3436 *Inorg. Chem.* **1981**, *20*, 3436-3439

Contribution from the Institut für Anorganische Chemie der Universität Hannover, D-3000 Hannover, West Germany,
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Reactions of Hydroxylamido-*O*,*N* Complexes of Vanadium(V) and of Molybdenum(VI) with Oxalic Acid. Crystal Structure of $(Et_2NHOH)_2[Mo_2O_4(Et_2NO)_2(C_2O_4)_2]$: A μ-Dioxo Complex Containing Two Pentagonal-Bipyramidal Molybdenum(VI) Ions

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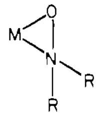
Received January 15, 1981

The reaction of $[O(VO(R_2NO)_2)_2]$ (R = ethyl, benzyl) with oxalic acid in ethanol yields colorless neutral complexes of vanadium(V) containing a bridging μ_4-oxalato ligand: $[(VO(R_2NO)_2)_2(C_2O_4)]$. The reaction of $MoO_2(Et_2NO)_2$ (Et = ethyl) in ethanol with oxalic acid yields pale yellow crystals of $(Et_2HNOH)_2[Mo_2O_4(Et_2NO)_2(C_2O_4)_2]$. This complex has been characterized by a single-crystal X-ray diffraction study. The complex crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^5—No. 14) with a = 11.593 (3) Å, b = 12.120 (3) Å, c = 12.045 (3) Å, β = 102.75 (2)°, V = 1650 Å^3, and ρ_{calcd} = 1.587 g cm^{-3} for Z = 2 and mol wt 788.5. Diffraction data were collected on a Syntex R3 diffractometer using θ–2θ scan and Mo Kα radiation, and the structure was solved by conventional methods, resulting in a final R factor of 0.051 for 2314 independent reflections. The structure consists of *N*,*N*-diethylhydroxylammonium cations and of binuclear dianions, $[Mo_2O_4(Et_2NO)_2(C_2O_4)_2]^{2-}$, upon which a center of symmetry is imposed crystallographically. the Mo(VI) ions are in a distorted pentagonal-bipyramidal environment containing an O,N-coordinated *N*,*N*-diethylhydroxylamido ligand, a bidentate oxalate anion, and a terminal and two bridging oxo ligands. The two terminal oxo ligands are in a trans position with respect to each other. The structure of the dianion may be regarded as two pentagonal bipyramids sharing an equatorial edge.

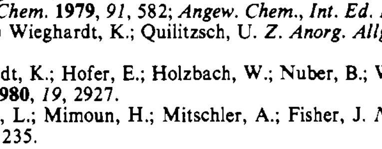
Introduction

In a series of papers we have investigated the structural chemistry of the hydroxylamido(1−) anion and its N-substituted derivatives with transition metals in high oxidation states, e.g., vanadium(V) and molybdenum(VI).[2-4] In general, it is found that the H_2NO^- anion as well as its *N*-alkyl or *N*,*N*-dialkyl derivatives are coordinated in the "side on" fashion (O,N-coordinated):[1-8]



M = V,[2b,4,5] Mo,[2c,3,4] Ru,[6] Pd,[7] , U[8]

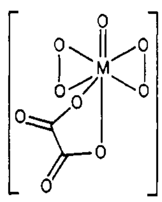
Hydroxylamine is isoelectronic with hydrogenperoxide; and from a structural point of view, the ligand properties of R_2NO^- are in many instances similar to those of coordinated peroxo groups. To illustrate this point, we must consider the following monoperoxo complex and the isostructural hydroxylamido complex of vanadium(V)—both of which have been characterized by single-crystal X-ray analyses.[5,9] In both complexes the vanadium(V) center is in a pentagonal-bipyramidal environment.



dipic = pyridine-2,6-dicarboxylate

Even colorless bis(hydroxylamido-*O*,*N*) complexes of vanadium(V) have been isolated[2b] to match the well-known yellow diperoxo complexes of vanadium(V):[10] $[(pic)VO(H_2NO)_2]^0$ and $[(pic)VO(O_2)_2]^{2-}$, where pic = picolinate anion.

