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Molybdenum and tungsten methoxo clusters with differently bonded methoxo groups. Crystal structure of $[Na(CH_3OH)_5]_2[Mo_6(\mu_3\text{-}Br)_8(OCH_3)_6]$

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Abstract

New molybdenum and tungsten methoxo clusters of the composition $[M_6(\mu_3\text{-}X)_8X_2(\mu\text{-}OCH_3)_{4/2}]\cdot 2CH_3OH$ (M = Mo, W; X = Cl, Br), $[Mo_6(\mu_3\text{-}X)_8(OCH_3)_2(\mu\text{-}OCH_3)_{4/2}]\cdot CH_3OH$ (X = Cl, Br) and $[Na(CH_3OH)_5]_2[Mo_6(\mu_3\text{-}Br)_8(OCH_3)_6]$ containing bridging (μ), both bridging and terminal, or terminal methoxo groups, respectively, have been prepared. The preparation procedures, spectroscopic and physical properties, including X-ray photoelectron spectra (XPS) have been correlated. The crystal structure has been solved for $[Na(CH_3OH)_5]_2[Mo_6(\mu_3\text{-}Br)_8(OCH_3)_6]$. The compound crystallizes in the triclinic crystal system. The structure is built of two $[Na(CH_3OH)_5]^+$ cations and the $[Mo_6(\mu_3\text{-}Br)_8(OCH_3)_6]^{2-}$ anion. All six-oxygen atoms from coordinated methoxo groups are acceptors of hydrogen of coordinated methanol molecules from the six neighbouring cations making a three-dimensional packing network.

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Keywords: Molybdenum clusters; Tungsten clusters; Methoxo complexes; X-ray crystal structures

1. Introduction

Systematic investigation of the reactions of hexanuclear halide cluster compounds, M_6X_{12} (M = Mo, W; X = Cl, Br) with alkoxide ions is missing in the literature. So far the data on the preparation of molybdenum cluster derivatives of the composition $Na_2[Mo_6X_8(OR)_6]$ (X = Cl, Br; R = CH_3, C_2H_5, C_6H_5) as well as $[Na(CH_3OH)_5]_2[Mo_6(OCH_3)_8(OCH_3)_6]$ are available [1]. For the latter compound and for $[Na(CH_3OH)_5]_2[Mo_6Cl_8(OCH_3)_6]$ the crystal structure determinations revealed the presence of the complex cation $[Na(CH_3OH)_5]^+$, with coordinated methanol molecules, and the cluster anions $[Mo_6(OCH_3)_8(OCH_3)_6]^{2-}$ and $[Mo_6Cl_8(OCH_3)_6]^{2-}$, respectively [2]. Structural data for molybdenum chloro cluster compounds with different alkoxo groups in the complex anion $[Mo_6Cl_8(OR)_6]^{2-}$ (R = CH_3, C_6H_5, C_9H_9, $C_{15}H_{11}$) are also known [3,4].

The idea for these investigations came from an earlier observation [5] that in diluted solutions a small amount of the methoxo cluster $[Mo_6(\mu_3\text{-}Cl)_8Cl_2(\mu\text{-}OCH_3)_{4/2}]\cdot 2CH_3OH$ was formed immediately after dissolution of Mo_6Cl_{12} in methanol. Usually, a clear solution was obtained first, but it became cloudy almost instantly. The pH value of this solution was ~2. The analytical and spectroscopic investigations of the solid indicated the presence of methoxo groups which appeared as a result of deprotonation of methanol molecules in the presence of Mo_6Cl_{12}. The reaction was incomplete with the yield of ~20%. In very concentrated solutions the formation of $Mo_6Cl_{12}\cdot 2CH_3OH$ was observed as the only product. The cluster Mo_6Br_{12} is not soluble in methanol, but reacts slowly with this solvent giving the

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crystalline substance $Mo_6Br_{12}\cdot 2CH_3OH$. Yet, the bromo methoxo cluster $[Mo_6(\mu_3\text{-}Br)_8Br_2(\mu\text{-}OCH_3)_{4/2}]\cdot 2CH_3OH$ formed if the suspension of Mo_6Br_{12} in methanol was refluxed for 16–20 h [5]. The yield was again not higher than ~20%.

We have systematically investigated the hexanuclear halide clusters of molybdenum and tungsten in the reactions with sodium methoxide and found out the existence of several solid phases having different numbers of methoxo groups and consequently, different physical and chemical properties.

2. Experimental

2.1. Materials

The starting substances and all the products are air and moisture sensitive. Therefore, all manipulations were performed by the use of an inert atmosphere dry-box, a high-vacuum manifold and Schlenk techniques, unless otherwise stated.

