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Activated Molybdenum–Molybdenum Quadruple Bonds. Synthesis, Structure, and Properties of [$Mo_2(O_2CMe)_2(en)_4$][$(O_2CMe)_2$]·en: A Solid-State Model for a Solvent-Shared Ion Pair

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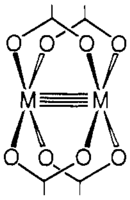
$Mo_2(O_2CMe)_4$ [Mo$\overset{4}{-}$Mo] reacts with neat ethylenediamine (en) to form [$Mo_2(O_2CMe)_2(en)_4$][$(O_2CMe)_2$]·en (**1**) in high yield. The $Mo_2(O_2CMe)_2(en)_4^{2+}$ ion in **1** contains a quadruply bonded Mo_2^{4+} center [Mo–Mo = 2.125 (1) Å] supported by two axial and two spanning en ligands in addition to two spanning acetates. The complex exists as an ion pair in which the displaced acetates are separated from the Mo_2 coordination sphere by the two spanning en ligands. The acetate counterions are hydrogen bonded to the spanning en ligands [N–O = 2.86 (2) Å (av)]. Compound **1** converts back to $Mo_2(O_2CMe)_4$ at 120 °C in the solid state. NMR studies show that dissociated and coordinated acetate ligands are present in neat en whereas, in D_2O, only dissociated en and acetate are observed. Crystal data for **1** (20 °C): a = 25.548 (7) Å, b = 9.277 (3) Å, c = 14.292 (4) Å, β = 107.43 (2)°, Z = 4, D_{calc} = 1.374 g/cm^3, and space group $C2/m$.

Multiple bonds between metal atoms of group 6 have been known for many years and are still a topic of current interest.[2] In particular, dinuclear tetracarboxylate complexes of Cr, Mo, and W that contain $\sigma^2\pi^4\delta^2$ M–M quadruple bonds have received a considerable amount of attention due to their interesting structural and spectroscopic properties.[2–6] A central feature of these compounds is the familiar paddle-wheel type structures (I)



I

formed by the spanning carboxylate ligands, but in this geometry, the nonlabile carboxylates block access to the reservoir of electrons that constitute the metal–metal bonds. As a result, little chemistry has been reported involving small organic substrates and quadruply bonded dimetal compounds.[7–9] In contrast, the organometallic chemistry of the Mo and W complexes containing sterically accessible M–M triple bonds is exceedingly rich.[10,11] We have been interested in developing the chemistry of the $M_2(O_2CMe)_4$ compounds (where M = Mo or W)[6,3] in the hope of exploiting the reducing potential of the electron-rich M–M quadruple bonds.

Aside from a slight solubility in DMF, $Mo_2(O_2CMe)_4$ is virtually insoluble in most polar and nonpolar solvents, but when it is dissolved in ethylenediamine (en), a rapid color change takes place and concentrated solutions of "$Mo_2(O_2CMe)_4$" can be attained. From these solutions, very air-sensitive, orange-yellow powders with a high en content are obtained in high yield. This new form of solvated "$Mo_2(O_2CMe)_4$" served as an Mo_2 source in the synthesis of [$Mo_4Te_{16}(en)_4^{2-}$][12] prompting us to investigate the nature of the $Mo_2(O_2CMe)_4$–en system in greater detail.

We report here the synthesis, structure, and properties of the [$Mo_2(O_2CMe)_2(en)_4$][$(O_2CMe)_2$]·en complex (**1**) containing two acetate counterions that are hydrogen bonded to two spanning en ligands. The compound serves as a solid-state model for a solvent-shared ion pair[13] where the spanning en ligands (solvent) are shared by the Mo_2^{4+} center and the displaced acetate anions. In the solid state, **1** converts back to $Mo_2(O_2CMe)_4$ with the loss of 5 equiv of en. Unlike the parent $Mo_2(O_2CMe)_4$ compound, this complex is very soluble in polar solvents, such as MeOH and H_2O, and is quite reactive toward certain organic molecules such as RC≡CH (where R = H, $SiMe_3$, and Ph). For example, we have recently isolated the remarkable [$Mo_2(\mu$-4-$MeC_6H_4CCH)(\mu$-$O_2CMe)(en)_4]^{3+}$ ion that contains *three* acetate counterions in the crystalline solid.[14] The relationship of **1** to Taube's[15] solvated Mo_2^{4+} species derived from $K_4Mo_2Cl_8$ is discussed.

Experimental Section

General Procedures. All reactions and sample manipulations were conducted under He or N_2 atmospheres with a combination of standard Schlenk techniques and Vacuum Atmospheres Co. glovebox systems. NMR spectra were recorded on a Bruker AM 360 spectrometer in 5-mm tubes at 23 °C. The ^1H and ^{13}C NMR spectra were referenced against an internal $Me_3Si(CD_2)_2CO_2Na$ (TSP) standard set at δ = 0.0 ppm. The IR spectra were recorded on an IBM 32 FTIR spectrometer. The samples were pressed into KI pellets and the spectra recorded under an N_2 atmosphere. The powder X-ray diffraction data were collected by using an airtight beryllium-windowed cell on a Phillips XRG-3000 powder diffractometer. Product identification was made by comparison with the XRD patterns of authentic samples. TGA data were obtained with a Perkin-Elmer TGS-2 thermogravimetric system installed in an N_2 drybox. The samples were run under an Ar purge at a heating rate of 10 °C/min. Elemental analyses were performed under an inert atmosphere by Schwarzkopf Microanalytical Laboratories, Woodside, NY. Crystallographic services were provided by Dr. Cynthia Day, Crystalytics Co., Lincoln, NE.

