concentration of the two chromium(V) chelates, the number of electrons transferred corresponding to both peaks was calculated[32] to be 2 in the acidity range 0.1–0.01 M. Moreover, with an identical concentration, the integrated area of the cathodic portion of the curve was found to be 1.8 times higher at pH 2.0 than at pH 4.0. Table III summarizes the electrochemical data in the pH range 1–2. In acidic solution the electrode processes then can be represented by

$$L_2Cr^{V}(O) + 2H^+ + 2e^- \xrightarrow{\text{irreversible}} L_2Cr^{III}(H_2O) \qquad (9)$$

$$LCr^{V}(O) + 2H^+ + 2e^- \xrightarrow{\text{irreversible}} LCr^{III}(H_2O) \qquad (10)$$

The reduction waves for both species shift anodically with increasing hydrogen ion concentrations, in accord with our picture. From the dependence of reduction potential on pH, the number of protons involved in the redox process can, in principle, by calculated. Assuming that the rate of electron transfer does not change with pH, an anodic shift of 60 mV is expected for the reduction peak potentials of both the mono and dichelate for a 10-fold increase in the hydrogen ion concentration. We note that at a constant scan rate (0.1 V s^{-1}) the reduction wave for the dichelate shifted 70 mV in the positive direction when $[H^+]$ is increased from 0.01 to 0.1 M. Likewise, a slightly higher anodic shift (90 mV) was observed for the reduction wave of the monochelate for a 10-fold increase in $[H^+]$.

The reason for the irreversibility of the Cr(V)/Cr(III) couple is open to question. The irreversibility may be due to the marked structural differences associated with these two oxidation states. Another possiblility is that in acidic solution ($[H^+]$ = 0.01–0.1 M) the released hydroxycarboxylic acid may modify the electrode surface such that the reduced species is electroinactive. This view may be supported by the presence of only a single reduction peak in voltammograms obtained in the hydroxycarboxylate buffer (pH 3.5) whereas a quasi-reversible behavior was observed in the unbuffered solution having identical pH. We await further evidence before choosing between these alternatives.

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Registry No. I^-, 84622-43-5; $L_2Cr^{IV}(O)$, 99495-02-0; $LiClO_4$, 7791-03-9; $(C_2H_5)_2C{=}O$, 96-22-0.

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[32] In this calculation it is assumed that the value of the diffusion coefficient of the Cr(V) complexes does not change significantly with changing pH and that the diffusion coefficient of the monochelate is not much different from that of the bis chelate.

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Direct Synthesis of Alkali-Metal and Ammonium Pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$, and First Synthesis and Structural Assessment of Alkali-Metal and Ammonium Difluorodiperoxytitanates(IV), $A_2[Ti(O_2)_2F_2]$

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Yellow alkali-metal and ammonium pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4), have been synthesized directly from the reaction of TiO_2 in 40% HF with 30% H_2O_2 at pH 6 maintained by the addition of the corresponding alkali metal or ammonium hydroxide. Novel alkali-metal and ammonium difluorodiperoxotitanates(IV), $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4), have been synthesized from the reaction of a solution of TiO_2 in 40% HF with 30% H_2O_2 at pH 9 maintained by the addition of the corresponding AOH, followed by precipitation with ethanol. The compounds are all diamagnetic and permit molar conductance measurements. The IR and laser Raman spectra suggest that the peroxide groups are bonded to the Ti^{4+} center in a triangular bidentate (C_{2v}) manner and that ν_{O-O} decreases with the increase in the number of coordinated peroxide groups.

There has been a considerable recent interest in metal complexes that contain peroxide.[1,2] Some of this interest originates from the probable biochemical significance of peroxymetal complexes[1,3] and the potential use of hetero ligand peroxymetal compounds containing macrocyclic ligands as models for biological systems.[3] Our interest in this area stems from developing suitable methods of syntheses and making assessment of structures of hetero ligand peroxymetal compounds. We have embarked on a research program designed to find suitable methods for syntheses. Within the context of the present work there are certain aspects of the chemistry of peroxytitanates(IV), as reported in the literature,[4,5] that remain unclear. Notably important among them are the lack of a direct method for synthesizing alkali-metal and ammonium pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$, and the absence of any reported existence of difluorodiperoxytitanate(IV) complexes, $A_2[Ti(O_2)_2F_2]$. Reported in this paper are a direct general method for the synthesis of $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4), and the synthesis, characterization, and assessment of structure of novel hetero ligand peroxytitanate(IV) compounds of the type $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4), and also a set of internally consistent data concerning the effect on ν_{O-O} modes with the increase in number of such groups coordinated to the Ti^{4+} center in going from $[Ti(O_2)F_5]^{3-}$ to $[Ti(O_2)_2F_2]^{2-}$. The syntheses have been achieved by conducting the reactions under two different, in each case specific, pH conditions.

