

## Experimental Section

**General Data.** Oxygen was excluded during all operations by using vacuum lines or a glovebox supplied with purified nitrogen. All solvents except methanol and water were dried over and distilled from sodium benzophenone ketyl. Methanol was dried over magnesium metal. Water and all solvents were degassed before use. IR spectra were recorded using a Mattson Galaxy Series FTIR 3000. NMR spectra were recorded on a Varian Unity Inova 400 MHz. Visible absorption spectra were recorded using a Hewlett Packard 8452A diode array spectrophotometer. The chemicals were used as purchased from Aldrich chemical except for 2,2,2-trichloroethanol, which was freshly distilled before use. The preparation of  $\text{K}_4\text{Mo}_2\text{Cl}_8$  was reported elsewhere.<sup>1</sup> The preparation of the Fréchet type dendrons was accomplished with an addition to the literature synthetic method.<sup>2</sup> This consisted of neutralizing excess  $\text{H}_2\text{SO}_4$  with a saturated  $\text{NaHCO}_3$  solution after the reaction to produce **D0**, followed by distillation of the excess 2,2,2-trichloroethanol under reduced pressure before the suggested literature purification and further stepwise syntheses. We were not able to obtain this compound in good yields otherwise.

The electrochemical measurements on the dendritic molecules were accomplished with a Bioanalytical Systems CV-50W workstation controlled by a 366 MHz Pentium based Gateway PC. The voltammetric experiments were performed in a 5.0 mL cell equipped with a glassy carbon working electrode ( $0.282 \text{ cm}^2$ ), a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode. The electroactive dendrimers were dissolved ( $0.001 \text{ mol L}^{-1}$ ) in dried benzonitrile also containing tetrabutylammonium

hexafluorophosphate (Fluka, >99%) as the supporting electrolyte (0.10 mol L<sup>-1</sup>). An argon atmosphere was maintained over the solutions throughout the electrochemical experiments. Ferrocene oxidized at 0.51 V under these conditions.

The mass spectral data were obtained at the Michigan State University Mass Spectrometry Facility which is supported, in part, by a grant (DRR-00480) from the Biotechnology Research Technology Program, National Center for Research Resources, National Institutes of Health.

**Preparation of Mo<sub>2</sub>(C<sub>7</sub>H<sub>5</sub>O<sub>4</sub>)<sub>4</sub> (D0).** A solution of K<sub>4</sub>Mo<sub>2</sub>Cl<sub>8</sub> (300 mg, 0.474 mmol) in 10 mL of distilled water was added to a solution of 3,5-dihydroxy benzoic acid (310 mg, 1.99 mmol) in 20 mL methanol. The resulting yellow solution was concentrated until a yellow product precipitated out of solution. This yellow product was filtered and vacuum dried and purified by subsequent recrystallization with a methanol/ benzene mixture. Yield 290 mg 76.12%; IR 3332 br, 1604 s, 1503 s, and 1407 s cm<sup>-1</sup>; <sup>1</sup>H NMR (D<sub>6</sub>-acetone) δ 8.41 (s, 8H, ArOH), 7.27 (d, 4H, J = 2 Hz, ArH), and 6.46 (t, 4H, J = 2 Hz, ArH); UV 432 nm (in THF). Anal. Calcd. for Mo<sub>2</sub>C<sub>28</sub>H<sub>20</sub>O<sub>16</sub>: C 41.81 ; H 2.51 Found : C 37.61 ; H 3.22. This analysis is very low but it is possible that **D0** was contaminated with KCl, as was evident in the crystal structure determination, and, in that case for **D0**·KCl: C 38.28; H 2.29. Traces of silicon grease were also evident in the NMR spectrum for this compound.

**Preparation of Mo<sub>2</sub>(C<sub>21</sub>H<sub>13</sub>O<sub>6</sub>)<sub>4</sub> (D1).** A solution of K<sub>4</sub>Mo<sub>2</sub>Cl<sub>8</sub> (200 mg, 0.316 mmol) in 10 mL of distilled water was added to a solution of dendron-1 (480 mg, 1.327 mmol) in 20 mL THF. An orange gum-like precipitate occurred almost immediately, and, the solution was stirred under N<sub>2</sub> for at least 30 min. The orange product was filtered and vacuum dried and re-crystallized in a THF/hexanes mixture. Yield 480 mg

