Synthesis, Structural Assessment and Reaction Chemistry of $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ containing η^2- and σ:σ-Bonded Peroxides

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The compound $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ has been synthesised from the reaction of $UO_3\cdot 4H_2O$ with H_2O_2 in an ammoniacal medium (pH 8–9), and characterised by chemical analysis and vibrational spectroscopy. Infrared and laser-Raman spectroscopy indicates both chelated and bridging peroxides. In aqueous solution the complex reacts with SO_2(g), CO_2(g) and NO_2(g) to produce $[UO_2(O_2)]\cdot 4H_2O$ as an intermediate, and a sulfato-, a carbonato- and presumably a nitrato-complex, respectively, of UO_2^{2+} as the final products.

The interactions which take place between UO_2^{2+} and hydrogen peroxide have been of interest for many years,[1–3] though this aspect of uranium chemistry appears to be highly complicated.[3] We have been interested in the peroxo chemistry of uranium and some of our previous publications have addressed the synthesis and characterisation of complex peroxouranates having fluoride,[4] sulfate and oxalate,[5] carbonate,[6] and amines or amino acids[7] as the coligands. While all these complexes were obtained as monoperoxo derivatives of the metal, a few diperoxouranium(VI) complexes with Schiff bases as coligands have been reported.[8] It was observed, during our earlier investigations, that peroxouranates possessing a $UO_2^{2+}:O_2^{2-}$ ratio of $1:>1$ are difficult to obtain. Our concern in this context was to develop a synthetic methodology for peroxouranium(VI) species containing $[U_2O_4(O_2)_3]^{2-}$ and evaluate the mode of co-ordination of the peroxo ligands using vibrational spectroscopy. In addition we aimed to study the reaction profile of such a complex with inorganic substrates like SO_2(g), CO_2(g) or NO_2(g) in aqueous media and to isolate the products at different stages of its reactions.

Here we describe studies on an anionic system $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$ including its synthesis, characterisation and reactivity with the chosen gaseous substrates.

Experimental

The chemicals used were of reagent grade quality. The water used for reactivity studies was deoxygenated by first boiling it under a nitrogen atmosphere and then cooling to room temperature followed by bubbling nitrogen gas through it for *ca.* 15 min. It was stored in an air-tight container.

Infrared spectra of the compounds were recorded on a nitrogen-purged Perkin Elmer 983 spectrophotometer as Nujol mulls between CsI plates or as KBr pellets between sodium chloride plates. Laser Raman spectra were recorded on a SPEX Ramalog model 1403 spectrometer using the 4880 Å line from a Spectra-Physics Model 165 argon-ion laser as the excitation source. The spectra were recorded at ambient temperatures from pressed pellets of the compounds. Molar conductances and pH values were measured as described earlier.[9]

Synthesis of $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$.—To $UO_3\cdot 4H_2O$ (1 g, 2.79 mmol) was added 30% H_2O_2 (12 cm^3, 105.78 mmol). The mixture was stirred for 5 min followed by dropwise addition of aqueous ammonia (sp.gr. 0.9) until a clear dark orange solution was obtained. The pH recorded at this stage was 8–9. Stirring was continued for *ca.* 10 min, and then a yellow microcrystalline product was precipitated by the addition of ice-cold ethanol (*ca.* 20 cm^3). After allowing to stand for 30 min, the precipitate was filtered off and washed three or four times with ethanol. It was dissolved in water (20 cm^3) and reprecipitated with ethanol (*ca.* 20 cm^3). The compound thus obtained was separated by centrifugation, washed three times with ethanol and finally dried *in vacuo* over concentrated H_2SO_4. Yield 0.7 g (65%).

The compound was deuteriated as follows: $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ (0.3 g) was dissolved in ^2H_2O (15 cm^3) and the solution stirred at ambient temperature for 7 h. The yellow solution was then allowed to stand for 48 h and finally dried in a vacuum desiccator.

