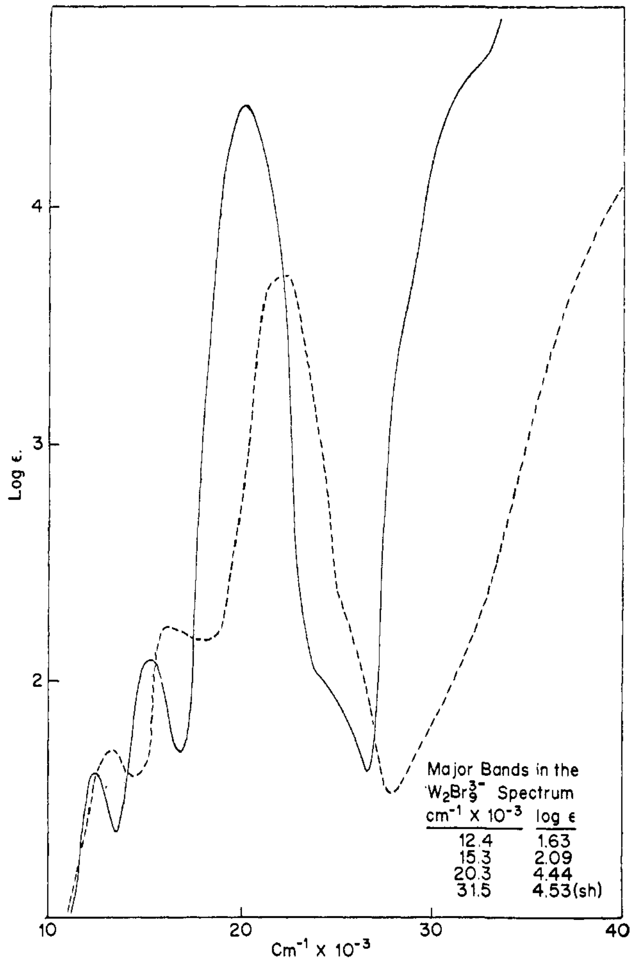
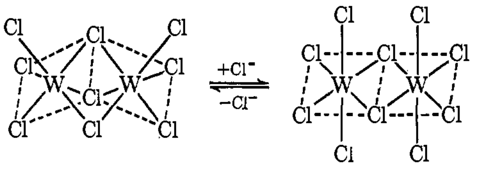


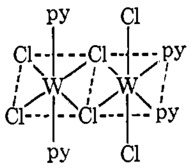
Figure 2. Absorption spectra of $K_3W_2Br_9$ (———) in ~0.1 *M* HBr solution and $K_3W_2Cl_9$ (- - - -) in water.

in their words, two bridge bonds probably would have to break in order to permit the necessary internal rearrangement. Alternatively, the equivalence could result from a dynamic equilibrium with an intermediate such as $W_3Cl_{14}^{5-}$ or WCl_5^{2-} (actually $W(H_2O)Cl_5^{2-}$). This mechanism was favored because of their observation that changes in the spectrum of $W_2Cl_9^{3-}$ were not usually accompanied by equivalent losses in the reducing strength of the solution, which ordinarily would be evidence for another species of W(III). König,[6] however, has shown that $K_5W_3Cl_{14}$ and possibly $K_2W(H_2O)Cl_5$ are mixtures of $K_3W_2Cl_9$ and $K_2W(OH)Cl_5$, an intensely red compound. He has also indicated that dramatic changes in the spectrum of $W_2Cl_9^{3-}$ can occur due to the formation of only small quantities of $W(OH)Cl_5^{2-}$ from the decomposition of $W_2Cl_9^{3-}$. Thus, major spectroscopic changes would not be accompanied by a major change in the reducing strength of a solution.

In the light of these observations, we can find no present reason to discard the first mechanism discussed by Hawkins and Garner, particularly since intramolecular exchange and exchange with free halide ion can be accomplished by breaking *only one* of three bridge bonds



wherein Cl^- is used for simplicity as the free halide ion.[7] The existence of a ten-coordinated dinuclear ion seems reasonable in view of the preparation[8] of $W_2Cl_6(py)_4$ and the subsequent X-ray examination[9] which showed the molecular structure to be



Similar steps with Br^- would also account for the formation of $W_2Br_9^{3-}$.

