Electronic Supplementary Information

Synthesis, structure and spectroscopic analyses of aquachloridodiperoxidomolybdate(VI)

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Table S1. Selected Interatomic Distances and Bond Angles in $[N(C_2H_5)_4][MoClO(O_2)_2(OH_2)]$ (**1**) and $[N(CH_3)(C_2H_5)_3][MoClO(O_2)_2(OH_2)]$ (**2**).

Table S2. Short contacts between aqua ligand and O atoms in **1** and **2**.

Table S3. Short (C)H-Cl contacts in **1** and **2**.

Figure S1. Structures of tetraethylammonium (**1**, above**)** and triethylmethylammonium (**2,** below**)** salts with numbering of non-H atoms.

Figure S2. FTIR spectra of **1** (above) and **2** (below), recorded as nujol paste on silicon wafers, with a spectral resolution of 4 cm^{-1}. The asterisks show the absorption band by nujol and organic ammonium.

Figure S3. TG/DTA charts of **1** (above, initial weight 3.43 mg) and **2** (below, initial weight 3.18 mg) in 150 mL min^{-1} air flow at 5°C min^{-1}.

Figure S4. ^{95}Mo NMR signal behaviour as a function of Cl/Mo ratio. at $[MoO_4^{2-}]_{tot}$ = 0.80 M, $[H_2O_2]_{tot}/[MoO_4^{2-}]_{tot}$ = 2.0 and pH = 1. $(NH_4)_6Mo_7O_{24}.4H_2O$ was used as molybdate source, hydrochloric acid and sodium hydroxide were used for pH adjustment.

Electronic Supplementary Material (ESI) for Dalton Transactions

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Atoms	Distances/Å	Atoms	Distances/Å
1			
Mo1-O1	1.675(2)	Mo1-O2	1.9643(19)
Mo1-O3	1.927(2)	Mo1-O4	1.939(2)
Mo1-O5	1.959(2)	Mo1-O6W	2.3505(18)
Mo1-Cl1	2.4004(6)		
Mo2-O7	1.6808(17)	Mo2-O8	1.958(2)
Mo2-O9	1.934(2)	Mo2-O10	1.944(2)
Mo2-O11	1.946(2)	Mo2-O12W	2.3982(18)
Mo2-Cl2	2.3878(7)		
2			
Mo1-O1	1.683(2)	Mo1-O2	1.958(2)
Mo1-O3	1.934(3)	Mo1-O4	1.930(3)
Mo1-O5	1.959(2)	Mo1-O6W	2.326(2)
Mo1-Cl1	2.3856(12)		

