(4) E. Sarkin, W. Rath, and H. Erlenmeyer, *Helv. Chim. Acta*, **35**, 1736 (1952).
(5) N. K. Dutt and A. K. Sen Gupta, *Z. Naturforsch., B*, **30b**, 769 (1975).
(6) G. Vicentini and A. B. Nascimento, *An. Acad. Bras. Cienc.*, **50**, 165 (1978).
(7) L. B. Zinner, *Cienc. Cult. (Sao Paulo)*, **50**, 705 (1978).
(8) S. J. Lyle and M. Md. Rahman, *Talanta*, **10**, 1177 (1963).
(9) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(10) Local versions of the following major programs were used in the solution and refinement of structures in this work: (a) SYNCOR, W. Schmonsees' program for data reduction; (b) FORDAP, A. Zalkins' Fourier program; (c) ORFLS and ORFEE, W. R. Busing, K. O. Martin, and H. A. Levy's full-matrix least-squares program and function and error program; (d) ORTEP, C. K. Johnson's program for drawing crystal models. Scattering factors for Sm(III) were taken from D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965), and those for the remaining atoms as well as the anomalous scattering terms for the Sm(III) ion were taken from "International Tables for X-ray Crystallography", Vol. IV, J. A. Ibers and W. Hamilton, Eds., Kynoch Press, Birmingham, England, 1974. The program HFINDR (A. Zalkin) was used to assign hydrogen positions 1.0 Å from carbon atoms with idealized angles.
(11) D. Prevorsek, *Bull. Soc. Chim. Fr.*, 765 (1958).
(12) H. Shindo, *Chem. Pharm. Bull.*, **5**, 472 (1957).
(13) Y. Kakiuti, S. Kida, and J. V. Guagliano, *Spectrochim. Acta*, **19**, 201 (1963).
(14) B. M. Gathehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).
(15) J. W. Moore, M. D. Glick, and W. A. Baker, Jr., *J. Am. Chem. Soc.*, **94**, 1858 (1972).
(16) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, 1972, p 1057.
(17) M. D. Lind, B. Lee, and J. L. Hoard, *J. Am. Chem. Soc.*, **87**, 1611 (1965).
(18) E. L. Muetterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967).

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Metal Isotope Shifts in the Raman Spectrum of $Mo_2(O_2CCH_3)_4$

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Metal isotope substitution has been widely used for the assignment of metal–ligand vibrations of coordination compounds, but the application of this technique to compounds containing M–M bonds is very limited.[2] In this work we report the results of a Raman study of $Mo_2(O_2CCH_3)_4$ in the normal isotopic (ca. ^{96}Mo) and ^{92}Mo forms. $Mo_2(O_2CCH_3)_4$ has a Mo–Mo bond distance of 2.09 Å resulting from the Mo–Mo quadruple bond supported by four bridging acetate groups. Cotton and co-workers assigned the Raman feature at 404 cm^{-1} as the symmetric Mo–Mo stretch, with no significant contribution from other stretching or bending modes, whereas Ketteringham et al. concluded that the Mo–Mo stretch contains about a 15% contribution from the $O_4M–MO_4$ deformation.[3,4] Also, the question is open as to whether the contrast between the broad spread of Mo–Mo stretching frequencies and the narrow range of Mo–Mo bond distances reflects trends in bonding or simply the influence of coupling of the Mo–Mo stretch to Mo–ligand displacement coordinates.[5]

The purpose of this study is to (1) confirm the assignments of metal-dependent vibrations, particularly the metal–metal stretching mode, (2) infer the extent of mixing between the M–M coordinate and other internal displacement coordinates, and (3) provide data which will permit a more precise solution of the normal-coordinate vibrational problem.

Experimental Section

The natural-abundance $Mo_2(O_2CCH_3)_4$ was prepared by refluxing acetic acid containing acetaldehyde with $Mo(CO)_6$.[6] The ^{92}Mo-substituted species was prepared from $^{92}Mo(CO)_6$ by using the same procedure. The $^{92}Mo(CO)_6$ was prepared by the reaction of $^{92}MoO_3$ with carbon monoxide at 14000 psi.[7]

