Oxodiperoxovanadate(v) Complexes with Bidentate Ligands

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Crystalline oxodiperoxovanadate(v) complexes containing co-ordinated 2,2′-bipyridine(bipy), 1,10-phenanthroline(phen), and oxalato-groups, $C_2O_4^{2-}$(ox), $M[VO(O_2)_2L],nH_2O$ (M = Na, K, or NH_4; L = bipy or phen; n = 2—5) and $M_3[VO(O_2)_2(ox)],2H_2O$ (M = K or NH_4), have been prepared. The complexes are formed in hydrogen peroxide solutions of trioxovanadate(v) ions in the presence of corresponding ligands. They are soluble in water, where molar conductivity measurements indicate the presence of 1 : 1 and 1 : 3 electrolytes, respectively. With large excesses of the bidentate nitrogen ligands, complexes are obtained, of simplest formula $LH_2[V_2O_2(O_2)_4L_2],6H_2O$ (L = bipy or phen), which do not contain a monomeric peroxovanadate(v) group. The oxodiperoxovanadate(v) complexes are not analogous nor isomorphous with eight-co-ordinate triperoxo-niobate(v) and -tantalate(v) complexes containing the same bidentate ligands and prepared under similar conditions.

PREVIOUSLY [1] we have shown that triperoxo-niobate(v) and -tantalate(v) complexes are formed in the presence of neutral bidentate nitrogen ligands, such as 2,2′-bipyridine and 1,10-phenanthroline respectively, and that mono- and di-peroxo-mixed-ligand complexes of Nb^V and Ta^V are generally obtained in the presence of more electronegative ligands, such as halide or oxalate ions. The triperoxo-complexes, $K[M(O_2)_3L]$ [M = Nb or Ta; L = 2,2′-bipyridine(bipy) or 1,10-phenanthroline(phen)] possess four bidentate ligands, and no terminal or bridging oxo-group. Their stereochemistry has been confirmed by X-ray structure determination.[2]

Our attention has been recently drawn to these complexes again, since several reports have appeared [3-7] dealing with mixed-ligand vanadium(v) peroxo-complexes. Our attempts to obtain eight-co-ordinate V^V derivatives analogous to those of Nb^V and Ta^V (ref. 1) failed, resulting perpetually in formation of hydrated oxodiperoxovanadate(v) complexes, involving one additional bidentate nitrogen or oxygen ligand, as reported here. However, it is of significance that all peroxo-complexes of V^V prepared previously [5-10] in acidic or neutral media contain a terminal or bridging oxo-group, *e.g.* $K_3[O\{VO(O_2)_2\}_2]$ [10] and $NH_4[VO(O_2)_2NH_3]$.[6a] These complexes of vanadium(v) are not analogous to those of Nb^V and Ta^V, formed under similar conditions, and such behaviour is anticipated because of the greater tendency of vanadium to form bonds to oxygen. On the other hand, peroxovanadate(v) complexes prepared in strong alkaline media, such as $K_3[V(O_2)_4]$, are members of an isomorphous series [9] comprising Cr^V, V^V, Nb^V, and Ta^V.

Triperoxovanadate(v) complexes have not been found in acidic solution,[11] but recently it was claimed that they existed in crystalline complexes involving eight-co-ordination and bidentate ligands [3] similar to those reported here and elsewhere.[4] Eight-co-ordination has not been confirmed so far by X-ray structure analysis [5-7] in mixed-ligand V^V complexes. Seven-co-ordination, however, expected for the oxodiperoxo-derivatives described here, seems to be more common for mixed-ligand peroxo-complexes, and the pentagonal bipyramidal arrangement has been found in V^V (refs. 5 and 6*b*) and Mo^{VI} (ref. 12*a*) complexes. If the peroxo-group were to be considered as monodentate [12b] then the co-ordination number in these complexes would be reduced to five, which is fairly common in vanadium(v) complexes.

