Two distinct measures of electronic structure have been known for the iridium–dioxygen bond: the O–O and O–Ir internuclear distances[3] and the O–O stretching frequency.[1] We have now added a third, the ^{17}O nuclear quadrupole resonances. Taken together, these experimental observations may decide whether the π-bonding model of Griffith[4] or the two-electron oxidative addition model of Gray[11] is the better formulation of the reversible O_2 bond in this system. Whether the inequivalence of the oxygen atoms' charge distributions is incidental or essential to reversible bonding is also an interesting question that similar experiments on other synthetic oxygen carriers may help answer.

Acknowledgment. We are indebted to the National Science Foundation for Grant BMS-75-01401 and to the Alfred P. Sloan Foundation for a fellowship to O.L. We thank L. Vaska and P. Price for their advice on sample preparation.

Registry No. $Ir(^{17}O{=}^{17}O)Cl(CO)(P[C_6H_5]_3)_2$, 35599-61-2.

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Oxygen-17 Nuclear Magnetic Resonance Spectra of Certain Oxomolybdenum(VI) Complexes and the Influence of the Multiplicity of the Mo–O Bond

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Received May 18, 1978

The line widths and the paramagnetic chemical shifts of the ^{17}O NMR signals for a series of mononuclear oxomolybdenum(VI) complexes are discussed. The chemical shifts are shown to be related to both the force constants for Mo–O stretching vibrations and the Mo–O bond distances. These relationships are attributed to a dependency of the chemical shift on the π-bond order of these bonds. In addition, enrichment of the complexes with both ^{17}O and ^{18}O has allowed a complete confirmation of some previous assignments of Mo–O stretching frequencies.

Introduction

Complexes of molybdenum are dominated by the presence of oxo ligands when that metal is in its higher oxidation states.[1,2] To a large degree, the stability of the Mo–O fragments is undoubtedly due to extensive multiple bonding between the constituent atoms which is indicated by the short Mo–O bond distances[1,2] and the large stretching force constants.[3] The possible importance of these fragments in the chemistries of the molybdo enzymes has been recognized.[1,4] Because of the prevalence of the oxo ligand, we have undertaken a study of the ^{17}O NMR spectra of simple, diamagnetic complexes as a complement to their known chemistries. The advent of Fourier transform techniques and convenient methods for ^{17}O enrichment from readily available sources remove many of the earlier difficulties experienced in ^{17}O NMR spectroscopy. These advantages are mitigated somewhat by the ever-present quadrupole moment of the ^{17}O nucleus which will result in a broadened NMR resonance when the electron distribution about the oxygen atom is not symmetric. Unless the molybdenum atom is at a site of cubic symmetry, the large[5] quadrupole moments of ^{95}Mo ($I = {}^5/_2$, 15.7%) and ^{97}Mo ($I = {}^5/_2$, 9.5%) can also induce efficient relaxation at an ^{17}O nucleus which will cause further broadening of the ^{17}O NMR resonance. Nevertheless, Klemperer and his colleagues have shown[6] with condensed molybdates that usable NMR signals can still be obtained and that the ^{17}O chemical shifts are related to the types of oxo ligands in the molecule. The present study of oxomolybdenum(VI) complexes is concerned principally with empirical observations about the influence of multiple bonding within a Mo–O fragment on the chemical shifts of the ^{17}O NMR signal.

Experimental Section

Materials. Chemicals were reagent grade and used without further purification. Enriched water was purchased from Monsanto Research Corp., Mound Laboratory. The isotopic composition was 25.2% ^{16}O, 43.4% ^{17}O, and 31.4% ^{18}O.

Table I. Chemical Shifts and Line Widths

complex	^{17}O, %	chemical shift,[a] ppm	$\Delta\nu_{1/2}$, Hz
MoO_4^{2-}	5	532 ± 1[b,c]	
$MoO_3(NTA)^{3-}$	1.5	701 ± 2[b,d]	81 ± 10
$MoO_3(IDA)^{2-}$	1.5	698 ± 2[b,e]	155 ± 10
$MoO_2(Etcys)_2$	12	921 ± 5[f]	1250 ± 60
	2	919 ± 5[g]	790 ± 60
$MoO_2(Et_2dtc)_2$	27	975 ± 5[f]	362 ± 15
$MoO_2(acac)_2$	2	1025 ± 5[g]	400 ± 30
$MoOCl_2(Etdtc)_2$	27	948 ± 5[f]	258 ± 15
$MoOBr_2(Et_2dtc)_2$	27	947 ± 5[f]	212 ± 15

[a] Downfield from external $H_2{}^{17}O$. [b] Measured in enriched water. [c] pH 10. [d] pH 8.4. [e] pH 7.0. [f] Measured in CH_2Cl_2. [g] Measured in DMF.

