Synthesis and Crystal Structure of $(pipzH_2)_2Mo_2Cl_8 \cdot 4H_2O$ (pipz = piperazine)

I. LEBAN and P. ŠEGEDIN

University Edvard Kardelj, Department of Chemistry, Murnikova 6, P.O.B. 537, Ljubljana, Yugoslavia

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The title compound $(pipzH_2)_2Mo_2Cl_8 \cdot 4H_2O$ *(pipz = piperazine), was isolated from the solution of* $(morphH)_2Mo_2Cl_6(H_2O)_2$ *in HCl 1:1 by addition of* $(pipzH_2)Cl_2$*. This reaction indicates the reversibility of the substitution of chloride ions in* $Mo_2Cl_8^{4-}$ *by water molecules.* $(pipzH_2)_2Mo_2Cl_8 \cdot 4H_2O$ *crystallizes in the Pbca space group, with* $a = 15.154(2)$, $b = 13.170(2)$, $c = 12.208(2)$ *Å and* $Z = 4$*. The structure was solved by the Patterson method and refined to the unweighted and weighted residuals of 0.050 and 0.048. The crystal structure is built from* $Mo_2Cl_8^{4-}$, $(pipzH_2)^{2+}$ *and* H_2O*. The Mo–Mo distance of 2.129(3) Å is the shortest one found in all structurally-characterised* $Mo_2X_8^{4-}$ *(X = Cl, Br) anions. Four independent Mo–Cl distances are 2.456(3), 2.445(3), 2.463(4) and 2.455(4) Å. The* $(pipzH_2)^{2+}$ *exists in a usual chair conformation. There is a network of hydrogen bonds of the type N–H···Cl, N–H···O, O–H···Cl and O–H···O between the ions and water molecules.*

Introduction

$(morphH)_2Mo_2Cl_6(H_2O)_2$ [1] is the first chlorodimolybdate(II) containing $Mo_2Cl_6(H_2O)_2^{2-}$ anion to be structurally characterised by X-ray diffraction. The Mo–Mo bond length is 2.118(1) Å, significantly shorter than the values found in chlorodimolybdates(II) containing $Mo_2Cl_8^{4-}$ anions such as $K_4Mo_2Cl_8 \cdot 2H_2O$ (2.138(4) Å) [2], $(enH_2)_2Mo_2Cl_8 \cdot 2H_2O$ (2.134(1) Å) [3], $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ (2.150(5) Å) [4]. The data suggest that the presence of the water molecules coordinated to the Mo_2^{4+} pair shortens the Mo–Mo bond. In order to further support the claim, synthesis and complete X-ray characterisation of several halodimolybdates(II) with similar organic cations was undertaken.

Experimental

$(morphH)_2Mo_2Cl_6(H_2O)_2$ [1] and $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ [4] as starting materials were prepared as described. Methods for characterisation of isolated products were as before [1].

$(pipzH_2)_2Mo_2Cl_8 \cdot 4H_2O$

2.0 mmol (1.24 g) of $(morphH)_2Mo_2Cl_6(H_2O)_2$ were dissolved in 80 ml of HCl 1:1 at room temperature. The solution was filtered on to 16.0 mmol of $(pipzH_2)Cl_2$ obtained from 3.07 g piperazine·$6H_2O$ and 15 ml of HCl 1:1. The mixture was left under vacuum on ice for 24 hours. The precipitate was filtered in air, washed with ethanol and dried in air at room temperature. The average yield was 42%. Recrystallization was made from the HCl 1:1 by the addition of $(pipzH_2)Cl_2$.

The same compound was obtained by the addition of $(pipzH_2)Cl_2$ to the solution of $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ in HCl 1:1. This procedure gave better yields. *Anal.* Calcd. (Found) for $(pipzH_2)_2Mo_2Cl_8 \cdot 4H_2O$: Mo, 26.51(26.4); Cl, 39.18(39.2); H_2O, 9.96(9.9). The water content was determined from the thermogravimetric analysis.

