ate-bridged Cu(II)–Cu(II) linkage.

Registry No. [Cu(O$_2$CCCl$_3$)$_2$(Tempo)]$_2$, 85803-18-5.

Supplementary Material Available: Tables of atomic positional parameters, observed and calculated structure factors, elemental analysis, anisotropic thermal parameters, and bond distances and angles (25 pages). Ordering information is given on any current masthead page.

Department of Chemistry   **Leigh C. Porter**
University of California   **Michael H. Dickman**
Irvine, California 92717   **Robert J. Doedens***

Quadruple Probing of Electronic Excited States by Magnetic Circular Dichroism (MCD), Linearly Polarized Luminescence (LPL), Linearly Polarized Excitation Luminescence (LPEL), and Optical Absorption Techniques: Pentacarbonyl(piperidine)tungsten(0), W(CO)$_5$pip

Sir:

Our laboratory[1,2] and another[3] have very recently shown that electronic absorption polarizations can be assigned directly for

^{1}E $\xleftarrow{\sigma}$ ^{1}A$_1$ excitations of synthetically and photochemically important tetragonal six-coordinate transition-metal carbonyl complexes M(CO)$_5$L (e.g., M = Cr, Mo, W; L = amines, phosphines, stibines, arsines) in optically *isotropic solutions.* Solution MCD spectroscopy was used for this purpose, and the quantum interpretation of the signs of Faraday *A* terms by means of reliable orbital angular momentum calculations of signs of $\langle L \rangle$ for excited states made possible the assignment of MO fates for one-electron excitation processes. These and indirect considerations led to this excited-state assignment of W(CO)$_5$L[1,2] in order of increasing energy (I < II < III):

I ^{3}E[a$_1$^{1}($\sim$d$_{z^2}$)e^3($\sim$d$_{xz}$,d$_{yz}$)] $\leftarrow$

$\qquad\qquad$ ^{1}A$_1$[e^4($\sim$d$_{xz}$,d$_{yz}$)] $\sim$440 nm

II ^{1}E[a$_1$^{1}($\sim$d$_{z^2}$)e^3($\sim$d$_{xz}$,d$_{yz}$)] $\leftarrow$

$\qquad\qquad$ ^{1}A$_1$[e^4($\sim$d$_{xz}$,d$_{yz}$)] $\sim$400 nm

III ^{1}A$_2$(T$_{1g}$)[b$_1$^{1}($\sim$d$_{x^2-y^2}$)b$_2$^{1}($\sim$d$_{xy}$)] $\leftarrow$

$\qquad\qquad$ ^{1}A$_1$[b$_2$^{2}($\sim$d$_{xy}$)] $\sim$340 nm

However, direct MCD-based polarization assignments availing excited-state symmetries of bands such as ^{1}A$_2$ $\leftarrow$ ^{1}A$_1$ (band III, vibronically electric dipole allowed) or

$$^1A_1 \xleftarrow[z]{\pi} {}^1A_1$$

(electric dipole axially z allowed, molecular C$_4$ and z axes coincident) cannot in general be made reliably for large molecules such as the present one and others. Such interpretations of Faraday *B* terms[4] involve summations over all virtual states (k) (spectators during specific state excitation,

(1) Schreiner, A. F.; Amer, S.; Duncan, W. M.; Ober, G.; Dahlgren, R. M.; Zink, J. *J. Am. Chem. Soc.* **1980,** *102,* 6871 and references therein.
(2) Schreiner, A. F.; Amer, S.; Duncan, W. M.; Dahlgren, R. M.; *J. Phys. Chem.* **1980,** *84,* 2688.
(3) Boxhoorn, G.; Stufkens, D. J.; van de Coolwijk, P. J. M.; Hezemans, A. M. F. *Inorg. Chem.* **1981,** *20,* 2778.
(4) *B* terms are given by

$$B_{j \leftarrow a} = \Sigma Im \left[\sum_{k \neq a} \frac{\langle k|u|a \rangle}{(E_k - E_a)} \cdot \langle a|m|j \rangle \times \langle j|m|k \rangle + \right.$$

$$\left. \sum_{k \neq j} \frac{\langle j|u|k \rangle}{(E_k - E_j)} \cdot \langle a|m|j \rangle \times \langle k|m|a \rangle \right]$$

where $u = L + 2S$ and $m = $ er for the valence electrons.

