Although there is an extensive range of metal–metal-bonded alkoxides, there are none reported with ortho-substituted aryl oxides. This prevents a precise comparison of the effect of changing oxygen to sulfur on the observed chemistry. However, complex I does not react with CO at room temperature in contrast to species such as $[Mo_2(O\text{-}i\text{-}Pr)_6]$, which forms a series of carbonyl complexes.[2a,b]

The electrochemistry of complex I was studied by cyclic voltammetry in thf solution with $[n\text{-}Bu_4N][BF_4]$ as supporting electrolyte and a platinum working electrode. The complex undergoes a one-electron reversible reduction at $E_{1/2} = -0.88$ V (vs. SCE calibrated vs. the ferrocene/ferrocenium couple at +0.54 V) followed by a further irreversible one-electron reduction at $E_p = -1.72$ V. The second irreversible reduction was accompanied by thiolate anion loss. Although CO does not react with the unreduced dimer, under CO the second reduction process becomes a two-electron process due to interaction with CO. However, there was no indication of interaction with N_2 at any redox level. No oxidation waves were observed at potentials up to +1.2 V.

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Registry No. I, 97352-51-7; I (salt entry), 97352-52-8; $[Mo_2(SC_6H_2Me_3)_6]$, 86350-27-8; $[Mo_2(SC_6H_2Me_3)_6]$ (salt entry), 97069-07-3; $MoCl_4$, 13320-71-3; $[Ph_4P][MoO(SC_6H_2\text{-}i\text{-}Pr_3)_4]$, 97352-54-0; Mo, 7439-98-7.

Supplementary Material Available: Tables of observed and calculated structure factors, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom positions (36 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Convenient Synthesis of *trans*-Diacidotetraammineruthenium(III) Complexes

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The chemistry of trans ruthenium(II) and ruthenium(III) tetraammine complexes has been the subject of extensive research over the past decade.[1] However, the reported synthesis[2] of *trans*-$[Ru(NH_3)_4Cl_2]Cl$, a key starting material in ruthenium ammine chemistry, was rather inefficient and inconvenient, involving several steps. We have recently found that high-valent ruthenium(VI) amine oxo complexes could easily be converted into the corresponding ruthenium(IV) and ruthenium(III) species.[3] Here an efficient synthetic procedure for *trans*-$[Ru(NH_3)_4X_2]^+$ (X = Cl, I, NCS) utilizing *trans*-$[Ru(NH_3)_4O_2]^{2+}$ as the starting material is described.

Experiment Section

Materials. Ruthenium(III) chloride trihydrate (Aldrich) was used as supplied. *trans*-$[Ru(NH_3)_4O_2]Cl_2$ was prepared according to the literature method.[4] All chemicals used were of reagent grade, and deionized water was used throughout the experiment.

***trans*-$[Ru(NH_3)_4Cl_2]Cl$.** A mixture of *trans*-$[Ru(NH_3)_4O_2]Cl_2$ (0.2 g) and ascorbic acid (2 g) in HCl (2 M, 15 cm^3) was stirred for 1 day. An orange microcrystalline solid gradually deposited upon standing (yield >60%). The purity of the complex was checked by comparing its molar extinction coefficient at 331 nm with the known value. Alternatively, $SnCl_2$ or 2-propanol could be used instead of ascorbic acid.

Table I. UV–Vis Absorption Spectra of Some *trans*-Diacidotetraammineruthenium(III) Complexes

complex	solvent	λ_{max}/nm (ϵ_{max}/cm^{-1} dm^3 mol^{-1})[a]
trans-$[Ru(NH_3)_4Cl_2]Cl$	HCl (1 M)	331 (5270)[b]
trans-$[Ru(NH_3)_4Br_2]Br$	HBr (0.1 M)	399 (5133)[b]
trans-$[Ru(NH_3)_4(NCS)_2]NCS$	H_2O	524 (12 600), 430 sh (1410), 330 br (770)
trans-$[Ru(NH_3)_4I_2]I$	H_2O	552 (5800), 425 sh (1190), 304 (12 100)

[a] Abbreviations: br, broad; sh, shoulder. [b] Isabirye, D. A. Ph.D. Thesis, University of Hong Kong, 1977.

***trans*-$[Ru(NH_3)_4I_2]I$.** An aqueous solution (20 cm^3) of *trans*-$[Ru(NH_3)_4O_2]Cl_2$ (0.1 g), ascorbic acid (2 g), and NaI (2 g) was stirred for 2 h. A dark violet-blue microcrystalline solid gradually deposited. This was filtered and purified from a hot (~70 °C) NaI solution (1 M) (overall yield >70%). Anal. Calcd for $[Ru(NH_3)_4I_2]I$: N, 10.17; I, 69.20. Found: N, 10.27; I, 68.90. IR: ν(NH) 3240, 3200, 3130 cm^{-1}; δ(NH) 1620 cm^{-1}.

