into a doublet separated by 6 cm.$^{-1}$ by the former instrument, trace a, which could not be resolved by the latter, trace b, Fig. 2. Also, in contrast to the ν_{CO} region, here we found unmistakeable indication of increased infrared activity for the mixed metal derivative. The molar absorptivities obtained from integrating a plot of log % transmission against cm.$^{-1}$ for the bands near 600 cm.$^{-1}$ gave the following results (for equimolar concentrations): the relative areas for the bands in this region were $Mn_2(CO)_{10}$:$Re_2(CO)_{10}$:$(CO)_5MnRe(CO)_5$, 1:1:1.5.

Acknowledgment.—We are indebted to Professor M. A. El-Sayed of this department for helpful discussions.

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Spectra of Manganese(III) Complexes. I. Aquomanganese(III) Ion and Hydroxide, Fluoride, and Chloride Complexes

BY J. P. FACKLER, JR., AND I. D. CHAWLA

Received March 16, 1964

The absorption spectrum of aqueous manganese(III) is described in the presence and absence of added halide ions. Addition of fluoride to solutions containing aqueous manganese(III) causes a distinct splitting of the ${}^5T_{2g} \leftarrow {}^5E_g$ (in O_h) to occur. This is shown to be consistent with the formation of MnF^{2+}, $Mn^{3+} + F^- = MnF^{2+}$ with $K \cong 10^6$ at ~23°. Jahn–Teller effects are thought to influence the observed spectra.

Introduction

Attempts to correlate spectral properties of tris(β-ketoenolato)manganese(III) complexes[1] with known spectra of manganese(III) species in an environment of ligands bonding through oxygen[1-7] caused us to reexamine the spectrum of aqueous manganese(III). Hexaaquomanganese(III) ion has been observed spectrally[2-4] in the species $CsMn(SO_4)_2 \cdot 12H_2O$. In these studies only one band in the 6000–30,000 cm.$^{-1}$ region of the spectrum was observed. It occurs at 21,000 cm.$^{-1}$ with a molar extinction of ~5 l. mole^{-1} cm.$^{-1}$. This band has been attributed[4] to the ${}^5T_{2g} \leftarrow {}^5E_g$ absorption expected in an octahedral symmetry.

Aqueous solutions thought to contain Mn^{3+} have been observed spectrally by Piper and Carlin[5] and Furlani and Ciana.[6] Ibers and Davidson[7] earlier reported the absorption spectrum of manganese(III) in 10 *N* hydrochloric acid. In each case two bands were observed, one near 20,000 cm.$^{-1}$, the other near 12,000 cm.$^{-1}$. The latter authors report molar extinctions of ~70 and ~340, respectively, for the low and high energy bands. Hatfield, *et al.*,[8] observed $MnCl_6^{3-}$ in a pressed salt pellet, finding no band at 12,000 cm.$^{-1}$ but observing bands at 17,540 and 22,400 cm.$^{-1}$. The latter band was thought to arise from "charge transfer." Runciman and Syme[9] recently reported the spectrum of $CrCl_2 \cdot 4H_2O$. This d^4 ion complex[10] shows three "crystal-field" bands at 77°K.

Recently Diebler and Sutin[11] published the solution spectrum of manganese(III) in perchloric acid. This spectrum, as well as the spectra of solutions containing added fluoride and chloride, suggests previous spectral assignments[5,6,8] for aqueous manganese(III) are incorrect.

Experimental

Preparation of Solutions.—Manganese(III) solutions were prepared by dissolving a weighed quantity of $Mn(ClO_4)_2 \cdot 6H_2O$ in water containing $HClO_4$ and adding a measured quantity of aqueous $KMnO_4$. In a typical experiment, 15.0 g. of $Mn(ClO_4)_2 \cdot 6H_2O$ (G. Frederick Smith) is dissolved in 25 ml. of water and 5.0 ml. of $HClO_4$ (60%) is added. To this solution 2.0 ml. of a water solution of $KMnO_4$ containing 1.0 mg./ml. is added. The resulting solution, which is ~1.44 *M* in $HClO_4$, remains stable for periods up to 1 week. Solutions containing added NaCl and NaF were prepared by adding the reagent grade salt directly to the solution.

