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Self-assembly of [Sn(OPMe₃)₃(CF₃SO₃)₂]₆ metallocyclic Sn(ɪɪ) hexamer stacks with CF₃-lined channel interiors†

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[Sn(OPMe₃)₃(CF₃SO₃)₂]₆ (**1**) self-assembles to form a highly unusual hexagonal metallocyclic array with bridging CF₃SO₃⁻ groups. The discrete hexamers stack along the *c*-axis to form hydrophobic CF₃-lined channels with an F···F distance across the channel diameter of 0.8 nm. This Sn(ɪɪ) complex is different from its Pb(ɪɪ) analogue, which instead forms a discrete, doubly CF₃SO₃-bridged dimer of formula, [{Pb(OPMe₃)₃(CF₃SO₃)}₂(μ-CF₃SO₃)₂] (**3**).

Main group chemistry has attracted considerable research effort in the last two decades in response to the desire for tailored precursors for p-block materials deposition, metal-free catalysts, and porous coordination polymers, in addition to exploring new classes of compounds and reaction chemistry.[1]

While many of the reported p-block complexes are derived from main group halide precursors with secondary bonding interactions to neutral group 15 and 16 donor ligands, replacing the halide with more weakly coordinating (less Lewis basic) anions, such as CF₃SO₃⁻, and the bulky fluorous tetra-arylborates and fluorous aluminates, *etc.*, can provide an entry to highly Lewis acidic p-block cations that are of interest in organic/organometallic chemistry,[2–5] while delocalised fluorous anions including CF₃SO₃⁻, SiF₆²⁻, PF₆⁻, *etc.*, can be used to lower the dimensionality of porous coordination polymers and metal–organic frameworks (MOFs).[6–9] Weakly coordinating anions, in which the negative charge is delocalised and diffuse, including triflate, fluorous tetra-arylborates and

fluorous aluminates, amongst others, have attracted considerable research effort in the field of organometallic chemistry.[2–5] They aid solubility in low polarity solvents and can facilitate stabilisation of highly reactive species such as the univalent [Ga(PPh₃)₃]⁺,[10] and [Ag(P₄)₂]⁺ cations,[11] as well as unusual homoleptic phosphine[12] or thioether complexes with alkali metal cations.[13]

The CF₃SO₃⁻ group has been used extensively as a weakly coordinating anion in work developing group 14 chemistry and cations thereof. Notable examples include the stabilisation of 'naked' Ge(ɪɪ) dications encapsulated within 2.2.2-cryptand,[14] Ge(ɪɪ) dications bearing N-heterocyclic carbenes,[15] and pnictines,[16] as well as tetravalent group 14 fluoride species with soft pnictine ligands.[17] We have also observed that the CF₃SO₃⁻ anion can engage in a range of different secondary interactions that play an important role in determining the speciation and structures adopted. For example, in [In(OTf)₂(Ph₃PO)₄]–[In{(OH₂)₄(OTf)₄}(Ph₃PO)₂], which forms a weakly associated 24-membered pseudo-macrocyclic ring *via* H-bonding between the coordinated water molecules and the CF₃SO₃⁻ anions.[18] In view of these observations, we became interested to investigate the coordination chemistry of the divalent group 14 ions (Ge, Sn, Pb) with the hard and sterically compact OPMe₃ ligand.

Reaction of Sn(CF₃SO₃)₂ with three mol equiv. of OPMe₃ in a weakly coordinating solvent such as CH₂Cl₂ or MeCN readily leads to the formation of a colourless crystalline solid, Sn(OPMe₃)₃(CF₃SO₃)₂, in high yield. Spectroscopic data for this species are presented in Fig. S3–S5 (ESI†) and discussed below. However, to probe the role of the CF₃SO₃⁻, single crystals suitable for X-ray analysis were grown either by diffusion of hexane into a CH₂Cl₂ solution or by vapour diffusion of Et₂O into an MeCN or MeNO₂, solution with several crystals grown from different batches and solvents all producing the same crystalline form.

