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## Structural Study of Two Crystal Forms of $[\text{Mo}_3\text{O}(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)(\text{CF}_3\text{SO}_3\text{H})_2 \cdot 5\text{H}_2\text{O}$

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The title cation has been prepared in aqueous solution by a previously described method, isolated on a cation-exchange resin, and eluted with 0.2 M trifluoromethanesulfonic acid. In separate experiments done in different laboratories by different workers crystals with the same composition,  $[\text{Mo}_3\text{O}(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)(\text{CF}_3\text{SO}_3\text{H})_2 \cdot 5\text{H}_2\text{O}$ , were obtained, but when one crystal from each batch was examined, they had slightly different cell dimensions. Both structures, **1** and **2**, were refined as fully as possible and shown to contain essentially identical trinuclear cations, with dimensions identical with those previously found in a  $\text{BF}_4^-$  salt. For the two crystals the dimensions of the orthorhombic unit cell (space group  $Pmn2_1$  and  $Z = 2$ ) were as follows (where the values of **1** and **2** are given in that order for each dimension):  $a = 13.699$  (2), 13.510 (4) Å;  $b = 8.092$  (3), 8.059 (4) Å;  $c = 20.010$  (12), 19.667 (6) Å;  $V = 2218$  (2), 2141 (2) Å<sup>3</sup>. There are different arrangements of the water molecules and trifluoromethanesulfonate ions in the two forms, which entail different hydrogen-bonding schemes.

### Introduction

A procedure for preparing the bicapped trimolybdenum cluster cation  $[\text{Mo}_3\text{O}(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+$  has previously been reported,<sup>2,3</sup> and the cation has been structurally characterized in the form of its nonhydrated  $\text{BF}_4^-$  salt. The cation can be obtained in a number of other compounds depending, primarily, on the acid used to elute the cation-exchange column. In this paper we report on crystals obtained when 0.2 M  $\text{CF}_3\text{SO}_3\text{H}$  was used to elute the trinuclear cation. As will be seen, this work has raised some nonroutine problems, which, unfortunately, are all too typical of this field. In our previously published work<sup>2-6</sup> we have, naturally, described structures that have been satisfactorily completed and our success in these cases has been due to the fact that no unduly puzzling problems have arisen. There are, however, a number of other compounds of the bicapped trimetal cations that have entailed crystallographic difficulties. Usually, in these cases, the cation itself has behaved satisfactorily, but the anions and (if present) water of hydration have presented problems.

The work reported here exemplifies some of the difficulties we have encountered with the arrangements of anions and water molecules. In this case a reasonably satisfactory reconciliation of the apparent inconsistencies has been achieved. An additional problem here is that in different preparations crystals that are very similar but evidently not identical have been obtained. Chemically, the differences are minor to the point of being insignificant, but in practical crystallographic terms they have been troublesome and time consuming to work out.

### Experimental Section

The reaction of  $\text{Mo}(\text{CO})_6$  with acetic acid, acetic anhydride, and triethylamine was carried out as previously described,<sup>3</sup> and the workup was also conducted in the same way until the red trinuclear cation had been collected on a column of 100-200 mesh Dowex 50w-X2 cation-exchange resin. A 0.2 M solution of trifluoromethanesulfonic (triflic) acid,  $\text{CF}_3\text{SO}_3\text{H}$ , was then used to elute the column. The red eluate was left to evaporate in a flat glass dish in air. This same procedure was carried out both in Haifa and in College Station, TX,

Table I. Crystallographic Parameters

| parameter                                   | cryst 1         | cryst 2          |
|---|-----------------|------------------|
| space group                                 | $Pmn2_1$        | $Pmn2_1$         |
| $a$ , Å                                     | 13.699 (2)      | 13.510 (4)       |
| $b$ , Å                                     | 8.092 (3)       | 8.059 (4)        |
| $c$ , Å                                     | 20.010 (12)     | 19.667 (6)       |
| $V$ , Å <sup>3</sup>                        | 2218 (2)        | 2141 (2)         |
| $d_{\text{calcd}}$ , g/cm <sup>3</sup>      | 1.911           | 1.980            |
| $Z$   | 2               | 2                |
| fw  | 1276.5          | 1276.5           |
| cryst size, mm                              | 0.5 × 0.4 × 0.3 | 0.4 × 0.2 × 0.15 |
| $\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup> | 10.74           | 11.13            |
| range $2\theta$ , deg                       | 1-50            | 1-50             |
| no. of unique data                          | 2577            | 3244             |
| no. of data, $F_o^2 > 3\sigma(F_o^2)$       | 1941            | 2286             |
| no. of variables                            | 246             | 278              |
| $R_1^a$                                     | 0.056           | 0.049            |
| $R_2^b$                                     | 0.072           | 0.061            |
| goodness of fit                             | 2.402           | 1.579            |
| largest shift <sup>c</sup>                  | 0.59            | 0.29             |

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $R_2 = [\sum w(|F_o| - |F_c|)^2] / \sum w|F_o|^2$  with  $w = \sigma(F_o)^2$ . <sup>c</sup> Shift expressed as fraction of esd.

without any significant difference that we are aware of.

The Texas batch of crystals was observed to contain both thin, seemingly hexagonal plates and prisms with well-defined faces. The thin plates, though birefringent, gave no detectable diffraction of X-rays. A prismatic crystal (**1**) was selected and used for all further work.

In Haifa a prismatic crystal (**2**) was also selected and used. Whether crystals of any other habit were also present in this batch is uncertain; none were noticed. A complete structure determination was carried out on crystal **2** in Haifa. However, when we recognized that the Texas crystal and the Haifa crystal were not identical, the Haifa crystal (**2**) was sent to Texas and the structure entirely re-determined using exactly the same equipment and programs as had been used for crystal **1**. The new work on crystal **2** gave results in essentially exact agreement with those obtained in Haifa, but refinement was carried a little further. We report here the results for both crystals using the data obtained in Texas.

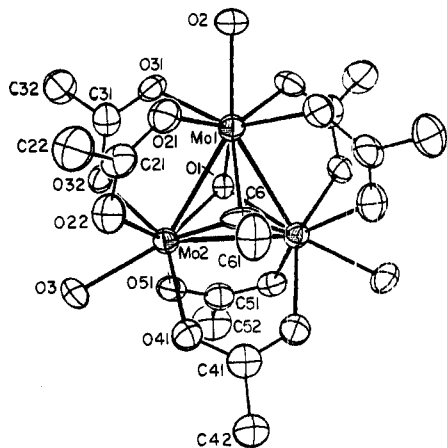
**X-ray Data Collection.** Crystal **1** was mounted inside a glass capillary tube above a column of the solution from which it had grown. Crystal **2** was sealed with epoxy cement to the end of a glass fiber. In all other respects the two crystals were handled in the same way and the data were all collected on an Enraf-Nonius CAD-4 automated diffractometer using Mo  $K\alpha$  radiation ( $\lambda_a = 0.71073$  Å) with a graphite-crystal monochromator in the incident beam. Other parameters pertaining to the data collection, crystal dimensions, and refinement procedure are summarized in Table I.

