As already mentioned the blue S_3^- entity can be formed in CsCl–AlCl₃ melts but not in NaCl–AlCl₃ and KCl–AlCl₃ melts. the most obvious reason for this difference is the higher chloride activity in the basic CsCl–AlCl₃ melts than in the NaCl–AlCl₃ and KCl–AlCl₃ melts (under comparable conditions). This perhaps makes ion B a more likely candidate. Also, S(–II) in basic melts is strongly bound to aluminum in polymeric structures of the $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ type (which for large values of n could be looked upon as $[AlSCl_2]_n^{n-}$). If we assume that the compound formed is $[S_3AlCl_4]^{2-}$ (ion B), the reaction giving this compound must be

$$[AlSCl_2]_n^{n-} + (5n/m)S_m + nAlCl_4^- + 2nCl^- \rightleftharpoons$$
$$2n[S_3AlCl_4]^{2-} \quad (1)$$
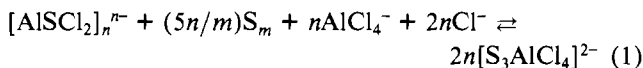
where m and n are integers, and most likely m is no larger than 8. It can immediately be seen that this reaction is favored by increasing basicity of the melt whereas a corresponding reaction involving ion A instead of ion B will be independent of the acidity–basicity of the melt.

The formation of $[S_3AlCl_4]^{2-}$ instead of the formation of $[S_3AlCl_3]^-$ is very surprising from a structural point of view since it involves a coordination number higher than 4 for Al(III). Therefore the question of the nature of the sulfur species formed cannot be considered to be completely settled.

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Polarized Electronic Absorption Spectra of Tetrakis(μ-trifluoroacetato)dimolybdenum(II) and Tetrakis(μ-trifluoroacetato)bis(pyridine)dimolybdenum(II)

DON S. MARTIN,* ROBERT A. NEWMAN, and PHILLIP E. FANWICK

Polarized spectra are reported for the 010 faces of $Mo_2(O_2CCF_3)_4$ and $Mo_2(O_2CCF_3)_4\cdot2C_5H_5N$ at 300 and 5 K. At 5 K bands at about 23 000 cm⁻¹ exhibit rich vibrational structure. The evidence available from earlier studies with $Mo_2(O_2CCH_3)_4$ provides a justification for assigning the transitions as weak electric dipole allowed with molecular z polarization under the local D_{4h} symmetry. The intensities are sufficiently low that Franck–Condon progressions based on vibronic origins have intensities comparable to the 0–0 progression. The polarization of the transition is that expected for the $^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta-\delta^*$) transition. The presence of a second electronic transition in this vicinity is also indicated.

Introduction

The dimeric complexes of molybdenum(II) possess the interesting quadruple bond between the Mo atoms. Generally, the recent scattered-wave Xα calculations[1-5] have indicated that the lowest energy electronic excitation in such dimers should be the $\delta \rightarrow \delta^*$ transition. A local symmetry of D_{4h} applies to a number of these dimeric complexes. Under this symmetry the spin-allowed $\delta \rightarrow \delta^*$ transition can be characterized as $^1A_{1g} \rightarrow {}^1A_{2u}$ ($b_{1g} \rightarrow b_{2u}$). It is therefore predicted to be an electric-dipole-allowed transition for the absorption of light polarized in the z direction; i.e., along the metal–metal bond.

Polarized optical absorption measurements[6,7] for single crystals containing $Mo_2Cl_8^{4-}$ and $Mo_2(SO_4)_4^{4-}$ with bridging sulfate ligands have indicated that the lowest energy observed absorption bands were z polarized, consistent with the $\delta \rightarrow \delta^*$ assignment. Also, the polarized spectra for $K_3Mo_2(SO_4)_4\cdot4H_2O^8$, for which there should be only one electron in the δ orbital, were consistent with a $\delta \rightarrow \delta^*$ assignment.

The assignment of the lowest energy band in the electronic absorption spectra of the tetrakis(μ-carboxylate) complexes has involved more controversy. A number of crystals have provided low-temperature spectra with rich vibrational detail so that from three to seven Franck–Condon progressions, with five to seven lines each, have been resolvable. For tetragonal crystals of tetrakis(μ-glycine)dimolybdenum(II) sulfate tetrahydrate, where z- and x,y-polarized lines were indicated unambiguously, the presence of lines in both polarizations of comparable intensity originally led to the conclusion that this band should not be assigned as a $\delta \rightarrow \delta^*$ transition.[9] This conclusion was apparently supported by the spectra recorded for tetrakis(μ-formato)dimolybdenum(II),[6] where the polarization ratio for the lowest observed line in the spectra was opposite to that expected for a z-polarized transition. In addition, Trogler et al.[10] reported single-crystal spectra for tetrakis(μ-acetato)dimolybdenum and a multicrystal unpolarized spectrum for tetrakis(μ-trifluoroacetato)dimolybdenum(II). They assigned the observed band as $\delta \rightarrow \pi^*$ ($^1A_{1g} \rightarrow {}^1E_g$). However, Martin et al.[11] were able to measure polarization ratios for the sharp line at longest wavelength for two different crystal faces of $Mo_2(O_2CCH_3)_4$, which was the origin of the most intense Franck–Condon progression. From this information the orientation of the transition moment for this line could be determined. It was

(1) Norman, J. G., Jr.; Kolari, H. J. *J. Chem. Soc., Chem. Commun.* **1975,** 649.
(2) Norman, J. G., Jr.; Kolari, H. J. *J. Am. Chem. Soc.* **1975,** *97,* 33.
(3) Mortola, A. P.; Mosowitz, J. W.; Rosch, N.; Cowman, C. D.; Gray, H. B. *Chem. Phys. Lett.* **1975,** *32,* 283.
(4) Noodleman, L.; Norman, J. G., Jr. *J. Chem. Phys.* **1979,** *70,* 4903.
(5) Norman, J. G., Jr.; Ryan, J. B. *J. Comput. Chem.* **1980,** *1,* 59.
(6) Cotton, F. A.; Martin, D. S.; Fanwick, P. E.; Peters, T. J.; Webb, T. R. *J. Am. Chem. Soc.* **1976,** *98,* 4681.
(7) Fanwick, P. E.; Martin, D. S.; Cotton, F. A.; Webb, T. R. *Inorg. Chem.* **1977,** *16,* 2103.
(8) Fanwick, P. E.; Martin, D. S.; Webb, T. R.; Robbins, G. A.; Newman, R. A. *Inorg. Chem.* **1978,** *17,* 2723.

