Electronic Supplementary Material (ESI) for Dalton Transactions.

Oxo-Molybdenum Complexes Obtained by Cl/O Interchange Between $MoCl_5$ and Carboxylic Acids: a Crystallographic, Spectroscopic and Computational Study

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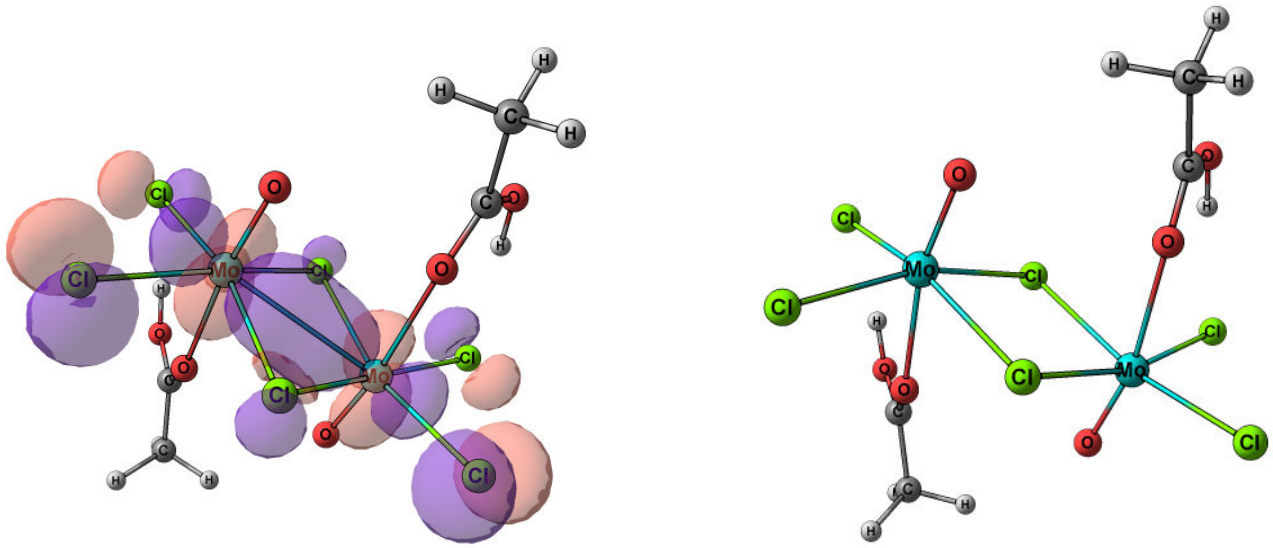
Supporting Information

Figure S1. DFT M06 calculated structures for **1a**, with implicit C-PCM solvation (CH_2Cl_2). Plot of HOMO for **1a-singlet** (surface isovalue = 0.04 a.u.).

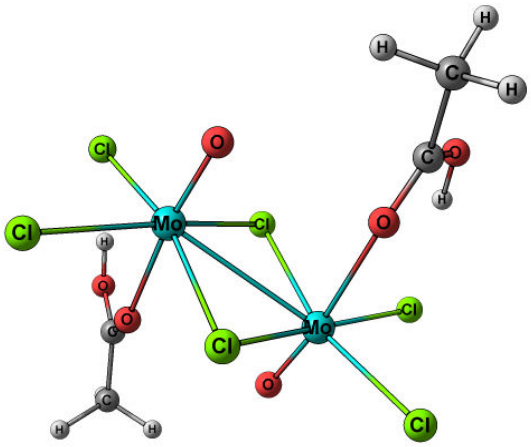


1a-singlet **1a-triplet**

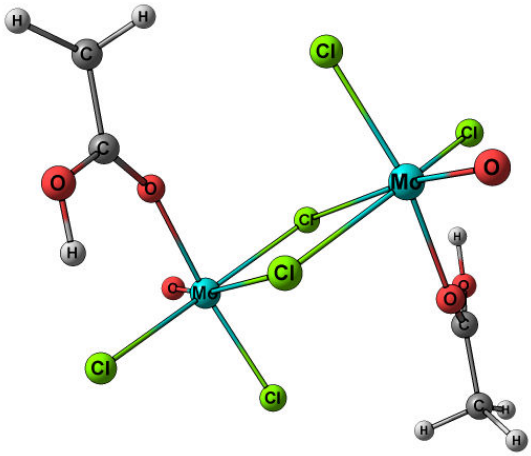
Table S1. Selected computed bond lengths (Å) and angles (°) for **1a** (M06/C-PCM), singlet-state. Values for the triplet state configuration are in parentheses.

