

Figure 7. The observed and calculated PES for $\text{Mo}_2(\text{OCH}_2\text{CMe}_3)_6$. The energy scale is for the experimental spectrum and the calculated values are arbitrarily shifted to match the lowest calculated ionization energy to the first observed maximum.

very different tendencies of the two systems to sacrifice $\text{M-M } \sigma$ bonding, which is the strongest component of the entire quadruple bond, in favor of $\text{M-L}_{\text{ax}} \sigma$ bonding are clearly implied by these results.

The calculation⁸⁵ for $\text{Cr}_2(\text{O}_2\text{CH})_4$ clearly shows the presence of a quadruple bond, in which the δ and π ($2b_{2g}$, $6e_u$) orbitals are close in energy. This feature and, indeed, all other key features of the calculated level pattern for a Cr-Cr distance of ca. 2.30 Å are in excellent accord with the observed PES⁸⁶ for gaseous $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$, and this close agreement provides powerful evidence that the calculation is reliable and

(86) D. C. Garner, I. H. Hillier, M. F. Guest, J. C. Green, and A. W. Coleman, *Chem. Phys. Lett.*, **41**, 91 (1976).

that there are indeed quadruple Cr-Cr bonds in the $\text{Cr}_2(\text{O}_2\text{CR})_4$ compounds.

Finally, in this extremely brief and selective sampling of theoretical results, we draw attention to the way in which SCF- $X\alpha$ -SW calculations have confirmed and quantified the simple qualitative picture of the triple Mo-Mo and W-W bonds in M_2X_6 species. Figure 7 shows the UV photoelectron spectrum of $\text{Mo}_2(\text{OCH}_2\text{CMe}_3)_6$ together with the calculated ionization energies for the seven highest energy levels. The fit, though not impeccable, is very satisfactory overall. The $5e_u$ orbital is the M-M π bonding orbital and the $4a_{1g}$ is the M-M σ bonding level, exactly as expected from the qualitative picture discussed earlier.

The first attempts to employ Hartree-Fock (so-called *ab initio*) methods for these multiple bonds have recently been reported.^{86,87a} For $\text{Cr}_2(\text{O}_2\text{CH})_4$ it is clear^{87a} that unless configuration interaction is included, erroneous results are obtained; this, of course, adds greatly to the expense of an already expensive calculation. For several second-row compounds, single configuration calculations have afforded results that are essentially in accord with SCF- $X\alpha$ -SW calculations as far as the qualitative order of levels is concerned.^{87b} No Hartree-Fock calculation has yet been tested in terms of its ability to account for electronic absorption or photoelectron spectra. In at least one case, $\text{Tc}_2\text{Cl}_8^{3-}$, an SCF- $X\alpha$ -SW calculation has been shown to give a virtually quantitative fit to the observed absorption spectrum,⁶² although it must be admitted that in other cases the agreement has not been as good.

Work in my own laboratory in this field has been supported by the National Science Foundation during the period covered. I am grateful to many talented co-workers, whose names may be found in the reference list, for their contributions to this work. It has been a privilege to collaborate with Professor D. S. Martin, Jr., of Iowa State University, Ames, and Professor Malcolm H. Chisholm of Princeton University in several phases of the work.

(87) (a) M. Benard and A. Viellard, *Nouv. J. Chim.*, **1**, 97 (1977); (b) M. Benard and A. Viellard, private communication.

Electronic Spectra and Photochemistry of Complexes Containing Quadruple Metal-Metal Bonds

WILLIAM C. TROGLER and HARRY B. GRAY*

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

Received June 22, 1977

Study of the nature of metal-metal interactions in cluster complexes has been an active area of research in our laboratory for 10 years. Our initial investigations involved $\text{Mn}_2(\text{CO})_{10}$ and related complexes containing

Harry Gray is the William R. Kenan, Jr. Professor at the California Institute of Technology. He studied with Fred Basolo and Ralph Pearson at Northwestern (1957-1960) and with Carl Ballhausen at the University of Copenhagen (1960-1961). He was Professor of Chemistry at Columbia University before joining the faculty of Caltech. He is now studying bioinorganic and photoinorganic oxidation-reduction reactions.

William C. Trogler was an undergraduate at The Johns Hopkins University. In 1974 he received B.A. and M.A. degrees and did research with Luigi G. Marzilli. Subsequently he obtained his Ph.D. at Caltech with Harry B. Gray. Now he is an Assistant Professor of Chemistry at Northwestern University.

single metal-metal bonds.^{1,2} We established that the electronic spectra of such binuclear complexes feature a relatively low-lying, intense absorption band that is not present in reference mononuclear systems. In the spectrum of $\text{Mn}_2(\text{CO})_{10}$, this band peaks at 29400 cm^{-1} ($\epsilon 2 \times 10^4$).²

Simple theoretical considerations taken together with the experimental finding that the absorption in

(1) G. P. Ceasar, R. A. Levenson, and H. B. Gray, *J. Am. Chem. Soc.*, **91**, 772 (1969).

(2) R. A. Levenson, H. B. Gray, and G. P. Ceasar, *J. Am. Chem. Soc.*, **92**, 3653 (1970).

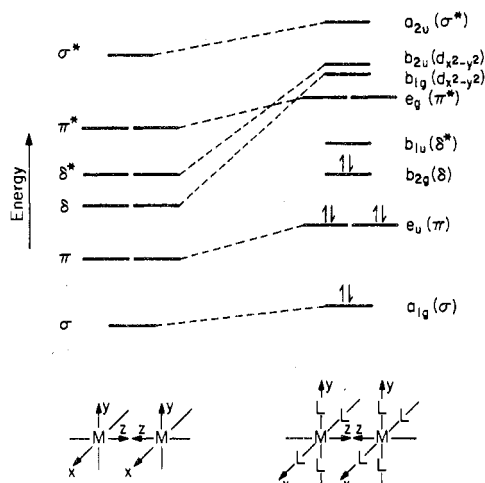


Figure 1. Relative energies of the d-derived molecular orbitals in $D_{\infty h} M_2$ and in a $D_{4h} M_2L_8$ complex. The ground state of a d^4-d^4 M_2L_8 complex is $^1A_{1g} (\sigma^2\pi^4\delta^2)$.

$Mn_2(CO)_{10}$ is MnMn-axis polarized led us to identify the band with the strongly allowed $\sigma \rightarrow \sigma^*$ transition, where σ and σ^* denote the d_{z^2} -derived bonding and antibonding molecular orbitals, respectively, that are associated with the MnMn single bond (σ^2 ground state). Subsequently, several investigations made it apparent that a general electronic spectral feature of all singly bonded MM units is an intense $\sigma \rightarrow \sigma^*$ absorption system.³⁻⁵ Furthermore, it is now well established that $\sigma \rightarrow \sigma^*$ excitation leads to dissociative homolytic cleavage of the MM bond.^{6,7}

More recently, we have made extensive studies of the electronic spectra of binuclear complexes containing very strong metal-metal bonds. In particular, we have concentrated on $Re_2Cl_8^{2-}$ and its close d^4-d^4 -bonded relatives, whose ground states Cotton showed⁸ in 1964 are quite reasonably described as possessing quadruple metal-metal bonds. In this Account we are concerned mainly with what we and others have learned about the nature of the electronic excited states of these strongly metal-metal-bonded complexes.

Basic Theoretical Considerations

The relative energies expected for the d-derived molecular orbitals of a homonuclear diatomic molecule are depicted on the left side of Figure 1. In the coordinate systems shown for the two atoms, σ , π , and δ bonding and antibonding molecular orbitals may be generated from the appropriate linear combinations of the d_{z^2} , (d_{xz}, d_{yz}), and ($d_{xy}, d_{x^2-y^2}$) functions, respectively. Introduction of eight ligands along the x and y axes to form a $D_{4h} M_2L_8$ complex significantly increases the energies of the $d_{x^2-y^2}$ -derived δ and δ^* orbitals, b_{1g} and b_{2u} (Figure 1). These two orbitals are primarily metal-ligand σ antibonding in character.

