT ligand as the middle deck; but the terminal decks are Cp derivatives.¶,‖,‡ Sandwich complexes (of the form ring–metal–ring) consisting of s-block elements and dianionic aromatic rings exclusively are unknown. Presumably, charge balance and lack of d/f orbital contributions make access to these species difficult.¶ The next generation of metallocenes would logically contain multiple metals between the decks to facilitate multi-electron redox processes.

Metallocene chemistry encompasses complexes with diverse architectures (Fig. 1), with species B accounting for the majority of known sandwich complexes. Sandwich complexes containing multiple metals between the decks that bind to each deck are very rare (A). The confirmed structure of a handful of such metallocenes exist, but contain only transition metals (Pd, Pt, Ni.

Fig. 1 Different types of metallocenes. Note that the aromatic ring shown is COT, however any aromatic ring could be substituted (Cp, Cp*, COT”, etc.). Species B represents the typical sandwich complex. Species A represents the multi-metal sandwich complex; C the extended sandwich; D the inverse sandwich; E the multi-deck sandwich complex.
or Mo). In such complexes, the number of sandwiched metals range from two to four and the sandwich consists of COT, cycloheptatriene, cyclononatetraenyl or benzene rings. In addition, a chloride or solvent molecule may bind to the sandwiched metals in a plane that is parallel to the aromatic rings. In another related [TiCOT] example, the COT rings are severely bent with the titanium atoms binding to make two separate fragments within the COT ring: a pentadienyl and an allenyl fragment. In addition, the bent structure also promotes a Ti–Ti bond. There are also a few examples of complexes that contain linear chains of (transition) metals capped by monoanionic or neutral aromatic ligands providing an extended sandwich complex (C). With this in mind, we report the first structurally confirmed example of a sandwich complex containing two lithium atoms sandwiched and bound between two decks, free of solvents and other Lewis bases and a related linear sodium chain. In addition to single crystal X-ray structure, multielectron NMR (solution and solid-state) as well as computational studies confirmed the structure, stability and the molecular dynamics. These results finally bring direct evidence of one of the most utilized organo-lithium precursors in lanthanide chemistry.

**Experimental**

**General methods**

Unless specified otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk or glovebox techniques. Glassware was oven dried before use. Hexane, toluene, and tetrahydrofuran (THF) were dried using activated alumina. C6D6 was purchased from Cambridge Isotopes and dried over calcium hydride. All chemicals were purchased from Thermofisher Scientific and used without further purification.

Liquid NMR spectra were acquired on a Bruker AVANCE spectrometer, operating at 500 MHz for 1H.

**Computational methods**

Solid phase density functional theory (DFT) calculations of the magnetic shielding (MS) and electric field gradient (EFG) tensors were performed using the gauge-including projector-augmented wave (GIPAW) DFT methodology as implemented in the CASTEP code. This method reproduces the periodicity of a solid using plane wave pseudopotentials as a basis and often yields more accurate solid-state NMR parameters. The PBE DFT functional was used along with on-the-fly generated pseudopotentials, a 610 eV kinetic energy cut-off and a 3 × 2 × 2 k-point grid. Li–Li indirect spin–spin coupling constants (J) were calculated using a simplified monomeric structural model at the B3LYP15/6-311++G** level of theory with the Gaussian 09 software (revision A.02).

The dynamic behaviour of the lithium ions in the COT sandwich was investigated with Gaussian 09 using the spin-restricted molecular orbital formalism. The crystal structure of 1 with the THF molecules removed was used as a starting point for geometry optimizations of 1. Gas-phase optimizations were performed at the B3LYP15/TZVP17 level. Wavefunction stability checks were performed to make sure that the calculated wavefunction corresponds to the electronic ground state (the stable keyword in Gaussian). The nature of stationary points obtained was confirmed by harmonic frequency calculations. Mayer bond orders were calculated using the AOMix software. Natural population analysis (NPA) was performed to evaluate atomic charges.

