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# Complexes of (Hydroxylamido-*O*,*N*)molybdenum(VI). Preparation and Crystal Structures of $[MoO(H(CH_3)NO)_2(HNC(S)N(CH_3)O)]$ and $[MoO(H(CH_3)NO)(HNC(S)N(CH_3)O)(H_2NC(S)N(CH_3)O)]\cdot H_2O$

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The reaction of the molybdate(VI) oxoanion in aqueous solutions (pH ~6) with N,N-substituted hydroxylamines affords colorless neutral complexes, $[MoO_2(R_1R_2NO)_2]$ ($R_1R_2NO = H(CH_3)NO^-$, $(CH_3)_2NO^-$, $(C_2H_5)_2NO^-$, $(C_6H_5CH_2)_2NO^-$). The hydroxylamido ligands are bonded via the nitrogen and oxygen atoms to the Mo(VI) center (O,N-coordination) in the solid state and also in solution as evidenced from their $^1H$ NMR spectrum. The reaction of $MoO_4^{2-}$ and *N*-methylhydroxylamine in the presence of $SCN^-$ at 80 °C affords red crystals of $[MoO(H(CH_3)NO)_2(HNC(S)N(CH_3)O)]$. The complex has been characterized by a three-dimensional X-ray diffraction study. The complex crystallizes in the tetragonal space group $I4_1/a$ ($C_{4h}^6$, No. 88) with $a = 15.121$ (5) Å, $c = 19.231$ (20) Å, $V = 4397$ Å$^3$, and $\rho$(calcd) = 1.862 g cm$^{-3}$ for $Z = 16$ and mol wt 308.2. Diffraction data were collected on an automated AED (Siemens) diffractometer using $\theta$–$2\theta$ scan and Mo K$\alpha$ radiation, and the structure was solved by conventional methods, resulting in a final $R$ factor of 6.4% for 1517 independent reflections. The structure consists of monomeric complexes of Mo(VI) in a distorted pentagonal-bipyramidal environment containing two *N*-methylhydroxylamido-*O*,*N* ligands, one terminal oxo ligand, and the O,N-coordinated dianion of *N*-methyl-*N*-hydroxylthiourea, $[HNC(S)N(CH_3)O]^{2-}$, forming a planar five-membered ring. The reaction of $[MoO_2(H(CH_3)NO)_2]$ with excess $H(CH_3)NOH$ and $SCN^-$ at 80 °C yields a different red complex of Mo(VI): $[MoO(H(CH_3)NO)(HNC(S)N(CH_3)O)(H_2NC(S)N(CH_3)O)]\cdot H_2O$. This complex has also been characterized by an X-ray diffraction study (experimental conditions as before). The complex crystallizes in the monoclinic space group $P2_1/a$ ($C_{2h}^5$, No. 14) with $a = 10.003$ (15) Å, $b = 14.313$ (6) Å, $c = 10.733$ (16) Å, $\beta = 116.38$ (4)°, $V = 1376.7$ Å$^3$, and $\rho$(calcd) = 1.859 g cm$^{-3}$ for $Z = 4$ and mol wt 385.3. The structure was solved by conventional methods, resulting in a final $R$ factor of 4.2% for 3255 independent reflections. The structure consists of monomeric complexes of Mo(VI) in a distorted pentagonal-bipyramidal environment. One *N*-methylhydroxylamido-*O*,*N* ligand, a terminal oxo group, and the O,N-coordinated dianion $[HNC(S)N(CH_3)O]^{2-}$ forming a planar five-membered ring are again bonded to a Mo(VI) center. In addition, the monoanion of *N*-methyl-*N*-hydroxylthiourea, $[H_2NC(S)N(CH_3)O]^-$, is O,S-coordinated and forms a nearly planar five-membered ring with the Mo(VI) ion. There is no evidence for the incorporation of the Mo(VI) into any delocalized system.

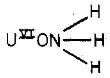
## Introduction

The structural chemistry of hydroxylamine and its N-substituted analogues functioning as ligands in transition-metal complexes is complex and not well understood. There is an inherent ambiguity concerning the mode of coordination: There are well-established examples of hydroxylamine being a neutral, monodentate ligand:[2-5]

$MNH_2OH$

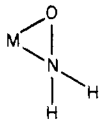
N-coordination[2-4]

M = Co(III), Pt(II), Ni(II)



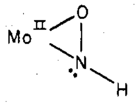
O-coordination[5]

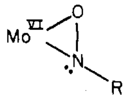
Hydroxylamine in its O-deprotonated form can also serve as a negatively charged ligand, $H_2NO^-$ (or $R_1R_2NO^-$). In this instance only the "side on" or $\eta^2$ O,N mode of coordination has been established by a number of X-ray diffraction studies to date:[6-10]



M = U(VI),[5,6] V(V),[7] V(I),[8] Mo(VI),[9] Mo(II)[10]

Furthermore, examples have been reported recently of complexes containing an O,N-coordinated hydroxylamido(2–) ligand:[11-13]





R = substituted phenyl rings

Finally, it has been recognized that reactions of molybdenum(VI) oxoanions with $H_2NOH$ in acidic and basic media afford nitrosyl complexes of the type $\{Mo–N{=}O\}^4$,[9;10,12,14]

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We report here a series of complexes of molybdenum(VI) containing N-substituted hydroxylamido(1−) ligands in the O,N mode of coordination.

## Experimental Section

**Preparation of Complexes.** The preparation of $[MoO_2(H(CH_3)NO)_2]$ (I) has been described elsewhere.[9]

**$[MoO_2((CH_3)_2NO)_2]$ (II).** The ligand *N,N*-dimethylhydroxylamine was prepared in situ. To a 0.15 M solution of *N,N*-dimethylamine in 200 mL of water was added $Na_2WO_4 \cdot 2H_2O$ (1 g). The solution was cooled to −10 °C, and within 30 min 130 mL of 30% $H_2O_2$ was added dropwise. The solution was stirred for another 30 min at −10 °C. The pH of the solution was adjusted to ~8 with $H_2SO_4$ (6 M) and stirred at 20 °C for 30 min. Then $Na_2MoO_4 \cdot 2H_2O$ (8 g) was added, and the pH of the solution was decreased to 5 with 6 M $H_2SO_4$. A colorless precipitate formed immediately, which was filtered off, washed with water, and dried over $P_2O_5$. (From the cooled (0 °C) filtrate a second batch of crystals precipitated after 24 h.) The yield was 86% (mp 203 °C dec). Anal. Calcd for $[MoO_2(C_2H_6N_2O_2)]$: C, 19.37; H, 4.88; N, 11.29; Mo, 38.67. Found: C, 19.5; H, 5.0; N, 11.4; Mo, 38.5.