(9) Cotton, F. A.; Martin, D. S.; Webb, T. R.; Peters, T. J. *Inorg. Chem.* **1976,** *15,* 1199.
(10) Trogler, W. C.; Solomon, E. I.; Trajberg, I.; Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1977,** *16,* 828.
(11) Martin, D. S.; Newman, R. A.; Fanwick, P. E. *Inorg. Chem.* **1979,** *18,* 2511.

found to be 34° away from the metal–metal bond or the molecular z axis. Also, the observed hot bands implied that this first line was electric dipole allowed rather than being of vibronic (Herzber–Teller) origin and was therefore the 0–0 line. It was concluded that the band was an electric-dipole-allowed transition with an unusually low transition moment so the vibronic lines were not orders of magnitude weaker as is the normal case for allowed transitions. The rotation of the transition moment for the 0–0 line by some 34° away from the molecular z axis was attributed to crystal field forces, since only Ī symmetry was required for the molecular site in the PĪ space group. The indicated molecular polarization was that which would be expected for the $\delta \rightarrow \delta^*$, $^1A_{1g} \rightarrow {}^1A_{2u}$, transition. Very recently, Manning and Trogler[12] have reported spectra for Mo$_2$(O$_2$CCH$_3$)$_4$ in a number of matrices at 10 K. In six different matrices they observed the strong progressions seen in crystal spectra, but in each matrix there is a weak progression based on an origin below the origin of these crystal progressions. From this evidence they propose that there is a second transition in this band. However, for the crystal sites the origin of this second band must be higher than the origin of the dipole-allowed band indicated in these crystal spectra. They also have questioned whether the allowed transition should be assigned as the $\delta \rightarrow \delta^*$.

The present study provides single-crystal spectra for two additional dimers with carboxylic bridges, viz., compounds with trifluoroacetate bridging ligands, one with the Mo$_2$(O$_2$CCF$_3$)$_4$ molecules and the other in which a pyridine nitrogen is bonded to each of the two terminal coordination sites of the dimer molecules. These spectra provide additional information relevant to the transition assignments for the carboxylate-bridged dimers.

Experimental Section

Mo$_2$(O$_2$CCF$_3$)$_4$ was prepared by the method of Cotton and Norman.[13] Since the dimers react so readily to add terminal ligands, the crystals for spectroscopy were prepared by sublimation in a stream of dry nitrogen at 180 °C. The crystals were exceedingly soft and fragile. Thin sections would readily cleave lengthwise. A good deal of twinning was observed as well. Crystals in air deteriorated in a few days so they were stored in a vacuum desiccator for many weeks. The crystals would disintegrate upon immersion in the refractive index standard liquids, so no measurements of the refractive indices were obtained. A number of thin needles, about 1 mm long, 100–200 μm wide, and less than 20 μm thick proved ideal for spectroscopic measurements. Several of the crystals, for which spectra were recorded, were cemented to glass fibers and mounted on the goniometer head of an automated four-circle X-ray diffractometer. From a series of oscillation photographs standard programs were utilized to establish the crystallographic axes. The measurements confirmed the triclinic cell reported by Cotton and Norman,[13] viz., $a/b/c$ = 8.392 (8)/9.209 (9)/5.568 (5) Å and $\alpha/\beta/\gamma$ = 91.18 (4)/100.561 (7)/89.670 (7)°. The spectroscopic face of the crystal for all cases measured was either the 010 or 0Ī0 face, and the long axis of the crystals coincided with the c axis. The extinctions between crossed polarizers occurred when one of the polarized planes was ca. 10° away from the needle or c axis. The extinction was not "pure" but shaded from red to violet to blue or vice versa as the crystal was rotated, indicative of a wavelength dependence for the vibration directions of the two plane-polarized electromagnetic waves transmitted by the crystal. The thickness of a crystal 10 ● 1 μm thick was measured by means of a calibrated eyepiece scale in the microscope. This crystal was observed to have a first-order orange interference color between crossed polarizers. Although interference colors were distorted somewhat by the color of the crystals, the retardation could be estimated at 505 nm by the observation of the colors with the $^1/_4\lambda$, the first-order red, and the wedge accessories for the polarizing microscope. The thicknesses of thinner crystals of Mo$_2$(O$_2$CCF$_3$)$_4$ were then estimated from the retardations indicated by their interference colors.
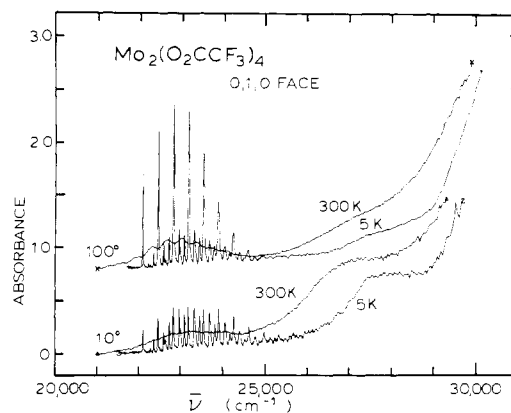

Figure 1. Crystal spectra for a Mo$_2$(O$_2$CCF$_3$)$_4$ crystal, 4 ± 1 μm thick. Molar absorptivities can be obtained by multiplying absorbances by 637. The polarizer angles are measured counterclockwise from the c axis for the 010 face viewed from the direction of the approaching light beam.
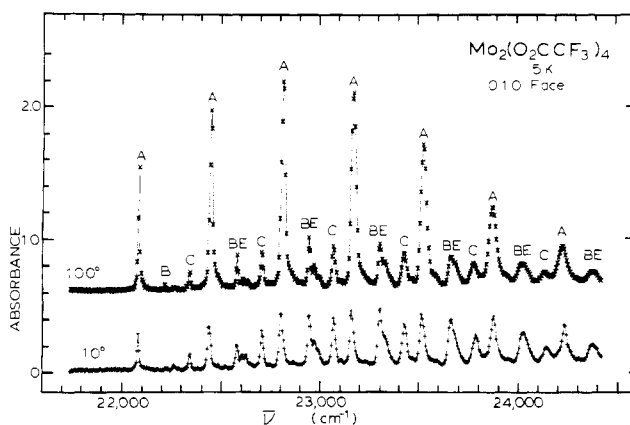
Figure 2. Resolution of vibrational structure in the first band for an Mo$_2$(O$_2$CCF$_3$)$_4$ crystal, 4 ± 1 μm thick.

