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Synthesis, Characterization and Reactions of Compounds, Containing Anion $[Mo_2Br_8H]^{3-}$. Crystal Structure of $(pipH)_3[Mo_2Br_8H]$ (pip = piperidine)

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Preparation and characterization of $(pyH)_3[Mo_2Br_8H]$ (py = pyridine) (**1**), $(pipH)_3[Mo_2Br_8H]$ (pip=piperidine) (**2**), and $(morphH)_2(H_7O_3)[Mo_2Br_8H]$ (morph=morpholine (**3**) are described. $(pipH)_3[Mo_2Br_8H]$ (**2**) crystallizes in the monoclinic space group $P2_1/c$ with a = 15.378(4), b = 12.149(7), c = 16.870(5) Å, β = 107.40(2)° and Z = 4; 1855 data with $I > 3\sigma(I)$ were refined to R = 0.069, R_w = 0.073. The structure of crystallographically asymmetric $[Mo_2Br_8H]^{3-}$ anion revealed a greater *trans* effect of the μ–H than that of the μ–Br, found also in the case of other $[Mo_2X_8H]^{3-}$, X = Cl, Br, I anions. Two reaction pathways dominate the chemistry of compounds containing $[Mo_2Br_8H]^{3-}$, as found in the studies of reactions with pyridine, HBr(aq) and CH_3COOH(aq) and they can be represented schematically as (a) $Mo_2^{6+} + H^- + H^+ \rightarrow Mo_2^{6+} + H_2$, and (b) $Mo_2^{6+} + H^- \rightarrow Mo_2^{4+} + H^+$.

INTRODUCTION

The compound dimolybdenum tetraacetate has been known for a long time to be an excellent starting material for the preparation of halodimolybdates (II) and halo complexes of molybdenum in higher oxidation states. All reactions of dimolybdenum tetraacetate with aqueous solutions of hydrogen halides can be divided into several groups.[1] One of them, namely oxidative addition of hydrohalic acids to the quadruply bonded molybdenum atoms, is represented by Eq. (1):

$$Mo_2(O_2CCH_3)_4 + 8\ HX \rightarrow Mo_2X_8H^{3-} + 3\ H^+ + 4\ CH_3CO_2H \qquad (1)$$

This reaction appears to be quantitative when carried out at temperatures of 60 °C and above, and with exclusion of oxygen. It constituted the first example of an oxidative-addition reaction involving a well-defined metal-metal multiple bond.[2]

The formally triply bonded bioctahedral hydride $Mo_2(\mu\text{–}H)(\mu\text{–}Cl)_2Cl_6^{3-}$ has been also obtained photochemically[3] and electrochemically[4] from 6 M HCl solutions of $Mo_2Cl_8^{4-}$.

Also these complexes were the subject of numerous structural,[5] spectroscopic,[6] and electrochemical[7] studies, while only few examples of articles dealing with bromo or iodo analogues can be found. $Cs_3[Mo_2Br_8H]$[8] was not only the first bromo analogue that was synthesized and characterized by X-ray diffraction studies (at that time formulated as $Cs_3Mo_2Br_8$), but also the compound extensively used for studies concerning the true identity of compounds containing $[Mo_2X_8H]^{3-}$ anion,[9] spectroscopic studies,[10] and as an useful precursor for the preparation of tetrabromodimolybdenum (II) complexes with different unidentate and bidentate ligands.[11] Preparation and structures of $(H_7O_3)[(CH_3)_4N]_2[Mo_2Br_8H]$[12] and $(H_7O_3)[(C_2H_5)_4N]_2[Mo_2I_8H]$[13] are reported. $Rb_3[Mo_2Br_8H]$ and $(Bu_4N)_3[Mo_2Br_8H]$ are briefly mentioned[6a] without any details on their preparation and properties. These compounds are, as far as we know, the only compounds containing $[Mo_2X_8H]^{3-}$, X = Br, I, that have been described. In this paper, we wish to report on the synthesis, characterization and reactivity of another three compounds containing anion $[Mo_2Br_8H]^{3-}$.

