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Supplementary Material Available: Tables of anisotropic temperature factors (2 pages). Ordering information is given on any current masthead page.

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Complex Peroxyuranates. Synthesis and Structural Assessment of Alkali-Metal and Ammonium Dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na), and Alkali-Metal and Ammonium Dioxoperoxy(oxalato)uranate(VI) Hydrates, $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$

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Received September 4, 1985

Yellow microcrystalline alkali-metal and ammonium dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na), and alkali-metal and ammonium dioxoperoxy(oxalato)uranate(VI) hydrates, $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K), have been synthesized from the reaction of the product obtained by treating an aqueous solution of $UO_2(NO_3)_2\cdot 6H_2O$ with alkali-metal or ammonium hydroxide, AOH, with 30% H_2O_2 and aqueous sulfuric acid and oxalic acid solution, respectively, in the mole ratio $UO_2(NO_3)_2\cdot 6H_2O$:H_2O_2:SO_4^{2-} or $C_2O_4^{2-}$ of 1:111:5 or 1, at pH 6 maintained by the addition of the corresponding alkali-metal or ammonium hydroxide. Precipitation was completed by the addition of ethanol. IR and laser Raman spectra suggest that the O_2^{2-} and SO_4^{2-} ions in $[UO_2(O_2)SO_4(H_2O)]^{2-}$ are bonded to the UO_2^{2+} center in a bridging and in a monodentate manner, respectively, while both the O_2^{2-} and $C_2O_4^{2-}$ ions in $[UO_2(O_2)C_2O_4]^{2-}$ bind the uranyl center in a bidentate chelated fashion. The complex peroxyuranates are diamagnetic and insoluble. The $A_2[UO_2(O_2)SO_4(H_2O)]$ compounds, unlike $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$, are stable up to 110 °C. Whereas H_2O in $A_2[UO_2(O_2)SO_4(H_2O)]$ is coordinated to the UO_2^{2+} center, it occurs as a water of crystallization in the corresponding peroxy oxalato compounds.

Introduction

Although uranium is the most important and useful of the actinide metals and is known to form simple peroxides,[1,2] its heteroligand peroxy chemistry seems to have been practically overlooked in earlier investigations.[1,2] This is probably because of the highly complicated nature of peroxyuranate chemistry[1] owing to the formation of a number of different species with a small variation of pH of the reaction solution. Peroxyuranates containing O_2^{2-}:U ratios of 1:1, 1:2, 2:1, 3:1, 3:2, and 5:2 were described in the literature,[1,2] of which $UO_2(O_2)\cdot nH_2O$ (n = 2, 4) appears to be the best characterized one. Recent experience in the field of peroxy–metal chemistry[3–6] advocates an enhanced stability of such compounds brought about by the coordination of heteroligands. Reports on heteroligand peroxyuranate compounds are rather scanty, except for the ones on (carbonato)- and (oxalato)peroxyuranates.[1]

The present work was undertaken to synthesize hitherto unknown peroxy(sulfato)uranates(VI) and improvise a direct route to peroxy(oxalato)uranates(VI), to make an assessment of their structures and to rationalize the IR and laser Raman spectra in terms of the modes of binding of O_2^{2-} and SO_4^{2-} or $C_2O_4^{2-}$ with the UO_2^{2+} center, and to make an internal comparison of the results to correlate with that of the previously reported $(NH_4)_2UO_4C_2O_4\cdot 3H_2O$.[7]

Experimental Section

The chemicals used were all reagent grade products. IR and laser Raman (LR) spectra were recorded on the instruments and by the methods described in our earlier papers.[3,6,8] LR spectra were recorded on solids owing to the insolubility of the compounds. Magnetic susceptibility measurements were made by the Gouy method; $Hg[Co(NCS)_4]$ was the calibrant. The pH of the reaction solutions was measured with a Systronics type 335 digital pH meter and also with pH indicator (BDH) paper.

