

despite the use of strong Lewis acids, no double bond migration of the silyl enol ethers takes place during the reaction with nitroolefins because of the mild reaction conditions. Ready accessibility of starting materials, high regioselectivity, good yields, and simple manipulation make the present 1,4-diketone synthesis a very useful method.

The following experimental procedure is illustrative of our 1,4-diketone synthesis. 1-Trimethylsilyloxycyclohexene<sup>7</sup> (170 mg, 1.0 mmol) was added dropwise to a cooled dry methylene chloride solution ( $-78^{\circ}$ ) of freshly distilled stannic chloride (260 mg, 1.0 mmol) and 2-nitropropene (131 mg, 1.5 mmol) over 5 min with stirring under nitrogen. The mixture was stirred at the same temperature for an additional hour and then warmed gradually to  $0^{\circ}$  over 2 h. Water (1.5 ml) was added and the resultant heterogeneous mixture was stirred at reflux for 2 h. Extraction with ethyl acetate was followed by washing with water and brine. Removal of the solvent left a residue, which was filtered through a short alumina column (Woelm, activity III) eluting with ether. Single distillation ( $80^{\circ}$ , 0.2 mm) of the eluate gave pure 2-acetyl-cyclohexanone<sup>9</sup> (131 mg, 85%).

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- This compound was prepared from 2-nitro-1-propanol, which was obtained, according to the reported procedure,<sup>16</sup> from nitroethane and formalin in 84% yield. Contrary to the literature,<sup>17</sup> **2a** could be stored without decomposition as low-melting crystals in a refrigerator for several months.
- Dehydration of nitroalcohols was carried out with phthalic anhydride.<sup>17</sup> The use of 1.35 equiv of the anhydride considerably improved the yields of nitroolefins, thus giving **2a**, **2b**, and **2c** from the corresponding nitroalcohols in 72, 82, and 60% yields, respectively.
- This nitroolefin was prepared from 3-nitro-2-butanol by dehydration (ref 5), selectively yielding an *E* isomer. The nitroalcohol was obtained in 90% yield by the reaction of nitroethane (0.42 mol) and aqueous acetaldehyde (85% assay, 0.3 mol) in methanolic potassium hydroxide (KOH 19.7 g, MeOH 120 ml) at room temperature for 22 h, followed by acidification with acetic acid and distillation (bp  $88-89^{\circ}$  (9 mm); lit.<sup>18</sup>  $92^{\circ}$  (10 mm)).
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## Electronic Spectra of Crystals of Dimolybdenum Tetraformate and the Tetrasulfatodimolybdenum(II) Ion

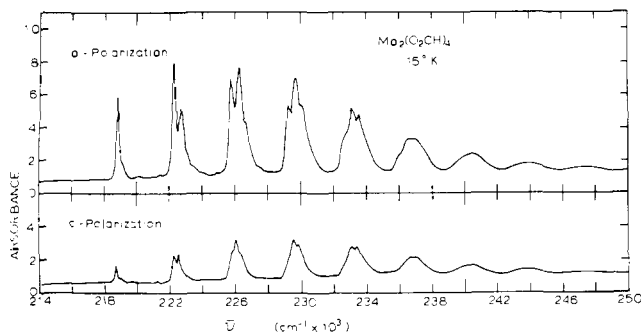
Sir:

For the quadruply bonded dirhenium and dimolybdenum complexes the lowest energy observed electronic transitions are in the visible region of the spectrum. A computation of one-electron energy states by Dubicki and Martin,<sup>1</sup> who used a SCCO-MO treatment for  $\text{Mo}_2(\text{O}_2\text{CMe})_4$ , indicated that the first transition would not be the  $\delta \rightarrow \delta^*$  transition. On the other hand more recent calculations by the SCF-X $\alpha$  scattered wave method by Norman and Kolarik<sup>2,3</sup> for  $\text{Mo}_2\text{Cl}_8^{4-}$  and for  $\text{Mo}_2(\text{O}_2\text{CH})_4$  have indicated the highest filled orbital is the  $\delta$  and the lowest unfilled orbital is the  $\delta^*$ . Polarized absorption spectra on single crystals containing these complexes can provide cogent evidence for assignment of the electronic transitions. The spin-allowed  $\delta \rightarrow \delta^*$  transition of  $\text{M}_2\text{X}_8$  complexes with  $D_{4h}$  molecular symmetry is  ${}^1A_{1g} \rightarrow {}^1A_{2u}$  and therefore will be dipole allowed with  $z$  polarization ( $z$  lies along the metal-metal bond). A few such measurements for compounds containing quadruply bonded dirhenium<sup>4,5</sup> and dimolybdenum<sup>6</sup> units suggest that for both  $\text{Re}_2\text{Cl}_6(\text{PET}_3)_2$  and  $\text{Re}_2\text{Cl}_8^{2-}$  the band in the visible spectrum may be assigned to the  $\delta \rightarrow \delta^*$  transition. For the  $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3^+)_4$  unit in  $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,<sup>7</sup> the results show that the lowest energy transition in the visible spectrum cannot be so assigned.<sup>6</sup> We wish to report here some new results that help to place the foregoing results in a broader context and thus clarify their significance.