Yellow-orange crystals of the compound Mo$_2$(O$_2$CCF$_3$)$_4$·2C$_5$H$_5$N were prepared by the method of Cotton and Norman.[14] Several small thin platelets were formed that were suitable for spectroscopy. Some crystals were mounted for X-ray diffraction. The unit cell coordinates were determined from 12 observed reflections and were found to be in good agreement with those reported by Cotton and Norman, viz, $a/b/c$ = 10.245 (8)/8.736 (7)/8.564 (8) Å and $\alpha/\beta/\gamma$ = 85.538 (9)/101.923 (9)/113.478 (1)°. the well-developed large faces were found to be 010 with the edges of the faces parallel to the a and c axes. A measurement of the thickness for the pyridine-adduct crystals was not accomplished.

Equipment and procedures for recording the polarized crystal spectra have been described previously.[8,15] The spectra with highly resolved vibrational features were recorded with slit settings on the Cary spectrophotometer that provided a dispersion of no more than 0.12 nm. The figures were prepared from absorbances punched on computer cards each 0.1 nm with a scan speed of 0.05 nm/s.

Results and Discussion

Spectra for Mo$_2$(O$_2$CCF$_3$)$_4$. Crystal spectra, recorded at 300 and 5 K for the 010 face of a crystal, 4 ± 1 μm thick, are shown in Figure 1. The lowest energy band observed at room temperature has a maximum at ca. 23 000 cm^{-1}. The band is somewhat more intense in the 100° polarization than at 10°, and weak vibrational structure for this band can be discerned at 100° but not for 10°. At 5 K this band develops a rich vibrational structure for both polarizations. In addition, there is a second band observable at 26 500 cm^{-1} in both polarizations and somewhat more intense in the 10° polarization. This band

(12) Manning, M. C.; Trogler, W. C., private communication.
(13) Cotton, F. A.; Norman, J. G., Jr. *J. Coord. Chem.* **1971**, *1*, 161.

(14) Cotton, F. A.; Norman, J. G., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 5697.
(15) Martin, D. S., Jr. *Inorg. Chim. Acta, Rev.* **1971**, *5*, 107.

Table I. Vibrational Details in the Absorption Band of
$Mo_2(O_2CCF_3)_4$ at 5 K

| progression line	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$,^{a} cm^{-1}
	21 960 w	(−120)
	21 990 w	(−90)
	22 030 w	(−50 cm)
A_0	22 080	
B_0	22 210 w	(130)
D_0	22 260 w	(180)
C_0	22 340	(260)
A_1	22 450	370
B_1-E_0	22 580	370-(500)
C_1	22 700	360
A_2	22 810	360
B_2-E_1	22 940	360
C_2	23 060	360
A_3	23 160	350
B_3-E_2	23 300	360
C_3	23 420	360
A_4	23 520	360
B_4-E_3	23 650	350
C_4	23 780	360
A_5	23 870	350
B_5-E_4	24 020	370
C_5	24 140	360
A_6	24 220	350
B_6-E_5	24 370	350
C_6	24 490	350
A_7	24 560	340
B_7-E_6	24 730	360
C_7	24 840	350
A_8	24 900	340
B_8-E_7	25 070	360
C_8	25 180	340
A_9	25 240	340
B_9-E_8	25 330	360
C_9-X	25 540	360
A_{10}	25 600	360

^{a} Values in parentheses give the difference, $\Delta\bar{\nu}$, from the A_0 line. Values without parentheses give the $\Delta\bar{\nu}$ values from the preceding line in the progression.

lies on the tail of a much more intense absorption that peaks beyond 30 000 cm^{-1}.

An extended plot of the low-energy region of the first band is presented in Figure 2, which shows the striking resolution of vibrational structure at 5 K. Wavenumbers for the individual lines are given in Table I. The separation of the origins of the B, C, and E progressions from the A origin are also given in the column, $\Delta\bar{\nu}$, which also lists the separation of the higher members of each progression from the preceding member. The maximum and minimum for the A_0 line occurred very close to the wave-directions indicated by the optical extinctions between the crossed polarizers of the polarizing microscope. The C and E lines were not strongly dependent upon the polarizer settings, but the polarization ratio for the A_0 line, $I_{A_0}(100°)/I_{A_0}(0°)$, was 3.4, where I_{A_0} represents the peak height.