Preparation of ^{17}O-Enriched Complexes. The enrichment of MoO_4^{2-} was accomplished by dissolving $Na_2MoO_4{\cdot}2H_2O$ in diluted ^{17}O-enriched water. Enriched samples of $MoO_3(NTA)^{3-}$ (NTA = nitrilotriacetate ligand) and $MoO_3(IDA)^{2-}$ (IDA = iminodiacetate ligand) were prepared by adding the requisite amount of ligand to a 0.9 M solution of MoO_4^{2-} in enriched water. The acidity of the solutions was then adjusted. Calculated enrichment levels and the pH of these solutions are included in Table I. Enrichment of the carboxylate oxygen atoms will not occur under these conditions because their exchange with the solvent is slow.[7]

The complexes which were examined in organic solvents were enriched and isolated prior to the NMR measurement. All of these complexes were identified by their infrared spectra. An enrichment of approximately 2% was achieved with $MoO_2(Etcys)_2$ (Etcys = ethyl ester of the cysteinate ligand) and $MoO_2(acac)_2$ (acac = acetylacetonate ligand) from solutions of MoO_4^{2-} and the ligand in diluted ^{17}O-enriched water. Highly enriched $MoO_2(Et_2dtc)_2$ (Et_2dtc = diethyldithiocarbamate ligand) was prepared by an unpublished method.[8] An extensively dried sample of $MoO_2(Et_2dtc)_2$ (0.5 g) was dissolved in 100 mL of dichloroethane which had been distilled from P_2O_5. To this solution, 0.075 mL of 43.4% ^{17}O-enriched water was

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added. Equilibration was accomplished by stirring for 4.5 h. The enriched compound was isolated by removing the solvent by distillation under vacuum. The calculated enrichment level is 27% ^{17}O and 20% ^{18}O assuming complete exchange had occurred. The solvent containing enriched water which was recovered was then used to enrich $MoO_2(Etcys)_2$ (0.5 g) by a similar procedure. The calculated enrichment of this compound in ^{17}O is 12%. Labeled $MoOCl_2(Et_2dtc)_2$ was prepared from a portion of the enriched $MoO_2(Et_2dtc)_2$. Dry HCl was bubbled into a solution of enriched $MoO_2(Et_2dtc)_2$ (0.1 g) in CH_2Cl_2 which had been distilled from P_2O_5. The anhydrous conditions ensured no loss of the label. Enriched samples of $MoOBr_2(Et_2dtc)_2$ were prepared in an analogous manner using dry HBr.

Instrumentation. All Fourier transform ^{17}O NMR spectra were obtained with a Varian Associates XL-100-15 FT spectrometer operating at 13.56 MHz and externally locked on a hexafluorobenzene signal. All spectra were obtained at approximately 30 °C from samples which were spun at about 10 revolutions/s. A delay time of 330 μs (10–12 data points) prior to data accumulation was used to eliminate pulse breakthrough on the samples dissolved in organic solvents. However, a delay time was not used for aqueous samples in order to minimize the baseline roll brought about by phase correction.

The following operating conditions apply to all samples other than MoO_4^{2-}. A sweep width of 15 151.5 Hz was used with the filter set at 20 kHz. Free induction decay was obtained using a radio-frequency pulse of 19 μs and a recycle time of 0.11 s. The data were accumulated as 2K data points in the time domain, transformed as 4K, and displayed as 2K in the frequency domain. Instrumental limitations required the pulse to be applied upfield of the resonances. The resulting spectra were reversed and required computer manipulation to be displayed correctly. The number of scans which were accumulated was variable (16–65K) and depended upon the line width of the observed signals and the level of enrichment. Exponential multiplication was applied to the data before Fourier transformation to enhance the signal-to-noise ratio at the expense of some line broadening. This effect is illustrated by the 227-Hz line width obtained for $MoOCl_2(Et_2dtc)_2$ without multiplication whereas the width was 258 Hz with multiplication. The signal-to-noise ratio increased by a factor of approximately 1.5. In general, exponential multiplication caused the line widths to increase by about 15%.

A recycle time of 1.0 s was used with MoO_4^{2-} to avoid saturation since the relaxation time of the ^{17}O nuclei in MoO_4^{2-} is 0.22 s.[9] To achieve greater digital resolution in determining the ^{95}Mo–^{17}O coupling constant, the data were accumulated as 4K data points, transformed as 8K, and displayed as 4K. A spectral width of 10 000 Hz and a filter of 12 000 Hz were used. No exponential multiplication was performed. With a 5% level of ^{17}O incorporation, it was necessary to accumulate only 256 scans to obtain an excellent signal-to-noise ratio.

