Synthesis, Characterisation, and Some Properties of Molecular Mixed-ligand Peroxo Complexes of Uranium(VI) containing Amines or Aminocarboxylic Acids as Coligands

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Molecular peroxo complexes of $[UO_2]^{2+}$, *viz.* $[UO_2(O_2)(phen)]$ (phen = 1,10-phenanthroline), $[UO_2(O_2)(bipy)]$ (bipy = 2,2'-bipyridyl), $[UO_2(O_2)(en)]$ (en = ethylenediamine), $[UO_2(O_2)(H_4edta)]$ (H_4edta = ethylenediamine-*NNN'N'*-tetra-acetic acid), and $[UO_2(O_2)(gly)]$ (gly = glycine), have been synthesised at different pH values of the reaction medium. They are diamagnetic. On the basis of spectroscopic evidence, both peroxide and each of the coligands, except gly, are co-ordinated to the metal in a bidentate manner, while gly occurs in its zwitterionic form and acts as a monodentate ligand. The complex $[UO_2(O_2)(gly)]$ oxidises triphenylphosphine, cyclohexene, styrene, and SO_2(g) to triphenylphosphine oxide, 1,2-cyclohexanediol, 1-phenylethylene glycol, and sulphate respectively.

Owing to an intrinsic interest in[1,2] and practical use of[3,4] peroxometal compounds there has been an upsurge of research in their chemistry. Although peroxoactinides are known,[5,6] molecular complexes are rather scanty.[7,8] This aspect of uranium is complicated[5] and $[UO_2(O_2)]\cdot nH_2O$ (n = 2 or 4) is best characterised. In addition $[UO_2(O_2)L]$ (L = Ph_3PO, Ph_3AsO, or pyridine *N*-oxide)[7] and a few diperoxouranium(VI) complexes with Schiff bases as coligands[8] are known. The compound $[UO_2(O_2)]\cdot 4H_2O$ oxidises olefins to epoxides and oxidative-cleavage products.[4] It has been observed[6] that $[UO_2]^{2+}$ reacts with H_2O_2 to generate '$UO_2(O_2)$' in solution and caused us to anticipate that a similar reaction in the presence of an appropriate coligand would provide an access to molecular peroxo-complexes of the metal. The present report deals with the synthesis, characterisation, and some properties of $[UO_2(O_2)(L{-}L)]$ [L–L = 1,10-phenanthroline (phen), 2,2'-bipyridine (bipy), ethylenediamine (en), or ethylenediamine-*NNN'N'*-tetra-acetic acid (H_4edta)] and $[UO_2(O_2)(gly)]$ (gly = glycine).

Experimental

The chemicals used were all reagent-grade products. Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer, laser Raman spectra on an instrument described earlier.[6] Magnetic susceptibility measurements were made by the Gouy method; using $Hg[Co(NCS)_4]$ as the calibrant. The pH values of the reaction solutions were measured with a Systronic type 335 digital pH meter and also with pH indicator paper (BDH).

Preparations.—Dioxoperoxo(1,10-*phenanthroline*)*uranium*(VI), $[UO_2(O_2)(phen)]$. To a solution of $UO_2(CH_3CO_2)_2\cdot 2H_2O$ (1.0 g, 2.36 mmol) in water (15 cm^3) was added an ethanolic solution (10 cm^3) of 1,10-phenanthroline monohydrate (0.47 g, 2.37 mmol). The whole was stirred for *ca.* 5 min whereupon a light yellow product began to appear. Hydrogen peroxide (30%; 15 cm^3; 132.35 mmol) was added and the mixture stirred for *ca.* 15 min. The pH of the solution was 3.5—4. Precooled ethanol (20 cm^3) was added for complete precipitation of the yellow microcrystalline $[UO_2(O_2)(phen)]$. The compound was separated by filtration, washed three or four times with ethanol, and dried *in vacuo* over concentrated H_2SO_4. Yield 1 g (91%).

(2,2'-*Bipyridine*)*dioxoperoxouranium*(VI), $[UO_2(O_2)(bipy)]$. The method was similar to that of $[UO_2(O_2)(phen)]$ except that 2,2'-bipyridine was used instead of 1,10-phenanthroline. Starting from $UO_2(CH_3CO_2)_2\cdot 2H_2O$ (1.0 g, 2.36 mmol) the yield of $[UO_2(O_2)(bipy)]$ was 1.7 g (94%).