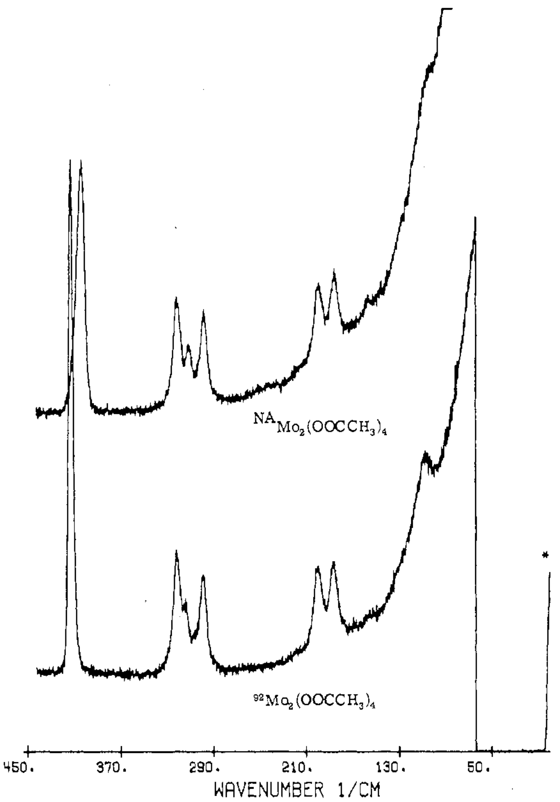

Figure 1. Room-temperature Raman spectra of $^{NA}Mo_2(O_2CCH_3)_4$ and $^{92}Mo_2(O_2CCH_3)_4$; * denotes the laser exciting line.

Table I. Raman Data for $^{NA}Mo_2(OOCCH_3)_4$ and $^{92}Mo_2(OOCCH_3)_4$[a]

$^{NA}Mo_2$-$(OOCCH_3)_4$	$^{92}Mo_2$-$(OOCCH_3)_4$	shift[b]
186	186	
200	200	
298	299	−1
311	314	−3
321	322	−1
404	413	−9

[a] Values in cm^{-1}; accuracy ±1.0 cm^{-1}. [b] Shift is for $\nu[^{NA}Mo_2(OOCCH_3)_4] - \nu[^{92}Mo_2(OOCCH_3)_4]$.

Raman spectra were collected on samples of natural-abundance (NA) and ^{92}Mo (97.4%) $Mo_2(O_2CCH_3)_4$ which were sealed under an inert atmosphere in 5-mm Pyrex tubes. Data were collected in the backscattering geometry with a Raman spectrometer which is described elsewhere.[8] The 514.5-nm Ar^+ ion laser line was employed for all spectra.

Results

The room-temperature spectra of the compounds are illustrated in Figure 1 and the data and isotope shifts summarized in Table I. The spectrum of the natural-abundance material is in good agreement with that reported by Cotton.[3] The band at 404 cm^{-1} in the natural-abundance $Mo_2(O_2CCH_3)_4$ spectrum appears at 413 cm^{-1} in $^{92}Mo_2(O_2CCH_3)_4$. Naturally abundant molybdenum contains 16% ^{92}Mo, five isotopes in the range 94 through 98, and 9% ^{100}Mo. The peak in the natural material is taken as representative of ^{96}Mo, which is in the middle of the most abundant group of isotopes.

A less intense triplet of absorptions occurring between 290–320 cm^{-1} is found 1–3 cm^{-1} higher in the compound containing the lighter molybdenum isotope. On the basis of simple consideration of reduced masses and relative force constants a larger isotopic shift is predicted for the Mo–Mo

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stretch than for the Mo–O stretch. Thus the large shift of the 404-cm^{-1} band confirms its origin as the Mo–Mo stretch, whereas the metal-isotope shifts of the bands in the 300-cm^{-1} region are comparable to those found for Mo–O stretch in mononuclear molybdenum compound.[9]

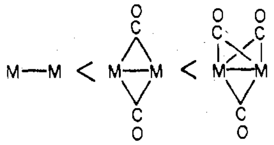
The 9-cm^{-1} shift of the Mo–Mo stretch is very close to that calculated for a Mo diatomic species, 8.7 cm^{-1}, where molybdenum masses are 92 and 96. If coupling of the Mo–Mo stretch with other coordinates were occurring, the size of the shift would be smaller. Therefore the present data provides direct evidence that the 404-cm^{-1} band represents a nearly pure Mo–Mo stretch, and this result favors the interpretation of Bratton, Cotton, Debau, and Walton, but because of sensitivity to experimental error the interpretation of Ketteringham et al. cannot definitely be ruled out. By contrast, the observed metal-isotope shift for $Fe_2(CO)_9$, 1.3 cm^{-1},[2] is much smaller than the value of 4.8 cm^{-1} calculated on the diatomic approximation for $^{54}Fe_2$ vs. $^{56}Fe_2$. To facilitate the comparison, we calculate the ratio of observed isotope shifts for $Mo_2(O_2CCH_3)_4$ to that of $Fe_2(CO)_9$, eq 1.

$$\frac{\nu[^{92}Mo_2(O_2CCH_3)_4] - \nu[^{NA}Mo_2(O_2CCH_3)_4]}{\nu[^{54}Fe_2(CO)_9] - \nu[^{56}Fe_2(CO)_9]} = \frac{9}{1.3} = 6.9 \qquad (1)$$

