Inorganica Chimica Acta, 57 (1982) 247–251
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Preparative and Structural Studies of Halodimolybdates(II). VII. Synthesis and Crystal Structures of $(morphH)_2Mo_2X_6(H_2O)_2$ (X = Cl, Br; morph = morpholine)

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Received May 12, 1981

$(morphH)_2Mo_2Cl_6(H_2O)_2$ (A) and $(morphH)_2Mo_2Br_6(H_2O)_2$ (B) (morph = C_4H_9NO) crystallize in the P1 space group with Z = 1 and comparable cell dimensions. Average Mo–Mo distance is 2.12(1) Å. Mo_2 pairs have two different orientations with respect to the position of the remaining atoms forming $Mo_2X_6(H_2O)_2^{2-}$ anion. Population factors for the disorded part are 14 and 33% for chloride and bromide. Mo–Cl and Mo–Br bond lengths average 2.43(1) and 2.57(1) Å. Mo–O(H_2O) distances are 2.20(1) Å and 2.23(1) Å (B). $Mo_2X_6(H_2O)_2^{2-}$ is located at the symmetry center.

Morpholinium cations are in the chair conformation. Cations and anions are connected by electrostatic interactions and weak hydrogen bonds.

$(morphH)_4Mo_2Cl_8$ and the compound with the chemical composition of $(morphH)_2Mo_2Br_{4.2}Cl_{1.8}(H_2O)_2$ were prepared. All compounds were characterized by chemical and physical methods.

Introduction

Halodimolybdates(II) with quadruply bonded molybdenum atoms contain $Mo_2X_8^{4-}$ or $Mo_2X_6(H_2O)_2^{2-}$ anion. The former was identified in $K_4Mo_2Cl_8\cdot 2H_2O$, $(enH_2)_2Mo_2Cl_8\cdot 2H_2O$, $(NH_4)_5Mo_2Cl_9\cdot H_2O$ and $(NH_4)_4Mo_2Br_8$ [1–4]. $Mo_2X_6(H_2O)_2^{2-}$ was found in $(picH)_2Mo_2Br_6(H_2O)_2$, $(picH)_2Mo_2J_6(H_2O)_2$, $(piH)_2Mo_2J_6(H_2O)_2$, $(pipH)_2Mo_2Br_6(H_2O)_2$ and $(piH)_3Mo_2Br_7(H_2O)_2$ [5–9]. From the knowledge obtained thus far $Mo_2X_6(H_2O)_2^{2-}$ seems to be the preferential product in the presence of organic cations.

Protonated morpholinium is the first cation that gives $(morphH)_2Mo_2Br_6(H_2O)_2$ as well as $(morphH)_2Mo_2Cl_6(H_2O)_2$ and $(morphH)_4Mo_2Cl_8$. It was therefore interesting to compare the $Mo_2X_6(H_2O)_2^{2-}$ (X = Cl, Br) pair to see whether the cation has any influence on the bonding parameters of the $Mo_2X_6(H_2O)_2^{2-}$ group or whether some trends could be identified in the relation between the halogen and the Mo–Mo distance.

Experimental

Compounds were analysed for Mo and halogens as described before [5]. Chlorine in the $(morphH)_2Mo_2Br_{4.2}Cl_{1.8}(H_2O)_2$ was determined after the removal of bromine with KJO_3 [10].

Interplanar spacings were obtained with Guinier de Wolf camera (Enraf Nonius) and CuK_α radiation. Intensities were estimated visually.

Thermal decomposition was followed on the Mettler instrument [11] in the flow of dried Ar with combined TG and DTA head and the platinum sample holder. Approximate weight of the sample was 100 mg, heating rate 2° min^{-1} and the reference substance α-Al_2O_3.

Infrared spectra were measured on the PE 521 instrument down to 300 cm^{-1} with samples suspended in the paraffin oil between CsBr plates.

$(NH_4)_5Mo_2Cl_9\cdot H_2O$, $Mo_2(CH_3COO)_4$ and $(NH_4)_4Mo_2Br_8$ were prepared following the published procedures [3, 4, 12].

