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Electronic Spectra of Tetrakis(μ-acetato)-dimolybdenum(II) in Matrices at 10 K

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The 23 000-cm^{-1} electronic absorption band system of $Mo_2(O_2CCH_3)_4$ has been studied in N_2, Ar, Kr, Xe, and CH_3Br matrices at 10 K. Five progressional origins A_0, B_0, C_0, D_0, and E_0 are found at 22 370, 22 090, 22 650, 22 710, and 22 910 cm^{-1} in argon at 10 K. Each origin exhibits a progression in the excited state a_{1g}(Mo–Mo) stretching vibration with an average value of 390 cm^{-1}. The A_0–B_0 separation varies as a function of matrix environment while the A_0–C_0, A_0–D_0, and A_0–E_0 differences do not. As the atomic number of the matrix increases so does the relative intensity of B_0. These data suggest that band B be attributed to a second spin-forbidden electronic transition. The a_{1g}(Mo–Mo) progressional frequency in the matrix spectra differs significantly from that of 370 cm^{-1} in the crystal spectrum. This is attributed to the lack of axial ligands in the matrices. A comparison of the relative intensities of the A_0, C_0, D_0, and E_0 origins shows C_0 and E_0 increase by similar amounts relative to A_0 and D_0, when the environment is changed from the crystal to the matrix. This results from the concomitant 700-cm^{-1} blue shift of these origins which decreases the energy gap to the dipole-allowed transitions (in the near ultraviolet) and leads to an increase in the intensity derived from Herzberg–Teller coupling. The electronic origin A_0 and the a_{1g}(Mo–O) component, D_0, would not be expected to show such an intensity increase. Direct support for the vibronic nature of the E progression is evident in vibronic interference between higher progressional members and the allowed electronic transitions at higher energy.

Introduction

Electronic spectra of binuclear molybdenum(II) carboxylate complexes have provided an interesting spectroscopic problem for over a decade. These complexes formally possess a quadruple metal–metal bond and the ground-state d-electron configuration $\sigma^2\pi^4\delta^2$ (see Figure 1). Dubicki and Martin initially examined several of these compounds, most notably $Mo_2(O_2CCH_3)_4$, by diffuse-reflectance spectroscopy at 77 K.[1] Aided by Hückel MO calculations, they assigned the weak, structured absorption ca. 23 000 cm^{-1} to a dipole-forbidden transition from the δ-bonding orbital to a σ-type nonbonding level. This assignment was made partly by analogy to the then accepted interpretation[2] of the $Re_2Cl_8^{2-}$ spectrum, which has now been revised.[3] Subsequently, a study of the polarized crystal spectra of the analogous glycinate complex supported the conclusion that the weak band near 23 000 cm^{-1} arose from a dipole-forbidden electronic transition.[4] The enabling vibrations which were invoked to explain the numerous vibronic origins had energies in excess of 1000 cm^{-1}; however, a recent paper[5] raises the possibility that an impurity defect is responsible for the weak *z*-polarized progression that was thought to be based on the true electronic origin. Subsequent polarized electronic absorption spectral studies of $Mo_2(O_2CH)_4$ also led to the conclusion that the 23 000-cm^{-1} band must arise from a dipole-forbidden transition.[6] At about this time Norman and Kolari[7] suggested a specific $\delta \rightarrow \pi^*$ assignment for this transition on the basis of Xα calculations. This was supported by an analysis of the hot bands in the electronic absorption spectra of $Mo_2(O_2CCH_3)_4$, $Mo_2(O_2CCF_3)_4$, and $Mo_2(O_2CH)_4$, in addition to single-crystal-polarized spectral studies of $Mo_2(O_2CCH_3)_4$.[8] The evidence suggested that the $\delta \rightarrow \pi^*$ ($^1A_{1g} \rightarrow {}^1E_g$) transition was split by the low-molecular site symmetry in the crystal ($\bar{1}$ in the case of $Mo_2(O_2CCH_3)_4$[9]). Low-energy ungerade vibrations (200–600 cm^{-1}) were invoked as the vibronically active modes.