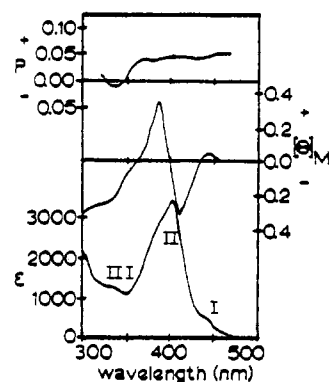**Figure 1.** MCD (θ), LPEL (*P*), and optical spectra of W(CO)$_5$pip (MCD and optical spectra at room temperature, LPEL spectrum at 80 K). [θ]$_M$ is the molar ellipticity in a field of 1 G, ϵ the molar absorptivity, and *P* the degree of polarization ($P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$). At 80 K about $^2/_3$ of band I is completely free of the tail of band II.

j $\leftarrow$ a) and involve electric $\langle$er$\rangle$ and magnetic $\langle L \rangle$ dipole integral evaluations (magnitudes and signs) that include spectator state functions |k$\rangle$, and |a$\rangle$ and |j$\rangle$, and the virtual MO's of |k$\rangle$ and |j$\rangle$, about nearly all of which little is known with certainty; also required for the *B* term evaluations are pure guesses about the correct one-to-one associations of ill-characterized excited-state and MO functions with spectator optical band energies, and many of these latter functions are not known at all in the vacuum-UV, for example.

Reasons such as the above prompted us to measure the linearly polarized luminescence (LPL) and linearly polarized excitation luminescence (LPEL) on our laboratory's computerized modular instrument of original design. *Combining LPL–LPEL results with MCD and optical data then led to new assignments as described.* The LPEL–LPL instrument consists of CW xenon-lamp excitation (chopped), stepper motor driven excitation ($^1/_4$ m) and emission ($^1/_4$ m, double dispersion) grating monochromators, order filters, UV–visible–near-infrared polarizers, a wavelength-slaved electrooptic modulator, dual lock-in phase-sensitive detection, and a microprocessor for control of monochromators and modulator, collection of voltage-to-frequency converted PMT signals, and multiscan averaging. Operating at 50 kHz, the modulator on alternate half-cycles samples $I_\parallel$ and $I_\perp$ of emitted light, which becomes incident on a fixed polarizer (P2) preceding the emission monochromator. P2 passes vector projections of $I_\parallel$ and $I_\perp$. The LPEL–LPL spectra are precisely free of monochromator and detector anisotropy effects and of detector dark current. We sought linear polarization data from LPEL–LPL especially for the nondegenerate excited states, e.g., A$_1$ $\xleftarrow{z}$ A$_1$, or electric dipole vibronically allowed states, e.g.

$$A_2(a_2^{vib} \text{ or } e^{vib}) \xleftarrow{\sigma \text{ or } \pi} A_1$$
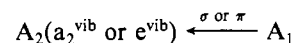
Our aspiration was realized by executing the following plan.

The molecular excitation polarization of band II ($\sim$400 nm) was already known to be $\sigma(x,y)$, or ^{1}E $\leftarrow$ ^{1}A$_1$, from the MCD.[1-3] Then the LPEL–LPL excitation and emission monochromators were set, respectively, to 400 nm (^{1}E $\leftarrow$ ^{1}A$_1$) and 535 nm (emission maximum[5] at 80 K). The degree of linear emission polarization,[6] *P*, of the frozen solution was found to be positive and ca. 0.05 (Figure 1), indicative of dominant $\sigma(x,y)$ emission, or $\bar{E}(^3$E) $\rightarrow$ A$_1$. $\bar{E}$ is one of the spin–orbit components ($\bar{E}$, $\bar{A}_1$, $\bar{A}_2$, $\bar{B}_1$, $\bar{B}_2$) of ^{3}E mentioned above. *The direct finding that this emission is molecularly in plane, $\sigma(x,y)$, polarized at 535 nm is a new observation,*