According to this simple model, a d^4-d^4 complex such as $Re_2Cl_8^{2-}$ possesses a quadruple metal-metal bond

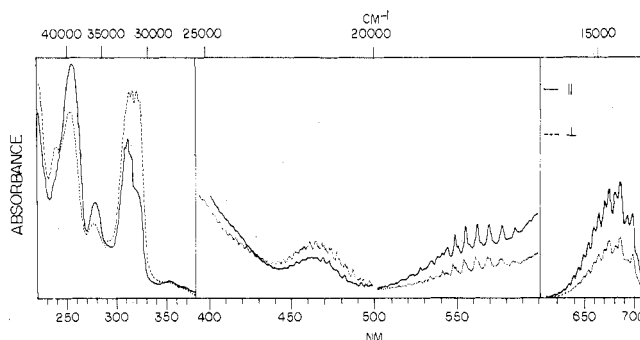


Figure 2. Single-crystal polarized electronic absorption spectra of $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ at 5 K (outer spectra) and 15 K (central portion). Three different crystals were used to obtain these spectra.

($\sigma^2\pi^4\delta^2$), as first proposed⁸ by Cotton to explain the diamagnetism, the eclipsed geometry, and the unusually short ReRe distance (2.24 Å) that are found. Estimates of the strengths of quadruple metal-metal bonds vary; there is no doubt, however, that such bonds are very strong in comparison to those of lower order involving heavy atoms. Recently, we proposed,⁹ based on a Birge-Sponer-type extrapolation of vibrational spectroscopic data, that the quadruple ReRe and MoMo bond dissociation energies fall in the ranges 115-130 and 110-160 kcal/mol, respectively.

The MO diagram (Figure 1) suggests that the lowest energy electric-dipole-allowed transition in d^4-d^4 binuclear complexes is $^1A_{1g} \rightarrow ^1A_{2u} (\delta \rightarrow \delta^*)$. The correctness of this prediction is now amply documented for nonbridged d^4-d^4 complexes, as we shall see.

Transitions to $\delta\delta^*$ Excited States

The polarized electronic absorption spectra of $Re_2Cl_8^{2-}$ are shown in Figure 2.⁹⁻¹¹ The lowest system in these spectra peaks at 14700 cm^{-1} ($\epsilon_{\text{max}} 1530$; $f = 0.023^{12}$) and is ReRe-axis polarized.¹⁰ The intensity of this absorption system is temperature independent,¹⁰ and the maximum shifts only 600 cm^{-1} to the red upon substitution of bromide for chloride ligands.¹¹ No lower energy electronic absorption bands of appreciable intensity are observed¹³ in the spectrum of $Re_2Cl_8^{2-}$. The main lines of experimental evidence, therefore, are consistent with a $^1A_{1g} \rightarrow ^1A_{2u} (\delta \rightarrow \delta^*)$ assignment¹⁰ for the 14700-cm^{-1} system. Furthermore, Clark and Franks have shown¹⁴ that excitation of $^1A_{1g} \rightarrow ^1A_{2u} (\delta \rightarrow \delta^*)$ leads to strong resonance enhancement of the totally symmetric ReRe stretching vibration, $a_{1g}(\text{ReRe})$, in the Raman spectrum of $Re_2Cl_8^{2-}$, as expected for an electric-dipole-allowed transition. At 5 K, two progressions in quanta of 248 cm^{-1} , attributable to $a_{1g}(\text{ReRe})$, are built on the 14700-cm^{-1} system.¹⁰ Reduction of the ReRe stretching vibrational frequency from the ground-state value^{14,15} of 272 cm^{-1} suggests that in the $^1A_{2u} (\delta\delta^*)$ excited state the metal-metal bond is slightly

(3) R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc.*, **97**, 6042 (1975).

(4) D. C. Harris and H. B. Gray, *J. Am. Chem. Soc.*, **97**, 3073 (1975).

(5) H. B. Abrahamson, C. C. Frazier, D. S. Ginley, H. B. Gray, J. Lilienthal, D. R. Tyler, and M. S. Wrighton, *Inorg. Chem.*, **16**, 1554 (1977), and references therein.

(6) M. S. Wrighton, *Top. Curr. Chem.*, **65**, 37 (1976); *Chem. Rev.*, **74**, 401 (1974); and references therein.

(7) C. R. Bock and E. A. Koerner von Gustorf, *Adv. Photochem.*, **10**, 221 (1977), and references therein.

(8) F. A. Cotton et al., *Science*, **145**, 1305 (1964); F. A. Cotton, *Inorg. Chem.*, **4**, 334 (1965).

(9) W. C. Trogler, C. D. Cowman, H. B. Gray, and F. A. Cotton, *J. Am. Chem. Soc.*, **99**, 2993 (1977).

(10) C. D. Cowman and H. B. Gray, *J. Am. Chem. Soc.*, **95**, 8177 (1973).

(11) A. P. Mortola, J. W. Moskowicz, N. Rosch, C. D. Cowman, and H. B. Gray, *Chem. Phys. Lett.*, **32**, 283 (1975).

(12) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).

(13) W. C. Trogler and H. B. Gray, unpublished observations.

(14) R. J. H. Clark and M. L. Franks, *J. Am. Chem. Soc.*, **98**, 2763 (1976).

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

Table I
Data for the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) Bands in Binuclear Complexes

Complex	Sample condition ^a	$\bar{\nu}_{\max}$, cm ⁻¹	ϵ_{\max}	f	a_{1g} (MM), cm ⁻¹	
					${}^1A_{1g}$	${}^1A_{2u}$
(<i>n</i> -Bu ₄ N) ₂ Re ₂ Cl ₈	crystal, 5 K	14 654 ^b	1530 ^c	0.023 ^c	272 ^d	248 ^b
(<i>n</i> -Bu ₄ N) ₂ Re ₂ Br ₈	crystal, 5 K	14 104 ^e			275 ^d	255 ^e
K ₂ Mo ₂ Cl ₈ ·2H ₂ O	crystal, 4 K	19 128 ^f	1050 ^g	0.015 ^h	346 ⁱ	336 ^f
(<i>n</i> -Bu ₄ N) ₂ Tc ₂ Cl ₈	polycrystalline (diffuse reflectance)	14 290 ^j				
Re ₂ Cl ₆ (PET ₃) ₂	crystal, 5 K	14 363 ^k			278 ^l	289 ^h
Mo ₂ Cl ₄ (PET ₃) ₄	KBr disk, 15 K	16 955 ^e	3015 ^m		342 ⁱ	320 ^e
K ₄ Mo ₂ (SO ₄) ₄ ·2H ₂ O	crystal, 15 K	19 400 ⁿ	170 ^o			
Mo ₂ (aq) ⁴⁺	10 ⁻² M HSO ₃ CF ₃	19 840 ^p	337 ^p			
Mo ₂ (en) ₄ Cl ₄	10 ⁻³ M HSO ₃ CF ₃	20 920 ^p	483 ^p			
(Li·Et ₂ O) ₂ Re ₂ (CH ₃) ₈	Et ₂ O	18 600 ^q	<1500 ^q			
(Li·Et ₂ O) ₄ Cr ₂ (CH ₃) ₈	Et ₂ O	22 000 ^q	<700 ^q			
(Li·Et ₂ O) ₄ Mo ₂ (CH ₃) ₈	Et ₂ O	19 500 ^q	<1500 ^q			
Mo ₂ (O ₂ CH) ₄	4:1 EtOH/MeOH, 80 K	30 600 ^r		0.03 ^r		
K ₂ Mo ₂ (SO ₄) ₄ ·3.5H ₂ O	KBr disk, 15 K	7 100 ^{o,s}	143 ^o		373,386 ^t	350,357 ^o
K ₂ Tc ₂ Cl ₈ ·2H ₂ O	CsI disk, 4 K	6 300 ^{s,u}				320 ^u

