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Contribution of a δ-Orbital Electron to a Quadruple Metal–Metal Bond. A Direct Experimental Measure from Vibrational Fine Structure in the δ Ionization of $Mo_2(O_2CCH_3)_4$[1]

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Abstract: The first observation of metal–metal vibrational fine structure in a photoelectron band is reported. Attention is focused on the predominantly metal "δ" ionization band (arising from production of the $^2B_{2g}$ positive ion state) of $Mo_2(O_2CCH_3)_4$. From our high-resolution and high signal-to-noise He I ionization data collection techniques, we have observed within this band approximately 20 members of the vibrational progression predominantly corresponding to the totally symmetric (a_{1g}) metal–metal stretching mode in the $^2B_{2g}$ positive ion state. The metal–metal stretching frequency is found to be lower in the $^2B_{2g}$ state than in the ground state, indicating an appreciable reduction of metal–metal bond strength upon the loss of the δ-bonding electron. This stretching frequency is also lower than that observed in the $^1A_{2u}$ ($\delta\delta^*$) electronic excited state of the neutral molecule as obtained from absorption techniques. A normal Franck–Condon analysis of the vibrational progression in the $^2B_{2g}$ positive ion state reveals that the equilibrium metal–metal bond distance is substantially longer than in the ground state of the molecule and, in addition, is longer than in the $^1A_{2u}$ electronic excited state. The comparatively low metal–metal vibrational frequency and long bond length indicate that, in addition to the change in bond order upon ionization, the change in the metal oxidation state also serves an important role in determining the strength of the resultant metal–metal interaction.

Metal–metal interaction and bonding are fundamentally important features of a wide variety of chemical systems and processes. The study of quadruply bonded metal–metal complexes is especially significant because three different types of metal bonding interactions—σ, π, and δ—are present in a single species. Ionization spectroscopy, especially UPS, is invaluable for obtaining experimental information relating to the electronic interactions and the bonding schemes for the metal–metal unit.[2] This technique also offers the possibility of directly probing the vibrational and equilibrium bond length characteristics of a particular positive ion state in the event that the vibrational progression(s) in that ionization band are resolved. When contrasted to the corresponding ground-state characteristics, the exact contributions of the individual electrons may be ascertained. Such vibrational resolution is commonly observed in the study of small symmetric molecules. Conventional UPS studies of transition-metal molecules, however, generally have not shown evidence of vibrational fine structure. This is due, in part, to the low frequency of such metal vibrations and the number of vibrational modes that may overlap and also to the limitations of the instruments used for these studies.

We have recently reported the first observation of vibrational fine structure in transition-metal–ligand valence orbitals in the mononuclear group 6B hexacarbonyls[3] and in $(C_5H_5)Re(CO)_3$.[4] Certain molecular, electronic, and vibrational characteristics have been identified which are favorable for observation of such structure in transition-metal complexes.[3] The vibrational progression is most clearly observed when excitation of only a single normal mode in a particular frequency range dominates the band contour. Although large molecules have a large number of normal modes, there are effective "selection rules" that severely restrict the number of modes that can lead to observable progressions, particularly for transition-metal complexes. The most important factor governing the occurrence of a progression is that a change in equilibrium bond distance must be caused by the particular ionization. The typical localization of metal-centered orbitals and normal vibrational modes dictates that most modes will not give extensive progressions.[3-5] Even if the particular orbital is delocalized, local electronic symmetry and normal mode symmetry can assist the observation of vibrational fine structure because the totally symmetric mode normally dominates. We have observed this effect in the photoelectron spectra of some mononuclear transition-metal complexes.[3,4] Lineberger et al.[5] have also observed this effect in the electron detachment spectra of $Ni(CO)_n{}^m$ (n = 1–3; m = 0 and −1), where only one vibrational mode, the totally symmetric C–O stretching mode, is significantly activated by the ionization process.

$Mo_2(O_2CCH_3)_4$ has ideal molecular, electronic, and vibrational characteristics for observation of fine structure.[6] In particular, the δ orbital is highly localized on the metals,[7-11] the totally symmetric Mo–Mo a_{1g} vibrational mode is localized on the metals,[12-17] and, as will be shown, the ionization of this orbital is accompanied by an appreciable bond distance change. This molecule also has a very favorable gas-phase stability for such ionization studies despite the moderately high temperatures re-

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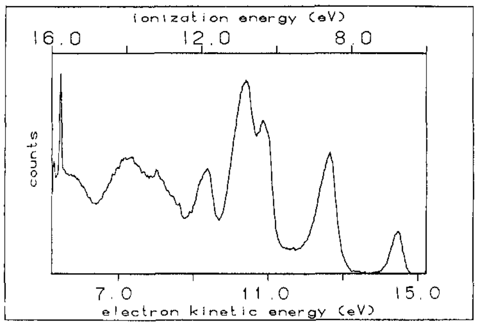

Figure 1. Valence He I photoelectron spectrum of $Mo_2(O_2CCH_3)_4$.