$(morphH)_4Mo_2Cl_8$

2×10^{-3} mol (1.25 g) of $(NH_4)_5Mo_2Cl_9\cdot H_2O$ were dissolved in 40 ml of 1:1 HCl cooled to 0 °C. The solution was filtered on to 3.2×10^{-2} mol of morphHCl obtained from 2.8 ml morpholine and 5.5 ml of conc. HCl. The reaction mixture was left at 5 °C for 24 hours. The crystalline product was vacuum filtered, washed with several portions of ether and dried under vacuum at room temperature. The average yield was 60%.

The same compound was obtained from $Mo_2(CH_3COO)_4$ and morphHCl in conc. HCl. This way gave better yields. *Anal.* Calcd. (Found) for $(morphH)_4Mo_2Cl_8$: Mo, 23.17(23.0); Cl, 34.25(34.1)%.

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*Part VI. J. V. Brenčič and P. Šegedin, *Vestn. Slov. Kem. Drus. 26*, 367 (1979) (in English).

TABLE 1. Crystal Data for $(morphH)_2Mo_2Cl_6(H_2O)_2$ (A), $(morphH)_2Mo_2Br_6(H_2O)_2$ (B) and $(morphH)_2Mo_2Br_{4.2}Cl_{1.8}(H_2O)_2$ (C).

	A	B	C
Formula	$C_8Cl_6H_{24}Mo_2N_2O_4$	$Br_6C_8H_{24}Mo_2N_2O_4$	$Br_{4.2}C_8Cl_{1.8}H_{24}Mo_2N_2O_4$
Formula weight	616.89	883.63	801.59
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	6.950(1)	7.111(1)	7.099(1)
b	8.328(2)	8.687(4)	8.570(2)
c	9.560(2)	9.795(3)	9.707(1)
α^0	110.06(2)	108.77(2)	108.811(12)
β	98.73(2)	99.55(2)	99.416(12)
γ	102.68(2)	103.12(2)	102.959(11)
Volume, $Å^3$	491.27	538.84	526.65
Dc, g cm^{-3}	2.085	2.723	2.527
Dm	2.07(3)	2.70(3)	2.51(3)
Z	1	1	1

$(morphH)_2Mo_2Cl_6(H_2O)_2$ (A)

8×10^{-4} mol (0.7 g) of $(morphH)_4Mo_2Cl_8$ were dissolved in 30 ml of cold 1:1 HCl and the liquid poured in the solution of 2×10^{-2} mol of morphHCl in 10 ml 1:1 HCl and left on ice for 24 hours. The product was filtered, washed with ether and dried under vacuum at room temperature. The average yield was 60%. *Anal.* Calcd. (Found) for $(morphH)_2Mo_2Cl_6(H_2O)_2$: Mo, 31.12(31.2); Cl, 34.48(34.8); H_2O, 5.84(5.5)%. The water content was determined from the thermogravimetric analysis.

$(morphH)_2Mo_2Br_{4.2}Cl_{1.8}(H_2O)_2$

The compound of this stoichiometry is the product of the reaction between 2×10^{-3} mol (1.25 g) of $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ dissolved in 20 ml 1:1 HBr cooled to 0 °C and 3.2×10^{-2} mol of morphHBr. After cooling for 24 hours on ice, the crystalline product was filtered, washed with ether and dried under vacuum at room temperature. Average yield: 50%. Recrystallization of the product from 1:1 HBr by the addition of morphHBr gave $(morphH)_2Mo_2Br_6(H_2O)_2$. *Anal.* Calcd. (Found) for $(morphH)_2Mo_2Br_{4.2}Cl_{1.8}(H_2O)_2$: Mo, 23,94(23.1); Cl, 7.96(8.3); H_2O, 4.49(4.2)%.

Recrystallization of $(morphH)_2Mo_2Br_{4.2}Cl_{1.8}(H_2O)_2$ from hydrobromic acid gave $(morphH)_2Mo_2Br_6(H_2O)_2$.

$(morphH)_2Mo_2Br_6(H_2O)_2$ (B)

10^{-3} mol (0.75 g) of $(NH_4)_4Mo_2Br_8$ were dissolved in 20 ml of cold ($\sim$5 °C) 1:1 HBr and the solution filtered on 2×10^{-2} mol of morphHBr. The reaction mixture was left on ice for 24 hours. The crystalline product was handled in the same way as described above. The same compound can also be prepared from $Mo_2(CH_3COO)_4$ and morphHBr in the conc. HBr. *Anal.* Calcd. (Found) for $(morphH)_2Mo_2Br_6(H_2O)_2$: Mo, 21.72 (21.5); Br, 54.26(53.6); H_2O, 4.08(4.0)%. The water content was determined from thermogravimetric analysis for both $(morphH)_2Mo_2Br_{4.2}Cl_{1.8}(H_2O)_2$ and $(morphH)_2Mo_2Br_6(H_2O)_2$.