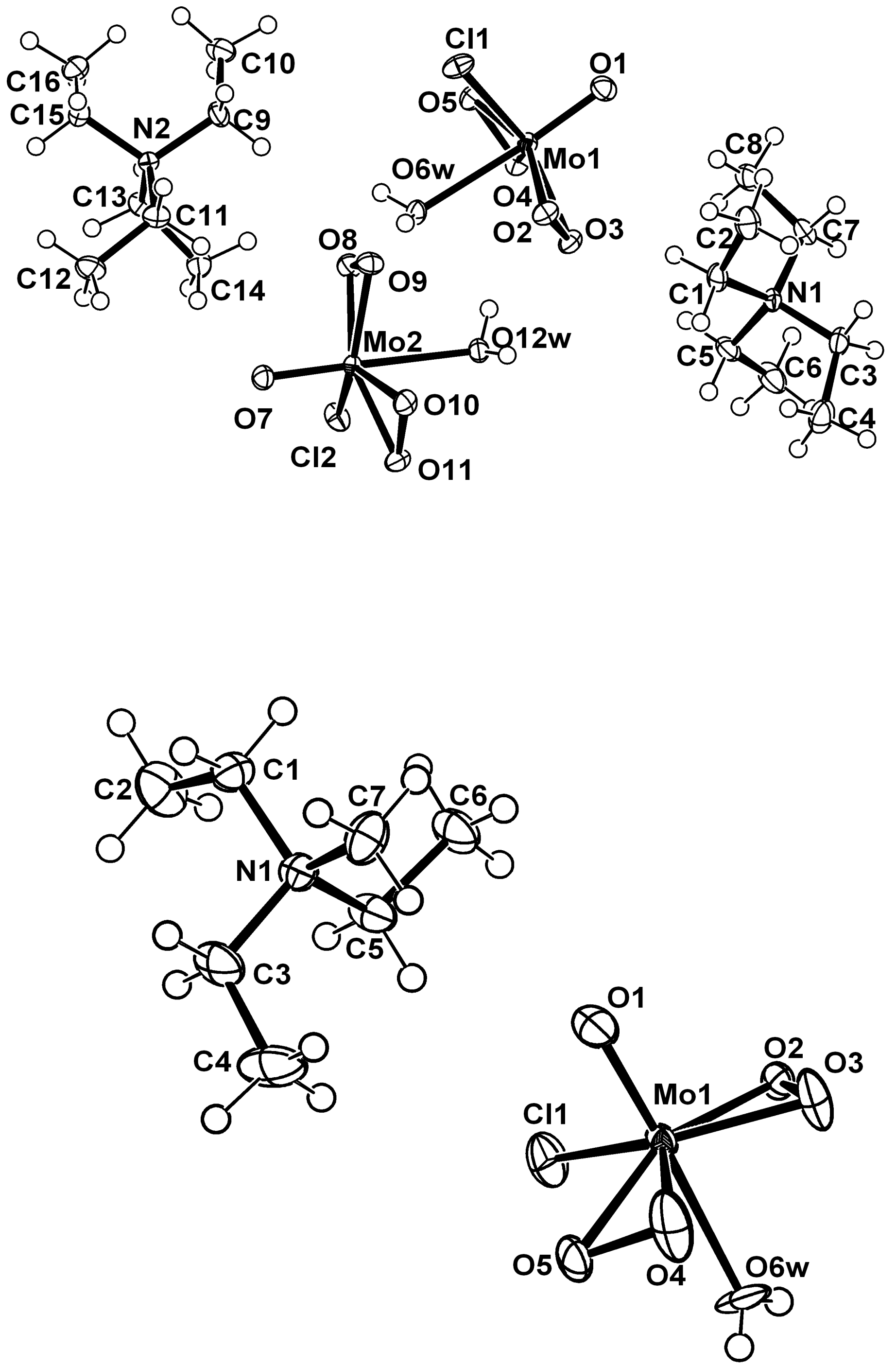
Atoms	Angles/°	Atoms	Angles/°
1			
O1-Mo1-O6W	175.91(8)	O1-Mo1-Cl1	94.56(7)
O6W-Mo1-Cl1	81.50(5)		
O7-Mo2-O12W	177.49(8)	O7-Mo2-Cl2	95.02(7)
O12W-Mo2-Cl2	82.48(5)		
2			
O1-Mo1-O6W	174.54(12)	O1-Mo1-Cl1	92.78(8)
O6W-Mo1-Cl1	81.81(9)		

Table S2. Short contacts between aqua ligand and O atoms in **1** and **2**.

Atoms	H--O distance/Å, O-H--O angle/°	Atoms	H--O distance/Å, O-H--O angle/°
1			
O6W-HW1A--O8	2.06(2), 162(4)	O6W-HW1B--O10(*x*-1, *y*, *z*)	2.006(17), 178(4)
O6W-HW1B--O11(*x*-1, *y*, *z*)	2.63(3), 145(3)	O12W-HW2A--O2	2.11(2), 164(4)
O12W-HW2B--O5(*x*+1, *y*, *z*)	1.992(18), 174(4)		
2			
O6W-HO6A--O5(0.5+*x*, 1.5-*y*, 1-*z*)	2.16(5), 154(5)	O6W-HO6B--O2(*x*-0.5, 1.5-*y*, 1-*z*)	2.18(5), 161(6)

Table S3. Short (C)H-Cl contacts in **1** and **2**.

Atoms	H--Cl length/Å, C-H--Cl angle/°	Atoms	H--Cl length/Å, C-H--Cl angle/°
1			
C11-H11B--Cl1(0.5+*x*, 0.5-*y*, -*z*)	2.77, 148.6	C13-H13A--Cl2(*x*-0.5, 1.5-*y*, -*z*)	2.76, 161.1
C6-H6C--Cl2(1-*x*, *y*-0.5, 0.5-*z*)	2.74, 153.7	C7-H7B--Cl2(1-*x*, *y*-0.5, 0.5-*z*)	2.64, 160.7
2			
C6-H6C--Cl1(1-*x*, *y*-0.5, 1.5-*z*)	2.79, 154.9	C5-H5A--Cl1	2.76, 155.2



