Hybrid organic–inorganic, hexa-arm dendrimers based on an Mo_6Cl_8 core

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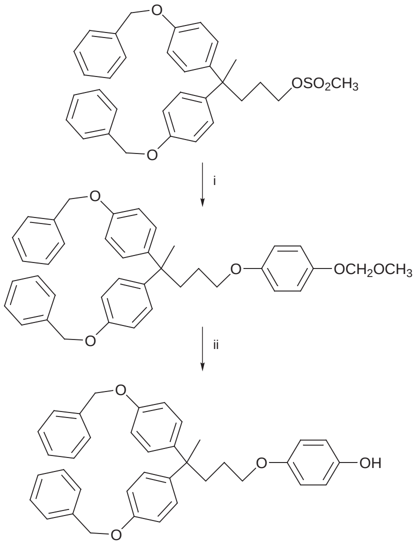
Dendrons with focal phenoxide groups were shown to substitute for triflate or methoxide ligands around an Mo_6Cl_8 core to form molecules of the form $Mo_6(\mu_3\text{-}Cl)_8(OR)_6$ where R = dendrons with zero to two hyperbranches, respectively; these molecules represent a new type of metal cluster core dendrimer with six arms and high symmetry.

Metals and inorganic clusters have served several roles in the construction of dendrimer structures.[1] These include acting as the linking elements, the peripheral elements and as the core element of dendrimers. When used as cores, metals and inorganic clusters have several documented functions.[1] They can be used as reporters of the interior environment of these molecules by virtue of their luminescent, electrochemical or magnetic properties. They can take advantage of the micro-environment of the dendrimer in catalysis applications. Moreover, they can utilize the dendrimer to control electron transfer.[2,3]

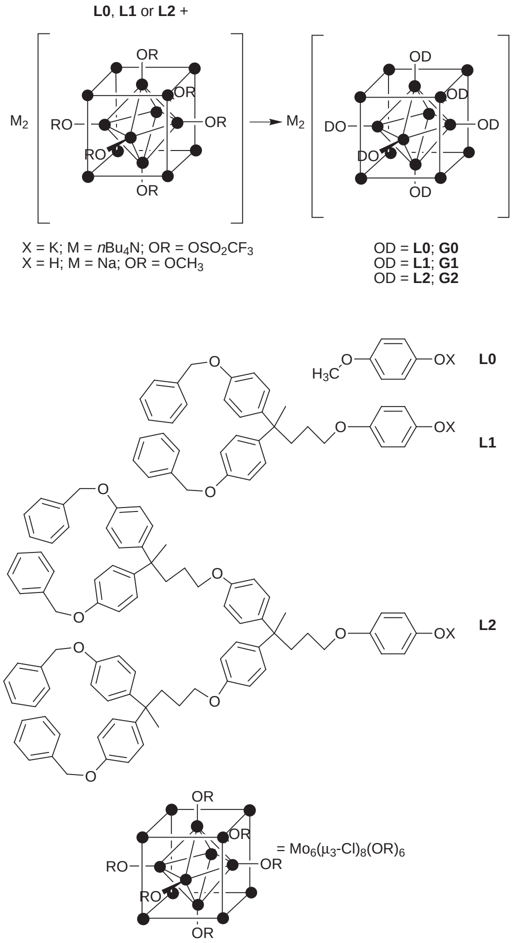
To these ends and others, a variety of metal and metal cluster core dendrimers have been prepared. These include dendrimers with porphyrin,[4–8] iron–sulfur,[2] metal tris-bipyridine[9] and octasilsesquioxane[10,11] cores. All of these syntheses rely on either a core that is tolerant of organic coupling reactions or a core that can undergo some type of ligand exchange to substitute dendritic ligands for smaller ligands. The ligand exchange route to dendrimers can be particularly attractive. In the iron–sulfur core dendrimers discussed above, ligand exchange of a bulky aliphatic thiol for a focally substituted aromatic thiol dendron resulted in virtually quantitative synthesis of molecules with molecular weights of up to 22 kD.[2]

Here we report that ligand exchange reactions around a metal cluster core of the form Mo_6Cl_8 can be employed to form molecules of the form $Mo_6(\mu_3\text{-}Cl)_8(OR)_6$ (R = dendrons with 0–2 hyperbranches), respectively. These six arm, pseudo-octahedral core dendrimers represent one of the first examples of this type.[12] The replacement of both methoxy by other alkoxy ligands[13–16] and of triflate by other alkoxy or carboxy ligands[17,18] at the corner positions of these clusters have been reported. Here, the use of such reactions in the synthesis of new hybrid organic–inorganic macromolecules is illustrated.