Quantitative measurements of the observed molar extinction as a function of added fluoride were obtained for two concentrations of acid and manganese(II). These data are summarized in Table I.

Spectral Studies.—Spectra were observed on a Cary Model 14 spectrophotometer at room temperature, ~23°. After ascertaining that the spectrum of manganese(II) in this perchloric acid medium was identical with the spectrum presented in the

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(9) W. A. Runciman and R. W. G. Syme, *Philosophical Mag.*, **8**, 605 (1963).

(10) The Cr^{2+} in $CrCl_2 \cdot 4H_2O$ is surrounded[9] by six ligands with point group symmetry C_{2h}. There are two long and two short Cr–O bonds.

(11) (a) H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964). This paper appeared during the preparation of the original manuscript. (b) D. R. Rossiensky, *J. Chem. Soc.*, 1181 (1963), reported the stability of aqueous manganese(III) solutions.

TABLE I

QUANTITATIVE DATA FOR ESTIMATION OF EQUILIBRIUM CONSTANTS

$[Mn^{2+}]$, *M*	$[ClO_4^-]$, *M*	Ionic strength	$C_{Mn^{3+}} \times 10^3$, *M*	$[H^+]$, *M*	$C_F \times 10^3$, *M*	ϵ_{Mn}^{470}
1.29	4.02	5.3	1.97	1.44	0	87
				1.43	7.4	53
				1.42	18.6	37
				1.40	40.9	27
				1.35	89.3	20
				1.23	212	16
0.345	5.81	6.1	2.04	5.12	0	66.5
				5.11	7.7	44.4
				5.10	19.2	33.1
				5.08	42.3	24.7
				5.03	92.4	15.7

literature,[12] subsequent runs were made by filling a matched 10-cm. cell with a solution containing $Mn(ClO_4)_2$ at the same concentration as the sample cell but with no added $KMnO_4$. It was found that the best procedure was to fill both cells with the manganese(II) solution and run a base line (see Fig. 2). Then 2.0 ml. of the $KMnO_4$ solution was added to the sample cell while adding 2.0 ml. of H_2O to the reference cell. When halide salts were added, equal quantities were introduced into each 10-cm. cell.

Results

Electronic transitions within the 3d configuration for "spin-free" manganese(II) species involve multiplicity changes, and hence they are very weak in intensity.[12] Maximum extinction coefficients are approximately 0.01–0.10 for octahedral species and approximately 0.1–10 for tetrahedral complexes. These low intensity absorptions enable[13] the more intense spectra of manganese(III) species to be observed (Fig. 1), even in the presence of large quantities of manganese(II). In Fig. 1 and 2a, the spectrum of a solution containing aqueous manganese(III) in 875-fold excess manganese(II) perchlorate and perchloric acid is presented. The manganese(II) absorbance is subtracted out.

Using oxidation potentials listed by Latimer,[14] an equilibrium constant of ~1.5 is calculated for reaction 1. Hence assuming 1 *M* Mn^{2+} and 1 *M* H^+ concentrations, it is readily shown that a 10^{-4} *M* initial concentration of MnO_4^- is converted nearly quantitatively to Mn^{3+}. Using this assumption, it is possible to calculate a molar extinction coefficient for the Mn^{3+} species. In Table II we have listed bands observed for manganese(III) in perchloric acid and with approximately 200-fold excess of added chloride or fluoride.

$$MnO_4^- + 4Mn^{2+} + 8H^+ = 5Mn^{3+} + 4H_2O \qquad (1)$$

It is readily apparent that the spectrum of Mn^{3+} in aqueous perchlorate is much more intense than the spectrum of $Mn(H_2O)_6^{3+}$ in the $CsMn(SO_4)_2 \cdot 12H_2O$ crystal.[3,4] The band at 21,000 cm.$^{-1}$ is 10–20 times stronger in solution than in the solid. There is evidence for a weak band near 14,500 cm.$^{-1}$ in solution which is absent from the crystal or may not have been observed due to experimental difficulties.