Mo_6X_{12} (X = Cl, Br) were prepared by the reduction of $MoCl_5$/NaCl or $MoBr_4$/NaBr mixtures with molybdenum metal powder [6], and W_6Cl_{12} by the reduction of WCl_4 with iron metal powder [7]. The original procedure comprising direct brominating of tungsten metal in a sealed quartz tube at elevated temperature in a two-zone oven was developed for W_6Br_{12}. Methanol (Mallinckrodt, Kemika) was dried by refluxing over sodium methoxide (Aldrich) and ethanol (Kemika) over sodium ethoxide formed by dissolving metal sodium in ethanol. Both solvents were then vacuum distilled on activated molecular sieves (4 Å) and stored under vacuum.

2.2. Synthesis of complexes

2.2.1. $[M_6(\mu_3\text{-}Cl)_8Cl_2(\mu\text{-}OCH_3)_{4/2}]\cdot 2CH_3OH$, M = Mo (**1**), W (**2**)

The cluster Mo_6Cl_{12} (0.500 g, 0.500 mmol) or W_6Cl_{12} (0.500 g, 0.327 mmol) was transferred to a round bottom flask in a dry-box. Methanol (15 ml) was distilled onto the substances on the vacuum line. The starting clusters slowly dissolved in the methanol and simultaneously with the dissolution process a certain amount of $[(M_6Cl_8)Cl_2(OCH_3)_2]\cdot 2CH_3OH$ formed, often mixed with $M_6Cl_{12}\cdot 2CH_3OH$ (at higher methanol volume portions deprotonation of methanol occurred as the only reaction process and methoxo clusters of the composition $[(M_6Cl_8)Cl_2(OCH_3)_2]\cdot 2CH_3OH$ formed in a 20% yield). Separately, methanol solutions of sodium methoxide were prepared by dissolving metal sodium (0.023 g, 1.000 mmol or 0.015 g, 0.654 mmol for Mo_6Cl_{12} and W_6Cl_{12}, respectively) in methanol (4 ml) under a stream of dry nitrogen. In the same atmosphere, using a syringe, these solutions were slowly added to the cluster suspensions. The pH value of both solutions was 7. For M = Mo the resulting solution did not become clear and in the course of 2–3 h the amount of precipitate increased. For M = W the initial precipitate dissolved immediately upon addition of sodium methoxide and a completely clear solution was obtained. Approximately 1 h later the solution became cloudy, indicating the beginning of $[(W_6Cl_8)Cl_2(OCH_3)_2]\cdot 2CH_3OH$ formation. The reaction mixtures for both clusters were left at normal conditions for 5 days. The colloid-like bright-yellow (for M = W the colour is slightly darker) precipitates were filtered off through a fine porosity fretted glass filter on the vacuum line and dried in a dynamic vacuum over 12 h period; the yield was 0.475 g (90%) for **1** and 0.461 g (89%) for **2**.

Anal. Calc. for $[(Mo_6Cl_8)Cl_2(OCH_3)_2]\cdot 2CH_3OH$ (**1**): C, 4.55; H, 1.34; Cl, 33.56; Mo, 54.49. Found: C, 4.63; H, 1.37; Cl, 32.94; Mo, 55.07%. IR data (nujol, cm^{-1}): 3310 m, br, 1179 m, 1081 sh, 1017 vs, 584 w, 510 w, 399 vs, 350 vs, 331 s, 296 m.

Anal. Calc. for $[(W_6Cl_8)Cl_2(OCH_3)_2]\cdot 2CH_3OH$ (**2**): C, 3.03; H, 0.89; Cl, 22.39; W, 69.65. Found: C, 2.93; H, 0.88; Cl, 21.98; W, 69.08%. IR data (nujol, cm^{-1}): 3310 m, br, 1175 w, 1080 sh, 1015 vs, 594 vw, 499 vw, 397 vs, 308 vs.

2.2.2. $[M_6(\mu_3\text{-}Br)_8Br_2(\mu\text{-}OCH_3)_{4/2}]\cdot 2CH_3OH$, M = Mo (**3**), W (**4**)

Mo_6Br_{12} (0.500 g, 0.326 mmol) or W_6Br_{12} (0.500 g, 0.242 mmol) were transferred to a round bottom flask in a dry-box and methanol (15 ml) was distilled onto the substances as described for **1** and **2**. The clusters did not dissolve in methanol. The orange coloured suspensions were usually left mixing for 2 h when their colour turned to orange-yellow, indicating the formation of the insoluble substances $M_6Br_{12}\cdot 2CH_3OH$. Upon addition of sodium methoxide (2 equiv.) solutions the clusters dissolved and clear solutions were obtained with an immediate formation of orange precipitates. The reaction mixtures were left for a further 24 h before separation. Filtering and drying were carried out the same as for **1** and **2**; the yield was 0.450 g (92%) for **3** and 0.448 g (91%) for **4**.

