

In retrospect, perhaps the most striking characteristic of the delicate orbital balance in Co(II) square-planar compounds is the dramatic effect of weak axial perturbations on the energy of  $|^2A_1 z^2\rangle$ . Clearly, the amplifying factor in this process must be attributed to d-s orbital mixing. It is not surprising that the creation of a singly occupied fairly destabilized antibonding orbital level

leads to facile oxidative-addition reactions.

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## Electronic Spectra of the Quadruply Bonded Group 6<sup>+</sup> Metal Dimers of 2-Methyl-6-oxypyridine

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The spectra of the quadruply bonded dimers  $M_2(mhp)_4$  ( $M = Cr, Mo$ ) have been recorded for THF solutions, for KBr pellets at 5 K, and for single crystals at 5 K. For  $M = Mo$ , a vibrational progression is observed on the  $\delta \rightarrow \delta^*$  transition in the solution and KBr pellet spectrum based on the metal-metal stretching frequency in the excited electronic state. The mean frequency of the vibration is decreased from 380  $cm^{-1}$  in the solid to 344 (11)  $cm^{-1}$  in solution, suggesting weak axial coordination by the solvent. The mass spectrum of  $Mo_2(mhp)_4$  prepared from  $Mo_2(O_2CCH_3)_4$  indicated that the compound is not pure but contains on average 18%  $Mo_2(mhp)_3(O_2CCH_3)$ . This material was found to account for several of the vibrational bands observed in the spectrum of the impure crystals of  $Mo_2(mhp)_4$ . The pure compound can be obtained from the reaction of  $(NH_4)_4Mo_2Cl_8 \cdot NH_4Cl$  with  $Na(mhp)$  in methanol. The chromium complex displays weak vibrational structure, with a mean spacing of 305 (13)  $cm^{-1}$  in the KBr pellet and 310 (12)  $cm^{-1}$  in the crystal. In the crystal spectra, the lowest energy transition is assigned as  $\delta \rightarrow \delta^*$ . The vibrational structure was assigned to a metal-ligand stretching vibration in the excited electronic state. No progression based on the Cr-Cr stretch was observed.

### Introduction

Structural and spectroscopic investigations of the quadruply bonded dimers of the group 6 metals indicate that these dimers can be classified into four broad categories depending on the types of ligands bound to the  $M_2$  unit. The similarity of the metal-metal bond lengths and electronic spectra of compounds within each class suggests that the bonding within each is similar and thus is a function of the ligand system used. The first and most widely studied class of group 6 dimers are those in which the dimetal unit is bridged by four carboxylates. A wide variety of alkane- and arenecarboxylates have been used as ligands. In the case of molybdenum, typical and metal-metal bond lengths are 2.09 Å.<sup>2</sup> These compounds are usually bright yellow. The reported 0-0 transitions for the first observed electronic transition ( $\delta \rightarrow \delta^*$ ) range from 20 500 to 22 080  $cm^{-1}$ .<sup>3-6</sup> The analogous carboxylates of chromium also appear to form a similar class. Surprisingly, the metal-metal distances in these dimers are longer than in the dimolybdenum compounds. Typical values for the chromium-chromium distance are 2.29-2.4 Å.<sup>2</sup> Unlike the molybdenum dimers, the color of the chromium dimers depends on the carboxylic acid used as the ligand. There has only been one study of the spectra of these compounds, and the assignments were not definitive.<sup>7</sup> Recently, the tungsten analogues have been prepared.<sup>8</sup>

The second class involves compounds of the type  $[M_2X_8]^{4-}$  where X is a univalent anion. Examples of such ligands are halides, pseudohalides, and alkyl ions. For the molybdenum compounds, the Mo-Mo bond distances range from 2.134 to 2.150 Å.<sup>2</sup> This distance is somewhat dependent on the counterion used. These compounds tend to be red, with the  $\delta \rightarrow \delta^*$  transition typically appearing at 19 000  $cm^{-1}$ .<sup>9</sup> The only chromium compound in this class is  $[Cr_2(CH_3)_8]^{4-}$ . For this dimer, the Cr-Cr distance was determined to be 1.980 Å.<sup>10</sup> The absorbance maximum on the  $\delta \rightarrow \delta^*$  transition of an  $Et_2O$  solution of the lithium salt was reported to be at 22 000  $cm^{-1}$  ( $\epsilon \cong 700 M^{-1} cm^{-1}$ ). The tungsten dimers are also known, but they are extremely

reactive and not readily amenable to study.<sup>11-13</sup>

The third class of dimers is of the form  $M_2X_4L_4$  where X is a halide and L is a neutral ligand such as a sulfide or phosphine. Compounds of this type are known for molybdenum and tungsten but not for chromium. For molybdenum the Mo-Mo bond lengths span the range 2.130 Å for  $Mo_2Cl_4(P(CH_3)_3)_4$ <sup>14</sup> to 2.144 Å for  $Mo_2Cl_4(S(C_2H_5)_2)_4$ .<sup>15</sup> These compounds are usually blue or green with an intense absorption at  $\sim 17 000 cm^{-1}$ . We are currently investigating the spectra of the compounds of this class.