(*Ethylenediamine*)*dioxoperoxouranium*(VI), $[UO_2(O_2)(en)]$. Uranyl nitrate hexahydrate, $[UO_2(NO_3)_2]\cdot 6H_2O$ (1.0 g, 1.99 mmol), was dissolved in water (15 cm^3) followed by the addition of aqueous ammonia (sp.gr. 0.9) until a yellow precipitate ceased to appear. The precipitate was filtered off and washed free from alkali and nitrate. An aqueous suspension (10 cm^3) of the yellow precipitate was treated with 5 N sulphuric acid solution (2 cm^3, 5.0 mmol). This was then filtered and cooled in an ice-bath. To the cold solution was added dropwise precooled ethylenediamine (3 cm^3, 49.92 mmol) with continuous stirring whereupon a light yellow product began to appear. To this an excess of 30% H_2O_2 (20 cm^3, 176.47 mmol) was added to obtain a clear orange-red solution. Stirring was continued for *ca.* 10 min while yellow microcrystalline $[UO_2(O_2)(en)]$ began to appear. The pH of the reaction medium was *ca.* 9. The compound was completely precipitated by adding cold ethanol (20 cm^3) and then left to stand for 30 min. The product was isolated by centrifugation, washed four times with ethanol, and finally dried *in vacuo* over concentrated H_2SO_4. Yield 0.7 g (92%).

(*Ethylenediamine*-NNN'N'-*tetra-acetic acid*)*dioxoperoxouranium*(VI), $[UO_2(O_2)(H_4edta)]$. To an aqueous suspension of the yellow product, obtained from $[UO_2(NO_3)_2]\cdot 6H_2O$ (1.0 g, 1.99 mmol) in a similar way to that described above, was added solid ethylenediamine-*NNN'N'*-tetra-acetic acid (0.58 g, 1.98 mmol) with stirring. The mixture was warmed over a steam-bath for *ca.* 15 min, and a lemon-yellow solution was obtained which was then cooled to room temperature. To this 30% H_2O_2 (15 cm^3, 132.35 mmol) was added and stirred for *ca.* 15 min whereupon a yellow microcrystalline product separated. The pH of the reaction solution was 2. The product was filtered off, washed four or five times with ethanol, and dried *in vacuo* over concentrated H_2SO_4. Yield 1 g (84%).

(*Glycine*)*dioxoperoxouranium*(VI), $[UO_2(O_2)(gly)]$. The yellow product from $[UO_2(NO_3)_2]\cdot 6H_2O$ (1.0 g, 1.99 mmol) was obtained in an analogous manner to that described under the synthesis of $[UO_2(O_2)(en)]$. An aqueous (10 cm^3) suspension of the product on treatment with 5 N H_2SO_4 (2 cm^3, 5.0 mmol) gave a clear solution. To this was added glycine (0.3 g, 3.99 mmol) and the solution was stirred for *ca.* 5 min followed by the addition of 30% H_2O_2 (15 cm^3, 132.35 mmol). Stirring was continued for 10 min whereupon a yellow product began to appear. The pH of the reaction medium was raised to *ca.* 6.5 by slow addition of a 20% solution of KOH. Addition of pre-cooled ethanol (50 cm^3) precipitated yellow microcrystalline $[UO_2(O_2)(gly)]$. The product isolation, purification, and drying were accomplished in similar ways to those described above. Yield 0.7 g (97%).

Elemental Analyses.—Uranium was estimated gravimetrically as U_3O_8.[9a] The peroxide content was determined by redox titration separately with standard $KMnO_4$ solution[9b] or cerium(IV) solution[9c] and the result was verified by iodometry.[9d] Carbon, hydrogen, and nitrogen were estimated by micro-analytical methods (Amdel Australian Micro Analytical Service, Port Melbourne, Victoria, Australia, and Micro Analytical Laboratories, Regional Sophisticated Instrumentation Centre, North-Eastern Hill University, Shillong).

Results and Discussion

Uranyl ion, $[UO_2]^{2+}$, reacts with H_2O_2 to produce '$UO_2(O_2)$',[6] and by conducting such reactions separately in the presence of each of the following coligands, phen, bipy, en, H_4edta, and gly, molecular peroxo complexes $[UO_2(O_2)(phen)]$, $[UO_2(O_2)(bipy)]$, $[UO_2(O_2)(en)]$, $[UO_2(O_2)(H_4edta)]$, and $[UO_2(O_2)(gly)]$ have been synthesised. It is important to note that the addition of H_2O_2 follows that of the coligand because the reverse order of addition is detrimental owing to a pronounced tendency to form sparingly soluble $[UO_2(O_2)]\cdot nH_2O$. Equally important in this context is the maintenance of an appropriate pH of the reaction solution. The role of ethanol was to bring about complete precipitation of the product.

Characterisation and Assessment of Structure.—The compounds are yellow, diamagnetic, e.s.r. silent, and sparingly soluble in water. They are partly soluble in organic solvents with $[UO_2(O_2)(gly)]$ being relatively more soluble. In the presence of dilute H_2SO_4 they dissolve in water, liberating H_2O_2. This facilitates determination of their active oxygen contents by redox titrations involving standard $KMnO_4$ or cerium(IV) solutions. The analysis results showed the UO_2^{2+}:O_2:heteroligand ratio as 1:1:1 in agreement with the formulae (Table).

