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Communications to the Editor

Synthesis of (Trifluoromethanesulfonato)pentaammineosmium(III): Osmium(III) Pentaammine Complexes

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We wish to communicate the high-yield synthesis (>95%) of $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, I, as a valuable intermediate for the preparation of $[Os(NH_3)_5L]^{m+}$ and $[Os(NH_3)_5LOs(NH_3)_5]^{n+}$ complexes.[1,2] The chemistry of the mononuclear and binuclear ruthenium analogues has been facilitated by the use of the substitution-labile $[Ru(NH_3)_5(OH_2)]^{2+}$ ion.[3] However, a similar strategy is not available for osmium because $[Os(NH_3)_5(OH_2)]^{2+}$ rapidly reduces water to H_2.[4,5] Our interest in the chemistry of osmium complexes stems from the greater π-bonding properties of Os(II) and Os(III) relative to the much studied ruthenium analogues. This prompted us to investigate the use of triflato (trifluoromethanesulfonato) complexes of Os(III), since similar complexes have proven to be extremely versatile synthetic intermediates in Co(III), Rh(III), Ir(III), Pt(IV), Cr(III), and Ru(III) chemistry.[6,7]

The typical approach for synthesis of the $[M(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ complexes has been to heat the $[M(NH_3)_5Cl]Cl_2$ complexes in neat CF_3SO_3H. While such a strategy also succeeds with $[Os(NH_3)_5Cl]Cl_2$, we find that Br_2 oxidation in neat triflic acid (CF_3SO_3H) of the readily prepared $[Os(NH_3)_5N_2]Cl_2$[8,9] is a more efficient and facile route. In a typical reaction, $[Os(NH_3)_5N_2]Cl_2$ (2 g) was dissolved cautiously in neat distilled CF_3SO_3H (4–5 mL), and after HCl evolution had subsided, Br_2 (~1 mL, excess) was added while N_2 was bubbled through the solution at room temperature. Gas evolution from the Br_2/CF_3SO_3H interface and a dark green intermediate[10] were observed during the ~1.5-h of reaction. Subsequent heating to 110 °C for 1 h drove off excess Br_2 and HBr to yield a yellow solution from which the triflate complex was precipitated by the cautious addition of anhydrous ether at 0 °C. The precipitate was collected and washed with ether to yield $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (≳95%) as a very pale yellow solid,[11] which was stored in a desiccator.

Table I. Reduction Potentials and UV–vis Absorption Spectra for Osmium(III) Pentaammine Complexes

complex[a]	E_f, mV[b]	UV–vis, nm[c]
$Os(NH_3)_5(OSO_2CF_3)^{2+}$		235.5 (843), 290 sh (108), 447 (55)[k]
$Os(NH_3)_5Cl^{2+}$	−850[d]	224 (200), 267 (2010)[l]
$Os(NH_3)_5(OH_2)^{3+}$	−730[d,e]	220 sh (1100)[m]
$Os(NH_3)_5(NCCH_3)^{3+}$	−250[f]	~225 sh (1700), 250 sh (790), 320 sh (44), 450 (4)[g,n]
$Os(NH_3)_5(py)^{3+}$	−395[g,h]	234 (4500), 266 (4300), 290 sh (2500)[g,h]
$Os(NH_3)_5(pyd)^{3+}$	−210[h,i]	~225 sh (3000), 256 (2500), 305 (3000), 420 sh (400)[g,h]
$Os(NH_3)_5(pyr)^{3+}$	−260[h,i]	228 (5100), 290 (2800)[g,h]
$Os(NH_3)_5(pz)^{3+}$	−90[h,i]	246 (1900), 282 (1500), 329 (1400)[g,h]
		248 (4400), 285 (3200), 332 (3100)[o]
$Os(NH_3)_5(pzH)^{4+}$	[j]	264 (5030), 324 (1860), 391 (4480), ~530 sh (650)[g]
$Os(NH_3)_5(pzMe)^{4+}$	+546[g]	268 (4900), 360 sh (2150), 420 (5000), ~600 sh (494)[g]

