$[^1H]$ and 62.83-MHz $[^{13}C]$ on a Bruker WM-250 spectrometer. Chemical shifts are based on residual solvent resonances. Melting points are corrected.

1,3,5-Tris(dimethylamino)-2,4,6-trinitrobenzene (1a).[5,29,30] A 500-mL round-bottom flask is charged with 1,3,5-tribromo-2,4,6-trinitrobenzene[31] (1 g) and 250 mL of ethanol. The solution is warmed gently and a 40% solution of dimethylamine in ethanol (5 equiv) is added dropwise. After 1 h the yellow solution is cooled and a precipitate forms (yield 70%). The yellow solid is collected by filtration and can be recrystallized from chloroform and hexane: mp >250 °C dec; ^1H NMR ($CDCl_3$) δ 3.40 (s).

1,3,5-Tris(diethylamino)-2,4,6-trinitrobenzene (1b).[29] A mixture of 1,3,5-trichloro-2,4,6-trinitrobenzene[31] (2.2g) and diethylamine (30mL) was heated at reflux under a blanket of argon for 24 h to give a yellow suspension. Addition of water prompted further precipitation. The suspension was filtered to give a yellow solid (2 g) that was washed with water and then dried. Recrystallization from hexane/ethanol yielded yellow needles: mp 99–100 °C (lit.[5] 99–100 °C); ^1H NMR (CD_2Cl_2) δ 1.33 (t, 18 H, ^3J = 7.2 Hz), 3.63 (q, 12 H, ^3J = 7.2 Hz).

X-ray Crystallography. Crystals of 1,3,5-tris(diethylamino)-2,4,6-trinitrobenzene were grown by slow evaporation from hexane/ethanol. A bright yellow crystal of approximately 0.06 × 0.18 × 0.51 mm was chosen for the X-ray measurements. Crystal data: $C_{18}H_{30}N_6O_6$, M = 426.6 g·mol^{-1}; monoclinic (space group $P2_1/c$); a = 10.005 (2) Å, b = 21.452 (5) Å, c = 10.544 (2) Å, β = 104.3° (2); and V = 2193.8 (8) Å^3, d_{calc} = 1.29 g·cm^{-3}, Z = 4. X-ray intensities were recorded at room temperature on a Nicolet R3m four-circle diffractometer applying Cu Kα radiation (λ = 1.54178 Å). A total of 2948 independent reflections were recorded with 3° ≤ 2θ ≤ 114° of which 2475 with $|F_0| > 3\sigma(F_0)$ were considered unique and observed. The structure was solved by direct methods with the SHELXTL software. All non-hydrogen atoms were refined anisotropically by using a block cascade least-squares procedure. Hydrogen atoms were included at ideal positions (C–H = 0.96 Å and C–C–H = 109.5°). R and R_w factors after refinement of 271 parameters were 0.046 and 0.053, respectively. The largest peak in the final Fourier difference map was 0.17 e·Å^{-3}.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-8510067) and the Presidential Young Investigator Award Program (Grant No. CHE-8857812) for support of this work.

Registry No. 1a, 121097-10-7; **1b**, 114396-18-8; 1,3,5-tribromo-2,4,6-trinitrobenzene, 83430-12-0; dimethylamine, 124-40-3; 1,3,5-trichloro-2,4,6-trinitrobenzene, 2631-68-7; diethylamine, 109-89-7.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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[29] Tris(dialkylamino)trinitrobenzenes are, in general, explosive! Extreme care should be taken when handling these materials. Do not prepare or store large quantities of these compounds. It is unadvisable to store these compounds in ground glass stoppered vials. Even though we have had no accidental detonations of **1a** or **1b**, we have been able to detonate a few milligrams of **1a** by striking it with a ball peen hammer on a hard surface.

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Communications to the Editor

Structural Characterization of the Pentamolybdate Anion, $[(MoO_4)_2\{Mo_3O_8(OMe)\}]^{3-}$, and Isolation of the $[Mo_3O_8(OMe)]^+$ Trinuclear Core in the Squarate Complex $[\{Mo_3O_8(OMe)\}(C_4O_4)_2]^{3-}$

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Received December 27, 1988

Polyoxoanions which are soluble in organic solvents are of continuing interest by virtue of their applications in the elucidation of pathways for interconversions of various polymetalate structural types[2] and in the development of the coordination chemistry of these species with organic substrate molecules.[3,4] The isopolymolybdate anions which can be synthesized or stabilized in organic solvents include the structurally characterized species $[Mo_2O_7]^{2-}$,[5] $[Mo_6O_{19}]^{2-}$,[6] and α-$[Mo_8O_{26}]^{4-}$[7] and the amorphous pentamolybdate $[Mo_5O_{17}H]^{3-}$.[8] In the course of investigations of polymolybdate–carbonyl interactions,[9,10] we have isolated a crystalline derivative of the pentamolybdate species, [(*n*-