Anal. Calc. for $[(Mo_6Br_8)Br_2(OCH_3)_2]\cdot 2CH_3OH$ (**3**): C, 3.20; H, 0.94; Br, 53.24; Mo, 38.35. Found: C, 3.14; H, 0.94; Br, 52.85; Mo, 38.12%. IR data (nujol, cm^{-1}): 3310 m, br, 1171 w, 1075 sh, 1016 vs, 807 w, 647 w, 390 vs, 276 m, 228 vs.

Anal. Calc. for $[(W_6Br_8)Br_2(OCH_3)_2]\cdot 2CH_3OH$ (**4**): C, 2.37; H, 0.70; Br, 39.39; W, 54.39. Found: C, 2.24; H, 0.73; Br, 39.15; W, 53.92%. IR data (nujol, cm^{-1}): 3310 m, br, 1170 vw, 1077 sh, 1017 vs, 568 vw, 394 s, 281 w, 236 m.

2.2.3. $[M_6(\mu_3\text{-}Cl)_8(OCH_3)_2(\mu\text{-}OCH_3)_{4/2}]\cdot CH_3OH$, M = Mo (**5**), W (**6**)

The procedure was the same as for **1** and **2**, but with addition of 4 sodium methoxide equivalents. The starting solids dissolved completely. The pH values of the resulting clear solutions were 9–10. These were evaporated to dryness on the vacuum line. The reaction products were mixtures of $[M_6Cl_8(OCH_3)_4]\cdot n CH_3OH$ and NaCl. In order to remove NaCl, ethanol (15 ml) was distilled onto the solids. The clusters dissolved completely and NaCl, remaining undissolved, was separated by vacuum filtration. Completely clear, yellow (for M = Mo) and dark-brown (for M = W), ethanol filtrates were evaporated to dryness on the vacuum line. Methoxo clusters were recovered by distilling methanol (15 ml) onto the solids. Finally, methanol was evaporated in vacuum and the remained clusters were dried in a dynamic vacuum over a 12 h period; the yield for **5** was 0.451 g (89%).

Anal. Calc. for $[Mo_6Cl_8(OCH_3)_4]\cdot CH_3OH$ (**5**): C, 5.91; H, 1.59; Cl, 27.93; Mo, 56.69. Found: C, 6.03; H, 1.65; Cl, 27.45; Mo, 56.83%. IR data (nujol, cm^{-1}): 3300 w, br, 1172 w, 1026 vs, 1014 sh, 471 m, 380 s, 350 sh, 334 s, 282 w.

For the cluster $[W_6Cl_8(OCH_3)_4]\cdot n CH_3OH$ (**6**) no satisfactory analytical data were obtained due to the partial decomposition of the cluster in an alkaline medium. IR data (nujol, cm^{-1}) for **6**: 3300 w, br, 1169 w, 1041 vs, 1002 sh, 469 vs, 395 vw, 300 vs, 224s.

2.2.4. $[M_6(\mu_3\text{-}Br)_8(OCH_3)_2(\mu\text{-}OCH_3)_{4/2}]\cdot CH_3OH$, M = Mo (**7**), W (**8**)

The starting procedure was the same as for **3** and **4**, using 4 sodium methoxide equivalents. A clear solution was obtained for M = Mo and over a period of 2–3 h an orange substance precipitated out. The suspension was left overnight, then filtered off and dried in a dynamic vacuum; the yield was 0.407 g (91%). For M = W, yellow $W_6Br_{12}\cdot 2CH_3OH$ dissolved slowly to provide a clear orange-yellow solution. No precipitate appeared after several days standing, so the volume was reduced in several successive steps, but crystallization never occurred until essentially all solvent was removed. Thus a pure product was not obtained, the mixture also containing NaBr. Efforts to separate the mixture were not successful.

Anal. Calc. for $[Mo_6Br_8(OCH_3)_4]\cdot CH_3OH$ (**7**): C, 4.38; H, 1.18; Br, 46.62; Mo, 41.99. Found: C, 4.28; H, 1.27; Br, 46.22; Mo, 42.17%. IR data (nujol, cm^{-1}): 3300 w, br, 1171 m, 1065 s, 1019 vs, 824 sh, 648 vw, 496 s, 396 vs, 267 m, 232 s, 221 s.

2.2.5. $[Na(CH_3OH)_5]_2[Mo_6(\mu_3\text{-}X)_8(OCH_3)_6]$, X = Cl (**9**), Br (**10**)

These clusters were prepared according to Ref. [1].

IR data (nujol, cm^{-1}) for **9**: 1164 w, 1048 vs, 473 vs, 349 s, 298 w, 250 w. IR data (nujol, cm^{-1}) for **10**: 1165 w, 1044 vs, 806 vw, 457 vs, 338 w, 290 w, 225 m, 208 m.

