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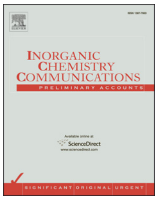

Synthesis, structure, and substitution reactivity of a new bi-oxo capped molybdenum cluster: $[Mo_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CCH_2Cl)_6(H_2O)_2(OH)]^+$

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ABSTRACT

A new bi-oxo capped molybdenum carboxylate, $[Mo_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CCH_2Cl)_6(H_2O)_2(OH)]^+$, was synthesized by refluxing $[Mo_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CCH_3)_6(H_2O)_3]^{2+}$ in chloroacetic acid for 20 h (T = 110 °C). Using ion-exchange chromatography (0.5 M $NaClO_4$ eluant), the trinuclear molybdenum ion was isolated and allowed to crystallize slowly (T = 4 °C) as the perchlorate salt (yield 23%). Upon dissolution of the compound in methanol-d_4, substitution of the terminal ligands for solvent occurs readily in which the observed exchange rate constant is $k_{obs}^{298K} = 5.3 \times 10^{-5}$ ($\pm$0.3) s^{-1} and activation parameters equal to $\Delta H^{\ddagger} = 130$ ($\pm$10) kJ mol^{-1} and $\Delta S^{\ddagger} = 111$ ($\pm$33) J mol^{-1} K^{-1}. From the kinetic data, we find that ligand substitution follows a dissociative pathway and that rates of substitution are faster than expected when compared to the molybdenum acetate analog. Herein, we report the synthesis, crystallographic study, and substitution reactivity of a new molybdenum bi-oxo capped cluster with bridging chloroacetate ligands.

Oxo-centered metal carboxylates ($[M_3(\mu_3\text{-}O) \times (\mu\text{-}O_2CR)_6L_3]^{z+}$; M = metal ion; L = terminal ligand; R = alkyl group; x = 1: single oxo-capped and x = 2: bi-oxo capped; abbreviated as $\mathbf{M_3}$) have long been studied for their redox chemistry [1–3], catalytic activity [4–6], and ligand substitution reactivity [7–10]. Despite a number of studies on $\mathbf{Cr_3}$ [11], $\mathbf{Ru_3}$ [12], $\mathbf{Rh_3}$ [13] and $\mathbf{Fe_3}$ [14] clusters (where R = halogenated alkyl group), the structure and reactivity of a bi-oxo capped $\mathbf{Mo_3}$ cluster with halogenated carboxylate ligands, to our knowledge, have not been reported before. Yet these clusters are particularly interesting since reports on similar $\mathbf{Rh_3}$ and $\mathbf{Cr_3}$ structures suggest that metal carboxylates with halogenated bridging ligands tend to be more inert to substitution [11,13]. For instance, Houston et al. found that $\mathbf{Rh_3}$ clusters with chloroacetate and dichloroacetate bridging ligands were significantly less reactive to water substitution (k^{298K} (R = CH_2Cl) = $5.0 \text{x} 10^{-4}$ s^{-1} and k^{298K} (R = $CHCl_2$) = 2.3×10^{-5} s^{-1}) when compared to the acetate-bridged trimer (k^{298K} (R = CH_3) = 5.6×10^{-3} s^{-1}) [13]. Similarly, Fujihara et al. found that rates of substitution for $\mathbf{Cr_3}$ carboxylates (R = H, CH_3, CH_2CH_3, CH_2Cl, $CHCl_2$, CH_2OCH_3, $C(CH_3)_3$, CH_2CHCl, $CH(CH_2CH_3)_2$) spanned over two orders of magnitude ($k = 2.4 \times 10^{-5}$ s^{-1} to 9.49×10^{-3} s^{-1}; T = 40 °C) and could be eloquently explained by examining Taft's electronic parameters for the alkyl chains [11]. Likewise, a recent manuscript by Inatomi et al. reported that rates for $\mathbf{Ru_3}$ (R = $CHCl_2$) were 105-fold smaller than $\mathbf{Ru_3}$ (R = CH_3) [12]. Based on these results, we were initially perplexed to find that the $[Mo_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CCH_2Cl)_6(H_2O)_2(OH)]^+$ cluster ($\mathbf{Mo_3}$ (R = CH_2Cl); Scheme 1) is roughly an order of magnitude more reactive to ligand substitution (k_{obs}^{298K} (R = CH_2Cl) = 5.3×10^{-5} s^{-1}) when compared to the molybdenum acetate analog (k^{298K} (R = CH_3) = 5.6×10^{-6} s^{-1}; H_2O exchange, ΔH = 126 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 77 J mol^{-1} K^{-1}) [15]. Herein we report on the facile synthesis for producing halogenated molybdenum carboxylates, comment on the mechanism, and suggest a reason for the enhanced substitution reactivity of the terminal ligands.