EXPERIMENTAL

Preparative Procedures

Dimolybdenum tetraacetate $Mo_2(O_2CCH_3)_4$[14] and $Cs_3[Mo_2Br_8]$[11c] were prepared as described. All commercial reagents were used as supplied. Mo was analyzed gravimetrically as $PbMoO_4$. Potentiometric titration with $AgNO_3$ was used for determination of Br. Interplanar spacings were obtained with the Guinier-de-Wolf camera (Enraf Nonius) and Cu $K\alpha$ radiation. Infrared spectra were measured on mineral oil mulls between CsBr plates using a Perkin-Elmer model 521 spectrometer in the range 4000–300 cm^{-1}. Electronic absorption spectra were obtained with the SPECORD M 40 (Carl Zeiss, Jena) spectrophotometer. Only from red phosphorus freshly distilled solutions of HBr were used for spectroscopic measurements and diluted with water when needed.

*Preparation of (pyH)$_3$[Mo$_2$Br$_8$H] (py=pyridine) (**1**)*

$Mo_2(O_2CCH_3)_4$ (1.00 g, 2.34 mmol) was dissolved with stirring in air in 20 ml of 9.0 M HBr. After one hour, the solution was filtered onto 25 mmol of pyHBr, obtained from 2.0 ml of pyridine and 3.0 ml 9.0 M HBr. The solution was then concentrated on the high vacuum line at 20 °C for 30 minutes and then left under vacuum at 5 °C for 20 hours. The brown crystalline product was filtered, washed with cold ethanol and ether and dried over night in evacuated desiccator over KOH. Average yield 1.87 g (75%). Crude product was recrystallized from 9.0 M HBr with addition of pyHBr. The average yield was 67%. *Anal.* Calcd. for $(pyH)_3[Mo_2Br_8H]$ (M_r = 1072.49): Mo 17.9; Br 59.6%; found Mo 18.0, Br 59.6%. From X-ray powder data, the following d spacings (Å) were observed (relative intensities in parentheses): 10.1 (2), 8.85 (8), 8.05 (10), 8.0 (1), 7.8 (3), 7.5 (1), 7.45 (1), 6.75 (3), 6.45 (4). IR spectra confirmed the presence of pyridinium cations.

*Preparation of (pipH)$_3$[Mo$_2$Br$_8$H] (pip=piperidine) (**2**)*

$Mo_2(O_2CCH_3)_4$ (1.00 g, 2.34 mmol) was dissolved in 17 ml of 9.0 M HBr by stirring for 1 hour in air. The obtained solution was added to 25 mmol of pipHBr (2.5 ml of piperidine and 3.0 ml of 9.0 M HBr) and then concentrated on the high vacuum line at 20 °C for 30 minutes and then left over night under vacuum at 5 °C. The crystalline product was filtered and dried without washing in air and then under reduced pressure over KOH for 20 hours. Average yield 1.88 g (74%). The crude product was recrystallized from 9.0 M HBr with average yield of 71%. *Anal.* Calcd. for $(pipH)_3[Mo_2Br_8H]$ (M_r = 1090.63): Mo 17.6, Br 58.6%; found Mo 17.5, Br 59.0%. The following d spacings (Å) were observed (relative intensities in parentheses): 9.7 (3), 9.4 (5), 8.85 (10), 8.15 (5), 8.05 (1), 7.5 (7), 7.35 (7), 6.7 (3), 6.45 (3), 6.3 (2). The observed values are in excellent agreement with those calculated from unit cell dimensions. IR spectra confirmed the presence of piperidinium cations.

*Preparation of (morphH)$_2$(H$_7$O$_3$)[Mo$_2$Br$_8$H] (morph=morpholine) (**3**)*

This compound was prepared and recrystallized in similar manner to **1** and **2**. Average yield of synthesis 82% (for recrystallization 69%). *Anal.* Calcd. for (morphH)$_2$(H$_7$O$_3$)[Mo$_2$Br$_8$H] (M_r = 1063.47): Mo 18.0, Br 60.1%; found Mo 17.8, Br 60.0%. The following *d* spacings (Å) were observed (relative intensities in parentheses): 11.75 (2), 10.3 (1), 9.2 (4), 8.5 (3), 8.0 (8), 7.85 (10), 7.5 (4), 6.95 (3), 6.6 (6). IR spectra confirmed the presence of morpholinium cations. The presence of hydrated proton $H_7O_3^+$ is confirmed by a strong broad maximum centred at 3450 cm^{-1} (ν(H$_2$O)), characteristic of compounds containing this cation.[15] The same stoichiometry is also found in several other μ-hydrido complexes, cited in the introduction.