2.3. Physical measurements

Infrared spectra (4000–200 cm^{-1}) were obtained with a Bomem MB-102 Fourier transformed infrared spectrometer equipped with CsI optics. Samples were prepared as Nujol mulls and mounted between CsI windows. The X-ray photoelectron spectra (XPS) were collected with a Physical Electrons Industries 5500 multitechniques surface analysis system, using a monochromatic Mg Kα source, and the binding energies were calibrated with C 1s = 284.6 eV, obtained from adventitious or combined carbon in the samples.

A suitable single crystal of $[Na(CH_3OH)_5]_2[Mo_6Br_8(OCH_3)_6]$ was selected at ambient conditions, then attached to the top of a glass capillary and cooled immediately in the cold nitrogen stream on the diffractometer. The data collection was performed on a Rigaku AFC6R diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation at 203 K. The unit cell dimensions were collected by least-square refinement on setting angles of 22 reflections with $12.84° < 2\theta < 19.03°$. Lorentz-polarization as well as absorption corrections based on ψ-scan were applied [8]. A successful solution by direct methods [9] provided the positions of Mo and Br. The other non-hydrogen atoms were located in alternating series of least-squares cycles and difference Fourier maps [10]. With the exception of C1, C2 and C3 other non-hydrogen atoms were refined with anisotropic displacement coefficients.

Detailed information about the crystal data and structure determination are summarized in Table 1. The molecular geometry was calculated by the PARST-96 programme [11] and the drawings were prepared by the ORTEP-3 for windows programme [12].

2.4. Chemical analyses

Molybdenum was determined gravimetrically as the 8-hydroxyquinolinate complex [13]. Tungsten was determined as WO_3 after decomposition of the sample with 3 mol dm^{-3} HNO_3. Chlorine and bromine were determined by potentiometric titration with a standard silver nitrate solution, after decomposition of the clusters with KOH and H_2O_2. Carbon and hydrogen were determined by in-house analysis in the Analytical Services Group in the Department of Chemistry, Iowa State University.

Table 1
Crystal data and experimental details of the data collection and refinement for **10**

Empirical formula	$C_{16}H_{58}Br_8Mo_6Na_2O_{16}$
Formula weight (g mol^{-1})	1767.44
Crystal system	triclinic
Space group	$P\bar{1}$ (2)
Unit cell dimensions	
a (Å)	10.811(3)
b (Å)	12.270(2)
c (Å)	10.776(3)
α (°)	97.31(2)
β (°)	119.36(2)
γ (°)	95.42(2)
V (Å^3)	1215.2(6)
Z	1
D_{calc} (Mg m^{-3})	2.415
Absorption coefficient (mm^{-1})	8.145
$F(0\,0\,0)$	836
Crystal size (mm)	0.30 × 0.20 × 0.20
θ range for data collection (°)	1.7–27.6
Index ranges	$-4=h=14$, $-15=k=15$, $-14=l=12$
Reflections collected	6022
Independent reflections	5601
R_{int}	0.057
Observed reflections [$I>2.0\sigma(I)$]	2239
Number of reflections used in refinement	5601
Number of parameters	215
R [a]	0.0652
wR_2 [b]	0.2310
Goodness-of-fit on F^2	1.03
Largest difference peak and hole (e Å^{-3})	−2.85, 2.55

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $wR_2=\{\Sigma[w(F_o{}^2-F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

3. Results and discussion

The hexanuclear halide clusters $M_6X_{12}=[M_6(\mu_3\text{-}X)_8X_2(\mu\text{-}X)_{4/2}]$ consist of M_6 octahedron, eight μ_3-X, two terminal X and two intermolecular μ-X atoms. Selective transformation of these species to methoxo clusters containing bridging (μ), both bridging and terminal, or terminal methoxo groups is possible. The formation of a particular methoxo cluster is a function of the number of $NaOCH_3$ equivalents added to M_6X_{12}. The reactions could be described by the following chemical equations:

$$[M_6(\mu_3\text{-}X)_8X_2(\mu\text{-}X)_{4/2}]+2NaOCH_3 \xrightarrow{CH_3OH} [M_6(\mu_3\text{-}X)_8X_2(\mu\text{-}OCH_3)_{4/2}]\cdot 2CH_3OH + 2NaX \quad (1)$$

$$[M_6(\mu_3\text{-}X)_8X_2(\mu\text{-}X)_{4/2}]+4NaOCH_3 \xrightarrow{CH_3OH} [M_6(\mu_3\text{-}X)_8(OCH_3)_2(\mu\text{-}OCH_3)_{4/2}]\cdot CH_3OH + 4NaX \quad (2)$$

$$[Mo_6(\mu_3\text{-}X)_8X_2(\mu\text{-}X)_{4/2}]+6NaOCH_3 \xrightarrow{CH_3OH} [Na(CH_3OH)_5]_2[Mo_6(\mu_3\text{-}X)_8(OCH_3)_6]+4NaX \quad (3)$$