Recently, a more careful study of the $Mo_2(O_2CCH_3)_4$ crystal spectrum proved the previously reported polarization ratios to be incorrect and suggested an alternate interpretation of the hot band data.[5] The polarization ratios reported[6] for a similar absorption feature in the electronic spectrum of $Mo_2(O_2CH)_4$ were also questioned. Unfortunately, Martin et al.[5] did not furnish absolute error limits for their deconvoluted polariztion ratios; the technique applied is sensitive to errors in the crystal thickness, corrections due to multiple reflections and dispersion of the refractive index.[10] The dipole-allowed $\delta \rightarrow \delta^*$ ($^1A_{1g} \rightarrow {}^1A_{2u}$) assignment was proposed for the 23 000-cm^{-1} absorption in the electronic spectra of dimolybdenum(II) carboxylates. This requires an allowed oscillator strength of less than 0.001 and that vibronic contributions dominate the spectrum. Subsequently, an analogous assignment was made for a leucine complex;[11] however, the authors did not comment about a number of weak spectral features observed *below* the supposed 0–0 transition in the published spectra. The intensities of these features are too great to be hot bands at the stated temperatures. Careful study of the unpolarized spectrum of $Mo_2(O_2CH)_4$ at low temperature also reveals a weak peak near the first electonic origin[8] that was not mentioned in the earlier study.[6] The $Mo_2(O_2CCF_3)_4$ complex also exhibits weak vibronic lines which are of *lower energy* than the first intense line in the electronic absorption spectrum. These features have been attributed to lower energy vibronic origins,[8] a second transition, or a defect site.[5] It is interesting that all the dimolybdenum(II) carboxylates examined, except for the acetate complex, contain extra anomalous weak vibronic lines. Since it appears that crystal-site properties may be important in these systems, we examined $Mo_2(O_2CCH_3)_4$ isolated in a variety of low-temperature matrices. These studies show that two electronic states contribute to the 23 000-cm^{-1} electronic absorption band of $Mo_2(O_2CCH_3)_4$.

Experimental Section

Optical spectra were recorded with a Cary 17D spectrophotometer, whose sample compartment was modified to accommodate the matrix apparatus. An Air Products Displex CS 202B closed-cycle helium

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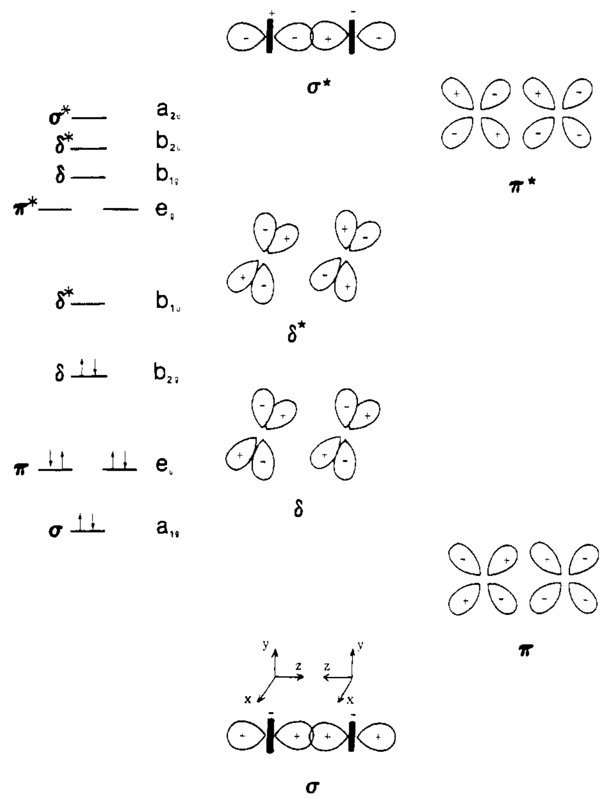