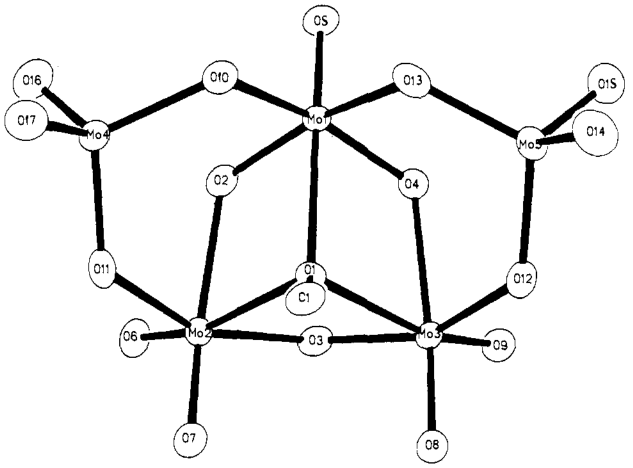

Figure 1. ORTEP view of the structure of $[\{Mo_3O_8(OMe)\}(MoO_4)_2]^{3-}$ (I), showing the atom-labeling scheme. Selected bond lengths (Å) and angles (deg) are as follows: Mo(1)–O(1), 2.446 (9); Mo(2)–O(1), 2.285 (9); Mo(3)–O(1), 2.303 (10); Mo(1)–O_b, 1.801 (14) (av); Mo(1)–O_b', 2.060 (15) (av); Mo(1)–O(3), 1.915 (12); Mo(2)–O(2), 2.237 (10); Mo(2)–O(11), 2.012 (13); Mo(3)–O(3), 1.923 (11); Mo(3)–O(4), 2.240 (9); Mo(3)–O(12), 1.976 (11); Mo(4)–O_b', 1.849 (12) (av); Mo(5)–O_b', 1.837 (11); O(1)–Mo(1)–O(5), 177.9 (6); O(6)–Mo(2)–O(1), 161.8 (6), O(9)–Mo(3)–O(1), 161.8 (5). O_b ≡ bridging oxo groups within $\{Mo_3O_8(OMe)\}^{1+}$ subunit; O_b' ≡ bridging oxo group of $(MoO_4)^{2-}$ subunits.

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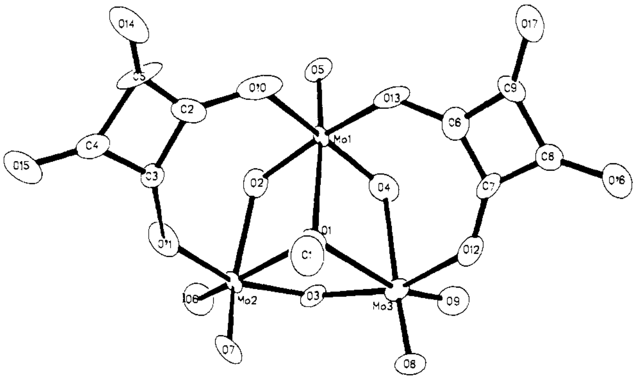

Figure 2. ORTEP view of the structure of $[\{Mo_3O_8(OCH_3)\}(C_4O_4)_2]^{3-}$ (II), showing the atom-labeling scheme.

$C_4H_9)_4N]_3[(MoO_4)_2\{Mo_3O_8(OMe)\}]$ (I). As anticipated, the coordinated $(MoO_4)^{2-}$ groups are readily displaced and reactions of I with squaric acid and pinacol yielded $[R_4N]_3[Mo_3O_8(OMe)(C_4O_4)_2]$ (II) and $[(n\text{-}C_4H_9)_4N]_2[Mo_3O_8(\text{pinacolate})_2]$ (III), respectively, whose structures are also reported herein.

The reaction of $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_7]$ with oxalic bis(cyclohexylidenehydrazide), $C_6H_{10}NNHC(O)C(O)NHNC_6H_{10}$, in CH_2Cl_2 followed by addition of ether/methanol afforded crystals of $[(n\text{-}C_4H_9)_4N]_3[(MoO_4)_2\{Mo_3O_8(OMe)\}]\cdot 0.5CH_2Cl_2$ (I) after standing for several hours.[11] The second crop of crystals, which formed over a period of 3 days, proved to be the carbonyl insertion product $[(n\text{-}C_4H_9)_4N]_3[Mo_4O_{15}(OH)(C_{14}H_{22}N_4)]$.