Upon addition of sodium methoxide (2 equiv.) solution to the cluster suspensions in methanol a selective exchange of two μ-X ($X_{4/2}$) atoms for two μ-methoxo groups has been found. The substitution is completed at $2NaOCH_3$/cluster, resulting in the formation of $[M_6(\mu_3\text{-}X)_8X_2(\mu\text{-}OCH_3)_{4/2}]\cdot 2CH_3OH$ (Eq. (1)). With this substitution reaction the two-dimensional nature of the starting cluster compounds remains unchanged. With the increase of methoxide ions concentration in the suspensions further exchange of two terminally coordinated halogen atoms takes place. The end of this substitution process occurs at $4NaOCH_3$/cluster, leading to the formation of two-dimensional methoxo clusters of the composition $[M_6(\mu_3\text{-}X)_8(OCH_3)_2(\mu\text{-}OCH_3)_{4/2}]\cdot CH_3OH$, with two bridging and two terminally coordinated methoxo groups present simultaneously (Eq. (2)). The W_6Br_{12} cluster differs from the other members in the series. A precipitate of $[W_6Br_8(OCH_3)_2(OCH_3)_{4/2}]\cdot CH_3OH$ never forms and the orange colour of the solution appears to be stable. In this case, we believe, a tighter binding of terminal ligands results in formation of the complex anion $[W_6(\mu_3\text{-}Br)_8Br_2(OCH_3)_2(\mu\text{-}OCH_3)_{4/2}]^{2-}$, which is so soluble as to prevent easy isolation. Further increase of the methoxide ions concentration causes the destruction of the two-dimensional cluster species and the formation of the monomeric $[Na(CH_3OH)_5]_2[M_6(\mu_3\text{-}X)_8(OCH_3)_6]$ methoxo clusters with six terminally coordinated methoxo groups exclusively (Eq. (3)). The latter refers mostly to molybdenum compounds, since there are great difficulties in isolating the analogous tungsten species. Namely, W_6Cl_{12} is unstable in an alkaline medium as evident by the change of the colour of the solution from bright-yellow to dark-brown. A dark precipitate is also formed indicating a partial decomposition of the cluster units. W_6Br_{12} is less sensitive to the influence of the methoxide ion concentration, but nevertheless, attempts to isolate methoxo clusters similar to **9** or **10** failed.

The IR spectra were very useful in recognizing various methoxo cluster species. The different nature of methoxo groups in compounds **5**–**8** is reflected in the appearance of two $\nu_{(C–O)}$ and two $\nu_{(M–O)}$ bands in the IR spectra [14]. The spectra of compounds **1**, **5** and **9** are given in Fig. 1. In the spectrum of $[Mo_6(\mu_3\text{-}Cl)_8Cl_2(\mu\text{-}OCH_3)_{4/2}]\cdot 2CH_3OH$ (**1**) (Fig. 1(a)) there is a shoulder at 1081 cm^{-1} and a strong absorption band at 1017 cm^{-1} originating from $\nu_{(C–O)}$ of the lattice held methanol molecules and μ-methoxo groups, respectively. The absorption band observed at 1026 cm^{-1} and a shoulder at 1014 cm^{-1} in the spectrum of $[Mo_6(\mu_3\text{-}$

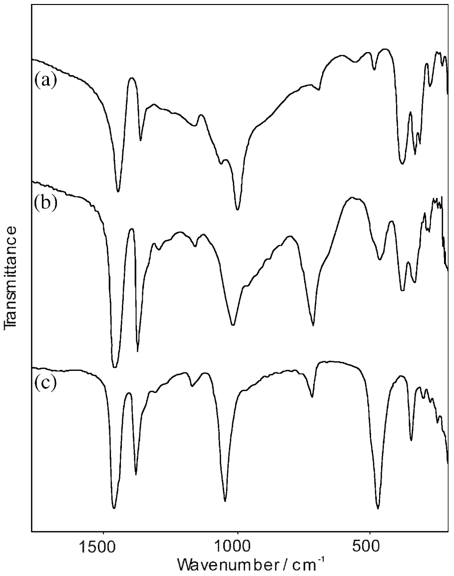

Fig. 1. Infrared spectra (1600–200 cm^{-1}) of compounds: (a) $[(Mo_6(\mu_3\text{-}Cl)_8Cl_2(\mu\text{-}OCH_3)_{4/2}]\cdot 2CH_3OH$ (**1**), (b) $[Mo_6(\mu_3\text{-}Cl)_8(OCH_3)_2(\mu\text{-}OCH_3)_{4/2}]\cdot CH_3OH$ (**5**), (c) $[Na(CH_3OH)_5]_2[Mo_6(\mu_3\text{-}Cl)_8(OCH_3)_6]$ (**9**).