Reactions of Compounds Containing $[Mo_2Br_8H]^{3-}$

Reactions with pyridine:

a) Reactions at room temperature. – 10 ml of pyridine was degassed on the high vacuum line and then frozen in a closed flask by liquid nitrogen. (pyH)$_3$[Mo$_2$Br$_8$H] (0.54 g, 0.50 mmol) ground to fine powder, was added and the evacuated flask slowly warmed to room temperature. The solution was stirred with a magnetic stirrer at room temperature for 20 hours. The green product was filtered off, washed with methanol and ether and dried under vacuum. Average yield was 0.34 g (82%). *Anal.* Calcd. for Mo$_2$Br$_4$py$_4$ (M_r = 827.92): Mo 23.2, Br 38.6%; found Mo 23.0, Br 38.7%. The compound was also identified by its IR spectrum and powder pattern.[16] When **2** and **3** were used as starting materials for this reaction, Mo$_2$Br$_4$py$_4$ was the only obtained product, but the yields were lower. In the case of the compound with morpholinium cation, the difference is significant. Evolution of small amounts of gas was observed when the reaction mixture containing compound **3** was warmed to room temperature.

If Cs$_3$[Mo$_2$Br$_8$H] was used as starting material, only unreacted Cs$_3$[Mo$_2$Br$_8$H] was present in the reaction mixture after stirring in vacuum for 20 hours.

b) Reactions at 100 °C. – The reaction mixture containing **1** (1.07 g, 1.00 mmol) and 20 ml of pyridine in vacuum was prepared as described under a) and then left under reflux at 100 °C in an evacuated glass ampoule for 30 minutes. The solution was then slowly cooled to room temperature, Mo$_2$Br$_4$py$_4$ was filtered in the air, washed with methanol and ether and dried under vacuum. Average yield 0.65 g (79%).

When the reaction was carried out under identical conditions with other starting materials, the same dependence of the obtained amount of Mo$_2$Br$_4$py$_4$ on the starting material used as at room temperature was observed. A major difference concerns Cs$_3$[Mo$_2$Br$_8$H] as starting material, which under these conditions also reacts completely. When the reaction was performed with (morphH)$_2$(H$_7$O$_3$)[Mo$_2$Br$_8$H], a small amount (~ 0.1 g) of red-brown crystalline product precipitated from the filtrate after filtration of Mo$_2$Br$_4$py$_4$ and washing with methanol. The compound was identified as orthorhombic modification of MoBr$_3$py$_3$[17] on the bases of its IR spectrum and powder pattern.

Reactions with 2.25 M HBr:

1.00 mmol of compound containing $[Mo_2Br_8H]^{3-}$ion (**1**, **2** or **3**) was added to 25 ml of degassed frozen 2.25 M HBr. The entire system was then evacuated and allowed to warm slowly to room temperature. When the HBr(aq) melted, the solution was stirred uniformly with a magnetic stirrer. The yellow-brown colour of solution slowly changed to intense green and the evolution of hydrogen gas was observed throughout the reaction. The gas generated was collected under water and under the reaction conditions (temperature, pressure, water pressure) the following amounts of evolved hydrogen were obtained (two independent experiments were carried out for each starting material):

Starting material	**1**	2	**3**
n(starting material)/mmol	1.00	1.00	1.00
n(H$_2$)/mmol	0.98 (2)	1.00 (2)	0.99 (2)

Reactions with $CH_3COOH(aq)$:

2 (0.55 g, 0.50 mmol) was dissolved in 20 ml of 4.4 M CH_3COOH in the air at room temperature. The solution had a yellow-green colour and formation of small amounts of gaseous H_2 was observed after a few seconds. After several minutes, the colour of solution turned to deep violet and slow precipitation of yellow $Mo_2(O_2CCH_3)_4$ began. After four hours, the product, identified by its IR spectrum and powder pattern as dimolybdenum tetraacetate, was filtered off in the air, washed with ethanol and dried in vacuum. A typical yield for this reaction is 79% (0.17 g).

