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Labile coodination dendrimers†

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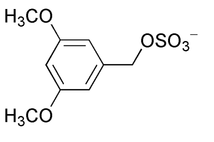
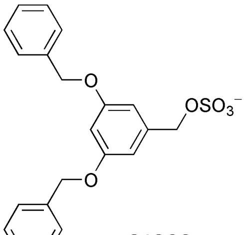
Addition of anionic benzylsulfate dendrons to dynamic mixtures of Ag$^+$ and triphosphine ligands results in the assembly of loosely-bonded cage–core dendrimers.

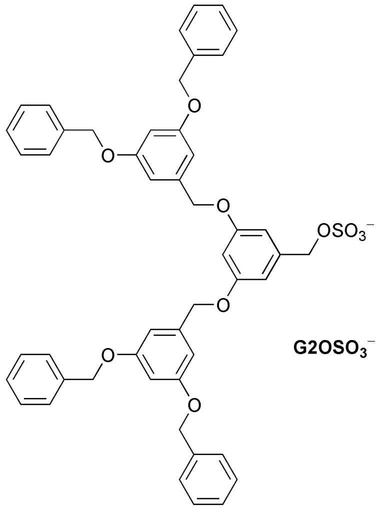
We recently reported a *T*-symmetry cage $[Ag_6(triphos)_4(anion)_4]^{2+}$ {triphos = $CH_3C(CH_2PPh_2)_3$} which assembles from six Ag$^+$ ions, four triphosphines and four templating oxo anions such as NO_3^-, ClO_4^- or OTf$^-$.[1] Due to the ever increasing attention given to dendrimers,[2] we have investigated this cage as a novel dendritic core, by using dendritic benzylsulfates, $ROSO_3^-$, given that their anionic potentially tripodal OSO_3^- groups could act as organising core templates in the presence of dynamic mixtures of Ag$^+$ cations and triphosphine ligands. Here we report on these complexes, which are unusually labile examples of metallo-dendrimers, undergoing reversible dendron exchange for available SbF_6 anions (Scheme 1).



