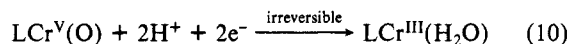
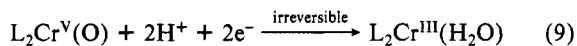


concentration of the two chromium(V) chelates, the number of electrons transferred corresponding to both peaks was calculated<sup>32</sup> to be 2 in the acidity range 0.1–0.01 M. Moreover, with an identical concentration, the integrated area of the cathodic portion of the curve was found to be 1.8 times 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



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, be calculated. Assuming that the rate of electron transfer does not change with pH, an anodic shift of 60 mV is expected for the

(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.

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<sup>-1</sup>) the reduction wave for the dichelate shifted 70 mV in the positive direction when [H<sup>+</sup>] 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<sup>+</sup>].

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 possibility is that in acidic solution ([H<sup>+</sup>] = 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.**  $\Gamma$ , 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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## 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<sub>4</sub>), have been synthesized directly from the reaction of TiO<sub>2</sub> in 40% HF with 30% H<sub>2</sub>O<sub>2</sub> at pH 6 maintained by the addition of the corresponding alkali metal or ammonium hydroxide. Novel alkali-metal and ammonium difluorodiperoxytitanates(IV),  $A_2[Ti(O_2)_2F_2]$  (A = K, NH<sub>4</sub>), have been synthesized from the reaction of a solution of TiO<sub>2</sub> in 40% HF with 30% H<sub>2</sub>O<sub>2</sub> 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<sup>4+</sup> center in a triangular bidentate (C<sub>2v</sub>) manner and that  $\nu_{O-O}$  decreases with the increase in the number of coordinated peroxide groups.

There has been a considerable recent interest in metal complexes that contain peroxide.<sup>1,2</sup> Some of this interest originates from the probable biochemical significance of peroxymetal complexes<sup>1,3</sup> and the potential use of hetero ligand peroxymetal compounds containing macrocyclic ligands as models for biological systems.<sup>3</sup> 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,<sup>4,5</sup> 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<sub>4</sub>), 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<sub>4</sub>), and also a set of internally consistent data concerning the effect on  $\nu_{O-O}$  modes with the increase in number of such groups coordinated to the Ti<sup>4+</sup> 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 measured 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<sub>4</sub>).** In a typical reaction, to a stirred cold solution of 2.0 g (25 mmol) of TiO<sub>2</sub> in 20 cm<sup>3</sup> (400 mmol) of 40% hydrofluoric acid, obtained by heating the mixture for ca. 20 min,

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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, $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	% found (% calcd)				IR, $\text{cm}^{-1}$	Raman, <sup>b</sup> $\text{cm}^{-1}$	assignt
		A or N	Ti	O <sup>a</sup>	F			
$(NH_4)_3[Ti(O_2)F_5]$	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	$\nu_{O-O}$ ( $\nu_1$ ) $\nu_{Ti-O_2}$ ( $\nu_3$ ) $\nu_{Ti-O_2}$ ( $\nu_2$ ) $\nu_{Ti-F}$ 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	$\nu_{O-O}$ ( $\nu_1$ ) $\nu_{Ti-O_2}$ ( $\nu_3$ ) $\nu_{Ti-O_2}$ ( $\nu_2$ ) $\nu_{Ti-F}$ 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	$\nu_{O-O}$ ( $\nu_1$ ) $\nu_{Ti-O_2}$ ( $\nu_3$ ) $\nu_{Ti-O_2}$ ( $\nu_2$ ) $\nu_{Ti-F}$ 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	$\nu_{O-O}$ ( $\nu_1$ ) $\nu_{Ti-O_2}$ ( $\nu_2$ ) $\nu_{Ti-O_2}$ ( $\nu_3$ ) $\nu_{Ti-F}$ 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	$\nu_{O-O}$ ( $\nu_1$ ) $\nu_{Ti-O_2}$ ( $\nu_2$ ) $\nu_{Ti-O_2}$ ( $\nu_3$ ) $\nu_{Ti-F}$ Ti-F def

<sup>a</sup> Peroxy oxygen. <sup>b</sup> Abbreviations: p, polarized band; dp, depolarized band.

was added 20  $\text{cm}^3$  (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  $\text{cm}^3$  (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  $\text{cm}^3$  (176.4 mmol) of 30%  $H_2O_2$  with stirring. To the solution was added the corresponding alkali-metal or ammonium hydroxide with occasional 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.<sup>6</sup> Titanium content in each of the compounds was estimated gravimetrically as  $TiO_2$ , after precipitation with cupferron.<sup>7</sup>

