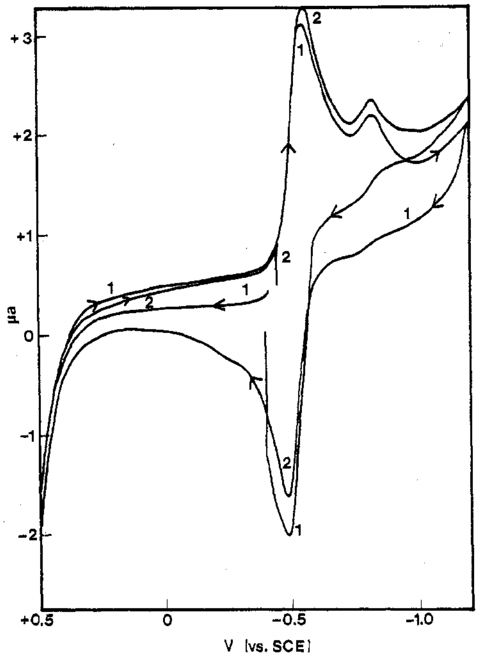

Figure 2. Cyclic voltammogram of $MoO(ox)_2(MePPh_2)$, after one-electron oxidation at +0.07 V (5.00×10^{-4} M in DMF, 0.10 M Et_4NCl): (1) anodic scan, beginning at -0.400 V; (2) cathodic scan, beginning at -0.450 V.

solution is allowed to stand, the oxidation peak at 0.037 V decreases in height at the expense of the oxidation peak at -0.435 V. After one-electron coulometric oxidation at 0.070 V, only the oxidation peak at -0.435 V remains (Figure 2); this peak and the reduction peak at -0.510 V are identical with those of $MoOCl(ox)_2$.[6] This is most likely due to the slow loss of the coordinated $MePPh_2$ ligand. Oxidation to the Mo(V) complex produces $MoOCl(ox)_2$, and subsequent rereduction gives only the Mo(IV) complex without $MePPh_2$. The changes in the cyclic voltammogram correspond in time to the changes noted above in the visible electronic spectrum for $MoO(ox)_2(MePPh_2)$ upon solution in DMF. For the other Mo(IV) complexes, the loss of coordinated $MePPh_2$ is apparently too rapid to observe during cyclic voltammetry.

Infrared Spectra. The infrared absorption frequencies for the MoO bands are found in the Table I. They occur at somewhat higher frequencies than the MoO bands of the molybdenum(V)-oxo or molybdenum(VI)-dioxo complexes.[11]

The $MoOCl_2L(MePPh_2)$ and $MoOL_2(MePPh_2)$ complexes described here form electron-transfer couples with the corresponding molybdenum(V)-oxo complexes $MoOCl_3L$ and $MoOClL_2$. The results are in agreement with the hypothesis of molybdenum(IV)-oxo and molybdenum(V))-oxo complexes being involved in rapid electron transfer at the molybdenum center of the molybdenum oxidases and nitrate reductase.[1-3]

Experimental Section

Materials. All solvents were spectrograde or were distilled before use. Et_3N, 8-aminoquinoline, Et_4NCl, and 8-hydroxyquinoline were purchased from Eastman, α,α'-bipyridyl and *o*-phenanthroline were from Aldrich, and $MePPh_2$ was purchased from Strem Chemicals.

Syntheses. $C_9H_7NS{\cdot}HCl$ (8-Mercaptoquinoline Hydrochloride). This ligand was synthesized according to the method of Kealey and Freiser.[12]

$MoOCl_2(bpy)(MePPh_2)$. This complex was prepared by addition of 0.50 g of α,α'-bipyridyl in 50.0 mL of dry EtOH to an equal volume of a hot solution equimolar in $MoOCl_2(MePPh_2)_3$ in dry EtOH, followed by gentle heating for 2 h under N_2. The solution was cooled and filtered, and the dark purple precipitate was washed with two 10-mL portions of pentane under N_2 and dried in vacuo overnight. Anal. Calcd for $MoC_{23}H_{21}Cl_2N_2OP$: C, 51,23; H, 3.93; Cl, 13.15; N, 5.19; P 5.74. Found: C, 50.73; H, 3.86; Cl, 13.28; N, 4.73; P, 5.36.

$MoOCl_2(phen)(MePPh_2)$. This complex was prepared in the same manner as $MoOCl_2(bpy)(MePPh_2)$. Anal. Calcd for $MoC_{25}H_{21}Cl_2N_2OP$: C, 53.51; H, 3.76; Cl, 12.59; N, 4.97; P, 5.50. Found: C, 52.48; H, 3.87; Cl, 12.30; N, 4.64; P, 5.84.

