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High oxidation state aqueous organometallics. Formation and structure of an oxo-centred Cp*Mo^{V} trinuclear cation by chemical reduction of Cp*$_2$Mo$_2$O$_5$

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Reduction of Cp*$_2$Mo$_2$O$_5$ by zinc/CF$_3$CO$_2$H in MeOH–H$_2$O yields a salt which is composed of [Cp*$_3$Mo$_3$O$_4$(O$_2$CCF$_3$)$_3$]$^+$ and [Zn$_2$(O$_2$CCF$_3$)$_6$]$^{2-}$ ions after crystallisation from THF–Et$_2$O.

High oxidation state organometallic chemistry is now a mature field with important applications to a variety of catalytic transformations.[1,2] Although many compounds in this class are stable in an aqueous environment and some have even been synthesised in water, their aqueous chemistry has rarely been investigated. Complex [Cp*$_2$Mo$_2$O$_5$][3,4] is one such example. We have recently described an improved aqueous synthesis,[5] the speciation of this compound in water[6] which highlighted the new species [Cp*MoO$_2$(OH)] and [Cp*MoO$_2$]$^+$, and an exploratory aqueous reductive electrochemistry study. An on-line voltammetric-ESMS investigation has indicated the formation of a wealth of new mixed oxo-Cp* complexes in oxidation states down to IV.[7] Therefore, we are now proceeding to explore synthetic chemical reductions under a variety of conditions. The first product that we have isolated, showing unexpected and unusual features, is reported in this contribution.

The compound is generated by zinc reduction in MeOH–H$_2$O containing trifluoroacetic acid and air-stable single crystals have been obtained from THF–Et$_2$O. † The structure of the compound has been elucidated by X-ray crystallography. ‡ It is composed of [(Cp*Mo)$_3$(μ_3-O)(μ-O)$_3$(μ-O$_2$CCF$_3$)$_3$]$^+$ (Fig. 1) and [Zn$_2$(μ-O$_2$CCF$_3$)$_4$(O$_2$CCF$_3$)$_2$]$^{2-}$ (Fig. 2) ions. The cation, of ideal C_{3v} symmetry, sits on a general position, while the dianion lies on inversion centers. The cation features an oxo-capped equilateral Mo$_3$ triangle where each metal has the formal oxidation state V (3 cluster electrons). Each edge is further bridged by an oxo and a trifluoroacetate ligand, and an η^5-Cp* ligand completes each metal's coordination sphere. No previous example seems available of a Mo$_3$ cluster, whatever the coordination sphere and geometry, where the metal oxidation state is as high as V.

The central Mo$_3$O$_4$ core is a quite typical archetype for Mo$_3$ clusters, but is mostly found for clusters containing 6 metal electrons (Mo^{IV}), *e.g.* the [Mo$_3$O$_4$(H$_2$O)$_9$]$^{4+}$ aqua ion.[8] Examples have also been described for lower oxidation states, notably 8-electrons (Mo$_3^{III,III,IV}$), but not for higher ones.[9] Previously reported clusters featuring triangular (Cp*Mo)$_3$ units include [(Cp*Mo)$_3$(μ-OH)$_n$(μ-O)$_{6-n}$]$^{2+}$ (n = 4, 5, 6; *e.g.* 5, 6 and 7-electron clusters),[10] the two related [Cp*$_4$Mo$_5$O$_{11}$] and [Cp*$_6$Mo$_8$O$_{16}$] clusters[10,11] containing the same 4-electron Mo$_3$(μ-O)$_6$ core, and [(CpMo)$_3$(μ_3-O)(μ-Cl)$_4$Cl$_3$].[12] None of these compounds contains a Mo$_3$O$_4$ core, nor has any of them the oxidation state V for all Mo centres. The related Mo^{IV} clusters [Cp$_3$Mo$_3$(μ_3-S)(μ-S)$_4$]$^+$ [13] and [(Cp*Mo)$_3$(μ_3-CH)(μ-CH$_2$)(μ-O)$_2$][14] are also known. The Mo$_3$(μ-O$_2$CR)$_3$ unit has precedents in non organometallic complexes with 6–9 cluster electrons, none of which contains a Mo$_3$(μ_3-O)(μ-O)$_4$ core.[15–18] The closest relative appears to be [Mo$_3$O$_4$(O$_2$CH)$_8$]$^{4-}$ (another compound of Mo^{IV}), having a single bridging and seven terminal (η^1) formato ligands.[19]