$Cl)_8(OCH_3)_2(\mu\text{-}OCH_3)_{4/2}]\cdot CH_3OH$ (**5**) originate from $\nu_{(C\text{–}O)}$ of terminal and μ-methoxo groups, respectively (Fig. 1(b)). The absorption band originating from $\nu_{(C\text{–}O)}$ of the one lattice-held methanol molecule in these complexes has not been resolved as it is for compounds **1**–**4**, and is probably masked by the broad $\nu_{(C\text{–}O)}$ band of methoxo groups. A strong and single absorption band present at 1048 cm^{-1} in the spectrum of $[Na(CH_3OH)_5]_2[Mo_6(\mu_3\text{-}Cl)_8(OCH_3)_6]$ (**9**) originates from $\nu_{(C\text{–}O)}$ of terminally coordinated methoxo groups only (Fig. 1(c)), as confirmed by the crystal structure determination. A similar situation is repeated in the 500–380 cm^{-1} region, where $\nu_{(Mo\text{–}O)}$ occurs. As expected, in compounds **1** and **9** there is just one absorption band in this region, located at 399 and 473 cm^{-1}, respectively. The first, located at lower wave numbers, corresponds to $\nu_{(Mo\text{–}O)}$ (oxygen from μ-methoxo groups) in **1** and the second one to $\nu_{(Mo\text{–}O)}$ (oxygen from terminal methoxo groups) in **9**. The presence of both terminal and bridging methoxo groups in compound **5** is confirmed by the appearance of two $\nu_{(Mo\text{–}O)}$ bands: at 471 and 380 cm^{-1}, respectively. The position of $\nu_{(Mo\text{–}(\mu_3\text{-}Cl))}$ absorption bands in the region of ~350 cm^{-1} is practically unaffected by the presence of bridging or terminal methoxo groups in these halide cluster species.

Table 2
XPS binding energies (eV) for cluster compounds

Compound	Mo 3d$_{5/2}$ [W 4f$_{7/2}$]	Cl 2p$_{3/2}$ [Br 3d$_{5/2}$]
$(Mo_6Cl_8)Cl_4(C_2H_5OH)_2$	229.7	198.5(t), 200.4(μ$_3$)
$(W_6Cl_8)Cl_4(C_2H_5OH)_2$	[32.8]	198.2(t), 200.4(μ$_3$)
$(Mo_6Br_8)Br_4(CH_3OH)_2$	229.5	[68.6(t), 70.5(μ$_3$)]
$(W_6Br_8)Br_4(C_2H_5OH)_2$	[32.7]	[68.5(t), 70.5(μ$_3$)]
1	228.7	197.9(t), 199.4(μ$_3$)
2	[32.3]	197.9(t), 200.1(μ$_3$)
3	228.6	[68.1(t), 69.7(μ$_3$)]
4	[32.2]	[68.0(t), 70.2(μ$_3$)]
5	229.3	200.1(μ$_3$)
6	[32.3]	197.9(t), 200.1(μ$_3$)
7	228.5	[69.9(μ$_3$)]

3.1. X-ray photoelectron spectra

Binding energies for metal and halogen atoms in the $(M_6X_8)X_4$ alcohol adducts and methoxo derivatives are given in Table 2. The observed Mo 3d$_{5/2}$ and W 4f$_{7/2}$ binding energies fall in the expected range, 228.5–229.7 eV [15] and 32.2–32.8 eV [16], respectively. In each of these cases the spectra indicated a single Mo 3d$_{5/2}$, 3d$_{3/2}$ or W 4f$_{7/2}$, 4f$_{5/2}$ doublet, reflecting the presence of only one metal atom species in the cluster units. However, in all cases except **5** and **7**, the presence of two halogen atom types could be discerned, as resolved from the spectrum deconvolution procedure. The μ$_3$-halogen atoms are found at higher energies, 199.4–200.4 eV for Cl 2p$_{3/2}$ and 69.7–70.5 eV for Br 3d$_{5/2}$, whereas the terminal halogen atoms are at lower binding energies, 197.9–198.5 and 68.0–68.6 eV, respectively [15]. The large binding energy difference between μ$_3$-halogen and terminal halogen atoms (t), 1.9 eV (average) for both Cl and Br, in these compounds suggests that all contain only nonbridging halogens in the terminal positions. (For reference, the Br 3d XPS data for Mo_6Br_{12} show three doublets with 3d$_{5/2}$ binding energies of 68.3, 69.7 and 70.7 eV). In turn, as also inferred from IR spectra, this implies that in compounds **1** to **4** the methoxo ligands must be bridging, as represented in $[M_6(\mu_3\text{-}X)_8X_2(\mu\text{-}OCH_3)_{4/2}]$. These data also confirm the absence of terminal halogen atoms in **5** and **7**, which show only one doublet peak with a binding energy characteristic of μ$_3$-halogen atoms. The Cl 2p$_{3/2}$ data for **6** reflect partial decomposition of the cluster, as noted in Section 2, with the resulting presence of terminal Cl atoms at a binding energy of 197.9 eV. XPS data for the alcohol adducts listed in Table 2 clearly indicate their formulation as $[M_6(\mu_3\text{-}X)_8X_4(ROH)_2]$ (R = Me or Et).