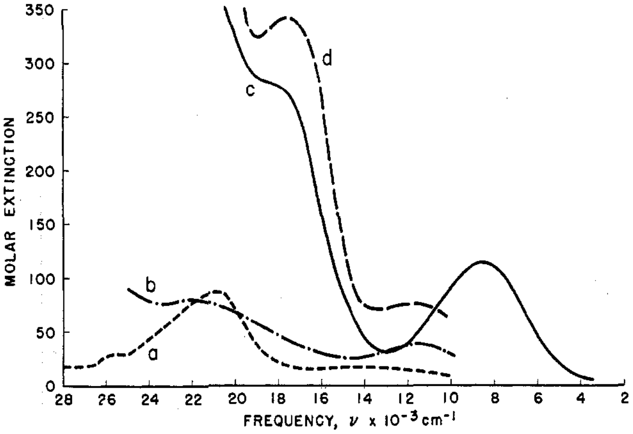

Fig. 1.—Visible spectra of some manganese(III) complexes: a, Mn^{3+}(aq) containing $MnOH^{2+}$(aq); b, Mn^{3+}(aq) with added chloride; c, manganese(III) dipivaloylmethane; d, Mn^{3+} in 10 *N* HCl, ref. 7.

TABLE II

Solution	$\bar{\nu} \times 10^{-3}$, cm.$^{-1}$	ε, l. mole^{-1} cm.$^{-1}$
Mn^{3+}, ClO_4^- ~6–1 *M* $HClO_4$	~14.5 (broad)	20–26[a]
	21.0	60–92
0.26 *M* NaCl added	11.7	36.5
	22.2	80
0.21 *M* NaF added	13.1	9
	18.6	19
	23.2	24

[a] Repeated runs fell within these limits. Solutions contain $MnOH^{2+}$ (see text).

Added chloride has a pronounced effect (Fig. 1, b) on the spectrum with the resulting solution showing a new band near 11,800 cm.$^{-1}$ with ε ~40. This type of spectrum is similar to that observed with the tris(β-ketoenolato)manganese(III) complexes[1] (Fig. 1, c) and to spectra of the solutions reported for aqueous Mn^{3+} oxalate by Piper and Carlin[5a] and Furlani and Ciana.[6] The peaks are in similar positions but have lower intensities than those reported by Ibers and Davidson[7] for Mn^{3+} in 10 *N* HCl. Fluoride (or better HF since solutions initially contained high concentrations of $HClO_4$) reduces the intensity of the major Mn^{3+} peak at 21,000 cm.$^{-1}$ and splits it into two distinct bands (Fig. 2, b–f). The broad band near 14,000 cm.$^{-1}$ does not seem to be affected strongly.

During this study Diebler and Sutin[11a] published the spectrum of aqueous manganese(III) in perchloric acid, obtained by the electrolytic oxidation of manganese(II). They suggested that the formation of $MnOH^{2+}$ is responsible for the variation in the molar extinction with changes in acidity. A hydrolysis constant K_1 for Mn^{3+}(aq) of ~5 was estimated.

From the data published by Diebler and Sutin[11a] and this work, it is possible to estimate, by graphical extrapolation, the molar extinction at 470 mμ of Mn^{3+}

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[12] See, for example, T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience, New York, N. Y., 1960.

[13] We are indebted to Professor J. Halpern for the suggestion.

[14] W. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1958.