EXPERIMENTAL

Preparations.—Ammonium oxalato-oxodiperoxovanadate(v), $(NH_4)_3[VO(O_2)_2(ox)],2H_2O$. Ammonium trioxovanadate(v), NH_4VO_3 (0·59 g), was dissolved with cooling in hydrogen peroxide (20%, 15 ml) and added to a solution (10 ml) of ammonium oxalate (0·71 g) in hydrogen peroxide

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(20%). Ethanol was then added gradually until a precipitate started to appear. The latter was redissolved with a small amount of hydrogen peroxide and the reaction mixture set aside to crystallize at 5 °C. Orange *crystals* obtained were filtered off and dried on the filter paper.

Potassium oxalato-oxodiperoxovanadate(v), $K_3[VO(O_2)_2(ox)],2H_2O$. Vanadium pentoxide (0·91 g) and potassium hydroxide (1·95 g) were dissolved in water (20 ml) and to this solution oxalic acid (1·26 g), dissolved in water (10 ml) and hydrogen peroxide (30%, 20 ml), was added. Precipitation was initiated by ethanol as above, the precipitate redissolved, and the reaction mixture set aside to crystallize at room temperature (large crystals) or in a cool place (small crystals). *Orange* crystals obtained were filtered off and dried on the filter paper.

Ammonium (2,2′-bipyridine)oxodiperoxovanadate(v), $(NH_4)[VO(O_2)_2(bipy)],4H_2O$. Ammonium trioxovanadate(v) (0·59 g) was dissolved under cooling in hydrogen peroxide (20%, 20 ml) and 2,2′-bipyridine (0·8 g), dissolved in ethanol (10 ml), was added with stirring. After 2—3 min, more ethanol (20 ml) was added and the reaction mixture set aside to crystallize at 5 °C. The yellow *crystals* obtained were filtered off, washed once with ethanol, and dried in air.

Ammonium oxodiperoxo(1,10-*phenanthroline*)*vanadate*(v), $(NH_4)[VO(O_2)_2(phen)],2H_2O$, was prepared similarly, but the amounts of water and hydrogen peroxide were reduced to half the above quantities because of the solubility properties of this complex. *Sodium*(2,2′-*bipyridine*)*oxodiperoxovanadate*(v), $Na[VO(O_2)_2(bipy)],5H_2O$ *and sodium oxodiperoxo*(1,10-*phenanthroline*)*vanadate*(v), $Na[VO(O_2)_2(phen)],5H_2O$, were again obtained as above, but crystallization took place more slowly. Crystals were dried on the filter paper in air.

Potassium (2,2′-*bipyridine*)*oxodiperoxovanadate*(v), $K[VO(O_2)_2(bipy)],5H_2O$. Vanadium pentoxide (0·91 g) and potassium hydroxide (0·65 g) were dissolved in water (10 ml), cooled, and, if necessary, the dissolution was completed with a small amount of hydrogen peroxide. To the clear, cool solution hydrogen peroxide (10 ml) and 2,2′-bipyridine (1·6 g) dissolved in ethanol (7—8 ml) were added. Pure *crystals* were obtained as described for the analogous oxalato-derivative of potassium. *Potassium oxodiperoxo*(1,10-*phenanthroline*)*vanadate*(v), $K[VO(O_2)_2(phen)],3H_2O$, was obtained similarly.

$(H_2bipy)[V_2O_2(O_2)_4(bipy)_2],6H_2O$. Vanadium pentoxide (0·46 g) was carefully dissolved in hydrogen peroxide (20%, 20 ml) and the resulting solution added dropwise to a hydrogen peroxide (30%, 20 ml) solution of 2,2′-bipyridine (present in an excess). The pH was not allowed to drop below 3. Orange *crystals* which formed immediately, and continued to form on setting aside the solution at 5 °C, were filtered off and dried in air. The complex $(H_2phen)[V_2O_2(O_2)_4(phen)_2],6H_2O$ was prepared similarly, but crystallization took place more slowly and the yield was lower.

Analyses.—Vanadium was determined in sodium and potassium salts gravimetrically by precipitation with ammonia in the presence of tannin. In the other complexes vanadium was determined by direct ignition to V_2O_5. The peroxide content of these complexes was determined in 1N-sulphuric acid by titration with 0·05M-Ce^{IV}. In complexes which also contained the oxalato-group, this titration yields the sum ($O_2^{2-} + C_2O_4^{2-}$) and the peroxide content was calculated from the oxalate content derived from carbon analysis. Iodometric determination of the peroxide content,[8] which also involves reduction of V^V, was carried out for the peroxo-complexes and several blanks containing NH_4VO_3, in 1N-sulphuric acid, by titration with 0·05N-$Na_2S_2O_3$. Sodium and potassium were determined by flame photometry, after the salts had been dissolved in water and the solution acidified with hydrochloric acid. Carbon, hydrogen, and nitrogen analyses were obtained from Central Microanalytical Laboratory, Institute ' Rudjer Bošković,' and all analytical data are shown in Table 1.

