Inorg. Chem. **1984**, *23*, 4683–4688

Contribution from the Departments of Chemistry, Boston College, Chestnut Hill, Massachusetts 02167, Boston University, Boston, Massachusetts 02215, and University of Cincinnati, Cincinnati, Ohio 45521

Synthesis and Structure of *trans*-$[O_2(TBP)_4Tc]^+$ (TBP = 4-*tert*-Butylpyridine) and Related Complexes

M. E. KASTNER,[1] P. H. FACKLER,[2] M. J. CLARKE,*[2] and E. DEUTSCH[3]

Received May 18, 1984

A series of complexes of the general type *trans*-$[O_2(py)_4Tc]^+$ have been prepared and characterized as to their structure and spectroscopic properties. An X-ray crystal structure determination has been made of *trans*-$[O_2(TBP)_4Tc]F_3CSO_3{\cdot}H_2O$ (TBP = 4-*tert*-butylpyridine), which crystallizes in the triclinic space group $P\bar{1}$ with cell constants of a = 13.876 (5) Å, b = 15.429 (4) Å, c = 11.822 (2) Å, α = 111.83 (2)°, β = 108.77 (2)°, and γ = 65.24 (2)°. The cell volume is 2092 (1) Å^3 with Z = 2. Weighted and unweighted R factors are 0.093 and 0.074, respectively. The coordination sphere about the Tc is nominally octahedral with average Tc=O and Tc—N bond lengths of 1.743 (6) and 2.15 (2) Å, respectively. The pyridines are twisted away from the O=Tc=O axis by varying degrees and form an average dihedral angle of 74° with a plane defined by the Tc and two adjacent nitrogen atoms. Broad bands appear in the electronic spectra of the complexes around 310 and 520 nm in ethanol, with the former probably arising from a ligand-to-metal charge-transfer transition and the latter an $^1A_1 \rightarrow {}^1B_2$ ligand field excitation. Infrared absorbances assigned to the asymmetric stretching of O=Tc=O occur at 818–828 cm^{-1}. ^{1}H NMR resonances are slightly deshielded relative to those of the free ligands. The solubilities of these complexes and the ease of substitution of the pyridine ligands are such that they are likely to be useful as synthetic materials for new species containing the *trans*-$[O{=}Tc{=}O]^+$ core.

Oxotechnetium(V) ions are prominent in the aqueous chemistry of this synthetic element and often occur in clinically used radiopharmaceuticals containing ^{99m}Tc.[4-7] In general, the monooxotechnetium(V) core is present in complexes containing π-donor ligands in the equatorial plane, while the *trans*-dioxotechnetium moiety obtains with π-acceptor ligands or ligands that do not form π bonds. While the full structures of two compounds containing the *trans*-$[O_2Tc^V]^+$ core have been reported,[8,9] these have contained chelating nitrogen ligands. Complexes with only monodentate nitrogen ligands provide a basis for "standard" Tc(V)–N bond lengths and are of interest as starting materials for other technetium species.[10] Synthetically useful materials should contain fairly labile equatorial ligands and be readily soluble in organic solvents that will maintain the *trans*-dioxotechnetium(V) core and prevent hydrolysis to the polymeric $[TcO_2]_n{\cdot}H_2O$.

In preparing a series of heterocyclic iminium salts of $[TcCl_6]^{2-}$, Kuzina et al. reported electronic absorption spectra at pH 4–5 suggestive of pyridine coordination.[11] On the basis of a preliminary elemental analysis and an infrared spectrum similar to that of $[O_2(py)_4Re]Cl{\cdot}10H_2O$ (where py = pyridine), it was concluded that the corresponding technetium compound had been obtained. In studies directed toward the synthesis of technetium complexes with imine ligands, it was observed that pyridine ligands containing strongly electron-withdrawing substituents in the para position added to $[OCl_4Tc]^-$ in alcoholic solutions to yield $[O(RO)Cl_2L_2Tc^V]$, where RO$^-$ is the anion of the alcohol and L is 4-nitro- or 4-cyanopyridine.[12] Continued reaction of these species in neat pyridine results in $[Cl(py)_4Tc{-}O{-}TcCl_4(py)]$ and other similar products[13] that constitute the black, water-insoluble, crystalline material alluded to in early studies of technetium ions with pyridine.[11]

In this work we report on an efficient synthesis of a variety of *trans*-dioxotetrakis(pyridine)technetium(V) complexes. Owing to the instability of many of these complexes with respect to pyridine loss and a desire for a synthetic starting material readily soluble in organic media, *trans*-$[O_2(TBP)_4Tc^V]F_3CSO_3{\cdot}H_2O$ was synthesized and subjected to a full structure determination by X-ray methods. The synthesis and spectrographic characterization of several other complexes of the general type *trans*-$[O_2(py)_4Tc]^+$ are also reported and related to earlier studies.[8,11-13]

Abbreviations: py, pyridine, AP, 4-aminopyridine; DMP, 4-(dimethylamino)pyridine; Pic, 4-methylpyridine (picoline); Lut, 3,5-dimethylpyridine (lutidine); TBP, 4-*tert*-butylpyridine; Im, imidazole; MeIm, methylimidazole; en, ethylenediamine; DMF, *N*,*N*-dimethylformamide.

Experimental Section

Synthesis. Complexes of the general type *trans*-$[O_2(py)_4Tc]Cl$ were typically prepared by combining 156 mg (0.31 mmol) of $[n\text{-}Bu_4N][OCl_4Tc]$[14] with 5 mL of the neat pyridine ligand in a 10-mL beaker. The solution was stirred for 10 min at room temperature until a yellow precipitate had formed. After filtration on a medium-porosity sintered-glass frit, the precipitate was dissolved in 5 mL of alcohol. Crystals were collected upon evaporation. Yields ranged from 81 to 92%. Single crystals of *trans*-$[O_2(py)_4Tc]Cl$ used for X-ray diffraction studies were obtained upon evaporation of a methanol solution of this material. The same material could also be made by a similar procedure starting with $(NH_4)_2TcCl_6$.[15]

For the aminopyridine ligands, which are solids at room temperature, 3.0 mmol of the ligand was stirred together with 0.37 mmol of $[n\text{-}Bu_4N][OCl_4Tc]$ in 20 mL of absolute ethanol at room temperature for 5 min. The resulting orange solution was subjected to rotary evaporation under vacuum to yield a pink solid that was suspended in 30 mL of benzene, in the case of the aminopyridine, and ice water, in the case of the (dimethylamino)pyridine, by vigorously scraping the sides of the flask. The suspension was subsequently filtered and washed with an additional 50 mL of solvent to remove all unreacted ligand. Crystallization of *trans*-$[O_2(AP)_4Tc]Cl{\cdot}2H_2O$ by evaporation from ethanol resulted in two types of crystals. Purple crystals (which were not characterized) formed on the top of the solution and the sides of the beaker, and red crystals formed at the bottom. One of the red crystals was studied by X-ray diffraction.