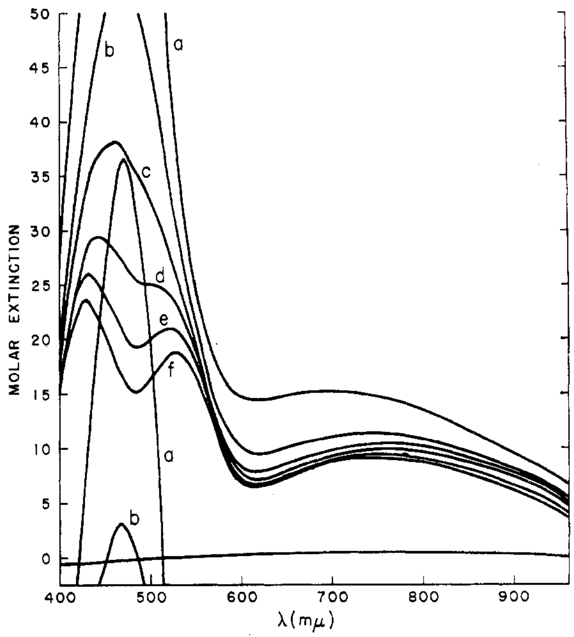

Fig. 2.—Visible spectrum of Mn^{3+}(aq) with added fluoride in ~1.44 M $HClO_4$: a, no NaF added, Mn^{3+}(aq) 2.0 × 10^{-3} M, Mn^{2+}(aq) 1.3 M; b, total fluoride 7.4 × 10^{-3} M; c, total fluoride 18.6 × 10^{-3} M; d, total fluoride 40.9 × 10^{-3} M; e, total fluoride 89.3 × 10^{-3} M; f, total fluoride 212 × 10^{-3} M.

(aq) and $MnOH^{2+}$(aq), as well as that of the species formed with added fluoride. These values are listed in Table III. Using extrapolated molar extinctions, calculation of the hydrolysis constant from Diebler and Sutin's data gave values between 1.8 and 5.1, decreasing with increasing acidity. Since other hydrolysis species besides $MnOH^{2+}$ might be expected at the low hydrogen ion concentrations, the lower value for K is probably the more reliable. Our results suggest that this constant is ~1.5, a value in good agreement with the value of Diebler and Sutin considering the fact that our solutions were prepared by quite different means.

Table III

Analyses of Spectral Data at 470 mμ

Species	ϵ^{470}, l. mole^{-1} cm.$^{-1}$	Obtained as intercept of
Mn^{3+}	54	ϵ_{obsd} *vs.* $1/[H^+]$
$MnOH^{2+}$	115	ϵ_{obsd} *vs.* $[H^+]$
MnF^{2+}	10	ϵ_{obsd} *vs.* $1/C_{NaF}$

Calculated equilibrium constants

	Ref. 11a[a]	This work[b]
$K_1 = \frac{[MnOH^{2+}][H^+]}{[Mn^{3+}]}$	1.8–5.1	1.7, 1.3
$K_2 = \frac{[MnF^{2+}][H^+]}{[Mn^{3+}][HF]}$	. . .	200–700

[a] Calculated from the data of ref. 11a, the low values were obtained at high acid strength, ionic strength I = 6.0 M. [b] K_1 measured at $[H^+]$ = 1.44 M, I = 5.3, and $[H^+]$ = 5.12 M, I = 6.1, respectively. K_2 = 250 ± 50 at $[H^+] \cong 1.44$ M, I = 5.3; K_2 = 540 ± 100 at $[H^+] \cong 5.1$ M, I = 6.1. These values vary somewhat with the choice of K_1, which was taken to be 1.3 for these calculations. We are indebted to Dr. David Holah for the data at high acidities.

Assuming a value of ~1.5 for the hydrolysis of Mn^{3+}(aq), it is possible quantitatively to correlate the spectrum observed upon adding sodium fluoride with the formation of MnF^{2+}(aq). Since the solutions observed contained large excesses of hydrogen ion, the weak acidity of HF(aq), $K_a \cong 5 \times 10^{-4}$, suggests all the fluoride is associated with HF(aq) and MnF^{2+}. Assuming MnF^{2+} is formed completely at large ratios of added fluoride to manganese(III), the molar extinction at 470 mμ was determined (Table III). From the observed reduction in the molar extinction (Table I) as a function of added fluoride, the equilibrium constant for the reaction $Mn^{3+} + HF = MnF^{2+} + H^+$ was calculated (Table III). This value suggests a dissociation constant for MnF^{2+} of $\sim 10^{-6}$, at ionic strengths near 6. Due to the fact that nonideal conditions were used in this study, the "constants" obtained, Table III note *b*, cannot be considered much better than order of magnitude values.

Attempts to analyze the spectral data assuming only Mn^{3+}(aq) and MnF^{2+} are the manganese(III) species present led to inconsistent results and caused us to assume at first that MnF_2^+ may be present. However, knowing that $MnOH^{2+}$ is present in substantial amounts,[11a] it was possible to obtain consistent results considering only Mn^{3+}(aq), $MnOH^{2+}$, and MnF^{2+}. In fact, a plot of $\epsilon^{\lambda}_{obsd}/f_c$ *vs.* $1/[HF]$ must not be linear if appreciable quantities of manganese(III) species other than MnF^{2+} are formed on adding fluoride (f_c is the fraction of MnF^{2+} formed as calculated at 470 mμ). Testing this relationship at 430, 470, and 520 mμ, reasonably good linearity is observed assuming $[HF] = C_F$. This supports the conclusion that the species responsible for the split band near 20,000 cm.$^{-1}$ is MnF^{2+}.