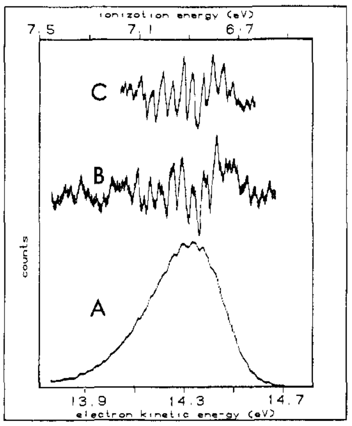

Figure 2. (A) Close-up view of the $^2B_{2g}$ ("δ") ionization band of $Mo_2(O_2CCH_3)_4$. (B) Fourier transform enhancement. (C) Residuals of fit (ROF) enhancement.

quired for sufficient vapor pressures. Here we report the first observation of vibrational fine structure in the ionization of metal–metal valence orbitals of dinuclear metal complexes, specifically the $2b_{2g}$ ("δ") orbital ionization of $Mo_2(O_2CCH_3)_4$, and discuss the implications derived from this information with regard to the contribution of an electron in the δ-bonding orbital to the total bonding between the metal centers.

Experimental Section

All experiments were performed on a GCA-McPherson ESCA-36 photoelectron spectrometer equipped with modifications as reported earlier.[3] These observations were also reproduced with our more recent modifications, which include improved detection circuitry, new digital power supplies for analyzer control, and more advanced computer hardware and software for data collection and reduction.[18] Operating temperatures were maintained at 190–200 °C with no decomposition of the sample. Resolution of the calibrant Ar $^2P_{3/2}$ ionization (15.759 eV) was 14–18 meV *during* all data collections. Sensitivity was consistently 200–300 counts per second over the top of the δ ionization band. Five independent data sets for the $^2B_{2g}$ ionization band were collected and reproduced at various times over a 10-month period. Our special data collection techniques have been reported previously.[3]

It is required that high spectral resolution be maintained while simultaneously sustaining high signal to noise at the temperatures required for the gas-phase investigation of the complexes over extended periods of time (several hours). It is especially important to have good instrumental stability (usually aided by careful temperature control prior to and during vaporization) and to "lock" any spectral drift with an internal calibrant. With our present instrumentation the vibrational spacing in the ionization band should be greater than about 150 cm^{-1} (18 meV) in order to be easily resolved.

Results

General Spectrum. Figure 1 shows the overall valence ionization region of $Mo_2(O_2CCH_3)_4$. This spectrum shows the same general valence ionization bands as the spectrum previously reported by Green and Hayes.[19] They assigned the lowest energy ionization band of this molecule to the $^2B_{2g}$ positive ion state (vertical ionization energy of 6.98 eV; this study) and the next ionization band to the ^2E_u positive ion state (vertical ionization energy of 8.68 eV; this study). These correspond to ionizations from orbitals predominantly associated with the Mo–Mo quadruple bond, representing the $2b_{2g}$ δ-bonding and $6e_u$ π-bonding orbitals, respectively. The location of the $^2A_{1g}$ ionization band corresponding to the σ bond (the $5a_{1g}$ orbital) is still not clear from this single spectrum. Figure 2 shows a close-up of the $^2B_{2g}$ δ band, after one of our high-resolution data collections. The structure on the contour of the band is clearly evident.

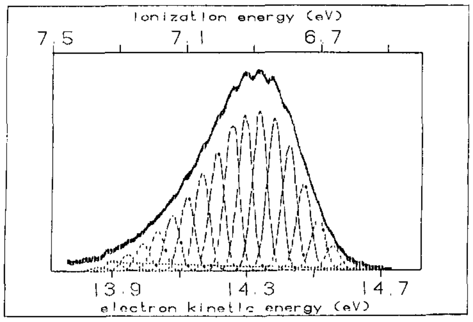

Figure 3. Spectral simulation analysis of the $^2B_{2g}$ ionization band of $Mo_2(O_2CCH_3)_4$ shown with the same data collection set as in Figure 2.

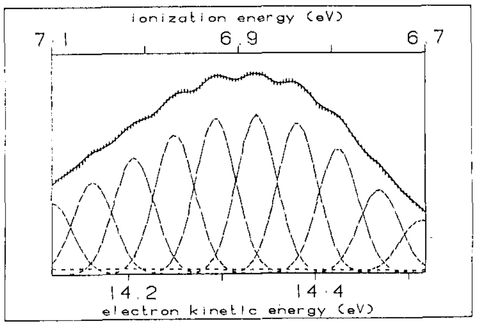

Figure 4. Close-up of the spectral simulation displaying the ten most intense vibrational components and the exactness of the simulation (solid line) to the data (vertical dashes) for the $^2B_{2g}$ ionization band of $Mo_2(O_2CCH_3)_4$.