All resonances appeared downfield from water and were assigned positive chemical shifts relative to external water.

Infrared spectra were recorded using a Perkin-Elmer 283 spectrometer. Values of the pH were measured with a Sargent pH meter equipped with a Corning 30070-1C electrode.

Results and Discussion

The experimental conditions and results are presented in Table I. With the exception of MoO_4^{2-}, no spin coupling was observed between ^{17}O and either ^{95}Mo or ^{97}Mo. In the case of MoO_4^{2-}, whose spectrum is found in Figure 1, we find a sharp center line at 532 ppm, whose width is somewhat less than 5 Hz, and six symmetrically disposed wing lines due to spin coupling between ^{95}Mo and ^{17}O. The coupling constant is 40 ± 1 Hz. Since the ratio of the magnetic moments of ^{97}Mo and ^{95}Mo is 1.02, we expect that the spin coupling constant between ^{97}Mo and ^{17}O should be approximately 41 Hz. However, the quadrupolar moment associated with ^{97}Mo is greater than that due to ^{95}Mo by a factor of 11.4.[5,10] The larger quadrupolar moment causes more efficient relaxation and does not allow the resolution of the satellite lines arising from spin coupling between ^{97}Mo and ^{17}O. Instead, this coupling results in a broad envelope which encompasses the total width of the spectrum. The general features of this spectrum, with the exception of the broad envelope, are in good agreement with previously reported spectra.[9,11] We attribute our observation of this envelope to a larger ^{17}O enrichment level (5 vs. 0.8%) and a larger magnetic field. We also note that while the ^{95}Mo NMR spectrum of MoO_4^{2-} contains resolved lines due to spin coupling, the ^{97}Mo NMR spectrum contains only a broad resonance which does not allow the observation of spin coupling.[5]

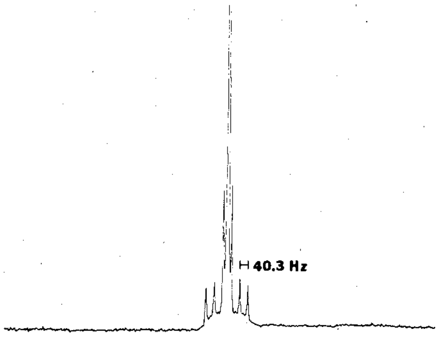

Figure 1. ^{17}O NMR spectrum of MoO_4^{2-}.

The ^{17}O NMR spectra of $MoO_3(NTA)^{3-}$ and $MoO_3(IDA)^{2-}$ were obtained under pH conditions which allowed considerable amounts of MoO_4^{2-} to be present. The latter was easily distinguished by the chemical shift of its ^{17}O resonance. No ^{95}Mo–^{17}O coupling was observed in this resonance, however, and its line width (44 Hz) was considerably larger than that obtained for MoO_4^{2-} at pH 10. The loss of coupling and increased line width have been previously attributed to hydrolysis.[5,9] Although the symmetries of both $MoO_3(NTA)^{3-}$ and $MoO_3(IDA)^{2-}$ are C_s[12,13] so that only two of the three oxo ligands are equivalent, only a single resonance was observed in each case. It is noteworthy, however, that the line width of the resonance due to $MoO_3(IDA)^{2-}$ is roughly twice that of the signal due to $MoO_3(NTA)^{3-}$.

Although line widths will be tied simultaneously to the magnitude of the electric field gradient at the ^{17}O nuclei, indirect effects from the ^{95}Mo and ^{97}Mo nuclei, the symmetry about each Mo–O bond, and the rate of tumbling, these effects should be relatively constant for these two complexes. However, the rates of both intramolecular and intermolecular exchange will also influence the relative line widths. We have previously shown from both ^1H and ^{13}C NMR studies that $MoO_3(NTA)^{3-}$ is fluxional ($k > 100\ s^{-1}$ at 25 °C) in nonaqueous solvents and that the symmetry of the transition state is either C_3 or C_{3v} wherein the oxo ligands become equivalent.[14] The presence of water has a large stimulatory effect on the rate of this exchange. In contrast, ^1H NMR studies have shown the rigid nature of $MoO_3(IDA)^{2-}$ in aqueous solution.[14,15] In the absence of ^{17}O exchange between solvent (H_2O) and $MoO_3(IDA)^{2-}$, two unresolved signals could then be housed under the single resonance envelope that was observed in the ^{17}O NMR spectrum of that complex. These signals should also be present with $MoO_3(NTA)^{3-}$ in the absence of intramolecular and intermolecular exchange. However, since intramolecular exchange is occurring rapidly, these signals should be averaged to produce a narrower line. Intermolecular, pH-dependent exchange between the solvent and the complex may also be responsible for the differing line widths since the spectrum of $MoO_3(IDA)^{2-}$ was obtained at pH 7.0 while that of $MoO_3(NTA)^{3-}$ was obtained at pH 8.4. If the exchange rate increases with increasing pH as is the case with MoO_4^{2-},[5,9] a broader line would be expected with $MoO_3(IDA)^{2-}$. We note, however, that a strict comparison with the behavior of MoO_4^{2-} is not particularly valid since it is believed that the exchange in that case is due to an expansion of the coordination number from 4 to 6.[5,9] The counterpart in the complexes with IDA or NTA would be expansion to

