in diethyl ether, while the NCS derivative requires a mixture of $EtOH-CH_2Cl_2$ to crystallize.

By carbonylation of $WCl_2(PMe_3)_4$ in a way similar to that described for $MoCl_2(PMe_3)_4$ for a period of 6–8 h, the complex dichlorodicarbonyltris(trimethylphosphine)tungsten(II), $WCl_2(CO)_2(PMe_3)_3$, can be obtained. Crystallization is achieved from petroleum ether–CH_2Cl_2 (3:1) at −30 °C (70% yield).

Metathesis with the appropriate potassium salts in acetone at room temperature affords the I, NCS, and NCO derivatives in ca. 40–50% yield.

B. Synthesis of $M(CO)(PMe_3)_2(S_2CNR_2)_2$ Complexes. Carbonylbis(trimethylphosphine)bis(dimethyldithiocarbamato)molybdenum(II), $Mo(CO)(PMe_3)_2(S_2CNMe_2)_2$. To a mixture of $MoCl_2(CO)_2(PMe_3)_3$ (0.45 g, ca. 1 mmol) and NaS_2CNMe_2 (ca. 4 mmol) is added 40 mL of acetone or THF via syringe. The suspension is stirred for ca. 4 h while a red color develops. Excess of PMe_3 (0.3 mL, ca. 3 mmol) is then added and the stirring continued for 12–18 h, at 40–50 °C. The solvent is stripped off in vacuo and the residue extracted with a diethyl ether–acetone mixture. Centrifugation and cooling at −30 °C give the product as red crystals in ca. 60% yield.

The compounds $Mo(CO)(PMe_3)_2(S_2CNR_2)_2$ (R = Et, *i*-Pr) were obtained as red crystals from Et_2O, in similar yields by an analogous procedure.

Starting with the chlorocarbonyltungsten(II) complex, $WCl_2(CO)_2(PMe_3)_3$, the corresponding tungsten compounds were prepared: $W(CO)(PMe_3)_2(S_2CNMe_2)_2$, red crystals from CH_2Cl_2–acetone; $W(CO)(PMe_3)_2(S_2CNEt_2)_2$, red crystals from Et_2O; $W(CO)(PMe_3)_2(S_2CN\text{-}i\text{-}Pr_2)_2$, red crystals from Et_2O–acetone.

C. Synthesis of $M(CO)_2(PMe_3)_2(S_2CNR_2)_2$ Complexes. Dicarbonyl(trimethylphosphine)bis(dimethyldithiocarbamato)molybdenum(II), $Mo(CO)_2(PMe_3)(S_2CNMe_2)_2$. $MoCl_2(CO)_2(PMe_3)_3$ (0.45 g, ca. 1 mmol) and NaS_2CNMe_2 (ca. 4 mmol) are mixed together, and 40 mL of THF or acetone is added. After it was stirred at room temperature for 4 h, the resulting dark red mixture is reacted at 50–60 °C with carbon monoxide at atmospheric pressure until the IR spectrum shows complete disappearance of the absorptions due to the monocarbonyl derivative $Mo(CO)(PMe_3)_2(S_2CNMe_2)_2$ (approximately 4 h). The suspension is then evaporated to dryness and the residue crystallized from Et_2O to give red crystals of the title compound.

The following complexes can be obtained by similar procedures: $Mo(CO)_2(PMe_3)(S_2CN\text{-}i\text{-}Pr_2)_2$, red crystals from Et_2O–acetone; $W(CO)_2(PMe_3)(S_2CNR_2)_2$, red crystals from Et_2O–acetone for R = Me and orange crystals from Et_2O for R = *i*-Pr. The S_2CNEt_2 derivatives can be obtained similarly, although they are usually obtained directly (red crystals from Et_2O) from the reactions of NaS_2CNEt_2 with the corresponding $MCl_2(CO)_2(PMe_3)_3$ (M = Mo, W) complexes. Yields are about 50–60%.