[a] py = pyridine, pyd = pyridazine = 1,2-diazine, pyr = pyrimidine = 1,3-diazine, pz = pyrazine = 1,4-diazine, pzH = 4-pyrazinium, pzMe = 4-methylpyrazinium. [b] Formal potentials vs. NHE. [c] Extinction coefficients in parentheses ($M^{-1}\ cm^{-1}$). [d] 0.3 M $NaCH_3SO_3$.[5] [e] pH 4.0, pH dependent due to deprotonation of the aqua group coordinated to Os(III), $pK_a(Os(NH_3)_5(OH_2)^{3+})$ = 5.2.[5] [f] 0.1 M NaCl. [g] 0.1 M HCl. [h] Reference 16. [i] pH ~9 $NaCH_3CO_2$, pH dependent due to protonation of terminal nitrogen in the Os(II) heterocycles. The Os(II) complexes have the following pK_a values: pydH, 3.7; pyrH, 2.1; pzH, 7.4. [j] Estimated to be +500 mV by comparison with $Os(NH_3)_5(pzMe)^{4+/3+}$. [k] Neat CF_3SO_3H. [l] Allen, A. D.; Stevens, J. R. *Can. J. Chem.* 1973, *51*, 92–98, water. [m] Reference 14. [n] Weak shoulders on the edge of a charge-transfer band trailing into the UV. [o] 0.01 M HCl.

The triflato complex was identified readily from IR spectral measurements, which showed no bands attributable to coordinated water or N_2, while bands due to the triflato group were split. In particular, bands appear at higher frequencies (1300–1400 cm^{-1}) in the asymmetric S=O stretching region, which are assigned to the coordinated triflato ligand.[12] This ligand on Os(III) is relatively labile to solvolysis reactions, and in acidic aqueous medium $[Os(NH_3)_5(OH_2)]^{3+}$ is formed with a first-order rate constant of $1.6 \times 10^{-3}\ s^{-1}$ at 25 °C (0.1 M CF_3SO_3H). Therefore, the Os(III) complex is the second most inert of the $[M(NH_3)_5(OSO_2CF_3)]^{2+}$ series, which follows a reactivity order of Ru(III) > Co(III) > Rh(III) ≳ Cr(III) > Os(III) > Ir(III).[7] Aquation of compound I in the solid state by atmospheric moisture occurs, but not so fast as to preclude normal handling in air. Aquation may be reversed to regenerate I by simply heating an aged sample in a vacuum oven at 120 °C for 1 day or by heating in neat triflic acid.

In nonbasic aprotic solvents, substitution to form the $[Os(NH_3)_5L]^{3+}$ ions proceeds in essentially quantitative yields.

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[1] Magnuson, R. H.; Lay, P. A.; Taube, H. submitted for publication in *J. Am. Chem. Soc.*

[2] Lay, P. A.; Magnuson, R. H.; Taube, H., to be submitted for publication.

[3] Taube, H. *Comments Inorg. Chem.* **1981**, *1*, 17–31.

[4] Gulens, J.; Page, J. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, *55*, 239–253.

[5] Gulens, J.; Page, J. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *67*, 215–230.

[6] Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470–476.

[7] Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M., submitted for publication in *Inorg. Chem.*; submitted for publication in *J. Chem. Soc., Chem. Commun.*

[8] Allen, A. D.; Stevens, J. R. *Can. J. Chem.* **1972**, *50*, 3093–3099. Bottomley, F.; Tong, S.-B. *Inorg. Synth.* **1976**, *16*, 9–13.

[9] Buhr, J. D.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2208–2212.

[10] If insufficient Br_2 is present, the binuclear dinitrogen mixed-valence species $[Os(NH_3)_5N_2Os(NH_3)_5]^{5+}$ is produced, which is readily recognized by an intense green coloration. Use of I_2, instead of Br_2, as oxidant tends to favor the formation of the binuclear dinitrogen complex. This represents the best method of synthesis of such a species, which has been synthesized previously in lower yield by a lengthier procedure (Richardson, D. E.; Sen, J. P.; Buhr, J. D.; Taube, H. *Inorg. Chem.* **1982**, *21*, 3136–3140). Synthesis of binuclear dinitrogen complexes by these methods will be reported in more detail elsewhere (Lay, P. A.; Magnuson, R. H.; Taube, H., to be submitted for publication).