***trans*-$[Ru(NH_3)_4(NCS)_2]NCS$.** An aqueous solution (20 cm^3) of *trans*-$[Ru(NH_3)_4O_2]Cl_2$ (0.1 g), ascorbic acid (2 g), and NaNCS (2 g) was stirred for 2–3 h. A dark violet-red solid gradually precipitated out. This was filtered off, washed with an ethanol–diethyl ether mixture (1:10), and dried under vacuum. Anal. Calcd for $[Ru(NH_3)_4(NCS)_2]NCS$: C, 10.50; H, 3.49; N, 28.56; S, 28.0. Found: C, 10.37; H, 3.33; N, 28.14; S, 28.4. IR: ν(NH) 3240, 3200, 3130 cm^{-1}; ν(C≡N) 2060 cm^{-1}; δ(NH) 1620 cm^{-1}, δ(NCS) 790 cm^{-1}.

Physical Measurements. Elemental analyses of the newly prepared compounds were performed by the Australian Microanalytical Service Unit. Infrared spectra were measured in Nujol mulls on a Perkin-Elmer 577 spectrophotometer (4000–200 cm^{-1}). Electronic absorption spectra of freshly prepared solutions were measured with a Beckman Acta CIII spectrophotometer and the results were tabulated in Table I.

Results and Discussion

Previous work of Taube and his co-workers[5] has shown that reduction of *trans*-$[Os(NH_3)_4O_2]Cl_2$ by $SnCl_2$ in HCl (6 M) produced *trans*-$[Os(NH_3)_4Cl_2]^+$. This synthetic method has been found to be more efficient for the general synthesis of *trans*-$[Ru(NH_3)_4X_2]^+$ (X = Cl, I, NCS). Other mild reductants, such as ascorbic acid and 2-propanol, can also very efficiently reduce *trans*-$[Ru(NH_3)_4O_2]^{2+}$, as it is a better oxidant than *trans*-$[Os(NH_3)_4O_2]^{2+}$.

The complex *trans*-$[Ru(NH_3)_4Cl_2$ prepared here is identical with that reported in the literature. The newly prepared *trans*-$[Ru(NH_3)_4I_2]I$ and *trans*-$[Ru(NH_3)_4(NCS)_2]NCS$ complexes are stable in the solid state and in acidic solutions. The similarities of their UV–vis absorption spectra with those of the reported *trans*-$[Ru(en)_2X_2]^+$[6] (X = I, NCS) support the assignment of a trans configuration. As expected, the ligand-to-metal charge-transfer energy of *trans*-$[Ru(NH_3)_4X_2]^+$ decreases in the order of X = Cl > Br > NCS > I (see Table I). *trans*-$[Ru(NH_3)_4(NCS)_2]NCS$ has also been characterized by its IR absorption bands at 2060 and 790 cm^{-1} assignable to ν(CN) and ν(CS), respectively.[7] It is difficult to ascertain whether it is an N- or S-bonded thiocyanate species. Preliminary redox kinetic work showed that this species is a good mediator for electron-transfer reactions,[8] a full account of which will be reported.

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(8) Che, C. M., unpublished results.

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Registry No. *trans*-[Ru(NH_3)$_4$$Cl_2$]Cl, 63251-19-4; *trans*-[Ru(NH_3)$_4$$I_2$]I, 97134-68-4; *trans*-[Ru(NH_3)$_4$(NCS)$_2$]NCS, 97134-70-8; *trans*-[Ru(NH_3)$_4$$O_2$]$Cl_2$, 38882-90-5.

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Extended Correlation between O–F Bond Energies and ^{19}F NMR Chemical Shifts in Fluoroxy Compounds

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Bond energies D_{RO-F} and ^{19}F NMR chemical shifts ϕ markedly depend on the nature of the R group in fluoroxy compounds. It has been shown[1] recently that the direct correlation between D_{RO-F} and ϕ, which is nearly linear over a wide (13 kcal/mol; 100 ppm) range, (1) may be taken as evidence of three-center bonding[2] in these species, (2) is consistent with changes in the electron population of the π^*-SOMO of OF, and (3) reveals the shortcomings of semiquantitative theories of paramagnetic shielding for the fluorine nucleus.[3]