The general features of the vibrational spectra of the compounds are the i.r. signatures for ν(O–O) (ν_1), ν(U–O_2) (ν_2), ν(U–O_2) (ν_3), and ν(U=O) (*trans*-linked O=U=O) modes at *ca.* 870s, *ca.* 600m, *ca.* 635w, and *ca.* 915s cm^{-1}, respectively. Complementary laser Raman signals at *ca.* 880, *ca.* 600, *ca.* 620, and *ca.* 920 cm^{-1} support the presence of '$UO_2(O_2)$' containing a chelated (C_{2v}) peroxide. the i.r. spectra also provide clear evidence for the co-ordinated heteroligands. The spectra of $[UO_2(O_2)(phen)]$ and $[UO_2(O_2)(bipy)]$ resemble the pattern typical of chelated phen and bipy, and concurrent with this ν(U–N) has been observed at *ca.* 270 cm^{-1}.[10] The absorptions related to en of $[UO_2(O_2)(en)]$ appear at 1 618s cm^{-1} owing to $\delta(NH_2)$, at 1 510m and 1 340m cm^{-1} due to $\delta(CH_2)$, and at 1 050 cm^{-1} assigned to ν(skeletal) modes characteristic of the chelated ligand[11] as opposed to a *trans*-bridging[12] one. The bands

Table. Analytical data for the complexes of uranium(VI) and structurally significant i.r. and laser Raman bands of $[UO_2(O_2)(en)]$, $[UO_2(O_2)(H_4edta)]$, and $[UO_2(O_2)(gly)]$

	Analysis (%)[a]							
Compound	U	O[b]	C	H	N	I.r. (cm^{-1})	Laser Raman (cm^{-1})	Assignment
$[UO_2(O_2)(phen)]$	49.50	6.40	30.10	1.65	5.80			
	(49.35)	(6.65)	(29.40)	(1.65)	(5.80)			
$[UO_2(O_2)(bipy)]$	52.15	7.15	26.25	1.80	6.15			
	(51.95)	(7.00)	(26.20)	(1.75)	(6.10)			
$[UO_2(O_2)(en)]$	65.65	9.10	6.65	2.20	7.90	910s	915	ν(O=U=O)
	(65.75)	(8.85)	(6.65)	(2.20)	(7.75)	880s	875	ν(O–O)(ν_1)
						610m	600	ν(U–O_2)(ν_2)
						630w	620	ν(U–O_2)(ν_3)
						1 618s		$\delta(NH_2)$
						1 510m		$\delta(CH_2)$
						1 340m		
						1 050s		ν(skeletal)
$[UO_2(O_2)(H_4edta)$	44.00	6.20	13.45	1.50	5.30	1 710s		$\nu(CO_2H)$
	(44.25)	(5.95)	(13.40)	(1.50)	(5.20)	910s	900	ν(U=O=O)
						870s	870	ν(O–O)(ν_1)
						615m	610	ν(U–O_2)(ν_2)
						635w	625	ν(U–O_2)(ν_3)
						260m		ν(U–N)
$[UO_2(O_2)(gly)]$	63.40	8.65	6.35	1.35	3.75	905s,br	910	ν(O=U=O)
	(63.10)	(8.50)	(6.35)	(1.35)	(3.70)	890s	880	ν(O–O)(ν_1)
						617m	600	ν(U–O_2)(ν_2)
						640w	620	ν(U–O_2)(ν_3)
						1 630		$\delta_{asym}(CO_2^-)$
						1 517		$\delta_{sym}(NH_3^+)$
						1 427		$\nu(CH_2)$
						1 385		$\nu_{sym}(CO_2^-)$
						1 112		$\rho_r(NH_3^+)$
						680		$\rho_w(CO_2^-)$
						597		$\delta(CO_2^-)$
						215		ν(U–O)

[a] Calculated values are given in parentheses. [b] Peroxo-oxygen.

originating from H_4edta in the spectrum of $[UO_2(O_2)(H_4edta)]$ are observed at 1 710s and at 260m cm^{-1} attributed to un-ionised, unco-ordinated $\nu(CO_2H)$[13] and ν(U–N),[8] respectively. This result and the absence of any peak at 1 590—1 650 cm^{-1} suggest that H_4edta occurs as a neutral ligand being bonded to the metal through its N atoms[14,15] only. The frequencies of gly in the spectrum of $[UO_2(O_2)(gly)]$ appear at 1 630s, 1 385s, 1 112m, 680m, and at 597m cm^{-1} owing to $\nu_{asym}(CO_2^-)$, $\nu_{sym}(CO_2^-)$, $\rho_r(NH_3^+)$, $\rho_w(CO_2^-)$, and $\delta(CO_2^-)$ modes, respectively. Notable are (*i*) the increase of $\nu_{asym}(CO_2^-)$, (*ii*) the decrease of $\nu_{sym}(CO_2^-)$, and (*iii*) the unaltered N–H stretching frequencies compared to those of free glycine. The observed spectral pattern and the band positions clearly indicate that gly occurs in its zwitterionic form $(NH_3^+CH_2CO_2^-)$[16] and co-ordinates through its carboxylic oxygen.[16] The complex probably exists as a polymer in the crystal lattice involving terminal oxo and the contiguous uranium atoms. Broadening of the ν(U=O) (*trans*-linked O=U=O) band supports this view.

