

Notes

First Synthesis and Structural Assessment of Alkali-metal Carbonatodioxoperoxouranate(vi) Monohydrates, $A_2[UO_2(O_2)(CO_3)] \cdot H_2O$, and Carbonato-oxodiperoxovanadate(v) Trihydrates, $A_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$

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The complexes $A_2[UO_2(O_2)(CO_3)] \cdot H_2O$ ($A = Na$ or K) have been synthesised from the reaction of the product obtained by treating $UO_2(NO_3)_2 \cdot 6H_2O$ with AOH and $AHCO_3$ (ratio $U : CO_3^{2-} = 1 : 4$) with an excess of 30% H_2O_2 at pH 7–8, and $A_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$ ($A = Na$ or K) have been synthesised by treating V_2O_5 with A_2CO_3 (ratio $V : CO_3^{2-} = 1 : 1.5$) and an excess of 30% H_2O_2 at pH ca. 7. They were precipitated with ethanol. The occurrence of *trans* $O=U=O$ and terminal $V=O$ in the $[UO_2(O_2)(CO_3)]^{2-}$ and $[VO(O_2)_2(CO_3)]^{3-}$ ions, respectively, and the presence of triangular bidentate O_2^{2-} and chelated bidentate CO_3^{2-} groups, have been ascertained from i.r. and laser Raman spectra. The complexes $A_2[UO_2(O_2)(CO_3)] \cdot H_2O$ can be dehydrated at ca. 100 °C, a temperature at which $A_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$ starts to decompose.

The complexity involved in the field of peroxouranates is an acknowledged problem.^{1,2} Few examples of peroxouranates have been reported, $[NH_4]_2[UO_2(O_2)(CO_3)] \cdot 2H_2O$ ³ being the only one for which the synthesis is available. In contrast, relatively more is known about complex peroxovanadates,^{4,5} and some peroxovanadates containing co-ordinated N-heterocyclic ligands have been very well characterised.⁵ However, $[VO(O_2)_2C_2O_4]^{3-}$ is to our knowledge the only peroxovanadate having an oxygen-containing ligand.^{5,6} Attempts to co-ordinate SO_4^{2-} with V^V in the presence of O_2^{2-} were unsuccessful,⁷ however, the simultaneous co-ordination of CO_3^{2-} and O_2^{2-} to V^V appeared to be possible under appropriate conditions.

Experimental

The chemicals used were all reagent-grade products. Magnetic susceptibilities and the pH of the reaction solutions were measured as described earlier.^{4,8} Molar conductances were measured using a Philips PR 9500 conductivity bridge. I.r. spectra were recorded on a Perkin-Elmer model 983 instrument. The laser Raman spectra were recorded at ambient temperatures on a SPEX Ramalog 1403 spectrometer using the line at 4 880 Å from a Spectra Physics model 165 argon laser as the excitation source. The sample was held either in a quartz capillary or in the form of a pressed pellet.

Synthesis of Alkali-metal Carbonatodioxoperoxouranate(vi) Monohydrates, $A_2[UO_2(O_2)(CO_3)] \cdot H_2O$ ($A = Na$ or K).— Powdered $UO_2(NO_3)_2 \cdot 6H_2O$ (1 g, 1.99 mmol) was dissolved in hot water (20 cm³) and a 20% solution of AOH ($A = Na$ or K) was added slowly with stirring until a yellow product ceased to appear. The solution was filtered while hot and the yellow product washed free from alkali. To a stirred water suspension of the product, $AHCO_3$ (8 mmol; ratio $U : CO_3^{2-} = 1 : 4$) was added and stirring continued for ca. 20 min. An excess of 30% H_2O_2 (30 cm³, 264.7 mmol) was added until a clear yellow solution was obtained. The pH of the solution was found to be 7–8. The solution was filtered and then cooled in an ice-bath for ca. 30 min. Addition of pre-cooled ethanol (ca. 50 cm³) led to the precipitation of a yellow microcrystalline solid which was filtered off, washed 3–4 times with ethanol, and then dried *in vacuo* over concentrated H_2SO_4 . The yields of $Na_2[UO_2(O_2)-$

$(CO_3)] \cdot H_2O$ and $K_2[UO_2(O_2)(CO_3)] \cdot H_2O$ were 0.7 (82) and 0.8 g (88%) respectively.