Vibrational Spacing Analysis. The spacings between the vibrational components are important in relation to the metal–metal bonding in the positive ion. The spacings were numerically analyzed by three techniques: Fourier transform analysis, "residuals of fit" (ROF) analysis,[3] and spectral simulation. Figure 2, in addition to showing the δ band, also shows the Fourier transform and the residuals of fit analyses directly above the band. The Fourier transform analysis involves treating the data as though it existed in the time domain, transforming it to the frequency domain, filtering out low-frequency components (corresponding to the broad-band profile), and transforming back to the time domain. This enhances the visibility of the vibrational progressions and allows for more precise numerical evaluation of the spacings. The ROF analysis may be roughly equated to a "manual" Fourier transform analysis. In this technique, the ionization band is fit with one or more broad Gaussian curves in order to obtain a smooth band representing the observed band's overall profile. The smooth band corresponds to the low-frequency components in the Fourier transformation. Subtracting the smooth overall band from the actual spectrum results in the isolation of the higher frequency vibrational components, as shown in Figure 2. Figure 3 illustrates the simulation of the ionization band. The spectral simulation involves fitting the ionization band with evenly spaced symmetric Gaussian curves that model the vibrational components, the sum of which simulates the ionization band. The vibrational spacing is simply the energy spacing between the peaks of the Gaussian curves. Figure 4 shows a close-up of the top of the spectral simulation of Figure 3 to further display the closeness of the fit to the actual spectrum. The 7–10 most apparent vibrational

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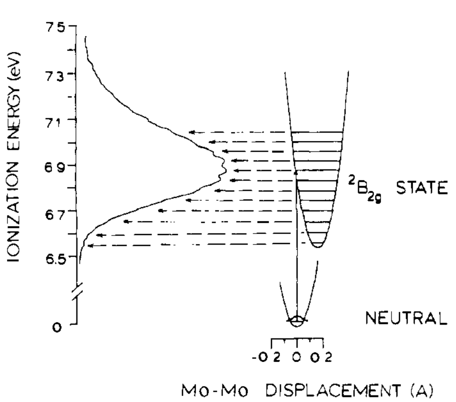

Figure 5. Illustration of the normal Franck–Condon analysis used to determine the magnitude of the Mo–Mo bond displacement in the $^2B_{2g}$ state of $Mo_2(O_2CCH_3)_4$. The vertical ionization is shown to the $\nu' = 7$ level in the $^2B_{2g}$ state.[27]

spacings over the tops of the ionization bands were generally used for statistical analysis in all three of our methods.

The vibrational spacing is determined to be 360 (10) cm^{-1} for the metal–metal vibrational mode in the $^2B_{2g}$ state (average vibrational spacings from five independent data sets: 355 (12) cm^{-1} by the Fourier transform method, 365 (8) cm^{-1} by the residuals of fit (ROF) method, and 355 (10) cm^{-1} by spectral simulation). It should be noted here that our technique is not sufficiently sensitive to detect small (<10 cm^{-1}) anharmonicity in the spacings.

The number of observable vibrational quanta between the adiabatic vibrational component ($\nu_0\{\text{neutral}\} \rightarrow \nu'_0\{\text{ion}\}$) and the vertical (most intense) component is important to the Franck–Condon analysis. Both the Fourier transform and the ROF analyses show eight observable quanta between the onset and the vertical vibrational component in this band. The spectral simulation indicates seven Gaussians between the most intense Gaussian and the first Gaussian on the low binding energy side of the band profile. It cannot be determined with certainty whether the first observed vibrational component is actually the adiabatic transition or instead is a transition to a higher vibrational level in the positive ion. Franck–Condon analysis (next section) shows that each increase in the assigned vertical transition in the range from $\nu' = 7$ to at least $\nu' = 20$ results in an increase of about 0.01 Å for the calculated Mo–Mo displacement. Nevertheless, on the basis of the observed vibrational spacing and comparison with other electronic states of the molecule (Discussion), we do not expect the actual bond distance change to be much greater than our analysis suggests.

Franck-Condon Analysis

Franck–Condon analysis[3,20–26] of this ionization band structure leads to a measure of the bond distance change upon ionization to the $^2B_{2g}$ state. This is shown diagrammatically in Figure 5.[27] The principles of our analysis are basically the same as those in other studies of vibrational structure in electronic excitations of quadruply bonded complexes.[28,29] It should be mentioned that these analyses contain some implicit assumptions regarding the relationship of the normal modes in the ground and excited states that may influence the value determined for the bond distance change. An evaluation of how these assumptions affect the results is presented in this section. An important point is that these assumptions do not significantly affect the *relative* changes in bond distances so that the results of the present study may be compared directly with the results of the other electronic excited studies.[28,29]

