

product (the ΔS^\ddagger values for the reactions of the aqua-oxo complexes are considerably more negative than those for the corresponding hydroxo-oxo complexes).⁷ The present ΔH^\ddagger value also falls on the linear plot. The present ΔS^\ddagger value is clearly more negative than those for the *cis*-hydroxo-oxo complexes and closer to the values for the *cis*-aqua-oxo complexes (the difference in charges of the complexes has been taken into account).

The effect of D₂O may be explained at least qualitatively in terms of the weaker V-O(aqua) bond in D₂O. Table V clearly indicates that the oxidation rate decreases with a decrease in the strength of V-O(aqua) bond.

Concluding Remarks. The existence of the hydrogen bond between the coordinated water and the adjacent phosphonate arm in [VO(pida)(H₂O)]²⁻ has been predicted by the pK_{a2} value. Ligand substitution and outer-sphere oxidation reactions show characteristic features that are reasonably understood by the existence of hydrogen bonding. This work stresses the importance

of mutual ligand interaction on the reactivity of metal complexes.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 58430010) to K.S. from the Ministry of Education, Science and Culture of Japan. We are indebted to Dr. Y. Hasegawa, School of General Education, Tohoku University, for the use of the stopped-flow spectrophotometer. Useful suggestions on the pK_a values by Professor K. Sawada, Department of Chemistry, Niigata University, are gratefully acknowledged.

Supplementary Material Available: Figure 2 (dependence of k_{obsd} on the concentration of NaNCS for the ligand substitution reaction of [VO(pida)(H₂O)]²⁻ with NCS⁻ at $I = 0.1$ M (NaClO₄) and at pH 5.7 \pm 0.2 ([VO(pida)(H₂O)]²⁻ = 2.0×10^{-3} M)) and Figure 4 (dependence of k_{obsd} on the concentration of [VO(pida)(H₂O)]²⁻ for the oxidation of [VO(pida)(H₂O)]²⁻ with [IrCl₆]²⁻ (2.75×10^{-5} M) in aqueous solution at $I = 0.1$ M (NaClO₄) and pH 5.7 \pm 0.2) (2 pages). Ordering information is given on any current masthead page.

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Direct Synthesis of Hexafluoroferrates(III) and Reaction of Thiocyanate and Fluoride with Iron(III) and Hydrogen Peroxide as an Access to Fluoro(sulfato)ferrates(III)

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Received March 11, 1986

The reaction of iron(III) hydroxide with alkali-metal or ammonium fluoride and 48% hydrofluoric acid in the presence of hydrogen peroxide, followed by the addition of ethanol, directly gives alkali-metal or ammonium hexafluoroferrates(III), A₃FeF₆ (A = Na, K, or NH₄), in very high yields. An investigation of the reaction of ammonium or potassium thiocyanate and 48% HF with iron(III) hydroxide in the presence of hydrogen peroxide has been carried out. Sulfate has been obtained as the oxidation product of SCN⁻, without involving reduction of iron(III) and providing an access to fluoro(sulfato)ferrates(III) of the types (NH₄)₂[Fe(SO₄)F₃] and K₃[Fe(SO₄)F₄]. Similar reactions with sulfates in lieu of thiocyanates, either in the presence of or in the absence of H₂O₂, do not afford fluoro(sulfato)ferrates(III), however. IR spectroscopy and laser Raman spectroscopy provide evidence for a chelated sulfate in each of the fluoro(sulfato)ferrates(III).

Introduction

The chemistry of fluoro and mixed-fluoro complexes of transition metals continues to attract much attention and to produce new and exciting results.¹⁻⁴ Although much of the very recent activity in this area is devoted to studies related to kinetics³ and magnetic properties,^{1,4} a great deal of effort is required for the search for direct synthetic procedures and for synthesis of novel fluoro and mixed-fluoro complex species. These are the prerequisites for an heuristic approach in this field of chemistry. Importance of such compounds as insulators and semiconductors have been emphasized in the literature,⁵ and pentafluoroferrates(III) have shown very interesting magnetic properties.¹

In some of our recent publications we have dealt with the synthesis and structural assessment of fluoronickelates(II),⁶ fluoromanganates(III),^{7,8} and mixed-fluoromanganates(III).^{2,9}

We have decided to extend our work to iron analogues. To the best of our knowledge, within the context of fluoroferrates(III), there exists no direct and simple method for the synthesis of hexafluoroferrates(III), FeF₆³⁻, thus limiting their accessibility. Moreover, mixed-fluoroferrates(III), for instance fluoro(sulfato)ferrates(III), have no reported existence.