Unit cell dimensions were determined by accurately centering 25 reflections in the  $2\theta$  range 17-36° (**1**) or 20-30° (**2**). Intensity data were measured by  $\omega$ - $2\theta$  scans. For crystal **1** scan widths were cal-

- (1) (a) Hebrew University. (b) Texas A&M University. (c) The Technion-Israel Institute of Technology.
- (2) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1981**, *103*, 243.
- (3) Bino, A.; Cotton, F. A.; Dori, Z.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 5779.
- (4) Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kaftory, M.; Kolthammer, B. W. S.; Kapon, M.; Reisner, G. *Inorg. Chem.* **1981**, *20*, 4083.
- (5) Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kaftory, M.; Reisner, G. *Inorg. Chem.* **1982**, *21*, 1912.
- (6) Ardon, M.; Cotton, F. A.; Dori, Z.; Fang, A.; Kapon, M.; Reisner, G.; Shaia, M. *J. Am. Chem. Soc.*, in press.

**Table II.** Positional Parameters and Their Estimated Standard Deviations for Structure 1 of[Mo<sub>3</sub>O(CCH<sub>3</sub>)(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)(CF<sub>3</sub>SO<sub>3</sub>H)<sub>2</sub>·5H<sub>2</sub>O

| atom   | x            | y             | z            |
|--------|--------------|---------------|--------------|
| Mo(1)  | 0.00000 (0)  | -0.11992 (15) | 0.00000 (0)  |
| Mo(2)  | -0.10037 (6) | 0.02306 (9)   | -0.10413 (8) |
| S(1)   | -0.2286 (3)  | -0.3790 (6)   | 0.1946 (2)   |
| S(11)  | 0.0000       | -0.1277       | 0.3999       |
| F(1)   | -0.3693 (12) | -0.471 (2)    | 0.1181 (11)  |
| F(2)   | -0.4042 (9)  | -0.270 (2)    | 0.1796 (11)  |
| F(3)   | -0.3089 (11) | -0.238 (2)    | 0.0944 (8)   |
| O(1)   | 0.0000 (0)   | -0.1570 (10)  | -0.0985 (5)  |
| O(2)   | 0.0000 (0)   | -0.2507 (15)  | 0.0968 (6)   |
| O(3)   | -0.2396 (6)  | 0.0869 (11)   | -0.1494 (4)  |
| O(21)  | -0.1115 (6)  | -0.0077 (10)  | 0.0597 (5)   |
| O(22)  | -0.1934 (6)  | 0.1085 (10)   | -0.0258 (4)  |
| O(31)  | -0.1073 (5)  | -0.3091 (10)  | -0.0087 (4)  |
| O(32)  | -0.1895 (5)  | -0.1947 (8)   | -0.0943 (4)  |
| O(41)  | -0.0812 (6)  | 0.2638 (10)   | -0.1433 (4)  |
| O(51)  | -0.0813 (6)  | -0.0403 (9)   | -0.2057 (4)  |
| O(71)  | -0.1545 (8)  | -0.4342 (16)  | 0.1478 (7)   |
| O(72)  | -0.2620 (13) | -0.5047 (23)  | 0.2378 (9)   |
| O(73)  | -0.2152 (11) | -0.2261 (24)  | 0.2228 (7)   |
| C(6)   | 0.0000 (0)   | 0.116 (2)     | -0.0377 (8)  |
| C(61)  | 0.0000 (0)   | 0.280 (2)     | 0.0026 (11)  |
| C(21)  | -0.1797 (9)  | 0.081 (2)     | 0.0353 (6)   |
| C(22)  | -0.2487 (10) | 0.165 (2)     | 0.0853 (7)   |
| C(31)  | -0.1765 (8)  | -0.309 (1)    | -0.0507 (6)  |
| C(32)  | -0.2433 (11) | -0.459 (2)    | -0.0544 (9)  |
| C(41)  | 0.0000 (0)   | 0.335 (2)     | -0.1549 (8)  |
| C(42)  | 0.0000 (0)   | 0.506 (2)     | -0.1820 (12) |
| C(51)  | 0.0000 (0)   | -0.063 (2)    | -0.2326 (8)  |
| C(52)  | 0.0000 (0)   | -0.132 (3)    | -0.3068 (9)  |
| C(71)  | -0.3318 (14) | -0.337 (3)    | 0.1461 (12)  |
| O(91)  | 0.179 (1)    | 0.243 (2)     | 0.3017 (9)   |
| O(92)  | 0.000 (0)    | 0.363 (5)     | 0.3417 (20)  |
| O(93)  | 0.412 (2)    | 0.964 (3)     | 0.7009 (16)  |
| C(171) | 0.0000       | -0.027        | 0.460        |
| F(11)  | 0.074        | 0.095         | 0.471        |
| F(12)  | 0.000        | -0.135        | 0.517        |
| O(171) | -0.095       | -0.211        | 0.4028       |
| O(172) | 0.000        | -0.011        | 0.3596       |

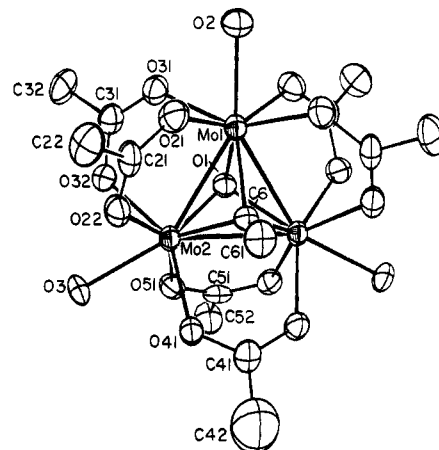
**Figure 1.** Structure and labeling scheme for the cation in structure 1 of [Mo<sub>3</sub>O(CCH<sub>3</sub>)(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)(CF<sub>3</sub>SO<sub>3</sub>H)<sub>2</sub>·5H<sub>2</sub>O.

culated as  $(0.75 + 0.35 \tan \theta)^\circ$  and scan speeds were in the range  $1.25\text{--}20.0^\circ/\text{min}$ . For crystal 2 the corresponding figures are  $(0.90 + 0.35 \tan \theta)^\circ$  and  $1.82\text{--}20.0^\circ/\text{min}$ . Standard reflections were measured every 100 data points or every hour, and in neither case was decay observed. Lorentz and polarization corrections were applied, but absorption was considered negligible.

