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Upper Electronic Excited States of Quadruply Bonded $M_2X_4(PMe_3)_4$ Complexes

Michael D. Hopkins,*[†] Vincent M. Miskowski,* and Harry B. Gray*

Contribution No. 7632 from the Arthur Amos Noyes Laboratory, California Institute of Technology, Pasadena, California 91125, and the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109. *Received July 22, 1987*

Abstract: The electronic spectra of $Mo_2X_4(PMe_3)_4$ (X = Cl, Br, I) and $W_2Cl_4(PMe_3)_4$ have been measured in solutions (300 and 77 K) and single crystals (300 and 5 K). Systematic shifts of the electronic transitions among the various compounds, analysis of polarizations and vibronic structure, and comparisons to calculations and photoelectron data have facilitated detailed assignments. Three strong, well-defined bands are assigned as follows: $^1(\delta \rightarrow \delta^*)$, ν_{max} 15000–17000 cm^{-1}, ϵ_{max} 3000–5000, strongly $\|z$-polarized, vibronically structured in $\nu(Mo_2) \sim 330$ cm^{-1}; $^1(\sigma(MP) \rightarrow \delta^*)$, ν_{max} 25000–34000 cm^{-1}, ϵ_{max} 4000–11000, strongly $\perp z$-polarized, weakly structured (in one case) in $\nu(MoP) \sim 180$–190 cm^{-1}; $^1(\pi \rightarrow \delta^*)$, ν_{max} 20000–23000 cm^{-1}, ϵ_{max} 200–500, strongly $\perp z$-polarized, weakly structured (in one case) in $\nu(Mo_2) \sim 320$ cm^{-1}. In addition, two weaker features are assigned to $^3(\sigma(MP) \rightarrow \delta^*)[\nu_{max}$ 23000–30000 cm^{-1}, weak shoulder, mixed polarization ($\perp z > \|z$), unstructured] and $^3(\sigma \rightarrow \delta^*)[\nu_{max}$ 18000–21000 cm^{-1}, mixed polarization ($\|z > \perp z$), sharply structured in $\nu(Mo_2)$ 330–350 cm^{-1}] transitions.

Electronic spectroscopic investigations of the $^1(\delta \rightarrow \delta^*)$ transitions of complexes containing quadruple metal–metal bonds have been the cornerstone of experimental efforts to elucidate the electronic characteristics of the δ-bond.[1–5] In contrast to the abundance of effort devoted to this one absorption band, however, studies leading to the assignments of the higher energy transitions in the absorption spectra of these systems have not been vigorously pursued.[6] This lack of activity is curious in view of the fact that analyses of the vibronic structure, intensities, and energies of such bands are of central importance in determining the electronic properties of not only the excited states that are populated by these transitions but also the one-electron orbitals between which these excitations occur. While carefully considered assignments for the bands lying to higher energy of $^1(\delta \rightarrow \delta^*)$ have been reached for a few quadruply bonded complexes (e.g., $Re_2Cl_8^{2-}$,[7,8] $Mo_2Cl_8^{4-}$,[9] $Mo_2(SO_4)_4^{4-}$[10]), no systematic studies of the dependence of the energies of these electronic excited states upon the nature of the coordination sphere and central dimetal unit have been carried out, as have been for the $^1(\delta \rightarrow \delta^*)$ bands of several classes of quadruply bonded compounds.[11,12]

We recently reported the initial results of a concerted effort to explore the extent to which the molecular and electronic structures of complexes of the $M_2X_4L_4$ type (M = Mo, W; X = Cl, Br, I; L = uncharged σ-donor ligand) are perturbed by ligand and metal, as manifested in the vibrational and electronic spectroscopic, crystallographic, magnetic, and photophysical properties of these species.[11,13] Our interest in this particular class of compounds is motivated by the fact that the wide range of derivatives available facilitates the delineation of metal–metal and metal–ligand localized electronic structural properties. We now bring this advantageous aspect of these species to bear on the problem of the nature of the higher energy electronic excited states of quadruply bonded dimers. Reported herein are the assignments of the electronic transitions present in the single-crystal polarized absorption spectra of $Mo_2Cl_4(PMe_3)_4$ and $Mo_2Br_4(PMe_3)_4$, as well as an analysis of the dependence of the energies, intensities, and vibronic structure of these bands on the nature of the halide ligand and metal.

Experimental Section

The compounds $Mo_2X_4(PMe_3)_4$ (X = Cl, Br, I)[11] and $W_2Cl_4(PMe_3)_4$[14] were prepared by standard procedures. Single-crystal absorption studies employed previously described[10] equipment and techniques.

Single crystals of $Mo_2Br_4(PMe_3)_4$ and $Mo_2Cl_4(PMe_3)_4$ were obtained by slow evaporation of toluene and dichloromethane solutions, respectively. The crystal thicknesses of $Mo_2Br_4(PMe_3)_4$ samples were measured with a micrometer. The crystal of $Mo_2Cl_4(PMe_3)_4$ that provided the data presented here did not survive warmup to room temperature after the experiment, so the crystal thickness (hence, crystal electronic absorption extinction coefficients) could not be determined. The crystal faces of these isomorphous ($C2/c$) dimers were determined by X-ray photographic methods and polarized optical microscopy. Polarized single-crystal spectra were recorded of their prominent (101) face; the molecular z axis is colinear with the crystallographic b axis, which is contained by this crystal face (see ref 11, Figure 1). Under the crystallographically imposed C_2 symmetry of these dimers, polarization parallel to molecular z ($\| b$) is rigorously split from that parallel to x- and $y(\perp b)$. Consistent with this, examination of the (101) crystal face under a polarizing microscope showed sharp extinctions parallel and perpendicular to b that transmitted dark blue and light greenish-yellow light, respectively. Although the molecular x and y directions are not strictly equivalent under C_2 symmetry, the deviations of the molecular structures of $Mo_2Cl_4(PMe_3)_4$ and $Mo_2Br_4(PMe_3)_4$ from D_{2d} symmetry, for which x and y are degenerate, are quite small.

We have not yet succeeded in obtaining crystals of $Mo_2I_4(PMe_3)_4$ and $W_2Cl_4(PMe_3)_4$ that are suitable for single-crystal spectroscopy.

Theory and Photoelectron Spectroscopy

Figure 1 summarizes the orbital energies resulting from two recent theoretical calculations[15,16] on the model complex Mo$_2$-

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[†] Present address: Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260.