Isolation of Dioxoperoxouranium(VI) *Tetrahydrate*, $[UO_2(O_2)]\cdot 4H_2O$ **1**.—Yellow $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ (1 g, 1.28 mmol) was dissolved in deoxygeneated water (20 cm^3). The aliquot of water used for reactivity studies was purged with the substrate gas prior to dissolving the complex, in order to avoid any decomposition of the compound before its contact with the substrate. In three separate experiments, SO_2(g), CO_2(g) or NO_2(g) was bubbled through the yellow solution with constant stirring until a microcrystalline product was precipitated from the solution. The pH at this stage was *ca.* 5. The precipitate was filtered off, washed repeatedly with ethanol, and then dried *in vacuo* over concentrated H_2SO_4. The yield of $[UO_2(O_2)]\cdot 4H_2O$ **1** was 0.7 g (73%).

Isolation of $[NH_4]_2[UO_2(SO_4)_2]\cdot 2H_2O$ **2**, $[NH_4]_2[UO_2(CO_3)_2]\cdot 5H_2O$ **3** *and a Nitrato Product*.—Through a solution of $[NH_4]_2[UO_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ (1 g, 1.28 mmol) in pretreated (as described above) deoxygenated water (20 cm^3) was passed a stream of SO_2(g), CO_2(g) or NO_2(g) until the yellow intermediate $[UO_2(O_2)]\cdot 4H_2O$ **1** which appeared at pH *ca.* 5 had redissolved, resulting into a clear solution. The pH of the solution was *ca.* 2 for SO_2(g) and *ca.* 3 for CO_2(g) or NO_2(g). Addition of precooled ethanol in each case resulted in the precipitation of a yellow microcrystalline compound. Starting from 1.0 g of $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$, the yield of $[NH_4]_2[UO_2(SO_4)_2]\cdot 2H_2O$ **2** was 1.0 g (80%), and that of $[NH_4]_2[UO_2(CO_3)_2]\cdot 5H_2O$ **3** was 1 g (73%). The uranyl nitrate product obtained from the reaction of $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ with NO_2(g) could not be assigned a definite formula.

Control Reactions.—(*a*) *Interaction with* N_2(g). A stream of

Table 1 Analytical and selected vibrational spectroscopic data

	Analysis[a] (%)				Spectral data (cm^{-1})		
Compound	N	U	O_2^{2-}	H	IR	Laser Raman	Assignment
$[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$	3.55	61.30	12.40	2.50	900s	905	ν(U=O) (*trans*-O=U=O)
	(3.60)	(61.00)	(12.30)	(2.60)	860s	855	ν(O–O) (triangular bidentate, C_{2v}, O_2^{2-})
					795w(br)	798	ν(O–O) (bridging, O_2^{2-})
					728w		δ(H–O–H) (ρ_r)
					490m	495	ν_2(U–O_2) } (triangular bidentate,
					465m	460	ν_3(U–O_2) } C_{2v}, O_2^{2-})
$[UO_2(O_2)]\cdot 4H_2O$	—	63.55	8.60	2.15	905s	900	ν(U=O) (*trans*-O=U=O)
		(63.65)	(8.55)	(2.15)	860m	860	ν(O–O) (chelating O_2^{2-})
					728m		δ(H–O–H) (ρ_r)
					615m	620	ν(U–O_2) (ν_2)
					597m	600	ν(U–O_2) (ν_3)
$[NH_4]_2[UO_2(SO_4)_2]\cdot 2H_2O$	5.35	44.50	36.25[c]	2.20	1150	1160	
	(5.25)	(44.44)	(35.95)	(2.25)	1120	1115	ν(S–O) (ν_3)
					1070	1075	
					920s	915	ν(U=O) (*trans*-U=O=O)
					677	670	
					618	625	ν(S–O) (ν_4)
					597	585	
$[NH_4]_2[UO_2(CO_3)_2]\cdot 5H_2O$	6.70	44.55	4.60[d]	3.75	1602	1595	ν(C–O) (ν_1)
	(6.75)	(44.55)	(4.5)	(3.80)	1209		ν(C–O) (ν_5)
					910s	905	ν(U=O) (*trans*-O=U=O)

[a] Calculated values are in parentheses. [b] Peroxo oxygen. [c] Sulfate. [d] Carbon.