**Structure Solution and Refinement.**<sup>7</sup> In each case the positions of two crystallographically independent molybdenum atoms, one in

**Table III.** Positional Parameters and Their Estimated Standard Deviations for Structure 2 of[Mo<sub>3</sub>O(CCH<sub>3</sub>)(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)(CF<sub>3</sub>SO<sub>3</sub>H)<sub>2</sub>·5H<sub>2</sub>O

| atom   | x            | y             | z            |
|--------|--------------|---------------|--------------|
| Mo(1)  | 0.00000 (0)  | -0.12172 (13) | 0.00000 (0)  |
| Mo(2)  | -0.10187 (5) | 0.02141 (8)   | -0.10574 (7) |
| S(1)   | -0.2215 (3)  | -0.3750 (5)   | 0.1952 (2)   |
| S(11)  | 0.0000 (0)   | -0.1396 (8)   | 0.3958 (3)   |
| F(1)   | -0.3690 (8)  | -0.474 (1)    | 0.1219 (7)   |
| F(2)   | -0.3979 (6)  | -0.261 (1)    | 0.1799 (6)   |
| F(3)   | -0.3114 (8)  | -0.244 (1)    | 0.0914 (6)   |
| O(1)   | 0.0000 (0)   | -0.1566 (10)  | -0.0997 (5)  |
| O(2)   | 0.0000 (0)   | -0.2545 (13)  | 0.0983 (5)   |
| O(3)   | -0.2439 (5)  | 0.0883 (9)    | -0.1524 (4)  |
| O(21)  | -0.1117 (5)  | -0.0074 (8)   | 0.0598 (4)   |
| O(22)  | -0.1955 (5)  | 0.1067 (8)    | -0.0265 (4)  |
| O(31)  | -0.1104 (5)  | -0.3086 (9)   | -0.0107 (4)  |
| O(32)  | -0.1920 (4)  | -0.1929 (8)   | -0.0964 (4)  |
| O(41)  | -0.0821 (5)  | 0.2638 (8)    | -0.1454 (4)  |
| O(51)  | -0.0815 (5)  | -0.0404 (8)   | -0.2097 (4)  |
| O(71)  | -0.1516 (6)  | -0.4426 (11)  | 0.1473 (5)   |
| O(72)  | -0.2573 (11) | -0.4913 (22)  | 0.2457 (7)   |
| O(73)  | -0.1974 (9)  | -0.2205 (18)  | 0.2189 (6)   |
| O(171) | -0.0887 (8)  | -0.2265 (18)  | 0.4032 (10)  |
| O(172) | 0.0000 (0)   | -0.0421 (23)  | 0.3368 (9)   |
| C(6)   | 0.0000 (0)   | 0.116 (2)     | -0.0404 (8)  |
| C(61)  | 0.0000 (0)   | 0.279 (2)     | -0.0031 (9)  |
| C(21)  | -0.1811 (7)  | 0.080 (1)     | 0.0358 (6)   |
| C(22)  | -0.2503 (8)  | 0.160 (1)     | 0.0870 (6)   |
| C(31)  | -0.1772 (7)  | -0.311 (1)    | -0.0529 (6)  |
| C(32)  | -0.2456 (9)  | -0.462 (1)    | -0.0576 (8)  |
| C(41)  | 0.0000 (0)   | 0.334 (2)     | -0.1561 (8)  |
| C(42)  | 0.0000 (0)   | 0.505 (2)     | -0.1860 (10) |
| C(51)  | 0.0000 (0)   | -0.065 (2)    | -0.2375 (7)  |
| C(52)  | 0.0000 (0)   | -0.134 (2)    | -0.3100 (8)  |
| C(71)  | -0.3301 (10) | -0.337 (2)    | 0.1454 (8)   |
| C(171) | 0.0000 (0)   | -0.009 (3)    | 0.460 (2)    |
| F(11)  | 0.078 (1)    | 0.101 (2)     | 0.4606 (9)   |
| F(12)  | 0.000 (0)    | -0.064 (4)    | 0.5268 (17)  |
| O(91)  | 0.1696 (8)   | 0.218 (1)     | 0.2923 (6)   |
| O(92)  | 0.0000 (0)   | 0.376 (3)     | 0.3452 (13)  |
| O(93)  | 0.0000 (0)   | -0.012 (1)    | 0.2006 (5)   |
| O(94)  | 0.0000 (0)   | 0.310 (3)     | 0.1805 (13)  |

**Figure 2.** Structure and labeling scheme for the cation in structure 2 of [Mo<sub>3</sub>O(CCH<sub>3</sub>)(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)(CF<sub>3</sub>SO<sub>3</sub>H)<sub>2</sub>·5H<sub>2</sub>O.

the mirror plane and the other on a general position, were derived from the three-dimensional Patterson function. The other atoms were then found in a series of alternating refinements and difference maps. There were some nonroutine problems with the CF<sub>3</sub>SO<sub>3</sub> and H<sub>2</sub>O units, and these will be explained in detail in the Results section that follows.

## Results

The two structures are not significantly different in any feature of chemical importance. The derived structural parameters of the trinuclear cation are identical, within error, for both. Tables II–V give the positional parameters, bond

(7) All crystallographic computing was done on a PDP 11/60 computer at Bertram Frenz and Associates, College Station, TX, using the Enraf-Nonius Structure Determination Package with local modifications.

Table IV. Bond Distances for  
 $[\text{Mo}_3(\text{O})(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)(\text{CF}_3\text{SO}_3\text{H})_2 \cdot 5\text{H}_2\text{O}$