Computer controlled CAD-4 (Enraf Nonius) counter diffractometer was used for collecting the data. 2861(A) and 3063(B) independent reflections bounded by a sphere in reciprocal space with $\theta = 30°$ were measured with MoK_α radiation. The number of measured reflections 193(A) and 1069(B) were such that a $I < 3\sigma(I)$. σ of an I value was taken from the counting statistics. The remaining reflections were used for the solution and refinement of the structure. Both sets of data were corrected for absorption.

The cell dimensions for A, B and $(morphH)_2Mo_2Br_{4.2}Cl_{1.8}(H_2O)_2$ were determined from the θ values of more than 20 randomly chosen reflections by the least squares analysis. The densities were determined by flotation in the mixture of suitable organic liquids.

The whole procedure of collecting the data was controlled by the PDP-8 computer.

Initial positions for molybdenum were taken from the isostructural $(pipH)_2Mo_2Br_6(H_2O)_2$ [8]. Fourier map calculated with the starting set gave the coordinates for all the atoms constituting $Mo_2X_6(H_2O)_2^{2-}$ anion. Combination of the Fourier and least squares techniques resulted in the final R_1 and R_2 values of 6.5 and 8.2% for A and 7.0 and 9.4% for B. No attempt was made to include the hydrogen atoms. Appropriate weighting scheme was applied in the later stages of refinement in order to minimize $W\Delta^2$ dependence of F_o and $\sin^2\theta$. $\Delta = (Fo - Fc)$. Scattering factors for neutral Mo, Cl, Br, C, N and

TABLE II. Fractional Atomic Coordinates for $(morphH)_2Mo_2X_6(H_2O)_2$, X = Cl (A); X = Br (B).

Atom	A					B				
	x	y	z	P.P.[a]	Beq ($Å^2$)[b]	x	y	z	P.P.[a]	Beq ($Å^2$)[b]
Mo_1	0.12931(1)	0.51524(6)	0.45432(5)	0.878(6)	1.75	0.13081(22)	0.51862(17)	0.46185(16)	0.690(6)	1.73
Mo_2	0.0645(4)	0.6231(4)	0.5961(3)	0.14(1)	1.87	0.0626(5)	0.6152(4)	0.5944(3)	0.33(1)	1.83
X_1	0.22586(19)	0.82345(17)	0.47490(16)	–	2.58	0.24019(20)	0.83257(15)	0.48570(16)	–	2.35
X_2	−0.03210(22)	0.42740(21)	0.18552(14)	–	2.92	−0.01429(22)	0.44280(19)	0.18069(14)	–	3.10
X_3	0.20615(20)	0.23043(18)	0.39226(16)	–	2.77	0.21607(21)	0.23708(17)	0.39887(15)	–	2.87
O_1	0.37831(60)	0.60954(65)	0.66119(53)	–	2.88	0.3689(14)	0.6052(14)	0.6731(12)	–	3.29
N_{11}	0.7989(9)	0.8190(8)	0.2668(6)	–	3.44	0.7939(19)	0.8142(16)	0.2594(12)	–	3.94
C_{11}	0.8724(10)	0.8091(9)	0.1260(7)	–	3.25	0.8650(26)	0.8157(22)	0.1271(16)	–	3.36
C_{12}	0.7500(11)	0.8834(11)	0.0351(8)	–	3.08	0.7416(29)	0.8896(25)	0.0373(18)	–	3.85
C_{13}	0.4648(10)	0.8082(12)	0.1306(8)	–	3.62	0.4646(29)	0.8063(30)	0.1258(18)	–	4.36
C_{14}	0.5748(11)	0.7288(11)	0.2261(8)	–	3.82	0.5698(27)	0.7221(25)	0.2180(18)	–	5.18
O_{11}	0.5375(8)	0.7905(8)	−0.0051(5)	–	3.94	0.5357(18)	0.7971(16)	−0.0051(11)	–	4.32

[a] Population parameters for the rest of the atoms are 1. [b] $Beq = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

TABLE III. Dimensions of the $Mo_2X_6(H_2O)_2^{2-}$ in $(morphH)_2Mo_2Cl_6(H_2O)_2$–A and $(morphH)_2Mo_2Br_6(H_2O)_2$–B.

