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Preparative and Structural Studies of Halodimolybdates(II). V. Crystal Structure of Bis(pyridinium) hexaiododiaquodimolybdate(II)

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A number of halodimolybdates(II) were prepared and characterised by X-ray diffraction during the last decade [1]. The dimolybdate(II) anion was identified in the form of $Mo_2X_8^{4-}$ (X = Cl, Br) [1, 2] or $Mo_2X_6(H_2O)_2^{2-}$ (X = Br, I) with two different structures [3–5]. The essential part of the structure is the short Mo–Mo bonding distance from 2.115(1) Å in $(picH)_2Mo_2I_6(H_2O)_2$ (picH stands for protonated 4-methylpyridine) [4] to 2.150(5) Å in $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ [1], and the eclipsed configuration of the atoms around the Mo_2 pair.

The present compound is the second example of iododimolybdates(II). X-ray structural analysis was undertaken for purposes of identification and comparison of the bond lengths between the two iododimolybdates(II).

Experimental

$(piH)_2Mo_2I_6(H_2O)_2$ was prepared from the solution of $(piH)_3Mo_2Br_7(H_2O)_2$ [5] in HI 1:1 by the addition of piHI prepared from pyridine and concentrated HI. The mixture was evaporated under vacuum until the crystals started to precipitate and left on ice for 24 hours. The precipitate was filtered in the air, washed with ether and dried under high vacuum at room temperature. Recrystallization is possible from the HI 1:1 by the addition of piHI.

The three dimensional data were collected on the single crystal sealed in the capillary. The compound has monoclinic space group $P2_1/c$ with: $a = 9.890(1)$, $b = 9.511(2)$, $c = 12.815(3)$ Å and $\beta = 97.50(2)°$, Z = 2. An Enraf-Nonius CAD-4 diffractometer with MoKα radiation was used and 1589 reflections from 2614 measured were applied to the solution and refinement of the structure. Phases were determined by direct methods (Multan) [6].

The structure was refined by the full-matrix least squares method, with anisotropic temperature factors for the heavy atoms, to R = 0.054 and $R_w = 0.061$ with the empirical weighting scheme similar to the one described elsewhere [3].

A table of observed and calculated structure factors may be obtained from the authors. Atomic and thermal parameters are listed in Tables I and II.

TABLE I. Fractional Atomic Coordinates and Isotropic Thermal Parameters ($\times 10^2$).[a]

Atom	x	y	z	U (Å^2)
Mo	0.41748(10)	0.52143(10)	0.44091(8)	–
I1	0.40168(10)	0.81023(8)	0.40835(7)	–
I2	0.20537(9)	0.53857(9)	0.56151(8)	–
I3	0.31406(10)	0.26624(8)	0.35568(7)	–
O	0.4941(10)	0.5309(10)	0.2882(8)	3.8(2)
N	−0.2188(19)	0.9409(20)	0.4145(15)	6.9(4)
C1	−0.1325(21)	0.8502(22)	0.4253(16)	6.2(4)
C2	−0.0140(26)	0.8559(27)	0.3901(20)	7.7(6)
C3	0.0146(26)	0.9696(28)	0.3348(21)	8.1(6)
C4	−0.0726(31)	1.0709(34)	0.3169(24)	9.7(7)
C5	−0.2020(26)	1.0641(29)	0.3615(20)	7.9(6)

[a] Isotropic temperature factors are of the form $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$.

TABLE II. Anistropic Temperature Parameters ($\times 100$).[a]

Atom	U11	U22	U33	U12	U13	U23
Mo	3.00(5)	1.86(4)	3.02(5)	0.05(3)	0.59(4)	−0.06(3)
I1	5.17(5)	2.13(4)	4.69(5)	0.69(3)	1.58(4)	0.75(3)
I2	3.61(5)	3.50(5)	5.58(6)	−0.15(3)	1.81(4)	0.03(4)
I3	5.12(5)	2.60(4)	3.74(5)	−1.01(3)	0.87(4)	−0.54(3)

[a] Temperature factors are of the form $[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \dots]$.

TABLE III. Dimensions of the $Mo_2I_6(H_2O)_2^{2-}$ in $(picH)_2Mo_2I_6(H_2O)_2$ (A) and $(pic)_2Mo_2I_6(H_2O)_2$ (B), in Å.

	A	B
Mo–Mo′	2.115(1)	2.116(1)
Mo–I1	2.784(1)	2.781(1)
Mo–I2	2.760(2)	2.768(2)
Mo–I3	2.797(1)	2.799(1)
Mo–O	2.188(11)	2.191(10)

Results and Discussion

Projection of the crystal structure in the xz plane and the numbering schemes are seen in Fig. 1.