The bond distance change that is determined is most strongly dependent on the quantum number of the vertical transition, which we will set as $\nu' = 7$ from the spectral simulation analysis assuming that the adiabatic ionization ($\nu_0 \rightarrow \nu'_0$) is observed. The calculated bond distance change is less sensitive to the exact shape of the positive ion potential well as calculated within a wide range of possible metal–metal vibrational frequencies (350–410 cm^{-1}) and dissociation energies (50–1000 kcal mol^{-1}). Using the observed vibrational spacing of 360 (10) cm^{-1} in the positive ion and a dissociation energy in the neighborhood of 300–500 kcal mol^{-1} gives a bond distance change of 0.18 Å. In the unlikely event that the force constant does not change from that in the ground state of the molcule, the resultant bond distance change is only decreased by 0.02 Å to a bond displacement of 0.16 Å. The calculated bond distance change assuming a bond dissociation energy of 50 kcal mol^{-1} is only 0.02 Å less than that calculated assuming a bond dissociation energy of 300 kcal mol^{-1} and more. The bond displacement results are equally insensitive to the harmonic oscillator vs. the Morse curve approximations of the potential well shape. These results are to be expected since the vibronic levels observed in the positive ion ($\nu' = 7$–10) are within the lower 5–10% of the potential well.

This first-order analysis treats the observed vibrational frequency and Franck–Condon progression as associated with a pure dimeric molybdenum stretch. It is possible that this vibrational mode includes mixing with the a_{1g} Mo–O stretch and/or the a_{1a} Mo–Mo–O deformation,[30] although other studies indicate that the extent of this mixing is likely to be small.[12–17,28] Isotope shift studies of the ground-state vibrational frequencies show that the a_{1g} metal–metal stretch in dimetal tetracarboxylates is nearly pure metal.[32] Thompson et al.[34] have reported that for large molecules, where it is likely that the molecular ion is very similar to the parent molecule, one may expect that the vibrational characteristics will also be similar.[35] It has also been stated on the basis of the vibrational frequency shifts in the $^1A_{2u}$ states of $Mo_2(O_2CCH_3)_4$ and $Mo_2(O_2CCF_3)_4$ that the metal–metal stretch is not dominated by mixing of other modes in this excited state. It has additionally been shown that the Mo–Mo stretch is a major contributor to the

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(27) A Boltzmann distribution analysis was employed which showed that at 200 °C the calculated contribution of hot bands (specifically $\nu_x\{\text{neutral}\} \rightarrow \nu'_0\{\text{ion}\}$ transitions, where $x > 0$) in a model Gaussian ionization band for this molecule does not change the number of vibrational quanta counted between the apparent adiabatic and the vertical ionizations. In short, our bond distance results are not influenced by hot bands.

(28) Trogler, W. C.; Solomon, E. I.; Trajberg, I.; Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1977**, *16*, 828.

(29) Martin, D. S.; Newman, R. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2511.

(30) Definitive a_{1g} Mo–O stretch and Mo–Mo–O deformation frequencies have yet to be verified for $Mo_2(O_2CR)_4$ complexes. Suspected values for both modes, however, are all ±300 cm^{-1} from the a_{1g} Mo–Mo stretch.[12,13,31]

(31) (a) Ketteringham, A. P.; Oldham, C. *J. Chem. Soc., Dalton Trans.* **1973**, 1067. (b) Ketteringham, A. P.; Oldham, C.; Peacock, C. J. *Ibid.* **1976**, 1640.

(32) A $^{92}Mo/^{96}Mo$ isotope shift Raman study of $Mo_2(O_2CCH_3)_4$ has shown that the absorption at 404–406 cm^{-1} is dominated by Mo–Mo stretch.[13] In addition, an $^{16}O/^{18}O$ isotope shift Raman study of $Ru_2(O_2CCH_3)_4Cl$ has indicated negligible influence on the predominantly Ru-Ru stretch.[33] This latter case is analogous to $Mo_2(O_2CCH_3)_4$ since the energy difference of the a_{1g} Ru–Ru stretch and a_{1g} Ru–O stretch approximates, and is actually slightly smaller than, the analogous $Mo_2(O_2CCH_3)_4$ stretch differences.[31] Unfortunately, the a_{1g} Ru–Ru–O deformation frequency was not resolved from this latter study.

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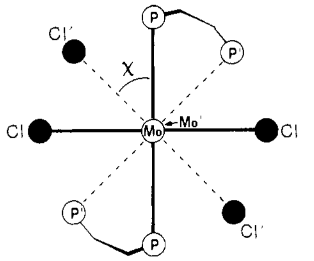
(35) In fact, IR and Raman spectral assignments have previously been made on the basis of observed vibrational structure in the valence photoelectron spectra. Derrick, P. J.; Asbrink, L.; Edquist, O.; Lindholm, E. *Spectrochim. Acta, Part A* **1971**, *27a*, 2525.

observed vibrational mode in the $^1A_{2u}$ $\delta\delta^*$ excited state by the recording of a dominant hot band at a spacing of about 400 cm^{-1} (the a_{1g} Mo–Mo stretch in the ground electronic state) from the adiabatic transition. In order to compare the distortion in the $^2B_{2g}$ positive ion state of $Mo_2(O_2CCH_3)_4$ with the results of other studies on the $^1A_{2u}$ state, it is most appropriate to discuss the distortion simply in terms of the metal–metal stretch. There is no indication of substantial mixing with other modes, but we do not rule out this possibility (vide infra).[36]