^a In most cases these conditions refer only to measurements of $\bar{\nu}_{\max}$ and ${}^1A_{2u}$ a_{1g} (MM); $\bar{\nu}_{\max}$ values are for room temperature measurements unless noted otherwise. ^b C. D. Cowman and H. B. Gray, *J. Am. Chem. Soc.*, **95**, 8177 (1973). ^c F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965). ^d R. J. H. Clark and M. L. Franks, *J. Am. Chem. Soc.*, **98**, 2763 (1976). ^e C. D. Cowman, W. C. Trogler, and H. B. Gray, *Israel J. Chem.*, **15**, 308 (1977). ^f P. E. Fanwick, D. S. Martin, F. A. Cotton, and T. R. Webb, *Inorg. Chem.*, **16**, 2103 (1977). ^g W. C. Trogler, D. K. Erwin, G. L. Geoffroy, and H. B. Gray, *J. Am. Chem. Soc.*, **100**, 1160 (1978). ^h W. C. Trogler, E. I. Solomon, I. Trajberg, C. J. Ballhausen, and H. B. Gray, *Inorg. Chem.*, **16**, 828 (1977). ⁱ R. J. H. Clark and M. L. Franks, *J. Am. Chem. Soc.*, **97**, 2691 (1975). ^j K. Schwochau, K. Hedwig, H. J. Schenk, and O. Greis, *Inorg. Nucl. Chem. Lett.*, **13**, 77 (1977). ^k C. D. Cowman, Ph.D. Thesis, California Institute of Technology, 1974. ^l Value reported for Re₂Cl₆(P(*n*-C₃H₇)₃)₂ and Mo₂Cl₄(PBu₃)₄: J. S. Filippo and H. J. Sniadoch, *Inorg. Chem.*, **12**, 2326 (1974); J. S. Filippo, H. J. Sniadoch, and R. L. Grayson, *ibid.*, **13**, 2121 (1974). ^m W. C. Trogler and H. B. Gray, *Nouv. J. Chim.*, **1**, 475 (1977). ⁿ F. A. Cotton, D. S. Martin, P. E. Fanwick, T. J. Peters, and T. R. Webb, *J. Am. Chem. Soc.*, **98**, 4681 (1976). ^o D. K. Erwin, G. L. Geoffroy, H. B. Gray, G. S. Hammond, E. I. Solomon, W. C. Trogler, and A. A. Zagars, *ibid.*, **99**, 3620 (1977). ^p A. R. Bowen and H. Taube, *Inorg. Chem.*, **13**, 2245 (1974). ^q A. P. Sattelberger and J. P. Fackler, *J. Am. Chem. Soc.*, **99**, 1258 (1977). ^r J. G. Norman, H. J. Kolari, H. B. Gray, and W. C. Trogler, *Inorg. Chem.*, **16**, 987 (1977). ^s The transition is ${}^2B_{2g} \rightarrow {}^2B_{1u}$ ($\delta \rightarrow \delta^*$). ^t A. Loewenschuss, J. Shamir, and M. Ardon, *Inorg. Chem.*, **15**, 238 (1976). ^u F. A. Cotton, P. E. Fanwick, L. D. Gage, B. Kalbacher, and D. S. Martin, *J. Am. Chem. Soc.*, **99**, 5642 (1977).

weakened. The MCD spectrum of Re₂Cl₈²⁻ in the 14 700-cm⁻¹ region is consistent with the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) assignment, as only a weak *B* term is observed.¹⁶

Analogous $\delta \rightarrow \delta^*$ absorption bands have been observed for a variety of other complexes that contain quadruple metal-metal bonds (Table I). The spectra of the related Re(III) derivatives, Re₂Br₈²⁻ and Re₂Cl₆(PET₃)₂, exhibit *z*-polarized bands at 14 104 and 14 363 cm⁻¹, which show progressions in 255- and 289-cm⁻¹ vibrations, respectively.¹⁶ A *z*-polarized¹⁷ band attributable¹⁰ to ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) is observed at 19 128 cm⁻¹ in the spectrum of Mo₂Cl₈⁴⁻, which at low temperatures exhibits a progression in a 336-cm⁻¹ vibration (a_{1g} (MoMo); ground state^{15,18} 346 cm⁻¹). The spectrum of Mo₂(SO₄)₄⁴⁻ exhibits a structureless absorption at 19 400 cm⁻¹.¹⁹ From the polarization data¹⁹ a ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) assignment is indicated; however, the intensity of this absorption is rather low ($\epsilon_{\max} \sim 170$).²⁰

The relatively low intensities of $\delta \rightarrow \delta^*$ absorption bands have caused some confusion. Generally, one-electron N \rightarrow V excitations of the bonding to antibonding kind give rise to very intense absorption

systems.²¹ Recently, we suggested²² that the diminished intensity of a band attributable to the $\delta \rightarrow \delta^*$ transition is a consequence of poor orbital overlap. Mulliken has shown²¹ that the oscillator strength (*f*) of a one-electron N \rightarrow V diatomic-like transition in a weak coupling or valence bond formalism may be approximated by

$$f = 1.096 \times 10^{11} \bar{\nu} s^2 r^2$$

where $\bar{\nu}$ is the transition energy in cm⁻¹, *s* is the orbital overlap, and *r* is the bond length in cm. As the δ overlap is on the order of 0.1 or less, a valence bond description is more appropriate than the MO model. Employing the above formula, one predicts oscillator strengths in the neighborhood of 10⁻² for typical values of *r* and $\bar{\nu}$.

Another point of interest is the location of the transition to the $\delta\delta^*$ triplet state, ${}^3A_{2u}$, or, more correctly, its A_{1u} and E_u spin-orbit components. Clark and Franks have proposed¹⁸ that a weak structured absorption at 6250 cm⁻¹ in the diffuse reflectance spectra of some, but not all, Mo₂Cl₈⁴⁻ salts is due to ${}^1A_{1g} \rightarrow {}^3A_{2u}$. An alternative placement of this transition is suggested by a recent single-crystal-polarized spectral study of K₄Mo₂Cl₈·2H₂O, which revealed¹⁹ an (*x,y*) polarized shoulder at $\sim 17 500$ cm⁻¹. It was pointed out¹⁹ that this shoulder, which falls on the low-energy side of ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$), could represent a transition to the E_u spin-orbit component of ${}^3A_{2u}$. Subsequently, we reported²³ the 1.3 K emission spectra of Re₂Cl₈²⁻,

(21) R. S. Mulliken, *J. Chem. Phys.*, **7**, 20 (1939).

(22) W. C. Trogler, E. I. Solomon, I. Trajberg, C. J. Ballhausen, and H. B. Gray, *Inorg. Chem.*, **16**, 828 (1977).

(16) C. D. Cowman, W. C. Trogler, and H. B. Gray, *Israel J. Chem.*, **15**, 308 (1977); C. D. Cowman, Ph.D. Thesis, California Institute of Technology, 1974.

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

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

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

(20) D. K. Erwin, G. L. Geoffroy, H. B. Gray, G. S. Hammond, E. I. Solomon, W. C. Trogler, and A. A. Zagars, *J. Am. Chem. Soc.*, **99**, 3620 (1977).

$\text{Re}_2\text{Br}_8^{2-}$, and $\text{Mo}_2\text{Cl}_8^{4-}$. In all three complexes, excitation of $^1A_{1g} \rightarrow ^1A_{2u}$ ($\delta \rightarrow \delta^*$) gives an emission band that does not overlap the 0-0 peak of the absorption system.²³ The emission band shape is similar to that of the $^1A_{1g} \rightarrow ^1A_{2u}$ ($\delta \rightarrow \delta^*$) absorption and the luminescent lifetimes are all on the order of 100 ns. Thus the emission may originate either from one of the spin-orbit components of $^3A_{2u}$ or from a distorted (approximately D_{4d}) $\delta\delta^*$ singlet state. It will require additional theoretical and experimental work to settle this matter.

