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Key indicators

Single-crystal X-ray study
 $T = 110$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.032
 wR factor = 0.075
Data-to-parameter ratio = 17.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Pentakis(tetraethylammonium) diaqua- μ_4 -malonato-
tetramalonatodi- μ_3 -oxo-di- μ -oxo-tetraoxopotassium-
tetramolybdenum acetonitrile disolvate

The title compound, $(\text{C}_8\text{H}_{20}\text{N})_5[\text{KM}_4\text{O}_8(\text{C}_3\text{H}_2\text{O}_4)_5] \cdot 2\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$, was obtained from a ligand substitution reaction of $[\text{Et}_4\text{N}]_3[\text{Mo}_3(\text{CO})_9(\text{OMe})_3]$ with malonic acid and subsequent reaction with oxygen and water. The structure contains two Mo^{5+} dimers bridged by a malonate group. Each Mo atom is ligated by an additional chelating malonate group, a terminal oxide and two bridging oxides. A potassium ion occupies the cavity formed by the bridging malonate group.

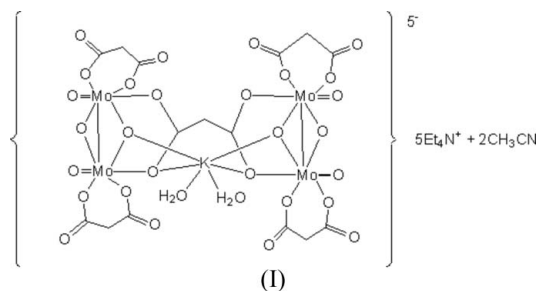
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Comment

Previously, we have presented the results of ligand exchange of the trianion of $[\text{Et}_4\text{N}]_3[\text{Mo}_3(\text{CO})_9(\text{OMe})_3]$, (II), with aryl alcohols (Adrian *et al.*, 2004). We were unable to isolate the products of the analogous reaction using dicarboxylic acids; therefore, we decided to allow the reaction mixture to be oxidized. In this study, we present the results of exchange with an organic acid and its subsequent reaction with oxygen. This resulted in the synthesis of the title compound, (I), which is illustrated in Fig. 1. Selected geometric parameters are presented in Table 1. All other bond lengths and angles are within expected ranges.



Compound (I) contains two dimolybdenum units bridged by a malonate dianion such that each O atom of the malonate group bonds to an Mo atom. Each Mo atom is ligated by an additional chelating malonate group, a terminal oxo ligand and two bridging oxo ligands. The final bond, which yields a seven-coordinate metal, is a metal–metal single bond of 2.5522 (4) Å for Mo1–Mo2 and 2.5526 (4) Å for Mo3–Mo4. The bridging malonate group creates a pocket, which is filled by an adventitious K ion. The angles about the Mo atoms reveal a distorted octahedral environment if the Mo–Mo bond is excluded. For the Mo1–Mo2 dimer, the *cis*-O–Mo–O angles range from 77.97 (6)° for O13–Mo2–O2 to 104.85 (8)° for the O8–Mo2–O5 angle. The *trans*-O–Mo–O angles range from 157.06 (7)° for O5–Mo2–O15 to a near-linear 174.01 (8)° for the O7–Mo1–O1 angle. For the Mo3–Mo4 dimer, the angles are similar. The bridging malonate

group is symmetric in its binding. The Mo—O distances cover a small range from 2.3023 (17) to 2.3405 (18) Å, while the C—O distances also cover a very small range from 1.257 (3) to 1.271 (3) Å. These distances are intermediate as compared with the C—O distances in the chelating malonate ligands and suggest the same bond order for each of the C—O bonds for the bridging malonate ligand. The chelating malonate ligands have very different C—O distances depending on whether the O atom is bound to the metal or not. On average the C—O(bound) distance is 1.303 (1) Å, while the average C—O(free) bond length is 1.229 (1) Å. This implies that the free CO has more double-bond character, as would be expected.

The K⁺ cation is coordinated by two water molecules, two of the bridging oxo ligands and two of the O atoms from the μ_4 malonate. The bond lengths to the K⁺ cation range from 2.779 (2) Å for O29 to 3.0786 (18) Å for O5. Five tetraethylammonium cations are present to balance the charge of the trianion. Compound (I) crystallizes with two molecules of acetonitrile in the asymmetric unit.

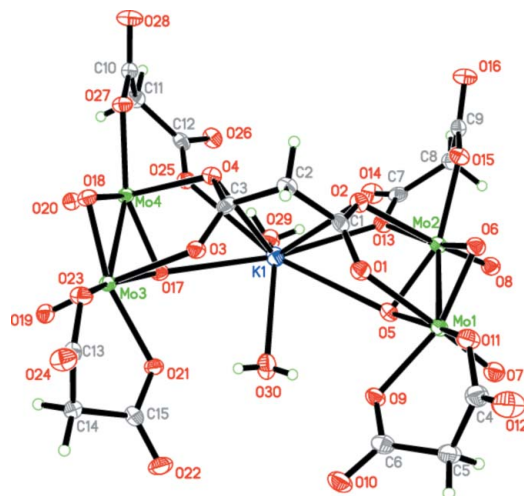


Figure 1
A view of the molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. Tetraethylammonium cations and acetonitrile molecules have been omitted.

Experimental

Compound (I) was obtained by the ligand exchange reaction of [Et₄N]₃[Mo₃(CO)₉(OMe)₃], (II), with three equivalents of malonic acid. In a typical experiment, (II) (0.100 g) was dissolved in CH₃CN (20 ml) and three equivalents of malonic acid in CH₃CN (15 ml) were added. This solution was stirred for 1 h at room temperature. The solvent was then removed at reduced pressure to about 5 ml. The complex was precipitated from solution by addition of diethyl ether (60 ml), resulting in an oily precipitate. Diffraction quality crystals of (I) were obtained by slow diffusion of diethyl ether into a concentrated acetonitrile solution in the presence of air.

