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Behaviour of Dimolybdenum Tetraacetate in Aqueous Solutions of Hydrogen Halides. Synthesis and Crystal Structures of $(pyH)_2[Mo_2(O_2CCH_3)_4Br_2]$ and two Modifications of $(pyH)_2[Mo_2(O_2CCH_3)_4I_2]$ (py=pyridine)*#

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The axial diadducts $(pyH)_2[Mo_2(O_2CCH_3)_4X_2]$, (py = pyridine, X = Br, I) were isolated from solutions of dimolybdenum tetraacetate in HX 1 : 1 after addition of pyridinium halide. $(pyH)_2[Mo_2(O_2CCH_3)_4Br_2]$ (*A*) crystallizes in the space group *I*4/m with $a = 0.9746(2)$ nm, $c = 1.3948(2)$ nm, $V = 1.32484$ nm^3 and $Z = 2$. Two modifications of the iodide analog were isolated. Triclinic modification (*B*) crystallizes in the space group $P\bar{1}$ with $a=1.0016(1)$ nm, $b = 1.0092(2)$ nm, $c = 1.6325(2)$ nm, $\alpha = 74.75(1)^\circ$, $\beta = 71.38(2)^\circ$, $\gamma = 61.12(2)^\circ$, $V = 1.35747$ nm^3 and $Z = 2$; tetragonal modification (*C*) in the space group *I*4/mcm with $a = 1.3086(1)$ nm, $c = 1.4712(1)$ nm, $V = 2.51933$ nm^3 and $Z = 4$. The Mo — X (X = Br, I) distances, found in anions $[Mo_2(O_2CCH_3)_4X_2]^{2-}$, 287.9(3) pm in *A*, 326.2(1) pm and 329.9(1) pm in *B*, and 320.4(1) pm in *C* are quite long, indicating only weak axial coordination. Accordingly, the Mo — Mo distances 210.2(1) pm in *A*, 210.3(1) pm in *B*, and 210.2(1) pm in *C* are only slightly longer than the Mo — Mo distance of 209.3(1) pm found in $Mo_2(O_2CCH_3)_4$.

INTRODUCTION

The compound dimolybdenum tetraacetate[1] has been known for a long time[2] 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 four groups:

1. Simple metathesis reactions, represented by eq. (1)[3]

$$Mo_2^{II}(O_2CCH_3)_4 + 8\,HX \rightarrow [Mo_2^{II}X_8]^{4-} + 4\,H^+ + 4\,CH_3CO_2H \tag{1}$$

2. Oxidative additions of hydrohalic acids to the quadruply bonded molybdenum atoms, eq. (2)[4–8]

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* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

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$$\mathrm{Mo_2^{II}\,(O_2CCH_3)_4 + 8\,HX \rightarrow [Mo_2^{III}\,X_8H]^{3-} + 3\,H^+ + 4\,CH_3CO_2H} \qquad (2)$$

3. Synthesis of chloromolybdates(III), eq. (3)[9]

$$\mathrm{Mo_2^{II}\,(O_2CCH_3)_4 + 11\,HCl + 1/2\,O_2 \rightarrow [Mo^{III}\,Cl_5\,(H_2O)]^{2-} +}$$
$$\mathrm{+ [Mo^{III}\,Cl_6]^{3-} + 5\,H^+ + 4\,CH_3CO_2H} \qquad (3)$$

4. Synthesis of oxotetrahalomolybdenum(V) compounds, eq. (4)[8,10]

$$\mathrm{Mo_2^{II}\,(O_2CCH_3)_4 + 8\,HX + 3/2\,O_2 \rightarrow 2\,[MoOX_4\,(H_2O)]^- + 2\,H^+ + 4\,CH_3CO_2H} \qquad (4)$$

In all cases the products of chemical reactions depend solely on the exact conditions such as temperature, acid concentration, and the cation used.

Although several chlorodimolybdates(II) were prepared by reaction (1) from dimolybdenum tetraacetate as the starting material (see [11] and references therein), only three bromodimolybdates(II)[11–13] and not a single iododimolybdate(II) were prepared in this way. This was the main reason for a detailed study of the behaviour of dimolybdenum tetraacetate in aqueous solutions of hydrogen halides.

EXPERIMENTAL

Dimolybdenum tetraacetate $Mo_2(O_2CCH_3)_4$ was prepared as described[1]. Mo was analysed gravimetrically as $PbMoO_4$. Potentiometric titration with $AgNO_3$ was used for determination of Br and I. Infrared spectra were measured on mineral oil mulls between CsBr plates using a Perkin-Elmer model 521 in the range 4000—300 cm^{-1}. Thermal decomposition was followed on the Mettler instrument[14] in a flow of dried Ar with a combined TG DTA head and the platinum sample holder. Approximate weight of the sample was 100 mg, heating rate 2 °C min^{-1} and the reference substance $\alpha - Al_2O_3$. Interplanar spacings were obtained with the Guinier-de-Wolf camera (Enraf Nonius) and CuKα radiation.

