the octahedral chloroaquo complexes of Ru(III).[15] Since the isomerization of $Pd(NH_3)_2Cl_2$ is rather fast[11] and relatively long times are required to establish solubility equilibrium, the aqueous solute and the $Pd(NH_3)_2Cl(H_2O)^+$ in the solubility experiments can be expected to be the equilibrium mixture of isomers, which could conceivably contain appreciable quantities of the *cis* forms. A similar argument applies to the aquation[5] of $PdCl_3(H_2O)^-$ because of the isomers of $PdCl_2(H_2O)_2$.

Muromtsev,[16] in studies at 10°, obtained a nearly constant solubility for $Pd(NH_3)_2Cl_2$, averaging 2.1×10^{-4} *M*, in HCl solutions ranging from 1 to 5%. Under these conditions both the base hydrolysis and aquation will be completely repressed, and the solubility measures x directly. Because of the above mentioned uncertainty regarding isomeric composition, however, it does not appear to be justified at this time to combine this value with that of the present work to obtain an enthalpy of solution of the neutral molecule.

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Preparation of Two Periodato Complexes of Iron(III)

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Iron(III) forms two complexes with periodate which are analogous to the corresponding cobalt(III) complexes. In acid solution the compound $H_3[Fe_4I_3O_{24}H_{12}]$ is formed, while in excess base, the compound $Na_5[Fe(H_2IO_6)_2(OH)_2]$ is formed. The latter is converted to the former on acidification with sulfuric acid. The magnetic susceptibilities of both indicate high spin d^5 electronic configurations of the iron(III) atoms.

Previous workers[1–8] have prepared anionic periodato complexes of Mn(IV), Co(III), Ni(IV), Cu(III), Ag(III), and Au(III). These complexes appear to fall readily into two classes, those formed in acidic solution and those formed in basic solution. The latter have metal-to-iodine ratios less than one and are clearly simple complexes of a conventional type. The former, on the other hand, have metal-to-iodine ratios equal to or greater than unity and appear to be condensed forms of simple complexes. In one case, *e.g.*, the complex of Co(III), the species formed in basic solution has been shown to be convertible to that formed in acid, the conversion being effected by a decrease in pH.[7]

Two analogous complexes of Fe(III) have now been prepared, and this paper reports their method of preparation and some of their properties.

Experimental

Preparation of the Complex Species Having an Fe/I Ratio of 4:3.—$Fe(NO_3)_3 \cdot 9H_2O$ ($^1/_{50}$ mole) was dissolved in 100 ml. of water, and $NaIO_4$ ($^1/_{50}$ mole) was dissolved in 100 ml. of water to which a few ml. of concentrated HNO_3 had been added. The solutions were heated to 80° and mixed slowly with stirring. A very insoluble yellow-ochre precipitate formed which was filtered, washed with three 50-ml. samples of 0.02 *M* HNO_3, then with absolute ethanol, and air dried. The precipitate set to a brown glass-like solid which was pulverized and allowed to stand over $CaCl_2$ in a desiccator for 24 hr. before being analyzed. *Anal.* Calcd. for $H_3[Fe_4I_3O_{24}H_{12}]$: Fe, 22.2; I, 37.9; equiv. wt., 35.89. Found: Fe, 21.3; I, 37.0; equiv. wt., 36.02; ratio Fe/I = 1.31.

Preparation of a Complex Species Having an Fe/I Ratio of 1:2.—$NaIO_4$ (0.04 mole) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.015 mole) were mixed as above. The resultant yellow viscous suspension was poured slowly with stirring into 150 ml. of a 10% NaOH solution; the color of the precipitate changed from ochre to a light yellow-green. The mother liquor was decanted and the complex was washed with small quantities of water. The air-dried precipitate set to a pale green

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(6) L. Malatesta, *Gazz. chim. ital.*, **71**, 467 (1941).

(7) C. J. Nyman and R. A. Plane, *J. Am. Chem. Soc.*, **83**, 2617 (1961).

(8) P. Ray and B. Sarma, *J. Indian Chem. Soc.*, **25**, 205 (1948).

"glass" which was pulverized and dried for 24 hr. in a desiccator over $CaCl_2$. After drying at 110° to constant weight, the sample was analyzed. *Anal.* Calcd. for $Na_5[Fe(H_2IO_6)_2(OH)_2]$: Fe, 8.5; I, 38.8; Na, 17.6; equiv. wt., 38.5. Found: Fe, 8.0; I, 38.3; Na, 17.3; equiv. wt., 38.4; ratio of I/Fe = 2.10.