Synthesis of Alkali-Metal and Ammonium Dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na). A 1.0-g (1.99-mmol) sample of $UO_2(NO_3)_2\cdot 6H_2O$ was dissolved in water (10–15 cm^3) followed by addition of 25% ammonium hydroxide solution or a concentrated solution of sodium hydroxide in the case of the Na^+ salt with stirring until the yellow precipitate ceased to appear. The yellow precipitate was filtered off and washed free of alkali-metal ion or ammonium ion and nitrate. To an aqueous suspension of the product was added 4 cm^3 (10 mmol) of 2.5 M H_2SO_4 solution to obtain a clear solution, which was stirred for ca. 5 min. A 25-cm^3 (220.5-mmol) sample of 30% H_2O_2 was added, while the U:SO_4^{2-}:H_2O_2 ratio was maintained at 1:5:111, and the solution was stirred for ca. 15 min followed by careful addition of the corresponding alkali-metal or ammonium hydroxide solution, AOH (A = NH_4, Na), until the pH was raised to 6, whereupon a yellow product just began to appear. An equal volume of ethanol was added with occassional stirring to obtain yellow microcrystalline alkali-metal or ammonium dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na), in high yields. Each compound was allowed to settle for ca. 20 min, separated by centrifugation, purified by washing with ethanol (3–5 times), and finally dried in vacuo over concentrated H_2SO_4.

Synthesis of Alkali-Metal and Ammonium Dioxoperoxy(oxalato)uranate(VI) Hydrates, $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K). The $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ compounds were prepared in a manner analogous to that described above for the synthesis of the peroxy(sulfato)uranate compounds. The two points of differences are that (i) a concentrated solution of oxalic acid ($H_2C_2O_4\cdot 2H_2O$) was used in lieu of the 2.5 M H_2SO_4 solution and (ii) a U:$C_2O_4^{2-}$:H_2O_2 ratio of 1:1:111 was maintained for the synthesis.

The amounts of reagents used for the syntheses and the yields of $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) and $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A

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Table I. Amounts of Reagents Used for the Syntheses of and the Yields Obtained for $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) and $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K)

compd	yield, g (%)	amt of $UO_2(NO_3)_2\cdot 6H_2O$, g (mmol)	amt of 30% H_2O_2, cm^3 (mmol)	amt of 2.5 M H_2SO_4, cm^3 (mmol)	amt of $H_2C_2O_4\cdot 2H_2O$, g (mmol)
$(NH_4)_2[UO_2(O_2)SO_4(H_2O)]$	0.8 (90)	1 (1.99)	25 (220.5)	4 (10)	
$Na_2[UO_2(O_2)SO_4(H_2O)]$	0.75 (82)	1 (1.99)	25 (220.5)	4 (10)	
$(NH_4)_2[UO_2(O_2)C_2O_4]\cdot H_2O$	0.8 (91)	1 (1.99)	25 (220.5)		0.25 (1.98)
$Na_2[UO_2(O_2)C_2O_4]\cdot H_2O$	0.8 (89)	1 (1.99)	25 (220.5)		0.25 (1.98)
$K_2[UO_2(O_2)C_2O_4]\cdot H_2O$	0.85 (87)	1 (1.99)	25 (220.5)		0.25 (1.98)

= NH_4, Na, K) compounds are summarized in Table I.

Elemental Analyses. Uranium was estimated gravimetrically as U_3O_8.[9a] The peroxide content was determined by redox titration with standard solutions of $KMnO_4$[9b] or Ce^{4+}.[9c] While sulfate was estimated gravimetrically as $BaSO_4$,[9d] oxalate was estimated volumetrically.[9e] Nitrogen, sodium, and potassium were estimated by the methods described in previous papers.[3]