While this mechanism has many attractive aspects, we do not presently rule out the alternative mechanism: the existence of a dynamic equilibrium between $W_2Cl_9^{3-}$ and some other unknown W(III) species.

Acknowledgment. This research was supported by the National Science Foundation under Grant No. GP-8519. We also acknowledge many helpful discussions with R. Saillant.

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(6) E. König, *Inorg. Chem.*, 2, 1238 (1963). König has suggested that the variety of red "W(III)" solutions, which have been reported in the past 40 years, are due to traces of his $W(OH)Cl_5^{2-}$ ion. Nevertheless, it is not clear in our minds that the case is completely solved.

(7) We do not mean to infer that another intermediate does not precede the ten-coordinate species. However, since the order of the reaction with respect to Cl^-, as well as the relative rates of the two exchange processes, is presently unknown, we prefer to indicate simply that exchange could occur by breaking only one bond. This requires that intramolecular exchange occurs at least as rapidly as exchange with free Cl^-, in agreement with the observed kinetic results.[2]

(8) R. Saillant, J. L. Hayden, and R. A. D. Wentworth, *Inorg. Chem.*, 6, 1497 (1967).

(9) R. B. Jackson and W. E. Streib, to be published.

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Received June 10, 1968

The Electron Spin Resonance Spectrum of $(FeF_6)^{3-}$ in Aqueous Solutions

Sir:

Relatively little work was done on the esr of Fe^{3+} ions in solutions.[1-3] This is mainly due to the large width of the resonance line, often exceeding 1000 G, which is normally observed. Consequently the signals are quite weak, and no hyperfine structure is observed from either the ^{57}Fe isotope (~2% atom) or from ligand nuclei in the coordination spheres. Information on the identity and properties of the species in the solution are extricated from such hyperfine structure.

In the present work we wish to indicate a case where a very narrow esr signal due to an Fe^{3+} complex in solution has been observed: when successively increasing amounts of NH_4F were added to an aqueous solution of $Fe(ClO_4)_3$ initially at pH 2, large variations in the intensity and width as well as the shape of the esr signal were observed.[4] When the $[F^-]/[Fe^{3+}]$ ratio exceeded 6, a

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(1) B. R. McGarvey, *J. Phys. Chem.*, 61, 1232 (1957).

(2) A. H. Zeltman and L. O. Morgan, *ibid.*, 70, 2807 (1966).

(3) G. R. Hertel and H. M. Clark, *ibid.*, 65, 1930 (1961).

(4) These effects are similar to those observed in solutions of Mn^{2+} in methanol (H. Levanon and Z. Luz, *J. Chem. Phys.*, in press) and will be described in more detail elsewhere.

new signal appeared, which consisted of seven equally spaced lines with binomial intensities. The splitting is evidently due to fluorine hyperfine interaction in the ferrihexafluoride ion $(FeF_6)^{3-}$. Evidence for this complex in aqueous solutions was previously obtained from solvent extraction[5] data. Our esr results substantiate this evidence and provide a more direct means for a quantitative study of its properties.

Typical spectra, recorded at room temperature, corresponding to solutions containing 0.04 M $Fe(ClO_4)_3$ and varying amounts of NH_4F are shown in Figure 1. By comparison with simulated spectra the fluorine hyperfine splitting was found to be 23.0 G. This is very close to the fluorine isotropic hyperfine interaction in $(FeF_6)^{3-}$ observed[6] in the solids $KMgF_3$ (25.7 G) and $KCdF_3$ (24.3 G). No satellites due to ^{57}Fe were observed. The line width (peak-to-peak separation of the derivative curve) of a single hyperfine component was about 11 G and the g value was 2.0036. The esr spectra of $(FeF_6)^{3-}$ were sensitive to pH: at high NH_4F concentration (pH 8–9), well-resolved lines were observed, but when the pH was less than 5 the $(FeF_6)^{3-}$ resonance disappeared.