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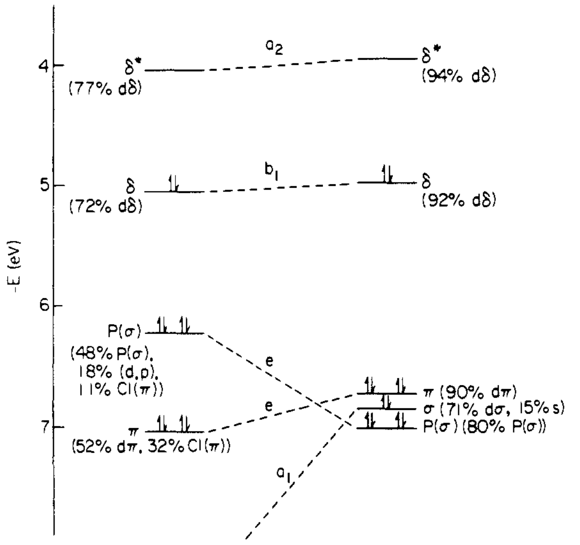

Figure 1. Comparison of calculated orbital energy levels for $Mo_2Cl_4(PH_3)_4$: left-hand side, ref 15; right-hand side, ref 16. Orbital parentages are for Mo levels unless specified otherwise.

Table I. Electronic Absorption Data for $M_2X_4(PMe_3)_4$ Compounds in 2-Methylpentane Solution at 300 K[a]

		band			
M	X	I[b]	II[b]	III	IV
Mo	Cl	17 090 (3110)	30 860 (3720)	22 680 (210)	25 300 (75)
	Br	16 720 (4060)	28 990 (6650)	21 880 (310)	*c*
	I	15 720 (5250)	25 350 (11 850)	20 240 (460)	19 530 (470)
W	Cl	15 150 (4170)	34 130 (9090)	20 275 (290)	*c*

[a] Energies are in cm^{-1}; extinction coefficients are given in parentheses. Bands III and IV are designated in Figures 3 and 4. [b] Reference 11. [c] Not resolved.

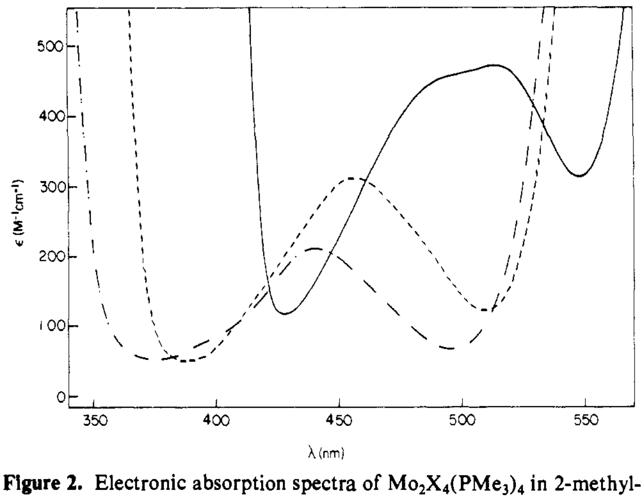

Figure 2. Electronic absorption spectra of $Mo_2X_4(PMe_3)_4$ in 2-methylpentane at room temperature in the region between bands I and II; X = I (—); X = Br (---); X = Cl(-····-).

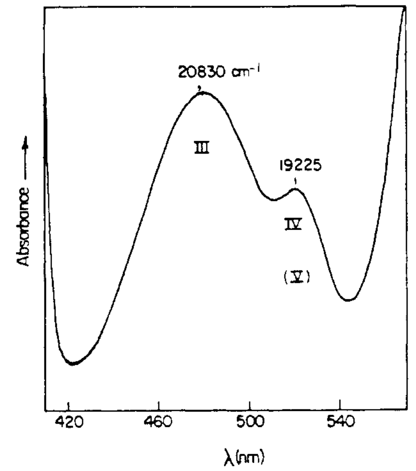

Figure 3. Electronic absorption spectrum of $Mo_2I_4(PMe_3)_4$ in 2-methylpentane at 77 K in the region between bands I and II.

$Cl_4(PH_3)_4$. While both calculations bear out the energetic ordering of metal–metal orbitals that is derived from qualitative theoretical considerations, namely $\delta^* > \delta > \pi > \sigma$, and are in excellent agreement as to the δ^*, δ, and π orbital energies, they differ in several crucial respects. First, the ordering of the orbitally degenerate $e(\pi(Mo_2))$ and $e(\sigma(MoP))$ levels is inverted in the two schemes, with the latter lying nearly 1 eV higher than the former in the Cotton calculation[15] but 0.3 eV below $e(\pi(Mo_2))$ in the energy level diagram arrived at by Ziegler.[16] More glaring is the large discrepancy in the placement of $\sigma(Mo_2)$; the Ziegler and Cotton calculations place it 0.1 and 4.4 eV, respectively, below $\pi(Mo_2)$. A SCF–Xα–SW calculation on $W_2Cl_4(PH_3)_4$, performed in the same fashion as that for its molybdenum analogue, also indicated a large energy gap between the metal–metal π and σ levels.[15]

Although the photoelectron data for $Mo_2Cl_4(PMe_3)_4$[15] and $W_2Cl_4(PMe_3)_4$[15,17] were originally interpreted within the framework of the SCF–Xα–SW results,[15] the spectrum of the latter compound has recently been shown to provide strong evidence for the near energetic equivalency of the metal–metal σ and π levels.[17] While the σ ionization of the molybdenum complex has not been observed (perhaps because it lies within the ionization envelope of the π level),[18] a similar conclusion would appear to be justified in light of the concensus on this point that has been reached from theoretical and photoelectron spectroscopic studies on related dimolybdenum systems.[19] The photoelectron data also indicate that $\sigma(MoP)$ lies below $\pi(Mo_2)$, again in agreement with the Ziegler calculation.

Taking the Ziegler calculation as our benchmark, we thus infer from the right-hand side of Figure 1 that four orbital transitions (eight electronic transitions, considering that both singlet and triplet excited states are possible) may occur below ~3 eV: the transitions from δ, π, σ, and $\sigma(MoP)$ to δ^* (where we have dropped the (Mo_2) designation for metal-based orbitals). Assuming that the calculations and/or photoelectron data give good one-electron energy separations, all of the designated transitions are reasonable candidates for near-UV–visible excitations, although there will be two-electron contributions to all transition energies, usually increasing them; the $^1(\delta \rightarrow \delta^*)$ transition energy is additionally subject to significant configuration interaction.[5] In addition to these transitions, past work[8] indicates $\delta \rightarrow \pi^*$ to be a candidate for a fairly low energy excitation. While none of the available theoretical or experimental work provides an estimate of a one-electron energy difference of these orbitals for the $Mo_2X_4(PMe_3)_4$ class of complexes, previous studies[8,10,20] on related systems suggest that this excitation lies to higher energy of $\pi \rightarrow \delta^*$.