In order to pursue this structural analogy between H_2NO^- and O_2^{2-} ligands, we attempted to prepare hydroxylamido-*O*,*N* complexes of vanadium(V) and of molybdenum(VI) containing oxalato ligands since the corresponding peroxo complexes are well characterized by X-ray analyses:



M = V(V); n = 3[11]
Mo(VI); n = 2[12]

Experimental Section

Abbreviations used are Et = ethyl and Bz = benzyl.

Preparation of Complexes. $[O(VO(Et_2NO)_2)_2]$. This complex has been prepared previously from the reaction of $VO(acac)_2$ or $(Et_2NCS_2)_3VO$ with Et_2NOH[4]. We found a simpler method giving good yields by reacting V_2O_5 (1.8 g) with 20 mL of Et_2NOH at 100 °C or, alternatively, by reaction of an aqueous solution (100 mL) of NH_4VO_3 (1.2 g) with Et_2NOH (3.6 g).

$[O(VO(Bz_2NO)_2)_2]$. *N*,*N*-Dibenzylhydroxylamine (10 g) was dissolved in a mixture of 250 mL of ethanol, 150 mL of water, and 100 mL of acetone. To this was added 1.2 g of NH_4VO_3 at 70 °C. A pale yellow precipitate formed which was filtered off, washed with ether, and air dried. The complex was recrystallized from chloroform. Anal. Calcd for $[C_{56}H_{56}N_4O_7V_2]$: C, 67.33; H, 5.65; N, 5.61; V, 10.19. Found: C, 68.8; H, 6.1; N, 5.8; V, 9.4.

$[(VO(Bz_2NO)_2)_2(C_2O_4)]$. $[V_2O_3(Bz_2NO)_4]$ (2.0 g) was dissolved in 40 mL of ethanol, and oxalic acid dihydrate (0.25 g) dissolved in 10 mL of ethanol was added with stirring. A colorless precipitate formed immediately which was filtered off, washed with ether, and air dried. The complex was recrystallized from chloroform; yield 1.5 g (70%). Anal. Calcd for $[C_{30}H_{28}N_4O_{10}V_2]$: C, 65.05; H, 5.27; N, 5.23; V, 9.51. Found: C, 64.6; H, 5.6; N, 5.1; V, 9.4.

$[(VO(Et_2NO)_2)_2(C_2O_4)]$. To a solution of $[V_2O_3(Et_2NO)_4]$ (1.0 g) in 30 mL of ethanol was added at 40 °C 5 mL of an ethanolic solution of oxalic acid dihydrate (0.13 g). From the cooled solution (0 °C), colorless crystals precipitated which were filtered off, washed

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Table I. Summary of Crystal Data and Intensity Collection for $(Et_2NHOH)_2[Mo_2O_4(Et_2NO)_2(C_2O_4)_2]$

(A) Crystal Parameters at 22 °C

$a = 11.593$ (3) Å $Z = 2$
$b = 12.120$ (3) Å   cryst system: monoclinic
$c = 12.045$ (3) Å   space group: $P2_1/c$ [C^5_{2h}–No. 14]
$\beta = 102.75$ (2)°   mol wt: 788.5
$V = 1650.7$ Å^3 mol formula $(C_4H_{12}NO)_2[C_{12}H_{20}Mo_2N_2O_{14}]$
$\rho_{calcd} = 1.587$ g cm^{-3}

(B) Measurement of Intensity Data

diffractometer: Syntex R3
radiation: Mo Kα ($\lambda = 0.7107$ Å)
data collctn: θ–2θ mode; 2θ range = 4–60°
scan rate: 2.8–11.4°/min
bkgd estimation: stationary crystal–stationary counter at the extremities of each 2θ scan; each for half the time taken for the 2θ scan
std reflctns: 2 reflctns remeasd after every 2h; inspection of these data revealed a decay of 20% over the exposure time; the data were corrected accordingly
reflctns collected: 2314 ($I \geq 2.5\ \sigma(I)$)
abs coeff: $\mu = 8.09$ cm^{-1}
goodness of fit = 1.68

with ether, and air dried; yield 0.48 g (84%). Anal. Found: C, 37.9; H, 7.0; N, 9.8; V, 17.6.