$MoO(ox)_2(MePPh_2)$. This complex was prepared by adding 25.0 mL of a dry EtOH slurry containing 1.70 g of $MoOCl_2(MePPh_2)_2$ to 1.13 g of 8-hydroxyquinoline and 0.80 mL of Et_3N (distilled) in 35.0 mL of dry EtOH. After being heated at rapid reflux under N_2 for 12 h, the solution was cooled, the deep wine precipitate was filtered, washed with two 10-mL portions of anhydrous diethyl ether, and dried in vacuo overnight. Anal. Calcd for $MoC_{31}H_{25}N_2O_3P$: C, 62.01; H, 4.20; N, 4.67; P, 5.16. Found: C, 61.77; H, 4.24; N, 4.73; P, 4.97.

$MoO(tox)_2(MePPh_2)$. This complex was prepared by adding 50.0 mL of dry CH_3CN containing 0.93 g of $C_9H_7NS{\cdot}HCl$ and 1.00 mL of Et_3N (distilled) to a slurry of 1.38 g of $MoOCl_2(MePPh_2)_3$ in 35.0 mL of dry CH_3CN. After the solution was stirred for 12 h at room temperature under N_2, the black-green precipitate was removed by filtration, washed with two 10-mL portions of anydrous diethyl ether, and dried in vacuo for 2 h. Anal. Calcd for $MoC_{31}H_{25}N_2OPS_2$: C, 58.66; H, 3.98; N, 4.43; P, 4.90; S, 10.14. Found: C, 56.53; H, 3.93; N, 4.35; P, 4.59; S, 9.60. This compound is unstable and must be stored under vacuum.

$(Et_4N)_2Mo(tdt)_3$. This complex was prepared by addition of a slurry of 0.665 g of $MoOCl_2(MePPh_2)_3$ in 25.0 mL of dry CH_3CN to 50.0 mL of a solution containing 0.350 g of 3,4-dimercaptotoluene and 0.45 mL of Et_3N (distilled) in dry CH_3CN. The mixture was stirred overnight at room temperature under N_2, 0.27 g of Et_4NCl was added, and the stirring was continued for 1 h. The bright blue precipitate was filtered, rinsed with three 10-mL portions of anhydrous diethyl ether, and dried in vacuo overnight. Anal. Calcd for $MoC_{37}H_{58}N_2S_6$: C, 54.25; H, 7.14; N, 3.42; S, 23.48. Found: C, 53.44; H, 7.33; N, 3.40; S, 22.11.

Electrochemical Measurements. Cyclic voltammetry and controlled-potential coulometry were performed as described previously.[7]

Acknowledgment. This work was supported by Grant GM 08347, National Institutes of Health.

Registry No. $MoOCl_2(bpy)(MePPh_2)$, 73953-23-8; $MoOCl_2(phen)(MePPh_2)$, 73953-24-9; $MoO(ox)_2(MePPh_2)$, 73953-25-0; $MoO(tox)_2(MePPh_2)$, 73953-26-1; $(Et_4N)_2Mo(tdt)_3$, 73970-85-1; $MoOCl_2(MePPh_2)_3$, 30859-03-1.

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Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida 32611

Synthesis of Methylhydrazine and 1,1-Dimethylhydrazine by the Reactions of Hydroxylamine-*O*-sulfonic Acid with Methyl- and Dimethylamine

Harry H. Sisler,* Milap A. Mathur, and Sampat R. Jain

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Interest in the synthesis of methylhydrazine and 1,1-dimethylhydrazine in nonaqueous solvents led us to investigate the reactions of hydroxylamine-*O*-sulfonic acid with methylamine and dimethylamine. Amination of primary and secondary amines by hydroxylamine-*O*-sulfonic acid forming the corresponding hydrazines is a known reaction.[1-3] Although there is apparently no report on the synthesis of 1,1-dimethylhydrazine by this method, methylhydrazine has been synthesized by the reaction of hydroxylamine-*O*-sulfonic acid

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Table I

components	% given by CDS-111 system	components	% given by CDS-111 system
methylamine	2.45	water	7.04
methanol	4.16	diglyme	24.71
methylhydrazine	53.92	others (including some gases)	7.42

with methylamine in aqueous KOH solutions.[1-3] The side products formed have, however, not been examined. Sisler et al.[4] have reported the amination of tertiary amines by hydroxylamine-*O*-sulfonic acid to form 1,1,1-trisubstituted hydrazinium sulfates, but they did not discuss any side products obtained in these reactions.