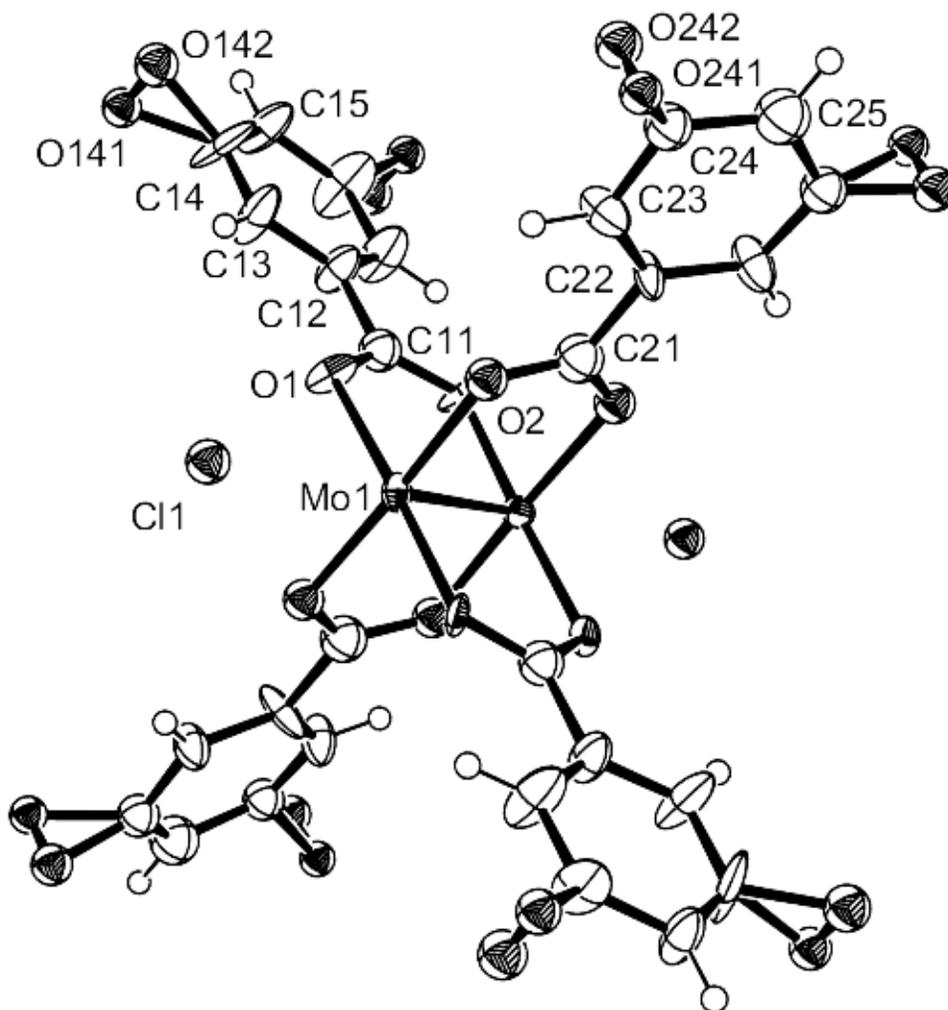
92.84 %; IR 1739 vs, 1696 sh, 1595 m, and 1255 br  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.40-7.68 (m, 16H,  $16 \times \text{ArH}$ ), 7.87 (d,  $J = 2$  Hz, 4H,  $\text{ArH}$ ), 7.99 (d,  $J = 2$  Hz, 4H,  $\text{ArH}$ ), 8.018 (d,  $J = 2$  Hz, 4H,  $\text{ArH}$ ), 8.068 (m, 4H,  $\text{ArH}$ ), 8.173 (m, 16H,  $\text{ArH}$ ), 8.27 (m, 4H,  $\text{ArH}$ ) ; UV 434 nm (in THF); mass spectrum (FAB)  $m/z$  1637 (ca. 100%). Anal. Calcd. for  $\text{Mo}_2(\text{C}_{21}\text{H}_{13}\text{O}_6)_4$ : C, 61.62; H, 3.18. Found: C, 58.08; H, 4.18. Note **D1**·KCl: C 58.99; H 3.06.

