comitant hydroxide oxidation that is responsible for cleavage. With regard to applications, this photoactivated reaction should make possible "footprinting" as a function of time. Most importantly, the differential cleavage of ColE1 DNA by enantiomers of $Co(DIP)_3^{3+}$ represents a clear example of a *conformation-specific* DNA cleaving molecule. This molecule will be useful in determining regions of Z-DNA conformation within long segments of native DNA. Moreover the high level of recognition of DNA conformation by these chiral inorganic complexes suggests to us the powerful application of stereospecificity in DNA drug design.

Acknowledgment. We are grateful to the National Institute of General Medical Sciences (GM 32203) for their financial support.

Nature of the Emissive Excited State of Quadruply Bonded $Mo_2X_4(PMe_3)_4$ Complexes

Michael D. Hopkins and Harry B. Gray*

Contribution No. 6957, Arthur Amos Noyes Laboratory
California Institute of Technology
Pasadena, California 91125

Received December 7, 1983

A totally convincing interpretation of the electronic emission spectra of quadruply bonded transition-metal dimers has not yet been achieved.[1-6] This is in contrast to the increasingly detailed understanding of the absorption spectra of these complexes that has been realized in recent years.[7,8] Conclusive assignment of the emissive state and establishment of its geometry have been hindered in these systems by the general observation of a lack of mirror symmetry between the emission and lowest energy absorption band. The sole unambiguous example of prompt fluorescence from the singlet $\delta\delta^*$ excited state to the δ^2 ground state was observed for $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ and was attributed to the fact that the arrangement and steric bulk of the ligands imposed a considerable barrier to certain geometrical distortions generally available to this excited state.[3] Our interest in determining the extent of ligand participation in these formally metal-localized excited states has led us to examine the electronic spectra of a number of derivatives of the $M_2X_4(PR_3)_4$ type.[9]

The electronic absorption spectrum of $Mo_2X_4(PMe_3)_4$ (X = Cl, Br, I)[10] exhibits a band attributable to the singlet $\delta^2 \rightarrow \delta\delta^*$ ($^1B_2 \leftarrow {}^1A_1$; D_{2d}) transition[3,7,11] as its lowest energy feature. This band both red shifts and increases in intensity according to Cl < Br < I (X = Cl, λ_{max} = 585 nm, f = 0.026; X = Br, λ_{max} = 598 nm, f = 0.032; X = I, λ_{max} = 636 nm, f = 0.040; 300 K, 2-methylpentane). Upon excitation of this transition, crystals and hydrocarbon solutions of $Mo_2X_4(PMe_3)_4$ display an intense red luminescence. The radiative efficiency of this luminescence is, by an order of magnitude, the highest yet observed for a quadruply bonded system (X = Cl, λ_{max} = 673 nm, ϕ = 0.26, τ = 140 ns; X = Br, λ_{max} = 671 nm, ϕ, = 0.16, τ = 90 ns; X = I, λ_{max} = 715 nm, ϕ = 0.12, τ = 30 ns; 300 K, 2-methylpentane).[12] The close agreement of the radiative rate constant with that calculated from the oscillator strength[13] of the $^1B_2 \leftarrow {}^1A_1$ transition, in addition to the substantial overlap of the emission spectrum with this band, strongly suggests assignment of the emission to $^1B_2 \rightarrow {}^1A_1$ fluorescence for all three complexes.