Another limiting description for the excited states defines the a_{1g} mode as two rigid MoO_4 units (similar to the type of analysis considered by Crosby et al.[25]). Employing this treatment yields metal–metal displacements of 0.08 and 0.13 Å for both the $^1A_{2u}$ and the $^2B_{2g}$ states, respectively. The description of the masses of the vibrating units in the a_{1g} Mo–Mo stretch is probably some value intermediate to the above two definitions, yielding a calculated displacement range of 0.13–0.18 Å for the $^2B_{2g}$ state and 0.08–0.11 Å for the $^1A_{2u}$ state.

The magnitude of these reported metal–metal bond lengthenings in the $^1A_{2u}$ and $^2B_{2g}$ states seems large in comparison to certain structural results of dimolybdenum complexes. Cotton et al.[37,38] were able to prepare and structurally characterize the series of $Mo_2(SO_4)^{n-}$ salts, where $n = 3$ and 4. In these complexes the formal bond orders are 3.5 ($\sigma^2\pi^4\delta$) and 4.0 ($\sigma^2\pi^4\delta^2$), respectively. As in the case of the molybdenum carboxylates, the metal–metal bonding orbitals in these sulfates are highly localized on the metals.[40] In this $Mo_2(SO_4)_4{}^{n-}$ series the Mo–Mo bond length was observed to increase only 0.05 Å from $Mo_2(SO_4)_4{}^{4-}$ (2.111 (1) Å) to $Mo_2(SO_4)_4{}^{3-}$ (2.164 (2) Å). Another interesting comparison is provided by recent work by Cotton and Powell[41] on $Mo_2X_4(P_2)_2$ systems (where X = Cl and Br and P_2 are bridging diphosphine ligands). They found that by increasing the torsional angle, χ, in the $L{-}Mo\overset{4}{-}Mo{-}L'$ unit, as shown in the following Newman projection a correlation may be made with the Mo–Mo bond length. Extrapolation to $\chi = 45°$, where the δ bond should be nonexistent (i.e., a formal bond order of 3.0), shows that the effect of the δ bond in these systems is to shorten the bond length by 0.055 (2) Å. The formal oxidation state and formal bond order of the molybdenum atoms in these systems are +2.0 and 3.0, respectively, as in the $\delta\delta^*$ state. Since the structurally characterized study[37,38] yields a value half of that in the $\delta\delta^*$ studies,[28,29] it appears that the Franck–Condon analysis overestimates the bond displacement by approximately a factor of 2.

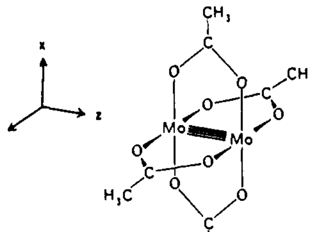


Admittedly, caution must be exercised in comparing these solid-state studies with our gas-phase studies. In the first comparison the two metal sulfate salts have differing numbers and positions of the potassium counterions, so that the effect of the oxidation state changes may be much different. There are also water molecules of solvolysis. The gas-phase studies, on the other hand, are not influenced at all by axial intermolecular interactions that exist in the crystalline solid lattice. In addition, these crystallographic studies of Mo–Mo bond lengths correspond to molecules with ligands other than carboxylates.

It is also possible that vibrational features in the excited states that are not included in the Franck–Condon analysis are leading to large metal–metal bond length determinations in the $^1A_{2u}$ and $^2B_{2g}$ states. As mentioned above, these analyses essentially treat the active normal mode which is responsible for the observed vibrational progression as being 100% composed of the internal a_{1g} Mo–Mo stretching mode in both the ground and excited states. If the contribution of other internal modes into the vibrational progression is nonnegligible, then the actual Mo–Mo displacement is a fraction of the calculated distortion since the normal coordinate mode is a weighted compilation of the activated internal coordinate modes. An extreme example of this was observed by Zink et al.[26] A semiclassical description and time-dependent approach to this problem has also been reported by Heller et al.[42-45] The a_{1g} internal coordinate modes of ν(Mo–Mo), ν(Mo–O), and $\delta(MoO_4)$ may combine to afford a missing mode effect (MIME) in this $^2B_{2g}$ state of $Mo_2(O_2CCH_3)_4$. It should be added, however, that preliminary PE experiments on the $Mo_2(S_2CCH_3)_4$ complex show a similar $^2B_{2g}$ ionization bandwidth and a similar vibrational frequency. Further PE and Raman studies must be done to determine the absolute validity of the Franck–Condon analysis, but this result also suggests that a relatively pure Mo–Mo stretch is likely. In any event, errors in our analysis due to a complex normal coordinate mode would also be present in the electronic studies with which we make our qualitative comparisons.[28,29] Therefore, the conventional analysis has been used.