The assignment of the A, B, C, and E progressions follows that used in our description of the tetrakis(μ-acetato)dimolybdenum(II) spectra. For that compound the A_0 line was the lowest energy absorption feature, extensive evidence was presented to indicate it might represent the 0–0 line of the $^1A_{1g}$ → $^1A_{2u}$ (b_{2g}, δ → b_{1u},δ*) transition. However, from a polycrystalline sample of $Mo_2(O_2CCF_3)_4$, Trogler et al.[10] reported that there were weak absorption features at lower energy than that of the A_0 line. Therefore, we have recorded spectra for a crystal, 105 μm thick, which are shown in Figure 3. There are three weak lines below the A_0 lines. Trogler et al.[10] observed the lines at 21 960 and 21 990 cm^{-1} but did not resolve the line at 22 030 cm^{-1} in their multicrystal, unpolarized spectra. (In general, the agreement in wavenumbers with their
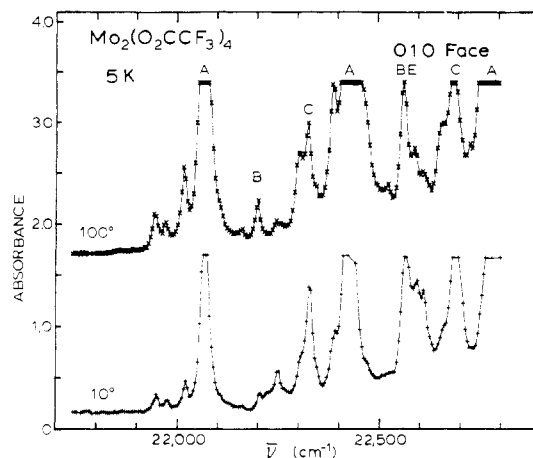
Figure 3. Spectra for a crystal of $Mo_2(O_2CCF_3)_4$, 105 μm thick.
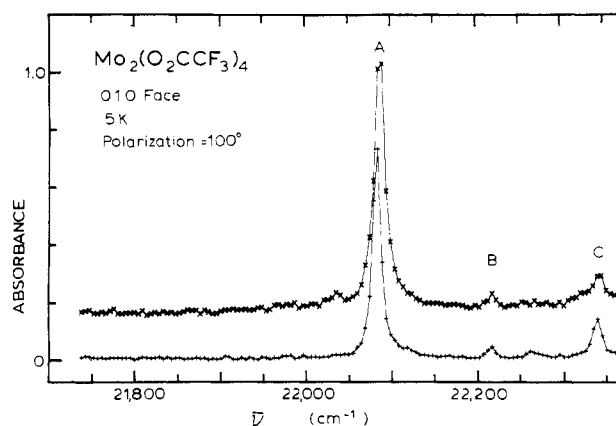
Figure 4. Comparison of the low-energy region of spectra for two different $Mo_2(O_2CCF_3)_4$ crystals. The lower spectrum is for the crystal of Figures 1 and 2.

values was within the uncertainty of the Cary Model 14 spectrophotometer of 10–20 cm^{-1}.) However, we found no evidence, even with thicker crystals, for a line at 21 860 cm^{-1}, which they assigned as the 0–0 line for the band.

It is possible that the weak peaks below A_0 might belong to a second transition of the sort that Manning and Trogler[12] proposed for $Mo_2(O_2CCH_3)_4$ from their matrix spectra. It has been difficult to make an accurate comparison of the relative heights of these three minor peaks with the major lines in the spectra because of the large differences in intensity. With a crystal for which the weak lines can be measured accurately, the strong lines are far beyond the instrumental capabilities. The crystal whose spectra are in Figure 1 had been prepared by sublimation only a few days before the spectra were measured. The low-energy portion of the 100° polarization is compared in Figure 4 with that for a crystal of comparable thickness obtained from a different preparation several months earlier. Although the older crystal was perhaps slightly thicker, the heights of the B_0 and C_0 lines were certainly not greatly different. The three weaker components, especially the line at 22 030 cm^{-1}, are evident in the older crystal spectrum but not discernible in the lower spectrum for the freshly prepared specimen. This evidence, although not overwhelmingly convincing, suggests that the weak components below the A_0 line are preparation dependent and that they can be attributed to defect components. A small fraction of the molecules might occupy somewhat different sites from the bulk component. We believe that a minority component is also responsible for a weak progression observed in a single-crystal spectrum of $[Mo_2(O_2CCH_3NH_3)_4](SO_4)_2 \cdot 4H_2O$ with an origin 940 cm^{-1} below that of the band for the majority component.
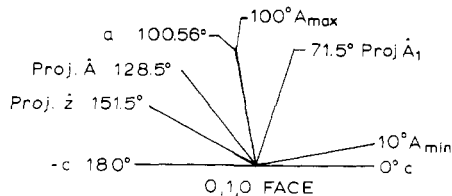
Figure 5. Crystal optics for Mo$_2$(O$_2$CCF$_3$)$_4$. Angles are measured counterclockwise from the c axis for an observer looking toward the 010 face.

Such a progression was not evident in the single-crystal spectra of the amino acid carboxylate complex Mo$_2$(L-leucine)$_4$$^{4+}$ ions reported by Bino et al.[16] although the sensitivity in that case was somewhat limited by the noise. Since no line was observed at 21 860 cm^{-1} for very thick (ca. 1 mm) crystals of Mo$_2$-(O$_2$CCF$_3$)$_4$, we believe this feature in the polycrystalline spectrum of Trogler et al. can be attributed to an impurity in their preparation.

The A_0 line has therefore been assigned as the 0–0 line of a weak, but electric-dipole-allowed, band for the majority component as in the case of the molybdenum(II) acetate. The B_0, C_0, and E_0 lines correspond to vibronic excitations that involve molecular vibrations of 130, 260, and 500 cm^{-1} respectively, for the excited-state vibrations. For molybdenum acetate crystals the B_0, C_0, and E_0 lines correspond to frequencies of 175, 275, and 545 cm^{-1}, respectively. There are a number of weaker lines, evident from the spectra presented in Figures 2 and 3, which have not been labeled or recorded in Table I.

The average spacing between successive lines in the Franck–Condon progressions is 356 ± 8 cm^{-1}. This spacing corresponds to the frequency for a totally symmetric vibration, presumably the metal–metal stretch, which has been observed to be 397 cm^{-1} for the ground electronic state by Cotton and Norman.[13] It is slightly lower than the value of 370 cm^{-1} observed in the spectra for Mo$_2$(O$_2$CCH$_3$)$_4$.

Since the single-crystal absorption spectra could only be recorded for one face, viz. the 010 or the equivalent 0$\bar{1}$0 face, it was not possible to determine the absolute orientation in space for the A_0 transition moment, as in the case of Mo$_2$-(O$_2$CCH$_3$)$_4$. Features of the crystal optics for the 010 face are shown in Figure 5. The polarization of the two linearly polarized light waves transmitted by the crystal were at 10 and 100°. The absorption of A_0 was greater for the 100° polarization, which was approximately coincident with the crystallographic axis a.

