Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis of Di- and Tetranuclear Oxido-Molybdenum(V) Complexes Containing *p*-Toluenesulfonates as Ligand: a Joint Spectroscopic, Crystallographic and Computational Study

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Supplementary Material

Figure 1S. DFT-optimized molecular structure (EDF2 functional) of $Mo_2O_2Cl_6[\mu\text{-}\kappa^2\text{-}1,4\text{-}Me(SO_3Me)C_6H_4]$, **1**, singlet-state configuration, and plot of HOMO molecular orbital (isovalue = 0.048 a.u.).

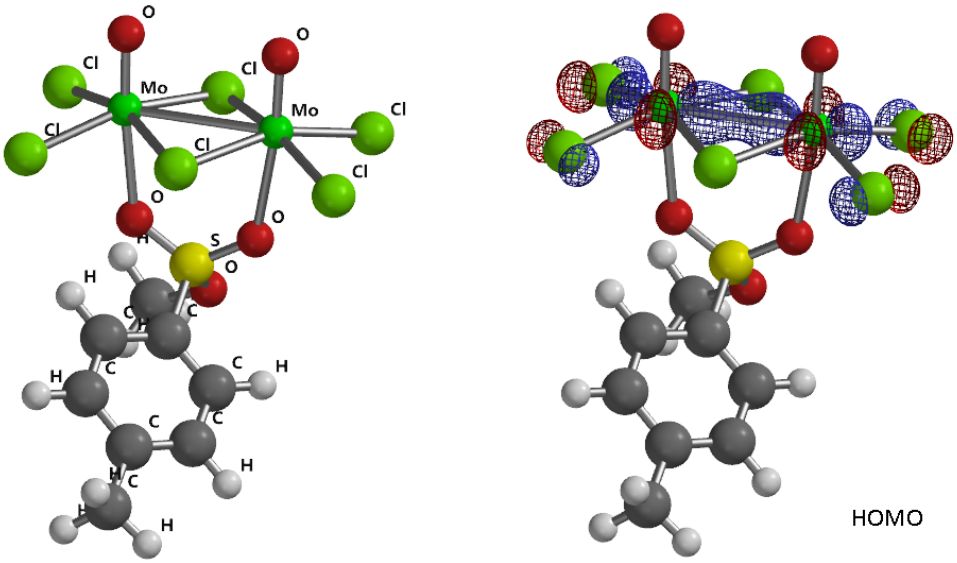


Table 1S. Selected computed bond lengths (Å) and angles (°) (EDF2 functional) of $Mo_2O_2Cl_6$[μ-κ^2-1,4-Me(SO_3Me)C_6H_4], **1** (singlet-state).

Mo-Mo	3.133
Mo=O	1.666 / 1.666
Mo-O(μ-1,4-Me(SO_3Me)C_6H_4)	2.422 / 2.461
Mo-Cl(terminal)	2.327 / 2.330 / 2.335 / 2.346
Mo-Cl(bridge)	2.487 / 2.493 / 2.492 / 2.496
Mo-Cl(bridge)-Mo	77.8 / 78.0
O=Mo-Cl(terminal)	101.8 / 101.6 / 101.5 / 101.7
O=Mo-Cl(bridge)	95.9 / 96.9 / 95.9 / 96.1
O=Mo-O(μ-1,4-Me(SO_3Me)C_6H_4)	174.0 / 173.3
S=O	1.465 / 1.474
S-O(CH_3)	1.600

Figure 2S. DFT-optimized molecular structure (EDF2 functional) of $Mo_2O_2Cl_6[\mu\text{-}\kappa^2\text{-}1,4\text{-}Me(SO_3Me)C_6H_4]$, **1**, triplet-state configuration, and plot of α-HOMO and α-HOMO-1 molecular orbitals (isovalue = 0.032 a.u.).