Discussion

The structure in the first ionization band of $Mo_2(O_2CCH_3)_4$ reported in this paper is the most striking example of a vibrational progression in a predominantly metal ionization that we have observed to this time. Vibrational structure of this type is to be expected if the ionization and normal vibrational mode are highly localized on the metal center and if an appreciable change in metal–metal bond strength occurs. The ionization is associated with removal of an electron from the $2b_{2g}$ molecular orbital of $Mo_2(O_2CCH_3)_4$, which primarily represents the δ-bonding interaction of the d_{xy} atomic orbitals of the two molybdenum centers as defined in the following SCF–Xα–SW,[7,8] SCF–Xα–DV,[46] and Hartree–Fock[9,10] calculations have been carried out on the prototype molecule $Mo_2(O_2CH)_4$ and the results indicate that the $2b_{2g}$ orbital is predominantly localized on the metal atoms. Hutchinson et al.[13] have shown from a Raman study of isotopically labeled Mo in $Mo_2(O_2CCH_3)_4$ that the totally symmetric a_{1g} Mo–Mo stretching vibration "represents nearly pure Mo–Mo



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[36] In the event that there is a nonnegligible mode mixing, the calculated displacement value becomes a compilation of the displacements along all activated coordinates. On the basis of structural studies of two other classes of quadruply bonded molybdenum dimers, $[Mo_2(SO_4)_4]^{n-}$ and $[Mo_2(HPO_4)_4]^{n-}$, where n = 2, 3, or 4, it has been shown that each successive oxidation decreases the Mo–O bond length[37-39] (undoubtedly due to a combination of tighter molybdenum function and to a decrease of the filled–filled Mo3d–O2p interactions). It is fully anticipated that the Mo–O distances will also decrease in $Mo_2(O_2CCH_3)_4$ upon the δ ionization process for the same reasons. It is again stressed, though, that these displacements will contribute to the observed Franck–Condon progression only if the a_{1g} modes mix, and then only to the extent of their corresponding contributions.

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Table I. Compilation of the Pertinent Data and Information for the Three Electronic Perturbations of $Mo_2(O_2CCH_3)_4$

electronic state	electronic description	formal bond order	ν_{Mo-Mo}, cm^{-1}	d_{Mo-Mo}, Å
$^1A_{1g}$ (ground state)	$\sigma^2\pi^4\delta^2$	4.0	406[a]	2.079 (3)[b]
$^1A_{2u}$ ($\delta \rightarrow \delta^*$)	$\sigma^2\pi^4\delta\delta^*$	3.0	390[c]	2.19[d]
$^2B_{2g}$ (δ ionization)[e]	$\sigma^2\pi^4\delta$	3.5	360 (10)	2.26 ± 0.02[f]

[a] Reference 12. [b] Reference 47. [c] Reference 48. [d] The bond distance change from ref 28 and 29 has been applied to the gas-phase Mo–Mo bond length from ref 47. [e] From this work. [f] The deviation value reported is a level of confidence and not a standard deviation.

stretch”. This interpretation, indicating a lack of substantial mode mixing in the a_{1g} vibration, was also favored by other authors.[12,14-17]

The important question concerns the extent that the δ bond contributes to the total metal–metal bond strength. The observation of vibrational structure in the δ ionization band reported herein reveals the actual effects on the bond force constant and the Mo–Mo bond length caused by the removal (photoionization) of a single $2b_{2g}$ electron, which comprises half of the δ bond. It is most useful to compare the a_{1g} vibrational mode frequency and the bond length of the $^2B_{2g}$ positive ion state of the molecule with the corresponding mode frequencies and bond lengths in two other electronic states: the ground ($^1A_{1g}$) and the $\delta\delta^*$ ($^1A_{2u}$) excited electronic states of the neutral molecule. These are gathered in Table I along with the formal bond orders for these three electronic perturbations of $Mo_2(O_2CCH_3)_4$. This comparison relates three electronic states, each with differing degrees of δ-bonding interactions. The $^1A_{1g}$ state contains a full δ bond, the $^2B_{2g}$ state contains half of a δ bond, and the $^1A_{2u}$ state contains the effective cancellation of the δ bond. The Mo–Mo bond lengths and vibrational frequencies have been taken, when available, from either gas-phase or matrix-isolation studies. These values are not importantly different from the results of other solid-state studies, but they provide the most direct comparison to gas-phase photoelectron spectroscopic studies, which do not involve intermolecular interactions.