**Preparation of  $\text{Mo}_2(\text{C}_{49}\text{H}_{29}\text{O}_{14})_4$  (D2).** A solution of  $\text{K}_4\text{Mo}_2\text{Cl}_8$  (200 mg, 0.316 mmol) in 10 mL of distilled water was added to a solution of dendron-2 (1117 mg, 1.327 mmol) in 20 mL THF. The solution was stirred under  $\text{N}_2$  for at least 30 min. The result orange gum-like precipitate was filtered and vacuum dried and recrystallized using THF/hexanes solution. Yield 1.03g, 91.71%; IR 1739 s, 1594 s, 1512 m, and 1244 br  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.40-7.68 (m, 60H,  $\text{ArH}$ ), 7.84-8.04 (m, 20H,  $\text{ArH}$ ), 8.07-8.40 (m, 36H,  $\text{ArH}$ ) ; UV 440 nm (in THF). Anal. Calcd. for  $\text{Mo}_2(\text{C}_{49}\text{H}_{29}\text{O}_{14})_4$ : C, 66.14; H, 3.16. Found: C, 64.35; H, 3.66. Note **D2**·KCl: C 64.84; H 3.22.

**Preparation of  $\text{Mo}_2(\text{C}_{105}\text{H}_{61}\text{O}_{30})_4$  (D3).** A solution of  $\text{K}_4\text{Mo}_2\text{Cl}_8$  (100 mg, 0.158 mmol) in 10 mL of distilled water was added to a solution of dendron-3 (1196 mg, 0.664 mmol) in 20 mL THF. The solution was stirred under  $\text{N}_2$  for at least 30 min. The result orange gum-like precipitate was filtered, dried under vacuum and recrystallized from a THF/hexanes solution. Yield 1.02g 87.37%; IR 1739 s, 1595 s, 1514 m, and 1256 br  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.40-7.58 (m, 88H,  $\text{ArH}$ ), 7.60-7.68 (m, 36H,  $\text{ArH}$ ), 7.86-7.91 (m, 12H,  $\text{ArH}$ ), 7.97-8.05 (m, 36H,  $\text{ArH}$ ), 8.15-8.24 (m, 72H,  $\text{ArH}$ ) ; UV 442 nm (in THF). Anal. Calcd. for  $\text{Mo}_2(\text{C}_{105}\text{H}_{61}\text{O}_{30})_4$ : C, 68.14; H, 3.30. Found: C, 66.59; H, 4.00. Note **D3**·KCl: C 67.52; H 3.29.

### Crystallographic Details.

Details of the X-ray spectrometer and associated analysis are given elsewhere.<sup>3</sup> A suitable crystal was identified, rolled in epoxy resin and mounted on a glass fibre. The windows program WinGX was used as the interface for the solution and refinement of the models.<sup>4a</sup> The data were first reduced and corrected for absorption using psi-scans<sup>5</sup> and then solved using the program *SIR97*.<sup>6</sup> The model was refined with *SHELXL97*.<sup>7</sup> The refinement was not straightforward. All non-H atoms were refined with anisotropic thermal parameters and H-atoms refined freely with isotropic thermal parameters. Some of the non-hydrogen atoms did not take anisotropic model refinement and thus these were refined with isotropic parameters. The likely sites for the K and Cl atoms were refined with occupancies consisting of 50% of each. The nature of the oxygen atom disorder was also readily apparent in a difference map and the two sites were refined at 50% occupancies. Several other space groups were also explored corresponding to various tetragonal body centered lattices (*I4*, *I* bar 4 and *I4/m*). None produced as good a model as the *F222* setting and, more importantly, the various models refined and the three dimensional arrangements were identical. A diagram of the molecule is depicted in Figure 1, the crystallographic data for **D0** is listed in Table 1 for the converged model in the final refinements and positional and anisotropic data are given in Tables 2 and 3 respectively.



**Figure 1.** An ORTEP3 for Windows<sup>4b</sup> representation of **D0**. H-atoms are represented by circles of arbitrary radii and ellipsoids are drawn at the 50% probability level.

Table 1. Crystal data and structure refinement for D0.