**$[MoO_2((C_2H_5)_2NO)_2]$ (III).** To a solution of $Na_2MoO_4 \cdot 2H_2O$ (7.2 g) in 50 mL of water was added 6.2 g of *N,N*-diethylhydroxylamine at 40 °C. The alkaline solution was neutralized by the dropwise addition of hydrochloric acid (6 M). A microcrystalline, colorless precipitate formed which was filtered off, washed with water, and dried in vacuo over $P_2O_5$ (mp 137 °C). An identical product was obtained when $MoO_3$ (1.4 g) was dissolved in 10 mL of *N,N*-diethylhydroxylamine (0.1 M) in water at 95 °C. Upon slow cooling of this solution to 10 °C, large, laminated crystals precipitated (yield 97%). Anal. Calcd for $[MoO_2(C_4H_{10}N_2O_2)]$: C, 31.59; H, 6.63; N, 9.21; Mo, 31.54. Found: C, 31.7; H, 6.5; N, 9.3; Mo, 31.6.

**$[MoO_2((PhCH_2)_2NO)_2]$ (IV).** This complex was prepared as described for complex III by using *N,N*-dibenzylhydroxylamine (mp 208 °C dec, yield 91%). Anal. Calcd for $[MoO_2(C_{14}H_{14}N_2O_2)]$: C, 60.87; H, 5.11; N, 5.07; Mo, 17.37. Found: C, 61.0; H, 5.2; N, 5.1; Mo, 17.1.

**$[MoO(H(CH_3)NO)_2(HNC(S)N(CH_3)O)]$ (V).** To a solution of $MoO_3$ (2.8 g) in 40 mL of 1 M NaOH was added solid NaSCN (8 g). At 75 °C *N*-methylhydroxylammonium chloride (8 g) was added in small amounts. The temperature was maintained at 80 °C for 5 min during which time the solution became deep red. Very slowly the temperature of the solution was decreased to 10 °C (4 °C/h). Red crystals of analytically pure V precipitated which were filtered off, washed with ethanol and ether, and air-dried (mp 140 °C dec, yield 63%). Anal. Calcd for $MoO(C_4H_{12}N_4O_3)$: C, 15.59; H, 3.93; N, 18.18; Mo, 31.13; S, 10.41. Found: C, 15.7; H, 3.9; N, 18.1; Mo, 30.8; S, 10.9

**$[MoO(H(CH_3)NO)(HNC(S)N(CH_3)O)(H_2NC(S)N(CH_3)NO)] \cdot H_2O$ (VI).** To a solution of $MoO_2(H(CH_3)NO)_2$ (I) (2.2 g) in 40 mL of water at 80 °C were added *N*-methylhydroxylammonium chloride (3 g) and NaSCN (4 g). After 3 min at this temperature, the solution became deep red. After slow cooling of the solution to 0 °C (4 °C/h), red crystals precipitated which were filtered off, washed with ethanol and ether, and air-dried (mp 127 °C dec, yield 75%). Anal. Calcd for $[MoO(C_5H_{13}N_5O_4S_2)] \cdot H_2O$: C, 15.59; H, 3.92; N, 18.18; Mo, 24.90; S, 16.65. Found: C, 15.6; H, 3.8; N, 18.5; Mo, 25.0; S, 16.3.

**Description of the X-ray Diffraction Studies and Solution of the Structures of V and VI.** The crystals selected for the structural analyses were of the approximate dimensions 0.08 × 0.07 × 0.19 mm (V) and 0.10 × 0.13 × 0.25 mm (VI). The unit cell parameters were obtained at 23 °C by least-squares refinements of the respective angular settings of 46 reflections of each crystal (Table I). Intensity data were collected on an automated diffractometer, AED (Siemens), and were corrected for Lorentz and polarization effects. No absorption correction was applied in view of the small absorption coefficients and crystal dimensions. The scattering factors for neutral atoms were corrected for both the real and the imaginary components of anomalous dispersion. The function minimized during least-squares refinement was $\sum(|F_o| - |F_c|)^2$.

No weighting scheme was applied in the refinement. The structures of V and VI were solved via three-dimensional Patterson syntheses which yielded the positions of the molybdenum atoms, respectively. Fourier syntheses revealed the locations of all remaining nonhydrogen atoms. Refinements[25] were carried out by using anisotropic thermal parameters for all nonhydrogen atoms. At this stage two difference Fourier syntheses revealed the positions of all hydrogen atoms, respectively. In the case of V refinement was continued with all hydrogen atoms included in calculated, idealized positions (based upon $d$(C–H) and $d$(N–H) of 0.95 Å, regular tetrahedral geometry about carbon atoms C1, C2, and C3, approximately tetrahedral geometry about N1 and N2, and a trigonal-planar geometry about N3, and isotropic temperature factors of $U = 0.08$). Convergence was reached with $R = \sum||F_o| - F_c||/\sum|F_o| = 0.064$. In the case of structure VI refinement was continued with positions of all hydrogen atoms and isotropic thermal parameters of these hydrogen atoms. Convergence was reached with $R = 0.042$.

**Table I.** Summary of Crystal Data and Intensity Collection for $[MoO(H(CH_3)NO)_2(HNC(S)N(CH_3)O)]$ (V) and $[MoO(H(CH_3)NO)(HNC(S)N(CH_3)O)(H_2NC(S)N(CH_3)O)] \cdot H_2O$ (VI)

A. Crystal Parameters at 23 °C

| | V | VI |
|---|---|---|
| $a$, Å | 15.121 (5) | 10.003 (15) |
| $b$, Å | | 14.313 (6) |
| $c$, Å | 19.231 (20) | 10.733 (16) |
| $\beta$, deg | | 116.38 (4) |
| $V$, Å$^3$ | 4397 | 1376.7 |
| cryst system | tetragonal | monoclinic |
| space group | $I4_1/a(C_{4h}^6$, No. 88) | $P2_1/a(C_{2h}^5$, No. 14) |
| $Z$ | 16 | 4 |
| $\rho$(calcd), g cm$^{-3}$ | 1.862 | 1.859 |
| mol wt | 308.2 | 385.3 |
| fw | $[MoC_4H_{12}N_4O_4S]$ | $[MoC_5H_{13}N_5O_4S_2] \cdot H_2O$ |