Registry No. $MoCl_2(CO)_2(PMe_3)_3$, 83828-53-9; $MoBr_2(CO)_2(PMe_3)_3$, 83828-52-8; $MoI_2(CO)_2(PMe_3)_3$, 83828-51-7; $Mo(NCO)_2(CO)_2(PMe_3)_3$, 88393-32-2; $Mo(NCS)_2(CO)_2(PMe_3)_3$, 88393-33-3; $WCl_2(CO)_2(PMe_3)_3$, 83828-56-2; $WI_2(CO)_2(PMe_3)_3$, 83828-54-0; $W(NCO)_2(CO)_2(PMe_3)_3$, 88393-34-4; $W(NCS)_2(CO)_2(PMe_3)_3$, 88393-35-5; $Mo(CO)_2(PMe_3)(S_2CNMe_2)_2$, 88393-36-6; $Mo(CO)_2(PMe_3)(S_2CNEt_2)_2$, 88393-37-7; $Mo(CO)_2(PMe_3)(S_2CN\text{-}i\text{-}Pr_2)_2$, 88393-38-8; $Mo(CO)(PMe_3)_2(S_2CNMe_2)_2$, 88393-39-9; $Mo(CO)(PMe_3)_2(S_2CNEt_2)_2$, 88393-40-2; $Mo(CO)(PMe_3)_2(S_2CN\text{-}i\text{-}Pr_2)_2$, 88393-41-3; $W(CO)_2(PMe_3)(S_2CNMe_2)_2$, 88393-42-4; $W(CO)_2(PMe_3)(S_2CNEt_2)_2$, 88393-43-5; $W(CO)_2(PMe_3)(S_2CN\text{-}i\text{-}Pr_2)_2$, 88393-44-6; $W(CO)(PMe_3)_2(S_2CNMe_2)_2$, 88393-45-7; $W(CO)(PMe_3)_2(S_2CNEt_2)_2$, 88393-46-8; $W(CO)(PMe_3)_2(S_2CN\text{-}i\text{-}Pr_2)_2$, 88393-47-9; $MoCl_2(PMe_3)_4$, 85185-53-1; $MoBr_2(PMe_3)_4$, 85185-54-2; $MoI_2(PMe_3)_4$, 85248-74-4; $WCl_2(PMe_3)_4$, 85798-76-1.

Supplementary Material Available: ^1H and $^{31}P\{^1H\}$ NMR spectra (13 pages). Ordering information is given on any current masthead page.

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The $[VO(O_2)_2Cl]^{2-}$–$[V(O_2)_3Cl]^{2-}$ Pair in Peroxyvanadium(V) Chemistry: Synthesis of the First Chloroperoxyvanadate(V) Compounds and Evidence for Diperoxyvanadate(V)–Triperoxyvanadate(V) Interconversion

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Alkali-metal and ammonium salts of yellow oxydiperoxychlorovanadates(V), $A_2[VO(O_2)_2Cl]$, and blue triperoxychlorovanadates(V), $A_2[V(O_2)_3Cl]$ (A = Na, K, or NH_4), have been synthesized, for the first time, by reacting V_2O_5 with alkali chloride, ACl, and hydrogen peroxide in varying concentrations of alkaline media. The three salts of the anion $[VO(O_2)_2Cl]^{2-}$ are comparatively more stable than those of the complex anion $[V(O_2)_3Cl]^{2-}$. Characterization of the compounds has been made from the results of elemental analyses, magnetic susceptibility measurements, and IR spectroscopic studies. The IR spectra suggest that the peroxy groups are bonded to vanadium(V) in a triangular bidentate manner and that the O–O bond order of peroxy ligands decreases with the increase in the number of peroxy ligands coordinated to the metal center. The conversion of $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$ and the reverse provide good evidence for the facile diperoxyvanadate(V)–triperoxyvanadate(V) interconversion.