(pyH)$_2$[Mo$_2$(O$_2$CCH$_3$)$_4$Br$_2$] (A)

A solution of $Mo_2(O_2CCH_3)_4$ in HBr 1 : 1 was prepared by the following procedure: 36 ml of HBr 1 : were degassed on the high vacuum line. The solution was in a closed flask frozen by liquid nitrogen. 2.0 g of $Mo_2(O_2CCH_3)_4$ (4.67 mmol) ground up to a fine powder were added, and the evacuated flask slowly warmed to room temperature. The suspension was stirred and after 5 hours $Mo_2(OCCH_3)_4$ had almost completely disolved. The solution was filtered onto 50.0 mmol of pyHBr obtained from 4.0 ml pyridine and 6.0 ml of conc. HBr (48%). The reaction mixture was left under vacuum at 5 °C for 24 hours. The crystalline product was filtered in air, washed with ether and dried under vacuum at room temperature. The average yield was 50%. Anal Calcd. (Found) for $(pyH)_2[Mo_2(O_2CCH_3)_4Br_2]$: Mo, 25.65 (25.88); Br, 21.36 (21.48)%. The same compound was obtained if the solution of $Mo_2(O_2CCH_3)_4$ in HBr 1 : 1 was prepared under modified conditions. If the solution was heated up to 80 °C or stirred over a longer period (20 hours), the yields of the reaction were practically the same. When the reaction was carried out in air, the yield was significantly lower (less than 10%).

(pyH)$_2$[Mo$_2$(O$_2$CCH$_3$)$_4$I$_2$]

a) *Triclinic Modification (B)*

A solution of $Mo_2(O_2CCH_3)_4$ in HI 1 : 1 with approximate concentration 0.1 mol/l was prepared by the procedure described above. 1.5 g of $Mo_2(O_2CCH_3)_4$ (3.50 mmol) was added to 25 ml HI 1 : 1 and the suspension stirred under vacuum for 5 hours. Undissolved dimolybdenum tetraacetate was filtered off and the solution added to 35.0 mmol of pyHI, obtained from 2.8 ml pyridine and 10.0 ml HI 1 : 1. The reaction mixture was left under vacuum at 5 °C for 24 hours. The yellow crystalline product was filtered, washed with ether and dried under vacuum. The average yield was 24%. Anal. Calcd. (Found) for $(pyH)_2[Mo_2(O_2CCH_3)_4I_2]$: Mo, 22.79 (22.07); I, 30.14 (30.58)%.

b) *Tetragonal Modification (C)*

2.0 g of $Mo_2(O_2CCH_3)_4$ (4.67 mmol) were stirred under vacuum with 55.0 ml of HI 1 : 1 over a period of 5 hours. Undissolved $Mo_2(O_2CCH_3)_4$ was filtered off and the solution of approximate concentration 0.07 mol/l was added to 50.0 mmol of pyHI obtained from 4.0 ml pyridine and 15.0 ml HI 1 : 1. Because this compound precipitated very slowly, the solution was left at 5 °C for 14 days. The dark red product was filtered, washed with ether and dried under vacuum. Average yield was 10%. Because of the small amounts of obtained product elemental analysis was not performed. The identity of the compound was checked by its powder patern only. IR spectrum and thermogravimetric analysis of the compound indicated the presence of small amounts of water but this was not confirmed by later crystal structure determination. All compounds are moderately stable in a dry atmosphere. They are soluble in water, methanol, ethanol, dimethylformamide, dimethylsulfoxide, pyridine, and too some extent in acetonitrile and nitromethane. Dissolution in water, methanol and ethanol is accompanied by conversion to dimolybdenum tetraacetate.

IR spectra of the solids confirmed the presence of pyridinium cations and acetate groups.

Crystal Structure Determination and Refinement

Precise cell dimensions were obtained by least-squares from the 2Θ values of 45 moderately high-order reflections in the range $10° < \Theta < 16°$ measured on an Enraf-Nonius CAD diffractometer ($MoK\alpha_1$ radiation, $\lambda = 70.926$ pm). Space groups were determined from the inspection of preliminary oscillation, Weissenberg and precession photographs. For the systematic absences the following space groups were selected: $I4/m$ (No. 87) for compound *A*, $P\bar{1}$ (No. 2) for compound *B* and $I4/mcm$ (No. 140) for compound *C*. Several attempts were also made in space groups with lower symmetry, but only the above proposed space groups gave a successful refinement.

Data were collected on a computer controlled CAD-4 diffractometer with $MoK\alpha$ radiation equipped with a graphite monochromator. Reflections were prescanned and then scanned in the $\omega - 2\Theta$ mode (moving crystal-moving counter) at different scan rates in order to obtain the count of 5000 within a specified maximum scan time. Details of the crystal data, data collection and reduction are given in Table I. The data were corrected in the usual way for changes in reference reflections and Lorentz-polarization effects. In the case of compounds *A* and *C* an exact absorption correction was also performed.