Although the synthesis of metal carboxylates has been studied for over three decades [16,17], the structures have been mostly restricted to molybdenum and tungsten clusters with simple alkyl chains. Recent studies have shown that the synthesis of new molybdenum (and tungsten) carboxylates can be accomplished by using the acetate-bridged cluster as a starting template [18,19]. By refluxing 1.0 g of $\mathbf{Mo_3}$ (R = CH_3) in the presence of chloroacetic acid (25 g; T = 110 °C for 20 h), we find that the bridging acetates readily exchange for chloroacetates giving the $\mathbf{Mo_3}$ (R = CH_2Cl) trimer with decent yield (23% yield based on $\mathbf{Mo_3}$ (R = CH_3)). Following ion exchange chromatography (0.5 M $NaClO_4$ eluant), red plates formed after several days (T = 4 °C) and were analyzed using X-ray crystallography, ^{1}H NMR, UV–vis and elemental analysis (full details are provided in the Supporting Data, Appendix 1).

The $\mathbf{Mo_3}$ (R = CH_2Cl) perchlorate salt (Fig. 1) crystallizes in the orthorhombic crystal system in space group $P2_12_12_1$, with the following unit–cell dimensions; a = 12.6963(9) Å, b = 14.2111(10) Å, c = 16.0429(11) Å, α,β,γ = 90°, and V = 2894.6(4) Å^3. Consistent with other $\mathbf{Mo_3}$ structures, the oxidation state of each Mo ion is (IV) giving

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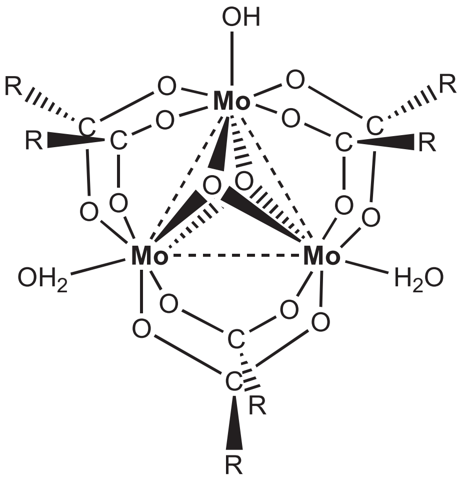

R = CH_2Cl; ClO_4^-

Scheme 1. Trinuclear molybdenum cluster.

a cluster cation that is monovalent [16,17,20]. Each Mo(IV) ion is bound through metal–metal bonding with μ_3-O ligands above and below the **Mo_3** plane. Also attached are bridging chloroacetate ligands, ligated waters and a bound hydroxo ligand. As a result, the trinuclear molybdenum unit contains *pseudo*-C_{2v} symmetry. Structural data for $[Mo_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CCH_2Cl)_6(H_2O)_2(OH)]ClO_4{\cdot}H_2O$ is summarized in Table 1.

Upon dissolving the crystals in methanol-d_4, the ^1H NMR spectrum immediately after dissolution shows one signal due to bridging chloroacetate protons (4.34 ppm; $\mu\text{-}O_2CCH_2Cl$) (Fig. 2, **inset**). After only 20 min at a slightly elevated temperature (306 K), substitution of the terminal ligands by the deuterated solvent results in new $\mu\text{-}O_2CCH_2Cl$ signals from the various substituted trimers (mono-substituted (*), di-substituted (o) and tri-substituted (T), Fig. 2). Similar NMR patterns for ligand substitution have been observed for other trinuclear transition metal complexes (**Mo_3**, **W_3**, **Rh_3**) [13,18,20]. Since quantifying the substitution reactivity of the unsubstituted complex (labeled as #, 4.34 ppm) was the focus of this study, the kinetics of the mono-, di-, and tri-substituted species was not quantified (description of NMR patterns is provided in Supporting Data; Fig. A.1).