If **1** and **3** are used as starting materials, the results are almost identical On the other hand, great dependence on the molarity of CH_3COOH solution was observed. Typical results for reations of 0.50 mmol of 2 with 20 ml of CH_3COOH solutions of different concentrations are shown below:

$c(CH_3COOH)$/mol l^{-1}	1.0	1.7	2.9	4.4	5.8	8.7
$m(Mo_2(O_2CCH_3)_4)$/g	0.11	0.13	0.16	0.17	0.165	0.16

At lower concentrations of CH_3COOH solutions, greater amounts of evolved gas were observed in the first stage of the reaction, accompanied by a more intense violet colour of solution in the second stage.

X-ray Crystallography

A prismatic dark brown crystal of compound **2**, with approximate dimension 0.40 x 0.26 x 0.18 mm, was used for data collection. Data were collected on a CAD-4 (Enraf Nonius) computer-controlled diffractometer with graphite monochromated Mo $K\alpha$ radiation. Details of crystal data and refinement are listed in Table I. The data were corrected for Lp effects and absorption. The absorption correction was based on crystal shape measurements. The Patterson vector map revealed the positions of Mo and Br atoms and the electron density map gave the positions of all nonhydrogen atoms. Nitrogen atoms of piperidinium cations could not be identified and all atoms were refined as carbon atoms isotropically. Hydrogen atoms in cations were included at calculated positions and were not refined. The position of μ-hydride in the anion was found in a final difference map. Attempts to refine it were unsucessful, so it was included without refinement. All calculations were carried out wiht X-RAY 76[18] and SHELX 76[19] systems of computer programs.

RESULTS AND DISCUSSION

Synthetic Studies

Three compounds containing $[Mo_2Br_8H]^{3-}$ anion: $(pyH)_3[Mo_2Br_8H]$ (py=pyridine) (**1**), $(pipH)_3[Mo_2Br_8H]$ (pip=piperidine) (**2**) and $(morphH)_2(H_7O_3)[Mo_2Br_8H]$ (morph=morpholine) (**3**) were isolated from the solutions of dimolybdenum tetraacetate, $Mo_2(O_2CCH_3)_4$ in 9.0 M HBr in the presence of an appropriate organic cation. All compounds were characterized by standard chemical and physical methods. The dark brown crystalline compounds are fairly stable in a dry atmosphere. They are very soluble in water and aqueous HBr solutions. Dissolution in water and dilute aqueous solutions of HBr is accompanied by evolution of hydrogen gas.

Oxidative addition of hydrobromic acid to the quadruply bonded molybdenum atoms in dimolybdenum tetraacetate, Eq. (1), may be considered formally as the combined result of two reaction steps:[5b]

TABLE I.

*Crystallographic data for $(pipH)_3[Mo_2Br_8H]$ (**2**)*

Empirical formula	$C_{15}H_{37}N_3Mo_2Br_8$
Molar mass (g mol^{-1})	1090.634
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
a/Å	15.378 (4)
b/Å	12.149 (7)
c/Å	16.870 (5)
β/°	107.40 (2)
Volume (Å^3)	3007.55
Z	4
T/°C	293 (2)
λ (Mo $K\alpha$)	0.7107
D_x/g cm^{-3}	2.408
D_m/g cm^{-3} (flotation)	2.41 (2)
Reference reflections	2 3 –3; 2 3 2; 0 3 3
Intensity decrease/%	–
Measured reflections	5762 ($+h$, $+k$, $\pm l$)
Unique data	3891
R for merging equivalent data	0.060
Observed reflections	1855 ($I > 3\sigma(I)$)
μ /cm^{-1}	113.53
Transmission factor range	0.0716–0.6393
$R(F)$	0.069
$R_w(F)$	0.073
Data-to-variable ratio	11.3
Min., max. peaks in final ΔF map (e^-/Å^3)	–0.67, 0.69

TABLE II.

