functions also contribute to the P–F bond, and the net result of this contribution is to facilitate the shift of electronic charge toward the F atoms.[9] This withdrawal of charge from the P atom mainly empties the 3p valence level and results in a π^* empty orbital with larger 3p character, which is as a consequence more suited to accept charge from the metal atom.[9] Both mechanisms lead to exactly the same result, i.e. the 3p participation being enhanced via the 3d orbitals, and it seems likely that they are contributing together to strengthen the Ni–P bond.

Hyperconjugation in the Ni–P Bonding. Hyperconjugation is a concept widely used in organic chemistry and in its classical form consists in the interaction of a π-type orbital with an empty p orbital, causing a lowering in energy.[24] This interaction can explain why a CH_3 group can stabilize a carbonium ion, etc. The substitution of the H atoms in the CH_3 group by a more electronegative element like F results in a CF_3 group, which in turn can stabilize an anion. However, this process will involve both the π (occupied) and the π^* (empty) orbitals of the CF_3 group. In CF_3, the π orbital has a small C 2p component and the π^* orbital a large C 2p character. The π^* orbital thus becomes more available for electron acceptance and can easily interact with an atom or radical with an excess of charge.

The valence electronic configuration of a CH_3^- group closely resembles that of the PH_3 molecule. The same is also valid for CF_3^- and PF_3. In PF_3 the pair of π orbitals that can interact with the π system of an anion are 4e (π) and the 7e (π^*). The P 3p component in 4e is very small while the 7e is largely a P 3p orbital with a small P 3d participation (see above). The interaction of a PF_3 molecule with a transition metal in a low oxidation state (an "anion") and the acceptance of charge into the P 3p orbital via the 7e π^* level may be considered as a kind of hyperconjugation process essentially analogous to the hyperconjugation in organic compounds.

Registry No. $Ni(PF_3)_4$, 13859-65-9; Ni, 7440-02-0; P, 7723-14-0.

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First Synthesis and Structural Assessment of Alkali-Metal Triperoxovanadates(V), $A[V(O_2)_3]$

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It is probably owing to biochemical significance,[1,2] and importance in the oxidation chemistry,[3] of peroxo–transition-metal compounds that the study on peroxovanadium chemistry has emerged as one of the active areas of research.[4-10] The vanadium–hydrogen peroxide system is complicated owing to the formation of peroxovanadates of varied compositions and colors with varying acidity or alkalinity of the reaction media.[7,11,12] The blue tetraperoxovanadate(V) $K_3[V(O_2)_4]$ has been known,[13] presumably having a structure analogous to that of $K_3[Cr(O_2)_4]$.[14] However, the triperoxovanadates(V) $A[V(O_2)_3]$ (A = alkali metal) have not been synthesized and isolated in the solid state although the hetero triperoxovanadates(V) $A_2[V(O_2)_3X]$ (X = F or Cl) have been reported recently.[15] In view of this it was thought that the successful synthesis and isolation of the blue $[V(O_2)_3]^-$ complex would provide some fundamental information concerning the minimum number of O_2^{2-} ligands, per V^{5+} center, required for the formation of a blue peroxovanadate(V) species. The present paper reports the synthesis, isolation in the solid state, and characterization of the blue alkali-metal triperoxovanadates(V) $A[V(O_2)_3]$ (A = Na or K).

Experimental Section

The chemicals used were all reagent grade (B.D.H., E. Merck) products. Infrared spectra were recorded on a Perkin-elmer Model 983 spectrophotometer. The laser Raman spectra were recorded on a SPEX Ramalog Model 1403 spectrometer. The 6328-Å Laser line from a helium–neon laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube and a photon-counting processing system. The spectra were recorded at ambient temperatures by making freshly prepared solutions of the samples or pressed pellets of the compounds. Molar conductance measurements were made with a Philips PR 9500 conductivity bridge. Magnetic susceptibilities were measured by the Gouy method using $Hg[Co(NCS)_4]$ as the standard. The UV–vis spectra were recorded on a Beckman Model UV-26 spectrophotometer.

Synthesis of Alkali-Metal Triperoxovanadates(V), $A[V(O_2)_3]$ (A = Na or K). Recommended Procedure. To finely powdered V_2O_5 was added an excess of 30% hydrogen peroxide, with slow stirring, in the molar ratio of $V_2O_5:H_2O_2$ as 1:42.5. Solid alkali-metal hydroxide, AOH, was slowly added to the above mixture under continuous stirring, until a blue color was developed (molar ratio $V_2O_5:H_2O_2:AOH$ as 1:42.5:(10–12)). The blue solution was then cooled in an ice-water bath for ca. 30 min, followed by the addition of an excess of precooled ethyl alcohol until the blue microcrystalline $A[V(O_2)_3]$ ceased to appear. The blue compound was separated by centrifugation, washed four or five times with cold ethanol, and finally dried in vacuo over phosphorus pentoxide. The reaction was monitored by IR spectroscopy. The complete disappearance of the sharp band at ca. 950 cm^{-1} due to $\nu_{V=O}$, in the product isolated from a small amount of the blue solution, indicates completion of the reaction.