As shown in Figure 1, the structure of the pentamolybdate (I)[12] consists of a trinuclear core $[Mo_3O_8(OMe)]^+$ coordinated to two bidentate bridging $(MoO_4)^{2-}$ groups. The complex anion displays three distinct Mo coordination environments: Mo(4) and Mo(5) display pseudotetrahedral coordination; molybdenum centers Mo(2) and Mo(3) are pseudooctahedral cis dioxo sites with the usual two short–two long–two intermediate bond length pattern; while the Mo(1) center is unique, exhibiting coordination to a single terminal oxo group, to two bridging oxo groups from the tetrahedral Mo centers, to two bridging oxo groups within the central trinuclear core, and to the triply-bridging methoxy group.

The infrared spectrum of (I) is nearly identical in the 500–1000-cm^{-1} region with that reported for the underivatized pentamolybdate $[Mo_5O_{17}H]^{3-}$ indicating structural isomorphism, rather than a structure related to $[(CH_3)_2AsMo_4O_{15}H]^{2-}$[13] as originally suggested.[8] In contrast to the marked solution instability of $[Mo_5O_{17}H]^{3-}$, solutions of I in dichloroethane are stable for several hours as monitored by infrared. The lability of $[Mo_5O_{17}H]^{3-}$ is a consequence, in part, of facile deprotonation, followed by dissociation and reaggregation to more solution stable structures. The enhanced stability of I may be related to the substitution of the OH^- subunit by CH_3O^-. However, the presence of two weakly bound $(MoO_4)^{2-}$ groups implies that these subunits may be readily displaced by appropriate ligands in a fashion analogous to that observed for $[(MoO_4)_2\{Mo_2(OR)_2(NNR)_4\}]^{2-}$.[14]

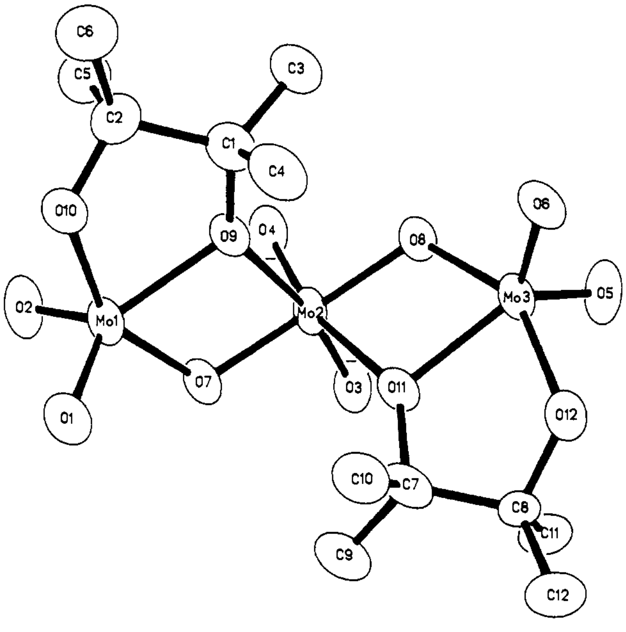

Figure 3. Perspective view of the structure of $[Mo_3O_8(C_6H_{12}O_2)_2]^{2-}$ (III), showing the atom-labeling scheme.

The bridging $(MoO_4)^{2-}$ units of I were readily replaced by squarate ligands in the presence of triethylamine to give $[(C_2H_5)_3NH]_3[Mo_3O_8(OMe)(C_4O_4)_2]$ (II),[15] a species which retains the $[Mo_3O_8(OMe)]^+$ core, as illustrated in Figure 2.[16] Although reminiscent of the well-documented trinuclear $[Mo_3O_4]^{4+}$ unit associated with Mo(IV) chemistry,[17] the $[Mo_3O_8(OMe)]^+$ core is a unique structural subunit in the chemistry of Mo(VI) polyoxoanions. The facile replacement of $(MoO_4)^{2-}$ by squarate may reflect analogous electronic and structural features of these subunits: both are dinegative anions capable of bidentate bridging or monodentate ligation modes, and the ligand "bite" distances are nearly identical at 3.10 Å. The analogy extends to several reported examples of structures exhibiting $(MoO_4)^{2-}$ subunits functioning as monodentate or bidentate ligands: $[Mo_2(OR)_2(NNR)_4(C_4O_4)_2]^{2-}$ may be prepared from $[\{Mo_2(OR)_2(NNR)_4\}(MoO_4)_2]^{2-}$ and $[Mo_4O_8(OCH_3)_2(HC_4O_4)_2(C_4O_4)_2]^{4-}$ from $[\{Mo_4O_8(OCH_3)_2\}(HMoO_4)_2(MoO_4)_2]^{4-}$.[18]