The last class of dimers involves anionic aromatic ligands in which an atom in the ring is directly bonded to the metal. Examples of such ligands are 2-methyl-6-oxypyridine (mhp) and 2,6-dimethoxyphenyl (DMP). These ligands stabilize dimers of all the group 6 metals, and these dimers have the shortest metal-metal bonds observed. In this paper, we present solution, low-temperature solid-state, and single-crystal spectra of the compounds  $Mo_2(mhp)_4$  and  $Cr_2(mhp)_4$ . Our aims in studying these spectra were twofold. First, we wished to determine how these spectra are related to those of other quadruply bonded

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\* The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

dimers. Second, we wished to determine why these ligands stabilize the metal dimers and result in such short metal-metal bond distances. While we were undertaking these studies, a paper on the spectra of  $M_2(\text{mhp})_4$  dimers was published by Manning and Trogler.<sup>16</sup> While our results are essentially in agreement with theirs, our interpretation of the assignments in some cases is different.

### Experimental Section

All solvents used were dried and distilled under nitrogen prior to use. All manipulations of solutions were done under a nitrogen atmosphere except as noted.

$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ ,<sup>17</sup>  $(\text{NH}_4)_4\text{Mo}_2\text{Cl}_8 \cdot \text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$ ,<sup>18</sup> and 2-methyl-6-hydroxypyridine<sup>19</sup> were prepared by literature methods.  $\text{Mo}_2(\text{mhp})_4$  and  $\text{Cr}_2(\text{mhp})_4$  were prepared by the previously reported preparations<sup>20</sup> and as follows:

**$\text{Mo}_2(\text{mhp})_4$ .** To 15 mL of methanol were added 0.08 g of sodium metal and 0.36 g of 2-methyl-6-hydroxypyridine. After all the sodium had reacted, 0.5 g of  $(\text{NH}_4)_4\text{Mo}_2\text{Cl}_8 \cdot \text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$  was added and the slurry was stirred for 4 h. The yellow-orange product was filtered in air and washed with water and ethanol. The isolated yield was 86%.

**$\text{Cr}_2(\text{mhp})_4$**  was prepared as above except  $\text{CrCl}_2$  (Alfa) was used as the chromium source. In this case, the reaction is nearly instantaneous in methanol. The compound was purified from the traces of chromium(III) by sublimation.

Crystals of  $\text{Mo}_2(\text{mhp})_4$  were grown from  $\text{CH}_2\text{Cl}_2$ /hexane mixtures and by slow evaporation of methylene chloride solutions. Crystals of  $\text{Cr}_2(\text{mhp})_4$  were obtained by sublimation at 225 °C at pressures less than  $10^{-6}$  torr.

### Spectra

Crystal spectra were recorded on a Cary 17-D spectrophotometer interfaced to a NOVA 1200 computer using procedures previously described.<sup>21</sup> Data were collected every 0.1 nm. Solution spectra were recorded on a Cary 14 spectrophotometer. Gaussian deconvolution was performed with a program based on the method of damped least squares.<sup>22</sup>

Crystal morphology was determined by indexing the crystals on the CAD-4 diffractometer and using that information to determine the faces on a Huber optical goniometer.

Mass spectra were obtained on a Vacuum Generators ZAB-2F double-focusing spectrometer. Raman spectra were recorded on a SPEX double-pass monochromator and photon-counting system. An argon laser was used as the excitation source.

### Results

**$\text{Mo}_2(\text{mhp})_4$ .** The spectra of  $\text{Mo}_2(\text{mhp})_4$  in THF solution and in KBr pellets were essentially identical. The observed band maxima and their molar absorptivities were 20 200  $\text{cm}^{-1}$  (2450  $\text{M}^{-1} \text{cm}^{-1}$ ), 24 700  $\text{cm}^{-1}$  (13 270  $\text{M}^{-1} \text{cm}^{-1}$ ), and 34 800  $\text{cm}^{-1}$  (25 900  $\text{M}^{-1} \text{cm}^{-1}$ ). The second band was asymmetric. Deconvolution revealed a peak at 27 030  $\text{cm}^{-1}$  ( $\epsilon = 5170 \text{ M}^{-1} \text{cm}^{-1}$ ). These spectra are in good agreement with those previously reported by Trogler and Manning.<sup>16</sup> However, not observed in the previous report is the vibrational fine structure on the lowest energy absorption in the solution spectrum. The structure is tabulated in Table I. The average separation was  $344 \pm 11 \text{ cm}^{-1}$ . This is substantially lower than the mean separation of 380  $\text{cm}^{-1}$  observed in the KBr pellet at 5 K.

This difference in the vibrational frequencies between the solution and the solid state is somewhat anomalous. The observed frequency of 380  $\text{cm}^{-1}$  in the KBr pellet is in good agreement with the previously reported value of 400 (13)  $\text{cm}^{-1}$  observed for  $\text{Mo}_2(\text{mhp})_4$  in rare-gas matrices.<sup>16</sup> The value for the Mo-Mo stretch in the electronic ground state has been reported as 425