The photoelectron data for $W_2Cl_4(PMe_3)_4$ indicate that the optical spectrum of this complex in the near-UV–visible region should display the same electronic transitions as are observed for $Mo_2Cl_4(PMe_3)_4$, with one important energetic distinction between the two: all metal–metal levels (such as δ^*) are indicated to be significantly destabilized relative to ligand levels in the tungsten

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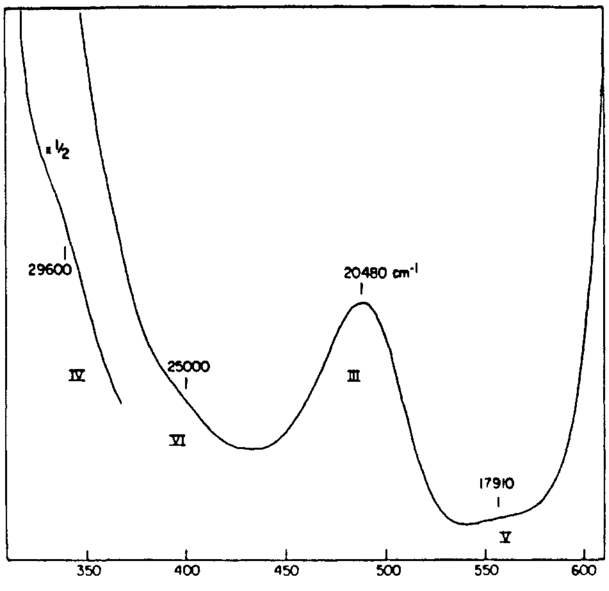

Figure 4. Electronic absorption spectrum of $W_2Cl_4(PMe_3)_4$ in 2-methylpentane at 77 K in the region between bands I and II.

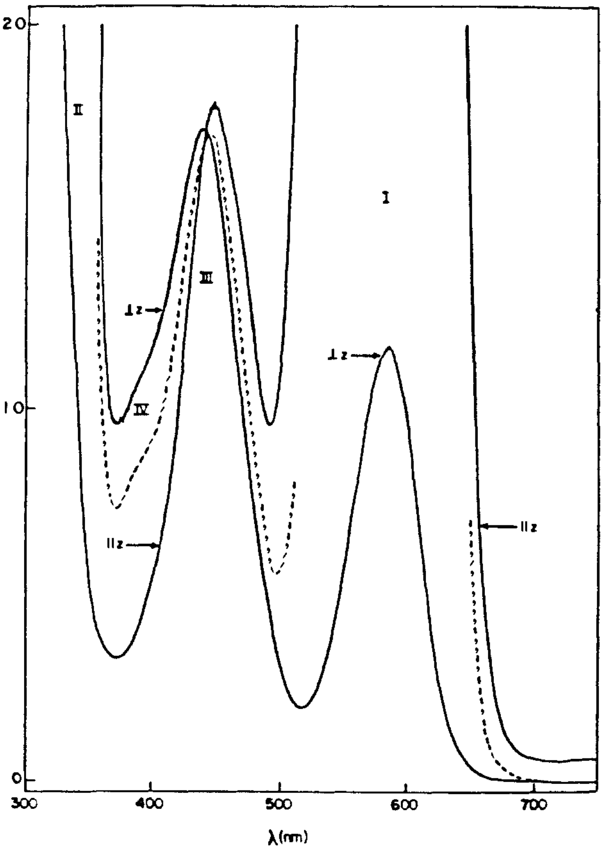

Figure 5. Single-crystal ((101) face) electronic absorption spectra of $Mo_2Cl_4(PMe_3)_4$ at room temperature. Band polarizations refer to the Mo–Mo axis. The $\parallel z$ spectrum is offset from the $\perp z$ spectrum by 0.06 optical density units. The dashed line is the calculated isotropic spectrum $^1/_3(\mathrm{OD}(\parallel z) + 2\ \mathrm{OD}(\perp z))$, with the $\perp z$ base line.

system. It is therefore expected that $\sigma(\mathrm{MP}) \rightarrow \delta^*$ will be strongly blue-shifted for $W_2Cl_4(PMe_3)_4$ relative to its position in molybdenum dimers, whereas metal–metal-localized excitations should shift to a smaller extent.

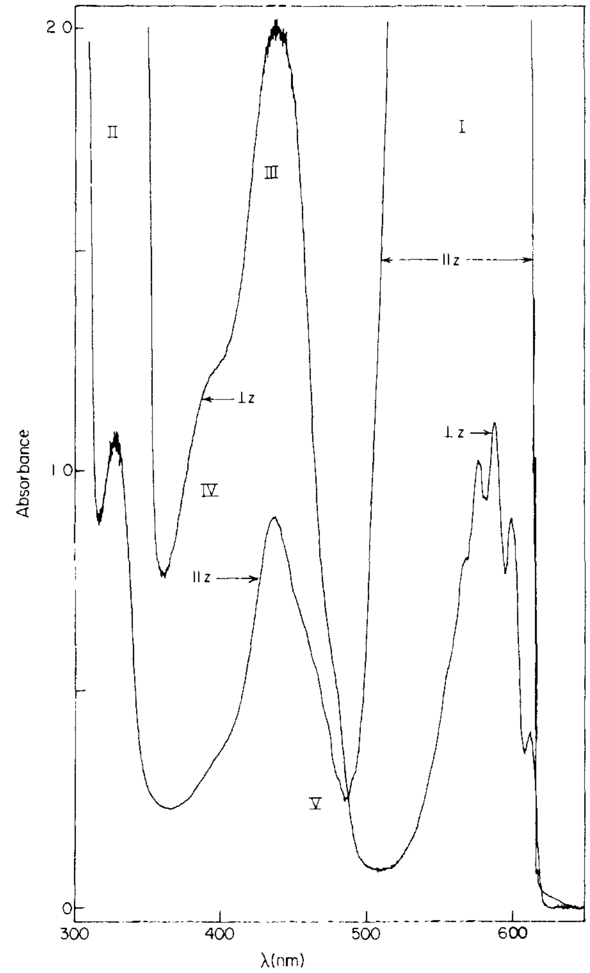

Figure 6. Spectra (Figure 5) at 5 K.

Solution Electronic Spectra

Solution electronic spectra of the $Mo_2X_4(PMe_3)_4$ complexes and $W_2Cl_4(PMe_3)_4$ are summarized in Table I. There are two dominant bands, labeled I and II, that have been discussed elsewhere.[11] The spectra additionally display a much weaker band of intermediate energy, labeled III, as shown in Figure 2 for the molybdenum compounds.

The spectra of $Mo_2Cl_4(PMe_3)_4$ and $Mo_2I_4(PMe_3)_4$ show very weak shoulders on the high- and low-energy flanks, respectively, of band III, which are designated as band IV. The relative intensity of band IV for the iodo complex is well-illustrated in a 77 K spectrum (Figure 3), where it is better resolved and clearly much weaker than band III.[21]

The compound $W_2Cl_4(PMe_3)_4$ does not display any resolved weak features other than band III in solution at room temperature, but a 77 K spectrum (Figure 4) shows three additional weak features labeled IV–VI.