The direct displacement of $(MoO_4)^{2-}$ units without concomitant structural rearrangement appears to be a unique feature of squarate ligand chemistry. In contrast, the reactions of I with various dialcohols invariably result in some structural reorganization or even reaggregation. For example, reaction of I with pinacol in CH_2Cl_2 yields the crsytalline species $[(n\text{-}C_4H_9)_4N]_2[Mo_3O_8(\text{pinacolate})_2]$ (III),[19] whose structure is shown in Figure

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(11) A solution of oxalic bis(cyclohexylidenehydrazide) (0.706 g, 2.5 mmol) in CH_2Cl_2 (5 mL) was added to $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_7]$ (2.00 g, 2.5 mmol) in CH_2Cl_2 (50 mL). After overnight stirring at room temperature, colorless transparent crystals of I were obtained upon addition of diethyl ether. Recrystallization from CH_2Cl_2/methanol/ether (3:2:1) afforded crystals of block habit in 30% yield. IR (KBr pellet, cm^{-1}) 2970 (s), 2880 (s), 1487 (s), 1375 (m), 935 (s), 925 (vs), 786 (s), 740 (s), 687 (s), 560 (m), 362 (m). Anal. Calcd for $C_{49.5}H_{112}N_3O_{17}ClMo_5$: C, 38.7; H, 7.30; N, 2.74. Found: C, 38.4; H, 7.05; N, 2.85.

(12) Crystal data for I, $C_{49.5}H_{112}N_3O_{17}ClMo_5$: monoclinic space group Cc, $a = 29.396$ (5) Å, $b = 17.400$ (4) Å, $c = 17.649$ (4) Å, $\beta = 123.88$ (1)°, $V = 7495.4$ (18) Å^3, $Z = 4$, $D_{calcd} = 1.19$ g cm^{-3}. Structure solution and refinement based on 4622 reflections with $F_o \gtrsim 6\sigma(F_o)$ (5436 collected, Mo Kα), $\lambda = 0.71073$ Å) gave $R = 0.052$.

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(15) An excess of squaric acid (0.44 g, 3.8 mmol) was added to a solution of $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_7]$ (2.00 g, 2.5 mmol) and triethylamine (0.67 g, 8.0 mmol) in methanol (50 mL). After stirring for 6 h at room temperature, diethyl ether was carefully layered over the solution. Upon standing at room temperature for 2 days, needle-shaped orange crystals of II were obtained in 65% yield. Alternatively, squaric acid may be added to I in methanol and treated as above to give $[(n\text{-}C_4H_9)_4N]_3[Mo_3O_8(OCH_3)(C_4O_4)_2]$ (IIa) in 60–70% yield. IR (KBr, cm^{-1}) 2960 (m), 1800 (m), 1680 (s), 1560 (s), 1535 (s), 1450 (s), 1045 (m), 930 (s), 905 (s), 800 (m), 770 (s), 740 (m); ^{17}O NMR (δ, ppm) 421 (O_3), 610 (O_2,O_4), 905 and 960 (O_5 to O_9). Anal. Calcd for $C_{57}H_{111}N_3O_{17}Mo_3$ (IIa): C, 49.0; H, 8.02; N, 3.01. Found: C, 48.7; H, 8.14; N, 3.11.

(16) Crystal data for (II), $C_{27}H_{51}N_3O_{17}Mo_3$ at 173 K: rhombohedral space group $R3c$ (hexagonal setting), $a = b = 38.276$ (6) Å, $c = 25.515$ (5) Å, $V = 32372.5$ (22) Å^3, $Z = 18$. Structure solution and refinement based on 4505 reflections with $F_o \geq 6\sigma(F_o)$ (5722 collected, Mo Kα) converged at $R = 0.072$.

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3.[19] The oxo-bridged triangular core associated with I and II is not retained, and significant structural reorganization is required to produce the "open" trinuclear structure of the anion of III. A notable feature of this structure is the presence of five-coordinate molybdenum centers, Mo(1) and Mo(3), with geometries intermediate between the idealized square-pyramidal and trigonal-bipyramidal limits.