The first question addressed here is whether the results for the  $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3^+)_4$  moiety can be considered representative for  $\text{Mo}_2(\text{O}_2\text{CR})_4$  species in general. We have therefore investigated the corresponding low-energy transition in dimolybdenum tetraformate.<sup>8</sup> Polarized spectra for  $\text{Mo}_2(\text{O}_2\text{CH})_4$  at 15 K are presented in Figure 1. The region observed corresponds to that previously studied for  $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ .<sup>6</sup> The crystal displayed well-formed 010 faces thus allowing measurement of polarizations parallel to the  $a$  and  $c$  axes. The Mo-Mo bond (which defines a molecular  $C_4$  axis, the  $z$  axis) is aligned  $33.4^{\circ}$  from the  $c$  axis. A  $z$ -polarized molecular transition would absorb in both the  $a$  and  $c$  crystal directions, with  $I_c/I_a = 4.3$  while an  $xy$ -polarized molecular transition would have  $I_c/I_a = 0.36$ .

The first absorption is a very narrow band with  $\nu_{1/2}$  of  $10 \text{ cm}^{-1}$  at  $21\,870$  in  $a$  and  $21\,880 \text{ cm}^{-1}$  in  $c$  polarization. This single band is followed by a pair of bands, each somewhat broader than the first, and then by a group of three bands. Three components can be identified in the fourth and fifth and possibly the sixth group. The spectrum appears to contain three progressions, with a separation of  $350 \pm 10 \text{ cm}^{-1}$  between the successive members of each progression. The low energy bands in each group comprise one progression. The second progression begins with the higher energy band in the pair and includes the intermediate energy members in the higher groups. The third progression includes the high energy members beginning with the third group.

The spectra must be associated with an electronic transition



**Figure 1.** Polarized crystal spectra for  $\text{Mo}_2(\text{O}_2\text{CH})_4$  at 15 K. Crystal thickness was  $0.9 \mu$ . Absorbances can be converted to molar absorptivities by multiplying by the factor  $1460 \text{ cm}^{-1} \text{ M}^{-1}$ .

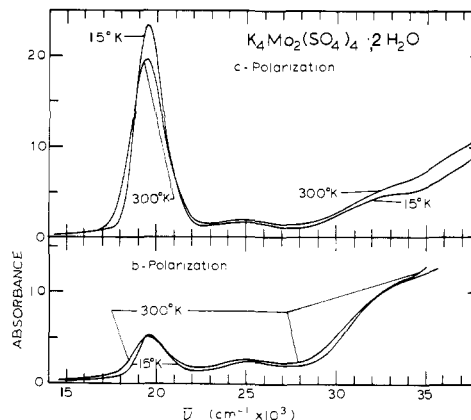
that is dipole forbidden in  $D_{4h}$  molecular symmetry but vibronically allowed by three asymmetric molecular vibrations, giving rise to a Franck-Condon progression based on a single totally symmetric,  $A_{1g}$ , molecular vibration, presumably the metal-metal stretch with frequency  $350 \pm 10 \text{ cm}^{-1}$  in the excited electronic state. Weaker vibrational components in spectra of thicker crystals will be discussed in a later report. There is no observed absorption at lower energies than the first sharp bands, even with a crystal thickness of  $20 \mu$ .