$(Et_2NHOH)_2[Mo_2O_4(Et_2NO)_2(C_2O_4)_2]$. To a solution of 1.5 g of $[MoO_2(Et_2NO)_2]^{3,4}$ in 30 mL of ethanol at 50 °C was added with stirring 0.45 g of oxalic acid dihydrate. Upon slow cooling of the pale yellow solution to 20 °C (~1°/h), crystals precipitated which were filtered off and air dried. These crystals decomposed slowly within 6 days to give a brownish power: IR ν(O—H) 3440 (m, br); ν(C—H) 2990 (w), 2950 (w), 2880 (vw); ν(N—H) 2750 (br, m); ν(C═O) 1700 (m), 1650 (vs), 1470 (w), 1435 (m), 1418 (m), 1400 (w); ν(C—O) 1286 (m), 1188 (vvw), 1170 (vw), 1107 (vvw), 1080 (vw), 1040 (m), 1025 (m), 975 (vw); ν(Mo═O) 942 (s), 907 (vw), 841 (vw), 795 (m), 775 (w), 682 (s), 575 (m), 510 (m) cm^{-1}. Anal. Calcd for $(C_4H_{12}NO)_2[Mo_2C_{12}H_{20}N_2O_{14}]$: C, 30.47; H, 5.62; N, 7.11; Mo, 24.34. Found: C, 30.6; H, 5.6; N, 7.1; Mo, 24.1.

X-ray Diffraction Study and Solution of the Structure

The crystal selected for the structural analysis was of the approximate dimensions 0.2 × 0.2 × 0.1 mm. The unit cell parameters were obtained at 22 °C by least-squares refinement of the respective angular settings of 25 reflections (Table I). Intensity data were collected on an automated diffractometer, Syntex R3. Three standard reflections were measured every 2 h. A decay of 20% was observed in the intensities of the standards, and the data were adjusted accordingly. Corrections for Lorentz and polarization effects but not for absorption were made.[18] The scattering factors for neutral atoms were corrected for both the real and the imaginary components of anomalous dispersion.[19] The function minimized during least-squares refinement was $\sum w_i(|F_o| - |F_c|)^2$ with final convergence to $R_1 = 0.051$ and $R_2 = 0.041$[20] ($w_i = 1/\sigma(F^2)$).

The structure was solved via a three-dimensional Patterson synthesis which yielded the positions of the molybdenum atoms. Subsequent Fourier syntheses revealed the locations of all remaining nonhydrogen atoms. Idealized positions of H atoms bound to carbon atoms were calculated (based upon d(C–H) of 0.97 Å and regular tetrahedral geometry about the C atoms) which were refined as rigid moiety with fixed isotropic thermal parameters ($U = 0.08$) for the H atoms and anisotropic thermal parameters for the C atoms. Refinements were carried out with the use of anisotropic thermal parameters for all other atoms. At this stage a difference Fourier Synthesis revealed the positions of two additional hydrogen atoms bound to the O and N atoms of the *N,N*-diethylhydroxylammonium cations, respectively. The refinement was continued with these positions and a fixed isotropic temperature factor ($U = 0.08$).

The final positional and thermal parameters are given in Table II, bond distances in Table III, and bond angles in Table IV. A list of observed and calculated structure factors is available as supplementary material.