Table II. Comparison of Chemical Shifts, Infrared Data, Mo–O Bond Distances, and Expected π-Bond Orders

complex	chemical shift, ppm	$\nu(\mathrm{Mo}{-}^{16}\mathrm{O})$,[a,b] cm^{-1}	force constant,[b,c] mdyn/Å	Mo–O, Å	π-bond order[d]
MoO_4^{2-}	532	894, 833[d]	5.89	1.76 (1)	0.75
$MoO_3(NTA)^{3-}$	701	893, 840[e]	5.98	1.736 (5)[f]	1
$MoO_3(IDA)^{2-}$	698				1
$MoO_2(Etcys)_2$	921	905, 874			1.5
$MoO_2(Et_2dtc)_2$	975	908, 877	6.46	1.696 (5)[g]	1.5
$MoO_2(acac)_2$	1025	935, 905	6.85	1.66 (2), 1.72 (2)[h]	1.5
$MoOCl_2(Et_2dtc)_2$	948	946 (949)	7.23 (7.28)	1.701 (4)[i]	~1.5[j]
$MoOBr_2(Et_2dtc)_2$	947	956 (949)	7.38 (7.28)	1.656 (5)[i]	~1.5[j]

[a] All frequencies are from the solid state except those in parentheses. [b] Parenthetic values are from solution data. [c] Calculated by methods in ref 3. [d] References 3 and 23. [e] Data pertains to $(MoO_3)_2EDTA^{4-}$ which has identical Mo–O bond lengths and MoO_3 bond angles. [f] Reference 12. [g] Reference 18. [h] Reference 19. [i] Reference 20. [j] See text.

a coordination number of 7 or 8. There is no evidence for direct exchange by way of this expansion at present. The actual effect of the pH on the line widths of the signals due to these complexes remains to be seen.

An explanation related to exchange may also apply to the solvent-dependent line widths which were observed with $MoO_2(Etcys)_2$. Three structural isomers of this complex are possible in principle. Two of these have C_2 symmetry while the third has no symmetry. The large line width which was observed for the complex in CH_2Cl_2 may be due in part to a relatively static distribution of these isomers. However, a narrower signal was observed in DMF. Since DMF is somewhat more viscous than CH_2Cl_2, an explanation in terms of viscosity is not appropriate, but it may be that isomerization is more facile in DMF. It is also of interest to note that the chemical shifts obtained in the two solvents are nearly identical.

We did not observe ^{17}O NMR resonances due to oxygen atoms from the carboxylate groups within $MoO_3(NTA)^{3-}$ and $MoO_3(IDA)^{2-}$ although these should probably occur in the vicinity of 250 ppm.[16] Neither did we observe a signal from the ligand oxygen atoms in $MoO_2(acac)_2$. Lack of lability toward ^{17}O incorporation, at least in the case of the carboxylate groups,[7] and large electrical field gradients are presumably responsible for our inability to locate these resonances.

The results in Table I indicate that the chemical shifts of the ^{17}O NMR signals for the oxo ligands in this series of mononuclear, oxomolybdenum(VI) complexes fall between 500 and 1050 ppm. Furthermore, the results in Table II indicate that the chemical shifts tend to increase with increasing values of the stretching frequencies (or more precisely, the force constants which can be calculated[3] from these frequencies) as well as with decreasing values of the Mo–O bond lengths.[12,17–20] The correlation between the latter and the chemical shifts is even more striking when it is realized that a linear relationship exists (Figure 2) if the data for $MoOBr_2(Et_2dtc)_2$ are excluded. An adequate explanation of the behavior of this compound is provided in a subsequent paragraph. However, the collective data in Table II provide strong, presumptive evidence for a relationship between the chemical shift and the bond order of the Mo–O bonds. Similar dependencies have been noted for the C–O bonds in organic compounds[21] and the Cr–O bonds in oxochromium(VI) complexes.[22]

