formation, those in the other, a $C_{2'}$ endo-trans-gauche conformation.[29]

Acknowledgment. We are grateful to Mr. R. Wasylishen for his help with the computer analyses and Dr. J.B. Rowbotham for his adaptation of a plotting routine for LAME and to the Faculty of Graduate Studies of the University of Manitoba for financial support. J. G. D. is grateful for the award of a Manitoba Fellowship. This work was supported by a grant from the National Research Council of Canada. We thank Dr. A. A. Grey of the Ontario Research Foundation for obtaining the 220-MHz spectra. We thank a referee for suggesting the inclusion of the statement regarding the low probability of the $C_{2'}$ endo conformation for those nucleosides which do not correlate.

(29) NOTE ADDED IN PROOF. A correction (*ca.* 1 Hz) for the effect of the electronegativity differential between 2′-H and 2′-OH should be applied to the $J_{1'2'}$ values of dU, IdC, and BrdU. A much smaller correction (<0.5 Hz) might be required for the corresponding $J_{3'4'}$ values. These corrections would shift the three points to the *left* in Figure 3 and to the *right* in Figure 2 but do not affect our qualitative conclusions. Further, since submission of this article we have analyzed spectra for thymidine (T), dihydrouridine (diHU), and arabinouridine (aU). Data for T and diHU correlate, although the latter does not have feature b in common with the correlating nucleosides. However, aU does not correlate; this suggests that the stereoconfiguration of the sugar is important insofar as the correlation is concerned.

F. E. Hruska,* A. A. Smith, J. G. Dalton
Chemistry Department, The University of Manitoba
Fort Garry, Manitoba, Canada
Received May 24, 1971

Emission from Tungsten Carbonyl Complexes

Sir:

Dissociative decay is a major deactivation pathway for electronic excited states of metal carbonyls.[1] Other facile nonradiative processes include reactions of coordinated ligands other than CO[1-3] and internal conversion where photoreaction quantum yields are less than unity.[4-6] In this communication we report the observation of emission from $W(CO)_5(L)$ compounds where L is a ketone, ether, amine, or pyridine. This is the first report of a radiative deactivation pathway for metal carbonyl complexes.

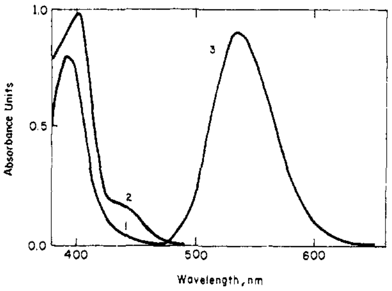

Figure 1. Room temperature absorption spectra of $Mo(CO)_5$(cyclohexylamine), curve 1, and $W(CO)_5$(cyclohexylamine), curve 2. Spectra recorded for $\sim 10^{-4}$ *M* isooctane solutions using 1-cm path cells. Curve 3 shows 77°K emission from $W(CO)_5$(cyclohexylamine). No emission could be seen from $Mo(CO)_5$(cyclohexylamine).

Preparation of the $W(CO)_5(L)$ compounds was achieved by photolysis of $W(CO)_6$ in the presence of the entering ligand.[1] Infrared spectra in the carbonyl region are in agreement with previously published data.[7] The uv–vis spectra of the complexes studied are similar, with a prominent feature being an intense absorption in the vicinity of 400 nm. Room-temperature emission from the complexes could not be detected, but upon cooling to 77°K all of the complexes exhibited an emission maximum between 510 and 545 nm.[8] The emission spectra show little or no structure and there is some overlap of the emission and absorption bands. Figure 1 shows typical emission and absorption spectra. Table I gives emission maxima as well as low-energy absorption maxima for a number of $W(CO)_5(L)$ species

Table I. Emission and Absorption Maxima for Some $M(CO)_5(L)$ Complexes

Compound	Absorption max, nm	Emission max, nm
$W(CO)_5(NEt_3)$	465, 428, 402	533
$Mo(CO)_5(NEt_3)$	393	*c*
$W(CO)_5(NHEt_2)$	438, 402	533
$Mo(CO)_5(NHEt_2)$	393	*c*
$W(CO)_5$(cyclohexylamine)	438, 402	533
$Mo(CO)_5$(cyclohexylamine)	393	*c*
$W(CO)_5$	436[a]	533
$W(CO)_6$	314, 334, 353[b]	*c*
$Mo(CO)_6$	313, 332, 347[b]	*c*
$W(CO)_5$(acetone)	406, 450	538
$W(CO)_5$(ethyl ether)	418, 456	533
$Mo(CO)_5$(ethyl ether)	407	*c*
$W(CO)_5$(pyridine)	440, 385	510
$W(CO)_5(S\text{–}Et_2)$	412, 386	545
$Mo(CO)_5(S\text{–}Et_2)$	377	*c*

[a] Reference 9. [b] Reference 13. [c] None detectable.