Studies of peroxyvanadium chemistry have generated considerable current interest[1-7] probably owing to the special biochemical significance[8,9] of peroxy–transition-metal complexes. Whereas most of the recent reports on peroxyvanadium chemistry deal with the studies in solutions,[2-7] the synthesis and structural assessment of such compounds have received only scant attention. Moreover, only a few heteroligand peroxy complexes of vanadium are known, in contrast to many such reported examples for the other transition metals.[9-11] Our interest in this area involving the synthesis, characterization, structural assessment, and study of the chemistry of peroxyvanadium compounds[12,13] has led to the synthesis of chloro-

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peroxy compounds of vanadium(V). In this paper we wish to report the synthesis of two series of chloroperoxyvanadium(V) compounds, viz., the yellow alkali-metal and ammonium oxydiperoxychlorovanadates(V), $A_2[VO(O_2)_2Cl]$, and the blue alkali-metal and ammonium salts of triperoxychlorovanadate(V), $A_2[V(O_2)_3Cl]$ (A = Na, K, or NH_4), the first chloroperoxy compounds of vanadium. Also reported in this paper are a set of internally consistent data regarding the effect on the ν_{O-O} mode of O_2^{2-} ligands with the increase in the number of such ligands in going from $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$ and the facile interconversion $[VO(O_2)_2Cl]^{2-} \rightleftarrows [V(O_2)_3Cl]^{2-}$, evidencing the ability of such compounds to undergo a basic formation reaction and an acidic dissociation reaction.

Experimental Section

The chemicals used in the present work were all reagent grade products (B.D.H., Merck, or Sarabhai M. Chemicals). Infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer separately in KBr and in Nujol media. Molar conductance measurements were made by using a Philips PR 9500 conductivity bridge. Magnetic susceptibility measurements were made by the Gouy method. The compound $Hg[Co(NCS)_4]$ was the calibrant.

Syntheses of $A_2[VO(O_2)_2Cl]$ (A = Na, K, or NH_4). Vanadium pentoxide and dry alkali chloride, ACl, taken in the molar ratio 1:2, were intimately mixed by powdering them together in an agate mortar. A concentrated solution of the corresponding alkali hydroxide, AOH, was then added to the mixed powder while the molar ratio V_2O_5:AOH was maintained at 1:10, and the resulting mixture was stirred at room temperature for ca. 10 min. Hydrogen peroxide (9% solution) was slowly added to the solution with constant stirring, with the molar ratio of V_2O_5:H_2O_2 rising ultimately to 1:14. Stirring was continued at room temperature for another 15 min followed by filtration to remove any undissolved residue. The clear solution was cooled at ice-bath temperatures for ca. 20 min. An excess of ethyl alcohol was then added to the cold solution with stirring until yellow-colored microcrystalline $A_2[VO(O_2)_2Cl]$ was obtained. The reaction container was allowed to cool at ice-bath temperatures for ca. 10 min. The compound was separated by centrifugation, washed several times with ethyl alcohol until it was free from alkali, and finally dried in vacuo over phosphorus pentoxide. The yields of $(NH_4)_2[VO(O_2)_2Cl]$, $Na_2[VO(O_2)_2Cl]$, and $K_2[VO(O_2)_2Cl]$ were 77%, 83%, and 77%, respectively.

Syntheses of $A_2[V(O_2)_3Cl]$ (A = Na, K or NH_4). The blue alkali-metal and ammonium triperoxychlorovanadates(V), $A_2[V(O_2)_3Cl]$, were synthesized in a manner analogous to that described above. The only difference was that the molar ratio V_2O_5:ACl:AOH:H_2O_2 was maintained at 1:2:15:14. The reaction was monitored by infrared spectroscopy. The disappearance of the sharp band at ca. 950 cm^{-1} owing to $\nu_{V=O}$ in the compound isolated from the reaction medium indicated completion of the reaction. The yields of $(NH_4)_2[V(O_2)_3Cl]$, $Na_2[V(O_2)_3Cl]$, and $K_2[V(O_2)_3Cl]$ were 85%, 80%, and 77%, respectively.

Conversion of Oxydiperoxychlorovanadate(V), $[VO(O_2)_2Cl]^{2-}$, to Triperoxychlorovanadate(V), $[V(O_2)_3Cl]^{2-}$, and Vice Versa. The interconversion reactions were studied with the $Na_2[VO(O_2)_2Cl]$ and $Na_2[V(O_2)_3Cl]$ compounds.

