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Note

A new aqueous molybdenum cluster with a $Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)$ trinuclear core

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ABSTRACT

Reaction of $Mo(CO)_6$ with propionic acid and propionic anhydride gives the expected μ_3-propylidyne capped molybdenum cluster as well as the unanticipated μ_3-ethylidyne capped molybdenum cation with bridging propionates, $[Mo_3(\mu_3\text{-}CR)(\mu_3\text{-}O)(\mu\text{-}O_2CCH_2CH_3)_6(H_2O)_3]Br\cdot 4H_2O$; R = CH_3 and CH_2CH_3. Due to the similarity in structure, both complexes crystallize together in the triclinic crystal system upon slow evaporation of NaBr solutions ($T = 277$ K). Herein, we report the synthesis, characterization, and crystallographic study of the carbon-capped clusters. To our knowledge, this study is the first to report a trinuclear molybdenum cation in which the μ_3-alkylidyne ligand is not the same chain length as the carboxylic acid used in the synthesis.

1. Introduction

Led by the seminal work of Bino and Cotton, acetate-bridged trinuclear molybdenum cluster cations with formula $[Mo_3(\mu_3\text{-}X)(\mu_3\text{-}Y)(\mu\text{-}O_2CCH_3)_6(H_2O)_3]^{z+}$, where X = Y = O, X = Y = CCH_3 and where X = O and Y = CCH_3, were discovered when $Mo(CO)_6$ was refluxed with a mixture of acetic acid and acetic anhydride [1–4]. Of these, the most intriguing molecular cation is the oxidized form of the *bi*-ethylidyne capped cluster (X = Y = CCH_3), which upon dissolution in water generates gaseous 2-butyne [5]. Mechanistically, it was proposed that the formation of 2-butyne was the result of a C–C coupling reaction in which free methyl carbyne radicals combined in solution [6]. Surprisingly, 2-butyne was not the only organic substrate found in solution, however. Other organic side-products including propyne, propene, acetaldehyde, and number of organics with short carbon chains (i.e. ethane and ethene) were detected as well. In our attempt to synthesize the *bi*-oxo capped propylidyne cluster, we discovered the co-crystallization of two molybdenum complexes, the *mono*-μ_3-CCH_2CH_3 and the unanticipated *mono*-μ_3-CCH_3 capped cluster *both* with bridging propionate ligands ($[Mo_3(\mu_3\text{-}CR)(\mu_3\text{-}O)(\mu\text{-}O_2CCH_2CH_3)_6(H_2O)_3]Br\cdot 4H_2O$ with R = CH_3 **1** and CH_2CH_3 **2**; Scheme 1). The discovery of **1** was entirely unexpected because the propionic acid–anhydride mixture used in the synthesis should yield only the propylidyne capped cluster, as previously reported by Bino and Gibson [7]. Our discovery of **1** may in fact support the carbyne radical coupling reaction in that the formation of the μ_3-CCH_3 capping group would require other reactive species to be present in solution besides propionic acid.

2. Results and discussion

Although the original synthesis reported by Bino and Gibson [7] was only slightly modified, we isolated both the μ_3-propylidyne capped cluster and μ_3-ethylidyne capped cluster. Due to their similarity in structure, **1** and **2** crystallize in the same crystallographic site as the tetrahydrate bromide salt. Fig. 1 shows thermal ellipsoid drawings for structures **1** (a) and **2** (b), in which the C(2a) atom position refers to the terminal methyl group of the μ_3-ethylidyne chain on **1** and the C(2) position refers to the methylene of the μ_3-propylidyne of **2**. Both molecular cations are trinuclear with *pseudo*-C_{3v} symmetry in which each Mo(IV) ion is bound through metal–metal bonding to give a central Mo_3 unit. Above and below the Mo_3 plane are two three-coordinate capping ligands, a μ_3-CR and a μ_3-O giving a slightly distorted trigonal bipyramid. In order for the cluster cations to be monovalent, each Mo ion must be in the (IV) oxidation state, which is consistent with other trinuclear molybdenum cations [4,8,9]. Ligated to each Mo(IV) are four bridging propionate ligands and a terminal water giving rise to nine-coordinate Mo(IV) cations.