Bond		**Angle**	
Mo---Mo	3.069 (3.763)	O=Mo–$Cl_{terminal}$	97.2 (100.6)
Mo=O	1.641 (1.642)		101.4 (103.9)
	1.641 (1.642)		97.2 (100.6)
Mo–OC	2.233 (2.262)		101.4 (103.9)
	2.233 (2.262)	O=Mo–$Cl_{bridging}$	94.4 (93.5)
Mo–$Cl_{terminal}$	2.337(2.308)		91.8 (91.2)
	2.401 (2.355)		94.4 (93.5)
	2.337 (2.308)		91.8 (91.2)
	2.401 (2.355)	O=Mo–O	172.4 (166.5)
Mo–$Cl_{bridging}$	2.461 (2.569)		172.4 (166.5)
	2.482 (2.558)	$Cl_{bridging}$–Mo–$Cl_{bridging}$	103.2 (84.5)
	2.461 (2.569)		103.2 (84.5)
	2.482 (2.558)	O–C–O	122.7 (123.0)
C=O	1.240 (1.238)		122.7 (123.0)
	1.240 (1.238)		
C–OH	1.304 (1.307)		
	1.304 (1.307)		
O–H	0.984 (0.981)		
	0.984 (0.981)		
OH---Cl	2.233 (2.296)		
	2.233 (2.296)		

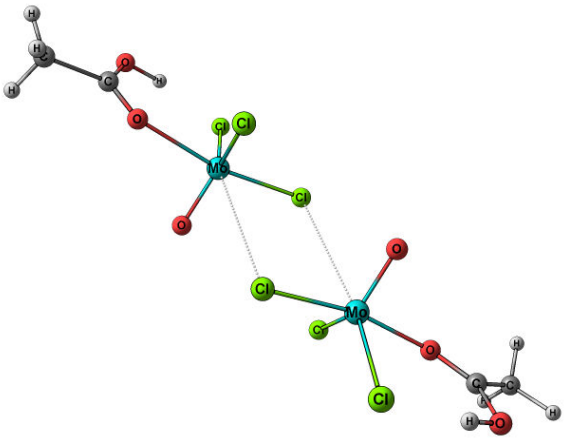
Figure S2. DFT M06 calculated structures for $[MoOCl_2(CH_3CO_2H)(\mu\text{-}Cl)]_2$ (singlet state, EDF2/LACVP**) and relative Gibbs free energy values (kcal mol^{-1}).