Binuclear complexes with metal-metal electronic structures of $\sigma^2\pi^4\delta$ and $\sigma^2\pi^4\delta^2\delta^*$ should result from one-electron oxidation and reduction, respectively, of the parent d^4-d^4 systems. A series of EPR studies by Cotton and Pedersen have shown²⁴ that this is probably the case for oxidized species such as $\text{Mo}_2(\text{SO}_4)_4^{3-}$ and $\text{Mo}_2(\text{O}_2\text{CC}_3\text{H}_7)_4^+$ and for the reduced species $\text{Tc}_2\text{Cl}_8^{3-}$, $\text{Re}_2(\text{O}_2\text{CPh})_4^+$, and $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4^+$. It is now apparent that a near-infrared electronic absorption band is characteristic of these one-electron reduction and oxidation products. Ebner and Walton have noted the presence of absorptions at 7100 cm^{-1} with molar extinction coefficients greater than 2000 in the spectra of $\text{Re}_2\text{X}_5(\text{PRPh}_2)_3$ ($\text{X} = \text{Cl}$ or Br).^{25,26} A spectral study of another reduced species, $\text{Tc}_2\text{Cl}_8^{3-}$, revealed an absorption at 6300 cm^{-1} ($\epsilon_{\text{max}} 630$), and, at low temperatures, a well-resolved 320-cm^{-1} vibrational progression was observed.²⁷

An absorption at 7100 cm^{-1} ($\epsilon_{\text{max}} 143$) is present²⁰ in the electronic spectrum of the oxidized species $\text{Mo}_2(\text{SO}_4)_4^{3-}$. At low temperatures this band system of $\text{Mo}_2(\text{SO}_4)_4^{3-}$ displays well-resolved vibrational progressions in quanta of 350 cm^{-1} . For comparison, the ground-state value²⁸ of $a_{1g}(\text{MoMo})$ for $\text{Mo}_2(\text{SO}_4)_4^{3-}$ is $\sim 380\text{ cm}^{-1}$. On the basis of the sharp molecular vibronic structure observed and the lack of any observable splitting of Mo signals in the X-ray photoelectron spectrum, we proposed²⁰ a $^2B_{2g} \rightarrow ^2B_{1u}$ ($\delta \rightarrow \delta^*$) rather than an intervalence charge transfer assignment for the near-infrared absorption system. It has also been suggested²⁷ that the 6300-cm^{-1} absorption in the $\text{Tc}_2\text{Cl}_8^{3-}$ spectrum is attributable to $\delta \rightarrow \delta^*$, and an analogous assignment appears likely for the near-IR bands in the spectra of the complexes examined by Ebner and Walton.^{25,26} It is interesting to note that the ϵ_{max} of the near-IR absorption is similar to that of the $\delta \rightarrow \delta^*$ band in corresponding complexes that possess a full quadruple metal-metal bond. For this reason, we prefer a $\delta \rightarrow \delta^*$ assignment for the 13000 cm^{-1} ($\epsilon_{\text{max}} 2600$) absorption in the spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4^-$ to the original proposal²⁹ that it is a metal-to-ligand charge transfer (MLCT) transition. The fact that this band is some 6000 cm^{-1} to the blue of those in the other examples cited is not surprising, as $\delta \rightarrow \delta^*$ in the

electronic spectrum of the parent compound is also positioned at much higher energy.³⁰

We will not review in any detail the various theoretical calculations^{11,31-34} of the ordering of the excited states in d^4-d^4 complexes, as these are discussed in the accompanying article by Cotton.³⁵ We do wish to comment, however, on the finding that the excitation energies to $^1A_{2u}$ ($\delta\delta^*$) states in $\text{Re}_2\text{Cl}_8^{2-}$,¹¹ $\text{Mo}_2\text{Cl}_8^{4-}$,³³ and $\text{Mo}_2(\text{O}_2\text{CH})_4$ ³⁴ are estimated by SCF-X α -SW calculations to be too low by at least 10000 cm^{-1} . One possible explanation for this discrepancy is that the X α method fails to account adequately for electron repulsion contributions to the $\delta \rightarrow \delta^*$ excitation energy in the closed-shell d^4-d^4 systems. This explanation is suggested by the fact that the $\delta \rightarrow \delta^*$ transition energies are much less in the one-electron oxidized and reduced species (vide supra). In these open-shell cases, electron repulsion effects will be similar for both the ground and excited states, because they each have one singly occupied orbital ($\delta \rightarrow \delta^*$ or $\delta^2\delta^* \rightarrow \delta\delta^{*2}$). In the closed-shell systems, the $\delta \rightarrow \delta^*$ excited state possesses two singly occupied δ -like orbitals, whereas the ground state has one doubly occupied δ orbital. A considerable amount of ionic character in the $^1A_{2u}$ state would effectively place both δ electrons on the same atom, leading to high repulsion energies. Therefore, it seems likely that such unfavorable electron repulsion effects contribute to the high energy of the $^1A_{2u}$ state for these systems. However, the exact origin of the destabilization of $^1A_{2u}$ still should be considered an open question, and one that should be examined thoroughly in future theoretical studies.

How Strong Is a δ Bond?

Both theoretical calculations³⁵ and experimental spectroscopic studies^{10,11,16,17} are consistent with the view that the δ and δ^* orbitals possess very little ligand character, being comprised almost entirely of weakly coupled metal d_{xy} functions. In the complexes where these weakly coupled orbitals contain an odd number of electrons, the $\delta \rightarrow \delta^*$ vertical excitation energy should be approximately equal to two times the δ bond dissociation energy. A bond dissociation energy approximated in this way represents an upper limiting value, as according to theory the antibonding orbital is destabilized to a greater extent than its bonding partner is stabilized. Taking values of 7100 and 6300 cm^{-1} for the $\delta \rightarrow \delta^*$ splittings in the odd-electron complexes $\text{Mo}_2(\text{SO}_4)_4^{3-}$ ²⁰ and $\text{Tc}_2\text{Cl}_8^{3-}$,²⁷ upper limits of 10 and 9 kcal/mol, respectively, are obtained for the one-half δ bond dissociation energies.

Forbidden Metal-Localized Transitions in $\text{M}_2\text{X}_8^{n-}$ Complexes

The MO diagram for a d^4-d^4 complex (Figure 1) suggests that many metal-localized transitions in addition to $\delta \rightarrow \delta^*$ might be observed in absorption

(23) W. C. Troglor, E. I. Solomon, and H. B. Gray, *Inorg. Chem.*, **16**, 3031 (1977).

(24) F. A. Cotton and E. Pedersen, *J. Am. Chem. Soc.*, **97**, 303 (1975), and references therein.

(25) J. R. Ebner and R. A. Walton, *Inorg. Chim. Acta*, **14**, L45 (1975).

(26) J. R. Ebner, D. R. Tyler, and R. A. Walton, *Inorg. Chem.*, **14**, 1987 (1975).

(27) F. A. Cotton, P. E. Fanwick, L. D. Gage, B. Kalbacher, and D. S. Martin, *J. Am. Chem. Soc.*, **99**, 5642 (1977).

(28) A. Loewenschuss, J. Shamir, and M. Ardon, *Inorg. Chem.*, **15**, 238 (1976).

(29) J. H. Baxendale, C. D. Garner, R. G. Senior, and P. Sharpe, *J. Am. Chem. Soc.*, **98**, 637 (1976).

(30) W. C. Troglor, Ph.D. Thesis, California Institute of Technology, 1977.

(31) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 924 (1967).

(32) L. Dubicki and R. L. Martin, *Aust. J. Chem.*, **22**, 1571 (1969).

(33) J. G. Norman and H. J. Kolari, *J. Chem. Soc., Chem. Commun.*, **303** (1974); *J. Am. Chem. Soc.*, **97**, 33 (1975).

(34) J. G. Norman, H. J. Kolari, H. B. Gray, and W. C. Troglor, *Inorg. Chem.*, **16**, 987 (1977), and references therein.