Experimental Section

The chemicals used were all reagent grade products. IR spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer. Laser Raman (LR) spectra were recorded on a Spex Ramalog Model 1402 spectrometer. The 4880-Å laser line from the Spectra-Physics Model 165 argon laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube followed by a photon-counting processing system. The sample was held either in a quartz capillary or in the form of a pressed pellet, unless otherwise stated, and the spectra were recorded at ambient temperatures. Molar conductance measurements were made in aqueous solution with a Philips PR 9500 conductivity bridge. The pH of the reaction solutions was measued with a Systronics Type 335 digital pH meter and also with pH indicator (BDH) paper.

Synthesis of Alkali-Metal and Ammonium Pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4). In a typical reaction, to a stirred cold solution of 2.0 g (25 mmol) of TiO_2 in 20 cm^3 (400 mmol) of 40% hydrofluoric acid, obtained by heating the mixture for ca. 20 min,

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[1] Djordgevic, C. *Chem. Br.* **1982**, *18*, 554.
[2] Campbell, N. J.; Capparelli, M. V.; Griffith, W. P.; Skapski, A. C. *Inorg. Chim. Acta* **1983**, *77*, L215.
[3] Guilard, R.; Latour, J.; Lecompte, C.; Marchon, J. *Inorg. Chem.* **1978**, *17*, 1228.
[4] Connor, J. A.; Ebsworth, E. A. V. *Adv. Inorg. Chem. Radiochem.* **1964**, *6*, 286.
[5] Clark, R. J. H.; Bradley, D. C.; Thornton, P. "The Chemistry of Titanium, Zirconium, and Hafnium"; Pergamon Press: Elmsford, NY, 1975; Pergamon Texts in Inorganic Chemistry, Vol. 19; p 378.

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Table I. Analytical Data, Molar Conductance Values, and Structurally Significant IR and Raman Bands of $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4) and $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4)

compd	molar conductance, Ω^{-1} cm^2 mol^{-1}	% found (% calcd) A or N	Ti	O^a	F	IR, cm^{-1}	Raman,^{b} cm^{-1}	assignt
$(NH_4)_3[Ti(O_2)F_5]$	365	18.51 (18.35)	21.2 (20.9)	14.2 (13.97)	41.8 (41.48)	905 vs 600 s 530 s 430 m 225 m	900 s (p) 590 m (dp) 530 s (p) 270 m	ν_{O-O} (ν_1) ν_{Ti-O_2} (ν_3) ν_{Ti-O_2} (ν_2) ν_{Ti-F} Ti–F def
$Na_3[Ti(O_2)F_5]$	350	28.1 (28.28)	19.3 (19.64)	13.6 (13.12)	38.4 (38.96)	900 vs 600 s 549 s 450 m 240 m	900 s (p) 600 m (dp) 525 s (p) 250 m	ν_{O-O} (ν_1) ν_{Ti-O_2} (ν_3) ν_{Ti-O_2} (ν_2) ν_{Ti-F} Ti–F def
$K_3[Ti(O_2)F_5]$	370	39.8 (40.14)	16.7 (16.39)	11.2 (10.95)	32.9 (32.51)	900 vs 600 s 530 s 430 m 230 m	900 s (p) 600 m (dp) 520 s (p) 270 m	ν_{O-O} (ν_1) ν_{Ti-O_2} (ν_3) ν_{Ti-O_2} (ν_2) ν_{Ti-F} Ti–F def
$(NH_4)_2[Ti(O_2)_2F_2]$	225	15.21 (15.06)	25.3 (25.75)	34.8 (34.4)	20.8 (20.43)	860 vs 830 s 620 s 510 s 450 m 250 m	860 s (p) 830 s (p) 600 s (p) 520 m (dp) 270 m	ν_{O-O} (ν_1) ν_{Ti-O_2} (ν_2) ν_{Ti-O_2} (ν_3) ν_{Ti-F} Ti–F def
$K_2[Ti(O_2)_2F_2]$	235	34.7 (34.28)	21.3 (21)	28.4 (28.06)	16.3 (16.66)	860 vs 840 s 620 s 500 s 430 m 250 m	860 s (p) 825 s (p) 600 s (p) 525 m (dp) 270 m	ν_{O-O} (ν_1) ν_{Ti-O_2} (ν_2) ν_{Ti-O_2} (ν_3) ν_{Ti-F} Ti–F def