Cell dimensions were obtained by least-squares from the 2θ values of 90 moderately high-order reflections measured on a CAD-4 (Enraf Nonius) computer-controlled diffractometer ($MoK\alpha_1$, $\lambda = 0.70926$ Å). The systematic absences (0kl: k = 2n + 1; h0l: l = 2n + 1; hk0: h = 2n) suggested the centrosymmetric space group Pbca (No. 61), which has been vindicated by the successful structure analysis. A prismatic violet-coloured crystal with approximate dimensions 0.22 × 0.20 × 0.18 mm was used for the data collection. Crystal data are given in Table I; details of data collection and data reduction are available from the Editor. The data were corrected for variations in reference reflections and the usual Lorentz-polarization effects, but not for absorption since the linear absorption coefficient $\mu = 19.00$ cm^{-1} and optimum crystal size ($t = 2/\mu$) = 1.05 mm.

The positions of Mo and 4 Cl were found in the Patterson map and a subsequent Fourier map revealed all non-hydrogen atoms. Atom parameters were refined by full-matrix least squares, minimizing $\Sigma w(|F_o| - k|F_c|)^2$, where w was chosen to keep $\Sigma w(\Delta F)^2$ uniform over the ranges of $(\sin \theta/\lambda)$ and $|F_o|$. At this stage the conventional $R = \Sigma(\Delta F)/\Sigma|F_o|$ was 0.06. A difference electron-density map located all the hydrogens of the water molecules and $(pipzH_2)^{2+}$ close to the expected positions. The positions of

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TABLE I. Crystal Data for $(pipzH_2)_2Mo_2Cl_8 \cdot 4H_2O$ at 293(1) K.

Formula	$C_8H_{32}Cl_8Mo_2N_4O_4$
Formula weight	723.87
Space group	Pbca (No. 61)
a, Å	15.154(2)
b	13.170(2)
c	12.208(2)
Volume, $Å^3$	2436.45
D_m (flotation), g cm^{-3}	1.96(2)
D_c, g cm^{-3}	1.973
Z	4
μ, cm^{-1}	19.00

TABLE II. Fractional Atomic Coordinates ($\times 10^5$ for Mo; $\times 10^4$ for Cl, O, N, C; $\times 10^3$ for H) and Equivalent or Isotropic Thermal Parameters ($\times 10^4$; $\times 10^3$ for H).

Atom	x	y	z	U_{eq} [10]	U_{iso}
Mo	51387(7)	48557(8)	58406(8)	203(5)	
Cl(1)	6607(2)	4066(2)	5813(2)	296(17)	
Cl(2)	4511(2)	3172(2)	6165(3)	289(16)	
Cl(3)	3857(2)	5474(3)	6885(3)	327(19)	
Cl(4)	5897(3)	6382(3)	6510(3)	366(21)	
O(1)	4128(9)	1214(9)	3881(10)	523(79)	
O(2)	6441(10)	5717(10)	8964(10)	673(93)	
N(1)	2448(9)	1036(10)	0562(11)	377(74)	
C(2)	2258(11)	1726(12)	1450(14)	399(96)	
C(3)	1273(10)	1871(11)	1622(11)	324(81)	
N(4)	0880(8)	2184(10)	0559(9)	332(69)	
C(5)	1054(10)	1423(12)	−0343(12)	358(87)	
C(6)	2026(11)	1313(12)	−0493(12)	362(87)	
H(1)	414(12)	078(11)	337(11)		69(31)
H(2)	386(11)	175(10)	366(13)		69(31)
H(3)	636(13)	608(12)	957(10)		69(31)
H(4)	630(12)	601(12)	833(10)		69(31)
H(11)	299(7)	087(13)	054(14)		57(17)
H(12)	227(11)	040(9)	064(13)		57(17)
H(21)	254(11)	148(12)	215(8)		57(17)
H(22)	252(10)	237(8)	136(13)		57(17)
H(31)	109(11)	116(7)	178(13)		57(17)
H(32)	107(10)	231(10)	224(10)		57(17)
H(41)	101(12)	275(9)	020(12)		57(17)
H(42)	031(7)	216(13)	068(12)		57(17)
H(51)	080(11)	169(11)	−103(9)		57(17)
H(52)	074(9)	079(9)	−010(13)		57(17)
H(61)	212(11)	078(10)	−104(11)		57(17)
H(62)	230(10)	192(9)	−077(12)		57(17)