**Solid-state NMR**

Solid-state NMR spectra were acquired on a 400 MHz Bruker AVANCE III spectrometer using a 4 mm triple resonance magic angle spinning (MAS) probe. The 7Li and 6Li NMR spectra were acquired using the simple pulse-acquire method with excitation pulses of 2.1 and 7.0 μs, respectively, and recycle delays of 20 s and 6 min, respectively. The chemical shifts were referenced to a 1 M solution of LiCl using solid LiCl as an external reference (δ = −1.06 ppm). Both spectra were acquired at a MAS rate of 5 kHz.

The 13C cross-polarization (CP) MAS NMR spectrum (Fig. S1, ESI†) was acquired while spinning at 8 kHz using a 3.5 μs 1H excitation pulse and a 2 ms contact time. A total of 500 transients were collected with a recycle delay of 2 s. The chemical shifts were referenced to TMS using solid glycine as an external reference (δ = 176.4 ppm).

The 29Si CPMAS NMR spectrum (Fig. S2, ESI†) was acquired while spinning at 5 kHz using a 1H excitation pulse of 3.5 μs and a 10 ms contact time. A total of 64 scans were collected with a recycle delay of 2 s. The chemical shifts were referenced to TMS using tetraakis(trimethylsilyl)silane as an external reference (δ = −9.9 ppm).

**X-ray crystallography**

Crystals were mounted in inert oil and transferred to the cold gas stream of the diffractometer. Unit cell measurements and intensity data were collected at 200 K on a Bruker-AXS SMART 1 k CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXL program suite. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms.

**Synthesis of 1**

The synthesis was previously reported, however, crystals were grown from 4:1 hexane–toluene at −35 °C. Crystals are extremely air sensitive. Elemental Analysis, Calcd(%) for C44H39Li4O4Si4: C 64.99, H 9.92; Found (%): C 65.19, H 8.94%.

**Crystal structure data for 1**

C44H39Li4O4Si4 crystal size: 0.29 × 0.23 × 0.17 mm³, triclinic, P1, a = 10.713(2), b = 11.295(3), c = 11.483(2) Å, α = 99.865 (12), β = 108.105(11), γ = 97.319(13)°, V = 1276.8(5) Å³.
$T = 200(2)$ K, $Z = 1$, $\rho = 1.058$ Mg m$^{-3}$, $\mu(\lambda = 0.071073$ Å) = 4.4447 mm$^{-1}$, 14794 reflections collected, 6090 $R(\text{int}) = 0.0386$, $R_1 = 0.0577$ and $wR_2 = 0.1536$ using 4083 reflections with $I > 2\sigma(I)$.

**Synthesis of 2**

386 mg of 1 (0.505 mmol) and 300 mg of anhydrous NaCl (5.13 mmol) were mixed together in 3 mL of THF. The resulting solution was stirred for 48 h at room temperature. The THF was then removed in vacuo and then 3 mL of toluene were added. The LiCl was filtered off through celite and hexane was added to the filtrate (making 4:1 hexane–toluene) until a white precipitate (making 4:1 hexane–toluene) was as an inverse sandwich with two lithium atoms coordinating with NaCl in tetrahydrofuran leads to the formation of 2. Large colourless, block crystals suitable for X-ray diffraction were grown from 4:1 hexane–toluene (to avoid interference from excess coordinating solvents). Clearly, the structure of 1 is not a dilithio salt, as previously assumed. Considering the importance of this simple precursor and length of time it has been used, clear evidence of its structure surprisingly does not exist.

Scheme 1: Synthetic route to tetralithio salt 1 and sodium chain 2.

Based on previous NMR studies, the assumed structure of 1 was as an inverse sandwich with two lithium atoms coordinating in an $\eta^8$ fashion to the COT$''$ faces with the number of coordinating THF molecules variable between 1 and 3.4,6 In order to accurately identify the structure of 1 (and 2), it was first thoroughly dried under vacuum and then recrystallized from non-coordinating solvents. As the solvent can influence the molecular structure, the use of non-coordinating solvents during crystallization becomes important in obtaining a complex that mimics the bulk material.22 Our own analysis of 1 via $^1$H and $^7$Li NMR (Fig. S1 and S2, ESI†) is consistent with previous reports. In contrast, the solid-state studies clearly reveal a bis metal metallocene, indicating a high probability that the solid and solution states do not match. The single crystal X-ray data collected at 200 K (Fig. 2) reveal a tetrametallic structure consisting of two lithium ions sandwiched between two COT$''$ rings and two additional lithium atoms on the outer COT$''$ faces. Overall, complex 1 has $S_2$ symmetry.