The positions of Mo atoms in *A* and *C* were deduced from the space group symmetry considerations, since the number of formula units in the crystal cell (Z) requires Mo_2 pairs to be located at a special position. Subsequent electron-density mapping revealed the positions of the remaining heavy atoms and atoms of acetate groups. The Patterson vector map revealed the positions of Mo and I atoms in compound *B*, and the electron-density map gave the complete structure. It was not possible to locate the atoms of pyridinium cations in compounds *A* and *C*. However, rings of electron density were observed around the positions 1/2 0 1/4 in *A* and around 0 0 0.1175 in *C*, which suggested a rotational and/or positional disorder of pyridinium cations (Figure 1). No such disorder was observed in compound *B*. The disorder was taken into account by including two regular six-membered rings, the first being rotated by 30° around the direction perpendicular to the ring plane with respect to the second one. The population factors for atoms were selected according to the stoichiometry of the compounds. (Population parameters for C(11), C(12), C(13) in *A* are 0.500, whereas for C(11), C(12), C(13) in *B* they are 0.750, 0.375 and 0.375, respectively). All the atoms of pyridinium cations were taken as carbons with fixed isotropic temperature factors in A, whereas in *B* and *C* they were allowed to move anisotropically. The structures were refined by full-matrix least-squares, minimizing the function $\Sigma w (|F_o| - k|F_c|^2)$, where the weighting function w was chosen to

TABLE I

Crystal and Intensity-measurement Data Summary

	COMPOUND		
	A	*B*	*C*
Molecular formula	$C_{18}H_{24}N_2O_8Mo_2Br_2$	$C_{18}H_{24}N_2O_8Mo_2I_2$	$C_{18}H_{24}N_2O_8Mo_2I_2$
Molecular weight	748.102	842.084	842.084
Crystal system	Tetragonal	Triclinic	Tetragonal
Space group	$I4/m$ (No. 87)	$P\bar{1}$ (No. 2)	$I4/mcm$ (No. 140)
Unit-cell parameters			
a (nm)	0.9746(2)	1.0016(1)	1.3086(1)
b (nm)	0.9746(2)	1.0092(1)	1.3086(1)
c (nm)	1.3948(2)	1.6325(2)	1.4712(1)
α (°)	90	74.75(1)	90
β (°)	90	71.38(2)	90
γ (°)	90	61.12(2)	90
Volume (nm^3)	1.32484	1.35747	2.51933
Z	2	2	4
D_x ($Mg \cdot m^{-3}$)	1.875	2.060	2.220
D_m ($Mg \cdot m^{-3}$) (flotation)	1.88(2)	2.04(2)	2.21(2)
Shape of crystal	Octahedral	Irregular prism	Prism
Size of crystal (mm)	$0.27 \times 0.27 \times 0.20$	$0.23 \times 0.20 \times 0.16$	$0.24 \times 0.295 \times 0.05$
$2\,\Theta$ scan width (°)	$0.7 + 0.3 \tan \Theta$	$0.8 + 0.2 \tan \Theta$	$0.7 + 0.2 \tan \Theta$
Scan rate (° min^{-1}):			
minimum	1.7	1.7	1.7
maximum	20.1	20.1	20.1
Background	1/4 of the scan time at each of the scan limits		
$2\,\Theta_{max}$ (°)	56	54	56
Maximum scan time (s)	40	45	40
Aperture (mm)	$2.4 + 0.9 \tan \Theta$	$2.5 + 0.9 \tan \Theta$	$2.4 + 0.9 \tan \Theta$
Reference reflections	$0\,2\,6;\ 1\,1\,5;\ \bar{2}\,3\,3$	$\bar{3}\,0\,\bar{3};\ \bar{2}\,\bar{2}\,\bar{4};\ 2\,\bar{1}\,\bar{2}$	$2\,\bar{2}\,6;\ 6\,0\,2;\ 4\,\bar{3}\,5$
Intensity descrease (%)	—	2.0	4.2
Measured reflections	$6369(\pm h, \pm k, \pm l)$	$12072\,(\pm h, \pm k, \pm l)$	$2539(+h, \pm k, +l)$
Average reflections	836	5665	843
Mean discrepancy on I (%)	2.9	4.2	5.2
Observed reflections	679	2888	560
Unobserved reflection	$157, I < 3\sigma(I)$	$2777, I < 5\sigma(I)$	$283, I < 3\sigma(I)$
$\sigma(I)$ based on		counting statistics	
μ (cm^{-1})	41.77	31.85	34.32
Absorption correction	done	—	done

keep $\Sigma w\,(\Delta F)^2$ uniform over the ranges of $(\sin \Theta/\lambda)$ and $|F_o|$. The function w in structures A and C was empirical and defined as

