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# Synthesis and Crystal Structure Determination of Sodium Molybdate Dihydrate

FRANCESCO CAPITELLI†, MD. SELIM and KALYAN K. MUKHERJEA*
*Department of Chemistry, Jadavpur University, Calcutta-700032, India*
*Fax: (91)(33)24146584; Tel.: (91)(33)24146193; E-mail: k_mukherjea@yahoo.com*

The compound sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) has been synthesized from aquous medium. Orange single crystal of the compound has been diffracted for structural analysis. The structure of the molecule has been determined with better refinement and the positions of the hydrogens of the $H_2O$ molecule have also been located.

**Key Words: Synthesis, Sodium molybdate dihydrate, X-ray crystal structure.**

## INTRODUCTION

Sodium molybdate dihydrates ($Na_2MoO_4 \cdot 2H_2O$) (SMO) are compounds known for their applications in agriculture, pigment industry and metal finishing fields. It also serves as a key reagent for alkaloids, biochemical field and in clinical diagnosis. In spite of such wide applications, the structural details have not gained much importance; only two crystal structures for SMO are known[1, 2]. Herein, the synthesis and the single-crystal X-ray analysis of new crystals of SMO is reported. The present structure is in agreement with the structure reported by Matsumoto *et al.*[2] with much improved R indices and additionally the positions of hydrogens have also been found out.

## EXPERIMENTAL

Molybdenum was estimated spectrophotometrically by the following standard method[3]. Sodium and $H_2O$ were determined by flame-photometric and thermodynamic methods respectively. The amounts of sodium, molybdenum and water are 19.10, 39.51 and 14.55% respectively while $Na_2MoO_4 \cdot 2H_2O$ requires 19.00, 39.66 and 14.87%, respectively.

**Preparation of the title compound:** 1 mM molybdic acid ($MoO_3$) was dissolved in minimum volume of triple distilled water (*ca.* 5 mL). To it was added 1 mM of organic thiolate (glutathione) dissolved in 3 mL of triple distilled water with constant stirring; the solution turned yellow and the resulting pH was 5.5. The pH of the solution was raised to 7.0 by adding dil. NaOH solution and the resulting solution was stirred for 30 min. To this solution, 80–100 mL of distilled ethanol was added and stirred for another 45 min, cooled in a refrigerator for 1 h and then filtered. The product was sticky and orange in colour.

The sticky orange mass was washed several times with distilled ethanol and finally with diethyl ether and dried in vacuum. On drying, an orange powder was obtained. This was soluble in water and was recrystallized twice.

†Institute of Crystallography-CNR, V. Amendola 122/o, 70126 Bari, Italy.

**Crystallization:** The orange powder was dissolved in distilled water to get a very concentrated solution. Distilled ethanol was added to it till turbidity and preserved in airtight condition for 2 min, when diffractable grade orange crystals were harvested for X-ray diffraction.

**X-ray crystallography:** X-ray data were collected at 293 K on colourless prismatic sample using a Nonius Kappa CCD area detector diffractometer, with $MoK_\alpha$ radiation ($\lambda = 0.71070$ Å), in $\phi$ and $\omega$ scan modes. Data were corrected for Lorentz and polarisation effects and for absorption effect. The structure was solved through the direct method procedure of SIR97[4] and refined by a full-matrix least-squares technique based on $F^2$, SHELXL-97[5]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were localised through difference-Fourier map and refined isotropically. Crystal data and structure refinement are reported in Table-1, while fractional atomic coordinates and equivalent isotropic parameters are reported in Table-2