Dimensions of the $Mo_2I_6(H_2O)_2^{2-}$ in the present compound agree closely with the dimensions found in $(picH)_2Mo_2I_6(H_2O)_2$ (see Table III). The angles and intraionic contacts within $Mo_2I_6(H_2O)_2^{2-}$ are also comparable. Pyridine ring is planar within 0.02 Å. Mean C–N and C–C distances are 1.34(6) and 1.37(6) Å. Interionic contacts smaller than 3.60 Å between

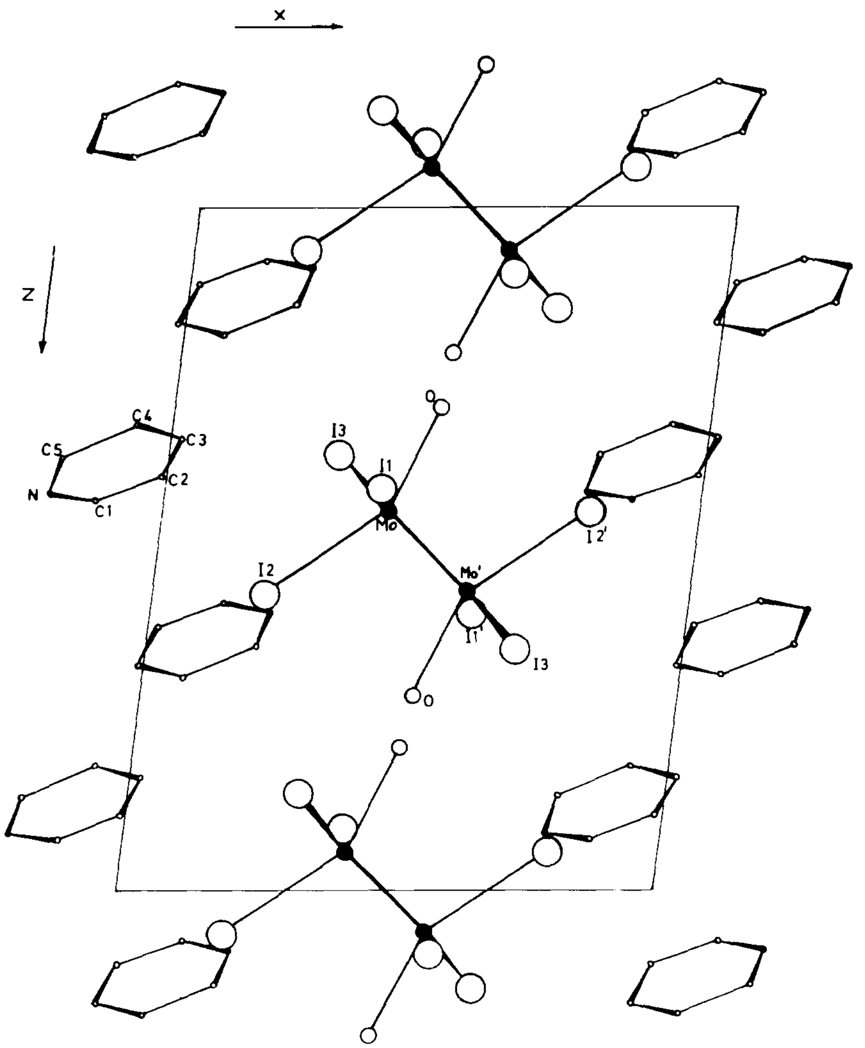

Fig. 1. Projection of the crystal structure in the xz plane and the numbering schemes.

$Mo_2I_6(H_2O)_2^{2-}$, $Mo_2I_6(H_2O)_2^{2-}$ and $C_5H_6N^+$ and $C_5H_6N^+$ ions are: O(x,y,z) to I1, I3 at (1 − x, 1/2 + y, 3/2 − z), 3.53 and 3.59 Å; to C5 at (−x, 1/2 + y, −1/2 + z), 3.27 Å; and 3.58 Å from C1(x,y,z) to C3 (−x, 1 − y, 1 − z). The first two values indicate the possibility of weak hydrogen bonding between $Mo_2I_6(H_2O)_2^{2-}$ ions.

The smallest contact not considering hydrogens between $Mo_2I_6(H_2O)_2^{2-}$ ions in $(picH)_2Mo_2I_6(H_2O)_2$ is 3.53 Å, and between cation and anion 3.30 Å. Both structures are close also in this respect.

Last but not least, equal dimensions of $Mo_2I_6(H_2O)_2^{2-}$ groups prove the correctness of both structures and the small influence of the cationic part on the bond length between quadruply bonded molybdenum atoms.

Acknowledgments

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