3.2. Molecular and crystal structure of **10**

$[Na(CH_3OH)_5]_2[Mo_6(\mu_3\text{-}Br)_8(OCH_3)_6]$ (**10**) crystallizes in the space group $P\bar{1}$. The cluster is isostructural to $[Na(CH_3OH)_5]_2[Mo_6(\mu_3\text{-}Cl)_8(OCH_3)_6]$ [2]. The structure consists of two $[Na(CH_3OH)_5]^+$ complex cations and the octahedral $[Mo_6(\mu_3\text{-}Br)_8(OCH_3)_6]^{2-}$ cluster anion. The octahedral cluster unit with the symmetry of $\bar{1}$ is defined by three crystallographically independent Mo atoms.

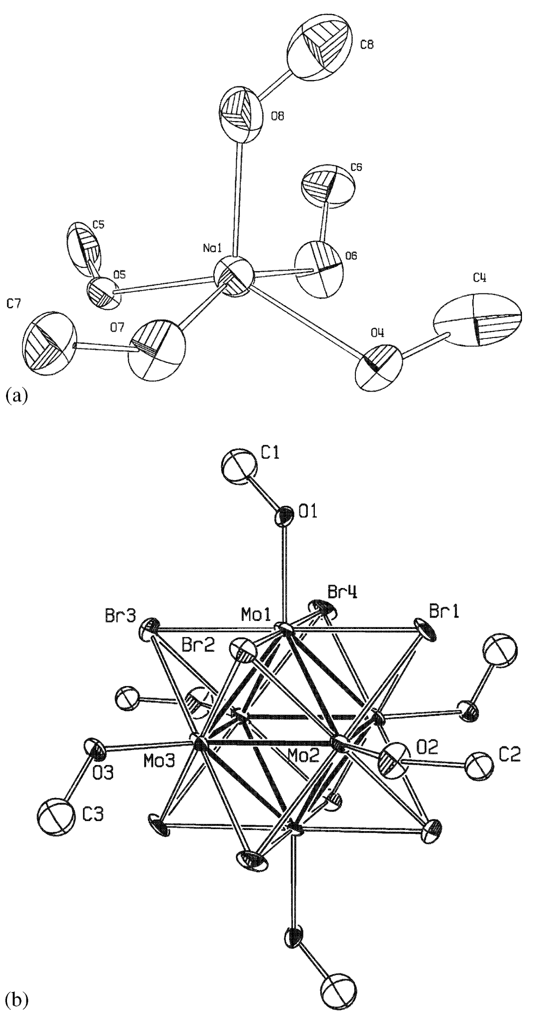

Fig. 2. The ORTEP plot of the $[Na(CH_3OH)_5]^+$ cation (a) and the $[Mo_6(\mu_3\text{-}Br)_8(OCH_3)_6]^{2-}$ anion (b) in **10**. Thermal ellipsoids are shown at 50% probability level.

Table 3
Selected bond lengths (Å) for **10**

Mo1–Mo2	2.630(2)
Mo1–Mo3	2.626(3)
Mo2–Mo3	2.632(3)
Mo1–Mo2^i	2.636(3)
Mo1–Mo3^i	2.630(2)
Mo2–Mo3^i	2.630(2)
Mo1–Br1	2.620(3)
Mo1–Br2	2.615(3)
Mo1–Br3	2.609(3)
Mo1–Br4	2.617(3)
Mo2–Br1	2.611(3)
Mo2–Br2	2.634(3)
Mo2–Br3^i	2.616(3)
Mo2–Br4^i	2.630(3)
Mo3–Br2	2.637(3)
Mo3–Br3	2.629(2)
Mo3–Br1^i	2.614(3)
Mo3–Br4^i	2.612(2)
Mo1–O1	2.07(1)
Mo2–O2	2.01(1)
Mo3–O3	2.06(2)
Na1–O7	2.32(2)
Na1–O8	2.25(2)
Na1–O4	2.41(2)
Na1–O5	2.27(2)
Na1–O6	2.37(2)

Symmetry code: (i) $1-x, -y, 2-z$.

Fig. 2 shows the structure of the cation and the anion with the atom numbering scheme, whereas Table 3 contains selected bond lengths. The Na atom in the cation is pentacoordinated by methanol O atoms with Na–O interatomic distances ranging from 2.25(2) Å to 2.41(2) Å. These values are close to those found for terminally bonded methanol molecules (average: 2.37(2) Å) in the cation of $[Na_2(CH_3OH)_9][Ta_6Cl_{12}(OCH_3)_6]\cdot 3MeOH$ [17]. The C–O interatomic distances of 1.34(4) Å to 1.45(3) Å for coordinated methanol molecules and of 1.39(3) Å to 1.45(2) Å for coordinated methoxo groups are as expected for a single C–O bond.