Bond lengths, Å	A	B
Mo_1-Mo_1'	2.118(1)	2.114(2)
Mo_2-Mo_2'	2.119(4)	2.116(4)
$Mo-X_1$	2.436(2)	2.581(2)
$Mo-X_2$	2.423(2)	2.581(2)
$Mo-X_3$	2.439(2)	2.560(3)
$Mo-O_1$	2.196(4)	2.229(8)
Mo_2-X_1	2.507(4)	2.637(4)
Mo_2-X_2	2.300(4)	2.472(4)
Mo_2-X_3'	2.453(4)	2.593(4)
Mo_2-O_1'	2.214(5)	2.218(11)
Bond angles, Deg		
$Mo_1'-Mo_1-X_1$	106.01(4)	107.1(1)
$Mo_1'-Mo_1-X_2$	100.67(4)	101.9(1)
$Mo_1'-Mo_1-X_3$	105.21(4)	106.4(1)
$Mo_1'-Mo_1-O_1$	101.52(13)	101.5(3)
$X_1-Mo_1-X_2$	87.96(6)	86.8(1)
$X_2-Mo_1-X_3$	89.71(6)	89.4(1)
$X_3-Mo_1-O_1$	85.06(14)	85.1(3)
$O_1-Mo_1-X_1$	85.41(15)	85.4(3)
$X_1-Mo_1-X_3$	148.58(5)	146.4(1)
$X_2-Mo_1-O_1$	157.80(14)	156.5(3)
$Mo_2'-Mo_2-X_1$	101.64(16)	103.6(2)
$Mo_2'-Mo_2-X_2$	108.33(18)	108.7(2)
$Mo_2'-Mo_2-X_3'$	104.35(14)	104.3(2)
$Mo_2'-Mo_2-O_1'$	100.42(20)	102.2(3)
$X_1-Mo_2-X_3'$	87.60(13)	86.9(1)
$X_2-Mo_2-X_1$	92.32(13)	91.1(1)
$X_3'-Mo_2-O_1'$	83.35(18)	84.3(4)
$X_2-Mo_2-O_1'$	83.78(19)	83.0(4)
$X_2-Mo_2-X_3'$	149.04(11)	147.1(1)
$X_1-Mo_2-O_1'$	154.87(17)	153.3(3)

O were taken [13]. Corrections for the anomalous dispersion were included [14].

A package of computer programs edited by Stewart was applied for all calculations [15]. Crystal data are in the Table I. Positional parameters and bond lengths are in Tables II, III. Hydrogen bonds are collected in the Table IV. Numbering scheme and the way the cations and anions are distributed in the unit cell can be seen on the Figs. 1 and 2. A listing of observed and final calculated structure factors together with anisotropic temperature parameters are available from the Editor.

TABLE IV. Hydrogen Bonds in the Structures of (morphH)$_2$Mo$_2$X$_6$(H$_2$O)$_2$ (X = Cl, A; X = Br, B) in Å.[a]

	A	B
N11 (x,y,z)–X1 (1 – x, 2 – y, 1 – z)	3.21(3.30)	3.36(3.40)
O1 (x,y,z)–X3 (1 – x, 1 – y, 1 – z)	3.10(3.27)	3.25(3.37)
O1 (x,y,z)–O11 (x, y, 1 + z)	2.92(3.04)	2.93(3.04)

[a] Values in parenthesis are sums of the average van der Waals radii taken from the ref. 22.

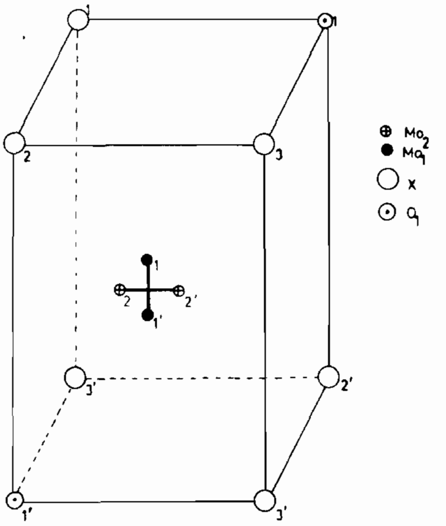

Fig. 1. Numbering scheme within the $Mo_2X_6(H_2O)_2^{2-}$ ion.