From the recovery point of view, it is preferable to synthesize methylhydrazine and 1,1-dimethylhydrazine in nonaqueous solvents. In this paper we report the syntheses of methylhydrazine and 1,1-dimethylhydrazine using hydroxylamine-*O*-sulfonic acid in bis(2-methoxyethyl) ether (diglyme) solutions. Besides the hydrazines, various side products are also formed. These products are believed to be formed by the subsequent oxidation of the hydrazines with hydroxylamine-*O*-sulfonic acid.

Experimental Section

Materials and Analyses. All solvents used were reagent grade. Hydroxylamine-*O*-sulfonic acid was supplied by Ventron, Alfa Division, and methylamine and dimethylamine were supplied by the Matheson Co. Diglyme was freshly distilled over CaH_2 before use.

The hydrazines were estimated by the iodate method.[5] The proton NMR spectra were recorded on a Varian Associates A-60-A spectrometer. The gas chromatographic data were obtained on a Varian Model 3700 gas chromatograph equipped with CDS-111 data analyzer and Soltic Model 252 integrating recorder. A 6 ft × $^1/_8$ in. Carbowax column having the composition 10% Carbowax 20 M + 5% KOH on Chrom-WAW, 80/100 mesh, was used. The chromatographs were obtained at the following parameters: injector temperature, 170 °C; column temperature, 80 °C; He flow rate, 20 mL/min; thermal conductivity detector temperature, 160 °C; thermal conductivity current, 150 mA; and filament temperature, 180 °C. A Nester/Faust spinning-band column was used for fractional distillation. Identification of the various products was achieved by comparing their proton NMR spectra and gas chromatographic retention times with those of known substances.

Reaction of Hydroxylamine-*O*-sulfonic Acid with Methylamine. In a typical experiment a 500-mL three-necked flask was equipped with a dropping funnel with a tip long enough to reach below the surface of the solvent, a dry ice–acetone-cooled condenser, and a nitrogen inlet. The flask was flushed with dry nitrogen for about 30 min; the nitrogen inlet was then removed from the central neck and was replaced by a mechanical stirrer; 300 mL of dry diglyme was added to the flask. The flask was cooled to −10 °C, and methylamine was bubbled through the diglyme until approximately 1.7 mol of CH_3NH_2 was collected. To this mechanically stirred solution was added 0.37 mol (42 g) of hydroxylamine-*O*-sulfonic acid in a 250-mL diglyme solution drop by drop at −10 °C. An exothermic reaction took place with the formation of a white solid. After the complete addition of the acid, the mixture was further stirred for 2 h and allowed to come to ambient temperature. The solid formed was filtered under nitrogen and recrystallized from aqueous methanol. It was found to be $(CH_3NH_3)_2SO_4$ by its sulfate analysis (SO_4^{2-}: calculated, 60.0%; found, 60.93%) and by comparing its melting point and ^1H NMR spectrum with those of an authentic sample of $(CH_3NH_3)_2SO_4$. The filtrate was analyzed for N–N bonded material by the acid iodate method. Total N–N bonded material found was 0.20 mol or 55% of theory on the basis of the hydroxylamine-*O*-sulfonic acid used. The solution was then distilled by using a spinning-band column, and the fraction distilling between 80 and 90 °C was collected. This fraction was examined by gas chromatography using the CDS-111 data system. Its composition is summarized in Table I.

Table II

components	% composition[a] 1st fraction (60–64 °C)	2nd fraction (69–90 °C)
other gases (N_2 etc.)	2.60	
dimethylamine	9.10	15.86
1,1-dimethylhydrazine	81.53	52.68
water		10.47
1,1,4,4-tetramethyl-2-tetrazene	1.44	3.64
diglyme	1.63	13.26

[a] % composition as given by the CDS-111 data system.

Table III

components	% composition[a] of the 2nd fraction (90–93 °C)
dimethylamine and other gases	7.05
1,1-dimethylhydrazine	49.45
water	13.33
1,1,4,4-tetramethyl-2-tetrazene	7.23
unidentified liquids plus diglyme	22.94

[a] % composition as given by the CDS-111 data system.

The above fraction (obtained between 80 and 90 °C) was redistilled by using a mini glass distillation apparatus with a Vigreux column and the fraction distilling between 87 and 90 °C collected. The proton NMR spectrum of this sample showed three peaks at δ 2.51, 3.30, and 3.65 downfield from internal tetramethylsilane. By comparing this NMR spectrum with the NMR spectrum of a known mixture of CH_3OH and CH_3NHNH_2, we assigned the peaks at δ 2.51 and 3.30 to N–CH_3 protons of methylhydrazine and O–CH_3 protons of methanol, respectively, and the peak at δ 3.65 was assigned to both NH and OH protons. The gas chromatography analysis of this product showed 84.3% methylhydrazine and 11.5% methanol; the remainder was methylamine, water, and diglyme.

