8 *M* HCl (aq), glass membrane, ammonia solution (varying NH_4^+ concentration during "titration"), asbestos-plugged capillary junction, ammonia solution (0.001 *M* $AgNO_3$, *ca.* 0.2 *M* KNO_3), Ag. A plot of emf *vs.* weight of added ammonium bromide for a "titration" of a KOH suspension is shown in Figure 3. The sharp inflection point corresponds to the point where the cloudiness due to KOH just disappeared, and the titer agrees within experimental error with that calculated from the weight of potassium converted to KOH. A curve of essentially the same shape was obtained for the titration of a solution of potassium amide with ammonium bromide. When a mixture of potassium hydroxide and potassium amide[9] was titrated, two distinct inflection points were observed, corresponding to the two different end points.

In view of the simplicity of the apparatus, the rapidity with which measurements can be made (electrode equilibrium was usually established within 20 sec), and the results described above, the use of cationic glass electrodes appears to be a promising method for measuring pH values in liquid ammonia. Clearly the method will facilitate end-point determination for acid–base titrations in ammonia. It is hoped that it will permit the determination of absolute p*K* values for acids in ammonia. It will be interesting to apply cationic glass electrodes to the determination of alkali metal ion concentrations (for example, in metal–ammonia solutions).

Acknowledgment. This work was supported by the U. S. Atomic Energy Commission.

(9) Prepared by adding a small amount of water to a potassium amide solution.

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The Synthesis of the $W_2Br_9^{3-}$ Ion

Sir:

Although $K_3W_2Br_9$ was described by Young in 1932,[1] no further mention of this compound or its reactions has appeared. Our own efforts to duplicate the synthesis briefly described by Young have resulted in insignificant yields of the desired compound. An alternate synthesis of $W_2Br_9^{3-}$ was provided by a consideration of the kinetic results of Hawkins and Garner,[2] who examined the exchange of radiochloride ion with $W_2Cl_9^{3-}$ in acid solution. Although the chlorine atoms in the dinuclear ion are not structurally equivalent, they were found to be kinetically equivalent. Guided by these results, we examined the simple halogen exchange reaction

$$W_2Cl_9^{3-} + 9Br^- \rightleftharpoons W_2Br_9^{3-} + 9Cl^-$$

in acid solution.

$K_3W_2Cl_9$ was dissolved in a saturated HBr solution at 0°. Samples were withdrawn periodically and insoluble $Rb_3W_2Cl_{9-x}Br_x$ was precipitated by the addition of RbBr. Equilibrium was attained after about 3 hr, whereupon the average composition[3] was $Rb_3W_2Cl_{0.9}Br_{8.1}$, as shown in Figure 1. However, when a moderate flow of gaseous HBr was maintained throughout the course of the reaction, complete exchange occurred within 24 hr. For synthetic purposes the reaction was conveniently performed at room temperature for an equal length of time. *Anal.* Calcd for $Rb_3W_2Br_9$: W, 27.37; Br, 53.54. Found: W, 27.6, 27.4; Br, 53.9, 53.7. Nearly quantitative yields were achieved. The magnetic moment was found to be 0.4 BM, which is identical with the magnetic moment of $Cs_3W_2Cl_9$. The paramagnetism of the latter was recently found[4] to be completely independent of temperature.

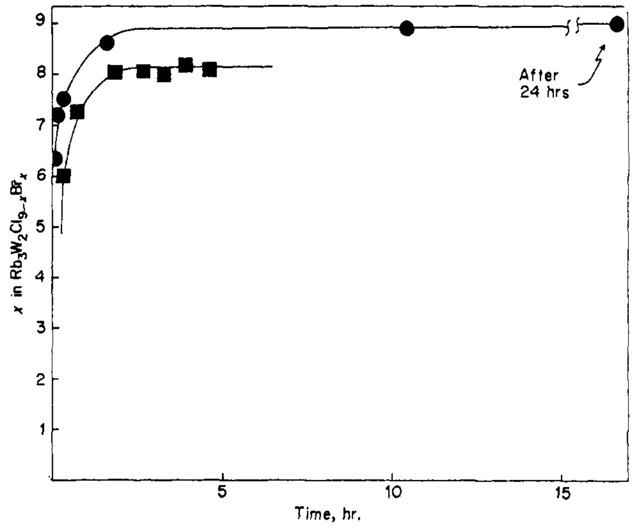

Figure 1. Rates of formation of $W_2Cl_{9-x}Br_x^{3-}$: ■, in a saturated HBr solution, and ●, in a saturated HBr solution with a continuous, moderate flow of gaseous HBr, at 0°.