$$w = w_F \cdot w_S$$

where

$$w_F\,(|F_o| < A) = (|F_o|/A)^C$$

$$w_F\,(|F_o| > B) = (B/|F_o|)^D$$

$$w_F\,(A < |F_o| < B) = 1.0$$

and

$$w_S\,(\sin \Theta < E) = (\sin \Theta/E)^H$$

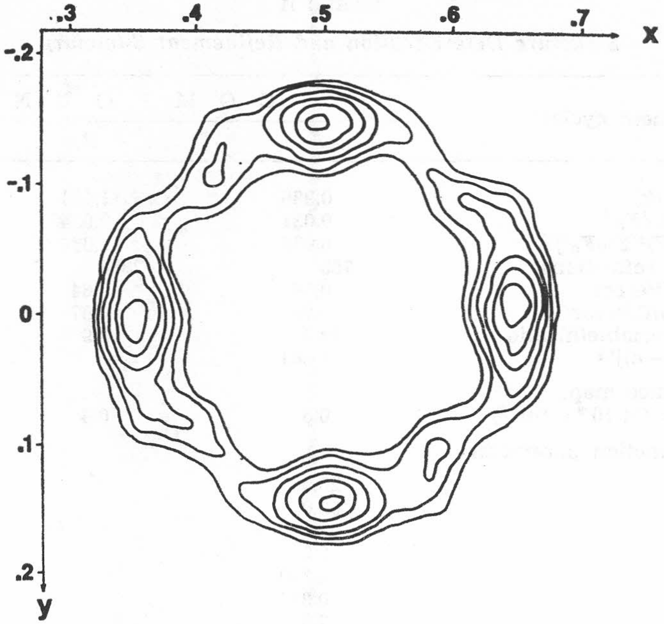

Figure 1. The section of the electron density map at $z = 0.2545$ for compound $(pyH)_2[Mo_2(O_2CCH_3)_4Br_2]$ (*A*). The largest value of electron density is 2.5×10^2 e·nm^{-3}. Lines of equal electron density are separated by 0.2×10^2 e · nm^{-3}.

$$w_S\,(\sin\Theta > G) = (G/\sin\Theta)^J$$

$$w_S\,(E < \sin\Theta < G) = 1.0$$

whereas in structure *B* the $w = [\sigma^2(F_o) + 0.003F_o^2]^{-1}$.

Details of refinement parameters with final R values are given in Table II. Scattering factors for H atoms were taken from reference[15] and for the others from reference[16]. Dispersion-correction factors were those from reference[17]. All calculations were carried out on the CDC CYBER 172 computer at RRC Ljubljana with X Ray 72[18] (for *A* and *C*) and SHELX 76[19] (for *B*) systems of computer programs.

Lists of structure factors F_O/F_C and anisotropic thermal parameters are available on request from the authors. Final fractional coordinates with U_{eq}[20] or U_{iso} are given in Table III.

RESULTS AND DISCUSSION

The dimolybdenum tetracarboxylates did not appear to have any great tendency to coordinate axial ligands. Only recently the synthesis and crystal structures of comopunds of the type $(N—n—Bu_4)_2\,[Mo_2(O_2CCF_3)_4X_2]$, (X = Br, I) were reported[21], but neither the acetate nor the benzoate compounds exhibit axial coordination. However, there are weak intermolecular interactions between the coordinated oxygen atoms and the axial positions of an adjacent molecule[22].

During systematic work on the behaviour of dimolybdenum tetraacetate in dilute aqueous solutions of hydrogen halides we succeeded in isolating compounds of general formula $(pyH)_2[Mo_2(O_2CCH_3)_4X_2]$, (X = Br, I). We believe

TABLE II

Structure Determination and Refinement Summary

Final refinement cycle:	COMPOUND *A*	COMPOUND *B*	COMPOUND *C*
Scale factor (k)	0.986	1.434	1.136
$R = \Sigma \mid \Delta F \mid / \Sigma \mid F_o \mid$	0.031	0.034	0.028
$R_w = [\Sigma w (\Delta F)^2 / \Sigma w F_o^2]^{1/2}$	0.036	0.034	0.032
Contributing reflections	705	2888	655
Average shift/error	0.16	0.64	0.044
Maximum shift/error	0.60	6.87	0.246
Data(m)-to-variable(n)ratio	24.3	9.9	13.4
$[\Sigma w (\Delta F)^2/(m-n)]^{1/2}$	1.061	—	1.139
Final difference map:			
Maximum $\Delta\varrho$ ($\times 10^{-3}$ e. nm^{-3})	0.5	0.4	0.7
Weighting-function parameter[a]			
A	20.0		70.0
B	62.0		100.0
C	1.0		1.0
D	2.5		2.0
E	0.320		0.36
G	0.321		0.50
H	2.5		2.0
J	1.0		1.0
K	0.01		0.01

[a] The weighting scheme w for compound *B* is $w = [\sigma^2 (F_o) + 0.003\, F_o^2]^{-1}$

that there are three main conditions which are characteristic for isolation of this type of compound: a) the concentration of HX, b) the concentration of anionic species in solution, and c) the choice of the appropriate cation. While in concentrated solutions of HX metathesis reactions (eq. (1)) and at higher temperatures oxidative additions of hydrohalic acids (eq. (2)) are preferable, in dilute solutions the rate of these reactions is much slower. Isolation of compounds containing the dimolybdenum tetraacetate molecule with axially coordinated halogen atoms from such solutions, prepared under mild conditions, indicates the possibility that axial coordination of halogen atoms is the first step in the mechanisms of all other reactions. It must be mentioned that compounds with different stoichiometries can be isolated from the same solutions of $Mo_2(O_2CCH_3)_4$ in dilute HX after addition of other organic cations or when the concentration of anionic species in solution is increased[23]. Evidently several different anionic species are present in solution under the same conditions. The isolation of a solid compound from such solution therefore depends mainly on its solubilitiy. Further investigations are in progress and the results will be reported.