The projection of the molecular z axis, i.e., the metal–metal bond, upon the 010 face lies at 151.5°. Thus, it is 51.5° from the wave direction at 100°, A_{max}, and only 38.5° from the wave direction at 10°. According to the oriented-molecule model, the predicted polarization ratio is

$$A(100°)/A(10°) = \cos^2 51.5°/\cos^2 38.5° = 0.63 \quad (1)$$

Thus, the higher absorption is predicted to be for the 10° polarization angle. This prediction is in serious disagreement with the observation of a polarization ratio of 3.4, which places the highest absorption at the 100° polarization angle. Hence, the question is raised, "Can this be the $\delta \rightarrow \delta^*$ transition?"

Further consideration was therefore given to the dimolybdenum tetraacetate crystal, where the transition moment was found to lie 34° away from the metal–metal bond. The major crystal field perturbation to the molecular D_{4h} symmetry can reasonably be attributed to the intermolecular interactions that exist in the one-dimensional chains of loosely bonded dimeric molecules along the short crystallographic axis in both

(16) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1980**, *19*, 1215.

Figure 6. Packing of dimers in the crystals of Mo$_2$(O$_2$CCF$_3$)$_4$ and Mo$_2$(O$_2$CCH$_3$)$_4$ to form loosely bound one-dimensional chains.

the acetate and the trifluoroacetate. The arrangement of the dimers in these chains is illustrated in Figure 6. Thus, an oxygen of the carboxylate in a neighboring molecule occupies the positions trans to the metal–metal bond. Each molecule can be considered as weakly linked to each adjacent neighbor in the chain by a pair of Mo···O interactions. The bonds are quite weak as evidenced by the intermolecular Mo–O distances, 2.72 Å in the trifluoroacetate and 2.645 Å in the acetate in contrast to the 2.0–2.1-Å intramolecular Mo–O bonds. The Mo–Mo–O angle along the stacking chains deviates considerably from 180°, being 161.0° in Mo$_2$(O$_2$OCC-F$_3$)$_4$[13] and 160.1° for Mo$_2$(O$_2$CCH$_3$)$_4$. For a characterization of the orientation of the transition moment for the A_0 vibrational line of Mo$_2$(O$_2$CCH$_3$)$_4$ (presumably the 0–0 line in the band), a righ-handed orthogonal set of molecular axes for the molecule is defined in the following way. The unit z axis, $\hat{z}$, was placed along the metal–metal bond. The molecular y axis was placed in the plane of the metal–metal bond and the bond from the metal to the oxygen that formed the weak bond in the chain. The unit transition-moment vector for Mo$_2$(O$_2$C-CH$_3$)$_4$ was given by the expression

$$\hat{A} = 0.1654\hat{x} - 0.5333\hat{y} + 0.8296\hat{z} \quad (2)$$

This transition moment is directed 33.9° away from the $\hat{z}$ axis. However, it is only 9.5° out of the molecular yz plane. A transition moment with this orientation on this Mo$_2$(O$_2$CCF$_3$)$_4$ molecule would have had a polarization ratio of $I(100°)/I$-(10°) equal to 7.3 compared to the observed value of 3.4.

The polarization ratio of 3.4 indicates that the transition moment lies in a plane normal to the 010 face at an angle, $\cot^{-1} 3.4^{1/2}$ or 28.5°, away from the A_{max} direction, as shown in Figure 5. The polarization ratio therefore places the transition moment in either of the two planes at 71.5 or 128.5°. Whereas any transition moment vector in the 71.5° plane must be at least 70.4° off the metal–metal bond, the vector at the intersection of the 128.5° plane and the molecular yz plane would lie 23.1° away from the metal–metal bond. It is therefore our contention that the intermolecular interactions provide a crystal field that rotates the transition moment for the δ–δ^* transition moment away from the Mo–Mo bond but keeps it close to the molecular yz plane. As shown in Figure 6, the rotation of the transition moment, $\hat{A}$, is away from the short axis translation axis. The net result of this shift is that, although the metal–metal bond is closer to the A_{min} extinction at 10°, the transition moment is actually closer to the 100°

Figure 7. High-energy region of the first band in a $Mo_2(O_2CCF_3)_4$ crystal, 105 μm thick. This was the same crystal whose spectra were shown in Figure 3.

extinction, so there has been a reversal of the polarization ratio. Perhaps, the 23° shift for $Mo_2(O_2CCF_3)_4$ compared to the 34° shift for $Mo_2(O_2CCH_3)_4$ is associated with a weaker intermolecular interaction that is reflected in the longer Mo–O distance, 2.72 vs. 2.645 Å, and the larger Mo–Mo···O angle, 161.0 vs. 160.1°.

In orthorhombic crystals of dimolybdenum tetraformate[17] the molecules do not occupy a site with inversion symmetry, so the definition of molecular axes is not so straightforward. The molecular z axis was placed along the metal–metal bond. The x axis was placed along the cross product of the vector connecting the two oxygens involved in the intermolecular chain interactions times the z axis. To account for the observed polarization ratio would require a transition moment in the yz plane that had been rotated as shown in Figure 6 by 39.1° away from the z axis. Without the inversion center the distances and angles to the t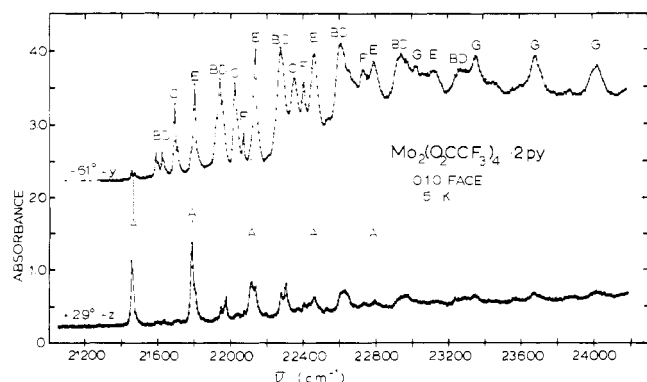erminally bonded oxygens are different for the opposite ends of the molecule, amounting to 2.646 and 2.643 Å and 159.2 and 159.3° respectively. The distances are very close to those in aceate crystals, but the smaller angles indicate a greater perturbation of the D_{4h} field consistent with a larger rotation of the transition moment. Thus, the data indicate a consistent pattern in the crystal field perturbation on the transition moments for the lowest line in this band for the three molecular carboxylate dimers of molybdenum(II).