The yield of $Na[V(O_2)_3]$ was 0.8 g (86%) obtained from the reaction of 0.5 g (2.7 mmol) of V_2O_5 with 13 cm^3 (114.6 mmol) of 30% H_2O_2 and 1.1 g (27.5 mmol) of NaOH, while that of $K[V(O_2)_3]$ was 0.9 g (90%) obtained from 0.5 g of V_2O_5 with 13 cm^3 of 30% H_2O_2 and 1.8 g (32 mmol) of KOH.

Elemental Analyses. Vanadium was determined volumetrically by redox titration with potassium permanganate.[15,16] The estimation of total peroxide content, in each compound, was accomplished by redox titrations with a standard cerium(IV) solution[17] and also separately with a standard potassium permanganate solution.[18] In a representative titrimetric procedure for the estimation of total amount of coordinated peroxide, a weighed amount of the sample under investigation was added to 100 cm^3 of cold distilled water, acidified with 2 cm^3 of concentrated sulfuric acid, containing ca. 1.5 g of boric acid. The whole was gently stirred on a magnetic stirrer and titrated with a standard potassium permanganate solution[17] or with a standard Ce^{4+} solution.[18] Sodium and potassium were determined by the methods described in our earlier paper.[15]

The results of elemental analyses, molar conductance values, IR and laser Raman band positions and their assignments are summarized in Table I.

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Table I. Analytical Data, Molar Conductance Values, and IR and Raman Bands of $A[V(O_2)_3]$ (A = Na or K)

compd	molar conductance, Ω^{-1} cm^2 mol^{-1}	% found (% calcd) A	V	O_A[a]	IR, cm^{-1}	Raman, cm^{-1}	assignt
$Na[V(O_2)_3]$	135	13.8	30.4	55.8	855 (s)	850	ν_{-O-O-} (ν_1)
		(13.53)	(29.98)	(56.49)	610 (s)	600	ν_{V-O_2} (ν_3)
					525 (s)	530	ν_{V-O_2} (ν_2)
$K[V(O_2)_3]$	140	21.2	27.8	52.1	855 (s)	860	ν_{-O-O-} (ν_1)
		(21.02)	(27.38)	(51.6)	610 (s)	610	ν_{V-O_2} (ν_3)
					530 (s)	530	ν_{V-O_2} (ν_2)

[a] Peroxo oxygen.

Results and Discussion

Albeit there has been a continued interest in the peroxovanadium chemistry, most of the recent reports deal with the aspects of solution chemistry[3,5–10] while information on synthesis, isolation in the solid state, characterization, and structural assessment of peroxovanadate compounds is rather scanty. The synthesis of blue alkali-metal triperoxovanadates(V), $A[V(O_2)_3]$ (A = Na or K), has been achieved from the reaction of V_2O_5 with 30% H_2O_2 in the presence of a relatively large concentration of alkaline medium with the molar ratio of V_2O_5:H_2O_2:AOH being maintained at 1:42.5:(10–12). A high concentration of AOH is necessary and conducive to the formation and then isolation of $A[V(O_2)_3]$ compounds. Although the V^{5+}–H_2O_2 solution assumes a blue color at a relatively lower concentration of AOH, the IR spectrum of the product isolated from it shows a band at ca. 950 cm^{-1} owing to $\nu_{V=O}$ in addition to those expected for the coordinated O_2^{2-}. This suggests that the formation of the triperoxovanadate(V), $[V(O_2)_3]^-$, complex is not complete; thus, it is required to add a further amount of alkali-metal hydroxide after the first appearance of blue color, however, not beyond the stipulated limit (see the Experimental Section). It may be noted that the change of color of V^{5+}–H_2O_2 solution, with the increase in concentration of alkaline medium, from yellow to blue clearly indicates that the complex $[VO(O_2)_2]^-$ is first formed and then is ultimately converted to the $[V(O_2)_3]^-$ complex. The complete disappearance of the $\nu_{V=O}$ at ca. 950 cm^{-1} in the IR and laser Raman spectra of the compound ensures completion of the reaction. Thus $A[V(O_2)_3]$ compounds were obtained by the addition of ethanol, which facilitates precipitation. Attempts to synthesize $NH_4[V(O_2)_3]$ were futile. Although a transitory blue solution was obtained by the addition of NH_4OH solution (sp gr 0.9), the color was practically discharged, with brisk evolution of oxygen, during workup. It is worthwhile to mention that the tetraperoxovanadate(V), $[V(O_2)_4]^-$, complex, as opposed to the triperoxo species, is formed[12,19] only at temperatures below 0 °C presumably in the presence of a relatively higher amount of alkaline medium.