The crystal structures of all isolated compounds of the type $(pyH)_2[Mo_2(O_2CCH_3)_4X_2]$, (X = Br, I) are built of $[Mo_2(O_2CCH_3)_4X_2]^{2-}$ anions and pyridinium cations. In the case of triclinic $(pyH)_2[Mo_2(O_2CCH_3)_4I_2]$ (*B*) there are two crystallographically independent forms of that anion (*I* and *II*). The packing of these units in the unit cells is shown in projections in Figure 2, 3 and 4 for compounds *A*, *B* and *C* respectively.

TABLE III

Fractional Atomic Coordinates ($\times 10^5$ for Mo, Br, I; $\times 10^4$ for O, C), Equivalent[20] or Isotropic Thermal Parameters (pm^2) with Estimated Standard Deviations in Parentheses

Atom	x	Y	z	U_{eq}/U_{iso}
		$(pyH)_2\,[Mo(O_2CCH_3)_4Br_2]$ (A)		
Mo(1)	0	0	7532(4)	383(3)
Br(1)	0	0	29290(5)	559(4)
O(1)	1581(4)	1484(4)	796(2)	646(17)
C(1)	2040(9)	1883(9)	0	782(45)
C(2)	3225(24)	2888(24)	0	2015(157)
C(11)	3594	0	2500	1076
C(12)	3801	713	2500	1076
C(13)	4287	1199	2500	1076
		Triclinic $(pyH)_2\,[Mo_2(O_2CCH_3)_4I_2]$ (B)		
Mo(1)	92004(9)	55969(8)	—4058(5)	535(4)
I(1)	68084(8)	73926(8)	—17164(4)	849(4)
O(1)	7740(7)	7281(7)	436(4)	618(33)
O(2)	9433(8)	6037(7)	1293(4)	677(33)
C(1)	8191(12)	7110(11)	1121(6)	690(51)
C(2)	7167(16)	8291(14)	1748(8)	1095(77)
O(3)	7918(7)	4306(7)	244(4)	732(33)
O(4)	9636(7)	3016(7)	1091(4)	677(33)
C(3)	8436(11)	3257(11)	844(6)	671(48)
C(4)	7659(15)	2212(15)	1268(8)	1248(74)
Mo(2)	4296(8)	38566(8)	52917(5)	474(3)
I(2)	—17726(8)	96862(7)	37246(4)	691(3)
O(5)	2658(6)	3319(6)	4438(4)	563(30)
O(6)	1768(7)	5732(6)	3825(4)	599(30)
C(5)	2866(11)	4394(10)	3881(6)	627(45)
C(6)	4439(11)	4067(12)	3272(7)	826(55)
O(7)	—245(7)	3225(6)	4404(4)	590(30)
O(8)	—1186(6)	5657(6)	3799(4)	552(29)
C(7)	—922(9)	4269(9)	3837(6)	558(42)
C(8)	—1406(13)	3859(12)	3200(6)	943(58)
C(11)	7072(16)	—433(13)	6145(8)	1023(72)
C(12)	7927(17)	197(16)	6062(9)	1197(88)
C(13)	7398(18)	1701(18)	5870(10)	1780(108)
C(14)	5899(22)	2573(11)	5726(10)	1544(112)
C(15)	4985(12)	1791(19)	5868(9)	1253(88)
C(16)	5666(17)	300(16)	6066(8)	1426(82)
C(21)	7745(29)	3146(22)	8447(13)	2435(141)
C(22)	6507(25)	3372(19)	9012(11)	1612(120)
C(23)	5956(15)	2266(24)	9332(9)	1586(106)
C(24)	6878(26)	921(18)	8987(12)	2262(128)
C(25)	8164(24)	803(21)	8392(12)	1472(138)
C(26)	8536(17)	1882(27)	8119(10)	1478(101)
		Tetragonal $(pyH)_2\,[Mo_2(O_2CCH_3)_4I_2]$ (C)		
Mo(1)	44320(3)	5680	0	232(3)
I(1)	27010(3)	22990	0	431(3)
O(1)	1394(2)	4805(2)	1047(2)	312(13)
C(1)	1011(3)	3989	1363(4)	297(17)
C(2)	1520(3)	3480	2164(4)	425(22)
C(11)	1055	0	1175	1607(211)
C(12)	528	914	1175	1571(365)
C(13)	914	528	1175	1138(244)