| atoms                     | dist, Å     |             |
|---------------------------|-------------|-------------|
|                           | structure 1 | structure 2 |
| Mo(1)–Mo(2)               | 2.752 (1)   | 2.748 (1)   |
| Mo(2)–Mo(2)'              | 2.750 (1)   | 2.753 (1)   |
| Mo(1)–O(1)                | 1.993 (7)   | 1.981 (9)   |
| –C(6)                     | 2.051 (9)   | 2.073 (11)  |
| –O(2)                     | 2.207 (8)   | 2.210 (9)   |
| –O(21)                    | 2.141 (6)   | 2.124 (6)   |
| –O(31)                    | 2.129 (5)   | 2.130 (6)   |
| Mo(2)–O(1)                | 2.007 (4)   | 1.992 (5)   |
| –C(6)                     | 2.054 (9)   | 2.031 (11)  |
| –O(3)                     | 2.173 (5)   | 2.194 (5)   |
| –O(22)                    | 2.135 (6)   | 2.121 (6)   |
| –O(32)                    | 2.153 (5)   | 2.121 (5)   |
| –O(41)                    | 2.116 (6)   | 2.120 (6)   |
| –O(51)                    | 2.112 (6)   | 2.122 (6)   |
| C(6)–C(61)                | 1.553 (15)  | 1.51 (2)    |
| O(21)–C(21)               | 1.276 (11)  | 1.261 (10)  |
| O(22)–C(21)               | 1.257 (10)  | 1.261 (11)  |
| C(21)–C(22)               | 1.535 (12)  | 1.518 (12)  |
| O(31)–C(31)               | 1.268 (10)  | 1.227 (10)  |
| O(32)–C(31)               | 1.281 (10)  | 1.296 (10)  |
| C(31)–C(32)               | 1.526 (12)  | 1.531 (12)  |
| O(41)–C(41)               | 1.273 (8)   | 1.263 (8)   |
| C(41)–C(42)               | 1.49 (2)    | 1.50 (2)    |
| O(51)–C(51)               | 1.251 (8)   | 1.246 (8)   |
| C(51)–C(52)               | 1.58 (2)    | 1.53 (2)    |
| S(1)–O(71)                | 1.451 (9)   | 1.440 (8)   |
| –O(72)                    | 1.411 (13)  | 1.450 (13)  |
| –O(73)                    | 1.373 (13)  | 1.369 (12)  |
| –C(71)                    | 1.75 (2)    | 1.790 (13)  |
| C(71)–F(1)                | 1.32 (2)    | 1.304 (15)  |
| –F(2)                     | 1.31 (2)    | 1.295 (14)  |
| –F(3)                     | 1.34 (2)    | 1.32 (2)    |
| S(11)–O(171) <sup>a</sup> | 1.46        | 1.395 (10)  |
| –O(172)                   | 1.24        | 1.40 (2)    |
| –C(171)                   | 1.46        | 1.64 (3)    |
| C(171)–F(11)              | 1.43        | 1.38 (2)    |
| –F(12)                    | 1.43        | 1.36 (4)    |

<sup>a</sup> The  $\text{CF}_3\text{SO}_3^-$  ion was not included in the last cycle of refinement, so no esd's for this group are reported. See text. For the other bonds, the numbers in parentheses are the estimated standard deviations in the least significant figures.

lengths, and bond angles for the two structures. Figures 1 and 2 show the labeling schemes for the cations in structures 1 and 2, respectively.

Structure 1 and structure 2 differ from each other in the arrangements of the five water molecules in the lattice. In structure 1, two of them, O(91) and O(93), are on general positions, and O(92) is on a special position, giving a total of ten in the unit cell. Structure 2 has three water oxygen atoms on crystallographic mirrors and one on a general position, again giving ten in the unit cell. This is equivalent to five molecules of water per trinuclear cation. Two of the water oxygen atoms of structure 1, O(91) and O(92), are on sites similar to two of those, O(91) and O(92), respectively, in structure 2. Table VI lists all contacts that are or might be considered too short to be simple nonbonded packing contacts.

In each crystal, the six trifluoromethanesulfonate groups are arranged so that two lie on a mirror plane and the other four on a general position. We have looked for indications as to where the two acid hydrogen atoms are located and have found that several possibilities can be considered. Thus, our formal way of writing the formula, with  $(\text{CF}_3\text{SO}_3)(\text{CF}_3\text{SO}_3\text{H})_2 \cdot 5\text{H}_2\text{O}$ , is simply a convenience. Alternative ways would have one or both of the acidic hydrogen atoms transferred to water molecules to give  $\text{H}_3\text{O}^+$  and/or  $\text{H}_5\text{O}_2^+$  ions; we shall discuss some of these in detail presently. The results given by the X-ray data do not allow an unequivocal choice in either 1 or 2.

**Structure 1.** The positional and thermal parameters of all atoms in the cationic trimer were well-defined, as were the parameters for the trifluoromethanesulfonate moiety that lies on the general position. The trifluoromethanesulfonate moiety on the mirror plane did not refine well, and a damping factor of 0.6 was used in an effort to establish the best coordinates for it. It was not included in the final least-squares cycle, for which no damping factor was employed and during which none of the remaining parameters was shifted by more than 0.59 times its standard deviation. There were no peaks of chemical significance in a difference Fourier map at the end of refinement.

Our inability to refine the positional parameters of the mirror-plane  $\text{CF}_3\text{SO}_3$  group in a way that would lead to a distinction—based on bond lengths—between its two parts (the  $-\text{CF}_3$  end and the  $-\text{SO}_3$  end) might seem to be an indication of a 2-fold disorder. However, O(171) of this group takes part in a hydrogen-bonding interaction, viz., O(3)–O(171), 2.69 Å, typical of O–H...O contacts, and this shows that the orientation of the group in the lattice is not arbitrary. Furthermore, an attempt to refine a model based on a rotated trifluoromethanesulfonate led to a wholly unacceptable result.

The general-position trifluoromethanesulfonate groups exhibit close contact between fluorine atom F(2) of one molecule and F(2) of the mirror-related equivalent. This distance, 2.62 (2) Å, is slightly less than the sum of the van der Waals radii of two fluorine atoms (2.70 Å). The hypothesis that this might imply the existence of an unprecedented type of hydrogen bond, C–F...H...F–C, has been considered. While we do not think such a possibility can be dismissed with certainty, we consider it more likely that this F(2)...F(2)' distance simply represents a nonbonded contact that is slightly shorter than usual.

A stereoview of an extended portion of structure 1 is presented in Figure 3. It shows at least one example of almost all of the nonbonded close contacts listed in Table VI. (The acetate groups, however, have been omitted for the sake of clarity.)

Structure 1 and structure 2 may each possess the unusual feature of a bifurcated hydrogen bond.<sup>8</sup> Atom O(91) has two nonbonded contacts, O(91)–O(3), 3.058 (13) Å, and O(91)–O(32), 2.785 (13) Å, that subtend an angle of 53° at O(91), with O(3) and O(32) separated by 2.62 Å. Given that O(91) has three other contacts at less than 3 Å, it is not likely that these two contacts involve more than a single hydrogen bond.

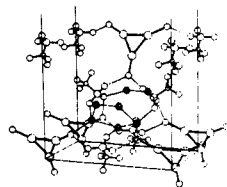
In attempting to develop an internally consistent hydrogen-bonding scheme, we must be constrained by the necessity of including all hydrogen atoms corresponding to the five water molecules as well as two more that (formally) are introduced by the two " $\text{CF}_3\text{SO}_3\text{H}$  molecules". However, these last two can be placed elsewhere, so long as we avoid unrealistic arrangements in which any one water oxygen atom is assigned more than three close protons. With these constraints in mind, we can proceed as follows, where we shall use the words donor and acceptor to denote the atoms that have short and long O to H distances, respectively. In this sense, we may say that water oxygen O(93) must be the donor toward acetate oxygen O(21) and that water oxygen O(91) must donate a proton to the bifurcated interaction with O(32) and O(3).