TABLE 1

Analytical data

Complex	Found (%)						Calc. (%)					
	C	H	N	($O_2^{2-}/2$)	V	Na/K	C	H	N	($O_2^{2-}/2$)	V	Na/K
$Na[VO(O_2)_2(bipy)],5H_2O$	29·9	5·0	7·0	8·1	12·7	5·9	30·0	4·5	7·0	8·0	12·7	5·8
$K[VO(O_2)_2(bipy)],5H_2O$	29·1	5·1	6·8	7·7	12·4	9·9	28·9	4·3	6·7	7·7	12·2	9·4
$NH_4[VO(O_2)_2(bipy)],4H_2O$	32·1	5·6	11·3	8·7	13·4		31·8	5·4	11·1	8·5	13·5	
$Na[VO(O_2)_2(phen)],5H_2O$	33·9	3·8	6·7	7·4	12·1	5·6	34·0	4·2	6·6	7·5	12·0	5·4
$K[VO(O_2)_2(phen)],3H_2O$	36·2	3·6	7·1	8·2	13·6	10·4	37·3	3·1	7·3	8·4	13·2	10·1
$NH_4[VO(O_2)_2(phen)],2H_2O$	39·9	5·8	11·1	8·5	13·6		39·5	4·4	11·5	8·7	13·9	
$K_3[VO(O_2)_2(ox)],2H_2O$	6·4	0·8		8·5	13·8	30·9	6·5	1·0		8·6	13·7	31·8
$(NH_4)_3[VO(O_2)_2(ox)],2H_2O$	7·8	4·6	13·8	10·8	16·7		7·8	5·2	13·6	10·4	16·5	
$(H_2bipy)[V_2O_2(O_2)_4(bipy)_2],6H_2O$	42·1	5·3	10·0	7·9	12·0		42·9	4·5	10·0	7·7	12·1	
$(H_2phen)[V_2O_2(O_2)_4(phen)_2],6H_2O$	49·1	5·1	9·8	7·3	11·4		48·4	4·3	9·4	7·2	11·4	

I.r. spectra were recorded on Perkin-Elmer model 337 and 651 spectrometers, as Nujol or hexachlorobutadiene mulls. Special care was taken to avoid decomposition of the complexes during the measurements, which was observed to occur with NaCl and KBr because of water and peroxo-reactions initiated by grinding, pressing, or heating the samples. Wherever possible Polythene plates were used. The conductivity of aqueous solutions was measured in the concentration range 3×10^{-4}—5×10^{-3}M, reproducible values being obtained; the water used had a conductivity lower than $3 \times 10^{-6}\ \Omega^{-1}\ cm^2$. *X*-Ray powder photographs were recorded, in a 0·3 mm capillary with Cu-K_α radiation, by a Philips 114·6 mm camera.

RESULTS

In hydrogen peroxide (10—20%) solutions of trioxovanadate(v) ions containing 2,2′-bipyridine, 1,10-phenanthroline, and oxalate ligands, the bidentate ligands enter the co-ordination sphere of V^V, together with one terminal oxo- and two peroxo-groups. Complexes of formulae $M[VO(O_2)_2L],nH_2O$ ($M = Na$, K, or NH_4; L = bipy or phen; $n = 2$—5) and $M_3[VO(O_2)_2(ox)],2H_2O$ (M = K or NH_4) were prepared from these solutions by precipitation with ethanol. Chemical tests described previously[1] show that no free peroxo-, oxalato-, or bidentate nitrogen ligands are present in the aqueous solutions of these complexes.