## RESULTS AND DISCUSSION

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR $Na_2MoO_4 \cdot 2H_2O$

| | |
|---|---|
| Empirical formula | $MoNa_2H_4O_6$ |
| Formula weight | 241.95 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system, space group | Orthorhombic, Pbca |
| Unit cell dimensions (Å) | a = 8.4780 (2); b = 10.5790 (3); c = 13.8300 (4) |
| | $\alpha = \beta = \gamma = 90°$ |
| Volume ($Å^3$) | 1240.40 (6) |
| Z, Calculated density (mg $m^{-3}$) | 8, 2.591 |
| Absorption coefficient ($mm^{-1}$) | 2.212 |
| F(000) | 928 |
| Crystal size (mm) | 0.43 × 0.12 × 0.12 |
| Theta range for data collection (°) | 3.80 to 30.03 |
| Limiting indices | $-11 \le h \le 11, -14 \le k \le 14, -19 \le l \le 18$ |
| Reflections collected/unique | 14579/1803 [R(int) = 0.0377] |
| Completeness to theta = 30.03 | 99.4% |
| Max. and min. transmission | 0.7772 and 0.4497 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 1803/0/98 |
| Goodness-of-fit on $F^2$ | 1.095 |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.0213$, $wR_2 = 0.0532$ |
| R indices (all data) | $R_1 = 0.0251$, $wR_2 = 0.0549$ |
| Largest diff. peak and hole ($eÅ^{-3}$) | 0.630 and –0.859 |

[1]Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (49)(7247)808666; E-mail: mailto:crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-415412.

TABLE-2
FRACTIONAL ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC PARAMETERS ($Å^2$)

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Mo1 | 0.5149 (2) | 0.19824 (2) | 0.02330 (1) | 0.01433 (7) |
| Na1 | 0.24269 (8) | 0.05067 (7) | –0.14798 (6) | 0.02300 (3) |
| Na2 | 0.65690 (9) | 0.49525 (7) | –0.08530 (5) | 0.02280 (2) |
| O1 | 0.4507 (2) | 0.1768 (1) | –0.0976 (1) | 0.0215 (3) |
| O2 | 0.5566 (2) | 0.3601 (1) | 0.0417 (1) | 0.0197 (3) |
| O3 | 0.3713 (2) | 0.1488 (1) | 0.1091 (1) | 0.0225 (3) |
| O4 | 0.6868 (2) | 0.1089 (1) | 0.0389 (1) | 0.0244 (3) |
| O5 | 0.2295 (2) | 0.1412 (2) | –0.2989 (1) | 0.0271 (3) |
| O6 | 0.0375 (2) | –0.0908 (2) | –0.1994 (1) | 0.0298 (3) |
| H51 | 0.276 (3) | 0.206 (3) | –0.317 (2) | 0.04 (1) |
| H52 | 0.153 (4) | 0.146 (3) | –0.320 (3) | 0.05 (1) |
| H61 | 0.059 (3) | –0.104 (3) | –0.252 (2) | 0.03 (1) |
| H62 | 0.047 (4) | –0.151 (3) | –0.182 (3) | 0.04 (1) |

Molybdenum cation is tetrahedrally surrounded by four oxygen atoms; Mo—O bond distances range from 1.751 (1) up to 1.778 (1) Å (Table-3), in good agreement with values reported elsewhere[1, 2]. There are two kinds of sodium cations: Na1 shows coordination number 5, forming a square pyramidal polyhedron; Na2 shows coordination number 6, forming an octahedron. Na—O bond distances range from 2.300–2.481 Å (Table-3), in good agreement with literature values[1, 4, 6].

The three-dimensional framework is built up by layers of sodium polyhedra down b, with molybdenum tetrahedra filling up resulting cavities. Strong hydrogen bonds involving water molecules and oxoanions (with H···· A distances ranging from 2.01 (3) up to 2.16 (3), (Table-4) complete the array.

Fig. 1 depicts the asymmetric unit of $Na_2MoO_4·2H_2O$ with atomic numbering scheme, while Figs. 2 and 3 depict the three-dimensional framework of $Na_2MoO_4·2H_2O$ down, respectively, c and a.