Cotton and Wing[3] have shown that the π-bond orders for each Mo–O bond within the *cis*-MoO_3 and *cis*-MoO_2 fragments are 1 and 1.5, providing possible π bonding by other donor atoms is ignored. Although Cotton and Wing have estimated the π-bond order of each Mo–O bond in MoO_4^{2-} to be close to unity,[3] a better estimate would appear to be 0.75.[23] The expected π-bond orders have been noted in Table II. These assignments indicate that Mo–O bond distances of approximately 1.76, 1.73, and 1.70 Å are characteristic of π-bond orders of 0.75, 1, and 1.5, respectively. Although the different Mo–O bond distances (Table II) within $MoO_2(acac)_2$ should be viewed with some caution since the data were obtained by film techniques,[19] their average value of 1.69 (2) Å is very close to the two identical bond lengths of 1.696 (5) Å found in $MoO_2(Pr_2dtc)_2$.[18] However, the data in Figure 2 suggest that the π-bond orders for each Mo–O bond in $MoO_2(acac)_2$ should be slightly more than those in $MoO_2(Et_2dtc)_2$. Both are taken to be 1.5 in Table II because of the uncertainties which are involved.

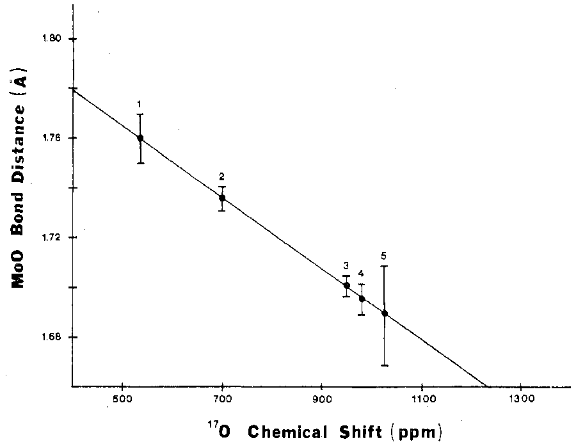

Figure 2. Dependence of the ^{17}O chemical shift on the Mo–O bond distances for (1) MoO_4^{2-}, (2) $MoO_3(NTA)^{3-}$, (3) $MoOCl_2(Et_2dtc)_2$, (4) $MoO_2(Et_2dtc)_2$, and (5) $MoO_2(acac)_2$. Possible errors (2σ) in the bond distances are included.

Turning attention next to complexes bearing a single oxo ligand, $MoOX_2(Et_2dtc)_2$ (X = Cl or Br), we expect the π-bond order for each Mo–O bond would exceed 1.5 in the absence of π bonding to other ligands and, in principle, a value of 2 could be achieved. However, the chemical shift and the Mo–O bond distance[20] (1.701 (4) Å) obtained for $MoOCl_2(Et_2dtc)_2$ fall within the ranges which are characteristic of complexes containing the *cis*-MoO_2 moiety. Both pieces of evidence indicate that the effective π-bond order is approximately 1.5. On the other hand, the corresponding bond length in $MoOBr_2(Et_2dtc)_2$ is 1.656 (5) Å[20] which is indicative of a π-bond order greater than 1.5. However, the chemical shift obtained for this compound is within experimental error identical with that of the chloro analogue. The differences in the solid state appear to be real since we found that the value of the Mo–O stretching frequency is 946 cm^{-1} for the chloro complex while it is 956 cm^{-1} for the bromo complex. Shifts due to isotopic labeling, which are presented subsequently, support these assignments. Both absorptions, however, appear at 949 cm^{-1} in CH_2Cl_2, the solvent used for the ^{17}O NMR measurements. Consequently, similar π-bond orders appear to be in effect when these compounds are in solution, and we estimate that the π-bond order for each is probably near 1.5.

The data in Table II also show that the chemical shifts tend to increase as the number of oxo ligands decreases, a trend which is explicable in terms of the general increases in π bonding which accompany the loss of each oxo ligand. This trend is not observed, of course, when complexes containing the *cis*-MoO_2 fragment are compared to those containing a single oxo ligand since the π-bond orders appear to remain roughly constant. The same general trend can be observed with $Mo_2O_7^{2-}$ and other condensed molybdates,[6,21,24] indicating that the total number of π bonds experienced at an oxo ligand also plays an important role in the chemical shifts observed for these compounds. However, the smooth relationship between chemical shifts and π-bond orders (as judged by bond distances), which was observed for the mononuclear complexes, is generally absent and other effects may also contribute to the chemical shifts. Nevertheless, it is particularly noteworthy that the chemical shift due to the totally encapsulated oxo ligand of $Mo_6O_{19}^{2-}$ is −32 ppm[6] while the long Mo–O bond distances[25] of approximately 2.3 Å are indicative of π-bond orders which must be close to zero.