Results and Discussion

The reaction of hydrogen peroxide with UO_2^{2+} leading to a complex peroxyuranate(VI) of a definite composition is highly dependent on the pH of the reaction medium. Thus, evaluation of an appropriate pH for successful synthesis of a peroxyuranate species is emphasized to be an important prerequisite. The suitable pH for bringing about coordination of both peroxide and sulfate or oxalate with the uranyl center was ascertained to be 6. The compounds isolated at a relatively lower pH (e.g., ca. 4) on being analyzed did not show the occurrence of peroxide to the desired level (i.e., $U:O_2^{2-}$ as 1:1), indicating therefore that the O_2^{2-} uptake process was in progress but did not reach the $U:O_2^{2-}$ ratio of 1:1. The peroxy(sulfato)uranates(VI) and peroxy(oxalato)uranates(VI) of the types $A_2[UO_2(O_2)SO_4(H_2O)]$ and $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = alkali metal or ammonium) have been synthesized by carrying out reactions among UO_2^{2+}, H_2O_2, and SO_4^{2-} and $C_2O_4^{2-}$, respectively, at pH 6 of the reaction solution maintained by addition of the corresponding alkali-metal or ammonium hydroxide, AOH. While ammonium hydroxide was used as a 25% solution (sp gr 0.88), sodium and potassium hydroxides were added as 10% solutions. The peroxide uptake process was monitored through chemical determination of active oxygen (O_2^{2-}) in the products isolated from the reaction solution at different pH. The method of synthesis of the complex peroxyuranates described in the present work is straightforward, does not involve any extra preparation step unlike in the method previously reported for the synthesis of peroxy(oxalato)uranates(VI)[7] (which required ammonium uranyl oxalate), and may serve as a paradigm for an access to other heteroligand peroxyuranates(VI). It is imperative to mention that, according to the present method, the complex peroxyuranates(VI) start appearing as soon as the solution attains pH 6; however, the addition of ethanol is required to achieve quick and nearly quantitative precipitation of the products. It must also be mentioned that similar compounds were obtained in low yields by allowing the reaction solutions, after adjusting their pH to 6, to stand for several hours at an ice–water temperature.

Characterization and Assessment of Structure. The $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) and $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K) compounds are all yellow microcrystalline products, practically insoluble in water. Their insolubility precludes molar conductance measurements. They do not seem to by hygroscopic, and while the $A_2[UO_2(O_2)SO_4(H_2O)]$ compounds are stable for a prolonged period, the oxalato compounds, $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$, start losing active oxygen with time (in days). Pyrolysis studies showed that $A_2[UO_2(O_2)SO_4(H_2O)]$ does not suffer any loss of water up to ca. 110 °C, whereas $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ begins to expel water around the same temperature, leading us to state that the H_2O molecule is rather loosely held in the latter compound. Both types of complex peroxyuranates(VI) readily decompose in dilute sulfuric acid, liberating hydrogen peroxide quantitatively, and thus facilitate determination of active oxygen content of the compounds. Chemical determination of active oxygen, considered to be very crucial to ascertain the number of O_2^{2-} groups coordinated to the UO_2^{2+} center, was accomplished by redox titrations involving a standard Ce^{4+} solution, and also separately with a standard $KMnO_4$ solution. The estimation was conducted in the presence of boric acid in order to prevent any loss of active oxygen. The results suggested the occurrence of one O_2^{2-} group per UO_2^{2+} center in each of the newly synthesized compounds. The compounds are all diamagnetic, in conformity with the presence of hexavalent uranium.

