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# Alkaline-Earth-Metal Complexes of 1,4,8,11-Tetraazacyclotetradecane-1,4,8,11-tetraacetic Acid, $H_4TETA$, and Crystal and Molecular Structure of $H_4TETA \cdot 6H_2O$ and $[Mg(H_2TETA)(H_2O)_4] \cdot 4H_2O$

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*Received August 9, 1990*

The macrocycle 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetic acid, ($H_4TETA$), reacts with alkaline-earth-metal salts in aqueous solutions to form $M(H_2TETA) \cdot nH_2O$ ($M$ = Mg, $n = 2$ and 8; $M$ = Ca, $n = 2$; and $M$ = Sr, $n = 2$; pH = 6–8), and $Ca_2TETA \cdot 3H_2O$ (pH = 10). IR and NMR spectral studies are reported which show the presence of protonated N and deprotonated carboxylate in these compounds. Crystals suitable for diffraction studies were isolated for $H_4TETA \cdot 6H_2O$ (I) and $[Mg(H_2TETA)(H_2O)_4] \cdot 4H_2O$ (II) and their structures are reported. I crystallizes as $\{-NH(CH_2COO)-(CH_2)_2-N(CH_2COOH)-(CH_2)_3-\}_2 \cdot 6H_2O$ in monoclinic space group $P2_1/c$ with $a = 11.6212$ (6) Å, $b = 14.6659$ (8) Å, $c = 7.8199$ (4) Å, $\beta = 102.445$ (2)°, and $Z = 2$. II crystallizes as $[Mg\{-NH(CH_2COO)-(CH_2)_2-N(CH_2COO)-(CH_2)_3-\}_2(H_2O)_4]_n \cdot [4H_2O]_n$ in triclinic space group $P\bar{1}$ with $a = 8.2377$ (5) Å, $b = 10.0088$ (6) Å, $c = 9.8980$ (6) Å, $\alpha = 106.492$ (2)°, $\beta = 72.951$ (2)°, $\gamma = 113.542$ (2)°, and $Z = 1$. The structures of I and II were solved by direct methods and refined to $R = 0.059$ and $R = 0.036$, respectively. Discrete centrosymmetric molecules are present in I as dizwitterions, whereas II consists of chains of centrosymmetric ligands bridging Mg atoms (on inversion centers) via carboxylate O atoms. The macrocycle adopts the same rectangular [3434] conformation in both crystals. However, N atoms occupy different relative positions in I and II, showing that the conformational congruence of the rings is independent of heteroatom location.

## Introduction

The title ligand belongs to a novel class of macrocyclic compounds that contain a metal selective cavity.[1] Potential applications of these molecules include use as reagents for complexometric titrations,[2] models for ion transport in biological systems,[3] and tools in medicine.[4,5] The first reported synthesis of $H_4TETA$ and several other tetraazamacrocycle-*N,N′,N″,N‴*-tetraacetic acids[6] indicated that these ligands are powerful complexing agents for alkaline-earth-metal ions.[6,7] The exceptional selectivity of $H_4TETA$ for calcium and strontium over magnesium[2,6] led us to develop an amperometric method for the determination of alkaline-earth-metal ions based on this reagent.[8]

$H_4TETA$ is a remarkably flexible molecule that binds metal ions in a variety of ways. A detailed investigation of the solution chemistry of this polyamine polycarboxylic acid has shown that protonated as well as deprotonated species are involved in complexation equilibria.[2] The protonation scheme for $H_4TETA$ has been established,[9] and kinetic studies indicate that the presence of a proton near the coordination site can markedly decelerate the total coordination process.[10]

Mononuclear terbium(III)[11] and binuclear copper(II)[12,13] complexes of $H_4TETA$ have been structurally characterized. In both cases, the ligand is fully deprotonated and all eight ligating groups are utilized. On the other hand, in a related dimethylated TETA analogue,[14] it has been suggested that metal ions such as Co(II) and Ni(II) are not bound to all four N atoms as might be expected. Rather, two of the acetate groups and only two N atoms are coordinated to the metal ion. To further elucidate the coordination chemistry of $H_4TETA$, we have synthesized and characterized the alkaline-earth-metal compounds $M(H_2TETA) \cdot nH_2O$, where M = Mg, Ca, and Sr, and $Ca_2TETA \cdot 3H_2O$. Spectroscopic data for these compounds and the crystal structures of $H_4TETA \cdot 6H_2O$ and $[Mg(H_2TETA)(H_2O)_4] \cdot 4H_2O$ are reported here.

## Experimental Section

**Reagents.** The parent cyclic tetraamine cyclam was prepared as described earlier.[15] Reagent grade $CaCl_2$ (Aldrich), $MgCl_2 \cdot 6H_2O$ (Baker), and $SrCl_2 \cdot 6H_2O$ (Fisher) were used as received without further purification. Solutions were prepared with freshly distilled water, and reactions were carried out under an atmosphere of purified $N_2$.

**Measurements.** IR spectra were recorded on a Perkin-Elmer 1310 infrared spectrometer as Nujol mulls. $^1H$ and $^{13}C$ NMR spectra were recorded in $D_2O$ on a Varian VXR-300 NMR spectrometer equipped with a multinuclear probe at 299.94 and 75.43 MHz, respectively. All chemical shifts are referenced to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard. An Orion research pH meter, Model 701A, equipped with a combination microelectrode was used for pH measurements. Solution pD was calculated as pH + 0.4.[16] Conductivity measurements were made on a YSI conductivity bridge, Model 31, by using a Pyrex cell that had been calibrated with 0.001 M KCl. Elemental analysis for C, H, and N was performed by Micro-Tech, Inc., Skokie, IL. Metal ion analysis was accomplished by digesting a complex in 12 M $HNO_3$, dissolving the resultant metal oxide in 1 mL of 6 M HCl, adjusting solution pH to 10 by addition of 5 mL of $NH_3/NH_4Cl$ buffer, and titrating with EDTA using calmagite as the indicator.[17]