We also anticipate that the trends which we have observed may be dependent upon the formal oxidation state of molybdenum. However, results for either dinuclear Mo(V) or mononuclear Mo(IV) are not available at this time.

Infrared Assignments. A recent investigation[26] using ^{18}O enrichment alone, indicated that molybdenum–terminal oxygen stretching frequencies occur between 800 and 970 cm^{-1} when ^{16}O is in natural abundance, in confirmation of previous assignments. Our preparations of complexes which were enriched in both ^{17}O and ^{18}O give us the means to provide still further confirmation of these assignments. For example, the spectrum of enriched $MoOCl_2(Et_2dtc)_2$ contains bands at 946, 922, and 898 cm^{-1} due to ^{16}O, ^{17}O, and ^{18}O labeling. When the molybdenum and ^{16}O atoms are treated as simple harmonic oscillators, the predicted frequencies of the harmonic oscillations of the MoO fragment in the ^{17}O- and ^{18}O-labeled complexes are then 922 and 900 cm^{-1}, respectively. Similarly, the spectrum of enriched $MoOBr_2(Et_2dtc)_2$ contains bands at 956, 932, and 908 cm^{-1} while the calculated values for the ^{17}O- and ^{18}O-labeled complexes are 932 and 909 cm^{-1}, respectively.

We have also considered the spectrum of enriched $MoO_2(Et_2dtc)_2$ which should contain 12 bands due to the symmetric and antisymmetric motions of six isotopic isomers. The actual spectrum is shown in Figure 3. The band at 917 cm^{-1}, which can barely be seen when ^{16}O is in natural abundance, is assigned to a vibration of the dithiocarbamate ligands since its position is invariant with varying levels of enrichment. The band at 908 cm^{-1}, arising from the symmetric stretching motion of $Mo^{16}O_2(Et_2dtc)_2$, is somewhat shifted from the previously found[25] value of 910 cm^{-1} due to partial deconvolution of the spectrum through isotopic dilution. The antisymmetric stretching frequency, taken from the spectrum of the complex when ^{16}O is in natural abundance, is 877 cm^{-1}. Finally, a band near 844 cm^{-1} in the spectrum of the latter is again assigned to a vibration of the dithiocarbamate ligands.

Cotton and Wing have assumed that the bent MoO_2 fragment can be treated as an isolated entity and that the interaction of stretching and bending motions of this entity can be ignored.[3] Using these assumptions and the general procedure given by Nakamoto,[27] we have calculated the requisite **G** and **F** matrices which are given below. In this

$$\mathbf{G} = \begin{bmatrix} {}^{1}/_{2}(\mu_0 + \mu_0') + \mu_{Mo}(1 + \cos\alpha) & (\mu_0 - \mu_0')/2 \\ (\mu_0 - \mu_0')/2 & {}^{1}/_{2}(\mu_0 + \mu_0') + \mu_{Mo}(1 - \cos\alpha) \end{bmatrix}$$

$$\mathbf{F} = \begin{bmatrix} f_{11} + f_{12} & 0 \\ 0 & f_{11} - f_{12} \end{bmatrix}$$

notation, μ_{Mo} is the reciprocal mass of the molybdenum atom while μ_0 and μ_0' are the reciprocal masses of the two oxygen atoms of the fragment. The angle α is taken from the crystallographic data[18] as 105.7°. The force constants f_{11} and f_{12} are identical in definition to those used by Cotton and Wing.[3]

