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Isomerization of a Lanthanide Complex using a Humming Top Guest Template: a Solid-to-Solid Reaction[†]

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SbPh₃Cl₂ is used to effect a dramatic rearrangement of the ligand sphere and “pancake bonding” in Ce(hfac)₃(5′-Br-pyDTDA)₂, by forming a 2:1 host-guest complex supported by numerous non-covalent contacts (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato-; 5′-Br-pyDTDA = 4-(5′-bromopyrid-2′-yl)-1,2,3,5-dithiadiazolyl). The host-guest complex forms quantitatively in a solvent-free solid-to-solid reaction and crystals are grown by sublimation.

Cram’s seminal work on cation recognition established the *principle of preorganization* as a pillar of contemporary supramolecular chemistry. While crown ethers and cryptands, pioneered by Pedersen¹ and Lehn,² exploit the *principle of complementarity*,³ these molecules do not have a rigid cavity and must change to an open conformation to accommodate an alkali metal cation. Cram showed that a preorganized host, with a geometry that requires little or no rearrangement, optimizes the stability of the host-guest species.⁴ Preorganization has since been used effectively for encapsulation of neutral molecules with a wide variety of applications such as waste stream remediation⁵ and drug delivery.⁶

Consider, however, the advantages of an opposite approach, of employing the host-guest formation to drive reorganization of the host. It is then possible to use co-crystallization of two molecules to deliberately effect changes in one or both of them. In this way, we can induce molecular isomerism,⁷⁻⁹ tautomerism,¹⁰ and formation of other species that might not otherwise be stable.¹¹ Since the physical properties (e.g., conductivity, magnetism, absorption spectrum) are often closely related to molecular geometry and intermolecular contacts, using a guest to template a host (or vice versa) is an attractive strategy for creating new materials with technologically relevant properties that can be altered and tuned. An energetic price must be paid for the molecular rearrangement, and an arsenal of weak, non-covalent

interactions may be required to stabilize the host-guest species. Once compatible reactants are found, however, reorganization and co-crystallization can occur easily, under mild conditions, and even as a direct reaction between two solids.

Herein, we report a representative example of a new family of co-crystals prepared by gentle heating of the solid host and guest components in a stoichiometric ratio. The host molecule (**1**) undergoes significant rearrangement of its coordination sphere, and of its intermolecular contacts, to accommodate a half molar equivalent of the guest. The solid-to-solid reaction proceeds quantitatively and the thermally stable 2:1 host-guest complex (**2**) is volatile enough to be sublimed, generating lustrous, red single crystals.

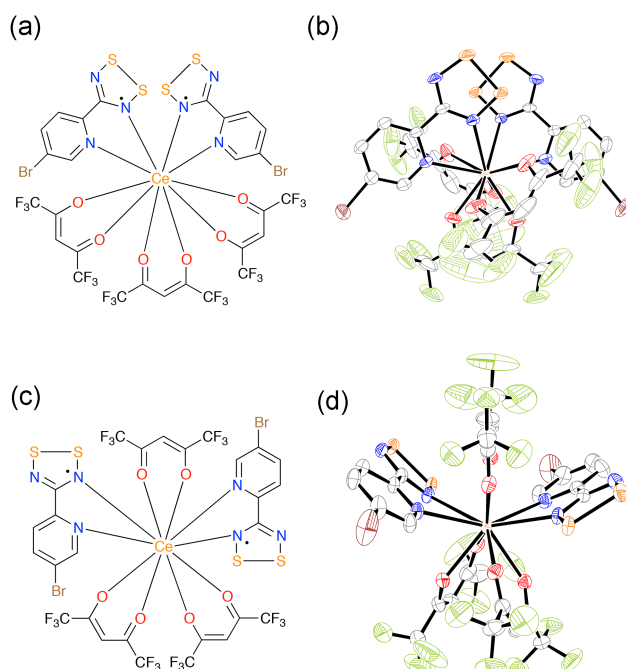


Fig. 1 Line drawings and ORTEP representations of the molecular structure of Ce(hfac)₃(5′-Br-pyDTDA)₂ as found in **1** (a) & (b) and in **2** (c) and (d). Relative ligand positions and orientations are dramatically different in the two isomers.