The complexes crystallize together in the triclinic crystal system with space group $P\bar{1}$ and the following unit-cell dimensions; $a = 11.6658(11)$ Å, $b = 13.7602(12)$ Å, $c = 13.7673(12)$ Å and

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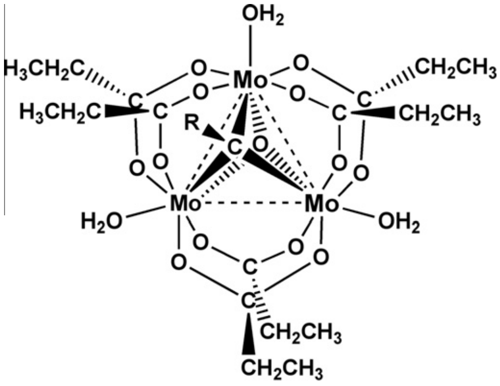

Br · $4H_2O$; R = CH_3 **1** and CH_2CH_3 **2**

Scheme 1. Molecular strructure of **1** and **2**.

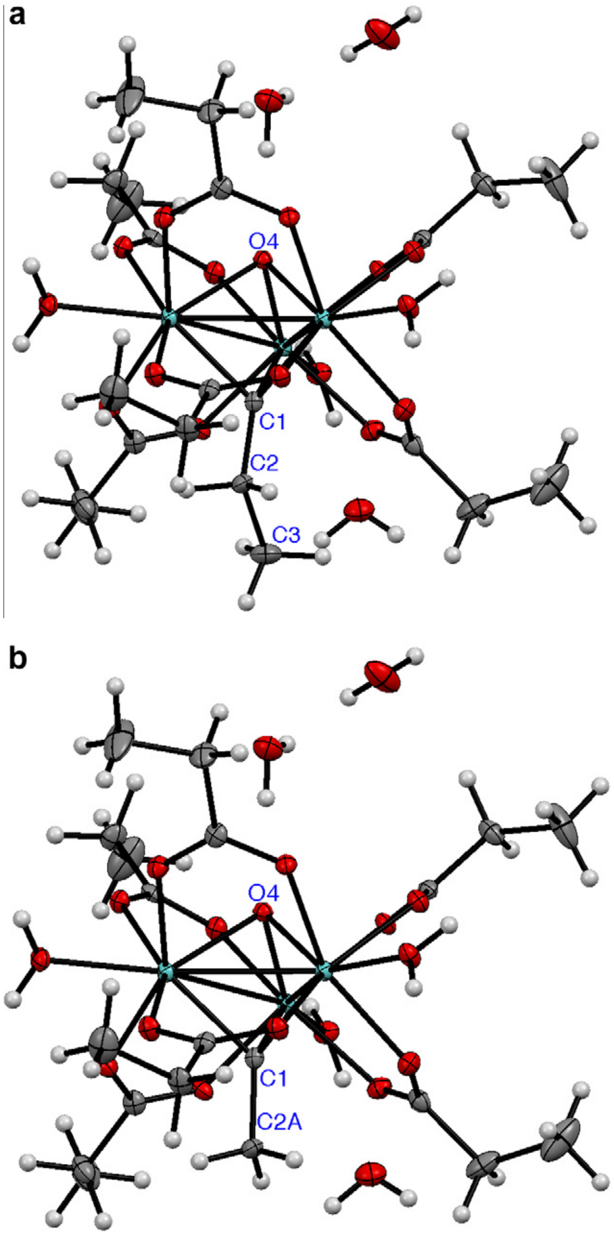

Fig. 1. Thermal ellipsoid plot of **1** (a) and **2** (b), in which the C(2a) atom position refers to the terminal methyl group of the μ_3-ethylidyne chain on **1** and the C(2) position refers to the methylene of the μ_3-propylidyne of **2**. Anisotropic displacement ellipsoids are shown at the 50% probability level.