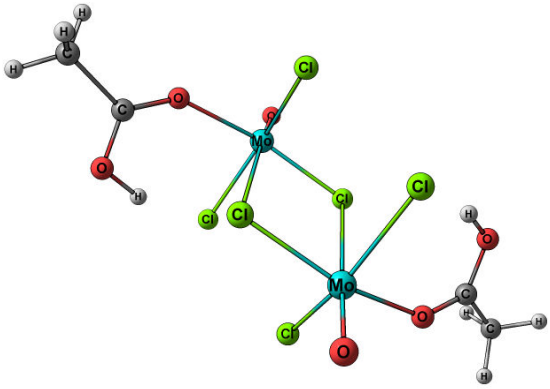
1a



1aB



1aC



1aD

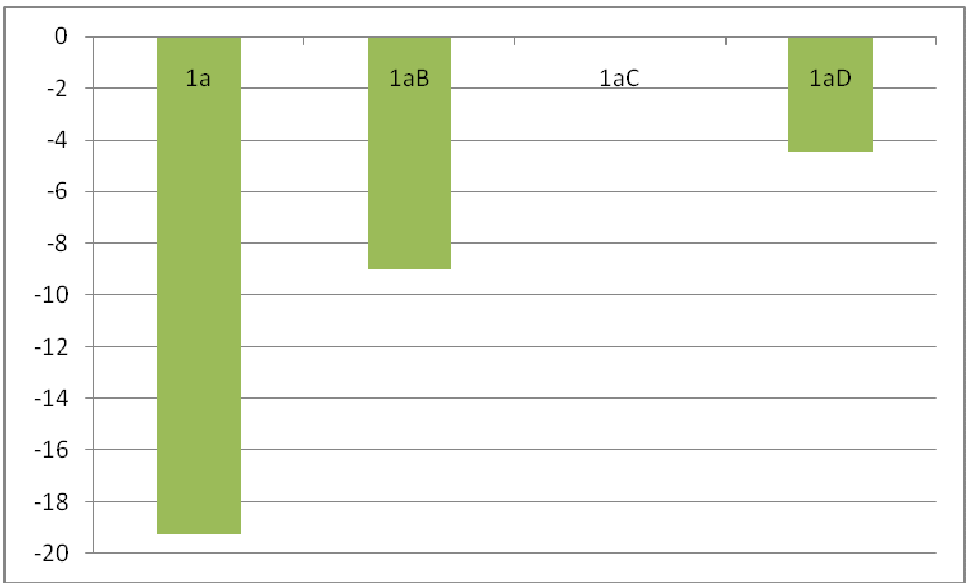
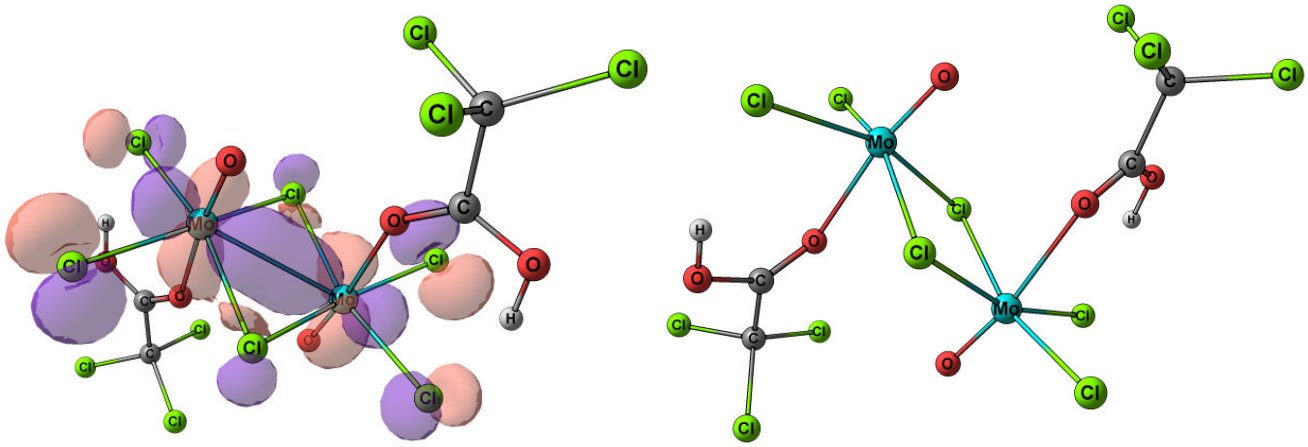


Figure S3. DFT M06 calculated structures for **1b**, with implicit C-PCM solvation (CH_2Cl_2). Plot of HOMO for **1b-singlet** (surface isovalue = 0.04 a.u.).