Equivalent Weight.—To a 0.1-g. sample of the complex, 2 g. of solid KI and 10 ml. of 1 *N* H_2SO_4 were added. The liberated I_2 was titrated after 12 hr. with 0.1 *N* $Na_2S_2O_3$ to a starch end point. An atmosphere of CO_2 minimized air oxidation of I_2.

Iodine.—Samples were dissolved in 5 ml. of 1 *M* Na_2SO_3 and 25 ml. of 1 *N* H_2SO_4, and after complete dissolution the excess SO_2 was removed by gentle boiling for 5 min. Iodide then was determined gravimetrically as AgI.

Sodium.—A weighed sample of complex was suspended in sulfur dioxide saturated water, and after complete dissolution the excess sulfur dioxide was removed by boiling. The solution was diluted to known volume and sodium was determined with a flame spectrophotometer.

Iron.—The mother liquors and washings remaining after the filtration of the AgI above were collected, the pH was adjusted with an acetic acid–acetate buffer, and the solution was diluted to known volume. The iron was determined spectrophotometrically using the standard *o*-phenanthroline procedure.

Results

The compound containing an Fe/I ratio of 1.31 (4/3) was prepared using a method essentially the same as that used by Malaprade[5] for the preparation of the corresponding cobalt(III) complexes. Attempts to prepare compounds with other Fe/I ratios by varying the relative amounts of iron and periodate in the starting solutions met with failure.

From the analytical data obtained, one can estimate both the empirical formula and the empirical formula weight for the compound. The percentage of iron gives a formula weight of 262 per iron atom. Similarly, the formula weight per iodine atom is 343. The Fe/I ratio of 4/3 (1.33) is closest to the observed 1.31, and therefore it is assumed that the simplest empirical formula contains four iron atoms and three iodine atoms. Thus the values of the formula weight obtained are $262 \times 4 = 1048$ and $343 \times 3 = 1029$. Further, after the iodide reduction of four iron(III) and three periodate ions, 28 equivalents of thiosulfate would be required to titrate the liberated iodine to iodide ion. From the observed oxidation–reduction equivalent weight of 36.03, the simplest empirical formula is 36.03×28, or 1009. Thus the values from three separate experimental procedures agree within 4%. A formulation analogous to that proposed for the corresponding cobalt complex would be $H_3[Fe_4I_3O_{24}H_{12}]$, and the formula weight of this compound is 1005, in close agreement with the observed values. This formula hence is proposed for this complex, and as a possible structure, that proposed by Evans[9] for $(NH_4)_6[TeMo_6O_{24}]\cdot 7H_2O$, or one similar to it, would account for the observed properties.

The magnetic susceptibility of the complex was determined by the Gouy method and a value of 4.3 ± 0.1 B.M. (corrected for diamagnetism) for μ_{eff} was obtained. Such a value for μ_{eff} can be taken to indicate an Fe(IV) complex, which would have a theoretical μ_{eff} of 4.9 B.M. However, the analytical determination of the oxidation–reduction equivalent weight would indicate Fe(III). A value of μ_{eff} corresponding to the theoretical spin-only value is not always achieved for Fe(III). Solutions of hydrolyzed Fe(III) compounds often give rise to an apparent μ_{eff} of about 4 B.M. This has been attributed to the dimer $Fe_2(OH)_2^{4+}$, which is claimed to be diamagnetic.[10] Other forms of hydrated ferric oxide and solid solutions of ferric oxide have been observed to give rise to low values of μ_{eff}. In the present case there are almost certainly oxygen bridges between iron atoms analogous to those in the dimer and in ferric oxide. Furthermore, the complex is not magnetically dilute. Both effects would lead to a low value for the effective magnetic moment.

The compound having a ratio of Fe/I of 1:2 was found to be produced when ratios of iron to periodate of 1:1 to 1:3 were mixed. At the 1:1 ratio, there was a small amount of excess iron and at the 1:3 ratio, there was a small amount of excess periodate. From the analysis for Fe, I, and oxidizing power, the formula for the complex was best formulated as $Na_5[Fe(H_2IO_6)_2(OH)_2]$; theoretical formula weight 655; experimental formula weight 653. When the salt was dried at less than 110°, varying amounts of water appeared to be present in the solid.

