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LETTER

Technetium(VII) nitridoperoxo complexes

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Transition metal peroxo complexes have been extensively studied because of their importance as stoichiometric or catalytic oxidants of organic compounds [1]. Oxoperoxo complexes have been prepared for a number of transition metals in the d^0 configuration, particularly Mo^{VI} where many complexes based on the $MoO(O_2)_2$ core have been structurally characterised [2]. Recently, we reported the preparation and structural characterisation of $Cs[TcN(O_2)_2Cl]$ [3], the first example of a transition metal nitridoperoxo complex, and, as far as we are aware, the only example of a stable peroxo complex of a metal in the +7 oxidation state. We now report the preparation of a series of technetium(VII) nitridoperoxo complexes and evidence for $[TcN(O_2)_2(OH)_2]$ in solution.

Experimental

Ammonium pertechnetate was supplied by Amersham International plc. Infrared spectra were recorded in KBr discs with a Perkin-Elmer 197 spectrophotometer. Microanalyses were performed by either the Australian Microanalytical Service or Chemical and Micro Analytical Services Pty. Ltd., Melbourne. Technetium analyses were performed by liquid scintillation counting with the appropriate correction made for counting efficiency. A Camag HVE system was used for the electrophoretic studies. $AsPh_4[TcNX_4]$ (X = Cl or Br), and nitridotechnetic(VI) acid were prepared by the methods of Baldas *et al.* [4, 5]. $Cs_2[TcNCl_5]$ was prepared by the literature method [6], except that the acetonitrile extract of the $TcO_4^-/NaN_3/HCl$ reaction was dissolved in the minimum amount of hot conc. HCl and precipitated by CsCl in hot conc. HCl.

$AsPh_4[TcN(O_2)_2Cl]$ (1)

Hydrogen peroxide (10%, 2 cm^3) was added to a solution of $AsPh_4[TcNCl_4]$ (148 mg, 0.232 mmol) in the minimum volume of CH_3CN. The colour changed from orange to yellow and the mixture was reduced in volume on a rotary evaporator. The pale-yellow precipitate was collected by filtration, washed with water, and dried under vacuum. Melting point (m.p.) decomposition commenced at *c.* 205 °C.

$AsPh_4[TcN(O_2)_2Br]$ (**2**) was similarly prepared by agitating a suspension of $AsPh_4[TcNBr_4]$ in CH_3CN/10% H_2O_2 until all the blue solid dissolved to give a yellow solution. The complex decomposed at *c.* 110 °C.

$[TcN(O_2)_2(bipy)]$ (3)

Nitridotechnetic(VI) acid prepared by the hydrolysis of $Cs_2[TcNCl_5]$ (72 mg, 0.129 mmol) was dissolved in 2 cm^3 of 10% H_2O_2. Addition of 2,2′-bipyridyl (100 mg, 0.637 mmol) in water gave a pale-yellow precipitate which was collected, washed with water and dried under vacuum.

$[TcN(O_2)_2(phen)]$ (**4**) was prepared by reaction with 1,10-phenanthroline·HCl.

Complexes **3** and **4** decomposed at *c.* 130 °C.

$(AsPh_4)_2[\{TcN(O_2)_2\}_2ox]$ (5)

Addition of $H_2C_2O_4 \cdot 2H_2O$ (75 mg in 1 cm^3 of water) to a solution of nitridotechnetic(VI) acid (0.12 mmol) in 10% hydrogen peroxide (3 cm^3) gave a pale-yellow solution. On addition of $AsPh_4Cl$ (98 mg, 0.234 mmol) a pale-yellow precipitate formed which was collected, washed with water and dried under vacuum. On heating the complex exploded at *c.* 140 °C.

Reaction of $AsPh_4[TcN(O_2)_2X]$ (X = Cl or Br) with $SOCl_2$

The nitridoperoxo complex (25 mg) was dissolved in 0.5 cm^3 of $SOCl_2$ to give an orange solution. Removal of the $SOCl_2$ and recrystallisation from CH_3CN/C_6H_6 (1:1) gave red crystals shown by their m.p. and IR spectrum to be identical with $AsPh_4[TcNCl_4]$.