An additional complication in the spectra for $Mo_2(O_2CCF_3)_4$ appeared in an examination of the vibrational structure in the high-energy portion of the first band, which is shown in Figure 7. At energies above A_7 the lines in the A progression for the 10° polarization do not match exactly the lines in the 100° polarization. Furthermore, the lines for 10° are narrower and higher than the lines for 100°, whereas for the early members in the progression, the 100° A lines are more intense. It has been concluded that the 10° lines represent a new progression that begins at about 24 240 cm⁻¹. Further evidence for new progressions is found in the C progression in the 10° polarization. The C_7 line is less intense than C_6 in Figure 7, but there is an increase in intensity for C_8, which has been attributed to a new X progression. Finally, there is a Y progression, the first line of which is seen in 10° polarization at 25 350 cm⁻¹. Since there are no H atoms in these molecules, it does not seem feasible to assign these new progressions to vibronically excited lines which would require vibrations with 2000–3000 cm⁻¹. Therefore, it is believed that these new progressions correspond to a different transition with somewhat lower intensity than

(17) Cotton, F. A.; Norman, J. G., Jr.; Stults, B. R.; Webb, T. R. *J. Coord. Chem.* **1976,** *5,* 217.

Figure 8. Polarized spectra for the 010 face of $Mo_2(O_2CCF_3)_4$· $2C_6H_5N$.

the one represented by the A, B, C, and E progressions. This additional transition might arise from a defect component in the crystal. On the other hand, it might represent a second transition in this region for $Mo_2(O_2CCF_3)_4$ in accordance with the suggestion for $Mo_2(O_2CCH_3)_4$ of Manning and Trogler based on their matrix spectra. Vibrational structure in the crystal spectra of $Mo_2(O_2CCH_3)_4$ was not as well resolved as for $Mo_2(O_2CCF_3)_4$ so that additional lines were not evident in the high-energy region of the band. It seems likely that any second transition is spin forbidden and may gain intensity from its proximity to a dipole-allowed transition. Presumably, the corresponding spin-allowed transition would lie under the intense absorption above 30 000 cm⁻¹. One point of concern is that no absorption corresponding to an $^1A_{1g} \rightarrow {}^3A_{2u}$ transition has been observed for any carboxylato.complex, even with very thick crystals. The only evidence for a spin-forbidden $\delta \rightarrow \delta^*$ transition is the luminescence band for polycrystalline $Mo_2(O_2CCF_3)_4$, peaking at 17 900 cm⁻¹, reported by Trogler et al.[10] No other luminescence spectrum for a dimolybdenum(II) carboxylate has been reported.

Because the 27 500-cm⁻¹ band evident in Figure 1 falls on the tail of a more intense band, its temperature dependence is not clearly indicated. The intensity of this band does seem consistent with an assignment as the electric-dipole-forbidden $^1A_{1g} \rightarrow {}^1E_g$ ($b_{1g},\delta \rightarrow e_u,\pi^*$) transition proposed for $Mo_2(O_2-CCH_3)_4$.

Spectra for $Mo_2(O_2CCF_3)_4$·$2C_5H_5N$. For the $Mo_2(O_2CC-F_3)_4$·$2C_6H_5N$ molecules the nitrogen atom of a pyridine is bonded to each molybdenum. The Mo–N distance is reported to be 2.548 Å,[14] considerably shorter than the terminal Mo···O distances in $Mo_2(O_2CCF_3)_4$ crystals. The Mo–Mo–N angle is 171.8°. Furthermore, the Mo–Mo distance is 2.129 Å, some 0.039 Å longer than in the simple trifluoroacetate dimer, indicative of a weakening of the metal–metal bond. A methanol or benzene solution of $Mo_2(O_2CCF_3)_4$ is yellow with absorption bands peaking at 22 900 and 23 200 cm⁻¹, respectively, which therefore corresponds closely to the structured crystal band characterized in the last section. However, in pyridine, the solutions are red and a band at 19 600 cm⁻¹ was reported.[14] An examination of our crystals indicated one extinction 29° from the a axis of the 010 face and the second one 61° across the a axis from the first. Spectra recorded for these polarizations are shown in Figure 8, designated at +29 and –61°, respectively. It can be seen that the absorption from 18 000 to 21 400 cm⁻¹ is a very weak, broad, featureless absorption with little difference in intensity between the two polarizations. However, at about 22 000 cm⁻¹ there is evident a band that at room temperature is much more intense in the –61° polarization. At 5 K this band possesses a very rich vibrational structure so the band presumably corresponds to the structured band of $Mo_2(O_2CCF_3)_4$ considered in the

Figure 9. Polarized spectra for the 010 face of Mo$_2$(O$_2$CCF$_3$)$_4$· 2C$_6$H$_5$N with an expanded scale to show details of the vibrational structure.

previous section. The vibrational structure is shown on an expanded wavenumber scale in Figure 9. The wavenumbers for the individual peaks are listed in Table II. The molecule lies in a $\bar{1}$ site. Since the bonded pyridine molecules may introduce a severe perturbation to the D_{4h} symmetry, a set of molecular axes was chosen in the following way. The metal–metal axis was retained as the z axis. The molecular x axis was taken perpendicular to the z axis and to the normal for the pyridine plane and was therefore parallel to the pyridine plane, and the y axis was orthogonal to x and z. The molecular z axis forms an angle of only 13.4° with the extinction at 29°. The calculated polarization ratio $[I(29°)/I(-61°)]_z$ is 47.1, and 97% of the absorption intensity occurs in this plane. The 29° spectrum has been labeled $\sim z$ in Figure 9 since that absorption is primarily due to the z-polarized absorption. For the −61° polarization, 71% of the y absorption occurs and 26% of the x-polarization. This spectrum has accordingly been labeled $\sim y$. The calculated polarization ratios, $I(-61°)/I(29°)$, are 15.5 and 35.6, respectively, for y and x polarization. In the case of two equal orthogonal transition moments normal to z (the usual x,y polarization absorption) the polarization ratio is predicted to be $I(-61°)/I(29°) = 18.3$.