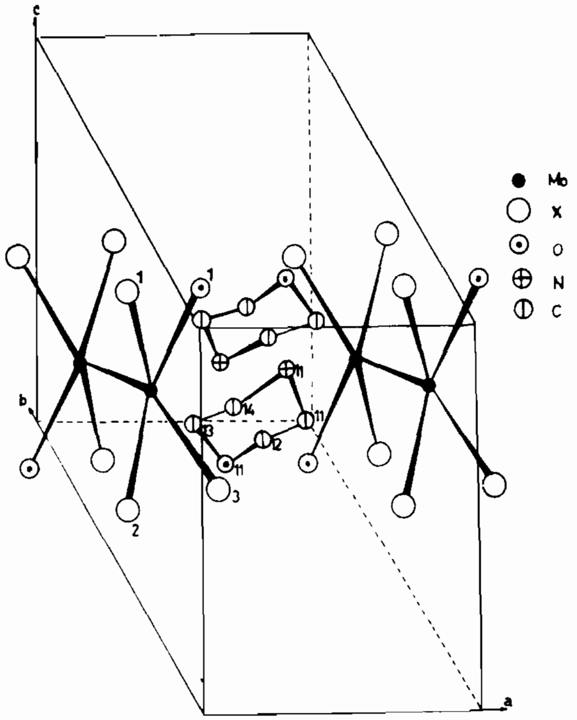

Fig. 2. Packing of the $Mo_2X_6(H_2O)_2^{2-}$ and $C_4H_{10}ON^+$ groups in the unit cell.

Results and Discussion

Organic cations are very suitable for the preparation of the halodimolybdates(II). Besides the appropriate solubility in the hydrohalic acid, large dimensions enable better separation between the anions in the solid state and the isolation of the specific $Mo_2X_6(H_2O)_2^{2-}$ anionic groups.

Both $Mo_2X_6(H_2O)_2^{2-}$ anions found in (morphH)$_2$-$Mo_2X_6(H_2O)_2$ have the usual structures found previously in (LH)$_2$Mo$_2$X$_6$(H$_2$O)$_2$ (L = 4-methylpyridine, piperidine; X = Br and L = 4-methylpyridine, pyridine, X = J) [5–8]. Both anions are located on the symmetry center with eclipsed configuration. Mo–Mo distances 2.118(1) (A) and 2.114(2) Å (B) are comparable to the average value 2.12(1) Å found in other (LH)$_2$Mo$_2$X$_6$(H$_2$O)$_2$ compounds [5–8]. It seems that the halogens have little influence on the Mo–Mo distance when the structure of the anion is the same. It is worth mentioning that the average Mo–Mo value found in $K_4Mo_2Cl_8 \cdot 2H_2O$, $(enH_2)_2$-$Mo_2Cl_8 \cdot 2H_2O$, $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ and $(NH_4)_4Mo_2$-Br_8 equals 2.14(1) Å [1–4]. The last four compounds contain $Mo_2X_9^{4-}$anion and steric conditions could be the reason for lengthening of Mo–Mo distance in $Mo_2X_8^{4-}$ group.

Mo_2 pairs within both $Mo_2X_6(H_2O)_2^{2-}$ anions are disordered in a specific way. About 14% of molybdenum pairs in the chloride and 33% in the bromide are oriented perpendicular to the main direction. Electron density maps showed the unique positions of the halogen atoms and water molecules. Disorder of this sort has been found before in $Mo_2Cl_8^{4-}$ [1], $Re_2Cl_8^{2-}$, $Re_2(CH_3)_8^{4-}$ and Re_2-Cl_4(diphos)$_2$ [16–18]. Mo–Mo distances of the second pair of molybdenum atoms are not much different from the main values 2.119(4) for (A) and 2.116(4) Å for (B). Also, Mo–O(H$_2$O) bond lengths remained unchanged. Larger deviations from the usual values were found in one Mo$_2$–X$_2$ distance which had the value 2.300(4) for the chloride and 2.472(4) Å for the bromide. X$_2$ is the halogen *trans* to the water molecule. While the Mo$_2$–Br$_2$

value is close to the smallest figure in the $Mo_2Br_4(LL)_2$ (LL = 1-diphenylphosphino-2-diphenylarsinomethane) 2.480(1) Å [19] the first one has no counterpart in the Mo(II) structural chemistry. The shortest Mo(II)–Cl distance was found in $Mo_4Cl_8[P(C_2H_5)_3]_4$ 2.373(5) Å [20]. All trials to locate and refine different positions for this particular chlorine atom were unsuccessful.