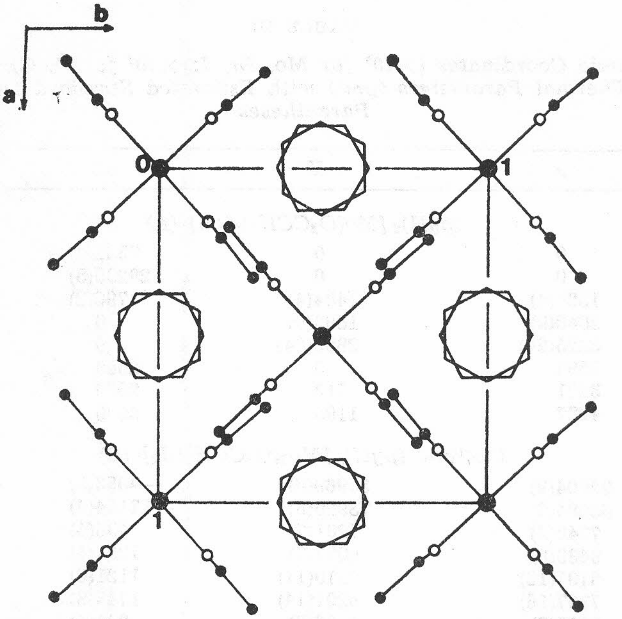

Figure 2. Projection of the structure of $(pyH)_2[Mo_2(O_2CCH_3)_4Br_2]$ (*A*) along [0 0 1] (Larger black circles Mo, smaller black circles C, smaller open circles O; bromine atoms, located along [0 0 1], are omitted for clarity).

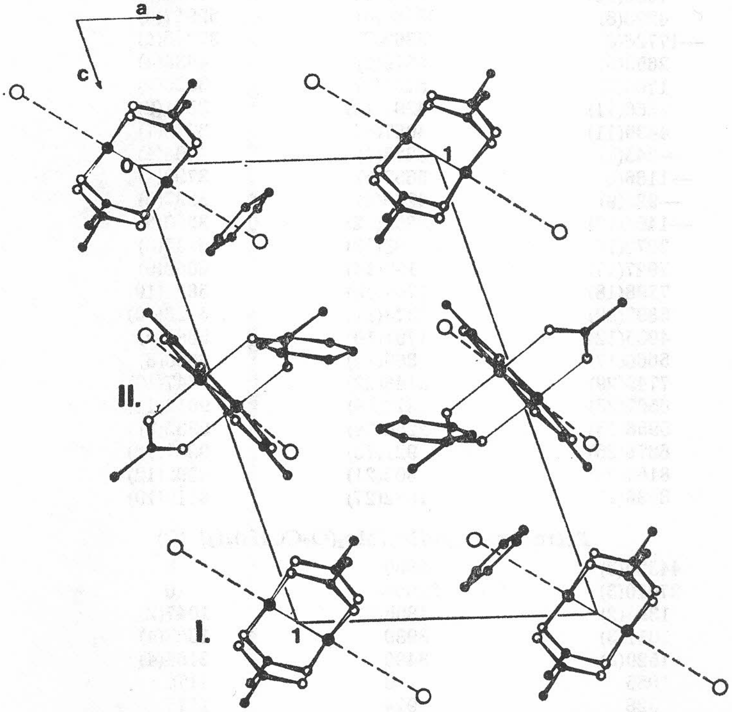

Figure 3. Projection of the structure of the triclinic modification of $(pyH)_2[Mo_2 \cdot (O_2CCH_3)_4I_2]$ (*B*) along [0 1 0]). Two crystallographically independent anions are denoted by I and II. (The atoms are marked in the same way as on Figure 2. I atoms are denoted by larger open circles).

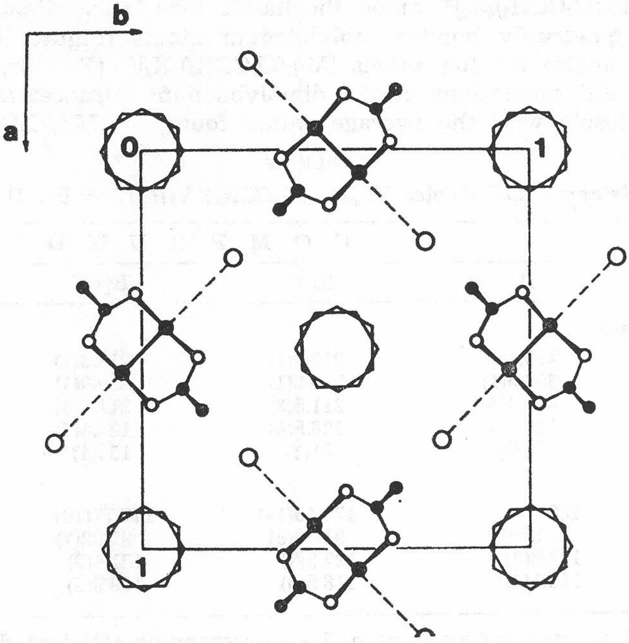

Figure 4. Projection of the structure of the tetragonal modification of $(pyH)_2[Mo_2 \cdot \cdot (O_2CCH_3)_4I_2]$ (*C*) along [0 0 1]. For clarity only half of the unit cell content is presented. (The atoms are marked in the same way as on Figure 3).