The distance between the sandwiched lithium ions is 2.84 Å, which surprisingly falls within 0.1 Å of the M–M bond range of other multi-metallic metallocenes.10 Such a distance is longer than a typical lithium–lithium bond length (2.10–2.50 Å);23 however, longer bond lengths are known.24 Thus this suggests that intra-sandwiched Li atoms are not metal bonded, this is

![Fig. 2](image-url)
further confirmed by solid state NMR as well as computational studies (vide infra). The average distance between a sandwiched lithium and an outer lithium atom is 4.31 Å, which is considerably longer than the distance between the two COT" centroids (4.00 Å). In addition, the distance between the outer lithium ions is 8.17 Å. The eight bond angles within the COT" ring vary from 129.6 to 137.4° as would be expected due to the silyl substituents on the ring. The COT" ring also displays a kink or deviation from planarity. The exact reason for this is unclear, although two possibilities exist. First, while the outer lithium atoms coordinate in an η3 mode, the bridging lithium atoms coordinate asymmetrically to the COT" rings in both an η4 and η3 fashion. As a result one COT" carbon is left uncoordinated on each ring by an inner lithium ion. Secondly, each COT" ring effectively has three lithium atoms coordinating to it, with two on one face and one on the other face. A simple electron push–pull model then explains the small deviation from planarity. Lastly, one carbon on each THF molecule is disordered.

Fig. S3 (ESI†) depicts that 1 packs in an ordered manner and that all the molecules point in a single direction. Each unique unit cell contains one molecule of 1. In addition, the lattice displays an AB packing with respect to the crystallographic c axis. The closest intermolecular lithium–lithium distance is approximately 7.8 Å and the furthest is 9.0 Å.

In order to further confirm and validate the structural features solid-state 6/7Li, 29Si, and 13C magic-angle spinning (MAS) NMR experiments complemented the XRD studies of 1. The 13C cross-polarization (CP) MAS NMR spectrum (Fig. S4, ESI†) distinguishes seven (of eight) unique carbon resonances (97.1, 95.3, 94.9, 93.8, 91.7, 85.1, and 84.3 ppm) attributable to the COT" dianion carbons and confirms the local C1 symmetry (of the COT" ring). The resonances at 69.5, 66.5, and 26.4 ppm correspond to the THF carbons. Finally the low-frequency peaks at 3.0 and 2.3 ppm are characteristic of the methyl groups attached to the two crystallographically distinct silicon sites. The 29Si CPMAS NMR spectrum (Fig. S5, ESI†) exhibits only a single broad resonance at −2.4 ppm indicating inadequate resolution for the chemically similar Si1 and Si2.

Note, due to the extreme air-sensitivity of 1, a small amount of decomposition occurred during the studies as observed in the spectra (Fig. S4 and S5, ESI†). Fig. 3 displays the 6/7Li MAS NMR spectra of 1 obtained at 9.4 T using two-dimensional one-pulse processing.25 This processing method aligns the spinning sidebands in the indirect dimension of a 2D NMR spectrum and indicates the relative size of the quadrupolar coupling constants for the two Li sites. In contrast to the solution 7Li NMR studies, the solid-state spectra clearly reveal two sharp lithium resonances at −8.5 and −12.3 ppm (±0.1 ppm).

As the 7Li NMR spectrum also contains numerous spinning sidebands originating from the satellite transitions (±3/2 ↔ ±1/2) these were simulated using the SIMPSON program in order to extract the EFG tensor parameters at these lithium sites.26 Fig. 4 displays a comparison of the simulated and experimental 7Li satellite transition spectroscopy (SATRAS)27 spectra. By simulating this SATRAS spectrum, it was also possible to extract the magnitudes of the 7Li quadrupolar coupling constants (CQ) of...
135 ± 5 kHz (Li1) and 164 ± 5 kHz (Li2) and the respective quadrupolar asymmetry parameters ($\eta_Q$) of 0.90 ± 0.05 (same for both Li sites).