Crystal data

(C₈H₂₀N)₅[KM₂O₈(C₃H₂O₄)₅]⁻ · 2C₂H₅N · 2H₂O
M_r = 1830.48
 Monoclinic, *P*2₁/*c*
a = 10.6052 (6) Å
b = 24.2012 (16) Å
c = 30.778 (2) Å
 β = 97.592 (4)°
V = 7830.3 (9) Å³
Z = 4

Data collection

Bruker APEX X8 area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
*T*_{min} = 0.856, *T*_{max} = 0.934
 128367 measured reflections

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.032
wR(*F*²) = 0.075
S = 1.04
 15993 reflections
 928 parameters
 H atoms treated by a mixture of independent and constrained refinement

D_x = 1.553 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 7542 reflections
 θ = 2.6–26.3°
 μ = 0.76 mm⁻¹
T = 110 (2) K
 Block, red
 0.20 × 0.15 × 0.09 mm

Table 1

Selected geometric parameters (Å, °).

Mo1—O7	1.6935 (19)	Mo3—O17	1.9416 (17)
Mo1—O5	1.9459 (18)	Mo3—O18	1.9506 (17)
Mo1—O6	1.9549 (18)	Mo3—O23	2.0941 (18)
Mo1—O11	2.0867 (18)	Mo3—O21	2.1134 (17)
Mo1—O9	2.0997 (17)	Mo3—O3	2.3304 (17)
Mo1—O1	2.3405 (18)	Mo3—Mo4	2.5526 (4)
Mo1—Mo2	2.5522 (4)	Mo4—O20	1.6960 (17)
Mo2—O8	1.6993 (18)	Mo4—O18	1.9360 (17)
Mo2—O6	1.9317 (18)	Mo4—O17	1.9415 (17)
Mo2—O5	1.9366 (17)	Mo4—O27	2.0990 (18)
Mo2—O15	2.1015 (18)	Mo4—O25	2.1167 (18)
Mo2—O13	2.1356 (17)	Mo4—O4	2.3036 (17)
Mo2—O2	2.3023 (17)	K1—O30	2.779 (2)
Mo3—O19	1.6947 (18)	K1—O29	2.826 (2)
O7—Mo1—O5	103.45 (8)	O19—Mo3—O17	103.90 (8)
O7—Mo1—O6	104.15 (8)	O19—Mo3—O18	104.32 (8)
O5—Mo1—O6	95.79 (7)	O17—Mo3—O18	96.29 (7)
O7—Mo1—O11	94.90 (8)	O19—Mo3—O23	97.14 (8)
O5—Mo1—O11	159.82 (7)	O17—Mo3—O23	157.16 (7)
O6—Mo1—O11	87.65 (7)	O18—Mo3—O23	86.88 (7)
O7—Mo1—O9	97.66 (8)	O19—Mo3—O21	95.33 (8)
O5—Mo1—O9	84.67 (7)	O17—Mo3—O21	84.77 (7)
O6—Mo1—O9	157.40 (7)	O18—Mo3—O21	159.39 (7)
O11—Mo1—O9	84.65 (7)	O23—Mo3—O21	84.54 (7)
O7—Mo1—O1	174.01 (8)	O19—Mo3—O3	172.85 (8)
O5—Mo1—O1	81.29 (7)	O17—Mo3—O3	81.00 (7)
O6—Mo1—O1	78.76 (7)	O18—Mo3—O3	80.05 (7)
O11—Mo1—O1	79.90 (7)	O23—Mo3—O3	77.28 (6)
O9—Mo1—O1	78.99 (7)	O21—Mo3—O3	79.80 (6)
O8—Mo2—O6	104.19 (8)	O20—Mo4—O18	105.00 (8)
O8—Mo2—O5	104.85 (8)	O20—Mo4—O17	104.58 (8)
O6—Mo2—O5	96.86 (7)	O18—Mo4—O17	96.78 (7)
O8—Mo2—O15	95.81 (8)	O20—Mo4—O27	96.20 (8)
O6—Mo2—O15	87.47 (7)	O18—Mo4—O27	86.34 (7)
O5—Mo2—O15	157.06 (7)	O17—Mo4—O27	157.33 (7)
O8—Mo2—O13	93.49 (8)	O20—Mo4—O25	93.61 (8)
O6—Mo2—O13	160.96 (7)	O18—Mo4—O25	160.11 (7)
O5—Mo2—O13	85.16 (7)	O17—Mo4—O25	85.03 (7)
O15—Mo2—O13	83.71 (7)	O27—Mo4—O25	84.71 (7)
O8—Mo2—O2	170.03 (8)	O20—Mo4—O4	168.71 (7)
O6—Mo2—O2	83.75 (7)	O18—Mo4—O4	84.47 (7)
O5—Mo2—O2	79.78 (7)	O17—Mo4—O4	79.94 (7)
O15—Mo2—O2	78.31 (7)	O27—Mo4—O4	78.02 (7)
O13—Mo2—O2	77.97 (6)	O25—Mo4—O4	76.32 (6)

The H atoms on the water molecules were located in difference Fourier maps and were allowed to refine isotropically [O–H = 0.74 (4) – 0.85 (4) Å. All the other hydrogen atoms were included in calculated positions and treated as riding atoms [C–H = 0.98–0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$].

Data collection: *APEX-II* (Bruker, 2003); cell refinement: *APEX-II*; data reduction: *SAINT-Plus* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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