(45) The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weighting factor, w, was defined as $1/\sigma^2(F_o) = 4.0F_o^2/\sigma^2(F_o^2)$. $\sigma^2(F_o^2)$ was determined from counting statistics as $\sigma^2(F_o^2) = \text{RLP}\{\text{TSC} + \text{BACK} + [P(\text{TSC} - \text{BACK})]^2\}$ where RLP is the reciprocal of the Lorentz and polarization correction, TSC is the total scan count, and BACK is the number of counts accumulated during background measurement during a period equivalent to the scan time. P was given a value of 0.04. See: W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957); P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(46) "International Tables for X-ray Crystallography", Vol. 4, Kynoch Press, Birmingham, England, 1974.
(47) J. Kleinberg, *Inorg. Synth.*, **7**, 107 (1963).
(48) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(49) Established by decoupling experiments.
(50) F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974).

Low-Temperature Electronic Spectra of Solid Tetrakis(dimethyldimethylenephosphonium)dimolybdenum and -dichromium

F. Albert Cotton* and Phillip E. Fanwick*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received April 20, 1979*

Abstract: The electronic absorption spectra of the title compounds, which contain quadruple Mo-Mo and Cr-Cr bonds, have been measured on crystalline powders pressed in KBr pellets at 5 K. The molybdenum compound has an absorption band at ca. 2000 cm^{-1} and the low-temperature spectra reveal no less than five resolved vibrational progressions, each of which has a spacing (345 cm^{-1}) associated with that totally symmetric vibration in the electronic excited state that is approximately describable as $\nu_{\text{Mo-Mo}}$. The Franck-Condon factors are of two different kinds, one associated with three of the progressions and the other with the two remaining ones. It is shown that this curious spectrum can be explained in detail using theory first discussed by Craig and Small for a transition where both orbitally allowed and vibronic contributions to intensity are of comparable magnitude. The analysis is much the same as that recently employed for the $Mo_2(O_2CCH_3)_4$ spectrum and adds valuable support to the assignment of the electronic transition occurring at ca. 20 000 cm^{-1} in both $Mo_2(O_2CCH_3)_4$ and $Mo_2[(CH_2)P(CH_3)_2]_4$ as the $^1A_{2u} \leftarrow {}^1A_{1g}$ ($\delta^* \leftarrow \delta$) transition. The spectrum of the chromium analogue is blemished by decomposition products and could not be analyzed.

Introduction

There is today a general, qualitative understanding of the nature of triple and quadruple bonds between transition-metal atoms, and to a certain degree even a quantitative understanding.[1] However, many points remain obscure and the interpretation of electronic absorption and photoelectron spectra still poses some challenging problems. This is especially true for the quadruply bonded dichromium compounds in general[2] and for certain of the quadruply bonded dimolybdenum compounds.

With regard to the latter, the tetracarboxylates, $Mo_2(O_2CR)_4$, have been particularly enigmatic. The first study[3] of their spectra using oriented crystals at low temperature was made by Cotton, Martin, Webb, and Peters, using $Mo_2(O_2CCHNH_3)_4(SO_4)_4 \cdot 4H_2O$; the lowest energy band, at ca. 20 000 cm^{-1}, was examined in detail. This band was shown to consist of vibrational progressions in *both z and xy polarizations*, with different origins in each, thus indicating an important role for vibronic (Herzberg-Teller) excitation in giving intensity to the band. Indeed, the observations were quite consistent with the assumption that the transition is purely vibronic and led, therefore, to the suggestion that the band should *not* be assigned to the $\delta^* \leftarrow \delta$ ($^1A_{2u} \leftarrow {}^1A_{1g}$) transition, since selection rules show that transition is electric dipole allowed with nonzero intensity for *z*-polarized light but no intensity in the *xy* plane.

This study was followed by the work of Trogler, Solomon, Trajberg, Ballhausen, and Gray,[4] who studied $Mo_2(O_2CCH_3)_4$. They also considered the transition to be purely vibronic in nature and proposed a specific assignment, viz., $\pi^* \leftarrow \delta$. Their spectra were much more complex and, hence, potentially informative because of the low symmetry of the crystal; but they did not fully account for all the details. This prompted Martin, Newman, and Fanwick[5] to reinvestigate the $Mo_2(O_2CCH_3)_4$ crystal spectrum.