Syntheses. $Mo_2(O_2CMe)_4$ was prepared by published methods.[6] Ethylenediamine was purchased from Aldrich (Gold Label, 99+%) and

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Table I. Fractional Coordinates for $[Mo_2(O_2CMe)_2(en)_4][(O_2CMe)_2]\cdot en$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	1601 (1)	0	1244 (1)	38 (1)
Mo(2)	1653 (1)	0	2756 (1)	37 (1)
O(1)	973 (2)	1571 (5)	942 (3)	46 (1)
O(2)	1025 (2)	1574 (5)	2510 (3)	47 (1)
N(1)	2183 (2)	1731 (7)	1124 (4)	53 (2)
N(2)	2271 (2)	1689 (7)	3383 (4)	52 (2)
N(3)	1337 (12)	0	−830 (16)	236 (16)
N(5)	1691 (5)	0	4656 (8)	109 (6)
C(1)	796 (2)	1970 (7)	1642 (5)	45 (2)
C(2)	296 (3)	2904 (10)	1434 (6)	65 (3)
C(3)	2388 (6)	2769 (12)	1909 (7)	124 (6)
C(4)	2604 (5)	2385 (13)	2820 (7)	114 (5)
C(5)	720 (12)	0	−1588 (21)	377 (54)
C(7)	12245 (7)	0	5081 (14)	178 (14)
O(3)	31162 (3)	1180 (7)	614 (6)	105 (3)
C(9)	333 (5)	0	455 (9)	59 (4)
C(10)	3895 (5)	0	281 (11)	71 (5)
O(4)	2001 (4)	3973 (11)	4698 (8)	218 (6)
C(11)	1779 (5)	5000	4386 (10)	86 (5)
C(12)	1199 (7)	5000	3651 (13)	117 (7)
N(4)	739 (18)	−1417 (10)	−2855 (22)	265 (76)
N(4)*	1416 (19)	0	4656 (8)	109 (6)
N(6)	568 (12)	1469 (18)	4626 (23)	109 (6)
C(6)	566 (15)	0	−2707 (20)	201 (19)
C(6)*	781 (15)	0	−2660 (18)	276 (102)
C(8)	708 (7)	0	4445 (16)	125 (10)

distilled under N_2 three times from CaH_2 and once from K_4Sn_9. The purified solvent was stored under a He atmosphere over 4-Å molecular sieves. Methanol-d_4 and D_2O were degassed under N_2 and used without further purification. $Me^{13}CO_2Na$ was purchased from Isotec Inc. and used without further purification.

Preparation of $[Mo_2(O_2CMe)_2(en)_4][(O_2CMe)_2]\cdot en$. In a typical experiment, $Mo_2(O_2CMe)_4$ [103 mg, 0.241 mmol] was dissolved in en (2 mL), producing an orange solution. The reaction mixture was warmed to 50 °C for 10 min and allowed to slowly cool to room temperature. After 12 h, the orange-yellow microcrystalline precipitate was isolated by removing the solvent and briefly drying the residual solid in vacuo (total yield 155 mg, 80%). Large, pale orange, chunky, X-ray quality crystals were obtained in lower yields by preparing saturated reaction mixtures at 100 °C and allowing the solutions to slowly cool to room temperature. Anal. Calcd for $Mo_2C_{18}H_{52}N_{10}O_8$ (five en): Mo, 26.34; C, 29.68; H, 7.20; N, 19.23. Found (fresh crystals): Mo, 26.57; C, 28.68; H, 6.83; N, 19.13. Anal. Calcd for $Mo_2C_{16}H_{44}N_8O_8$ (four en): C, 28.76; H, 6.63; N, 16.77. Found (aged powder): C, 28.67; H, 7.51; N, 16.68.

Crystallographic Studies. In an N_2 glovebox, a suitable crystal was glued to the inside of a thin-walled glass capillary and sealed under N_2. Routine $2\theta-\omega$ data collection was carried out on a computer-controlled four-circle Nicolet Autodiffractometer with graphite-monochromated Mo Kα X-radiation. A 2° scan range was used.

The data were processed on a Data General S-200 computer. Lorentz and polarization corrections were applied; however, absorption and intensity decay corrections were not necessary and not performed. Solution and refinement of the structure were accomplished by using only data with $I > 3\sigma(I)$. The crystallographic data are summarized in Table III.

Crystals of **1** are monoclinic and display systematic absences consistent with the *C*-centered space groups *C*2 (No. 5), *Cm* (No. 8), and *C*2/*m* (No. 12). Solution and refinement of the structure were attempted "from scratch" in all three space groups. The structure was solved and refined in both the noncentrosymmetric *C*2 (R_F = 0.046; R_{wF} = 0.056) and the centrosymmetric *C*2/*m* (R_F = 0.056; R_{wF} = 0.070) whereas attempted solutions in *Cm* were unsuccessful. In the *C*2/*m* solution, both axial en ligands were disordered about the crystallographic mirror plane and the en solvate molecule was not located. In the *C*2 solution, the en solvate

Table II. Selected Bond Distances (Å) and Angles (deg) for $[Mo_2(O_2CMe)_2(en)_4][(O_2CMe)_2]\cdot en$[a]

A	B	dist (*C*2)[b]	dist (*C*2/*m*)[c]
Mo(1)	Mo(2)	2.125 (1)	2.124 (1)
Mo(1)	O(1)	2.11 (1)	2.115 (4)
Mo(1)	O(1)′	2.13 (1)	
Mo(2)	O(2)	2.08 (2)	2.120 (4)
Mo(2)	O(2)′	2.14 (1)	
Mo(1)	N(1)	2.16 (1)	2.230 (6)
Mo(1)	N(1)′	2.28 (1)	
Mo(2)	N(2)	2.19 (2)	2.214 (6)
Mo(2)	N(2)′	2.26 (2)	
Mo(1)	N(3)	2.84 (2)	2.84 (2)
Mo(2)	N(5)	2.69 (1)	2.69 (1)
O(1)	C(1)	1.25 (3)	1.268 (9)
O(1)′	C(1)′	1.31 (3)	
O(2)	C(1)	1.34 (3)	1.258 (7)
O(2)′	C(1)′	1.20 (2)	