Gauge-including projector-augmented wave (GIPAW) DFT calculations$^{16,28}$ of the lithium electric field gradient and magnetic shielding tensors allowed for assignment of the spectral resonances to the lithium sites in the structure. The results are in good agreement with the experiment, although the quadrupolar coupling constants are overestimated; Li1, $C_Q = -196.1$ kHz and Li2, $C_Q = 258.2$ kHz. The calculated asymmetry parameters are also very close to the experimental ones at 0.989 and 0.941 for Li1 and Li2, respectively. In this case, the calculated chemical shifts (which were converted from the MS values with the use of an absolute shielding scale)$^{27}$ are in near quantitative agreement with the experiment. GIPAW DFT predicts chemical shifts of $-9.1$ ppm for the Li1 and $-13.7$ ppm for the Li2.

From these calculations we can reasonably assign the resonance at $-12.3$ ppm to the lithium ions inside the sandwich whereas the peak at $-8.5$ ppm corresponds to the lithium ions coordinated to the THF molecules. These chemical shifts are also consistent with the work of Johnels et al. which demonstrated that lithium ions in sandwich type complexes experience chemical shifts around $-12$ ppm whereas those bound to a single ring appear at approximately $-8$ ppm.$^{29}$ In contrast to the work of Johnels et al., the quadrupolar asymmetry parameters obtained, are far from axial symmetry (i.e. $\eta_Q = 0$). This highlights the fact that, unlike in Cp complexes, the lithium ions are not found in the center of the ring and instead coordinate in $\eta^3$ and $\eta^4$ fashions, as reproduced by our calculations.

In order to determine the possibility of a Li–Li bonding interaction, we also performed through-bond $^7$Li–$^7$Li heteronuclear double-quantum filtered experiments. There was not an observable signal, in agreement with the DFT calculations that predict a miniscule $J$-coupling constant of $-0.016$ Hz. This suggests that there is no bonding interaction between the lithium ions inside the rings. However, a lack of signal in these experiments does not unequivocally rule out some Li–Li interaction.

Previous studies have alluded to or demonstrated a fluxional behaviour between metal centres in similar systems.$^{10b,11,30}$ In order to probe dynamic behaviour of the lithium ions in structure 1, DFT calculations at the B3LYP/TZVP level of theory were conducted to obtain the energy minima and the corresponding transition states (Fig. 5). The calculated minimum energy structure has a very similar geometry to the X-ray structure of 1. The calculated value for the Li2–Li2a internuclear distance (3.10 Å) is longer than the value from the X-ray structure (2.84 Å). There is only a repulsive electrostatic interaction between these two lithium ions. The lithium ions inside the COT$^\prime$ sandwich exhibit weak covalent bonding with the carbon atoms of the COT$^\prime$ ligands (the corresponding Li–C bond orders are between 0.07 and 0.14). The NPA-derived charges of these two lithium atoms (+0.78 au) are consistent with this description of Li–COT$^\prime$ interactions. The transition structure corresponding to the concerted movement/rotation of two lithium ions inside the COT$^\prime$ sandwich was located. The calculated energy barrier for the circular rotation of the lithium ions around the COT$^\prime$ rings is 3.5 kcal mol$^{-1}$ (Fig. 5).

Based on periodic trends and the relative size difference between lithium and sodium cations, one would expect compound 2 to be isostructural with 1, yet unexpectedly, 2 forms long linear chains along the crystallographic $a$ axis (Fig. S6–S8, ESI†). Powder XRD evidence, in a previous report, indicates that lithium and sodium cations behave identically and form linear polymeric chains with cyclopentadienyl ligands.$^{7}$ The larger potassium, cesium, and rubidium derivatives form zig-zag chains, that interact with neighbouring chains. Potassium also forms the same type of zig-zag chains with $\eta^4$-bridging COT$^\prime$ rings.$^{31}$ The repeating units in the linear sodium chains are very different than the unit in tetrametallic 1. The structure of 2 (Fig. 6) contains a COT$^\prime$ ring with a sodium ion binding $\eta^3$ to each face as an inverse sandwich. Two THF molecules coordinate to each sodium centre, thus bridging it to another sodium

Fig. 5 DFT-calculated structures of the energy minimum and the transition state for 1. Hydrogen atoms omitted for clarity. The red arrow indicates lithium atomic movements that correspond to the imaginary frequency mode (70 cm$^{-1}$) of the transition state.