The first and second generation ligands (**L1** and **L2**) used to prepare the six-arm dendrimers were prepared by reacting the previously reported[19] focally substituted dendron mesylates (mesylate = OSO_2CH_3) with mono-methoxymethyl hydroquinone followed by deprotection of the methoxymethyl group (Scheme 1). Molecules **G0**, **G1** and **G2** (named corresponding to the generation of dendrimer they represent) were prepared by ligand exchange with either triflate-capped $[nBu_4N]_2[Mo_6$-



Scheme 1 Preparation of focally-substituted phenol dendrons. Sequence is shown for the preparation of **L1**. Preparation of **L2** is performed in an identical fashion. *Reagents and conditions*: i, HOC_6H_4OMOM (1 equiv.), K_2CO_3 (6 equiv.), 18-crown-6 (0.2 equiv.), dry acetone, reflux 60 h; ii, MeOH–THF–HCl, reflux overnight.



Scheme 2 Preparation of dendrimers. *Reagents and conditions* for $[nBu_4N]_2$**G*x*** (*x* = 0, 1, 2): 10 equiv. **L*x*** (*x* = 0, 1 2), excess KH, THF, r.t., N_2, 30 min then $[nBu_4N]_2Mo_6Cl_8(OSO_2CF_3)_6$, THF, r.t., N_2 overnight, ppt $KOSO_2CF_3$, washing with toluene, filter and ppt product washed with Et_2O. *Reagents and conditions for* Na_2**G*x*** (*x* = 0, 1, 2): 10 equiv. **L*x*** (*x* = 0, 1, 2), $Na_2Mo_6Cl_8(OMe)_6$, MeOH–toluene or MeOH–1,2-dichlorobenzene, 80–90 °C, overnight, N_2, Et_2O ppt.

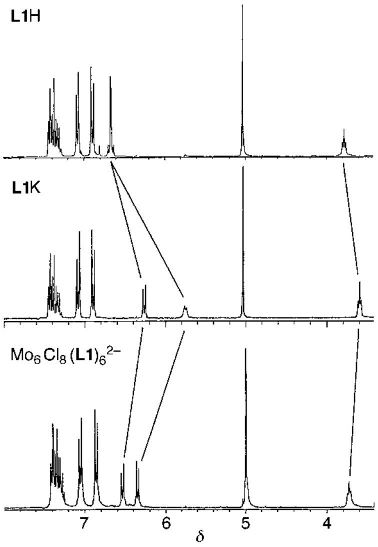


Fig. 1 Series of ^1H NMR spectra illustrating the distinct shifts in the resonances of the focal aromatic ring protons upon deprotonation and attachment to the cluster. Rapid exchange was ruled out by adding excess ligand and observing two distinct sets of peaks.

$Cl_8(OSO_2CF_3)_6]$[17] or methoxy-capped $Na_2[Mo_6Cl_8(OMe)_6]$[20] clusters (Scheme 2).

Deprotonation and subsequent reaction of a slight excess of ligand with the triflate-capped cluster resulted in complete exchange in the case of the $[n\text{Bu}_4\text{N}]_2$**G0** and $[n\text{Bu}_4\text{N}]_2$**G1** molecules.[21] This series of reactions is nicely illustrated by the series of ^1H NMR spectra shown in Fig. 1. Complete precipitation of potassium triflate coproduct was found to be essential as this reaction was determined to be reversible. NMR samples of pure **G1** in THF-d^8 were found to undergo ligand loss when a few equivalents of potassium triflate were added to this solution. Moreover, only partial exchange was observed when **L2** was employed as evidenced by broad ^1H NMR signals of the multiple, overlapping, partially substituted species. These two latter features limited the utility of this reaction in our hands.