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.<sup>4</sup> This is probably the reason why not much is known about peroxytitanates.<sup>4,5</sup> 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.<sup>8,9</sup> 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,<sup>4,5</sup> which results in an extra preparation step. From our experience in the field of peroxymetalate chemistry,<sup>6</sup> 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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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  $A_3[Ti(O_2)F_3]$ , 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  $\nu_{O-O}$  mode in the IR spectrum to a lower frequency (ca.  $860\text{ cm}^{-1}$ ) compared to that (ca.  $900\text{ cm}^{-1}$ ) typical of  $A_3[Ti(O_2)F_3]$  complexes (Table I). The product isolated at pH values between 6 and 8 showed two  $\nu_{O-O}$  modes at ca.  $900$  and ca.  $860\text{ cm}^{-1}$ , 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  $A_3[Ti(O_2)F_3]$  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  $[Ti(O_2)F_3]^{3-}$  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  $A_3-[Ti(O_2)F_3]$  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 measurements, and the conductances of  $A_3[Ti(O_2)F_3]$  ( $A = Na, K, NH_4$ ) and  $A_2[Ti(O_2)_2F_2]$  ( $A = K, NH_4$ ) have been found to lie in the range  $350\text{--}370$  and  $220\text{--}240\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ , 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  $A_3[Ti(O_2)F_3]$  and the  $A_2[Ti(O_2)_2F_2]$  cases, respectively.

The O-O and metal-O<sub>2</sub> 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  $A_3[Ti(O_2)F_3]$  compounds exhibit peaks at ca.  $900$ , ca.  $600$ , and ca.  $530\text{ cm}^{-1}$ , and the corresponding peaks for the  $A_2[Ti(O_2)_2F_2]$  compounds appear at ca.  $860$  and  $830$ , ca.  $610$ , and ca.  $520\text{ cm}^{-1}$ . The peaks at ca.  $900$  or  $860$  and  $830\text{ cm}^{-1}$  have been assigned to  $\nu_{O-O}$ , while the ones at ca.  $600$  or  $610\text{ cm}^{-1}$  and at ca.  $530$  or  $520\text{ cm}^{-1}$  correspond to  $\nu_{Ti-O_2}$  modes of coordinated peroxide. The band at ca.  $430\text{ cm}^{-1}$  observed only in the IR spectra of the compounds has been attributed to the  $\nu_{Ti-F}$  mode. The assignments are in order.<sup>6,10,11</sup> The observed positions of  $\nu_{O-O}$

and  $\nu_{Ti-O_2}$  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 ( $\nu_1, \nu_{O-O}$  stretching, and  $\nu_2, \nu_{Ti-O_2}$  symmetric stretching) are polarized, while the  $B_2$  mode ( $\nu_3, \nu_{Ti-O_2}$  asymmetric stretching) is depolarized in the Raman spectra.<sup>11</sup> The  $\nu_1$  mode occurs at  $800\text{--}900\text{ cm}^{-1}$ , and the  $\nu_2$  and  $\nu_3$  modes fall in the region  $500\text{--}600\text{ cm}^{-1}$ . 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.  $600\text{ cm}^{-1}$  for the  $A_3[Ti(O_2)F_3]$  have been attributed to the  $\nu_2$  and  $\nu_3$  modes, respectively, of  $\nu_{Ti-O_2}$ , while the signals at ca.  $610$  and ca.  $520\text{ cm}^{-1}$  for  $A_2[Ti(O_2)_2F_2]$  have been assigned respectively to the  $\nu_2$  and  $\nu_3$  modes of  $\nu_{Ti-O_2}$ . 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  $\nu_2$  and  $\nu_3$ . 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  $[Ti(O_2)F_3]^{3-}$  and  $[Ti(O_2)_2F_2]^{2-}$  retain their structural identity also in solution. The splitting of  $\nu_{O-O}$  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.  $430\text{ cm}^{-1}$  in the IR spectra of each of the compounds has been assigned to  $\nu_{Ti-F}$ . However, a counterpart could not be observed in the corresponding LR spectra. The band at ca.  $250\text{ cm}^{-1}$  most likely owes its origin to a Ti-F deformation mode. A clear shift of  $\nu_{O-O}$  from ca.  $900$  to ca.  $850\text{ cm}^{-1}$  in going from  $[Ti(O_2)F_3]^{3-}$  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  $\pi_p$  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  $\pi_p$  ( $O_2^{2-}$ ) 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  $A_3[Ti(O_2)F_3]$  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  $[Ti(O_2)F_3]^{3-}$  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.**  $(NH_4)_3[Ti(O_2)F_3]$ , 18639-68-4;  $Na_2[Ti(O_2)F_3]$ , 99398-68-2;  $K_3[Ti(O_2)F_3]$ , 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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