$Nb_2(OCH_3)_{10}$ nor $Ta_2(OCH_3)_{10}$ crystallizes. Identical crystals were also obtained from nonequimolar mixtures of the symmetric alkoxides. Their ir spectrum shows the presence of both ν(Nb–O) and ν(Ta–O) stretching frequencies (550 and 511 cm^{-1}, respectively).[5]

When dissolved in various solvents, the crystals give NMR spectra which are identical with those observed with *equimolar* mixtures of the symmetric alkoxides dissolved in the same solvent.

That the isolated solid does *not* consist of mixed crystals of both symmetric dimers is further borne out by mass spectral analysis. Figure 2 compares the mass spectrum of compound I with those measured on the symmetric alkoxides $Nb_2(OMe)_{10}$ and $Ta_2(OMe)_{10}$. The molecular ion is found at *m/e* 584 (20.6%) (expected for $NbTa(OMe)_{10}$: 584.09). Other fragments containing *both* niobium *and* tantalum atoms were identified at *m/e* 582, 488, 486, 431, 429, 367, 365, and 276 (loss of CH_3OH, CH_2O, or $(CH_3)_2O$), while *none* of the higher mass fragments containing two tantalum atoms (*m/e* 641, 610, 595, 549, 519, 503, 495, 482, 467, 454, 439) or two niobium atoms (*m/e* 465, 434, 419, 388, 373, 326, 311, 297, 280, 264, 262, 218, 217), which are found in the spectra of the symmetric alkoxides,[6] were detected in the spectrum of I.

The molar equilibrium distributions of the three species in solution were determined from the NMR spectra for various Nb:Ta ratios and in several solvents. Average values (10 samples examined) for the equilibrium constant $\bar{K} = [NbTa(OMe)_{10}]^2/[Nb_2(OMe)_{10}][Ta_2(OMe)_{10}]$ are 3.1 ± 0.7 (toluene), 6.2 ± 0.3 (acetonitrile), and 5.4 ± 0.3 (octane) at −30°C. These values are close to the value of 4 which would correspond to a random association of the $Nb(OMe)_5$ and $Ta(OMe)_5$ monomers. This is interpreted to mean that the replacement of one niobium atom by a tantalum atom, or vice versa, in the symmetric dimers does not drastically alter their structures and suggests that tantalum may be used as a label in polynuclear niobium compounds and vice versa.

Experimental Section

All manipulations were carried out under dry nitrogen. The symmetric alkoxides were synthesized as reported in the literature.[1] Solvents were purified and dried by standard methods. NMR spectra (δ in ppm, TMS as internal standard) were recorded on JEOL C-60 HL and Varian HA-100 spectrometers equipped with a variable-temperature attachment. Quantitative evaluations of the concentrations in equilibrated mixtures were performed by cutting and weighing of Xerox copies of several spectra each time. Ir spectra were measured on Nujol mulls on a Beckman IR 12 spectrometer. Mass spectra were obtained on an AEI MS 902 apparatus under 70 eV at a source temperature of 200°C.

Crystalline Niobium Tantalum Decamethoxide (I). Niobium pentamethoxide (442 mg, 1.78 mmol) and tantalum pentamethoxide (485 mg, 1.44 mmol) were dissolved in dry octane (12 ml). Deposition of colorless crystals occurs slowly at room temperature. The crystalline product was filtered after 2 months, washed with petroleum ether, and dried under vacuum: mp 110°C; ir (Nujol): 1160, 1100 (ν(C–CR)); 880, 800, 720; 550 (ν(Nb–O)), 511 (ν(Ta–O)) cm^{-1}. $NbTa(OCH_3)_{10}$ is very unstable in air. It is soluble in toluene or acetonitrile and insoluble in aliphatic hydrocarbons.

Acknowledgment. We wish to thank Dr. Nixon (Brighton) for having measured the mass spectra of compound I.

Registry No. $NbTa(OMe)_{10}$, 56348-61-9; $Nb_2(OMe)_{10}$, 18533-43-2; $Ta_2(OMe)_{10}$, 18533-42-1.