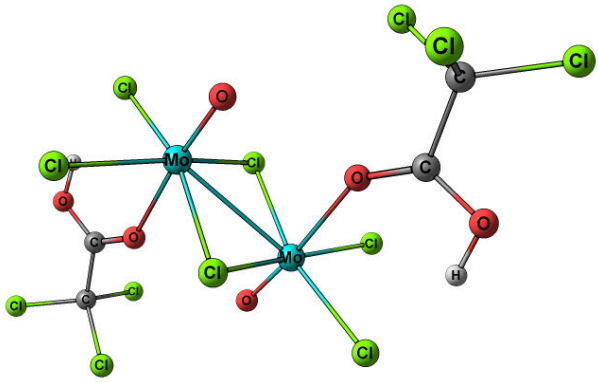


1b-singlet **1b-triplet**

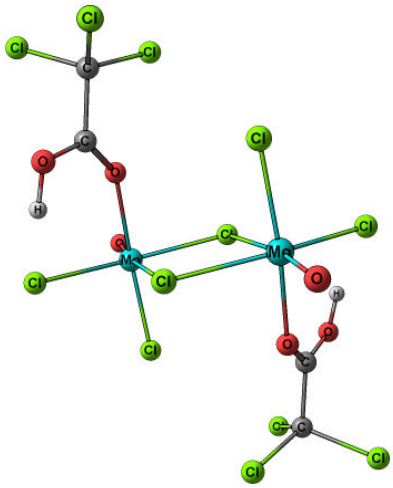
Table S2. Selected computed bond lengths (Å) and angles (°) for **1b** (M06/C-PCM), singlet-state. Values for the triplet state configuration are in parentheses.

Bond		**Angle**	
Mo---Mo	3.059 (3.779)	O=Mo–$Cl_{terminal}$	98.4 (100.9)
Mo=O	1.634 (1.635)		101.7 (103.8)
	1.634 (1.635)		98.4 (100.5)
Mo–OC	2.323 (2.373)		101.7 (103.4)
	2.323 (2.361)	O=Mo–$Cl_{bridging}$	94.7 (96.1)
Mo–$Cl_{terminal}$	2.398 (2.352)		94.9 (96.4)
	2.341 (2.304)		94.7 (96.7)
	2.398 (2.354)		94.9 (94.7)
	2.341 (2.305)	O=Mo–O	174.5 (169.9)
Mo–$Cl_{bridging}$	2.448 (2.519)		174.5 (170.8)
	2.460 (2.538)	$Cl_{bridging}$–Mo–$Cl_{bridging}$	102.9 (83.2)
	2.448 (2.516)		102.9 (83.1)
	2.460 (2.534)	O–C–O	126.5 (126.6)
C=O	1.222 (1.220)		126.5 (126.6)
	1.222 (1.219)		
C–OH	1.292 (1.297)		
	1.292 (1.297)		
O–H	0.989 (0.985)		
	0.989 (0.984)		
OH---Cl	2.182 (2.252)		
	2.181 (2.224)		

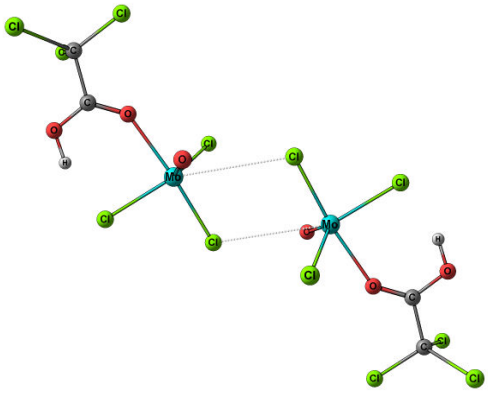
Figure S4. DFT M06 calculated structures for $[MoOCl_2(CCl_3CO_2H)(\mu\text{-}Cl)]_2$ (singlet state, EDF2/LACVP**) with implicit C-PCM solvation (CH_2Cl_2), and relative Gibbs free energy values (kcal mol^{-1}).