---

(1) Boston University. Present address: Department of Chemistry, Bucknell University, Lewisburg, PA 7837.

(2) Boston College.

(3) University of Cincinnati.

(4) Deutsch, E.; Libson, K. *Comments Inorg. Chem.* **1984**, *3*, 83–103.

(5) Clarke, M. J.; Fackler, P. H. *Struct. Bonding (Berlin)* **1982**, *50*, 57–77.

(6) Davison, A.; Jones, A. G. *Int. J. Appl. Radiat. Isot.* **1982**, *33*, 875–882.

(7) Deutsch, E.; Libson, K.; Jurisson, S.; Lindoy, L. *Prog. Inorg. Chem.* **1983**, *30*, 75–139.

(8) Kastner, M. E.; Lindsay, M. J.; Clarke, M. J. *Inorg. Chem.* **1982**, *21*, 2037–2040.

(9) Zuckman, S. A.; Freeman, G. M.; Troutner, D. E.; Volkert, W. A.; Holmes, R. A.; Van Derveer, D. G.; Barefield, E. K. *Inorg. Chem.* **1981**, *20*, 2386.

(10) Trop, H. S.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1980**, *19*, 1993–1997.

(11) Kuzina, A. F.; Oblova, A. A.; Spitsyn, V. I. *Russ. J. Inorg. Chem.* **1972**, *17*, 1377–1379.

(12) Fackler, P. H.; Kastner, M. E.; Clarke, M. J. *Inorg. Chem.* **1984**, *23*, 3968.

(13) Kastner, M. E.; Fackler, P. H.; Podbielski, L.; Charkoudian, J.; Clarke, M. J., to be submitted for publication.

(14) Cotton, F. A.; Davison, A.; Day, V. W.; Gage, L. D.; Trop, H. S. *Inorg. Chem.* **1979**, *18*, 3024.

(15) Libson, K.; Barnett, B. L.; Deutsch, E. *Inorg. Chem.* **1983**, *23*, 1695.

0020-1669/84/1323-4683$01.50/0

Table I. Elemental Analyses for *trans*-$[O_2L_4Tc]X\cdot(H_2O)_n$[a]

ligands				% anal.	
L	X	*n*	element	calcd	found
TBP	F_3CSO_3	1	C	52.97	52.69
			H	6.48	6.37
			N	6.67	6.49
			S	3.82	3.88
py	Cl		C	46.30	46.22
			H	4.66	4.59
			N	10.80	10.80
			Cl	6.83	6.81
			Tc	19.1	18.9
Pic	Cl		C	48.61	49.38
			H	5.78	5.74
			N	9.45	9.05
			Cl	5.98	7.74
			Tc	16.7	16.8
Lut	Cl		C	54.86	53.65
			H	6.25	6.20
			N	9.14	8.85
			Cl	5.78	6.05
			Tc	16.1	16.4
AP	Cl	2	C	41.50	41.13
			H	4.86	4.85
			N	19.36	19.12
			Cl	6.12	5.95
			Tc	17.1	16.2
DMP	Cl	4	C	46.25	45.43
			H	6.65	6.27
			N	15.41	15.10
			Cl	4.88	5.25
			Tc	13.6	13.4

[a] py = pyridine, Pic = 4-methylpyridine (picoline), Lut = 3,5-dimethylpyridine (lutidine), AP = 4-aminopyridine, DMP = 4-(dimethylamino)pyridine, TBP = 4-*tert*-butylpyridine.

Elemental analyses were also performed on the red crystals. Elemental analyses for all compounds are listed in Table I.

The compound *trans*-$[O_2(TBP)_4Tc]F_3CSO_3\cdot H_2O$ was prepared by dissolving 0.35 g of $[n\text{-}Bu_4N][OCl_4Tc]$ and 2 g of $Li(F_3CSO_3)$ in 60 mL of ethanol to which was added 6 mL of neat 4-*tert*-butylpyridine (graciously donated by the Reilly Chemical Corp.) and an ethanolic solution of 2 mL of this ligand that had been neutralized with 6 M F_3CSO_3H. The resultant brown solution was stirred at room temperature for 30 min, and 60 mL of water added. Yellow crystals covered with a brown oil deposited overnight. After decantation of the supernatant, the brown oil was removed from the crystals by successive rinsings with ethylacetate, toluene, and heptane. The yellow crystals of the desired product were then dissolved in a minimum amount of warm 8/2/1 toluene/dichloromethane/4-*tert*-butylpyridine. Following filtration, heptane was added until incipient precipitation, with large yellow crystals resulting upon slow cooling. These were collected by filtration and washed successively with toluene, heptane, and diethyl ether; yield 260 mg (45%).

Pure *trans*-$[O_2(TBP)_4Tc]F_3CSO_3\cdot H_2O$ is very soluble in CH_2Cl_2, ethanol, methanol, and THF, with some decomposition occurring in the latter three solvents. It is soluble in ethylacetate, slightly soluble in toluene and 1-butanol, and insoluble in heptane, diethyl ether, CCl_4, xylene, and water, with decomposition in the latter. Single crystals were grown by layering a solution of 4-*tert*-butylpyridine in heptane over a solution of the product and 4-*tert*-butylpyridine in CH_2Cl_2 and then letting the layers slowly diffuse together. Upon prolonged exposure to air, some of these crystals changed to a red color.

