Table IV

reacn time	% yield	
	$(CH_3)_2NN{=}NN(CH_3)_2$	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	H_2O	$CH_3NHN{=}CH_2$ 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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Double Refractory Bimetallic Clusters: Optical and Extended Hückel Molecular Orbital Studies of the MoNb Molecule

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

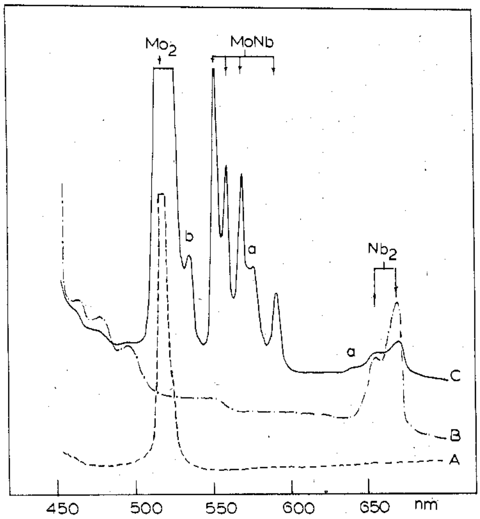

Figure 1. Low-energy optical absorption spectra of the products formed in the matrix codepositions (A) Mo/Ar $\simeq 1/10^3$, (B) Nb/Ar $\simeq 1/10^3$, and (C) Mo/Nb/Ar $\simeq 1/1/10^3$ at 10–12 K showing the bands ascribed to Mo_2, Nb_2, and MoNb. The lines labeled "a" are thought to be unstable matrix sites of MoNb and Nb_2, and "b" depicts a trace amount of Mo_3.

model theory and heterogeneous catalysis.[1] In view of the exciting potential that multimetallic cluster systems hold for improving a variety of heterogeneous reactions which operate with unimetallic catalysts,[2] it is important to develop new chemical and physical methods for improving our understanding of these multicomponent systems at the atomic level.

It would appear that a useful insight into the electronic and molecular properties of few-atom, multimetallic clusters can be obtained by a combination of metal-vapor cryochemical techniques with a suitable form of spectroscopy such as UV-visible,[3] ESR,[4] or Mössbauer.[5] We have recently demonstrated that very small, unimetallic and bimetallic clusters can be generated and trapped by simultaneously codepositing metal vapors with either a low-temperature, weakly interacting matrix[1,3] or a functionalized liquid polymer at close to room temperature.[6] In rare-gas supports, the clusters can be fabricated either during the deposition process[1,3] or within the solid matrix by annealing[1,3] and cryophotoaggregation[1,7] procedures.

Table I. Optimized Parameters Used in the Extended Hückel Calculations of Mo_2, MoNb, and Nb_2[a]

metal	orbital	orbital exponent	H_{ii}, eV
Nb	4p	3.566	−39.56
	4d	2.070	−6.00
	5s	1.351	−6.40
	5p	0.992	−4.00
Mo	4p	3.761	−44.39
	4d	2.105	−7.00
	5s	1.409	−7.00
	5p	0.994	−4.25

[a] Compared to previous EHMO calculations,[3] only the 4d-orbital exponents have been adjusted downward by a value of one unit, in a designed attempt to increase the d-orbital involvement in the bonding schemes of these heavy-metal diatomics and to match the d-orbital splitting energies obtained in related SCF-Xα-SW calculations.[3]

Up to the present time, bimetallic cluster matrix research has involved, at most, only one refractory metal component. While this study was under completion, Gupta and Gingerich[8] reported a Knudsen effusion mass spectrometric investigation of the MoNb molecule generated in the high-temperature molybdenum–niobium–carbon system. The matrix optical spectrum, together with extended Hückel molecular orbital calculations of MoNb, constitutes the subject matter of this brief note.