Solid-State Electronic Spectra

We have obtained polarized single-crystal absorption spectra of $Mo_2Cl_4(PMe_3)_4$ and $Mo_2Br_4(PMe_3)_4$—hereafter we will usually refer to these compounds as the chloride and bromide—and alkali-halide pellet spectra in the region of bands I and II (which are too intense in their allowed polarizations to be measured for

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(21) These weak features are genuine transitions of the $Mo_2X_4(PMe_3)_4$ chromophore: absorption and $^1(\delta^* \rightarrow \delta)$ fluorescence[13a] excitation spectra are identical for $\lambda > 250$ nm.

(22) Reproductions of the low-temperature, $\perp z$-polarized single-crystal spectra in the region of band I for $Mo_2Cl_4(PMe_3)_4$ and $Mo_2Br_4(PMe_3)_4$ are available as supplementary material.

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(24) The $\parallel z$ temperature-dependent intensity of the band is about the same as that of the forbidden polarization, vibronically induced intensities of bands I and II. For our assignments of bands I, II, and III, the off-polarization vibronically active vibrations would be of e symmetry. Examples of such intensity approaching that of the dipole-allowed electronic transition are the $^1(\delta \rightarrow \delta^*)$ transitions of compounds of the $Mo_2(O_2CR)_4$ class;[3] the vibronically induced intensity seen for such systems is similar to that observed here.

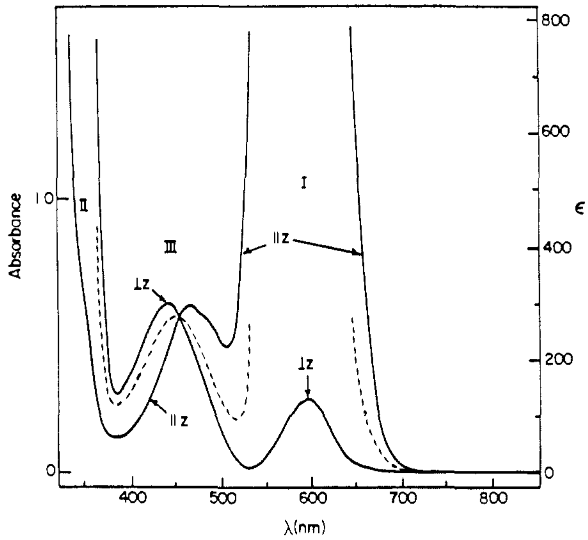

Figure 7. Single-crystal ((101 face) electronic absorption spectra of $Mo_2Br_4(PMe_3)_4$ at room temperature. Band polarizations refer to the Mo–Mo axis. The dashed line is an isotropic spectrum calculated by $^1/_3(\epsilon(\|z) + 2\epsilon(\perp z))$.

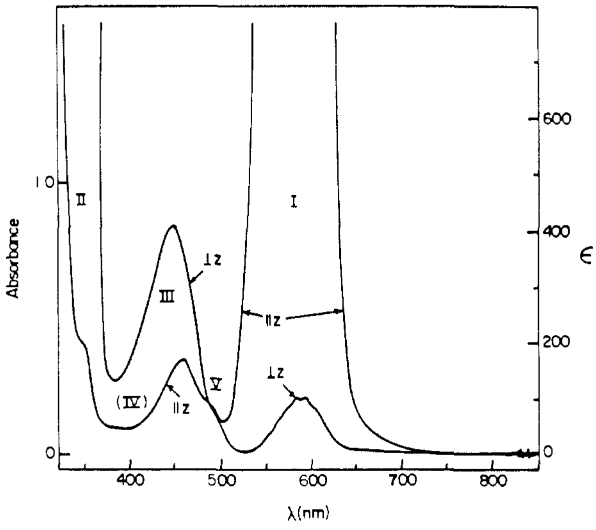

Figure 8. Spectra (Figure 7) at 40 K.

Table II. Electronic Absorption Data for Single Crystals of $Mo_2X_4(PMe_3)_4$ at 5 K[a]

	band				
X	I	II	III	IV	V
Cl	17070	30400	22880	25600	21050
	(∥)	(⊥)	(⊥)	(⊥ > ∥)	(∥ > ⊥)
Br	16800	28600	21830	~23500?	20400
	(∥)	(⊥)	(⊥)	⊥?	(∥ > ⊥)

[a] Energies are in cm^{-1}; the dominant polarizations relative to molecular z axis are given in parentheses. Bands I–V are designated in Figures 6 and 8.

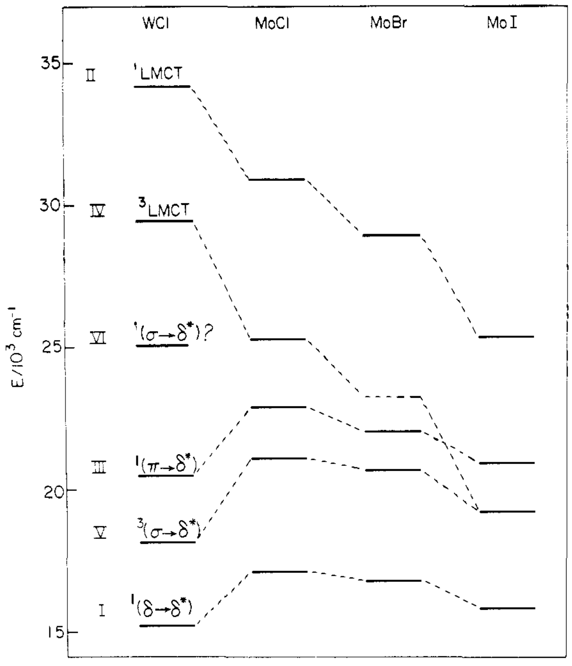

Figure 9. Correlation of excited states for the compounds of this study. Band designations are defined in Figures 3–8. LMCT ≡ (σ(MP) → δ*).

crystals) for all four compounds. The weaker absorption bands that lie between these intense features were ill-defined in the pellet spectra.

Polarized single-crystal spectra are presented in Figures 5–8. Much of the finer vibronic structure is not well represented in these reproductions, and high-resolution expansions will be subsequently presented. These spectra display bands I–IV, which are clearly analogous to those seen in solution (Table I), together with an extremely weak feature (band V) near 475 nm that is only observed in the helium-temperature spectra. The band positions observed in the crystal spectra are summarized in Table II. Calculated room temperature isotropic spectra ($^1/_3(\epsilon(\|z) + 2\epsilon(\perp z))$) are included in Figures 5 and 7; they agree well with the solution spectra. The close agreement of the isotropic extinction coefficient of band III for $Mo_2Br_4(PMe_3)_4$ in solution and crystals encourages us to assume the same for the chloride, in which case 1.0 optical density (OD) unit corresponds to $\epsilon = 140$ in Figures 5 and 6.