(35) F. A. Cotton, *Acc. Chem. Res.*, **11**, 225 (1978).

spectral experiments. Two, in particular, that would be expected to fall at relatively low energies are the forbidden transitions $\delta \rightarrow \pi^*$ and $\pi \rightarrow \delta^*$. Thus, after we had completed our studies of the 14 700-cm⁻¹ system in the spectrum of Re₂Cl₈²⁻, we turned our attention to the three regions of weak absorption between 16 000 and 25 000 cm⁻¹ (middle panel, Figure 2). The first weak band of (n-Bu₄N)₂Re₂Cl₈ peaks at 17 675 cm⁻¹ and at 15 K consists of three progressions in a 225-cm⁻¹ excited state a_{1g}(ReRe) stretching vibration built on three origins.⁹ Two of the progressions are polarized parallel and one perpendicular with respect to the ReRe molecular axis. The band red-shifts by only 200 cm⁻¹ in (n-Bu₄N)₂Re₂Br₈.⁹ These results suggest that the transition in question is metal-localized, and further that the excited state possesses greater antibonding character than ¹A_{2u}($\delta\delta^*$), as reflected by the diminished value of a_{1g}(ReRe). Recall that this vibration is 248 cm⁻¹ in the ¹A_{2u} state. The presence of several vibronic origins and the weakness of the 17 675-cm⁻¹ band suggest an electric-dipole-forbidden, vibronically enabled transition. A ¹A_{1g} → ¹E_g ($\delta \rightarrow \pi^*$) assignment was adopted,⁹ as $\delta \rightarrow \pi^*$ would be expected to lie lower than $\pi \rightarrow \pi^*$ (vide infra; 39 215 cm⁻¹). A $\delta \rightarrow \pi^*$ assignment is also preferred over $\pi \rightarrow \delta^*$, as the X α calculation shows that the π orbital possesses substantial halogen character (% Cl: π , 44; π^* , 19).¹¹

The next absorption band, in order of increasing energy, in the spectrum of Re₂Cl₈²⁻ is another weak (ϵ_{\max} 65) system centered at 20 940 cm⁻¹ (Figure 2).⁹ Only perpendicularly polarized progressions of ~400 cm⁻¹ are built on this system.⁹ This high frequency clearly is not attributable to a_{1g}(ReRe), and was assigned to an excited state a_{1g}(ReCl) stretch (ground state^{14,15} 357 cm⁻¹). The a_{1g}(ReCl) assignment suggests in turn that the electronic transition is to an unoccupied, ReCl-type orbital. The vibronic nature of the transition is supported by its low intensity, the presence of several vibronic origins, and the red shift and intensity increase between 15 and 298 K. A corresponding absorption is also observed⁹ at 19 150 cm⁻¹ in the spectrum of (n-Bu₄N)₂Re₂Br₈. It was pointed out⁹ that this 1790-cm⁻¹ red shift upon halide substitution parallels the 1400–1500-cm⁻¹ red shift of the d_{xy} → d_{x²-y²} transition in (n-Bu₄N)OsNX₄ (X = Cl, Br). Therefore, a ¹A_{1g} → ¹A_{1u} ($\delta \rightarrow d_{x^2-y^2}(b_{2u})$) assignment was adopted.⁹ We note here for the sake of completeness that weak absorptions observed in the 22 000–24 000-cm⁻¹ region of the spectrum of K₄Mo₂Cl₈·2H₂O have been in part ascribed to the ¹A_{1g} → ¹A_{2g} ($\delta \rightarrow d_{x^2-y^2}(b_{1g})$) transition.^{17,33}

Proceeding to higher energy in the electronic spectrum of Re₂Cl₈²⁻ (Figure 2), we see an extremely weak progression at about 23 650 cm⁻¹. This weak system is partly obscured by the tail of a more intense absorption band. The progressional frequency of 185 cm⁻¹ is attributed⁹ to a symmetrical bending mode, a_{1g}(ReReCl). This band is tentatively assigned⁹ to the electric-dipole-forbidden transition ¹A_{1g} → ¹E_g ($\pi \rightarrow \delta^*$). Excitation of a_{1g}(ReReCl) is consistent⁹ with the considerable halogen character of the π orbital that was found in the X α calculation.¹¹ Part of a weak absorption system between 22 000 and 24 000 cm⁻¹ in the spectrum of Mo₂Cl₈⁴⁻ has been assigned to ¹A_{1g} → ¹E_g ($\pi \rightarrow \delta^*$) on the basis of the results from an X α calculation.³³ Also, an extremely weak absorption at 13 600

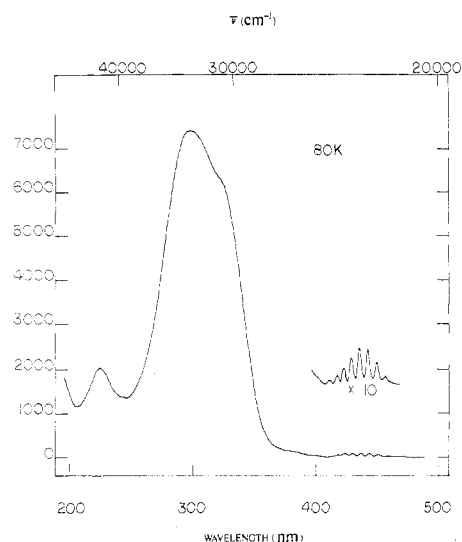


Figure 3. Electronic absorption spectrum of Mo₂(O₂CH)₄ in a 4:1 EtOH/MeOH glass at 80 K.

cm⁻¹ in the spectrum of Tc₂Cl₈³⁻ has been attributed to a $\pi \rightarrow \delta^*$ excitation.²⁷

Spectra of Mo₂(O₂CR)₄ Complexes

The electronic spectra of Mo₂(O₂CR)₄ (R = H, CH₃, CD₃, CF₃) complexes puzzled us for a long time. These complexes, which are isostructural with Cu₂(O₂CCH₃)₄, contain four bridging carboxylate ligands.³⁴ Unlike the electronic spectra of other species that contain quadruple metal-metal bonds, there is no absorption in the 14 000–21 000-cm⁻¹ region. Furthermore, no electronic absorption bands of appreciable intensity have been detected at lower energy.³⁴ The first feature in the solution electronic absorption spectra of these species is a weak band centered at 22 700 cm⁻¹ (ϵ_{\max} ~ 100). This band in the frozen solution spectrum³⁰ of Mo₂(O₂CH)₄ is shown in Figure 3. Dubicki and Martin observed³² a single vibrational progression of 350 cm⁻¹ built on the 22 700-cm⁻¹ band in the 77 K diffuse reflectance spectrum of Mo₂(O₂CCH₃)₄. They were not able to identify whether the progressional mode is due to a MoMo or a MoO stretching vibration, and no firm assignment for the 22 700-cm⁻¹ absorption system was reached; however, it was concluded that this absorption is not attributable to a $\delta \rightarrow \delta^*$ transition, thereby placing the latter at higher energy. More direct evidence that this weak absorption system is not $\delta \rightarrow \delta^*$ has come from the polarized crystal spectral studies of Mo₂(O₂CCH₂NH₃)₄(SO₄)₂·4H₂O and Mo₂(O₂CH)₄.^{19,36}

Our measurements of the polarized spectra of a crystal of Mo₂(O₂CCH₃)₄, as well as films of Mo₂(O₂-CCD₃)₄, Mo₂(O₂CCF₃)₄, and Mo₂(O₂CH)₄ at 15 K, allowed us to propose a specific assignment for the 22 700-cm⁻¹ absorption band. The energy of this absorption system does not depend significantly on the nature of the carboxylate ligand (Figure 4), implying that a metal-localized excitation is involved. From a comparison of the shifts of the progressional frequency and ground-state IR and Raman fundamentals, it is apparent that the vibration responsible for the excited-state progression is a_{1g}(MoMo).²² A hot band is observed 390 cm⁻¹ to the red of the first intense vibronic

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

Table II
Data for the ${}^1A_{1g} \rightarrow {}^1E_g$ ($\delta \rightarrow \pi^*$) Bands in Binuclear Complexes