Conversion of $Na_2[VO(O_2)_2Cl]$ to $Na_2[V(O_2)_3Cl]$. Sodium oxydiperoxychlorovanadate(V) (0.5 g, 2.4 mmol) was dissolved in a concentrated solution of sodium hydroxide (2.2 g, 5.5 mmol) followed by immediate addition of 9% hydrogen peroxide (30.0 mL, 79.4 mmol); a blue solution was obtained. The solution was cooled at ice-bath temperatures for ca. 15 min, and then an excess of ethyl alcohol was added to precipitate the blue sodium triperoxychlorovanadate(V), $Na_2[V(O_2)_3Cl]$. The compound was separated by centrifugation, washed several times with ethyl alcohol, and finally dried in vacuo.

Reconversion of $Na_2[V(O_2)_3Cl]$ to $Na_2[VO(O_2)_2Cl]$. A blue solution was obtained by dissolving 0.3 g (1.3 mmol) of sodium triperoxychlorovanadate(V) in 30 mL (79.4 mmol) of 9% hydrogen peroxide containing 3.3 g (83 mmol) of sodium hydroxide. Dilute hydrochloric acid (1 N) was added dropwise until the solution became permanently yellow. The solution was cooled at ice-bath temperatures for ca. 20 min followed by the addition of an excess of ethyl alcohol to produce the yellow sodium oxydiperoxychlorovanadate(V), $Na_2[VO(O_2)_2Cl]$. The compound was isolated and purified in a similar manner to that described above.

Interconversion of $Na_2[VO(O_2)_2Cl] \rightleftarrows Na_2[V(O_2)_3Cl]$ was also studied in the following manner. The yellow solution was first prepared by the reaction of V_2O_5 with NaCl, NaOH, and 9% H_2O_2 with the molar ratio maintained at 1:2:10:14. Addition of an excess of ethyl alcohol to a part of the solution afforded the yellow sodium oxydiperoxychlorovanadate(V), $Na_2[VO(O_2)_2Cl]$. To the remaining solution was added more sodium hydroxide in the form of its concentrated solution (total molar ratio of V_2O_5:ACl:AOH:H_2O_2 as 1:2:15:14), and a blue solution was obtained. The blue solution was divided into two parts, and an excess of alcohol was added to one part of it to produce the sodium triperoxychlorovanadate(V), $Na_2[V(O_2)_3Cl]$. Dropwise addition of dilute hydrochloric acid (1 N) to the other part of the solution until it turned permanently yellow, followed by the addition of ethyl alcohol, gave the yellow sodium oxydiperoxychlorovanadate(V), $Na_2[VO(O_2)_2Cl]$. Both the basic formation (peroxide, O_2^{2-} uptake) and the acidic dissociation (deperoxygenation) reactions were performed at ice-bath temperatures.

Elemental Analyses. Vanadium analysis was done volumetrically, after expelling the peroxy oxygen and separating chloride, by titration with a standard potassium permanganate solution as described in our previous paper.[13] The peroxide content of the compounds was determined by redox titration with a standard Ce^{4+} solution[14] and chloride by Volhard's method.[15] Sodium, potassium, and nitrogen were determined by the methods described in our earlier paper.[13] The analytical data and the IR band positions are summarized in Table I.

Results and Discussion

Synthesis. It has been emphasized in the literature[11] very recently that only a few heteroligand peroxyvanadium compounds have been known although there have been many such examples for other transition metals. It is possible that vanadium presents a different story owing to the uncertain nature of peroxyvanadium species in solutions of varying pH.[5,16,17] An elementary consideration in the course of our studies[12,13] mainly involving the synthesis and structural assessment of peroxyvanadium compounds suggested that hitherto unknown chloroperoxyvanadium compounds could be synthesized under suitable conditions. Moreover, we were interested in ascertaining the mimimum number of peroxy groups responsible for the formation of blue peroxyvanadates about which no mention was made in any of the studies made in solutions.[5,16,17]

