Preparation and Structure of $Cs[TcN(O_2)_2Cl]$; the First Example of a Nitridoperoxo Complex

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Reaction of $Cs_2[TcNCl_5]$ with hydrogen peroxide yields the chloronitridoperoxo complex $Cs[TcN(O_2)_2Cl]$, which has been shown by single-crystal *X*-ray analysis to have a distorted pentagonal pyramidal co-ordination geometry with the nitrogen atom in the apical position.

Transition metal peroxo complexes have been extensively studied, in particular those of titanium, niobium, tantalum, chromium, molybdenum, and tungsten.[1] Although oxoperoxo complexes are well established, chloro-oxoperoxo complexes are rare with examples being the salts of $[Cr^{VI}O(O_2)_2Cl]^-$ and $[V^{V}O(O_2)_2Cl]^{2-}$, which are moderately stable.[2,3] The nitrido analogues of oxoperoxo complexes have not, to date, been observed. We now report the preparation and structure of the technetium complex $Cs[Tc^{VII}N(O_2)_2Cl]$ (**1**), 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.

Yellow–orange crystals of (**1**), suitable for *X*-ray analysis,† were prepared in high yield by dissolving $Cs_2[TcNCl_5]$[4] (280 mg, 0.5 mmol) in 5 cm^3 of 10% hydrogen peroxide and allowing the yellow solution slowly to evaporate at room temperature in an evacuated desiccator over solid KOH. The structure of the anion in (**1**) is shown in Figure 1. The co-ordination about the technetium atom is best described as a distorted pentagonal pyramid with the nitrido ligand in the apical position [$Tc{\equiv}N$ = 1.63(2) Å]. The peroxo ligands are sideways bound with O(1)–O(2) = 1.41(2) Å, O(3)–O(4) = 1.46(2) Å, and Tc–O(mean) = 1.95 Å. The peroxo 'bite' angles are 42.6(5)° for O(1)–Tc–O(2) and 43.9(6)° for O(3)–Tc–O(4). The Tc–Cl distance of 2.355(4) Å is similar to those observed in other technetium chloro complexes.[5] The peroxo and chloro ligands lie essentially in a plane (r.m.s.d. ± 0.09 Å, $\chi^2 = 76$) with the technetium atom being displaced by 0.45 Å above the plane. This displacement is no doubt a manifestation of the large *trans* influence of the nitrido ligand.[6] A similar situation was found for the chromium oxoperoxo complex, $[Cr^{VI}O(O_2)_2(\text{pyridine})]$, where the oxo ligand results in the displacement of the chromium atom by 0.51 Å from the basal plane.[7] The IR spectrum of (**1**) in the solid state showed peaks at 1063 ($Tc{\equiv}N$), 910 (O–O), 894 (O–O) and 657 {sym[$Tc(O_2)$]} cm^{-1}.

Initially, we attempted the structure determination of $(AsPh_4)[TcN(O_2)_2Cl]$ (**2**), prepared by the reaction of hydrogen peroxide with $(AsPh_4)[TcNCl_4]$. However, in this tetragonal salt, all of the ligand atoms of the anion were

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† *Crystal data* for (**1**): $ClCsNO_4Tc$, $M = 345.27$, orthorhombic, space group $P2_12_12_1$, $a = 6.376(2)$, $b = 8.552(2)$, $c = 11.406(3)$ Å, $U = 621.9(3)$ Å^3, $D_c = 3.69$ g cm^{-3}, $Z = 4$. Intensity data were measured at 21(1) °C with Cu-K_α radiation (graphite-crystal monochromator, $\lambda = 1.5418$ Å) on a Rigaku-AFC four-circle diffractometer. The crystal had well developed faces of type (102), (010), and $(10\bar{2})$ with perpendicular distances between faces of 0.125, 0.175, and 0.25 mm, respectively. Intensity data were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by the heavy-atom method, and full-matrix least-squares refinement with SHELX-76 converged at $R = 0.045$ and $R_w = 0.058$ for 615 observed terms. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

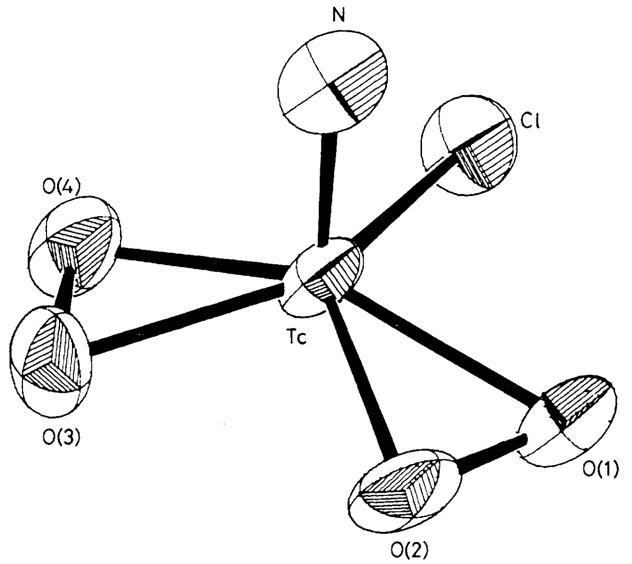

Figure 1. ORTEP diagram for $[TcN(O_2)_2Cl]^-$ showing the 50% probability thermal ellipsoids. Distances (Å): Tc–O(1) 1.953(15), Tc–O(2) 1.942(14), Tc–O(3) 1.929(12), and Tc–O(4) 1.961(14). Angles (°): O(1)–Tc–Cl 85.6(4), O(4)–Tc–Cl 87.3(5), O(2)–Tc–O(3) 90.3(6), N–Tc–O(1) 104.5(8), N–Tc–O(2) 102.5(8), N–Tc–O(3) 103.4(8), N–Tc–O(4) 105.0(8), and N–Tc–Cl 99.3(6).

disordered over four tetrahedral co-ordination sites and hence the structure could not be resolved satisfactorily. The IR spectrum of (**2**) showed peaks, in addition to those arising from the cation, at 1069, 897, and 653 cm^{-1}.

Complex (**1**) is very water-soluble and when dissolved in conc. HCl was converted to $[TcNCl_4]^-$ which was recovered, on the addition of $AsPh_4Cl$, as the insoluble $(AsPh_4)[TcNCl_4]$. Complex (**2**) dissolved in thionyl chloride and removal of the solvent gave a quantitative yield of $(AsPh_4)[TcNCl_4]$. Complex (**1**), on heating, began to decompose at *ca.* 110 °C with decrepitation and exploded at 160 °C. The salt (**2**), however, was rather more stable and only began to decompose at *ca.* 205 °C. The relative stability of the $[TcN(O_2)_2Cl]^-$ anion is indicative of the low oxidising power of the $[Tc^{VII}N]^{4+}$ core. The nitrido ligand (N^{3-}) is a powerful π-electron donor which effectively stabilises metals in high oxidation states.[6] Reaction of $Cs_2[TcOCl_5]$[8] with 10% hydrogen peroxide did not yield $Cs[Tc^{VI}O(O_2)_2Cl]$ but resulted only in the isolation of $CsTcO_4$.

We are currently investigating the chemistry of technetium nitridoperoxo complexes with a variety of ligands.

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