Figure 1. Qualitative energy level scheme for metal-localized molecular orbitals in the D_{4h} $Mo_2(O_2CCH_3)_4$ complex along with sketches of the types of metal–metal overlap. The b_{1g} (δ) and b_{2u} (δ*) orbitals, derived from metal $d_{x^2-y^2}$ atomic functions, point at the ligands and are of metal–ligand σ* character.

refrigerator cooled a sapphire window, affixed with indium gaskets to the cold station, to 10 K. The matrix furnace was built to specification by the Northwestern University Physics Department machine shop. A standard 7.6-cm o.d. vacuum flange was used for the furnace base, with a Macor (from Corning) ceramic disk machined to seal off one end. Feedthroughs for the furnace heater, thermocouple, and quartz crystal microbalance were drilled in the ceramic. Insulating ceramic supports for the cylindrical oven were epoxyed (Perkin-Elmer Ultratorr) to the inside surface of the ceramic. The oven consisted of a 1-cm o.d. stainless-steel cylinder of 3-cm height. A 6-mm diameter hole was bored from one end to within 2 mm of the opposite end. Two molecular beam ports 5 mm long and of 1-mm i.d. were inserted through the walls of the cylinder at its midpoint. The furnace and beam ports were wrapped with Nichrome wire (1.62 Ω/ft) and covered with a glass braid. A slotted brass cylinder fit over the Nichrome wire to secure the wrappings. The snugly fitting oven cap was machined from stainless steel and contained a chromel/alumel thermocouple. In operation we found the $Mo_2(O_2CCH_3)_4$ first sublimed onto the cap, which was slightly colder than the oven body. This was considered an advantage because it provided an in situ sublimation prior to deposition, which permits the release of trapped (volatile) impurities. One oven beam port pointed toward the ceramic base, above which a quartz crystal microbalance[12] was affixed. This provided a quantitative measure of the solid flow rate. The other beam port pointed toward the sapphire window, when the flange which held the oven was attached to the can assembly (vide infra). A brass can (5-cm o.d., 0.16-cm walls, and 4.7-cm height) was attached to the other 7.6-cm vacuum flange and joined to a short (18 mm) run of 19-mm i.d. pipe that contained a disk to collimate the the molecular beam to a 5-mm diameter. Two 0.08-cm diameter gas nozzles mixed the matrix gas with this beam ca. 4 cm from the cold sapphire window. The narrow end of the brass can assembly was hard soldered to a flange designed to fit the commerical vacuum shroud of the CS 202B. Gas-flow rates could be regulated with disks containing a hole of precision diameter held (by O-rings in a gasket assembly) in the matrix gas line. Kinetic theory of flow through an orifice requires holes of 0.025- and 0.040-mm diameter for flow rates of 2.9 and 7.3 mmol/h for argon gas with a 300-torr back-pressure (most experiments used the former flow rate). An experimental check of the theoretical flow rates showed negligible error (±10%) occurred by using the ideal gas equation

$$\text{flow rate} = \frac{P(A_0)}{(2\pi M_r RT)^{1/2}}$$

where P is the pressure, A_0 the area of the hole, M_r the molecular weight, T the temperature, and R the gas constant.

Gaseous argon (99.9998%), krypton (99.995%), nitrogen (99.999%), and xenon (99.995%) were obtained from Airco Corp. Methyl bromide (99.5%) was purchased from Matheson. Background pressure in the matrix apparatus (monitored by a cold cathode gauge) was ca. 10^{-6} torr under operating conditions. Tetrakis(μ-acetato)-dimolybdenum(II) was prepared by a literature method.[5]

Table I. Energies (cm^{-1}) of Band Origins for $Mo_2(O_2CCH_3)_4$ Isolated in Matrices at 10 K

