and 0.1 M pmdien) has succeeded by use of ascorbate in CO-saturated solution at pH 10. No reduction of the Cu^{II} complex was possible in the absence of CO. This explains why we did not see the two-step 1e redox reaction in the polarography of the Cu^{II} and Cu^{I} complexes with pmdien in CH$_3$CN (only)-containing aqueous solution.

Comparison of [Cu(dien)(CO)]$^+$ (1) and [Cu(pmdien)(CO)]$^+$ (8). Finally, **8** was isolated as the crystalline perchlorate salt from *aqueous* solution (see Experimental Section). A molecular model suggests a tetrahedral structure for **8** similar to that established (by X-ray study) for **1**.[5] The colorless solid **8**(ClO$_4$) gradually turned to blue in the air. However, such oxidation of **8** is apparently slower than that of the previous **1**. The infrared ν_{CO} signals occur at 2082 cm^{-1} (KBr pellet) and 2088 cm^{-1} (in H$_2$O) for **8** and 2080 cm^{-1} (in THF or Nujol) for **1**,[5] suggesting a common end-on CO bonding to Cu^{I}.[11] CO dissolved in H$_2$O failed to show a definite ν_{CO} band due to perturbation with H$_2$O. The ν_{CO} (gas) value is reported at 2170 cm^{-1}.[20] If pmdien were a much weaker σ-donor (or stronger π-acceptor) than dien, we would anticipate a stronger Cu^{I}–CO bonding for **8**, which would be reflected in a higher ν_{CO} value.[22] A characteristic UV absorption in aqueous solution occurs at λ_{max} 275 nm (ϵ 3900) for **8**, while no such UV behaviors in solution were reported for previous

Cu^{I}–CO complexes, including **2**.

Concluding Remarks

The present study has disclosed that the tridentate tertiary saturated amine pmdien is an appropriate ligand to sustain Cu^{I} with the aid of a monodentate π-ligand such as CH$_3$CN or CO in neutral *aqueous* solutions as monomeric, four-coordinate Cu^{I} complexes. The good separation between the two 1e redox systems by **8** may open up some applications such as a new CO-gas sensor.

The results clearly point out that a N-peralkylated tridentate open-chain tertiary amine (pmdien) stabilizes Cu^{I} in aqueous solutions more than the nonalkylated counterpart (dien). A direct comparison of the [Cu(L)(CO)]$^+$ formation constants failed due to the instability of the dien system **1** in aqueous solution. However, a similar ν_{CO} frequency of the Cu^{I}-bound CO indicates similar donor (to Cu^{I}) effects for pmdien and dien. The stability of the Cu^{I}/pmdien system **8** against water or other hostile ligands seems due to the steric and/or hydrophobic effects of permethylation. This result suggests that the analogous effect observed in tetraaza macrocyclic complexes[4,12,13] is not due to an increase of the cavity of the macrocyclic ligand but rather to the steric hindrance and/or hydrophobicity of the methylated ligands.

Supplementary Material Available: Calculation procedure for Cu^{I} complex formation constants (3 pages). Ordering information is given on any current masthead page.

(22) The infrared ν_{CO} band for the CO adduct of [Cu(cimetidine)]$^+$ (containing an imidazole ligand)[3] was observed at 2097 cm^{-1} in CO-saturated aqueous solution (Kimura, E.; Koike, T. Unpublished results).

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Syntheses of Pentaammineosmium(III) and -osmium(II) Complexes: Pentaammine(trifluoromethanesulfonato-O)osmium(III)

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The triflato complex [Os(NH$_3$)$_5$(OSO$_2$CF$_3$)](CF$_3$SO$_3$)$_2$ is prepared in 95–100% yield by either the Br$_2$ or O$_2$ oxidation of [Os(NH$_3$)$_5$(N$_2$)]Cl$_2$ in neat CF$_3$SO$_3$H or the substitution reaction of [Os(NH$_3$)$_5$Cl]Cl$_2$ in neat CF$_3$SO$_3$H. Solvation rates are rather rapid in comparison to those of other Os(III) complexes, with k_{obs} = 8.8 × 10^{-4} s^{-1} at 25 °C in 1 M aqueous CF$_3$SO$_3$H. The solvation rate constants have been recorded for a number of solvents; however, basic solvents cause disproportionation reactions, which limits the range of solvents in which this reaction can be studied. In the case of [Os(NH$_3$)$_5$(acetone)]$^{3+}$, a second first-order reaction is observed, which is believed to involve the condensation of acetone with an ammine ligand. A large variety of pentaammineosmium(III) complexes can be prepared either by the direct reaction of the triflato complex with the neat ligand or by the use of relatively labile solvent complexes as intermediates. These reactions are not suitable for basic ligands because of the disproportionation problems. Complexes with many anionic ligands are prepared readily by heating the triflato complex in aqueous solutions of HX or acidified NaX solutions. The osmium(II) analogues are prepared readily from the reduction of the osmium(III) complexes. The shifts in the Os(III/II) redox potentials of the complexes containing the π-acid ligands compared to [Os(NH$_3$)$_6$]$^{3+/2+}$ are more positive than the corresponding shifts in the ruthenium analogues. This indicates the greater extent of π-back-bonding for Os(II), as compared to Ru(II). The reactivity patterns of the Os(III) and Ru(III) complexes also indicate that π-back-bonding is significant for Os(III), but not for Ru(III). The [Os(NH$_3$)$_5$(acetone)]$^{3+/2+}$ and [Os(NH$_3$)$_5$(dmso)]$^{3+/2+}$ complexes exhibit oxidation-state-dependent linkage isomerization reactions. The electronic absorption spectra of both the Os(III) and Os(II) complexes with π-acid ligands are dominated by MLCT transitions, which occur at lower energies for the former. The electronic transitions that occur within the t$_2$ subset of the 5d orbitals are observed in the near-IR region. They are due to the effects of spin–orbit coupling on the t$_2^5$ electronic configuration and are an order of magnitude more intense for the complexes with π-acid or π-base ligands than those where the ligand shows little or no tendency to π-bond.

Introduction

Although the known chemistry of [Ru(NH$_3$)$_5$L]$^{n+}$ in both the Ru(II) and Ru(III) oxidation states is quite extensive, the corresponding osmium chemistry is not as well-known.[1] This disparity has arisen partially from the historical difficulty in preparing osmium(III) pentaammine complexes[1-4] and partially from the instability of many Os(II) complexes to oxidation by water or to ligand reduction.[4-6] In particular, the instability of [Os-

(NH$_3$)$_5$(OH$_2$)]$^{2+}$ to oxidation by water[5,6] has limited its use as an effective synthetic intermediate, unlike the Ru(II) analogue.