Synthesis of Alkali-metal Carbonato-oxodiperoxovanadate(v) Trihydrates, $A_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$ ($A = Na$ or K).— In a typical synthesis a mixture of V_2O_5 (1 g, 5.5 mmol) and A_2CO_3 (16.5 mmol; ratio $V : CO_3^{2-} = 1 : 1.5$) was dissolved in 30% H_2O_2 (15 cm³, 132.4 mmol) giving a clear yellow solution. The solution was filtered and the filtrate cooled in an ice-bath for ca. 15 min. An excess of pre-cooled ethanol was added with stirring until the yellow microcrystalline $A_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$ ($A = Na$ or K) was completely precipitated. The stirring and cooling were continued for another 30 min. The compounds were isolated, purified, and dried similarly to the peroxouranates. The yields of $Na_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$ and $K_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$ were 3 (87) and 3.2 g (80%) respectively.

Elemental Analysis.—The determinations of uranium,⁸ and of vanadium, peroxide, carbon, sodium, and potassium,⁴ were as described earlier. The elemental analyses, molar conductances, and structurally significant i.r. and Raman bands are summarised in the Table.

Results and Discussion

The importance of the pH for the successful synthesis of peroxo-metal compounds has been emphasised,^{4,9,10} and it was shown very recently that a relatively high pH favoured co-ordination of O_2^{2-} with UO_2^{2+} (ref. 8) and VO^{3+} .^{4,10} In the present case, pH > 6 was considered conducive in order to prevent the reaction $CO_3^{2-} + 2H^+ \longrightarrow CO_2 + H_2O$. Thus pH ca. 7 was found to be suitable for the syntheses. It is imperative that the products isolated at pH 4 or 5 either did not show the presence of CO_3^{2-} at all or did to a very small extent, indicating that co-ordination of the CO_3^{2-} ligand might have just commenced. However, the reaction of UO_2^{2+} with hydrogen peroxide and $AHCO_3$ ($A = Na$ or K) at pH 7–8, and that of V_2O_5 with H_2O_2 and A_2CO_3 at pH 7, followed by the addition of alcohol which facilitated precipitation, afforded $A_2[UO_2(O_2)(CO_3)] \cdot H_2O$ and $A_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$ respectively in very high yields. Attempts to synthesise the ammonium salts of the complex ions were not successful. Corresponding salts of Rb^+ and

Table. Analytical data, molar conductances, structurally significant i.r. and laser Raman bands of $A_2[VO_2(O_2)(CO_3)] \cdot H_2O$ and $A_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$ ($A = Na$ or K)