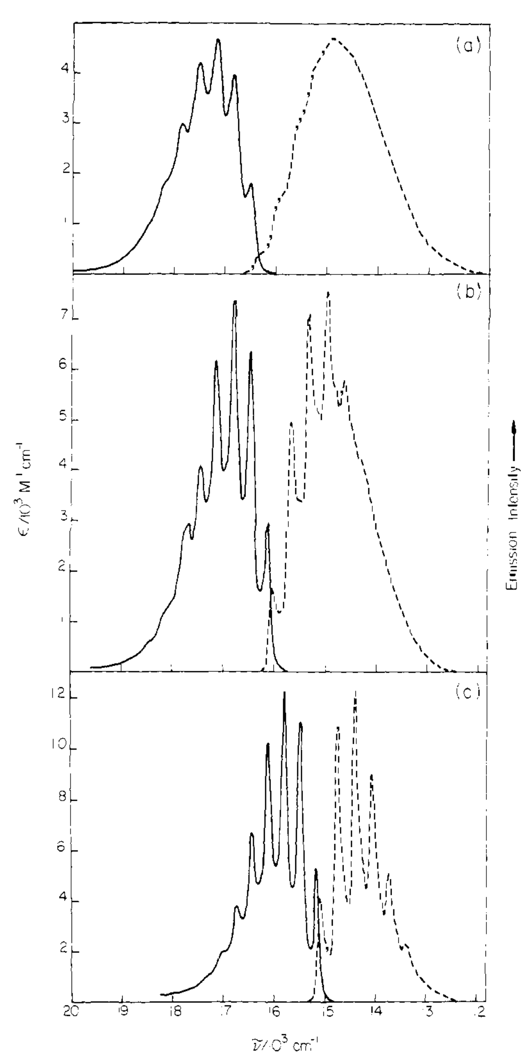


Figure 1. Absorption (—) and corrected emission (---) spectra of $Mo_2X_4(PMe_3)_4$ in 2-methylpentane at 77 K: (a) X = Cl; (b) X = Br; (c) X = I.

Vibrational fine structure is resolved in both the $^1B_2 \leftarrow {}^1A_1$ and $^1B_2 \rightarrow {}^1A_1$ bands of $Mo_2X_4(PMe_3)_4$ at low temperature. At 77 K the absorption and emission spectra (Figure 1) progress in a single mode, with spacings corresponding to the metal-metal stretching frequencies of the excited and ground states, respectively.[14] In the absorption spectra of all three complexes, the Franck-Condon factors calculated from the relative intensities

---

[1] Trogler, W. C.; Solomon, E. I.; Gray, H. B. *Inorg. Chem.* **1977**, *16*, 3031-3033.

[2] Trogler, W. C.; Solomon, E. I.; Trajberg, I.; Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1977**, *16*, 828-836.

[3] Miskowski, V. M.; Goldbeck, R. A.; Kliger, D. S.; Gray, H. B. *Inorg. Chem.* **1979**, *18*, 86-89.

[4] Morgante, C. G.; Struve, W. S. *Chem. Phys. Lett.* **1979**, *63*, 344-346.

[5] Manning, M. C.; Trogler, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 5311-5320.

[6] Fraser, I. F.; Peacock, R. D. *Chem. Phys. Lett.* **1983**, *98*, 620-623.

[7] Trogler, W. C.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 232-239.

[8] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

[9] Presented in part: Hopkins, M. D.; Gray, H. B. *Abstr. Pap.-Am. Chem. Soc.* **1983**, *186th*, INOR 115.

[10] The complexes were prepared by treating $Mo_2(O_2CCH_3)_4$ with excess trimethylphosphine and halotrimethylsilane, following the route to $Mo_4X_8(PR_3)_4$ (Ryan, T. R.; McCarley, R. E. *Inorg. Chem.* **1982**, *21*, 2072-2079).

[11] Spectroscopic studies on single crystals of $Mo_2Br_4(PMe_3)_4$ have been performed (Miskowski, V. M., unpublished results). The 598-nm band is found to be polarized parallel to the Mo-Mo axis, consistent with the $^1B_2 \leftarrow {}^1A_1$ assignment.

[12] The origin of the unexpected increase of the emission lifetime and quantum yield of $Mo_2Cl_4(PMe_3)_4$ relative to the electronically similar $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_4$[3] has been investigated through variable-temperature lifetime measurements of the complexes $Mo_2Cl_4(PR_3)_4$ (R = Me, Et, *n*-Pr, *n*-Bu)[9] (Hopkins, M. D.; Gray, H. B., unpublished results). The nonradiative rate constants (k_{nr}) of all complexes follow the expression

$$k_{nr} = k_0 + k_1 \exp(-E_a/kT)$$

and appear to have very similar values of E_a and k_0. The trimethylphosphine complex differs from the other three by having a smaller value of k_1. An interpretation of the "phosphine sensitivity" of k_1 is not yet available.