Our observation of an a_{1g} Mo–Mo vibrational frequency of 360 (10) cm^{-1} in the ionization band arising from the $^2B_{2g}$ state indicates a substantial decrease in the metal–metal bonding ability upon δ ionization compared to the $^1A_{1g}$ ground state (404–406 cm^{-1}).[12,13] The conventional Franck–Condon analysis of this band's vibrational progression reveals a bond length increase of 0.18 ± 0.02 Å relative to the $^1A_{1g}$ ground-state bond length of 2.079 (3) Å.[47]

Comparison of the $^2B_{2g}$ state (δ ionization) with the $^1A_{2u}$ state ($\delta\delta^*$ excitation) is also significant. Gray[14-16] and others[17] have shown experimentally that the δ^* orbital is predominantly metal in character. Norman et al.[7,8] also have calculated with the SCF–Xα–SW method that the δ^* orbital is similar in metal character to the δ orbital (86% vs. 89%). Therefore, it is reasonable that excitation to the $\delta\delta^*$ state represents effective cancellation of the δ bond. The electronic studies at low temperatures[28,29] indicate that the change in metal–metal interaction and the amount of molecular distortion in the $\delta\delta^*$ $^1A_{2u}$ state are less than for the $^2B_{2g}$ state. The a_{1g} vibrational frequency is only lowered from 404–406 cm^{-1} in the neutral molecule[12,13] to 390 cm^{-1} upon electronic promotion of this matrix-isolated molecule to the $^1A_{2u}$ excited state[48] and to 370 (5) cm^{-1} in the analogous single-crystal electronic study.[28,29] Trogler et al.[28] and Martin et al.[29] have shown, using a Franck–Condon analysis the same as ours, that the Mo–Mo equilibrium bond distance is subsequently increased by about 0.11 Å by this electronic promotion. It should be noted that the vertical transition for $\delta\delta^*$ excitation ($^1A_{1g} \rightarrow {}^1A_{2u}$) is to the $\nu' = 2$ level, whereas the vertical transition for δ ionization is to the $\nu' = 7$ level, indicative of the greater bond displacement in the $^2B_{2g}$ positive ion state.

It is immediately apparent from Table I and the preceding discussion that the trends in the Mo–Mo stretching frequencies and bond lengths in these electronic perturbations do not run parallel with simplified bond order formalism. This formalism suggests that both the Mo–Mo stretching frequency and bond length for the $^2B_{2g}$ state should fall between those values for the ground and the $^1A_{2u}$ electronic states. In fact, the bond distance change in the $^2B_{2g}$ state is longer (by nearly a factor of 2) and the a_{1g} vibrational frequency is lower than the corresponding values in the other two electronic states. Clearly, the formal bond order change is not sufficient to explain the large frequency change and bond lengthening.

The additional important factor to consider is the effective oxidation state of the metal centers in these three states of the molecule. Upon the electronic transition to the $^1A_{2u}$ excited state, the metals' local total electron density environment is not appreciably altered since the $2b_{1u}$ (δ^*) orbital to which the electron was promoted is of comparable metal character to the δ orbital. In other words, the effective oxidation state of the two metals has not been perturbed by promotion to the $^1A_{2u}$ state. Ionization of the neutral molecule to the $^2B_{2g}$ positive ion state, however, involves the total removal of a “δ” electron from the molecular system. This process increases the effective oxidation state of the two metals, leading to stabilization of the metal levels and contraction of the metal orbitals. Contraction of the metal orbitals not only lowers the overlap involved in the $2b_{2g}$ δ-bonding orbital, in which only one electron now resides, but also reduces the overlap in the doubly degenerate $6e_u$ orbitals involved in π bonding between the metals. The reduced overlap of these orbitals in the $^2B_{2g}$ positive ion state understandably lowers the total bond strength between the two metals and results in the larger than anticipated changes in the Mo–Mo vibrational stretching frequency and bond distance in the $^2B_{2g}$ state.

Analogous arguments of this contraction of the metal orbitals have previously been used in the bonding comparisons of Mo_2 vs. Mo_2^{4+} systems,[49] in the bonding comparisons of $[Mo_2(SO_4)_4]^{n-}$ and $[Mo_2(HPO_4)_4]^{n-}$, where n = 2, 3, or 4,[50] and also in the $M(CO)_6$ vs. $M(CO)_6^+$ systems where M = Cr, Mo, and W.[3] This effect was particularly important in the latter study, which showed disproportionately large metal–carbon bond lengthening with the removal of a single, predominantly metal electron from the d^6 t_{2g} configuration. In this case the effective oxidation state increase at the metal center reduced the π-back-bonding ability of the remaining metal d electrons to the carbonyls.

In brief summary, we have reported the first observation of vibrational fine structure in a metal–metal photoionization band. The vibrational frequency observed in the $^2B_{2g}$ positive ion state of $Mo_2(O_2CCH_3)_4$ was found to be 360 (10) cm^{-1}, which is substantially lower than the vibrational frequency in the neutral molecule. Franck–Condon vibrational progression analysis shows a substantial lengthening of the metal–metal bond. An evaluation of this conventional analysis suggests that partial inclusion of other internal modes may be necessary for precise determination of the change in metal–metal bond distance. Nonetheless, it is clear that the metal–metal bond is weakened more from removal of an electron from the δ-bonding orbital ($^1A_{1g} \rightarrow {}^2B_{2g}$) than from the $\delta\delta^*$ ($^1A_{1g} \rightarrow {}^1A_{2u}$) excitation process. Both the change in metal–metal bond order upon $2b_{2g}$ ionization and the change in the metal oxidation state are important in determining the contribution of the δ-bonding electron to the metal–metal interaction.