The material crystallises in the trigonal space group (*P3̄*) and the structure determination shows that it self-assembles into discrete hexamers, [Sn(OPMe₃)₃(CF₃SO₃)₂]₆ (**1**) (Fig. 1(a))

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† Electronic supplementary information (ESI) available: Full experimental, spectroscopic and microanalytical data for the new complexes, together with the X-ray crystallographic parameters and simulated and experimental powder X-ray patterns for the Sn(ɪɪ) hexamer. Experimental methods and characterisation data are provided in the ESI, along with the crystallographic parameters (Table S1), alternative views of the structure of [Sn(OPMe₃)₃(CF₃SO₃)₂]₆ (Fig. S1), simulated and experimental PXRD patterns for [Sn(OPMe₃)₃(CF₃SO₃)₂]₆ (Fig. S2). Cif files for the crystal structures are available from the Cambridge Crystallographic Data Centre with CCDC numbers 2169639 ([Sn(OPMe₃)₃(CF₃SO₃)₂]₆, **1**) and 2169640 ([{Pb(OPMe₃)₃}₂(CF₃SO₃)(μ-CF₃SO₃)₂], **3**). For ESI and crystallographic data in CIF or other electronic format see DOI: **https://doi.org/10.1039/d2ce01029a**
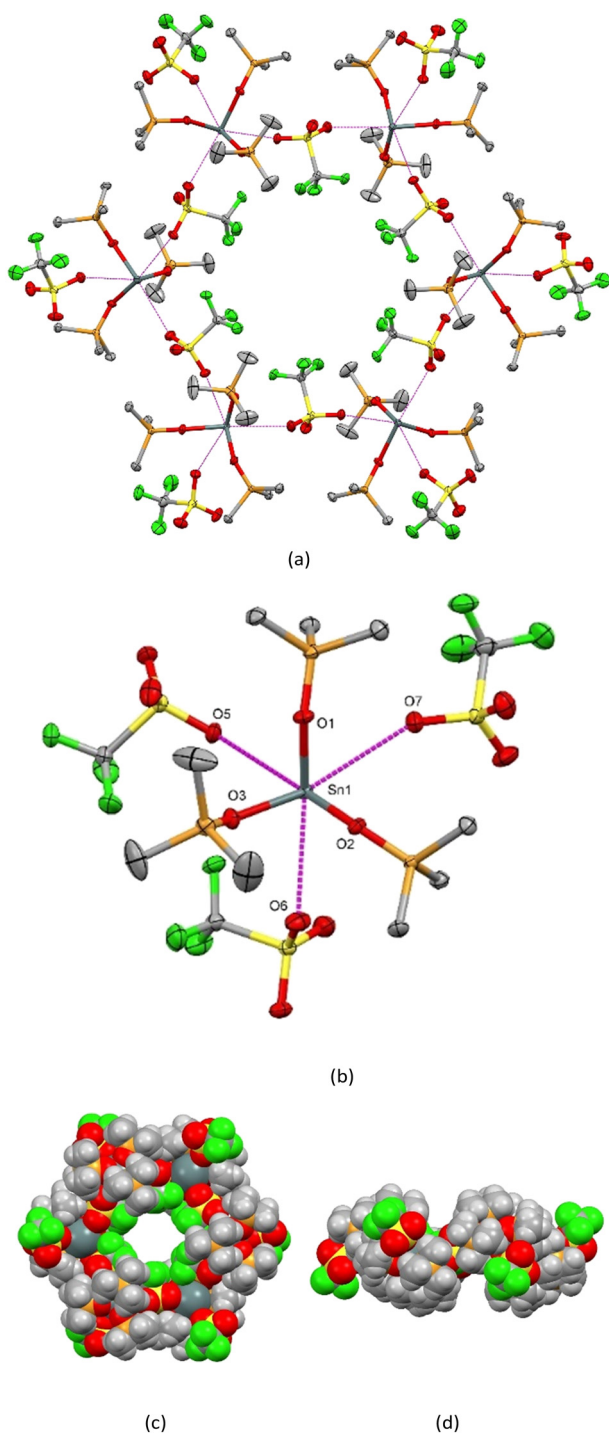
Fig. 1 (a) View of the hexameric assembly adopted by [Sn(OPMe$_3$)$_3$(CF$_3$SO$_3$)$_2$]$_6$ (**1**) *via* the bridging CF$_3$SO$_3^-$ groups; (b) the coordination environment at Sn(II) with the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å): Sn1–O1 = 2.1557(11), Sn1–O2 = 2.1670(10), Sn1–O3 = 2.0943(11), Sn1···O5 = 2.8578(12) (bridging), Sn1···O6 = 3.0277(13) (bridging), Sn1···O7 = 3.0822(12) (terminal); selected bond angles (°): O1–Sn1–O2 = 82.15(4), O1–Sn1–O3 = 85.97(4), O2–Sn1–O3 = 87.49(4); (c) space-filling diagram of a discrete hexamer – top view; (d) space-filling diagram of a discrete hexamer – edge view.