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Raman Spectrum of Matrix-Isolated S_2O. Evidence for the Formation of S_3 and SO_2 from S_2O

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Disulfur monoxide, once mistaken as sulfur monoxide,[1,2] has now been well characterized.[3-6] In the infrared spectrum of gaseous S_2O, Jones[2] observed two bands at 1165 and 679 cm^{-1}. Later, these were correctly assigned to ν_1 (S–O stretching vibration) and ν_2 (S–S stretching vibration) by Blukis and Myers.[5] The frequency of the bending vibration, ν_3, was first estimated from the microwave spectrum of gaseous S_2O by Meschi and Myers;[4] however, a more precise frequency (388 cm^{-1}) was obtained from the infrared spectrum of a frozen film at 77 K.[5] Despite the fact that the sulfur oxides are very good Raman-scattering species, the Raman spectrum of S_2O has not been reported to date. The reason for this is probably due to the fact that S_2O is not very stable, and it is usually prepared in very small quantities by passing SO_2 (or S + SO_2) through an electronic discharge.

The objective of the present study was to observe the Raman spectrum of matrix-isolated S_2O by preparing relatively large amounts through the direct synthesis from thionyl chloride and silver sulfide. However, in addition to obtaining the spectrum of matrix-isolated S_2O, we also obtained information on the bimolecular reaction of two S_2O molecules through changes in the spectra as a function of the *M/A* (matrix:active species) ratio and by limited diffusion experiments.

Disulfur monoxide, S_2O, was prepared by passing thionyl chloride, $SOCl_2$, over warm Ag_2S. $SOCl_2$ (J. T. Baker, purified) and Ar (Matheson, 99.998%) were used without further purification. The vapor of $SOCl_2$ was mixed with Ar to obtain the desired matrix ratios by standard manometric procedures. Ag_2S was precipitated from aqueous $AgNO_3$ by adding aqueous Na_2S; the precipitate was washed with hot distilled water several times and dried on a hot plate. Ag_2S was dried again in situ under vacuum at ~200°C for 1 hr prior to each experiment. The gaseous mixture of $SOCl_2$ and Ar were passed through Ag_2S contained in a horizontal Pyrex tube (1-cm o.d., 20 cm long), and the reaction products were cocondensed with Ar onto an OFHC copper cold finger (20 K) in a hydrogen Cryotip cell[7] at the rate of 6–8 mmol/hr. The Ag_2S in the tubing was heated by a nichrome winding, and the temperature was varied from room temperature to 150°C. Because of the higher partial pressure of $SOCl_2$ at lower *M/A* (Ar:$SOCl_2$) ratios, a higher Ag_2S temperature was used in order to make the reaction between $SOCl_2$ and Ag_2S more complete. The temperature of Ag_2S was 150°C at *M/A* = 25 and 50, 120°C at *M/A* = 100, 70°C at *M/A* = 140, and 23°C (room temperature) at *M/A* = 250 and 500.

Raman spectra were measured using a Spex Industries

Model 1401 double monochromator with photon-counting detection and a CRL Model 52-A argon ion laser. The 4880-Å laser line (~100 mW power at the sample) was used to obtain all of the spectra. However, the fact that the observed bands were due to Raman scattering was confirmed by measuring several spectra using the 5145-Å laser line as the exciting source. Frequencies of the observed bands were calibrated by the emission lines[8] of a neon lamp.

Raman spectra of the products from the reaction of $SOCl_2$ with Ag_2S isolated in an Ar matrix at Ar:$SOCl_2$ (*M*/*A*) ratios of 50, 100, 250, and 500 are shown in Figure 1. The observed frequencies and assignments are listed in Table I.

