relatively limited solubility in most other solvents. No extinction coefficients were determined for the fluoro complex because of stability problems; this was not unexpected considering the relatively low stability of $Cr(CO)_5Cl^-$ in the same solvent. The higher stability of $Cr(CO)_5OH^-$ was surprising. $W(CO)_5F^-$ is reasonably stable in solution but follows the expected stability order I > Br > Cl > F. The spectra of the complexes (except for $Cr(CO)_5OH^-$) match the expected pattern in number of peaks and relative intensities.[25,26] We are unable to account for the fact that while the spectra of the $W(CO)_5X^-$ (X = halide, OH) complexes are all similar, the only band seen for $Cr(CO)_5OH^-$ is at much higher energy than in the $Cr(CO)_5X^-$ (X = halide) complexes. The limitation of the K-dibenzo-18-crown-6 cation in ultraviolet spectroscopy is illustrated by the hydroxo spectra.

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Registry No. [Dibenzo-18-crown-6-K][$W(CO)_5OH$], 54964-71-5; [dibenzo-18-crown-6-K][$Cr(CO)_5OH$], 55000-28-7; [dibenzo-18-crown-6-K][$W(CO)_5F$], 54964-72-6; dibenzo-18-crown-6, 14187-32-7; $Et_4N[W(CO)_5F]$, 54964-73-7; $Et_4N[Cr(CO)_5F]$, 54964-74-8.

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Reduction of μ-Superoxo-bis[pentaamminecobalt(III)] by Hexaammineruthenium(II) and a Correlation of Kinetic Data for Two Series of Redox Reactions

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The classification of electron-transfer reactions into either inner-sphere or outer-sphere categories is generally based upon the nature of primary reaction products,[1] including in some cases the identification of binuclear intermediates,[2] as well as information regarding the lability or inertness of metal ion reactants.[3] In addition there are now several examples in which the less restrictive criteria of linear free energy correlations[4] have been successful in providing a means of differentiating between mechanisms.[5-7] These correlations have hitherto been established for reactions involving two reductants, for example, Cr^{2+} and V^{2+}, with a common series of oxidants.[8,9]

Such correlations should also apply, but are less well established,[10] for the converse situation in which the reactions of two oxidant species with a common series of reductants are compared. Here we seek to test further this possibility and in doing so report data for the reduction of the μ-superoxo-bis[pentaamminecobalt(III)] complex by $Ru(NH_3)_6^{2+}$.

Experimental Section

Hexaammineruthenium(III) trichloride (Johnson Matthey Chemicals Ltd.) was purified as previously described[11] (λ_{max} 275.5 nm, ϵ 472 M^{-1} cm^{-1}) and reduced to hexaammineruthenium(II) (λ_{max} 275 nm, ϵ 640 M^{-1} cm^{-1}) using a Jones reductor column, containing amalgamated zinc shot (Hopkin and Williams, Analar grade), under argon gas.[12]

The μ-superoxo-bis[pentaamminecobalt(III)] complex was prepared by oxidation of μ-peroxo-bis[pentaamminecobalt(III)] chloride in situ using ammonium peroxodisulfate, $(NH_4)_2S_2O_8$.[13] The perchlorate salt was isolated and solutions ca. 0.01 *M* in 0.1 *M* $HClO_4$ were made up immediately (λ_{max} 670 nm, ϵ 890 M^{-1} cm^{-1}) and stored at −5° in a light-proof flask.

The stoichiometry of the reaction was shown to be 1:1 by treating freshly generated $Ru(NH_3)_6^{2+}$ with an excess of the μ-superoxo complex and measuring the absorbance change at 670 nm. The μ-peroxo complex which is formed is unstable in acid solution,[14] and when excess $Ru(NH_3)_6^{2+}$ is used, further reaction occurs with the oxygen released.[11] Absorbance changes corresponding to the reaction of the μ-superoxo complex and the subsequent decomposition of the μ-peroxo intermediate were monitored on a Durrum-Gibson stopped-flow spectrophotometer. Concentrations of $Ru(NH_3)_6^{2+}$ pertaining to each run were checked immediately following stopped-flow runs by addition to an excess of μ-superoxo complex and measuring the absorbance change at 670 nm.