Since it was first shown that the triflato (trifluoromethanesulfonato) ligand of [Cr(OH$_2$)$_5$(OSO$_2$CF$_3$)]$^{2+}$ is comparable in

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reactivity to the perchlorato ligand as a leaving group,[7] the lability of the triflato ligand has found use in the syntheses of cobalt amine complexes.[8-13] More recently, triflato complexes of many of the other substitution-inert oxidation states of transition-metal ions have been prepared and have been found to be equally useful synthetic intermediates.[11-26] The properties and use of [Os-$(NH_3)_5(OSO_2CF_3)$]$^{2+}$, as a synthetic intermediate, have been reported on briefly.[23-26] In this paper, details of its synthesis, reactivity, and general synthetic utility are discussed; its use in the synthesis of N-heterocyclic complexes is detailed elsewhere.[26]

Experimental Section

Materials and Reagents. CF_3SO_3H (3M Co.), sulfolane, N,N-dimethylformamide, and triethyl phosphate were vacuum-distilled prior to their use.[8,9] Acetone and dmso, both of AR grade, were dried over 4-Å molecular sieves for at least 48 h before use. Acetonitrile (Aldrich, spectroscopic grade) and benzonitrile (AR) were passed through a column of neutral alumina and stored over the same. The aqueous hydro-halic acids used were all of AR grade. Analytical grade diethyl ether and OsO_4 (Alfa) were used as received. High-purity argon was used for all manipulations involving the Os(II) complexes and was deoxygenated (Cr^{2+}) and dried (H_2SO_4) prior to its use.

Instrumentation. Cyclic voltammograms were performed by using a PAR Model 173 potentiostat with a PAR Model 175 universal programmer as a function generator. The responses were recorded on a PAR Omnigraphic X-Y recorder or a Tektronix single-beam storage oscilloscope and camera for fast scan rates (>500 mV s^{-1}). A three-electrode system was used, which incorporated a glassy-carbon or carbon-paste working electrode, a platinum wire as the auxiliary electrode, and the SCE as a reference electrode. In nonaqueous solvents, the reference electrode was separated from the working compartment by a salt bridge containing the same solvent and electrolyte as those in the bulk solution. The ferrocenium/ferrocene couple was used as an internal standard in nonaqueous solvents.[27] For bulk electrolysis, the PAR 173 potentiostat was used in conjunction with a PAR 179 digital coulometer, either a Hg pool or a Pt basket being used as the working electrode. A BAS 100 electrochemical analyzer was also used in some experiments.

Infrared spectra were recorded as KBr disks on either a Perkin-Elmer Model 621 IR spectrometer or a Nicolet 7199 FTIR spectrometer. The latter was also used for the recording of the near-IR spectra in KBr disks. Absorption spectra (UV, visible, and near-IR) were recorded by using a Beckman Model 5270 spectrophotometer. The spectra in the near-IR region were recorded for samples pelletized in KBr or CsI and/or dissolved in 0.1 M DCl/D$_2$O solutions. Spectra of air-sensitive complexes were obtained by reducing the complexes with Zn(Hg) or [Ru(NH$_3$)$_6$]$^{2+}$ in a Zwickel flask under an argon atmosphere and then transferring the

solutions directly to a Beckman spectrophotometer cell.[28,29]

Reaction Kinetics. Rates of substitution reactions were measured on the Beckman spectrophotometer by dissolving solid [Os(NH$_3$)$_5$(OSO$_3$C-F$_3$)](CF$_3$SO$_3$)$_2$ in the appropriate solvent, which had been preequilibrated at 25 °C. The solution was filtered prior to the measurement of the reaction kinetics, and the temperature was maintained constant (±0.1 °C) by the use of a thermostated water bath. The consecutive first-order reactions that were observed in the case of the complex in acetone were treated by the published graphical method.[30]

Synthesis. (NH$_4$)$_2$[OsCl$_6$][31] is prepared from OsO$_4$ and is used for the synthesis of [Os(NH$_3$)$_5$(N$_2$)]Cl$_2$ by a modification[23,32] of the previously published methods.[2,3,33] [Os(NH$_3$)$_5$Cl]Cl$_2$ is prepared from [Os(N-H$_3$)$_5$(N$_2$)]Cl$_2$ by the oxidation of the dinitrogen complex in aqueous HCl.[34]

Caution! The precipitation of the Os complexes as their perchlorate salts should be strictly avoided, as they are unpredictably explosive and present an extreme safety hazard.

[Os(NH$_3$)$_5$(OSO$_2$CF$_3$)](CF$_3$SO$_3$)$_2$. Method 1. To [Os(NH$_3$)$_5$(N$_2$)]Cl$_2$ (2.0 g, 5.3 mmol), contained in a 50-mL two-necked round-bottomed flask fitted with an Ar or N$_2$ gas bubbler, is added distilled[8,9] anhydrous CF$_3$SO$_3$H (10 mL). Liquid Br$_2$ (0.5 mL, 10 mmol, 4-fold excess) is added to the yellow or pale green solution, and N$_2$ immediately begins to evolve from the interface of the Br$_2$ and CF$_3$SO$_3$H layers. The pale green color that is sometimes observed results from an impurity of the mixed-valence species [(NH$_3$)$_5$OsN$_2$Os(NH$_3$)$_5$]$^{5+}$, but under the reaction conditions this compound is also converted to the [Os(NH$_3$)$_5$-(OSO$_2$CF$_3$)]$^{2+}$ ion. A constant flow of N$_2$ or Ar is commenced in order to stir the solution while the temperature is maintained around the boiling point of Br$_2$, ~50-60 °C. The gas flow is stopped periodically to determine if the evolution of N$_2$ gas has ceased from the interface of the two layers. When the evolution has ceased (~0.5-1 h), the solution is heated to 110 °C in an oil bath, and a constant gas flow is maintained in order to drive off excess Br$_2$ and the HBr that has been produced in the reaction. After the brown fumes have ceased and no Br$_2$ remains in the bottom of the flask, the solution is cooled to room temperature. It is then cooled in an ice bath to ~5 °C. Anhydrous diethyl either (~30 mL) is added dropwise to the rapidly stirred solution. (*Caution!* This a very exothermic addition, and due care must be exercised to avoid too rapid addition of the diethyl ether). A white to cream-colored precipitate begins to form immediately. The precipitate is collected on a medium-porosity frit and is air-dried. For larger scale reactions, it is best to let the precipitate settle and decant off most of the solvent through the frit. The filtrate may be kept for recovery of CF$_3$SO$_3$H as the Na$^+$ salt.[8,9] The solid is washed with copious quantities of anhydrous diethyl ether until the washings are colorless and then dried (yield 3.7 g, 96%). At this point, the compound is quite suitable as a synthetic intermediate, but it may be purified by boiling a suspension in chloroform, as follows. Any lumps in the solid are broken up by grinding with a mortar and pestle. A suspension of the powder is stirred in boiling chloroform (AR, 50 mL) for ~0.5 h, in order to remove any coprecipitated Et$_2$O·CF$_3$SO$_3$H. The fine powder is collected on a medium-porosity frit, washed once with chloroform (10 mL), and dried in air. Anal. Calcd for C$_3$H$_{15}$F$_9$N$_5$O$_9$S$_3$Os: C, 4.98; H, 2.09; N, 9.69; S, 13.31; F, 23.66. Found: C, 5.3; H, 2.1; N, 9.7; S, 13.1; F, 23.0. The compound is stored in a desiccator over P$_4$O$_{10}$ or silica gel in order to prevent absorption of atmospheric moisture, which will form [Os(NH$_3$)$_5$(OH$_2$)](CF$_3$SO$_3$)$_3$ in the solid state. However, this process is very slow, and the compound may be manipulated readily without the precautions necessary for working in a moisture-free atmosphere.