Electronic spectral data for $[Mo_2Br_8H]^{3-}$ complexes

Compound	Solvent	λ_{max} / nm ; ε / M^{-1} cm^{-1} (in parentheses)				
		1	2	3	4	5
1	9.0 M HBr	258 ($29x10^3$)	307 ($7.8x10^3$)	353sh ($3.8x10^3$)	442 (1953)	785 (174)
	CH_3CN	256 ($22x10^3$)	310 ($8.4x10^3$)	343sh ($5.2x10^3$)	450 (2320)	794 (202)
2	9.0 M HBr	261 ($17x10^3$)	309 ($8.0x10^3$)	353sh ($2.9x10^3$)	442 (1987)	785 (187)
	CH_3CN[a]	270	309	341sh	449	795
3	9.0 M HBr	261 ($19x10^3$)	309 ($8.2x10^3$)	353sh ($3.9x10^3$)	442 (1934)	785 (181)
	CH_3CN	252 ($19x10^3$)	310 ($9.4x10^3$)	342sh ($5.7x10^3$)	450 (2340)	797 (195)
$Cs_3[Mo_2Br_8H]$	9.0 M HBr	245 ($19x10^3$)	305 ($7.0x10^3$)	352sh ($3.3x10^3$)	442 (1784)	785 (170)
	CH_3CN[a]	266	310	340sh	449	790

[a] – becuase of the lower compound solubility in CH_3CN, the exact concentration of the solution was not estimated

$$Mo_2(O_2CCH_3)_4 + 4\ HBr + 3\ Br^- \rightarrow \text{»}Mo_2Br_7^{3-}\text{«} + 4\ CH_3COOH \quad (2)$$

$$\text{»}Mo_2Br_7^{3-}\text{«} + HBr \rightarrow [Mo_2Br_8H]^{3-} \quad (3)$$

The true identity of bromodimolybdate(II) species in solution after the first reaction stage – simple metathesis reaction, Eq. (2), is dubious, but we believe that a mixture of two anionic species, $[Mo_2Br_8]^{4-}$ and $[Mo_2Br_6(H_2O)_2]^{2-}$, which have been also isolated in solid compounds,[20] is present. The second stage – oxidative addition of HBr to bromodimolybdate(II), Eq. (3), is slower, thus being the rate determining step of the whole process. In the case of the synthesis of $Cs_3[Mo_2Br_8H]$, the whole process is completed in less than 45 minutes at an elevated temperature (60 °C).[9] Even at room temperature, the yields of the $[Mo_2Br_8H]^{3-}$ synthesis from dimolybdenum tetraacetate are very high at reasonable reaction times. This is probably due to the fact that the oxidative addition of HBr to bromodimolybdate(II) ions is much faster than the reaction of HCl with $[Mo_2Cl_8]^{4-}$.[21]

The electronic absorption spectra of isolated compounds in solution were studied in more detail. Characteristic electronic absorption spectra of $[Mo_2Br_8H]^{3-}$ in 9.0 M HBr and acetonitrile are given in Figure 1 while all the relevant absorption bands of the complexes in 9.0 M HBr and CH_3CN solutions are presented in Table II. All the complexes studied present five-band electronic spectra with maxima reasonably red shifted with respect to their chloro analogues. Positions and molar absorbances of maxima 4 and 5 were usually reported[6d,g;7a,22] and the only reported values for $[Mo_2Br_8H]^{3-}$ in 6 M HBr[23] 435 nm (2200 $M^{-1}cm^{-1}$) and 772 nm (176 $M^{-1}cm^{-1}$) are in excellent agreement with our results.