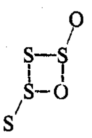
The reaction of $SOCl_2$ with Ag_2S has been used for preparing S_2O by others,[6,9,10] and it was found to be a very effective method. Since S_2O is not a stable molecule, Schenk and Steudel[11,12] have suggested that S_2O decomposes into sulfur and SO_2 according to the reaction

$$2S_2O \rightarrow 3S + SO_2 \tag{1}$$

In our experiments, higher *M*/*A* ratios and lower preparation temperatures were used to eliminate the self-decomposition of S_2O, i.e., under these conditions the intensities of the bands due to S_2O increased relative to those of SO_2. The relative intensities of the bands at 1157, 673, and 382 cm^{-1} increase with increasing *M*/*A* ratios, and the frequencies agree with the vibration frequencies of S_2O from previous infrared measurements.[5,13,14] Thus, these three bands are assigned to S_2O: 1157 cm^{-1} as S–O stretching vibration (ν_1), 673 cm^{-1} as S–S stretching vibration (ν_2), and 382 cm^{-1} as bending vibration (ν_3).

The products other than S_2O from the reaction between $SOCl_2$ and Ag_2S are SO_2 and a sulfur species which come from the decomposition of S_2O according to eq 1. At lower *M*/*A* ratios the concentration of S_2O is higher and this increases the bimolecular reaction between two S_2O molecules. Consequently, this increases the amount of SO_2 and the sulfur species. In addition to the band due to SO_2 at 1145 cm^{-1} (symmetric stretching vibration), a strong band at 583 cm^{-1} appears in all of the spectra. As the relative intensities of the bands due to S_2O decrease with the decreasing of *M*/*A* ratios, the relative intensity of this band increases. Furthermore, in limited diffusion experiments (Figure 1c and f) the band at 583 cm^{-1} as well as the band due to SO_2 at 1145 cm^{-1} increased in intensity at the expense of the bands due to S_2O.

Previously, Meyer and coworkers[15] observed the absorption band progression of S_3 in the visible spectrum of high-temperature sulfur vapor. From these data they calculated that the frequency of one of the stretching vibrations of S_3 in the ground electronic state should be at ~590 cm^{-1}. This agrees very well with the value of 583 cm^{-1} we observed in the Raman spectra, which suggests that S_3 is formed during the self-decomposition of S_2O. This seems reasonable, if we consider that a bimolecular reaction between two S_2O molecules would likely go through a complex such as



to form SO_2 and S_3.

We also measured infrared spectra of S_2O at *M*/*A* ratios of 70, 200, and 500. Bands due to SO_2 increased as those due to S_2O decreased with decreasing *M*/*A* ratios and in limited diffusion experiments. We had hoped to detect bands due to the other vibrations of S_3; however, we could not make any definite assignments. The reason for this is that sulfur species generally have low extinction coefficients in infrared spectra, whereas they are very good Raman scatterers.