Discussion

Previous investigations[5-7] thought to present the spectrum of $Mn(H_2O)_6^{3+}$ must be considered incorrect. Solutions prepared by starting[5,6] with $Mn(C_2O_4)_3^{2-}$ suggest the presence of a strong low-energy band which is absent (a band near 14,000 cm.$^{-1}$ occurs with low intensity, however) in aqueous manganese(III).

While the spectrum of Mn^{3+}(aq) was not observed directly in this study due to hydrolysis, the data suggest that $Mn(OH)^{2+}$ and Mn^{3+}(aq) have very similar spectra, the latter compound having a molar extinction about one-half that of $Mn(OH)^{2+}$. The spectrum (Fig. 1, a) appears to be that of a solution containing nearly equal quantities of Mn^{3+}(aq) and $Mn(OH)^{2+}$. Chloride, Fig. 1, b, causes the growth of a band near 11,000 cm.$^{-1}$, not unlike the spectra reported previously for aqueous manganese(III). In view of the ability of manganese(III) to complex ions in the solution, *e.g.*, OH^- or F^-, it is likely that the band near 11,000 cm.$^{-1}$ arises from a manganese(III) species containing chloride. This is substantiated by the spectrum of manganese(III) in 10 N HCl, Fig. 1, d. The low-energy band observed[5-7] by others undoubtedly arises from species of the MX_n^{3-n} type.

The 21,000 cm.$^{-1}$ band occurring in the manganese-

(III) solutions in perchloric acid comes from the $^5T_{2g} \leftarrow {}^5E_g$ (in O_h) transition. It is the only spin-allowed transition expected in spin-free d^4 systems of this symmetry. The intensity of the band in $Mn^{3+}(aq)$ and $MnOH^{2+}$ is enormous, especially in view of the extinction of ~5 reported in $CsMn(SO_4)_2 \cdot 12H_2O$. The decrease in intensity in going from $MnOH^{2+}$ to $Mn^{3+}(aq)$ is consistent with the diminished mixing of metal 3d and 4p functions on going to a higher symmetry. However, the intensity is much too large in the $Mn^{3+}(aq)$ to be accounted for by vibronic mechanisms alone.

In $Cr^{2+}(aq)$, Runciman and Syme[9] have observed "a broad intense band at 14,300 cm.$^{-1}$," which is resolved in $CrCl_2 \cdot 4H_2O$ at 77°K. into bands at 13,100, 15,200, and 18,940 cm.$^{-1}$. A low-energy band not observed by Runciman and Syme appears as a shoulder on the main peak in solution.[15] Thus the solution spectrum of $Cr^{2+}(aq)$ is very similar to that of $Mn^{3+}(aq)$. If one assumes the Dq ratio for Cr^{2+}/Mn^{3+} is insensitive to molecular distortions from octahedral symmetry, the ratio of 0.68 is in reasonable agreement[16] with Dq ratios for V^{2+}/Cr^{3+}, 0.71 and Mn^{2+}/Fe^{3+}, 0.59.

The distinct splitting of the $^5T_{2g} \leftarrow {}^5E_g$ (in O_h) transition into two components in the MnF^{2+} species is quite interesting in view of the fact that water and fluoride appear at similar positions in the spectrochemical series. The reduction in intensity may reflect less molecular orbital bond formation in the fluoride complex compared with the aqueous and chloride species.

Since high-spin d^4 systems contain a degenerate ground state in octahedral symmetry, Jahn–Teller distortions are expected.[17] If this distortion is static in nature and sufficiently large, one might expect to see up to four "visible" bands arising from transitions to the three components of $^5T_{2g}$ and the other component of ^5E_g in low symmetry. Perhaps the three bands observed in $CrCl_2 \cdot 4H_2O$ at 77°K. are such spin-allowed transitions. Furthermore, the two peaks near 20,000 cm.$^{-1}$ in MnF^{2+} must arise from transitions to a symmetry split $^5T_{2g}$ level.