**Synthesis of $H_4TETA \cdot 6H_2O$.** The ligand was synthesized by reacting cyclam with chloroacetic acid in aqueous alkaline solution. A cold aqueous solution of NaOH (2.80 g, 70 mmol in 10 mL) was added dropwise with stirring to 10 mL of a cold aqueous solution of chloroacetic acid (2.50 g, 26 mmol). This reaction mixture was added dropwise with stirring to 20 mL of a cold aqueous solution of cyclam (1.00 g, 5.0 mmol). The resulting solution was filtered, transferred to a round-bottom flask, and heated on a water bath for 6 h at 80 °C. After the reaction mixture was cooled to room temperature, the pH was adjusted to 0.8 with 2 M HCl and then raised to 3.0 by addition of 2.0 M $NH_4OH$. The desired product was obtained as a white crystalline solid when the reaction mixture was allowed to stand overnight at −4.0 °C. The solid was collected by filtration, washed with several small portions of water, and air-dried. Yield: 69% (1.50 g, 3.47 mmol). Decomposition temperature: 307-309 °C (lit. 313 °C).[2]

Purification of $H_4TETA$ was achieved by dissolving the ligand in a minimum amount of 1.0 M HCl and precipitating it at the isoelectric point. A quantity of $H_4TETA$ (1.50 g, 3.47 mmol) was dissolved in 1.0 M HCl and the pH adjusted to 3.0 with 1.0 M $NH_4OH$. Large crystals of $H_4TETA \cdot 6H_2O$ formed when the reaction mixture was allowed to

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**Table I.** Crystallographic Data

| | I | II |
|---|---|---|
| chem formula | $C_{18}H_{44}N_4O_{14}$ | $C_{18}H_{46}MgN_4O_{16}$ |
| fw | 540.6 | 598.9 |
| space group | $P2_1/c$ (No. 14) | $P\bar{1}$ (No. 2) |
| $a$, Å | 11.6212 (6) | 8.2377 (5) |
| $b$, Å | 14.6659 (8) | 10.0088 (6) |
| $c$, Å | 7.8199 (4) | 9.8980 (6) |
| $\alpha$, deg | 90 | 106.492 (2) |
| $\beta$, deg | 102.455 (2) | 72.951 (2) |
| $\gamma$, deg | 90 | 113.542 (2) |
| $V$, Å$^3$ | 1301.5 (1) | 702.2 (1) |
| $T$, °C | 22 | 22 |
| $\lambda$, Å | 1.5418 | 1.5418 |
| $Z$ | 2 | 1 |
| $\rho_{obsd}$, g·cm$^{-3}$; $\rho_{calcd}$, g·cm$^{-3}$ | 1.37 (2); 1.38 | 1.41 (2); 1.39 |
| $\mu$, cm$^{-1}$ | 13.1 | 11.6 |
| transm factors | 1.00–0.88 | 1.00–0.91 |
| $R$ | 0.059 | 0.036 |
| $R_w$ | 0.083 | 0.046 |

stand overnight at −4.0 °C. Anal. Calcd for $C_{18}H_{44}N_4O_{14}$: C, 40.00; H, 8.15; N, 10.37; $H_2O$, 20.0. Found: C, 40.87; H, 8.00; N, 10.59; $H_2O$ (by mass loss at 120 °C), 19.7.

**Preparation of $MgH_2TETA·nH_2O$, $n = 2, 8$.** A solution of $H_4TETA$ (432 mg, 1.00 mmol) in 15 mL of 0.1 M NaOH was added dropwise to a stirred solution of $MgCl_2·6H_2O$ (203 mg, 1.00 mmol) in 5.0 mL of water. The pH of the reaction mixture was raised to 8.7 with 0.1 M NaOH, and the resulting solution was heated on a water bath for 12 h at 80 °C. The solution volume was reduced to 5.0 mL and white crystals formed when the solution was allowed to stand at room temperature. The crystals were collected by filtration and washed twice with cold water. Yield: 79% (380 mg, 0.79 mmol). The compound was recrystallized by dissolving it in a minimum amount of water (pH ~ 6.0) and allowing the saturated solution to evaporate slowly at room temperature over a period of several days. The dihydrate was obtained upon air drying overnight at 80 °C. Anal. Calcd for $MgC_{18}H_{34}N_4O_{10}$: C, 44.05; H, 6.93; N, 11.42; Mg, 4.96. Found: C, 44.56; H, 6.85; N, 11.47; Mg, 5.05.

The crystal of $MgH_2TETA·8H_2O$ used for the X-ray analysis was obtained as described above except that drying was accomplished at room temperature. A phase that crystallized at higher pH also grew into well-formed crystals, but these crystals lost crystallinity upon standing in air even for short periods of time.

**Synthesis of $CaH_2TETA·2H_2O$ and $SrH_2TETA·2H_2O$.** These compounds were prepared as described above by substituting $CaCl_2$ or $SrCl_2$ for $MgCl_2$ and carrying out the reaction at pH 6.0 and 7.5, respectively. The complexes were recrystallized from water and air-dried at 80 °C. X-ray quality crystals of these compounds were not obtained under various drying conditions. Yields were 65%. Anal. Calcd for $CaC_{18}H_{34}N_4O_{10}$: C, 42.68; H, 6.72, N, 11.07; Ca, 7.98. Found: C, 42.38, H, 6.58; N, 10.97; Ca, 8.35. Anal. Calcd for $SrC_{18}H_{34}N_4O_{10}$: C, 39.02; H, 6.14; N, 10.12. Found: C, 39.33; H, 6.06; N, 10.32.

**Synthesis of $Ca_2TETA·3H_2O$.** A solution of $H_4TETA$ (432 mg, 1.0 mmol) in 15 mL of 0.1 M NaOH was added dropwise to a stirred solution of $CaCl_2$ (532 mg, 2.0 mmol) in 5.0 mL of water at room temperature. After the pH of the reaction mixture was adjusted to 10.2 with 0.1 M NaOH, the solution was heated on a water bath at 80 °C with stirring for 12 h. The solution volume was reduced to 5.0 mL, and a white solid precipitated when the solution was allowed to stand overnight at −4.0 °C. The solid was collected by filtration, washed with several portions of water, and dried overnight at 120 °C. Recrystallization from water at pH 10.5 afforded the compound as a white microcrystalline solid. Yield before recrystallization: 74.7% (420 mg, 0.75 mmol). Anal. Calcd for $Ca_2C_{18}H_{34}N_4O_{11}$: C, 38.42; H, 6.04; N, 9.96; Ca, 14.26. Found: C, 39.08; H, 6.10; N, 10.16; Ca, 14.33.