B. Measurement of Intensity Data[a]

diffractometer: AED (Siemens)
radiation: Mo K$\alpha$ ($\lambda = 0.7107$ Å)
data collcn: $\theta$–$2\theta$ mode
$2\theta$ range: V, 4–60°; VI, 4–68°
scan rate: 2.85–11.4°/min.
scan width: $[\theta(K\alpha) + 0.20 + 0.228 \tan\theta]^\circ - [\theta(K\alpha) - 0.15 - 0.116 \tan\theta]^\circ$
bkgd estimation: stationary crystal, stationary counter at the extremities of each $2\theta$ scan; each for half the time taken for the $2\theta$ scan
std reflcns: 2 every 2 h; no decay observed
rflcns collected: V, 1517; VI, 3255 ($I \geq 3.0\sigma(I)$)
abs coeff: V, 13.5 cm$^{-1}$; VI, 12.4 cm$^{-1}$

C. Structure Refinement

| | V | VI |
|---|---|---|
| largest shift/esd | 0.008 | −0.016 |
| largest peak,[b] e/Å$^3$ | 0.41 | 0.33 |

[a] No absorption corrections were deemed to be necessary in either case. [b] Largest peak in the final difference Fourier map.

The final positional and thermal parameters are given in Table II for structure V and in Table III for structure VI. Lists of observed and calculated structure factors are available as supplementary material.

## Results and Discussion

**Preparation and Characterization of Complexes.** The preparation and crystal structure of $[MoO_2(H(CH_3)NO)_2]$ have been described elsewhere[9] (see eq 1). In the solid state

$$MoO_4^{2-} + 2[H_2(CH_3)NOH]^+ \rightarrow [MoO_2(H(CH_3)NO)_2]^0 + 2H_2O \quad (1)$$

two *N*-methylhydroxylamido(1−) ligands are coordinated via an oxygen and a nitrogen atom, respectively, to a *cis*-dioxomolybdenum(VI) moiety.

Reaction 1 can be generalized to readily yield *cis*-dioxomolybdenum(VI) complexes with two N,N-substituted hydroxylamido(1−) ligands as is shown in reaction 2. Complexes

$$MoO_4^{2-} + 2H^+ + 2R_1R_2NOH \rightarrow [MoO_2(R_1R_2NO)_2]^0 + 2H_2O \quad (2)$$

$$R_1 = R_2 = CH_3\ (II),\ CH_2CH_3\ (III),\ CH_2C_6H_5\ (IV)$$

II–IV form colorless crystals which are soluble in dimethyl sulfoxide and chloroform but only very slightly soluble in

**Table II.** Final Positional Parameters and Anisotropic Thermal Parameters for $[MoO(H(CH_3)NO)_2(HNC(S)N(CH_3)O)]$ (V)[a]

| atom | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| Mo | 0.34324 (6) | 0.40573 (6) | 0.07713 (6) | 0.0284 (4) | 0.0383 (5) | 0.0425 (5) | 0.0010 (4) | −0.0015 (4) | 0.004 (4) |
| S | 0.1055 (2) | 0.4212 (2) | 0.2276 (2) | 0.044 (2) | 0.047 (2) | 0.043 (2) | 0.003 (1) | 0.006 (1) | 0.003 (1) |
| O1 | 0.3717 (6) | 0.3074 (5) | 0.0146 (4) | 0.053 (5) | 0.051 (5) | 0.049 (5) | −0.004 (4) | 0.017 (4) | −0.001 (4) |
| O2 | 0.3762 (5) | 0.4841 (6) | 0.0004 (4) | 0.048 (5) | 0.062 (5) | 0.048 (5) | 0.003 (4) | 0.007 (4) | −0.010 (4) |
| O3 | 0.2158 (5) | 0.4028 (5) | 0.0446 (4) | 0.036 (4) | 0.046 (4) | 0.033 (4) | 0.004 (3) | 0.002 (3) | −0.002 (3) |
| O4 | 0.4307 (5) | 0.4081 (5) | 0.1306 (5) | 0.035 (4) | 0.056 (5) | 0.067 (6) | −0.002 (4) | −0.017 (4) | 0.002 (4) |
| N1 | 0.3320 (6) | 0.2679 (6) | 0.0727 (5) | 0.042 (5) | 0.039 (5) | 0.059 (6) | 0.002 (5) | 0.008 (5) | 0.003 (4) |
| N2 | 0.3466 (7) | 0.5410 (7) | 0.0525 (6) | 0.051 (6) | 0.042 (6) | 0.075 (8) | −0.003 (5) | −0.002 (6) | −0.004 (5) |
| N3 | 0.2636 (5) | 0.4205 (6) | 0.1631 (5) | 0.033 (4) | 0.042 (5) | 0.037 (5) | 0.002 (4) | −0.005 (4) | −0.001 (4) |
| N4 | 0.1482 (6) | 0.4056 (6) | 0.0924 (5) | 0.035 (5) | 0.043 (5) | 0.043 (5) | 0.003 (4) | −0.004 (4) | 0.000 (4) |
| C1 | 0.3864 (9) | 0.2021 (8) | 0.1090 (8) | 0.056 (8) | 0.045 (7) | 0.086 (11) | 0.013 (7) | −0.010 (7) | 0.008 (6) |
| C2 | 0.4149 (9) | 0.6026 (9) | 0.0776 (8) | 0.079 (9) | 0.053 (8) | 0.091 (11) | 0.004 (8) | −0.006 (9) | −0.019 (7) |
| C3 | 0.0613 (7) | 0.3889 (8) | 0.0666 (7) | 0.032 (6) | 0.066 (8) | 0.055 (8) | 0.008 (7) | −0.006 (5) | 0.004 (5) |
| C4 | 0.1763 (7) | 0.4166 (6) | 0.1578 (5) | 0.041 (5) | 0.024 (5) | 0.040 (6) | 0.002 (4) | 0.009 (4) | 0.008 (4) |

| | $x$ | $y$ | $z$ | | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| H10 | 0.2814 (6) | 0.2319 (6) | 0.0831 (5) | H21 | 0.3904 (10) | 0.6391 (9) | 0.1136 (8) |
| H20 | 0.3016 (7) | 0.5851 (7) | 0.0584 (6) | H22 | 0.4359 (10) | 0.6393 (9) | 0.0404 (8) |
| H30 | 0.3028 (5) | 0.4289 (6) | 0.2018 (5) | H23 | 0.4632 (9) | 0.5688 (9) | 0.0962 (8) |
| H11 | 0.3531 (9) | 0.1791 (8) | 0.1475 (8) | H31 | 0.0195 (7) | 0.3928 (8) | 0.1040 (7) |
| H12 | 0.4392 (9) | 0.2300 (8) | 0.1259 (8) | H32 | 0.0602 (7) | 0.3303 (8) | 0.0473 (7) |
| H13 | 0.4019 (9) | 0.1547 (8) | 0.0782 (8) | H33 | 0.0460 (7) | 0.4310 (8) | 0.0312 (7) |