A determination of the magnetic susceptibility of the solid $Na_5[Fe(H_2IO_6)_2(OH)_2]$ by the Gouy method gave a value of 5.9 ± 0.2 B.M., which is very close to the "spin-only" value of 5.91 corresponding to five unpaired electrons of iron(III). In this complex the iron probably is octahedrally bound to two hydroxide ions and to two bidentate periodate ions.

To further demonstrate the similarity between the cobalt(III) and iron(III) complexes it was

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[9] H. T. Evans, *J. Am. Chem. Soc.*, **70**, 1292 (1948).

[10] L. Mulay and P. W. Selwood, *ibid.*, **77**, 2693 (1955).

found possible to convert $Na_5[Fe(H_2IO_6)_2(OH)_2]$ to $H_3[Fe_4I_3O_{24}H_{12}]$. Qualitatively, it was shown that addition of acid to the 1:2 complex caused it to change color from yellow-green to the characteristic ochre of the 4:3 complex. The mother liquor gave a white precipitate with tetraphenylarsonium chloride, indicative of free periodate. A semiquantitative experiment showed that the amount of periodate liberated on acidification of the 1:2 complex was in good agreement with that expected theoretically. Two 0.194-g. samples of the 1:2 complex were taken, acidified with 10 ml. of 1 *N* H_2SO_4, and allowed to stand for 24 hr. The 4:3 complex was filtered off, and to the filtrate (*ca.* 500 ml.) at about 80° was added 35 g. of NaCl, making the solution about 1.5 *M* with respect to the latter. A 50% excess of tetraphenylarsonium chloride solution (20 ml. of a solution of 1 g. in 100 ml.) was added slowly with stirring. The precipitate was filtered (after the solution had stood overnight) and dried at 110°. The amount of IO_4^- found in both instances was 0.073 g., and the amount which theoretically would be liberated if the reaction proceeded stoichiometrically was 0.071 g. The discrepancy is well within experimental error and the results indicate conversion according to the equation

$$4Na_5[Fe(H_2IO_6)_2(OH)_2] + 15H^+ \longrightarrow H_3[Fe_4I_3O_{24}H_{12}] + 5IO_4^- + 20Na^+ + 12H_2O$$

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The Preparation and Properties of Some Oxovanadium(IV) Complexes

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The preparation of the complexes $VO(ClO_4)_2 \cdot 5C_5H_5NO$, $VOCl_2 \cdot 2(C_6H_5)_3PO$, $VO(ClO_4)_2 \cdot 4(C_6H_5)_3PO$, $VOCl_2 \cdot 4(C_6H_5)_3AsO$, $VO(ClO_4)_2 \cdot 4(C_6H_5)_3AsO$, and $VOCl_2 \cdot 3(CH_3)_2SO$ are reported. Arguments for structural assumptions are based upon measurements of their visible and infrared spectra, magnetic moments, and conductances in polar solvents.

Introduction

In an extension of earlier work with oxygen donor species[1-3] we attempted to prepare some addition compounds of vanadium(III). In each case the product was a complex of VO^{2+} ion, when atmospheric oxygen was not excluded during the syntheses. While the preparative work with VO^{2+} complexes was going forward, Ballhausen and Gray[4] reported a detailed analysis of the electronic spectrum of the vanadyl ion based on a molecular orbital model, in contrast to Jørgensen's[5] analysis based on simple tetragonal distortion of a cubic crystal field.

Experimental

Reagents.—Reagent grade chemicals were used without further purification except in the cases noted.

Methylene chloride, used as a solvent for spectral measurements, was dried over calcium chloride and saturated with dry nitrogen.

Triphenylarsine oxide and triphenylphosphine oxide were prepared by similar procedures[6] from Eastman "White Label" triphenylarsine and triphenylphosphine, respectively. Pyridine N-oxide, obtained from K and K Chemical Company, was purified by vacuum distillation and stored in a moisture-free container.

Vanadium(III) chloride 6-hydrate was a student preparation.[7]

Analyses.—The complexes were decomposed for vanadium analyses by digestion with a mixture of concentrated H_2SO_4, HNO_3, and $HClO_4$. The digested sample was diluted to volume, treated with 30% H_2O_2, allowed to

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