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[†]Electronic Supplementary Information (ESI) available: synthetic and crystallographic details for **1** and **2**; Tables S1-S3. See DOI: 10.1039/x0xx00000x

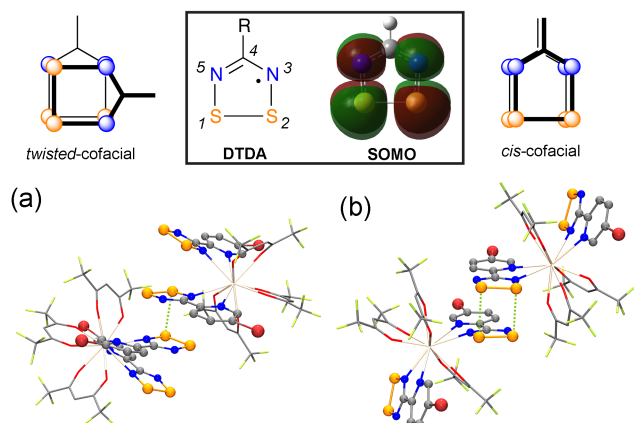


Fig. 2 Top: Cartoon representations of generic "pancake bonding" motifs, a generic DTDA heterocycle, and the singly occupied molecular orbital (SOMO). Bottom: Excerpts from the crystal structures of (a) **1** and of (b) **2** illustrating the "pancake bonding"; green dotted lines used to highlight S...S contacts.

Supramolecular interactions supporting the host-guest structure include electrostatic contacts, "pancake bonding" of radical moieties, and halogen-halogen contacts.

The host molecule, $\text{Ce}(\text{hfac})_3(5'\text{-Br-pyDTDA})_2$ **1**, is a 10-coordinate complex of Ce(III) with two 5'-Br-pyDTDA ligands¹² (Fig.1). The paramagnetic DTDA moiety has a propensity to form diamagnetic [DTDA]₂ π -stacked dimers via "pancake bonding"¹³ (Fig.2) which can be regarded as a supramolecular synthon.¹⁴⁻¹⁶ In the structure of **1**, each of the coordinated 5'-Br-pyDTDA ligands is engaged in "pancake bonding" with a neighbouring molecule. The *twisted cofacial* geometry observed for the "pancake bonding" in **1** is a motif in which the two DTDA rings are rotated by $\sim 90^\circ$ with respect to one another (Fig.2), one of four common orientations¹⁷ providing optimal overlap of the two DTDA singly occupied molecular orbitals (SOMOs). The arrangement of the 5'-Br-pyDTDA ligands about the Ce(III) centre is unusual, however. The DTDA heterocycles of the two coordinated ligands are partially eclipsed in what might appear to be a *twisted cofacial* arrangement, but the staggered geometry and long distances are inconsistent with "pancake bonding" (Table S3).

$[\text{Ce}(\text{hfac})_3(5'\text{-Br-pyDTDA})_2] \cdot 0.5[\text{SbPh}_3\text{Cl}_2]$ **2**, the host-guest complex, is formed quantitatively by heating a finely ground stoichiometric mixture of **1** and SbPh_3Cl_2 under reduced

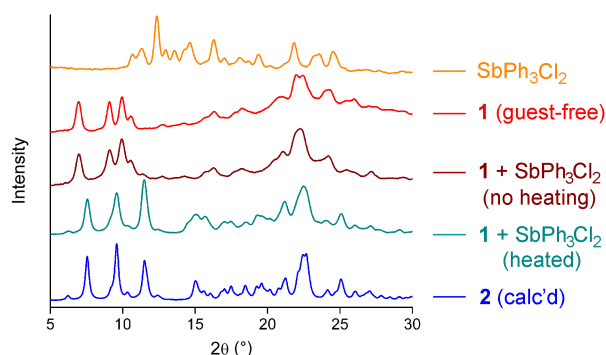


Fig. 3 PXRD intensities (top to bottom): guest SbPh_3Cl_2 ; guest-free host **1**; finely ground stoichiometric mixture of SbPh_3Cl_2 (guest) and **1** (guest-free host); heated mixture, clearly showing conversion to **2**; calculated powder pattern of **2** from single crystal analysis.