A	B	dist (*C*2)[b]	dist (*C*2/*m*)[c]
O(3)	C(9)	1.28 (4)	1.22 (1)
O(3)′	C(9)	1.19 (4)	
O(4)	C(11)	1.27 (3)	1.13 (1)
O(4)′	C(11)	1.07 (3)	
N(1)	C(3)	1.63 (2)	1.45 (1)
N(1)′	C(3)′	1.25 (3)	
N(2)	C(4)	1.65 (3)	1.48 (1)
N(2)′	C(4)′	1.33 (3)	
C(3)	C(4)	1.41 (2)	1.30 (1)
C(3)′	C(4)′	1.30 (3)	
N(1)	O(3)	2.87 (3)	2.85 (1)
N(1)′	O(3)′	2.85 (3)	
N(2)	O(4)	2.80 (3)	2.88 (1)
N(2)′	O(4)′	3.03 (3)	

A	B	C	angle (*C*2)[b]	angle (*C*2/*m*)[c]
Mo(2)	Mo(1)	O(1)	91.2 (4)	91.1 (1)
Mo(2)	Mo(1)	O(1)′	91.3 (4)	
Mo(2)	Mo(1)	N(1)	106.9 (3)	103.8 (2)
Mo(2)	Mo(1)	N(1)′	102.5 (2)	
Mo(1)	Mo(2)	O(2)	90.9 (4)	91.0 (1)
Mo(1)	Mo(2)	O(2)′	91.4 (4)	
Mo(1)	Mo(2)	N(2)	104.9 (5)	103.4 (2)
Mo(1)	Mo(2)	N(2)′	102.2 (5)	
Mo(2)	Mo(1)	N(3)	169.1 (5)	170.3 (4)
Mo(1)	Mo(2)	N(5)	178.1 (2)	178.6 (2)
O(1)	Mo(1)	O(1)′	87.1 (6)	87.1 (2)
O(1)	Mo(1)	N(1)	84.2 (5)	88.3 (2)
O(1)′	Mo(1)	N(1)′	92.2 (5)	

A	B	C	angle (*C*2)[b]	angle (*C*2/*m*)[c]
O(1)	Mo(1)	N(3)	78.0 (6)	81.9 (3)
O(1)′	Mo(1)	N(3)	89.1 (6)	
N(1)	Mo(1)	N(1)′	92.0 (4)	92.2 (3)
N(1)	Mo(1)	O(1)′	166.3 (4)	164.5 (2)
N(1)′	Mo(1)	O(1)	160.0 (5)	
N(1)	Mo(1)	N(3)	71.5 (5)	82.8 (3)
N(1)′	Mo(1)	N(3)	88.4 (5)	
Mo(2)	N(5)	C(7)	126 (1)	129 (1)
N(1)	C(3)	C(4)	112 (1)	123 (1)
N(1)′	C(3)	C(4)	136 (3)	
N(2)	C(4)	C(3)	111 (1)	121 (1)
N(2)′	C(4)′	C(3)′	132 (1)	

[a] The primed and unprimed pairs of atoms are crystallographically equivalent in the *C*2/*m* description by virtue of the mirror plane at $y = 0$ but are independent in the *C*2 description. These atoms are labeled as a and b pairs in the *C*2 section of the Supplementary Material. [b] Results from the solution and refinement in space group *C*2. [c] Results from the solution and refinement in space group *C*2/*m*.

Table III. Summary of Crystallographic Data for $[Mo_2(O_2CMe)_2(en)_4][(O_2CMe)_2]{\cdot}en$[a]

empirical formula	$Mo_2O_8C_{18}H_{52}N_{10}$
space group	$C2/m$-No. 12 [$C2$-No. 5]
temp, °C	20
cell dimens (at 20 °C)	
a, Å	25.548 (7)
b, Å	9.277 (3)
c, Å	14.292 (4)
β, deg	107.43 (2)
Z, molecules/cell	4
vol, Å^3	3232 (2)
calcd density, g/cm^3	1.374
wavelength, Å	0.71069
mol wt	728.46
linear abs coeff, mm^{-1}	0.80
R_F	0.056 [0.046]
R_{wF}	0.070 [0.056]
totl. no of reflcns	3929
no. of reflcns with $I > 3\sigma(I)$	2454
no. of params	180 [320]
goodness-of-fit last cycle	1.40 [1.68]

[a] Numbers in brackets correspond to the $C2$ solution.

was clearly visible (albeit disordered) and the axial en ligands were less disordered, but the bond distances of the en solvate molecule and axial en ligands had to be fixed at idealized values to achieve convergence. In addition, the pseudocentricity observed in the difference Fourier syntheses had to be manually removed in order to refine to the structure. As a result, the atom positions diverged from those found for the $C2/m$ solution to give several unreasonable bond distances and angles (see Table II) and unrealistic ligand conformations (i.e. a planar spanning en ligand). However, analysis of the Wilson plots, bond distances, bond angles, and ligand conformations suggest that the centric $C2/m$ description is the correct one despite the somewhat higher residuals. The higher residuals in the $C2/m$ description could be due in part to the noninclusion of the en solvate molecule. The gross structural features are the same in both descriptions. Full details of both refinements, including comparative figures from both solutions, are given in the supplementary material.

