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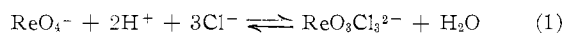
The Trioxotrichlororhenate(VII) Ion¹

BY D. E. GROVE, N. P. JOHNSON, AND G. WILKINSON

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The majority of oxygen-containing rhenium(VII) compounds can be considered to be perturbations of the perrhenate ion, ReO_4^- , e.g., $\text{ReO}_3\text{N}^{2-}$, ReO_3S^- , ReO_3X ($\text{X} = \text{F}, \text{Cl}, \text{Br}$), and Re_2O_7 . Seven-coordinate ReF_7 ,^{2,3} six-coordinate ReOF_6 ,⁴ and five-coordinate ReO_2F_3 ⁴ have been described, but no compound of stoichiometry $\text{ReO}_3\text{X}_3^{2-}$ has been described, although Peacock,⁵ when reporting the ReO_2F_4^- ion, considered that $\text{ReO}_3\text{F}_3^{2-}$ should be capable of existence; both of the isoelectronic ions $\text{WO}_3\text{F}_3^{3-}$ and OsO_3F_3^- are known.^{6,7}

The dissolution of perrhenic acid in concentrated hydrochloric acid saturated with hydrogen chloride produces a yellow solution from which cesium chloride precipitates a pale yellow solid of stoichiometry $\text{Cs}_2[\text{ReO}_3\text{Cl}_3]$. The formation of the ion can be written



The salt dissolves in water or base to give a clear solution without formation of black ReO_2 suggesting that a rhenium(VII) species is present. The salt turns white on exposure to the atmosphere.

The octahedral ion may have two possible geometrical isomers: *cis* (C_{3v}) and *trans* (C_{2v}). Simplified group theory (omitting site symmetry considerations) predicts that the *cis* ion should have 15 normal vibrations of species $4\text{A}_1 + \text{A}_2 + 5\text{E}$, the 5 E vibrations being doubly degenerate, and that there should be two infrared- and Raman-active metal-oxygen and metal-chlorine stretching modes. Similarly, the *trans* ion should have 15 normal vibrations of species $6\text{A}_1 + \text{A}_2 + 4\text{B}_1 + 4\text{B}_2$ with three infrared- and Raman-active metal-oxygen and metal-chlorine stretches.

The infrared spectrum consists of an extremely broad absorption centered around 890 cm^{-1} with a band width of about 100 cm^{-1} . In the $400\text{--}250\text{ cm}^{-1}$ region bands were found at 314 (sh), 320 (vs), 334 (m), 360 (sh), and 370 (s) cm^{-1} , but it was not possible to distinguish between Re-Cl stretching bands and O-Re-O deformation modes.

The Raman spectrum of the solid has two sharp bands at 925 (vs) and 895 (s) cm^{-1} in the metal-oxygen stretching region and a series of bands below 400 cm^{-1} at 387 (s), 366 (vs), 297 (s), 220 (vs), 187 (vs), and 154 (s) cm^{-1} . The two sharp bands in the metal-oxygen

stretching region is good evidence for a *cis* (C_{3v}) configuration of the $\text{ReO}_3\text{Cl}_3^{2-}$ ion.

The preparation of the analogous fluoro anion was attempted but without success even when liquid hydrogen fluoride was used as the solvent. (The Raman spectrum of a solution of sodium perrhenate in 15% hydrogen fluoride was that of the unperturbed ReO_4^- ion.) Addition of a solution of cesium fluoride to a solution of perrhenic acid both in concentrated hydrofluoric acid with some additional liquid hydrogen fluoride present did not give an immediate precipitate. If the mixture was kept cool, large white crystals separated out after about 1 week. Analytical, infrared, and X-ray data confirmed that these crystals were cesium perrhenate. Using other cations, $(\text{C}_6\text{H}_5)_3\text{As}^+$ gave an immediate precipitate of the perrhenate, but R_4N^+ and Rb^+ gave no precipitate at all. The two most likely explanations as to why the fluoride cannot be obtained are: (i) the ion is too susceptible to hydrolysis so that an equilibrium such as that of eq 1 is over to the left; (ii) the salts are too soluble relative to the corresponding perrhenate to be obtained in the solid state.