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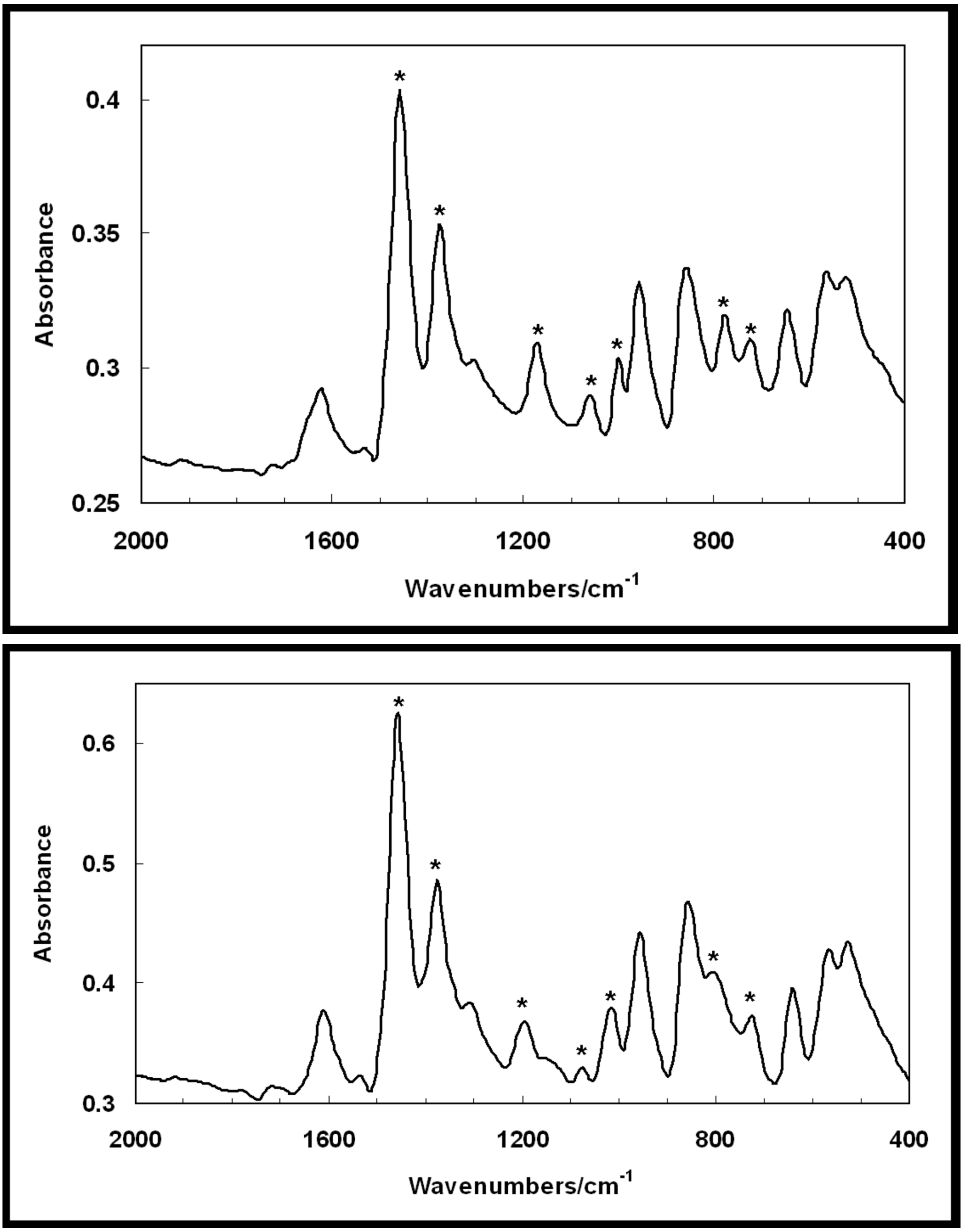