Molar conductivity measurements in water (Table 2) indicate the presence of 1 : 1 and 3 : 1 electrolytes, respectively, as expected. Hydrated, transparent yellow crystals of these mixed-ligand peroxo-complexes can be kept in air for several days, but over drying agents they loose crystallinity, becoming a fine powder. Nevertheless, set aside at room temperature over phosphorous pentoxide *in vacuo*, most of the peroxo-oxygen is retained and they loose water. On gentle heating above 50 °C, all the complexes gradually decompose, loosing water and oxygen simultaneously. Dehydration of these complexes is hence a complex process. Thermal gravimetric and differential thermal analysis measurements too involve gradual decomposition and, therefore, the water content of those complexes cannot be derived from them. The number of water molecules reported is deduced from chemical analysis only and is not therefore entirely reliable.

TABLE 2

Some properties of oxodiperoxovanadate(V) complexes

Complex	λ	Tentative assignment of pertinent i.r. bands (cm^{-1})			
	$\Omega^{-1}\ cm^2\ mol^{-1}$	$\nu(V{=}O)$	$\nu_1(O{-}O)$	$\nu_3(MO_2)$	$\nu_2(MO_2)$
$Na[VO(O_2)_2(bipy)],5H_2O$	110	945vs	895m, 872vs	623m	588s
$K[VO(O_2)_2(bipy)],5H_2O$	114	930vs	875s, 856vs	621m	582s
$NH_4[VO(O_2)_2(bipy)],4H_2O$	118	930vs	870s, 858vs	622m	585s
$Na[VO(O_2)_2(phen)],5H_2O$	98	940vs	880s, 858vs	628m	588s
$K[VO(O_2)_2(phen)],3H_2O$	109	925vs	870s, 854vs	635m	590m
$NH_4[VO(O_2)_2(phen)],2H_2O$	112	930vs	870s, 850vs	636m	588m
$K_3[VO(O_2)_2(ox)], 2H_2O$	365	930vs	877s, 852vs	631s	585s
$(NH_4)_3[VO(O_2)_2(ox)],2H_2O$	396	932vs	882s, 864vs	634s	591s
$(H_2bipy)[V_2O_2(O_2)_4(bipy)_2],6H_2O$	192	945s	890s, 845s		
$(H_2phen)[V_2O_2(O_2)_4(phen)_2],6H_2O$	187	935s	890s, 840s		

Under similar conditions, but with excesses of 2,2′-bipyridine and 1,10-phenanthroline, respectively, crystalline orange-yellow oxoperoxovanadate(V) complexes were prepared, corresponding by analysis to the simplest formula $(LH_2)[V_2O_2(O_2)_4L_2],6H_2O$ (L = bipy or phen). These complexes, containing co-ordinated and protonated nitrogen ligands (as cations), may be represented by other formulae, compatible with the spectral and analytical data. For example, they can be formulated as $(LH_2)H_2[O\{VO(O_2)_2(bipy)\}_2],5H_2O$ in view of a structure found in dimeric peroxovanadate complexes.[5] In water, solutions of these complexes show a conductivity larger and smaller than expected for 1 : 1 and 2 : 1 electrolytes respectively, implying that here conductivity data are of not much significance. There are no similar model salts with which the conductivity values of these complexes could be compared,[13] and it is also possible that these complexes are weak electrolytes, where conductivity data become meaningless. Insight into the molecular structure of these polymeric oxoperoxovanadate(V) complexes can be obtained only by *X*-ray structure analysis.

In Table 2 tentative assignment of relevant bands found in the i.r. spectra is given, conforming well with previous reports of spectra of the co-ordinated oxo- and peroxo-groups.[10, 14–17] An acceptable value for the stretching frequency of the terminal V=O group is observed (Tables 2 and 3) and it has been found that this absorption band is rather broad in these complexes. Bands below 900 cm^{-1}, which do not belong to the ligands L, have been assigned to ν_1, ν_2, and ν_3 of the co-ordinated peroxo-group (Table 2). Spectra of the 2,2′-bipyridine complexes are straightforward in this respect, since 2,2′-bipyridine does not absorb significantly between 1000 and 800 cm^{-1}. The case of the oxalate ligand is similar, and even 1,10-phenanthroline, which displays a strong band at 850 cm^{-1}, does not obscure the assignments since this band is not shifted on co-ordination.