V = 1771.6(3) $Å^3$. Solid-state ratios were calculated and found to be roughly 0.50:0.50, which is supported by ^1H NMR integrations. Structural data shows that the Mo–C(μ_3-C) mean distance for the mixed crystal is 2.0600(2) Å, which is comparable to the *mono*-ethylidyne, *bi*-ethylidyne and *mono*-propylidyne molybdenum clusters [2,3,7]. However, we do find some slight differences in metal–metal bonding. Metal–metal distances are in the range of 2.7658(4)–2.7690(4) Å, which are comparable to Mo–Mo bonds in both the single-ethylidyne (2.752 Å) [3] and single-propylidyne cluster compounds (2.742 Å) [7], but shorter than Mo–Mo distances in the *bi*-ethylidyne capped cation (2.815–2.892 Å) [2]. We also find that the average Mo–OH_2 bond distance is 2.1384(18) Å, which is much longer than the mean distance reported for the *bi*-oxo capped acetate and propionate bridged clusters [4]. Bond angles in the Mo_3 core range from 59.938(10)° to 60.051(9)°. Angles for the slightly distorted trigonal bipyramid range from 84.29(9)° to 84.51(9)° for the Mo-(μ_3-C)–Mo unit and 87.55(6)–87.62(6)° for the Mo-(μ_3-O)–Mo unit. Select structural data for $[Mo_3(\mu_3\text{-}CR)(\mu_3\text{-}O)(\mu\text{-}O_2CCH_2CH_3)_6(H_2O)_3]Br\cdot 4H_2O$; R = CH_3 and CH_2CH_3 along with related structures is given in Table 1.

Solution NMR data show that **1** and **2** crystallize as a 0.50:0.50 mixture based on ^1H NMR integrations. The ^1H NMR spectrum (Fig. 2) clearly shows four sets of quartets and triplets from bridging propionate protons (μ-$O_2CCH_2CH_3$). Due to the symmetry of the single-carbon capped structures, two sets of μ-$O_2CCH_2CH_3$ protons are observed for each cluster, giving rise to a total of four sets μ-$O_2CCH_2CH_3$ protons with slightly different chemical shifts (inset, Fig. 2). We assign the two overlapping quartets furthest downfield at 2.440 ppm to μ-$O_2CCH_2CH_3$ protons near μ_3-O caps from both **1** and **2**. We assign the two remaining quartets near 2.380 ppm to μ-$O_2CC\mathbf{H_2}CH_3$ protons near μ_3-CCH_3 and μ_3-CCH_2CH_3 capping ligands. The quartet furthest upfield at 2.375 ppm is assigned to the μ-$O_2C\mathbf{CH_2}CH_3$ protons on **2** because the ethyl substituent on the capping ligand is a stronger electron-donating group than the methyl substituent. Also observed in the same region is a singlet at 2.420 ppm, which is assigned to the μ_3-$CC\mathbf{H_3}$ protons. Perhaps the most compelling piece of evidence, however, is the ^{13}C NMR spectrum (Fig. 3). Two signals from the three-coordinate capping carbons, μ_3-$\mathbf{C}CH_3$ and μ_3-$\mathbf{C}CH_2CH_3$, are observed downfield at 304.1 and 299.5 ppm, respectively, and are consistent with previously reported μ_3-CR chemical shifts [3]. The ratios of the two peaks are nearly equal, however, we recognize that ^{13}C NMR data are not quantitative. Also shown on the ^{13}C NMR spectrum, are signals from the methyl and methylene carbons on the μ_3-$C\mathbf{C}H_3$ and μ_3-$C\mathbf{C}H_2\mathbf{C}H_3$ capping groups. DEPT-135 data confirm all ^{13}C NMR assignments (Supporting Fig. 1).