Caution! All syntheses were performed with ^{99}Tc, which is a β-emitting isotope with a half-life of 2.15×10^5 yr. Precautions for handling this material are described elsewhere.[8]

Compound Characterization. All elemental analyses (except for ^{99}Tc) were performed by the Stanford Microanalytical Laboratory, Stanford, CA, or Schwartzkopf Microanalytical, Woodside, NY. Technetium analyses were performed by standard scintillation counting techniques after oxidizing the material to $[TcO_4]^-$.[12] Infrared spectra were taken on a Perkin-Elmer Model 599B grating spectrophotometer in CsI pellets. UV–visible spectra were obtained on a Perkin-Elmer Model 575 spectrometer equipped with a digital background corrector and a thermostated sample cell. ^1H NMR spectra were recorded on a Varian FT-80A Fourier transform spectrometer. All spectra were recorded at room temperature. Magnetic susceptibility measurements were performed on a Cahn Model 7500 electrobalance with a 14 502-G magnet.

Table II. Crystallographic Data for *trans*-$[O_2(TBP)_4Tc]F_3CSO_3\cdot H_2O$

formula	$H_{54}C_{37}N_4O_6F_3S(Tc)$
fw	838.93
cryst dimens	$0.35 \times 0.25 \times 0.12$
color	orange-yellow
radiation source (Cu Kα)	$\lambda = 1.5418$ Å
τ, cm^{-1}	37.8
transmission factors	0.39–0.64
diffractometer	Syntex $P2_1$
space group	$P\bar{1}$
cell const: a, b, c, Å	13.876 (5), 15.429 (4), 11.822 (2)
α, β, γ, deg	111.83 (2), 108.77 (2), 65.24 (2)
V, Å^3	2092 (1)
Z	2
d_{calcd}, g/cm^3	1.332
d_{obsd}, g/cm^3	1.33
total no. of observns	4441
no. of obsd reflcns[a]	3682
scan mode	θ–2θ
2θ range, deg	3–100
scan width above and below Kα	0.7
scan rate, deg/min	2–12
no. of variables in least squares	472
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$[b]	0.074
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma\lvert w(F_o)^2\rvert]^{1/2}$	0.093
goodness of fit = $[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$	8.0

[a] Reflections with $F_o > 3\Sigma(F_o)$ were retained as observed and used in the solution and refinement of the structure. [b] Function minimized: $\Sigma w(F_o - F_c)$.

Structure Determination. Intensity data were measured on an automated diffractometer with background counts collected at the extremes of the scan for half the time of the scan. Data were collected in the hemisphere $+h,\pm k,\pm l$. Three standard reflections were measured every 50 reflections during the course of the measurements. Pertinent crystallographic data are summarized in Table II. The initial choice of the centrosymmetric space group $P\bar{1}$[16] was confirmed during the subsequent structure determination.

The structure was solved by standard heavy-atom techniques, with the position of the Tc atoms deduced from an initial Patterson map and all other non-hydrogen atoms found in a series of difference Fourier maps.[17] The *trans*-$[O_2(TBP)_4Tc^V]^+$ cations are located at centers of symmetry at (0, 0, 0) and ($^1/_2$, 0, 0) with only half of each molecule in the asymmetric unit. The triflate ($F_3CSO_3^-$) anion is at a general location, and very large thermal parameters reflect the freedom of this species to rotate. The water molecule is also in a general location. The final model used anisotropic thermal parameters for all non-hydrogen atoms, and calculated positions for the four hydrogen atoms in the plane of each pyridine ring (C–H = 0.95 Å, $B(H) = B(C) + 1.0$ Å^2) were included in subsequent refinement cycles as fixed contributors. The 36 hydrogen atoms on the terminal methyl groups are not included in the calculations. The structure was refined by full-matrix least-square methods,[18,19] and errors were estimated.[20] The

---

(16) Henry, N. F. M.; Lansdale, K. "International Tables for X-ray Crystallography"; 2nd ed.; Kynoch Press: Birmingham, England, 1965; Vol. I, p 75.

(17) Hubbard, C. R.; Quicksall, C. O.; Jacobson, R. A. "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFPROJ, ALFFII and FRIEDEL", Report IS-2625; Ames Laboratory: Iowa State University, Ames, IA, 1971.

(18) Lapp, R. L.; Jacobson, R. A. "ALLS, A Generalized Crystallographic Least Squares Program", Report No. IS-4708 UC-4; National Technical Information Service: Springfield, VA, 1979.

(19) The atomic form factor for hydrogen was from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1975**, *17*, 3175. Form factors for other elements were from: Cromer, P. T.; Mann, J. L. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.

Table III. Atomic Coordinates in the Unit Cell of *trans*-$[O_2(TBP)_4Tc]F_3CSO_3 \cdot H_2O$