**Crystallography.** X-ray diffraction data were measured on a modified four-circle Picker diffractometer using Ni-filtered Cu radiation, $\lambda$ = 1.5418 Å, without a monochromator. Lattice parameters were determined at 22 °C from $\pm 2\theta$ scans of 18 reflections (for I) and 26 reflections (for II) ranging from 60 to 70°. Intensity data were collected by the $\theta$–$2\theta$ scan method with $2\theta$ ranging from −65 to 120°. Crystal decay was checked by monitoring intensities of four standard reflections and was found to be negligible. Empirical corrections for absorption were applied based on $\phi$ scan data taken at $\chi$ = 90°. Intensities were considered to be observed for reflections with $I > 3\sigma(I)$. The distribution of intensities for II suggested a centrosymmetric structure so determination was initiated in space group $P\bar{1}$. The successful solution of II in $P\bar{1}$ supports that assignment. The structures were solved by direct methods (MULTAN)[18] and refined by least-squares methods (SHELX76).[19] Scattering

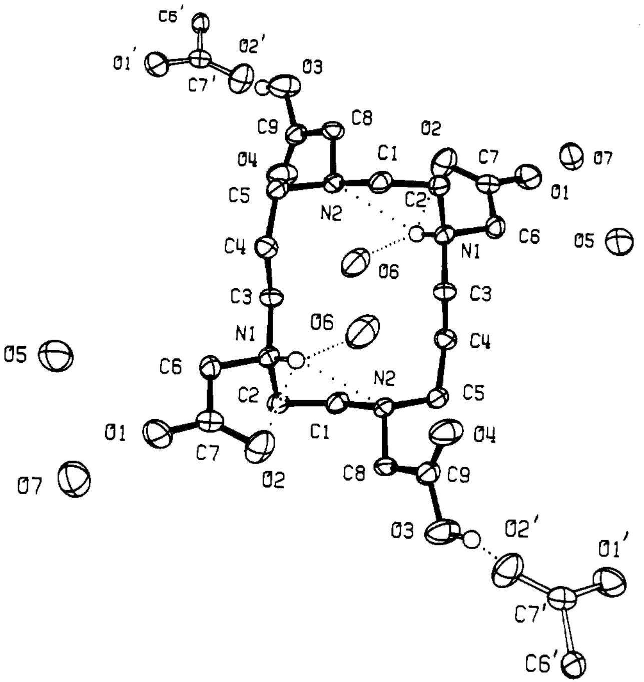

**Figure 1.** ORTEP plot of $H_4TETA·6H_2O$, structure I, with 50% probability thermal ellipsoids. Only hydrogen atoms bonded to N(1) and O(3) are shown. Hydrogen bonds are indicated by dotted lines and atoms from adjacent molecules have primed labels.

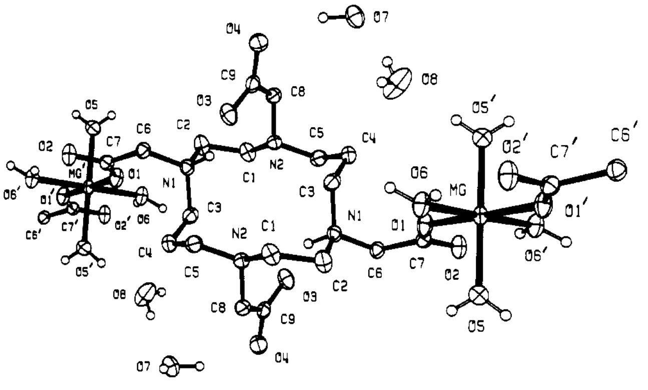

**Figure 2.** ORTEP plot of $[Mg(H_2TETA)(H_2O)_4]·4H_2O$, structure II, with 40% probability thermal ellipsoids. Only hydrogen atoms bonded to N and O are shown. Atoms not contiguous to a single formula unit are labeled with primes.

factors and anomalous dispersion corrections were taken from ref 20. Additional crystallographic information is shown in Table I. Methylene H atoms were placed in idealized positions ($d$(C–H) = 0.95 Å) and given fixed isotropic temperature factors of 0.040 Å$^2$ in both structures. Only non-methylene H atoms bonded to N(1) and carboxylate O(3) atoms were found in electron density difference maps of structure I, and their coordinates and a common temperature factor were refined. Subsequent difference maps for structure I were featureless so H atoms from water were not located. In structure II all non-methylene H atoms were located and refined with fixed temperature factors of 0.050 Å$^2$. Final values of refined coordinates for I and II are listed in Tables II and III respectively, and selected bond distances and torsion angles are listed in Table V. Table VI contains information on H bonding for the two structures. Figures 1 and 2 show ORTEP[21] diagrams of the structures, and Figure 3 is an ORTEP diagram of the H bonding scheme for II.

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**Table II.** Final Atomic Coordinates (×$10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $H_4TETA·6H_2O$ (I)

| atom[a] | $x$ | $y$ | $z$ | $U_{eq}$[b,c] |
|---|---|---|---|---|
| O(1) | 4068 (3) | 2400 (1) | 2166 (2) | 43 (2) |
| O(2) | 1887 (3) | 1383 (2) | 1727 (2) | 46 (2) |
| O(3) | 2597 (3) | 236 (1) | 10241 (2) | 46 (2) |
| O(4) | 990 (3) | 957 (1) | 8707 (2) | 46 (2) |
| O(5) | 6474 (4) | 3311 (1) | 3972 (2) | 58 (3) |
| O(6) | 1882 (3) | −571 (2) | 3212 (2) | 55 (3) |
| O(7) | 6649 (3) | 2225 (1) | 5922 (2) | 48 (2) |
| N(1) | 1317 (3) | 1332 (1) | 3940 (2) | 24 (2) |
| N(2) | 1948 (3) | −344 (1) | 7161 (2) | 23 (2) |
| C(1) | −1983 (3) | 1209 (2) | 3478 (2) | 27 (2) |
| C(2) | −399 (3) | 1810 (2) | 3481 (2) | 26 (2) |
| C(3) | 1586 (3) | 1120 (2) | 5235 (2) | 26 (2) |
| C(4) | 3242 (3) | 574 (2) | 5695 (2) | 29 (2) |
| C(5) | 3372 (3) | 249 (2) | 6966 (2) | 28 (2) |
| C(6) | 2774 (3) | 1916 (2) | 3694 (2) | 29 (2) |
| C(7) | 2906 (3) | 1896 (2) | 2400 (2) | 29 (2) |
| C(8) | 2227 (3) | −513 (2) | 8433 (2) | 26 (2) |
| C(9) | 1857 (3) | 323 (2) | 9116 (2) | 28 (2) |
| H(1) | −2164 | 1057 | 4452 | 40 |
| H(2) | −2902 | 1530 | 3072 | 40 |
| H(3) | −471 | 2397 | 4030 | 40 |
| H(4) | −437 | 2031 | 2589 | 40 |
| H(5) | 1666 | 1753 | 5717 | 40 |
| H(6) | 478 | 731 | 5378 | 40 |
| H(7) | 3247 | −13 | 5137 | 40 |
| H(8) | 4362 | 998 | 5666 | 40 |
| H(9) | 3392 | 846 | 7513 | 40 |
| H(10) | 4588 | −118 | 7236 | 40 |
| H(11) | 2549 | 2611 | 3930 | 40 |
| H(12) | 3997 | 1676 | 4228 | 40 |
| H(13) | 1368 | −1057 | 8579 | 40 |
| H(14) | 3572 | −715 | 8758 | 40 |
| H(15) | 1335 (44) | 821 (26) | 3541 (30) | 54 (7) |
| H(16) | 2417 (47) | 748 (25) | 694 (32) | 54 (7) |