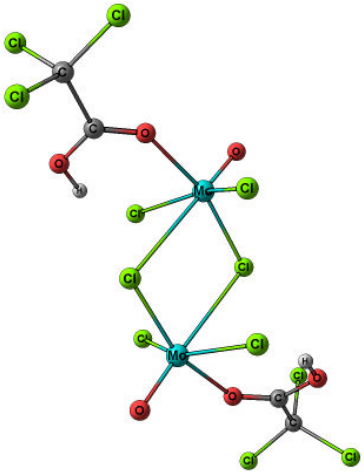
1b



1bB



1bC



1bD

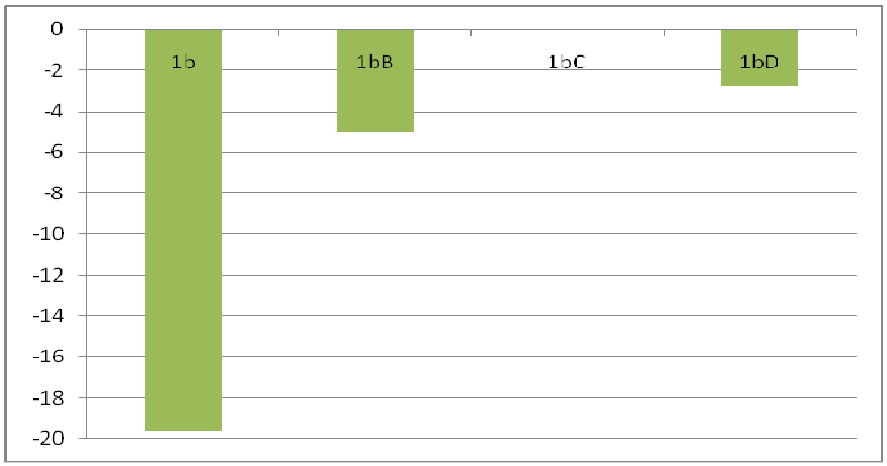


Figure S5. DFT M06 calculated structure of $Mo_2O_2Cl_6(\mu\text{-}\kappa^1\text{-}CH_3CO_2H)$, **2a** (triplet state), with implicit C-PCM solvation (CH_2Cl_2).

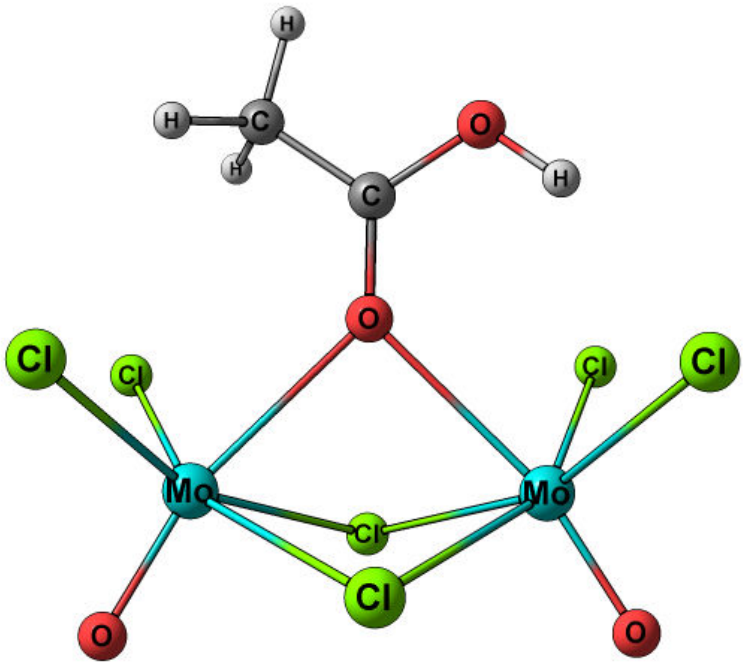
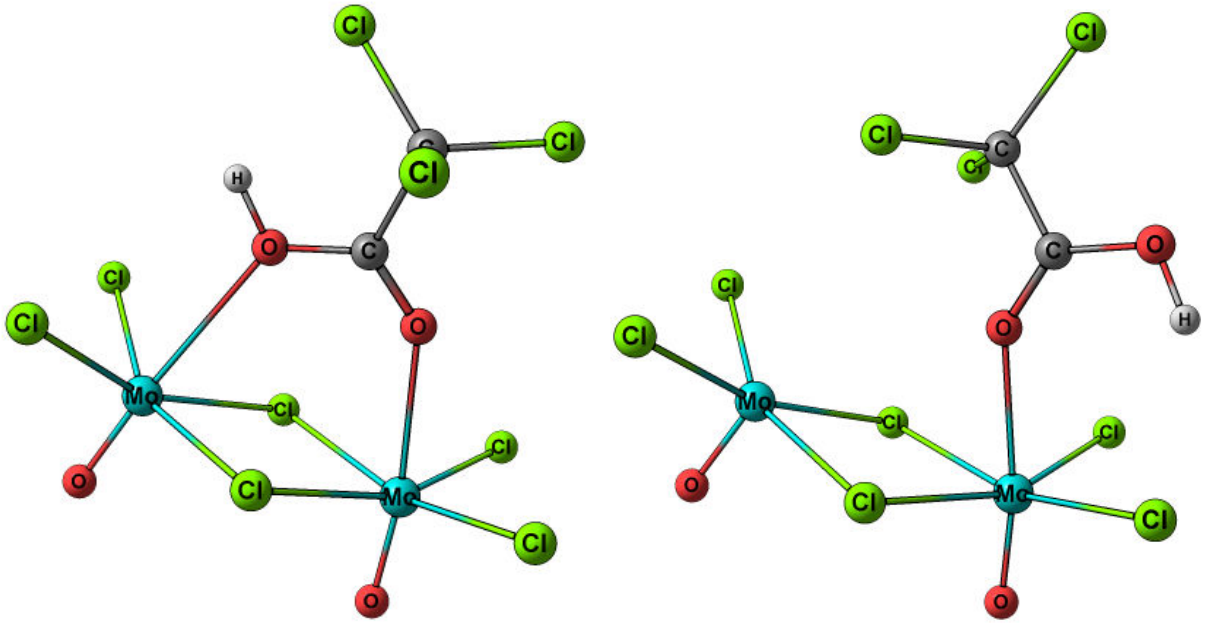