No attempt was made to obtain the bromide or iodide since perrhenic acid partially oxidizes these hydrogen halides and is itself reduced.

Experimental Section

Infrared spectra of Nujol mulls were recorded using Perkin-Elmer 457 and Grubb-Parsons "Spectromaster" instruments; Raman spectra were obtained using a Cary Model 81 spectrometer with an He-Ne laser source.

Dicesium Trioxotrichlororhenate(VII).—Rhenium metal (Johnson, Matthey Ltd. 99.5%) (2 g) was dissolved in 100 vol of aqueous hydrogen peroxide and the solution of perrhenic acid was evaporated to dryness on a hot plate. The residue was dissolved in 10 M hydrochloric acid (10 ml) and the solution was saturated with hydrogen chloride. To the resulting yellow solution was added a solution of cesium chloride (4 g) in hydrogen chloride saturated aqueous HCl (10 ml). The mixture was allowed to stand overnight. The yellow crystalline product was collected under an atmosphere of hydrogen chloride, washed with 10 M HCl, and dried *in vacuo* over P_2O_{10} (4.15 g, 58%). *Anal.* Calcd for $\text{Cs}_2[\text{ReO}_3\text{Cl}_3]$: Cl, 17.5; Cs, 43.8; O, 7.9; Re, 30.7. Found: Cl, 17.1; Cs, 43.8; O, 7.8; Re, 30.6.

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Fluoro Complexes of Manganese(III) in Acid Perchlorate Solution¹

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Previous workers^{2,3} have noted a doublet in the visible spectrum of Mn(III) in excess fluoride, which has

(1) The authors gratefully acknowledge support of Grant GM-08893-07 from the National Institute of General Medical Sciences, Public Health Service.

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been assigned to a splitting of the ${}^5T_{2g} \leftarrow {}^5E_g$ (in O_h) transition in the $MnF_{aq}{}^{2+}$ species.² However, the proximity of F^- , OH^- , and H_2O in the spectrochemical series and the observation⁴ that OH^- does not produce a splitting of the spectrum in $MnOH_{aq}{}^{2+}$ suggest the absence of splitting in the spectrum of the species $MnF_{aq}{}^{2+}$. We have therefore reanalyzed the spectral data at constant ionic strength in terms of equilibria involving the $Mn(OH)F_{aq}{}^+$ ion in addition to those previously postulated.²

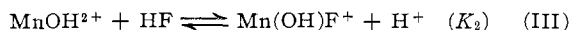
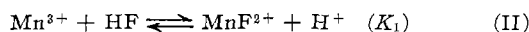
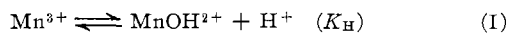
Experimental Section

Reagents.—The preparation and standardization procedures for perchloric acid, manganese(III) solutions, and the perchlorates of manganese(II), iron(II), and barium were as previously described.⁵ Sodium fluoride (Fisher Certified reagent grade) was used without further purification to make up stock solutions. The manganese(III) solution to be used was always freshly prepared by electrolysis of an acidic solution of a large excess of $Mn(II)$.⁴