Table II. Final Positional and Thermal[a] Parameters for $(Et_2NHOH)_2[Mo_2O_4(Et_2NO)_2(C_2O_4)_2]$[b]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	0.04726 (5)	0.07668 (4)	0.09911 (4)	0.0327 (3)	0.0351 (2)	0.0366 (2)	−0.0014 (3)	0.0082 (2)	0.017 (4)
O1	0.2112 (3)	0.43355 (3)	0.5313 (3)	0.028 (2)	0.057 (3)	0.038 (2)	−0.007 (2)	0.012 (2)	−0.007 (2)
O2	0.1836 (4)	0.4857 (3)	0.7331 (3)	0.035 (3)	0.054 (3)	0.035 (2)	−0.009 (2)	0.004 (2)	−0.008 (2)
O3	0.3939 (4)	0.5031 (4)	0.5671 (3)	0.037 (3)	0.106 (4)	0.056 (3)	−0.021 (3)	0.013 (2)	−0.021 (3)
O4	0.3639 (4)	0.5570 (4)	0.7844 (4)	0.052 (3)	0.133 (5)	0.055 (3)	−0.034 (3)	0.006 (2)	−0.037 (3)
O5	0.1299 (3)	0.2830 (3)	0.6602 (3)	0.044 (3)	0.036 (2)	0.046 (2)	0.003 (2)	−0.000 (2)	0.004 (2)
O6	0.0373 (3)	0.5812 (3)	0.5558 (3)	0.036 (2)	0.031 (2)	0.040 (2)	−0.003 (2)	0.003 (2)	0.000 (2)
O7	−0.0509 (3)	0.4275 (4)	0.6866 (3)	0.047 (3)	0.056 (2)	0.044 (2)	0.000 (2)	0.020 (2)	−0.02 (3)
O8	0.4489 (5)	0.3407 (6)	0.2375 (5)	0.085 (6)	0.158 (6)	0.102 (4)	−0.068 (4)	0.058 (4)	−0.054 (5)
N1	0.0295 (4)	0.2474 (4)	0.5800 (4)	0.055 (4)	0.034 (3)	0.040 (3)	0.005 (2)	0.010 (3)	0.001 (3)
N2	0.4044 (5)	0.3784 (6)	0.3322 (5)	0.046 (4)	0.103 (6)	0.051 (4)	−0.026 (3)	0.012 (3)	−0.016 (4)
C1	0.2988 (5)	0.4819 (5)	0.5942 (4)	0.045 (4)	0.058 (4)	0.032 (3)	−0.005 (3)	0.005 (3)	0.003 (3)
C2	0.2827 (6)	0.5111 (5)	0.7153 (5)	0.056 (5)	0.054 (4)	0.046 (4)	−0.005 (3)	0.017 (4)	−0.001 (4)
C3	0.0576 (6)	0.2003 (5)	0.4746 (5)	0.067 (5)	0.043 (4)	0.043 (4)	−0.001 (3)	0.011 (4)	0.005 (4)
C4	0.1436 (7)	0.1034 (5)	0.4994 (6)	0.097 (7)	0.061 (5)	0.057 (4)	−0.001 (4)	0.023 (4)	0.019 (5)
C5	0.0562 (6)	0.6879 (6)	0.8679 (5)	0.063 (5)	0.044 (4)	0.055 (4)	−0.006 (3)	0.013 (4)	0.009 (4)
C6	0.1801 (6)	0.6995 (6)	0.9376 (6)	0.060 (5)	0.074 (5)	0.087 (6)	−0.010 (4)	0.010 (5)	0.024 (5)
C7	0.3758 (7)	0.2778 (7)	0.3923 (7)	0.085 (6)	0.086 (7)	0.093 (6)	−0.025 (5)	0.029 (5)	−0.003 (6)
C8	0.4822 (8)	0.2163 (8)	0.4476 (8)	0.118 (10)	0.107 (8)	0.157 (10)	−0.010 (7)	0.023 (8)	0.021 (7)
C9	0.3018 (7)	0.4528 (8)	0.2942 (6)	0.068 (6)	0.129 (9)	0.043 (4)	−0.001 (5)	0.014 (4)	−0.006 (6)
C10	0.3323 (9)	0.5565 (8)	0.2453 (8)	0.102 (8)	0.142 (10)	0.082 (6)	0.019 (7)	−0.004 (6)	−0.016 (8)