Reaction of Hydroxylamine-*O*-sulfonic Acid with Dimethylamine in Diglyme. In a typical reaction, dimethylamine (1.78 mol) was condensed at −78 °C in a three-necked flask previously flushed with nitrogen. The flask had a sintered-glass frit at the bottom connected through a side tube for filtration. After the amine was diluted with 50 mL of cold diglyme, a solution of hydroxylamine-*O*-sulfonic acid (17.3 g, 0.15 mol) in 150 mL of diglyme was added dropwise with vigorous stirring over a period of 1 h at −78 °C. The reaction occurred smoothly with the separation of a white solid. After complete addition of the hydroxylamine-*O*-sulfonic acid solution, the reaction mixture was brought to room temperature with constant stirring. The excess amine was allowed to escape, and the liquid was filtered with suction. After 5 g of solid KOH was added, the filtrate was distilled on a spinning-band column. The distillate was collected in two fractions which were examined by gas chromatography (Table II). The lower boiling fraction (60–64 °C) contained 81.5% 1,1-dimethylhydrazine with a considerable amount of more volatile material. This corresponds to an overall yield of about 35% of the hydrazine on the basis of the hydroxylamine-*O*-sulfonic acid used. Its diglyme content was 1.63%, and it contained water as well as diglyme and one more component which was not identified. The proton NMR spectrum of the lower boiling fraction gave only two peaks, viz., at δ 2.60 and 3.16 downfield from internal tetramethylsilane, which may be assigned to 1,1-dimethylhydrazine. The solid material which was highly hygroscopic was washed several times with ether and was dried under vacuum. It contained SO_4^{2-} and gave evidence for the presence of N–N bonds in trace amounts by the iodate method. Washing with ethanol removed the N–N bonded material. On the basis the NMR spectrum of the insoluble portion in D_2O, the material appeared to be dimethylammonium sulfate.

Reaction of Hydroxylamine-*O*-sulfonic Acid with Dimethylamine. The reaction of a solution of 17.3 g of hydroxylamine-*O*-sulfonic acid in 150 mL of diglyme with 1.8 mol of the pure dimethylamine also was carried out. The reaction mixture was treated in a manner similar

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Table IV

reacn time	% yield $(CH_3)_2NN=NN(CH_3)_2$	% yield H_2O
10 min	2.00	1.70
30 min	2.70	2.70
70 min	0.83	1.25
10 days	0.00	

Table V

reacn time	% yield CH_3OH	% yield H_2O	% yield $CH_3NHN=CH_2$ or its dimer
10 min	40.55	0.31	3.83
45 min	36.78	0.10	1.55
20 h	33.13	1.78	4.62

to that of the previous experiment. The first fraction, distilling between 60–63 °C, was found to be almost pure 1,1-dimethylhydrazine with a trace of dimethylamine as shown by its gas chromatogram and NMR spectrum. The gas chromatographic data for the second fraction (Table III), distilling between 90 and 93 °C, showed 13 peaks besides those attributable to 1,1,4,4-tetramethyl-2-tetrazene and diglyme. The presence of these components was confirmed by the proton NMR spectrum of the mixture.

Reaction of Hydroxylamine-*O*-sulfonic Acid with 1,1-Dimethylhydrazine. In order to determine the source of water and 1,1,4,4-tetramethyl-2-tetrazene in the reaction of dimethylamine with hydroxylamine-*O*-sulfonic acid, we carried out the reaction of dimethylhydrazine with hydroxylamine-*O*-sulfonic acid under conditions similar to those of the dimethylamine reaction. A 500-mL three-necked flask was equipped with a nitrogen inlet and outlet and a dropping funnel with its tip long enough to reach below solution level in the flask. The assembly was flushed with nitrogen for 30 min. Six grams (100 mmol) of freshly distilled dimethylhydrazine dissolved in 100 mL of dry diglyme was placed in the flask and the solution kept at −10 °C. Hydroxylamine-*O*-sulfonic acid, 5.7 g (50 mmol), was dissolved in 50 mL of diglyme, transferred to the dropping funnel, and added dropwise to the continuously stirred solution of dimethylhydrazine over a period of 45 min. The reaction was immediate with the formation of a white precipitate of $[(CH_3)_2NNH_3HSO_4]$, water, and 1,1,4,4-tetramethyl-2-tetrazene. Discarding the solvent peak from the gas chromatographic analysis of the reaction mixture, we estimated the yields of water and tetramethyl-2-tetrazene (Table IV).