The bimetal-vapor-matrix cocondensation methods used in the present study have been described previously.[3] Niobium and molybdenum (99.99%) both supplied by McKay, New York, were evaporated by direct heating of the metal filaments in a vacuum furnace, dual-quartz-crystal microbalance assembly.[3] UV–visible spectra were recorded on a standard Unicam SP8000 spectrophotometer in the range 200–700 nm. The sample was condensed onto a NaCl optical window cooled to 10–12 K by means of a Displex closed-cycle helium refrigeration unit, with the deposition temperature monitored by a 1/0.07 atom % Au–Fe thermocouple embedded in a drilled cavity close to the center of the sample window.

In an earlier study we have described the matrix optical spectra of Nb, Nb_2, Mo, Mo_2 and Mo_3[3,7,9] and have discussed the experimental difficulty of vaporizing niobium resistively and quantitatively at roughly 50 °C below its melting point. Typical low-energy optical spectra of Mo/Ar and Nb/Ar $\simeq 1/10^3$ mixtures are shown in Figure 1A,B and depict the major absorptions of Mo_2 and Nb_2 in the presence of the parent atomic species (the latter seen best in the higher energy regions of the spectra[3,7,9]). From a series of Nb/Mo/Ar cocondensations over a wide range of concentration ratios, one observes besides the characteristic absorptions of Nb_2 and Mo_2 a series of remarkably clear spectral features at 551, 558, 568, 575, and 590 nm, energies intermediate between those of Nb_2 and Mo_2, which appears to be associated with a bimetallic cluster species, Mo_xNb_y. The line at 575 nm as well as a weak absorption at 640 nm (labeled "a" in Figure 1) vanishes upon thermally annealing the matrix at 25 K and probably depicts the presence of one or more unstable matrix sites of the new species.

One is thus left with *four* well-resolved new lines whose energy spacing seems much too large to represent part of a vibronic progression of a Mo_xNb_y cluster species. Resistance of this quartet to thermal annealing would argue against a site-splitting phenomenon. Under the high-dilution conditions chosen in these experiments one would expect the production

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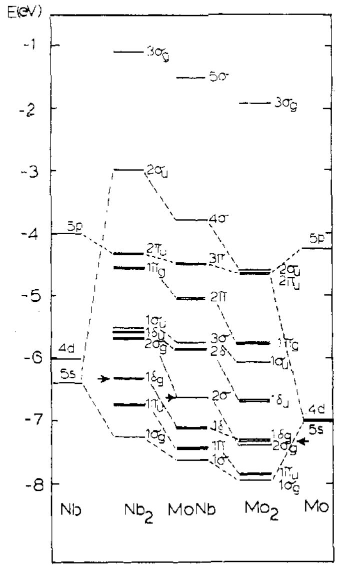

Figure 2. EHMO schemes for Mo_2, MoNb, and Nb_2 calculated at the minimum-energy geometries of 2.40, 2.30, and 2.20 Å, respectively (see text). Arrows indicate HOMO'S.

of trinuclear and higher clusters to be negligible. Therefore with a fair degree of confidence one can associate the new absorptions centered around 570 nm with the bimetallic molecule MoNb. Support for this proposal stems from comparisons with the optical spectra of the CrMo molecule which also shows a well-resolved, low-energy absorption (with similar splittings) located essentially midway between those of the respective parent diatomic absorptions,[3] a situation analogous to that discovered for a wide range of bimetallic cluster complexes.[10] Such an averaging effect for the transition energies of MoNb relative to Mo_2 and Nb_2 is not unreasonable for closely related atomic components having similar electronic configurations (Nb, $4d^45s^1$; Mo, $4d^55s^1$) and comparable valence orbital ionization potentials (Table I). One should note that an averaging effect of the bond dissociation energies of Mo_2, MoNb, and Nb_2 has recently been observed mass spectrometrically,[8] which is understandable since the ionic contribution to the Mo–Nb bond strength is calculated to be less than 1 kcal mol^{-1} from Pauling's formula[11] based on the electronegativity difference between Nb and Mo.