A reasonable point of departure for interpreting the remaining contacts is the assumption that the particularly short contact between O(93) and its mirror-related O(93)', 2.42 (4) Å, indicates the presence of an  $\text{H}_5\text{O}_2^+$  ion. Then O(93) can still donate a hydrogen atom to O(21) and also to triflate oxygen O(73), which, in keeping with the assumption above

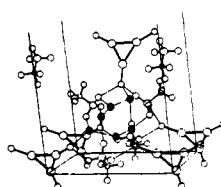
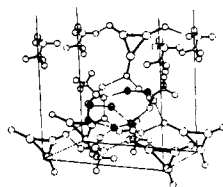
Table V. Bond Angles for [Mo<sub>3</sub>O(CCH<sub>3</sub>)(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)(CF<sub>3</sub>SO<sub>3</sub>H)<sub>2</sub>·5H<sub>2</sub>O

| atoms              | angle, deg  |             | atoms                             | angle, deg  |             |
|--------------------|-------------|-------------|-----------------------------------|-------------|-------------|
|                    | structure 1 | structure 2 |                                   | structure 1 | structure 2 |
| Mo(2)-Mo(1)-Mo(2)' | 59.96 (3)   | 60.12 (3)   | O(22)-Mo(2)-O(32)                 | 81.9 (2)    | 81.8 (2)    |
| -O(1)              | 46.7 (1)    | 46.4 (2)    | -O(41)                            | 92.7 (2)    | 92.7 (2)    |
| -C(6)              | 48.0 (2)    | 47.3 (3)    | -O(51)                            | 149.2 (2)   | 149.4 (2)   |
| -O(2)              | 150.02 (2)  | 149.94 (2)  | O(32)-Mo(2)-O(41)                 | 149.1 (2)   | 148.7 (2)   |
| -O(21)             | 83.5 (2)    | 83.2 (2)    | -O(51)                            | 87.7 (2)    | 88.1 (2)    |
| -O(21)'            | 126.9 (2)   | 126.4 (2)   | O(41)-Mo(2)-O(51)                 | 81.5 (2)    | 81.1 (2)    |
| -O(31)             | 84.0 (1)    | 82.6 (2)    | Mo(1)-O(1)-Mo(2)                  | 86.9 (2)    | 87.5 (3)    |
| -O(31)'            | 125.8 (2)   | 125.0 (2)   | Mo(2)-O(1)-Mo(2)'                 | 86.5 (2)    | 87.4 (3)    |
| O(1)-Mo(1)-C(6)    | 77.1 (4)    | 75.6 (5)    | Mo(1)-C(6)-Mo(2)                  | 84.2 (3)    | 84.1 (4)    |
| -O(2)              | 142.7 (3)   | 142.9 (4)   | -C(61)                            | 127.1 (9)   | 128 (1)     |
| -O(21)             | 128.0 (2)   | 127.6 (2)   | Mo(2)-C(6)-Mo(2)'                 | 84.1 (4)    | 85.3 (6)    |
| -O(31)             | 79.1 (2)    | 78.6 (2)    | -C(61)                            | 130.4 (4)   | 129.5 (5)   |
| C(6)-Mo(1)-O(2)    | 140.3 (4)   | 141.5 (5)   | Mo(1)-O(21)-C(21)                 | 123.3 (5)   | 124.2 (6)   |
| -O(21)             | 79.1 (3)    | 79.1 (3)    | Mo(2)-O(22)-C(21)                 | 124.6 (6)   | 124.5 (6)   |
| -O(31)             | 129.7 (2)   | 128.0 (3)   | O(21)-C(21)-O(22)                 | 125.4 (8)   | 125.1 (9)   |
| O(2)-Mo(1)-O(21)   | 73.4 (2)    | 74.1 (2)    | -C(22)                            | 116.9 (8)   | 116.5 (9)   |
| -O(31)             | 74.2 (2)    | 75.2 (2)    | -C(22)                            | 117.6 (9)   | 118.4 (8)   |
| O(21)-Mo(1)-O(21)' | 91.0 (4)    | 90.6 (4)    | Mo(1)-O(31)-C(31)                 | 124.7 (5)   | 126.4 (6)   |
| -O(31)             | 81.9 (2)    | 82.2 (2)    | Mo(2)-O(32)-C(31)                 | 124.9 (5)   | 124.6 (5)   |
| -O(31)'            | 147.5 (2)   | 149.2 (2)   | O(31)-C(31)-O(32)                 | 123.9 (7)   | 123.2 (7)   |
| O(31)-Mo(1)-O(31)' | 87.3 (3)    | 88.9 (3)    | -C(32)                            | 118.6 (7)   | 119.8 (8)   |
| Mo(1)-Mo(2)-Mo(2)' | 60.02 (2)   | 59.94 (2)   | O(32)-C(31)-C(32)                 | 117.3 (8)   | 116.9 (8)   |
| -O(1)              | 46.3 (2)    | 46.1 (3)    | Mo(2)-O(41)-C(41)                 | 126.3 (6)   | 125.8 (6)   |
| -C(6)              | 47.9 (3)    | 48.6 (3)    | O(41)-C(41)-O(41)'                | 122 (1)     | 123 (1)     |
| -O(3)              | 148.6 (2)   | 149.0 (2)   | -C(42)                            | 119.1 (5)   | 118.6 (6)   |
| -O(22)             | 83.0 (2)    | 83.0 (2)    | Mo(2)-O(51)-C(51)                 | 124.1 (6)   | 125.2 (7)   |
| -O(32)             | 82.5 (1)    | 83.1 (2)    | O(51)-C(51)-O(51)'                | 126 (1)     | 124 (1)     |
| -O(41)             | 127.2 (2)   | 127.0 (2)   | -C(52)                            | 117.1 (6)   | 117.9 (6)   |
| -O(51)             | 124.4 (2)   | 124.4 (2)   | O(71)-S(1)-O(72)                  | 113.6 (7)   | 115.0 (8)   |
| Mo(2)-Mo(2)'-O(1)  | 46.7 (1)    | 46.3 (2)    | -O(73)                            | 116.8 (7)   | 114.2 (6)   |
| -C(6)              | 48.0 (2)    | 47.3 (3)    | O(72)-S(1)-O(73)                  | 116.1 (9)   | 116 (1)     |
| -O(3)              | 151.3 (2)   | 151.0 (2)   | O(71)-S(1)-C(71)                  | 105.5 (7)   | 104.2 (6)   |
| Mo(2)'-Mo(2)-O(22) | 126.6 (2)   | 126.6 (2)   | O(72)-S(1)-C(71)                  | 102.5 (8)   | 102.3 (7)   |
| -O(32)             | 124.5 (1)   | 125.0 (2)   | O(73)-S(1)-C(71)                  | 99.3 (8)    | 103.0 (7)   |
| -O(41)             | 82.9 (2)    | 82.8 (1)    | S(1)-C(71)-F(1)                   | 113 (1)     | 112 (1)     |
| -O(51)             | 82.9 (2)    | 82.5 (2)    | -F(2)                             | 114 (1)     | 112 (1)     |
| O(1)-Mo(2)-C(6)    | 76.7 (3)    | 76.4 (4)    | -F(3)                             | 111 (1)     | 112.3 (9)   |
| -O(3)              | 142.9 (2)   | 143.7 (3)   | F(1)-C(71)-F(2)                   | 105 (1)     | 108 (1)     |
| -O(22)             | 127.1 (3)   | 127.0 (3)   | -F(3)                             | 105 (2)     | 106 (1)     |
| -O(32)             | 77.8 (2)    | 78.8 (2)    | F(2)-C(71)-F(3)                   | 109 (1)     | 107 (1)     |
| -O(41)             | 127.2 (2)   | 126.8 (2)   | O(171)-S(11)-O(171)' <sup>a</sup> | 125         | 118 (1)     |
| -O(51)             | 78.1 (3)    | 78.4 (3)    | -O(172)                           | 112         | 111.6 (7)   |
| C(6)-Mo(2)-O(3)    | 140.4 (3)   | 139.9 (3)   | -C(171)                           | 103         | 104 (1)     |
| -O(22)             | 78.8 (3)    | 79.5 (3)    | O(172)-S(11)-C(171)               | 96          | 106 (1)     |
| -O(32)             | 128.3 (3)   | 129.8 (4)   | S(11)-C(171)-F(11)                | 121         | 115 (2)     |
| -O(41)             | 79.6 (3)    | 78.6 (4)    | -F(12)                            | 108         | 122 (2)     |
| -O(51)             | 128.9 (3)   | 127.5 (3)   | F(11)-C(171)-F(11)'               | 90          | 100 (2)     |
| O(3)-Mo(2)-O(22)   | 72.8 (3)    | 72.9 (2)    | -F(12)                            | 107         | 101 (2)     |
| -O(32)             | 74.6 (2)    | 74.6 (2)    |                                   |             |             |
| -O(41)             | 74.7 (2)    | 74.3 (2)    |                                   |             |             |
| -O(51)             | 76.4 (2)    | 76.6 (2)    |                                   |             |             |