Table I. Vibrational Structure of  $\text{Mo}_2(\text{mhp})_4$

| $\lambda$ , nm | $\tilde{\nu}$ , $\text{cm}^{-1}$ | sep, $\text{cm}^{-1}$ |                                  |
|----------------|----------------------------------|-----------------------|----------------------------------|
| Solution (THF) |                                  |                       |                                  |
| 515            | 19 420                           | 340                   |                                  |
| 506            | 19 760                           | 360                   |                                  |
| 497            | 20 120                           | 330                   |                                  |
| 489            | 20 450                           | 340                   |                                  |
| 481            | 20 790                           | 350                   |                                  |
| 473            | 21 140                           | $344 \pm 11$ (av)     |                                  |
| KBr Pellet     |                                  |                       |                                  |
| 517.4 (3)      | 19 330 (12)                      | 380                   |                                  |
| 507.3          | 19 710                           | 380                   |                                  |
| 497.8          | 20 090                           | 380                   |                                  |
| 488.5          | 20 470                           | 380                   |                                  |
| 479.6          | 20 850                           | 380                   |                                  |
| 471.0          | 21 230                           | 380                   |                                  |
| 462.8          | 21 610                           | 380 (av)              |                                  |
| Crystal        |                                  |                       |                                  |
| $\lambda$ , nm | $\tilde{\nu}$ , $\text{cm}^{-1}$ | $\lambda$ , nm        | $\tilde{\nu}$ , $\text{cm}^{-1}$ |
| 510.9          | 19 580                           | 505.6                 | 19 780                           |
| 510.1          | 19 600                           | 503.5                 | 19 860                           |
| 509.5          | 19 630                           | 502.0                 | 19 920                           |
| 507.2          | 19 710                           | 501.6                 | 19 940                           |
| 506.4          | 19 750                           | 500.6                 | 19 970                           |

$\text{cm}^{-1}$  from the Raman spectrum and 420 (4)  $\text{cm}^{-1}$  from the emission spectrum. This is slightly greater than the  $\sim 400 \text{ cm}^{-1}$  observed in carboxylic acid complexes,<sup>23,24</sup> as is to be expected since the Mo-Mo bond length is slightly shorter in the  $\mu$ -tetramethylhydroxypyridinato complexes. Therefore, the value of 380  $\text{cm}^{-1}$  observed in the electronic excited state in the KBr pellet is in agreement with the value of 350–370  $\text{cm}^{-1}$  observed for the excited state of the carboxylate dimers.<sup>5,6</sup> However, the value of 344  $\text{cm}^{-1}$  is exceedingly low. One possibility is that the solvent, THF, is weakly coordinating to the axial positions. For the case of  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ , it was observed that weak axial coordination by pyridine lowered the excited-state Mo-Mo stretch by  $\sim 25 \text{ cm}^{-1}$ .<sup>6</sup> Certainly, the fact that the value in  $\text{Mo}_2(\text{mhp})_4$  is lower in THF supports the concept of weak solvent coordination. However, the methyl groups of the ligand were expected to block the axial sites.

Crystals of  $\text{Mo}_2(\text{mhp})_4$  suitable for spectroscopy were grown by evaporation of methylene chloride solutions. The crystals were thin plates with a thickness of  $\sim 5$ – $10 \mu\text{m}$ . When indexed, the unit cell was identical with that previously reported,<sup>20</sup> and the observed face was determined to be the (1,0,-1) face. In this face of a monoclinic crystal, the extinction directions are required by symmetry to be parallel and perpendicular to the  $b$  axis. The calculated polarization ratios are as follows: for a  $z$ -polarized transition, 4.4/1 for  $b_{\parallel}/b_{\perp}$ ; for an  $x,y$ -polarized transition, 4.3/1 for  $b_{\perp}/b_{\parallel}$ . The similarity in these ratios is accidental. For the lowest energy transitions, the maximum intensity was along the  $b$  axis and the intensity ratio was  $\sim 2/1$ . The difference between the calculated and observed values of the polarization ratio probably reflects the fact that the high polarization was nearly too intense to measure. The spectrum was affected by stray light and perhaps polarizer leakage. However, the transition is  $z$  polarized and is therefore assigned as  $\delta \rightarrow \delta^*$ . The low polarization is illustrated in Figure 1, and the observed vibrational structure is tabulated in Table I. Even in the low polarization only a small portion of this transition could be scanned before the absorbance was greater than the stray light level. However, at 400  $\text{cm}^{-1}$  10

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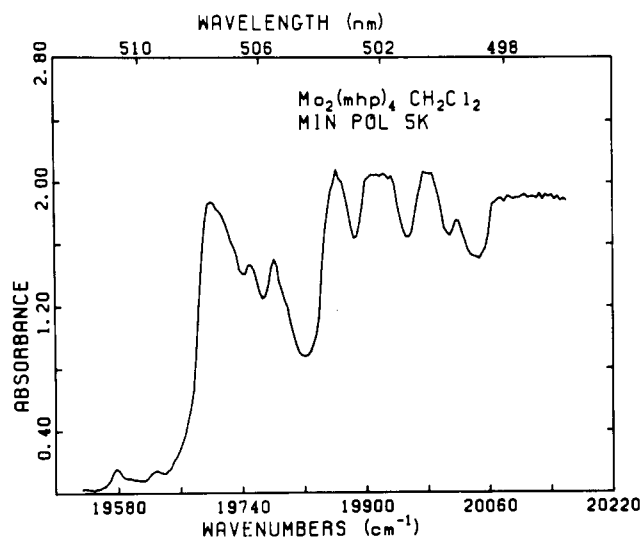


Figure 1. First electronic transition in the crystal of  $\text{Mo}_2(\text{mhp})_4 \cdot \text{CH}_2\text{Cl}_2$  as observed in the (1,0,-1) face at 5 K. The maximum polarization is parallel to the  $b$  axis.

vibrational components were observed. The first fairly weak feature was observed at  $19\,500\text{ cm}^{-1}$  and was well polarized. There were several other very weak features before an intense absorption at  $19\,710\text{ cm}^{-1}$ . From this point on, only intense components were observed.

