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The Preparation, Characterisation and Reactions of Chlorotetrakis(thiourea)nitridotechnetium(V) Chloride

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Technetium(V) complexes containing the $Tc{=}O^{3+}$ core are well known, and many of these complexes have been prepared by ligand substitution reactions of $TcOX_4^-$ (X = Cl, Br) [1]. Substitution reactions of the $Tc^{VI}NCl_4^-$ anion have recently been shown to provide a general route to complexes containing the $Tc{\equiv}N$ core [2]. The reaction of thiourea (tu) with pertechnetate in the presence of HCl has been used to prepare $[Tc^{III}(tu)_6]Cl_3$ [3]. This complex has been used to prepare a variety of low-valent technetium complexes. We now report the preparation of chlorotetrakis(thiourea)nitridotechnetium(V) chloride, $[TcN(tu)_4Cl]Cl$, and its use for the preparation of $Tc^V{\equiv}N$ complexes by substitution in aqueous solution. The complex, $[TcN(tu)_4Cl]Cl$, is the first example of a metal nitrido complex containing the thiourea ligand.

Experimental

Ammonium [^{99}Tc] pertechnetate (58 mg ml^{-1} in 0.1 mol l^{-1} NH_4OH solution) was obtained from Amersham International plc. Infrared spectra were determined for KBr disks on a Perkin-Elmer 197 spectrophotometer. Conductivity measurements were performed in 1×10^{-3} mol l^{-1} solution at 25 °C using a Crison 522 conductivity meter. The microanalysis was performed by the Australian Microanalytical Service, Melbourne.

Chlorotetrakis(thiourea)nitridotechnetium(V) Chloride

Ammonium pertechnetate (58 mg, 0.32 mmol) was mixed with concentrated HCl (36% *w/w*, 20 ml), and then NaN_3 (200 mg, 3.1 mmol dissolved in 0.5 ml water) was carefully added to the mixture. The mixture was heated under reflux for 15 min and the orange–red solution allowed to cool. HCl was removed in a rotary evaporator and the residue extracted with 2 × 5 ml of CH_3CN. Thiourea (190 mg, 2.5 mmol dissolved in 1 ml water) was added to the orange–red CH_3CN solution to give a deep olive-green colour which rapidly faded to give a mass of fine orange crystals. The crystals were collected by filtration and washed with CH_3CN and dried in a dessicator. Yield 148 mg (95% based on Tc). Recrystallization from water:ethanol (1:10) containing added thiourea (*ca.* 0.2 mol l^{-1}) gave orange crystals, melting point (m.p.) 210–212 °C. *Anal.* Calc. for $C_4H_{16}N_9Cl_2S_4Tc$: C, 9.84; H, 3.30; N, 25.82; Cl, 14.52; S, 26.26. Found: C, 10.18; H, 3.40; N, 26.05; Cl, 14.1; S, 26.2%. IR: ν_{max} 3420vs, 3290vs, 3140vs, 1631vs, 1420vs, 1394vs, 1042s ($Tc{\equiv}N$), 704s cm^{-1}. Conductivity (10^{-3} mol l^{-1}): dimethylformamide, $\Lambda_M = 68$ ohm^{-1} cm^2 mol^{-1}; water, $\Lambda_M = 725$ ohm^{-1} cm^2 mol^{-1}; methanol, $\Lambda_M = 195$ ohm^{-1} cm^2 mol^{-1}.

Dichlorobis(triphenylphosphine)nitridotechnetium(V)

$[TcN(tu)_4Cl]Cl$ (50 mg, 0.10 mmol dissolved in a mixture of 2 ml of water and 2 ml of ethanol) was added to a solution of PPh_3 (55 mg, 0.21 mmol in 5 ml of ethanol). The mixture was heated under reflux for 5 min and the fawn precipitate collected by filtration and washed with hot ethanol and dried. Yield 70 mg (96% based on Tc), m.p. 230–231 °C (literature values 231–232 °C [2], 227 °C [4]). IR: ν_{max} 1480vs, 1433vs, 1094vs, 1088vs ($Tc{\equiv}N$), 750s, 742vs, 707s, 690vs cm^{-1}.

Bis(diethyldithiocarbamato)nitridotechnetium(V)

$Na[S_2CNEt_2]\cdot 3H_2O$ (200 mg, 0.89 mmol in 1 ml of water) was added in one lot to $[TcN(tu)_4Cl]Cl$ (50 mg, 0.10 mmol) dissolved in 3 ml of water. A milky-yellow precipitate formed immediately and the mixture was extracted with 2 × 5 ml of $CHCl_3$. The yellow $CHCl_3$ solution was dried over anhydrous Na_2SO_4, evaporated to dryness and the yellow residue suspended in a little ethanol and collected by filtration. Yield 38 mg (91% based on Tc). Recrystallization from $CHCl_3$:EtOH (1:1) gave yellow crystals, m.p. 253–254 °C (lit. m.p. 254–256 °C [2], 253–254 °C dec. [5]). IR: ν_{max} 1512vs, 1438s, 1283s, 1205s, 1070vs ($Tc{\equiv}N$) cm^{-1}.