Method 2. To [Os(NH$_3$)$_5$Cl]Cl$_2$ (1.0 g, 2.6 mmol) in a 50-mL two-necked round-bottomed flask is added carefully distilled trifluoro-methanesulfonic acid (5 mL, 57 mmol). The stirred reaction mixture is heated to 120 °C while a flow of N$_2$ is maintained through the solution. After 1 h, the gas bubbler is removed, the flask is stoppered to prevent too much evaporation of CF$_3$SO$_3$H, and the heating is continued for 10-15 h at 120 °C. The nitrogen bubbler is replaced in order to allow the solution to cool to room temperature under a stream of nitrogen. It is cooled further in an ice bath until the temperature reaches ~5 °C. Anhydrous diethyl ether (40 mL) is added cautiously in a dropwise fashion to the rapidly stirred solution. The complex is filtered on a

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medium-porosity sintered-glass funnel, initially by gravity, and the filtration is completed by using a water aspirator. The white powder is washed and purified, as before (the yield is quantitative). Its nature was confirmed by a comparison of its properties with those obtained in the previous experiment.

A similar procedure is used to convert other halo, aqua, and acido complexes to the triflato complex. This is useful for the regeneration of the osmium starting material.

$[Os(NH_3)_5Cl](CF_3CO_2)_2\cdot2CF_3CO_2H$. $[Os(NH_3)_5Cl]Cl_2$ (1.0 g) is dissolved in 0.001 M CF_3CO_2H (50 mL) and absorbed onto a column of SP-Sephadex C-25 (2-cm diameter × 20 cm). The column is washed with distilled water (1 L), and the complex is eluted with 0.2 M CF_3C-O_2H. The eluant is evaporated to dryness on a rotary evaporator (40–50 °C) to yield a white powder. The solid is washed with diethyl ether onto a sintered-glass frit and dried in vacuo over P_4O_{10}. Anal. Calcd for $C_8H_{17}N_5O_8F_{12}ClOs$: C, 12.56; Cl, 4.63; F, 29.8; H, 2.24; N, 9.16. Found: C, 12.92; Cl, 4.78; F, 27.37; H, 2.41; N, 9.21. This salt is much more soluble than other salts of the chloro complex and is used for crystallization of other salts such as $[Os(NH_3)_5Cl](S_2O_6)$. (Anal. Calcd for $ClH_{15}N_5O_6S_2Os$: C, 0.00; Cl, 7.53; H, 3.21; N, 14.87; S, 13.62. Found: C, 0.00; Cl, 7.22; H, 3.17; N, 14.30; S, 13.62) and for N-deuteration of the ammines.

$[Os(ND_3)_5Cl]Cl_2$. $[Os(NH_3)_5Cl](CF_3CO_2)_2\cdot2CF_3CO_2H$ (100 mg) is dissolved in D_2O (5 mL), and after 4 min, 4 drops of concentrated DCl is added. The solution is heated to near boiling and is allowed first to cool slowly to room temperature and then to cool in ice to yield yellow crystals. Full deuteration (≥90%) was established from the absence of N–H stretches in its IR spectrum and the microanalytical data. Anal. Calcd for $[Os(ND_3)_5Cl]Cl_2$: D, 7.61; N, 17.65; Cl, 26.80, C, 0.00. Found: C, 7.49; N, 17.42; Cl, 26.67; C, 0.00.

$[Os(ND_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ is prepared from $[Os(ND_3)_5Cl]Cl_2$, as described in method 2. This may be used to prepare the perdeuterated pentaammine complexes.

$[Os(NH_3)_6](CF_3SO_3)_3$ and $[Os(NH_3)_6]Cl_3$. $[Os(NH_3)_5(OSO_2CF_3)]$-$(CF_3SO_3)_2$ (0.10 g, 0.14 mmol), is placed in a 100-mL two-necked round-bottomed flask, and the flask and solid are heated in a vacuum oven at 110 °C. A second 100-mL two-necked round-bottomed flask is connected to a KOH drying tower and placed in a dish containing dry ice. Liquid ammonia (~40 mL) is transferred to this flask, and the flask is stoppered. The flask containing the osmium complex is removed from the vacuum oven with heat-resistant gloves while it is still hot. It is then connected to the outlet of the KOH drying tower, and the outlet from the flask is connected to a KOH drying tube. The dry ice dish is removed from the flask containing the liquid ammonia. By placement of this flask in a water bath for short periods of time (~15–20 °C), ~10 mL of the liquid is evaporated and allowed to pass through the flask containing the osmium complex. This procedure should be extended for 15–30 min in order to prevent loss of compound by the gas flow. The outlet of the flask is connected to a mercury bubbler that is arranged to maintain a small positive pressure (~80 Torr), and ammonia (~20 mL) is condensed into the flask containing the osmium complex by cooling the flask in a dry ice bath. The bath is removed, and the solution is left at room temperature for 5–6 h. After the mercury bubbler has been removed, the solvent is evaporated by warming in a water bath at ~20 °C. The off-white solid remaining is collected by washing the interior of the flask with diethyl ether (2 × 10 mL) and is collected on a medium-porosity sintered-glass frit. After air-drying, the yield is 0.10 g (98%). Anal. Calcd for $C_3H_{18}F_9N_6O_9S_3Os$: C, 4.87; H, 2.45; N, 12.36. Found: C, 4.7; H, 2.6; N, 11.3. Depending on the purity of the triflato complex used in this procedure, the product may be highly colored. The impurities giving rise to this coloration are not easily removed by recrystallization, and the complex is purified by cation-exchange chromatography, as follows. The crude triflate salt (0.10 g, 0.14 mmol) is dissolved in 0.01 M CF_3CO_2H (100 mL) and is absorbed onto a column of Dowex 50W-X2, 200–400 mesh, H^+ form (Fluka) (2-cm diameter × 10 cm). The column is washed with 0.01 M CF_3CO_2H (100 mL) and then 0.1 M HCl (1 L), and the colorless complex is eluted with 3 M HCl (~500 mL). The movement of the band down the column may be monitored visually by the movement of the white band against the colored background of the resin. Alternatively, it may be monitored by using UV detection at 220 nm. The eluate containing the complex is evaporated to dryness on a rotary evaporator (water bath 50–60 °C). The crude chloride residue is dissolved in 0.001 M CF_3CO_2H (1 mL), and this solution is heated to 70–80 °C. Concentrated HCl (12 M, 0.5 mL) is added, and the solution is allowed to cool to room temperature and is then cooled further in an ice bath for 2 h. The white precipitate is collected on a sintered-glass microfilter, washed with ethanol (2 × 5 mL) and diethyl ether (2 × 5 mL), and air-dried. The yield is 0.046 g (85%). Anal. Calcd for $H_{18}N_6Cl_3Os$: C, 0.00; H, 4.55; N, 21.09; Cl, 26.67. Found: C, 0.00; H, 4.47; N, 20.89; Cl, 26.63.