	x	y	z		x	y	z
H3A	0.0168 (9)	0.1833 (5)	0.4246 (5)	H7B	0.3295 (7)	0.3103 (7)	0.4407 (7)
H3B	0.0937 (6)	0.2613 (5)	0.4444 (5)	H8A	0.4652 (8)	0.1502 (8)	0.4847 (8)
H4A	0.1511 (7)	0.0713 (5)	0.4286 (6)	H8B	0.5402 (8)	0.2589 (8)	0.4992 (8)
H4B	0.1135 (7)	0.0492 (5)	0.5438 (6)	H8C	0.5121 (8)	0.1973 (8)	0.3818 (8)
H4C	0.2196 (7)	0.1283 (5)	0.5406 (6)	H9A	0.2562 (7)	0.4032 (8)	0.2394 (6)
H5A	0.0342 (6)	0.6114 (5)	0.8619 (5)	H9B	0.2565 (7)	0.4738 (8)	0.3485 (6)
H3B	0.0483 (6)	0.7184 (5)	0.7931 (5)	H10A	0.2645 (9)	0.6015 (8)	0.2150 (7)
H6A	0.2297 (6)	0.6607 (6)	0.8965 (6)	H10B	0.3634 (9)	0.527 (8)	0.1839 (7)
H6B	0.1931 (6)	0.6714 (6)	1.0138 (6)	H10C	0.3917 (9)	0.6005 (8)	0.2937 (7)
H6C	0.1990 (6)	0.7768 (6)	0.9397 (6)	H1	0.525 (6)	0.583 (5)	0.635 (5)
H7A	0.3249 (7)	0.2369 (7)	0.3327 (7)	H2	0.510 (5)	0.581 (5)	0.777 (4)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.
[b] Fixed isotropic thermal parameter for all hydrogen atoms with $U = 0.08$ Å^2.

Table III. Bond Distances (Å)

	Anion Bonds		
Mo1-O1	2.233 (4)	O3-C1	1.244 (8)
Mo1-O2	2.133 (3)	O4-C2	1.242 (7)
Mo1-O5	2.010 (4)	O5-N1	1.406 (5)
Mo1-O6	1.980 (4)	N1-C3	1.492 (8)
Mo1-O6′	1.907 (3)	N1-C5	1.475 (9)
Mo1-O7	1.714 (4)	C1-C2	1.552 (9)
Mo1-N1	2.149 (4)	C3-C4	1.526 (10)
O1-C1	1.258 (6)	C5-C6	1.502 (9)
O2-C2	1.253 (9)	Mo1-Mo1′	3.033 (1)
	Cation Bonds		
N2-O8	1.427 (9)	O8-H2	1.09 (6)
N2-C7	1.492 (11)	C7-C8	1.469 (12)
N2-C9	1.482 (11)	C9-C10	1.464 (13)
N2-H1	0.95 (7)		
	Hydrogen Bonds		
N2-O3	2.783 (8)	O8-O4	2.563 (8)

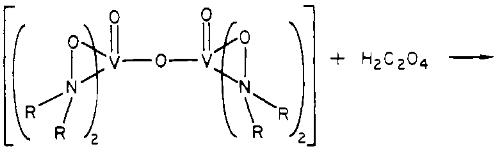
Table IV. Bond Angles (Deg)