The blue triperoxovanadates(V) $A[V(O_2)_3]$ (A = Na or K) are diamagnetic in line with the occurrence of quinquevalent vanadium and, unlike the $A_2[V(O_2)_3X]$ (X = F or Cl)[15] and $A_3[V(O_2)_4]$[19] compounds, are stable in water. Whereas $A_2[V(O_2)_3X]$[15] and $A_3[V(O_2)_4]$[19] do not permit molar conductance measurements, the values for the $A[V(O_2)_3]$ compounds, at ambient temperatures, were found to lie in the range 130–140 Ω^{-1} cm^2 mol^{-1}, suggesting their 1:1 electrolytic nature, in complete agreement with the formulas. The estimation of peroxide content is emphasized to be very crucial in order to fix the number of O_2^{2-} groups bound to the V^{5+} center. The results of peroxide determination, accomplished by redox titrations[17,18] involving Ce^{4+} and potassium permanganate, conspicuously suggested the occurrence of three peroxide groups per V^{5+} center in each of the new compounds. The UV–vis spectra of the solutions recorded before isolation of the compound and of that obtained by redissolving the compound were similar and showed absorptions at 560 and 192 nm with the molar absorption coefficients being 84.3 and 1.04 × 10^4, respectively. This indicates that the complex species formed in solution and that isolated in the solid state are identical. The electronic spectral data for $[V(O_2)_4]^{3-}$ are not available in the literature, thus precluding comparison with those of $[V(O_2)_3]^-$.

The characteristic features of the IR and laser Raman (LR) spectra are the absorption at ca. 850 cm^{-1} owing to ν_{-O-O-}[20] and the two absorptions at ca. 600 and ca. 530 cm^{-1} due to ν_{V-O_2}[20] with all three originating from the coordinated peroxide groups. The typical pattern of the spectra suggests that each of the O_2^{2-} ligands is bonded to the V^{5+} center in a triangular bidentate manner. The –O–O– and metal–O_2 bonds are important spectroscopic probes for molecular structure assessment of peroxometal compounds and are amenable to direct IR and LR spectroscopy. Considering C_{2v} to be the local symmetry of a coordinated O_2^{2-} group, three vibrations, viz. ν_1 (ν_{-O-O-}), ν_2 (ν_{V-O_2}), and ν_3 (ν_{V-O_2}), are expected to be active in both IR and Raman spectra,[20] with the ν_1 and ν_2 modes being polarized in the latter and appearing comparatively more sharp and intense than ν_3 mode. Accordingly, the LR signals at ca. 850, ca. 530, and ca. 600 cm^{-1} have been assigned respectively to the ν_1, ν_2, and ν_3 modes of the coordinated O_2^{2-} ligands. The solution LR spectra of $A[V(O_2)_3]$ compounds resemble those of the corresponding solids, suggesting that the complex anion $[V(O_2)_3]^-$ possesses the same structure in the solid state as well as in solution. Further, the absence of any band at ca. 950 cm^{-1} due to $\nu_{V=O}$, especially in the LR spectra in which it would be very strong on account of the large polarizability changes involved in the V—O bond, renders it certain that the complex does not contain any V=O group.

It may be inferred that a minimum of three O_2^{2-} groups, coordinated to a V^{5+} center, is required for the formation of a blue color in the V^{5+}–H_2O_2 system. The complex $[V(O_2)_3]^-$ ion, unlike the $[V(O_2)_4]^{3-}$ species, retains its identity both in solution as well as in the solid state. The $[V(O_2)_3]^-$ ion may have a hexacoordinated monomeric structure with the O_2^{2-} groups being bonded to the V^{5+} center in a triangular bidentate manner.

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Registry No. $Na[V(O_2)_3]$, 96760-79-1; $K[V(O_2)_3]$, 96760-80-4.

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Electrochemistry and Spectroelectrochemistry in CH_3CN and Aluminum Chloride/*N*-(1-Butyl)pyridinium Chloride Molten Salts of Films Prepared by Electrochemical Polymerization of Tris(5-amino-1,10-phenanthroline)iron(II)

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The incorporation of transition-metal complexes into polymer films on electrodes has received considerable attention in recent

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