To our knowledge, this study is the first to report a trinuclear molybdenum cation in which the μ_3-alkylidyne ligand is not the same chain length as the carboxylic acid used in the synthesis. In order for the μ_3-CCH_3 capping group to form, other reactive species besides propionic acid are likely present in solution. This is not surprising given that Bogoslavsky et al. [6] found that carbon-capped molybdenum clusters produce a large number of organic products including short chain alkanes, alkenes, alkynes and acids when dissolved in water. We suspect that the μ_3-ethylidyne capping cluster forms from reaction of a cluster fragment with an organic side product, such as acetic acid, that may have been generated from the combination of free carbynes radicals in solution. This is entirely possible given our reaction was run under aqueous conditions and allowed to rest for nearly 24 h. Our discovery of the μ_3-ethylidyne capping cluster may support the proposed carbyne radical coupling reaction and suggests that the formation of μ_3-alkylidyne capped-clusters requires much further investigation.

Table 1
Select bond distances (Å) and angles (°) for $[Mo_3(\mu_3\text{-}CR)(\mu_3\text{-}O)(\mu\text{-}O_2CCH_2CH_3)_6(H_2O)_3]Br{\cdot}4H_2O$; R = CH_3 and CH_2CH_3 and related structures.

$[Mo_3(\mu_3\text{-}X)(\mu_3\text{-}Y)(\mu\text{-}O_2CZ)_6(H_2O)_3]^{n+}$	Mo–Mo	Mo–C(μ_3-C)	Mo–O(μ_3-O)	Mo–OH_2	Mo-(μ_3-CZ)–Mo, Mo-(μ_3-O)–Mo
X = CCH_3, CCH_2CH_3, Y = O, Z = CH_2CH_3[a]	2.7676(4)	2.060(2)	1.9997(16)	2.1384(18)	84.29(9)–84.51(9) 87.55(6)–87.62(6)
X = CCH_2CH_3, Y = O, Z = CH_2CH_3 [b]	2.742(4)	2.05(4)	1.98(2)	–	– –
X = CCH_3, Y = O, Z = CH_3[c]	2.752(1)	2.044(7)	1.983(4)	2.164(4)	84.6(3)–84.8(3) 87.8(2)–87.9(2)
X = CCH_3, Y = CCH_3, Z = CH_3[d]	2.815(7)–2.892(1)	2.052(10)–2.083(6)	–	2.197(5)–2.147(8)	87.98(8) –
X = O, Y = O, Z = CH_3[e]	2.766(2)	–	2.004(6)	2.083(10)	– 87.0(4)
X = O, Y = O, Z = CH_2CH_3[e]	2.752(2)	–	1.984(4)	2.144(4)	– 87.4(4)–88.3(5)

[a] This work. Average values are given and average deviations from the mean are given in parentheses.
[b] Ref. [7].
[c] Ref. [3].
[d] Ref. [2], a range is reported for three structures with different counterions and/or oxidation numbers.
[e] Ref. [4].

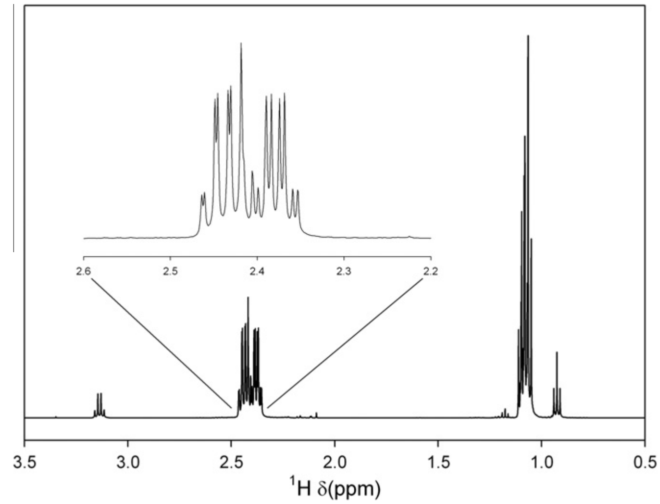

Fig. 2. ^1H NMR spectrum of the co-crystallized cations, $[Mo_3(\mu_3\text{-}CR)(\mu_3\text{-}O)(\mu\text{-}O_2CCH_2CH_3)_6(H_2O)_3]^+$ R = CH_3 and CH_2CH_3. Due to the symmetry of both complexes, the propionate ligands are not all chemically equivalent resulting in two sets of μ-$O_2CCH_2CH_3$ protons per complex. The highlighted region (2.2–2.6 ppm) shows four quartets from the μ-$O_2CC\mathbf{H_2}CH_3$ protons and a singlet from the μ_3-$C\mathbf{CH_3}$ ligand. Small impurity peaks are observed around 2.1 and 1.2 ppm.