O1-Mo1-O2	72.9 (1)	Mo1-O6-Mo1′	102.6 (2)
O1-Mo1-O5	79.3 (2)	O5-N1-C3	113.5 (5)
O1-Mo1-O6	81.1 (1)	O5-N1-Mo1	65.0 (2)
O1-Mo1-O6′	86.5 (1)	O5-N1-C5	113.0 (4)
O1-Mo1-O7	163.2 (1)	C3-N1-Mo1	115.9 (4)
O1-Mo1-N1	95.5 (2)	C3-N1-C5	117.9 (5)
O2-Mo1-O5	79.0 (1)	Mo1-N1-C5	119.8 (4)
O2-Mo1-O6	81.2 (1)	O3-C1-O1	125.3 (5)
O2-Mo1-O6′	152.3 (2)	C2-C1-O1	114.8 (6)
O2-Mo1-O7	90.3 (2)	O3-C1-C2	119.8 (5)
O2-Mo1-N1	118.0 (2)	O4-C2-O2	125.7 (6)
O5-Mo1-O6	155.4 (1)	C1-C2-O2	114.2 (5)
O5-Mo1-O6′	115.7 (2)	C1-C2-O4	120.1 (6)
O5-Mo1-O7	97.3 (2)	C4-C3-N1	112.6 (5)
O5-Mo1-N1	39.3 (2)	C6-C5-N2	111.5 (5)
O6-Mo1-O6′	77.4 (2)	C7-N2-O8	106.5 (6)
O6-Mo1-O7	97.2 (2)	C9-N2-O8	110.8 (5)
O6-Mo1-N1	158.7 (1)	H1-N2-O8	94 (4)
O6′-Mo1-O7	109.6 (2)	C9-N2-C7	113.4 (6)
O6′-Mo1-N1	81.4 (2)	H1-N2-C7	118 (4)
O7-Mo1-N1	91.9 (2)	H1-N2-C9	113 (4)
C1-O1-Mo1	116.6 (4)	H2-O8-N2	95 (3)
C2-O2-Mo1	120.8 (4)	C8-C7-N2	112.3 (7)
N1-O5-Mo1	75.7 (2)	C10-C9-N2	113.5 (7)

Results and Discussion

Preparation of Complexes. The reaction of *N*,*N*-diethylhydroxylamine with V_2O_5 at 100 °C yields quantitatively yellow crystals of the composition $[O(VO(Et_2NO)_2)_2]$. The same product may be obtained from an aqueous solution of NH_4VO_3 and Et_2NOH. This complex has been described previously and characterized by X-ray analysis.[4] The binuclear structure again resembles the structure of the corresponding peroxo complex $[O(VO(O_2)_2)]^{4-}$.[13] If *N*,*N*-dibenzylhydroxylamine is used, yellow crystals of the neutral complex $[O(VO(Bz_2NO)_2)_2]$ can be isolated.

Solutions of these neutral hydroxylamido-*O*,*N* complexes in ethanol react with oxalic acid forming colorless, microcrystalline precipitates which can be recrystallized from chloroform.



$+ H_2C_2O_4 \longrightarrow$

R = ethyl or benzyl

$[(VO(R_2NO)_2)_2(C_2O_4)] + H_2O$ (1)

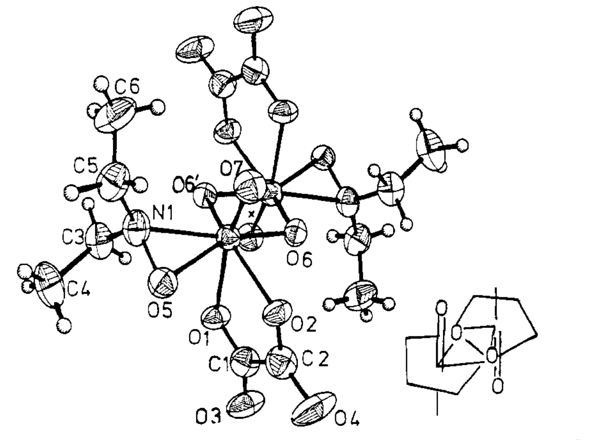
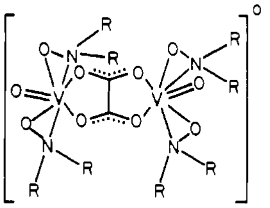


Figure 1. Perspective view of the dianion $[Mo_2O_4(Et_2NO)_2(C_2O_4)_2]^{2-}$ (× denotes a center of symmetry).