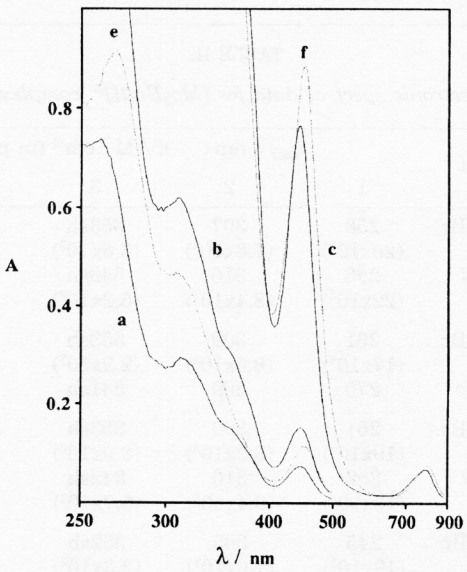

Figure 1. Electronic absorption spectra of $(morphH)_2(H_7O_3)[Mo_2Br_8H]$, compound **2** in 9.0 M HBr (—) and CH_3CN (····); c(**2**) = a) 3.81×10^{-5} M, b) 7.62×10^{-5} M, c) 3.81×10^{-4} M, e) 5.19×10^{-5} M, f) 3.83×10^{-4} M.

TABLE III.

Dimensions of the $[Mo_2Br_8H]^{3-}$ anion in $(pipH)_3[Mo_2Br_8H]$ 2[a]

Bond lengths/Å			
Mo(1)–Mo(2)	2.385(4)		
Mo(1)–Br(1)	2.637(5)	Mo(2)–Br(1)	2.610(5)
Mo(1)–Br(2)	2.634(4)	Mo(2)–Br(2)	2.659(4)
Mo(1)–Br(3)	2.530(5)	Mo(2)–Br(6)	2.554(5)
Mo(1)–Br(4)	2.544(4)	Mo(2)–Br(7)	2.540(4)
Mo(1)–Br(5)	2.633(5)	Mo(2)–Br(8)	2.637(4)
Mo(1)–H	2.00	Mo(2)–H	1.80
Bond angles/deg			
Mo(1)–Br(1)–Mo(2)	54.1(1)	Mo(1)–Mo(2)–Br(6)	117.2(2)
Mo(1)–Br(2)–Mo(2)	53.5(1)	Mo(1)–Mo(2)–Br(7)	111.1(2)
Mo(1)–H–Mo(2)	77.5	Mo(1)–Mo(2)–Br(8)	135.6(2)
H–Mo(1)–Br(5)	177.1	Mo(2)–Mo(1)–Br(3)	115.4(2)
H–Mo(2)–Br(8)	169.5	Mo(2)–Mo(1)–Br(4)	113.2(1)
Br(1)–Mo(1)–Br(2)	90.3(1)	Mo(2)–Mo(1)–Br(5)	135.4(4)
Br(1)–Mo(2)–Br(2)	90.3(1)		

[a] – The position of μ–H in the anion from a final difference map was not refined

Reactions of $[Mo_2Br_8H]^{3-}$

Two reactions dominate the chemistry of $[Mo_2Br_8H]^{3-}$. The first reaction takes place in the presence of an appropriate proton donor and can be schemtically represented by Eq. (4):

$$Mo_2^{6+} + H^- + H^+ \rightarrow Mo_2^{6+} + H_2 \qquad (4)$$

The evolution of hydrogen in reactions of compounds containing $[Mo_2X_8H]^{3-}$, X = Cl, Br with water or dilute aqueous solutions of HX, in which the oxidation number of molybdenum remains unchanged, is clear evidence for the presence of bridging hydrogen. As a matter of fact, this reaction, combined with deuterium labelling experiments, led to recognition of the true identity of compounds of this type.[9] Determination of the amount of evolved hydrogen gas in the case of the reaction of $[Mo_2Br_8H]^{3-}$ with 2.25 M HBr has shown that the reaction is quantitative under the applied conditions. The characteristic green colour and visible spectra of the solution after the reaction support the formation of dihydroxy-bridged molybdenum(III) dimer $Mo_2(\mu\text{-}OH)_2Br_x(H_2O)_{8-x}^{(x-4)-}$. The inverse dependence of the reaction rate on $[H^+]$, found in kinetic studes of reaction of $Rb_3[Mo_2Cl_8H]$ with dilute HCl soluions,[22] is consistent with H_2O playing the role of proton donor in this reaction. This proposal is supported by the observation that the same reaction takes place if pure water is used instead of dilute solutions of HX. Thus, the reactions of compounds containing $[Mo_2Br_8H]^{3-}$ anion with dilute solutions of HBr can be represented by the following reaction:

$$[Mo_2Br_8H]^{3-} + (10-x)\ H_2O \rightarrow Mo_2(\mu\text{–}OH)_2Br_x(H_2O)_{8-x}^{(x-4)-} + H_2 + (8-x)\ Br^- + H^+ \quad (5)$$

The second reaction, schematically shown with Eq. (6), which is characteristic of the

$$Mo_2^{6+} + H^- \rightarrow Mo_2^{6+} + H^+ \quad (6)$$

chemistry of $[Mo_2Br_8H]^{3-}$ anion, is the reversal of the oxidative addition of a proton to the quadruply bonded pair of molybdenum atoms, Eq. (1). This reaction dominates in reactions of compounds containing $[Mo_2Br_8H]^{3-}$ anion with pyridine and aqueous solutions of CH_3COOH.

It has been known for a long time that the reaction of $Cs_3[Mo_2X_8H]$, X = Cl, Br with pyridine leads to formation of neutral complexes with stoichiometry $Mo_2X_4py_4$.[11a,23] The reaction was conducted at an elevated temperature (110 °C) and the authors[11a] propose that pyridine may, at least in part, be responsible for the reduction of $[Mo_2X_8H]^{3-}$ to $Mo_2X_4py_4$. The results of our studies can be summarized in the following conclusions: (*1*) All synthesized compounds react with pyridine at room temperature to give $Mo_2Br_4py_4$. After 6 hours, the yield of the reaction is not substantially affected by prolonged reaction times. At an elevated temperature (100 °C), the reaction is much faster. $Cs_3[Mo_2Br_8H]$ does not react with pyridine at room temperature even at much longer reaction times (20 hours). Low solubility of this compound in pyridine is probably the only reason for this observation. (*2*) We believe that the hydride ion plays the role of reducing agent, thus giving a very neat stoichiometry of the reaction represented by Eq. (7) for compound **1**:

$$(pyH)_3[Mo_2Br_8H] + 5\ py \rightarrow Mo_2Br_4py_4 + 4\ pyHBr \quad (7)$$

A similar reaction takes place with $(pipH)_3[Mo_2Br_8H]$.

(*3*) Significantly lower yields, the observed evolution of hydrogen gas and formation of $MoBr_3py_3$ as side product in the reaction of **3** wih pyridine indicate two simultaneous reactions. The presence of the strong proton donor $H_7O_3^+$ is the evident reason for the significant role of reaction (8) in the reaction of **3** with pyridine:

$$(morphH)_2(H_7O_3)[Mo_2Br_8H] + 6\ py \rightarrow 2\ MoBr_3py_3 + H_2 + 2\ morphHBr + 3\ H_2O \quad (8)$$

The reaction is similar to the reaction of $[Mo_2Br_8H]^{3-}$ in 2.25 M HBr, with $H_7O_3^+$ playing the role of proton donor in this case. Where water molecules act as proton donors, compounds of Mo^{III} with one or more μ-hydroxo bridges are formed. (*4*) San Filippo *et al.*[11a] have described the synthesis of *mer*-$MoBr_3py_3$ from $Cs_3[Mo_2Br_8H]$ and pyridine at 200 °C after 8 hours. The absence of a possible proton donor and the fact that hydrogen gas evolution was not observed exclude the Eq. (4) pathway. Although the reactions were carried out under anaerobic conditions, the authors suggest that the presence of dissolved oxygen is one of the possible reasons for oxidation of $Mo_2Br_4py_4$ formed in the first reaction stage. We did not observe any formation of $MoBr_3py_3$ from $Cs_3[Mo_2Br_8H]$ and degassed pyridine, when the reactions were carried out in glass tubes, sealed under vacuum, at 200 °C for 24 hours or even more. Thus, we believe that oxygen is the most probable oxidant in the case of the observed formation of $MoBr_3py_3$ from $Cs_3[Mo_2Br_8H]$.