The positions of the two Mo atoms were determined by heavy-atom Patterson techniques. The remaining heavy atoms were located by a combination of least-square refinements and difference Fourier syntheses. Many of the hydrogen atoms were visible in the latter Fourier maps—11 of which were included as fixed-atom contributors in the final refinements. After refinement, the positions of the remaining hydrogen atoms, including the en N–H hydrogens, were calculated by assuming ideal geometries and distances (N–H = 0.90 Å and C–H = 0.96 Å). The terminal atoms on both axial en ligands appear to be disordered in the lattice and have at least two preferred positions. Occupancy factors for N(4), N(4)*, C(6) and C(6)* were refined in least-squares cycles and then normalized to the following values: N(4), 0.40; N(4)*, 0.10; C(6), 0.38; and C(6)*, 0.12. Carbon atom C(5) must also be disordered, but the positions corresponding to C(6) and C(6)* could not be resolved and the listed coordinates presumably represent the average position of C(5). The second nitrogen atom on both en ligands [N(4) and N(6)] were statistically disordered across the mirror at $y = 0$. The anisotropic refinement of the data was conducted in blocked diagonals with convergence residuals of $R_F = 0.056$ and $R_{wF} = 0.070$. The top five peaks in the final difference Fourier map (1.16–0.78 e/Å^3) were within 1.07 Å of a Mo atom. There were no other peaks above background level (0.70 e/Å^3).

Results and Discussion

Synthesis. Pale yellow $Mo_2(O_2CMe)_4$ readily dissolves in (reacts with) en forming orange solutions that, upon evaporation of the solvent, yield orange-yellow microcrystalline $[Mo_2(O_2CMe)_2(en)_4][(O_2CMe)_2]{\cdot}en$ (**1**) according to eq 1. Large pale-orange

$$Mo_2(O_2CMe)_4 + \text{neat en} \rightarrow [Mo_2(O_2CMe)_2(en)_4][(O_2CMe)_2]{\cdot}en \quad (1)$$

crystals of **1** can be isolated in high yield by preparing concentrated solutions of "$Mo_2(O_2CMe)_4$" in hot en (ca. 100 °C) and allowing the mixture to slowly cool to room temperature. The air-sensitive **1** forms concentrated orange to red-orange solutions when dissolved in H_2O, MeOH, or en. The complex has been characterized by IR and ^1H and ^{13}C NMR spectroscopy, elemental analysis, thermal gravimetric analysis (TGA), and powder and single-crystal X-ray diffraction.

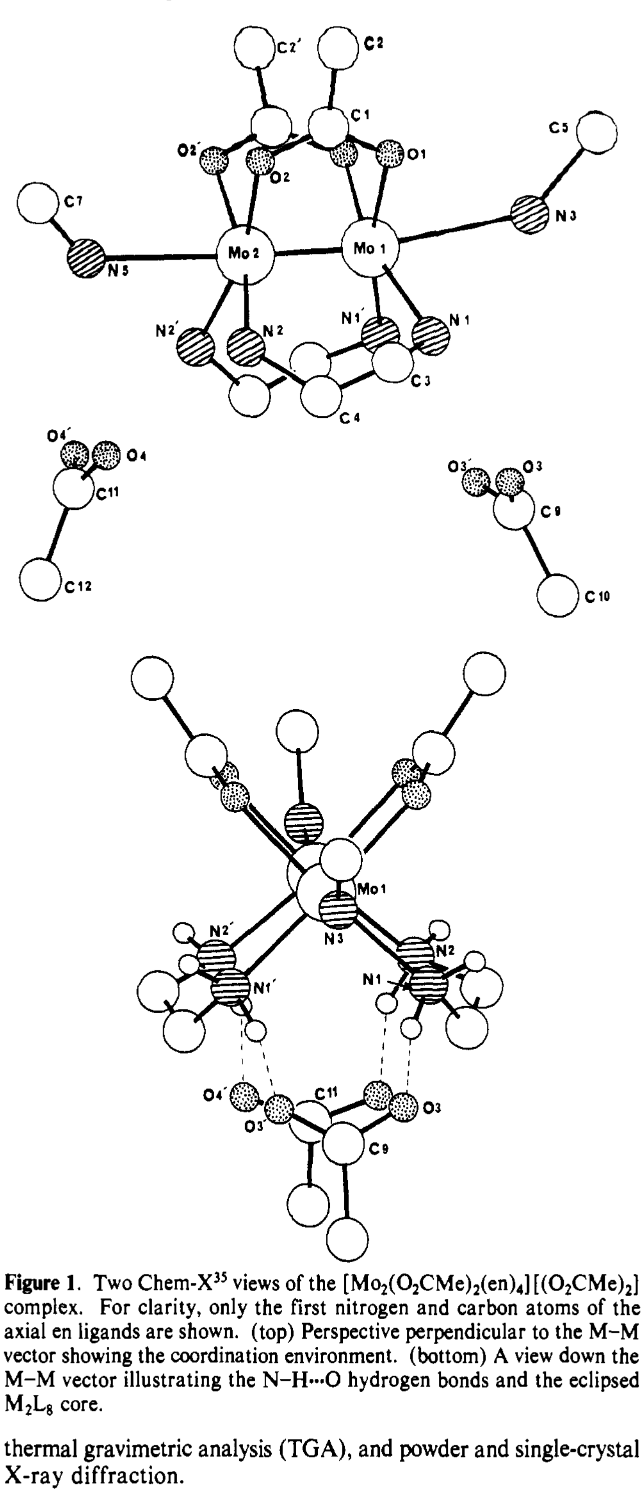


Figure 1. Two Chem-X[35] views of the $[Mo_2(O_2CMe)_2(en)_4][(O_2CMe)_2]$ complex. For clarity, only the first nitrogen and carbon atoms of the axial en ligands are shown. (top) Perspective perpendicular to the M–M vector showing the coordination environment. (bottom) A view down the M–M vector illustrating the N–H···O hydrogen bonds and the eclipsed M_2L_8 core.