	N_2	Ar	Kr	Xe	CH_3Br	crystal[a]
			Band Origins			
B_0	22 070	22 090	22 100	22 050	21 930	21 880
A_0	22 310	22 370	22 370	22 360	22 200	21 700
B_1	22 450	22 470	22 480	22 430	22 310	NO[b]
C_0	22 590	22 650	22 640	22 640	22 480	21 980
D_0	NO	22 710	NO	NO	NO	22 020
A_1	22 700	22 760	22 760	22 750	22 580	22 080
E_0	22 850	22 910	22 920	22 920	22 760	22 250
			Band Origins Relative to A_0			
B_0	−240	−280	−270	−310	−270	180
A_0	0	0	0	0	0	0
B_1	140	100	110	70	110	NO
C_0	280	280	270	280	280	280
D_0	NO	330	NO	NO	NO	320
A_1	390	390	390	390	380	380
E_0	540	550	550	560	560	550

[a] Taken from ref 5. [b] NO = not observed.

Results and Discussion

This work constitutes the first matrix isolation study of a binuclear metal–carboxylate complex. Five different host lattices were employed: N_2, Ar, Kr, Xe, and CH_3Br, with dilutions typically ranging from 500:1 to 800:1. A representative spectrum, taken in argon, is shown in Figure 2 and compared with the spectrum of a polycrystalline film. The energies of individual vibronic lines are summarized in Table I. Important differences and similarities exist. Both the crystal and matrix spectra display a weak, highly structured absorption (Figure 2) with five major origins. All origins exhibit progressions in the a_{1g}(Mo–Mo) stretching vibration. The average vibrational frequency in the matrix, 390 cm^{-1}, is significantly greater than that of 370 cm^{-1} in the crystal spectrum. We attribute this increase in the metal–metal stretching frequency to a difference in axial ligation (Ar in the matrix and oxygen from a neighboring carboxylate[9] in the crystal). Stronger axial ligands are known to weaken the metal–metal bond.[13a] Bonding to antibonding transitions involving metal-localized orbitals may increase in energy with an increase in the metal–metal bond strength.[13b] This could also account for the 700-cm^{-1} blue shift of the band system in the matrix relative to the crystal.

From the data in Table I, it is evident that the A_0-C_0, A_0-D_0, and A_0-E_0 separations are nearly identical for both crystal and matrix spectra. This rules out an earlier suggestion that peaks C_0 and E_0 were vibronic origins built upon a site splitting of a degenerate electronic origin.[8] Rather, they must be vibra-