$[Os(NH_3)_5(OH_2)](CF_3SO_3)_3$. $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.30 g, 0.42 mmol) is added to a 0.1 M aqueous solution of CF_3SO_3H (1 mL) contained in a 15-mL beaker. The solution is boiled for 5 min. After being cooled to room temperature, the solution is cooled further to ~5 °C in an ice bath. Neat CF_3SO_3H (1 mL) is added slowly in dropwise fashion while the solution is stirred rapidly. A white precipitate of $[Os(NH_3)_5(OH_2)](CF_3SO_3)_3$ begins to form immediately. The solution is cooled in an ice bath for 1 h, and the precipitate is collected on a medium-porosity sintered-glass funnel. After air-drying, the solid is washed thoroughly with anhydrous diethyl ether (4 × 10 mL) and air-dried. The yield is 0.2 g (65%). Anal. Calcd for $C_3H_{17}F_9N_5O_{10}S_3Os$: C, 4.87; H, 2.31; N, 9.46. Found: C, 5.0; H, 2.4; N, 8.95. IR (cm^{-1}): ν_{O-H} 3580. The remaining $[Os(NH_3)_5(OH_2)](CF_3SO_3)_3$ is precipitated by the addition of diethyl ether (6 mL). The precipitate is treated as above to give an essentially quantitative overall yield (0.30 g, 98%) of the complex.

$[Os(NH_3)_5(CH_3CN)](CF_3SO_3)_3$. $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.5 g, 0.69 mmol) is added to spectrophotometric grade acetonitrile (Aldrich) (2 mL) containing several drops of trifluoromethanesulfonic anhydride (triflic anhydride), all contained in a 10-mL test tube. (The use of triflic anhydride can be avoided by rigorously drying the acetonitrile over freshly regenerated 4-Å molecular sieves overnight or by passing the solvent through an alumina column prior to the reaction with the triflato complex.) The suspension of the triflato complex is rapidly stirred by using a magnetic stirring bar, and the solvent is protected from the atmospheric moisture by sealing with an appropriate serum cap. The mixture is kept stirred overnight, and the white precipitate is removed with diethyl ether (4 × 5 mL) and is filtered on a medium-porosity frit. The precipitate is washed two more times with anhydrous diethyl ether and air-dried. The yield is 0.5 g (90%). Anal. Calcd for $C_5H_{18}F_9N_6O_9S_3Os$: C, 7.86; H, 2.38; N, 11.00. Found: C, 7.8; H, 2.5; N, 10.7. IR (cm^{-1}): ν_{C-H} 2960, $\nu_{C≡N}$ 2295.

$[Os(NH_3)_5(PhCN)](CF_3SO_3)_3$ is prepared in a manner similar to that for the acetonitrile complex, except distilled benzonitrile is used. IR (cm^{-1}): $\nu_{C≡N}$ 2243.

$[Os(NH_3)_5\{OP(OEt)_3\}](CF_3SO_3)_3$. $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (100 mg) is added to dry distilled triethyl phosphate (5 mL). The solution is protected from the atmosphere and stirred at 25 °C for 3 h (6 half-lives). Alternatively, the solution is heated at 60 °C for 30 min. Dry distilled chloroform (230 mL) is added dropwise with stirring while dry Ar is passed through the solution. The solid is collected, washed with dry chloroform, and dried in vacuo over P_4O_{10}. (Chloroform is used instead of diethyl ether in the isolation because the complex is moderately soluble in triethyl phosphate/diethyl ether solutions.) The yield is 90%. Anal. Calcd for $C_9H_{24}N_5O_{13}F_9S_3Os$: C, 11.9; H, 3.3; N, 7.7. Found: C, 11.6; H, 3.2; N, 8.0. IR (cm^{-1}): ν_{C-H} 2930, 2995; ν_{P-OEt} 986.

$[Os(NH_3)_5(dmf)](CF_3SO_3)_3$ and $[Os(NH_3)_5(dmso)](CF_3SO_3)_3$ are prepared in a manner similar to that for the triethyl phosphate complex, except the triflato complex is dissolved in the appropriate solvent and anhydrous diethyl ether and is used to precipitate the complex. The yield is ~95%, in each instance.

Preliminary attempts at preparing $[Os(NH_3)_5(acetone)]^{3+}$ and $[Os(NH_3)_5(sulfolane)]^{3+}$ have been only partially successful. Isolations of the complexes by the above methods have, as yet, only led to impure products.

$[Os(NH_3)_5Cl]Cl_2$, $[Os(NH_3)_5Br]Br_2$, and $[Os(NH_3)_5I]I_2$, Method 1. $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (100 mg) is dissolved in 2–3 mL of a hot (90 °C) solution that is ~0.1 M in the appropriate hydrohalic acid. The solutions is maintained at this temperature for 15 min and then is allowed to cool slowly to room temperature. It is then cooled in an ice bath at 5 °C for ~1 h. The crystals are collected, washed with acetone, and dried at the pump. Anal. Calcd for $[Os(NH_3)_5Cl]Cl_2$ ($H_{15}N_5Cl_3Os$): C, 0.00; H, 3.96; N, 18.35; Cl, 27.86. Found: C, 0.00; H, 3.82; N, 17.89; Cl, 27.80. Larger crystals suitable for X-ray diffraction and single-crystal spectroscopy are grown by dissolving $[Os(N-H_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ in 0.001 M CF_3CO_2H and after 2 h at 25 °C adding a few drops of concentrated hydrohalic acid. The appropriate crystals grow slowly over 1–2 weeks as the aqua complex formed initially is converted slowly to the halo complex.

Synthetic methods similar to those described in the preceding sections are also suitable for the synthesis of a range of other acido complexes and for the preparation of the N-deuterated complexes from $[Os(ND_3)_5(O-SO_2CF_3)](CF_3SO_3)_2$.

Microanalyses. These were performed by the Stanford University and Australian National University Microanalytical Services.

Results

Syntheses and Characterization. The complex $[Os(NH_3)_5(O-SO_2CF_3)](CF_3SO_3)_2$ is prepared in essentially quantitative yield by the bromine oxidation of $[Os(NH_3)_5N_2]Cl_2$ in neat CF_3SO_3H.

Table I. IR Data in KBr Disks for [Os(NH₃)₅(OSO₂CF₃)](CF₃SO₃)₂

assgnt	freq, cm⁻¹ ᵃ
ν(N–H)	3300 (s)
δ_{as}(N–H)	1620 (m)
δ_{s}(N–H)	1370 (s), 1355 (m)
ν_{as}(OSO, ligand)	1338 (m), 1320 (s)
ν_{as}(OSO, anion)	1280 (s), 1235 (s), 1220 (s)
ν(C–F)	1185 (s), 1160 (sh)
ν_{s}(OSO)	1032 (s), 1018 (s)
ρ_r(NH₃)	873 (m), 850 sh, 838 (s)
	638 (s), 630 (s), 582 (m)
	523 (s), 500 (w)
ν(M–N) + δ(N–M–N)	370 (w), 360 (w)
ν(M–O)	324 (w)

ᵃ Abbreviations: m, medium; s, strong; sh, shoulder; w, weak.

Table II. Rate Constants for Solvation of [Os(NH₃)₅(OSO₂CF₃)]²⁺ at 25 °C

solvent	10⁴k, s⁻¹	solvent	10⁴k, s⁻¹
H₂O	8.8	acetone	21
triethyl phosphate	4.9		5.0ᵃ

ᵃ This rate constant refers to the following reaction in which the solvent condenses with the complex.

