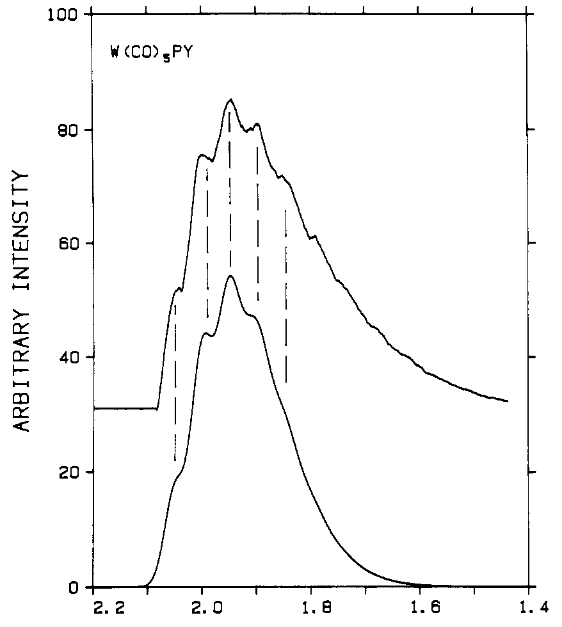

Figure 1. Top: Experimental emission spectrum of W(CO)$_5$py at 10 K. Bottom: Calculated spectrum.

time-dependent wave packet (with $\phi(0) = \phi$) evolving on the lower, multimode potential surface. Under the assumption of harmonic modes displaced by δ but otherwise the same in both electronic states, the overlap $\langle\phi|\phi(t)\rangle$ factors into two overlaps, one for each mode:

$$\langle\phi|\phi(t)\rangle = \langle\phi_{432}|\phi_{432}(t)\rangle\langle\phi_{599}|\phi_{599}(t)\rangle \qquad (2)$$

The evolution of these overlaps is shown in Figure 2. In each case, an initial decay is followed by a recurrence peaked at $t' = 2\pi/\omega'$, where ω' is the frequency of the mode. The occurrence is caused by the return of the moving-wave packet to its starting position. The product of the two overlaps, shown in Figure 2, occurs at $t = 0$ and $t \simeq \pm 2\pi/\omega_M$, where ω_M is the MIME 550-cm^{-1} frequency. The Fourier transform gives a regular 550 ± 7 cm^{-1} spacing in the frequency domain.

The spectrum calculated with $\delta_{432} = 1.82$, $\delta_{599} = 1.55$, and $\Gamma = 130$ cm^{-1}, shown in Figure 1, gives an excellent fit.[5] An excellent fit can also be obtained by using three of the observed totally symmetric normal-mode frequencies.[6] By changing the displacements, it is possible to tune the MIME frequency by more than 100 cm^{-1} in this case.

The MIME effect, although previously unrecognized, is not uncommon.[7] The main requirements for the MIME effect are (1) at least two displaced modes and (2) vibronic resolution

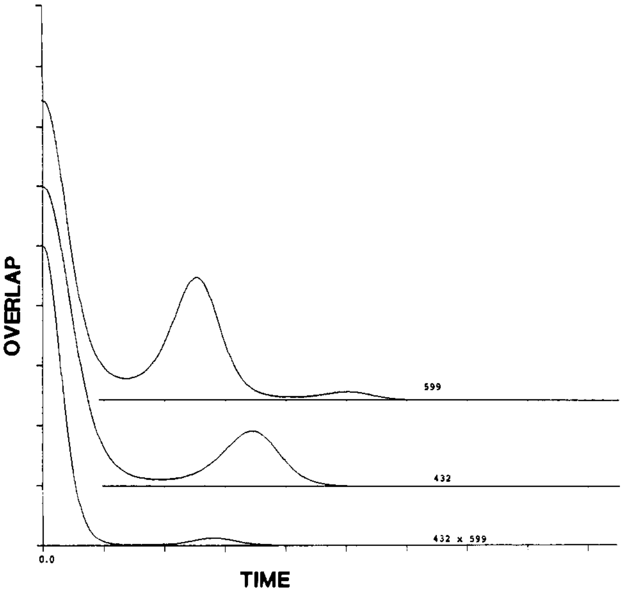

Figure 2. Top: Overlap $\langle\phi_{599}|\phi_{599}(t)\rangle e^{-\Gamma^2t^2/2}$ vs. t. Middle: $\langle\phi_{432}|\phi_{432}(t)\rangle e^{-\Gamma^2t^2/2}$ vs. t. Bottom: Product $\langle\phi|\phi(t)\rangle$ (see eq 2) of the above two overlaps. The Fourier transform gives the spectrum in the frequency domain shown in Figure 1 containing the 550-cm^{-1} MIME frequency.

on the order of that in Figure 1 caused by the damping.