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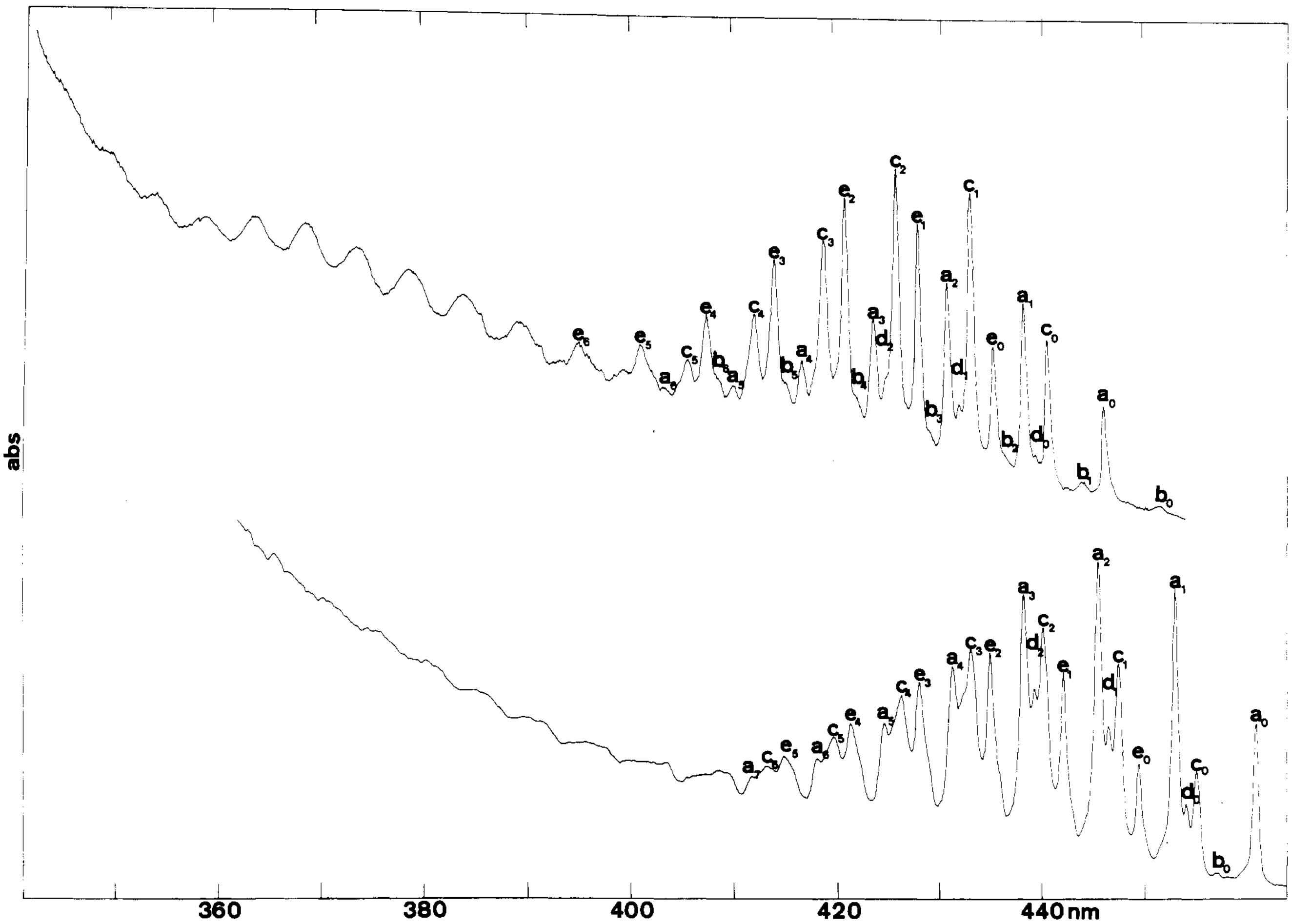

Figure 2. Electronic absorption spectra of $Mo_2(O_2CCH_3)_4$ as a polycrystalline film on a quartz flat (lower spectrum), and diluted 1:700 in an argon matrix on a sapphire substrate (upper spectrum). Instrumental resolution was 0.03 nm, the practical limit of the Cary 17D spectrometer. Both spectra were measured at 10 K. Five major excited-state progressions in the a_{1g}(Mo–Mo) stretch are designated a, b, c, d, and e.

tional origins based upon a single electronic origin; most probably that is A_0 according to the studies of Martin et al.[5] The 280-cm^{-1} A_0–C_0 spacing may be assigned to a molybdenum–oxygen stretch.[14] Considering the large A_0–E_0 splitting (550 cm^{-1}), a carboxylate mode must be responsible for vibronic origin E_0. Previous work on the vibrational spectrum of copper acetate suggests this frequency be attributed to either the carboxylate bend or rock.[15] Peak D_0 has been assigned[5] to an a_{1g}(Mo–O) stretch built upon A_0. Upon careful inspection of the electronic spectrum, it is apparent that the D progressional frequency is less than either A or C. Notice how in the low-energy region of the band (Figure 1) D_0 lies midway between C_0 and A_1; however, at higher energies (e.g., D_2) the D progression becomes buried under the C progression. This further confirms the assignment of D_0 to an a_{1g}(Mo–O) vibration on A_0. Coupling between a_{1g}(Mo–Mo) and the a_{1g}(Mo–O) vibrations could slightly alter the a_{1g}(Mo–O) frequency when many quanta of a_{1g}(Mo–Mo) are simultaneously excited.