[a] H(1) through H(14) are bonded in successive pairs to C(1) through C(6) and C(8). Their positions were calculated and not refined. H(15) and H(16) are bonded to N(1) and O(3) respectively, and their coordinates were refined. [b] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$. [c] H(1) through H(14) have fixed isotropic temperature factors. A common temperature factor was assigned to H(15) and H(16) and refined.

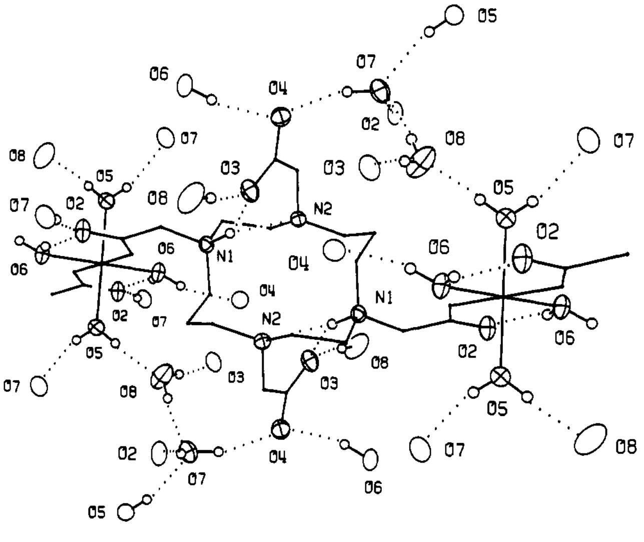

Figure 3. ORTEP plot of the hydrogen-bonding scheme for $[Mg(H_2TETA)(H_2O)_4]·4H_2O$, structure II, with 40% probability thermal ellipsoids. The main formula unit has the same orientation as in Figure 2 and atoms not participating in H bonding have been reduced to points. Participant atoms outside of the main formula unit are drawn so their ellipsoids only show an outer border envelope. Hydrogen bonds are indicated by dotted lines.

**Table III.** Final Atomic Coordinates (×$10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $MgH_2TETA·8H_2O$ (II)

| atom[a] | $x$ | $y$ | $z$ | $U_{eq}$[b] |
|---|---|---|---|---|
| Mg | 0 | 0 | 0 | 23 (1) |
| O(1) | 2264 (2) | 1236 (2) | 806 (2) | 32 (2) |
| O(2) | 4707 (2) | 1237 (2) | −918 (2) | 36 (2) |
| O(3) | 7276 (2) | 3284 (2) | 3894 (2) | 39 (2) |
| O(4) | 8060 (2) | 1929 (2) | 4850 (2) | 48 (2) |
| O(5) | −205 (3) | 1893 (2) | −280 (2) | 46 (2) |
| O(6) | −1563 (2) | 201 (2) | 2066 (2) | 33 (2) |
| O(7) | 8319 (3) | 2403 (2) | 7756 (2) | 41 (2) |
| O(8) | 91 (4) | 4363 (3) | 1756 (3) | 57 (3) |
| N(1) | 4247 (3) | 2806 (2) | 2941 (2) | 28 (2) |
| N(2) | 4064 (2) | 2985 (2) | 5889 (2) | 26 (2) |
| C(1) | 2424 (3) | 2130 (3) | 5309 (3) | 35 (2) |
| C(2) | 2875 (3) | 1568 (3) | 3704 (2) | 35 (3) |
| C(3) | 3437 (3) | 3942 (2) | 3044 (3) | 33 (2) |
| C(4) | 4630 (4) | 5112 (3) | 2126 (3) | 40 (3) |
| C(5) | 3662 (4) | 3807 (3) | 7352 (3) | 34 (3) |
| C(6) | 5123 (3) | 2221 (3) | 1459 (2) | 29 (2) |
| C(7) | 3921 (3) | 1513 (2) | 363 (2) | 26 (2) |
| C(8) | 5138 (3) | 2075 (3) | 5785 (2) | 31 (2) |
| C(9) | 6995 (3) | 2496 (3) | 4775 (2) | 30 (2) |
| H(1) | 1647 | 1195 | 5839 | 40 |
| H(2) | 1634 | 2832 | 5511 | 40 |
| H(3) | 3426 | 701 | 3513 | 40 |
| H(4) | 1655 | 1127 | 3283 | 40 |
| H(5) | 2162 | 3378 | 2697 | 40 |
| H(6) | 3205 | 4495 | 4154 | 40 |
| H(7) | 3795 | 5754 | 2216 | 40 |
| H(8) | 4897 | 4697 | 1101 | 40 |
| H(9) | 2914 | 4281 | 7319 | 40 |
| H(10) | 2954 | 3205 | 8104 | 40 |
| H(11) | 6253 | 3135 | 1063 | 40 |
| H(12) | 5609 | 1399 | 1542 | 40 |
| H(13) | 5338 | 2188 | 6848 | 40 |
| H(14) | 4382 | 931 | 5397 | 40 |
| H(15) | 5206 (37) | 3217 (30) | 3538 (29) | 50 |
| H(16) | −514 (40) | 1915 (32) | −955 (31) | 50 |
| H(17) | −34 (38) | 2708 (33) | 295 (32) | 50 |
| H(18) | −1436 (36) | 981 (30) | 2790 (29) | 50 |
| H(19) | −2571 (42) | −134 (33) | 1997 (30) | 50 |
| H(20) | 8309 (36) | 2065 (30) | 6806 (29) | 50 |
| H(21) | 7294 (42) | 2027 (33) | 8118 (31) | 50 |
| H(22) | −751 (42) | 4124 (32) | 2436 (31) | 50 |
| H(23) | 441 (39) | 5259 (33) | 1847 (30) | 50 |

[a] H(1) through H(14) are bonded in successive pairs to C(1) through C(6) and C(8). Their positions were calculated and not refined. H(15) is bonded to N(1), and H(16) through H(23) are bonded in successive pairs to O(5) through O(8) respectively, and these H coordinates were refined. [b] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$, except for H atoms, which have fixed isotropic factors.