Compound	Molar conductance ^a / $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	Analysis ^b (%)				I.r. (cm^{-1})	Laser Raman (cm^{-1})	Assignment
		A	U or V	O ^c	C			
$Na_2[VO_2(O_2)(CO_3)] \cdot H_2O$	255(20)	10.45 (10.8)	56.2 (55.85)	7.8 (7.5)	2.85 (2.8)	1 580s	1 570	$\nu(C-O) \nu_1, A_1$
						1 325m		$\nu(C-O) + \delta(O-C-O)$
								ν_5, B_2
						920s	930	$\nu(O=U=O)$
						890s	880	$\nu(O-O) \nu_1$
						615m	600	$\nu(U-O_2) \nu_3$
$K_2[VO_2(O_2)(CO_3)] \cdot H_2O$	245(20)	17.3 (17.1)	52.25 (51.95)	7.2 (7.0)	2.6 (2.6)	1 570s	1 570	$\nu(C-O) \nu_1, A_1$
						1 330m		$\nu(C-O) + \delta(O-C-O)$
								ν_5, B_2
						925s	930	$\nu(O=U=O)$
						885s	885	$\nu(O-O) \nu_1$
						610m	600	$\nu(U-O_2) \nu_3$
$Na_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$	370(7)	23.2 (21.95)	16.7 (16.2)	20.65 (20.4)	3.85 (3.8)	1 580s	1 580	$\nu(C-O) \nu_1, A_1$
						1 340s		$\nu(C-O) + \delta(O-C-O)$
								ν_5, B_2
						940s	940	$\nu(V=O)$
						865s	870	$\nu(O-O) \nu_1$
						620s	600	$\nu(V-O_2) \nu_3$
$K_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$	375(7)	32.6 (32.4)	14.55 (14.05)	18.2 (17.65)	3.35 (3.3)	1 585s	1 580	$\nu(C-O) \nu_1, A_1$
						1 335s		$\nu(C-O) + \delta(O-C-O)$
								ν_5, B_2
						945s	940	$\nu(V=O)$
						865s	865	$\nu(O-O) \nu_1$
						625s	600	$\nu(V-O_2) \nu_3$
	530	$\nu(V-O_2) \nu_2$						

^a Temperature ($^{\circ}\text{C}$) in parentheses. ^b Calculated values are in parentheses. ^c Peroxo-oxygen.

Cs^+ could be obtained by the method analogous to that used for Na^+ and K^+ . Strong desiccation of the compounds over concentrated H_2SO_4 did not remove the water of crystallisation. Pyrolysis of $A_2[VO_2(O_2)(CO_3)] \cdot H_2O$ at 100°C expelled the water molecule without changing the composition of the complex ion, while at the same temperature the $A_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$ started to decompose through the loss of both O_2^{2-} and H_2O .

The molar conductances of $A_2[VO_2(O_2)(CO_3)] \cdot H_2O$, lying in the range $240\text{--}255 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ at room temperature, are as expected and attest to the stability of the complexes. The room-temperature molar conductances of $A_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$ were higher than the expected values, indicating rapid decomposition. The values obtained at *ca.* 7°C , *ca.* $370 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ were, however, as expected, suggesting that the complex peroxovanadates are stable in solution only at low temperatures.

The complexes $A_2[VO_2(O_2)(CO_3)] \cdot H_2O$ and $A_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$ tend to absorb moisture slowly. The compounds are diamagnetic, in conformity with the occurrence of U^{VI} and V^{V} respectively. The results of the peroxide estimations, by redox titrations^{4,8,10} involving separate standard potassium permanganate and cerium(IV) solutions, suggest the presence of one peroxide per U^{VI} and two peroxides per V^{V} in the corresponding complexes.

The i.r. spectra of $A_2[VO_2(O_2)(CO_3)] \cdot H_2O$ show bands at *ca.* 920s , *ca.* 890s , and *ca.* 610m and *ca.* 550s cm^{-1} due to $\nu(\text{O}=\text{U}=\text{O})$, *trans*,^{8,11} $\nu(\text{O}-\text{O})$, and $\nu(\text{U}-\text{O}_2)$ modes^{8,10,12} respectively, at *ca.* 1580s , *ca.* 1330m , *ca.* 1050s , *ca.* 750m , *ca.* 675m , and *ca.* 415cm^{-1} due to $\nu(\text{C}-\text{O})$, $\nu(\text{C}-\text{O}) + \delta(\text{O}-\text{C}-\text{O})$, $\nu(\text{C}-\text{O})$, ring deformation + $\nu(\text{U}-\text{O})$, $\delta(\text{O}-\text{C}-\text{O}) + \nu(\text{U}-\text{O})$, and $\nu(\text{U}-\text{O})$ respectively originating from the co-ordinated bidentate carbonate,¹³ and at *ca.* 3455m and *ca.* 1630s cm^{-1}