Fig. 6 X-ray structure of 2. Hydrogen atoms omitted for clarity. Na = orange, Si = green, O = red. Na1–Na1a 3.86 Å, Na1–Na1 3.53 Å, Na1–COT$^\prime$ centroid 1.93 Å, O1–O2 3.17 Å, Si1–C2 1.86 Å, Si1–C6 1.88 Å, COT$^\prime$ centroid–COT$^\prime$ centroid 7.39 Å, Na1–COT$^\prime$ centroid–Na1a 180.0°, Na1–O1–Na1a 94.9°, Na1–O2–Na1a 97.4°, Na1–C1–Na1a 93.6, O1–Na1–O2 83.8°.
ion to complete the repeating unit. The structure also exhibits local $C_{3v}$ symmetry.

The Na1–Na1a distance is 3.86 Å and is longer than the distance between the sodium atoms coordinating to the THF molecules (Na1–Na1, 3.53 Å) because of the electronic repulsion from the dianionic COT’’ ring versus the neutral THF molecules. The COT’’ $\text{centroid - COT’’ } \text{centroid}$ distance in 2 (7.39 Å) is logically longer than in 1 because of the absence of solvent between the COT’’ rings in 1. The bond angles in the COT’’ ring deviate slightly from the ideal 135° (131.53 to 136.80°), again attributable to the two silyl group substituents. These groups also account for the approximate 2.5° difference between the two $\text{Na - Ox - Na}$ bonds ($x = 1$ or 2). Clearly, the silyl groups disallow 2 from being perfectly $C_{3v}$, but there is a C2 axis and mirror plane along the crystallographic c axis. Compound 2 is perfectly linear along the crystallographic a axis exemplified by the 180° angle between Na1–COT’’ $\text{centroid - Na1a}$. The chains form an AB packing arrangement and the inter-chain distance as measured between two sodium ions are 10.1 Å (between 2 chains in the A layer) and 11.1 Å (between 2 chains in the A and B layer). Fig. S6–S8(ESH) best display this arrangement. To allow for a tighter lattice the silyl groups orient upwards in one layer and down on the adjacent layer looking down the a axis. The unique crystallographic cell contains four monomeric Na–COT’’ units corresponding to 4 chains.

Conclusion

In summary, after 22 years the elusive structure of Li2COT’’ is finally known as tetralithio salt 1. The discrepancy between the solid and solution phase studies point toward an ion-paired intermediate in solution. More importantly, the solid-state identity of 1 will eliminate the need to generate it in situ, thereby reducing the propensity for unwanted side products (from the use of "BuLi"). In general, this may also open new applications for the COT/COT’’ ligand outside of molecular chains. For instance, recent reports demonstrate the first organo-f M(COT)L (M = Er, Np, Dy; L = Cp* or COT) make interesting single-molecule magnets (SMMs), and more broadly, organometallic SMMs are relatively unexplored. Also, a 3.5 kcal mol$^{-1}$ rotational energy barrier between the inner lithium atoms points to a possibility of having a rich dynamic behaviour in such sandwich systems.

This report also marks the first definitive evidence for multiple alkali metals sandwiched between decks in a metallocene. Of note, Edelmann et al. previously proposed a linear polymeric (K$_2$DME$_2$COT’’)$_n$ structure based on combustion analysis and solution $^1$H NMR. However, other structures are also consistent with the data, for instance (DME)K(COT’’)$_2$K(DME), for which there is precedent in similar lithium versions. In contrast to 1, 2 appears as an inverse sandwich unit linked by two THF molecules.

In conjunction with other reports, incrementally altering the ionic radius of a metal allows for fine-tuning of the molecular architecture. The monocationic radius of lithium is 68 pm, sodium is 95 pm and potassium is 133 pm. These values correspond to sandwich structures of discrete molecules (Li), linear chains (Na), and intermingling zig-zag chains (K). Pinpointing the exact number at which each structural transition occurs is difficult. However, based on the ionic radii in other examples of multimetallic metallocenes (involving COT and Cp), we can reasonably assume transition metals can form such sandwich structures while lanthanide and actinides preferentially could form linear systems.

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Notes and references