**Table IV.** Infrared Absorption Bands ($cm^{-1}$)[a,b]

| $H_4TETA$[c] | $MgH_2TETA·8H_2O$ | $CaH_2TETA·2H_2O$ | $SrH_2TETA$[c] | assignt |
|---|---|---|---|---|
| 2500 m, br | 2640 m, br | 2580 m, br | 2610 m, br | $-NH^+$ comb |
| 1732 vs | | | | |
| 1720 sh | | | | –COOH str |
| 1630 s, br | | | | |
| | 1620 vs | 1625 s | 1605 s | $-COO^-$ str |
| | 1590 s | 1575 s | 1588 vs | |

[a] Recorded as Nujol mulls. [b] Key: w, weak; m, medium; s, strong; vs, very strong; br, broad; comb, intercombination band; str, stretch. [c] Dried at 120 °C.

## Results

Alkaline-earth-metal complexes of $H_4TETA$ were obtained as white polycrystalline solids when stoichiometric quantities of ligand and metal chloride were mixed in approximately neutral (pH 6.0–8.0) aqueous solution. The predominate ligand species in these solutions is the diprotonated form of the acid,[2] and the empirical formula of isolated solids is $MH_2TETA·2H_2O$. Neutral complexes of this stoichiometry were expected although protonated complexes of this type for the alkaline-earth-metal ions have not been observed in solution.[2] The hydrates are insoluble in most organic solvents and readily lose water above room temperature. A change in the drying procedure for the Mg product resulted in crystals of $Mg(H_2TETA)·8H_2O$ suitable for diffraction studies.

**Table V.** Selected Bond Distances (Å) and Torsion Angles (deg) for $H_4TETA\cdot6H_2O$ (I) and $MgH_2TETA\cdot8H_2O$ (II)

| | | | |
|---|---|---|---|
| Compound I | | | |
| O(1)–C(7) | 1.246 (3) | N(1)–C(3) | 1.507 (3) |
| O(2)–C(7) | 1.242 (3) | N(1)–C(6) | 1.501 (3) |
| O(3)–C(9) | 1.317 (3) | N(2)–C(1) | 1.472 (3) |
| O(4)–C(9) | 1.189 (3) | N(2)–C(5) | 1.469 (3) |
| N(1)–C(2) | 1.507 (3) | N(2)–C(8) | 1.468 (3) |
| N(2)–C(1)–C(2)–N(1) | 54.4 | N(1)–C(3)–C(4)–C(5) | 172.1 |
| C(1)–C(2)–N(1)–C(3) | 67.5 | C(3)–C(4)–C(5)–N(2) | −60.1 |
| C(2)–N(1)–C(3)–C(4) | −175.6 | C(4)–C(5)–N(2)–C(1) | −64.8 |
| | | C(5)–N(2)–C(1)–C(2) | 171.2 |
| Compound II | | | |
| Mg–O(1) | 2.028 (2) | N(1)–C(2) | 1.515 (3) |
| Mg–O(5) | 2.069 (2) | N(1)–C(3) | 1.500 (3) |
| Mg–O(6) | 2.076 (2) | N(1)–C(6) | 1.498 (3) |
| O(1)–C(7) | 1.245 (3) | N(2)–C(1) | 1.463 (3) |
| O(2)–C(7) | 1.252 (3) | N(2)–C(5) | 1.464 (3) |
| O(3)–C(9) | 1.250 (3) | N(2)–C(8) | 1.470 (3) |
| O(4)–C(9) | 1.248 (3) | | |
| N(2)–C(1)–C(2)–N(1) | 49.2 | N(1)–C(3)–C(4)–C(5) | 69.9 |
| C(1)–C(2)–N(1)–C(3) | 66.4 | C(3)–C(4)–C(5)–N(2) | 59.0 |
| C(2)–N(1)–C(3)–C(4) | 171.8 | C(4)–C(5)–N(2)–C(1) | −170.7 |
| | | C(5)–N(2)–C(1)–C(2) | 167.2 |

A calcium compound of stoichiometry $Ca_2TETA\cdot3H_2O$ was obtained from strongly basic solutions of $H_4TETA$ containing 2 equiv of calcium ion. Consistent with a formulation in which all acidic functionalities of the ligand are deprotonated, the infrared spectrum of this calcium complex shows no absorption bands attributable to $-NH^+$ or $-COOH$ groups. In the carboxylate region of the spectrum, only a single strong broad absorption band attributable to ionized and/or complexed carboxylate appears at 1590 $cm^{-1}$. While it is likely that N is coordinated to calcium in this compound,[2,10] we have been unable to obtain suitable crystals to confirm this crystallographically.

**Infrared Spectra.** A partial listing of the infrared spectra of $H_4TETA$ and the alkaline-earth-metal compounds are given in Table IV. The compounds exhibit two strong bands in the carbonyl region and a characteristic $-NH^+$ intercombination band. Carbonyl group frequencies for polyamino polycarboxylic acids have been established by Nakamoto,[22] and while it is not possible to differentiate unambiguously between free and coordinated carboxylate groups, it is clear from the data that all carboxylic groups are deprotonated in the alkaline-earth-metal compounds. The carboxylate groups are not equivalent, and the higher carbonyl frequencies may signify coordination to metal. Similar spectra obtained for these compounds suggest that similar modes of carboxylate coordination are present in all cases. The spectra indicate the presence of protonated N, but do not provide information about N coordination. In view of the structure of II, it appears unlikely that the N atoms are bonded to the metal ion.