The A_0–B_0 separation varies, not only between the matrix and crystal spectra but also between different matrices as well (see Table I). The A_0–B_0 spacing decreases by at least 460 cm^{-1} in the argon matrix relative to the crystal. The analogy with B_0 in the crystal is not, however, unambiguous because of its weak intensity. It is possible that the analogue of B_0 in the crystal lies at even higher energies beneath the more intense A, C, D, and E progressions. Martin et al.[5] attributed B_0 in the crystal spectrum to a Mo–Mo–O bending vibration built on A_0; however, they did note that it possessed a transition moment oriented quite differently (in the triclinic crystal) from A_0, C_0, D_0, or E_0. It was this unusual presence of three polarization ratios that led Trogler et al.[8] to the split-state ($\delta \rightarrow \pi^*$) hypothesis. These difficulties are resolved if B_0 in the crystal spectrum is assigned to a second electronic state. The environmental sensitivity of the A_0–B_0 separation is also consistent with A and B belonging to different electronic states. Relative peak intensities (Table II) agree with this interpretation.

Table II. Intensities of Band Origins in Crystalline and Matrix-Isolated $Mo_2(O_2CCH_3)_4$

	RI[a]			RI[a]	
band	crystal	Ar matrix	band	crystal	Ar matrix
A_0	1.0	1.0	D_0	0.11	0.07
B_0	0.02	0.11	A_1	1.50	1.86
C_0	0.64	1.50	E_0	0.53	1.24

[a] RI denotes intensity relative to origin A_0, as estimated from the peak maxima. The data for the crystal used the spectrum of a polycrystalline film.

Peaks A_0 and D_0 appear to exhibit the same relative intensity in the crystal and matrix, which is consistent with their identification as the pure electronic origin and an a_{1g} vibronic component, respectively. Matrix peaks C_0 and E_0, which have identical crystal polarization characteristics,[5,8] possess intensities which are increased by similar amounts compared to those in the crystal (Table II). This supports their assignment to Herzberg–Teller components built upon A_0, as first ad-

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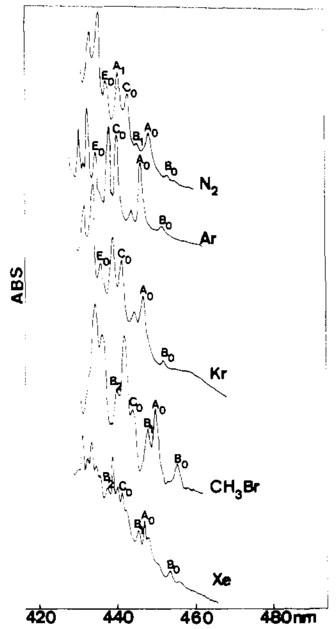

Figure 3. Expanded view of band origins in the electronic absorption spectra of $Mo_2(O_2CCH_3)_4$ isolated in N_2, Ar, Kr, CH_3Br, and Xe matrices at 10 K.

vanced by Martin et al.[5] The blue shift of the band origins in the matrix decreases the energy gap between these features and the allowed transitions (in the ultraviolet spectral region) to produce the expected increase in vibronic intensity. Vibronic progression E (and less dramatically, C) also exhibits an unusual interference phenomenon when it begins to overlap with excited states to higher energy. Notice the relatively longer progression[16] (Figure 2) to below 350 nm, whereas the A and D progressions have disappeared by 400 nm. This further supports the assignment of E_0 to a non totally symmetric vibronic origin based upon A_0. Interference effects such as these[17] are well documented in the electronic spectra of organic molecules[18] when a weak transition overlaps with an intense one (from which it steals intensity). Note that the 350–390-nm "interference" progression is not as evident in the crystal spectrum as in the matrix, presumably because of the red shift of the A_0–E_0 band origins.