It is well documented that the diatomic approximation is less satisfactory for the first transition series M–M-bonded compounds than for heavier metal analogues, because ligands which tend to ride with the metal exert a greater percentage effect on the lighter metals.[10] On the basis of complete vibrational analyses for other first-row carbonyls,[5] it is estimated that the effective mass change caused by the carbonyl ligands accounts for somewhat less than 1 cm^{-1} in the Fe–Fe isotopic shift. Accordingly, we increase the observed shift for the iron system by 1 cm^{-1} to account for the contributions from terminal CO ligands. With this correction the ratio given in eq 1 becomes 3.9. This mass-corrected shift ratio is to be compared to the theoretical ratio of shifts calculated on a diatomic approximation, eq 2.

$$\frac{\nu(^{92}Mo_2) - \nu(^{96}Mo_2)}{\nu(^{54}Fe_2) - \nu(^{56}Fe_2)} = \frac{8.7}{4.8} = 1.8 \qquad (2)$$

The disparity between the mass-corrected isotopic frequency shift ratio and that calculated on the diatomic approximation resides in the fact that even after mass correction, the shift for $Fe_2(CO)_9$ is far less than that expected on a diatomic model. Apparently the internal displacement coordinates associated with the metal-bridging ligand system contribute far more to the M–M restoring force for $Fe_2(CO)_9$ than for $Mo_2(O_2CCH_3)_4$. One obvious origin of this difference is the geometry of the C-atom bridge in $Fe_2(CO)_9$ which directs a significant component of Fe–C stretch along the Fe–Fe axis. By contrast, the three-atom bridge in $Mo_2(O_2CCH_3)_4$ should be much more compliant. Additional evidence for the influence of CO bridges is available from the observed trends in M–M stretching frequencies for first-row single-bonded carbonyls which follow the order:[5]



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Registry No. $^{NA}Mo_2(O_2CCH_3)_4$, 14221-06-8; $^{92}Mo_2(O_2CCH_3)_4$, 70046-80-9.

References and Notes

(1) (a) Abilene Christian University. (b) Northwestern University.
(2) C. B. Cooper, III, S. Onaka, D. F. Shriver, L. Daniels, R. L. Hance, B. Hutchinson, and R. Shipley, *Inorg. Chim. Acta*, **24**, L92 (1977).
(3) W. Bratton, F. A. Cotton, M. Debeau, and R. A. Walton, *J. Coord. Chem.*, **1**, 121 (1971).
(4) A. P. Ketteringham, C. Oldham, and C. J. Peacock, *J. Chem. Soc., Dalton Trans.*, 1640 (1976).
(5) D. F. Shriver and C. B. Cooper, III, "Advances in Infrared and Raman Spectroscopy", R. J. H. Clark and R. E. Hester, Eds., Heyden and Sons, in press.
(6) T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).
(7) A. P. Hagen, T. S. Miller, D. L. Terrell, B. Hutchinson, and R. L. Hance, *Inorg. Chem.*, **17**, 1369 (1978).
(8) D. R. Greig, G. C. Joy III, and D. F. Shriver, *J. Chem. Phys.*, **67**, 3189 (1977).
(9) Dennis Beaver, Thesis, Abilene Christian University, Abilene, TX, 1973.
(10) T. G. Spiro, *Prog. Inorg. Chem.*, **11**, 1 (1970).

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Carbon-13 and Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy of Some (η^5-Cyclopentadienyl)nitrosyl Complexes of the Group 6B Elements[1a]

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During the past few years there have been considerable advances in the detection of nitrogen-15 NMR signals at the natural-abundance level.[2] Consequently, it is reasonable to expect that ^{15}N NMR spectra can be obtained for transition-metal nitrosyl complexes. Furthermore, these spectra should provide detailed structural and electronic information about the nitrosyl species in much the same way that ^{13}C NMR spectra elucidate the properties of transition-metal carbonyl compounds.[3] We now report the results of the first ^{15}N NMR study of some organometallic nitrosyl complexes, namely, (η^5-cyclopentadienyl)nitrosyl derivatives of chromium, molybdenum, and tungsten, and we also compare the ^{15}N and ^{13}C chemical shifts exhibited by these compounds.

Experimental Section

All of the compounds studied were of reagent-grade purity. The $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$ and $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ (M = Cr, Mo, W) complexes[4] $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$[5] and $(\eta^5\text{-}C_5H_5)Mo(CO)(PPh_3)(NO)$[6] were prepared by published methods, and their purity was checked by elemental analyses. The infrared spectra of the complexes were recorded on a Perkin-Elmer 457 spectrophotometer and calibrated with the 1601-cm^{-1} band of polystyrene film.

^1H and ^{13}C NMR spectra were obtained with Varian Associates T60 and CFT20 spectrometers, respectively. The latter instrument was operated under conditions of proton decoupling with a deuterium lock. No relaxation reagent was employed during the measurement of ^{13}C NMR chemical shifts relative to internal solvent. The ^1H and ^{13}C NMR chemical shifts are reported in ppm downfield from $(CH_3)_4Si$. ^{15}N NMR spectra were recorded at a frequency of 18.25 MHz with a Bruker WH-180 pulse spectrometer that has been

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