	coordinates[a]		
atom	*x*	*y*	*z*
Tc1	0	0	0
Tc2	$^1/_2$	0	0
O1	−0.1326 (5)	0.0839 (5)	−0.0070 (6)
O2	0.3792 (5)	−0.0045 (5)	0.0075 (6)
N1	0.0591 (7)	0.1132 (6)	0.1338 (7)
N2	0.0206 (7)	0.0508 (6)	−0.1336 (7)
N3	0.5337 (7)	0.0577 (6)	0.1996 (7)
N4	0.4187 (7)	0.1505 (6)	−0.0133 (7)
C1	−0.0040 (9)	0.1994 (8)	0.1969 (10)
C2	0.0332 (11)	0.2787 (8)	0.2699 (10)
C3	0.1371 (10)	0.2723 (8)	0.2834 (9)
C4	0.2019 (9)	0.1810 (9)	0.2205 (11)
C5	0.1636 (10)	0.1064 (8)	0.1487 (10)
C6	0.1735 (11)	0.3607 (9)	0.3623 (10)
C7	0.1772 (16)	0.3764 (12)	0.4994 (12)
C8	0.2931 (12)	0.3401 (11)	0.3481 (14)
C9	0.0968 (15)	0.4547 (10)	0.3180 (15)
C10	0.1045 (10)	0.0035 (8)	−0.1905 (11)
C11	0.1240 (10)	0.0369 (9)	−0.2685 (11)
C12	0.0590 (9)	0.1265 (8)	−0.2925 (10)
C13	−0.0302 (10)	0.1766 (9)	−0.2336 (13)
C14	−0.0444 (10)	0.1357 (9)	−0.1580 (13)
C15	0.0792 (11)	0.1675 (9)	−0.3835 (12)
C16	0.0211 (14)	0.2808 (9)	−0.3562 (14)
C17	0.0279 (14)	0.1128 (12)	−0.5168 (12)
C18	0.2043 (11)	0.1409 (11)	−0.3703 (13)
C19	0.4932 (9)	0.0384 (7)	0.2730 (10)
C20	0.5125 (10)	0.0763 (9)	0.4003 (10)
C21	0.5763 (9)	0.1365 (8)	0.4605 (10)
C22	0.6156 (9)	0.1552 (8)	0.3852 (10)
C23	0.5942 (9)	0.1166 (8)	0.2573 (10)
C24	0.5986 (12)	0.1766 (10)	0.6023 (11)
C25	0.6441 (20)	0.2582 (14)	0.6477 (13)
C26	0.6805 (15)	0.0857 (12)	0.6552 (13)
C27	0.4925 (14)	0.2137 (14)	0.6550 (13)
C28	0.3114 (10)	0.1930 (8)	−0.0172 (10)
C29	0.2585 (11)	0.2931 (10)	−0.0183 (11)
C30	0.3164 (13)	0.3502 (9)	−0.0164 (10)
C31	0.4242 (11)	0.3020 (10)	−0.0161 (11)
C32	0.4718 (10)	0.2053 (9)	−0.0139 (11)
C33	0.2585 (14)	0.4599 (9)	−0.0221 (15)
C34	0.2515 (22)	0.4626 (13)	0.8501 (19)
C35	0.6910 (21)	0.4808 (12)	0.9183 (25)
C36	0.1346 (24)	0.4977 (14)	0.9878 (28)
S	0.7368 (3)	0.3347 (3)	0.3481 (5)
F1	0.5315 (8)	0.3786 (7)	0.3313 (11)
F2	0.5860 (9)	0.5032 (9)	0.4160 (13)
F3	0.5866 (14)	0.4319 (15)	0.2233 (20)
O3	0.7372 (8)	0.2466 (7)	0.2640 (11)
O4	0.7462 (19)	0.3258 (20)	0.4794 (15)
O5	0.8015 (9)	0.3843 (9)	0.3571 (12)
C37	0.6019 (14)	0.4148 (15)	0.3469 (24)
O6	0.6882 (8)	0.2539 (7)	0.9795 (10)

[a] The numbers in parentheses are the estimated standard deviations.

final data/parameter ratio was 7.8. A final difference Fourier synthesis was judged to be free of significant features, with the highest peaks occurring near the anion and no clearly defined hydrogens around the methyl carbon.

Final values of atomic coordinates in the asymmetric unit of the structure are given in Table III. A listing of the final and observed structure amplitudes (×10), thermal factors, bond distances, bond angles, and calculated hydrogen atom positions are available in Tables Is–Vs, respectively, of the supplementary material.

Table IV. Electronic Spectral Parameters for *trans*-$[O_2L_4Tc]^{\bullet}$ Ions in Ethanol

L	λ_{max}, nm	ϵ,[a] M^{-1} cm^{-1}
pyridine	207	8.02×10^3
	210	7.40×10^3
	248 (sh)	1.01×10^4
	253	1.11×10^4
	259	1.10×10^4
	264 (sh)	8.14×10^3
	305	3.33×10^3
	457	2.36×10^2
4-picoline	214	1.35×10^4
	248	1.08×10^4
	252 (sh)	1.07×10^4
	256 (sh)	1.05×10^4
	307	6.10×10^3
	466	5.08×10^2
3,5-lutidine	216	1.38×10^4
	252 (sh)	8.42×10^3
	269	1.57×10^4
	276 (sh)	1.16×10^4
	309	5.05×10^3
	468	4.00×10^2
4-*tert*-butylpyridine	212	1.77×10^4
	233 (sh)	1.54×10^4
	245 (sh)	1.32×10^4
	250	1.37×10^4
	255	1.40×10^4
	317	5.05×10^3
	469	1.85×10^2
4-aminopyridine	209	3.69×10^4
	250	4.32×10^4
	262	3.96×10^4
	305	5.86×10^3
	522	3.00×10^2
4-(dimethylamino)pyridine	211	2.88×10^4
	260	4.65×10^4
	284	3.17×10^4
	316	1.62×10^4
	512	2.64×10^2

[a] Precision of molar absorptivities is 5%.

Table V. ^1H NMR Data for *trans*-$[O_2L_4Tc]^+$ in Methanol-d_4[a]

L	assgnt	δ[a]	no. of protons	no. of peaks in mult	$^3J_{H-H}$, Hz
pyridine	H(2,6)	9.23	2	2	5.1
	H(4)	7.91	1	3	7.3
	H(3,5)	7.55	2	3	6.7
picoline	H(2,6)	8.95	2	2	6.5
	H(3,5)	7.36	2	2	6.1
	CH_3	2.43	3	1	
lutidine	H(2,6)	8.81	2	1	
	H(4)	7.63	1	1	
	CH_3	2.29	6	1	
4-*tert*-butylpyridine	H(2,6)	9.04	2	2	5.8
	H(3,5)	7.57	2	2	6.1
	CH_3	1.31	9	1	
4-aminopyridine	H(2,6)	8.14	2	2	6.7
	H(3,5)	6.54	2	2	6.5
4-(dimethylamino)pyridine	H(2,6)	8.04	2	2	6.0
	H(3,5)	6.60	2	2	6.0
	CH_3	2.99	6	1	6.0

[a] Positions are given relative to tetramethylsilane at 37 °C.

Data were also collected on *trans*-$[O_2(py)_4Tc]Cl$ and *trans*-$[O_2(AP)_4Tc] \cdot 2H_2O$. The former appears to be isomorphous with the analogous rhenium compound and crystallizes in a *C*-centered monoclinic cell (probably *Cc*) with cell constants $a = 13.618$ (4) Å, $b = 12.001$ (4) Å, $c = 7.778$ (4) Å, and $\beta = 116.38$ (5)°. Other data: d_{calcd} for $H_{24}C_{20}N_4O_4ClTc$ ($Z = 2$) = 1.51 g/cm^3; d_{obsd} = 1.51 g/cm^3. The aminopyridine complex appeared to crystallize in $P2_12_12_1$, with $a = 25.979$ (7) Å, $b = 16.515$ (5) Å, and $c = 10.877$ (3) Å.