G0OSO$_3^-$

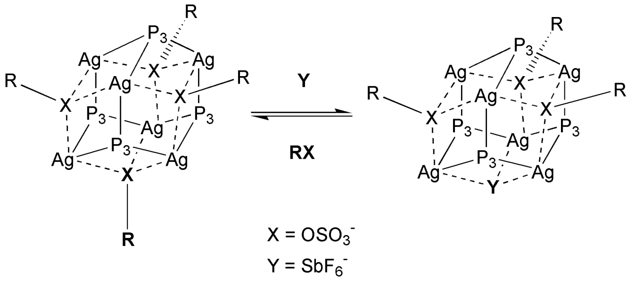


G1OSO$_3^-$



G2OSO$_3^-$

G0, G1 and **G2** alcohol-functionalised dendritic wedges[3] were readily converted to the corresponding benzylsulfate salts $[C_5H_5NH]$[**G*n*OSO$_3$**] (*n* = 0, 1, or 2) by reaction with pyridine sulfur trioxide. Titrations of these wedges into 6:4 $AgSbF_6$/triphos mixtures in $CDCl_3$–CD_3CN solutions were monitored by ^{31}P NMR spectroscopy, and the results of the **G1OSO$_3^-$** titration are shown in Fig. 1. Clearly, successive additions of one equivalent of **G1OSO$_3^-$** transform the dynamic mixture into a single symmetrical species with well resolved Ag–P coupling. Parallel results were obtained for **G0OSO$_3^-$** and **G2OSO$_3^-$**. ^{31}P NMR data for the resulting cage complexes were very similar,‡ and consistent with the previously reported Ag_6 cages with inorganic oxo anions.[1] However, for both **G0OSO$_3^-$** and **G1OSO$_3^-$**, full conversion to their corresponding complexes required five rather than the stoichiometric four equivalents of the anion, and for **G2OSO$_3^-$** fifteen equivalents were required. The requirement for more than four equivalents suggests that the weak coordinating ability of the sulfate groups, combined with steric effects for **G2OSO$_3^-$**, could be causing reversible coordination of the wedges at the cage core, as depicted in Scheme 1. Unfortunately, ^{19}F NMR signals were very broad due to the quadrupolar Sb nuclei, and gave no information on whether the 'vacant' core sites generated were, in fact, occupied by the available SbF_6 anions. Solid samples were obtained by diethyl ether precipitation of 6:4:6 Ag–triphos–**G*n*OSO$_3^-$** solutions.‡ The crystalline products were washed with methanol to remove any excess of **G*n*OSO$_3^-$** and pyridinium salt by-products. For **G1OSO$_3^-$**, elemental analysis of the dried solid material, **1**, suggested the overall composition $[Ag_6(triphos)_4$(**G1OSO$_3$**)$_3(SbF_6)][SbF_6]_2\cdot 1.5CHCl_3$,‡ *i.e.* containing only three wedges. Therefore, even though ^{31}P NMR spectra showed the main species present in solution to be the fully saturated cage, there was clearly dissociation of **G1OSO$_3^-$** which led to precipitation of the less soluble 'unsaturated' complex. Once redissolved, ^{31}P and ^{1}H NMR spectroscopies confirmed that only three **G1OSO$_3^-$** units were present per cage in this material (the spectra were identical to those for the *in situ* prepared 6:4:3 mixture). ESMS spectra showed, in addition to the saturated cage, peaks for the SbF_6-substituted species $[Ag_6(triphos)_4$(**G1SO$_3$**)$_3(SbF_6)]^{2+}$ and $[Ag_6(triphos)_4$(**G1OSO$_3$**)$_2(SbF_6)_2]^{2+}$ (see ESI†).



Scheme 1

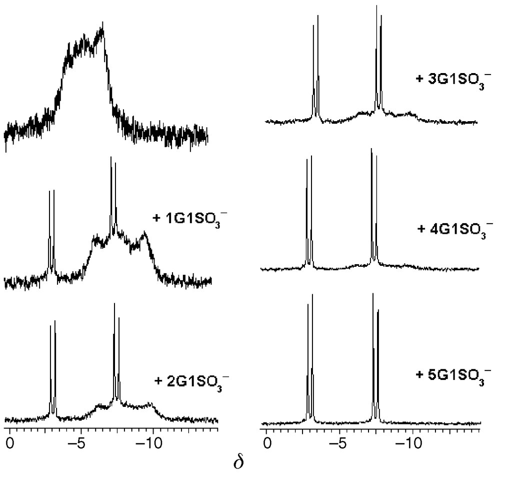


Fig. 1 ^{31}P NMR titration of $[C_5H_5NH]$**[G1OSO$_3$]** into a 6:4 $AgSbF_6$–triphos mixture in 4:1 $CDCl_3$–CD_3CN.

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† Electronic supplementary information (ESI) available: ESMS spectrum of **1** and dendron NMR data. See http://www.rsc.org/suppdata/cc/b1/b107658m/

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Crystals suitable for X-ray analysis were obtained by slow diethyl ether diffusion into a 6 : 4 : 4 $AgSbF_6$–triphos–$\mathbf{G1OSO_3}^-$ solution in $CHCl_3$–CH_3NO_2, and the molecular structure determined§ is shown in Fig. 2. The Ag_6(triphos)$_4$ core was well resolved, with bond lengths and angles similar to those for the OTf^- cage.[1] However, only two $\mathbf{G1OSO_3}^-$ units had full occupancy, each being unsymmetrically tripodally coordinated to three Ag^+ centres with Ag–O distances in the range 2.44(2)–2.78(2) Å. Another core site unexpectedly contained a tripodal hydrogensulfate anion, $HOSO_3^-$ (Ag···O distances in the range 2.57–2.66 Å), which apparently arose from slow hydrolysis of $\mathbf{G1OSO_3}^-$ (no detectable hydrolysis occurred in wet $CDCl_3$–CH_3CN solutions of $\mathbf{G1OSO_3}^-$, or 6 : 4 : 6 $AgSbF_6$–triphos–$\mathbf{G1OSO_3}^-$ mixtures, but aqueous suspensions of $\mathbf{G1OSO_3}^-$ did hydrolyse to the corresponding alcohol up to 5% after 3 days). Although the hydrogen atom could not be located it is suspected to form a strong hydrogen bond to a co-crystallised diethyl ether molecule (O···O separation 2.29(4) Å).