Spectral Measurements.—All measurements were carried out using matched 100-mm quartz cells in a Cary Model 14 spectrophotometer in a temperature-controlled room at $23 \pm 1^\circ$. Spectra were obtained in the range 300–600 nm using blank solutions containing all the components except $Mn(III)$. In most cases the ionic strength of solutions was adjusted to 5.35 *M* by addition of $Mn(II)$. Replacing some of the $Mn(II)$ by Na^+ or Ba^{2+} had no apparent effect on the spectra at constant acidity and ionic strength; consequently, manganese(II)-fluoride complexes may be neglected in the analysis of the data. The observed extinction coefficients were a minimum at *ca.* 350 nm, and only the data in the region 400–540 nm were deemed sufficiently accurate to justify a detailed analysis. The concentration ranges used were: $[Mn(III)] = (0.83\text{--}2.00) \times 10^{-3}$ *M*, $[HF] = (2.00\text{--}21.2) \times 10^{-2}$ *M*, $[HClO_4] = 0.63\text{--}5.00$ *M*, $[Mn(II)] = 0.03\text{--}1.53$ *M*, $[Na^+] = 0\text{--}0.50$ *M*, and $[Ba(II)] = 0\text{--}0.20$ *M*, with $\mu = 5.35$ *M*. The results of Fackler and Chawla² were in good agreement with our spectral measurements under the same conditions, the observed molar extinction coefficient *E* varying between 10.8 and 52.5 $M^{-1} cm^{-1}$ in the spectral range used for detailed analysis.

Results

If we assume that the equilibria



exist under the experimental conditions, with $K_H = [MnOH^{2+}][H^+]/[Mn^{3+}]$, $K_1 = [MnF^{2+}][H^+]/[Mn^{3+}][HF]$, and $K_2 = [Mn(OH)F^+][H^+]/[MnOH^{2+}][HF]$, then it can be shown that

$$E([H^+]^2 + K_H[H^+] + K_1[H^+][HF] + K_H K_2[HF]) = \frac{\epsilon_1[H^+]^2 + \epsilon_2 K_H[H^+] + \epsilon_3 K_1[HF][H^+] + \epsilon_4 K_H K_2[HF]}{\epsilon_1[H^+]^2 + \epsilon_2 K_H[H^+] + \epsilon_3 K_1[HF][H^+] + \epsilon_4 K_H K_2[HF]} \quad (1)$$

where ϵ_1 , ϵ_2 , ϵ_3 , and ϵ_4 are the molar extinction coefficients of Mn^{3+} , $MnOH^{2+}$, MnF^{2+} , and $Mn(OH)F^+$, respectively. Equation 1 may be rearranged to give

$$\frac{\gamma}{[HF]} = E(K_1[H^+] + K_2 K_H) - (\epsilon_3 K_1[H^+] + \epsilon_4 K_H K_2) \quad (2)$$

where $\gamma = [H^+](\epsilon_1[H^+] + \epsilon_2 K_H - E[H^+] - EK_H)$ can be calculated.^{4,6} Linear plots of $\gamma/[HF]$ vs. *E* (assuming that $[HF]$ is equal to the total added fluoride

concentration) were obtained at each wavelength, and each plot had a negative intercept as required by eq 2. The slopes S_λ and the intercepts I_λ of each plot at fixed wavelength are functions of acidity (eq 3 and 4) and

$$S_\lambda = K_1[H^+] + K_2 K_H \quad (3)$$

$$I_\lambda = \epsilon_3 K_1[H^+] + \epsilon_4 K_H K_2 \quad (4)$$

examples of plots of these functions are shown in Figure 1. The values of K_1 and K_2 obtained in this way at