Reactivity.—In general terms, metal peroxo complexes are anticipated to be potential oxygen donors to organic substrates, although so far only a few have proved to be reactive. In order that such a compound be reactive, two important criteria, (*i*) solubility in organic solvents and (*ii*) co-ordinative unsaturation of the metal, are expected to be satisfied. Among the complexes reported herein, $[UO_2(O_2)(gly)]$ has the highest solubility and the metal centre is apparently five-co-ordinated. Accordingly, a few oxidation reactions were carried out involving this complex in a nitrogen atmosphere. Thus in a stoicheiometric reaction between $[UO_2(O_2)(gly)]$ and triphenylphosphine in acetonitrile the substrate underwent facile oxidation at ambient temperature, and a white crystalline product was isolated in high yield. The product is highly soluble in organic solvents and free from uranium as ascertained by chemical tests. The distinctive feature of the i.r. spectrum of the product, as against that of PPh_3, is a strong band at 1 190 cm^{-1}. This is typical of the P–O stretching mode of $O{=}PPh_3$,[17] supporting the contention that PPh_3 has been oxidised to $OPPh_3$. The compound melts at 157 °C which matches that reported for $OPPh_3$.[17] These results and those of the elemental analyses establish the identity of the compound as triphenylphosphine oxide. One of the striking features of $[UO_2(O_2)(gly)]$ is its ability to oxidise ethylinic compounds at room temperature. For instance, the stoicheiometric oxidation of cyclohexene in the presence of formic acid (85% aqueous solution) followed by work up of the reaction solution afforded a white crystalline product whose melting point was 104 °C. The ^{1}H n.m.r. spectrum of the compound in D_2O showed signals at δ 0.7—2.1 and 3.3, while its mass spectrum exhibited the molecular ion peak at m/z 116. On the basis of these results as well as a comparison with those given in literature[18] the identity of the compound has been ascertained to be *trans*-1,2-cyclohexanediol. A similar reaction involving styrene as the substrate gave a white crystalline product with melting point 70 °C. Its ^{1}H n.m.r. spectrum in $CDCl_3$ exhibited signals at δ 4.7 and 7.3, and the mass spectrum showed the molecular ion at m/z 138. These values are quite characteristic and compare very well with those of the 1,2-glycol obtained from styrene.[18] Accordingly, the compound has been characterised as 1-phenylethylene glycol. It is relevant that such oxidations are otherwise accomplished with H_2O_2 and formic acid.[19] It is believed that the reaction proceeds through the formation of an epoxide followed by hydrolysis to produce the diol or 1,2-glycol, as obtained. The products have been isolated in *ca.* 48% yield.

The complex $[UO_2(O_2)(gly)]$ in the absence of air also oxidises $SO_2(g)$ to sulphate in an aqueous medium. Thus, bubbling of $SO_2(g)$ through an aqueous suspension of the complex produced a clear yellow solution. Work up of the solution yielded a yellow crystalline compound which did not contain peroxide or glycine as ascertained from its i.r. and laser Raman spectra. The results of chemical analysis confirmed the presence of sulphate with the stoicheiometry of $UO_2^{2+}:SO_4^{2-}$ being 1:1. In accord with this the empirical formula of the compound was $UO_2SO_4{\cdot}3H_2O$. I.r. and laser Raman spectra displayed ν(U=O) at *ca.* 930 cm^{-1} (*trans*-linked O=U=O), while for sulphate the ν_3 and ν_4 modes were split into three bands each and appeared at *ca.* 1 220, *ca.* 1 145, *ca.* 1 040 cm^{-1} and *ca.* 650, *ca.* 605, *ca.* 585 cm^{-1}, respectively, suggesting the occurrence of chelated sulphate[20] in the compound. It is evident therefore that the co-ordinated peroxide reacted with $SO_2(g)$ to give a chelated sulphate. Uranyl sulphate trihydrate dissolves in water and treatment of the solution with aqueous ammonia precipitates uranium quantitatively, whereas SO_4^{2-} remains in solution from which $(NH_4)_2SO_4$ has been isolated by concentrating the mother-liquor.

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