It is also prepared quantitatively by the reaction of [Os(NH₃)₅-(OH₂)](CF₃SO₃)₃, [Os(NH₃)₅Cl]Cl₂, and other halo complexes in neat triflic acid.

The presence of coordinated triflate is established from the IR spectra given in Table I, which show peaks at 1338 and 1320 cm⁻¹, characteristic of the triflato ligand.[13] The [Os(NH₃)₅-(OSO₂CF₃)]²⁺ complex is relatively labile for an Os(III) complex and, in the O-donating solvents that we have studied, undergoes solvation reactions that are first order with respect to Os(III) with $t_{1/2} \sim$ 10–30 min at 25 °C (see Table II). The relative lability of the triflato complex makes it a valuable intermediate for the syntheses of [Os(NH₃)₅(solvent)]³⁺ complexes. Thus, such reactions result in high yields of the desired products, provided the solvent is dry. The syntheses of [Os(NH₃)₆]³⁺, [Os(NH₃)₅-(OH₂)]³⁺, [Os(NH₃)₅(NCCH₃)]³⁺, [Os(NH₃)₅(NCPh)]³⁺, [Os(NH₃)₅(dmf)]³⁺, [Os(NH₃)₅(dmso)]³⁺, and [Os(NH₃)₅{OP-(OEt)₃}]³⁺ are achieved by this method. The acetone and sulfolane complexes were not obtained pure because of the susceptibility of these complexes to aquation by water as an impurity in the preparation and isolation of the complexes and because of the reactivity of the former complex. The triethyl phosphate complex is also very susceptible to aquation, and the solvents and atmosphere used in the synthesis have to be very dry in order to obtain the pure product.

In the case of [Os(NH₃)₆]³⁺ and [Os(NH₃)₅(OH₂)]³⁺, the identities of the products were established by comparison of their electrochemical and spectral properties with authentic samples.[5,6,34] The presence of the nitrile group in [Os(NH₃)₅(NCCH₃)]³⁺ and [Os(NH₃)₅(NCPh)]³⁺ is established by the presence of the νC≡N stretch in the IR spectra (KBr disks) at 2295 and 2243 cm⁻¹, respectively. Similarly, the presence of coordinated OH₂ and OP(OEt)₃ is established by the presence of characteristic ligand bands in the IR spectra (Experimental Section) and the absence of bands due to coordinated CF₃SO₃⁻. The osmium(III) nitrile complexes show less than 2% hydration of the nitrile ligand in 0.02 M HCl at 25 °C over 2 h (electrochemistry and UV spectroscopy). Therefore, the rate constant for the acid hydrolysis of the nitrile ligand is ≤10⁻⁶ s⁻¹ at 25 °C.

Various acidopentaammineosmium(III) complexes are prepared conveniently, and in essentially quantitative yields, by heating [Os(NH₃)₅(OSO₂CF₃)]²⁺ in a hot aqueous solution of the appropriate hydrohalic acid. The syntheses of [Os(NH₃)₅X]X₂ (X = Cl⁻, Br⁻, I⁻) are reported as examples of this reaction. Again, the complexes were characterized by a comparison of their properties with those of authentic samples,[34,35] and, in the case

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Table III. Vis/UV Data for Os(III) Complexes

complex	λ_{max} (ϵ_{max})ᵃ
[Os(NH₃)₆]³⁺	221 (760)³⁴
[Os(NH₃)₅(OH₂)]³⁺	220 sh (1100)³⁴
[Os(NH₃)₅Cl]²⁺	267 (2.00 × 10³)³⁴
	267 (2.01 × 10³), 244 (200)³⁵
[Os(NH₃)₅Br]²⁺	314 (1.87 × 10³)³⁴
	262 (67), 314 (1.87 × 10³)³⁵
[Os(NH₃)₅I]²⁺	407 (1.97 × 10³)³⁴
	271, 300, 407 (1.97 × 10³)³⁵
[Os(NH₃)₅(OSO₂CF₃)]²⁺	235.5 (843), 290 sh (108), 447 (55)ᵇ
[Os(NH₃)₅(NCCH₃)]³⁺	~225 sh (1700), 250 sh (790),
	320 sh (44), 450 (4)ᶜ
[Os(NH₃)₅(NCPh)]³⁺	223 (13 000), 275 sh (9100), 281 (9400),
	290 sh (9300), 338 sh (1100),
	361 sh (500), 330 sh (1900)ᵈ

ᵃ λ_{max} in nm; ϵ_{max} in M⁻¹ cm⁻¹ in parentheses. ᵇ Neat CF₃SO₃H. ᶜ 0.1 M HCl. ᵈ Reference 37; 0.1 M CF₃SO₃H/MeOH.

Table IV. Near-IR Data for Os(III) Complexes

complex	λ_{max} (ϵ_{max})ᵃ
[Os(NH₃)₆]³⁺	1745*, 2008*, 2200*ᵇ
[Os(NH₃)₅(OH₂)]³⁺	1225, 1740, 1850, 1930*, 2030*, 2090,
	2180, 2480ᵇ
[Os(NH₃)₅I]²⁺	1878 (170)ᶜ
[Os(NH₃)₅(OSO₂CF₃)]²⁺	1190 (~2.5)ᵈ
	1190 (2.5), 1680 (2), 1760 (3.6), 1820
	(5.3), 1880 (6.6), 1960 (11.2), 2060
	(6.6), 2140 (6.0), 2420 (2.6)ᵇ,ᵉ
[Os(NH₃)₅(CH₃CN)]³⁺	1390, 1750, 1840, 1900, 1960, 2050,
	2150, 2430ᵇ
	~1240 (4), 1408 (9), ~1560 (6), 1760
	(13), 1825 sh (11), 1875 (12), 1901
	(13), 1992 sh (24), 2077 (390), 2140
	sh (17.5), 2215 sh (8), 2455 (6)ᶠ
[Os(NH₃)₅(NCPh)]³⁺	2096ᵍ

ᵃ λ_{max} in nm; ϵ_{max} in M⁻¹ cm⁻¹ in parentheses; in KBr, the major peaks are denoted by an asterisk. ᵇ KBr disk. ᶜ Reference 34; this is the major peak of a complex vibronic band structure. ᵈ Neat CF₃SO₃-H. ᵉ Arbitrary values based on the value of ϵ in neat CF₃SO₃H. ᶠ 0.1 M DCl/D₂O. ᵍ Reference 37; KBr; this is the major peak of a complex vibronic band structure.