The shape and pattern of the peroxo-group bands in these diperoxovanadium complexes is characterized by one strong absorption, showing an additional medium-intensity peak, resolved on the higher-frequency side, separated from the main peak by only *ca.* 10 cm^{-1}. This pattern is quite different from that observed in triperoxo-mixed-ligand niobate and tantalate complexes[1] where a strong doublet is observed as a distinct feature of (O–O) stretching frequencies, the two peaks being separated by *ca.* 40 cm^{-1}. Assignment of ν_2 and ν_3 is somewhat less well established.[10] Values given in Table 2 were arrived at by choosing additional bands, observed in the expected region on comparison with the spectra of free bidentate ligands L, which seemed to be in agreement with previous findings.[10] As with Nb^V and Ta^V derivatives,[1] spectra indicate the presence of bidentate 2,2′-bipyridine, 1,10-phenanthroline, and oxalato-groups, respectively. The spectra of these oxodiperoxovanadate complexes are actually rather similar to those shown by triperoxo- and diperoxo-vanadate complexes, $M[V(O_2)_3L],nH_2O$ ($M = NH_4$, K, or Na; L = bipy, phen, or ox; n = 1—7) and $(NH_4)_2[(bipy)_2H_2V_2O_{11}]$-$3H_2O_2,3H_2O$ respectively.[3, 4]

Complexes containing protonated nitrogen ligands as cations display a very rich i.r. spectrum, expected from interaction of the vibrational modes of the protonated and co-ordinated nitrogen ligands. However, the presence of bridging V–O–V group vibrational modes (broad background absorption between 900 and 750 cm^{-1}), terminal V=O stretching frequencies (Table 2), and ν_1(O=O) is indicated by the spectra. The existence of co-ordinated and protonated nitrogen bases in these complexes is hinted at by the presence[15] and/or splitting of bands at 2350 (broad), 1600, and 765 cm^{-1}.

Peroxide analysis in these systems is of crucial importance, since the number of peroxo-groups per vanadium atom may be deduced from it. Our experiments showed that iodine titration of ammonium (2,2′-bipyridine)oxodiperoxovanadate(V) requires exactly 5 electron-equivalents,

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which corresponds to 2·5 peroxo-group equivalents. Peroxide analysis with Ce^{IV}, however, resulted in the consumption of 4 electron-equivalents, corresponding to two peroxo-groups per vanadium atom. The same results were obtained for other mixed-ligand peroxo-complexes, implying reactions (1) and (2). Accordingly, the consumption of

$$VO(O_2)_2^-(aq) + 5I^- + 8H^+ \longrightarrow VO^{2+}(aq) + 2{\cdot}5I_2 + 4H_2O \quad (1)$$

$$VO(O_2)_2^-(aq) + 4Ce^{4+}(aq) + H_2O \longrightarrow VO_2^+(aq) + 2O_2 + 2H^+ + 4Ce^{3+}(aq) \quad (2)$$

5 equivalents according to (1) is due to the reduction of two peroxo-groups and to the reduction of V^V to V^{IV}. Oxidation with Ce^{IV}, on the other hand, involves peroxo-groups only, showing the presence of two O_2^{2-} per vanadium ion.

In order to verify the above conclusions, we titrated several blanks (no peroxo-complexes; sulphuric acid media) containing trioxovanadate(v) ions (NH_4VO_3) in the presence and absence of 2,2′-bipyridine. Iodine formation observed in such blanks corresponded approximately to 1 electron equivalent (slightly greater than one, probably due to catalytic iodine formation). These results show that vanadium(v) is reduced almost quantitatively under the described conditions. In addition, solutions at the end of the titration had a characteristic green-blue colour, expected for V^{IV}. Based on this analytical evidence and combined with i.r. spectral data on the presence of the V=O group, the complexes have been formulated as the oxodiperoxo-derivatives.