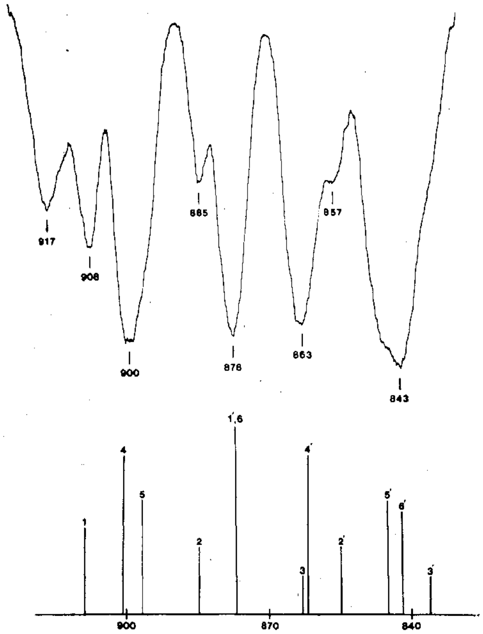

Figure 3. Comparison of the observed and calculated infrared spectrum of $MoO_2(Et_2dtc)$ which had been enriched in both ^{17}O and ^{18}O. The calculated spectrum contains bands due to the symmetric and antisymmetric Mo–O stretching motions of (1 and 1′) $Mo^{16}O_2(Et_2dtc)_2$, (2 and 2′) $Mo^{17}O_2(Et_2dtc)_2$, (3 and 3′) $Mo^{18}O_2(Et_2dtc)_2$, (4 and 4′) $Mo^{16}O^{17}O(Et_2dtc)_2$, (5 and 5′) $Mo^{16}O^{18}O(Et_2dtc)_2$, and (6 and 6′) $Mo^{17}O^{18}O(Et_2dtc)_2$. Bands due to the dithiocarbamate ligands occur at 917 and 844 cm^{-1}. The latter is contained in the band centered at 843 cm^{-1} in the spectrum of the enriched complex.

Table III. Calculated Stretching Frequencies for Isotopic Isomers of $MoO_2(Et_2dtc)_2$

complex	composition, %	ν_s, cm^{-1}	ν_a, cm^{-1}
$Mo^{16}O_2(Et_2dtc)_2$	15.2	(908)[a]	(877)[a]
$Mo^{17}O_2(Et_2dtc)_2$	12.2	885	855
$Mo^{18}O_2(Et_2dtc)_2$	6.6	863	836
$Mo^{16}O^{17}O(Et_2dtc)_2$	27.6	901	862
$Mo^{16}O^{18}O(Et_2dtc)_2$	20.0	897	845
$Mo^{17}O^{18}O(Et_2dtc)_2$	18.1	877	842

[a] Observed frequencies.

The calculated values of f_{11} and f_{12}, which were obtained from the stretching frequencies of $Mo^{16}O_2(Et_2dtc)_2$, are 6.46 and 0.481 mdyn/Å, respectively. The calculated values for the frequencies of the remainder of the isotopic isomers which are given in Table III are compared with the observed spectrum in Figure 3. The intensities of the bands were taken to be proportional to the calculated abundance of each complex (see Table III). Equivalent intensities were assigned to bands due to symmetric and antisymmetric vibrations although the antisymmetric band is slightly more intense in practice. The agreement between the calculated and observed spectra clearly provides unambiguous support for the original spectroscopic assignments.

Acknowledgment. Support from NSF Grant No. CHE 75-08188-A01 is gratefully acknowledged. We are also grateful to Dr. J. W. McDonald for providing us with his unpublished method of obtaining high levels of enrichment.

Registry No. MoO_4^{2-}, 14259-85-9; $MoO_3(NTA)^{3-}$, 67316-58-9; $MoO_3(IDA)^{2-}$, 19709-67-2; $MoO_2(Etcys)_2$, 22775-78-6; $MoO_2(Et_2dtc)_2$, 18078-69-8; $MoO_2(acac)_2$, 17524-05-9; $MoOCl_2(Et_2dtc)_2$, 57146-54-0; $MoOBr_2(Et_2dtc)_2$, 53548-92-8; $Mo^{17}O_2(Et_2dtc)_2$, 68975-39-3; $Mo^{18}O_2(Et_2dtc)_2$, 63912-66-3; $Mo^{16}O^{17}O(Et_2dtc)_2$, 68975-40-6; $Mo^{16}O^{18}O(Et_2dtc)_2$, 68975-41-7; $Mo^{17}O^{18}O(Et_2dtc)_2$, 68975-42-8; ^{17}O, 13968-48-4.