N_2(g) was passed through a solution of $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ (1 g) in water (20 cm^3) for 2 h. The yellow solution remained unchanged, and on addition of ethanol (*ca.* 20 cm^3) afforded a yellow microcrystalline product. This was filtered off and dried *in vacuo* over concentrated H_2SO_4. The product was found to be similar to the starting compound.

(*b*) *Attempted reactions with* $[NH_4]_2SO_4$, $[NH_4]_2CO_3$ *and* NH_4NO_3. The procedure used in the following experiment was typical. A mixture of $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ (0.64 mmol) and $[NH_4]_2SO_4$ (1.3 mmol) was dissolved in water (15 cm^3). A stream of N_2(g) was passed through the yellow solution for *ca.* 40 min with stirring. The mixture was then allowed to stand for 2 h at room temperature. Addition of ethanol (8 cm^3) with stirring gave a yellow precipitate which was filtered off, washed with ethanol, and dried in a vacuum desiccator over silica gel. The compound was found to be exactly the same as the starting complex $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$.

The results of the experiments involving $[NH_4]_2CO_3$ and NH_4NO_3 were similar. In other words, the product obtained in each case was $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$.

Elemental Analyses.—Uranium was estimated gravimetrically as U_3O_8[10a] and also as uranyl quinolin-8-olate.[10a] The peroxide content was determined by redox titrations either with standard $KMnO_4$ solution or cerium(IV) solution and the result verified by iodometry. The active oxygen content was estimated in the presence of boric acid to avoid any loss of peroxide. Carbon, hydrogen and nitrogen were estimated by the Microanalytical Laboratory, Department of Chemistry, Shillong. Sulfate was estimated gravimetrically as $BaSO_4$.[10b]

Results and Discussion

Uranium(VI) exists as UO_2^{2+} in aqueous solution and interacts with hydrogen peroxide. The nature of the peroxo species formed depends largely on the pH. Thus, in order to obtain a peroxouranium complex of a particular composition, it is necessary to ascertain the appropriate pH. In previous work[7] the monoperoxo species '$UO_2(O_2)$' was shown to exist at pH 6–7. In view of this it was anticipated that a relatively higher pH (> 7) might lead to the formation of the desired complex possessing a $UO_2^{2+}:O_2^{2-}$ ratio of 2:3. Indeed the reaction of $UO_3\cdot 4H_2O$ with H_2O_2 at pH 8–9, maintained by the addition of aqueous ammonia, afforded the new complex $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ in high yield. Recrystallisation of the product yielded a pure compound which analysed very well (Table 1).

The complex is stable both in the solid state and in solution. The electrical conductance of the recrystallised product in water was 265 Ω^{-1} cm^2 mol^{-1} at 20 °C and the value remained unchanged over 7 h.

Infrared spectroscopy appears to be a very sensitive method to prove the identity of peroxometalates. For $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ the presence of a *trans* O=U=O arrangement is evidenced by a strong band at 900 cm^{-1}. The compound also exhibits two distinct vibrations at 860s and 795w(br) cm^{-1}, respectively, characteristic of the ν(O–O) mode of chelated[11] and bridging[12] peroxo ligands. We were interested also to locate the ν_2 and ν_3 modes of the chelated peroxo group. These have been observed in the 500–400 cm^{-1} region (Table 1). Notable in this context is the rather small separation between the two vibrations which requires slow scanning to avoid overlap. The bands of the co-ordinated water have been observed at 728w (rocking mode) and at 325 cm^{-1} (U–OH_2 stretch). The ν(O–H) and δ(H–O–H) vibrations were observed in the expected positions, although the ν(O–H) region was complicated because of the presence of both co-ordinated and lattice water molecules as well as the overlap of ν_1 and ν_3 modes of NH_4^+. However, the ν_4 mode of NH_4^+ has been clearly observed at 1400 cm^{-1}.

The infrared spectrum of the deuteriated species was recorded under similar conditions. The only band which showed a significant shift was the U–OH_2 stretch (from 325 to 312 cm^{-1}) providing evidence for the occurrence of co-ordinated water.