For some additional insight into the electronic architecture of MoNb, a series of EHMO calculations was performed on MoNb by employing input parameters which had been spectroscopically optimized with respect to the parent diatomics, Mo_2 and Nb_2 (Table I). The resulting energy-level schemes for Mo_2, MoNb, and Nb_2 calculated at the minimum-energy geometries are illustrated in Figure 2. One should note here that the modified EHMO parameters listed in Table I give rise to a d-orbital splitting which more closely resembles that found in related SCF–Xα–SW calculations.[3] On the basis of these ground-state, low-spin energy level diagrams, one can determine a set of optical assignments which are internally consistent with the absolute energy values as well as the spectral trends observed for Mo_2, MoNb, and Nb_2 (Table II). However, because of the changes in electronic configuration involving formally 10-, 11-, and 12-valence-electron diatomics, the spectral correlations are not as straightforward as those derived for the related 12-valence electron Cr_2, CrMo, and Mo_2 series of molecules.[3]

Table II. Calculated and Observed Optical Transitions for Nb_2, MoNb, and Mo_2 in Solid Argon

molecule	assignt[a]	calcd transtn energy, cm^{-1}	obsd transtn energy	
			cm^{-1}	nm
Nb_2	$1\sigma_g \rightarrow 1\sigma_u$	13 967	14 992	667
			15 290	654
	$1\sigma_g \rightarrow 2\pi_u$	23 690	23 809	420
	$1\sigma_g \rightarrow 2\sigma_u$	34 370	35 714	280
MoNb[b]	$1\sigma \rightarrow 3\sigma$	15 302	16 949	590
	$2\sigma \rightarrow 3\pi$	17 210	17 605	568
	$1\pi \rightarrow 2\pi$	19 175	17 921	558
	$1\sigma \rightarrow 2\pi$	20 970	18 148	551
	$2\sigma \rightarrow 4\sigma$	22 858		
Mo_2	$2\sigma_g \rightarrow 2\sigma_u$	22 419	19 305	518
	$1\sigma_g \rightarrow 2\sigma_u$	26 945	32 467	308
	$1\pi_u \rightarrow 3\sigma_g$	48 001	43 103	232

[a] Note that, with the modified EH parameters used in these calculations, the assignments of the optical bands of Nb_2 and Mo_2 differ from those reported previously.[3] [b] Note that the electric dipole allowed $1\delta \rightarrow 2\pi$ transition of MoNb, although falling within the spectroscopic range of interest (calculated 16 487 cm^{-1}), is expected to have a low oscillator strength and is therefore not assigned.

On a final note, it is interesting that the potential energy calculations of the present study support the concept that these refractory metal diatomic molecules are likely to have high bond orders and bond strengths as seen from the computed bond dissociation energies of 171, 72, and 123 kcal mol^{-1} for Mo_2, MoNb, and Nb_2, respectively. These values can be compared with those obtained mass spectrometrically by Gupta et al., that is, 96.5 ± 5, 108 ± 6, and 122 ± 2.4 kcal mol^{-1}, respectively. Thus, the EHMO calculations of the present study are unable to reproduce either the experimental trend in bond energies or the absolute values of the bond energies of these refractory molecules, although the experimental order $D(Nb_2) > D(MoNb) > D(Mo_2)$ is somewhat unexpected for molecules which are purported to have multiple bond orders of 5, $5^1/_2$, and 6, respectively.[3,8] SCF–Xα–SW and/or ab initio studies of these heavy-metal diatomics would seem warranted to illuminate this puzzling aspect of the work.

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Registry No. Nb_2, 12596-70-2; Mo_2, 12596-54-2; MoNb, 68777-39-9.

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Wavelength Dependence of Photohydrolysis and Luminescence Quantum Yields of Tris(bipyridine)chromium(III) Ion

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The photohydrolysis of $Cr(bpy)_3^{3+}$ (bpy = bipyridine) in basic media to give $Cr(bpy)_2(OH)_2^+$ has been assigned as a reaction from the ^2E (approximate O_h microsymmetry) state which is luminescent and relatively long-lived (τ = 63 μs in deaerated solution).[1] This is the only photosubstitution re-