Martin et al. showed that a correct analysis of the acetate crystal spectrum is possible only when it is recognized that one is dealing with a very unusual, though not entirely unprecedented, situation in which the orbital electric dipole and vibronic intensities are of comparable magnitude. This has a number of ramifications, including the appearance of overlapping progressions having different Franck-Condon factors. Unfortunately, the glycinate crystals first studied were so symmetrical and the spectra so simple that it was impossible to discover the true nature of the transition and the conclusion drawn in that study, though incorrect, was entirely justified by the meager data.

On the basis of their analysis, Martin et al. were led to the conclusion that the $\delta^* \leftarrow \delta$ transition in $Mo_2(O_2CR)_4$ compounds does, indeed, give rise to the lowest energy band in the visible spectrum at ca. 20 000 cm^{-1}. This conclusion is in accord with the general picture that has emerged for $\delta^* \leftarrow \delta$ transitions in M-M quadruple bonds and, in particular, fits nicely with the assignments for other species containing Mo-Mo quadruple bonds, viz., $[Mo_2Cl_8]^{4-}$,[6,7] $[Mo_2(SO_4)_4]^{4-}$,[8] and $[Mo_2(CH_3)_8]^{4-}$,[9] and with the results of SCF-Xα-SW calculations.[10]

Even though the spectral analysis and the assignment made by Martin et al. are reasonable, internally consistent, and satisfying, the fact that they hinge on a phenomenon so unusual as to be justifiably called anomalous might have the undesirable effect of allowing some lingering doubt to survive. It is, therefore, of importance that we can report another example of the same "anomalous" spectroscopic behavior, but one which is so straightforward and clear that it should serve both to erase any doubt about the aptness of the analysis of Martin

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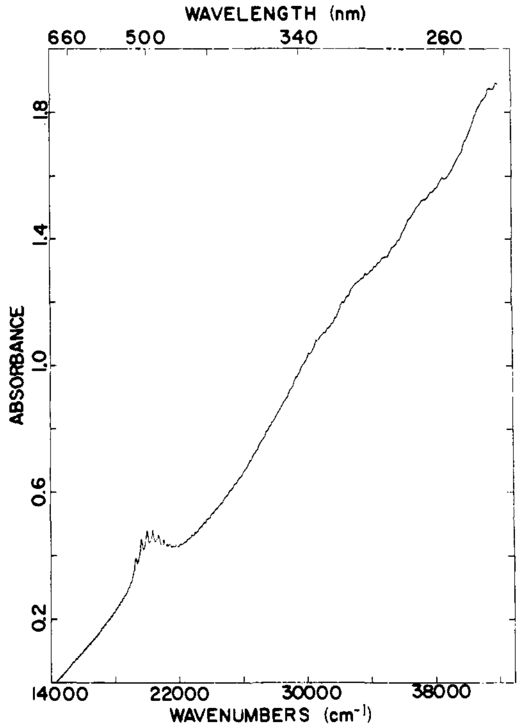
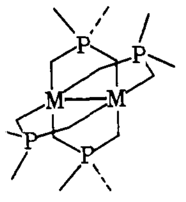


Figure 1. The electronic absorption spectrum of $Mo_2[(CH_2)_2P(CH_3)_2]_4$ at 5 K.

et al., in the case of $Mo_2(O_2CCH_3)_4$, and to illustrate the phenomenon in its prototypal simplicity.

Our work deals with the quadruply bonded molecules $M_2[(CH_2)_2P(CH_3)_2]_4$ with M = Cr and Mo, the structures of which have been accurately determined[11] and are represented schematically by **1**. These compounds were discovered



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several years ago by Kurras and co-workers,[12] who have more recently reported their electronic absorption spectra in solution.[13] We have carried out measurements of the spectra of these compounds as solids incorporated into pressed wafers of KBr. Dr. Kurras kindly supplied the samples used.

Experimental Procedure

Potassium bromide wafers containing the $M_2[(CH_2)_2P(CH_3)_2]_4$ compounds were made by grinding each compound with KBr in an argon atmosphere and transferring the ground mixture, still in an inert atmosphere, to a standard hydraulic press. The pressed pellets of the molybdenum compound displayed no decomposition during this process, but those of the chromium compound decomposed noticeably, changing from bright yellow to a drab yellow-brown color. Spectra were recorded on about ten pellets for the chromium compound, and one was deliberately allowed to decompose thoroughly so as to show what features are due to decomposition products.