Results and Discussion

The reaction was monitored at the 296-nm peak of the μ-superoxo complex, ϵ 2.45 × 10^4 M^{-1} cm^{-1}.[15] At this wavelength two stages were observed, the first of which is assigned to (1). The $Ru(NH_3)_6^{2+}$ was in at least eightfold

$$Ru(NH_3)_6^{2+} + (NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5^{5+} \rightarrow Ru(NH_3)_6^{3+} + (NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5^{4+} \qquad (1)$$

excess and the ionic strength maintained at $I = 0.1$ *M* using $LiClO_4$–$HClO_4$. Plots of absorbance changes, log $(A_t - A_\infty)$, against time were linear to at least 80% completion and yielded first-order rate constants. A threefold variation of [$Ru(NH_3)_6^{2+}$], which was the maximum it was possible to achieve, indicated a first-order dependence on reductant and a rate law (2). Values of *k* at temperatures 1.5–15° are given in Table

$$\text{rate} = k[Ru(NH_3)_6^{2+}][\mu\text{-}O_2^-] \qquad (2)$$

I. The two stages were less well separated at the higher temperatures, and as confirmation of our procedure and in order to ensure that a correct A_∞ was being used, a full consecutive reaction treatment was carried out for a number of runs.[16] Rate constants in Table I are seen to be independent of [H^+] in the range 0.01–0.10 *M*. The range of concentrations of H^+ and ClO_4^- as well as the range of temperatures over which reliable data could be obtained was restricted by the stability of $Ru(NH_3)_6^{2+}$.[17] Activation parameters, $\Delta H^\ddagger = 0.8 \pm 0.5$ kcal mol^{-1} and $\Delta S^\ddagger = -25.8 \pm 1.8$ cal K^{-1} mol^{-1}, were obtained by a least-squares treatment (no weighting factor).

The second stage of reaction corresponds to the decomposition of the primary product, the μ-peroxo-bis[penta-

Table I. Kinetic Data for the First Stage in the Reduction of μ-Superoxo-bis[pentaamminecobalt(III)] by Hexaammineruthenium(II) [$I = 0.1\ M$ (LiClO$_4$), λ 296 nm]^a

Temp, °C	[H$^+$], M	10^5[Ru(NH$_3$)$_6^{2+}$], M	10^6[μ-O$_2^-$], M	$10^{-6}k$, M^{-1} sec^{-1}
1.5	0.01	4.19	2.87	2.71 (2)
	0.01	5.43	6.90	2.55 (2)
	0.01	5.56	5.73	2.65 (2)^b
	0.05	11.85	6.90	2.90 (2)
	0.08	6.56	6.90	2.62 (3)
5.0	0.05	6.22	6.90	2.92 (3)
	0.08	11.62	6.15	2.95 (2)
10.0	0.01	4.49	2.87	2.99 (2)
	0.05	6.46	6.90	2.84 (2)
15.0	0.10	5.32	6.15	3.01 (2)

[a] Number of runs which have been averaged are indicated in parentheses. [b] [Cl$^-$] = 0.01 M.