<sup>a</sup> The CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> ion was not included in the final refinement cycle, and so the esd's in its parameters are not reported. For all other angles, the numbers in parentheses are the estimated standard deviations in the least significant figures.



**Figure 3.** Extended stereoscopic view of structure 1 of [Mo<sub>3</sub>O(CCH<sub>3</sub>)(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)(CF<sub>3</sub>SO<sub>3</sub>H)<sub>2</sub>·5H<sub>2</sub>O. Oxygen atoms from water molecules are drawn with crossed surfaces for identification.



**Figure 4.** Extended stereoscopic view of structure 2 of [Mo<sub>3</sub>O(CCH<sub>3</sub>)(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)(CF<sub>3</sub>SO<sub>3</sub>H)<sub>2</sub>·5H<sub>2</sub>O. Water oxygen atoms are drawn with crossed surfaces for identification.

and the requirement of electrical neutrality, has no hydrogen atom of its own. The remaining O(93) contact is a donor type to water oxygen O(91) and is longer (2.900 (23) Å) than the rest. Atom O(91) is involved as a donor in the bifurcated interaction noted above and must also be a donor in its interaction, 2.67 (2) Å, with triflate oxygen O(72). We can

balance charge and account for the longer O(91)-O(93) interaction by postulating that O(91) is a hydronium ion in half its occurrences and is a neutral water molecule in the other half. The remaining hydrogen bonds in structure 1 can be interpreted simply in terms of this scheme; but it should be noted that other possibilities are available. The notion of

**Table VI.**  $[\text{Mo}_3\text{O}(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_-$   
 $(\text{CF}_3\text{SO}_3\text{H})_2 \cdot 5\text{H}_2\text{O}$  Nonbonded Contacts

| atom 1      | atom 2 | dist, Å    | coordinates of atom 2       |
|-------------|--------|------------|-----------------------------|
| Structure 1 |        |            |                             |
| O(2)        | O(71)  | 2.780 (10) | $x, y, z$                   |
| O(2)        | O(71)  | 2.780 (10) | $-x, y, z$                  |
| O(3)        | O(73)  | 2.862 (11) | $-1/2 - x, -y, -1/2 + z$    |
| O(3)        | O(171) | 2.694      | $-1/2 - x, -y, -1/2 + z$    |
| O(3)        | O(91)  | 3.058 (13) | $-1/2 + x, -y, -1/2 + z$    |
| O(21)       | O(93)  | 2.865 (23) | $-1/2 + x, 1 - y, -1/2 + z$ |
| O(32)       | O(91)  | 2.785 (13) | $-1/2 + x, -y, -1/2 + z$    |
| O(72)       | O(91)  | 2.666 (16) | $-x, -1 + y, z$             |
| O(73)       | O(93)  | 2.778 (33) | $-1/2 + x, 1 - y, -1/2 + z$ |
| O(172)      | O(92)  | 3.045      | $x, y, z$                   |
| O(91)       | O(93)  | 2.900 (23) | $1/2 - x, 1 - y, -1/2 + z$  |
| O(92)       | O(91)  | 2.750 (17) | $x, y, z$                   |
| O(92)       | O(91)  | 2.750 (17) | $-x, y, z$                  |
| O(93)       | O(93)  | 2.416 (36) | $1 - x, y, z$               |
| Structure 2 |        |            |                             |
| O(2)        | O(71)  | 2.724 (10) | $x, y, z$                   |
| O(2)        | O(71)  | 2.724 (10) | $-x, y, z$                  |
| O(2)        | O(93)  | 2.803 (13) | $x, y, z$                   |
| O(3)        | O(73)  | 2.860 (11) | $-1/2 - x, -y, -1/2 + z$    |
| O(3)        | O(171) | 2.748 (13) | $-1/2 - x, -y, -1/2 + z$    |
| O(3)        | O(91)  | 2.939 (12) | $-1/2 + x, -y, -1/2 + z$    |
| O(32)       | O(91)  | 2.885 (11) | $-1/2 + x, -y, -1/2 + z$    |
| O(71)       | O(94)  | 2.929 (17) | $x, -1 + y, z$              |
| O(72)       | O(91)  | 2.781 (17) | $-x, -1 + y, z$             |
| O(172)      | O(93)  | 2.688 (18) | $x, y, z$                   |
| O(92)       | O(91)  | 2.822 (16) | $x, y, z$                   |
| O(92)       | O(91)  | 2.822 (16) | $-x, y, z$                  |
| O(93)       | O(94)  | 2.631 (24) | $x, y, z$                   |

disorder among the hydrogen atoms can help explain the difficulty in refining the trifluoromethanesulfonate that lies on the mirror plane, and, to a lesser extent, the water oxygen atoms. The scheme presented here leads, additionally, to the conclusion that the long (3.045 (44) Å) contact between O(91) and O(172) does not involve a hydrogen atom. This follows from the requirement of electrical neutrality.