Spectra were recorded on a Cary 17D spectrophotometer equipped with an R928 photomultiplier tube. Low temperatures were achieved using a Janis Research Co. super vari-temp cryostat. Temperature was determined and controlled to ±1 K with a Lakeshores Cryogenic Model DRC-7C temperature controller. The spectrophotometer was interfaced to a Nova 1200 computer through a locally designed adaptation of an MDB Systems Nova interface board. The computer had previously been interfaced to a Texas Instruments thermal printer and a PERTEC tape drive using the computer control supplied by Syntex Analytical Instruments for the Syntex AD-1 autodensitometer. Absorbance data were obtained from the BCD output of the Cary 17-D and the wavelength was determined by counting the monochromator stepping motor pulses and using these data to augment an entered initial value. The spectral output was recorded on magnetic tape and after processing was plotted on a Calcomp plotter at the Texas A&M Data Processing Center.

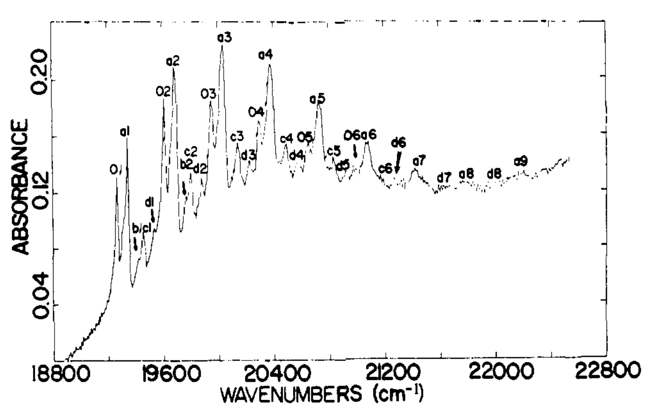

Figure 2. An expanded view of the electronic absorption spectra of $Mo_2[(CH_2)_2P(CH_3)_2]_4$ in the 20 000-cm⁻¹ region.

Results

According to the recently reported[13] solution spectra of the dichromium and dimolybdenum compounds, the molybdenum compound has transitions with maxima at 19 950 cm^{-1} (ϵ 660 cm^{-1} M^{-1}), 32 600 (1805), 36 600 (5675), and 46 400 (11 800).

The pellet spectrum of the molybdenum compound at 5 K is shown in Figure 1. A well-resolved band was observed at ≈20 000 cm^{-1}. In addition shoulders were observed at about 32 000, 35 000, and 38 500 cm^{-1}. The band at 38 500 cm^{-1} was not resolved in the reported room temperature solution spectrum, but the band at 36 600 cm^{-1} was asymmetric and probably hid this feature.

The transition at 20 000 cm^{-1} displayed vibrational structure even in the room temperature solution spectrum. The frequency of the vibrational spacing was reported to be 320 cm^{-1}. The vibrational structure observed for the pellet is shown in Figure 2. This figure is drawn from data collected every 0.2 nm and the resolution is slightly less than that observed on the spectrophotometer strip chart recorder. The structure is remarkably well resolved for a KBr pellet. Five different origins can be observed and one series can be followed for nine members. The vibrational frequencies for the progressions are listed in Table I.

All five Franck-Condon progressions are based on a single totally symmetric stretching mode with a frequency of 345 cm^{-1}. This is somewhat larger than the 320 cm^{-1} previously reported[13] but is more consistent with the values observed for the metal-metal stretching frequency in other quadruply bonded molybdenum dimers. The 345 cm^{-1} for the ylide complex is lower than the 350-355 cm^{-1} observed in the electronic spectrum of the dimolybdenum tetracarboxylates[4,5] but greater than that observed[6] in $Mo_2Cl_8^{4-}$. This intermediate magnitude in the excited state is consistent with the magnitudes in the ground states. The $Mo_2(O_2CR)_4$ compounds have the highest ν_{Mo-Mo} values[15] (ca. 400 cm^{-1}) while $[Mo_2Cl_8]^{4-}$ has a much lower frequency[7] (ca. 350 cm^{-1}, varying slightly with the counterion in the crystal). The Raman spectrum[16] of $Mo_2[(CH_2)_2P(CH_3)_2]_4$ has a band at 388 cm^{-1} that may be assigned to ν_{Mo-Mo}.

