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Quadruply Bonded Dimolybdenum Atoms Surrounded by Dendrons: Preparation, Characterization, and Electrochemistry

Teerayuth Liwporncharoenvong and Rudy L. Luck*

Department of Chemistry
Michigan Technological University
1400 Townsend Drive, Houghton, Michigan 49931

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There have been numerous reports dealing with the molecular architecture of dendrimers.[1] More recently, a review article on dendrimers[2a] and another on metallodendrimers[2b] have highlighted the present areas under investigation. There have been reports on the syntheses of dendrimers containing redox-active cores or peripheries.[3−7] In these cases, the redox-active cores consisted of the ferrocene subunit,[3b−d] an $[Fe_4S_4\text{-}(S\text{-}Dend)_4]^{2-}$ core,[4a] a $[Ru(bpy)_3]^{2+}$ unit,[5] a functionalized silsesquioxane core,[6] and on the periphery, a cobaltocenium functionality[3a] and ferrocene.[7] Other interesting core designs utilized a $[Re_6Se_8]^{2+}$ cluster,[8] a "Mo_6Cl_8" core,[9] and the cyclophosphazene unit.[10] The attribute of light harvesting and energy transfer with dendrimers has been explored,[11] and the use of metallo-containing fragments as dendrons with ferrocenyl[12] and platinum-acetylide units[13] has also been noted.

The rigidity of the central core of the various dendrimers is of interest to us as most of the metallodendrimers discussed contained dendrons secured to the central atom or core unit by one σ bond. A multiply bonded dimetal core center,[14] stabilized with bridging ligands, i.e., two σ bonds, clearly affords one of the best opportunities out of the myriad of possibilities to form a stable rigid center core. Due to pioneering work, largely the domain of basic research,[15] we now have a wide variety of dimetallic center transition metals to choose from and we first utilized the Mo_2^{4+} core as this was already well-defined.[14] Further, we decided to use a convergent approach to dendrimer synthesis, though depending on the metallodendrimer, either convergent or divergent strategies may be employed.[16] Our strategy was to employ four Fréchet-type dendritic polyesters[17] in varying lengths as dendrons to stabilize the Mo_2^{4+} core.

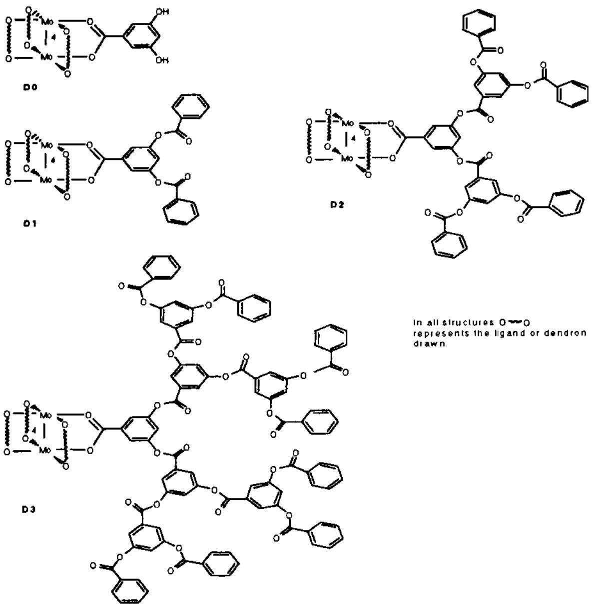

Figure 1. Structural representations of **D0**, **D1**, **D2**, and **D3**.

To that end molecules **D0**, **D1**, **D2**, and **D3** (Figure 1) were synthesized following the reaction shown in eq 1. This kind of substitution chemistry on the Mo_2^{4+}core was detailed previously by using a variety of smaller ligands.[18]

$$K_4Mo_2Cl_8 + 4\ \text{dendron} \rightarrow Mo_2(\text{dendron})_4 + 4KCl \quad (1)$$

The single-crystal X-ray determined structure of **D0** was completed[19] and this molecule cocrystallized with one molecule of KCl resulting in a fascinating three-dimensional square-honeycombed array. The arrangement of the 3,5-dihydroxybenzoate ligands around the Mo_2^{4+}core was, as anticipated, entirely planar affording D_{4h} symmetry to **D0**. The unique arrangement of the crystal packing results from the arrangement of the hydroxy groups toward the K^+ or Cl^- atoms and a more detailed discussion of this is provided in the Supporting Information.

Under the routine synthetic conditions reported, satisfactory elemental analyses (low in %C) were not obtained on **D0**−**D3**. As qualitative evidence for Cl^- was found in **D1**−**D3** (i.e., by the observation of a white precipitate in reacting solutions of the respective dendrimers with $AgClO_4$) it is likely that KCl was not completely removed during purification. **D0** did crystallize with

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* To whom correspondence should be addressed. Phone (906) 487-2309 (voice), (906) 487-2061 (fax). E-mail: rluck@mtu.edu.

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(19) Othorhombic, $F222$, yellow, $a = 13.060(3)$ Å, $b = 19.961(6)$ Å, $c = 19.985(6)$ Å, 291 K, $Z = 8$, $R = 0.079$, GOF $= 1.212$.