Results

Spectra. Infrared absorptions assigned to the asymmetric stretch of O═Tc═O are between 818 and 828 cm^{-1} and are within the range typical for O═M═O vibrations of this type, where M = Tc or Re.[5,21–23] Electronic absorption bands and

---

(20) Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFFE: A Fortran Crystallographic Function & Error Program", Report ORNL-TM-306; Oak Ridge National Laboratory: Oak Ridge, TN, 1964.

Table VI. Selected Bond Distances and Angles in *trans*-$[O_2(TBP)_4Tc]F_3CSO_3 \cdot H_2O$

bond type	dist, Å	bond type	angle, deg
Tc1-O1	1.748 (6)	O1-Tc1-N1	90.4 (3)
Tc2-O2	1.737 (6)	O1-Tc1-N2	89.6 (3)
Tc1-N1	2.129 (7)	N1-Tc1-N2	84.7 (3)
Tc1-N2	2.142 (7)	O2-Tc2-N1	89.7 (3)
Tc2-N3	2.158 (7)	O2-Tc2-N4	89.8 (3)
Tc2-N4	2.157 (7)	N4-Tc2-N3	88.8 (3)

[a] The numbers in parentheses are the estimated standard deviations in the last significant figure.

molar absorptivities are listed in Table IV. ^1H NMR spectra are summarized in Table V and indicate a slight deshielding effect of the *trans*-$[O_2Tc]^+$ moiety, which is attenuated by distance.

Investigation of the redox behavior of these complexes by cyclic voltammetry in DMF, employing a variety of electrodes, yielded only solvent peaks. Magnetic susceptibility measurements by the Faraday method at 14 502 G revealed all compounds to be diamagnetic.

Structure. Figure 1 illustrates the computer-drawn[24] models of the two independent *trans*-$[O_2(TBP)_4Tc^V]^+$ cations. Bond distances and angles in the coordination sphere are summarized in Table VI. (Complete bond distance and angle tables are available as Tables IIIs and IVs in the supplementary material.) The structural drawing clearly shows the distorted-octahedral geometry of *trans*-$[O_2(TBP)_4Tc^V]^+$. Both crystallographically unique cations are at centers of symmetry: (0, 0, 0) for Tc1; ($^1/_2$, 0, 0) for Tc2. The average Tc=O bond distance is 1.743 (5) Å, and the average Tc–N, 2.15 (2) Å. The pyridine rings are twisted away from the O=Tc=O axis and form dihedral angles with the equatorial Tc–N plane of 71.2, 75.4, 62.6, and 86.9° for the rings associated with N1, N2, N3, and N4, respectively. The water molecule of solvation is hydrogen bonded to an oxygen atom of cation 1 (O6–O1 = 2.8 Å). The water molecule is also close to the triflate anion (O6–O3 = 3.2 Å, O6–F3 = 3.4 Å). Nonbonded contacts for the rest of the atoms are greater than 3.5 Å.

Discussion

Synthesis and Spectra. The high yields of complexes of the general type *trans*-$[O_2(py)_4Tc]Cl$ by the direct combination of $[n\text{-}Bu_4N][OCl_4Tc]$ with the neat pyridine ligand or the pyridine ligand in ethanol solution suggests these as general methods. However, the latter approach with pyridines containing electron-withdrawing substituents can yield complexes of the type *trans*-$[O(RO)Cl_2L_2Tc]$, where RO^- is the anion of the alcohol and L is the pyridine ligand.[12] Water must be present in the reaction mixture to provide the oxygen atom to convert the technetium core from the $[TcO]^{3+}$ of $[OCl_4Tc]^-$ to the $[O{=}Tc{=}O]^+$ of *trans*-$[O_2(py)_4Tc]Cl$; however, sufficient quantities are often already present in the solvents or available from the atmosphere.

Both the 4-*tert*-butylpyridine and 4-(dimethylamino)pyridine complexes, and to some extent the other complexes, have the desired solubility characteristics for good starting materials to deliver the *trans*-dioxotechnetium(V) core. Since workup and recrystallization of *trans*-$[O_2(py)_4Tc]^+$ required the presence of excess ligand and the distinct odor of pyridine was present in solid samples of all but the aminopyridine complexes, it is clear that the pyridine ligands of these complexes are easily replaced. HPLC analysis in either aqueous or methanol/water eluants was impossible, since the compounds decompose in water or on the column to give the pyridine ligand and an insoluble Tc-containing material.

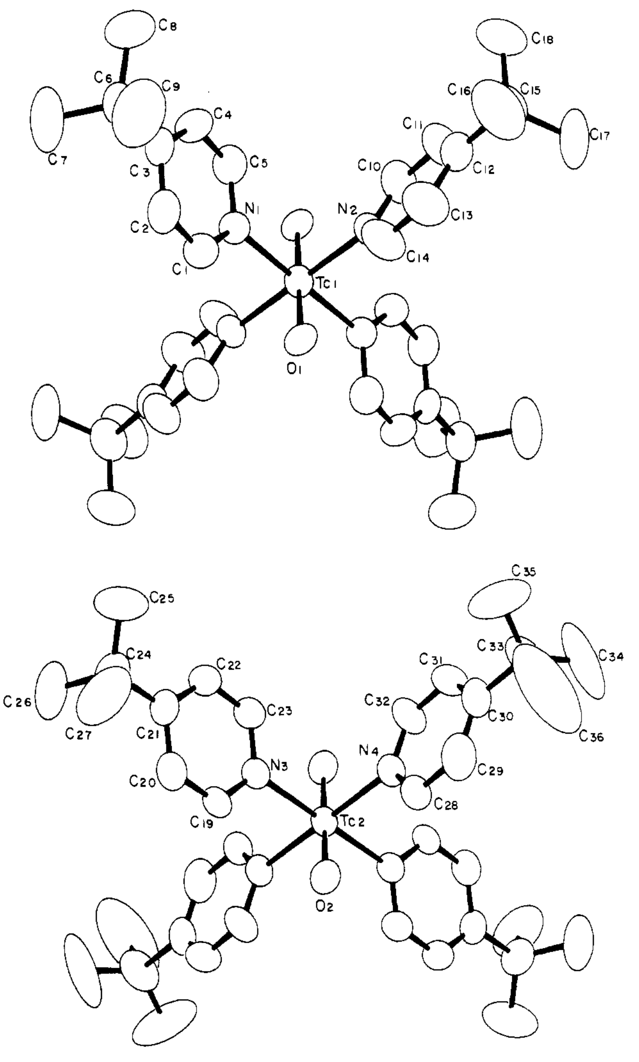

Figure 1. ORTEP diagrams of the two independent ions of *trans*-$[O_2(TBP)_4Tc^V]^+$; thermal ellipsoids drawn at 50% probability.[24]