The hydrogen bonds among the water molecules in structure 1 connect them into a five-membered ring, as Figure 3 shows. There are, in addition, larger cyclic arrays consisting of both covalent and nonbonded interactions, as the figure also shows.

**Structure 2.** In the refinement of structure 2, as in that of structure 1, the parameters of the trinuclear cation were well established. In this case, however, all atoms—including the mirror-resident trifluoromethanesulfonate group—were refined in the final cycle of least-squares refinement. In the last cycle, no parameter was shifted by more than 0.29 times its estimated standard deviation; also, no difference Fourier peaks of significance appeared after the final refinement.

The trifluoromethanesulfonate group on the crystallographic mirror plane in structure 2 did not refine with bond lengths that would distinguish the  $-\text{CF}_3$  end from the  $-\text{SO}_3$ . However, as with structure 1, the hydrogen-bonding interactions, O(3)–O(171), 2.748 (13) Å, and O(93)–O(172), 2.688 (18) Å, serve to distinguish one end from the other and to show that the orientation of this group in the lattice is not arbitrary.

Atom F(2) of the triflate group, which resides on a general position, is at a distance of 2.759 (17) Å from its mirror-related equivalent. This distance is greater than twice the van der Waals radius of fluorine.

Figure 4 gives a stereoscopic view of the packing in structure 2. (Again, the acetate groups have been omitted for clarity.) The atoms O(91) and O(92) are at positions similar to those of the corresponding atoms in structure 1. In this case, however, there are two more water molecules—each on a mirror plane—instead of one more on a general position. As a result, there is not a five-membered ring of oxygen atoms, as there is in structure 1.

**Table VII.** Structure Parameters of the  
 $[\text{Mo}_3\text{O}(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+$  Ion<sup>a</sup>

| dist, Å                            | this work |            | BF <sub>4</sub> ·9H <sub>2</sub> O<br>compd <sup>3</sup> |
|------------------------------------|-----------|------------|--|
|                                    | cryst 1   | cryst 2    |  |
| Mo–Mo(av)                          | 2.751 [1] | 2.750 [2]  | 2.752 (1)  |
| Mo–( $\mu_3$ -O)                   | 2.000 [7] | 1.986 [6]  | 1.983 (4)  |
| Mo–CCH <sub>3</sub>                | 2.053 [2] | 2.052 [21] | 2.044 (7)  |
| Mo–O <sub>2</sub> CCH <sub>3</sub> | 2.131 [6] | 2.123 [2]  | 2.12 [1]   |
| Mo–OH <sub>2</sub>                 | 2.19 [1]  | 2.202 [8]  | 2.164 (4)  |
| C–CH <sub>3</sub>                  | 1.55 (2)  | 1.51 (2)   | 1.52 (1)   |

<sup>a</sup> Values in parentheses connote esd's.  $[x]$  means  $x^2 = \Sigma \Delta_i^2 / (n - 1)$  for the deviations,  $\Delta_i$ , of  $n$  independent values.

As before, the hydrogen-bonding pattern in structure 2 can be analyzed in more than one way. The scheme presented here is one of several plausible arrangements. A logical assignment of donors and acceptors in the hydrogen bonds of structure 2 can begin with the assignment of a hydrogen to atom O(71) of the triflate on a general position.<sup>9</sup> This leads immediately to charge balance and establishes O(71) as the donor in its interaction with water oxygen O(94). Atom O(94) is a donor to O(93), which itself donates two hydrogen atoms, one to coordinated oxygen atom O(2) and the other to mirror-plane triflate oxygen atom O(172). Water oxygen atom O(92) donates to O(91), which in turn is a donor in its interactions with O(72) and in the bifurcated contact with O(32) and O(3). The remaining nonbonded contacts (Table VI) can be explained unambiguously by following this scheme.

Other donor–acceptor arrangements are possible in structure 2, and there are plausible schemes involving protonated water molecules. We will not discuss any other schemes here, however, since the X-ray data do not unequivocally support one model over another.

## Discussion

We are at a loss to explain the formation of such similar but not identical crystals, having the same chemical composition, under what would normally be termed identical conditions of crystallization. The two differ only in details of the arrangement of the water molecules of crystallization and are presumably of nearly equal free energy. The occurrence of a given compound in different crystal structures is, of course, a well-known phenomenon, but usually the structures are distinctly different (involving different space groups, for example) and are formed under different conditions. We are not aware of any precedent for the situation reported here.

The existence and dimensions of the  $[\text{Mo}_3\text{O}(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+$  ion were previously established in a study<sup>3</sup> of the nonhydrate of the BF<sub>4</sub><sup>−</sup> salt. In this compound there were no crystallographic difficulties or anomalies and much collateral evidence was presented to confirm the charge of 1+, the diamagnetism, and the authenticity of the CCH<sub>3</sub> capping group. The present work, despite the crystallographic difficulties pertaining to some of the CF<sub>3</sub>SO<sub>3</sub><sup>−</sup> moieties and water molecules, gave in each crystal a sharply defined image of the trinuclear cation. That this is, indeed, the same cation as found previously in the BF<sub>4</sub><sup>−</sup> salt is attested by the fact that in all three structures the dimensions are identical. In most cases the agreement is much closer than the 3σ limit, as shown by the data in Table VII.

**Acknowledgments.** We thank the National Science Foundation and the U.S.-Israel Binational Science Foundation for

(9) This is not necessarily inconsistent with the accepted rules of acid–base behavior. Crystals were grown by evaporation of solvent from a solution of the cation and triflic acid in water. The crystals formed in a viscous liquid presumed to be either a eutectic mixture or a solution of water in acid. In either case, it is not unreasonable to assume the existence of acid molecules.

support of this work. We also thank Dr. J. M. Williams and Dr. M. Beno of Argonne National Laboratory for some useful discussions and some help with graphics.

Registry No.  $[\text{Mo}_2\text{O}(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)(\text{CF}_3\text{SO}_3\text{H})_2 \cdot 5\text{H}_2\text{O}$ , 82598-68-3.

SO<sub>3</sub>H)<sub>2</sub>·5H<sub>2</sub>O, 82598-68-3.

**Supplementary Material Available:** Tables of structure factors and thermal vibration parameters for both crystals (23 pages). Ordering information is given on any current masthead page.