Solid-State Structure. Two ball-and-stick drawings of $[Mo_2(O_2CMe)_2(en)_4][(O_2CMe)_2]$ are shown in Figure 1. Fractional coordinates and selected bond distances and angles are listed in Table I and II, respectively. A summary of the crystallographic data is given in Table III.

Crystals of **1** are monoclinic, and the structure was solved and refined in both the noncentrosymmetric $C2$ ($R_F = 0.046$; $R_{wF} = 0.056$) and the centrosymmetric $C2/m$ ($R_F = 0.056$; $R_{wF} = 0.070$) space groups. The $C2/m$ description provides a much more chemically reasonable solution and was therefore chosen as the correct space group despite the somewhat higher final residuals. The lower residuals in the $C2$ description could result in part from the inclusion of the en solvate molecule, which was not located in the $C2/m$ solution. The gross structural features are the same for both solutions and the resulting bond distances and angles from the two refinements are given in Table II for comparison.

The compound possesses C_{2v} symmetry with a crystallographically imposed mirror plane defined by Mo(1), Mo(2), N(3), N(5),

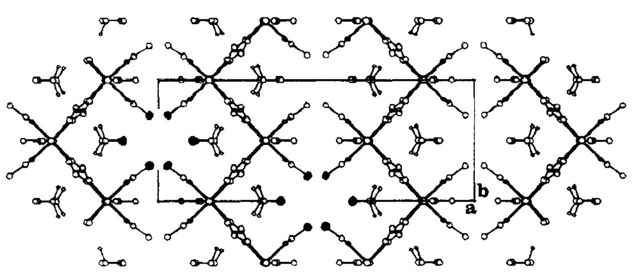


Figure 2. A [001] projection of the unit cell of $[Mo_2(O_2CMe)_2(en)_4][(O_2CMe)_2]\cdot en$ showing the cavity that hosts the disordered en solvate molecule. The large shaded balls are the acetate methyl carbon atoms that line the vacant cavity in the crystal lattice. The van der Waals separations between the acetate counterions methyl groups are ca. 5 Å along the *a* direction and 6 Å in the *c* direction.

and the four carbon atoms of the nonbonded acetate counterions. The mirror plane renders the two spanning en ligands and the two spanning acetate ligands equivalent. The second carbon and nitrogen atoms of the axial en ligands were disordered about the mirror plane and are not shown in Figure 1. The lengths of the asymmetric axial Mo–N contacts of 2.84 (2) and 2.69 (1) Å are similar to those observed in the $[Mo_2(O_2CMe)_2(MeCN)_6]^{2+}$ ion [2.745 (10) and 2.772 (8) Å][16] and the $^1_\infty[Mo_2(O_2CMe)_4(Me_2NCH_2CH_2NMe_2)]$[17] polymer [2.73 (1) Å] but are long in comparison to the axial Mo–N distances in $Mo_2(O_2CCF_3)_4(py)_2$ [2.55 (1) Å].[18] The Mo_2^{4+} center is supported by two cis spanning en ligands [Mo–N = 2.22 (2) Å (av)] and two cis spanning acetate ligands [Mo–O = 2.12 (1) Å (av)] with an M_2L_8 core similar to those in other dimetal carboxylate and halide compounds.[1] The metal–metal distance of 2.124 (1) Å in **1** is consistent with the presence of a Mo–Mo quadruple bond.[1,19] The disordered en solvate molecule (not located in the *C*2/*m* description) resides in the cavity formed by the acetate methyl groups as shown in Figure 2.

Of particular note in the structure of **1** are the two acetate counterions that were displaced from the Mo_2 center of the parent $Mo_2(O_2CMe)_4$ by the en solvent. Their oxygens are bonded to the N–H hydrogens of the spanning en ligands (Figure 1B) with N···O separations [2.86 (2) Å] typical of normal N–H···O hydrogen bonds.[20] The charge separation and coordination environment are not unlike those in the $[Mo_2(O_2CMe)_2(MeCN)_6]^{2+}$ and $[Rh_2(O_2CMe)_2(py)_6]^{2+}$ ions,[16,21] except that hydrogen bonding is absent in the latter two.

The thorough synthetic, structural, and theoretical studies by Cotton and co-workers involving the $Mo_2X_4(L\frown L)_2$ compounds (where X = halide and $L\frown L$ = a spanning diphosphine) clearly illustrate the correlation between metal–metal bond strength (δ overlap) and the angle of internal rotation about the metal–metal bond (χ) away from the eclipsed conformation at $\chi = 0°$.[19,22-26] Their studies show that maximum δ overlap occurs in the eclipsed conformation ($\chi = 0°$), illustrated by II, and the minimum δ overlap occurs in the staggered form ($\chi = 45°$), which is illustrated by III. The degree of rotation χ is strongly influenced by the number of atoms in the $PR_2(CH_2)_nPR_2$ bridge [where n = 1–3].[19,26] Minimizing the ring strain in these systems is apparently more important than maximizing δ overlap in the M–M bond. Thus, the number of methylene units (n) in the diphosphine ligand essentially determines χ (for $n = 1$, $\chi = 0°$; for $n = 2$, $\chi \approx 36°$; for $n = 3$, $\chi \approx 23°$).[26,27] In addition, when ethylene-bridged diphosphine ligands are used (dppe, dmpe), a second isomer is often formed that contains chelating diphosphines with eclipsed M_2L_8 cores (IV).[28] The two spanning acetate ligands in **1** prohibit rotation about the M–M vector, resulting in an eclipsed geometry. Therefore, the two fused six-membered rings formed by the spanning en ligands are forced into planar ($\chi = 0°$) N–Mo–Mo–N arrangements [N(1)–Mo(1)–Mo(2)–N(2) dihedral angle = 0.5 (9)°] with considerable ring strain.[29] In this geometry, however,