Kinetic data were collected by monitoring the ^1H NMR signal of the unsubstituted complex (labeled #; $\mu\text{-}O_2CCH_2Cl$; 4.34 ppm) as a function of time. Rate constants were calculated by using the integrated rate law for a first-order reaction (details in supporting information, Table A.1, Fig. A.2). Using variable-temperature NMR (T = 296, 306.0, 313.0 K), activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for substitution were determined by plotting $\ln(k_{obs}/T)$ vs. 1/T (Fig. 3).

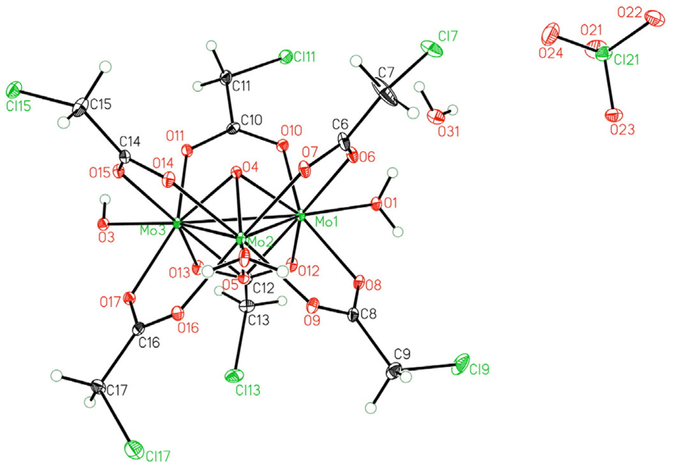

Fig. 1. Thermal ellipsoid plot of **Mo_3** (R = CH_2Cl) crystallized as the perchlorate salt.

Table 1
Crystallographic data, data collection, and structure refinement for $[Mo_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CCH_2Cl)_6(H_2O)_2(OH)]ClO_4{\cdot}H_2O$ (**CCDC 985107**).

Crystal data	
Empirical formula	$C_{12}H_{17}Cl_6Mo_3O_{17}{\cdot}ClO_4{\cdot}H_2O$
Formula weight (g mol^{-1})	1051.24
Crystal system	Orthorhombic
Space group	$P\,2_1\,2_1\,2_1$
a (Å)	12.6963(9)
b (Å)	14.2111(10)
c (Å)	16.0429(11)
α (°)	90°
β (°)	90°
γ (°)	90°
V (Å^3)	2894.6(4)
Z	4
ρ_{calc} (g cm^{-3})	2.412
F (000)	2048
μ (mm^{-1})	2.019
Data collection	
Radiation (Å)	Mo Kα, 0.71073
T (K)	90(2)
θ range (°)	2.5–27.5
Monochromator	Fine focused sealed tube
Unique data	34231
Observed data, (I > 2σ(I))	6497
Refinement	
No. of reflections	6666
No. of refined parameters	451
Final agreement factors:	$R(F_{all}) = 1.91\%$, $wR(F^2_{all}) = 4.13\%$
	$R(F_o > 4^{\delta}(F_o)) = 1.81\%$, $wR(F2) = 4.10\%$
Goodness-of-fit (GOF)	1.028
$\Delta\rho_{max}$	0.86 e Å^{-3}
$\Delta\rho_{min}$	−0.87 e Å^{-3}

