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Synthesis, characterization and reactivity of some novel dinuclear mixed-ligand peroxouranium(VI) complexes

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Abstract—Novel anionic dinuclear mixed-ligand peroxo complexes of the type $[(UO_2)_2(O_2)_3L(H_2O)_2]^{3-}$ (L = Histidinate, aspartate, salicylate, Imidazolate and glutamate) have been synthesised from the interaction of uranyl ion (UO_2^{2+}) with peroxide (O_2^{2-}) in the presence of the respective coligand (L) at pH 9–10. The sparingly soluble complexes were characterized by elemental analyses, FT-IR, laser Raman (LR) and UV–vis spectroscopy and solution electrical conductance measurements. Based on these studies, a double bridged dinuclear structure involving one peroxo and the mixed ligand L (*via*-COO^-) has been tentatively proposed. Infra-red coupled with LR spectra evidenced structurally different metal bound peroxides (η^2 and $\sigma:\sigma$). An aqueous solution of the salicylate and aspartate complexes have been shown to convert triphenylphosphine (PPh_3), cyclohexene, styrene and SO_2 to the corresponding $OPPh_3$, 1,2 cyclohexanediol, phenylethyleneglycol and SO_4^{2-}, respectively. © 1997 Elsevier Science Ltd

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Peroxoactinide chemistry is rather complicated [1–3]. For instance, synthesis of well defined peroxouranium complex is marred by formation of host of different species of varying U : O_2^{2-} stoichiometry with slight change in reaction solution pH [2]. Uranium occurring predominantly as uranyl [UO_2^{2+}] in aqueous solutions is known to afford a number of mixed-ligand mono-peroxo derivatives with fluoride [4], sulfate and oxalate [5], carbonate [6], amines and amino acids as coligand. Few peroxouranium(VI) complexes with phosphine and arsine [8], and Schiff bases [9] as coligand have also been reported. Conversion of atmospheric dioxygen to a μ-η^2, η^2-peroxobridge leading to the formation of dinuclear peroxouranates(VI) has recently attracted much interests [10–13]. Prompted by a recent success [14] on the synthesis of $[U_2O_4(O_2)_3(H_2O)_2]^{4-}$, we embarked on the synthesis of mixed ligand peroxouranium(VI) [$UO_2^{2+} : O_2^{2-} : 1 : > 1$] complexes. In this report, we include a pH-based strategy for the synthesis of hitherto unknown dinuclear organoperoxoderivatives $[(UO_2)_2(O_2)_3L(H_2O)_2]^{3-}$ containing peroxo (O_2^{2-}) ligand in different binding modes. In addition, reactivity studies involving representative complexes towards some chosen substrates are described.

EXPERIMENTAL

Reagent grade chemicals were used. Deoxygenated water was used for reactivity studies. Infrared spectra of the compounds were recorded on a Perkin–Elmer 1605 series FT-IR instrument in KBr pellets. Laser Raman spectra were recorded for solids using 4880 Å laser line from a Spectra-Physics 165-09 argon laser. Electronic spectra were obtained by a Hitachi U-3210 spec model spectrophotometer. Solution electrical conductances (10^{-3} M) were measured using a Systronics 304 digital direct reading conductometer. The pH values of the reaction solutions were recorded on a Systronics 335 digital pH-meter.

Uranium was estimated as uranyl oxinate [15]. Peroxo oxygen was determined by $KMnO_4$ titration and verified further by iodometry. Microanalyses on carbon, nitrogen and hydrogen were obtained from

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Central Drug Research Institute (CDRI), Lucknow. Potassium contents were estimated by Perkin–Elmer-2380 Atomic Absorption Spectrophotometer.

A general synthetic procedure for $(NH_4)_3[(UO_2)_2(O_2)_3L(H_2O)_2]$ (L = His, Asp, Salcy, Im, Glu)

A 1.0 g (2.36 mmol) of $UO_2(CH_3COO)_2 \cdot 2H_2O$ was dissolved in *ca* 20 cm^3 of water and filtered to remove any undissolved residue. To this clear yellow solution thus obtained, was added the coligand (4.72 mmol) dissolved in warm water instantly resulting in the formation of yellow product (a reddish solution in the case of salicylic acid). 10 cm^3 of 30% H_2O_2 was added and the mixture stirred for 15 min. The pH 3 recorded at this stage was slowly raised by dropwise addition of aqueous ammonia (sp. gr. 0.9) until a clear yellow solution (pH 9–10) is reached. Addition of 20 cm^3 precooled ethanol afforded yellow microcrystalline products. These were filtered off, washed with ethanol and dried *in vacuo* over P_4O_{10}. The yields were 60–70%.