We have also found weak emission from $W(CO)_5$ itself. Tungsten pentacarbonyl was produced in a methylcyclohexane glass at 77°K by photolysis of $W(CO)_6$ as previously reported.[9,10] The 533-nm emission, however, could not be detected until the excess CO was removed. The lack of emission before removing the trapped CO is probably related to the fact that regeneration of $W(CO)_6$ can be achieved *via* long-wavelength photolysis of the $[W(CO)_5 + CO]$ in the low-temperature glass.[11] The CO in the cage may be weakly interacting as an O-bonded ligand or in a π-type configuration. We have not been able to detect emission from complexes with L = olefins or acetonitrile.

---

(1) E. Koerner von Gustorf and F. W. Grevels, *Fortschr. Chem. Forsch.*, **13**, 366 (1969).

(2) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3285 (1971).

(3) W. Jennings and B. Hill, *ibid.*, **92**, 3199 (1970).

(4) A. P. Garratt and H. W. Thompson, *J. Chem. Soc.*, 1817 (1934).

(5) W. Strohmeier and D. von Hobe, *Chem. Ber.*, **94**, 2031 (1961).

(6) W. Strohmeier and D. von Hobe, *Z. Phys. Chem. (Frankfurt am Main)*, **34**, 393 (1962).

(7) "Organic Synthesis *via* Metal Carbonyls," Vol. I, I. Wender and P. Pino, Ed., Wiley, 1968, and references cited therein.

(8) Emission spectra were obtained by using an Aminco-Bowman spectrophotofluorometer or the optical detection system of a Cary 17. Excitation spectra were obtained with the Aminco instrument, and excitation maxima agreed well with absorption maxima for the compounds. Relative emission intensities were estimates, the emission spectra being obtained by exciting at 400 nm. All emission spectra were obtained at 77°K.

(9) M. A. Graham, A. J. Rest, and J. J. Turner, *J. Organometal. Chem.*, **24**, C54 (1970).

(10) (a) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, **84**, 3589 (1962); (b) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *ibid.*, **85**, 1014 (1963).

(11) M. Wrighton, G. S. Hammond, and H. B. Gray, unpublished observations.

The corresponding molybdenum and chromium compounds fail to emit. One important difference in these compounds is their lack of prominent shoulders on the 400-nm absorption band (Figure 1). Assuming effective C_{4v} symmetry and a relatively weak axial ligand field, the intense absorption at ~400 nm is assigned as the $^1A_1(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2a_1)$ transition.[12] The heavy-metal effect[13] leads us to assign the low-energy shoulder in the tungsten compounds as the corresponding singlet → triplet absorption. The metal effect as well as the overlap of the emission and absorption are consistent with assigning the emission as the $^3E(e^3b_2^2a_1) \rightarrow {}^1A_1(e^4b_2^2)$ transition. An emission lifetime has not been measured, but emission could not be seen when using a chopper.[14] Triplet lifetimes of d^6 systems are often short,[15] and with the large spin-orbit coupling in tungsten we expect fast radiative decay.

The fact that the emitting state is of the same energy for the $W(CO)_5(L)$ complexes strongly suggests that the axial ligand field is dominated by the CO trans to L. Such dominance by strongly π-bonding axial ligands in tetragonal complexes has been noted previously[16] in reference to electronic absorption spectra. In the present case the effect is particularly striking because of the similarity of free $W(CO)_5$ and $W(CO)_5(L)$. However, the emission intensity data given in Table II demonstrate that the ligand L does play an important role in relative rates of nonradiative and radiative decay. The role of the ligand here is twofold: (1) the ligand apparently can stabilize the C_{4v} $W(CO)_5$ group, *cf.* $W(CO)_5$ *vs.* $W(CO)_5(NEt_3)$; and (2) the ligand can provide facile nonradiative decay pathways such as high-energy vibrational modes or chemical reaction, *cf.* $W(CO)_5(NH_3)$ *vs.* $W(CO)_5(NEt_3)$ and $W(CO)_5$(pyridine) *vs.* $W(CO)_5$(*trans*-2-styrylpyridine).[17]

Table II. Emission Intensities for Some $W(CO)_5(L)$ Complexes

Complex	Intensity[a]
$W(CO)_5$	Weak
$W(CO)_5(NH_3)$	Weak
$W(CO)_5(NEt_3)$	Strong
$W(CO)_5$(pyridine)	Strong
$W(CO)_5$(*trans*-2-styrylpyridine)	*b*

[a] Under similar, but not, identical conditions. [b] No emission detectable.