The spin Hamiltonian for the Fe^{3+} sextet in a nearly octathedral field is[7] (assuming only a small tetragonal distortion)

$$\mathcal{H} = g\beta HS + D\left(S_z^2 - \frac{35}{12}\right) + \frac{1}{6}a\left(S_x^4 + S_y^4 + S_z^4 - \frac{707}{16}\right)$$

In solutions the first term gives the position of the esr line which is normally close to that of the free electron, while the last two terms determine the line width. McGarvey[1] has shown that for Fe^{3+} the quartic term, a, contributes very little to the electronic relaxation, and the main effect on the line width arises from the modulation of the zero-field splitting parameter D. The relatively small line width observed in $(FeF_6)^{3-}$ is of the same order as that often found in Mn^{2+} complexes.[4,8,9] For the latter case it was proposed[10] that the electronic relaxation occurs by distortion of the symmetric structure of the complex *via* collisions with other molecules. If the same mechanism is also dominant in $(FeF_6)^{3-}$, an upper limit for the root-mean-square fluctuation of the zero-field parameter, D, may be calculated from the equation[4]

$$1/T_2 = 6.4D^2\tau$$

where T_2 is the transverse electronic relaxation time and τ is the mean lifetime between collisions ($\sim 2 \times 10^{-12}$ sec).[10] Substituting the experimental value for $1/T_2$ gives $\sqrt{\overline{D^2}} = 0.02\ \text{cm}^{-1}$.

The large width of the esr resonance of Fe^{3+} hydrate is partly due to dimerization[11] but may also be caused by large deviations from cubic symmetry of the monomeric species. This will result in a significant static zero-field splitting interaction which provides an effective relaxation mechanism.[1] This deformation can be caused by the formation of both inner- and outer-sphere ion-pair complexes or by the acid dissociation of the hydrate, thus forming species of the type $[Fe(OH)(H_2O)_5]^{2+}$. All three possibilities are quite likely for the Fe^{3+} hydrate. The situation with $(FeF_6)^{3-}$ is, however, quite different; here there is no strong tendency to complex with other ions, and the geometry of the complex is more symmetric and can better resist deformation by collisions with neighboring molecules. It is quite likely that other Fe^{3+} complexes having high symmetry and tightly bound ligands will also exhibit narrow esr lines in solutions.

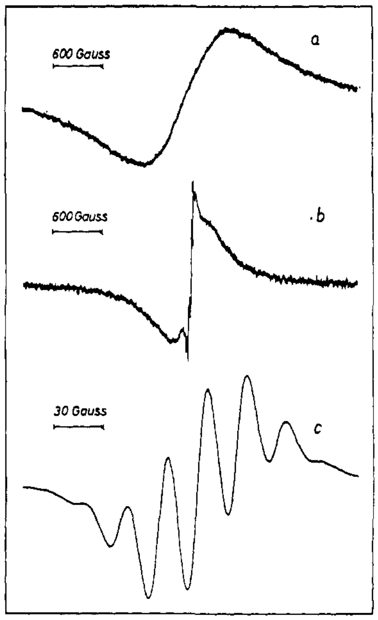

Figure 1. Fe^{3+} esr spectra in aqueous solutions. Spectrum a is for a 0.04 M $Fe(ClO_4)_3$ solution. Spectra b and c are for solutions containing the same amounts of $Fe(ClO_4)_3$ as in solution a and 0.36 and 2.0 M NH_4F, respectively. Note the different sweep width of spectrum c; at a greater sweep width of this spectrum no broad line signal was observed.

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Received July 5, 1968

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(5) I. A. Shevchuk, N. A. Skripnik, and V. I. Martsobha, *Zh. Anal. Khim.*, 22, 6, 891 (1967); see also R. E. Connick and W. H. McVey, *J. Am. Chem. Soc.*, 71, 3182 (1949).

(6) T. P. P. Hall, W. Hayes, R. W. H. Stevenson, and J. Wilkens, *J. Chem. Phys.*, **38**, 1977 (1963).

(7) B. Bleaney and K. W. H. Stevens, *Rept. Progr. Phys.*, **16**, 108 (1953).

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(10) N. Bloembergen and L. O. Morgan, *ibid.*, **34**, 842 (1961).

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Mechanism of the Intramolecular Reorientation Process in σ-Cyclopentadienylmetal Complexes

Sir:

The facile rearrangement of metal–carbon bonds in σ-cyclopentadienylmetal complexes, which manifests intself in the nmr equivalence of cyclopentadienyl protons in these substances, has heretofore been regarded as proceeding through either a dipolar metal–