The correspondence of the infrared spectra of these complexes with that reported in an early study indicates these compounds to be analogous.[11] The asymmetric O=Tc=O stretching frequencies are similar to those observed in other *trans*-dioxotechnetium(V) compounds.[8,10,21,28] The electronic spectra reported in Table IV are also similar to those of other *trans*-dioxotechnetium(V) complexes with imidazole and bidentate amine ligands.[8,28] Ligand field transitions are expected around 790, 600, and 490 nm, but the former two are of such low intensity as to not be easily observable, especially in unstable compounds.[25,26]

The transitions centered at 510–520 nm probably involve an $^1A_1 \to {}^1B_2$ ligand field transition with some increase in intensity owing to the loss of inversion symmetry by random twisting of the pyridine rings in solution or intensification by "stealing" from the charge-transfer band around 315 nm. Transitions around 315 nm appear in essentially all *trans*-

---

(21) Jezowska-Trzebiatowska, B.; Hanuza, J.; Baluka, M. *Acta Phys. Pol. A* **1970**, *A38*, 563–593.

(22) Hanuza, J.; Baluka, M.; Jezowska-Trzebiatowska, B. *Acta Phys. Pol. A* **1972**, *A42*, 537–551.

(23) Jezowska-Trzebiatowska, B.; Hanuza, J. *J. Mol. Struct.* **1973**, *19*, 109–142.

(24) Johnson, C. K. "ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(25) d → d transitions assuming the Tc(V) to be in a site of C_{4v} symmetry are expected at approximately (λ, nm (ε, M^{-1} cm^{-1})) 790 ($^1A_1 \to {}^1E_2$, $\epsilon \simeq 2$), 600 ($^1A_1 \to {}^1A_2$, $\epsilon \simeq 2$), and 490 ($^1A_1 \to {}^{B}{}_2$, $\epsilon \simeq 20$).

(26) Baluka, M.; Hanuza, J.; Jezowska-Trzebiatowska, B. *Bull. Acad. Pol. Sci., Ser. Sci., Chim.* **1972**, *20*, 217–278.

Table VII. Tc≡O, Tc=O, Tc–O, and Tc–N Bond Distances and Tc–O Stretching Frequencies in Selected Oxotechnetium(V) Complexes[a]

no.	complex	coordn no.	$\nu_{Tc=O}$, cm^{-1}	bond dist, Å				ref
				Tc≡O	Tc=O	Tc–O	Tc–N	
1	$[TcOCl_4]^-$	5	1020	1.610 (4)				33
2	$[TcO(O_2C_6H_4)_2]$	5	970	1.622 (7)		1.954 (5)		34
3	$[TcOCl((sal)_2en)]$	5	960	1.63 (1)		1.993 (9)	2.02 (1)	35
4	$[TcOCl(OPhSal)]^e$	5	980	1.634 (7)		1.948 (5)	2.055 (6)	36
5	$[TcO(SCH_2CH_2S)_2]^-$	5	940	1.64 (1)				37
6	$[TcO(OH_2)((acac)_2en)]$	6	960	1.648 (2)		2.020 (2)	2.001 (2)	35
7	*cis*-$[TcOCl(quin)_2]^e$	6	945	1.649 (3)		1.947 (3) 1.99 (3)^c	2.179 (3) 2.215 (3)^b	38
8	$[Tc(HBPz)Cl_2O]$	6	970	1.656 (3)			2.088 (3) 2.259 (4)	39
9	$[TcO(pencil)_2]$	5	981	1.657 (4)		2.214 (4)	2.20 (2)^b	31
10	$[TcO(EDTA)_2]^{2+\ d}$	7	960	1.66		2.03 2.16	2.35^b	32
11	$[TcO(SCH_2CH_2O)_2]^-$	5	948	1.662 (5)		1.945 (20)		40
12	$[TcOCl(PhSal)_2]^+$	6	951	1.67 (1)		1.99 (1) 1.94 (1)	2.12 (1) 2.19 (1)	41
13	$[TcO(SCH_2COS)_2]^-$	5	950	1.672 (8)				42
14	$[TcO(BIT)]^-$	5		1.679 (5)				43
15	$[TcO(OEt)Br_2(Npy)]$	6	938	1.684 (2)		1.855 (6)^i	2.14 (1)	12
16	$[Tc(Im)_4O_2]^+$	6	810		1.71 (2)		2.15 (2)	28
17	$[Tc(MeIm)_4O_2]^+$	6	812		1.71 (2)		2.15 (2)	28
18	$[Tc(TBP)_4O_2]^{\bullet}$	6	821		1.74 (1)		2.15 (1)	44
19	$[Tc(en)_2O_2]^+$	6	833		1.746 (1)^g 1.77 (4)^h		2.15 (2) 2.15 (2)	8
20	$[Tc(cyclam)O_2]^+$	6	790		1.75 (3)		2.13 (3)	9
21	$[TcO_2(CN)_4]^{3-}$	6	827		1.75			6
22	$[Tc(dmg)_3SnCl_3OH]$	7				2.03	2.09	45
24	$[Tc(OH)(MDP)]_n^{-\ f}$					2.01 (3)		46