Because of the large number of vibrational components observed, it appeared likely that the  $\text{Mo}_2(\text{mhp})_4$  synthesized from  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  was not pure. Therefore, the mass spectrum of the compound was examined. The main parent peaks beginning at  $M/z$  616 represented  $\text{Mo}_2(\text{mhp})_4$  and were identical with those previously reported.<sup>20</sup> Two very weak impurities (less than 0.5%) at higher mass were  $\text{MoW}(\text{mhp})_4$  centered about  $M/z$  710–720 and  $\text{Mo}(\text{mhp})_3(\text{dmhp})$  where dmhp is the anion of dimethylhydroxypyridine. The tungsten impurity comes from the molybdenum hexacarbonyl initially used to synthesize the molybdenum acetate. An intense set of peaks was observed 49 mass units lower than the parent peaks for  $\text{Mo}_2(\text{mhp})_4$ . The ratio of the intensity of this set of peaks to the parent peaks for  $\text{Mo}_2(\text{mhp})_4$  remained constant when the electron accelerating voltage was decreased from 70 to 12 V, suggesting these peaks were not due to fragmentation. Analysis of the isotopic ratios and the masses lead to their assignment as the parent peaks of  $\text{Mo}_2(\text{mhp})_3(\text{O}_2\text{CCH}_3)$ . The ratio of the two parent peak groups suggested that this impurity made up  $\sim 18\%$  of the sample. Different preparations of  $\text{Mo}_2(\text{mhp})_4$  gave essentially the same mass spectrum.

The originally reported elemental analyses for  $\text{Mo}_2(\text{mhp})_4$  are also consistent with the presence of the impurity of  $\text{Mo}_2(\text{mhp})_3(\text{O}_2\text{CCH}_3)$ .<sup>20</sup> Both the carbon and nitrogen analyses are too low and show a much greater deviation from the expected values than those reported for  $\text{Cr}_2(\text{mhp})_4$  and  $\text{W}_2(\text{mhp})_4$  in the same paper. If it is assumed that this deviation is totally because of the acetate impurity, the nitrogen and carbon analyses suggest that the sample contained 29% and 10% impurity, respectively. This is in agreement with the observed 18%.

In order to prepare pure  $\text{Mo}_2(\text{mhp})_4$  as new synthesis was devised. The compound was prepared by reacting  $\text{Mo}_2\text{Cl}_8^{4-}$  with  $\text{Na}(\text{mhp})$  in methanol. Since each univalent mhp anion replaces two chlorides, any compounds resulting from partial substitution would be anionic and could be removed by subliming the pure  $\text{Mo}_2(\text{mhp})_4$  from the mixture. The mass spectrum of the initially isolated  $\text{Mo}_2(\text{mhp})_4$  prepared from  $\text{Mo}_2\text{Cl}_8^{4-}$  did not display the parent peaks for the acetate impurity. Therefore, those peaks at mass 575 result from this impurity and not a fragment. Of course, any impurities from only partial substitution of the chlorides would not be observed in the mass spectrum.

Removing the acetate impurity from the  $\text{Mo}_2(\text{mhp})_4$  has almost no effect on the solution and KBr pellet spectra. However, the

Table II. Vibrational Structure of  $\text{Cr}_2(\text{mhp})_4$

| KBr Pellet     |                                  |                                  |                               |
|----------------|----------------------------------|----------------------------------|-------------------------------|
| $\lambda$ , nm | $\tilde{\nu}$ , $\text{cm}^{-1}$ | sep, $\text{cm}^{-1}$            |                               |
| 475.0 (3)      | 21 053 (12)                      | 320                              |                               |
| 468.0          | 21 370                           | 310                              |                               |
| 461.2          | 21 680                           | 310                              |                               |
| 454.8          | 21 990                           | 300                              |                               |
| 448.6          | 22 290                           | 280                              |                               |
| 443.0          | 22 570                           | 310                              |                               |
| 437.0          | 22 880                           | 305 $\pm$ 13 (av)                |                               |
| progressn no.  | $\lambda$ , nm                   | $\tilde{\nu}$ , $\text{cm}^{-1}$ | sep, $\text{cm}^{-1}$         |
| A <sub>0</sub> | 475.0 (3)                        | 21 050 (12)                      |                               |
| A <sub>1</sub> | 467.8                            | 21 380                           | 330                           |
| B <sub>0</sub> | 466.3 (weak)                     | 21 450                           | 400                           |
| A <sub>2</sub> | 461.3                            | 21 680                           | 300                           |
| B <sub>1</sub> | 459.5                            | 21 760                           | 310                           |
| A <sub>3</sub> | 454.6                            | 22 000                           | 320                           |
| B <sub>2</sub> | 453.2                            | 22 070                           | 310                           |
| A <sub>4</sub> | 448.3                            | 22 310                           | 310                           |
| B <sub>3</sub> | 447.0                            | 22 370                           | 300                           |
| C <sub>0</sub> | 446.0                            | 22 420                           | 1370                          |
| A <sub>5</sub> | 442.5                            | 22 600                           | 290                           |
| C <sub>1</sub> | 439.5                            | 22 750                           | 330                           |
| A <sub>6</sub> | 436.3                            | 22 920                           | 320                           |
| C <sub>2</sub> | 433.8                            | 23 050                           | 300                           |
| A <sub>7</sub> | 430.6                            | 23 220                           | 300                           |
| C <sub>3</sub> | 428.0                            | 23 360                           | 310                           |
|                |                                  |                                  | 310 $\pm$ 12 (av)             |
| broad          |                                  | struct                           |                               |
|                | 424 (1)                          | 23 570                           |                               |
|                | 419                              | 23 850                           | 280                           |
|                | 412 (2)                          | 24 260                           | 410                           |
|                | 407                              | 24 540                           | 280                           |
|                | 401                              | 24 940                           | 400                           |
|                | 395                              | 25 270                           | 330                           |
|                |                                  |                                  | 340 $\pm$ 63 (av)             |
| av A-B sep     |                                  |                                  | 385 $\pm$ 13 $\text{cm}^{-1}$ |
| av A-C sep     |                                  |                                  | 1368 $\pm$ 5 $\text{cm}^{-1}$ |