Because of the very facile oxidation of chloride to chlorine by hydrogen peroxide in the presence of an acidic medium, we thought that an alkaline medium should be conducive to the synthesis of chloroperoxyvanadium compounds. In accord with the synthetic strategy, the reactions of V_2O_5 with ACl, AOH, and 9% H_2O_2 in the molar ratios of V_2O_5:ACl:AOH:H_2O_2 of 1:2:10:14 and 1:2:15:14 gave rise to the formation of the yellow $[VO(O_2)_2Cl]^{2-}$ and blue $[V(O_2)_3Cl]^{2-}$ species, respectively. The complex ions were isolated in the solid state as their alkali-metal and ammonium salts by the addition of ethyl alcohol. The role of alcohol was to facilitate precipitation of the compounds. In the course of our work we observed that the blue color of the vanadium–hydrogen peroxide system, in the presence of Cl^- ion, was obtained with a relatively lower concentration of the alkaline medium at a comparatively higher temperature. However, the higher temperature was not considered favorable for the synthesis of such compounds over an enhanced concentration of alkaline

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Table I. Analytical Data and Structurally Significant IR Bands of $A_2[VO(O_2)_2Cl]$ and $A_2[V(O_2)_3Cl]$ (A = Na, K, or NH_4)

	% found (% calcd)					
compd	A or N	V	O_A[a]	Cl	IR, cm^{-1}	assignt
$(NH_4)_2[VO(O_2)_2Cl]$	13.21	24.82	32.13	17.92	970 (s)	ν_{V-O}
	(13.84)	(25.16)	(31.61)	(17.51)	870 (s)	$\}\nu_{O-O}$
					885 (s)	
					610 (s)	ν_{V-O_2}
					415 (s)	ν_{V-Cl}
					3160 (m)	ν_3
					3045 (s)	ν_1
					1400 (s)	ν_4
$Na_2[VO(O_2)_2Cl]$	22.21	24.34	31.33	16.28	955 (s)	ν_{V-O}
	(21.65)	(23.99)	(30.14)	(16.69)	875 (s)	$\}\nu_{O-O}$
					885 (s)	
					610 (s)	ν_{V-O_2}
					410 (s)	ν_{V-Cl}
$K_2[VO(O_2)_2Cl]$	31.57	20.21	26.88	14.78	970 (s)	ν_{V-O}
	(31.97)	(20.83)	(26.17)	(14.49)	875 (s)	$\}\nu_{O-O}$
					890 (s)	
					615 (s)	ν_{V-O_2}
					415 (s)	ν_{V-Cl}
$(NH_4)_2[V(O_2)_3Cl]$	12.43	22.79	44.66	16.72	855 (s)	ν_{O-O}
	(12.82)	(23.32)	(43.94)	(16.23)	620 (s)	ν_{V-O_2}
					410 (s)	ν_{V-Cl}
					3155 (m)	ν_3
					3040 (s)	ν_1
					1400 (s)	ν_4
$Na_2[V(O_2)_3Cl]$	20.92	22.85	42.93	15.22	860 (s)	ν_{O-O}
	(20.13)	(22.31)	(42.04)	(15.52)	615 (s)	ν_{V-O_2}
					420 (s)	ν_{V-Cl}
$K_2[V(O_2)_3Cl]$	30.83	20.31	36.13	13.25	855 (s)	ν_{O-O}
	(30.06)	(19.58)	(36.90)	(13.63)	620 (s)	ν_{V-O_2}
					415 (s)	ν_{V-Cl}

[a] Peroxy oxygen.

medium. The fact that a very high concentration of the alkaline medium leads to the formation of the triperoxy species $[V(O_2)_3Cl]^{2-}$ while the relatively lower concentration of the alkaline medium produces $[VO(O_2)_2Cl]^{2-}$ suggests that a very high alkaline medium probably helps replacement of the last oxygen from the $[VO(O_2)_2Cl]^{2-}$ by a $O_2{}^{2-}$ group, thereby favoring the formation of $[V(O_2)_3Cl]^{2-}$, or that the oxo oxygen of the $[VO(O_2)_2Cl]^{2-}$ species is converted to the third peroxy ligand by abstracting an oxygen of hydrogen peroxide. It is difficult for us to say, in the absence of any direct evidence, which of the two mechanisms is more probable. However, the fact that oxygen exchange on vanadium(V) is very slow[6] and the strength of the V–O multiple bond is high, as evident from the IR spectroscopic studies of oxovanadium(V) complexes,[12,18] indicates that the latter mechanism may be more likely. It is, therefore, evident that under the appropriate conditions, the heteroperoxyvanadium(V) compounds of the types $A_2[VO(O_2)_2Cl]$ and $A_2[V(O_2)_3Cl]$ can be synthesized and that a minimum number of three peroxy groups are required for the formation of blue peroxyvanadium compounds. We expect that a similar synthetic strategy can be applied for the synthesis of other heteroperoxyvanadium(V) compounds.