We correlate the data of Tables I and II, together with that of Figure 4, in Figure 9. The indicated assignments will be justified in the following sections. Considerable evidence as to the nature of bands I and II has already been presented.[11]

Band I

Band I, the $^1(\delta \rightarrow \delta^*)$ transition,[13a] is very strongly z-polarized. Assuming isotropic extinction coefficients on the order of those observed in solution (Table I), the $\|z/\perp z$ polarization ratio to be inferred from Figures 5–8 is ~100. Moreover the $\perp z$ component of both compounds undergoes a distinct decrease in oscillator strength upon cooling from 300 to 5 K, indicating that it is vibronically induced. This $\perp z$ component shows[22] a broad progression in quanta of ~340 cm^{-1}, which is attributable to the excited-state $\nu_1(Mo_2)$ (ground-state values: X = Cl, $\nu = 355\ cm^{-1}$; X = Br, $\nu = 352\ cm^{-1}$);[11] similar values are observed for this progression in a hydrocarbon glass at 77 K,[13a] and both the ν_1 frequency reduction in the excited state and the length of the progressions are typical of $^1(\delta \rightarrow \delta^*)$ transitions. It seems likely that multiple vibronic origins of e symmetry contribute to the poor resolution of the broad features. The $\|z$ vibronic structure is much sharper but difficult to interpret; it will be discussed in a separate publication. Importantly, we see no evidence for any features in this region not attributable to $^1(\delta \rightarrow \delta^*)$, so any other electronic transitions located near or within the $^1(\delta \rightarrow \delta^*)$ absorption envelope must be extremely weak.

Band II

Band II is very strongly $\perp z$-polarized. The weak $\|z$ component, which appears at roughly the same wavelength as the intense band II of solutions (Table I) for both the chloride and bromide, is resolved only at low temperature. Although its thermal behavior is not established, the finding that the intensity of the $\|z$ component is similar to that of the vibronically induced intensity of band I supports the idea that it is vibronically induced.

The strong $\perp z$-polarization of band II supports the ligand-to-metal charge-transfer (LMCT) assignment e(σ(MP) → δ*) that was arrived at previously.[11] As noted, the fact that II strongly blue-shifts upon substitution of W for Mo in $M_2Cl_4(PMe_3)_4$ (Table I) is uniquely consistent with an LMCT assignment. Moreover,

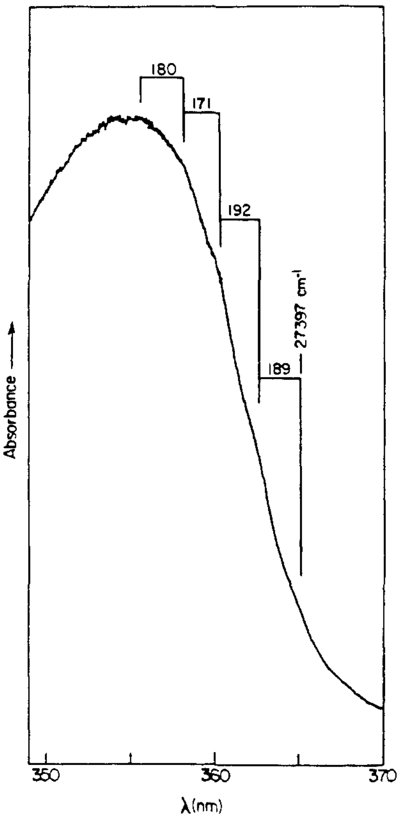

Figure 10. Absorption spectrum of a KBr pellet of $Mo_2Br_4(PMe_3)_4$ in the band II region at 5 K.

the halide dependence of the energy, intensity, and bandwidth of II is accounted for by the increasing mixing of this CT state with $\pi(X) \rightarrow \delta^*$ states as the energy of the latter decreases along the series Cl > Br > I. True $\pi(X) \rightarrow \delta^*$ LMCT transitions display much larger shifts along this series,[1,23] so a fairly small amount of mixing is involved, except for the iodide. We note that the $Mo_2Cl_8^{4-}$ ion does not display any intense CT absorptions below ~300 nm,[9,20] which is also consistent with the $\sigma(MP) \rightarrow \delta^*$ assignment for band II. Additional support for this assignment is provided by the low-temperature pellet spectrum of band II of the bromide complex (Figure 10), in which a ~180–190-cm^{-1} vibronic progression is seen as a series of shoulders. While this frequency is clearly too low to be $\nu_1(Mo_2)$ (ν_1 = 352 cm^{-1}) and too high to be $a_1\nu_2(MoBr)$ (ν_2 = 159 cm^{-1}), it is similar to the 235-cm^{-1} frequency that has been attributed to the $a_1\nu(MoP)$ mode of the chloride;[11] since a considerable force-constant reduction is expected in a P → Mo excited state, the ~180–190-cm^{-1} frequency is very reasonable for $\nu(MoP)$.

Band IV

We now consider one consequence of our assignment of band II. Because of its high intensity, band II must be the $^1(\sigma(MP) \rightarrow \delta^*)$ transition, and there will thus be a corresponding transition of triplet multiplicity to lower energy. It should be distinguished by a ligand dependence similar to that of the singlet transition and it will, of course, be much weaker than the spin-allowed transition. Since $^1A_1 \rightarrow {}^3E$ is orbitally allowed in both $\|z$- and $\perp z$-polarizations (via the B_2 and E spin–orbit components of ^3E), it should, moreover, be of mixed polarization.

We note from Figure 9 that band IV of the solution spectra shows a ligand dependence similar to that of band II, and dissimilar to those of the other absorptions. In addition, band IV is observed in the crystal spectra of the chloride to have mixed polarization, with the intensity in $\perp z$-polarization somewhat greater than $\|z$. We thus assign band IV to the $^3(\sigma(MP) \rightarrow \delta^*)$ transition. Unfortunately, no vibronic structure was seen, and the thermal behavior is obscured by surrounding bands.

An analogue for band IV is not well-defined in the crystal spectra of the bromide complex. Band III of these spectra is slightly asymmetric to shorter wavelength, perhaps hinting at a broad band IV near 425 nm.