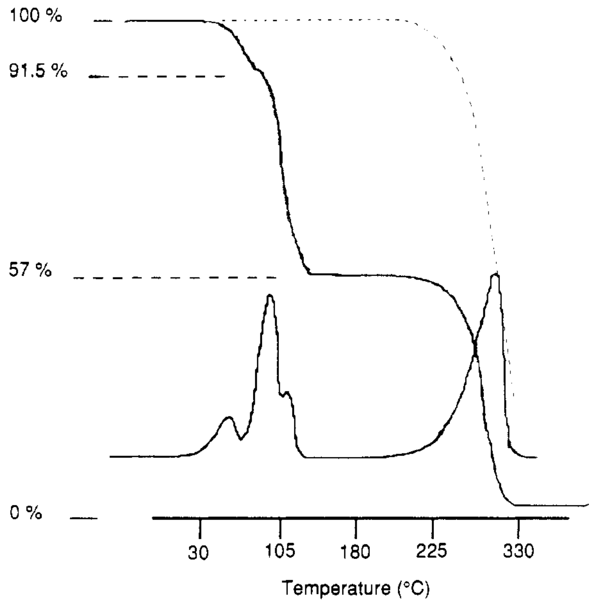
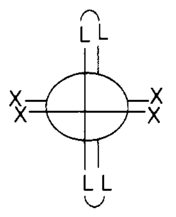
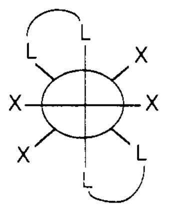


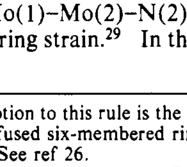
Figure 3. Plot of percent weight loss versus temperature and the first derivative [d(% wt)/d*T*] for the thermal decomposition of $[Mo_2(O_2CMe)_2(en)_4][(O_2CMe)_2]\cdot en$ (solid line) and $Mo_2(O_2CMe)_4$ (dotted line). The experiments were run under an Ar purge.



II



III



IV

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(29) There is significant thermal motion associated with atoms C(3) and C(4) in the direction normal to the N–C vectors. The unreasonable C(3)–C(4) distance of 1.31 Å is no doubt a consequence of this motion and the quality of the structure. If a realistic C–C distance is imposed on these atoms, the N–C–C angles of the spanning en ligands become even larger than the observed 122 (2)°.

the amine hydrogen atoms are in ideal positions to form strong hydrogen bonds to the nonligated acetate counterions. The ring strain could be relieved and M–M δ bonding maintained if the en ligands were chelating (IV), as in the related compounds $(\text{dmpe})_2\text{Mo}_2(\text{O-}i\text{-Pr})_4$[30] and $\alpha\text{-Re}_2\text{Cl}_4(\text{dppe})_2$,[31] instead of spanning. However, the chelating geometry would disrupt the hydrogen-bonding network that stabilizes the acetate counterions in the crystal lattice.[32] Similarly, adaptation of less strained boat conformations of the $\overline{\text{MoMoNH}_2(\text{CH}_2)_2\text{NH}_2}$ rings, analogous to those observed in $\text{Mo}_2\text{I}_4(\text{dppe})_2$,[26] would also compromise hydrogen bonding. Hydrogen bonding is obviously a driving force in the formation of **1** in solution and a dominant structural feature in the solid state. Attempts to exchange the acetate counterions with other non-hydrogen-bonding anions, such as BPh_4^- and PF_6^-, have been unsuccessful to date.

Solid-State Thermal Reactivity. As previously noted, compound **1** is thermally unstable in the solid state in that crystalline samples tend to powder rapidly at room temperature. Furthermore, analytical studies show that aged powdered samples (ca. 2 weeks at room temperature) contain lower en contents (ca. four en per Mo_2) than freshly crystallized samples (five en per Mo_2). This thermal instability is supported by TGA studies that show rapid loss of en at low temperatures. A plot of percentage weight loss versus temperature for a freshly prepared sample of **1** (Figure 3) establishes that the first 1 equiv of en has been completely removed (loss of 8.5%) at 75 °C and the remaining 4 equiv of en are expelled in two steps between 85 and 130 °C. The remaining pale yellow residue (57% of original mass) was identified as $\text{Mo}_2(\text{O}_2\text{CMe})_4$ by powder X-ray diffraction (XRD). The XRD peak widths are indicative of particle sizes greater than 100 Å. Upon further heating, the entire residue sublimes (230 °C, 1 atm Ar) yielding pale yellow, microcrystalline $\text{Mo}_2(\text{O}_2\text{CMe})_4$. When slow heating rates are employed, small amounts (<10%) of an unidentified, amorphous black residue are obtained.

The stepwise sequence in which the amine ligands are expelled (Figure 3) stimulates speculation as to their identity. A possible scenario in agreement with the data and chemical intuition would be initial expulsion of the disordered en solvate molecule followed by the expulsion of the weakly bound axial en ligands and finally those in the more tightly bound spanning positions. The second weight-loss regime corresponds to the expulsion of four en molecules and occurs in two steps (first derivative plot in Figure 3); however, we cannot determine the magnitude of weight loss in each of these steps (i.e. −2 and −2 or −1 and −3, etc.). It is interesting to note that, during this process, the unbound acetate counterions must rotate 90° and migrate ca. 4.0 Å in the solid state to re-form $\text{Mo}_2(\text{O}_2\text{CMe})_4$.