Table II. Summary of Rate Constants (25°) for the Reduction of Hexaaquoiron(III) (k_{Fe}) and μ-Superoxo-bis[pentaamminecobalt(III)] Complex (k_{S})^i

Reductant	k_{Fe}, M^{-1} sec^{-1}	k_{S}, M^{-1} sec^{-1}	Ref
Ru(NH$_3$)$_6^{2+}$	4.3×10^5	3.7×10^6	*a, b*
V^{2+}	1.8×10^4	9.6×10^4	*c, d*
Eu^{2+}	6.8×10^3	3.0×10^4	*d, e*
Cr^{2+}	2.3×10^3	2.3×10^3	*d, f*
Fe^{2+}	4.0	5.8×10^{-2}	*g, h*

[a] Reference 23; data extrapolated to 25°, $I = 0.1\ M$. [b] This work; $I = 0.1\ M$. [c] Reference 24. [d] Reference 19. [e] D. W. Carlyle and J. H. Espenson, *J. Am. Chem. Soc.*, **90**, 2272 (1968). [f] G. Dulz and N. Sutin, *ibid.*, **86**, 829 (1964). [g] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952); $I = 0.55\ M$. [h] R. Davies and A. G. Sykes, *J. Chem. Soc. A*, 2831 (1968); $I = 2.0\ M$. [i] The ionic strength (I) was 1.0 M except as stated.

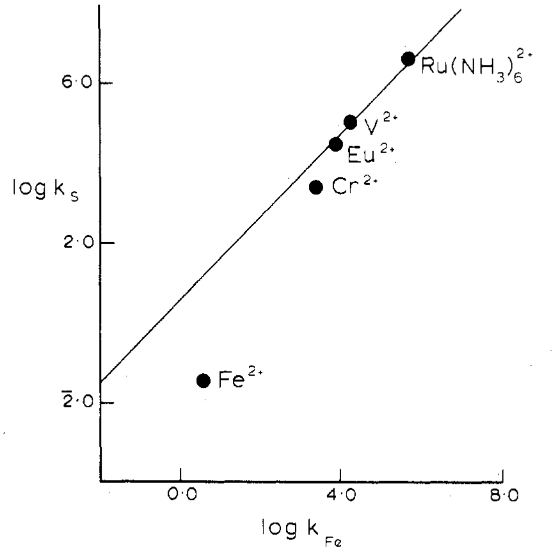

Figure 1. Linear correlation of rate constants for the reduction of the μ-superoxo-bis[pentaamminecobalt(III)] complex (k_{S}) and Fe(H$_2$O)$_6^{3+}$ (k_{Fe}), by a common series of reductants.

amminecobalt(III)] complex,[18] as in (3). First-order rate

$$(\mathrm{NH_3})_5\mathrm{Co{-}O_2{-}Co(NH_3)_5}^{4+} \xrightarrow{\mathrm{H^+,\ H_2O}} 2\mathrm{Co}^{2+} + 10\mathrm{NH_4}^+ + \mathrm{O_2} \qquad (3)$$

constants (k_{dec} = 5.1 sec^{-1} at 1.5°, [H$^+$] = 0.01 M) are dependent on [H$^+$], but full details have not as yet been investigated. Reaction 3 is also observed as a second stage in the Cr^{2+}, V^{2+}, and Eu^{2+} reduction of the μ-superoxo complex.[19]

The rate constant for the reduction of the μ-superoxo complex by Ru(NH$_3$)$_6^{2+}$ of 3.7×10^6 M^{-1} sec^{-1} at 25° (extrapolated value) and the low lability at both the Ru(II)[20] and Co(III) centers ensure that the reaction is outer sphere. Data for a series of metal ion reductions of the μ-superoxo-bis[pentaamminecobalt(III)] complex are now available, with rate constants (k_{S}) at 25° spanning several orders of magnitude. Rate constants (k_{Fe}) for the reduction of hexaaquoiron(III) ([H$^+$]-independent paths) are also available, Table II. Although a plot of log k_{S} against log k_{Fe}, Figure 1, gives a satisfactory linear correlation (4), or for the aquo