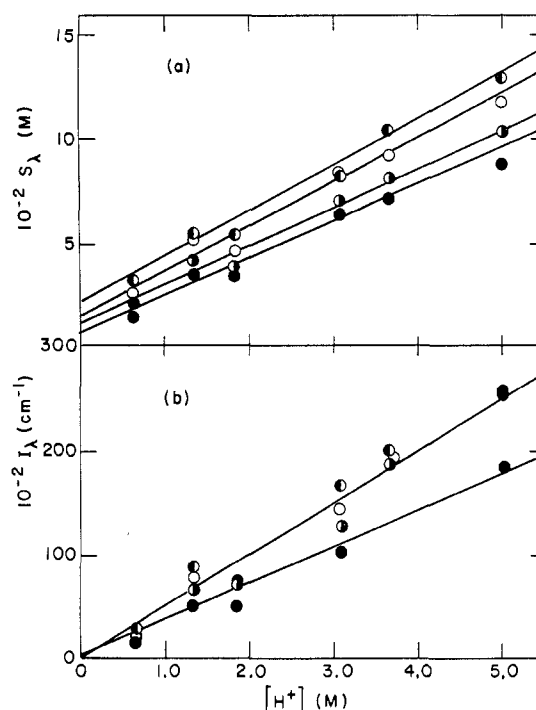


Figure 1.—Plots of (a) $10^{-2}S_\lambda$ vs. $[H^+]$ and (b) $10^{-2}I_\lambda$ vs. $[H^+]$ for spectral data at the following wavelengths: \bullet , 460 nm; \circ , 470 nm; \circ , 480 nm; \bullet , 500 nm.

wavelengths in the range 400–560 nm are shown in Table I, and the spectra of MnF^{2+} and $Mn(OH)F^+$ calculated from eq 4 using the individual values of K_1 and K_2 at each wavelength are shown in Figure 2. The average values over the wavelength range are $K_1 = (1.6 \pm 0.1) \times 10^2$ and $K_2 = (1.9 \pm 0.3) \times 10^2$. The nature of the analysis makes the precision of the value of K_2 much less than that of K_1 since the former is calculated from an intercept. Nevertheless, the appearance of an intercept in plots of eq 3 at every wavelength (see Figure 1a) strongly suggests that an equilibrium involving the species $Mn(OH)F^+$ must be taken into account in the interpretation of the spectral data.

Discussion

Although few complexes of $Mn(III)$ have been completely characterized in solution, it is worthwhile to compare the present results with those obtained for other systems.

Important information concerning the stabilities of several $Mn(III)$ complexes has been obtained from a study of the $Mn(III)$ -catalyzed oxidation of oxalic acid

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TABLE I
ESTIMATES OF EQUILIBRIUM CONSTANTS AT 23°
AND $\mu = 5.35 M$ AT VARIOUS WAVELENGTHS

Wavelength, nm	$10^{-2}K_1$	$10^{-2}K_2^a$
400	1.8	3.5
420	1.4	1.6
440	1.1	2.6
460	1.9	1.1
470	2.1	2.2
480	2.0	1.8
500	1.7	0.8
520	1.5	2.2
540	1.1	1.2
Av	1.6 ± 0.1	1.9 ± 0.3

^a The value $K_H = 0.90 M$ has been assumed at $\mu = 5.35 M$ and 23°.⁶

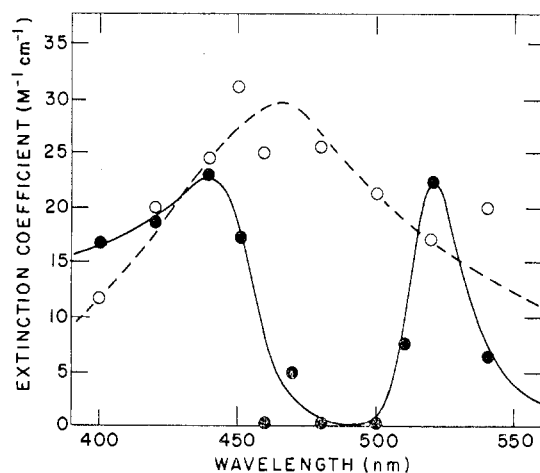
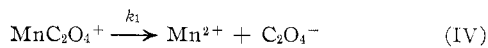
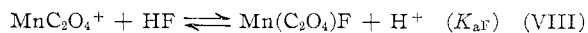
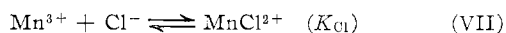
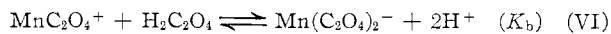
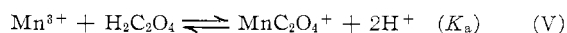