Other Mo–Mo, Mo–X and Mo–O(H_2O) bond lengths are as usual.

Both morpholinium cations are in the chair conformation. The central carbon atoms are planar within 0.01 Å, the angle between the planes defined by oxygen and two carbon atoms and nitrogen and the next carbon atom is only 5°. Bonding distances within the cations average 1.51(2), 1.50(2) and 1.43(2) Å for C–C, C–N and C–O. All angles are about 110(2)°.

Besides the electrostatic interactions between anions and cations weak hydrogen bonds exist between nitrogens of the morpholinium cation and halogen atom of the anion, oxygen atom of the coordinated water molecule and the halogen and finally between water oxygen and morpholinium oxygen. Distances between the mentioned atoms are smaller from the sum of the van der Waals radii (see Table IV). All other non-bonded contacts are significantly longer.

Infrared spectra of $(morphH)_2Mo_2Cl_6(H_2O)_2$, $(morphH)_2Mo_2Br_6(H_2O)_2$, $(morphH)_4Mo_2Cl_8$ and $(morphH)_2Mo_2Br_{4.2}Cl_{1.8}(H_2O)_2$ show the expected bands of the protonated morpholine, weak but definite bands where O–H valence vibrations are expected and strong peaks located at 305 cm^{-1} and 280 cm^{-1} in the spectra of $(morphH)_2Mo_2Cl_6(H_2O)_2$ and $(morphH)_4Mo_2Cl_8$ which probably contain large contribution of Mo–Cl vibration. Bromides have no absorption in this region.

The results of the thermal decomposition reflect the loosely bound water molecule. Decomposition of $(morphH)_2Mo_2Br_6(H_2O)_2$, $(morphH)_2Mo_2Cl_6(H_2O)_2$ starts at 87 and 120 °C. Maxima of the endothermic peaks are at 128 and 165 °C and the decomposition ends with a flat step at 140 and 175 °C. Although Mo–O$(H_2O)_2$ bond lengths are 2.229(8) and 2.214(5) for the bromide and chloride we do not dare to relate this difference directly to the bond strengths of the coordination bond between molybdenum and oxygen. Another explanation for the greater thermal stability of $(morphH)_2Mo_2Cl_6(H_2O)_2$ is based on the stronger hydrogen bond between oxygen of the water molecule O 1 (x, y, z) to Cl 3 (1 – x, 1 – y, 1 – z) which corresponds to 95% of the value taken for the sum of van der Waals radii. In the bromide this value is 97%.

$(picH)_2Mo_2J_6(H_2O)_2$ decomposes to $(picH)_2Mo_2J_6$ already at 80 °C (maximum of the endothermic peak) [21] and a general trend that the stability drops from chloride to iodide could reflect the inductive effect or intramolecular hydrogen bonds O(H_2O)–X as well.

Some halodimolybdates(II) show definite ability to form compounds containing two different halogen atoms. First example was $(pipH)_2Mo_2Br_{6-x}Cl_x$-$(H_2O)_2$ (X = 0.3; pipH = piperidinium cation) [8]. Recrystallization of $(morphH)_2Mo_2Br_{4.2}Cl_{1.8}(H_2O)_2$ as well as $(pipH)_2Mo_2Br_{6-x}Cl_x(H_2O)_2$ from the hydrobromic acid solutions gave the pure bromodimolybdates(II). Besides the analytical results the unit cell dimensions and experimental density as well support the identity of the $(morphH)_2Mo_2Br_{4.2}Cl_{1.8}(H_2O)_2$. Average value for X was taken as 1.8 with the probable uncertainty of 0.1. The reason why the same halodimolybdate(II) anion contains different proportions of the bromide to chloride remains unexplained.

Acknowledgement

We are indebted to Boris Kidrič Foundation and University of Ljubljana for assistance.

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