Identification code	D0
Empirical formula	C28 H20 Cl1 K1 Mo2 O16
Formula weight	878.89
Temperature	291(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $F 2 2 2$
Unit cell dimensions	a = 13.060(3) Å    alpha = 90 deg. b = 19.961(6) Å    beta = 90 deg. c = 19.985(6) Å    gamma = 90 deg.
Volume	5210(2) Å <sup>3</sup>
Z, Calculated density	8, 1.120 Mg/m <sup>3</sup>
Absorption coefficient	0.659 mm <sup>-1</sup>
F(000)	1744
Crystal size, color	0.2 x 0.2 x 0.1 mm, yellow
Theta range for data collection	2.03 to 22.42 deg.
Limiting indices	0<=h<=14, 0<=k<=21, -1<=l<=21
Reflections collected / unique	1014 / 1012 [R(int) = 0.0191]
Completeness to theta = 22.42	100.0 %
Absorption correction	Psi-scan
Max. and min. transmission	0.8991 and 0.7707
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1012 / 0 / 93
Goodness-of-fit on F <sup>2</sup>	1.212
Final R indices [I>2sigma(I)] <sup>a</sup>	R <sub>1</sub> = 0.0790, wR <sub>2</sub> = 0.2367 <sup>b,c</sup>
R indices (all data)	R <sub>1</sub> = 0.1034, wR <sub>2</sub> = 0.2517
Absolute structure parameter	-0.5(6)
Extinction coefficient	0.0009(2)
Largest diff. peak and hole	1.633 and -0.769 e.Å <sup>-3</sup>

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<sup>a</sup>R<sub>1</sub> =  $\sum(F_o - F_c) / \sum(F_o)$ . <sup>b</sup>wR =  $[\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$ . <sup>c</sup>w =  $1 / [\sigma^2(F_o^2) + (0.1484 * P)^2 + 126.77 * P]$ , where P =  $(F_o^2 + 2 * F_c^2) / 3$ .

Table 2. Atomic coordinates ( x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for **D0**.<sup>a</sup>

	x	y	z	U(eq)
Mo(1)	1694(2)	2500	2500	19(1)
K(1) <sup>b</sup>	-648(5)	2500	2500	36(2)
Cl(1) <sup>b</sup>	-648(5)	2500	2500	36(2)
O(1)	1646(9)	1451(5)	2520(20)	26(3)
C(11)	2500	1143(12)	2500	32(6)
C(12)	2500	383(12)	2500	36(7)
C(13)	1592(17)	57(10)	2450(50)	52(10)
C(14)	1611(17)	-621(11)	2450(40)	59(11)
O(141)	650(20)	-951(14)	2580(30)	28(9)
O(142)	690(30)	-952(18)	2175(19)	34(10)
C(15)	2500	-990(13)	2500	46(9)
O(2)	1648(9)	2503(18)	1450(5)	28(3)
C(21)	2500	2500	1146(13)	39(6)
C(22)	2500	2500	396(11)	36(8)
C(23)	1593(16)	2410(20)	65(10)	36(8)
C(24)	1582(15)	2376(12)	-623(10)	33(6)
O(241)	640(20)	2590(30)	-948(13)	25(9)
O(242)	700(30)	2183(19)	-963(18)	30(10)
C(25)	2500	2500	-980(15)	46(7)

$${}^a U_{eq} = \left(\frac{1}{3}\right) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j. \quad {}^b \text{atom refined at 50\% occupancy.}$$

Table 3. Full Listings of Anisotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>) for **D0**.

	U11	U22	U33	U23	U13	U12
Mo(1)	13(1)	23(1)	20(1)	4(3)	0	0
K(1)	38(4)	35(3)	33(3)	15(11)	0	0
Cl(1)	38(4)	35(3)	33(3)	15(11)	0	0
O(1)	22(6)	13(5)	44(8)	1(18)	-20(20)	5(5)
C(12)	20(13)	25(13)	62(18)	0	-10(70)	0
C(13)	28(10)	21(10)	110(30)	0(30)	10(40)	-5(9)
C(14)	34(11)	28(10)	110(30)	-20(30)	-30(40)	-12(10)
C(15)	27(15)	21(13)	90(30)	0	-20(70)	0
C(22)	23(15)	70(20)	12(12)	0	0	-20(50)
C(23)	21(9)	60(30)	25(10)	-6(17)	-2(9)	8(18)

The Temperature Factor has the Form of Exp(-T) Where  $T = 8\pi^2 U_{iso} \cdot (\text{Sin}(\theta) / \lambda)^2$  for Isotropic Atoms and  $T = 2\pi^2 \sum_i \sum_j U_{ij} h_i h_j a_i^* a_j^*$ , for Anisotropic Atoms.  $a_i^*$  are Reciprocal Axial Lengths and  $h_i$  are the Reflection Indices.

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