**NMR Spectra.** The $^1H$ NMR spectra of the alkaline-earth-metal compounds in $D_2O$ show the same number of resonances at approximately the same chemical shifts, intensities, and splitting patterns as the free ligand. The assignment of peaks is relatively straightforward from their relative intensities and splitting patterns.[9] The resonance of the methylene $\beta$-protons of the propylene chain appears as a quintuplet (4 H) at $\delta$ 1.8–1.9 while the $\alpha$-protons appear as a triplet (8 H) at $\delta$ 3.04–3.14. The ethylenic protons give rise to a singlet (8 H) at $\delta$ 3.10–3.20. The methylene protons of the acetate group also give rise to a singlet (8 H) at $\delta$ 3.40–3.54.

The $^{13}C$ NMR spectra of the compounds show a pH dependency, but when recorded at the same pH, the spectra of free ligand and complexes are nearly identical. Above pH 5.0, only four lines are observed in the $^{13}C$ spectra of these compounds. The lowest field resonance at $\delta$ ~178 is assigned to the carboxylate carbon of the acetate group while the methylene carbon of this group appears at $\delta$ ~59. The methylene carbons $\alpha$ to nitrogen appear at $\delta$ ~54.7 and those $\beta$ to nitrogen are at $\delta$ ~25.4. At lower pH, two separate resonances are observed for the $\alpha$-carbons.

Species in solution are undergoing rapid exchange on the NMR time scale, and it was not possible to slow this exchange sufficiently at 5 °C to observe signals for discrete entities. Alkaline-earth-metal complexes are expected to be labile, and the TETA ligand would be involved in rapid protonation equilibria as well as interconversion between different ring conformations. In a series of experiments, solutions containing equimolar mixtures of free ligand and complex were recorded over the pH range 4.0–9.0. In all cases, separate signals for ligand and complex were not observed. We were also unable to observe separate signals for coordinated and free carboxylate groups as reported for nonlabile lanthanide complexes of TETA.[23] On the basis of these observations, it is not possible to obtain definitive structural information about the species in solution, but the concentration of a neutral $MH_2TETA$ complex must be quite low. Conductivity measurements indicate that these compounds are strong electrolytes ($\Lambda \sim 125\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$) in solution.

**Crystal Structures.** Figure 1 shows the structure of I and part of the H bonding scheme. The macrocyclic ring is centered on a crystallographic inversion site so only half of the atoms in the formula are unique, the other half being symmetry related. The ring adopts a rectangular [3434] conformation[24] where C(2) and C(5) mark corner positions. The acetate groups extend laterally from the ring, and water molecules O(6) occupy prominent positions above and below the ring opening. Amine N(1) and carboxylate O(3) are protonated while amine N(2) and the remaining carboxylate O atoms are not. This feature is duplicated by symmetry and functions to make I a molecular dizwitterion. The protonation of N(1) results in longer C to N(1) bond lengths as compared to C to unprotonated N(2) bond lengths (Table V). The protonation of O(3) results in a longer C(9)–O(3) bond and a shorter C(9)–O(4) bond as compared to the two remaining carboxylate O atoms bonded to C(7), which have intermediate bond lengths. The proton on O(3) is strongly H bonded to O(2)′ [at *x*, *y*, 1 + *z*] from an adjacent molecule and acts to knit the molecular units together laterally. The proton on N(1) has a more complex H bonding pattern in that it services a triad of atoms [O(2), O(6) and N(2) at -*x*, -*y*, 1 − *z*]. This is denoted by dotted lines in Figure 1, and the various parameters are listed in Table VI.

Subsequent electron density difference maps for I did not reveal positions of water H atoms, and disordered water molecules might be the cause. However, a complete H-bonding scheme can be developed on the basis of nearest non-H neighbor contacts and geometry. For example, water O(6) has contact distances that are less than 3 Å to N(1), O(4) [at -*x*, -*y*, 1 − *z*] and O(7)′ [at 1 − *x*, -*y*, 1 − *z*] (Figure 1). Atom O(7)′ is not shown in Figure 1 at this position because it covers other atoms. These four atoms are almost coplanar, and angles about O(6) as vertex average 118 ± 20°. In addition, the proton from N(1) is 2.318 (4) Å distant from O(6) and the N(1)–H(15)–O(6) angle is 158.6 (4)°. It is concluded that O(6) participates in three H bonds, accepting one from N(1) and donating two to O(4) and O(7)′. Similarly, very reasonable H-bonding assignments can be made for all other water molecules so disorder is not necessarily present in I. The complete H-bonding scheme is tabulated to Table VI.

Figure 2 shows the structure of II. In this structure, the macrocyclic ring is centered on an inversion site and Mg lies directly on an inversion center. Thus only half of the atoms in the formula are unique, the other half being symmetry related. The macrocyclic ring has the same sequence of torsion angles as found in structure I (see Table II) so a [3434] conformation is present here as well. However, C(2) and C(4) mark corner positions in II so that the N atoms are at different relative locations as compared to structure I. The orientations of the acetate groups (relative to the ring) also change so that one group extends laterally

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**Table VI.** Hydrogen-Bonding Scheme for $H_4TETA \cdot 6H_2O$ (I) and $MgH_2TETA \cdot 8H_2O$ (II)