Electrophoresis

Paper electrophoretic separations on solutions of nitridotechnetic acid in 10% hydrogen peroxide were performed for 30 min at 600 V with 0.5 M *p*-toluenesulfonic acid as the supporting electrolyte. Since a single paper strip was required to dissipate 30–40 W, intimate contact with the cooling surface was maintained by an air pressure-bag system.

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Results and discussion

We have recently reported the preparation of $Cs[TcN(O_2)_2Cl]$ by the reaction of $Cs_2[TcNCl_5]$ with H_2O_2. X-ray crystallography established a distorted pentagonal-pyramidal coordination geometry with sideways bound peroxo ligands and with the nitrido ligand in the apical position [3]. A series of Tc^{VII} nitridoperoxo complexes has now been prepared either by the reaction of $AsPh_4[TcNX_4]$ ($X=Cl$ or Br) with H_2O_2 or by substitution of $[TcN(O_2)_2(OH_2)_2]$ (**6**). The nitridoperoxo formulations are based on the microanalytical data (Table 1) and the IR spectra (Table 2). Strong absorptions in the region 1069–1035 cm^{-1} confirm the presence of the Tc≡N group. The ν(O–O) absorptions occur at 912–894 cm^{-1} and $\nu_{sym}(TcO_2)$ as generally weak but characteristic peaks at 665–647 cm^{-1}. In Mo peroxo complexes ν(O–O) occurs at 895–845 cm^{-1} [2]. Complexes **1** and **2** most likely have the pentagonal-pyramidal geometry of $Cs[TcN(O_2)_2Cl]$, whereas complexes **3** and **4**, which contain the bidentate 2,2′-bipyridyl or 1,10-phenanthroline ligands, most likely have pentagonal-bipyramidal geometry. These geometries are characteristic of $[MO(O_2)_2L]$ and $[MO(O_2)_2LL']$ ($M=V$, Cr or Mo) complexes [7].

The oxalate complex **5** is dimeric, and we propose a structure consisting of two $[TcN(O_2)_2]$ units bridged either by a bidentate or tetradentate oxalate. A similar structure has been found for $K_4[Mo_2O_2(O_2)_4(C_4H_2O_6)]\cdot 4H_2O$ ($C_4H_2O_6$ = tartrate-(4−)) where the two $MoO(O_2)_2$ units are bridged by a tetradentate tartrate [8]. Tetradentate oxalato ligands have been shown to bridge two [TcN(ox)–O–TcN(ox)] units in the cyclic tetramer $(AsPh_4)_4[Tc_4N_4(O)_2(ox)_6]$ [9].

Hydrolysis of $Cs_2[TcNCl_5]$ has been reported to give a brown chloride-free precipitate of nitridotechnetic(VI) acid (**7**) [5] for which the dimeric di µ-oxo structure $[TcN(OH)(OH_2)(\mu\text{-}O)_2TcN(OH)(OH_2)]$ has been proposed [5, 10]. Solutions of **7** in 10% H_2O_2 are pale-yellow and most likely contain the $[TcN(O_2)_2(OH_2)_2]$ (**6**) species. The formation of **6** may be described by the reaction

$$\underset{\mathbf{7}}{[Tc_2N_2O_2(OH)_2(OH_2)_2]} + 5H_2O_2 \longrightarrow \underset{\mathbf{6}}{2[TcN(O_2)_2(OH_2)_2]} + 4H_2O$$

The analogous Mo oxoperoxo complex has been formulated as $[MoO(O_2)_2(OH_2)_2]$ in solution [11] and the structure of $[MoO(O_2)_2(OH_2)_2]\cdot$(18-crown-6)$\cdot H_2O$ has been reported [12]. However, the water molecule in the *trans* axial position of **6** is likely to be only weakly bound due to the stronger *trans*-influence of the nitrido ligand relative to the oxo ligand. The *trans*-influence of the oxo ligand is evident in the pentagonal-bipyramidal structure of $[MoO(O_2)_2(OH_2)_2]\cdot$(18-crown-6)$\cdot H_2O$ where the equatorial and axial $Mo–OH_2$ distances are 2.084 and 2.325 Å, respectively.