3. Experimental methods

3.1. Synthesis

To a mixture of propionic acid (50 mL) and propionic anhydride (50 mL), $Mo(CO)_6$ (1.0 g) was added and refluxed gently for 8 h. The reaction mixture was allowed to cool to room temperature overnight and was then diluted to 400 mL with deionized water and reduced in volume via rotary evaporation. Following evaporation under reduced pressure, the residue was diluted once again with 300 mL of deionized water and loaded onto a Dowex 50WX2 ion-exchange column for separation. Upon elution with a 0.5 M NaBr solution, two bands (orange and red) were observed with decent separation. When the orange product was reduced slowly via rotary evaporation, small orange micro-crystals formed from solution. The microcrystalline product was filtered, washed and dried for characterization (^1H NMR, ^{13}C NMR, DEPT-135, and UV–Vis). In order to produce well-formed crystals suitable for X-ray analysis however, a portion of the orange solution was allowed to reduce down for two months until small orange-red plates formed (T = 277 K). An unoptimized yield of less than 10% was determined. All attempts to separate compound **1** from **2** failed. The synthesis and crystallization of the co-crystallized complexes is reproducible with a slight variation in molecular composition (see Supporting Fig. 2).

3.2. Crystallographic study

Single crystal X-ray diffraction data were collected using a Bruker SMART1000 [10] CCD system at T = 90 K (Mo Kα, λ = 0.71073 Å). A total of 28,856 reflections were collected and corrected for Lorentz and polarization effects in SAINT [10] and absorption using crystal faces and Blessing's method as incorporated into the program SADABS [11–13] with 13421 unique. The SHELXTL [14] program package was implemented to determine the probable space group and set up the initial files. System symmetry, lack of systematic absences and intensity statistics indicated the centrosymmetric triclinic space group $P\bar{1}$ (No. 2). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms attached to carbon atoms were idealized and those attached to oxygen atoms had their distances fixed but their positions were free to refine throughout the final refinement process. The nearly overlapping atom combination of C(2a)/C(2), in which C(2a) atom is the terminal methyl in **1** and the C(2) atom is the methylene in **2**, was found to refine well to 0.50:0.50. Variations of this model allowed it to refine to extremes as large as 0.58:0.42 but in these cases the C(2) and C(2a) atom thermal parameters began to flatten while the C(3) began to increase in size. The 0.5:0.5 model appears to be best overall. The C(2a) methyl group had its hydrogen finally idealized but various attempts were made to begin them in eclipsing positions with distance restraints (DFIX/SADI) but the atoms preferred to adopt the final positions here. Terminal methyl groups C(6), C(9), C(12), C(15), C(18) and C(21) possessed varying levels of libration that all appear to be normal and tests for disorder proved fruitless. The hydrogen atoms attached to the oxygen atoms also had their distances restrained with DFIX instructions. All full occupancy hydrogen atoms had their thermal parameters refined. Crystallographic data, details of data collection, and refinement are given in Table 2 and further information regarding data collection and refinement can be found in the Supplementary material.