Spectroscopic Studies. The NMR and IR data for compound **1** and other selected, model compounds are given in Tables IV and V, respectively.

The ^{13}C NMR spectra for **1** in en and D_2O are significantly different, and neither spectrum is consistent with the solid-state structure. In neat en, three carboxylate MeCO_2 carbon resonances are observed at 176.6, 181.6, and 184.0 ppm. The two peaks at 181.6 and 184.0 ppm are broad whereas the third peak at 176.6 ppm is quite sharp and has a chemical shift virtually identical with that of $(\text{NH}_4)(\text{O}_2\text{CMe})$ in the same solvent (176.7 ppm). The two broad carboxylate resonances occur downfield of the $(\text{NH}_4)(\text{O}_2\text{CMe})$ signals, which is consistent with an acetate spanning an M–M multiple bond.[33] A similar pattern is observed for the acetate $\mathit{Me}\text{CO}_2$ ^{13}C nuclei, which exhibit only one very broad resonance and one sharp resonance. These data suggest that dissociated and coordinated acetate ligands are present in ethylenediamine solutions. When $\text{Me*CO}_2\text{Na}$ (where *C is 99+ atom % ^{13}C) was added to an en solution of **1**, only the free acetate resonances were enhanced and there was no change in the appearance of the two other acetate absorptions after 12 h at 25 °C. The broadness of the downfield ^{13}C resonances could result from either inter- or intramolecular exchange of coordinated acetate ligands (i.e. isomer interconversion, dimer–tetramer equilibria, or arm-on–arm-off acetate fluxionality); however, the ^{13}C labeling studies suggest that exchange between free and coordinated acetates is very slow at room temperature. It is unclear what compound or compounds are present in en solutions.

Table IV. NMR Data for Selected Compounds

		chem shift, δ		
		$^{13}\text{C}\{^1\text{H}\}$ in en	$^{13}\text{C}\{^1\text{H}\}$ in D_2O	^1H in D_2O
$\text{Mo}_2(\text{O}_2\text{CMe})_4(\text{en})_5$	$\text{O}_2\mathit{C}\text{Me}$	176.68, 181.6 (br) 184.0 (br)	172.6	
	$\text{O}_2\text{C}\mathit{Me}$	25.3, 24 (br)	14.5	1.89
	en		33.2	2.76
free en	en		33.2	2.66
$\text{NH}_4(\text{O}_2\text{CMe})$	$\text{O}_2\mathit{C}\text{Me}$	176.7	171.4	
	$\text{O}_2\text{C}\mathit{Me}$	24.9	13.6	1.92

Table V. Infrared Data

	ν, cm^{-1}		
	compd **1**	$\text{Na}(\text{O}_2\text{CMe})$	$\text{Mo}_2(\text{O}_2\text{CMe})_4$
antisymmetric	1566, 1527	1585	1526
symmetric	1431, 1394	1414	1437

The ^{1}H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for **1** in D_2O show one set of acetate resonances that are quite sharp and have chemical shifts similar to those for $(\text{NH}_4)(\text{O}_2\text{CMe})$ in the same solvent.

The solid-state IR spectrum for **1** (Table V) is characterized by two sets of bands assignable to the symmetric and antisymmetric O–C–O stretching vibrations for complexed and uncomplexed acetates. Comparison with the model compounds $\text{Mo}_2(\text{O}_2\text{CMe})_4$ and $\text{Na}(\text{O}_2\text{CMe})$ suggest that the bands at 1527 and 1431 cm^{-1} are due to the spanning acetate ligands on **1** and those at 1566 and 1394 cm^{-1} to the unbound acetate counterions.

Conclusion

$\text{Mo}_2(\text{O}_2\text{CMe})_4$ reacts with neat en at room temperature to form the $[\text{Mo}_2(\text{O}_2\text{CMe})_2(\text{en})_4][(\text{O}_2\text{CMe})_2]\cdot\text{en}$ complex (**1**) in high yield. Under mild thermal conditions (ca. 120 °C), compound **1** reverts back to $\text{Mo}_2(\text{O}_2\text{CMe})_4$ in the solid state. The complex has an unusual solid-state structure incorporating two acetate counterions that are hydrogen bonded to the spanning en ligands.

The extent of acetate displacement in solution is not clear; however, NMR studies suggest that solvent-for-acetate substitution is more extensive in D_2O than in en. This observation is consistent with the findings of Taube and Bowen nearly 2 decades ago.[15] Their studies showed that stable, red solutions of aquated Mo_2^{4+} could be produced from $\text{K}_4\text{Mo}_2\text{Cl}_8\cdot2\text{H}_2\text{O}$ in 0.1M aqueous trifluoromethanesulfonic acid. Furthermore, they prepared a compound of composition $\text{Mo}_2(\text{en})_4\text{Cl}_4$ that forms stable, yellow-orange aqueous solutions that presumably contain $\text{Mo}_2(\text{en})_4^{4+}$ ions.[15] Except for a few ligand exchange reactions, the chemistry of these compounds remains unexplored.

It appears that the ability of the polar en solvent to displace the acetate ligands from the coordination sphere of the Mo_2 center in **1** tends to activate the complex toward reactions with external small organic molecules such as terminal alkynes. The potential of these solvated Mo_2^{4+} ions for use as 8-e reductants in polar

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solvents is intriguing, and our preliminary studies show that the chemistry of these compounds is quite rich.