Bis(8-quinolinethiolato)nitridotechnetium(V)

8-quinolinethiol·HCl (45 mg, 0.23 mmol) dissolved in a mixture 3 ml of water and 0.1 ml conc. HCl was added to a solution of $[TcN(tu)_4Cl]Cl$ (50 mg, 0.10 mmol) in 3 ml of water. A brown precipitate formed which turned yellow–orange when the mixture was heated on a water bath for 2 min. The mixture was extracted with 2 × 5 ml of $CHCl_3$ and the $CHCl_3$ extract dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was suspended in ethanol and collected by filtration. Yield 33 mg (74% based on Tc). Recrystallization from $CHCl_3$:EtOH (1:1) gave fine orange crystals, m.p. 335–337 °C dec. IR: ν_{max} 1494vs, 1453vs, 1366m, 1298s,

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1212m, 1063s, (Tc≡N), 1000s, 821vs, 774vs, 689s cm^{-1}.

Results and Discussion

The reaction of an excess of thiourea with the $TcNCl_4^-$ anion in acetonitrile gives an orange crystalline product whose composition determined by elemental analysis is consistent with the formula $TcN(tu)_4Cl_2$. This reaction may be performed by the use of $AsPh_4[TcNCl_4]$ but it is more convenient to use the acetonitrile extract of the $TcO_4^-/HCl/N_3^-$ reaction which contains the $TcNCl_4^-$ ion and has previously been described by us [2]. The $TcN(tu)_4Cl_2$ complex was shown to be cationic by its electrophoretic migration and the choice between the two formulations $[TcN(tu)_4]Cl_2$ and $[TcN(tu)_4Cl]Cl$ is based on conductivity measurements. The molar conductivity of the complex in dimethylformamide is 68 ohm^{-1} cm^2 mol^{-1} which is consistent with the suggested Λ_M range at 10^{-3} mol l^{-1} of 65–90 ohm^{-1} cm^2 mol^{-1} for a 1:1 electrolyte in this solvent (*cf.* the suggested range of Λ_M = 130–170 ohm^{-1} cm^2 mol^{-1} for a 2:1 electrolyte) [6]. The complex is thus formulated as the six-coordinate $[TcN(tu)_4Cl]Cl$. The presence of the Tc≡N group is confirmed by the IR absorption at 1042 cm^{-1}, this value being consistent with the presence of a ligand *trans* to the nitrido group [2]. The reaction of thiourea with $TcNCl_4^-$ results in the reduction of Tc^{VI} to Tc^V; this behaviour has been observed for the reaction of $TcNCl_4^-$ with other reducing ligands such as PPh_3 and NCS^- [2]. The preparation of $[TcO(tmtu)_4](PF_6)_3$ (tmtu = *N,N,N',N'*-tetramethylthiourea), an oxo analogue of $[TcN(tu)_4Cl]Cl$, by the reaction of tmtu with NH_4TcO_4 in the presence of HCl has been reported [7].

The preparation of Tc≡N complexes by substitution reactions has, to date, been based on $[TcNCl_2(PPh_3)_2]$ and $TcNX_4^-$ (X = Cl, Br) as starting materials [2, 4, 8–11]. Use of $TcNX_4^-$ may, however, result in the oxidation of ligands. Thiourea ligands are labile and $[Tc(tu)_6]Cl_3$ and $[TcO(tmtu)_4](PF_6)_3$ have been used for the preparation of a variety of Tc complexes [3, 7]. $[TcN(tu)_4Cl]Cl$ is readily soluble in water to give strongly acid solutions. The pH of a 10^{-3} mol l^{-1} solution is *ca.* 2.8 indicating extensive hydrolysis, which is also evidenced by the high Λ_M of 725 ohm^{-1} cm^2 mol^{-1}. In methanol solution, hydrolysis is less extensive, Λ_M = 195 ohm^{-1} cm^2 mol^{-1}. Recrystallization of $[TcN(tu)_4Cl]Cl$ from ethanol–water mixtures leads to slow decomposition unless the recrystallization is performed in the presence of added thiourea. Substitution reactions of $[TcN(tu)_4Cl]Cl$ may, however, be performed in aqueous solution in good yield. Reactions of $[TcN(tu)_4Cl]Cl$ with PPh_3, $Na[S_2CNEt_2]$ and 8-quinolinethiol give the $[TcNCl_2(PPh_3)_2]$, $[TcN(S_2CNEt_2)_2]$ and $[TcN(C_9H_6NS)_2]$ complexes in good yield. These complexes have been previously prepared by substitution and concomitant reduction of $TcNCl_4^-$ [2].

The X-ray crystal structure of $[Tc(tu)_6]Cl_3 \cdot 4H_2O$ has established that the six thiourea ligands in this complex are S-bonded to the technetium atom [3]. In the IR spectrum of $[TcN(tu)_4Cl]Cl$ we have assigned the peak at 704 cm^{-1} to a C=S stretching mode. In free thiourea this absorption occurs at 730 cm^{-1} and the shift to lower frequency in metal thiourea complexes is indicative of S-bonding [12]. Further evidence of S-bonding in $[TcN(tu)_4Cl]Cl$ is provided by the splitting of the C=S stretching peak that occurs at 1412 cm^{-1} in thiourea into two peaks at 1420 and 1394 cm^{-1} [12].

The water solubility of $[TcN(tu)_4Cl]Cl$ and the ease of substitution make the ^{99m}TcN complex a potentially useful starting material for the preparation of ^{99m}TcN-radiopharmaceuticals by substitution reactions. The use of the ^{99m}TcN–thiourea complex for this purpose will be described elsewhere.

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