The fourth core site contained both $\mathbf{G1OSO_3}^-$, at 50% occupancy, and SbF_6^-, at 25% occupancy, as shown in Fig. 2 (a and b, respectively). An additional SbF_6^- at 25% occupancy was located some distance from the cage core, but in a position which blocked any coordination of $\mathbf{G1OSO_3}^-$ at the fourth site. The 'coordinated' SbF_6 anion is very weakly bonded in an unsymmetrical tripodal fashion to three silver centres with the Ag–F distances being 2.46(3), 2.72(2) and 2.72(3) Å (sum of F and Ag covalent radii = 2.24 Å, sum of van der Waals radii = 3.19 Å). There are very few structurally characterised SbF_6^- metal complexes,[4] and none in the Cambridge Crystallographic Database that involve coordination (even weak) to three metals. The crystal structure suggests that the large central core separates the $\mathbf{G1OSO_3}^-$ wedges sufficiently that they are unlikely to repel each other sterically, but that $\mathbf{G2OSO_3}^-$ could indeed result in steric crowding, consistent with the NMR titration described above. Although the elemental analysis, NMR spectra and the ESMS results of material **1** show that this crystal structure does not accurately represent the bulk material, it does provide a model for the dendritic complexes observed in solution, and confirms the novel aspect of dendron exchange for SbF_6^-. Although the connectivity in the core is unambiguous, care should be taken making detailed conclusions from the rest of the structure.

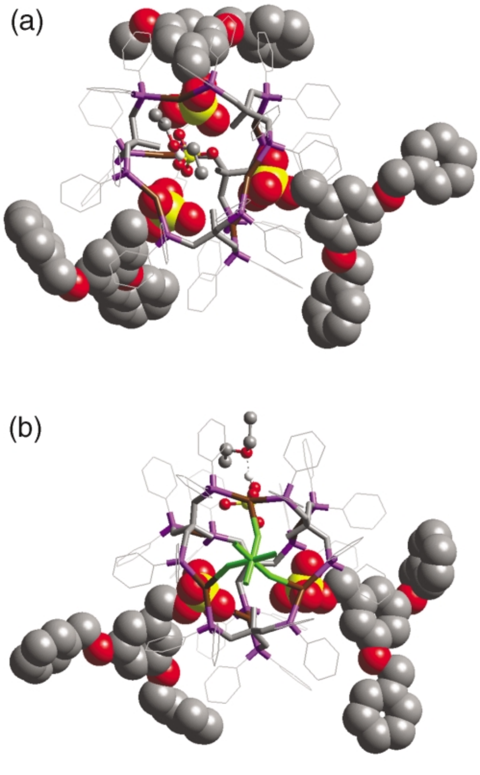

Fig. 2 Molecular structures of $[Ag_6(\text{triphos})_4(\mathbf{G1OSO_3})_3(HOSO_3)]^{2+}$ (a) and $[Ag_6(\text{triphos})_4(\mathbf{G1OSO_3})_2(SbF_6)(HOSO_3)]^{2+}$ (b) showing cage cores (cylinder), dendritic groups (space filling) and triphos phenyl substituents (lines). Ag = brown, P = pink, SbF_6 = green, S = yellow, O = red.