We are currently pursuing studies of the solution properties of the pentamolybdate (I) and of its potential applications as a synthetic precursor.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE8514634).

Registry No. I, 120904-99-6; II, 120881-76-7; IIa, 120881-80-3; III, 120881-78-9; $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_7]$, 64444-05-9; $C_6H_{10}NNHC(O)C(O)NHNC_6H_{10}$, 370-81-0.

Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, and thermal parameters for I, II, and III (18 pages); tables of observed and calculated structure factors (51 pages). Ordering information is given on any current masthead page.

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(19) Pinacol (1.18 g, 1.0 mmol) was added to a solution of I (6.50 g, 0.5 mmol) in CH_2Cl_2 (75 mL), and the solution was stirred for 24 h at room temperature. After addition of ether and standing for 5 days, colorless translucent crystals of III were obtained in 30% yield. IR (KBr, cm^{-1}) 2930 (s), 2865 (m), 1475 (m, br), 1375 (vs), 1075 (m), 1010 (s), 910 (sh), 900 (vs), 780 (s, br). Anal. Calcd for $C_{44}H_{96}N_2O_{12}Mo_3$: C, 46.7; H, 8.48; N, 2.47. Found: C, 46.4; H, 8.29; N, 2.36.

(20) Crystal data for (III), $C_{44}H_{96}N_2O_{12}Mo_3$: monoclinic space group $P2_1/n$, $a = 17.137$ (5) Å, $b = 17.513$ (5) Å, $c = 18.878$ (5) Å, $\beta = 91.01$ (2)°, $V = 5665.8$ (25) Å^3, $Z = 4$, $D_{calcd} = 1.33$ g cm^{-3}. Structure solution and refinement based on 4056 reflections with $F_o \geq 6\sigma(F_o)$ (7861 collected, Mo Kα) converged at $R = 0.064$.

Observation of a Stepwise Double Proton Transfer in Oxalamidine Which Involves Matched Kinetic HH/HD/DD Isotope and Solvent Effects

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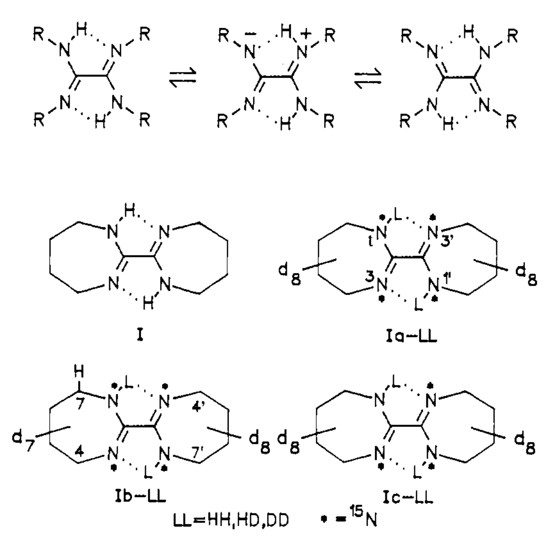

Figure 1. The stepwise double-proton-transfer in oxalamidine (OA, R = H), tetraphenyloxalamidine (TPOA, R = phenyl),[6] and I.[29]

The determination of kinetic HH/HD/DD isotope effects[1-5] is an important tool in the elucidation of the mechanisms of double-proton-transfer reactions.[1-28] Depending on the molecular reaction systems, smaller or larger deviations from the so-called rule of the geometric mean (RGM),[17,19] which states that the isotopic rate constants are related by $k^{HH}/k^{HD} = k^{HD}/k^{DD}$, have been observed.[1-5] These deviations were particularly strong in the case of the symmetric double proton transfer in porphyrine (POR)[1] and azophenine (AP),[4] where $k^{HH} > k^{HD} \simeq k^{DD}$. This finding was first interpreted in terms of a synchronous tunneling process.[1] It can, however, also be explained by formal kinetics in terms of two consecutive single proton-transfer steps via a metastable intermediate.[1,4] The proton in flight contributes a primary kinetic isotope effect P and the bound proton a secondary isotope effect S to the reaction rates according to[1,4]

$$k^{HH}/k^{DD} = P{\cdot}S,\ k^{HD}/k^{DD} = 2/(S^{-1} + P^{-1}),\ P \gg S \simeq 1 \quad (1)$$

Evidence for a stepwise double proton transfer in POR and AP has been obtained by theoretical calculations[24-28] and in the case of POR also by simulation of the Arrhenius curves with use of various tunnel models.[10,24,25] However, eq 1 is not able to describe

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