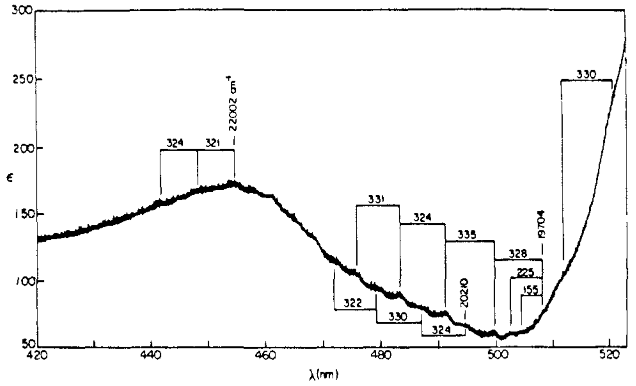

Figure 11. The $\|z$-polarized absorption spectrum of a single crystal of $Mo_2Br_4(PMe_3)_4$ at 5 K showing the weak bands at high resolution. The 330-cm^{-1} interval indicated on the far right of the figure is part of the $\nu(Mo_2)$ progression of the $^1(\delta \rightarrow \delta^*)$ transition.

Band III

Band III appears in both $\|z$- and $\perp z$-polarizations, but with markedly different temperature dependences. In $\perp z$-polarization, the peak intensity increases and the band sharpens at low temperature for both the chloride and bromide, which is indicative of a dipole-allowed transition, while in $\|z$-polarization the intensity clearly decreases at low temperature. The absorption maximum appears to be at longer wavelength in $\|z$- than in $\perp z$-polarization at room temperature, but this disparity is greatly reduced at 5 K, suggesting that it is due to overlap with adjacent bands (particularly $^1(\delta \rightarrow \delta^*)$) that sharpen considerably at low temperature.

The energy of band III varies with metal and halide in a similar fashion to that of the $^1(\delta \rightarrow \delta^*)$ transition (band I), which implies that III is metal–metal-localized. This fact, in conjunction with its dipole-allowed character in $\perp z$-polarization, leads us to assign band III to the $^1(\pi \rightarrow \delta^*)$ transition. The low intensity of $^1(\pi \rightarrow \delta^*)$ is understandable both in terms of the very weak mutual overlap of the π- and δ-symmetry orbitals and by its correlation to a dipole-forbidden transition in the parent D_{4h} symmetry of quadruply bonded complexes.[24]

The $^1(\pi \rightarrow \delta^*)$ transition would be expected to exhibit a longer vibronic progression in $\nu(Mo_2)$ than that of $^1(\delta \rightarrow \delta^*)$ as a result of the depopulation of the more strongly metal–metal-bonding π orbital. Although the band envelope of the chloride complex is featureless, we do see some vibronic structure for the bromide complex, as shown in Figure 11. While the $\|z$-polarization of the bromide has a highly structured shoulder (band V) with weak structure persisting into band III, it seems unreasonable that the band V structure could extend to as short a wavelength as observed. Moreover, the intervals found in the ~460–470-nm region are irregular, suggesting that vibronic structure due to the two different electronic transitions overlaps here. Accordingly, we have picked out a ~320-cm^{-1} progression near the maximum of band III, consistent with assignment to a $\nu(Mo_2)$ that is slightly lower than that of the $^1(\delta\delta^*)$ state (vide supra).

Our $^1(\pi \rightarrow \delta^*)$ assignment for band III makes the splitting of the $^1(\pi \rightarrow \delta^*)$ and $^1(\sigma(MP) \rightarrow \delta^*)$ transitions for $Mo_2Cl_4(PMe_3)_4$ and $W_2Cl_4(PMe_3)_4$ roughly 1 and 1.7 eV, respectively, versus respective 0.7 and 1.3 eV energy gaps measured for the π and $\sigma(MP)$ levels by photoelectron spectroscopy.[15] The agreement is satisfactory, given that contributions to the energies of interconfigurational transitions arising from two-electron terms will only approximately cancel when the difference in energy is taken. The $^1(\pi \rightarrow \delta^*)$ assignment is also consistent with that recently arrived at for the analogous transition in the absorption spectrum of $Mo_2(SO_4)_4^{4-}$.[10] While the energy of the $^1(\pi \rightarrow \delta^*)$ transition of this complex is higher (λ_{max} = 400 nm) than any of the corresponding absorptions of the $M_2X_4(PMe_3)_4$ series, the energy difference between $^1(\pi \rightarrow \delta^*)$ and $^1(\delta \rightarrow \delta^*)$ of the sulfato-bridged dimer (5580 cm^{-1}) is nearly identical with that observed for $Mo_2Cl_4(PMe_3)_4$ (5590 cm^{-1}), consistent with our observations of the similar dependences of the energies of metal–metal-localized transitions (Figure 9).

It is worth considering this last point in more detail for the $^1(\pi \rightarrow \delta^*)$ transitions of the $Mo_2X_4(PMe_3)_4$ class, in light of our previous discussions of the ligand dependence of the energies and intensities of their $^1(\delta \rightarrow \delta^*)$ transitions.[5,11] This series provides an important benchmark for analyzing such electronic structural perturbations due to the fact that the metal–metal distances of these species are virtually identical, lying in the range 2.125–2.130 Å.[11] As noted elsewhere, the modest red shift of the $^1(\delta \rightarrow \delta^*)$ transition as a function of halide (Cl → Br, ΔE = 370 cm^{-1}; Br → I, ΔE = 1000 cm^{-1}) is due to both a reduction in the two-electron terms that contribute to the energy of this transition and to its mixing with a $\pi(X) \rightarrow \delta^*$ state from which the inherently weak $^1(\delta \rightarrow \delta^*)$ transition also increasingly steals intensity along this series.[5,11] While the energy of this intensity-lending state has yet to be determined, calculations on $Mo_2Cl_4(PH_3)_4$ place the splitting of the $b_1(\pi(Cl))$ and $a_2(\delta^*)$ orbitals in the 3.7–4.5-eV range,[15,16] whereas the $^1(\delta \rightarrow \delta^*)$ transition of the corresponding trimethylphosphine derivative is located at ~2 eV; the energy gap between intensity-lending and -stealing states is thus ~1.5–2.5 eV. In contrast, $^1(\pi \rightarrow \delta^*)$ possesses the same polarization and symmetry, as well as a common orbital, as $^1(\sigma(MP) \rightarrow \delta^*)$ (band II); this latter state lies only 0.6–1.0 eV above $^1(\pi \rightarrow \delta^*)$, so larger energy and intensity perturbations are expected. Consistent with this argument is the fact that the magnitude of the red shift of $^1(\pi \rightarrow \delta^*)$ (Cl → Br, ΔE = 800 cm^{-1}; Br → I, ΔE = 1640 cm^{-1}; Table I) along this series is slightly larger than that of $^1(\delta \rightarrow \delta^*)$. While the intensities of these bands are more difficult to compare due to the differing contributions from underlying absorptions, particularly for $Mo_2I_4(PMe_3)_4$, there does appear to be roughly a 50% increase in the intensity of $^1(\pi \rightarrow \delta^*)$ on substitution of bromide for chloride in $Mo_2X_4(PMe_3)_4$.