crystal spectra changed drastically. First, it proved impossible to record the absorption spectrum of crystals as thin or slightly thinner than those of the impure  $\text{Mo}_2(\text{mhp})_4$ . Even in the low polarization, the absorption was always greater than 3. Second, no vibrational components were observed at energies lower than the sharp rise at  $\sim 510\text{ nm}$ . The weak bands observed in the impure crystals must be due to the impurity. Therefore, the first intense component at  $19\,710\text{ cm}^{-1}$  can be assigned as the 0-0 band in  $\text{Mo}_2(\text{mhp})_4$ . This is in good agreement with the values of  $19\,690\text{ cm}^{-1}$  reported by Manning and Troglar.

$\text{Cr}_2(\text{mhp})_4$ . The solution spectrum of  $\text{Cr}_2(\text{mhp})_4$  is illustrated in Figure 2. The broad band with a maximum at  $22\,470\text{ cm}^{-1}$  was the lowest energy transition observed. This feature was composed of two overlapping transitions: one at  $22\,320\text{ cm}^{-1}$  ( $\epsilon = 320\text{ M}^{-1}\text{ cm}^{-1}$ ) and one at  $24\,815\text{ cm}^{-1}$  ( $\epsilon = 160\text{ M}^{-1}\text{ cm}^{-1}$ ). The only higher energy feature observed was a shoulder at  $29\,850\text{ cm}^{-1}$  ( $\epsilon = 400\text{ M}^{-1}\text{ cm}^{-1}$ ). No vibrational structure was observed in the solution spectrum. However, weak vibrational fine structure was observed in KBr pellets at 5 K with a mean separation of  $305 \pm 13\text{ cm}^{-1}$ . The wavelengths are tabulated in Table II.

Crystals of  $\text{Cr}_2(\text{mhp})_4$  grown from methylene chloride solutions were not suitable for spectroscopy. Besides being poorly shaped, they tended to darken even when stored under nitrogen. Therefore crystals were grown by sublimation. These crystals did not contain methylene chloride in the unit cell. The structure for unsolvated  $\text{Cr}_2(\text{mhp})_4$  grown from chlorobenzene was reported previously<sup>25</sup>

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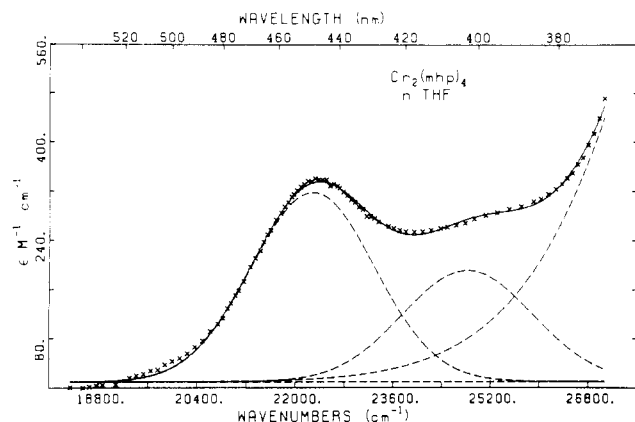


Figure 2. Solution spectrum of  $\text{Cr}_2(\text{mhp})_4$  in THF.