Within statistical limits the Mo_6 octahedron is regular, with Mo–Mo bond lengths in the range 2.626(3) Å to 2.636(3) Å (average: 2.631 Å). These values are appropriately short and close to the values observed in $(TBA)_2[(Mo_6Br_8)F_6]$ and $(TBA)_2[Mo_6Br_8(NO_3)_6]$ (TBA = tetrabutylammonium), with the average Mo–Mo bond lengths of 2.615(6) Å and 2.622(1) Å, respectively [18,19]. Short Mo–Mo distances are usually associated with longer Mo–(μ_3-Br) bond lengths. Indeed, the Mo–(μ_3-Br) distances for the eight μ_3-bromine atoms in $[Na(CH_3OH)_5]_2[Mo_6(\mu_3\text{-}Br)_8(OCH_3)_6]$, being in the range of 2.609(3) Å to 2.637(3) Å (average: 2.620 Å), belong to the longest observed for the $[Mo_6Br_8]^{4+}$ cluster derivatives [18–20]. For comparison, the average Mo–(μ_3-Br) bond length in $(Mo_6Br_8)Br_4\cdot 2H_2O$ is 2.606(2) Å [21]. The angles Br1–Mo1–Br3 and Br4–Mo1–Br2 of 179.49(10)° and 179.52(11)°, respectively, indicate four μ_3-Br atoms (one face of the cube) being located in the same plane as the molybdenum atoms. The angles Mo–Br–Mo are close to 60° (average: 60.35°).

Since all corners of the Mo_6 octahedron are coordinated by identical ligands, a small distortion of the Mo_6 octahedron and the observed differences in the Mo–O bond lengths may be the consequence of the hydrogen bonding system. The hydrogen bonding network consists of oxygen atoms from all coordinated methoxo groups and hydrogen atoms from coordinated methanol molecules in the $[Na(CH_3OH)_5]^+$ cations. Each cluster anion is surrounded by six cations (Fig. 3). The oxygen atom O1 is involved in two hydrogen bonds with methanol molecules coordinated to the same Na atom: [O4–H4···O1, 2.68(2) Å] and [O7–H7···O1, 2.73(3) Å]. A hydrogen bond of similar length (2.73(2) Å) is formed between O8–H8···O2^{iii} [symmetry code: (iii) $x, y, z-1$]. The shortest hydrogen bond (2.65(2) Å) is formed between O5–H5···O3^i [symmetry code: (i) $1+x, y, z$].

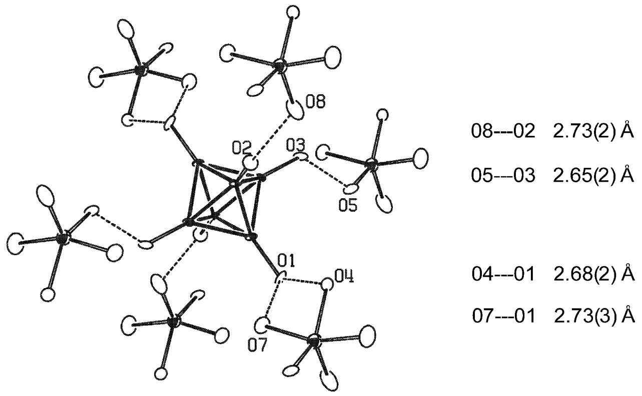

Fig. 3. Closest O–H···O contacts involving methanol molecules and methoxo groups in $[Na(CH_3OH)_5]_2[Mo_6(\mu_3\text{-}Br)_8(OCH_3)_6]$ (**10**). The C and H atoms have been omitted for clarity.

The oxygen atom O6 is involved in the intercation hydrogen bond [O6–H6···O4^{ii}, 2.75(2) Å, symmetry code: (ii) $2-x$, $1-y$, $2-z$]. The oxygen atom O7 is the only one involved in a hydrogen bond with a μ_3-bromine atom [O7–H7···Br1, 3.51(2) Å].

The Mo–O interatomic distances are the function of the number of hydrogen bonds involved and are longer when the oxygen atoms are involved in more than one hydrogen bond. The longest distance (2.07(1) Å) observed for Mo1–O1 is the consequence of the involvement of O1 in two hydrogen bonds. The angles O–Na–O are also dependent on the hydrogen bonding network. The lowest value of 79.4(6)° has been found for the angle O4–Na1–O7, since both of these oxygen atoms are involved in hydrogen bonds with the same oxygen atom (O1).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 199099. Copies of this information may be obtained free of charge from The Director, CCDC , 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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