comprising six pseudo-octahedrally coordinated Sn(II) centres with three mutually *fac* OPMe$_3$ ligands (d(Sn–OPMe$_3$) = 2.094(1), 2.156(2), 2.167(1) Å) and three weakly bound, CF$_3$-SO$_3^-$ groups (Fig. 1(b)). Two of the triflates bridge between adjacent Sn centres to form the cyclic arrangement (d(Sn···OO$_2$SCF$_3$) = 2.858(1), 3.028(2) Å), while the third is bonded terminally (d(Sn···OO$_2$SCF$_3$) = 3.082(1) Å).

Notably, the CF$_3$ groups from the six bridging CF$_3$SO$_3^-$ anions all point towards the central void of the metallocyclic hexamer, with the F···F distance across the void diameter being 8.019(2) Å (ESI† Fig. S1). These hexamers stack along the crystallographic *c*-axis, resulting in a structure with hydrophobic CF$_3$-lined nanochannels. There are no significant interactions between the hexamers. The structure determination showed the void to contain ~1 disordered hexane molecule per hexamer unit. The crystal has a void volume of 6.1% determined by PLATON.[19] Brunauer–Emmett–Teller (BET) surface area analysis performed on compound (**1**) after heating the powdered samples *in vacuo* at 80 °C overnight revealed no appreciable N$_2$ sorption.

Although the cyclic hexamer is very unusual, it is readily reproduced from different product batches and *via* crystallisation from different solvent systems. There is no evidence for other polymorphs and powder X-ray diffraction from the bulk product gives a good phase match to the pattern simulated from the single crystal structure (ESI† Fig. S2).

The corresponding Ge(II) and Pb(II) complexes, M(OPMe$_3$)$_3$(CF$_3$SO$_3$)$_2$, were also prepared; the former from GeCl$_2$(dioxane), Me$_3$SiO$_3$SCF$_3$ and OPMe$_3$ in a 1:2:3 molar ratio, and the latter directly from Pb(CF$_3$SO$_3$)$_2$ and 3 mol equiv. of OPMe$_3$. The Ge(OPMe$_3$)$_3$(CF$_3$SO$_3$)$_2$ (**2**) is a low-melting, waxy solid, therefore it was not possible to obtain diffraction data for this compound. Its spectroscopic and microanalytical data are consistent with the formulation shown (Fig. S4†), although it is not possible to confirm from the spectra whether the CF$_3$-SO$_3^-$ groups are coordinated. In the case of Pb(II), a white powdered solid was isolated and assigned as [{Pb(OPMe$_3$)$_3$(CF$_3$-SO$_3$)}$_2$(μ-CF$_3$SO$_3$)$_2$] (**3**) based on its X-ray crystal structure (below) and elemental analysis, with solution NMR spectroscopic data also consistent with this (Fig. S5†). Despite the stoichiometry of the product being the same as for the Sn(II) analogue, the X-ray crystal determination reveals that it adopts a very different structure from the Sn(II) hexamer.

In this case the Pb(II) complex is a discrete dimer with two CF$_3$SO$_3^-$ bridges (Fig. 2(a)), and with distorted octahedral coordination at each Pb centre *via* three OPMe$_3$ ligands (d(Pb–OPMe$_3$) = 2.3218(17), 2.3295(17), 2.3628(18) Å), and three longer O-bound CF$_3$SO$_3^-$ groups (two μ^2-bridging and one terminal) located around 2.8–3.0 Å from the Pb atoms. Fig. 2(b) shows the packing arrangement in the *bc*-plane, but illustrating that the triflate CF$_3$ groups decorate the upper and lower surfaces at the interfaces between the layers.