Acknowledgment. This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research (Contract No. AF OSR-71-1958), and the Army Research Office—Durham.

---

[12] D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3364 (1971).

[13] N. A. Beach and H. B. Gray, *ibid.*, **90**, 5713 (1968).

[14] Samples with lifetimes $\geq 10^{-3}$ sec could have been easily observed.

[15] P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970).

[16] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **2**, 426 (1963).

[17] *trans*-2-Styrylpyridine is N bonded to $W(CO)_5$.

[18] NIH trainee.

Mark Wrighton,[18] G. S. Hammond, Harry B. Gray*
Contribution No. 4273
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91109

Received June 21, 1971

Zero-Field Splitting in Hexaureavanadium(III) Bromide Trihydrate

Sir:

The measurement of specific heats at low temperatures offers an important and unambiguous method for the determination of relatively large zero-field splittings in paramagnetic systems, for the sign as well as the magnitude of the splitting may be determined. The present report, the first attempt to determine the zero-field splitting in $V(urea)_6Br_3 \cdot 3H_2O$ (I), presents an example of this procedure. This molecule, with a $^3A_2$ ground state,[1] suffers a trigonal distortion which may be described by the zero-field spin Hamiltonian ($S = 1$)

$$\mathcal{H} = D[S_z^2 - (1/3)S(S + 1)] + E(S_x^2 - S_y^2)$$

The resulting set of energy levels may be used, following standard procedures,[2] to calculate the magnetic contribution to the specific heat.

The specific heat of a 5.819-g single-crystal sample[3] of I is displayed in Figure 1. Measurements were made by the method of discontinuous heating, and temperatures were measured with a calibrated germanium resistance thermometer. The specific heat of the isomorphous[1,4] $Fe(urea)_6Cl_3 \cdot 3H_2O$ (II),[5] which was measured from 4.5 to 30°K, offered no indication of a magnetic contribution to the specific heat; this was anticipated, as the small zero-field splitting of the ^6S ion should not contribute a Schottky term in this temperature region, and cooperative magnetic effects should be important only at lower temperatures. Thus,

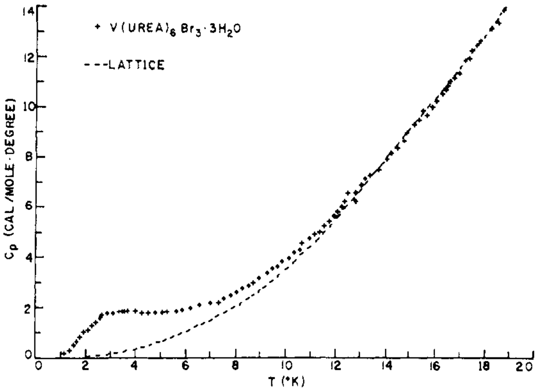

Figure 1. The measured specific heat of $V(urea)_6Br_3 \cdot 3H_2O$. Fewer than 10% of the experimental points below 6° are illustrated here. The dashed curve indicates the lattice contribution as estimated by the corresponding-states procedure.

---

[1] R. Dingle, P. J. McCarthy, and C. J. Ballhausen, *J. Chem. Phys.* **50**, 1957 (1969). These authors investigated "$V(urea)_6Br_3$," but an elemental analysis was not provided for this material. Conversations with Dr. Dingle and Professor Ballhausen suggest that in all probability the substance discussed in this reference is the same as the compound reported here.

[2] E. S. R. Gopal, "Specific Heats at Low Temperatures," Plenum Press, New York, N. Y., 1966.

[3] *Anal.* Calcd: V, 7.22; Br, 34.02; C, 10.21; H, 4.25; N, 23.84. Found: V, 7.04; Br, 35.43; C, 10.05; H, 4.19; N, 23.80.

[4] Y. Okaya, R. Pepinsky, Y. Takeuchi, H. Kuroya, A. Shimada, P. Gallitelli, N. Stemple, and A. Beevers, *Acta Crystallogr.*, **10**, 798 (1957).

[5] A 4.621-g single crystal. *Anal.* Calcd: Fe, 9.69; Cl, 18.45; C, 12.49; H, 5.24; N, 29.15. Found: Fe, 9.63; Cl, 18.9; C, 12.59; H, 4.56; N, 29.30.