Synthesis of $K_3[(UO_2)_2(O_2)_3L(H_2O)_2]$ (L = His, Asp, Im)

The complexes were accessed similar to those obtained for NH_4-countercation except that the pH raise was effected by addition of 20% KOH solution instead of *aq.* NH_3.

Deuteration study

A little amount of the complex $(NH_4)_3[(UO_2)_2(O_2)_3Asp(H_2O)_2]$ was dissolved in 1 cm^3 of D_2O and magnetically stirred at ambient temperature for 24 h. Addition of absolute ethanol then afforded the $(NH_4)_3[(UO_2)_2(O_2)_3Asp(D_2O)_2]$ species as evidenced from IR spectrum.

RESULTS AND DISCUSSION

The reaction solution pH plays a crucial role in determining the number of 'peroxo' group per uranyl $[UO_2^{2+}]$ centre in the coordination sphere. It has, however, been ascertained in some recent works [10,16], that a relatively higher pH (>7) favour products that incorporates more than one 'peroxo' ligand in the desired complexes. The strategy adopted for the synthesis is based on the prior formation of a UO_2^{2+}–L complex and its subsequent interaction with O_2^{2-} at pH 9–10 maintained by aqueous ammonia. When KOH is used, the complexes could be obtained as their potassium salt at least in the cases of imidazole, histidine and aspartic acid. The products were all obtained as yellow microcrystalline solids in high yields. Satisfactory analytical data were obtained for all compounds and are concordant with the formulations. The products isolated at lower pH gave inconsistent analyses. Addition of H_2O_2 prior to that of the coligand, however, gave in all cases, the known [14] stable $[U_2O_4(O_2)_3(H_2O)_2]^{4-}$. The solids are stable for months as ascertained by periodic determination of peroxide. Except for those with aspartate and salicylate, rest were only partially soluble in water. The solution electrical conductance (10^{-3} M) in water at 25°C was 340 Ω^{-1} cm^2 mol^{-1}, concurrent with 3 : 1 electrolytic nature of the complexes. The conductance values did not alter over 1d attesting their stability in solution as well. The UV-vis spectrum of an aqueous solution of $(NH_4)_3[(UO_2)_2(O_2)_3Asp(H_2O)_2]$ showed a rather broad band at 450 nm assigned to $O_2^{2-} \rightarrow UO_2^{2+}$ (LMCT) charge transfer transition. The absorption patterns were not affected even when the solution is heated to 100°C and spectrum recorded.

The FT-IR spectra of the complexes revealed diagnostic features (Table 1). The $\nu(U{=}O)$ mode observed at 890 cm^{-1} is in line with the presence of trans-linked O=U=O moiety [17]. The bands at 865 cm^{-1} and 795 w cm^{-1} were assigned to $\nu(O{-}O)$ stretching mode of chelated (η^2) [18] and bridging ($\sigma:\sigma$) [19] type peroxide. This spectroscopic criterion to distinguish different coordination mode (chelated and bridging) of peroxide has been rather useful [14,16,20]. The deformation mode (ν_4) associated with NH_4^+ was identified at 1400 cm^{-1}. Observance of two bands at 3445 s, br, cm^{-1} [$\nu(O{-}H)$] and 1640 cm^{-1} [$\delta(H{-}O{-}H)$] and any absorption near *ca.* 725 cm^{-1} attributable to rocking (ρ_r) mode of H_2O suggested its coordination to uranyl centre [21]. Pyrolytic studies carried out to determine number and nature of water molecules in the complexes did not prove useful owing to simultaneous loss of both peroxide and water near 100°C. The laser Raman spectra recorded on solids to discern the nature of metal–ligand vibration provided evidence for the occurrence of trans $[O{=}U{=}O]^{2+}$ core (910 cm^{-1}), η^2 (850 cm^{-1}) and $\sigma:\sigma$ type peroxide (790 cm^{-1}). With the excitation line (4880 Å) used other bands could not be detected probably owing to low intensity.

The IR spectrum of the deuterated, $(NH_4)_3[(UO_2)_2(O_2)_3Asp(D_2O)_2]$ showed a shift of $U{-}OH_2$ stretching mode (330 cm^{-1} to 310 cm^{-1}), further attesting the presence of 'aquo' ligands. Marked differences in the vibrational spectral features in the region 1600–1700 cm^{-1} of the complexes containing organic coligand with those of the corresponding free ligand (HL) indicated their coordination to the uranyl centre. The C,H,N microanalyses indicated one coligand per two metal centre. This led us to conjecture their occurrence in the complexes as bridging ligands. However, in order to be able to function as bidentate bridges, deprotonation must precedes coordination. A relatively high pH (8–9) condition used for the synthesis of the complexes and the solution electrical conductance values (340 Ω^{-1} cm^2 mol^{-1}, 3 : 1 type) indeed show the anionic nature of the ligand in the complexes.