Figure 2.—Derived spectra of MnF_{aq}^{2+} (○) and $Mn(OH)F_{aq}^{+}$ (●).

by chlorine^{7a} and bromine.^{7b} The rate-determining step in this reaction is⁷ the first-order decomposition of the monoaxalato complex



The observed rate of reaction at constant acidity varies with the concentrations of added oxalic acid and chloride or fluoride ions, and the data of Taube⁷ can now be rationalized by combining reactions I–III with



In the absence of added chloride or fluoride ion we have obtained the values of k_1 , K_a , and K_b of 11.9 min^{-1} , $1.64 \times 10^5 M$, and $45 M$, respectively. Comparison of these estimates with those obtained by Taube^{7b} in the absence of reaction I shows that the principal effect of its inclusion in the calculations is to increase the value of K_a . The kinetic data^{7b} in the presence of up to a 10^5 -fold excess of chloride only require the additional equilibrium VII, with $K_{Cl} = 13.5 \pm 0.5 M^{-1}$ at $\mu = 2 M$ and 25°. In the presence of added fluoride the data is accounted for by the additional equilibria II, III, and VIII with $(2K_1 + K_2K_H) = 1.1 \times 10^3 M$ and

(7) (a) H. Taube, *J. Am. Chem. Soc.*, **70**, 1216 (1948); (b) H. Taube, *ibid.*, **70**, 3928 (1948).

$K_{aF} = 118$ at $\mu = 2 M$ and 25°. Individual values of K_1 and K_2 cannot be obtained from the original^{7b} kinetic data since the acidity was kept constant at 2.0 M. However, the present results for $\mu = 5.35 M$ suggest that $K_1 \approx K_2$, whereupon we calculate $K_1 \approx K_2 \approx 370$ at $\mu = 2 M$ and 25°. The stability constants for fluoride complexation thus appear to increase with decreasing total ionic strength. The value of the composite stability constant obtained from spectral measurements by Fackler and Chawla² is consistent with these estimates, since it was obtained at varying ionic strength and acidity.

The ratio $K_1/K_2 = K_H/K_{FH}$, where $K_{FH} = [Mn(OH)F^+][H^+]/[MnF^{2+}] \approx 1.1 M$ at $\mu = 5.35 M$ and 23°, shows that the presence of F^- results in little change in the acidity of the remaining water molecules of the inner sphere. This conclusion is consistent with the similarity of the spectra of Mn_{aq}^{3+} , $MnOH_{aq}^{2+}$, $MnCl_{aq}^{2+}$, and MnF_{aq}^{2+} in both the visible and the uv regions.

The splitting of the visible spectrum of $Mn(OH)F_{aq}^{+}$ is presumably⁸ due to splitting of the 3E_g (and possibly ${}^5T_{2g}$) level by tetragonal distortion. It is not possible to assess the importance of *cis-trans* isomerism in this complex in the absence of data on other mixed-ligand complexes of this type. However, it should be noted that the high-spin⁹ complex $Mn(CYDTA)OH^{2-}$ has a spectral maximum at 448 nm which moves to 510 nm on protonation.¹⁰ Changes in the spectra of the aquo species in the presence of very large excesses of chloride,^{3,11} where higher order chloro complexes are formed, suggest that cumulative effects of negative charge can indeed cause measurable spectral changes in mixed complexes of Mn(III).

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A High-Pressure Form of Palladium Disulfide

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An orthorhombic palladium disulfide (I) ($a = 5.46$, $b = 5.54$, $c = 7.53 \text{ \AA}$) may be prepared by heating palladium dichloride and excess sulfur at 450° in an evacuated quartz tube for 4 days.² The structure of the palladium disulfide so prepared^{3,4} [space group D_{2h}^{15} (Pbca)] is derived from the pyrite structure, which places the cation in a nearly perfect octahedral environment, by elongation of one of the fourfold octahedral axes.⁵

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