Both the energy (ca. 20 000 cm^{-1}) of the electronic transition and the fact that all progressions are built on the metal-

Table I. Frequencies of Vibrational Components in the Absorption Spectrum of $Mo_2[(CH_2)_2P(CH_3)_2]_4$

band	cm^{-1}	$\Delta\nu$[a] (band-band)	$\Delta\nu'$[b] (origin to band)
0-1	19 268		
a-1	19 346		75
b-1	19 421		153
c-1	19 455		187
d-1	19 535		267
0-2	19 616	347	
a-2	19 693	346	77
b-2	19 771	349	155
c-2	19 802	346	186
d-2	19 881	345	265
0-3	19 956	340	
a-3	20 040	347	88
b-3	20 121	350	164
C-3	20 147	345	190
d-3	20 227	345	270
0-4	20 296	340	
a-4	20 387	347	91
c-4	20 492	344	195
d-4	20 576	349	279
0-5	20 644	347	
a-5	20 730	342	85
c-5	20 833	341	189
d-5	20 925	348	280
0-6	20 990	346	
a-6	21 075	345	84
c-6	21 173	339	182
d-6	21 277	351	285
a-7	21 418	343	
d-7	21 631	354	
a-8	21 763	344	
d-8	21 978	347	
a-9	22 148	385	
av $\Delta\nu$		345.6 ± 3.5	

[a] Difference between two successive bands in the same series. [b] Difference between a band and the nearest origin (0-progression) member.

metal stretching frequency provide support for an assignment as $^1A_{2u} \leftarrow {}^1A_{1g}$ ($\delta^* \leftarrow \delta$).

While only one vibrational frequency is observed in the Franck-Condon progressions, it is obvious that there are two different sets of Franck-Condon intensities. The 0-0 transition (labeled **0**-1 in Figure 2) is about three-quarters as intense as the pseudoorigin labeled **a**-1. Yet by the third and fourth members this intensity ratio has changed. The fact that there are two sets of intensities is also borne out by the fact that the **0** progression maximizes in the second member while the **a** progression maximizes in the third. Furthermore, the series labeled **a** can be observed for nine members while the origin series (**0**) shows only six members.

The existence of different Franck-Condon factors in progressions built on the same vibration is a situation analogous to that observed in $Mo_2(O_2CCH_3)_4$,[5] where it was explained by using the totally symmetric vibration as the basis of a Franck-Condon series and also for Herzberg-Teller coupling for the dipole allowed contributions.

The theory of such a situation was first discussed by Craig and Small.[17] As they noted, it is possible to expand the transition moment $M_{fg}(Q)$ in a Maclauren series and truncate after the second term to yield

$$\mathbf{M}_{fg}(Q) = \mathbf{M}_0 + \mathbf{m}_i Q_i \text{ where } \mathbf{m}_i = \left(\frac{\delta M}{\delta Q_i}\right)_{Qi} = 0$$

Since the intensity of a transition is proportional to the transition moment squared and assuming the adiabatic Born-Oppenheimer approximation, one may write

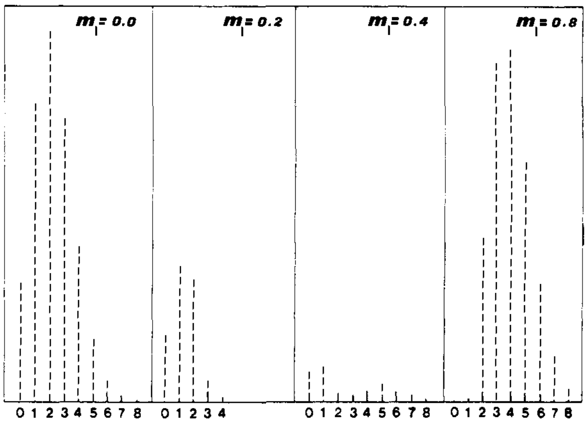

Figure 3. Intensities calculated for vibrational progressions. See text for discussion of method and parameter choices.