Albeit complex peroxy(oxalato)uranates(VI) have been reported,[7] we became interested in them not only to explore the feasibility of their being obtained by a method analogous to that improvised for the hitherto unknown peroxy(sulfato)uranates(VI) but also to spectroscopically evaluate the mode of bonding of O_2^{2-} with UO_2^{2+} in the compounds. The infrared and laser Raman spectra of all the compounds were recorded in the range 4000–200 and 2000–150 cm^{-1}, respectively. The significant features of the IR spectra of the $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) compounds involve absorptions of coordinated sulfate, coordinated water, and the U=O stretch. The appearance of medium-intensity ν_1 and ν_2 modes of S–O stretchings at ca. 980 and ca. 450 cm^{-1}, respectively, and the splitting of ν_3 and ν_4 into two bands each (Table II), as opposed to the absence of ν_1 and ν_2 and the presence of unsplit ν_3 and ν_4 modes in the ionic sulfate, provide strong evidences for the lowering of the symmetry of SO_4^{2-} from T_d to C_{3v} and also for its occurrence as a coordinated unidentate ligand in the complex peroxy(sulfato)uranates(VI). A very strong absorption, in addition to the sulfate ligand bands, was observed at ca. 895 cm^{-1} and assigned to the $\nu_{U=O}$ stretching (trans-linked O=U=O group).[11] The LR spectra of $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) complement the IR spectra by exhibiting SO peaks at ca. 970 and ca. 440 cm^{-1} owing to ν_1 and ν_2 and at ca. 1040, ca. 1140, ca. 600, and ca. 650 cm^{-1} due to the ν_3 and ν_4 modes of a coordinated SO_4^{2-} (C_{3v}) ligand. A very strong peak observed at ca. 900 cm^{-1}, because of large polarizability changes involved in the U–O bond, is attributed to the $\nu_{U=O}$ (trans-linked O=U=O) mode. The presence of coordinated water causes the distinct appearance of ν_{O-H} and δ_{H-O-H} modes, which occur in the IR spectra as medium-intensity bands at 3160 and 1630 cm^{-1}. The lowering of ν_{O-H} frequencies and broadening of δ_{H-O-H} bands relative to those of free water suggest a clear possibility of intramolecular hydrogen bonding[12,13] involving uranyl oxygens. This might be a reason for lowering of $\nu_{U=O}$ as well. Especially noteworthy, over and above the patterns just discussed, is the absence of any band in the IR or LR spectra of the peroxy(sulfato)uranates(VI) in the range 890–800 cm^{-1}, a position where ν_{O-O} would appear if peroxide ligand were coordinated in the triangular bidentate (C_{2v}) manner commonly encountered in peroxy compounds of V(V)[3,5,14] and Ti(IV),[6,14,15] for example. This causes us to infer that the O_2^{2-} ligand is present as a bridging group

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Table II. Analytical Data and Structurally Significant IR and Raman Bands of $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) and $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K)

compd	% found (% calcd)				IR, cm^{-1}	Raman, cm^{-1}	assignt
	A or N	U	O_A[a]	SO_4 or C_2O_4			
$(NH_4)_2[UO_2(O_2)SO_4(H_2O)]$	6.32	52.38	7.3	21.62[b]	890 (s)	900	$\nu_{U=O}$
	(6.2)	(52.64)	(7.08)	(21.24)[b]	790 (w, br)	780	ν_{O-O}
					980 (m)	970	(ν_1) ν_{S-O}
					440 (m)	440	(ν_2)
					1130 (s)	1140	(ν_3)
					1040 (s)	1040	
					640 (s)	650	(ν_4)
					605 (s)	600	
					3160 (m)		ν_{O-H}
					1630 (m)		δ_{H-O-H}
$Na_2[UO_2(O_2)SO_4(H_2O)]$	9.55	51.82	7.2	20.93[b]	895 (s)	950	$\nu_{U=O}$
	(9.95)	(51.51)	(6.93)	(20.79)[b]	780 (w, br)	780	ν_{O-O}
					975 (m)	970	(ν_1) ν_{S-O}
					445 (m)	450	(ν_2)
					1140 (s)	1140	(ν_3)
					1040 (s)	1040	
					645 (s)	640	(ν_4)
					600 (s)	600	
					3160 (m)		ν_{O-H}
					1630 (m)		δ_{H-O-H}
$(NH_4)_2[UO_2(O_2)C_2O_4]\cdot H_2O$	6.34	53.82	7.5	20.11[c]	880 (s)	890	$\nu_{U=O}$
	(6.31)	(53.59)	(7.2)	(19.82)[c]	860 (s)	850	ν_{O-O}
					610 (s)	600	ν_{U-O_2}
					3455 (m)		ν_{O-H}
					1640 (s)		δ_{H-O-H}
$Na_2[UO_2(O_2)C_2O_4]\cdot H_2O$	10.42	52.73	7.3	19.63[c]	890 (s)	890	$\nu_{U=O}$
	(10.13)	(52.42)	(7.05)[c]	(19.39)[c]	860 (s)	860	ν_{O-O}
					600 (s)	600	ν_{U-O_2}
					3460 (m)		ν_{O-H}
					1640 (s)		δ_{H-O-H}
$K_2[UO_2(O_2)C_2O_4]\cdot H_2O$	16.33	48.66	6.8	18.4[c]	890 (s)	880	$\nu_{U=O}$
	(16.08)	(48.95)	(6.58)	(18.1)[c]	850 (s)	860	ν_{O-O}
					600 (s)	600	ν_{U-O_2}
					3455 (m)		ν_{O-H}
					1640 (m)		δ_{H-O-H}