Complex	Sample condition ^a	$\bar{\nu}_{\max}$, cm^{-1}	ϵ_{\max}	f	$a_{1g}(\text{MM})$, cm^{-1}	
					${}^1A_{1g}$	1E_g
$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$	Thin film, 15 K	22 436 ^b	120 ^c		406 ^d	370 ^b
$\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$	Thin film, 15 K	22 472 ^b				370 ^b
$\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$	Thin film, 15 K	22 791 ^b	120 ^e	0.0011 ^b	397 ^e	355 ^b
$\text{Mo}_2(\text{O}_2\text{CH})_4$	Thin film, 15 K	22 653 ^b	100 ^f	0.0008 ^g	406 ^f	360 ^b
$\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4 \cdot (\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	Crystal, 15 K	22 830 ^h	100 ⁱ		393 ⁱ	345 ^h
$(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$	Crystal, 15 K	17 675 ^j	<60 ^j		272 ^h	225 ^j
$(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Br}_8$	Crystal, 15 K	17 475 ^j			275 ^h	

^a Refers to measurements of $\bar{\nu}_{\max}$ and 1E_g $a_{1g}(\text{MM})$ only. ^b W. C. Trogler, E. I. Solomon, I. Trajberg, C. J. Ballhausen, and H. B. Gray, *Inorg. Chem.*, **16**, 828 (1977). ^c L. Dubicki and R. L. Martin, *Aust. J. Chem.*, **22**, 1571 (1969). ^d W. K. Bratton, F. A. Cotton, M. Debeau, and R. A. Walton, *J. Coord. Chem.*, **1**, 121 (1971). ^e F. A. Cotton and J. G. Norman, Jr., *ibid.*, **1**, 161 (1971). ^f F. A. Cotton, J. G. Norman, B. R. Stults, and T. R. Webb, *ibid.*, **5**, 217 (1976). ^g J. G. Norman, H. J. Kolari, H. B. Gray, and W. C. Trogler, *Inorg. Chem.*, **16**, 987 (1977). ^h F. A. Cotton, D. S. Martin, T. R. Webb, and T. J. Peters, *ibid.*, **15**, 1199 (1976). ⁱ F. A. Cotton and T. R. Webb, *ibid.*, **15**, 68 (1976). ^j W. C. Trogler, C. D. Cowman, H. B. Gray, and F. A. Cotton, *J. Am. Chem. Soc.*, **99**, 2993 (1977). ^k R. J. H. Clark and M. L. Franks, *ibid.*, **98**, 2763 (1976).

component in the spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$. The temperature dependence of the intensity of this hot band is consistent with population of a $206 \pm 20 \text{ cm}^{-1}$ vibration. In the spectrum of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, the polarization of this band is identical with that of the first intense vibronic peak, and in the spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, an extremely weak absorption attributable to the 0-0 transition is observed 190 cm^{-1} to the blue of the hot band. This conclusively shows that the transition is allowed in the Herzberg-Teller sense and therefore is electric dipole forbidden.²² Comparison with the IR spectra of these complexes establishes that the 190-cm^{-1} quantum is associated with an a_{2u} (MoMoO) bending vibration.²² As this vibration lowers the symmetry of the Mo_2L_8 chromophore, it is reasonable that it would be important in a vibronic coupling mechanism. The presence of two kinds of perpendicular polarization is believed to be the result of low symmetry site splitting of a degenerate electronic state.²²

We learned more about the nature of the degenerate electronic excited state associated with the 22700-cm^{-1} system by studying the emission spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ at 1.3 K.²² Importantly, there is an 1800-cm^{-1} gap between the 0-0 peaks in the absorption and the a_{1g} (MoMo)-structured emission systems, and the emission has a long lifetime (2 ms). On the basis of these results, we proposed that the emission band is due to a triplet-singlet transition and that the excited state associated with the 22700-cm^{-1} absorption system is the corresponding singlet. The specific assignment adopted for the 22700-cm^{-1} absorption system is ${}^1A_{1g} \rightarrow {}^1E_g$ ($\delta \rightarrow \pi^*$), as X α calculations on $\text{Mo}_2(\text{O}_2\text{CH})_4$ have indicated that $\delta \rightarrow \pi^*$ falls below $\pi \rightarrow \delta^*$ and, more importantly, only the former transition is strongly metal-localized (% Mo: δ , 89; π^* , 96; π , 65; δ^* , 86).³⁴ Furthermore, the calculations suggest that the shoulder at 30600 cm^{-1} (Figure 3) with an oscillator strength of approximately 0.03 is attributable to the $\delta \rightarrow \delta^*$ excitation.³⁴ Data obtained from studies of the $\delta \rightarrow \pi^*$ absorption system in several $\text{Mo}_2(\text{O}_2\text{CR})_4$ complexes are compared with those obtained for $\text{Re}_2\text{Cl}_8^{2-}$ and $\text{Re}_2\text{Br}_8^{2-}$ in Table II.

Transitions to $\pi\pi^*$ and $\sigma\sigma^*$ Excited States

Both back-of-the-envelope (Figure 1) and sophisticated^{11,33,34} theories predict that the $\pi \rightarrow \pi^*$ and

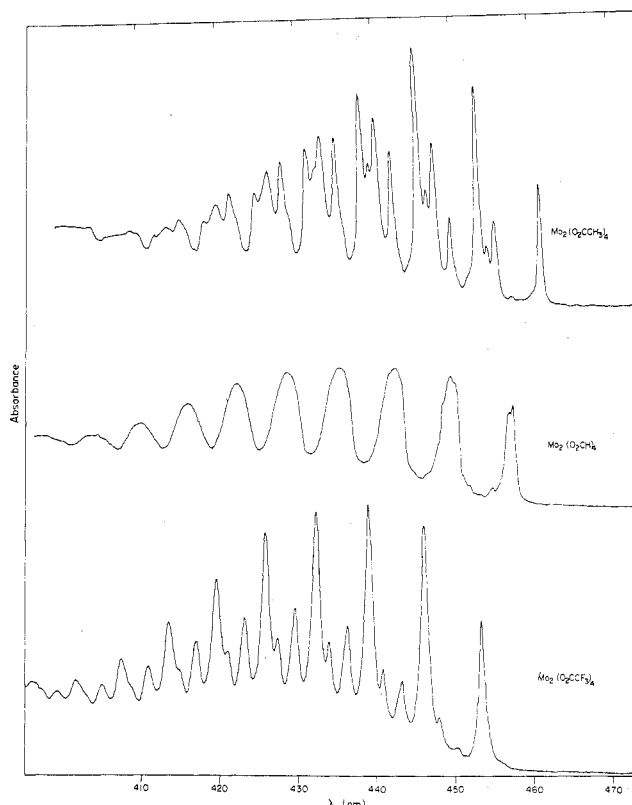


Figure 4. Electronic absorption spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CH})_4$, and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ in the 470-400-nm region. Spectra were obtained at 15 K for samples that had been sublimed onto a quartz window.

$\sigma \rightarrow \sigma^*$ transitions in $d^4\text{-}d^4$ complexes will occur at much higher energies than $\delta \rightarrow \delta^*$. The limited studies that have been made in the higher energy regions of the spectra of quadruply bonded complexes are in accord with this expectation. Once again, the best-studied complex from an experimental point of view is $\text{Re}_2\text{Cl}_8^{2-}$, where we have proposed that the z -polarized band centered at 39215 cm^{-1} (Figure 2) is due to the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\pi \rightarrow \pi^*$) transition.¹¹ The modest red shift of this band to 37735 cm^{-1} in the crystal spectrum of $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Br}_8$ is consistent with the 44.4% Cl character calculated (X α) for the π orbital of $\text{Re}_2\text{Cl}_8^{2-}$.¹¹ The X α calculations performed by Norman and Kolari have suggested that the intense absorption at energies above 34000 cm^{-1} in the spectrum of $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ is due

at least in part to a $\pi \rightarrow \pi^*$ excitation (the calculated $\pi \rightarrow \pi^*$ energy in $\text{Mo}_2\text{Cl}_8^{4-}$ is $39\,400\text{ cm}^{-1}$).³³ A well-resolved band with an oscillator strength of 0.02 occurs at about $44\,000\text{ cm}^{-1}$ in the solution spectra of $\text{Mo}_2(\text{O}_2\text{CR})_4$ complexes.^{30,32,34} On the basis of an $X\alpha$ calculation, this band was assigned to the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\pi \rightarrow \pi^*$) transition.³⁴ The relative order of the $\pi \rightarrow \pi^*$ energies for the complexes discussed is parallel to that for $\delta \rightarrow \delta^*$ transitions.