[a] Isotropic, fixed temperature factor is $U = 0.08$ Å² for all hydrogen atoms. The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

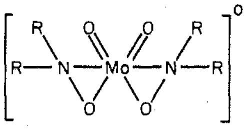
**Table III.** Final Positional and Anisotropic Thermal Parameters for $[MoO(H(CH_3)NO)(HNC(S)N(CH_3)O)(H_2NC(S)N(CH_3)O)]\cdot H_2O$ (VI)

| atom | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| Mo | 0.14058 (4) | 0.10453 (3) | 0.22848 (4) | 0.0308 (2) | 0.0303 (2) | 0.0350 (2) | 0.0023 (2) | 0.0162 (1) | −0.003 (2) |
| S1 | 0.0854 (1) | 0.14586 (8) | 0.4261 (1) | 0.0442 (6) | 0.0370 (6) | 0.0403 (6) | −0.0060 (5) | 0.0215 (5) | −0.0055 (5) |
| S2 | 0.3700 (2) | −0.1301 (1) | 0.1041 (2) | 0.0429 (7) | 0.0605 (8) | 0.0494 (7) | −0.0001 (6) | 0.0221 (6) | 0.0179 (6) |
| O1 | 0.0286 (4) | 0.1505 (3) | 0.0358 (3) | 0.050 (2) | 0.048 (2) | 0.044 (2) | 0.011 (2) | 0.028 (2) | 0.012 (2) |
| O2 | 0.2722 (4) | 0.0088 (2) | 0.3670 (3) | 0.039 (2) | 0.039 (2) | 0.034 (2) | 0.002 (1) | 0.015 (1) | 0.005 (1) |
| O3 | −0.0447 (3) | 0.0192 (2) | 0.1953 (3) | 0.038 (2) | 0.039 (2) | 0.033 (2) | −0.002 (1) | 0.019 (1) | −0.007 (1) |
| O4 | 0.2658 (4) | 0.1928 (2) | 0.2859 (4) | 0.041 (2) | 0.037 (2) | 0.071 (3) | −0.002 (2) | 0.028 (2) | −0.008 (1) |
| O5 | 0.0495 (8) | 0.8195 (4) | 0.2821 (6) | 0.124 (5) | 0.055 (3) | 0.070 (3) | −0.003 (3) | 0.037 (3) | −0.021 (3) |
| N1 | −0.0351 (4) | 0.1965 (3) | 0.1086 (4) | 0.041 (2) | 0.040 (2) | 0.048 (2) | 0.011 (2) | 0.026 (2) | 0.008 (2) |
| N2 | 0.2070 (4) | 0.0158 (3) | 0.1200 (4) | 0.037 (2) | 0.042 (2) | 0.035 (2) | 0.004 (2) | 0.016 (2) | 0.008 (2) |
| N3 | 0.3420 (4) | −0.0565 (3) | 0.3194 (4) | 0.036 (2) | 0.040 (2) | 0.040 (2) | 0.004 (2) | 0.016 (2) | 0.009 (2) |
| N4 | −0.1272 (4) | 0.0307 (2) | 0.2676 (4) | 0.036 (2) | 0.043 (2) | 0.041 (2) | 0.001 (2) | 0.021 (2) | −0.007 (2) |
| N5 | −0.1515 (5) | 0.0912 (3) | 0.4558 (5) | 0.062 (3) | 0.047 (3) | 0.057 (3) | −0.002 (2) | 0.042 (2) | −0.006 (2) |
| C1 | −0.0226 (8) | 0.2994 (4) | 0.1135 (8) | 0.076 (4) | 0.040 (3) | 0.096 (5) | 0.021 (3) | 0.058 (4) | 0.016 (3) |
| C2 | 0.3031 (5) | −0.0539 (3) | 0.1842 (5) | 0.030 (2) | 0.041 (2) | 0.040 (2) | 0.002 (2) | 0.016 (2) | 0.001 (2) |
| C3 | 0.4262 (5) | −0.1269 (4) | 0.4199 (6) | 0.056 (3) | 0.046 (3) | 0.043 (3) | 0.007 (2) | 0.014 (2) | 0.015 (2) |
| C4 | −0.0761 (5) | 0.0835 (3) | 0.3796 (5) | 0.044 (2) | 0.031 (2) | 0.040 (2) | 0.004 (2) | 0.025 (2) | 0.001 (2) |
| C5 | −0.2637 (6) | −0.0254 (4) | 0.2148 (6) | 0.044 (3) | 0.058 (3) | 0.055 (3) | −0.006 (3) | 0.026 (2) | −0.019 (2) |

| atom | $x$ | $y$ | $z$ | $U$,[a] Å² | atom | $x$ | $y$ | $z$ | $U$,[a] Å² |
|---|---|---|---|---|---|---|---|---|---|
| H1 | −0.126 (7) | 0.175 (4) | 0.070 (6) | 0.09 (2) | H13 | −0.044 (7) | 0.323 (4) | 0.185 (6) | 0.07 (2) |
| H2 | 0.168 (5) | 0.017 (4) | 0.040 (5) | 0.04 (1) | H31 | 0.486 (7) | −0.151 (4) | 0.391 (7) | 0.09 (2) |
| H3 | −0.116 (6) | 0.126 (4) | 0.526 (5) | 0.04 (1) | H32 | 0.477 (7) | −0.101 (4) | 0.509 (6) | 0.07 (2) |
| H4 | −0.208 (7) | 0.049 (4) | 0.453 (6) | 0.07 (2) | H33 | 0.378 (7) | −0.168 (4) | 0.435 (6) | 0.08 (2) |
| H6 | 0.022 (10) | 0.781 (6) | 0.261 (9) | 0.10 (2) | H51 | −0.310 (6) | −0.019 (4) | 0.107 (5) | 0.05 (1) |
| H8 | −0.033 (11) | 0.856 (7) | 0.235 (10) | 0.15 (2) | H52 | −0.295 (7) | −0.018 (4) | 0.304 (6) | 0.08 (2) |
| H11 | 0.067 (7) | 0.319 (4) | 0.107 (6) | 0.08 (2) | H53 | −0.231 (7) | −0.085 (4) | 0.218 (6) | 0.08 (2) |
| H12 | −0.087 (7) | 0.314 (5) | 0.010 (7) | 0.09 (2) | | | | | |