The subject of this paper is the direct synthesis of alkali-metal and ammonium hexafluoroferrates(III), A₃FeF₆ (A = Na, K, or NH₄), and an account of the reaction of thiocyanate and hydrofluoric acid with iron(III) in the presence of hydrogen peroxide, with the latter leading to the first synthesis of fluoro(sulfato)ferrates(III).

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer. The laser Raman (IR) spectra were recorded on a SPEX Ramalog Model 1403 spectrometer. The 4880-Å laser line from a Spectra-Physics Model 165 argon laser was used as the excitation source. The light scattered at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube followed by a photon-count processing system. The spectra were recorded at ambient temperatures by making pressed pellets of the compounds. Magnetic susceptibilities were measured by the Gouy method, using Hg[Co(NCS)₄] as the calibrant.

Synthesis of Alkali-Metal and Ammonium Hexafluoroferrates(III), A₃FeF₆ (A = Na, K, or NH₄). Anhydrous iron(III) chloride (1.0 g, 6.2 mmol) was dissolved in water (5 cm³) with gentle warming. Ammonium hydroxide solution (sp gr 0.9, 7 cm³, excess) was added slowly with continuous stirring. The mixture was heated on a steam bath for 15 min,

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and the precipitate of iron(III) hydroxide was then filtered off and washed with water until free from chloride.

The moist iron(III) hydroxide, alkali-metal or ammonium fluoride, AF (36.9 mmol), and 30% hydrogen peroxide (12 cm³, 105.7 mmol) were placed in a polyethylene beaker provided with a polyethylene cover. An amount of 1.3 cm³ (31.2 mmol) of 48% hydrofluoric acid was added dropwise with stirring to obtain a clear solution. The solution was stirred magnetically for a further period of ca. 15 min. Addition of about 20 cm³ of ethanol to the above solution precipitated very light yellowish white alkali-metal or ammonium hexafluoroferrate(III), A₃FeF₆. The compound was separated by filtration, washed three to four times with ethanol, and finally dried in vacuo over P₄O₁₀. The yields of Na₃FeF₆, K₃FeF₆, and (NH₄)₃FeF₆ were 1.1 g (75%), 1.4 g (79%), and 1 g (72%), respectively. Anal. Calcd for Na₃FeF₆: Na, 28.89; Fe, 23.38; F, 47.73. Found: Na, 28.55; Fe, 23.47; F, 47.91. Estimated oxidation state of Fe: 2.9. μ_{eff} : 5.8 μ_{B} . IR (cm⁻¹): 480 s ($\nu(\text{Fe-F})$), 292 m ($\delta(\text{F-Fe-F})$). Anal. Calcd for K₃FeF₆: K, 40.85; Fe, 19.45; F, 39.7. Found: K, 40.48; Fe, 19.87; F, 40.1. Estimated oxidation state of Fe: 3. μ_{eff} : 5.9 μ_{B} . IR (cm⁻¹): 475 s ($\nu(\text{Fe-F})$), 290 m ($\delta(\text{F-Fe-F})$). Anal. Calcd for (NH₄)₃FeF₆: N, 18.76; Fe, 24.93; F, 50.89. Found: N, 18.91; Fe, 25.22; F, 51.45. Estimated oxidation state of Fe: 3. μ_{eff} : 5.8 μ_{B} . IR (cm⁻¹): 497 s ($\nu(\text{Fe-F})$), 290 m ($\delta(\text{F-Fe-F})$), 3160 m, 3045 s, and 1400 s (ν_3 , ν_1 , and ν_2 modes of NH₄⁺).

Reactions of ASCN (A = K or NH₄) with Iron(III) Hydroxide, Aqueous HF, and Hydrogen Peroxide. Iron(III) hydroxide was prepared from 1.0 g of anhydrous iron(III) chloride in a similar way as described above.