Booth possible pathways, Eqs. (4) and (6), are characteristic of the reactions of $[Mo_2Br_8H]^{3-}$ with aqueous solutions od CH_3COOH. Evolution of H_2 is observed in the

initial stage of the reaction and dimolybdenum tetraacetate is the product of the reaction. Relatively high yields of the $Mo_2(O_2CCH_3)_4$ formation in the case of reactions of compounds **1–3** with $CH_3COOH(aq)$ are in accord with the dominant role of reaction (6). At lower concentrations of CH_3COOH solutions, the influence of reaction (4) becomes more significant due to the lower concentration of hydrated protons in these solutions.

It is worth mentioning that reactions of $[Mo_2X_8H]^{3-}$, X = Cl, Br with $CH_3COOH(aq)$ are not significant only because they illustrate the reversibility of oxidative addition of a proton to the quadruple Mo–Mo bond but also because they offer an efficient route for regeneration of $Mo_2(O_2CCH_3)_4$, the starting material for all these investigations.

X-ray

The dinuclear anion $[Mo_2Br_8H]^{3-}$ has the known bioctahedral structure. Although there is no crystallographic symmetry imposed upon the dimeric anion, its overall symmetry is very nearly C_{2v}. All dimensions of the $[Mo_2Br_8H]^{3-}$ ion in **2**, given in Table III, are in excellent agreement with those found in $(H_7O_3)[CH_3)_4N]_2[Mo_2Br_8H]$.[12] Abscence of any significant interionic interactions in both structures is the possible reason for this observation. There are three different sets of Mo–Br distances, with the average values Mo–$Br_{t,H}$ 2.635, Mo–$Br_{t,Br}$ 2.542, and Mo–Br_b 2.635 Å, indicating a greater *trans* effect of the μ–H than that of the μ–Br.

Three independent piperidinium cations lie in the unit cell, with small distortions from the usually observed chair conformation in one of them.

Supplementary material – Tables with atomic coordinates, anisotropic thermal parameters of Mo and Br atoms, dimensions of piperidinium cations and structure factors (18 pages) are available from the authors on request.

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SAŽETAK

Sinteza, karakterizacija i reakcije spojeva koji sadrže anion $[Mo_2Br_8H]^{3-}$. Kristalna struktura $(pipH)_3[Mo_2Br_8H]$ (pip=piperidin)

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Opisana je priprava i karakterizacija (pyH)$_3$[Mo$_2$Br$_8$H](py=piridin) (**1**), (pipH)$_3$[Mo$_2$Br$_8$H] (pip=piperidin) (**2**) i (morphH)$_2$(H$_7$O$_3$)[Mo$_2$Br$_8$H] (morph = morfolin). (pipH)$_3$[Mo$_2$Br$_8$H] kristalizira u monoklinskoj prostornoj grupi $P2_1/c$ sa a = 15.378(4), b = 12.149(7), c = 16.870(5)Å, β = 107.40(2) i Z = 4; 1855 podataka s $I > 3\sigma(I)$, utočnjeno je do R_w = 0.073. Struktura kristalografski asimetričnog aniona $[Mo_2Br_8H]^{3-}$, pokazala je veći *trans*-efekt za μ–H nego za μ–Br, što je nađeno i u slučaju drugih $[Mo_2X_8H]^{3-}$ aniona (X = Cl, Br, I). Proučavanjem reakcija s piridinom, HBr(aq) i CH_3COOH (aq) nađeno je da dva reakcijska puta prevladavaju u kemiji spojeva koji sadrže $[Mo_2Br_8H]^{3-}$, a mogu se shematski prikazati kao: (a) $Mo_2^{6+} + H^- + H^+ \rightarrow Mo_2^{6+} + H_2$ i (b) $Mo_2^{6+} + H^- \rightarrow Mo_2^{4+} + H^+$.