[a] Isotropic temperature factor. The form of the thermal anisotropic ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

water. The structures of II–IV in the solid state are thought to be analogous to I. In the infrared the *cis*-dioxo group,



I

$MoO_2$, generally exhibits two strong bands at 900–950 cm⁻¹ ($\nu_s$(Mo=O) and $\nu_{as}$(MoO);[15] see Table IV) but in some cases only one broad band is discernible.

The structures of I–IV in solution are unambiguously deduced to be the same as in the solid state from their ¹H NMR spectra at 23 °C (Table IV). The ¹H NMR spectra of I–IV exhibit the expected chemical shifts and multiplicities for the coordinated hydroxylamido(1−) ligands. For the protons of the methyl groups in I a doublet with $J$ = 4.3 Hz at $\delta$ 2.74 is observed due to the coupling with the NH protons at $\delta$ 8.92. A double resonance experiment proved this assignment to be correct. The magnitude of the observed coupling constant is in good agreement with reported values for NH–$CH_3$ coupling.[16] No such coupling is possible in II; consequently, only one singlet at $\delta$ 3.04 for four equivalent methyl groups is

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(15) Griffith, W. P.; Wickins, T. D. *J. Chem. Soc. A* **1968**, 400.

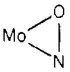
(16) Dudek, G. O.; Volpp, G. P. *J. Am. Chem. Soc.* **1963**, *85*, 2697.

**Table IV.** Spectroscopic Data of Complexes I–VI

| | | | $^1$H NMR[b] | | | |
|---|---|---|---|---|---|---|
| no. | complex | infrared spectrum ($\nu$, cm$^{-1}$)[a] | H | $CH_3$ | $CH_2$ | $C_6H_5$ |
| I | $[MoO_2(H(CH_3)NO)_2]$ | $\nu$(N–H) 3220 (s), 3120 (s)<br>$\nu$(Mo=O) 920 (s), 932 (vs) | 8.92 q[c] | 2.74 d | | |
| II | $[MoO_2((CH_3)_2NO)_2]$ | $\nu$(Mo=O) 910 (vs) | | 3.40 s[d] | | |
| III | $[MoO_2((C_2H_5)_2NO)_2]$ | $\nu$(Mo=O) 905 (vs) | | 1.24 t[d] | 3.07 m, 3.29 m | |
| IV | $[MoO_2((PhCH_2)_2NO)_2]$ | $\nu$(Mo=O) 900 (vs) | | | 4.11 d,[d] 4.23 d | 7.43 m |
| V | $[MoO(H(CH_3)NO)_2$-$(HNC(S)N(CH_3)O)]$ | $\nu$(N–H) 3240 (vs), 3020 (s), 2980 (s), 2800 (vs)<br>$\nu$(C=S) 1375 (vs)<br>$\nu$(Mo=O) 926 (s) | *e* | | | |
| VI | $[MoO(H(CH_3)NO)$-$(HNC(S)N(CH_3)O)$-$(H_2NC(S)N(CH_3)O)]\cdot H_2O$ | $\nu$(O–H) and $\nu$(N–H) 3580 (m), 3420 (m), 3380 (m), 3270 (s), 3170 (vs), 3000 (m), 2805 (s)<br>$\delta(NH_2)$ 1625 (s), 1580 (s)<br>$\nu$(C=S) 1350 (s) | *e* | | | |

[a] KBr disks; selected bands ((s) = strong; (vs) = very strong). [b] Inner standard TMS and $\delta$ scale (d = doublet; m = multiplet; s = singlet). [c] Measured in $(CD_3)_2SO$. [d] Measured in $CDCl_3$. [e] Decomposition of complexes in solution.

observed. This is regarded as excellent evidence that the symmetrical structure (as has been established in the solid state for I) is retained in solution. The $^1$H NMR spectra of III and IV are more complex. It is true that all substituents at the two nitrogen atoms of the hydroxylamido ligands are equivalent, but due to the hindered inversion of the nitrogen atoms the methylene protons are in a diastereomorphic environment; i.e., they are diastereotopic[17] and couple. Therefore, an AB system with $\delta$ 4.11 and 4.23 and a coupling constant of $J$ = 14 Hz is observed for the benzylic methylene protons in IV. The same steric conditions are valid for III, but due to an additional coupling of the methylene protons with the methyl group an $ABX_3$ spectrum is observed. These findings also preclude the mechanistic possibility of rapid dissociation and subsequent recombination of chemical bonds within the



ring in solution. Such a mechanism would cancel the hindrance of the inversion of the nitrogen atoms, and no AB and $ABX_3$ spectra for III and IV, respectively, should be observed.

When molybdate(VI) oxoanions are reacted with *N*-methylhydroxylammonium chloride and sodium thiocyanate in acidic aqueous solution at 80 °C, a deep red solution is obtained from which red crystals precipitate upon cooling. From the elemental analysis the composition is deduced: $MoC_4H_{12}N_4O_4S$. In the infrared spectrum no bands due to coordinated $SCN^-$ ligands were detected. The X-ray diffraction study reveals that two *N*-methylhydroxylamido(1–) ligands, a terminal oxo group, and the dianion of *N*-methyl-*N*-hydroxylthiourea are coordinated to a Mo(VI) center (eq 3). The ligand *N*-methyl-*N*-hydroxylthiourea is thought to

$$MoO_4^{2-} + 3H^+ + 3H(CH_3)NOH + SCN^- \rightarrow [MoO(H(CH_3)NO)_2(HNC(S)N(CH_3)O)] + 3\,H_2O \quad (3)$$

be generated by nucleophilic attack of the *N*-methylhydroxylamine at the carbon center of H—N=C=S in the presence of Mo(VI). The infrared spectrum of V exhibits a $\nu$(C=S) stretching frequency at 1375 cm$^{-1}$ and $\nu$(Mo=O) at 926 cm$^{-1}$. The complex is insoluble in water but dissolves with concomitant decomposition in $Me_2SO$. Since V cannot be redissolved in common solvents (ethanol, ether, benzene, acetone, etc.), it has not been possible to obtain the UV–visible or NMR spectrum. No other reaction products have been isolated from the above reaction solution; V appears to be the major product.