[a] Peroxy oxygen. [b] SO_4 [c] C_2O_4.

connecting the contiguous UO_2^{2+} centers through an infinite -U-O-O-U-O-O-U- chain in the crystal lattice. Fortunately the appearance of a broad, rather weak band at 790–750 cm^{-1} in the IR and LR spectra of the compounds lends support to our arguments in favor of a bridging peroxide[16] group.

The IR and LR spectra of the complex peroxy(oxalato)uranates(VI), $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K), were studied particularly to ascertain the mode of bonding of the O_2^{2-} ligand to the UO_2^{2+} center in the complex. It is pertinent to mention here that the earlier reports on peroxy(oxalato)uranates(VI)[7] suggested the presence of a bridging peroxide. The IR and LR spectra of the newly synthesized peroxy(oxalato)uranates(VI) showed distinctly strong and sharp bands at ca. 890, ca. 860, and ca. 600 cm^{-1}, in each of the compounds, which have been assigned to the $\nu_{U=O}$ (trans-linked O=U=O)[11] and peroxy modes[3,5,14,15] ν_{O-O} and ν_{U-O_2} respectively. The definite presence, shapes, and positions of ν_{O-O} and the complementary ν_{U-O_2} modes in the regions stipulated for the presence of triangularly bonded bidentate peroxide led us to draw an inference that the O_2^{2-} group is bonded to the UO_2^{2+} center, in each of the $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ compounds, in a triangular bidentate (C_{2v}) manner. The IR modes due to the coordinated $C_2O_4^{2-}$ ligand are quite straightforward and unequivocal, showing the presence of a chelated oxalto group,[17,18] and thus further discussion on this is redundant. The ν_{O-H} and δ_{H-O-H} bands in the IR spectra of the compounds resemble in their shapes and positions those generally observed for uncoordinated water.[19,20] This result, as well as the facile loss of water as evident from the pyrolysis studies, suggest that the H_2O molecule in $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ occurs as lattice water and probably is not coordinated to the uranyl center. The solubility property of the compounds suggests a fair possibility of a polymeric structure of the complex species $[UO_2(O_2)(C_2O_4)]^{2-}$ through a -U=O···U=O···U=O··· interaction.

Conclusions

Yellow microcrystalline, diamagnetic complex peroxyuranates(VI) $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) and $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K) can be synthesized from the reaction of UO_2^{2+} and H_2O_2 with H_2SO_4 and $H_2C_2O_4\cdot 2H_2O$, respectively, at pH 6 maintained by the addition of the corresponding AOH (A = NH_4, Na, K). The compounds are insoluble.

The peroxy(sulfato)uranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$, are comparatively more stable than the corresponding peroxy(oxalato)uranates(VI), $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$; the former does not lose H_2O upto 110 °C, a temperature at which the latter undergoes dehydration. Both compounds decompose in dilute sulfuric acid, quantitatively liberating H_2O_2.