The high polarization ratios for the individual vibrational lines between the two spectra indicate that the waves for the two indicated polarization angles contain relatively pure components. The lowest energy line observed is the A_0 peak at 21 460 cm^{-1}. A Franck–Condon progression containing five lines based on this origin is discernible. The A_0 line is very weak at −61° and indeed seems hardly more intense than what appears to be a phonon component peaking at ca. 21 475 cm^{-1}. The other features in the 29° polarization spectrum correspond to weak components associated with much more intense lines at −61°. Thus, the polarization ratios are consistent with the A lines having molecular z-polarized absorption with no discernible crystal field rotation of the transition moment and all the other lines having x or y polarization. These results are consistent with the assignment of the A_0 peak as the 0–0 line in an electric-dipole-allowed transition similar to the case for Mo$_2$(O$_2$CCF$_3$)$_4$ and Mo$_2$(O$_2$CCH$_3$)$_4$. The lack of crystal field perturbation in this case would result from the single terminal bond on each Mo without the packing in one-dimensional chains. Presumably, the high intensity for the x,y-polarized lines results from coupling with the aromatic molecules through the π-electron system, which does not give enhancement of intensity for the z polarization.

It is interesting to compare the indicated vibrational frequencies from these spectra with those for Mo$_2$(O$_2$CCF$_3$)$_4$. First of all, the average of 19 indicated Franck–Condon spacings correspond to a totally symmetric vibration of 331 ± 9 cm^{-1}. This value is 25 cm^{-1} lower than the 356-cm^{-1} value for Mo$_2$(O$_2$CCF$_3$)$_4$. The Raman value for the ground-state

Table II. Details in the Absorption Band of Mo$_2$(O$_2$CCF$_3$)$_4$·2C$_5$H$_5$N at 5 K

progression line[a]	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$,[b] cm^{-1}
A_0	21 460	
B_0	21 590	(130)
D_0	21 620	(160)
C_0	21 690	(230)
A_1	21 790	330
E_0	21 800	(340)
BD_1	21 940	340 (480)
C_1	22 020	330
F_0	22 070	(610)
A_2	22 110	320
E_1	22 130	330
BD_2	22 280	340
C_2	22 350	330
F_1	22 400	330
A_3	22 460	350
E_2	22 460	330
BD_3	22 610	330
F_2	22 730	330
A_4	22 790	330
E_3	22 790	330
BD_4	22 920	310
G_0	23 030	(1570)
E_4	23 120	330
BD_5	23 270	350
G_1	23 350	320
G_2	23 670	320
G_3	24 010	340

[a] A progression was read from the $\sim z$ polarization. All other lines were read from the $\sim y$ polarization. [b] Values in parentheses give the difference, $\Delta\bar{\nu}$, from the A_0 line. Values without parentheses give the $\Delta\bar{\nu}$ from the preceding line in the progression.

stretching frequency is 367 cm^{-1}.

In the −61° spectrum there is a pair of weak equally intense peaks, B_0 and D_0, at 130 and 160 cm^{-1} above the origin whereas for Mo$_2$(O$_2$CCF$_3$)$_4$ there was only a single peak at 130 cm^{-1}. There is only a single peak resolved, BD_1 in Table II, and the very large increase in intensity over B_0 and D_0 suggests that BD_1 may be the origin of a separate progression beginning at 21 900 cm^{-1}. The shoulders on the high and low side of this peak may be the B and D lines. If this is the case, the origin of this new progression would be 480 cm^{-1} above the band origin and might compare to the E_0 peak of Mo$_2$-(O$_2$CCF$_3$)$_4$ at 500 cm^{-1} above the origin. The large peak, E_0, 340 cm^{-1} above the origin in the −61° spectrum does not seem to have a counterpart in the Mo$_2$(O$_2$CCF$_3$)$_4$ spectra. The C_0 line, 230 cm^{-1} above the origin, corresponds closely to the C_0 line of Mo$_2$(O$_2$CCF$_3$)$_4$ at 280 cm^{-1}. The G progression is the dominant feature in the high-energy portion of the band. The first term in the progression is 1570 cm^{-1} above the origin. The other carboxylate dimers have not shown such a high-intensity progression originating so far above the band origin. This may be evidence of a second electronic transition similar to that suggested for the Mo$_2$(O$_2$CCF$_3$)$_4$ crystals, which did however have a somewhat higher origin. Thus, there are close similarities in the frequencies of some vibrations of Mo$_2$(O$_2$CCF$_3$)$_4$ and Mo$_2$(O$_2$CCF$_3$)$_4$·2(C$_5$H$_5$N) but also some clear differences in that the pyridine adduct has some additional intense lines.

The other carboxylate dimers have shown evidence of a weak transition around 26 000 cm^{-1}. The rather sharp unstructured band peaking at 25 700 cm^{-1} in z polarization is rather exceptional. In the −61° spectrum the absorption is rising rapidly in this region, and it is not clear how much intensity can be attributed to this band although it seems definitely less intense than the 29° component.

The weak absorption from 17 000 to 21 000 cm^{-1} is responsible for a good part of the yellowish-orange color of the crystals. The intensity of the color appears to be much higher

in the red pyridine solutions, where Garner et al.[18] have indicated some partial replacement of trifluoroacetate ligands by pyridine has occurred. The weak absorption in the crystals may therefore result from the incorporation of a very minor impurity component with additional pyridine substitution into the molecules.