$$\begin{aligned}\mathbf{M}_{g0,fv_i'} = {} & [\mathbf{M}_0{}^2\langle g0||fv_i'\rangle^2 \\ & + 2\mathbf{M}_0 m_i\langle g0||fv_i'\rangle\langle g0|Q_i|fv_i'\rangle \\ & + \mathbf{m}_i{}^2\langle g0|Q_i|fv_i'\rangle^2]\prod_{j\neq i}\langle g0||fv_j'\rangle^2 \quad (1)\end{aligned}$$

The functions $\langle g0|$ and $|fv_i'\rangle$ represent the 0th vibrational level in the ground electronic potential and the v_ith vibration in the final electronic state, respectively. Usually only the first term of eq 1 is observed in a dipole-allowed transition. For a dipole-forbidden transition $M_0 = 0$ and only the third term provides observed intensity. However, for a dipole-allowed transition only, Q_i can be a totally symmetric vibration and all three terms can provide intensity.

The presence of the additional terms will distort the Franck-Condon progressions for the dipole-allowed components. Since the series labeled **0** is the progression with the lowest energy it is taken to be the dipole-allowed origin and band **0**-1 is the 0-0 transition. Therefore, the series labeled **0** can be a distorted series. The series labeled **a**, **c**, and **d** all display similar intensity ratios and are assigned as vibronic in origin arising from coupling where Q_i is an e_g vibration in the C_{4h} symmetry of the molecule. These progressions are not distorted by additional coupling and display the unperturbed Franck-Condon intensities. The series labeled **b** appears to have intensity ratios similar to those of **0** and is, therefore, also assumed to be based on a totally symmetric vibration.

Franck-Condon and Herzberg-Teller overlap intergrals were evaluated from Hutchisson's[18] formula by the method of Yeung.[19] The ground-state metal-metal stretching frequency was assumed to be 388 cm^{-1} from the Raman spectrum, and the excited-state frequency was the observed 345 cm^{-1}. The reduced mass was taken to be that of two molybdenum atoms, i.e., 48 amu. The calculations were made assuming various values for the change, Δr, in the equilibrium bond distance between the ground and excited electronic states. The best agreement was obtained with $\Delta r = 0.092$ Å, which is in good agreement with the value of about 0.1 Å observed for $Mo_2(O_2CCH_3)_4$.[4,5] The results for several values of $m_i\Delta r/M_0$ (indicated as m_i in the figure) are shown in Figure 3.

The intensities for the pure Franck-Condon progression are in good agreement with those observed for the progressions **a**, **c**, and **d**. Similarly when $m_i\Delta r/M_0 = 0.2$, the calculated series has a shape similar to that observed for the **0** progression. It is to be noted that larger values of $m_i\Delta r/M_0$ give rise to progressions having a quite different appearance. The value of 0.2 is slightly less than the 0.3 observed in $Mo_2(O_2CCH_3)_4$,[5] but this is not surprising since the $\delta^* \leftarrow \delta$ transition in the solution spectrum of the ylide compound has an intensity of 660 cm^{-1} M^{-1} vs. only about 120 cm^{-1} M^{-1} in $Mo_2(O_2CCH_3)_4$. The fact that this vibronic coupling is occurring at all in a band of this intensity is in itself interesting.

The Raman spectrum[16] of the molybdenum compound, in addition to providing a value for ν_{Mo-Mo} in the ground state, gives data from which we may construct a plausible account of the origins of each of the four progressions (**a–d**) that do not begin with the 0–0 transition. The origin of the **a** progression, **a**-1, is at 75 cm^{-1} above the 0-0 transition (peak **0**-1). The Raman spectrum was recorded only down to ca. 100 cm^{-1} and thus we must assume, but cannot check, that there is a fundamental vibration of about this frequency. This vibration would have to be of e_g symmetry because of the Franck–Condon factors of the **a** progression (vide supra), It is assigned as an e_g ring deformation mode. The next origin peak, labeled **b**-1, has a frequency of 153 cm^{-1} above the 0-0 band. In the Raman spectrum a strong band is observed at 144.6 cm^{-1}. As this is a vibration of a_1 symmetry it may reasonably be assigned to the totally symmetric Mo–C bending frequency. The other observed origins are 187 and 267 cm^{-1} above the 0-0 band. Bands are observed in the Raman spectrum at 190.1 and 274.8 cm^{-1}, both of which bands must be of e_g symmetry. The 190.1-cm^{-1} vibration may be assigned as the e_g Mo–C bending mode and the 274.8-cm^{-1} band as an e_g Mo–C stretching mode. The progressions labeled **b, c,** and **a** are weak because they are only weakly coupled to the change in the metal–metal distance that results from the $\delta^* \leftarrow \delta$ excitation.