Table S3. Selected computed bond lengths (Å) and angles (°) for **2a** (triplet state, M06/C-PCM).

Bond		**Angle**	
Mo=O	1.634	O=Mo–$Cl_{terminal}$	103.5
	1.632		103.3
Mo–OC	2.489		102.9
	2.510		105.2
Mo–$Cl_{terminal}$	2.310	O=Mo–$Cl_{bridging}$	99.0
	2.312		99.3
	2.312		96.7
	2.341		98.3
Mo–$Cl_{bridging}$	2.538	O=Mo–O	164.5
	2.528		166.7
	2.507	$Cl_{bridging}$–Mo–$Cl_{bridging}$	80.8
	2.508		81.8
C=O	1.253	Mo–O–Mo	91.5
C–OH	1.299	O–C–O	123.0
O–H	0.982		
OH---Cl	2.259		

Figure S6. DFT M06 calculated structures for $Mo_2O_2Cl_6(CCl_3CO_2H)$ (triplet state), with implicit C-PCM solvation (CH_2Cl_2).



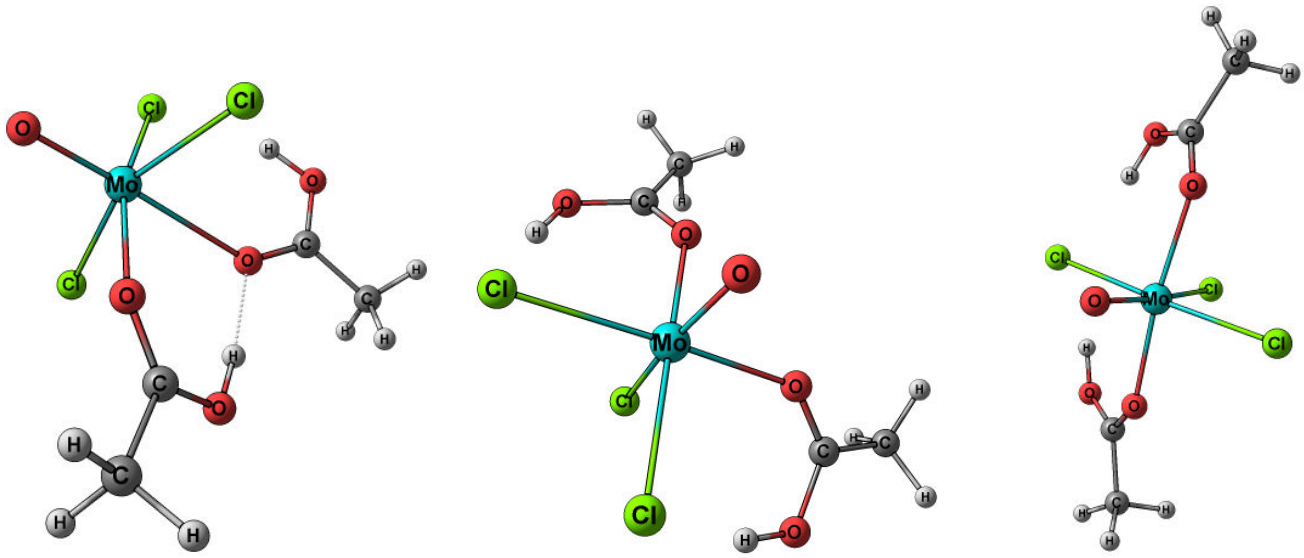
2b **2bA**

*G(**2bA**)-G(**2b**) = +16.5 kcal mol^{-1} (M06/C-PCM calculations)*