The peroxide group in $[UO_2(O_2)SO_4(H_2O)]^{2-}$ is bonded to the UO_2^{2+} center in a bridging manner, while the O_2^{2-} in $[UO_2(O_2)C_2O_4]^{2-}$ is bound to UO_2^{2+} in a triangular bidentate fashion. The SO_4^{2-} in the peroxy(sulfato)uranates(VI) occurs as a coordinated unidentate ligand, whereas the $C_2O_4^{2-}$ in the corresponding peroxy(oxalato)uranates(VI) acts as a bidentate chelating ligand.

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The H_2O molecule in the former complex is coordinated, but in the $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ case it is present as lattice water.

The complex species $[UO_2(O_2)SO_4(H_2O)]^{2-}$ very likely has a hexacoordinated polymeric structure through a –U–O–O–U–O–O–U– chain containing peroxide bridges. The complex $[UO_2(O_2)C_2O_4]^{2-}$ ion may be a hexacoordinated monomer; however, the possibility of a polymeric structure through a weak –U=O···U=O··· interaction cannot be totally ruled out.

Acknowledgment. Financial support from the Department of Atomic Energy is gratefully acknowledged. The authors thank the CSIR, New Delhi, for awarding fellowships to M.B. and R.N.D.P. and Professor A. L. Verma of the Department of Physics for extending his laser Raman facilities.

Registry No. $(NH_4)_2[UO_2(O_2)SO_4(H_2O)]$, 102149-54-2; $Na_2[UO_2(O_2)SO_4(H_2O)]$, 102149-56-4; $(NH_4)_2[UO_2(O_2)C_2O_4]$, 94535-39-4; $Na_2[UO_2(O_2)C_2O_4]$, 102149-57-5; $K_2[UO_2(O_2)C_2O_4]$, 102149-58-6.

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Redox and Spectral Properties of the Cis and Trans Isomers of the Osmium(VI) Dioxo Complex $[(bpy)_2Os(O)_2](ClO_4)_2$

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Received February 20, 1986

The cis and trans isomers of $[(bpy)_2Os(O)_2](ClO_4)_2$ (bpy = 2,2′-bipyridine) have been prepared and characterized and their redox properties in aqueous solution investigated by using electrochemical techniques. Plots of $E_{1/2}$ vs. pH for a series of redox couples that appear involving oxidation states II–VI are revealing both in terms of the relative stabilities of the various oxidation states for each isomer and in terms of the relative stabilities of the cis and trans isomers in different oxidation states. The cis isomer undergoes bpy ligand loss in aqueous solution on a time scale of minutes by chelate ring opening followed by ligand loss. Upon reduction to Os(III) or Os(II) the trans isomer is unstable with respect to isomerization to the cis isomer. Comparisons of the redox properties of the isomeric pair give insight into the factors that dictate the relative stabilities of oxidation states and suggest possibilities for the control of the redox potentials, which play a key role in the ability of polypyridyl oxo complexes of ruthenium and osmium to act as redox catalysts.

Introduction

In recent work we have shown that access to a series of metal oxo complexes of Ru and Os is possible based on oxidation of the corresponding aqua complexes, e.g., reaction 1 (b = bpy, 2,2′-bipyridine).[1] In most accessible pH domains, the oxidation process

$$[b_2(py)Ru^{II}{-}OH_2]^{2+} \xrightarrow{-e^-,\ -H^+} [b_2(py)Ru^{III}{-}OH]^{2+} \xrightarrow{-e^-,\ H^+} [b_2(py)Ru^{IV}{=}O]^{2+} \quad (1)$$

is accompanied by proton loss and stabilization of higher oxidation states by electronic donation from bound hydroxo or oxo groups. Synthetically, this approach to the preparation of metal oxo complexes has the advantage of starting with the synthetically accessible lower oxidation states to give higher oxidation states that are frequently good stoichiometric or even catalytic oxidants.