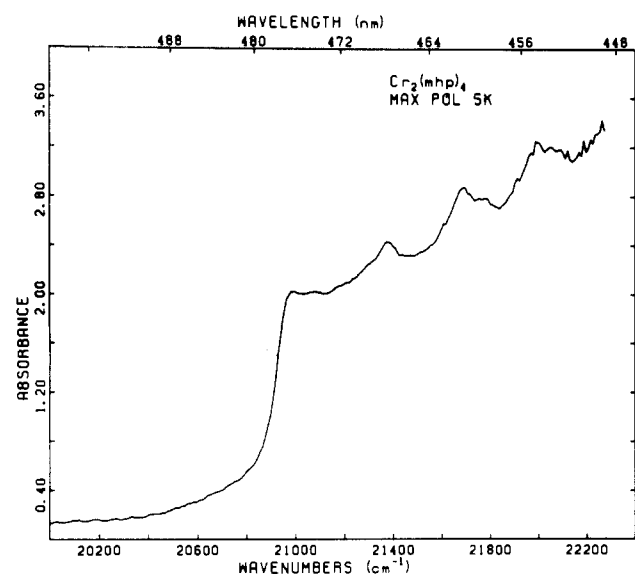


Figure 3. First electronic transition in the crystal of  $\text{Cr}_2(\text{mhp})_4$  as observed in the (1,-1,0) face at 5 K. The maximum polarization is perpendicular to the  $c$  axis.

and was identical with that of the sublimed crystals. The observed face was (110). Measurements with the polarizing microscope indicated that one extinction direction was nearly parallel to the  $c$  axis. The calculated polarization ratios are as follows: for a  $z$ -polarized transition, 13.4/1 for  $c_{\perp}/c_{\parallel}$ ; for an  $x,y$ -polarized transitions, 1.8/1 for  $c_{\parallel}/c_{\perp}$ .

The crystal spectrum of  $\text{Cr}_2(\text{mhp})_4$  is shown in Figure 3. As the crystals were rather thick ( $\sim 30 \mu\text{m}$ ), only the lowest energy features could be observed in the more intense polarization. However, in the perpendicular polarization the entire band was recorded. The maximum intensity was observed perpendicular to the crystallographic  $c$  axis. The dichroism seems to be rather large. Internal reflection<sup>26</sup> was observed in all the crystals studied, which made accurate determination of the zero absorbance impossible. However, the polarization ratio appears to be greater than 5/1. The transition is thus  $z$  polarized.

As in the molybdenum dimer, vibrational structure is observed. However, the appearance of this structure is radically different in  $\text{Cr}_2(\text{mhp})_4$ . In the case of the molybdenum compound, the fine structure appears as well-resolved peaks with a large peak-to-valley ratio. In the case of the chromium dimer, the vibrational components appear as small distortions in the overall Gaussian absorption band. This suggests that the individual components are broad and overlap to a substantial degree. This structure was reproducible in appearance and energy for four different crystals. The proposed progressional assignments are listed in Table II. The 0-0 band is at  $21050 \text{ cm}^{-1}$ , in agreement with Manning and

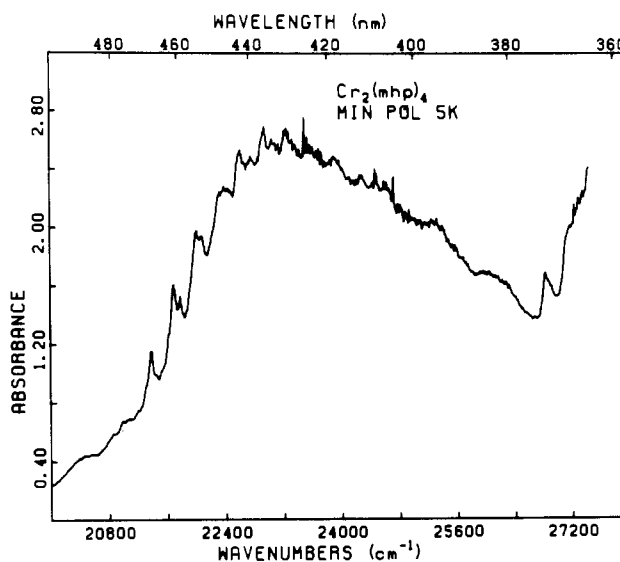


Figure 4.

Trogler.<sup>16</sup> Two other origins are observed: one  $385 (13) \text{ cm}^{-1}$  and one  $1368 (5) \text{ cm}^{-1}$  above the 0-0 band. The origin at  $385 \text{ cm}^{-1}$  is clearly vibronic in origin and probably corresponds to the  $391\text{-cm}^{-1}$  band observed in the infrared spectra. The origin at  $1368 \text{ cm}^{-1}$  probably represents the origin for the second electronic transition observed in the solution spectrum. The broad structure is the tail end of the transition from the 0-0 band for the  $\delta \rightarrow \delta^*$  overlapping with this new set of peaks. The appearance of a second electronic transition overlapping the  $\delta \rightarrow \delta^*$  has been observed previously in the dimolybdenum tetracarboxylates<sup>6,27</sup> and has been attributed to the vibronic transition  $\pi \rightarrow \delta^*$  or  $\delta \rightarrow \pi^*$ .