$$\log k_{\mathrm{S}} = 1.61 \log k_{\mathrm{Fe}} - 2.09 \qquad (4)$$

ions alone (5), we have chosen to draw a line of slope 1.0

$$\log k_{\mathrm{S}} = 1.75 \log k_{\mathrm{Fe}} - 2.39 \qquad (5)$$

through the Ru(NH$_3$)$_6^{2+}$, V^{2+}, and Eu^{2+} points only. Our reasons for adopting this approach are as follows. Data for the V^{2+} and Eu^{2+} reductions of seven common oxidants, including Co(NH$_3$)$_6^{3+}$ and Co(NH$_3$)$_5$py^{3+} (which react by an outer-sphere mechanism) and the μ-superoxo complex and Fe(H$_2$O)$_6^{3+}$, give a good linear correlation (6).[21] Similarly

$$\log k_{\mathrm{V}} = 1.01 \log k_{\mathrm{Eu}} + 0.51 \qquad (6)$$

rate constants for the μ-superoxo and Fe(H$_2$O)$_6^{3+}$ oxidants are in excellent agreement with the linear correlation for outer-sphere V^{2+} and Ru(NH$_3$)$_6^{2+}$ reductions as previously illustrated (eq 7).[5] Data for outer-sphere reductions of V^{2+}

$$\log k_{\mathrm{V}} = 0.89 \log k_{\mathrm{Ru}} - 0.95 \qquad (7)$$

and Cr^{2+} also give a good correlation (8).[22] From (6)–(8)

$$\log k_{\mathrm{V}} = 1.02 \log k_{\mathrm{Cr}} + 1.13 \qquad (8)$$

it can be concluded that four out of five of the μ-superoxo reactions of Table II are outer sphere. Furthermore the Ru(NH$_3$)$_6^{2+}$ reduction of Fe(H$_2$O)$_6^{3+}$ is outer sphere since both reactants are insufficiently labile.[23] Along with this assignment it has previously been concluded that the reaction of V^{2+} with Fe(H$_2$O)$_6^{3+}$ is outer sphere.[24] Now the slopes of (6)–(8) are close to unity, and it can therefore be concluded that the points for Ru(NH$_3$)$_6^{2+}$, V^{2+}, Eu^{2+}, and Cr^{2+} in Figure 1 should lie on or close to a line of slope unity, and certainly not as in (4) or (5). The line which we have drawn gives good correspondence for the points Ru(NH$_3$)$_6^{2+}$, V^{2+}, and Eu^{2+} but is less satisfactory for Cr^{2+} and Fe^{2+}. The deviation of almost one logarithmic unit for the Cr^{2+} point is perhaps marginal bearing in mind that NaClO$_4$ and not LiClO$_4$ was used to adjust the ionic strength for the Cr^{2+} reduction of Fe(H$_2$O)$_6^{3+}$. The deviation from the line of slope unity is more extensive for the Fe^{2+} point. If it can be assumed that outer-sphere Fe^{2+} reductions should lie on the line of slope unity, then the deviation observed can be explained by too high a k_{Fe} value. This may result from the Fe^{2+} exchange with Fe(H$_2$O)$_6^{3+}$ taking advantage of a more favorable inner-sphere pathway.

Thus the evidence presented here suggests that the Fe^{2+} reduction of Fe(H$_2$O)$_6^{3+}$ ([H$^+$]-independent pathway) may well proceed by inner-sphere electron transfer. It has previously been noted that for the Fe^{2+}–Fe^{3+} exchange a mechanism involving H atom transfer with the generation of FeOH^{2+} and FeH$_3$O^{3+} is unlikely on energetic grounds.[25] There are at present no other examples in which it has been demonstrated that a water ligand bridges two metal ion reactants in an inner-sphere electron-transfer process. Previously Toppen and Linck[26] have failed to detect a reaction path corresponding to the Cr^{2+} reduction of Co(NH$_3$)$_5$H$_2$O^{3+}, and the reaction observed proceeds entirely via Co(NH$_3$)$_5$OH^{2+}.

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Registry No. $Ru(NH_3)_6{}^{2+}$, 19052-44-9; $(NH_3)_5CoO_2Co(NH_3)_5{}^{5+}$, 12259-09-5.