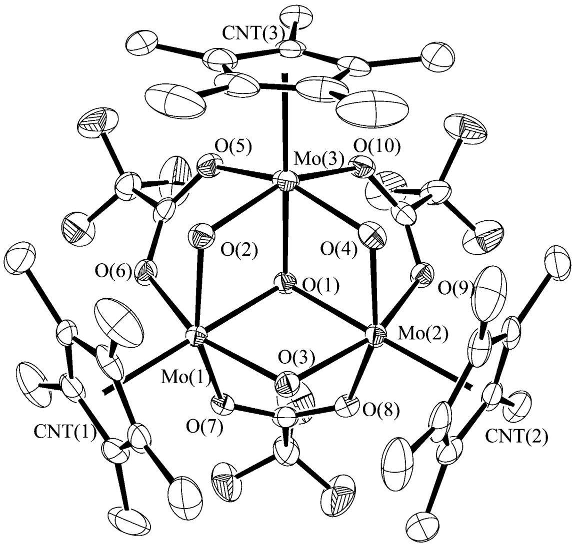
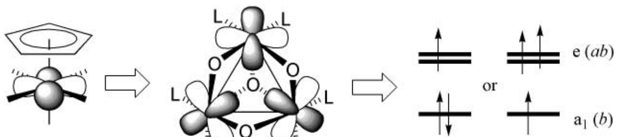


Fig. 1 ORTEP[26] view of the [Cp*$_3$Mo$_3$O$_4$(O$_2$CCF$_3$)$_3$]$^+$ cation. Relevant averaged parameters: Mo–Mo, 3.1287(15); Mo–CNT (Cp* centroid), 2.069(5); Mo–O(1), 2.032(6); Mo–(μ-O), 1.95(1); Mo–O(acetate), 2.183(10); C–O, 1.249(4) Å; CNT–Mo–O(1), 177.63(12); Mo–(μ-O)–Mo′, 106.9(4); Mo–(μ_3-O)–Mo′, 100.7(3)°.

The Mo–Mo distance indicates little or no direct metal–metal bonding. The absence of a strong interaction may be easily understood on a qualitative basis, imagining the formal assembly of the [(CpMo)$_3$(μ_3-O)(μ-O)$_3$L$_6$] cluster (L = terminal ligand) from three mononuclear CpML$_5$ fragments (see Scheme 1). The Cp* ligand occupies the position *trans* to the capping



Scheme 1 Orbital interactions in [(CpMo)$_3$(μ_3-O)(μ-O)$_3$L$_6$] clusters.

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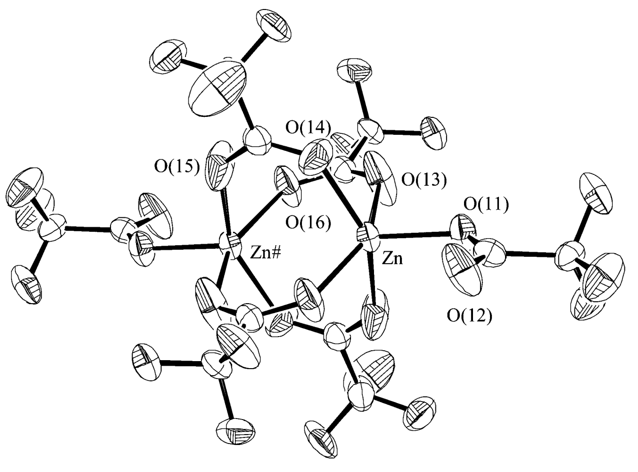

Fig. 2 ORTEP view of the $[Zn_2(O_2CCF_3)_6]^{2-}$ anion. Relevant averaged parameters: Zn ··· Zn, 3.228(5), Zn–O(bridging), 2.05(2); Zn–O(terminal), 1.926(3); C–O(br.), 1.214(14); C–O(term.), 1.243(5); C=O, 1.207(5) Å; O(br.)–Zn–O(br.)′ (*cis*), 86.4(9); O(br.)–Zn–O(br.)′ (*trans*), 150.9(2), O(11)–Zn–Zn#, 166.7(1)°.

O atom for each metal. Only one orbital (d_{xy}) is available to accommodate metal electrons and the three resulting cluster orbitals can only establish weak π/δ type interactions (see Scheme 1). The most favourable scenario for metal–metal bonding features two weakly bonding (a_1) and one antibonding (e) electron. Both $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3L_9]$ (Mo–Mo around 2.5 Å for 6 cluster electrons) and $[(CpM)_3(\mu\text{-}O)_6]$ type clusters (Mo–Mo = 2.7–2.8 Å for 4 to 6 electrons), on the other hand, possess more and better oriented orbitals for metal–metal bonding.[10,20] The Mo–(μ-O), Mo–(μ_3-O) and Mo–O($COCF_3$) distances are slightly longer in our $[Cp^*{}_3Mo_3O_4(O_2CCF_3)_3]^+$ cluster relative to the previously cited related Mo^{IV} clusters. The weaker Mo–Mo interactions probably play a more important role than the expected smaller ionic radius for determining these distances.