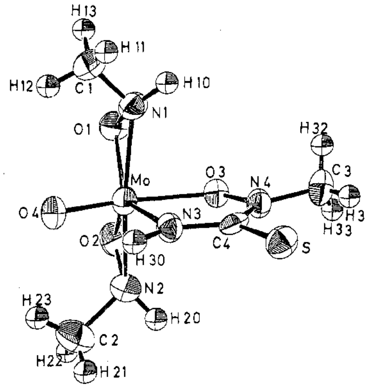


**Figure 1.** Structure of $[MoO(H(CH_3)NO)_2(HNC(S)N(CH_3)O)]$, showing 50% probability ellipsoids and the atom labeling scheme.

When complex I is reacted in slightly acidic solution with *N*-methylhydroxylammonium chloride and NaSCN at 80° C, again a red solution is obtained from which red crystals precipitate upon cooling. The composition of VI, $MoC_5H_{15}N_5O_5S_2$, is indicated by the elemental analysis. The infrared spectrum shows a strong band at 1350 cm$^{-1}$ which is assigned to a $\nu$(C=S) stretching frequency. As is shown by an X-ray diffraction study, one *N*-methylhydroxylamido(1–), an oxo ligand, and the monoanion as well as the dianion of *N*-methyl-*N*-hydroxylthiourea are coordinated to Mo(VI). One molecule of water of crystallization is present (eq 4).

$$[MoO_2(H(CH_3)NO)_2] + 2SCN^- + 2H^+ + H(CH_3)NOH \rightarrow [MoO(H(CH_3)NO)(HNC(S)N(CH_3)O)(H_2NC(S)N(CH_3)O)]\cdot H_2O \quad (4)$$

Complex VI is also not soluble in water or any of the common organic solvents, and a UV-visible spectrum or an $^1$H NMR spectrum has not been obtained. VI is the only isolable product from the above reaction mixtures in good yields.

**Description of the Structures of V and VI.** The structure of $[MoO(H(CH_3)NO)_2(HNC(S)N(CH_3)O)]$ (V) consists of well-separated monomers. There are no significant intermolecular nonbonded contacts in the unit cell. Figure 1 shows the complex to have pentagonal-bipyramidal geometry with two *N*-methylhydroxylamido(1–) ligands coordinated via the oxygen and nitrogen atoms, respectively, in equatorial positions. Thus the hydroxylamido(1–) ligands adopt the now well-known O,N-coordination.[5-11] The oxygen atom is deprotonated whereas one hydrogen atom is bonded to the nitrogen atom which shows a very distorted tetrahedral environment. The averaged O–N distance of 1.40 Å and a C–N distance of 1.48 Å indicate normal single bonds within the coordinated hy-

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[17] Mislow, K. "Introduction to Stereochemistry"; W. A. Benjamin: New York, 1965; p 86.

**Table V.** Bond Angles (Deg) of $[MoO(H(CH_3)NO)_2(HNC(S)N(CH_3)O)]$

| | | | |
|---|---|---|---|
| O1–Mo–O2 | 86.5 (3) | Mo–N1–C1 | 127.6 (8) |
| O1–Mo–O3 | 90.2 (3) | O1–N1–C1 | 115.4 (9) |
| O1–Mo–O4 | 102.7 (4) | Mo–N1–O1 | 64.8 (5) |
| O1–Mo–N1 | 40.3 (4) | Mo–N2–O2 | 64.6 (5) |
| O1–Mo–N2 | 126.5 (4) | Mo–N2–C2 | 123.9 (8) |
| O1–Mo–N3 | 134.7 (3) | O2–N2–C2 | 113.7 (10) |
| O2–Mo–O3 | 91.3 (3) | C4–N3–Mo | 121.1 (7) |
| O2–Mo–O4 | 104.5 (4) | N4–O3–Mo | 120.0 (6) |
| O2–Mo–N1 | 126.3 (4) | N1–O1–Mo | 74.9 (5) |
| O2–Mo–N2 | 40.1 (4) | N2–O2–Mo | 75.3 (6) |
| O2–Mo–N3 | 133.6 (3) | C4–N4–O3 | 113.3 (8) |
| O3–Mo–O4 | 160.1 (4) | C3–N4–O3 | 116.5 (8) |
| O3–Mo–N1 | 83.6 (3) | C3–N4–C4 | 129.9 (9) |
| O3–Mo–N2 | 88.5 (4) | N4–C4–S | 122.8 (8) |
| O3–Mo–N3 | 72.1 (3) | N3–C4–S | 124.0 (8) |
| O4–Mo–N1 | 96.3 (4) | N3–C4–N4 | 113.2 (9) |
| O4–Mo–N2 | 95.7 (4) | | |
| O3–Mo–N3 | 88.1 (4) | | |
| N1–Mo–N2 | 164.3 (4) | | |
| N1–Mo–N3 | 95.4 (4) | | |
| N2–Mo–N3 | 95.2 (4) | | |

**Table VI.** Bond Distances (Å) of $[MoO(H(CH_3)NO)_2(HNC(S)N(CH_3)O)]$

| | | | |
|---|---|---|---|
| Mo–O1 | 1.961 (8) | O1–N1 | 1.402 (13) |
| Mo–O2 | 1.962 (8) | O2–N2 | 1.399 (14) |
| Mo–O3 | 2.027 (7) | O3–N4 | 1.374 (11) |
| Mo–O4 | 1.677 (8) | N4–C4 | 1.339 (14) |
| Mo–N1 | 2.093 (9) | N4–C3 | 1.427 (14) |
| Mo–N2 | 2.101 (10) | C4–N3 | 1.326 (13) |
| Mo–N3 | 2.058 (9) | N1–C1 | 1.466 (16) |
| C4–S | 1.718 (11) | N2–C2 | 1.473 (17) |

droxylamido ligands of structures V and VI. The average Mo–N distance of 2.10 Å and the Mo–O distance of 1.97 Å may be used as internal standards for Mo–N and Mo–O single-bond lengths. The small bite angles of *N*-methylhydroxylamido(1–) ligands at 40.3, 40.1, or 39.1° (see Tables V and IX) are ideally suited for the occupation of equatorial positions of a pentagonal bipyramid.[5,6,8-11]

The dianion of *N*-methyl-*N*-hydroxylthiourea, $HNC(S)N(CH_3)O$, is coordinated via one nitrogen atom (equatorial position) and one oxygen atom in the axial position, forming a five-membered ring with the Mo(VI) center. The second axial position is occupied by a terminal oxo ligand. The two three-membered rings of the hydroxylamido ligands occupy four positions within the pentagonal plane (plane 1, Table VII) with N3 in the fifth position 0.38 A out of this plane, probably due to the steric requirements of the five-membered ring.