A metal-localized $\sigma \rightarrow \sigma^*$ type transition has never been observed in the spectrum of a quadruply bonded complex, which is consistent with the fact that $X\alpha$ calculations consistently predict that this excitation falls in the as yet unexplored vacuum ultraviolet region.

Ligand $\rightarrow \delta^*$ and $\delta \rightarrow$ Ligand Charge-Transfer Transitions

Next we turn our attention to the charge-transfer transitions in M_2L_8 complexes. The δ and δ^* orbitals are, respectively, the highest occupied and lowest unoccupied molecular orbitals. Therefore, it is not surprising that charge-transfer transitions that originate or terminate in the δ or δ^* orbitals have been observed.

First, the ligand-to-metal charge transfer (LMCT) excitations will be considered. The symmetry-adapted ligand π and σ -like orbitals are:

$$\sigma_{\parallel} = \pi_{\parallel} = a_{1g} + b_{1g} + e_g + a_{2u} + b_{2u} + e_u$$

$$\pi_{\perp} = a_{2g} + b_{2g} + e_g + a_{1u} + b_{1u} + e_u$$

where π_{\parallel} and π_{\perp} denote orbitals that lie in a plane containing and perpendicular to the metal-metal axis, respectively. Only LMCT transitions from the b_{2g} or one of the three e_g ligand orbitals to the lowest unoccupied b_{1u} (δ^*) level are electric dipole allowed. Intense (x,y) polarized absorption bands at $30\,870$ and $23\,630\text{ cm}^{-1}$ in the 5 K polarized crystal spectra of $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ (Figure 2) and $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Br}_8$, respectively, have been assigned to the LMCT transitions ${}^1A_{1g} \rightarrow {}^1E_u$ ($e_g\pi_{\parallel}, \pi_{\perp} \rightarrow \delta^*$).¹¹ Consistently, an MCD A term is associated with these bands. The dependence of the transition energy on the nature of the halide, of course, confirms the LMCT assignment.

The Norman-Kolari $X\alpha$ calculation of $\text{Mo}_2\text{Cl}_8^{4-}$ predicts³³ the two ${}^1A_{1g} \rightarrow {}^1E_u$ ($e_g\pi_{\parallel}, \pi_{\perp} \rightarrow \delta^*$) transitions to fall at $37\,500$ and $38\,600\text{ cm}^{-1}$. In accord with this prediction, an A term is observed¹⁶ at $37\,000\text{ cm}^{-1}$ in the MCD spectrum of $\text{Mo}_2\text{Cl}_8^{4-}$ in 6 M HCl. Alternatively, the MCD A term could represent a spin-forbidden LMCT transition to an excited state of E_u symmetry. A charge-transfer transition to δ^* has also been proposed²⁷ to account for part of the system centered at $31\,400\text{ cm}^{-1}$ in the absorption spectrum of $\text{Tc}_2\text{Cl}_8^{3-}$.

We will consider next the two peaks at $27\,000$ and $28\,100\text{ cm}^{-1}$ (ϵ_{max} of 400 in CH_3CN solution)⁹ in the spectrum of $\text{Re}_2\text{Cl}_8^{2-}$ (Figure 2). These absorptions shift to $21\,290$ and $22\,080\text{ cm}^{-1}$, respectively, in the spectrum of $\text{Re}_2\text{Br}_8^{2-}$.⁹ Owing to the small separation between the two bands, their LMCT character, and the polarization along the ReRe axis, $e_g\pi_{\parallel}$ and π_{\perp} (halide) $\rightarrow \delta^*$ (${}^1A_{1g} \rightarrow A_{2u}$ (a, b^3E_u)) assignments were proposed.⁹

Complex absorption systems at $35\,700$ and $26\,300\text{ cm}^{-1}$ in the spectra of $\text{Re}_2\text{Cl}_8^{2-}$ (Figure 2) and $\text{Re}_2\text{Br}_8^{2-}$, respectively, also appear to be due to electric-dipole-allowed LMCT transitions.¹⁶ Because of the mixed (x,y,z) polarization and the complex MCD signal observed, we suggested¹⁶ that the absorption system

contains two transitions, ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\text{Cl}(\pi_{\perp}) \rightarrow \delta^*$) and ${}^1A_{1g} \rightarrow {}^1E_u$ ($\text{Cl}(\sigma) \rightarrow \delta^*$).

A charge-transfer transition to a metal orbital other than δ^* has been proposed¹⁷ for the relatively weak absorption band at $28\,800\text{ cm}^{-1}$ in the spectrum of $\text{Mo}_2\text{Cl}_8^{4-}$ that is polarized along the MoMo axis; the intensity of this band is independent of temperature. For the reasons given, a ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\text{Cl}(\pi) \rightarrow d_{x^2-y^2}$) assignment was adopted.¹⁷ Examination of the polarized absorption spectra of a crystal of $(\text{NH}_4)_4\text{Mo}_2\text{Br}_8$ ³⁷ would provide useful additional information about the charge-transfer transitions in the binuclear Mo(II) halides.

Transitions of the MLCT type in the spectra of d^4-d^4 complexes have been identified only for the Mo(II) carboxylates. The most intense feature ($\epsilon_{\text{max}} \sim 7000$, $f = 0.19$) in the spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$ (Figure 3) peaks at $33\,500\text{ cm}^{-1}$.³⁴ The proposed assignment of this band, ${}^1A_{1g} \rightarrow {}^1E_u$ ($\delta \rightarrow \pi^*\text{CO}(e_u)$), is based on the results of an $X\alpha$ calculation.³⁴ Similar bands are observed in the spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$,³² $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$,³⁸ $\text{Mo}_2(\text{O}_2\text{CPh})_4$,³² and $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4$.³⁹

Photochemistry of Quadruply Bonded Complexes

Recent work in our laboratory has demonstrated that ultraviolet irradiation of binuclear molybdenum(II) complexes, in general, results in oxidation of the Mo_2^{4+} unit.^{20,40,41} For example, 254-nm irradiation of $\text{Mo}_2(\text{SO}_4)_4^{4-}$ and $\text{Mo}_2(\text{aq})^{4+}$ in acidic aqueous solutions yields $\text{Mo}_2(\text{SO}_4)_4^{3-}$ and $\text{Mo}_2(\text{aq})(\mu\text{-OH})_2^{4+}$, respectively.⁴¹ In each case the reduction product is molecular hydrogen. Similar UV irradiation of $\text{Mo}_2\text{X}_8^{4-}$ ($\text{X} = \text{Cl}, \text{Br}$) in aqueous HX solution produces $\text{Mo}_2\text{X}_8\text{H}^{3-}$, which breaks down thermally to give H_2 and $\text{Mo}_2(\text{aq})(\mu\text{-OH})_2^{4+}$. We have also shown that UV excitation of $\text{Mo}_2\text{Cl}_4\text{P}_4$ ($\text{P} = \text{PET}_3, \text{P}(n\text{-Bu})_3$, and PETPh_2) in chlorocarbon solvents yields trichloro-bridged dimolybdenum(III) complexes.⁴¹ Irradiation ($\lambda \leq 366\text{ nm}$) of $\text{Re}_2\text{Cl}_8^{2-}$ in acetonitrile solution does not result in photooxidation, however. In this case photocleavage of the ReRe bond occurs, producing monomeric rhenium(III) complexes.⁴² Subsequent flash kinetic spectroscopic investigations have suggested that ReRe bond rupture does not occur by a dissociative pathway, but rather is assisted by one or more acetonitrile solvent molecules.⁴³ All the photooxidation and photocleavage processes thus far observed involve upper excited states of the d^4-d^4 bonded complexes, as in no case have we found any reaction associated with a $\delta \rightarrow \delta^*$ transition.