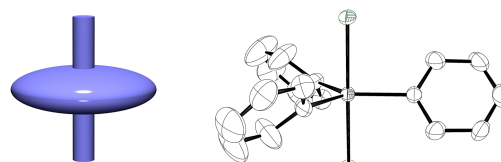


Fig. 4 Right: Cartoon of a generic "humming top" shape. Left: ORTEP representation of SbPh_3Cl_2 as found in **2**.

pressure. Following the reaction by PXRD (Fig.3), it is clear that an unreacted admixture of components exists after grinding for 2h, but that after heating for 1 week (110°C ; 10^{-1} Torr), the solid-to-solid reaction has essentially gone to completion. Single crystals of **2** are readily formed by sublimation. The volatile host-guest complex appears to sublime quantitatively, with no evidence of decomposition, or of co-sublimed starting materials.

As illustrated in Fig. 1, a dramatic rearrangement of the ligand sphere of the host $\text{Ce}(\text{hfac})_3(5'\text{-Br-pyDTDA})_2$ occurs in order to accommodate the SbPh_3Cl_2 guest. In **2**, the 5'-Br-pyDTDA ligands form "pancake bonds" with neighbouring complexes, but unlike **1**, the [5'-Br-pyDTDA]₂ pairs adopt a *cis-cofacial* geometry in which the two DTDA rings are aligned in the same direction ($\sim 0^\circ$ rotation with respect to one another, Fig.2). Thus, rearrangement of the dimers, involving breaking and re-making of "pancake bonds", must also occur in order to accommodate the guest. It is worth noting that reversible making/breaking of "pancake bonds" has been observed as a function of temperature in the related $\text{La}(\text{hfac})_3(\text{pyDTDA})_2$ complex.¹⁸

The guest SbPh_3Cl_2 has a molecular shape that can be described as a "humming top" structure (Fig.4),[†] and is therefore a good candidate for the design of inclusion complexes. The "humming top" is the simplest shape in a well-known family of "wheel-and-axle" molecules, which act as versatile hosts owing to their awkward shapes. Co-crystallization with another small molecule helps to optimize crystal packing, thus "wheel-and-axle" molecules readily form solid clathrates.²⁰ As might be expected, another feature common to molecules that behave as versatile hosts is polymorphism of their non-porous, single-component structures.²¹⁻²⁶ Both polymorphism and the tendency to form inclusion complexes apparently stem from the less than ideal crystal packing of the single-component species. At least three polymorphs of SbPh_3Cl_2 are known,²⁷⁻²⁹ as well as structures of at least three co-crystals,³⁰⁻³² providing evidence that SbPh_3Cl_2 behaves as anticipated. In **2**, SbPh_3Cl_2 is both a guest and a template facilitating the rearrangement of the host structure.

Wheel-and-axle hosts and their clathrates are frequently designed with specific intermolecular interactions, such as halogen bonding³³ and hydrogen bonding.³⁴ Examining the structure of **2**, it is possible to identify several important host-guest and host-host interactions that, in addition to van der Waals forces, contribute favourably to the co-crystalline arrangement and are likely to help drive the solid-to-solid reaction (Fig.5).

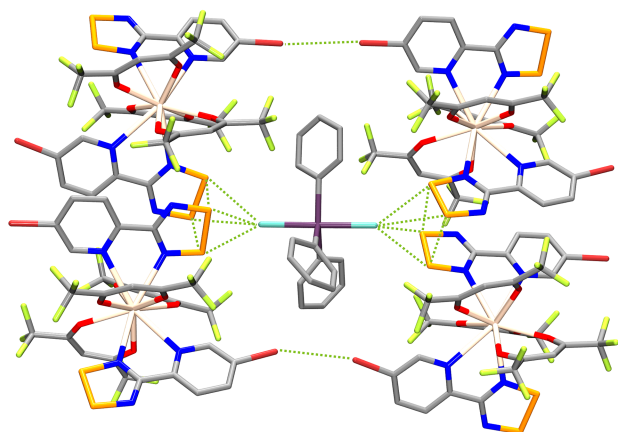


Fig. 5 Excerpt from the crystal structure of **2**, illustrating important non-covalent interactions (green dashed lines): S...S contacts related to "pancake bonding", electrostatic Cl...S contacts, and Br...Br contacts.