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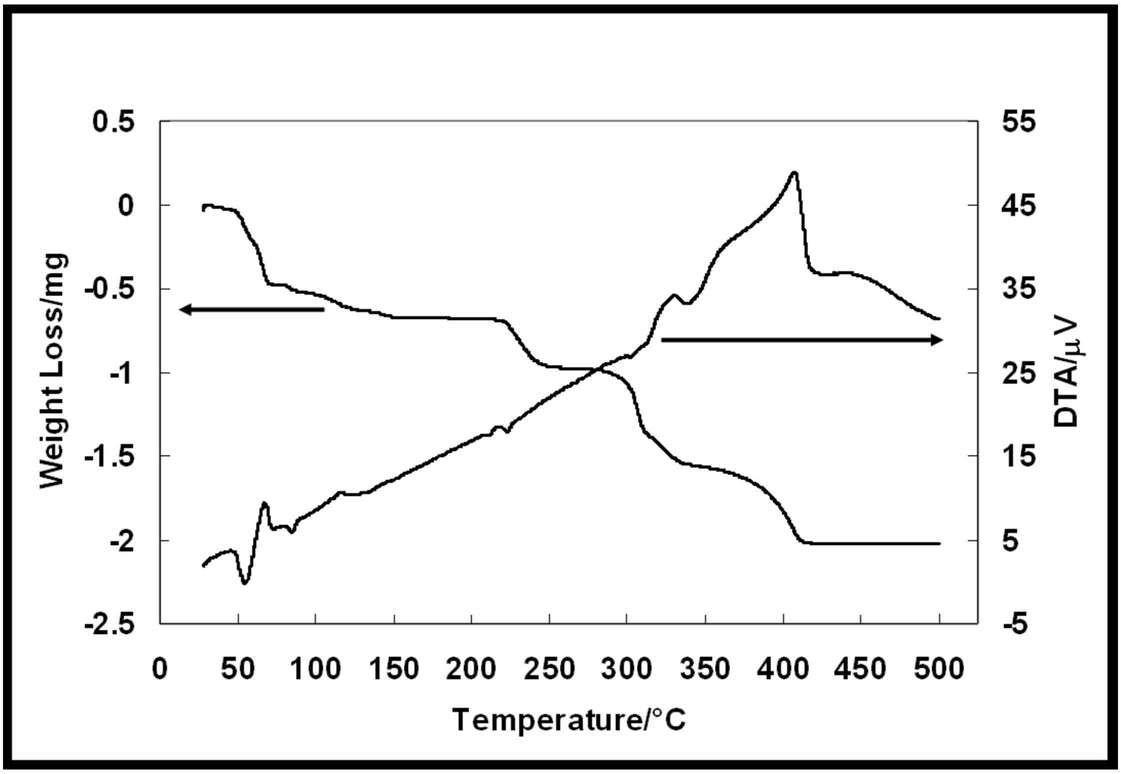