Table S4. Selected computed bond lengths (Å) and angles (°) for **2b** (triplet state, M06/C-PCM).

Bond		**Angle**	
Mo=O	1.635	O=Mo–OC	171.7
	1.630	O=Mo–OH	175.9
Mo–OC	2.409	O=Mo–$Cl_{terminal}$	103.0
Mo–OH	2.745		103.4
Mo–$Cl_{terminal}$	2.306		104.4
	2.310		104.6
	2.312	O=Mo–$Cl_{bridging}$	96.5
	2.316		96.2
Mo–$Cl_{bridging}$	2.502		101.8
	2.497		103.0
	2.544	O–C–O	122.1
	2.541		
C=O	1.208		
C–OH	1.317		
O–H	0.978		

Figure S7. DFT M06 calculated structures for $MoOCl_3(\kappa^1\text{-}CH_3CO_2H)_2$, **3a**, with implicit C-PCM solvation (CH_2Cl_2), and relative Gibbs free energy values (kcal mol^{-1}, M06/C-PCM calculations).



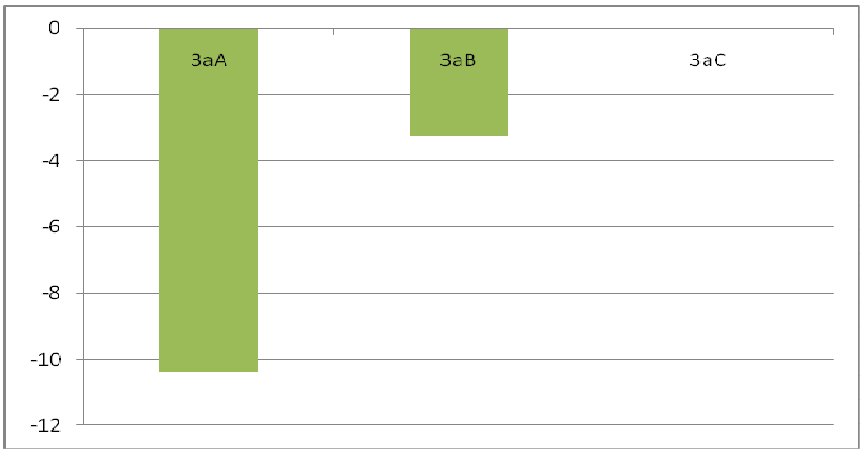
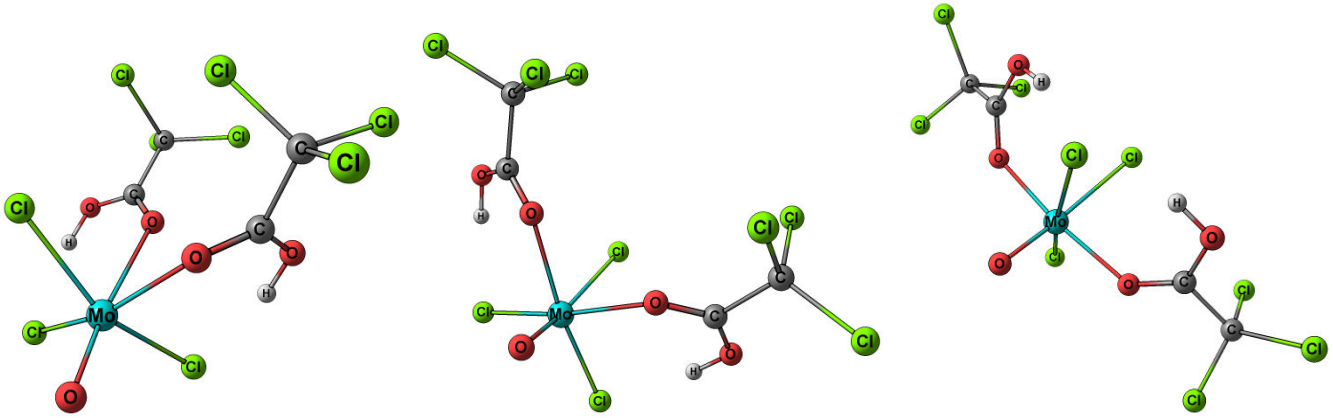