Table V. Vis/UV Data for Os(II) Complexes

complex	λ_{max} (ϵ_{max})ᵃ
[Os(NH₃)₅(CH₃CN)]²⁺	228 (1.2 × 10⁴), 280 sh (3.2 × 10³),
	320 sh (1.2 × 10³)
	390 sh (2.0 × 10²)ᵇ
[Os(NH₃)₅(PhCN)]²⁺	401 (1.03 × 10⁴), 507 (3.0 × 10³)ᵇ
	239 (1.8 × 10⁴), 258 sh, 290 sh, 403
	(1.0 × 10⁴), 509 (3.4 × 10³)ᶜ
[Os(NH₃)₅(η²-acetone)]²⁺	457, 327ᵈ

ᵃ λ_{max} in nm; ϵ_{max} in M⁻¹ cm⁻¹ in parentheses. ᵇ This work; 0.1 M HCl. ᶜ Reference 37; CH₃OH. ᵈ Reference 40.

of the chloro complex, by X-ray crystallography.[36]

Table III contains UV/visible data on the Os(III) complexes. The spectra of the complexes are typified by a high-energy transition around 220–240 nm with weaker shoulders at longer wavelengths. The halo complexes also exhibit LMCT bands involving the halo ligands.[34,35]

Table IV contains the near-IR spectral data for the Os(III) complexes. All show a large number of transitions, but the intensity varies greatly. For the complexes without π-bonding ligands, the intensity of the transitions are typically 10 M⁻¹ cm⁻¹. However, the major transitions at 2000–2100 nm in the π-acid complexes have intensities typically between 10² and 10³ M⁻¹ cm⁻¹. Similarly, the near-IR transitions of the complexes with π-base ligands (Cl⁻, Br⁻, I⁻) are much more intense than those due to [Os(NH₃)₆]³⁺, [Os(NH₃)₅(OSO₂CF₃)]²⁺, and [Os(NH₃)₅-(OH₂)]³⁺.

(36) Hambley, T. W.; Lay, P. A. *Inorg. Chem.* **1986,** *25,* 4553–4558.

Table VI. Redox Potentials of Osmium and Ruthenium Pentaammine Complexes in Aqueous Media at 25 °C

complex	$E_{1/2}$, V vs NHE[a]	
	Ru	Os
$[M(NH_3)_6]^{3+/2+}$	+0.051 (0.00)[38]	-0.78 (0.00)[5,6]
$[M(NH_3)_5(OH_2)]^{3+/2+}$	+0.066 (0.02)[38]	-0.73 (0.05)[5,6]
$[M(NH_3)_5Cl]^{2+/+}$	-0.042 (-0.09)[38]	-0.86 (-0.08)[5,6]
$[M(NH_3)_5Br]^{2+/+}$	-0.034 (-0.085)[38]	
$[M(NH_3)_5I]^{2+/+}$		-0.79 (-0.01)[5,6]
$[M(NH_3)_5(NCCH_3)]^{3+/2+}$	+0.426 (0.38)[39]	-0.25 (0.53)[d]
$[M(NH_3)_5(NCPh)]^{3+/2+}$	+0.485 (0.43)[39]	-0.20 (0.58)[d]
$[M(NH_3)_5(dmso)]^{3+/2+}$	+1.0 (0.95)[b,42]	

[a] Potential vs the appropriate $[M(NH_3)_6]^{3+/2+}$ couple in parentheses. [b] S-bound isomer. [c] O-bound isomer. [d] 0.1 M HCl; this work.

Table VII. Redox Potentials of Solvent Complexes vs Fc⁺/Fc in the Appropriate Solvent

complex	E, V vs Fc⁺/Fc	
	Ru	Os
$[Mn(NH_3)_5(acetone)]^{3+/2+}$	-0.337[a,b,c]	>-0.36[c,e]
	-0.477[a,b,d]	-1.24[d,e]
$[M(NH_3)_5(dmf)]^{3+/2+}$	-0.66[f]	-1.49[f]
$[M(NH_3)_5(dmso)]^{3+/2+}$	+0.104[g,h,j]	-0.42[g,h]
	-0.768[h,i,j]	-1.77[h,i]

[a] Refernce 41. [b] 0.1 M Bu₄NBF₄ in acetone. [c] C,O-bound acetone. [d] O-bound acetone. [e] Reference 58; acetone; corrected for the potential of the Fc⁺/Fc redox couple. [f] 0.1 M Bu₄NBF₄ in dmf. [g] Putative S-bound isomer. [h] 0.1 M Bu₄NBF₄ in dmso. [i] O-bound isomer. [j] Lay, P. A.; Powell, D. A. Unpublished results.

The Os(II) complexes, with nitrile ligands, are prepared by the reduction of the Os(III) complexes with Zn(Hg). The spectra, Table V, exhibit several intense charge-transfer transitions.[37]

Kinetics of the Substitution Reactions of $[Os(NH_3)_5$-$(OSO_2CF_3)]^{2+}$. The solvation reactions of $[Os(NH_3)_5$-$(OSO_2CF_3)]^{2+}$ were monitored for at least 4 half-lives at 25 °C. The reactions could not be followed in basic solvents, such as pyridine, because of the rapid base-catalyzed disproportionation reactions, even in the presence of added CF₃SO₃H. In the case of the acetone complex, a second first-order reaction followed the initial solvation reaction and the solution turned yellow. This yellow complex is very susceptible to aquation, the yellow color disappearing rapidly on the addition of water.

Electrochemistry. The electrochemistry of the water-soluble Os(III) complexes, and their Ru(III) analogues, are summarized in Table VI. As is the case with the N-heterocyclic complexes,[26] there is a positive shift in the redox potential of the M(III/II) couple of the complexes with π-acid ligands in comparison to the $[M(NH_3)_6]^{3+/2+}$ couples. However, the shift is not as large for complexes with nitrile ligands as compared to N-heterocyclic ligands (where the shift for Os is approximately twice as large as the shift for Ru[38,39]). This contrasts with the results for the π-base ligands (Cl⁻, Br⁻, I⁻), where the negative shifts relative to $[M(NH_3)_6]^{3+/2+}$ are comparable for the two metal ions.

The electrochemistry of some of the solvent complexes in the appropriate solvent are summarized in Table VII. The redox potentials are quoted vs the Fc⁺/Fc couple as an internal standard. Some of the solvent complexes exhibit rearrangement reactions, as is evidenced by the irreversibility of the responses in the cyclic voltammograms. The linkage isomerizations of the acetone complexes from an η^1-(O-bound) to an η^2-(C,O-bound) acetone ligand on reduction of M(III) to M(II) have been discussed elsewhere.[40,41] An isomerization also occurs following the re-

duction of $[Os(NH_3)_5(dmso)]^{3+}$ to the Os(II) complex. The putative S-bound isomer has an $E_{1/2}$ value (-0.42 V vs Fc⁺/Fc in dmso) that is 230 mV more negative of $E_{1/2}$ for the $[Os(NH_3)_5(N_2)]^{3+/2+}$ couple in the same solvent. Similar differences in redox potentials have been observed for the ruthenium analogues ($[Ru(NH_3)_5(N_2)]^{3+/2+}$ and $[Ru(NH_3)_5(dmso-S)]^{3+/2+}$) in aqueous media.[42] The couple for $[Os(NH_3)_5(dmso-O)]^{3+/2+}$ is more than a volt negative of that observed for the "S-bound" isomer and is less reversible. This is similar to the behavior observed for the analogous ruthenium dmso complexes, except that the separations of the two redox couples are about 50% larger in the case of Os as compared to Ru (Table VII). The kinetics and thermodynamics of these reactions will be discussed in a future paper. No evidence is observed for a similar linkage isomerization reaction for the dmf complexes. The $[Os(NH_3)_5(dmf)]^{3+}$ reduction is reversible in dmf when Bu₄NBF₄ is used as the background electrolyte but is irreversible when Bu₄NClO₄ is used as the background electrolyte.