The most surprising aspect of the spectrum of  $\text{Cr}_2(\text{mhp})_4$  is the spacing of the vibrational progressions. In the KBr pellet, the mean separation was  $305 \pm 13 \text{ cm}^{-1}$ . In the crystal there was only one Franck-Condon progression built on each origin. The progression had an average energy of  $310 \pm 12 \text{ cm}^{-1}$ . The Cr-Cr stretch in the ground state was reported to be at  $556 \text{ cm}^{-1}$ .<sup>20</sup> If the  $310\text{-cm}^{-1}$  progression is attributed to an excited-state Cr-Cr stretch, it represents a reduction of 44% in the stretching frequency. However, the observed Franck-Condon progression does not indicate a comparable large distortion in the bond length. The possibility that the Raman spectrum was misassigned was investigated by Trogler and Manning who concluded that the band at  $556 \text{ cm}^{-1}$  is not the metal-metal stretch because it is observed in the infrared spectrum and also in  $\text{Mo}_2(\text{mhp})_4$  and  $\text{mhp}$  itself. We agree with this contention. However, they concluded that the Cr-Cr stretch is most likely a band at  $340 \text{ cm}^{-1}$ . This does not appear to be a reasonable assignment. There is a regular pattern to the bond distances for the series  $\text{M}_2(\text{mhp})_4$  where  $\text{M}_2 = \text{Cr}_2, \text{CrMo}, \text{Mo}_2, \text{MoW},$  or  $\text{W}_2$ . Therefore, there is no reason to expect that the chromium dimer should have a lower metal-metal stretching frequency than the Mo-Mo or Mo-Cr dimers. A more reasonable assignment is to attribute this to either a Cr-N or Cr-O totally symmetric stretch. The range for such stretching frequencies is quite large. For example the Cr-N stretch is  $465 \text{ cm}^{-1}$  in  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ <sup>28</sup> but drops to  $219 \text{ cm}^{-1}$  in polymeric  $\text{Cr}(\text{py})_2\text{Cl}_2$ .<sup>29</sup> A similar broad range is observed in metal-oxygen stretches.<sup>30</sup> Therefore, the best approach is to use dimers similar in structure for an estimate of these stretching frequencies. For the case of metal-oxygen stretching frequencies, the totally symmetric Mo-O stretches for an  $\text{Mo}_2\text{O}_8$  skeleton were calculated to be at  $321\text{-}328 \text{ cm}^{-1}$ .<sup>24</sup> Similarly, a recent study of the vibrational and electronic spectra of  $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$  placed the totally symmetric Rh-O mode at  $343 \text{ cm}^{-1}$  in the ground state

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and at  $\sim 300\text{ cm}^{-1}$  in the  $\pi^*\delta^*(\text{Rh}_2) \rightarrow \sigma^*(\text{Rh-O})$ .<sup>31</sup>

The case of  $\text{Tc}_2(\text{hp})_4\text{Cl}$  ( $\text{hp} = 2\text{-oxypyridine}$ ) provides an even better model. The totally symmetric metal-ligand vibrations were identified at 319 and 295  $\text{cm}^{-1}$  in the Raman and 298 and 264  $\text{cm}^{-1}$  in the electronic spectrum.<sup>21</sup> This dimer also provides a precedent for observing a Franck-Condon progression based on a metal-ligand mode on the  $\delta \rightarrow \delta^*$  transition. In  $\text{Tc}_2(\text{hp})_4\text{Cl}$  the 0-0 band of the first transition ( $\delta \rightarrow \delta^*$ ) occurred at 12 190  $\text{cm}^{-1}$ .<sup>21</sup> This is much lower than that observed in either the molybdenum or chromium dimer. However, the metal-metal bond order in this technetium compound is only 3.5. The reduction in bond order decreases the energy of the  $\delta\text{-}\delta^*$  separation.<sup>33</sup> The total of 11 different origins were observed in the vibrational fine structure. Built on each origin were two Franck-Condon progressions. One progression displayed a separation of 337  $\text{cm}^{-1}$  and was attributed to the metal-metal stretch. A second progression was based on frequency of 298  $\text{cm}^{-1}$  and was attributed to a metal-ligand totally symmetric stretching mode. In addition, all the combination bands based on these two frequencies were observed. The slight increase of the metal-ligand mode to 310  $\text{cm}^{-1}$  in the chromium dimer is consistent with the reduction in the reduced mass as compared to technetium dimer. The appearance of a Franck-Condon progression based on a metal-ligand mode would suggest that the  $d_{xy}$  orbitals, which are usually thought of as only forming the metal-metal  $\delta$  bond, must be involved in metal-ligand bonding. The failure to observe the metal-metal stretch in the  $\delta \rightarrow \delta^*$  transition of  $\text{Cr}_2(\text{mhp})_4$  suggests there may be little change in the ground- and excited-state potential wells along this normal coordinate. It is expected that the Cr-Cr "quadruple" bond in this "supershort" dimer has but a small  $\delta$  component and that the Cr-Cr bond would not be significant lengthened upon excitation of an electron from the  $\delta$  to the  $\delta^*$  orbital. This is consistent with the contention that the  $\delta$  bond in this and related species contributes negligibly to the shortness of the metal-metal bond.<sup>34,35</sup>

It appears that there is no band in the Raman spectrum that can be assigned to a pure Cr-Cr stretch. This situation would not be unique. Studies on the triply bond compounds  $\text{M}_2(\text{N}(\text{CH}_3)_2)_6$  ( $\text{M} = \text{Mo}, \text{W}$ ) and their deuterated equivalents proved that the metal-metal stretching mode was not observed in the Raman spectra.<sup>2</sup> More germanely, dimers of the type  $\text{Mo}_2(\text{xhp})_4$  (where x is a group other than a methyl) did not display a metal-metal stretch in the Raman spectrum.<sup>29</sup>