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Table 1. Visible Spectra and Electrochemical Data[a]for **D0−D3**

complex	MW	UV−Vis[b]	SR[c]	E_{pc}/mV	E_{pa}/mV	$E_{1/2}$/mV	ΔE_p/mV	i_{pc}/μA	i_{pa}/μA	(i_{pc}/i_{pa})[d]
Mo_2(acetate)$_4$	428.06	434	50	415	481	448	66	1.39	1.68	0.83
D0	804.34	432	50	497	563	530	66	1.59	1.93	0.83, 0.83, 0.87, 0.90
D1	1637.20	434	50	588	681	635	93	1.26	1.79	0.70, 0.85, 0.90, 0.94
D2	3558.62	440	50	664	758	711	94	2.46	2.90	0.85, 0.86, 0.92, 0.98
D3	7402.36	442	50	785	852	819	67	2.41	3.55	0.68, 0.63, 0.50, 0.43

[a] Electrochemical data are listed using notations detailed in ref 20. [b] nm, THF. [c] BAS CV 50 electrochemical analyzer, SR= scan rate, glassy carbon working electrode, a platinum wire auxiliary electrode, a Ag/AgCl reference electrode, 0.001 mol L^{-1} tetrabutylammonium hexafluorophosphate in dried benzonitrile as supporting electrolyte (0.10 mol L^{-1}), ferrocene oxidized at 510 mV under these conditions. [d] Values for **D0−D3** are listed at scan rates of 50, 100, 500, and 1000 mV/s, respectively.

1 mol of KCl. Further, the molecular ion for **D1** was observed by using FAB-MS techniques. **D2** and **D3** could not be identified by either FAB-MS or MALDI-TOF techniques. On one occasion we were able to obtain crystals of **D1**; however, these decomposed prematurely before suitable crystallographic data were obtained. Unfortunately, crystals of **D2** and **D3** have not so far been obtained.

D1−D3 are the first examples of dendrimers containing quadruply bonded metal atoms at the core and thus constitute a new class of metallo-dendrimer. All compounds contained absorptions with a linear increase from **D0** of 432 nm to **D3** at 442 nm and **D0−D2** exhibited reversible oxidations, Table 1. The reversibility at the electrode for the oxidation in these carboxylate systems, as indicated by the fact that (i_{pc}/i_{pa}) is close to unity[20] for **D0−D2** (for the rate of scanning that accounts best for molecular diffusion away from the working electrode and rate of electron transfer), stands in contrast to the quasireversible waves previously reported for other dimolybdenum tetracarboxylate-bridged (DMTC) systems.[21] Since the voltammogram for **D0** obtained in THF was quasireversible ($E_{1/2}$/mV = 479 mV, ΔE_p/mV = 274 mV), this may simply be a reflection of the stability afforded by using benzonitrile (recently shown to be a constructive solvent[22] for these DMTC systems) as the solvent for the voltammetric measurements. Interestingly enough, the cyclic voltammogram for Mo_2(acetate)$_4$ measured in benzonitrile, previously reported as quasireversible in dmf[23] and described as similar to the quasireversible results obtained for dimolybdenum tetrabutyrate[21c] which were measured in CH_3CN, CH_2Cl_2, and EtOH, also consisted of a reversible oxidation, Table 1. This different nature of the oxidation (i.e., reversible and quasireversible) in different solvents for the Mo_2^{4+} core bridged by various carboxylic acids was previously noted.[23] Finally, as one-electron-oxidized compounds of DMTC molecules have been synthesized, these reversible results are not unexpected.[24]

Similar to what was observed previously in a series of redox-active dendrimers,[3b] the bigger the molecule the more positive the potential at which oxidation occurred as indicated by the increase in $E_{1/2}$ values in Table 1. It was previously noted in the case of a ferrocene subunit that oxidation is more difficult as the ferrocene is buried inside the aliphatic region of the dendrons, in this case alkanethiolate self-assembled monolayers.[25] The increasing difficulty with the oxidation in going from **D0** to **D3** (which also correlates with the order of increasing stability on exposure to the atmosphere, i.e., **D3** is the most stable) is possibly a reflection of the further distance the electron has to travel from the metal core to the working electrode as opposed to some electronic difference due to the different dendrons. It is noteworthy that the values for (i_{pc}/i_{pa}) for **D3** deviated the most from unity with increasing scan rate. This is probably because the increased speed in rate of scanning was too fast to account for the time it takes the electron to diffuse through the large dendrons on **D3**. As **D3** should exhibit the slowest rate of molecular diffusion in solution compared to the others, the slowest scan rate (i.e., at 10 mV/s, $(i_{pc}/i_{pa}) = 0.70$) did contain the (i_{pc}/i_{pa}) value closest to unity. It is also of interest if the dendrons wrap around themselves producing a spherical geometry or are arranged in a plus sign arrangement. The ^{1}H NMR resonance data (Supporting Information) do become broader from **D0** to **D3** suggesting hindered rotation, which may reflect the fact that a plus sign arrangement (resulting in increasing nuclear relaxation) pertains in solution.

One intriguing aspect of **D3** is that thin films (qualitatively homogeneous) consisting of 2% solution by weight of **D3** in polycarbonate (obtained by dipping glass slides into solutions of both polymers in THF) are more anisotropic as evident in polarized light than films of polycarbonate obtained by using identical procedures. Perhaps the dendrons on **D3** are held between the backbone chain of the polycarbonate framework and this results in a parallel arrangement of the Mo_2^{4+} vectors. This attribute, a more detailed electrochemical analysis, and the syntheses of dendrimers containing other transition metals multiply bonded as the core, perhaps leading to a new area of supramolecular chemistry,[26] are currently under investigation.

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Supporting Information Available: Experimental and full crystallographic details (PDF) and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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