Characterization and Structural Assessment. The alkali-metal and ammonium oxydiperoxychlorovanadates(V), $A_2[VO(O_2)_2Cl]$, are yellow microcrystalline compounds, and the similar salts of triperoxychlorovanadates(V), $A_2[V(O_2)_3Cl]$, are blue. The salts of the anion $[VO(O_2)_2Cl]^{2-}$ are generally more stable than those of the anion $[V(O_2)_3Cl]^{2-}$. A comparison of the properties of chloroperoxyvanadates(V) with those of the corresponding fluoroperoxyvanadates(V)[12,13] reveals that the most notable difference that result from changing the hetero ligand from F^- to Cl^- is the fall in stability, with the difference being more pronounced in the cases of heterotriperoxyvanadate(V) compounds. While the alkali-metal and ammonium salts of fluorotriperoxyvanadate(V) are stable for prolonged periods,[13] those of the chloroperoxyvanadate(V) are unstable. $A_2[V(O_2)_3Cl]$ (A = NH_4 or K) decomposed to a yellow microcrystalline product. The decomposition products have not yet been clearly identified; however, they have been found to contain peroxy groups, as evidenced by the results of chemical determination and IR spectroscopy, but definitely not to the extent of three peroxy ligands per vanadium. The stability of the compounds was ascertained by periodically estimating their peroxide content and recording their IR spectra. The determination of peroxide content of such compounds is considered to be crucial in order to decide the number of such groups coordinated to the metal center. The peroxide estimation was accomplished by redox titration with a standard cerium(IV) solution,[14] the results of which conclusively suggested the presence of two peroxy ligands per V^{5+} ion in the yellow compounds and three peroxy groups per V^{5+} ion in the blue compounds. The diamagnetic nature of the compounds, as evidenced by their magnetic susceptibility measurements, ensures that the vanadium occurs in its +5 oxidation state in each of the newly synthesized compounds.

The IR spectra of the three salts of the yellow $[VO(O_2)_2Cl]^{2-}$ ion resemble each other very closely (Table I), indicating thereby that the compounds are similar both structurally and stoichiometrically. The absorptions occurring in the four characteristic regions, viz. at 955–970, 870–890, 610–615, and 410–415 cm^{-1}, are well precedented in the literature and have been assigned respectively to ν_{V-O} of the terminally bonded V=O group,[12,18,19] to the ν_{O-O} mode of

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coordinated peroxy ligands,[12,20] to ν_{V-O_2},[20] and to ν_{V-Cl}.[21] The three extra vibrations at 3160 (m), 3045 (s), and 1400 (s) cm^{-1} in the case of the ammonium salt have been attributed to the ν_3, ν_1, and ν_4 modes of NH_4^+. The spectral pattern is in order and conforms well with the formula $A_2[VO(O_2)_2Cl]$.

The spectra of the three salts of the $[V(O_2)_3Cl]^{2-}$ anion also resemble each other very strongly, showing absorptions in the regions 855–860, 615–620, and 410–420 cm^{-1}, respectively, owing to the presence of coordinated peroxide and chloride ligands, and the peaks are assigned to the ν_{O-O}, ν_{V-O_2}, and ν_{V-Cl} modes. The three extra modes for the NH_4^+ ion in the case of the ammonium salt were also observed in their usual positions. The spectral pattern and the band positions resemble those of the analogous $A_2[V(O_2)_3F]$ compounds,[13] suggesting that both the triperoxychlorovanadates(V) and triperoxyfluorovanadates(V) probably have structural similarity.