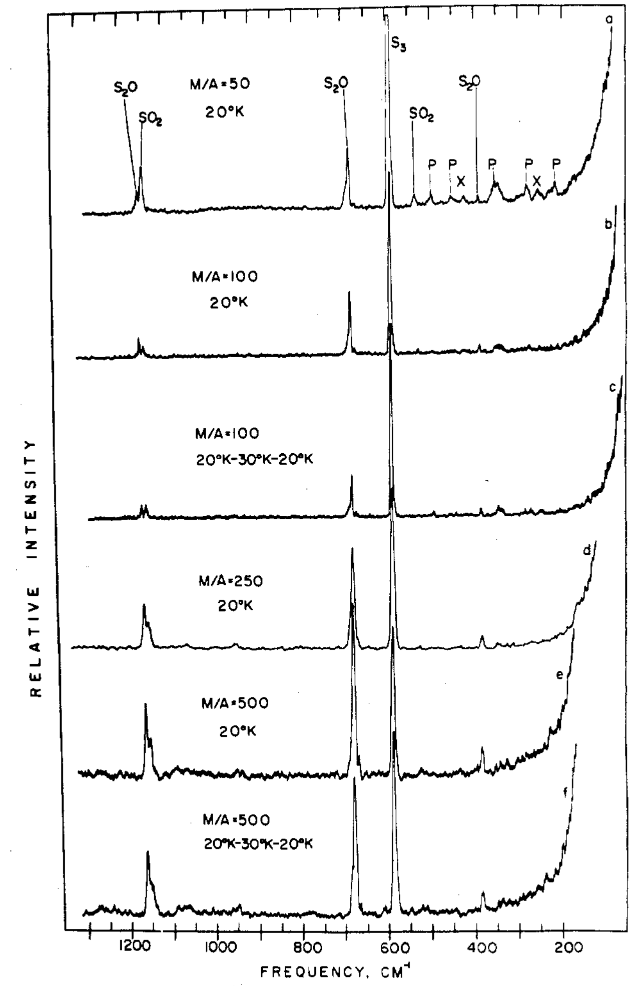


Figure 1. Raman spectra of S_2O and S_3 matrix-isolated in Ar at 20 K. c and f were measured after temperature cycling to 30 K for 30 min. Slit widths; a, 4 cm^{-1}; b and c, 3.5 cm^{-1}; d, 5.5 cm^{-1}; f, 5 cm^{-1}. P = $SOCl_2$; X = ?.

Table I. Observed Raman Frequencies of Matrix-Isolated S_2O and S_3

ν, cm^{-1}	Assignment	ν, cm^{-1}	Assignment
1157	S_2O, ν_1	410	?
1145	SO_2, ν_1	382	S_2O, ν_3
673	S_2O, ν_1	345	$SOCl_2$
662	S_3, ν_3?	334	?
583	S_3, ν_1	250	$SOCl_2$
523	SO_2, ν_2	243	?
486	$SOCl_2$	205	$SOCl_2$
440	$SOCl_2$		

The present results strongly support the self-decomposition of S_2O by reaction 1; i.e., it forms SO_2 and S_3 through a bimolecular reaction with itself. Furthermore, they support our previous results[16] in which S_2O was formed by passing SO_2 through a radiofrequency discharge. In those experiments we also observed a band at 583 cm^{-1}, which we assigned to S_3.

Acknowledgment. We wish to express our appreciation to the National Science Foundation for a matching grant which made possible the purchase of the Raman instrumentation.

Registry No. S_2O, 20901-21-7; SO_2, 7446-09-5; S_3, 12597-03-4.

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Proton Magnetic Resonance Spectrum of Magnesium Acetylacetonate in Chloroform-*d*. Evidence for Conformational Equilibrium

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It has been known for some time that the proton magnetic resonance (^{1}H NMR) spectra of most bis and tris diamagnetic metal acetylacetonate (abbreviated as "acac") complexes consist of a pair of singlets.[1,2] One is due to the $-CH_3$ protons and the other to the ring proton (Figure 1). The intensity ratio of the two signals is 6:1. The chemical shifts of these protons are relatively insensitive to the solvent used and to the particular metal in the complex.[3,4] An exception to these observations has, however, been noted. Eaton[4] has reported that Mg(acac)$_2$, dissolved in $CDCl_3$, exhibits two peaks due to methyl resonances. This doubling was ascribed to nonequivalent methyl groups and it was concluded that the compound was not symmetric. Other investigators have reported the ^{1}H NMR spectrum of Mg(acac)$_2$ in dimethyl-d_6 sulfoxide and observed only one peak attributable to methyl resonances.[5]

A possible explanation for the observed solvent dependence of the ^{1}H NMR spectrum of Mg(acac)$_2$ can be based on the existence of a solvent-dependent equilibrium between two geometrical isomers of the bis-bidentate chelate system. According to this explanation, the two methyl resonances in $CDCl_3$ can be attributed to the presence of significant concentrations of both isomers, whereas the single methyl resonance observed in dimethyl-d_6 sulfoxide would indicate that one isomer is preferred in this solvent.

There are two preferred molecular symmetries for bis-acetylacetonate complexes. The four oxygens of the acac ligands may be arranged in a distorted tetrahedral configuration around the metal atom (D_{2d} symmetry) or they may be placed in one plane (D_{2h} symmetry). Detailed structural data indicating which form is more stable in the gas phase or in solution do not exist. Semiempirical molecular orbital calculations have been performed in the CNDO/2 approximation[7] on both the D_{2d} and D_{2h} structure types, and it was found that the D_{2d} isomer was more stable than the D_{2h} by ~0.45 eV (~10 kcal/mol).[8] It is possible to convert one isomer into the other by a 90° rotation of one acac ring as a whole about the metal atom.