The Raman spectrum of the compound was recorded on a solid sample. This exhibited signals at 905 cm^{-1} [ν(U=O) (*trans*-O=U=O)], 855 [ν(O–O)], 495 [ν_2(U–O_2)] and 460 cm^{-1} [ν_3(U–O_2)]. The signal at 798 cm^{-1} is attributed to the ν(O–O) mode of the bridging peroxo group. These results compliment not only the IR patterns but also point to the peroxo-bridged dinuclear nature of the complex $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$. In addition, each UO_2^{2+} centre is co-ordinated to a chelated peroxo and an aqua ligand.

Reactions of $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ *with* $SO_2(g)$, $CO_2(g)$ *and* $NO_2(g)$.—Peroxometal complexes are expected to exhibit a variety of reactions. In a previous report[9] the reaction of a highly peroxygenated vanadium(v) complex, $[V(O_2)_3]^-$, with $SO_2(g)$ was described. In the present work an aqueous solution of $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ was treated separately with $SO_2(g)$, $CO_2(g)$ and $NO_2(g)$. On bubbling $SO_2(g)$ through the solution the compound interacted immediately as evidenced by the formation of a yellow solid at pH *ca.* 5 which reacted further with the substrate to form a soluble complex at pH *ca.* 2. Based upon these observations, two separate experiments involving $SO_2(g)$ were conducted. In the first the reaction was arrested at the stage when the solution attained a pH value of *ca.* 5 with a spontaneous precipitation of a yellow compound, **1**. In another experiment, the flow of $SO_2(g)$ was continued beyond the point of formation of **1** until the latter had redissolved completely, to afford a soluble complex at pH *ca.* 2. From this solution the compound **2** was isolated. Interestingly, **1** contained only peroxide but **2** contained sulfate and did not have peroxide as ascertained by a combination of chemical analyses and vibrational spectroscopy.

Compounds **1** and **2** have been characterised as $[UO_2(O_2)]\cdot 4H_2O$ and $[NH_4]_2[UO_2(SO_4)_2]\cdot 2H_2O$, respectively; **1** corresponds to one of the best characterised peroxouranium compositions and the results of the analyses and vibrational spectroscopy are in excellent agreement with those reported in the literature.[13] Compound **2** was diamagnetic and the chemical tests on it indicate the presence of uranium(VI). Thus, unlike the $[V(O_2)_3]^- + SO_2(g)$ reaction,[9] no reduction of the metal centre has taken place. This difference can be rationalised in terms of redox potentials. In aqueous acid solutions the E° values for the UO_2^{2+}–UO_2^{+} and V^V–V^{IV} couples are +0.05 and +1.00 V,[14] respectively, whereas that for the SO_4^{2-}–$SO_2\cdot xH_2O$ couple is +0.17 V.[14] Since systems with higher electrode potentials are expected to be reduced by systems with lower electrode potentials, the reduction of vanadium(v) to vanadium(IV) but not of UO_2^{2+} to UO_2^{+} by SO_2 is quite logical.

It has been commented that 'few physical data are available for known uranyl(VI) sulfato complexes'.[15] It was therefore desirable to study the properties of compound **2**. The solution electrical conductance of 260 Ω^{-1} cm^2 mol^{-1} is consistent with a 2:1 electrolyte. The invariant solution conductivity over a period of 10 d attests to the stability of the compound. Vibrational spectroscopy provides clear evidence supporting the formulation of the complex. While ν(U=O) (*trans*-O=U=O) was observed at 920s cm^{-1}, the ν_3 and ν_4 modes of co-ordinated SO_4^{2-} each gave three bands at 1070s, 1120s, 1150s and 597s, 618m, 677s cm^{-1}, respectively. This pattern is in line with the C_{2v} symmetry of the ligand. The appearance of ν_3 bands at lower wavenumbers (< 1200 cm^{-1}) compared with those of chelated SO_4^{2-} points to the occurrence of a bridging SO_4^{2-} ligand. The results of a laser Raman spectroscopic investigation provided further support for this. The Raman signal at 915 cm^{-1} assigned to ν(U=O) (*trans*-O=U=O) and three signals each for ν_3 (1075, 1115 and 1160 cm^{-1}) and ν_4 (585, 625, 670 cm^{-1}) are consistent with the proposed mode of bonding of the sulfato group. In addition, the ν(O–H) and δ(H–O–H) vibrations of the lattice water appeared in the expected positions, while the ν_4 mode of NH_4^+ was observed at 1400s cm^{-1} in the IR spectrum. Although the identity of compounds **1** and **2** has been ascertained without difficulty, the $[U_2O_4(O_2)_3(H_2O)_2]^{2-} + SO_2(g)$ reaction must involve several complicated steps.