Alternative explanations must be considered. Similar behavior in all matrices is strong evidence against the B progression being due to a specific lattice impurity site, in addition to the fact that there are no C_0 or E_0 origins built upon B_0. Any arguments based upon aggregates can be discarded due to the results of annealing experiments (at one-third of the matrix melting point) and concentration studies (complex: Ar ratios of 1:400 to 1:4000 were examined). All aggregates are found to absorb to lower energy than the truly isolated species and display much broader line widths. Deposition conditions were also varied (at 10 K and at one-third of the matrix melting point), and only in the case of xenon did the relative intensities of vibronic lines changes. In xenon each peak splits into two components (Figure 3), and the relative intensities of the split components are sensitive to annealing. We believe that two different matrix sites are present in the xenon host lattice. Assignment of B to an impurity also seems unlikely since such a species must either be present in all matrix gases or a compound with physical properties nearly identical with $Mo_2(O_2CCH_3)_4$ that is present in samples from several preparations. For these reasons, we prefer the conclusion that B is a distinct electronic state in dimolybdenum(II) acetate.

An important clue to the nature of the excited electronic state responsible for B is its relative intensity in different matrices. When the atomic number of the matrix increases, so does the relative intensity of B (Figure 3). This "heavy-atom" effect[19] suggests a "spin-forbidden" assignment.

We have established that *two distinct electronic transitions contribute to the 23 000-cm^{-1} electronic absorption of $Mo_2(O_2CCH_3)_4$*. The matrix experiments support the conclusion of Martin et al.[5] that A_0 be assigned to a pure electronic origin, D_0 be assigned to an a_{1g}(Mo–O) vibronic origin, and C_0 and E_0 be assigned to non-totally symmetric vibronic components. Origin B_0 is derived from a different electronic state, and is probably "spin forbidden". It is not clear whether A_0 is a weak dipole-allowed origin or also a spin–orbit component derived from a "triplet". According to GVB–CI calculations[20] of $Re_2Cl_8^{2-}$, the $\delta^1\delta^{*1}(^3A_{2u})$ and $\delta^1\delta^{*1}(^1A_{2u})$ states are located at 2800 and 23 150 cm^{-1} respectively. A recent spectroscopic study[21] of $Cr_2(O_2CCH_3)_4(H_2O)_2$ places these two states much closer in energy: ca. 16 000 and 25 800 cm^{-1}, respectively. Available theoretical studies[1,7,22] of $Mo_2(O_2CH)_4$ have not considered multiplet effects, and a detailed assignment of the electronic spectra of dimolybdenum(II) carboxylates must await relativistic calculations. An earlier suggestion[7] that configuration interaction between the $\delta \rightarrow \pi^*$ (^1E_g) and $\pi \rightarrow \delta^*$ (^1E_g) states lower $\delta \rightarrow \pi^*$ into the 23 000-cm^{-1} spectral region must be reconsidered. These two states are described by wavefunctions $|...\pi^4\delta^1\pi^{*1}|$ and $|...\pi^3\delta^2\delta^{*1}|$, that differ by *three* spin orbitals, and therefore cannot have nonzero off-diagonal matrix elements with the Hamiltonian that consists of one and two electron operators.

Acknowledgment. We thank the Research Corp. for partial support of this work.

Registry No. $Mo_2(O_2CCH_3)_4$, 14221-06-8.

Supplementary Material Available: Tables of the vibronic peak energies for the 23 000-cm^{-1} electronic absorption band system of $Mo_2(O_2CCH_3)_4$ in nitrogen, argon, krypton, xenon, and methyl bromide matrices at 10 K (5 pages). Ordering information is given on any current masthead page.

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(16) The oscillations are not interference fringes due to the matrix thickness as evidenced by their absence in the region of nonabsorption (wavelengths below 450 nm) and their persistence in matrices of different thickness.

(17) As an alternative interpretation, we note that a Jahn–Teller distortion of an E electronic state might lead to a double-humped absorption band shape: Longuet-Higgins, H. C.; Öpik, U.; Pryce, M. L. H.; Sack, R. A. *Proc. R. Soc. London, Ser. A* **1958**, *244*, 1–16. The possibility of a third transition must also be acknowledged.

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