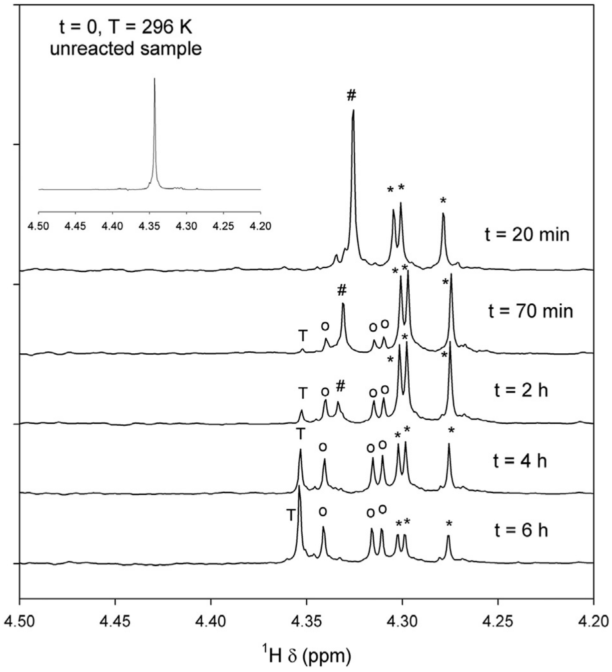

Fig. 2. ^1H NMR spectra after the dissolution of **Mo_3** in methanol-d_4 (T = 306 K). The signal at 4.34 ppm is due to the unsubstituted trimer. After completion, the integration for the tri-substituted signal equals the integration of the unsubstituted signal.

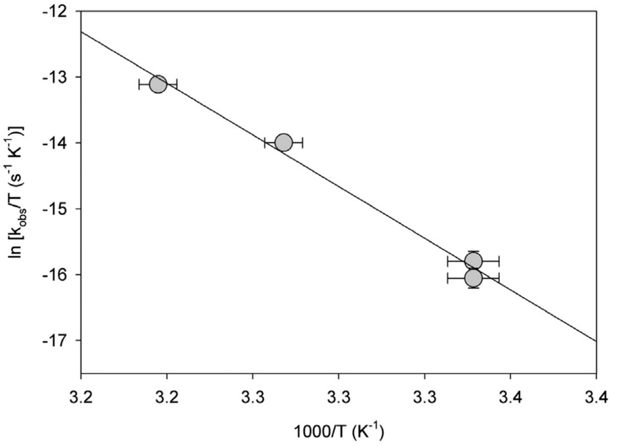

Fig. 3. Temperature dependence of the observed rate constant for ligand substitution at **Mo_3** ($R = CH_2Cl$).

We find from the ^1H NMR data that the observed rate constant for substitution of the unsubstituted complex is $k_{obs}^{298K} = 5.3 \times 10^{-5}$ s^{-1} and activation parameters are highly positive ($\Delta H^‡ = 130(\pm 10)$ kJ mol^{-1} and $\Delta S^‡ = 111$ (± 33) J mol^{-1} K^{-1}). Positive activation parameters suggest a dissociative (D or I_D) substitution mechanism, which is consistent with other **Mo_3** cluster studies that report highly positive activation enthalpies, entropies, and/or volumes (Table 2). A dissociative activation state is not surprising considering that the Mo(IV) ions that make up the triangular unit are nine-coordinate and the bond angle between the terminal ligand and bridging group (H_2O-Mo-μ-O_2CCH_2Cl) is roughly 75–77°. Approach of an incoming ligand in an associative pathway seems unlikely given the steric hindrance about the Mo(IV) ion.

We find that rates of substitution at **Mo_3** are nearly an order of magnitude faster when compared to the molybdenum acetate trimer (k^{298K} ($R = CH_3$) $= 5.6 \times 10^{-6}$ s^{-1}; H_2O exchange). Previous reports on **Rh_3** and **Cr_3** have shown that clusters with halogenated substituents on the carboxylate bridges tend to be more inert to substitution than those that possess electron donating alkyl chains [11,13]. For example, rate constants for ligand substitution at **Rh_3** chloroacetate and dichloroacetate clusters are one to two orders of magnitude smaller (k^{298K} ($R = CH_2Cl$) $= 5.6 \times 10^{-4}$ s^{-1}; k^{298K} ($R = CHCl_2$) $=$ 2.3×10^{-5} s^{-1}) when compared to the **Rh_3** acetate trimer ($k^{298K} =$ 5.6×10^{-3} s^{-1}) [13]. These data suggest that the inductive ability of the aliphatic substituents heavily influences the kinetic reactivity of the ligated waters. However, this comparison was made among clusters that were in the fully protonated form.