The moist iron(III) hydroxide and solid potassium or ammonium thiocyanate, ASCN (12.4 mmol), were mixed thoroughly in a polyethylene beaker. To this was slowly added 13 cm³ (114.6 mmol) of 30% hydrogen peroxide with occasional stirring. Stirring was continued until effervescence ceased to appear. An amount of 1.4 cm³ (33.6 mmol) of 48% hydrofluoric acid was added dropwise to obtain a clear solution that was stirred magnetically for ca. 15 min followed by the addition of 25 cm³ of ethanol to afford a grayish white oily mass. The oily mass was separated by decantation and solidified by repeated treatment with ethanol and scratching for about 20 min. The product was isolated and dried in a manner similar to that described under the synthesis of A₃FeF₆. Elemental analyses were consistent with the formulations K₃[Fe(SO₄)F₄] and (NH₄)₂[Fe(SO₄)F₃] for the products of reactions with KSCN and NH₄SCN, respectively. The yield of K₃[Fe(SO₄)F₄] was 1 g (47%), and that of (NH₄)₂[Fe(SO₄)F₃] was 0.7 g (47%). Anal. Calcd for K₃[Fe(SO₄)F₄]: K, 33.98; Fe, 16.18; SO₄, 27.83; F, 33.02. Found: K, 33.58; Fe, 16.51; SO₄, 28.21; F, 33.22. Estimated oxidation state of Fe: 3. μ_{eff} : 5.7 μ_{B} . IR (cm⁻¹): 980 m (ν_1), 451 m (ν_2), 1225 s, 1131 s, 1020 s (ν_3), 669 m, 611 s, 599 s (ν_4), 490 s ($\nu(\text{Fe-F})$). Raman (cm⁻¹): 970 (ν_1), 450 (ν_2), 1220, 1130, 1020 (ν_3), 670, 610, 600 (ν_4) (ν_1 - ν_4 are referring to SO₄²⁻ modes). Anal. Calcd for (NH₄)₂[Fe(SO₄)F₃]: N, 11.44; Fe, 22.79; SO₄, 39.2; F, 46.53. Found: N, 11.51; Fe, 22.83; SO₄, 39.42; F, 46.85. Estimated oxidation state of Fe: 3. μ_{eff} : 5.6 μ_{B} . IR (cm⁻¹): 975 m (ν_1), 450 m (ν_2), 1223 s, 1130 s, 1010 s (ν_3), 670 m, 610 s, 600 s (ν_4), 495 s ($\nu(\text{Fe-F})$), 3160 m, 3040 s, 1400 s (ν_3 , ν_1 , and ν_2 modes of NH₄⁺). Raman (cm⁻¹): 980 (ν_1), 450 (ν_2), 1220, 1135, 1010 (ν_3), 675, 615, 600 (ν_4).

Results and Discussion

Direct Synthesis of Hexafluoroferrates(III), A₃FeF₆ (A = Na, K, or NH₄). The three principal types of binary fluoro complexes of iron(III), viz. FeF₆³⁻, FeF₅²⁻, and FeF₄⁻, are documented in the literature, of which the pentafluoroferrate(III) species is most easily accessible.¹⁰ In the context of the present work, it is evident that no direct route to hexafluoroferrate(III) seems to be available. The recommended method¹¹ requires first the synthesis of the FeF₅²⁻ complex, which on treatment with molten alkali-metal hydrogen fluoride, AHF₂, yields the corresponding hexafluoroferrate(III), A₃FeF₆. It has now been possible for us to show that iron(III) hydroxide can be made to react with alkali-metal or ammonium fluoride, AF (A = Na, K, or NH₄), and aqueous hydrofluoric acid in the presence of an excess of hydrogen peroxide to afford directly alkali-metal or ammonium hexafluoroferrates(III), A₃FeF₆, in yields higher than those obtained by the earlier method.¹¹ An excess of 30% hydrogen peroxide (vide Experimental Section) was necessary as this also provided an appropriate medium for conducting the reactions. A similar volume maintained by using dilute hydrogen peroxide solutions

was found to be detrimental to the synthesis. The role of alkali-metal or ammonium fluoride, AF, was to provide counterions, A⁺, as well as to enhance the F⁻ ion concentration of the reaction medium, while that of hydrofluoric acid was to dissolve iron(III) hydroxide and also, of course, to supply fluoride ions. Strategically more important is the key role played by H₂O₂ in the successful synthesis of hexafluoroferrates(III). It is believed that pentafluoroferrate(III) is first formed, which coordinates with a peroxide (O₂²⁻) ligand, presumably to form an unstable peroxyfluoroferrate(III) intermediate. This unstable peroxy intermediate then reacts with F⁻ ions available in the solution, rupturing the iron-peroxide bond with concomitant formation of a new metal-fluoride bond, ultimately leading to the formation of the FeF₆³⁻ complex species. At present this interpretation is admittedly speculative; however, the fact that similar reactions in the absence of hydrogen peroxide, even in the presence of relatively higher concentrations of fluoride ions, yield only pentafluoroferrates(III) definitely lends support to the contention. Moreover, recently while working on some peroxyfluorometalates,¹² we observed that a peroxyfluorometalate complex could serve as a precursor for a binary fluoro-metalate species (cf. Ti(O₂)F₃³⁻ + F⁻ → TiF₆²⁻), providing thereby a sort of a rationale for the present synthesis. Because of the higher yields of products obtained by the new method, which is also easy to manipulate, this synthetic approach offers advantages over the method described in the literature.¹¹