Addition of 2,2′-bipyridyl or 1,10-phenanthroline to solutions of **6** gave **3** and **4** while addition of $AsPh_4Cl$ gave a precipitate of **1**. Evaporation of a solution of **6** at room temperature resulted in decomposition. Solutions of **6** are acidic, corresponding to the equilibrium,

$$\underset{\mathbf{6}}{[TcN(O_2)_2(OH_2)_2]} \longleftrightarrow [TcN(O_2)_2(OH)(OH_2)]^- + H^+ \qquad (1)$$

Electrophoresis in 0.5 M *p*-toluenesulfonic acid showed the presence of a single species with a slight migration towards the cathode, indicating partial protonation of **6** at this acidity. Electrophoresis in 0.1 M sodium *p*-toluenesulfonate, pH 7.0, resulted

TABLE 1. Yields and analytical data for complexes containing the $[TcN(O_2)_2]$ core[a]

Complex	Yield (%)	Elemental analyses: found(calc.) (%)					
		C	H	N	Tc	O	X
$AsPh_4[TcN(O_2)_2Cl]$ (1)	78	48.4	3.5	2.3	16.5	10.6	6.1
		(48.4	3.4	2.4	16.6	10.7	6.0)
$AsPh_4[TcN(O_2)_2Br]$ (2)	78	44.7	3.1	2.5	15.3	9.9	12.9
		(45.0	3.2	2.2	15.5	10.0	12.5)
$[TcN(O_2)_2(bipy)]$ (3)	60	35.85	2.41	12.67	29.5		
		(36.06	2.42	12.62	29.7)		
$[TcN(O_2)_2(phen)]$ (4)	70	38.71	2.17	11.23	27.2		
		(40.36	2.26	11.77	27.7)		
$(AsPh_4)_2[\{TcN(O_2)_2\}_2ox]$ (5)	71	50.20	3.35	2.02	16.4	15.62	
		(49.69	3.34	2.32	16.4	15.89)	

[a] bipy = 2,2′-bipyridyl, phen = 1,10-phenanthroline, ox = oxalate, X = Cl or Br.

TABLE 2. Typical IR stretching frequencies for $[TcN(O_2)_2L]^{n-}$ complexes

Complex	$\nu(Tc \equiv N)$ (cm^{-1})	$\nu(O–O)$ (cm^{-1})	$\nu_{sym}(TcO_2)$ (cm^{-1})
$Cs[TcN(O_2)_2Cl]$ [2]	1063	910, 894	657
$AsPh_4[TcN(O_2)_2Cl]$ (1)	1069	905, 898	653
$AsPh_4[TcN(O_2)_2Br]$ (2)	1069	905, 894	647
$[TcN(O_2)_2(bipy)]$ (3)	1045^a	912, 902	665
$[TcN(O_2)_2(phen)]$ (4)	1035	901	659
$(AsPh_4)_2[\{TcN(O_2)_2\}_2ox]$ (5)	1051	900	659

^{a}Cannot be unambiguously assigned due to superimposition of ligand frequencies.

in migration towards the anode, consistent with equilibrium (1). The pH of a 0.0107 M solution of **6** (in 10% H_2O_2) was 1.97, which corresponds to essentially complete dissociation. The pK_as of $[MoO(O_2)_2(OH_2)_2]$ and $[WO(O_2)_2(OH_2)_2]$ have been reported as 1.85 and 0.12, respectively [13].

Solutions of **6** were only slowly hydrolysed to TcO_4^- at room temperature. Electrophoresis showed that 13 min after dissolution of **7** in 10% H_2O_2 ([Tc] = 0.025 M) the TcO_4^- content was 1.0% which increased to 4% after 48 h. After 7, 21 and 51 days the TcO_4^- content was 8, 21 and 34%, respectively. The Tc^{VII} complexes $[TcO_3Cl(L\text{-}L)]$ (L-L = bipy or phen) and $[TcO_3Br(bipy)]$ have been reported to be readily hydrolysed to TcO_4^- [14]. When dissolved in $SOCl_2$, $AsPh_4[TcN(O_2)_2X]$ (X = Cl or Br) was reduced to Tc^{VI} with the formation of $AsPh_4[TcNCl_4]$.