Discussion

Syntheses and Reactivity. The lability of triflato complexes has been well documented, and they have proven to be valuable synthetic intermediates in the syntheses of Co(III), Cr(III), Rh(III), Ir(III), Ru(III/II), and Os(III/II) complexes.[7-26] The use of $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ has enabled the syntheses in moderate-to-high yields of many complexes of the osmium pentaammine series that have not been characterized previously. The preferred synthetic route to the triflato complex differs from that of the other pentaammine(triflato)metal(III) complexes, which have been prepared from the corresponding pentaammine chloro complexes in neat CF₃SO₃H.[7-26] Since $[Os(NH_3)_5Cl]Cl_2$ is obtained from $[Os(NH_3)_5(N_2)]Cl_2$, it is best to use the dinitrogen complex directly in the synthesis of the triflato complex. $[Os(NH_3)_5(N_2)]Cl_2$ is obtained from OsO₄ in ~80-90% yield (based on OsO₄),[2,3,23,32,33] and its conversion to $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ is quantitative, giving an 80-90% overall yield of $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, starting from OsO₄.

The synthesis itself relies on the lability of the dinitrogen ligand bound to Os(III).[43] Thus, as the $[Os(NH_3)_5(N_2)]^{2+}$ complex is oxidized to $[Os(NH_3)_5(N_2)]^{3+}$, the dinitrogen group leaves and is replaced by a triflato ligand. Triflic acid is a much stronger acid and is less volatile than HBr or HCl, which evaporate. Therefore, no other ligands can compete for coordination in the sixth position in the early stages of the reaction, with the exception of $[Os(NH_3)_5N_2]^{2+}$ itself. Thus, the green color of the mixed-valence ion, $[(NH_3)_5OsN_2Os(NH_3)_5]^{5+}$, is observed in the initial stages of the reaction, but this is also oxidized by Br₂ to $[(NH_3)_5OsN_2Os(NH_3)_5]^{6+}$. The 6+ ion then decomposes to the triflato complex and dinitrogen in a 2:1 molar ratio.[44] By control of the oxidation reaction, a convenient method for preparing $[(NH_3)_5OsN_2Os(NH_3)_5]Cl_5$ is obtained.[45] The dinitrogen complexes can also be oxidized to the triflato complex by dioxygen, although this reaction is somewhat slower than that with Br₂.

The oxidation of cis-$[Os(NH_3)_4(N_2)_2]^{2+}$ is performed in a similar manner to form cis-$[Os(NH_3)_4(OSO_2CF_3)_2]^+$. This is also prepared from cis-$[Os(NH_3)_4Cl_2]Cl$, while trans-$[Os(NH_3)_4$-$(OSO_2CF_3)Cl]^+$ is prepared from trans-$[Os(NH_3)_4Cl_2]^+$. The syntheses and properties of the tetrammine complexes and their Ru(III) analogues will be reported elsewhere.[46]

The triflato complex is regenerated from $[Os(NH_3)_5Cl]Cl_2$ by reactions similar to those reported for other chloro complexes, and this is convenient for the recovery of side products in synthetic

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reactions. It is also a useful method for preparing the deuterated triflato complex (see Experimental Section), which is used for the syntheses of deuterated pentammine complexes.

While the osmium(III) triflato complex is useful for the synthesis of a large number of pentaammineosmium(III) complexes, base-catalyzed disproportionation reactions are more troublesome[26,47,48] for ligands that are stronger Brønsted bases than those reported here (e.g. pyrazine and pyridine). More elaborate synthetic procedures are appropriate in these instances.[26] However, this is not a problem in the synthesis of $[Os(NH_3)_6]^{3+}$, even though the ligand is quite basic. There are probably three reasons for this: (i) $[Os(NH_3)_6]^{3+}$ is likely to be less acidic than are the $[Os(NH_3)_5(N\text{-heterocycle})]^{3+}$ complexes by analogy to Ru chemistry,[47] and thus, the deprotonation preequilibrium is less favored. (ii) $[Os(NH_3)_6]^{3+}$ is much more difficult to reduce to the osmium(II) complex than are the $[Os(NH_3)_5(N\text{-heterocy-cle})]^{3+}$ complexes.[4,24,26] (iii) The Os(IV) complexes formed in the disproportionation equilibrium will tend to be stabilized by donation of electron density from the deprotonated amine to the π^*-orbitals of the N-heterocyclic ligand.[24] Such stabilization is not available in the hexaammine complex. Thus, factor i tends to minimize the extent of the deprotonation preequilibrium for $[Os(NH_3)_6]^{3+}$, while points ii and iii will tend to reduce the disproportionation equilibrium constant for $[Os(NH_3)_6]^{3+}$, in comparison to $[Os(NH_3)_5(N\text{-heterocycle})]^{3+}$. The preparation of $[Os(NH_3)_5(OH_2)]^{3+}$ requires acidic conditions because $[Os(NH_3)_5(OH_2)]^{3+}$ is much more acidic than $[Os(NH_3)_6]^{3+\,49}$ and, therefore, is more susceptible to disproportionation.

The synthesis of the acetone complex is difficult, as the complex is suceptible to subsequent chemical reactions. Although the nature of the product is uncertain at present, it likely is formed by condensation of an acetone molecule with a coordinated ammine. Such a reaction has been observed with $[Os(NH_3)_6]^{3+}$ in acetone and results in the formation of an imine complex.[50] The imine complex, in the Os(III) oxidation state, would be expected to undergo rapid hydrolysis in the presence of water, which is consistent with its rapid decomposition upon the addition of water to its acetone solution. The condensation reaction is also consistent with the development of redox couples more positive than that for the reduction of $[Os(NH_3)_5(\text{acetone})]^{3+}$, in aged solutions. However, the reaction may also involve a condensation reaction between the acetone ligand and uncoordinated acetone. One or both of these reactions may be in operation, and the exact nature(s) of the reaction(s) cannot be determined without further evidence. The chemistry that follows the formation of the acetone complex, combined with its high relative lability, makes it difficult to obtain the complex in the pure form, but the lability of this complex is highly desirable for its use as a synthetic intermediate. As a consequence of its relative lability compared to those of other pentaammineosmium(III) complexes, the acetone complex is used in the synthesis of a large variety of mononuclear and binuclear Os(III) and Os(II) complexes.[23-26,40,45,51-53] For substitution reactions that are slow, it is best to use alternative synthetic methods, both because of the condensation reaction and because the increase in the amount of water in the solvent with time (from these and other condensation reactions). The latter results in the substitution of the acetone ligand to form an inert aqua complex, which is also susceptible to other side reactions, especially in the presence of basic ligands.

The sulfolane and triethyl phosphate complexes are also useful synthetic intermediates, but reactions in the corresponding solvents tend to be slower than those in acetone. Triethyl phosphate, and its complex with pentaammineosmium(III), can act as ethylating reagents,[51] which lowers the yield in the synthesis of complexes with diazines. It is likely that the complex is more active as the ethylating agent than as the solvent, since the coordination of trimethyl phosphate to M(III) complexes is known to catalyze strongly the nucleophilic cleavage of the organophosphate O–C bonds.[54,55] This aspect is being investigated further.