Using a modification of conditions reported in the literature,[13–16,22] reaction of the ligands **L0**, **L1** and **L2** with $Na_2[Mo_6Cl_8(OCH_3)_6]$ resulted in complete exchange for all molecules prepared. In the case of Na_2**G0**, a 98% yield of an analytically pure product was obtained, and crystals suitable for X-ray structure determination were obtained (Fig. 2).[23] Bond lengths and angles similar to those reported for related Mo_6Cl_8-core structures were found (*e.g.* Mo–Cl 2.48–2.50 Å, Mo–O 2.04–2.09 Å).[13,16,24]

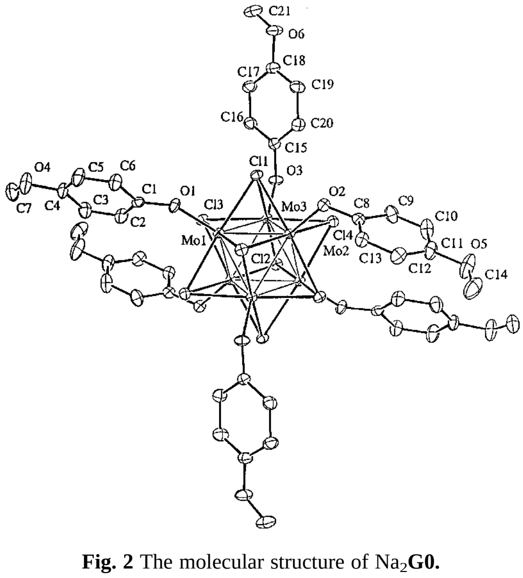


Fig. 2 The molecular structure of Na_2**G0**.

Dendrimers were characterized by NMR and mass spectrometry (MS). We found electrospray MS to be most convenient as a strong parent ion signal could be obtained. The charge on the clusters as well as perhaps their hydrophobicity[25] were probably beneficial factors in the success of these characterization experiments.

In conclusion, it has been shown that high-symmetry metal cluster cores can be used in the preparation of hybrid organic–inorganic dendrimers. In the case of an Mo_6Cl_8 core, the choice of ligand exchange reaction was found to be important to the success of making higher molecular weight dendrimers.

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22 To a suspension of $Na_2[Mo_6Cl_8(OMe)_6]$ (80 mg, 0.073 mmol) in a solution of **L***x* (x = 1, 2) (0.47 mmol) in 1,2-dichlorobenzene (3 ml), 3 ml of anhydrous methanol was added with stirring. The resulting mixture became clear immediately, and was further stirred overnight under a partial vacuum of 100 mTorr. This allowed solvents and by-product methanol to be removed slowly, and a yellow solid remained. The residue was dissolved into 4 ml of toluene, and filtered under nitrogen to remove the unreacted starting cluster, and then 10 ml of Et_2O was added to the filtrate. The precipitate was collected and washed with toluene–Et_2O. The product was further purified by precipitation from toluene–Et_2O several times (yield: 92% for **G1**). Molecule **G0** was prepared similarly except that DMF was substituted for 1.2-dichlorobenzene.
23 *Crystal data* for $Mo_6Cl_8C_{60}H_{79}O_{16.5}Na_2$ (Na**G0**·4THF·2Et_2O): M = 1969.50, monoclinic, space group $C2/c$, a = 22.9666(19), b = 18.1932(18), c = 18.1761(19) Å, U = 7509.8(12) Å^3, T = 148 K, Z = 4, μ = 1.33 mm^{-1}, 8106 reflections measured, 6108 of which had intensities $> 1.0\ \sigma(I)$ and were considered observed. The structure was refined using full matrix least squares based on F. The final R and R_w were 0.036 and 0.041 respectively. CCDC 182/1218. See: http://www.rsc.org/suppdata/cc/1999/877/ for crystallographic files in .cif format.
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