[11] Anal. Calcd for $C_3H_{15}F_9N_5O_9S_3Os$: C, 4.98; H, 2.09; N, 9.69; S, 13.31; F, 23.66. Found: C, 5.30; H, 2.06; N, 9.69; S, 13.10; F, 22.98.[15]

[12] This frequency region is typical of the asymmetric S=O stretching region of sulfonate ester groups. Dolphin, D.; Wick, A. "Tabulation of Infrared Spectral Data"; Wiley: New York, 1977; Chapter 7.1, p 469.

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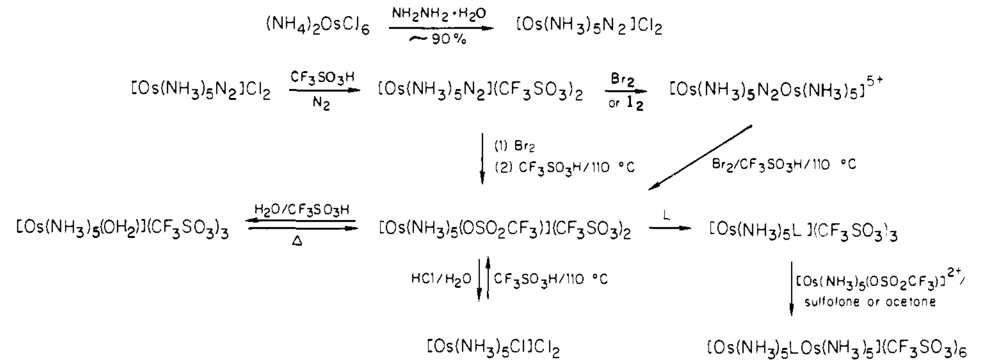
Scheme I



However, addition of CF_3SO_3H to the more basic solvents (H_2O, pyridine, pyrazine) is necessary to suppress base-catalyzed disproportionation reactions, which ultimately lead to multiple substitution and/or oligimerization.[9,13,14] In poorly coordinating solvents such as sulfolane, acetone, or triethyl phosphate, other ligands may be substituted, leading to preparations in moderate to excellent yields. This approach has also been applied successfully to the synthesis of binuclear decaammine complexes.[1,2] The overall chemistry is summarized in Scheme I, and spectral and electrochemical properties of selected complexes prepared by the above methods are presented in Table I.[15] Although most of these complexes have been reported previously,[14,16] the above methods represent the simplest and highest yield preparative routes. It is also worth noting that the intensities of some of the electronic absorption bands of the N-heterocyclic complexes as measured by us are greater than those reported elsewhere.[16] Near-IR spectral properties for several Os(III) complexes have been reported,[14,16] and their absence in analogous d^6 Os(II) complexes supports their assignment as intra t_{2g} transitions split by spin–orbital coupling and/or the symmetry requirement of the ligand field in the pentaammine complexes. The presence of such bands serves as a useful diagnostic tool for the Os(III) oxidation state. In general, a medium-intensity ($\epsilon \sim 10^2$ M^{-1} cm^{-1}) narrow transition occurs at ~2100 nm, along with other weaker transitions for the complexes containing π-acceptor ligands. For those where π-bonding is weak (e.g., $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ and $[Os(NH_3)_5(OH_2)]^{3+}$), only weak ($\epsilon \lesssim 10$ M^{-1} cm^{-1}) transitions have been observed.[17]

An interesting aspect of the redox chemistry is the range of potentials at which the osmium complexes with π-acceptor ligands are reversibly reduced.[16] In particular, the $[Os(NH_3)_5(CH_3CN)]^{3+/2+}$ couple ($E_f = -0.25$ vs. NHE) occurs at a potential that should make it a useful, fast, outer-sphere, and weakly colored redox reagent. Further, the redox potentials of the N-heterocyclic complexes makes them ideal candidates for the study of surface-enhanced Raman spectroscopy at silver electrodes, where very strong signals are observed. Some of these signals are sensitive to the electrode potential around E_f for the Os(III)/Os(II) couple.[18]