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Inorganic Compounds Containing the Trifluoroacetate Group. IV.[1] Preparation and Properties of Arsenic Tris(trifluoroacetate), $As(O_2CCF_3)_3$, and Related Compounds

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Trifluoroacetato complexes of the group 5 elements which have been prepared previously included $Bi(O_2CCF_3)_3$, $Na[Bi(O_2CCF_3)_4]$, and $Na[AsO(O_2CCF_3)_2]$ which were obtained by reaction of the corresponding oxide with trifluoroacetic anhydride.[2] Goel et al.[3,4] have prepared $R_3Sb(O_2CCF_3)_2$ (where R = Me or Ph) and several other carboxylato derivatives by metathesis between R_3SbX_2 (X = halide) and AgO_2CCF_3 in MeOH (R = Me) or C_6H_6 (R = Ph) solution and reported ir spectral, conductometric, and molecular weight data. The tris(carboxylato) complexes $As(O_2CCHF_2)_3$[5] and $M(O_2CH)_3$[6] (M = Sb or Bi) have been synthesized, the former by heating $Hg(CHF_2CO_2)_2$ with As and the latter by refluxing M_2O_3 with HCO_2H. However, attempts to prepare $As(O_2CCH_3)_3$ from $AsCl_3$ and CH_3CO_2H produced a mixture of $(CH_3CO_2)_xAsCl_{3-x}$ (where x = 1 or 2) derivatives which were not readily separable.[7] Cullen[8] has prepared $Me_2As(O_2CCF_3)$ by the reaction of Me_2AsCl and AgO_2CCF_3 and showed that, while the compound distilled at its boiling point (136°) under nitrogen, at 205° it decomposed giving some Me_2AsCF_3. This note reports a study of the preparation and properties of $As(O_2CCF_3)_3$ and an extension of this work to the corresponding P, Sb, and Bi compounds.

Experimental Section

All manipulations were carried out under an atmosphere of dried nitrogen. Anhydrous CF_3CO_2H (Koch-Light) and trifluoroacetic anhydride (Koch-Light) were used without further purification. Reagent grade $AsCl_3$ and PCl_3 were purified by distillation under reduced pressure and $SbCl_3$ by sublimation under a dynamic vacuum at 65° (10^{-2} Torr); $BiCl_3$ was purified by the addition of excess $SOCl_2$ and refluxing for 2 hr, followed by the evaporation of excess $SOCl_2$. CH_2Cl_2 and $CHCl_3$ were distilled from CaH_2, and THF was distilled from Na wire, immediately prior to use. Ir spectra were recorded on Perkin-Elmer 225 and 457 spectrometers calibrated with polystyrene film, and mass spectra were obtained on an AEI MS12 instrument using a 70-eV beam. ^1H NMR spectra were measured on a Perkin-Elmer R12A instrument at 60 MHz using TMS as an internal standard, and ^{19}F NMR spectra, on a Varian HA-100 instrument at 100 MHz using $C_6H_5CF_3$ as an internal standard.

Preparation of Arsenic Tris(trifluoroacetate), $As(O_2CCF_3)_3$. $AsCl_3$ (3.9 g, 21.5 mmol) was dissolved in CH_2Cl_2 (50 ml), AgO_2CCF_3[9] (14.9 g, 67.5 mmol) was added, and the mixture was stirred for 4 hr at room temperature. The precipitate of AgCl was then filtered off and the bulk of the CH_2Cl_2 distilled from the filtrate at 40° (760 Torr) to afford a viscous, pale yellow oil. Fractional distillation under reduced pressure afforded as the least volatile fraction a transparent, crystalline, extremely hygroscopic solid, mp 45.5–46.0°, in 70% yield. Anal. Calcd for $C_6F_9O_6As$: C, 17.4; F, 41.3; As, 18.1. Found: C, 17.1; F, 41.4; As, 18.1.