3.3. Characterization

^1H NMR data were collected with 16 scans, 90° pulse width of 11.50 μs and relaxation delay of 1.0 s. ^1H NMR assignments are as follows (δ in ppm, multiplicity, integration, assignment in D_2O): 0.93, triplet, 3H, μ_3-$CCH_2C\mathbf{H_3}$; 1.06–1.10, four sets of overlapping

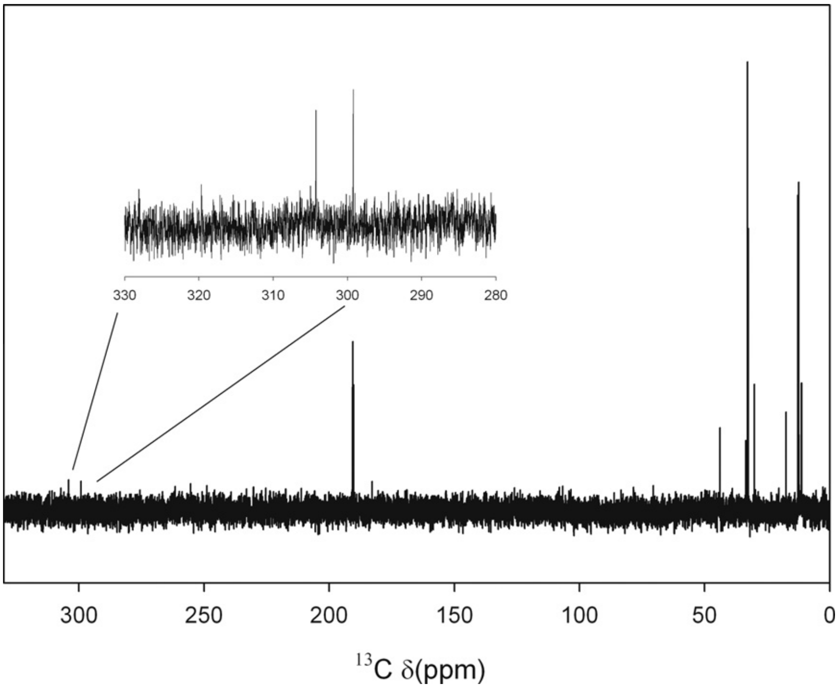

Fig. 3. ^{13}C NMR spectrum of the crystallized molybdenum cations. The highlighted region (330–280 ppm) shows two peaks downfield from the three coordinate capping carbons (304 ppm, μ_3-**C**CH_3 and 299 ppm, μ_3-**C**CH_2CH_3). Several small impurity peaks are detected from residual propionic acid at 11.2, 30.1, and 180 ppm. In order to improve signal to noise, the highlighted region showing the alkylidyne signals was collected for a longer period of time.

Table 2
Crystallographic data, data collection, structure refinement for $[Mo_3(\mu_3\text{-}CR)(\mu_3\text{-}O)(\mu\text{-}O_2CCH_2CH_3)_6(H_2O_3)]Br\cdot 4H_2O$; R = CH_3 and CH_2CH_3 (CCDC 865599).

Crystal data	
Empirical formula	$C_{41}H_{80}Mo_6O_{32}\cdot 8(H_2O)\cdot 2(Br)$
Formula weight (g mol^{-1})	1964.64
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	11.6658(11)
b (Å)	13.7602(12)
c (Å)	13.7673(12)
α (°)	60.0511(12)
β (°)	88.9275(12)
γ (°)	70.2585(13)
V (Å^3)	1771.6(3)
Z	1
ρ_{calc} (g cm^{-3})	1.841
F(000)	984
μ (mm^{-1})	2.25
Data collection	
Radiation (Å)	Mo, Kα, 0.71073
T (K)	90(2)
θ Range (°)	2.3–27.5
Monochromator	fine focused sealed tube
Unique data	8131
Observed data ($I > 2\sigma(I)$)	6953
Refinement	
Number of reflections	8131
Number of refine parameters	501
Fine agreement factors	$R[F^2 > 2\sigma(F^2)] = 0.024$, $wR(F^2) = 0.056$
Goodness-of-fit (GOF)	1.09
$\Delta\rho_{max}$ (e Å^{-3})	0.88
$\Delta\rho_{min}$ (e Å^{-3})	−0.55