The results of elemental analyses are consistent with the formula of the compounds. The chemically estimated oxidation state, accomplished by iodometry, was found to lie between 2.9 and 3.1, in agreement with the occurrence of iron(III). They are high-spin complexes with magnetic moments of 5.8–5.9 μ_{B} and conform well with the values reported in the literature.¹³ The IR spectra of the compounds exhibit a very strong but somewhat broad band at 470–497 cm⁻¹, assigned to $\nu(\text{Fe-F})$,¹⁴ and a strong band around 290 cm⁻¹, attributed to $\delta(\text{F-Fe-F})$. These are in conformity with those observed earlier¹⁴ on similar compounds.

Reactions of SCN⁻ and F⁻ with Iron(III) Hydroxide and Hydrogen Peroxide. There was some concern regarding the reaction of thiocyanate with iron(III), and consequently, results of some very recent studies¹⁵ have shown the possibility of oxidation of SCN⁻ to trithiocyanate (SCN)₃⁻, a rather unstable intermediate, by iron(III). Our principal concern was to investigate the main product of oxidation of thiocyanate in the presence of fluoride ions and iron(III) with a hope to get an access to mixed-ligand fluoro(sulfato)ferrates(III). This became necessary because our attempts to synthesize such mixed-ligand complexes from the reaction of sulfate and fluoride with iron(III) in an acidic medium had failed, unlike in the case of manganese(III).⁹ The products obtained therefrom were found to be only pentafluoroferrates(III) that did not contain any sulfate. Accordingly, chemical oxidation of SCN⁻ to SO₄²⁻ in the presence of F⁻ ions and iron(III) was undertaken. Hydrogen peroxide was chosen as the oxidant because not only is it capable of oxidizing SCN⁻ to sulfate,^{16,17} but also it helps iron to retain its trivalent state.

Initial studies of the reaction of SCN⁻ with iron(III) hydroxide, hydrofluoric acid, and hydrogen peroxide were carried out in a slightly alkaline medium but were found to be complicated owing to apparent side reactions leading to contamination of the reaction products, although the oxidation of thiocyanate did take place. Subsequent experiments were therefore carried out in acidic media. During the reaction of ASCN (A = K or NH₄) and iron(III) hydroxide with aqueous HF and hydrogen peroxide, SCN⁻ was oxidized to SO₄²⁻ and metal hydroxide went into solution with

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the solution becoming practically colorless. The reactions ultimately led to the synthesis of new compounds (vide Experimental Section) that analyze as $K_3[Fe(SO_4)F_4]$ and $(NH_4)_2[Fe(SO_4)F_3]$ as obtained from KSCN and NH_4SCN , respectively, providing an access to mixed-ligand fluoro(sulfato)ferrates(III). Presumably, here again an intermediate peroxyfluoroferrate(III) species is first generated, which then participates, through its coordinated peroxy group, in the oxidation of SCN^- finally to afford the heteroligand fluoro-ferrates(III).

A study of the vibrational spectra of the reaction products revealed the complete absence of $\nu(CN)$ at ca. 2120 cm^{-1} , and the IR and laser Raman (IR) spectral patterns were very similar to other metal sulfato complexes. When sulfate is coordinated, its symmetry is lowered from T_d to C_{3v} or C_{2v} ¹⁸ depending on whether it binds the metal center in a monodentate or a bidentate fashion.¹⁸ In the case of C_{2v} symmetry of sulfate, its ν_3 and ν_4 modes are split into three bands each while the ν_1 and ν_2 modes appear with medium intensity. Although both bridging and chelating sulfato ligands have C_{2v} symmetry, they can generally be distinguished on the basis of their IR and Raman spectra since ν_3 vibrations for chelating bidentate sulfato complexes occur at higher energies than those of bridging sulfato complexes.¹⁸ In the IR and IR spectra of the newly synthesized compounds each of the ν_3 and ν_4 vibrations was split into three bands with the ν_3 modes lying at ca. 1225 , ca. 1130 , and ca. 1020 cm^{-1} . A comparison with other types of sulfato complexes¹⁹ indicates that these

vibrations fall at rather high energies for ν_3 modes and therefore suggests that SO_4^{2-} binds the iron(III) center in a chelating bidentate manner. Another common feature of fluoro(sulfato)ferrates(III) is the band at ca. 495 cm^{-1} , which has been assigned to the $\nu(Fe-F)$ mode arising from the presence of coordinated fluoride ligands.