The preparation of complexes based on the $TcN(O_2)_2$ core is surprising in view of the ease with which H_2O_2 oxidises lower valent Tc compounds to the stable TcO_4^- [15]. Reaction of $AsPh_4[TcOCl_4]$ or $Cs_2[TcOCl_5]$ with 10% H_2O_2 resulted only in the isolation of $AsPh_4[TcO_4]$ or $Cs[TcO_4]$. Also, reaction of M_2O_7 and MO_4^- (M = Tc or Re) with H_2O_2 has not been reported to yield any peroxo species although the reaction of metal oxides or oxymetallate anions with H_2O_2 is a general route to peroxo complexes of the Group V and VI metals [2, 16, 17].

The $Tc^{VII}N(O_2)_2$ core is isoelectronic with $Mo^{VI}O(O_2)_2$ and, in view of the high oxygen transfer reactivity of the latter, it will be of interest to compare the reactivity of $[TcN(O_2)_2(OH_2)_2]$ and $[TcN(O_2)_2(OH)(OH_2)]^-$ with $[MO(O_2)_2(OH_2)_2]$ and $[MO(O_2)_2(OH)(OH_2)]^-$ (M = Mo or W) [18]. The nitrido ligand (N^{3-}) is very effective in stabilising higher oxidation states [19] and the low oxidising power of the $[TcN(O_2)_2]$ core is evident in the stability of $AsPh_4[TcN(O_2)_2Br]$. A number of fluoro and chloro peroxo complexes have been reported [7] but the only other bromoperoxo complex appears to be $(AsCH_3Ph_3)[CrO(O_2)_2Br]$ [17].

References

1 K. A. Jørgensen, *Chem. Rev., 89* (1989) 431.

2 E. I. Stiefel, in G. Wilkinson, R. D. Gillard and J. A. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Vol. 3, Pergamon, Oxford, 1987, Ch. 36.5. p. 1375.

3 J. Baldas, S. F. Colmanet and M. F. Mackay, *J. Chem. Soc., Chem. Commun.,* (1989) 1890.

4 J. Baldas, J. F. Boas, J. Bonnyman and G. A. Williams, *J. Chem. Soc., Dalton Trans.,* (1984) 2395.

5 J. Baldas, J. F. Boas and J. Bonnyman, *Aust. J. Chem., 42* (1989) 639.

6 J. Baldas, J. Bonnyman and G. A. Williams, *Inorg. Chem., 25* (1986) 150.

7 H. A. O. Hill and D. G. Tew, in G. Wilkinson, R. D. Gillard and J. A. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Vol. 2, Pergamon, Oxford, 1987, Ch. 15.2. p. 315.

8 A. C. Dengel, W. P. Griffith, R. D. Powell and A. C. Skapski, *J. Chem. Soc., Chem. Commun.,* (1986) 555.

9 J. Baldas, S. F. Colmanet and M. F. Mackay, *J. Chem. Soc., Dalton Trans.,* (1988) 1725.

10 J. Baldas, J. F. Boas and J. Bonnyman, unpublished results.

11 L. M. Schwane and R. C. Thompson, *Inorg. Chem., 28* (1989) 3938.

12 C. B. Shoemaker, D. P. Shoemaker, L. V. McAfee and C. W. DeKock, *Acta Crystallogr., Sect. C, 41* (1985) 347.

13 M. A. Islam and R. C. Thompson, *Inorg. Chem., 28* (1989) 4419.

14 A. Davison, A. G. Jones and M. J. Abrams, *Inorg. Chem., 20* (1981) 4300.

15 R. D. Peacock, *The Chemistry of Technetium and Rhenium,* Elsevier, Amsterdam, 1966.

16 N. J. Campbell, A. C. Dengel and W. P. Griffith, *Polyhedron, 8* (1989) 1379.

17 R. Armstrong and N. A. Gibson, *Aust. J. Chem., 21* (1968) 897.

18 A. F. Ghiron and R. C. Thompson, *Inorg. Chem., 27* (1988) 4766.

19 K. Dehnicke and J. Strähle, *Angew. Chem., Int. Ed. Engl., 20* (1981) 413.