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electronic studies of several quadruply bonded complexes (ref 46). The computer program used to perform the Fourier transform analyses was written and developed by Mr. Glen E. Kellogg, Chemistry Department, University of Arizona. We also acknowledge the Department of Energy, Contract DE-ACO2-80ER10746, and the University of Arizona for partial support of this work. D.L.L. is an Alfred P. Sloan Fellow.

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Specification of the Bonding Cavities Available in Metal-Binding Sites: A Comparative Study of a Series of Quadridentate Macrocyclic Ligands

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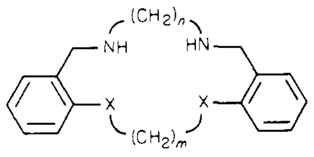
Abstract: A method for specifying the size of bonding cavities available to metal ions in metal-binding sites has been applied to a series of seven nickel(II) complexes of dibenzo-substituted quadridentate macrocycles and two free ligands. The procedure allows the goodness-of-fit of a metal ion for the binding site to be estimated by correcting the "hole size" of the donor set for the radii of the donor atoms. For the series of macrocyclic ligands considered, the resulting "bonding cavity" radii are shown to increase by ~0.05 Å for each additional atom in the inner great ring. Changing the donor atom type is found to have a relatively small influence on bonding cavity radii. Data from three new X-ray structure determinations of 14-membered macrocyclic species are considered in the survey; the structures determined are the nickel chloride complex of 3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclotetradecane [Ni(O-en-N-enH_4)Cl_2], the nickel thiocyanate complex of 3,4:9,10-dibenzo-1,5,8,12-tetraazacyclotetradecane [Ni(N-en-N-enH_4)$(NCS)_2$], and the metal-free macrocyclic ligand (N-en-N-enH_4). The conformation of metal-free (N-en-N-enH_4) is very similar to that in its nickel complex [Ni(N-en-N-enH_4)$(NCS)_2$] and also to that found for the related O_2N_2 ligand in [Ni(O-en-N-enH_4)Cl_2]. Both the N_4 and O_2N_2 14-membered ligands impose a ring-size constriction on the coordinated high-spin Ni(II) ion; this constriction is more severe for the O_2N_2 ligand. [Ni(O-en-N-enH_4)Cl_2]·$CHCl_3$: space group $P\bar{1}$, $a = 11.525$ (3) Å, $b = 11.307$ (3) Å, $c = 9.757$ (2) Å, $\alpha = 106.74$ (2)°, $\beta = 90.78$ (2)°, $\gamma = 103.22$ (2)°, $R = 0.075$ for 1233 four-circle diffractometer data with $F \geq \sigma(F)$. [Ni(N-en-N-enH_4)$(NCS)_2$]: space group $C2/c$, $a = 15.280$ (4) Å, $b = 9.765$ (2) Å, $c = 15.488$ (4) Å, $\beta = 108.13$ (3)°, $R = 0.038$ for 2151 four-circle diffractometer data with $F \geq \sigma(F)$. (N-en-N-enH_4): space group $P2_1/c$, $a = 11.844$ (3) Å, $b = 8.118$ (2) Å, $c = 17.788$ (4) Å, $\beta = 100.53$ (3)°, $R = 0.068$ for 1049 four-circle diffractometer data with $F \geq \sigma(F)$.

The fit of a metal ion for its surrounding coordination shell is a parameter of major importance in influencing the chemical properties of the resulting metal complex. While in simple ligand systems it is normally found that the respective donor atoms take up positions that yield near ideal metal–ligand bond lengths, this is often not the case when the ligands are restricted by steric constraints. Constraints of this type have been postulated to be the origin of unusual behavior in a range of metal-containing systems in both chemistry and biochemistry. In previous work, Busch et al.[2] have used force-field calculations to probe such constraints in Ni(II) and Co(III) complexes of tetraaza macrocycles.

We have been concerned with the theoretical and practical aspects of the use of macrocyclic ligands as metal ion selective reagents and have also been concerned with matching ring sizes in such ligands to the radii of particular metal ions. As part of this study, X-ray structure determinations of a series of closely related macrocyclic compounds **1** containing O_2N_2-, N_4-, and S_2N_2-donor sets have been completed[3-5] and a simple procedure developed for assessing the fit of the metal ion for a given macrocyclic cavity. A particular aim of these studies has been to correlate the hole-size variations in macrocycles of the general type **1** with the previously documented transition metal ion chemistry of these systems.[6-10] In the latter studies unusual, and potentially useful, ring-size discrimination effects have been observed in both the thermodynamic and kinetic behavior of a number of such compounds.[9,10]



1, X = O, NH, S; $n = 2, 3$; $m = 2$–4

A comparison of the macrocycle hole size in the dibromonickel(II) complex of **1** (X = O; $n = m = 3$) with that in its

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