Severe experimental problems were encountered in recording spectra of $Cr_2[(CH_2)_2P(CH_3)_2]_4$ because this compound is far more sensitive to air than its molybdenum analogue. All KBr pellets showed some evidence of decomposition, and, in fact, the pellets appeared to decompose faster than the pure compound, which suggests that interaction with the KBr is significant. In any case the quality of the spectra obtained was quite low,

The previously published solution spectra displayed only two well-resolved bands at 22 100 and 46 000 cm^{-1}. At 5 K weak vibrational fine structure was observed on the band at 22 100 cm^{-1}. The separation between the peaks was ca. 400 cm^{-1} and there appear to be several progressions. However, the quality of the spectra was too poor to allow a firm conclusion as to whether the lowest energy feature at 19 700 cm^{-1} is truly the 0–0 band. In addition, the spectrum of a totally decomposed pellet displayed the same intense feature at 22 000 cm^{-1} but without the vibrational structure. It is assumed then that this band is due to the decomposition product. As its maximum occurs where the band in the reported solution spectrum occurs, there is clearly some ground for uncertainty as to the genuineness of this feature in the solution spectrum.

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References and Notes

(1) See: Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225. Trogler, W. C.; Gray, H. C. *Ibid.*, **1978**, *11*, 232. Chisholm, M. H.; Cotton, F. A. *Ibid.* **1978**, *11*, 356.

(2) Cotton, F. A.; Stanley, G. G. *Inorg. Chem.* **1977**, *16*, 2668.

(3) Cotton, F. A.; Martin, D. S.; Webb, T. R.; Peters, T. J. *Inorg. Chem.* **1976**, *15*, 1199.

(4) Trogler, W. C.; Solomon, E. I.; Trajberg, I. B.; Ballhausen, C. J.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 828.

(5) Martin, D. S.; Newman, R. A.; Fanwick, P. E. *Inorg. Chem.*, in press.

(6) Fanwick, P. E.; Martin, D. S.; Cotton, F. A.; Webb, T. R. *Inorg. Chem.* **1977**, *16*, 2103.

(7) Clark, R. J. H.; Franks, M. L. *J. Am. Chem. Soc.* **1975**, *97*, 2691.

(8) Cotton, F. A.; Martin, D. S.; Fanwick, P. E.; Peters, T. J.; Webb, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 4681.

(9) Sattelberger, A. P.; Fackler, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 1258.

(10) (a) Norman, J. G., Jr.; Kolari, H. J. *J. Am. Chem. Soc.* **1975**, *97*, 33. (b) Norman, J. G., Jr.; Kolari, H. J.; Gray, H. B.; Trogler, W. C. *Inorg. Chem.* **1977**, *16*, 987.

(11) Cotton, F. A.; Ilsley, W.; Rice, G. W. *Inorg. Chem.*, in press.

(12) Kurras, E.; Rosenthal, V.; Mennenga, H.; Oehme, G. *Z. Chem.* **1974**, *14*, 160. Kurras, E.; Mennenga, H.; Oehme, G.; Rosenthal, U. *J. Organomet. Chem.* **1975**, *84*, C13.

(13) Böhmer, W.-H.; Madeja, K.; Kurras, E.; Rosenthal, U. *Z. Chem.* **1978**, *18*, 453.

(14) Fanwick, P. E.; Martin, D. S.; Cotton, F. A.; Webb, T. R. *Inorg. Chem.* **1977**, *16*, 2103.

(15) Bratton, W. K.; Cotton, F. A.; Debeau, M.; Walton, R. A. *J. Coord. Chem.* **1971**, *1*, 121.

(16) We thank Professor D. F. Shriver for making this measurement.

(17) Craig, D. P.; Small, G. J. *J. Chem. Phys.* **1969**, *50*, 3827.

(18) Hutchisson, E. *Phys. Rev.* **1930**, *36*, 410.

(19) Yeung, E. S. *J. Mol. Spectrosc.* **1973**, *45*, 142.