While the syntheses of the nitrile complexes are performed conveniently in the neat solvent, they can also be prepared by adding the triflato complex to acetone solutions of the nitrile ligand. This is a convenient method for the preparation of binuclear complexes containing the dicyanobenzene[53] and 1,4-dicyanobicyclo[2.2.2]octane complexes.[56]

The dmso and dmf complexes have several possible coordination modes. The former can bind through the O- or S-donors[42] or, possibly, by an η^2-S,O-binding mode. Similarly, the dmf complex can bind through O or N or an η^2-N,O mode, although binding through N is unlikely due to steric factors. Generally, oxygen binding is preferred by the M(III) oxidation state,[42,57] and this appears to be the case in this instance. The irreversibility of the reduction of $[Os(NH_3)_5(\text{dmf})]^{3+}$ that is observed at slow scan rates in 0.1 M tetrabutylammonium perchlorate solutions of dmf may be due to oxygen-transfer reactions between the osmium(II) complex and the perchlorate anion to form $[Os(NH_3)_5O]^{2+}$. This is supported by the lack of the growth of another couple at more positive potentials that could be attributed to a linkage isomer for scan rates where irreversible behavior is observed. The dmf ligand itself has been shown to undergo such oxygen-transfer reactions, but on a much slower time scale.[58] Therefore, the evidence suggests that only the O-bound isomer of the dmf complex exists for both Os(II) and Os(III). By contrast, the O-bound dmso complex undergoes a linkage isomerization reaction on reduction to the Os(II) complex. The thermodynamically stable form of the Os(II) complex has the ligand in either an S- or S,O-binding mode. Both isomers are distinct possibilities as η^2-bonding is common in Os(II)[37,40,58-61] and as S-bonding is also common for M(II) complexes.[42] The exact nature of this isomerization is under investigation, and the products will be examined by X-ray crystallography.

The synthesis of acido complexes is also achieved readily from the reaction of aqueous solutions of the appropriate acid with $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$. This route relies on the generation of $[Os(NH_3)_5(OH_2)]^{3+}$, which subsequently undergoes a slower anation reaction. Previous methods for the syntheses of $[Os(NH_3)_5X]X_2$ have involved the prolonged reaction of NH_3 on $(NH_4)_2[OsBr_6]$ or $(NH_4)_2[OsCl_6]$ at elevated temperatures and pressures.[62,63] More recently, the oxidation of $[Os(NH_3)_5(N_2)]Cl_2$,[3-35] or the anation of the potentially explosive $[Os(NH_3)_5(OH_2)](ClO_4)_3$[34] complex in the appropriate hydrohalic acid, has been employed. The method described here is more convenient, higher yielding, and more rapid than those published previously. While the specific examples given here are for the halo complexes, such reactions also work with other acido ligands. However, for acids that can be obtained in their neat form, e.g. carboxylic acids, sulfonic acids, etc., the reaction is best performed in the neat acids. The chemistry of the carboxylato complexes,

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including the dehydration of the formato complexes to carbonyl complexes, will be reported in a subsequent paper.[53]

Reaction Kinetics. The solvation reactions of $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ are slow, for a triflato complex,[7,8,13,64] and only the Ir(III) complex undergoes slower reactions of the $[M(NH_3)_5(OSO_2CF_3)]^{2+}$ complexes.[13] This appears to be one of the few examples of the substitution kinetics of Os(III) complexes being investigated. The complex $[Os(NH_3)_5Cl]^{2+}$ is very slow to undergo aquation with $k \sim 10^{-8}$ s^{-1} (at 25 °C).[34] This is also evidenced by the recrystallization of $[Os(NH_3)_5Cl](S_2O_6)$ by the dissolution of $[Os(NH_3)_5Cl](CF_3CO_2)_2$ in aqueous $S_2O_6{}^{2-}$ solutions at 90 °C. The difference in the aquation rates between $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ and $[Os(NH_3)_5Cl]^{2+}$ [34] is similar to the observed differences for their Ir(III) counterparts.[13,64]

Electrochemistry. The stabilization by π-acid ligands of Ru(II) and Os(II), relative to the higher oxidation states, has been noted already.[26] The stabilization of Os(II) is even greater than is evidenced by these shifts in the redox potentials, because Os(III), but not Ru(III), complexes are also stabilized by π-back-bonding. This has been established by the stability of the osmium(III) nitrile complexes to acid hydrolysis, as compared to that of Ru(III) complexes,[53] and also other evidence.[44,65] The nitrile $\nu_{C\equiv N}$ resonance, in the Os(III) complexes, is at a frequency similar to that of the Ru(III) complexes, but IR data alone are not good indicators of the extent of π-back-bonding.[66] However, evidence for strong π-back-bonding in Os(II) is seen in the large shift to lower frequency of $\nu_{C\equiv N}$ in the Os(II) complex as compared to in the Ru(II) complex.[37] While the IR evidence for π-back-bonding in Os(III) is not evident, the electrochemistry and chemical reactivities show the importance of π-back-bonding in both Os(III) and Os(II). By contrast, π-bonding with π-base ligands has been found to be comparable for Ru(III) and Os(III),[36] at least for Cl$^-$. The clear implication is that the shifts in the M(III)/M(II) redox potentials of $[M(NH_3)_5X]^{2+/+}$, relative to $[M(NH_3)_6]^{3+/2+}$,

should be comparable for a given halo ligand. Indeed, Table VI shows this to be the case.

Spectroscopy. The UV/vis spectra of the Os(III) complexes do not show many well-defined features. With the exception of the spectrum of the $[Os(NH_3)_5(NCPh)]^{3+}$ complex,[37] they are mostly dominated by transitions at 220–240 nm, the nature of which is uncertain at present. Their intensities ($\sim 10^3$ M^{-1} cm^{-1}) tend to eliminate the possibility that they are pure d–d transitions. The lack of significant absorption of the $[Os(NH_3)_5(NCCH_3)]^{3+}$ complex above ~ 300 nm, combined with the high chemical stabilities and rapid redox chemistry of the $[Os(NH_3)_5(NCCH_3)]^{3+/2+}$ couple, makes $[Os(NH_3)_5(NCCH_3)]^{2+}$ a very useful reductant for spectroscopic studies.

The electronic transitions that arise from the effects of spin–orbit coupling on the ground state of the $t_2{}^5$ electronic configuration occur in the near-IR region. For $[Os(NH_3)_6]^{3+}$, there should be a single transition (assuming O_h symmetry), whereas the lower symmetry (C_{4v}, or less) of the pentaammine complexes requires that the degeneracy of the E spin–orbit state is lifted.[34] Thus, there should be two near-IR transitions for these complexes. An analysis of the near-IR spectra presented here by the use of MCD, deuteration, and single-crystal experiments confirms these general expectations,[67] with the complex band structure observed in the near-IR being due to vibronic coupling within these transitions. However, there are some complications due to different site symmetries within the same crystal for $[Os(NH_3)_6]^{3+}$.[67] An interesting feature is that the transitions between spin–orbit states in the complexes with either π-acid or π-base ligands are much more intense than those in complexes with ligands that have little or no tendency to π-bond. This is consistent with a significant contribution of π-bonding to the tetragonal splitting of the degenerate spin–orbit states, which mixes charge-transfer character into the spin–orbit transitions.

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