Table 1. Structurally significant spectral data for two selected complexes

Compound	IR (cm^{-1})	IR (cm^{-1})	Assignment
$(NH_4)_3[(UO_2)_2(O_2)_3\,His(H_2O)_2]$	890 s	910	$\nu(U{=}O)$
	865 s	850 s	$\nu(O{-}O)$
			C_{2v}, chelated O_2^{2-}
	725 w		$\rho_r(H_2O)$
	795 m	790 m	$\nu(O{-}O)$ bridging O_2^{2-}
	1405 s		$\nu_4(NH_4^+)$
	1488 s		$\nu_s(COO^-)$
	1593 s		$\nu_a(COO^-)$
	1640		$\delta(H{-}O{-}H)$
	3445		$\nu(O{-}H)$
$(NH_4)_3[(UO_2)_2(O_2)_3\,salcy(H_2O)_2]$	895 s	898	$\nu(U{=}O)$
	870 s	860	$\nu(O{-}O)$, C_{2v}, O_2^{2-}
	730 w		$\rho_r(H_2O)$
	796 m	800	$\nu(O{-}O)$, bridging O_2^{2-}
	1405 s		$\nu_4(NH_4^+)$
	1450 s		$\nu_s(COO^-)$
	1585 s		$\nu_a(COO^-)$

In the compounds containing amino acids as coligands, the absence of any band in the IR spectra near *ca* 300–350 cm^{-1} other than $\nu(U{-}OH_2)$ (*vide infra*) assignable to $\nu(U{-}N)$ stretching mode rules out coordination *via* N-donor site. The ν_{N-H} features in the vicinity of 3000 cm^{-1} are complicated by the features of H_2O and NH_4^+ precluding their assignment. Comparison with the IR spectra of the free ligands revealed that, except for the carboxylic (-COOH) features (1600–1700 cm^{-1}), the rest were relatively unaltered in the complexes. The ν_a (COO^-) and ν_s (COO^-) observed at *ca* 1590 and 1445 cm^{-1}, respectively, and the difference, 145 cm^{-1} $(\nu_a - \nu_s)$ is rather characteristic of bridging carboxylate ligand [22]. This does not, however, exclude the possibility of an unsymmetrical bridge involving both amino and ($-NH_2$) and carboxylic (-COOH) function of the coligands. The salicylate complex is also presumably 'carboxylato' bridged [c.f. $\Delta\nu(COO^-) = 133$ cm^{-1}, Table 1]. Absence of N—H stretching mode of imidazole near 3100 cm^{-1} in the spectrum of $K_3[(UO_2)_2(O_2)_3\,Im(H_2O)_2]$ is suggestive of the occurrence of imidazolate as bridging ligand (N,N donor) in the complex [23].

Based on analytical, spectroscopic and conductance data, the most plausible structure of the complexes seems to involve doubly bridged dinuclear framework with each uranyl centre bound by a side on chelated peroxide (C_{2v}) and an aquo ligand.

The potential of peroxouranium(VI) complexes as oxotransfer agents *vis-à-vis* those of peroxo complexes of lighter transition metals have only been explored in a few cases [7,14,24]. The complexes containing aspartate and salicylate as coligands were relatively more water soluble (10^{-2} M) and thus suited well for some typically chosen *oxo*-transfer reactions. The reaction of PPh_3 with an aqueous solution of the complexes yielded $OPPh_3$ as evidenced by TLC, its m.p. and a band at 1190 cm^{-1} for $\nu(P{=}O)$ in its IR spectrum. Under slightly acidic condition, the complexes oxidised cyclohexene to 1,2 cyclohexenediol and styrene to phenylethyleneglycol [IR, $\nu(O{-}H)$: 3460 cm^{-1}]. The complexes in solution when treated with a stream of SO_2 (g) and the compound isolated therefrom revealed occurrence of SO_4^{2-} as evidenced by chemical test and its IR spectrum. No definite stoichiometry could be established for the sulfate compound. Magnetic susceptibility measurements and an unaltered ν $[O{=}U{=}O]$ (IR 900 cm^{-1}) suggested no reduction of the metal centre. This is also expected as the E^0 value for the UO_2^{2+}–UO_2^+ couple (+0.05 V) is far off from that of SO_2–SO_4^{2-} (−0.17 V] [25]. The reactivity studies were done under N_2-purged conditions to rule out any aerial oxidations. The catalytic activity of the complexes compare well with those reported [7,24] with similar systems, in terms of reaction time and conversion yield.

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