triplets, 36H, μ-$O_2CCH_2C\mathbf{H_3}$; 2.38–2.44, four sets of overlapping quartets, 24H, μ-$O_2CC\mathbf{H_2}CH_3$; 2.42, singlet, 3H, μ_3-$CC\mathbf{H_3}$; 3.14, quartet, 2H, μ_3-$CC\mathbf{H_2}CH_3$. ^{13}C NMR data were collected with 60000 scans and 80000 scans, pulse width of 9.25 μs and delay of 2.0 s. DEPT-135 spectra were collected with 60000 scans, 90°pulse of 9.25 μs and 180° tip of 18.50 μs with a delay of 2.0 s. ^{13}C/DEPT NMR assignments are as follows (δ in ppm, assignment in D_2O, in-phase/out-of-phase/null from DEPT-135): 12.38, 12.44, 12.51, 12.75, μ-$O_2CCH_2\mathbf{C}H_3$, in-phase; 17.49, μ_3-$CCH_2\mathbf{C}H_3$, in-phase; 32.57, 32.60 (overlap of 2 signals), 32.82, μ-$O_2C\mathbf{C}H_2CH_3$, out-of-phase; 33.59, μ_3-$C\mathbf{C}H_3$, in-phase; 43.92, μ_3-$C\mathbf{C}H_2CH_3$, out-of-phase; 190.23, 190.55, 190.57, 190.69, μ-$O_2\mathbf{C}CH_2CH_3$, null; 299.22, μ_3-$\mathbf{C}CH_2CH_3$, null; 304.25, μ_3-$\mathbf{C}CH_3$, null. All chemical shifts are reported relative to TSP. An electronic spectrum was collected and shows a broad signal at 378 nm with two shoulders 332 and 454 nm (*T* = 295 K). *Anal.* Calc. for $Mo_6O_{40}C_{41}H_{96}Br_2\cdot NaBr$: Mo, 27.8; C, 23.8; H, 4.6. Found: Mo, 27.4; C, 22.9; H, 4.1%. The mass percents were slightly lower than expected most likely due to residual NaBr from the crystallization process. Regardless, microanalysis data gave the expected Mo:C stoichiometry (Mo:C, 1.0:6.7) based on the molecular formula obtained from crystallography (Mo:C, 1.0:6.8).

Acknowledgments

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Appendix A. Supplementary material

CCDC 865599 contains the supplementary crystallographic data for $[Mo_3(\mu_3\text{-}CR)(\mu_3\text{-}O)(\mu\text{-}O_2CCH_2CH_3)_6(H_2O)_3]Br\cdot 4H_2O$; R = CH_3 and CH_2CH_3. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.03.037.

References

[1] A. Bino, M. Ardon, I. Maor, M. Kaftory, Z. Dori, J. Am. Chem. Soc. 98 (1976) 7093.
[2] M. Ardon, A. Bino, F.A. Cotton, Z. Dori, M. Kaftory, B.W.S. Kolthammer, M. Kapon, G. Reisner, Inorg. Chem. 20 (1981) 4083.

[3] A. Bino, F.A. Cotton, Z. Dori, B.W.S. Kolthammer, J. Am. Chem. Soc. 103 (1981) 5779.
[4] M. Ardon, A. Bino, F.A. Cotton, Z. Dori, M. Kaftory, Inorg. Chem. 21 (1982) 1912.
[5] A. Bino, M. Ardon, E. Shirman, Science 308 (2005) 234.
[6] B. Bogoslavsky, O. Levy, A. Kotlyar, M. Salem, F. Gelman, A. Bino, Angew. Chem., Int. Ed. 51 (2012) 90.
[7] A. Bino, D. Gibson, Inorg. Chim. Acta 65 (1982) L37.
[8] G. Powell, D.T. Richens, Inorg. Chem. 32 (1993) 4021.
[9] J.R. Houston, D.T. Richens, W.H. Casey, Inorg. Chem. 45 (2006) 7962.
[10] Bruker SMART (version 5.054) and SAINT (version 7.68a), Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
[11] R.H. Blessing, Acta Crystallogr., Sect. A 51 (1995) 33.
[12] G.M. Sheldrick, SADABS 2008/1, Universität Göttingen, Göttingen, Germany, 2008.
[13] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
[14] G.M. Sheldrick, SHELXTL, version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA, 2002.