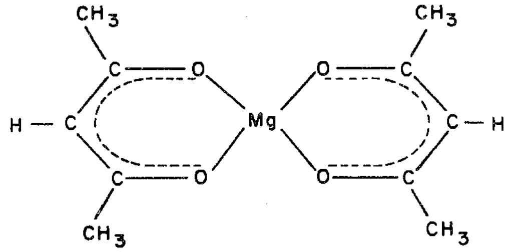

Figure 1. Structure of Mg(acac)$_2$.

To examine the possibility of whether one methyl resonance of Mg(acac)$_2$ in $CDCl_3$ is in fact due to the $-CH_3$ protons of a D_{2d} isomer and the other to a D_{2h} isomer, the ^{1}H NMR spectra of a series of bis-acetylacetonate comlexes were recorded in a variety of solvents. Since the chemical shift of the methyl groups on an acac ring appears to depend primarily on the geometry of the complex and not on the identity of the central metal ion, it seemed reasonable to compare the shifts of some D_{2d} and D_{2h} complexes with the values found for Mg(acac)$_2$.

It is known that Be(acac)$_2$ adopts a D_{2d} conformation[9] and that Ca(acac)$_2$ and Ba(acac)$_2$ probably are of D_{2h} symmetry.[1] It is also known that, in the absence of polymerization, four-coordinate zinc β-diketonates are D_{2d}.[10,11]

A final test for conformational equilibrium may be made by obtaining the chemical shifts of protons in unsymmetric β-diketone ligands.[12] If one of the $-CH_3$ groups on each chelating ring in Figure 1 is replaced by a phenyl group, one obtains the benzoylacetone complex (abbreviated as "bzac"). If this chelate were found in the D_{2h} form, two methyl resonances would be observed, while only one should be observed if the D_{2d} conformation were adopted. The ^{1}H NMR spectrum of this complex was also recorded in a variety of solvents.

Experimental Section

All β-diketonates were prepared according to the standard methods summarized by Fernelius and Bryant,[6] and their purity was checked by ir spectroscopy. All solvents were NMR quality and used without further purification. Due to the low solubility of the chelates in $CDCl_3$, only saturated solutions could be employed. Chemical shifts were measured relative to TMS using a Varian A-60A spectrometer, whose probe temperature was 36°C. The variable-temperature NMR spectra were measured on a JEOL PS100P/EC-100 pulsed Fourier transform spectrometer, having a spectral range of 1 kHz and using 4000 data points in the frequency domain. Temperature control was effected with a JEOL JNMVT3B model, and the probe temperature was measured with a Yellow Springs Instrument thermistor. The temperatures quoted are accurate to ±1°C.

Results and Discussion

The ^{1}H NMR chemical shifts of Mg(acac)$_2$, Be(acac)$_2$, Zn(acac)$_2$, Ca(acac)$_2$, and Ba(acac)$_2$ in various solvents are collected in Table I. It may be seen that the shifts tend to cluster in two groups: one occurring from 102 to 110 Hz (1.70–1.83 ppm) downfield from TMS and the other from 116 to 121 Hz (1.93–2.02 ppm). All bis complexes exhibit one methyl resonance in one group or the other, but only Mg(acac)$_2$ in $CDCl_3$ shows resonances in both groups.

It is apparent from Table I that D_{2h} methyl resonances occur between 102 and 110 Hz, while D_{2d} protons are found between 116 and 121 Hz. Thus, one may assign the methyl resonance of Mg(acac)$_2$ in $CDCl_3$ at 108 Hz to a D_{2h} isomer and the peak at 121 Hz to a D_{2d} isomer. Mg(acac)$_2$ was quite soluble in dimethyl sulfoxide, acetone, dioxane, and pyridine, and the resulting chemical shifts indicate the presence of only a D_{2h} isomer. One expects these solvents to coordinate directly to

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