Thus the expected mononuclear complex $[VO(R_2NO)_2C_2O_4]^-$ is not formed under these conditions but a neutral, binuclear complex with a bridging tetradentate μ_4-oxalato ligand, two O,N-coordinated hydroxylamido(1−) ligands, and a terminal oxo group per vanadium(V) center. The infrared spectra support the proposed structure: two ν(C–O) stretching frequencies at 1660 and 1300 cm^{-1} are consistent with a tetradentate oxalato group;[14] a strong band at 980 cm^{-1} indicates the presence of a V=O moiety. If it is assumed that R_2NO^- ligands like the O_2^{2-} ligand preferentially occupy equatorial positions of a pentagonal bipyramid whereas a terminal oxo group is located in an axial position, we propose a binuclear structure for the $[C_2O_4(VO(R_2NO)_2)_2]$ complexes in which one oxygen atom of the oxalato bridge occupies an equatorial and another an axial position at each vanadium(V) ion. Two pentagonal bipyramids are connected via an oxalato ligand.[15]



The reaction of $MoO_2(Et_2NO)_2$[3,4] with oxalic acid in ethanol also affords colorless crystals. The elemental analysis would be compatible with the composition $[MoO(Et_2NO)_2(C_2O_4)]H_2O$ which implies a monomeric, seven-coordinate structure as has been established by X-ray diffraction of $K_2[MoO(O_2)_2C_2O_4]$.[12] However, the infrared spectrum exhibits some peculiarities which indicate a more complex structure. The facts that two broad bands at 3440 and 2750 cm^{-1} of medium intensity and that over P_2O_5 in vacuo the complex does not loose water of crystallization are in conflict with the above structure.

Therefore, it was decided to carry out a single-crystal X-ray analysis which finally revealed a structure containing *N*,*N*-diethylhydroxylammonium cations and the binuclear dianion $[Mo_2O_4(Et_2NO)_2(C_2O_4)_2]^{2-}$ (vide infra).

$$2MoO_2(Et_2NO)_2 + 2H_2C_2O_4 \rightarrow (Et_2HNOH)_2[Mo_2O_4(Et_2NO)_2(C_2O_4)_2] \quad (2)$$

Description of the Structure. The structure of $(Et_2HNOH)_2[Mo_2O_4(Et_2NO)_2(C_2O_4)_2]$ consists of four *N*,*N*-diethylhydroxylammonium cations and of two binuclear dianions of $[Mo_2O_4(Et_2NO)_2(C_2O_4)_2]^{2-}$ in the elemental cell.

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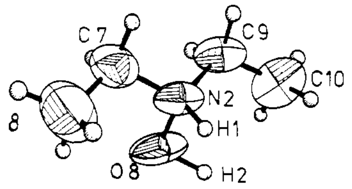

Figure 2. Perspective view of the cation $(Et_2HNOH)^+$.

Figures 1 and 2 show perspective views of the anion and cation, respectively. The dianion has a crystallographically imposed center of symmetry. Each molybdenum(VI) center is in a distorted pentagonal-bipyramidal environment of two bridging and one terminal oxo groups (O6, O6′, O7), a "side on" coordinated *N*,*N*-diethylhydroxylamido(1−) ligand, and a bidentate oxalato ligand.