There was also some evidence for methanol formation; on long standing the tetrazene disappeared, and the yield of methanol approached theoretical.

Reaction of Hydroxylamine-*O*-sulfonic Acid with Methylhydrazine. With the procedure described above, a sample of 4.6 g (100 mmol) of methylhydrazine and 5.7 g (50 mmol) of hydroxylamine-*O*-sulfonic acid were reacted in 150 mL of diglyme. The reaction products were examined by gas chromatographic analysis. The results were as shown in Table V. Further confirmation of H_2O and CH_3OH was obtained by adding a drop of each to a sample of the reaction mixture and observing that the areas under the peaks assigned to water and methanol did, in fact, increase.

Results and Discussion

The results obtained show that both methylhydrazine and 1,1-dimethylhydrazine can be obtained by the reaction of hydroxylamine-*O*-sulfonic acid with the corresponding amines and can be conveniently recovered from diglyme solution. The reaction with methylamine may be represented as

$$NH_2OSO_2OH + 3CH_3NH_2 \rightarrow CH_3NHNH_2 + (CH_3NH_3)_2SO_4$$

Besides the methylhydrazine and methylammonium sulfate which are formed as the major products of the reaction with methylamine, methanol and water are also observed as minor products. It is interesting to note that methanol has also been reported as an oxidation product of methylhydrazine by metal oxides.[6] Further, both water and methanol were observed in a recent study of the oxidation of methylhydrazine by oxygen in this laboratory.[7] It was presumed that these two products were produced by the reaction of hydroxylamine-*O*-sulfonic acid with some of the methylhydrazine produced by the amination of the amine. That this is, indeed, the case was confirmed by carrying out the reaction of hydroxylamine-*O*-sulfonic acid with methylhydrazine under reaction conditions similar to those of the amine reaction as described above.

Similarly, the side products observed in the case of the dimethylamine–hydroxylamine-*O*-sulfonic acid reaction included water and 1,1,4,4-tetramethyl-2-tetrazene. Water is also observed in the atmospheric oxidation[8] of 1,1-dimethylhydrazine, and 1,1,4,4-tetramethyl-2-tetrazene is formed as a major product when 1,1-dimethylhydrazine is oxidized by mercuric oxide[9] or one of the halogens.[10] Further, both these products were observed when 1,1-dimethylhydrazine was oxidized in oxygen.[7] It was, therefore, presumed that water and 1,1,4,4-tetramethyl-2-tetrazene were formed as oxidation products of some of the 1,1-dimethylhydrazine by hydroxylamine-*O*-sulfonic acid. This was confirmed by carrying out the reaction of hydroxylamine-*O*-sulfonic acid with dimethylhydrazine under conditions similar to those of the dimethylamine reaction. As shown in the Experimental Section, water and 1,1,4,4-tetramethyl-2-tetrazene were indeed formed by the reaction of dimethylhydrazine with hydroxylamine-*O*-sulfonic acid.

It is interesting to note that the methyl- and 1,1-dimethylhydrazine hydrazones of formaldehyde are not observed in the reactions of hydroxylamine-*O*-sulfonic acid with methyl- and dimethylamines, respectively. These hydrazones are known to be major oxidation products of methylhydrazine and 1,1-dimethylhydrazine by chloramine,[11] oxygen,[7,8] or mercuric oxide.[9] However, the methylhydrazone of formaldehyde or its dimer is a minor product of the reaction of hydroxylamine-*O*-sulfonic acid with methylhydrazine.

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Registry No. NH_2OSO_2OH, 2950-43-8; CH_3NH_2, 74-89-5; $(CH_3)_2NH$, 124-40-3; CH_3NHNH_2, 60-34-4; $(CH_3)_2NNH_2$, 57-14-7; $(CH_3)_2NN{=}NN(CH_3)_2$, 6130-87-6; $(CH_3NH_3)_2SO_4$, 33689-83-7; $((CH_3)_2NH_2)_2SO_4$, 37773-96-9; CH_3OH, 67-56-1; H_2O, 7732-18-5.

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Contribution from Lash Miller Chemical Laboratories and
Erindale College, University of Toronto, Toronto,
Ontario, Canada M5S 1A1

Double Refractory Bimetallic Clusters: Optical and Extended Hückel Molecular Orbital Studies of the MoNb Molecule

Werner E. Klotzbücher and Geoffrey A. Ozin*

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Very small transition-metal clusters of precisely defined dimensions are of wide-ranging interest in, for example, cluster