X-Ray powder photographs do not indicate isomorphism of analogous oxodiperoxo-salts and they show, as expected, a different powder pattern from those of the analogous potassium triperoxo-niobate and -tantalate complexes.[1]

DISCUSSION

The results show that, under similar conditions, vanadium(v) does not behave as Nb^V and Ta^V in hydrogen peroxide solutions. This finding is not new and conforms well with the established pattern in the co-ordination chemistry of the early transition metals. Oxodiperoxovanadate complexes have been reported previously[8,11] and by composition they correspond to some Cr^{VI}, Mo^{VI}, and W^{VI} peroxo-complexes which exhibit co-ordination numbers of six and seven.[5,6,12] It is important to specify the difficulties involved in the characterization of V^V peroxo-complexes, which may cause misinterpretation of experimental results. The dilemma lies in postulating the presence of a peroxo-group or an oxo-group. The principal experimental evidence used to distinguish between these two alternatives involves i.r. assignments of V=O and O=O stretching frequencies, and chemical analysis for the peroxo-group. Information obtained from spectral or analytical measurements may be ambiguous for the reasons briefly described below.

The terminal M=O group stretching frequency appears for the early transition metals in the vicinity of the most characteristic co-ordinated peroxo-group, the O–O stretching frequency ν_1. Wrong assignment of the strong bands between 1000 and 850 cm^{-1} can therefore lead to false conclusions on molecular composition. Since the peroxo-complexes are much too large to allow reliable application of theoretical treatments, and too complex for isotopic substitution, empirical assignments based on a comparison of the spectra of several analogous complexes remain ' educated guesses ' widely used in spectral studies of transition-metal peroxo-complexes.

Methods of peroxo-group analysis in transition-metal peroxo-complexes have been summarized.[8] Titration with Ce^{IV} seems to be satisfactory for vanadium systems, but the iodometric method in general cannot be trusted,[8] since, in particular, in peroxovanadate complexes it results in the simultaneous reduction of vanadium (for the V^V–V^{IV} couple, $E^0 = 1{\cdot}0$ V). The use of iodometric analysis for the complexes described here may well indicate a wrong number of peroxo-groups, since the titration, combined with various errors involved in the analytical procedures, can imply the consumption of 6-electron-equivalents, corresponding to the presence of three peroxo-groups.

TABLE 3

Metal–oxygen stretching frequencies found for the terminal oxo-group in some vanadium(v) complexes

Complex	ν(V=O)/cm^{-1}	Ref.
VOF_3	1058	*a*
$VOCl_3$	1035	*a*
$VOBr_3$	1025	*a*
$[VO(OH)(oxin)_2]$ [b]	952	*a*
$CsVOF_4$	1023 1016	*c*
VOF_5^{2-}	989	*c*
$VO(NO_3)_3$	1007	6*b*
$VO(NO_3)_3MeCN$	1010	6*b*
$(Hpy)[VOCl_4]$ [d]	967	*e*
$[Hquin)[VOCl_4]$	970	*e*
$[Hisoquin)[VOCl_4]$	972	*e*
$[Et_4N)[VOCl_4]$	965	*e*
$VO(CH_2SiMe_3)_3$	985	*h*
$K_4[O\{VO(O_2)_2\}_2]$	963 951	10*a*
$[NH_4)_4[O\{VO(O_2)_2\}_2]$	990 970	4
$(NH_4)_2[(bipy)_2H_2V_2O_{11}]3H_2O_2,3H_2O$	950 930	4

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The V=O stretching frequencies given in Table 2 fall in the expected region (Table 3). The complexity and range of absorption of the individual bands observed for the peroxo-complexes is hard to explain, and probably implies different interactions of vibrational modes. The peroxo-group frequencies given in Table 2 agree well with previously observed values.[1,10a] Differences observed in the pattern of these bands, on comparison with the triperoxo-niobate and -tantalate complexes, have to be expected because of the different number of peroxo-groups and the different symmetry involved. Additional support for the presence of only two peroxo-groups in the present complexes is the fact that their powder photographs do not indicate isomorphism with the analogous triperoxo-niobate and -tantalate complexes,[1] which would be expected if these two series of complexes were of identical composition. The peculiarly formulated ammonium (2,2′-bipyridine)peroxovanadate[4] (Table 3) and ammonium (2,2′-bipyridine)triperoxovanadate[3] seem to resemble, according to the i.r. spectra and some other properties reported, the ammonium (2,2′-bipyridine)oxodiperoxovanadate complex prepared in this study. The *X*-ray structure analysis[3] of the (2,2′-bipyridine)triperoxovanadate is, of course, of great interest.

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