hydrogens with two common isotropic temperature factors were included in the refinement, as well as the bond length constraints for O–H, N–H and C–H bonds. The final R and $R_w = (\Sigma w(\Delta F)^2/\Sigma w F_o^2)^{1/2}$ were 0.050 and 0.048 respectively; the weighting function was $w = 1.0/[\sigma^2(F_o) + 0.0006\ F_o^2]$. The final difference synthesis revealed 2 peaks with electron density of 0.66 and 0.32 $e.Å^{-3}$ at distances 1.06 and 0.99 Å from the Mo atom. In the final refinement cycle, the average and maximum shift/error ratios for the refined parameters were 0.150 and 1.05 respectively, using a common temperature factor for H atoms. Scattering factors for neutral Mo, Cl, O, N and C were taken from reference [5] and for H from [6]. Corrections for anomalous dispersion were also included [7].

All calculations were performed on a DEC-10 computer at RCU Ljubljana with the SHELX-76 system [8]. The DATCOR program of XRAY-80 [9] was used for data reduction. Positional parameters and selected interatomic distances and angles are given in Tables II, III. Hydrogen bonds are collected in the Table IV. A view of the crystal unit cell along the [010] direction can be seen in Fig. 1. A listing of observed and final calculated structure factors, together with anisotropic temperature parameters, is available from the Editor.

Results and Discussion

Synthesis of $(pipzH_2)_2Mo_2Cl_8 \cdot 4H_2O$ from $(morphH)_2Mo_2Cl_6(H_2O)_2$ as a starting material indicates that the substitution of chloride ions in $Mo_2Cl_8{}^{4-}$ by water molecules is a reversible reaction, which can be represented by:

$$Mo_2Cl_8{}^{4-} + 2H_2O \rightleftharpoons Mo_2Cl_6(H_2O)_2{}^{2-} + 2Cl^-$$

The addition of the specific cation to the solutions of chlorodimolybdates(II) in HCl 1:1 causes the precipitation of chlorodimolybdates(II) with either $Mo_2Cl_8{}^{4-}$ or $Mo_2Cl_6(H_2O)_2{}^{2-}$ as a basic structural unit. The solubility and the concentration of HCl are probably the only two factors which determine the type of the resulting products.

The crystal structure of $(pipzH_2)_2Mo_2Cl_8 \cdot 4H_2O$ is built from $Mo_2Cl_8{}^{4-}$, $(pipzH_2)^{2+}$ and H_2O. All dimensions of $Mo_2Cl_8{}^{4-}$ ion are similar to those found in other compounds containing this entity [4]. It is worth mentioning that the Mo–Mo distance 2.129(3) Å is the shortest one, even shorter than that found in $(NH_4)_4Mo_2Br_8$ [11], which is 2.135(2) Å. The short Mo–Mo distance is probably due to lack of axial coordination to the Mo–Mo quadruple bond. Having compared several halodimolybdates(II), it can be also noticed that the type of halogen has no dominant influence on the length of Mo–Mo bond.

The $(pipzH_2)^{2+}$ exists in a usual chair conformation. The bond lengths, valency and torsional angles are normal and close to values recently published for several compounds containing piperazinium dications [12].

Besides the electrostatic interactions between $(pipzH_2)^{2+}$ and $Mo_2Cl_8{}^{4-}$ ions, there is also a network of hydrogen bonds of the type N–H···Cl, N–H···O, O–H···Cl and O–H···O between the ions and water molecules (see Table IV). Only those distances are

TABLE III. Dimensions of the $Mo_2Cl_8^{4-}$ and $(pipzH_2)^{2+}$ Ions.