The intensities of all components are higher in  $a$  polarization than in  $c$ , but the ratios of the height of the members of the second or intermediate progression to the height of the members of the first or third progressions are smaller in  $a$  polarization than in  $c$ . It thus appears likely that the low and high energy vibrations provide vibronic states attained by a transition with  $xy$  molecular polarization and the intermediate vibration provides states attained by  $z$  polarized transitions. Apparently, crystal phonon effects and perhaps the proximity of the  $xy$ -polarized transition yields enhancement of the intensity seen for this  $z$  polarized transition in the  $a$  crystal polarization.

The results for  $\text{Mo}_2(\text{O}_2\text{CH})_4$  are thus fundamentally the same as those for the glycine complex and we conclude that the data for the latter (which are much more easily interpreted because of the exceptionally favorable alignment) can be taken as representative. There was not observed with  $\text{Mo}_2(\text{O}_2\text{CH})_4$  the weak  $z$  polarized progression due to a crystal field perturbation and which included the 0-0 line that was seen with the  $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ . The absence of this crystal field progression is presumably due to the much weaker electrostatic field of low symmetry that exists in the molecular crystal of  $\text{Mo}(\text{O}_2\text{CH})_4$  than in the ionic crystal of the glycine complex.

The other question we deal with here is whether the different assignment of the lowest transition for  $\text{Mo}_2(\text{O}_2\text{CR})_4$  vs.  $\text{Mo}_2\text{Cl}_8^{4-}$  is due simply to the change of ligand atoms from Cl atoms to linked O atoms, or whether the specific nature of the carbonyl group and its possible  $\pi$  interactions with the  $\text{Mo}_2$  unit<sup>3</sup> are important. We have therefore examined a crystal of  $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ .<sup>9</sup> For the cleavage face identified by x-ray crystallography as 100, polarizations along the  $b$  and  $c$  axes are shown in Figure 2. The molecular axes lie at angles of  $23.7^\circ$  to the  $c$  axis. In the absence of crystal effects a  $z$ -polarized transition would appear in both crystal polarizations with  $I_c/I_a = 5.2$  and an  $xy$  polarized transition would have  $I_c/I_a = 1/5.2$ .

At room temperature the band at  $19\,400 \text{ cm}^{-1}$  is about four times as intense in  $c$  polarization as in  $b$ . The band narrows and the peak height increases by 15% in  $c$  polarization for 15 K whereas the peak height is scarcely changed for  $b$  polarization by cooling. The integrated intensity scarcely changes with temperature. Thus, the data are consistent with the assignment of this band to the  $\delta \rightarrow \delta^*$  transition.



**Figure 2.** Polarized crystal spectra at 300 and 15 K for  $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ . Crystal thickness was  $15 \mu$ . Absorbances can be converted to molar absorptivities by multiplying by the factor 180.

On the basis of the results reported here, the following important points concerning the electronic spectra of quadruply bonded dimolybdenum systems are now clear. (1) Carboxylato-bridged quadruply bonded systems show a characteristic difference from most others in that the lowest energy visible absorption band is not due to the  $\delta \rightarrow \delta^*$  transition but rather to an orbitally forbidden, vibronically allowed transition. (2) This result is general for all  $\text{Mo}_2(\text{O}_2\text{CR})_4$  even though a detailed vibronic analysis is difficult in most cases because of unfavorable alignment of the molecules in the crystal. (3) Since the band at  $20\,000\text{--}25\,000 \text{ cm}^{-1}$  in  $\text{Mo}_2(\text{O}_2\text{CR})_4$  species is not due to the  $\delta \rightarrow \delta^*$  transition, it is most likely due to a  $\delta \rightarrow X^*$  or  $X \rightarrow \delta^*$  transition, where X and  $X^*$  refer to MO's containing substantial contributions from carbonyl  $\pi$  orbitals. (4) The special electronic character of the carbonyl ligands is shown by the fact that the transition with about the same energy in  $\text{Mo}_2(\text{SO}_4)_4^{4-}$  does have polarization properties which allow it to be assigned to the  $\delta \rightarrow \delta^*$  transition. (5) Presumably, in the  $\text{Mo}_2(\text{O}_2\text{CR})_4$  systems the  $\delta \rightarrow \delta^*$  transition must be responsible for part of the absorption previously<sup>4,6</sup> reported in the region of  $30\,000 \text{ cm}^{-1}$ .<sup>10</sup>

## References and Notes

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