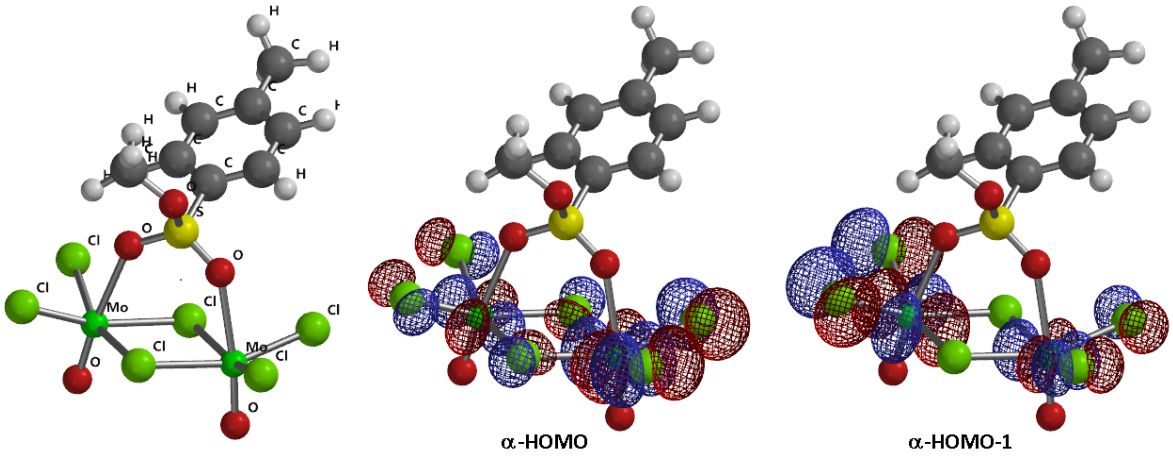
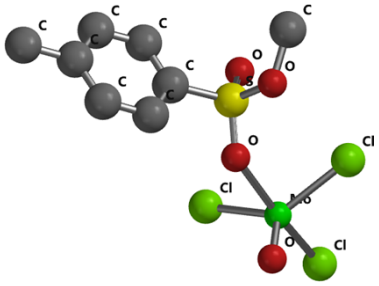


Table 2S. Selected computed bond lengths (Å) and angles (°) (EDF2 functional) of [$MoOCl_2$(μ-Cl)(κ^1-1,4-Me(SO_3Me)C_6H_4)]$_2$, **2**.

Mo...Mo	3.825
Mo=O	1.672 / 1.670
Mo-O(1,4-Me(SO_3Me)C_6H_4)	2.330 / 2.355
Mo-Cl(terminal)	2.327 / 2.315 / 2.323 / 2.320
Mo-Cl(bridge)	2.546 / 2.535 / 2.539 / 2.557
Mo-Cl(bridge)-Mo	97.1 / 97.9
O=Mo-Cl(terminal)	101.4 / 101.0 / 100.6 / 101.9
O=Mo-Cl(bridge)	97.4 / 94.5 / 94.9 / 97.7
O=Mo-O(1,4-Me(SO_3Me)C_6H_4)	170.8 / 170.3
S=O(Mo)	1.474 / 1.481
S=O	1.450 / 1.450
S-O(CH_3)	1.617 / 1.613

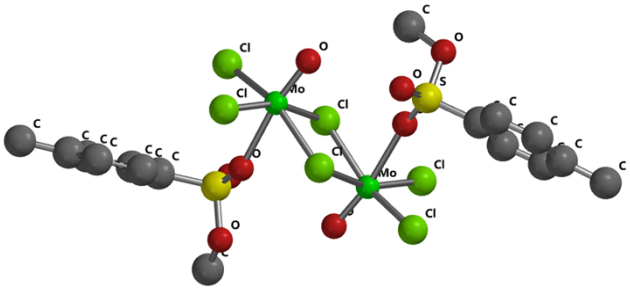
Figure 3S. DFT-calculated possible structures (EDF2 functional) of $MoOCl_3[1,4\text{-}Me(SO_3Me)C_6H_4]$ and relative energy values (kcal/Mo moles). Hydrogen atoms have been omitted for clarity.



$MoOCl_3[\kappa^1\text{-}1,4\text{-}Me(SO_3Me)C_6H_4]$

Monomer -2457.89731

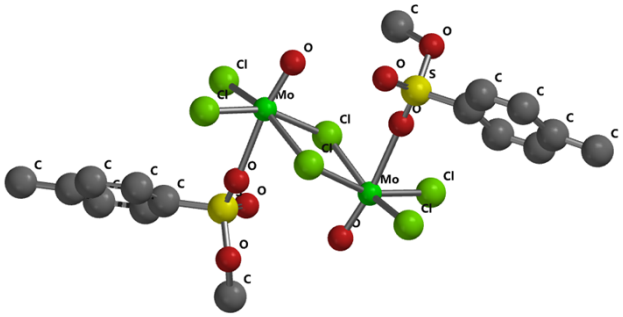
0.0 kcal mol^{-1}



$[MoOCl_2(\mu\text{-}Cl)(\kappa^1\text{-}1,4\text{-}Me(SO_3Me)C_6H_4)]_2$ (**2**)