Noteworthy is the absence, to the best of our knowledge, of any report on the reaction of a peroxometal complex with $CO_2(g)$ in an aqueous medium. We conducted the reaction between an aqueous solution of $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ and CO_2 (see Experimental section). The reaction went smoothly and a similar behaviour was observed as in the previous reaction. Thus, a yellow product was formed at pH *ca.* 5 which redissolved on passing $CO_2(g)$ through the solution with a concomitant lowering of pH to *ca.* 3. Addition of ethanol to the resulting solution provided a yellow compound **3**. Subsequently, two more reactions were conducted under similar experimental conditions to isolate the intermediate species at pH *ca.* 5 and the product **3** from the final solution (pH *ca.* 3). While the intermediate was characterised as exactly analogous with **1**, compound **3** was found to be a new carbonato complex, $[NH_4]_2[UO_2(CO_3)_2]\cdot 5H_2O$. The IR spectrum of **3** gave bands assigned to NH_4^+, lattice water, *trans*-O=U=O, and co-ordinated carbonate. A notable feature was the large separation between ν_1[A_1, ν(C–O)] at 1602 cm^{-1} and ν_5 [B_2, (C–O) + δ(O–C–O)] at 1209 cm^{-1}. The Raman spectrum showed in addition to the ν(U=O) (*trans*-O=U=O) signal at 905, a band at 1595 cm^{-1} assigned to the ν(C–O) (ν_1, A_1) mode of co-ordinated CO_3^{2-}. The large separation between the ν_1 and ν_5 modes of CO_3^{2-} in the IR spectrum and the appearance of the ν_1 mode in the Raman spectrum are striking and suggest[6,16] that the carbonato ligands are chelated in **3**.

Subsequently a similar reaction of the complex with $NO_2(g)$ was conducted. The substrate reacted with the complex to produce an isolable intermediate at pH *ca.* 5 which gave similar analyses to those for **1**, and as in the previous reactions redissolved on further bubbling of $NO_2(g)$ through the solution with a simultaneous lowering of the pH to *ca.* 3. Work-up of this solution afforded a microcrystalline product **4**. Unfortunately a well defined stoichiometric formula could not be assigned, although the presence of UO_2^{2+} and co-ordinated NO_3^- was evident from the vibrational spectra. Nitratoactinide complexes are generally very weak and the formation of such a complex requires a high nitrate concentration.[17]

Control Reactions.—Several control experiments were conducted to throw more light on the reactions described above. Interestingly, the complex $[NH_4]_2[U_2O_4(O_2)_3(H_2O)_2]\cdot 4H_2O$ was recovered unchanged when $N_2(g)$ was passed through its aqueous solution for an extended period and also in three separate experiments involving bubbling of $N_2(g)$ through aqueous solutions of the complex containing also $[NH_4]_2SO_4$, $[NH_4]_2CO_3$ or NH_4NO_3. These observations reveal the stability of the starting material. Thus, the substrate gases $SO_2(g)$, $CO_2(g)$ and $NO_2(g)$ must play a role in the reactions. Since the three gases are acidic in solution, it is quite likely that the corresponding acids convert the peroxouranate into $[UO_2(O_2)]\cdot 4H_2O$ **1**. This then reacts with the anions derived from the acid anhydrides to afford the sulfato and carbonato complexes obtained and presumably a nitrato product.

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