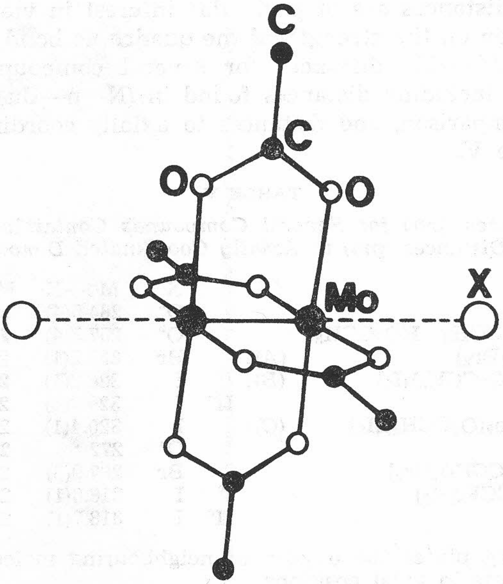

Figure 5. View of the $[Mo_2(O_2CCH_3)_4X_2]^{2-}$, (X = Br, I) anion. The halide ions X^- are axially coordinated to the quadruply bonded molybdenum atoms.

In the $[Mo_2(O_2CCH_3)_4X_2]^{2-}$ anion the halide ions is coordinated axially to each of the quadruply bonded molybdenum atoms (Figure 5). The bond distances and angles for the anions $[Mo_2(O_2CCH_3)_4X_2]^{2-}$ (X = Br, I) are given in Table IV). All dimensions of the dimolybdenum tetraacetate part of the anion agree closely with the average values found for $Mo_2(O_2CCH_3)_4$.[22]

TABLE IV

Bond Distances and Angles in $[Mo_2(O_2CCH_3)_4X_2]^{2-}$ (X = Br, I) Anions

	COMPOUND			
	A	*BI*^{a,b}	*BII*^{a,b}	*C*
a) *Distances (pm)*				
Mo — Mo^i	210.1(1)	210.3(1)	210.3(1)	210.2(1)
Mo — X	303.5(1)	326.2(1)	329.9(1)	320.4(1)
Mo — O	211.4(4)	211.8(3)	211.6(3)	213.0(3)
Cl — O	126.0(4)	126.5(6)	127.4(5)	126.8(4)
Cl — C2	151(2)	151(1)	150(1)	151(1)
b) *Angles (°)*				
Mo — Mo^i — X	180	178.15(14)	177.77(10)	180
Mo — Mo^i — O	91.35(6)	91.69(9)	91.62(7)	91.59(7)
O — Cl — O	123.8(8)	122.9(7)	121.4(9)	122.1(4)
O — Cl — C2	118.1(4)	118.5(5)	119.3(4)	118.9(3)

[a] The weighted average values $\bar{x}$ with the corresponding standard deviations $\sigma(\bar{x})$ were calculated as $\bar{x} = \sum_i x_i/\sigma_i^2) / (\sum \sigma_i^{-2})$ and $\sigma(\bar{x}) = (1/\sum_i \sigma_i^{-2})^{1/2}$

[b] Two crystallographically independent anions are present in compound *B*

[i] Mo^i is related to Mo by the center of symmetry

The Mo—Mo distances are of particular interest in view of the influence of axial coordination on the strength of the quadruple bond between molybdenum atoms. The Mo—Mo distances for several compounds containing the $Mo_2(O_2CCH_3)_4$ unit, including distances found in $(N—n—Bu_4)_2[Mo_2(O_2CCF_3)_4X_2]$, (X = Br, I) for comparison, and distances to axially coordinated donor atoms are given in Table V.

TABLE V

The Mo—Mo Distances (pm) for Several Compounds Containing the $Mo_2(O_2CCR_3)_4$ Unit and Distances (pm) to Axially Coordinated Donor Atoms X

Compound		X	Mo—X	Mo—Mo	Ref.
$Mo_2(O_2CCH_3)_4$		O^a	264.5(4)	209.3(1)	22
$Mo_2(O_2CCH_3)_4 \cdot NaO_2CCH_3 \cdot HO_2CCH_3$		O^b	257.5(4)	209.3(1)	27
$(pyH)_2[Mo_2(O_2CCH_3)_4Br_2]$	(*A*):	Br	303.5(1)	210.1(1)	This work
triclinic $(pyH)_2[Mo_2(O_2CCH_3)_4I_2]$	(*B*): I^c	I	326.2(1)	210.3(1)	This work
	II^c	I	329.9(1)	210.3(1)	This work
tetragonal $(pyH)_2[Mo_2(O_2CCH_3)_4I_2]$	(*C*):	I	320.4(1)	210.2(1)	This work
$Mo_2(O_2CCF_3)_4$		O^a	272	209.0(4)	26
$(N—n—Bu_4)_2[Mo_2(O_2CCF_3)_4Br_2]$		Br	287.9(3)	213.4(2)	21
$(N—n—Bu_4)_2[Mo_2(OCCF_3)_4I_2]$	I^c	I	318.0(1)	214.0(2)	21
	II^c	I	318.7(1)	213.6(2)	21