In a preliminary communication we noted an extensive redox chemistry of this kind based on $[(bpy)_2M(OH_2)_2]^{2+}$ (M = Ru or Os) which extended from oxidation states II through VI.[1c] In this paper we elaborate on the Os chemistry and note the existence of cis and trans isomers of $[(bpy)_2Os^{VI}(O)_2]^{2+}$. The cis isomer appears to be the first example of a d^2 *cis*-dioxo complex.

Experimental Section

Materials. Burdick and Jackson spectrograde acetonitrile was distilled under argon over P_2O_5 on a Vigreaux column. Ce(IV) perchlorate in perchloric acid solution (0.5 N) was purchased from G. F. Smith Chemical Co. Buffer solutions for electrochemical and spectroscopic measurements were prepared from $HClO_4$ acid solutions with $LiClO_4$ added as additional electrolyte (pH 0–2) and mono-, di-, and tribasic phosphate (pH 3–12) to maintain a minimum ionic strength of 0.1 M. The pH measurements were made with a radiometer pHM62 pH meter. All other materials were obtained as reagent grade and used without further purification.

Elemental Analysis. Microanalyses were conducted by Galbraith Laboratories, Knoxville, TN.

Preparations. The syntheses of $(bpy)_2OsCO_3$ and $(phen)Os(O)_2(OH)_2$ have been described previously.[2,3]

***cis*-$[(bpy)_2Os(O)_2](ClO_4)_2$.** To 10 mL of 2 M $HClO_4$ was added 50 mg (0.089 mmol) of bpy_2OsCO_3. The resulting solution was degassed with argon for 15 min and then filtered through a medium glass frit. To the stirred filtrate was added 1 mL of 0.5 N cerium(IV) perchlorate in perchloric acid solution. The green microcrystalline precipitate was filtered off, washed with 3 × 3 mL portions of ether, and then dried in vacuo. Yield: 34 mg, 52%. Anal. Calcd for $OsC_{10}H_{16}O_{10}Cl_2$: C, 32.71; H, 2.18; N, 7.63; Cl, 9.68. Found: C, 32.57; H, 2.35; N, 7.39; Cl, 9.58.

***trans*-$[(bpy)_2Os(O)_2](ClO_4)_2$.** To 20 mL of rigorously dry acetonitrile was added 50 mg (0.068 mmol) of *cis*-$[(bpy)_2Os(O)_2](ClO_4)_2$. The solution was heated at gentle reflux for 20 min with magnetic stirring under an inert argon atmosphere. After this time the solution was allowed to cool to room temperature and the resulting precipitate filtered onto a medium glass frit. Dry conditions are essential as bipyridine loss from *cis*-$[(bpy)_2Os(O)_2]^{2+}$ and subsequent dimer formation upon heating to yield the dioxo-bridged dimer $[(bpy)(O)_2Os]_2O_2^{4+}$ is competitive with isomerization. The beige solid was washed with 1 mL of ether and dried in vacuo. Yield: 24 mg, 48%. Anal. Calcd for $OsC_{10}H_{16}O_{10}Cl_2$: C, 32.71; H, 2.18; N, 7.63; Cl, 9.68. Found: C, 32.83; H, 2.18; N, 7.65; Cl, 9.46.

Measurements. Aqueous solutions of *cis*-$[(bpy)_2Os(OH_2)_2]^{2+}$ were prepared by dissolving the appropriate amount of $(bpy)_2OsCO_3$ in acidic solution. The diaqua complex is formed by protonation and loss of carbonate as CO_2

$$(bpy)_2Os(CO_3) + 2H^+ + H_2O \rightarrow [(bpy)_2Os(OH_2)_2]^{2+} + CO_2$$

Spectroscopy. Routine UV–vis spectra were recorded in quartz cells at room temperature on a Bausch and Lomb Model 210 spectrophotometer. Proton NMR spectra were recorded on a Bruker 250-MHz Fourier transform spectrometer and referenced to either Me_4Si or DSS accordingly. Spectra were recorded within $^1/_2$ h of sample preparation. IR measurements were obtained as KBr pellets or Nujol mulls on a Nicolet Model 20 DX FTIR.

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