The pattern of photochemical behavior that is developing for quadruply bonded binuclear complexes sharply contrasts with the prominence of dissociative photocleavage pathways^{6,7} in singly bonded systems such as $\text{Mn}_2(\text{CO})_{10}$. The failure to observe dissociative photocleavage in d^4-d^4 binuclear complexes is not really

(37) J. V. Brencic, I. Leban, and P. Segedin, *Z. Anorg. Allg. Chem.*, **427**, 85 (1976).

(38) F. A. Cotton and J. G. Norman, *J. Coord. Chem.*, **1**, 161 (1971).

(39) F. A. Cotton and T. R. Webb, *Inorg. Chem.*, **15**, 68 (1976).

(40) W. C. Trogler and H. B. Gray, *Nouv. J. Chim.*, **1**, 475 (1977).

(41) W. C. Trogler, G. L. Geoffroy, D. K. Erwin, and H. B. Gray, *J. Am. Chem. Soc.*, **100**, 1160 (1978).

(42) G. L. Geoffroy, H. B. Gray and G. S. Hammond, *J. Am. Chem. Soc.*, **96**, 5565 (1974).

(43) R. H. Fleming, G. L. Geoffroy, H. B. Gray, A. Gupta, G. S. Hammond, D. S. Kliger, and V. M. Miskowski, *J. Am. Chem. Soc.*, **98**, 48 (1976).

surprising, as it is now clear that strong metal-metal bonding persists in the low-lying $\delta\delta^*$ and $\delta\pi^*$ excited states. This is evidenced by the sharp vibronic structure that is built on $\delta \rightarrow \delta^*$ and $\delta \rightarrow \pi^*$ systems and the fact that the a_{1g} metal-metal stretching vibration is diminished by only 10–20% in the excited states in question. Rapid conversion of upper metal-localized excited states to these inactive ones greatly reduces the probability of metal-metal bond cleavage. It is possible that a transition to a $\sigma\sigma^*$ state might result in bond cleavage; however, this will be difficult to test. Recall that a band attributable to $\sigma \rightarrow \sigma^*$ has never been observed in the electronic spectra of d^4 - d^4 complexes, and it is presumed to lie at wavelengths shorter than 200 nm.

Concluding Remarks

In this Account we have emphasized the role that electronic spectroscopic and photochemical studies have played in the development of our present understanding of the nature of quadruple metal-metal bonds. The results have established that the lowest metal-localized electronic transitions in prototypal complexes ($\text{Re}_2\text{X}_8^{2-}$, $\text{Mo}_2\text{X}_8^{4-}$, $\text{Mo}_2(\text{SO}_4)_4^{4-}$, $\text{Mo}_2(\text{O}_2\text{CR})_4$) are derived from

$\delta \rightarrow \delta^*$, $\delta \rightarrow \pi^*$, and $\pi \rightarrow \delta^*$ transitions, with the energy order $\delta \rightarrow \delta^* < \delta \rightarrow \pi^*$ in all cases except $\text{Mo}_2(\text{O}_2\text{CR})_4$. The $\delta\delta^*$ singlet states lie about 14 000 cm^{-1} (40 kcal/mol) above the ground state in the binuclear $\text{Re}(\text{III})$ complexes, and at about 19 000 cm^{-1} (54 kcal/mol) in $\text{Mo}_2\text{Cl}_8^{4-}$, $\text{Mo}_2\text{Br}_8^{4-}$,⁴¹ and $\text{Mo}_2(\text{SO}_4)_4^{4-}$. The $\delta\pi^*$ singlet states lie about 17 000 cm^{-1} (49 kcal/mol) above the ground state in $\text{Re}_2\text{X}_8^{2-}$ and at about 22 000 cm^{-1} (63 kcal/mol) in several $\text{Mo}_2(\text{O}_2\text{CR})_4$ complexes. Analysis of the vibronic structure of the $\delta \rightarrow \delta^*$ and $\delta \rightarrow \pi^*$ bands has shown that the metal-metal bond strengths, which are relatively large in the ground states (>100 kcal/mol), are not weakened appreciably (<20%) in $\delta\delta^*$ and $\delta\pi^*$ excited states. Photoactivity is not associated with either of these lower excited states in the complexes examined to date.

It is a special pleasure to acknowledge the many contributions Dr. Charles D. Cowman made in the early stages of this research. We also thank Dr. R. J. H. Clark and Professors F. A. Cotton, W. A. Goddard III, D. S. Martin, Jr., J. G. Norman, Jr., and E. I. Solomon for helpful discussions and for sending us preprints of their works. Our work was supported by the National Science Foundation. This Account is Contribution No. 5616 from the Arthur Amos Noyes Laboratory.

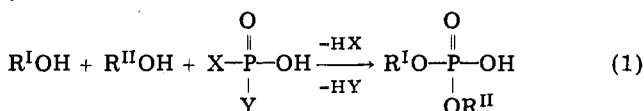
Phosphorylation by Means of Cyclic Enediol Phosphates¹

FAUSTO RAMIREZ* and JAMES F. MARECEK

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794

Received August 29, 1977

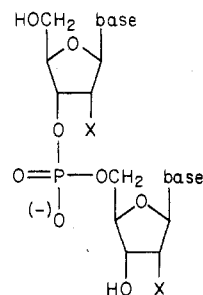
Several classes of important biological compounds, for example the nucleic acids and the phospholipids, are diesters of phosphoric acid. Consequently the nonenzymatic conversion of two alcohols into a phosphodiester (eq 1) as a route to these compounds has attracted the attention of the organic chemist for many years.²



The nucleic acids are linear polymers in which pentoses of adjacent nucleoside units are interconnected by 3'→5' phosphodiester bridges (1). The first synthesis of a dinucleoside phosphate containing the natural 3'→5' internucleotide bond was carried out by Michelson and Todd³ in 1955, and since that time much effort has been expended in improving the synthetic methodology.⁴ Despite recent advances, there still remains a need for more versatile phosphorylation procedures.

Fausto Ramirez has been Professor of Chemistry at the State University of New York (Stony Brook) since its foundation in 1959. He was born in Zulueta, Cuba, attended the University of Havana, and received a Ph.D. degree from the University of Michigan in 1950, working with W. E. Bachmann. He received further training under A. Burger at the University of Virginia. His research has dealt with the chemistry of phosphorus.

James F. Marecek is an Associate Research Director at Stony Brook. He was born in Berwyn, Ill., and received a Ph.D. degree from Case Western Reserve University in 1971, working with Dean L. Griffith.



1, X = H or OH

A second important class of phosphodiesters are the phospholipids (see Chart I). Found in biological membranes, they are composed of *O*-acyl or *N*-acyl derivatives of three types of polyols: glycerol, di-

(1) Supported by grants from the National Institutes of Health (GM 20672) and the National Science Foundation (MPS73-04944 and CHE76-16785).

(2) (a) H. G. Khorana, "Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest", Wiley, New York, N.Y., 1961; (b) D. M. Brown, *Adv. Org. Chem.*, 3, 75 (1963); (c) F. Cramer in "Newer Methods of Preparative Organic Chemistry", Vol. 3, W. Forest, Ed., Academic Press, New York, N.Y. 1964; (d) K. Sasse in "Methoden der Organischen Chemie", Vol. 12, Part 2, E. Muller, Ed., Georg Thieme Verlag, 1964; (e) V. M. Clark, D. W. Hutchinson and D. E. Wilson, *Angew. Chem., Int. Ed. Engl.*, 4, 240 (1965).

(3) A. M. Michelson and A. R. Todd, *J. Chem. Soc.*, 2632 (1955).

(4) (a) F. Cramer, *Angew. Chem., Int. Ed., Engl.*, 5, 173 (1966); (b) K. L. Agarwal, A. Yamazaki, P. J. Cashion, and H. G. Khorana, *Angew. Chem., Int. Ed. Engl.*, 11, 451 (1972); (c) R. J. Zhadanov and S. M. Zhenodorova, *Synthesis*, 222 (1975); (d) V. Amarnath and A. B. Broom, *Chem. Rev.*, 77, 183 (1977); (e) M. Ikehara, *Acc. Chem. Res.*, 7, 92 (1974).