The ν_{O-O} absorptions in the spectrum of each of the compounds occur in the region stipulated for the presence of triangularly bonded O_2^{2-} ligands,[12,13,20] leading us to conclude that in each of them the peroxy group is bonded to the vanadium(V) center in a triangular bidentate manner. A perusal of the spectra of the two series of compounds revealed that those of $A_2[V(O_2)_3Cl]$ compounds completely lack the absorption at ca. 950 cm^{-1} of ν_{V-O}. This conforms to the formula $A_2[V(O_2)_3Cl]$. The other difference was the shift, though small, in the positions of ν_{O-O} modes to a relatively lower region in the cases of the blue peroxy compounds (Table I). Whereas the ν_{O-O} absorptions for $A_2[VO(O_2)_2Cl]$ compounds lie in the region 870–890 cm^{-1}, those for the $A_2[V(O_2)_3Cl]$ compounds lie in the region 855–860 cm^{-1}. The fall in the ν_{O-O} frequency suggests a decrease in the O–O bond order of the coordinated peroxy ligands with the increase in the number of peroxy groups bound to the vanadium(V) center.

Conversion of $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$ and the Reverse. Evidence for Facile Diperoxyvanadate(V)–Triperoxyvanadate(V) Interconversion. Having obtained the yellow oxydiperoxychlorovanadates(V), $A_2[VO(O_2)_2Cl]$, and the blue triperoxychlorovanadates(V), $A_2[V(O_2)_3Cl]$, we thought it would be interesting to study the conversion of $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$ and vice versa. We chose the sodium salts of the anions for such studies because of their stabilities. It was observed that under suitable conditions (vide Experimental Section) $Na_2[VO(O_2)_2Cl]$ can be easily converted to $Na_2[V(O_2)_3Cl]$, which again can be reconverted to $Na_2[VO(O_2)_2Cl]$. The oxydiperoxychlorovanadate(V)–triperoxychlorovanadate(V) interconversion reactions were found to be quite facile, thereby affording a very good example of a process involving a basic formation reaction and an acidic dissociation reaction. Although both compounds are formed in the presence of alkaline medium and an excess of hydrogen peroxide, it is the large excess of alkaline medium that favors the formation of the triperoxyvanadium(V) species. The peroxide uptake and the deperoxygenation reactions can be best monitored by IR spectroscopy. The complete conversion of the $[VO(O_2)_2Cl]^{2-}$ species to $[V(O_2)_3Cl]^{2-}$ is ascertained by observing the complete disappearance of the ν_{V-O} band at ca. 950 cm^{-1} in a small amount of the compound isolated from the solution. The reverse reaction, i.e., the process $[V(O_2)_3Cl]^{2-} \rightarrow [VO(O_2)_2Cl]^{2-}$, was confirmed not only by observing the color change of the solution from blue to yellow but also by noting the appearance of the new band at about 950 cm^{-1} owing to ν_{V-O} and the shift of the ν_{O-O} absorption toward a relatively higher frequency.

It may be concluded that under the conditions described above, the complex species responsible for yellow and blue colors are $[VO(O_2)_2Cl]^{2-}$ and $[V(O_2)_3Cl]^{2-}$, respectively. In each of the compounds the peroxy ligands are bonded in a triangular bidentate manner to the V^{5+} center. The complex species $[VO(O_2)_2Cl]^{2-}$ may be a hexacoordinated monomer or it may as well be a polymer through a weak V–O–V or a weak V–Cl–V bridging. Similarly the complex species $[V(O_2)_3Cl]^{2-}$ may be a heptacoordinated monomer or it may have a polymeric structure through a weak V–Cl–V interaction. The $[VO(O_2)_2Cl]^{2-} \rightleftarrows [V(O_2)_3Cl]^{2-}$ interconversion provides a good example of a process that involves a basic formation reaction and an acidic dissociation reaction of peroxyvanadium(V) compounds.

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Registry No. $(NH_4)_2[VO(O_2)_2Cl]$, 88336-57-6; $Na_2[VO(O_2)_2Cl]$, 88326-64-1; $K_2[VO(O_2)_2Cl]$, 88326-65-2; $(NH_4)_2[V(O_2)_3Cl]$, 88326-66-3; $Na_2[V(O_2)_3Cl]$, 88326-67-4; $K_2[V(O_2)_3Cl]$, 88326-68-5.

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