| D | H | A | D–H[a] | D··A[a] | H··A[a] | D–H··A[b] | sym transformation |
|---|---|---|---|---|---|---|---|
| Compound I | | | | | | | |
| N(1) | H(15) | O(2) | 0.883 | 2.704 | 2.388 | 101.39 | |
| | | N(2) | | 2.976 | 2.618 | 105.33 | $-x, -y, 1 - z$ |
| | | O(6) | | 2.978 | 2.138 | 158.61 | |
| O(3) | H(16) | O(2) | 0.946 | 2.557 | 1.641 | 161.69 | $x, y, 1 + z$ |
| O(5) | | O(1) | | 2.834 | | | |
| | | O(3) | | 3.008 | | | $1 - x, {}^1/_2 + y, {}^3/_2 - z$ |
| O(6) | | O(7) | | 2.777 | | | $1 - x, -y, 1 - z$ |
| | | O(4) | | 2.859 | | | $-x, -y, 1 - z$ |
| O(7) | | O(5) | | 2.751 | | | |
| | | O(1) | | 2.780 | | | $x, {}^1/_2 - y, {}^1/_2 + z$ |
| Compound II | | | | | | | |
| N(1) | H(15) | O(3) | 1.009 | 2.742 | 1.812 | 151.46 | |
| | | N(2) | | 2.835 | 2.281 | 113.21 | |
| O(5) | H(16) | O(7) | 0.790 | 2.820 | 2.057 | 162.36 | $x - 1, y, z$-1 |
| | H(17) | O(8) | 0.838 | 2.658 | 1.853 | 171.97 | |
| O(6) | H(18) | O(4) | 0.892 | 2.811 | 1.987 | 152.99 | $x - 1, y, z$ |
| | H(19) | O(2) | 0.777 | 2.807 | 2.081 | 155.59 | $-x, -y, -z$ |
| O(7) | H(20) | O(4) | 0.905 | 2.837 | 1.967 | 160.47 | |
| | H(21) | O(2) | 0.793 | 2.783 | 1.991 | 175.66 | $x, y, 1 + z$ |
| O(8) | H(22) | O(3) | 0.823 | 2.728 | 1.911 | 171.75 | $x - 1, y, z$ |
| | H(23) | O(7) | 0.811 | 2.920 | 2.116 | 170.54 | $1 - x, 1 - y, 1 - z$ |

[a] Distances in angstrom units. [b] Angles in degrees.

and bonds to Mg through O(1), while the other group is more normal to the ring. The bonding to Mg results in chains of alternating Mg and ring units running through the crystal. Two water molecules, O(5) and O(6), complete the coordination sphere about the centrosymmetric Mg and cause a compressed pseudooctahedral arrangement.

Positions of all H atoms bonded to N and O in II were revealed in subsequent electron density difference maps. N(1) is protonated, and as in I, N(1) has longer bonds to C than does unprotonated N(2) (Table V). None of the carboxylate O atoms are protonated, and all have identical C–O bond lengths. The complete H-bonding network of II is illustrated in Figure 3 and tabulated in Table VI. Note that O(1), which is bonded to Mg, does not participate in this scheme, that O(7) takes part in four H bonds, and that the proton from N(1) makes a bifurcated intramolecular H bond to the carboxylate O(3) and to the adjacent N(2).

## Discussion

Force field calculations for 14-member rings show that two conformations of similar strain enthalpies are possible.[25] These are designated as [3434] or [77] according to the sequence of torsion angles.[24] I and II have the [3434] conformation, and the most significant difference in the structures is the relative location of heteroatoms in the rings. A similar comparison can be made between TETA in its terbium(III) complex[11] and the macrocyclic polyether 1,4,8,11-tetraoxacyclotetradecane,[26] which have the [77] conformation. Apart from the location of the heteroatoms, there are only minor differences in ring conformation. In the Tb complex, all N and acetate groups of TETA are coordinated, and all acetate groups are on the same side of the plane defined by N atoms.[11] These structures, plus that reported for a binuclear copper TETA complex,[12,13] demonstrate the remarkable flexibility of this ligand and the rich variety of coordination modes it can assume. The [3434] conformation may be preferred when the macrocyclic portion of TETA is not coordinated to a metal ion.

The H bonding schemes of I and II have important similarities. In both structures, the protonated amine N(1) makes an intramolecular H bond to N(2). In both structures, N(1) also makes a second H bond to an O atom. In the case of I, the O atom is water O(6), which is positioned above and below the ring opening. In the case of II, the O atom is intramolecular carboxylate O(3), which is similarly positioned above and below the ring opening. The geometry of this H-bonded trio of N(1), N(2), and the O atom is very similar in both structures and implies that it is an important feature for the development of the crystal. In structure II the remaining carboxylate group is bonded to Mg, and this results in chains of centrosymmetric ligands bridging Mg atoms. In structure I the two unique carboxylate groups are H bonded intermolecularly, and this results in chains of centrosymmetric ligands bridged by H bonds. These parallel conditions in H bonding may be the reason why the macrocycle adopts the same conformation in both structures.

Titration curves for $H_4$TETA and its complexes indicate that acidic protons are lost first from trans acetic acid moieties pendent to unprotonated N atoms. Subsequent protons are lost from protonated trans N atoms.[9] Our infrared data and structural results verify this ionization sequence. NMR studies further indicate that two N atoms of the TETA macrocycle are essentially unprotonated in acidic media.[9] An important question to be answered is whether their very low basicity is due to participation in H bonding, electrostatic repulsions, or some combination of these. The unprotonated amine in structure I is N(2). It occupies a crowded site in the molecule where it has three nonbonded neighbor atoms closer than 3 Å [H(15), N(1), and O(4)] and two more closer than 3.3 Å [C(3) and O(6)] (Figure 1). Given the number of close neighbor atoms about N(2) plus the H bond to H(15), its basicity can not be tied to any single factor but seems to be dependent on several competing factors.

The coordination of TETA to Mg in structure II occurs exclusively through the carboxylate groups and does not involve N atoms from the ring. This is not unexpected because in complexes of metal ions such as Mg(II) the binding is predominately electrostatic and interactions between M and N are generally weak. An additional factor to be associated with the exo-annular coordination of Mg is H bonding. Note in Figure 3 that there is an intramolecular H bond between protonated N(1) and acetate O(3). O(3) is part of the uncomplexed carboxylate group pendent to N(2). This places acetate groups above and below the ring and sterically restricts access to its internal cavity. The ring opening is further obstructed by H bonds between water O(6) and acetate O(4) [at $x - 1, y, z$] from an adjacent macrocycle. In view of this steric hinderance, coupled with the protonation of two amines, it is not surprising that coordination of TETA to Mg occurs exclusively through the carboxylate groups.

The monoprotonated form of TETA is several orders of magnitude more reactive than higher protonated species. The low reactivity of the diprotonated ligand has been attributed to a combination of the presence of a proton near the active site and strict conformational requirements for coordination.[10] Kinetic

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data also indicate that formation of metal complexes of macrocyclic ligands containing pendent acetate arms involves a rapid preequilibrium established through coordination to a carboxylate group. The structure of $[Mg(H_2TETA)(H_2O)_4]\cdot 4H_2O$ reported here may be representative of this type of kinetic species.

**Acknowledgment.** M.R.M. is grateful for support as a Searle Postdoctoral Fellow, and E.J.Z., for support as a Loyola University Dissertation Fellow.