We wish to report now that an extended set of data, including an experimental measurement of ϕ in NO_2OF ($\phi = 220$)[4] together with existing values for F_2O_2 ($D_{O-F} = 18$ kcal/mol; $\phi = 825$)[5] and FOH (54 kcal/mol; 21 ppm),[5a,6] confirms the above conclusions but requires an improved correlation to account for the extremely large spans of both parameters. A nonlinear least-squares fit[7] of the S-shaped D vs. ϕ plot (Figure 1) leads to the expression

$$D = 37.1 + 18.1 \tanh [(222.7 - \phi)/117.5] \qquad (1)$$

This correlation provides a useful predictor of the O–F bond energies of fluoroxy compounds from readily accessible spectroscopic data.[8] It also represents a critical test of ab initio calculations of magnetic shielding constants for heavy nuclei.[10]

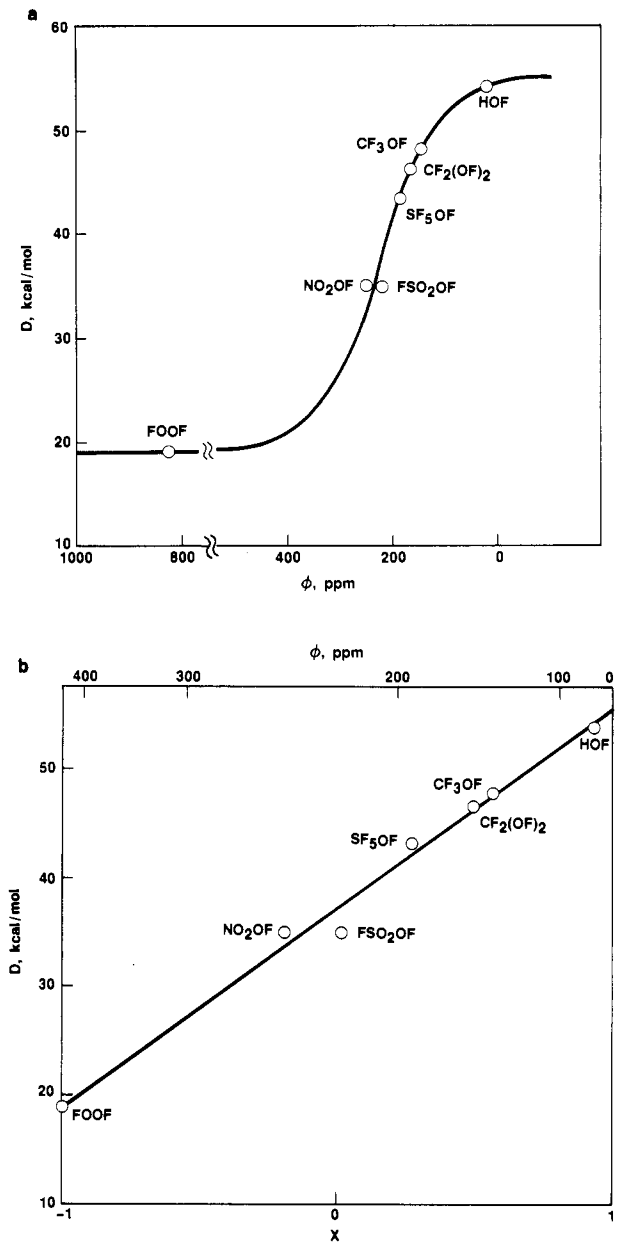

Figure 1. (a) Spectroscopic dissociation energies D_{O-F} vs. ^{19}F NMR chemical shifts ϕ for fluoroxy compounds. (b) D_{O-F} vs. X, where X is tanh [(222.7 − ϕ)/117.5]. The parameters have been determined by using the Marquardt algorithm.[7]

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Registry No. NO_2OF, 7789-26-6.

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(4) Determined for neat liquid NO_2OF at 84.6 MHz using $CFCl_3$ as external standard. The measured shift increased from 218.7 ppm at −95 °C to 219.6 ppm at −45 °C. Positive shifts are downfield from $CFCl_3$.

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(8) Thus for example, from experimental observations[9] and an assumption that the marginally stable SF_5OOF decomposes by $SF_5OOF = SF_5OO\cdot + F$ (k_1), followed by the fast reactions $SF_5OO\cdot = SF_5\cdot + O_2$ and $SF_5\cdot + F = SF_6$, we predict from the expression[1] $\log [k_1\ (s^{-1})] \sim 15.3 - E/(10^{-3}\ 4.575\ T)$ a value for D of about 22 kcal/mol, in good agreement with the one derived from eq. 1 for $\phi = 330$. Obviously, overall rates of gas-phase chain reactions or heterogeneous decompositions are partially controlled by D values. The relatively large errors (±1 kcal/mol and probably larger in the case of F_2O_2) usually associated with D values would normally preclude using any such correlation to estimate NMR chemical shifts with a precision comparable to those attained by direct measurement. Notice, however, that ϕ in F_2O_2 changes by about 40 ppm from neat liquid to infinite dilution.[5b]

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