[a] Abbreviations: Ph, C_6H_5; Et, C_2H_5; quin, 2-methyl-8-hydroxyquinoline; Im, imidazole; MeIm, 1-methylimidazole; cyclam, 1,4,8,11-tetraazacyclotetradecane; pencil, penicilamine; dmg, dimethylglyoxime; TBP, *tert*-butylpyridine; Npy, 4-nitropyridine; HBPz, hydrotris(1-pyrazolyl)borate; Pc, 4-methylpyridine; BIT, $[SCH_2CON(CH_2)_2NCOCH_2S]^{2-}$; $(sal)_2en$, *N,N'*-ethylenebis(acetylacetone imine); $(acac)_2en$, *N,N'*-ethylenebis(salicylideneamine); OPhSal, *N*-(2-hydroxyphenyl)salicylideneaminate; PhSal, *N*-phenylsalicylideneaminato. [b] Elongation due to trans effect. [c] Bond lengthening due to steric effects. [d] Seven-coordinate complex. [e] Cis oxo and chloro ligands. [f] Polymer, Tc(IV) or Tc(V). [g] Chloride salt. [h] Iodide salt. [i] Partial double bonding.[12]

dioxotechnetium(V) complexes with nitrogen ligands.[8] While these are somewhat more intense in the pyridine complexes, this is at least partly due to their overlap with the pyridine ligand bands. Since these vary relatively little with the nitrogen ligand, they may be due to oxo to Tc(V) charge-transfer transitions. The more intense bands at 260–280 nm vary with the pyridine ligand and are probably due to pyridine to Tc(V) charge-transfer transitions. These overlap somewhat with the pyridine $\pi \rightarrow \pi^*$ transitions at 250–260 nm. The slight deshielding of the pyridine ring protons is likely due to both an electron-withdrawing effect of the Tc(V) and the anisotropic magnetic field generated by circulation of electrons between π orbitals in the oxotechnetium core, which is fairly large in complexes of the type $[O(RO)Cl_2(py)_2Tc^V]$.[12]

While the lack of an electrochemically observable reduction process is somewhat surprising for a metal ion in a fairly high oxidation state, this is typical for complexes with oxotechnetium(V) cores. It appears from this that the kinetic overvoltage for electron transfer to oxotechnetium(V) from an electrode surface is quite large, perhaps owing to the lack of a suitable acceptor for the oxo groups or an inherently large Franck–Condon barrier. In contrast, it seems to be relatively easy to chemically reduce this general type of complex, since heating or long standing in a neat pyridine ligand spontaneously produces a mixed-valent material containing at least one Tc in a lower oxidation state.[13] It has also been observed that nitropyridine complexes of Tc(V) in alcohol undergo aerial oxidation to yield $[TcO_4]^-$.[12] This may account for the poor results often obtained in attempting to prepare analytically pure samples of this type of complex. If pyridine is lost, some crystalline samples of these complexes may contain other technetium ions. Solid-state transformations also appear likely since many of these materials exuded a distinct pyridine odor and vacuum desiccation produces an irreversible change in the complex, resulting in a material that cannot be recrystallized.

Structure. The overall structure clearly defines *trans*-$[O_2(TBP)_4Tc^V]^+$ and related ions to be tetragonally distorted-octahedral complexes, with the oxygen atoms in trans positions and the pyridine rings twisted in a pinwheel arrangement. The structure of *trans*-$[O_2(TBP)_4Tc]F_3CSO_3{\cdot}H_2O$ is similar to that of *trans*-$[O_2(py)_4Re]Cl{\cdot}2H_2O$,[27] with both having nearly identical average M–N and M=O bond distances. The average twisting of the pyridine rings from the O=M=O axis (~16°) is very similar to that observed in the rhenium compound (~15°), except that the rings are tilted in the same direction. This degree of twist is attributed to packing forces since it is sufficiently far from the steric limit of 28°, which occurs when the α-carbon of one ring approaches within 3.4 Å of a similar carbon on an adjacent pyridine. The hydrogen bonding of the water molecule of solvation to the oxygen of cation 1 (O6–O1) is analogous to that observed to the oxygen atoms of the *trans*-dioxotechnetium(V) cations in the structures of *trans*-$[O_2(Im)_4Tc]Cl{\cdot}2H_2O$ and *trans*-$[O_2(1\text{-}MeIm)_4Tc]Cl{\cdot}3H_2O$.[28]

Table VII summarizes Tc(V)—O and Tc(V)—N bond distances available from single-crystal structure analyses. Considering that two d_π orbitals are available for bonding to axial oxygen atoms, it is likely that the monooxo, square-pyramidal complexes (5-coordinate) represent at least partial triple bonding between the Tc(V) and oxygen.[12,29] An average of these bond distances (1.644 (24) Å) is not statistically different from an average of those involving a halo or hydroxo

---

(27) Calvo, C.; Krishnamachari, N.; Lock, C. J. L. *J. Cryst. Mol. Struct.* **1971**, *1*, 161–172.

(28) Fackler, P. H.; Kastner, M. E.; Lindsay, M. J.; Clarke, M. J. *Inorg. Chim. Acta*, in press.

(29) Lock, C. J. L.; Turner, G. *Can. J. Chem.* **1977**, *55*, 333–339.

ligand trans to the oxo (1.654 (17) Å). Therefore, an average Tc=O bond length is taken to be 1.65 (2) Å. Complexes containing the *trans*-dioxotechnetium(V) core (entries 16-21) exhibit a fairly narrow range of Tc=O bond distances and the average of these, 1.74 (2) Å, can now be considered standard for this core. Technetium-oxygen single-bond distances exhibit considerable variation, which is sometimes due to partial double bonding, as is probable in $[O(CH_3CH_2O)Br_2(4\text{-nitropyridine})_2Tc^V]$,[12] or steric strain, as in $[TcO(\text{pencil})_2]$[31] and $[Tc(EDTA)]^{2+}$.[32] Excluding these complexes, the average Tc-O distance is 1.98 (3) Å. Bond lengths for Tc(V)-N fall into a fairly wide range (2.00-2.35 Å), with the extremes resulting from chelate effects. The average of all Tc-N distances (2.14 (8) Å) is not appreciably different from that including only sterically unhindered nitrogen ligands (2.15 (1) Å for entries 15-18), which should be taken as the standard length.

Acknowledgment. This work was supported by PHS Grants CA-24344 and GM-26390 at Boston College. The diligent work of Dr. T. Brennan (Boston University) and Dr. A. F. Garafalo (Massachusetts College of Pharmacy) in attempting to solve the structure of *trans*-$[O_2(AP)_4Tc]Cl\cdot 2H_2O$ is also gratefully appreciated. E.D. gratefully acknowledges support from the NIH (Grant No. HL-21276) and the FDA (through an interagency agreement to the DOE, BNL).