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Registry No. W(CO)$_5$(py), 14586-49-3.

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(5) For convenience we transform to dimensionless normal coordinates:

$$\delta_k = \left(\frac{m_k\omega_k}{\hbar}\right)^{1/2}\Delta_k$$

The Gaussian damping Γ, due to relaxation into other modes, the "bath", etc., causes the magnitude of the recurring overlap to decrease with time as shown in Figure 2.

(6) The three frequencies used were 408 cm^{-1} (ν(M–C), A$_1$), 432 cm^{-1} (ν(M–C), A$_1$), and 599 (δ(MCO), A$_1$) with $\delta_{408} = 1.2$, $\delta_{432} = 1.1$, $\delta_{599} = 1.8$, $\Gamma = 120.0$.

(7) (a) Yersin, H.; Otto, H.; Zink, J. I.; Gliemann, G. *J. Am. Chem. Soc.* **1980**, *102*, 951. An observed vibronic spacing of 304 cm^{-1} in K$_2$PtCl$_4$ is not the expected 329-cm^{-1} (ν(M–Cl), A$_{1g}$) normal mode. The observed vibronic spacing of 395 cm^{-1} in K$_3$[Co(CN)$_6$] is not the expected 408-cm^{-1} (ν(M–CN), A$_{1g}$) normal mode. (b) Eyring, G.; Schmidtler, H. H. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 597. An observed 455-cm^{-1} progression in [Rh(NH$_3$)$_6$]Cl$_3$ cannot be assigned to a vibrational mode of the molecule.

Preparation and Structure of Ditungsten Tetrabenzoate Bis(tetrahydrofuranate)

Sir:

We wish to report here the relatively simple and convenient preparation, in high yield and high purity, of a quadruply bonded ditungsten tetracarboxylate compound, $W_2(O_2CC_6H_5)_4(THF)_2$. We also describe the molecular structure, accurately determined by X-ray crystallography.

The history of attempts to make stable compounds containing W$\overset{4}{-}$W (quadruple) bonds covers a period of more than 20 years.[1] It records many failures and frustrations and relatively few successes; most of the latter are recent and in several cases would have to be considered only qualified successes. Thus, in 1977 compounds containing the $[W_2(CH_3)_8]^{4-}$ and $[W_2Cl_n(CH_3)_{8-n}]^{4-}$ ions were characterized:[2] these were the first authenticated compounds containing W$\overset{4}{-}$W bonds, but they are extraordinarily unstable, both chemically and thermally. The first stable, useful compound was W$_2$(mhp)$_4$ (mhp = 2-oxy-6-methylpyridine), reported[3] in 1978, and then in 1980 stable compounds of the class

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(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; pp 137-144.

(2) Collins, D. M.; Cotton, F. A.; Koch, S. A.; Millar, M.; Murillo, C. A. *Inorg. Chem.* **1978**, *17*, 2017 and earlier papers cited therein.

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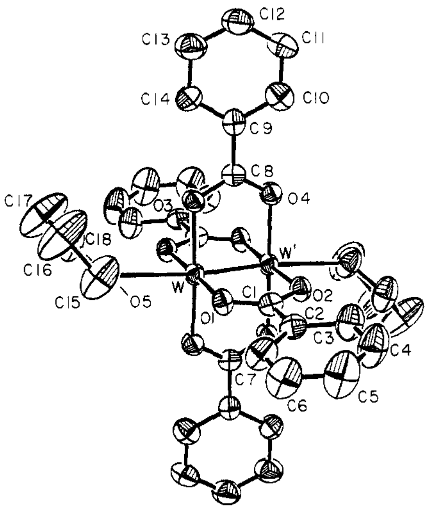

Figure 1. Structure of $W_2(O_2CC_6H_5)_4(THF)_2$ drawn by using the program ORTEP with each atom represented by its ellipsoid of thermal vibration scaled to enclose 40% of the electron density.

$W_2Cl_4(PR_3)_4$ were discovered and characterized.[4,5] However, continued failure, despite many attempts, to prepare a $W_2(O_2CR)_4$ compound was striking—and also discouraging. It seemed impossible to believe that such compounds could not exist. Finally, in 1981 there appeared the first report[6] of the synthesis and characterization of such a compound, viz., $W_2(O_2CCF_3)_4$. Unfortunately, the preparative procedure is an arduous one, reported to give only 20% yield and, in our hands, never more than 5%.