The axial terminal oxo ligands in V and VI have quite short Mo–O distances (1.68 Å), indicating considerable multiple-bond character. This is in good agreement with a number of monomeric molybdenum(VI)–oxo complexes[9,12,18,19] adopting a pentagonal-bipyramidal geometry. With use of the argumentation presented by Wentworth and co-workers,[21,22] a bond order of slightly greater than 2.5 seems to be effective, implying that the bond is probably best written as Mo$\overset{\leftarrow}{=}$O. In this way, the metal atom attains an 18-electron configuration. In general it has been observed that terminal oxo groups of this kind exert a large trans effect,[18] but in V the distance of Mo–O3 (2.03 Å) indicates only a relatively small effect—if any at all. It is noted that the Mo–N3 distance is still longer (2.06 Å). From this we conclude that both Mo–O3 and Mo–N3 are single bonds and no incorporation of the metal into any delocalized ring system has occurred.[20] The five-membered ring $\overline{\mathrm{MoON(CH_3)C(S)NH}}$ is not exactly planar (see plane 2, Table VII) with the C3 atom 0.23 A and the S atom 0.07 A out of the plane. The three canonical forms of the dianion of *N*-methyl-*N*-hydroxylthiourea, d, e, and f (Chart I), suffice to fully characterize the bonding situation: the C4–S, C4–N3, and C4–N4 distances are intermediate between single- and double-bond lengths whereas N4–C3 and N4–O3 distances are typical single-bond lengths, respectively.

**Chart I**

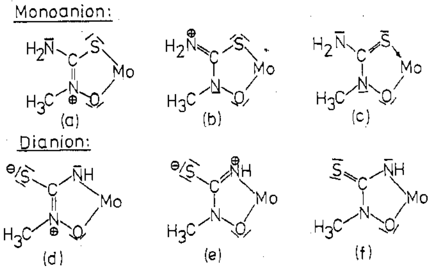

**Table VIII.** Bond Distances (Å) of $[MoO(H(CH_3)NO)(HNC(S)N(CH_3)O)(H_2NC(S)N(CH_3)O)]\cdot H_2O$

| | | | |
|---|---|---|---|
| Mo–S1 | 2.489 (2) | H1–N1 | 0.87 (7) |
| Mo–O1 | 1.976 (3) | H2–N2 | 0.76 (5) |
| Mo–O2 | 2.020 (3) | H3–N5 | 0.84 (5) |
| Mo–O3 | 2.114 (3) | H4–N5 | 0.82 (7) |
| Mo–N1 | 2.114 (4) | H6–O5 | 0.62 (9) |
| Mo–N2 | 2.026 (5) | H8–O5 | 0.92 (9) |
| Mo–O4 | 1.691 (3) | H11–C1 | 0.98 (8) |
| S1–C4 | 1.714 (5) | H12–C1 | 1.03 (6) |
| S2–C2 | 1.699 (6) | H13–C1 | 0.95 (8) |
| O1–N1 | 1.376 (7) | H31–C3 | 0.87 (9) |
| O2–N3 | 1.393 (6) | H32–C3 | 0.94 (6) |
| O3–N4 | 1.371 (7) | H33–C3 | 0.83 (7) |
| N1–C1 | 1.476 (7) | H51–C5 | 1.04 (5) |
| N2–C2 | 1.344 (6) | H52–C5 | 1.14 (8) |
| N3–C2 | 1.325 (7) | H53–C5 | 0.91 (7) |
| N3–C3 | 1.443 (6) | | |
| N4–C4 | 1.316 (6) | | |
| N4–C5 | 1.464 (7) | | |
| N5–C4 | 1.340 (9) | | |

The structure of $[MoO(H(CH_3)NO)(HNC(S)N(CH_3)O)(H_2NC(S)N(CH_3)O)]\cdot H_2O$ (VI) consists also of well-separated monomers and one additional molecule of water of crystallization per formula unit. Figure 2 shows the complex to have a distorted pentagonal-bipyramidal geometry but with only one *N*-methylhydroxylamido(1–) ligand in the equatorial position, bond distances and bond angles of the latter being

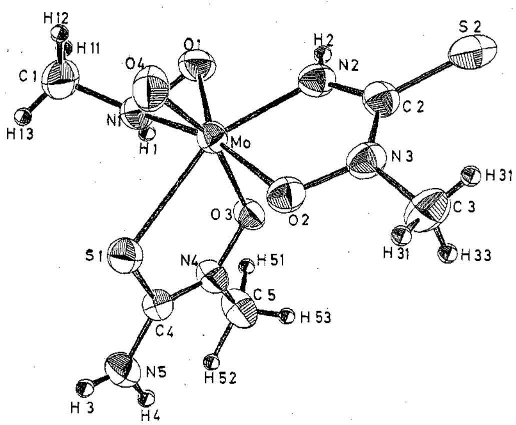

**Figure 2.** Structure of $[MoO(H(CH_3)NO)(HNC(S)N(CH_3)O)(H_2NC(S)N(CH_3)O)]$, showing 50% ellipsoids for all nonhydrogen atoms and the atom labeling scheme.