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## Structural and Bonding Studies of the Hexachlorobis( $\mu$ -chloro)( $\mu$ -hydrido)dimolybdenum(III) Ion, $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$

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The preparations and structures of two compounds containing the  $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$  ion are reported. The pyridinium salt,  $(\text{C}_5\text{NH}_6)_3[\text{Mo}_2\text{Cl}_8\text{H}]$  (1), crystallizes in space group  $P\bar{1}$  with  $a = 10.550$  (1) Å,  $b = 15.162$  (2) Å,  $c = 8.392$  (1) Å,  $\alpha = 99.14$  (1)°,  $\beta = 111.68$  (1)°,  $\gamma = 81.22$  (1)°,  $V = 1225.1$  (5) Å<sup>3</sup>, and  $Z = 2$ . Using 2786 reflections and 257 variables, refinement led to  $R_1 = 0.026$  and  $R_2 = 0.040$ . The mean values of important dimensions of the  $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$  ion are Mo-Mo = 2.371 (1) Å, Mo-Cl<sub>b</sub> = 2.492 (4) Å, Mo-Cl<sub>t</sub>(trans to Cl) = 2.389 (11) Å, Mo-Cl<sub>t</sub>(trans to H) = 2.489 (15) Å, Mo-H = 1.68 (6) Å, and  $\angle\text{Mo-H-Mo} = 89.6$  (3)°. The second compound,  $[\text{N}(\text{C}_2\text{H}_5)_4]_2[\text{H}_5\text{O}_2][\text{Mo}_2\text{Cl}_8\text{H}]$  (2), crystallizes in space group  $Pnma$  with  $a = 15.436$  (3) Å,  $b = 10.578$  (2) Å,  $c = 19.233$  (2) Å,  $V = 3140$  (2) Å<sup>3</sup>, and  $Z = 4$ . For the  $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$  ion, the principal dimensions are Mo-Mo = 2.384 (1) Å, Mo-Cl<sub>b</sub> = 2.474 (1) Å, Mo-Cl<sub>t</sub>(trans to Cl) = 2.398 (4) Å, Mo-Cl<sub>t</sub>(trans to H) = 2.517 (1) Å, Mo-H = 1.793 (4) Å, and  $\angle\text{Mo-H-Mo} = 83.3$  (2)°. Using the average dimensions of the  $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$  ion calculated from those reported here for structure 2, an SCF-X $\alpha$ -SW calculation has been carried out to learn more about the electronic structure of this ion and to make comparisons with the earlier results of Ginsberg on the  $[\text{Mo}_2\text{Cl}_9]^{3-}$  ion.

### Introduction

The  $[\text{Mo}_2\text{X}_8\text{H}]^{3-}$  ions, X = Cl, Br, were discovered in 1969 and 1973, respectively,<sup>2,3</sup> but only in 1976 was their true identity as  $\mu$ -H complexes established.<sup>4</sup> In their alkali metal salts these anions occupy sites of  $6m2$  ( $D_{3h}$ ) symmetry and are disordered, thus making it impossible to establish their true structures. It was only in 1979<sup>5</sup> that the  $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$  ion was structurally characterized in a compound,  $(\text{C}_5\text{NH}_6)_3[\text{Mo}_2\text{Cl}_8\text{H}]$ , in which there was no crystallographic symmetry greater than its own inherent  $C_{2v}$  symmetry (actually, in this instance, no crystallographic symmetry whatever) imposed upon it. It was possible in this case, and also in another compound<sup>6</sup> where a crystallographic mirror plane passes through the midpoint of the Mo-Mo bond, to locate and refine isotropically the  $\mu$ -H atom. Subsequently we have obtained another compound containing the  $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$  ion and obtained a third characterization, again including the  $\mu$ -H atom. In this paper we present that structure as well as a full report on the pyridinium compound, which had been given only in preliminary form earlier, and compare the three independent structures. In addition, because of (a) the chemical importance<sup>7</sup> of the  $[\text{Mo}_2\text{X}_8\text{H}]^{3-}$  ions and (b) the peculiar relationship that they have to the  $[\text{Mo}_2\text{X}_9]^{3-}$  ions,<sup>8,9</sup> in which all bridging groups are halide ions (4-electron donors) instead of only two halide ions and an H<sup>-</sup> ion (2-electron donor), we wanted to make a detailed comparison of the bonding in the two cases,  $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$  and  $[\text{Mo}_2\text{Cl}_9]^{3-}$ . An SCF-X $\alpha$ -SW study of the

Table I. Crystallographic Parameters

| parameter                                   | compd 1               | compd 2               |
|---|-----------------------|-----------------------|
| space group                                 | $P\bar{1}$            | $Pnma$                |
| $a$ , Å                                     | 10.550 (1)            | 15.436 (3)            |
| $b$ , Å                                     | 15.162 (2)            | 10.578 (2)            |
| $c$ , Å                                     | 8.392 (1)             | 19.233 (2)            |
| $\alpha$ , deg                              | 99.14                 | 90.0                  |
| $\beta$ , deg                               | 111.68                | 90.0                  |
| $\gamma$ , deg                              | 81.22                 | 90.0                  |
| $V$ , Å <sup>3</sup>                        | 1225.1 (5)            | 3140 (2)              |
| $d_{\text{calcd}}$ , g/cm <sup>3</sup>      | 1.943                 | 1.637                 |
| $Z$   | 2                     | 4                     |
| fw  | 716.8                 | 774.0                 |
| cryst size, mm                              | 0.3 × 0.2 × 0.2       | 0.6 × 0.3 × 0.2       |
| $\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup> | 21.61                 | 14.71                 |
| range $2\theta$ , deg                       | $0 < 2\theta \leq 45$ | $0 < 2\theta \leq 50$ |
| no. of unique data                          | 2952                  | 3834                  |
| no. of data, $F_o^2 > 3\sigma(F_o^2)$       | 2786                  | 2485                  |
| no. of variables                            | 257                   | 160                   |
| $R_1$                                       | 0.026                 | 0.035                 |
| $R_2$                                       | 0.040                 | 0.049                 |
| goodness of fit                             | 1.008                 | 1.222                 |
| largest shift <sup>a</sup>                  | 0.04                  | 0.01                  |

<sup>a</sup> Ratio of shift to esd of a positional parameter in the last cycle of refinement.

latter has recently been published by Ginsberg,<sup>10</sup> and we have now carried out such a study on  $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$ .

### Procedures

**Preparations.** The two compounds were prepared in practically the same way.  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  (0.20 g) was dissolved in 50 mL of hot (60 °C) 12 M hydrochloric acid. To this solution was added either pyridinium hydrochloride (0.20 g) or tetraethylammonium chloride (0.20 g). The solutions were then cooled and evaporated in a stream of nitrogen, giving either dark brown crystals of 1 or yellow-brown crystals of 2.

**Crystal Structure Determinations.** These were carried out routinely as described in detail many times before.<sup>11</sup> Data were collected on

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