$K_3W_2Br_9$ can be prepared as brown, hexagonal plates by similar methods but with lower yields due to its higher solubility. In agreement with Young,[1] we find that aqueous solutions of this compound, in the absence of air, are brown when concentrated, but appear orange to pink upon dilution. In the presence of air aqueous solutions are almost immediately decomposed. The spectrum of the compound in dilute HBr solution (Figure 2) is similar to that of $K_3W_2Cl_9$. The lattice constants for the hexagonal unit cell were found from X-ray powder photographs (Cu Kα radiation) to be $a = 7.6$ Å and $c = 17.5$ Å. For $K_3W_2Cl_9$,[5] $a = 7.17$ Å and $c = 16.25$ Å.

A mechanism for the formation of $W_2Br_9^{3-}$ from $W_2Cl_9^{3-}$ remains in some doubt. To account for the equivalent exchange of the chlorine atoms in $W_2Cl_9^{3-}$, Hawkins and Garner[2] considered two possibilities. In the first, the kinetic equivalence could result from an intramolecular exchange of the chlorine atoms in the dinuclear ion concurrent with the exchange with free chloride ion. This possibility was discounted because,

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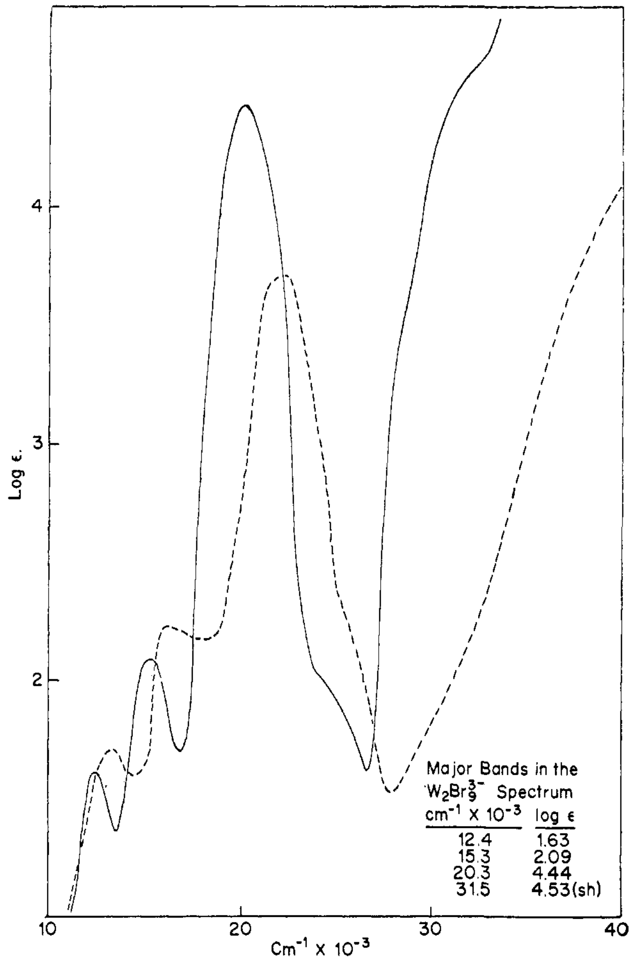
(1) R. C. Young, *J. Am. Chem. Soc.*, **54**, 4515 (1932). Young describes his synthesis as similar to that used for $K_3W_2Cl_9$, *i.e.*, the reduction of W(VI) with Sn in HCl solutions.

(2) G. L. Hawkins and C. S. Garner, *ibid.*, **80**, 2946 (1958). The order of the reaction with respect to Cl^- was not obtained because of the high concentrations of HCl present in solution.

(3) The samples were decomposed in dilute basic peroxide solutions. Following acidification, Cl^- and Br^- were determined potentiometrically with $AgNO_3$. From synthetic mixtures of these ions, it was determined that both ions could be determined simultaneously up to compositions corresponding to $W_2Cl_{0.5}Br_{8.5}^{3-}$. Beyond this composition, Cl^- could only be obtained by difference.

(4) R. Saillant and R. A. D. Wentworth, *Inorg. Chem.*, **7**, 1606 (1968).

(5) W. H. Watson and J. Waser, *Acta Cryst.*, **11**, 689 (1958).

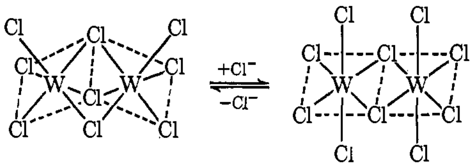


cm^{-1} x 10^{-3}	log ε
12.4	1.63
15.3	2.09
20.3	4.44
31.5	4.53(sh)

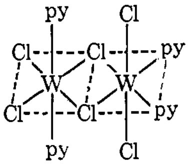
Figure 2. Absorption spectra of $K_3W_2Br_9$ (———) in ~0.1 *M* HBr solution and $K_3W_2Cl_9$ (– – – –) in water.

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

Sir:

Relatively little work was done on the esr of Fe³⁺ 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 Fe³⁺ 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 Mn²⁺ in methanol (H. Levanon and Z. Luz, *J. Chem. Phys.*, in press) and will be described in more detail elsewhere.