Polarized single-crystal spectra never prove transition assignments absolutely. At best, one establishes the molecular polarizations. For the carboxylate dimers of molybdenum(II) the rather uncommon and spectacular resolution of vibrational structure in the lowest electronic absorption band at low temperatures has provided convincing evidence that the major component of this band is a weak electric-dipole-allowed transition derived from molecular *z* polarization. The intensity is sufficiently weak that vibronically excited lines have intensities comparable to the 0–0 progresions. The polarization of the band is that expected for a $\delta \rightarrow \delta^*$ transition. The exceptionally low intensity does pose some questions. It may result from some electron density transfer from metal to carboxylate orbitals. The empty carboxylate π^* orbitals can form a B_{2g} symmetry-adapted LCAO, which can interact with the filled δ-bonding orbitals. Since the transition is essentially an intermetallic electron transfer between the Mo d_{xy} orbitals, this removes electron density from between the metals where the overlap in the transition moment integral occurs. Evidence is also accumulating that at least one other transition occurs

in the vicinity of this weak dipole-allowed transition.

The studies of the molybdenum(II) carboxylate dimers have emphasized the need to investigate a number of closely related systems. This is especially true because of the low-symmetry crystal sites that have been encountered. It has been clearly demonstrated that intermolecular interactions can shift transition moment vectors away from the expected molecular axes in specific cases. Also defect components in crystals of individual compounds have only been recognized when results from several systems have been compared. The present evidence indicates that this observed transition is a weak but electric-dipole-allowed $^1A_{1g} \rightarrow {}^1A_{2u}$ transition under D_{4h} symmetry. Such an assignment is also consistent with the most recent theoretical treatments of orbital energies. However, the uncertainties present in this assignment and questions about possible additional transitions in this energy region clearly indicate that further experimental and theoretical studies of these interesting systems should be very worthwhile.

Registry No. Tetrakis(μ-trifluoroacetato)dimolybdenum, 36608–07–8; tetrakis(μ-trifluoroacetato)bis(pyridine)dimolybdenum, 39176–71–1.

(18) Garner, C. D.; Senior, R. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1171.

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Infrared Spectra of Molecular Oxygen Adducts of (Tetraphenylporphyrinato)manganese(II) in Argon Matrices

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The infrared spectra of Mn(TPP) and Mn(TPP)O₂ were measured in Ar matrices at ~15 K. Splittings of the Mn(TPP) vibrations upon oxygenation are attributed to the lowering of symmetry from D_{4h} to C_{2v}. The O₂ stretching bands of Mn(TPP)^{16}O₂ and its ^{18}O₂ analogue are located at 983 and 933 cm⁻¹, respectively. Oxygen isotope scrambling experiments confirmed the symmetric, side-on coordination of the O₂ in Mn(TPP)O₂. All attempts to synthesize superoxo adducts of Mn(TPP) and Mn(TPP)Cl via matrix cocondensation reactions were not successful.

In 1976, Hoffman, Weschler, and Basolo[2] first discovered the reversible oxygenation of (tetraphenylporphyrinato)manganese(II) (Mn(TPP)py + O₂ ⇌ Mn(TPP)O₂ + py) in toluene solution at low temperatures using electronic and ESR spectroscopy. They proposed the Mn^{IV}(O₂$^{2-}$) formulation with a side-on coordination of the peroxide ion. Although their formulation and structure were challenged by Dedieu and Rohmer,[3] subsequent ESR studies on molecular oxygen adducts of Mn(*p*-substituted-TPP) and Mn(OEP) (OEP = octaethylporphyrinato anion) by Hoffman et al.[4] confirmed their original report. Furthermore, recent charge iterative extended Hückel MO calculations by Hanson and Hoffman[5] suggest that the most probable geometry of the Mn(TPP)O₂ core is one in which the Mn atom is ca. 0.5 Å above the pyrrole plane with the peroxo O–O bond staggered with respect to the

pyrrole nitrogens. Jones et al.[6] attempted to determine the $\nu(O_2)$ (ν, stretch) of Mn(TPP)O₂ in toluene solution as well as in Nujol mulls using IR difference spectroscopy. The 803-cm⁻¹ band, which was obtained by subtracting the IR spectrum of Mn(TPP) from that of Mn(TPP)(^{18}O₂), was assigned to the $\nu(^{18}O_2)$ of the dioxygen complex. Unfortunately, the corresponding $\nu(^{16}O_2)$ band could not be observed because of overlap with the solvent band at 844 cm⁻¹.

Our previous studies report the preparation and IR spectra of "base-free" adducts such as Co(TPP)O₂,[7] Co(OEP)O₂,[8] Co(J-en)O₂ (J-en = N,N'-ethylenebis(2,2-diacetyl-ethylideneaminato)anion),[9] and Co(acacen)O₂ (acacen = N,N'-ethylenebis(acetylacetone iminato)anion)[10] using the matrix cocondensation method. The advantages of this method

(1) (a) Marquette University. (b) Northwestern University.
(2) Hoffman, B. M.; Weschler, C. J.; Basolo, F. *J. Am. Chem. Soc.* **1976**, *98*, 5473. Weschler, C. J.; Hoffman, B. M.; Basolo, F. *Ibid.* **1975**, *97*, 5278.
(3) Dedieu, B. M.; Rohmer, M. M. *J. Am. Chem. Soc.* **1977**, *99*, 8050.
(4) Hoffman, B. M.; Szymanski, T.; Brown, T. G.; Basolo, F. *J. Am. Chem. Soc.* **1978**, *100*, 7253.
(5) Hanson, L. K.; Hoffman, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 4602.

(6) Jones, R. D.; Budge, J. R.; Ellis, P. E.; Linard, J. E.; Summerville, D. A.; Basolo, F. *J. Organomet. Chem.* **1979**, *181*, 151.
(7) Kozuka, M.; Nakamoto, K. *J. Am. Chem. Soc.* **1981**, *103*, 2162.
(8) Urban, M. W.; Nakamoto, K.; Kincaid, J. *Inorg. Chim. Acta* **1982**, *61*, 77.
(9) Nakamoto, K.; Nonaka, Y.; Ishiguro, T.; Urban, M. W.; Suzuki, M.; Kozuka, M.; Nishida, Y.; Kida, S. *J. Am. Chem. Soc.* **1982**, *104*, 3386.
(10) Urban, M. W.; Nonaka, Y.; Nakamoto, K. *Inorg. Chem.* **1982**, *21*, 1046.