Because of the problems in obtaining pure  $\text{Mo}_2(\text{mhp})_4$ , the mass spectrum of  $\text{Cr}_2(\text{mhp})_4$  was also studied. Material prepared by the literature preparation contained less than 0.5%  $\text{Cr}_2(\text{mhp})_3(\text{O}_2\text{CCH}_3)$ . However, a set of impurity peaks were observed in older samples that had darkened noticeably. These began at  $M/z$  374 and displayed an intensity ratio that was inconsistent with that of a chromium dimer. Analysis of the pattern revealed that they could be assigned to the compound  $\text{Cr}(\text{mhp})_3$ . When the electron-accelerating voltage was decreased to 18 V, the ratio of this group to that of the parent  $\text{Cr}_2(\text{mhp})_4$  remained unchanged. In addition, the peaks at  $M/z$  374 were virtually absent in freshly prepared samples. In samples over 1 year old they represented 10% of the sample. In any case, this material was readily removed by sublimation.

### Discussion

One aspect of this study is a comparison of the electronic transition energies in the group 6 dimers  $\text{M}_2(\text{mhp})_4$ . These dimers

are quite useful for such a study since their properties are periodic. The bond distances reported were 1.870 (3), 2.065 (1), and 2.161 (1) Å for the isostructural chromium, molybdenum, and tungsten dimers. Therefore, it is not surprising that the lowest energy electronic transitions are regular in both their energy and their intensity. The energies are 22 470, 20 160, and 18 000  $\text{cm}^{-1}$  for the chromium, molybdenum, and tungsten dimers while the molar absorptivities are 320, 2450, and  $>17\,000\text{ M}^{-1}\text{ cm}^{-1}$ . Sattelberger and Fackler<sup>36</sup> have shown that a plot of  $\delta \rightarrow \delta^*$  transition energy vs. M-M bond length results in a straight line for complexes of the type  $[\text{M}_2(\text{CH}_3)_8]^{n-}$  ( $\text{M} = \text{Mo}, \text{Cr}, \text{Re}$ ). A similar relationship appears to be the case here. Since this transition in the polarized crystal spectra of the molybdenum and chromium dimers is  $z$  polarized, the transition is assigned as  $\delta \rightarrow \delta^*$  ( ${}^1\text{B}_2 \leftarrow {}^1\text{A}_1$  under  $D_{2d}$  symmetry). This transition is dipole allowed. However, in spectroscopic studies of other quadruply bonded dimers it has been found to be quite weak.<sup>5,6</sup> The one major difference is the vibrational structure observed in  $\text{Cr}_2(\text{mhp})_4$ . However, it has been observed previously that the spectra of the tetracarboxylates of chromium were quite different from those of the molybdenum and tungsten dimers.<sup>7</sup>

The reasons for the decrease in the energy of the  $\delta \rightarrow \delta^*$  transition with increasing atomic number are not obvious. The overlap of the  $d_{xy}$  orbitals in the case of chromium is expected to be much less than in the case of the heavier metals. Therefore, it would be expected that chromium should have the smallest  $\delta\text{-}\delta^*$  separation. This is supported by calculations done on bare dinuclear dimers with no ligands. The results of Bursten and Cotton suggest that the  $\delta\text{-}\delta^*$  separation is much smaller in the dichromium molecule as compared to dimolybdenum.<sup>34</sup> They then considered the effects of reducing the charge on the metal by  $\sigma$  donation into the  $d_{x^2-y^2}$  orbitals. It was observed that a reduction in charge would increase the  $\delta\text{-}\delta^*$  separation slightly, with a maximum separation in dichromium occurring at 1.33 eV with a total ionic charge of 1+. However, this separation is still less than the minimal  $\delta\text{-}\delta^*$  separation of  $\sim 5$  eV observed in  $\text{Mo}_2^{4+}$ . They also commented that there were two other methods for altering the charge on the metals. The ligands can donate charge to the empty metal-metal antibonding orbitals and/or the ligands can accept charge from the occupied metal-metal bonding orbitals. The results of the spectra of  $\text{Tc}_2(\text{hp})_4\text{Cl}$  and  $\text{Cr}_2(\text{mhp})_4$  suggest at least one, if not both, of these two alternative methods are at work.

The presence of acetate impurities in dimolybdenum compounds synthesized by displacement of acetate ligands is not unique to  $\text{Mo}_2(\text{mhp})_4$ . Sattelberger has observed a similar problem in  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ .<sup>37</sup> Abbott noted that tetrakis(trifluoromethanesulfonato)dimolybdenum(II) was extremely difficult to purify when prepared from molybdenum acetate.<sup>38</sup> The crystal spectra of  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ ,<sup>6,27</sup>  $\text{Mo}_2(\text{O}_2\text{CH})_4$ ,<sup>4</sup> and  $\text{Mo}_2(\text{Gly})_4$ <sup>4+39</sup> all displayed anomalous weak vibrational components that were located at lower energy than the 0-0 band. It appears likely that these are due to acetate impurities.

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**Registry No.**  $\text{Mo}_2(\text{mhp})_4$ , 67634-80-4;  $\text{Cr}_2(\text{mhp})_4$ , 67634-82-6;  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ , 14221-06-8;  $(\text{NH}_4)_4\text{Mo}_5\text{Cl}_8 \cdot \text{NH}_4\text{Cl}$ , 40902-25-8; 2-methyl-6-hydroxypyridine, 3279-76-3.

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