[a] Peroxy oxygen. [b] Abbreviations: p, polarized band; dp, depolarized band.

was added 20 cm^3 (176.4 mmol) of 30% H_2O_2 at ca. 20 °C. After the solution was stirred for ca 10 min at 20 °C, the corresponding alkali-metal or ammonium hydroxide, AOH, was added in small portions with slow stirring until the pH of the solution was raised to 6, whereupon yellow microcrystalline alkali-metal or ammonium pentafluoroperoxytitanate(IV), $A_3[Ti(O_2)F_5]$, was precipitated in a very high yield. While sodium or potassium hydroxide was added in the form of powder, ammonium hydroxide was added as its concentrated solution (specific gravity 0.9). The cooling bath was removed, and the compound was separated by centrifugation, washed three times with ethanol, and finally dried in vacuo over concentrated sulfuric acid. The yields of $(NH_4)_3[Ti(O_2)F_5]$, $Na_3[Ti(O_2)F_5]$, and $K_3[Ti(O_2)F_5]$ were 5.5 g (96%), 5.5 g (90%), and 6.5 g (89%), respectively.

Synthesis of Alkali-Metal and Ammonium Difluorodiperoxytitanates(IV), $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4). In a typical procedure, representative of the general method, 1.0 g (12.5 mmol) of TiO_2 was dissolved in 10 cm^3 (200 mmol) of 40% HF by warming over a steam bath for ca. 20 min. The clear solution was cooled to ca. 20 °C followed by the addition of 20 cm^3 (176.4 mmol) of 30% H_2O_2 with stirring. To the solution was added the corresponding alkali-metal or ammonium hydroxide with occassional stirring, in a manner analogous to that mentioned under the synthesis of $A_3[Ti(O_2)F_5]$, until the pH of the reaction solution was raised to 9. The color of the solution first turned red and then yellow, giving a yellow precipitate at pH ca. 6, which slowly went into solution, with simultaneous decrease in the intensity of color, with the progress of addition of alkaline medium. The ultimate color of the solution at pH 9 was very faint yellow. Addition of ethanol to this solution afforded a very faint yellowish white microcrystalline alkali-metal or ammonium difluorodiperoxytitanate(IV) compound, $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4), in a nearly quantitative yield. The isolation, purification, and drying of the compounds were accomplished in similar manners as described earlier in this section. Yields of $(NH_4)_2[Ti(O_2)_2F_2]$ and $K_2[Ti(O_2)_2F_2]$ were 2.2 g (94%) and 2.6 g (91%), respectively.

Elemental Analyses. Peroxide, fluoride, nitrogen, sodium, and potassium were estimated by the methods described earlier.[6] Titanium content in each of the compounds was estimated gravimetrically as TiO_2, after precipitation with cupferron.[7]

The analytical data, molar conductance values, and structurally significant IR and Raman band positions along with their assignments are summarized in Table I.

Results and Discussion

The complexity involved in the chemistry of the Ti–H_2O_2 system is evident from the different color reactions observed with small variation of pH.[4] This is probably the reason why not much is known about peroxytitanates.[4,5] Pentafluoroperoxytitanate(IV), $[Ti(O_2)F_5]^{3-}$, is the most often quoted example of a typical peroxytitanate compound, albeit a few more have also been reported.[8,9] However, no direct method of and the optimum pH required for the synthesis of the complex are known to date. The procedure recommended and generally used for the purpose requires the $[TiF_6]^{2-}$ complex as the essential precursor,[4,5] which results in an extra preparation step. From our experience in the field of peroxymetalate chemistry,[6] and also considering some of the known aspects of titanium chemistry, it was expected that the pentafluoroperoxytitanate(IV) complexes could be synthesized directly from TiO_2 under appropriate conditions. The strategy for the present reaction was that TiO_2 would dissolve in aqueous HF, forming fluorotitanate(IV), in situ, which without isolation would then be made to react with H_2O_2, under a favorable pH of the reaction medium, to afford the complex $[Ti(O_2)F_5]^{3-}$. The reaction took place accordingly and afforded yellow microcrystalline alkali-metal and ammonium pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4), in very high yields. The procedure is straightforward and simple, and the suitable pH for the synthesis was found to be 6. The spontaneous separation of the compound from the reaction solution at pH 6 is an additional advantage of the method.

In order to synthesize hitherto unknown fluoroperoxytitanate(IV) complexes containing two peroxy groups bonded per Ti^{4+} center, the reaction of a solution of TiO_2 in 40% HF was

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(6) Chaudhuri, M. K.; Ghosh, S. K. *Inorg. Chem.* **1982**, *21*, 4020; *J. Chem. Soc., Dalton Trans.* **1984**, 507.