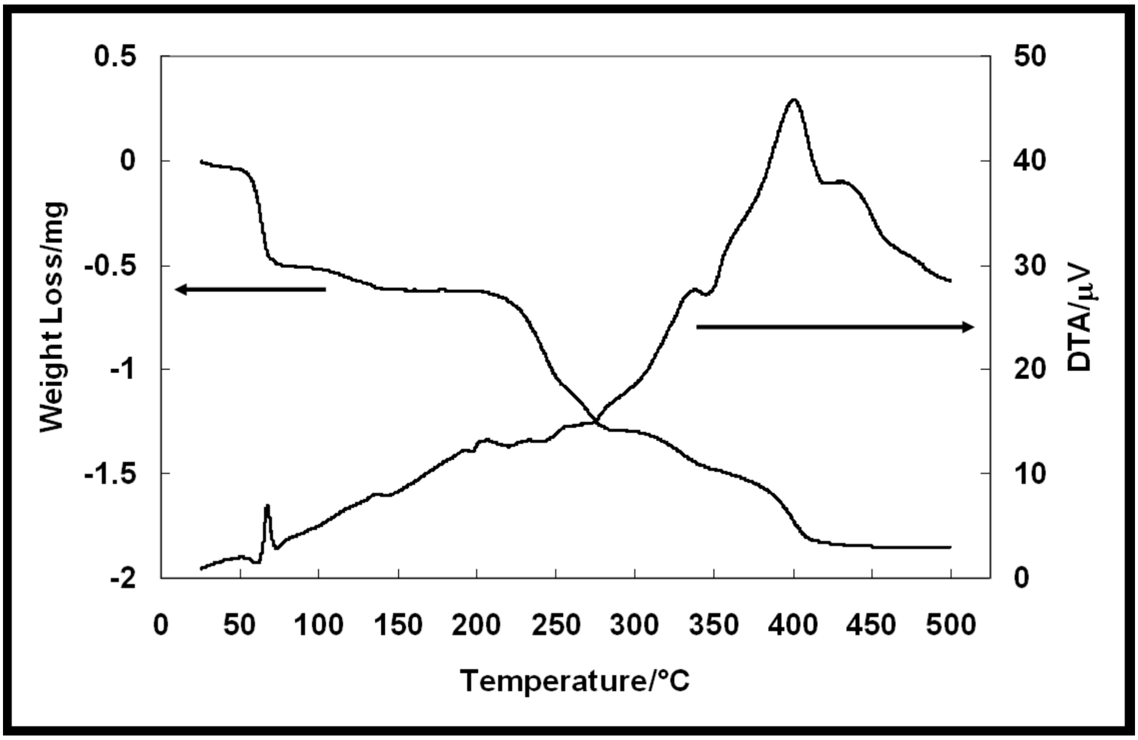

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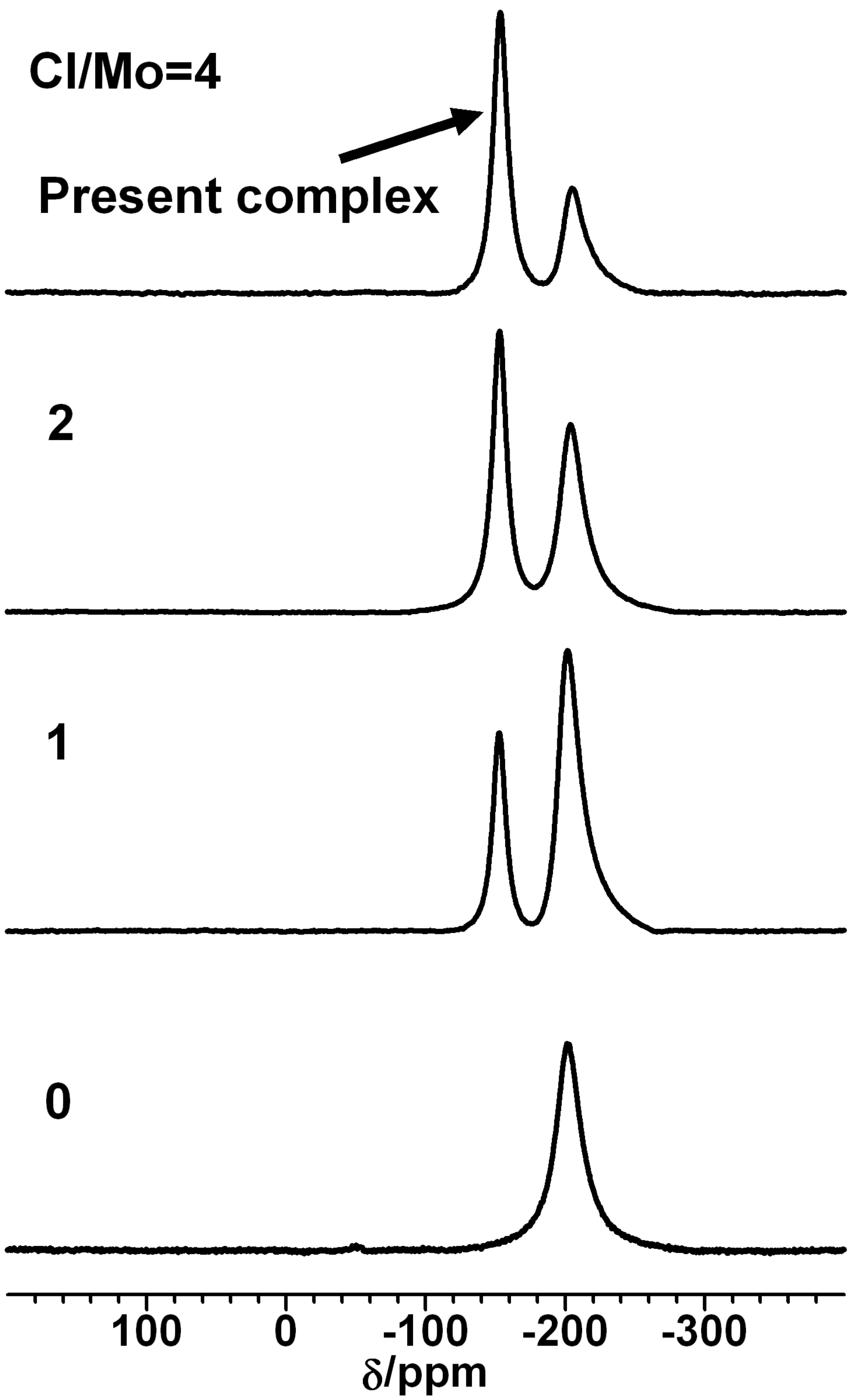

Figure S4. [95]Mo NMR behaviour as a function of Cl/Mo ratio at $[MoO_4^{2-}]_{tot}$ = 0.80 M, $[H_2O_2]_{tot}/[MoO_4^{2-}]_{tot}$ = 2.0 and pH = 1. $(NH_4)_6Mo_7O_{24}.4H_2O$ was used as molybdate source, and hydrochloric acid and sodium hydroxide were used for pH adjustment.