Registry No. *trans*-$[O_2(TBP)_4Tc]F_3CSO_3\cdot H_2O$, 93383-84-7; *trans*-$[O_2(py)_4Tc]Cl$, 93383-85-8; *trans*-$[O_2(pic)_4Tc]Cl$, 93383-86-9; *trans*-$[O_2(lut)_4Tc]Cl$, 93383-87-0; *trans*-$[O_2(AP)_4Tc]Cl\cdot 2H_2O$, 93383-88-1; *trans*-$[O_2(DMP)_4Tc]Cl$, 93383-89-2; $[n\text{-}Bu_4N][OCl_4Tc]$, 71341-65-6.

Supplementary Material Available: Listings of calculated and observed structure factor amplitudes for *trans*-$[O_2(TBP)_4Tc]F_3CSO_3\cdot H_2O$, temperature factors for non-hydrogen atoms, complete listings of bond distances and angles, hydrogen atom positions, and infrared and Raman spectral data (Tables Is-VIs) (29 pages). Ordering information given on any current masthead page.

---

(30) Reference deleted in revision.

(31) Franklin, K. J.; Howard-Lock, H. E.; Lock, C. J. L. *Inorg. Chem.* **1982**, *21*, 1941.

(32) Deutsch, E. A.; Elder, R. C.; Packard, A., unpublished work.

(33) Cotton, F. A.; et al. *Inorg. Chem.* **1979**, *18*, 3024.

(34) DePamphilis, B. V. Ph.D. Thesis, Massachusetts Institute of Technology, 1981.

(35) Jurrison, S.; Lindoy, L. F.; Dancey, K. P.; McPartlin, M.; Tasker, P. A.; Uppal, D. K.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 227-231.

(36) Bandoli, G.; Mazzi, U.; Wilcox, B. E.; Jurrison, J. C.; Deutsch, E., submitted for publication.

(37) Smith, J. E.; Byrne, E. F.; Cotton, F. A.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5570.

(38) Wilcox, B. E.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 2962-2967.

(39) Thomas, R. W.; Davison, A.; Trop, H. S.; Deutsch, E. A. *Inorg. Chem.* **1980**, *19*, 2840.

(40) Davison, A.; Jones, A. G.; DePamphilis, B. V. *Inorg. Chem.* **1981**, *20*, 1617.

(41) Bandoli, G.; Mazzi, U.; Clemente, D. A.; Roncari, E. *J. Chem. Soc., Dalton Trans.* **1982**, 2455.

(42) DePamphilis, B. V.; Jones, A. G.; Davis, M. A.; Davison, A. *J. Am. Chem. Soc.* **1978**, *100*, 5570.

(43) Davison, A.; et al. *J. Ncl. Med.* **1983**, *23*, 801-809.

(44) This work.

(45) Deutsch, E. A.; Elder, R. C.; Lange, B. A.; Vall, M. J.; Lay, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 4287.

(46) Libson, K.; Deutsch, E.; Barnett, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 2476.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Molecular and Electronic Structures of Two 16-Electron Complexes of Tungsten(II): $WBr_2(CO)_2(C_7H_8)$ (C_7H_8 = Norbornadiene) and $WBr_2(CO)_2(PPh_3)_2$

F. A. COTTON* and J. H. MEADOWS

Received April 27, 1984

The previously reported reaction of $WBr_2(CO)_4$ with norbornadiene has been reinvestigated and found to give monomeric $WBr_2(CO)_2(C_7H_8)$ (**1**). Compound **1** crystallizes from CH_2Cl_2 in the monoclinic space group $P2_1/n$ with lattice dimensions a = 7.506 (7) Å, b = 12.643 (8) Å, c = 12.296 (6) Å, β = 99.60 (7)°, V = 1150 (2) Å^3, and Z = 4. The structure was refined to R_1 = 0.032 and R_2 = 0.038. Compound **1** is a diamagnetic d^4 complex having a pseudo-octahedral geometry with its CO ligands trans to each other. Compound **1** also has relatively short W-Br (2.493 (1) and 2.489 (1) Å) bond lengths. Another 16-electron d^4 tungsten complex, $WBr_2(CO)_2(PPh_3)_2$ (**2**), was also structurally characterized. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with lattice dimensions a = 9.418 (5) Å, b = 10.021 (4) Å, c = 19.898 (6) Å, α = 90.54 (3)°, β = 112.80 (3)°, γ = 92.02 (4)°, V = 1730 (1) Å^3, and Z = 2. The structure was refined to R_1 = 0.064 and R_2 = 0.072. Compound **2** has an overall geometry greatly distorted from octahedral. Fenske-Hall type molecular orbital calculations were performed on models of **1** and **2** to determine the principal factors responsible for the removal of t_{2g} orbital degeneracy. The calculational results predict a lowest energy allowed transition between orbitals separated by ca. 3 eV for both **1** and **2**. This transition is assigned to visible transitions observed at 565 and 545 nm for **1** and **2**, respectively. The calculations indicate that the LUMO-HOMO separation in **1** can be attributed to metal d to CO π^* and olefin π^* back-donation, which results in the lowering of two orbitals preferentially. In **2** it appears that the strong distortions from octahedral symmetry, especially the P-M-P angle of only 128°, are as important as π bonding in giving the singlet ground state.

Introduction

Work in this laboratory involving d^4 transition-metal complexes has largely focused on the tendency of this electronic configuration to form multiple metal-metal bonds.[1a] Bond orders between the metal atoms as high as quadruple may be formed when a high degree of electron density is placed on the metal centers and the metal valence orbitals can overlap sufficiently. A basic question that we hope to answer by these studies is what are the electronic requirements (limitations) for forming multiple metal-metal bonds. The lack of complexes containing both multiple metal-metal bonds and π-acidic ligands (e.g., CO) shows that these structural components tend to be generally incompatible for reasons that have been discussed.[1b]

With this historical backdrop we were surprised to see a recent report that $WBr_2(CO)_4$ reacts with diolefins (L-L =

---

(1) (a) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982. (b) Cotton, F. A. *ACS Symp. Ser.* **1983**, *No. 211*, 209.