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Supplementary Material Available: For both the *C*2 and *C*2/*m* structures, ORTEP and Chem-X[35] drawings of **1** and complete listings of bond distances, bond angles, fractional coordinates, and anisotropic thermal parameters (25 pages); listings of calculated and observed structure factors for the *C*2 and *C*2/*m* structures (22 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Properties of $Fe_2Te_3(CO)_6^{2-}$ Containing the Unusual μ_2-η^1-Te_2^{2-} Ligand

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$Fe(CO)_3(\eta^4$-butadiene) reacts with excess K_2Te_4 in ethylenediamine in the presence of crypt to form $[Fe_2Te_3(CO_6)][(K\cdot crypt)_2]\cdot{}^1/_2$en in good yield. The $Fe_2Te_3(CO)_6^{2-}$ anion (**1**) contains two square-pyramidal Fe centers joined along a common basal edge via μ-Te and μ_2-η^1-Te_2 ligands. The Fe–Fe distance in **1** is 2.63 (1) Å. IR spectroscopic studies are suggestive of at least two detectable transient species during the formation of **1** with an overall t_∞ of ca. 18 h. The complex does not form in the absence of crypt. The $Fe_2Te_3(CO)_6^{2-}$ anion remains intact when dissolved. Crystal data: a = 11.531 (7) Å, b = 22.098 (12) Å, c = 25.341 (13) Å; α = 85.22 (4)°, β = 84.60 (4)°, γ = 84.39 (5)°, space group $P\bar{1}$, and Z = 4.

Introduction

We have recently shown that soluble main-group polyanions can be used to form metalized polymers[1] and metastable solids with tunable conductivities[2] by soluble deposition techniques at ambient temperatures. As an extension of this work, we have been preparing transition-metal main-group polyanions to investigate their structures and properties as well as their utility in forming new metastable materials.[3,4] Of particular interest are transition-metal polytelluride complexes, which are currently few in number in contrast to the large family of transition-metal polysulfide complexes.[5] The virtue of using such molecular precursors in the formation of binary solids is exemplified by the convenient low-temperature synthesis of FeTe and $FeTe_2$ from $[Cp(Et_3P)(CO)Fe]Te_n$ compounds reported by Steigerwald.[6] As a result of the effects of ourselves and others, a few transition-metal polytelluride anions have recently been prepared including $Mo_4Te_{16}(en)_4^{2-}$,[7] $Pd(Te_4)_2^{2-}$,[8] *trans*-$Cr(CO)_2(\eta^2$-$Te_2)_2^{2-}$,[9] $NbTe_{10}^{3-}$,[10a] $Cr(Te_4)(CO)_4^{2-}$,[10b] and $Cr_3Te_{24}^{3-}$.[11] The complexes were synthesized from various transition-metal complexes in solution reactions with soluble polytelluride ions. These compounds provide an unusual assortment of clusters with unprecedented structures and, with the exception of $Pd(Te_4)_2^{2-}$, have no analogues in the polysulfide systems.[5] We report here the synthesis, structure, and properties of the unusual $Fe_2Te_3(CO)_6^{2-}$ ion, which extends this class of transition-metal polytelluride anions.

Experimental Section

General Data. All reactions were conducted in a Vacuum Atmospheres Co. drybox under dry oxygen-free He atmospheres. The IR spectra were recorded on a Perkin-Elmer 283 infrared spectrophotometer under an N_2 purge. The solid-state spectra were obtained from pressed KI pellets. The solution spectra were recorded in an airtight CaF_2 cell in ethylenediamine (en) solvent. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Chemicals. $Fe(CO)_3(\eta^4$-butadiene) was purchased from Aldrich Chemicals and used without further purification. The melt of nominal composition K_2Te_4 was prepared by fusing a stoichiometric ratio of the elements under a He atmosphere in a quartz tube. The ethylenediamine solvent was purchased from Aldrich (Gold Label, 99+%), distilled three times from CaH_2 and once from K_4Sn_9, and stored under He. Crypt[12] was purchased from Fluka and used without further purification.

Preparation of $[Fe_2Te_3(CO)_6][(K\cdot crypt)_2]\cdot{}^1/_2$en. K_2Te_4 (78 mg, ca. 0.13 mmol) was extracted into en (ca. 2 mL), producing a reddish purple solution. Approximately 80% of the intermetallic compound went into solution. $Fe(CO)_3(\eta^4$-butadiene) (52 mg, 0.27 mmol) was added dropwise to the polytelluride solution. While the mixture was being stirred, crypt (100 mg, 0.27 mmol) was added as a solid. A slight reddening of the solution was observed upon addition of crypt. The solution was stirred for 24 h at room temperature and then filtered twice. After an additional 24 h, long dark needles of $[Fe_2Te_3(CO)_6][(K\cdot crypt)_2]\cdot{}^1/_2$en were isolated by removing the solvent and washing with en (2 × 1 mL). The crystals were dried in vacuo (crystalline yield, 86 mg, 46%). Large, chunky crystals of $(K\cdot crypt)_2Te_x$ are often formed when large excesses of K_2Te_4 are employed in the synthesis.[13] This material is more soluble in en than the iron-telluride product and can be washed away. IR data (KI pellet), cm^{-1}: 1995 (s), 1950 (s), 1922 (s), 1898 (s), 1886 (s). IR data (en solution, CaF_2 cell), cm^{-1}: 2000 (m), 1971 (m), 1957 (s), 1924 (m), 1909 (m). Anal. Calcd for $K_2Fe_2Te_3C_{43}H_{76}O_{18}N_5$: Fe, 7.3; Te, 25.1; C, 33.8; H, 5.0; N, 4.6. Found: Fe, 7.3; Te, 25.4; C, 34.9; H, 5.3; N, 4.5.

Structural Studies. A dark, almost black, irregularly-shaped crystal of $[Fe_2Te_3(CO_6)][(K\cdot crypt)_2]\cdot{}^1/_2$en, having approximate dimensions of 0.2 × 0.3 × 0.5 mm, was mounted in a glass capillary with its long axis

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