Two of these pentagonal bipyramids share an equatorial edge; the molybdenum ions are bridged by two μ-oxo ligands. Whereas $Mo_2O_5^{2+}$ structural moieties with one linear or bent μ-oxo bridge and two terminal cis dioxo ligands per Mo(VI) are known,[16] this appears to be the first example containing the $Mo_2O_4^{4+}$ moiety with two μ-oxo bridges and one terminal oxygen per Mo(VI) ion. Interestingly, these two terminal oxygen atoms (O7 and O7′) are in trans position relative to each other. In the chemistry of molybdenum(V), the $Mo_2O_4^{2+}$ moiety is quite common, but the terminal oxo groups are found to be nearly exclusively in the cis position.[16]

The two oxo bridges are not quite symmetrical; the two $Mo-O_b$ distances are at 1.980 (4) and 1.907 (3) Å. This may be due to the fact that O6 is trans to the nitrogen atom of the coordinated hydroxylamido ligand (N1) whereas an oxygen atom of the oxalate anion (O2) is in the trans position to the second bridging oxygen atom O6′.

The $Mo-O_t$ distances at 1.714 (4) Å are relatively long and may represent a bond order of 2.0.[17] The terminal oxo groups exerts a pronounced trans effect: the two Mo–O distances to the oxalate ligand are at 2.233 (4) (axial position, trans to O7) and 2.133 (3) Å (equatorial position).

The *N*,*N*-diethylhydroxylamido(1−) ligand adopts the O,N-coordination as in the six-coordinate complex $MoO_2(Et_2NO)_2$.[4] The reported bond distances are very similar to those reported here. The N1–O5 distance of 1.406 (5) Å is characteristic for a N–O single bond.

The oxalate ligands are bidentate; their bonding situation is very similar to that in $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$—a monobridged six-coordinate oxalato complex of molybdenum(VI).[17] The Mo–O1 distance of 2.233 (4) Å and that of Mo–O2 at 2.133 (3) Å compare also well with the respective distances in the $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$ anion (2.19. and 2.09 Å) although it is noted that due to increased crowding some lengthening of all bonds is observed for the seven-coordinate structure as compared to the six-coordinate complex (~2%).

The N–O distances of the *N*,*N*-diethylhydroxylammonium ions (1.427 (8) Å) and of the "side on" coordinated Et_2NO^- anions (1.406 (5) Å) are very similar. This shows that protonation of the nitrogen and of the oxygen atoms gives rise to only minor lengthening of the N–O bond as compared to coordination of these two atoms to a molybdenum center as anion Et_2NO^-.

There are two short hydrogen bonds in the structure connecting the cations and the dianions: N2–H1···O3 2.783 (8) Å and O8–H2···O4 2.563 (8) Å. O3 and O4 are oxygen atoms of the oxalato ligands at the periphery of the dianions. These hydrogen bonds are formed in such a manner that hydrogen bonds are formed between the first cation via its nitrogen atom to O3 of the oxalate ligand of the first dianion and between the second cation via its oxygen atom and O4 of the same oxalate ligand as before. Figure 2 illustrates that the two hydrogen atoms of the cations, H1 and H2, adopt the eclipsed rather than the staggered conformation. This is caused by the strong hydrogen-bonding scheme. The weaker hydrogen bond is linear (O3···H1–N2) and not symmetrical whereas the O8–H2···O4 bond is unsymmetrical but bent.

Acknowledgment. Financial support of this research from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. $(Et_2NHOH)_2[Mo_2O_4(Et_2NO)_2(C_2O_4)_2]$, 78624-44-9; $(VO(Bz_2NO)_2)_2(C_2O_4)$, 78610-26-1; $(VO(Et_2NO)_2)_2(C_2O_4)$, 78610-27-2; $O(VO(Bz_2NO)_2)_2$, 78610-28-3; $O(VO(Et_2NO)_2)_2$, 75346-30-4; $MoO_2(Et_2NO)_2$, 74081-86-0.

Supplementary Material Available: A list of the observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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(18) Computations were performed on a NOVA 3 (general data) computer using SHELXTL (G. M. Sheldrick, Göttingen, 1979).

(19) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(20) $R_1 = \sum||F_o| - |F_c||/\sum|F_o| \times 100$. $R_2 = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2} \times 100$.