Close contacts between the Cl^- atoms of SbPh_3Cl_2 and the S^+ atoms of the "pancake bonded" DTDA moieties can clearly be identified in **2**. Similar electrostatic contacts are very common in other crystalline DTDA-based compounds,³⁵⁻³⁷ and are observed in chloride salts of closed-shell DTDA⁺ cations³⁸ as well as mixed valent co-crystals of DTDA radicals and cation chlorides.^{39, 40}

Evidently, *cis-cofacial* "pancake bonds" also contribute to the lattice enthalpy of **2**, however they are formed at the expense of *twisted co-facial* "pancake bonds" in **1** (Fig. 3). It is worth noting, however, that the number of $\text{Cl}^- \dots \text{S}^+$ contacts in **2** is optimized by the *cis-cofacial* dimerization motif (Fig. 5).

In **2**, the large, non-polar phenyl rings of SbPh_3Cl_2 occupy space between the $-\text{CF}_3$ groups of host molecules, acting as a buffer between non-polarizable F atoms. Although anion- π interactions are known to stabilize inclusion compounds,⁴¹ specific contacts between F^- atoms and phenyl rings are not immediately obvious in **2**. Any proximity of these groups is likely a packing requirement, not a contact of significance.

Finally, Br...Br contacts between host molecules, well within the sum of van der Waals radii (Table S3), are apparent in **2** (Fig. 5). Similar halogen-halogen contacts (excluding F...F) are established supramolecular synthons,⁴²⁻⁴⁴ successfully employed in crystal engineering.⁴⁵⁻⁴⁹ The proximity and directionality of the Br...Br contacts in **2** support their identification as another factor contributing to the stability of the host-guest complex.

This work demonstrates that the use of irregular molecular shapes (e.g., "humming top") in the design of supramolecular solids can be a more powerful strategy than once imagined. Wheel-and-axle species can be used not only to promote co-crystallization but to template a chemical change, such as isomerisation, in another species. Once complementary functional groups are deliberately introduced to promote multiple weak interactions in the binary solid, it is possible to compensate for the energetic cost of reorganization.

This work also provides a valuable demonstration of a chemical change (isomerization) in a lanthanide complex, achieved easily, reproducibly, and quantitatively under mild conditions, without solvents. Annealing-assisted solid-state

reactions can be useful for accessing enantiomers, polymorphs and clathrates that are not formed by traditional solution-based techniques.^{50, 51} Since the physical properties of many lanthanide complexes (e.g., magnetism, luminescence) are quite sensitive to ligand geometry,^{52, 53} rearrangement of the ligand sphere might be used to optimize lanthanide-based material functionality. Further development of such systems may lead to a new class of switchable materials, where physical properties of a solid, defined by the lanthanide cation and its immediate coordination sphere, may be controlled by another, chemically inert, molecular species.

Notes and references

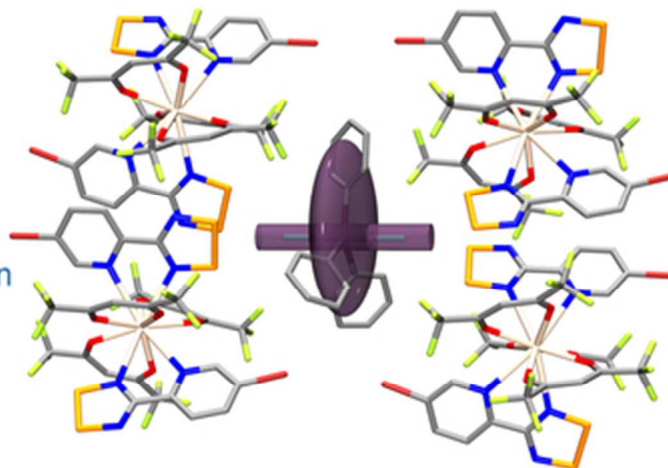
- ‡ The descriptive term, "humming top" structure, refers to the general shape of the molecule and is not intended to imply rotor-like motion.
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Humming Top
Guest Template

Electrostatic,
Pancake Bond,
&
Halogen-halogen
Contacts

Solvent-Free
Synthesis



39x19mm (300 x 300 DPI)