Triplet, O *trans* to $1,4\text{-}Me(SO_3Me)C_6H_4$

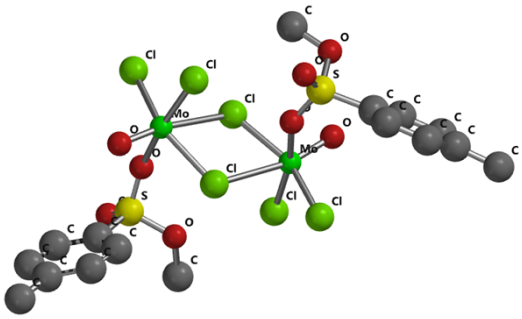
-6.4 kcal mol^{-1}



$[MoOCl_2(\mu\text{-}Cl)(\kappa^1\text{-}1,4\text{-}Me(SO_3Me)C_6H_4)]_2$

Singlet, O *trans* to $1,4\text{-}Me(SO_3Me)C_6H_4$

+3.7 kcal mol^{-1}



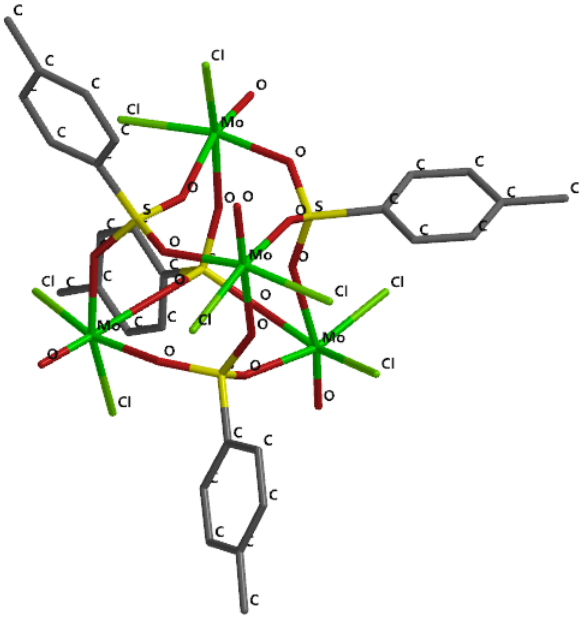
$[MoOCl_2(\mu\text{-}Cl)(\kappa^1\text{-}1,4\text{-}Me(SO_3Me)C_6H_4)]_2$

Triplet, O *cis* to $1,4\text{-}Me(SO_3Me)C_6H_4$

-3.0 kcal mol^{-1}

The geometry optimization of dinuclear complexes with bridging 1,4-$Me(SO_3Me)C_6H_4$ ligands and of dinuclear complexes with bridging Cl ligands and 1,4-$Me(SO_3Me)C_6H_4$ ligands in trans position respect to μ-Cl led to couples of mononuclear complexes.

Table 3S. Selected computed bond lengths (Å) and angles (°) for $Mo_4O_4Cl_8[\mu_3$-1,4-$Me(SO_3)C_6H_4]_4$, **3**.



	PBEPBE	EDF2
Mo=O	1.690 / 1.691 / 1.692 / 1.696	1.669 / 1.669 / 1.671 / 1.673
Mo-O (μ-1,4-$Me(SO_3)C_6H_4$)	2.203 / 2.205 / 2.268 / 2.182 / 2.209 / 2.291 / 2.201 / 2.190 / 2.297 / 2.177 / 2.193 / 2.345	2.147 / 2.154 / 2.311 / 2.139 / 2.140 / 2.297 / 2.141 / 2.168 / 2.324 / 2.138 / 2.164 / 2.371
Mo-Cl	2.316 / 2.337 / 2.318 / 2.334 / 2.319 / 2.333 / 2.322 / 2.327	2.314 / 2.333 / 2.316 / 2.323 / 2.334 / 2.314 / 2.335 / 2.315
O=Mo-Cl	101.8 / 102.4 / 101.3 / 102.6 / 101.2 / 102.2 / 101.3 / 101.5	100.5 / 100.7 / 101.3 / 101.2 / 101.1 / 101.0 / 101.8 / 100.6
O=Mo-O (μ-1,4-$Me(SO_3)C_6H_4$)	89.2 / 93.0 / 165.9 / 92.2 / 92.6 / 167.1 / 90.8 / 92.4 / 166.6 / 90.8 / 91.7 / 167.2	95.8 / 92.9 / 169.5 / 93.5 / 91.6 / 169.5 / 94.0 / 95.6 / 168.2 / 91.3 / 94.8 / 167.7
S-O	1.499 / 1.495 / 1.477 / 1.498 / 1.481 / 1.498 / 1.481 / 1.494 / 1.501 / 1.479 / 1.504 / 1.498	1.480 / 1.504 / 1.511 / 1.504 / 1.479 / 1.505 / 1.502 / 1.478 / 1.509 / 1.483 / 1.506 / 1.506