Polymetallic cages previously used as dendrimer cores are $Fe_4S_4(SR)_4$, $Ru_6Se_8L_6$ and $Mo_6Cl_8(OR)_6$.[5] Due to the essentially irreversible metal–ligand coordination in these cages, the resulting dendrimers are non-labile with respect to dendron binding.

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Notes and references

‡ ^{31}P NMR (121.47 MHz, $CDCl_3$–CD_3NO_2, 298 K), δ_P/ppm and $^1J(^{109}Ag–^{31}P)$/Hz: $[Ag_6(\text{triphos})_4(\mathbf{G0OSO_3})_4]^{2+}$ −6.56, 540; $[Ag_6(\text{triphos})_4(\mathbf{G1OSO_3})_4]^{2+}$; −6.47, 541; $[Ag_6(\text{triphos})_4(\mathbf{G2OSO_3})_4]^{2+}$ −6.40, 540. *Preparation and characterising data* for $\{Ag_6(\text{triphos})_4(\mathbf{G1OSO_3})_3(SbF_6)_3\}$ **1**: to a clear solution of $AgSbF_6$ (103 mg, 0.3 mmol) and triphos (125 mg, 0.2 mmol) mixture in 1 : 1 CH_3NO_2–$CHCl_3$ (2 ml) was added a solution of $[C_5H_5NH][\mathbf{G1OSO_3}]$ (144 mg, 0.3 mmol) in $CHCl_3$ (1.5 ml). The product was crystallised by vapour diffusion of diethyl ether into this mixture over 2 days. The off-white crystalline solid was collected, washed with methanol and dried *in vacuo* overnight. Yield: 185 mg, 73%. Microanalysis for $C_{227}H_{213}F_{18}O_{18}P_{12}S_3Ag_6Sb_3\cdot1.5CHCl_3$: found (calc.) C 52.4 (52.5), H 4.0 (4.1), S 2.4 (1.8), Cl 2.9 (3.0)%. $^{31}P\{H\}$ NMR (121.47 MHz, $CDCl_3$, 298 K): δ −5.72 (dd, $^1J(^{109}Ag–^{31}P)$ 541 Hz. Positive FAB (*m*/*z*): $[Ag_6(\text{triphos})_4(\mathbf{G1SO_3})_3(SbF_6)]^{2+}$, 2290. Crystals for X-ray analysis were grown in a similar way over 3 weeks.

§ *Crystal data* for **2**: $C_{219.45}H_{213.05}Ag_6F_{15.30}O_{19.70}P_{12}S_{3.45}Sb_{2.55}$, M = 4896.18, monoclinic, space group $P2_1/n$, a = 27.4440(12), b = 25.3852(11), c = 34.8363(15) Å, U = 22722.7(17) Å^3, T = 150(2) K, Z = 4, μ = 9.91 mm^{-1}, Synchrotron radiation (CLRC Daresbury Laboratory Station 9.8, λ = 0.6923 Å) Bruker AXS SMART CCD diffractometer,[6] narrow frame ω rotations, and were corrected semiempirically for absorption and incident beam decay (transmission 0.72–0.87), 53647 reflections collected, 19642 unique (R_{int} = 0.0905). The final R_1 = 0.1305 (for 11319 reflections $I > 2\sigma(I)$), wR_2 = 0.3440 for 1209 parameters. The core of the molecule was well resolved, allowing anisotropic refinement of the Ag, P, S, Sb, O (attached to S) and C (linking the P) atoms. All other Sb atoms were also refined anisotropically. The isotropic displacement parameters of the rest of the molecule reflect the inherent disorder in the system, which lead to the data only being significant to $2\theta_{max}$ = 38°, even with synchrotron radiation. In addition one peripheral phenyl group in the partial $\mathbf{G1SO_3}^-$ could not be found. CCDC reference number 166377. See http://www.rsc.org/suppdata/cc/b1/b107658m/ for crystallographic data in CIF or other electronic format.

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