For further characterization, the oxidation state of iron was estimated chemically by an iodometric method and magnetic moments were measured at room temperature. While the chemically estimated oxidation state of iron was found to be 3, the magnetic moments of the compounds were found to be ca. $5.7\ \mu_B$, suggesting the occurrence of high-spin iron(III). These results adduce additional support to the identity of the fluoro(sulfato)ferrates(III).

Concluding Remarks. Under the appropriate experimental conditions hexafluoroferrates(III) of the type A_3FeF_6 ($A = Na, K, \text{ or } NH_4$) can be directly synthesized in high yields, providing an easy access to such compounds. Reactions of potassium or ammonium thiocyanate with iron(III) hydroxide, aqueous hydrofluoric acid, and hydrogen peroxide have resulted in the production of hitherto unknown fluoro(sulfato)ferrates(III). These compounds provide excellent prospects as materials for further studies of their physical properties and for a comparison with those of the binary fluorometalates(III). In this way an insight into the fluorochemistry of iron may be gained.

Acknowledgment. The authors thank the Council of Scientific and Industrial Research, New Delhi, India, for the award of a research fellowship to N.S.I.

Registry No. Na_3FeF_6 , 20955-11-7; K_3FeF_6 , 13815-30-0; $(NH_4)_3FeF_6$, 13815-28-6; $K_3[Fe(SO_4)F_4]$, 103852-34-2; $(NH_4)_2[Fe(SO_4)F_3]$, 103852-35-3; KSCN, 333-20-0; NH_4SCN , 1762-95-4.

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Complexation Kinetics of Highly Substituted Acyclic, Monocyclic, and Bicyclic Tetraamines with Copper(II) in Basic Aqueous Media

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Received January 24, 1986

The complex formation kinetics of copper(II) with 1,1,10,10-tetramethyl-1,4,7,10-tetraazadecane (Me_4 trien), 1,1,4,7,10,10-hexamethyl-1,4,7,10-tetraazadecane (Me_6 trien), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane ($(N-Me)_4$ cyclam), and 1,4,7,10-tetraaza-13,18-dioxabicyclo[8.5.5]eicosane (cryptand $2_N.1_O.1_O$) have been studied in strongly basic media (0.075–0.40 M NaOH) at $25.0\text{ }^\circ\text{C}$. All ligands, with the possible exception of $(N-Me)_4$ cyclam, react with both $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$, and for a given ligand, $Cu(OH)_3^-$ is 10 to >300 times more reactive than $Cu(OH)_4^{2-}$. For Me_4 trien reacting with either $Cu(OH)_3^-$ or $Cu(OH)_4^{2-}$ and Me_6 trien reacting with $Cu(OH)_3^-$, the rate-determining step is proposed to be Jahn-Teller inversion after formation of the first Cu(II)–nitrogen bond. The rate-determining step appears to shift to second-bond formation for the reaction of Me_6 trien with $Cu(OH)_4^{2-}$. For the cyclic ligands, $(N-Me)_4$ cyclam and $2_N.1_O.1_O$, second-bond formation or multiple desolvation is proposed as the rate-determining step for reactions with $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$. The kinetics of the hydroxide-catalyzed dissociation of the copper(II) complex of 1,4,7,10-tetraaza-13,16,21,24-tetraoxabicyclo[8.8.8]hexacosane (cryptand $2_N.2_O.2_O$) have been studied at $I = 0.5$ (NaClO₄–NaOH) and $25.0\text{ }^\circ\text{C}$. For 0.12–0.25 M hydroxide, the reaction shows a third-order dependence on hydroxide ion concentration. The effects of methyl substitution at nitrogen and bicyclic ligand structure on the formation rate constants are discussed.

Introduction

There has been renewed interest in the kinetics of the reactions of divalent copper ion with linear and cyclic polyamines. The earlier studies have been reviewed,² and recent work has focused on the acid-catalyzed dissociation of Cu(II) polyamine complexes^{3–11} and the formation and isomerization reactions of Cu(II)

with cyclic tetraamines in strongly basic media.^{12–14} The latter studies are an extension of the work of Lin et al.,¹⁵ who employed highly basic media to avoid the effects of ligand protonation in

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