The spectrum of MnF^{2+} is consistent with a C_{4v} symmetry for the molecule, in which the t_{2g} level splits up into e (d_{xz}, d_{yz}) and b_2 (d_{xy}) while e_g splits into b_1 ($d_{x^2-y^2}$) and a_1 (d_{z^2}). Assuming fluoride interacts less with the metal d orbitals than does water (in accord with the spectrochemical series), a natural ordering of these levels would be the following: $b_1 > a_1 > b_2 > e$. Since the axial fluoride and water give rise to an average tetragonal effect, it is possible to treat the system in a manner analogous to the treatment of Ballhausen.[18] This leads to $Dq = 1860$ cm.$^{-1}$, $Ds = 2530$ cm.$^{-1}$, and $Dt = 600$ cm.$^{-1}$. However, assuming the axial orbitals are destabilized by the fluoride, a Dq of only ~1000 cm.$^{-1}$ is calculated. Since this value is unreasonable, the level scheme suggested appears appropriate and indicates a very substantial ground state splitting of ^5E_g (in O_h).

The absence of perceptible splitting of the $^5T_{2g} \leftarrow {}^5E_g$ band in the aqueous complexes, even though the band is broad and shows a rather large intensity, suggests an interpretation may be made in terms of a dynamical Jahn–Teller effect.[17,19] (It is significant that the $^2T_{2g} \leftarrow {}^2E_g$ (in O_h) transition in $Cu^{2+}(aq)$ is unusually broad[20] and somewhat more intense than Laporte forbidden transitions for other aqueous complexes.)

Liehr[17] has formulated the possible consequences of a Jahn–Teller effect in terms of a barrier potential to minima exchange, β, and the Jahn–Teller force, α. In summary, if α and β are large the molecule should remain in a permanently distorted configuration and display resultant anisotropic physical properties. With α small and β large some "static" distortion is expected resulting in probable broadening of bands. With α large but β moderate to small, "static" distortions may not persist unless crystalline or other forces in effect increase the magnitude of β. With α and β both small, isotropic properties of "normal" octahedral complexes would be expected.

The spectral data presented here suggest that the Jahn–Teller force, α, may be quite large (as expected in $t_{2g}{}^3e_g$ configurations) but that β is moderate to small in manganese(III) and chromium(II) aqueous complexes. Thus the low-energy band near 14,000 cm.$^{-1}$ in $Mn^{3+}(aq)$ could represent transitions within the ^5E_g level of O_h symmetry. The broad nature of this and the 20,000 cm.$^{-1}$ band suggests vibrational exchange occurs among the three expected distorted configurations of lowest energy in $Mn^{3+}(aq)$. Hence the "average" effect is the spectrum which might be expected by superposition of spectra from molecules having varying degrees of molecular distortion from octahedral symmetry. Solidification of $CrCl_2 \cdot 4H_2O$ at 77°K. or addition of fluoride to Mn^{3+} to form MnF^{2+} presumably creates an additional barrier to minima exchange, causing these substances to display anisotropic absorption spectra characteristic of distorted (from O_h) species. The bonding similarity of OH^- and OH_2 may be the reason the $^5T_{2g} \leftarrow {}^5E_g$ band is not split in $MnOH^{2+}$, or perhaps no well-defined minima are present.

The low-energy band observed in β-ketoenolate complexes of manganese(III) may be due to dynamical reductions[21] from a D_3 symmetry. Some evidence currently available[1] suggests static effects are not responsible for this band in solutions (Fig. 1).[21a] These spectra will be presented in a future paper along with other

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(21a) NOTE ADDED IN PROOF.—The recent publication by B. Morosin and J. R. Brathovde, *Acta Cryst.*, **17**, 705 (1964), of the X-ray crystal structure of tris(2,4-pentanediono)manganese(III) indicates that static distortions do not produce the band in the crystals either.

studies on d^4 systems currently being made in these laboratories.[22]

Acknowledgment.—The authors acknowledge the support of the National Science Foundation for this study. Discussions with Dr. A. D. Liehr and Professors K. Knox and D. Whitman are greatly appreciated.