[a] The crystal packing places the oxygen of neighbouring molecules of dimolybdenum tetracarboxylate in axial positions

[b] **One of the oxygen atoms in acetic acid/acetate dimers is axially coordinated to each of the molybdenum atoms**

[c] Two crystallographycally independent molecules are present in this compound

The insensitivity of the molybdenum-to-molybdenum quadruple bond in dimolybdenum tetracarboxylates to axial coordination is well documented[24]. This effect could be correlated with a shielding effect due to the electron-rich region close to the Mo atom, which is visible along the Mo—Mo axis on the external side of each Mo atom in the computed density map of $Mo_2(O_2CCH_3)_4$,[25] so protecting the metal from the approach of a ligand in an axial direction. Therefore only weak interactions with ligands in axial positions are expected and accordingly only small changes in the Mo—Mo distance could be possible. Inspection of distances cited in Table V confirmed this expectation.

The Mo—X (X = Br, I) distances, found in anions $[Mo_2(O_2CCR_3)_4X_2]^{2-}$, (R = H, F; X = Br, I), are quite long, indicating only weak axial coordination. The Mo—Br distances of 287.9(3) pm (R = F) and 303.5(1) pm (R = H) are significantly longer than the 260.4(1) pm distance in $[Mo_2Br_8]^{4-}$[28] or the 257(2) pm found $[Mo_2Br_6(H_2O)_2]^{2-}$[11,29-31]. Similarly, the Mo—I bonds at 318.0(1)), 318.7(1) pm, (R = F) and 326.2(1), 329.9(1), 320.4(1) pm, (R = H) are much longer than 278 pm found in $[Mo_2I_6(H_2O)_2^{2-}$[32,33]. These distances also indicate weaker interactions in tetraacetato compounds in comparison to their tetrafluoroacetato analogs. Accordingly, the changes in the Mo—Mo distances in tetrafluoroacetate diadducts are greater than in tetraacetate diadducts. Although these changes are rather small, they are meaningful with respect to their standard deviations. The Mo—Mo distance of 209.3(1) pm in $Mo_2(O_2CCH_3)_4$[22] is approximately 1 pm shorter than the Mo—Mo distance found in $[Mo_2(O_2CCH_3)_4X_2)^{2-}$, (X = Br, I) anions, while the corresponding difference in the case of tetrafluoroacetate analogs is 4—5 pm. On this basis it could also be concluded that the interaction of oxygen atoms of neighbouring molecules in axial positions, observed in $Mo_2(O_2CCH_3)_4$ and $Mo_2(O_2CCF_3)_4$, is weaker than the corresponding interaction with halide ions in their diadduct anions. The steric factor may be the main reason for this conclusion.

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POVZETEK

Obnašanje dimolibdenovega tetraacetata v vodnih raztopinah vodikovih halogenidov. Sinteze in kristalne strukture $(pyH)_2[Mo_2(O_2CCH_3)_4Br_2]$ in dveh modifikacij $(pyH)_2[Mo_2(O_2CCH_3)_4I_2]$ (py = piridin)

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Aksialne diadukte $(pyH_2)[Mo_2(O_2CCH_3)_4X_2]$, (py = piridin, X = Br, I) smo izolirali iz raztopin dimolibdenovega tetraacetata v HX 1 : 1 po dodatku piridinijevega halogenida. $(pyH)_2[Mo_2(O_2CCH_3)_4Br_2]$ (*A*) kristalizira v prostorski skupini *I*/4m z $a = 0.9746(2)$ nm, $c = 1.3948(2)$ nm, $V = 1.32484$ nm^3 in $Z = 2$. Izolirali smo dve modifikaciji jodidnega analoga. Triklinska modifikacija (*B*) kristalizira v prostorski skupini $P\bar{1}$ z $a = 1.0016(1)$ nm, $b = 1.0092(2)$ nm, $c = 1.6325(3)$ nm, $\alpha = 74.75(1)^\circ$, $\beta = 71{,}38(2)^\circ$, $\gamma = 61.12(2)^\circ$, $V = 1.35747$ nm^3 in $Z = 2$; tetragonalna modifikacija (*C*) v prostorski skupini *I*/4 mcm z $a = 1.3086(1)$ nm, $c = 1.4712(1)$ nm, $V = 2.51933$ nm^3 in $Z = 4$. Mo—X (X = Br, I) razdalje v anionih $[Mo_2(O_2CCH_3)_4X_2]^{2-}$, 287.9(3) pm v *A*, 326.2(1) pm in 329.9(1) pm v *B* in 320.4(1) pm v *C* so zelo dolge, kar kaže na šibko aksialno koordinacijo. V skladu s tem so razdalje Mo—Mo 210.1(1) pm v *A*, 210.3(1) pm v *B* in 210.2(1) pm v *C* le malo daljše od razdalje 209.3(1) pm v $Mo_2(O_2CCH_3)_4$.