TABLE-3
BOND LENGTHS (Å) AND ANGLES (°) FOR $Na_2MoO_4·2H_2O$

| | | | |
|---|---|---|---|
| Mo1-O4 | 1.751 (1) | Na1-O6 | 2.403 (2) |
| Mo1-O2 | 1.767 (1) | Na2-O3$^3$ | 2.395 (2) |
| Mo1-O1 | 1.772 (1) | Na2-O2 | 2.419 (2) |
| Mo1-O3 | 1.778 (1) | Na2-O5$^4$ | 2.423 (2) |
| Na1-O5 | 2.300 (2) | Na2-O2$^5$ | 2.446 (2) |
| Na1-O1 | 2.319 (2) | Na2-O6$^6$ | 2.456 (2) |
| Na1-O4$^1$ | 2.341 (2) | Na2-O4$^7$ | 2.481 (2) |
| Na1-O2$^2$ | 2.354 (2) | | |

Symmetry: (1) –x + 1, –y, –z; (2) x – 1/2, –y + 1/2, –z; (3) x + 1/2, –y + 1/2, –z; (4) –x + 1, y + 1/2, –z – 1/2; (5) –x + 1, –y + 1, –z; (6) –x + 1/2, y + 1/2, z; (7) –x + 3/2, y + 1/2, z.

TABLE-4
HYDROGEN BONDS FOR $Na_2MoO_4 \cdot 2H_2O$

| | D–H | D...A | H...A | D–H...A |
|---|---|---|---|---|
| O5-H51...O3$^{I}$ | 0.83(3) | 2.828(2) | 2.01(3) | 167(3) |
| O5-H52...O1$^{II}$ | 0.71(3) | 2.790(2) | 2.08(3) | 170(3) |
| O6-H61...O3$^{III}$ | 0.76(3) | 2.827(2) | 2.07(3) | 176(3) |

Equivalent positions: I: x, –y + 1/2, +z – 1/2; II: x – 1/2, +y, –z – 1/2;
III: –x + 1/2, –y, +z – 1/2; IV: –x + 1/2, +y – 1/2, +z.

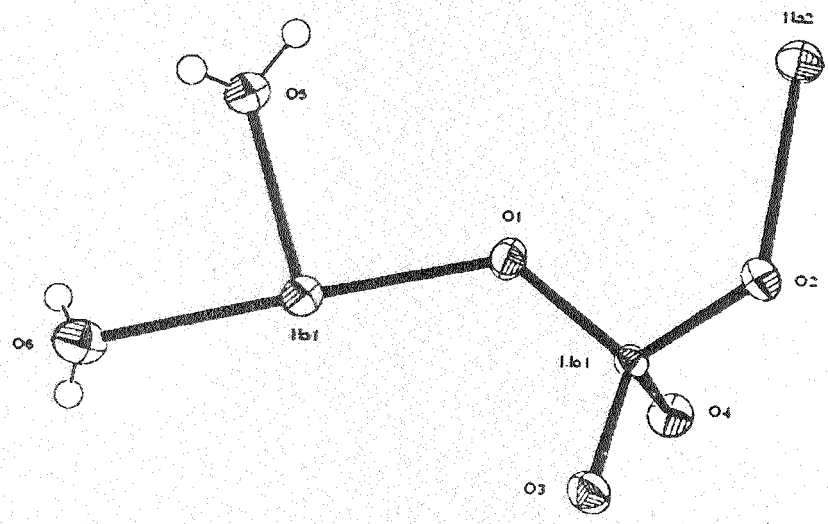


Fig. 1. Asymmetric unit with atomic numbering scheme for $Na_2MoO_4 \cdot 2H_2O$. Thermal ellipsoids are drawn at 50% probability level