(7) Vogel, A. I. "A Text Book of Quantitative Inorganic Analysis"; Longmans, Green and Co.: New York, 1962; p 544.

(8) Sala-Pala, J.; Edwards, A. J.; Guerchais, J. E. *Bull. Soc. Chim. Fr.* **1973**, 1545.

(9) Jere, G. V.; Gupta, G. D.; Raman, V.; Santhamma, M. T. *Indian J. Chem., Sect. A* **1978**, *16A*, 435.

conducted at a much higher concentration of the alkaline medium (pH 9) with the anticipation that an increased pH would favor and facilitate introduction of more than one O_2^{2-} group into the coordination sphere of Ti^{4+} at the expense of some F^- ligands already bonded to the metal. Thus the synthesis of difluorodiperoxytitanate(IV) complexes, $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4), was achieved at pH 9. That pH 9 is conducive to the synthesis was ascertained from the facts that $A_3[Ti(O_2)F_5]$, which formed at pH 6, started becoming first pale and ultimately very pale at pH 9 and that the product isolated at pH 9 showed a clear shift of the ν_{O-O} mode in the IR spectrum to a lower frequency (ca. 860 cm^{-1}) compared to that (ca. 900 cm^{-1}) typical of $A_3[Ti(O_2)F_5]$ complexes (Table I). The product isolated at pH values between 6 and 8 showed two ν_{O-O} modes at ca. 900 and ca. 860 cm^{-1}, suggesting thereby that the peroxide uptake process is in progress but is not complete until pH 9. A plausible mechanism, in view of the compounds isolated at pH 6 and 9 as $A_3[Ti(O_2)F_5]$ and $A_2[Ti(O_2)_2F_2]$, respectively, is that a fluorotitanate(IV) complex is first formed, from the reaction of TiO_2 with 40% HF, which subsequently undergoes stepwise peroxygeneration to afford $[Ti(O_2)F_5]^{3-}$ and $[Ti(O_2)_2F_2]^{2-}$. This certainly indicates that O_2^{2-} can displace some of the F^- around a Ti^{4+} center at higher pH values. It is quite reasonable to assume that other hetero ligand peroxy complexes of titanium could be obtained directly from TiO_2; syntheses of such compounds are under study. Also, since the diperoxytitanates(IV) undergo deperoxygenation with lowering of pH (<7) of the medium, mixed species (e.g. fluoro(sulfato)-, fluoro(oxalato)-, and fluoro(acetylacetonato)titanates(IV)) should be readily accessible.

Characterization and Assessment of Structure. Yellow $A_3[Ti(O_2)F_5]$ and light yellow $A_2[Ti(O_2)_2F_2]$ are soluble in water, and at room temperature they do not exhibit any noticeable tendency for hydrolysis. They permit molar conductance measuremetns, and the conductances of $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4) and $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4) have been found to lie in the range 350–370 and 220–240 Ω^{-1} cm^2 mol^{-1}, respectively, in conformity with their formulas. The diamagnetic nature of the compounds, as evidenced by the results of magnetic susceptibility measurements, supports the view that titanium occurs in its +4 oxidation state in each of the newly synthesized compounds. The peroxide estimation, accomplished by redox titrations separately involving a standard potassium permanganate and a standard Ce^{4+} solution, conspicuously suggests the presence of one or two peroxide groups per formula weight of the $A_3[Ti(O_2)F_5]$ and the $A_2[Ti(O_2)_2F_2]$ cases, respectively.