(5) Wrighton, M.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1971,** *93,* 4336.
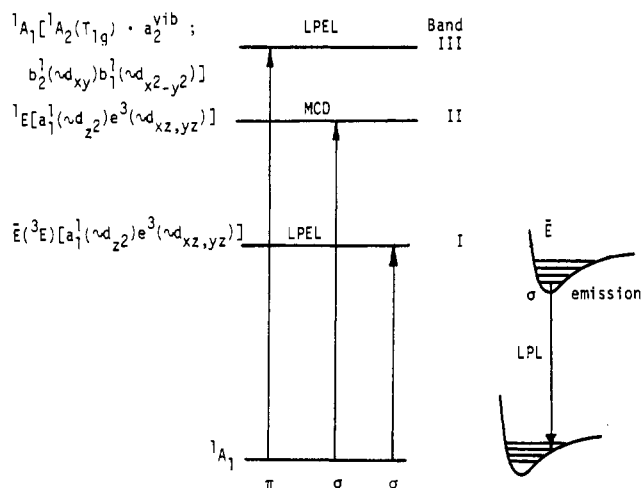(6) Albrecht, A. C. *J. Mol. Spectrosc.* **1961,** *6,* 84.

Figure 2. Direct excited state (and MO) assignments based on the quadruple-probe data of MCD, LPL, LPEL, and optical absorption techniques.

since in principle it might equally well have been $\pi(z)$ polarized. With this knowledge the emission monochromator was held at 535 nm and the excitation monochromator was scanned several times in the averaging mode for each of several solutions over the absorption region of bands I ($\sim$430 nm), II ($\sim$400 nm), and III ($\sim$340 nm). Figure 1 shows the positive degree of polarization,[6] P ($P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$), for bands I and II, but P is negative for band III. These results now enable us to make two new direct polarization excitation assignments for which *direct* assignments were not previously possible. Thus *it is found now that the degree of polarization, P, of band I is experimentally the same as of* $^1E \leftarrow {}^1A_1$ *(band II)*, for which reason band I, previously suggested[1-3,5] to be $^3E \leftarrow {}^1A_1$ (vide supra), *is dominated by molecular in-plane* $\sigma(x,y)$ *polarization*, or $\bar{E}(^3E) \leftarrow {}^1A_1$. On the basis of group theory band I might equally well have been dominated by out-of-plane $\pi(z)$ polarization, e.g., $\bar{A}_1(^3E) \leftarrow {}^1A_1$, to one of the energy-distinct spin–orbit components of ^3E. Previously observed[1,3] *A*-term-like MCD intensity for band I could not unambiguously be ascribed to a genuine *A* term of $\bar{E} \leftarrow A_1$ or to opposite signed *B* terms of adjacent spin–orbit components of a $^3\Gamma$ state such as ^3E.

The second new direct polarization assignment for optical excitation is that of band III ($\sim$335 nm). The polarization of $^1E \leftarrow {}^1A_1$ (band II) and $\bar{E} \to A_1$ from MCD and P of the LPEL–LPL experiments having been established, *the negative degree of polarization establishes that band III ($\sim$335 nm) is* $\pi(z)$ *polarized corresponding to excitation* $A_1 \xleftarrow{} A_1$. If III is the transition $^1A_2(T_{1g})[b_2{}^1(\sim d_{xy})b_1{}^1(\sim d_{x^2-y^2})] \leftarrow {}^1A_1$ as proposed,[1,2] then the present experimental polarization finding leads to the *new conclusion that the electric dipole enabling vibronically coupled vibration is of symmetry* $a_2{}^{vib}$, e.g., $^1A_2(a_2{}^{vib}) \xleftarrow{} {}^1A_1$ or $^1A_2 \xleftarrow{} {}^1A_1(a_2{}^{vib})$, ruling out the alternative group theoretically possible coupling vibration(s) of symmetry e^{vib}, e.g., $^1A_2(e^{vib}) \xleftarrow{} {}^1A_1$. The a_2 vibration of $W(CO)_5N$ is one of the type $\delta(W-C-O)$. The measured polarization does not support an assignment[3] $^1E[b_1{}^1(\sim d_{x^2-y^2})e^3] \leftarrow {}^1A_1$, since it requires P to be positive. The above amplitudes of P are below the extrema of depolarization-free ones,[6] $+^1/_7$ ($E_1 \leftarrow A_1$) and $-^1/_3$ ($A_1 \leftarrow A_1$), and will be discussed in our next paper.