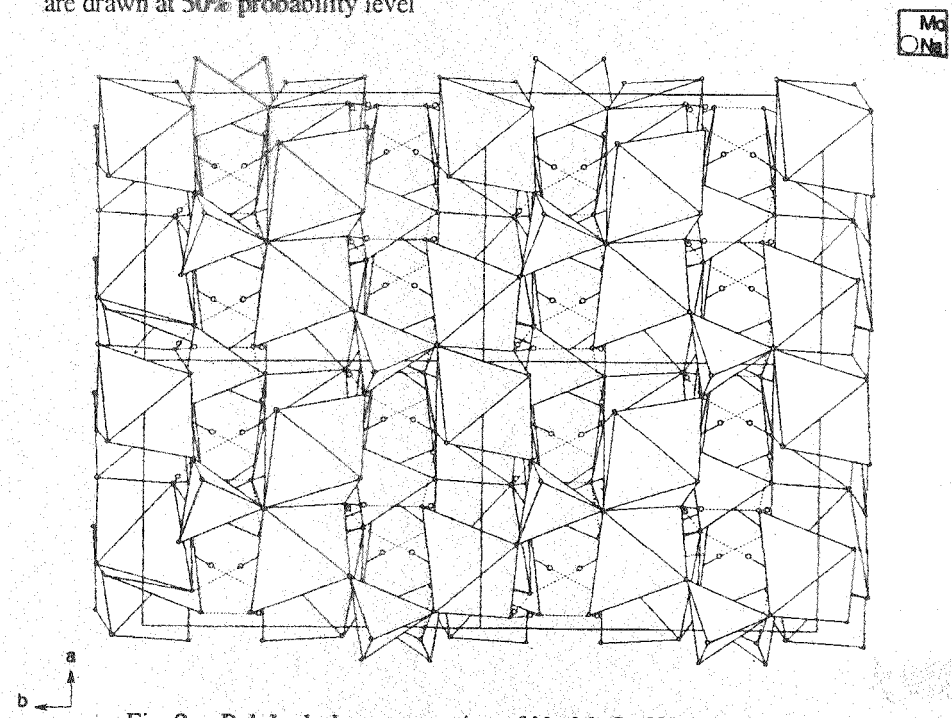


Fig. 2. Polyhedral representation of $Na_2MoO_4 \cdot 2H_2O$ down c

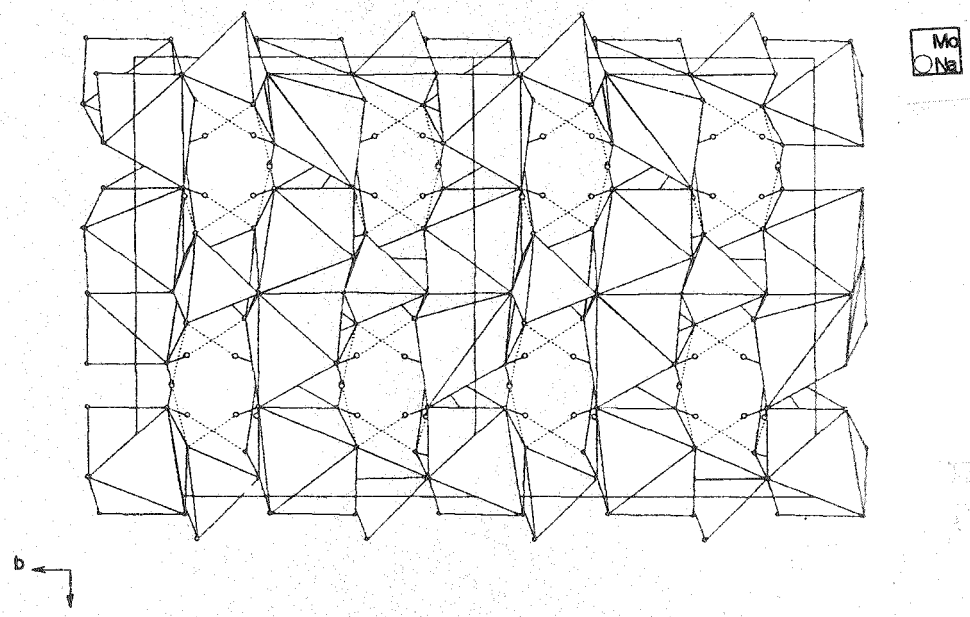


Fig. 3. Polyhedra representation of $Na_2MoO_4 \cdot 2H_2O$ down a

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