It has been our view for several years that much of the difficulty with the preparation and stability of compounds containing the $\mathrm{W}\overset{4}{-}\mathrm{W}$ bonds is due to the weakness of the δ component of that bond and the consequent readiness with which oxidative addition of acid occurs. This view has recently received strong experimental support.[7,8] In accordance with this belief, we have been trying to synthesize $W_2(O_2CR)_4$ compounds under strictly nonacidic conditions. It was, indeed, only under such conditions that the synthesis of $W_2(O_2CCF_3)_4$ succeeded,[6] and as recent examples of the disastrous effect of acid, the reaction of the otherwise very stable compounds W_2(2,4-dimethyl-6-oxypyrimidinate)$_4$ and $W_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ with acids promptly and completely destroys the $\mathrm{W}\overset{4}{-}\mathrm{W}$ bonds,[4,9] leaving in one case a double bond and in the other case single bonds.

Our work has led to a procedure for the convenient preparation on a large scale of pure $W_2(O_2CC_6H_5)_4(THF)_2$. This substance is accessible enough and stable enough that it should become a desirable intermediate in further syntheses, which is unlikely to be the case with the trifluoroacetate.

In the preparation of $W_2(O_2CC_6H_5)_4(THF)_2$ all operations must be carried out in absence of air. In a representative procedure 5 g of WCl_4 was treated with 2 equiv of 0.4% sodium amalgam in 300 mL of THF at −20 °C. To the resulting gray-blue solution was added 4.45 g of sodium benzoate. This reaction mixture was allowed to warm to room temperature with constant stirring (about 0.5 h), and the resulting purple solution was filtered through Celite to remove sodium chloride and mercury. A 25-mL portion of the filtrate was transferred to a Schlenk tube and covered with 20 mL of hexane. Slow diffusion of the hexane into the THF solution over a period of 3 days to 1 week produced large, well-formed orange crystals. The yield of this highly crystalline product was about 0.35 g (ca. 55%). The solid is moderately sensitive to air and moisture but in solution the sensitivity is very great.

The compound crystallizes in space group $P2_1/c$ with 2 molecules in a unit cell of dimensions a = 9.511 (7) Å, b = 17.716 (7) Å, c = 10.843 (3) Å, and β = 109.52 (4)°. The structure was refined to $R_1 = 0.033$ and $R_2 = 0.042$ with 2011 reflections having $I > 3\sigma(I)$. The centrosymmetric molecule is shown in Figure 1. Its important dimensions, averaged for D_{4h} symmetry in the $W_2(O_2C-)_4(O)_2$ central portion of the molecule are W–W = 2.196 (1) Å, W–O(carbox) = 2.077 [6] Å, W–O(THF) = 2.628 (8) Å, ∠W–W–O(carbox) = 90.6 [3]°, and ∠W′–W–O(THF) = 169.7 (2)°. These distances may be compared with those in the molybdenum analogue,[10] $Mo_2(O_2CC_6H_5)_4$, which, in the above order are, 2.100 (1) Å, 2.107 [2] Å, 2.663 (6) Å, 91.8 [4]°, and 169.9 (1)°. As is very typical in such comparisons, the W–W bond length is about 0.10 Å longer, while the other dimensions are practically the same in the two compounds. The two crystallographically independent W–W distances in the trifluoroacetate were 2.207 (2) and 2.211 (2) Å.

After some additional physical and chemical studies are completed, a full report will be submitted.

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Registry No. $W_2(O_2CC_6H_5)_4(THF)_2$, 82752-90-7.

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Synthetic Metals Based on Tetramethyltetraselenafulvalene (TMTSF): Synthesis, Structure (T = 298 and 125 K), and Novel Properties of $(TMTSF)_2H_2F_3$

Sir:

We report the synthesis and molecular structure as a function of temperature (T = 298 K and 125 K) of the unique tetramethyltetraselenafulvalene[1] organic radical cation salt $(TMTSF)_2H_2F_3$ (**1**). The relationship between the structure and the unusual physical properties of **1**, and of its sometimes superconducting congeners, is also discussed. The structural data for all 2:1 salts of $(TMTSF)_2X$, X = monovalent anion, reported to date indicate that they are *isostructural* (triclinic, space group $P\bar{1}$) and contain anions having octahedral or tetrahedral symmetry.[2] Despite their close structural simi-

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[1] TMTSF is $\Delta^{2,2'}$-bi-4,5-dimethyl-1,3-diselenolylidene.