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(23) The total number of π bonds experienced by a metal through its d orbitals is given simply by the number of d orbitals which can participate in π bonding. The π-bond order experienced by a single ligand belonging to a set of equivalent ligands will then be the total number of π bonds experienced by the metal divided by the number of equivalent ligands. No problems occur when this principle is applied to the Mo–O bonds within an octahedron. A more complex situation, however, exists in a tetrahedral oxo complex since the e and t_2 orbitals of the metal are both capable of π bonding but to a different extent. Thus, the e orbital will contribute two π bonds of one type while the t_2 orbitals will contribute three of another type. Fortunately, the differences are easily related by a consideration of the resulting overlap populations. According to perturbation theory, these will be proportional to $[\langle\psi_{Mo}{}^0|\mathcal{H}|\psi_O{}^0\rangle G(\gamma,\pi)]/[E_{Mo}{}^0 - E_O{}^0]$, where $G(\gamma,\pi)$ is the symmetry-dependent group overlap integral and the remaining symbols have their usual meaning and refer to the d_π orbitals of molybdenum and the p_π orbitals of each oxo ligand. Since it is reasonable to assume that the matrix element is itself proportional to $G(\gamma,\pi)$, the overlap population is then proportional to $[G(\gamma,\pi)]^2$. The relative effectiveness of π bonding due to t_2 and e orbitals is then $[G(t_2,\pi)]^2/[G(e,\pi)]^2 = {}^1/_3$ if ligand–ligand overlap is neglected. The total number of equivalent π bonds experienced by the metal is then $2 + (3)(1/3) = 3$ which indicates that the π-bond order for a single Mo–O bond is 0.75. The relative effectiveness of π bonding within this tetrahedron may now be compared to that of the hypothetical octahedral complex $MoO_6{}^{6-}$. The total overlap population due to π bonding in the latter will be proportional to $3[G(t_{2g},\pi)]^2$ or $12[S(d_\pi,p_\pi)]^2$, where $S(d_\pi,p_\pi)$ is the two-atom overlap integral. The overlap population resulting from π bonding to a single ligand is then proportional to $2[S(d_\pi,p_\pi)]^2$. The total overlap population for the tetrahedral complex is proportional to $3[G(e,\pi)]^2$ or $8[S(d_\pi,p_\pi)]^2$. Since there are now only four oxo ligands, the overlap population for a single Mo–O bond is identical with that found for the octahedron. These results suggest that π-bond orders for either geometry have an equivalent basis. (See C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory", W. A. Benjamin, New York, Chapter 8.) Furthermore, application of these principles to the terminal oxo groups of $Cr_2O_7{}^{2-}$ (assuming with Kidd[22] that the bridging oxo ligand does not experience π bonding) and CrO_2Cl_2 results in π-bond orders of 1 and 1.5, respectively. Fortunately, the chemical shifts of these oxo ligands still vary linearly with the new π-bond orders.
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Infrared Spectra of the $M^+BrF_2^-$ and $M^+IF_2^-$ Ion Pairs in Solid Argon

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Received November 1, 1978

Infrared absorptions for the trihalide anions BrF_2^- and IF_2^- have been observed in experiments codepositing an argon/fluorine mixture and the alkali bromide and alkali iodide salt vapors onto a cesium iodide window at 15 K. Infrared bands in the 520–530-cm^{-1} region and the 360–365-cm^{-1} region are assigned to the symmetric $FBrF^-$ and asymmetric $BrFF^-$ species, respectively, in the $M^+BrF_2^-$ ion pair. In the alkali iodide experiments, the analogous bands were observed in the vicinity of 505 cm^{-1} for M^+FIF^- and near 355 cm^{-1} for M^+IFF^-. In most experiments, a band was observed at 550 cm^{-1} which has been previously assigned to the $M^+F_3^-$ species, a product of the secondary reaction of MF with fluorine. These results are compatible with the following reaction scheme: $MX + F_2 \rightarrow M^+XFF^- \rightarrow M^+FXF^- \rightarrow MF + XF$. Salt reactions with HF impurity also produced the M^+FHX^- bihalide complexes.

Introduction

Alkali halide salt–halogen molecule matrix reactions have been used to synthesize the trihalide species $M^+X_3^-$ including the least stable trifluoride anion.[1-3] Studies of the mixed ClF_2^-, Cl_2F^-, $ClBr_2^-$, and Cl_2Br^- species have suggested that both symmetric and asymmetric mixed $M^+X_2Y^-$ species are formed in these reactions.[1,2] Reactions of alkali bromides and iodides with fluorine were done to synthesize the new $M^+BrF_2^-$ and $M^+IF_2^-$ species which are described in this paper.

Experimental Section

The cryogenic refrigerators, vacuum systems, and high-temperature ovens have been described previously.[4] RbI, CsI, RbBr (Research Organic/Inorganic Chemical Corp.), KBr (Harshaw Chemical), KI (J. T. Baker), NaBr (Mallinckrodt), CsBr (Orion), NaCl (J. T. Baker), and NaI (Mallinckrodt) were outgassed from the Knudsen cell at or above the experimental evaporation temperature for several hours prior to the experiment. Evaporation temperatures, chosen to give 1 μ of salt vapor pressure, were CsBr (490 °C), CsI (450 °C), RbBr (460 °C), RbI (430 °C), KBr (500 °C) KI (505 °C), NaBr (520 °C), NaI (450 °C), and NaCl (520 °C). Fluorine (Matheson), after removal of condensables at 77 K, was diluted in argon to $Ar/F_2 = 400/1$ in a stainless steel vacuum system.

Fluorine samples were codeposited at 3 mmol/h with alkali halide salt vapor on an optical window at 15 K for 18–22-h periods. Infrared spectra were recorded on a Beckman IR-12 infrared spectrophotometer with an accuracy of ±1 cm^{-1}. Samples were photolyzed with a filtered

0020-1669/79/1318-0988$01.00/0