Solution ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra (Fig. S3–S5†) for the complexes dissolved in CD$_2$Cl$_2$ (for **1** and **2**) or CD$_3$CN (for **3**) each show only one OPMe$_3$ environment, with the ^{31}P{^{1}H} chemical shifts showing a marginal low frequency
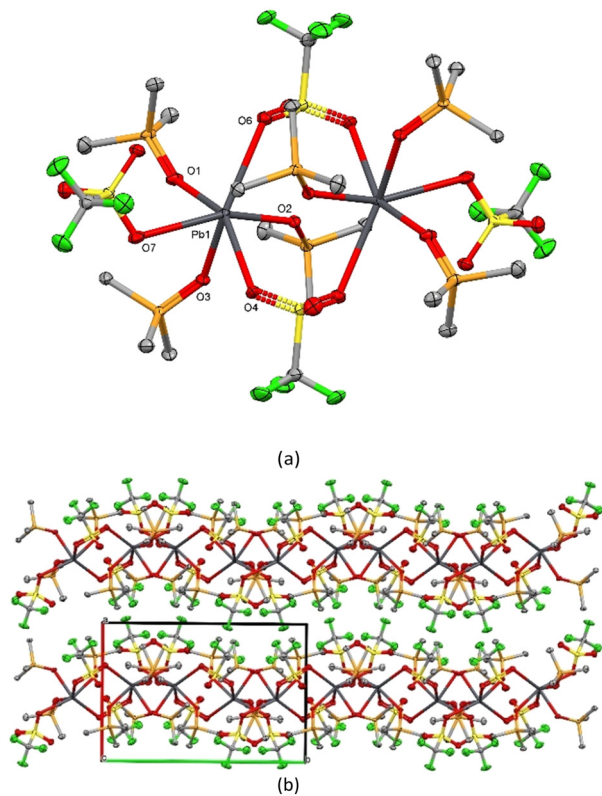
Fig. 2 (a) View of the structure of the [{Pb(OPMe₃)₃(CF₃SO₃)}₂(μ-CF₃SO₃)₂] dimer (**3**) with the atom labelling scheme. Selected bond lengths (Å): Pb1–O1 = 2.3628(18), Pb1–O2 = 2.3295(17), Pb1–O3 = 2.3218(17), Pb1–O4 = 2.7325(19), Pb1⋯O6 = 2.889(2) Pb1⋯O7 = 2.888(2). Selected bond angles (°): O1–Pb1–O2 = 97.35(6), O1–Pb1–O3 = 76.97(6), O2–Pb1–O3 = 80.09(6); (b) view of the *bc* plane showing the CF₃ groups aligned on the top and bottom surfaces.

shift upon going down group 14 from (**2**; Ge) → (**1**; Sn) → (**3**; Pb). The ^{19}F$\{^1$H$\}$ NMR shifts are sharp singlets at *ca.* −79 ppm in all three cases, consistent with ionic $CF_3SO_3^-$,[16] suggesting triflate dissociation in solution. The ^{119}Sn NMR resonance for (**1**) occurs at −793 ppm, similar to the chemical shifts reported for Sn(II) phosphines and phosphine chalcogenides with SbF_6^- anions.[20]

The formation of the [Sn(OPMe₃)₃(CF₃SO₃)₂]₆ metallocycle identified in this work was very unexpected and the weakly coordinating $CF_3SO_3^-$ linkers clearly play an important role in its assembly. Very recently Itoh and co-workers described a series of fluorous oligoamide nanorings with diameters ranging from 0.9–1.9 nm, which undergo supramolecular polymerisation in bilayer membranes forming nanochannels with a similar dense F-atom coverage of the interior walls as observed in our hexamer assemblies. Notably, Itoh *et al.* showed that the 0.9 nm channels exhibit a water permeation flux two orders of magnitude higher than those of aquaporins and carbon nanotubes.[21] It should be noted that the covalent oligoamide nanorings are rather more robust compared to the weakly coordinated hexameric assemblies reported in our work. Nevertheless, these results indicate that the incorporation of CF₃ groups can promote highly hydrophobic molecu-

lar and supramolecular nanochannels with fluorine-rich interior walls. There is also a growing interest in the development of both fluorous porous materials, as well as Sn-based MOFs for a range of applications.[4–6,22–24]

Our current work aims to understand the different behaviours observed for (**1**)–(**3**) in this work and to explore how modifying the pnictogen and/or the organic substituents influences the speciation with divalent group 14 triflates, and whether altering the denticity and architecture of the pnictine oxide increases the scope for developing other novel assemblies.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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