[13] Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814-822.

[14] ν_1(MoMo) ($^1B_2$): X = Cl, 335 (10); X = Br, 340 (10); X = I, 320 (5) cm^{-1}. ν_1(MoMo) ($^1A_1$): X = Cl, 358 (2); X = Br, 353 (2); X = I, 345 (2) cm^{-1} (Raman, λ_{ex} = 514.5 nm, C_6H_6 solution).

0002-7863/84/1506-2468$01.50/0

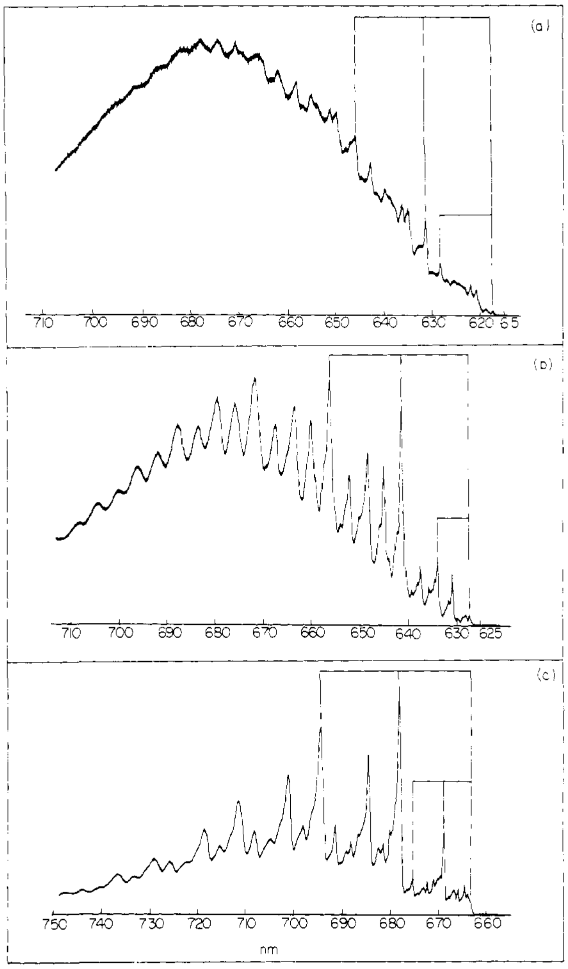


Figure 2. Emission spectra of polycrystalline $Mo_2X_4(PMe_3)_4$ at ca. 5 K (uncorrected for spectrometer response). The ν_1(MoMo) progression-forming mode and the $a_1\nu_2$(MoX) subprogression are identified. Fluorescence in the region of the electronic origin is strongly quenched by self-absorption. (a) X = Cl; (b) X = Br; (c) X = I.

of the progression members are nearly identical, indicating a similar excited-state distortion along the metal-metal axis in each case. The intensity distribution in the emission spectra, however, is a highly sensitive function of ligand. Progressive broadening of the individual vibronic transitions of the bromo and chloro complexes results in the striking deviation of their absorption and emission spectra from the mirror-image relationship displayed by the spectra of the iodo complex. Examination of the high-resolution emission spectrum of $Mo_2X_4(PMe_3)_4$ at 5 K (Figure 2) reveals that a remarkable number of other vibrational modes are Franck-Condon active and that the broadening observed for the bromo and chloro complexes arises from an increasing redistribution of intensity from the ν_1(MoMo) progression-forming mode into these vibronic sidebands. Although assignment of these additional vibrational modes is incomplete at present, each spectrum displays a major subprogression corresponding to the symmetric Mo-X stretching coordinate.[15]

