Multidecker sandwich compounds assembled into nano-rings

Sandwich compounds are molecules in which two planar molecular rings sandwich a metal ion ‘filling’ between them. The chemistry of these compounds has been extended by the assembly of nano-rings from 18 identical sandwich-type building blocks.

The project

Chemical structures known as sandwich complexes generally consist of two planar aromatic ligands (aromatic ligands) on either side of a central metal ion. This situation is reminiscent of a sandwich, with the flat aromatic ligands acting like two slices of bread and the metal atom like a filling. Sandwich complexes are a cornerstone of modern organometallic chemistry. Since the 1950s, these molecules, particularly ferrocene, which consists of an iron atom and two cyclopentadienyl ligands (rings made of five atoms), have had an important role in many applications, including synthesis, catalysis, electrochemistry and polymer chemistry.

Imagine adding layers of filling and bread to a sandwich to create triple-decker and multidecker sandwiches (gravity permitting). Similarly, sandwich complexes have previously been constructed as triple- and quadruple-decker compounds. Longer stacks approaching one-dimensional molecular wires have also been reported. But, what about assembling a multidecker sandwich in a circular form?

The discovery

Recently, we assembled the first quadruple-decker sandwich complexes that comprised metals from the lanthanide family of elements, and realized that these stacks deviate from linearity by about 20 degrees for the central sandwich unit. Assuming that the magnitude and unidirectional character of this bending, which is caused by asymmetric aromatic ligands, is retained when more units are added, 18 units should form a circular system. We realized that a ‘half-sandwich’ complex, consisting of just one planar aromatic ligand and one metal ion, covered by solvent molecules on the open side, would be a suitable precursor.

When we removed solvent molecules from the half-sandwich complex, the remaining compounds self-assembled into the predicted 18-membered ring structure. We call this new class of compounds cyclocenes. We used various metals ions with similar sizes and charges, and found that rings can form from complexes containing the lanthanides samarium (Fig. 1a) or europium, or the alkaline-earth metal strontium. And, remarkably, rings made with europium ions (Fig. 1b) show orange luminescence at room temperature. However, not all solvent molecules could be removed from half sandwiches featuring ytterbium, resulting in a completely different structural motif. Quantum-chemical calculations using TURBOMOLE (https://turbomole.org) confirmed that the specific shape of the aromatic ligand defines the angle between half-sandwich units, and showed that short-range interactions, known as dispersive interactions, contribute a major part of the bond energy between them. Calculations also explained why a ring structure, and not a one-dimensional zigzag chain, is formed: a crucial amount of binding energy that is gained during ring closure is not gained when a non-cyclic structure is formed.

Future directions

Previously, research into functional multidecker compounds has been restricted by the strict structural limitation to linear motifs. With a pathway towards cyclic multidecker sandwich compounds, such research can now be extended towards finding highly functional complexes, nano-rings or switchable molecular gateways and channels. Given the luminescence of europium-containing rings, future circular rings might have electroluminescent properties, for example. Our design approach is based on the structurally induced bending of self-assembled chains of the isolated half-sandwich units. Therefore, the concept could be transferred to other metals and ligands, further increasing the synthetic scope and the range of possible applications for sandwich nano-rings. Cyclocenes could thus become a crucial part of the materials-science toolbox.

Realistically, we have made just the first step in the synthesis of a new class of compounds. As is always the case in chemical synthesis, surprises (good and bad) will come with further exploration. Thus, it is too early to discuss the final impact of our work. Nevertheless, having synthesized this new class of cyclic sandwich compounds, we now aim to build rings of different sizes and to encapsulate large molecules inside the rings. We also plan to study more of the cyclocenes’ physical properties.

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The authors present a new class of organometallic molecule, showing that multidecker complexes can cyclize into nano-rings. The work is the culmination of years of effort by the inorganic community towards ever-larger multidecker sandwich complexes. Its elegance lies in a careful synthetic protocol for isolating complexes that, to my eye, would be extremely hard to handle and characterize. These results should spark a hunt for similar compounds containing different elements. (CC BY 4.0)

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Figure 1 | Structures of circular sandwich compounds. Sandwich compounds comprise a metal ion sandwiched between two planar molecular rings (aromatic ligands). Here, circular rings dubbed cyclocenes have been made from multidecker sandwich complexes, by stacking together half sandwiches comprising just the metal ion and one aromatic ligand. The molecular structures of these 18-membered cyclocenes are shown for two centre metals and from different perspectives to better visualize the circular structures (although they exhibit the same arrangement of half-sandwich units). Hydrogen atoms are omitted, and SiPr3-groups of the aromatic ligands are displayed near-transparently for clarity. a. The samarium-containing compound (2-Sm); samarium is shown in green. b. The europium-containing compound (2-Eu); europium is shown in orange.

We explored half-sandwich complexes containing lanthanides because little was known about them. A key factor was the use of substituted cyclooctatetraenes (eight-membered aromatic ligands), which we previously introduced for, among other things, synthesizing quadruple-decker complexes. These ligands enhance the solubility of the final product and induce the bending needed to form cyclocenes. Manfred Kappes's group in Karlsruhe enabled the investigation of the rings’ photophysical properties. A crucial question was what drives ring formation, and quantum-chemical calculations by F.W.’s group in Marburg showed that it is driven by the gain in energy brought about by ring closure. Refining the structures of the rings, obtained through single-crystal X-ray crystallography, took several months, owing to solvent molecules in the ring centre and the disorder of atoms along the outer rim. Furthermore, the calculations of the properties of these huge ring systems were made possible with only moderate computer resources and reasonable energy consumption, thanks to highly efficient modern quantum-chemistry software (such as TURBOMOLE; https://turbomole.org).

P.R. and F.W.

It’s not often that molecules stand out in their own right, rather than being useful components or reagents in a wider scheme, but these cyclic sandwich compounds certainly do. The way in which they are rooted in metallocenes — familiar to all chemists — but bend, literally, the expected linear geometry to make rings is satisfying and striking in equal measure.

Claire Hansell, Senior Editor and Team Manager, Nature