Bands V and VI

Band V is well-defined only in the low-temperature crystal spectra. It appears in $\perp z$-polarization as a shoulder with little or no trace of vibronic structure (Figures 6 and 8). Although it is similarly weak in $\| z$-polarization, it is nonetheless impressively vibronically structured, displaying long progressions in $\nu(Mo_2)$. These lines of band V are distinguishable from the tail of band I because they are much sharper than the high quantum number lines of the latter. The average value of $\nu(Mo_2)$ for the bromide (Figure 11) is about 330 cm^{-1}, which is similar to that seen for its $^1(\delta \rightarrow \delta^*)$ transition.[13a,25] In addition to the progression in $\nu(Mo_2)$ built on the 19704-cm^{-1} electronic origin, lines are found 225 and 155 cm^{-1} to higher energy; a second progression in $\nu(Mo_2)$ is based upon these origins, with the two lines not being individually resolved beyond one quantum of $\nu(Mo_2)$ (at 20210 cm^{-1}). The 155-cm^{-1} interval probably corresponds to ν(MoBr) (ground-state $a_1\nu$(MoBr) = 159 cm^{-1}[11]).

Band V of the chloride (Figure 12) is slightly better resolved than that of the bromide, and its vibronic structure is even more complicated. Progressions in $\nu(Mo_2)$ are observed based upon two closely spaced origins at 20048 and 20214 cm^{-1}, as well as upon one ~275-cm^{-1} quantum (ν(MoCl); ground-state $a_1\nu_2$(MoCl) = 274 cm^{-1})[11] based upon each of these two origins. Curiously, the average value of $\nu(Mo_2)$ in the excited state (~350 cm^{-1}) is very similar to that of the ground state (355 cm^{-1}) and considerably higher than the ~330-cm^{-1} value seen[13a,25] for the $^1(\delta \rightarrow \delta^*)$ transition.

The vibronic structure of band V, while establishing it as a metal–metal transition, bears no resemblance to that seen for any of the other electronic transitions. In particular, the relatively high value of $\nu(Mo_2)$ for the excited state argues against assignments such as $\delta \rightarrow \pi^*$, $^3(\pi \rightarrow \pi^*)$, or $^1(\delta^2 \rightarrow \delta^{*2})$, which are among the possibilities that are suggested by the various[8,15,16,20] calculations; population of these excited states should result in a metal–metal force-constant reduction greater than that of the $^1(\delta\delta^*)$ state, whereas a small frequency reduction is observed for band V. Moreover, the low oscillator strength of the band and its mixed polarization suggest a forbidden transition. The most likely assignment that we can conceive of, and one without precedent for the electronic spectra of quadruply bonded dimers, is the $\sigma \rightarrow \delta^*$ excitation (Figure 1), which is orbitally forbidden ($A_1 \rightarrow A_2$). Calculations[16] predict that ionization of the σ level will result in a *decrease* in metal–metal distance, so an exceptionally small decrease in $\nu(Mo_2)$ would be predicted for $\sigma \rightarrow \delta^*$.

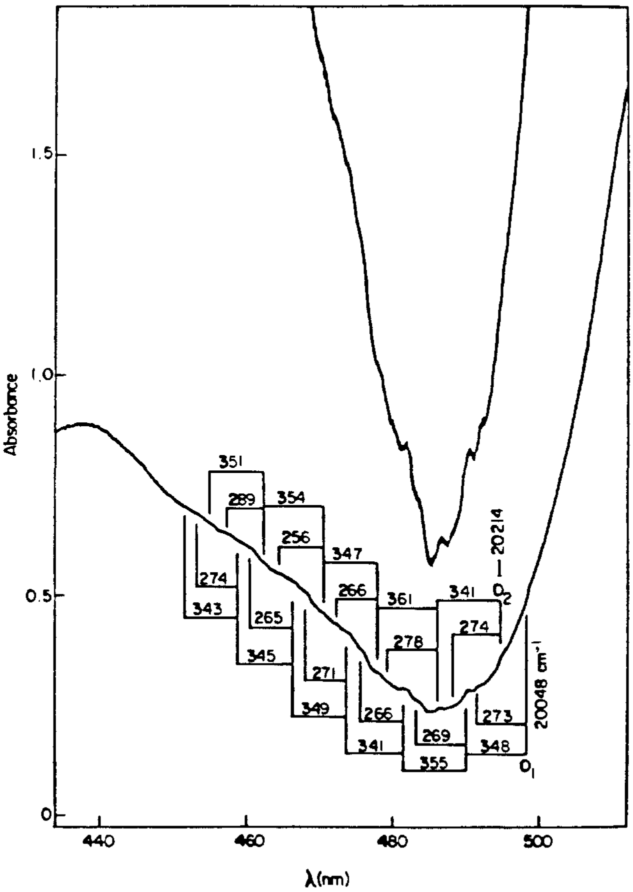

Figure 12. The $\| z$-polarized absorption spectrum of a single crystal of $Mo_2Cl_4(PMe_3)_4$ at 5 K showing weak bands at high resolution. The upper trace is an expansion of the lower trace.

That the effect of populating δ^* in this transition should have an opposing effect, namely an increase in metal–metal distance, to that of depopulating σ might be connected to the surprisingly large difference in excited-state $\nu(Mo_2)$ seen for the chloride and bromide; since the net effect is the difference of (small) opposing effects, ligand perturbations might be especially important. As noted elsewhere,[11] G matrix mixing of $\nu_1(M_2)$ and $\nu_2(MX)$, as well as halide-induced changes in the effective reduced mass of the M_2 oscillator, may affect the metal–metal stretching frequency.

A remaining question is whether the observed excited state is of singlet or triplet multiplicity. We think it likely that band V is $^1A_1 \rightarrow {}^3A_2$, since the photoelectron data[15,17] indicate the σ level to be more stable than π, suggesting that $^1(\sigma \rightarrow \delta^*)$ should lie to higher energy of $^1(\pi \rightarrow \delta^*)$ (band III). A candidate for $^1(\sigma \rightarrow \delta^*)$ of $W_2Cl_4(PMe_3)_4$ is band VI (Figure 4); the ~0.6 eV energy gap between bands III and VI in this complex is in good agreement with the 0.4-eV separation of σ and π levels obtained from photoelectron data.[17] Moreover, the implied singlet–triplet splitting is similar to that inferred for other metal–metal-localized transitions of this type.[10] If band VI varies position as do the other

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(25) Hopkins, M. D. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1986.