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**Table IX.** Bond Angles (Deg) of $[MoO(H(CH_3)NO)(HNC(S)N(CH_3)O)(H_2NC(S)N(CH_3)O)]\cdot H_2O$

| | | | | | |
|---|---|---|---|---|---|
| O1–Mo–S1 | 125.1 (1) | C4–S1–Mo | 99.5 (2) | N2–C2–S2 | 124.7 (4) |
| O2–Mo–S1 | 81.5 (1) | N1–O1–Mo | 75.8 (2) | N3–C2–S2 | 123.1 (3) |
| O2–Mo–O1 | 151.3 (2) | N3–O2–Mo | 117.0 (3) | N3–C2–N2 | 112.3 (5) |
| O3–Mo–S1 | 76.8 (1) | N4–O3–Mo | 122.6 (2) | H31–C3–N3 | 106 (4) |
| O3–Mo–O1 | 88.2 (1) | C1–N1–Mo | 124.4 (3) | H32–C3–N3 | 111 (4) |
| O3–Mo–O2 | 88.2 (1) | C1–N1–O1 | 116.4 (5) | H32–C3–H31 | 112 (6) |
| N1–Mo–S1 | 86.1 (1) | H1–N1–Mo | 119 (4) | H33–C3–N3 | 117 (4) |
| N1–Mo–O1 | 39.1 (2) | H1–N1–O1 | 102 (5) | H33–C3–H31 | 110 (7) |
| N1–Mo–O2 | 164.6 (2) | H1–N1–C1 | 115 (4) | H33–C3–H32 | 101 (6) |
| N1–Mo–O3 | 80.1 (1) | C2–N2–Mo | 120.8 (3) | C4–N4–O3 | 120.0 (4) |
| N2–Mo–S1 | 153.3 (1) | H2–N2–Mo | 120 (4) | C5–N4–O3 | 114.0 (4) |
| N2–Mo–O1 | 77.6 (2) | H2–N2–C2 | 119 (4) | C5–N4–C4 | 125.8 (5) |
| N2–Mo–O2 | 74.0 (1) | C2–N3–O2 | 115.6 (4) | N4–C4–S1 | 119.9 (5) |
| N2–Mo–O3 | 91.6 (2) | C3–N3–O2 | 114.5 (4) | N5–C4–S1 | 119.5 (3) |
| N2–Mo–N1 | 115.9 (2) | C3–N3–C2 | 128.9 (5) | N5–C4–N4 | 120.6 (5) |
| O4–Mo–S1 | 85.5 (2) | H11–C1–N1 | 111 (4) | H3–N5–C4 | 118 (4) |
| O4–Mo–O1 | 96.7 (2) | H12–C1–N1 | 100 (4) | H4–N5–C4 | 119 (5) |
| O4–Mo–O2 | 95.9 (1) | H12–C1–H11 | 91 (6) | H4–N5–H3 | 119 (7) |
| O4–Mo–O3 | 161.0 (2) | H13–C1–H12 | 123 (6) | H51–C5–N4 | 105 (3) |
| O4–Mo–N1 | 92.1 (2) | H13–C1–H11 | 120 (5) | H52–C5–N4 | 100 (3) |
| O4–Mo–N2 | 107.4 (2) | H13–C1–N1 | 110 (4) | H52–C5–H51 | 141 (4) |
| | | | | H53–C5–N4 | 104 (4) |
| | | | | H53–C5–H51 | 96 (5) |
| | | | | H53–C5–H52 | 107 (6) |

identical with those of structure V within experimental error (Tables VIII and IX). The dianion of *N*-methyl-*N*-hydroxylthiourea is coordinated as a bidentate ligand via an oxygen and a nitrogen atom to the Mo(VI) center. The Mo–O2 distance is also shorter than the Mo–N2 bond length, contrasting a structure reported in ref 23 where a Mo(VI)–N distance with double-bond character is reported. Although in VI the ligand $HNC(S)N(CH_3)O^-$ occupies two equatorial positions of the pentagonal plane (plane 1, Table X), the bonding situation is the same as in structure V: no evidence for a delocalized ring system incorporating the metal can be found. The canonical forms d, e, and f can satisfactorily account for the near planarity of the five-membered ring. In addition, it is shown that the carbon atom C2 has an exactly planar environment (plane 4, Table X) whereas the planarity of N3 is less well clear-cut (plane 5, Table X).

The most interesting feature of structure VI is the fact that a second ligand of *N*-methyl-*N*-hydroxylthiourea—in its monodeprotonated form—is coordinated via a sulfur atom and an oxygen atom to the Mo(VI) ion. The sulfur atom lies in an equatorial position whereas the oxygen atom of the ligand together with a terminal oxo group occupies the axial positions. The observed Mo–S1 and Mo–O3 bond distances again preclude the participation of the Mo(VI) in a delocalized ring system. They represent pure single-bond lengths.[23,24] Thus, the canonical forms a, b, and c account for the distances C4–S4, C4–N5, and C4–N4 which are intermediate between single- and double-bond lengths and for the distances N4–O3 and N4–C5 which are single-bond lengths. Contrary to V the terminal oxo group of structure VI does exert a substantial trans effect (Mo–O3 = Mo—O1 = 0.14 (1) Å), and Mo–O3 is now longer than the Mo–N2 bond length. It is not clear to us why the two compounds behave so differently.

In general, some lengthening of all bonds might be expected due to increased crowding when seven-coordinate structures are compared with similar six-coordinate complexes. In our complexes V and VI this seems not to be the case, at least not for the coordinated hydroxylamido(1–) ligands and the terminal oxo groups. All Mo–X bond lengths involved are within experimental error the same as in $[MoO_2(H(CH_3)NO)_2]$, a six-coordinate structure.[9]

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**Note Added in Proof.** After this paper had been accepted for publication, a paper by Mimoun et al. appeared describing the preparation and crystal structure of III which confirms the proposed structure (Saussine, L.; Mimoun, H.; Mitschler, A.; Fisher, J. *Nouv. J. Chim.* **1980**, *4*, 235).

**Registry No.** I, 70631-31-1; II, 74081-85-9; III, 74081-86-0; IV, 74081-87-1; V, 74096-66-5; VI, 74081-88-2; $Na_2MoO_4$, 7631-95-0; $MoO_3$, 1313-27-5.

**Supplementary Material Available:** Tables VII and X, several unweighted least-squares planes of structures V and VI, and listings of observed and calculated structure factor amplitudes for structures V and VI (31 pages). Ordering information is given on any current masthead page.

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(25) Computations were performed on a NOVA 3 (General Data) computer using SHELX (G. M. Sheldrick, Cambridge, England, 1976) and ORTEP (Johnson, C. K. Report ORNL-3794, Oak Ridge National Laboratory: Oak Ridge, Tenn., 1965).