In summary, the ready synthesis of the relatively air-stable $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ complex has provided a convenient and high-yielding entry into the pentaammineosmium and decaamminediosmium series of complexes. This greatly facilitates assessing the impact of π-donor effects on osmium relative to analogous ruthenium complexes and provides ready access to other significant comparisons including mixed-valence interactions,[1,2] redox chemistry,[2,16] reactions of coordinated ligands, and substitution and linkage isomerization processes.

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Registry No. I, 83781-30-0; $[Os(NH_3)_5N_2]Cl_2$, 20611-50-1; $[Os(NH_3)_5(OH_2)](CF_3SO_3)_3$, 83781-31-1; $[Os(NH_3)_5(CH_3CN)](CF_3SO_3)_3$, 83781-33-3; $[Os(NH_3)_5(pz)](CF_3SO_3)_3$, 83781-35-5; $[Os(NH_3)_5(pzMe)](BF_4)_4$, 83781-37-7; $[Os(NH_3)_5(py)]^{3+}$, 83781-38-8; $[Os(NH_3)_5(pyd)]^{3+}$, 70252-41-4; $[Os(NH_3)_5(pyr)]^{3+}$, 83781-39-9; $[Os(NH_3)_5(pzH)]^{4+}$, 83781-40-2.

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(13) Lay, P. A.; Magnuson, R. H.; Sargeson, A. M.; Taube, H., unpublished observations.

(14) Buhr, J. D. Ph.D. Thesis, Stanford University, Stanford CA, 1978.

(15) $[Os(NH_3)_5(OH_2)](CF_3SO_3)_3$ has $\nu(OH_2)$ at 3400–3500 cm^{-1}. Anal. Calcd for $C_3H_{17}F_9N_5O_{10}S_3Os$: C, 4.87; H, 2.31; N, 9.46. Found: C, 4.96; H, 2.39; N, 8.95. $[Os(NH_3)_5(CH_3CN)](CF_3SO_3)_3$ has $\nu(C{\equiv}N)$ at 2295 (w) cm^{-1}. Anal. Calcd for $C_5H_{18}F_9N_6O_9S_3Os$: C, 7.86; H, 2.38; N, 11.0. Found: C, 7.8; H, 2.5; N, 10.7. $[Os(NH_3)_5pyrazine](CF_3SO_3)_3{\cdot}H_2O$: Anal. Calcd for $C_7H_{21}F_9N_7O_{10}S_3Os$: C, 10.26; H, 2.58; N, 11.95. Found: C, 10.4; H, 2.6; N, 12.0. $[Os(NH_3)_5(methylpyrazinium)](BF_4)_4$: Anal. Calcd for $C_5H_{22}B_4F_{16}N_7Os$: C, 8.37; H, 3.09; N, 13.66. Found: C, 8.4; H, 3.1; N, 13.5. All microanalyses were performed by the Stanford University microanalyst. With some complexes, it is necessary to use the Kirsten–Dumas method in order to obtain satisfactory analytical figures (Lay, P. A.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 6161–6164).

(16) Sen, J.; Taube, H. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 125–135.

(17) Detailed investigations of the near-IR spectral region of the Os(III) complexes is underway. Winkler, J. R.; Gray, H. B.; Lay, P. A.; Magnuson, R. H.; Taube, H., work in progress.

(18) Farquharson, S.; Lay, P. A.; Magnuson, R. H.; Taube, H.; Weaver, M. J., to be submitted for publication.

Electron Transfer across Polypeptides. 4. Intramolecular Electron Transfer from Ruthenium(II) to Iron(III) in Histidine-33 Modified Horse Heart Cytochrome c

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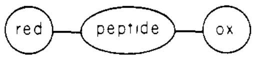
We have demonstrated that intramolecular rates of electron transfer can be significantly altered when different peptide units separate the same donor and acceptor metal ions as shown schematically in I.[1-5] In an attempt to extend this work to



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