(26) An alternative assignment for band VI that merits consideration is $^1(\delta \rightarrow \pi^*)$, which has not been identified in any of our spectra. We note that $^1(\delta \rightarrow \pi^*)$ should probably be less intense than $^1(\pi \rightarrow \delta^*)$ for these compounds, since it does not share an orbital with $^1(\sigma(MP) \rightarrow \delta^*)$, and hence to first order cannot steal intensity from this type of allowed, x,y-polarized transition.[27]

(27) Fenske, R. F. *J. Am. Chem. Soc.* **1967**, *89*, 252–256.

metal–metal transitions then Figure 9 indicates that it would be obscured by intense charge-transfer transitions for all other compounds of this study.[26]

Comparisons to Related Systems

While no single-crystal absorption experiments have been undertaken for other quadruply bonded dimers possessing mixed halide/phosphine coordination spheres, a circular dichroism study of the torsionally distorted β-$Mo_2X_4(PP)_2$ complexes (X = Cl, Br; PP = chiral bridging diphosphine) has been reported.[28] Although direct comparisons of band positions among the spectra of the β-$Mo_2X_4(PP)_2$ and $Mo_2X_4(PMe_3)_4$ compounds are difficult due to the fact that the former series has a greater number of absorption features, the spectra of the chiral compounds display an intense ($\epsilon > 3000$) feature at 370–380 nm that has been assigned[28] to $\pi_{yz} \rightarrow \delta^*$.[29] Since this absorption band also appears in the spectrum of D_2 β-$Mo_2Cl_4(dmpe)_2$[13c] at nearly the same position, and with equal intensity, as band II of the latter compound's D_{2d} rotamer, $Mo_2Cl_4(PMe_3)_4$, we conclude that these bands instead correspond to P → Mo excitations.

Relevant to our findings for $M_2X_4(PMe_3)_4$ systems are the results of spectroscopic studies on the $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$ ions. The low-temperature single-crystal spectra of $K_4[Mo_2Cl_8]\cdot 2H_2O$[9] show an exceedingly weak feature near 450 nm that might be $^1(\pi \rightarrow \delta^*)$, which is dipole-forbidden in D_{4h} symmetry. A moderately intense ($\epsilon \sim 200$) feature of mixed polarization at 345 nm was attributed to a ^3E_u excited state, with the corresponding ^1E_u state being assigned to the strong *x,y*-polarized absorption whose maximum ($\lambda < 330$ nm) was far too intense to be recorded. The triplet assignment seems reasonable, but we suggest that an $e_g(\pi(Cl)) \rightarrow \delta^*$ assignment for the intense band is far more likely to be correct than the proposed[9] $\pi \rightarrow d_{x^2-y^2}$ assignment. The crystal spectrum of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ has been extensively studied,[4,7,8] and several weak ($\epsilon < 100$) features are found in the 400–600-nm region. While two of them are highly vibronically structured in $\nu(Re_2)$, and therefore quite certain to be metal–metal-localized transitions, their interpretation is complicated by crystal disorder, so experimental assignments are not very secure. A band near 570 nm has been assigned to $^1(\pi \rightarrow \delta^*)$, perhaps overlapping with $^1(\delta \rightarrow \pi^*)$. A similarly highly vibronically structured band has been reported[4] at a similar wavelength for $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$. Since $^1(\pi \rightarrow \delta^*)$ is dipole-forbidden in D_{4h} symmetry, the very low intensity is reasonable, but additional work needs to be done on these systems. In particular, the possibility of a $\sigma \rightarrow \delta^*$ assignment should be considered for the 570-nm band.

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Registry No. $Mo_2Cl_4(PMe_3)_4$, 67619-17-4; $Mo_2Br_4(PMe_3)_4$, 89707-70-0; $Mo_2I_4(PMe_3)_4$, 89637-15-0; $W_2Cl_4(PMe_3)_4$, 73133-20-7.

Supplementary Material Available: ⊥ *z*-polarized single-crystal absorption spectra of $Mo_2Cl_4(PMe_3)_4$ and $Mo_2Br_4(PMe_3)_4$ in the region of their $^1(\delta \rightarrow \delta^*)$ transition at ca. 5 K (2 pages). Ordering information is given on any current masthead page.

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[28] Agaskar, P. A.; Cotton, F. A.; Fraser, I. F.; Manojlouic-Muir, L.; Muir, K. W.; Peacock, R. D. *Inorg. Chem.* **1986**, *25*, 2511–2519.

[29] The designation of this transition arises because the degenerate $\pi_{xz,yz}$ level in molecules of the parent D_{2d} symmetry may be split in the D_2 symmetry of the diphosphine-bridged species. Judging by the high d-orbital character of the π level calculated by Ziegler[16] (Figure 1), a large splitting would not be expected, since a pure metal-dπ level is invariant to rotation about the metal–metal bond.

Electronic Structure of Tetrakis(isopropylthio)thieno[3,4-*c*]thiophene Studied by Photoelectron and Electronic Absorption Spectroscopies Combined with MO Calculations

Tsunetoshi Kobayashi,[*1a] **Kenji Ozaki,**[1b] **and Shigeo Yoneda**[*1b]

Contribution from the Institute of Physical and Chemical Research, Wako, Saitama 351-01, Japan, and Department of Applied Chemistry, University of Osaka Prefecture, Sakai, Osaka 591, Japan.

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Abstract: Photoelectron and electronic absorption spectra of tetrakis(isopropylthio)thieno[3,4-*c*]thiophene (I) were measured. On the basis of these data combined with MO calculations the ground- and excited-state electronic structures of this compound containing two thiophene rings uniquely fused with each other were studied in detail. The He I photoelectron spectrum of I shows the bands at 6.72, 7.89–8.71, and 9.14 eV in the ionization energy scale. On the basis of the photoelectron spectrum it was concluded that the CSC planes relevant to the isopropylthio groups are twisted out by about 60° from the parent ring plane. The first band, the energy of which is as low as that of tetrathiafulvalene, corresponds to the ionization from the HO-π-MO almost completely localized on the 1-, 3-, 4-, and 6-carbon atoms of the parent framework. The electronic absorption spectrum of I in hexane shows the first band at 2.46 eV, this band being assigned to the $^1B_{3u} \leftarrow {}^1Ag$-like (mainly LU-$\pi$-MO ← HO-$\pi$-MO) transition almost localized on the parent ring system. It is concluded that compound I is as effective as tetrathiafulvalene for the electron-donating ability and reflects strongly the electronic character of the unknown parent compound, thieno[3,4-*c*]thiophene, for the relatively low energy phenomena such as chemical reactions relevant to HOMO and/or LUMO. Combination of photoelectron and electronic absorption spectroscopies assisted by MO calculations is effective in elucidating electronic structure of molecules as demonstrated in this work.

Among various types of spectroscopies photoelectron spectroscopy is the most powerful tool for studying occupied molecular orbitals for it gives almost directly orbital energy diagrams if we follow Koopmans' theorem.[2] In this paper electronic structure

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