1) $Mo_2Cl_8^{4-}$ ion			
Distances, Å		Angles, Deg	
Mo–Cl(1)	2.456(3)	Mo^i–Mo–Cl(1)	104.0(1)
Mo–Cl(2)	2.445(3)	Mo^i–Mo–Cl(2)	104.0(2)
Mo–Cl(3)	2.463(4)	Mo^i–Mo–Cl(3)	106.5(1)
Mo–Cl(4)	2.455(4)	Mo^i–Mo–Cl(4)	105.5(1)
Mo–Mo^i	2.129(3)		
2) $(pipzH_2)^{2+}$ ion			
Distances, Å		Angles, Deg	
N(1)–C(2)	1.44(2)	C(6)–N(1)–C(2)	114(1)
C(2)–C(3)	1.52(2)	N(1)–C(2)–C(3)	112(1)
C(3)–N(4)	1.49(2)	C(2)–C(3)–N(4)	108(1)
N(4)–C(5)	1.51(2)	C(3)–N(4)–C(5)	112(1)
C(5)–C(6)	1.49(2)	N(4)–C(5)–C(6)	109(1)
C(6)–N(1)	1.48(2)	C(5)–C(6)–N(1)	110(1)
Torsional angles[a], Deg			
C(6)–N(1)–C(2)–C(3)	55(2)		
N(1)–C(2)–C(3)–N(4)	–54(2)		
C(2)–C(3)–N(4)–C(5)	57(2)		
C(3)–N(4)–C(5)–C(6)	–60(2)		
N(4)–C(5)–C(6)–N(1)	55(2)		
C(5)–C(6)–N(1)–C(2)	–55(2)		

^{i}Mo^i is related to Mo by the center of symmetry. [a]The torsional angle is taken as positive if the bond in front has to be rotated clockwise to eclipse the rear bond.

considered as hydrogen bonds which are smaller than the sum of the average van der Waals radii taken from ref. [13].

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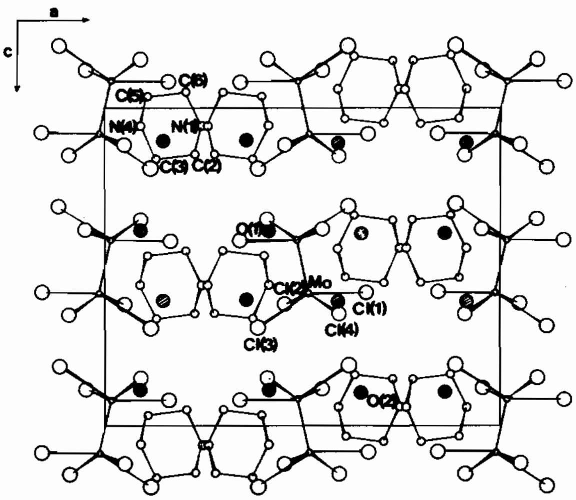

Fig. 1. A view of the unit cell of $(pipzH_2)_2Mo_2Cl_8{\cdot}4H_2O$ along [010].

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TABLE IV. Hydrogen Bonds.

D–H···A		Distances[a], Å			Angles, Deg
		D–A	D–H	H···A	D–H···A
N(1)–H(12)···O(2)	(–1/2 + x, 1/2 – y, 1 – z)	2.83	0.89	1.99	156
N(4)–H(41)···Cl(1)	(–1/2 + x, y, 1/2 – z)	3.19	0.89	2.31	168
N(4)–H(41)···Cl(2)	(–1/2 + x, y, 1/2 – z)	3.23	0.89	2.87	106
N(4)–H(42)···O(1)	(–1/2 + x, y, 1/2 – z)	3.02	0.88	2.24	147
O(1)–H(2)···Cl(4)	(1 – x, 1 – y, 1 – z)	3.20	0.86	2.50	140
O(2)–H(3)···O(1)	(1 – x, –1/2 + y, 1/2 – z)	2.84	0.89	2.40	150
O(2)–H(4)···Cl(4)	(x, y, z)	3.23	0.89	2.36	167

[a]Estimated standard deviations for distances D–A, D–H, H···A are *ca.* 0.02, 0.2 and 0.1 Å; for angles D–H···A 15°, respectively.