Significant deviations of electronic spectra from mirror symmetry have been observed previously in the octahalodimolybdate and -dirhenate family of ions.[1,3,4,6] This behavior was attributed to a Duschinsky effect[16] originating from an excited-state distortion that was large relative to that of a species exhibiting symmetric spectra. In light of the above absorption spectroscopic and photophysical evidence that all three $Mo_2X_4(PMe_3)_4$ derivatives possess similar, relatively slightly distorted excited-state geometries, the unprecedented "variable mirror symmetry" exhibited by their spectra is thus quite surprising. We suggest that a large part of the observed deviation in the spectral intensity profiles of these species arises from the varying degrees of coupling present between the ν_1(MoMo) and $a_1\nu_2$(MoX) vibrational modes in the ground and excited states of each complex.[17] Specifically, larger *apparent* Huang-Rhys factors for the ν_2(MoX) subprogression would be anticipated as the difference in frequency between the two modes decreases. Accordingly, the asymmetric spectra of the chloro complex indicate that these modes are strongly coupled to different extents in the ground and excited states. In contrast, the symmetric spectra of the iodo complex show that the two modes are largely decoupled.

We note in closing that Fraser and Peacock have found[6] that the progression-forming mode is ν_2(MoCl) rather than ν_1(MoMo) in the emission spectrum of $Mo_2Cl_8^{4-}$. As an alternative to the proposed reassignment[6] of the $\delta\delta^*$ emission, we suggest that the variation in the coupling of these two modes in the ground and $\delta\delta^*$ excited states of $Mo_2Cl_8^{4-}$ is even greater than that observed here for $Mo_2Cl_4(PMe_3)_4$.

Acknowledgment. We gratefully acknowledge the contributions Vince Miskowski and Tom Zietlow have made to this work, mainly through helpful discussions, and we thank R. D. Peacock for providing us with a preprint of ref 6. This research was supported by National Science Foundation Grant CHE81-20419. M.D.H. thanks the Sun Co. for providing a graduate fellowship.

---

[15] $a_1\nu_2$(MoX): X = Cl, 284 (5); X = Br, 165 (5); X = I, 143 (5) cm^{-1}.

[16] Ballhausen, C. J. "Molecular Electronic Structures of Transition Metal Complexes"; McGraw-Hill: New York, 1979; Chapter 1.

[17] Such coupling has been invoked to explain the electronic absorption and resonance Raman spectra of diruthenium(II,III) tetracarboxylate (Clark, R. J. H.; Ferris, L. T. H. *Inorg. Chem.* **1981**, *20*, 2759-2771. Miskowski, V. M.; Loehr, T. M.; Gray, H. B., unpublished results).

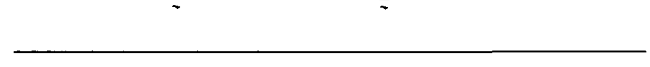
2-Alkoxybenzo-1,3-dithiole 1,1,3,3-Tetraoxide, a Carbonyl 1,1-Dipole Synthon

Barry M. Trost* and Peter Quayle

McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received December 28, 1983
Revised Manuscript Received February 22, 1984

Acyl sulfones **3** are an almost unknown class of compounds.[1] Their potential as acylating agents led us to explore methods to generate them that did not depend upon oxidation.[1,2] The possibility that unmasking an alkoxybis(sulfonyl)methane such as **2** could generate **3** in situ and that alkylation of **1** should provide an entry to **2** led us to propose that **1** could be a useful carbonyl 1,1-dipole synthon[3,4] as summarized in eq 1. Of great importance



(1)

---

[1] Schank, K.; Frisch, A.; Zwanenburg, B. *J. Org. Chem.* **1983**, *48*, 4580. Schank, K.; Werner, F. *Justus Liebigs Ann. Chem.* **1980**, 1477; **1979**, 1927 and references therein. For sulfonyl formates and related compounds, see: Ferdinand, G.; Schank, K. *Synthesis* **1976**, 408. Barton, D. H. R.; Manly, D. P.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1568. Ferdinand, G.; Schank, K.; Weber, A. *Justus Liebigs Ann. Chem.* **1975**, 1484. Olijnsma, T.; Engberto, J. B. F. N.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 897. Senning, A.; Sorenson, O. N.; Jacobsen, C. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 734. Gaul, R. J.; Fremuth, W. J. *J. Org. Chem.* **1961**, *26*, 5103.

[2] Cf.: Kumamoto, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2111. Minato, H.; Kodama, H.; Miura, T.; Kobayashi, M. *Chem. Lett.* **1977**, 413. However, acyl sulfoxides are believed to be the intermediates in these reactions.