[22] Originally it was thought that tetrahedral species may be producing the low-energy bands in manganese(III) complexes. However, data now available on $CrI_2 \cdot 2CH_3CN$ with excess I^- suggest this probably is not the case.

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Vibrational Spectrum of the Hexafluorogermanate Ion

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The existence of the GeF_6^{2-} ion in acid solution has been demonstrated from an examination of the Raman effect. The three-line spectrum expected for a regular octahedral complex was observed, although slow secondary processes, presumably hydrolysis and HF–Pyrex glass interactions, were evident from the time dependent appearance of a number of other Raman lines. A complete vibrational analysis of the active fundamental modes of GeF_6^{2-} was possible by considering solid phase infrared spectra of NH_4^+, K^+, Rb^+, Cs^+, and Ba^{2+} hexafluorogermanates. In these, consideration of space group and site group selection rules was essential for a satisfactory interpretation of the observed spectra.

The most probable structure for an MX_6^{2-} (X = halogen) ion is a regular octahedron (O_h point group) or a slightly distorted octahedron (D_{4h} point group). In the latter, axial M–X bonds would be longer or possibly shorter than the equatorial ones. Especially in the case of the GeF_6^{-2} and $GeCl_6^{2-}$ ions, there is the possibility that the D_{4h} model might prevail over the more spherically symmetrical O_h model. It can be argued, for example, that diffuse vacant 4d orbitals would not contract sufficiently in the field of the fluorines or chlorines to form six equivalent sp^{3}d^2 orbitals.

The results of early X-ray diffraction work[2-4] on GeF_6^{2-} compounds suggested that subtle differences between axial and equatorial Ge–F bond lengths existed, but these could not be evaluated. On the other hand, conductance measurements[5] and other solution studies[6] do not unambiguously establish the existence of the GeF_6^{2-} species in solution. Accordingly, it seemed attractive to explore some of these problems using vibrational spectroscopic methods.

Experimental

Fluorogermanic acid solutions and the barium and cesium hexafluorogermanates were made by standard methods[4,7] and X-ray powder patterns agreed with published data. The ammonium salt was crystallized from an NH_4F–H_2GeF_6 solution at 85° rather than at lower temperatures with the expectation that the octahedral form would be formed in preference to the more usual hexagonal form.[2,8] The potassium and rubidium salts were from Sylvania Electric Products, Inc., Towanda, Pennsylvania, and were used as received.

Raman displacements from the 4358 Å. Hg line were obtained photoelectrically using a Cary Model 81 spectrophotometer. Although fresh fluorogermanic acid solutions, which had been prepared in polyethylene containers, seemed clear when they were first put in the glass Raman sample tubes, colloidal particles soon formed. This unavoidably resulted in high noise levels and a strong background intensity. The determination of depolarization factors, especially for the two weaker lines, was therefore precluded.

Infrared spectra from 2000 to 250 cm.$^{-1}$ were recorded with a Perkin-Elmer Model 421 spectrophotometer and samples were pressed in CsI disks. The absence of cleavage planes and the softness of cesium iodide made it difficult to reduce the particle size except by prolonged grinding with an agate mortar and pestle. The spectrum of $BaGeF_6$ was also recorded on a sample prepared as a Nujol mull pressed between polyethylene plates.

Results and Discussion

Selection Rules and Raman Spectra.—If the GeF_6^{2-} species belongs to the O_h point group, the irreducible representation of internal motion is

$$\Gamma = a_{1g}(R,p) + e_g(R,dp) + 2f_{1u}(IR) + f_{2g}(R,dp) + f_{2u}(\text{inactive})$$

whereas for D_{4h} symmetry[9]

$$\Gamma = 2a_{1g}(R,p) + 2a_{2u}(IR) + b_{1g}(R,dp) + b_{2g}(R,dp) + b_{2u}(\text{inactive}) + e_g(R,dp) + 3e_u(IR)$$

Raman results which appear in Table I and Fig. 1 show quite clearly that the most probable structure for the

TABLE I

RAMAN SPECTRUM OF THE GeF_6^{2-} ION

Frequency, cm.$^{-1}$	627	454	318
Assignments	ν_1 (a_{1g})	ν_2 (e_g)	ν_5 (f_{2g})

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[1] Summer visitor at Bell Telephone Laboratories, Inc., 1963.

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