The enhanced lability of the **Mo_3** ($R = CH_2Cl$) trimer is most likely due to the bound hydroxide. When an anionic ligand is attached, the charge density on the overall complex is reduced resulting in a decrease in the ion–dipole interaction between the metal and the neighboring aqua ligands. This effect has been well documented in the literature for simple monatomic ions and can be as large as a 10^4-fold rate enhancement [21,22,22a),22b),23,24]. For instance, Xu et al. found that rates of water exchange for $Cr(H_2O)_5(OH)^{2+}$ were two orders of magnitude faster when compared to the fully protonated form (k^{298K} ($Cr(H_2O)_6^{3+}$) $= 1.8 \times 10^{-4}$ s^{-1}; k^{298K} ($Cr(H_2O)_5(OH)^{2+}$) $= 2.4 \times 10^{-6}$ s^{-1}) and activation parameters suggested a more dissociative activation state ($\Delta H^‡ = 111$ kJ mol^{-1}, $\Delta S^‡ =$ 55.6 J mol^{-1} K^{-1} and $\Delta V^‡ = +2.7$ cm^3 mol^{-1}) [23]. Similarly, rates of water substitution for the $Al(H_2O)_6^{3+}$ ion are enhanced by several orders of magnitude when the first hydration shell contains a bound hydroxo (k^{298K} ($Al(H_2O)_6^{3+}$) $= 1.29$ s^{-1}); k^{298K} ($Al(H_2O)_5(OH)^{2+}$) $=$ 3.1×10^4 s^{-1}) or a negatively charged anion such as F^- (k^{298K} ($Al(H_2O)_5(F)^{2+}$) $= 1.1 \times 10^2$ s^{-1}; k^{298K} ($Al(H_2O)_4(F)_2^+$) $= 1.96 \times$ 10^4 s^{-1}) [24]. Perhaps the most notable, however, is the aqueous rhodium dimer ($[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$, albeit in this case the hydroxide is not terminal but bridging two metals [25]. The labilizing influence of the bound hydroxide produced rates that are 10^2 faster (k^{298K} (trans-H_2O) 8.5×10^{-7} s^{-1}; k^{298K} (cis-H_2O) 5.4×10^{-7} s^{-1}) [26] when compared to the hexaaqua rhodium ion (k^{298K} ($Rh(H_2O)_6^{3+}$) $= 2.2 \times$ 10^{-9} s^{-1}) [27]. At this time, a comparison between protonated and deprotonated **Mo_3** clusters cannot be made because exchange rates have only been measured for a small number of clusters [7,7a),7b), 8–13] and there have been no reports on the substitution rates of the first hydrolysis species. Our conclusion that water exchange is enhanced by the bound hydroxide, however, is consistent with a number of studies that report 10^2–10^4 rate enhancements for monomeric and polyatomic ions with hydoxo ligands. Future work focuses on a full pH dependence study in which substitution rates for the fully protonated **Mo_3** ($R = CH_2Cl$) cluster will be compared to other **Mo_3** trimers currently being quantified ($R = CH_2CH_3$, $CH_2CH_2CH_3$, and CH_2CH_2Cl).

Acknowledgments

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Supplementary material

CCDC 985107 contains the supplementary crystallographic data for $[Mo_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CCH_2Cl)_6(H_2O)_2(OH)]ClO_4$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated such as detailed experimental procedures can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche.2014.08.021.

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Table 2
Ligand substitution for a selected number of bi-oxo capped molybdenum clusters, $[Mo_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CR)_6\ L_3]^{z+}$ where $R = CH_3$ or CH_2Cl.

Mo_3	Attached ligand (L)	Incoming ligand	k^{298K} (s^{-1})	$\Delta H^‡$ (kJ mol^{-1})	$\Delta S^‡$ J mol^{-1} K^{-1}	Mechanism
$R = CH_2Cl$	η-OH_2	CD_3OD	5.3×10^{-5}	130	111	I_D or D[a]
$R = CH_3$	η-O_2CCH_3	D_2O	7.2×10^{-6}	126	80	I_D[b]
$R = CH_3$	η-OH_2	$C_2O_4^{2-}$	8×10^{-6}	120	85	I_D[c]
$R = CH_3$	η-OH_2	SCN^-	9.4×10^{-6}	141	131	I_D[c]
$R = CH_3$	η-OH_2	$^{17}OH_2$	5.6×10^{-6}	126	77	I_D[c,d]

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[b] Reference [7b].
[c] Reference [15].
[d] Reference [7a].

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