Table S5. Selected computed bond lengths (Å) and angles (°) for **3aA** (M06/C-PCM).

Bond		Angle	
Mo=O	1.638	O=Mo–OC	176.4
Mo–O (*trans* oxo)	2.455		97.4
Mo–O (*cis* oxo)	2.116	O=Mo–Cl	99.1
Mo–Cl	2.310		101.0
	2.377		101.5
	2.367	O–C–O	123.4
C=O	1.247		122.7
	1.241		
C–OH	1.303		
	1.296		
O–H	0.985		
	0.994		
OH---O	1.698		

Figure S8. DFT M06 calculated structures for $MoOCl_3(\kappa^1\text{-}CCl_3CO_2H)_2$, **3b**, with implicit C-PCM solvation (CH_2Cl_2), and relative Gibbs free energy values (kcal mol^{-1}, M06/C-PCM calculations).



3bA **3bB** **3bC**

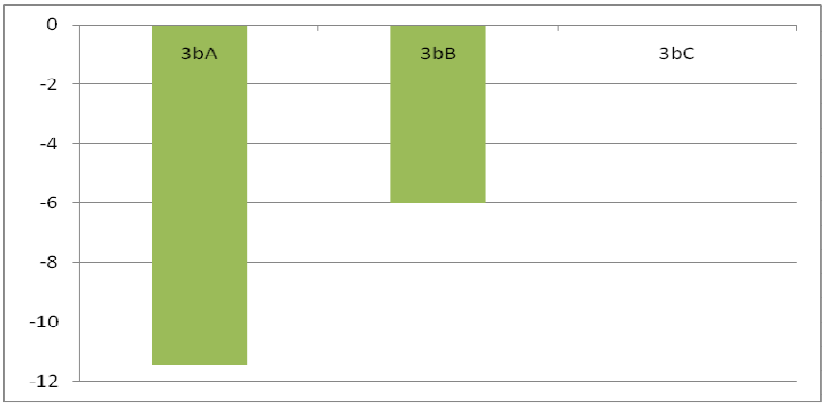


Table S6. Selected computed bond lengths (Å) and angles (°) for **3bA** (M06/C-PCM).

Bond		**Angle**	
Mo=O	1.635	O=Mo–OC	168.9
Mo–OC (*trans* oxo)	2.426		96.8
Mo–OC (*cis* oxo)	2.169	O=Mo–Cl	100.4
Mo–Cl	2.355		102.7
	2.406		102.4
	2.346	O-C-O	126.7
C=O	1.220		127.1
	1.233		
C–OH	1.296		
	1.282		
O–H	0.986		
	0.995		