**Supplementary Material Available:** Tables listing anisotropic temperature factors, additional crystallographic information, and bond distances and angles for I and II (7 pages); tables of calculated and observed structure factors for I and II (21 pages). Ordering information is given on any current masthead page.

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# Electron Transfer. 110. Oxidations of Trinuclear Aquomolybdenum(IV)

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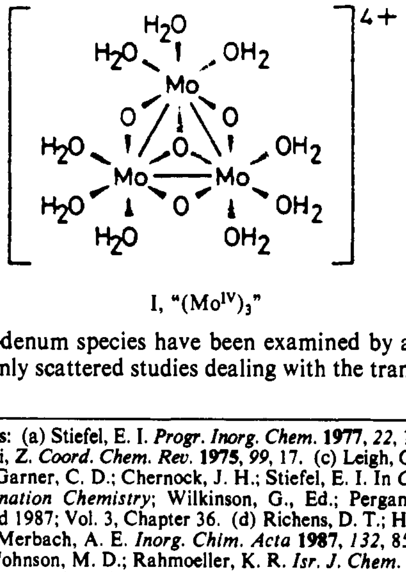
*Received March 22, 1991*

The trimeric cation of molybdenum(IV), $Mo_3O_4(OH_2)_9{}^{4+}$, (structure I) readily reacts with oxyhalogen species and metal-center oxidants in aqueous acid. Conversions are to Mo(VI), even with the oxidants in deficiency. Reductions of $BrO_3^-$ and $ClO_3^-$ are to the respective halide ions, whereas $H_5IO_6$ is reduced rapidly to $IO_3^-$, which is then reduced much more slowly. Kinetic patterns for oxidations by $BrO_3^-$ and $H_5IO_6$ (rate law 6 in text) indicate that these reactions entail conversion of the reductant ($pK_A = 0.7$ at $\mu = 2.0$ M) into its conjugate base, which forms a 1:1 complex with both oxyhalogens. Oxidation by V(V) appears to utilize two paths with transition states differing by a single $H^+$; an observed $[V(V)]^2$ dependency points to reaction via an unusually reactive vanadium(V) dimer. Oxidation by Fe(III) is unobservably slow in HTos or HCl but is markedly accelerated by thiocyanate, suggesting a specific bridging role for Fe(III)-bound $NCS^-$. Both $(Mo^{IV})_3$ and its anation product $(Mo^{IV})_3$–NCS are oxidized by $FeNCS^{2+}$, and both paths require loss of two protons. Oxidation by Cr(VI) is seen to pass through a strongly absorbing intermediate ($\epsilon_{530} = 3 \times 10^3\ M^{-1}\ cm^{-1}$ in 1 M HTos), which decays unimolecularly ($k = 1 \times 10^2\ s^{-1}$ at $[H^+] = 1.0$ M). The behavior of this intermediate is consistent with its formulation as a complex of Cr(IV) associated with a partially oxidized molybdenum cluster (e.g. $Mo^{IV}Mo^{IV}Mo^{VI}$). Although all oxidations of $(Mo^{IV})_3$, by both 1e and 2e reagents, yield three $Mo^{VI}$'s (a net change of six units), rates are generally determined by the initial redox act. Succeeding electron transfers and breakup of partially oxidized Mo clusters proceed too rapidly to affect the kinetic picture.

Among the lower oxidation states of molybdenum,[1] there is continuing interest in Mo(IV), in part because of evidence that complexes of this state intervene in bioconversions catalyzed by the molybdoenzymes xanthine oxidase and xanthine dehydrogenase.[2] However, it is now recognized[3] that the aqueous chemistry of this state is dominated by the pink trinuclear ion $[Mo_3O_4(OH_2)_9]^{4+}$ (I). Although redox reactions involving aquomolybdenum species have been examined by a number of workers,[4] only scattered studies dealing with the transformations of "$(Mo^{IV})_3$" (I) have been described, possibly because preparations of this species from available materials require sequences of several steps. Reactions of $(Mo^{IV})_3$ with the strongly oxidizing $1e^-$ acceptors $IrCl_6{}^{2-}$, $Fe(phen)_3{}^{3+}$, and $Fe^{III}(aq)$ have been reported, and there are indications that both inner- and outer-sphere paths may operate.[5]



I, "$(Mo^{IV})_3$"

The present contribution deals with oxidations of the trinuclear molybdenum(IV) cation I using both oxyhalogen species and metal-center oxidants.

## Experimental Section

**Materials.** Sodium chlorate (Baker and Adamson), sodium bromate (Sargent), sodium metaperiodate (MCB), sodium dichromate (MCB), ammonium metavanadate (Aldrich), iron(III) perchlorate (Alfa), and *p*-toluenesulfonic acid (HTos, Aldrich) were used as received. The sodium salt, $Na^+Tos^-$ was prepared from the parent acid by neutralization with NaOH. The corresponding lithium salt was generated by treatment of the acid with $Li_2CO_3$ and then recrystallized twice from water. All solutions were prepared in distilled water that had been boiled for at least 1 h and then sparged with $N_2$ for 4 h.

To prepare solutions of $[Mo_3O_4(OH_2)_9]^{4+}$, the known Mo(III) complex $(NH_4)_2MoCl_5(OH_2)$[6] was treated with $Na_2MoO_4\cdot 2H_2O$ in 2 M HCl as described by Richens and Sykes.[3d,7] The resulting mixture of chloromolybdenum(IV) complexes, designated $Mo_3O_4Cl_n{}^{(4-n)+}$, was allowed to undergo aquation in aqueous 0.5 M HTos for 24 h under $N_2$. The preparation was then subjected to cation exchange chromatography under $N_2$, using Dowex 50W-X2. Impurities ($Mo_2O_4{}^{2+}$ and chloro complexes) were removed by washing successively with 0.5 and 1.0 M HTos, after which the desired aquo trimer, $(Mo^{IV})_3$, was eluted with 2.0 M HTos. The eluted solution was stored under $N_2$ at 0–4 °C and was found to be stable for 15 days under these conditions. Solutions were standardized spectrophotometrically at 505 nm; $\epsilon_{max} = 63\ M^{-1}\ cm^{-1}$ per Mo (189 per trimer).

**Stoichiometric Studies.** The stoichiometries of the reactions with the several oxo anions were determined, taking $(Mo^{IV})_3$ in excess, by adding a measured deficiency of the oxidant to $(Mo^{IV})_3$, waiting for completion

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