The assignment composite is summarized in Figure 2. The generalization inherent in these results resides in the fact that the analysis should be applicable to similar excitation and emission bands of all nominally "$nt_{2g}{}^6$" low-spin tetragonal complexes, ML_5X and *trans*-ML_4XY, including other carbonyl complexes.

In summary, it is shown that multiply probing electronic excited states by LPL, LPEL, MCD, and optical absorption techniques can lead to complementing and definitive new information of great importance to photochemists as well as spectroscopists. For the present case of $W(CO)_5pip$ it became possible to make direct polarization assignments of a sequence of three absorption and one emission state and to associate the MO's with them. The direct polarized measurements for excitation bands I and III are new, as is that of the dominant σ polarization of the emission band. The photochemical implication of excitations I and II is dominantly σ labilization (with some xz, yz π labilization) of the axial N–W–CO, with magnitudes of effects W–N > W–CO as photochemically found. The implications of excitation III are equatorial W–CO σ labilization and π labilization of in-plane (xy) type. However, these one-electron effects are distributed over four W–CO bonds. Also, since there is only one photoemission band, it is considered that at 80 K there is no emission corresponding to excitation III. Thus, the lower quantum yields[7,8] (e.g., $W(CO)_5L + L' \to W(CO)_5L' + L$) with excitation III compared to excitation II may be due to $^{1,3}A_2$ nonradiative losses, $^{1,3}A_2 \rightsquigarrow {}^{*3}E"[(\sim d_{z^2})^1(\sim d_{xz}, d_{yz})^3]$, detracting from internal conversion to the most likely photoreactive state, "^3E".

(7) Wrighton, M. S. *Chem. Rev.* **1974**, *74*, 401.
(8) Darensbourg, D. J.; Murphy, M. A. *Inorg. Chem.* **1978**, *17*, 884.

Department of Chemistry   **Sten A. Wallin**
North Carolina State University   **Anton F. Schreiner***
Raleigh, North Carolina 27650

Selective Molecular Oxygen Oxidation of Alkyl Sulfides to Sulfoxides Catalyzed by Dichlorotetrakis(dimethyl sulfoxide)ruthenium(II)

Sir:

In the past, attempts to use metal-based catalysts to promote the selective oxidation of dialkyl sulfides to their sulfoxides have met with only limited success. Known catalysts for this oxidation suffer not only from slow rates but also from poor selectivities with high levels of sulfone as byproducts. We have found that the Ru(II) complex *cis*-dichlorotetrakis(dimethyl sulfoxide)ruthenium in alcohol solvents is an excellent catalyst for the selective molecular oxygen oxidation of dialkyl sulfides to their sulfoxides. The observed reaction rates at 100 °C and 100 psig O_2 pressure are much faster than reported rates for other metal catalysts such as $RuCl_3{}^{1,2}$ or $RuCl_2(Ph_3)_3$.[1] In addition, unlike metal-based literature catalysts,[1] the *cis*-$RuCl_2(Me_2SO)_4$ complex[4,5] affords high selectivities for the

(1) Ledlie, M. A.; Allum, K. G.; Howell, I. V.; Pitkethly, R. C. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1734-8.
(2) Contrary to ref 3, $RuCl_3 \cdot xH_2O$ (when reduced with H_2 to ensure that all Ru present is in the +3 oxidation state[3]) will not function as a catalyst. This offers further support for the presence of Ru(IV) since the authors of ref 3 were very likely dealing with a Ru(IV) contaminant as active catalyst material in their work.[3]
(3) Harrod, J. F.; Ciccone, S.; Halpern, J. *Can. J. Chem.* **1961**, *39*, 1372.
(4) James, B. R.; Ochiai, E.; Rempel, G. I. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 781-4.
(5) The complex used in the catalytic studies was recrystallized from MeOH and has been shown to possess a cis–chloro arrangement with two S-bonded Me_2SO groups trans to the chloride ligands, one axial Me_2SO O-bonded, and the other axial Me_2SO S-bonded: Mercer, A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2480-3.