The $[Zn_2(O_2CCF_3)_6]^{2-}$ structure is also worthy of brief comment. Structurally characterised lantern-type $Zn_2(\mu\text{-}O_2CR)_4L_2$ precedents (R = CH_3, CH=CHCH_3; L = py, py-4-CN, quin) show slightly shorter Zn–Zn distances (2.89–2.98 Å),[21–23] though a direct bonding interaction is precluded by the closed-shell configuration of Zn^{2+}. An incipient interaction between the Zn^{2+} centres and the "free" C=O groups may be responsible for a slight misalignment between the Zn–O(term.) and Zn–Zn axes.

Given the low coordinating ability of $CF_3CO_2^-$, its facile dissociation in an aqueous environment, leaving a $[(Cp^*Mo)_3O_4]^{4+}$ core, may be expected. However, an electrospray mass spectrometric (ESMS) study of the compound (positive mode) shows the envelope of the structurally characterised cation in either THF, MeCN, or MeCN–MeOH (see Fig. 3a).§ MS investigations reveal the successive loss of $Cp^*MoO_2(O_2CCF_3)$, CF_3CO_2H, CF_3CO_2H, and H_2O. Under negative detection mode, the major envelope corresponds to a $[(Cp^*Mo)_3(O)_4(O_2CCF_3)_5]^-$ species which derives from the tranfer of two $CF_3CO_2^-$ ions from the Zn dianion. When the same experiment was carried out in the presence of 0.28 M CF_3CO_2H, however, the monoanions $[Zn(O_2CCF_3)_3]^-$ and $[Zn_2(O_2CCF_3)_5]^-$ were observed (see Fig. 3b).

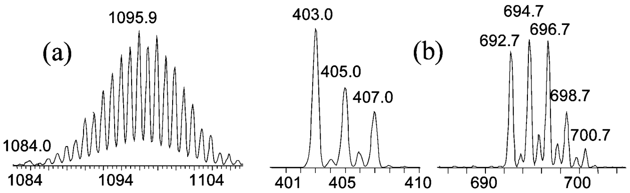

Fig. 3 Excerpts of the ESMS of the title compound in MeCN in the presence of 0.28 M CF_3CO_2H. (a) Positive detection mode. (b) Negative detection mode.

The Cp^*Mo^{V} moiety in combination with oxo ligands is already known in dinuclear (*e.g.* $[Cp^*MoO_2]_2$)[24] and mononuclear (*e.g.* $[Cp^*MoOCl_2]$)[25] complexes. Dinuclear and mononuclear oxo-carboxylato Cp^*Mo^{V} species were also detected in our recent EC-ESMS study,[7] whereas a trinuclear one was not. Whether a relationship between these smaller fragments and the trinuclear complex shown here exists and under which conditions one may be able to interconvert these species are questions for future investigations. Another interesting and related question is the lability of the capping oxo ligand, since this is extremely inert in the large class of $Mo^{IV}{}_3O_4$ clusters.[8] We also wish to isolate larger quantities of salts containing this cation to investigate its magnetic properties.

As a final remark, we underline the robustness of the Cp*Mo bond, which remains intact upon long reaction times under strongly acidic aqueous conditions. This feature is encouraging for the future development of catalytic and electrocatalytic processes with Cp*Mo systems in an aqueous environment.

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Notes and references

† $[Cp^*{}_2Mo_2O_5]$ (0.15 g, 0.28 mmol) dissolved in MeOH–H_2O (1 : 1, 10 ml) was treated under argon with Zn powder (1.5 g, 23 mmol) and concentrated CF_3CO_2H (10 drops). Three-day stirring at rt yielded a green suspension. After filtration and drying, the solid was extracted with THF and, after filtration, addition of heptane yielded a blue precipitate. A small amount of single crystals of the title compound were obtained by diffusion of an ether layer into a blue THF solution at rt.

‡ Crystal data. $C_{42}H_{45}F_{18}O_{16}Mo_3Zn$, M = 1500.97, monoclinic, a = 11.8671(1), b = 11.7975(1), c = 37.6903(5) Å, β = 95.767(1)°, U = 5250.01(9) Å^3, T = 110 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 1.28 mm^{-1}, 20526 reflections measured, 11521 unique (R_{int} = 0.039) which were used in all calculations. The final $wR(F^2)$ was 0.096 (all data). CCDC reference number 178376. See http://www.rsc.org/suppdata/dt/b2/b203583a/ for crystallographic data in CIF or other electronic format.

§ MS investigations were carried out with a Finnigan (San Jose, USA) LCQ quadrupole ion trap mass spectrometer equipped with a Protana (Odense, Denmark) nano-electrospray ionization (ESI) interface. Tip and sampling cone potentials were −1.5 kV and −50 V (negative mode), 1.5 kV and 23 V (positive mode), respectively. The mass analyzer was scanned from *m*/*z* 100 to 2000 (5 total microscans). Maximum injection time into ion trap was 50 ms. Sample injection flow rate was 1 μL min^{-1}.

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