The mass spectrum of the compound was obtained by dissolving a sample of CH_2Cl_2 and injecting a portion of the solution through a serum cap into the warmed inlet of the mass spectrometer. Peaks were observed at the following m/e values (with relative intensities) and assigned as 396 (25) $As_4O_6{}^+$, 301 (30) $As(O_2CCF_3)_2{}^+$, 300 (10) $As_4{}^+$, 220 (10) $AsO_2(O_2CCF_3)^+$, 207 (25) $AsF(O_2CCF_3)^+$, 188 (50) $As(O_2CCF_3)^+$, in addition to peaks corresponding to further fragmentation products, including m/e 91 (100) AsO^+. Ir spectra were recorded for a sample sublimed as a thin film onto a NaCl window cooled to ca. −196° and contained in an ir gas cell (Table I) and also for samples dissolved in CH_2Cl_2 and CS_2 at room temperature. The ^{19}F NMR spectrum of the compound dissolved in $CHCl_3$ consisted of a single resonance 76.8 ppm upfield of $CFCl_3$, within the range 74–79 ppm upfield of $CFCl_3$ typical[12] of trifluoroacetate compounds.

Preparation of Trivinylarsonium Trifluoroacetate, $[(H_2C{=}CH)_3AsH]O_2CCF_3$. The reaction between $(H_2C{=}CH)_3As$ and CF_3CO_2H was investigated as an alternative synthetic route to $As(O_2CCF_3)_3$. $(H_2C{=}CH)_3As$ (2.4 g) was prepared[10] by the reaction of $AsCl_3$ and $(H_2C{=}CH)MgBr$ in THF and was then added to a mixture of CF_3CO_2H (10 ml) and $(CF_3CO)_2O$ (1 ml); this solution was refluxed for 3 hr. The excess solvent was then evaporated at ca. 72° (760 Torr), and the residue was extracted with CH_2Cl_2 and filtered before distillation of solvent at ca. 40° (760 Torr). On allowing the resulting viscous solution to stand at −10° for 2 hr, large platelike crystals were deposited. These crystals were filtered and washed with pentane; traces of solvent were removed by pumping (10^{-3} Torr) at room temperature; yield 2.45 g, 65% based on $(H_2C{=}CH)_3As$; mp 154–156° dec. Anal. Calcd for $C_8H_{10}AsF_3O_2$: C, 35.5; H, 3.7; As, 27.8. Found: C, 35.2; H, 3.5; As, 27.6. The mass spectrum was recorded at 100° and contained peaks at m/e 157, 156, 129, 102, and 75, corresponding to the fragments $(H_2C{=}CH)_3AsH^+$ and $(H_2C{=}CH)_nAs^+$ (where n = 3, 2, 1, or 0), respectively, and at m/e 113, 97, 94, and 69 corresponding to $CF_3CO_2{}^+$, CF_3CO^+, $CF_2CO_2{}^+$, and $CF_3{}^+$ fragments, respectively. The ^1H NMR spectrum of $[(H_2C{=}CH)_3AsH](CF_3CO_2)$ in $CDCl_3$ solution consisted of a singlet at τ 6.9, assigned to the As–H hydrogen atom, and 12 resolved peaks centered at τ 3.5 which resemble those obtained for $(H_2C{=}CH)_4Sn$ and $(H_2C{=}CH)_2Sn(O_2CCF_3)_2$.[11]

Preparation of Arsenic Tris(trifluoroacetate)–2,2'-Bipyridyl, $As(O_2CCF_3)_3 \cdot N_2C_{10}H_8$. $As(O_2CCF_3)_3$ (2.07 g, 5 mmol) was dissolved in $CHCl_3$ (10 ml) and a solution of 2,2'-bipyridyl (0.78 g, 5 mmol) in $CHCl_3$ (5 ml) was added; the resulting solution was stirred for 0.5