due to $\nu(\text{O}-\text{H})$ and $\delta(\text{H}-\text{O}-\text{H})$ modes of unco-ordinated water. The laser Raman spectra, recorded in the solid state because of low solubility, exhibited peaks at *ca.* 930cm^{-1} assigned to $\nu(\text{O}=\text{U}=\text{O})$,^{8,11} at 880 , *ca.* 600 , and *ca.* 550cm^{-1} due to $\nu(\text{O}-\text{O})$, ν_1 , $\nu(\text{U}-\text{O}_2)$, ν_3 , and $\nu(\text{U}-\text{O}_2)$, ν_2 respectively,¹² and at *ca.* 1570cm^{-1} due to $\nu(\text{C}-\text{O})$ (ν_1, A_1) of co-ordinated CO_3^{2-} . The distinction between the ν_2 and ν_3 modes of $\nu(\text{U}-\text{O}_2)$ was made on the basis of the sharpness and intensity of the peaks, that at *ca.* 550cm^{-1} being the sharpest and most intense. The i.r. spectra of $A_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$ show $\nu(\text{V}=\text{O})$, terminal at *ca.* 940s cm^{-1} , $\nu(\text{O}-\text{O})$, ν_1 at 865s cm^{-1} , and the two $\nu(\text{V}-\text{O}_2)$, ν_2 , and ν_3 modes at *ca.* 525s and *ca.* 620s cm^{-1} due to co-ordinated O_2^{2-} groups. The bands at *ca.* 1585s , *ca.* 1340s , *ca.* 1050s , *ca.* 740m , *ca.* 695w , and *ca.* 395m cm^{-1} have been attributed to $\nu(\text{C}-\text{O})$, $\nu(\text{C}-\text{O}) + \delta(\text{O}-\text{C}-\text{O})$, $\nu(\text{C}-\text{O})$, ring deformation + $\nu(\text{V}-\text{O})$, $\delta(\text{O}-\text{C}-\text{O}) + \nu(\text{V}-\text{O})$, and $\nu(\text{V}-\text{O})$ modes¹³ respectively, while those at *ca.* 1640s and *ca.* 3450m cm^{-1} have been assigned to $\delta(\text{H}-\text{O}-\text{H})$ and $\nu(\text{O}-\text{H})$ modes of unco-ordinated water.¹⁴ The laser Raman spectra of $A_3[VO(O_2)_2(CO_3)] \cdot 3H_2O$ exhibit a strong peak at 940cm^{-1} assigned to $\nu(\text{V}=\text{O})$, peaks at *ca.* 870 , *ca.* 600 , and *ca.* 530cm^{-1} attributed to the $\nu(\text{O}-\text{O})$, ν_1 , $\nu(\text{V}-\text{O}_2)$, ν_3 , and $\nu(\text{V}-\text{O}_2)$, ν_2 modes¹² respectively of the co-ordinated O_2^{2-} , and a peak at *ca.* 1580cm^{-1} assigned to the $\nu(\text{C}-\text{O})$, ν_1 , A_1 mode of co-ordinated CO_3^{2-} . The facile loss of water at 100°C and the resemblance of the peak shapes and positions of $\delta(\text{H}-\text{O}-\text{H})$ and $\nu(\text{O}-\text{H})$ with those of unco-ordinated water^{14,15} suggest that the water molecules are not co-ordinated. The typical pattern of absorptions due to the co-ordinated O_2^{2-} ,^{4,8,12} and those due to co-ordinated CO_3^{2-} ,¹³ especially the appreciable separation between $\nu_1(A_1)$ and $\nu_5(B_2)$ modes (Table) and also the appearance of a Raman peak at *ca.* 1575cm^{-1} due to $\nu(\text{C}-\text{O})$ (ν_1, A_1), render it certain that both the peroxide (O_2^{2-}) as well as the carbonate (CO_3^{2-}) ligands

are bonded to the metal centres in a bidentate chelated (C_{2v}) manner.

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