The O–O and metal–O_2 vibrations of peroxymetal compounds are important spectroscopic probes for molecular structure assessment in such systems and are amenable to direct study by IR and Raman spectroscopy. Typically the IR and laser Raman (LR) spectra of the $A_3[Ti(O_2)F_5]$ compounds exhibit peaks at ca. 900, ca. 600, and ca. 530 cm^{-1}, and the corresponding peaks for the $A_2[Ti(O_2)_2F_2]$ compounds appear at ca. 860 and 830, ca. 610, and ca. 520 cm^{-1}. The peaks at ca. 900 or 860 and 830 cm^{-1} have been assigned to ν_{O-O}, while the ones at ca. 600 or 610 cm^{-1} and at ca. 530 or 520 cm^{-1} correspond to ν_{Ti-O_2} modes of coordinated peroxide. The band at ca. 430 cm^{-1} observed only in the IR spectra of the compounds has been attributed to the ν_{Ti-F} mode. The assignments are in order.[6,10,11] The observed positions of ν_{O-O} and ν_{Ti-O_2} are those that one would expect to observe for a triangularly bonded O_2^{2-}. Considering C_{2v} being the local symmetry of coordinated O_2^{2-} ligand, three vibrations (two A_1 and one B_2) are expected to be IR and Raman active, of which the two A_1 modes (ν_1, ν_{O-O} stretching, and ν_2, ν_{Ti-O_2} symmetric stretching) are polarized, while the B_2 mode (ν_3, ν_{Ti-O_2} asymmetric stretching) is depolarized in the Raman spectra.[11] The ν_1 mode occurs at 800–900 cm^{-1}, and the ν_2 and ν_3 modes fall in the region 500–600 cm^{-1}. On the basis of the sharpness and intensity of the observed LR signals and Raman polarization measurements on solutions, the frequencies at ca. 530 and ca. 600 cm^{-1} for the $A_3[Ti(O_2)F_5]$ have been attributed to the ν_2 and ν_3 modes, respectively, of ν_{Ti-O_2}, while the signals at ca. 610 and ca. 520 cm^{-1} for $A_2[Ti(O_2)_2F_2]$ have been assigned respectively to the ν_2 and ν_3 modes of ν_{Ti-O_2}. It is probably the changes in stoichiometry of Ti:O_2:F, and the structures of the complex ions, as one goes from the mono- to the diperoxy species, that cause the frequency reversal of ν_2 and ν_3. Since the LR spectra of the solids as well as their solutions, recorded under identical conditions, do not reveal any notable change in the pattern of the spectra or in the positions of the signals, it is believed that the complex species $[Ti(O_2)F_5]^{3-}$ and $[Ti(O_2)_2F_2]^{2-}$ retain their structural identity also in solution. The splitting of ν_{O-O} in the case of the $A_2[Ti(O_2)_2F_2]$ compounds very likely originates from the coupling of the in-phase–out-of-phase vibrations of the two coordinated peroxo groups. A medium-intensity band at ca. 430 cm^{-1} in the IR spectra of each of the compounds has been assigned to ν_{Ti-F}. However, a counterpart could not be observed in the corresponding LR spectra. The band at ca. 250 cm^{-1} most likely owes its origin to a Ti–F deformation mode. A clear shift of ν_{O-O} from ca. 900 to ca. 850 cm^{-1} in going from $[Ti(O_2)F_5]^{3-}$ to $[Ti(O_2)_2F_2]^{2-}$ is a clean indication of a decrease in the O–O bond order with an increase in the number of coordinated O_2^{2-} groups. Since peroxide ligands bind to Ti through donation from two antibonding π_p orbitals, Ti^{4+} will become a worse acceptor with increasing number of O_2^{2-} ligands. This will make Ti^{4+} withdraw less electron density from the antibonding π_p (O_2^{2-}) orbitals, which will increase their repulsive character and in turn will weaken the O–O bond. Hence, O_2^{2-} multisubstitution should result in weakening of the O–O bond, as observed in the present work.

It may be inferred that fluoroperoxytitanates(IV) of the types $A_3[Ti(O_2)F_5]$ and $A_2[Ti(O_2)_2F_2]$ can be synthesized directly from the reactions of TiO_2, 40% HF, and hydrogen peroxide at pH 6 and 9, respectively, adjusted by the addition of the corresponding alkali-metal or ammonium hydroxide, AOH. While the complex $[Ti(O_2)F_5]^{3-}$ ion may be a heptacoordinated monomer, the complex species $[Ti(O_2)_2F_2]^{2-}$ may have a hexacoordinated structure. However, the chances of polymeric structures of the complexes through weak –Ti–F–Ti– interactions cannot be totally ruled out. The O_2^{2-} group, in each case, is bonded to the Ti^{4+} center in a triangular bidentate (C_{2v}) manner, with the O–O bond order being decreased by the increase in the number of each groups coordinated to the metal center.

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Registry No. $(NH_4)_3[Ti(O_2)F_5]$, 18639-68-4; $Na_3[Ti(O_2)F_5]$, 99398-68-2; $K_3[Ti(O_2)F_5]$, 12021-39-5; $(NH_4)_2[Ti(O_2)_2F_2]$, 99416-55-4; $K_2[Ti(O_2)_2F_2]$, 99416-56-5.

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[10] Griffith, W. P. *J. Chem. Soc.* **1964**, 5248.

[11] Griffith, W. P.; Wickins, T. D. *J. Chem. Soc.* **1967**, 590; **1968**, 397.