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The Synthesis and Characterization of Dimethylthiourea and Tetramethylthiourea Complexes of Technetium

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Introduction

Recently, we reported the synthesis and characterization of salts of the $[Tc(S{-}thiourea)_6]^{+3}$ ion [1]. An X-ray structure determination of $[Tc(S{-}thiourea)_6]Cl_3{\cdot}4H_2O$ showed that the six thiourea molecules are S-bonded in a roughly octahedral arrangment [2]†. We now have extended these studies to be substituted thioureas, N,N'-dimethylthiourea (dmtu) and N,N,N',N'-tetramethylthiourea (tmtu). The use of the Tc(V) cation, $[TcO(tmtu)_4]^{3+}$ as a starting material for the preparation of other Tc(V) species is described.

Experimental

Technetium as $NH_4{}^{99}TcO_4$ was obtained as a gift from New England Nuclear (NEN), Billerica, MA. All manipulations were carried out in laboratories approved for low-level radioactivity (^{99}Tc is a weak β-emitter with a half life of 2.12×10^5 years and a particle energy of 0.292 MeV) and all precautions followed have been detailed elsewhere [3, 4]. Melting points were obtained with a Mel-Temp apparatus and are uncorrected.

Preparation of Oxotetrakis(tetramethylthiourea)technetium(V)hexafluorophosphate

To a 50 ml beaker were added water (20 ml), 12 *N* HCl (4.0 ml) and tmtu (0.36 g, 2.7 mmol). To the stirred solution 0.5 ml of 0.418 *M* NH_4TcO_4 (0.21 mmol) was added after the tmtu had dissolved. After 30 min of stirring, the deep red solution was filtered and 0.5 g of NH_4PF_6 in water (5.0 ml) was added to the filtrate. The resulting red-orange precipitate was isolated by suction filtration, washed with water (5.0 ml) and dried *in vacuo*. This material was recrystallized by evaporation of an acetone/2N HCl (3:1 v/v, the 2 *N* HCl was 0.02 *M* in tmtu) solution. Yield of $[TcO(tmtu)_4](PF_6)_3$, 0.16 g (0.14 mmol), 67% based on Tc; mp > 200 °C dec. This compound is soluble in acetonitrile and acetone. *Anal.*: Calcd for $C_{20}H_{48}F_{18}N_8OP_3S_4Tc$: C, 22.26; H, 4.49; N, 10.39; S, 11.89. Found: C, 22.28; H, 4.52; N, 10.34; S, 11.93. Optical spectrum (acetonitrile): 520 nm ($\epsilon = 1.2 \times 10^3$ L mol^{-1} cm^{-1}), 393 (5.9×10^3), 256 (6.3×10^4). IR spectrum (KBr): 2930(w), 1605(s), 1500(w), 1465(m), 1455(m), 1405(m), 1385(m), 1255(m), 1205(w), 1165(m), 1100(m), 1050(w), 975(s), 840(s), 600(w), 555(s) cm^{-1}. Conductivity (acetonitrile, 10^{-3} M): $\Lambda_M = 419$ ohm^{-1} cm^2 mol^{-1}.

Preparation of Hexakis(N,N'-dimethylthiourea)technetium(III)hexafluorophosphate

This complex was prepared similarly to $[TcO(tmtu)_4](PF_6)_3$ using dmtu (27:1 excess over $[TcO_4]^-$) in 66% yield. The reaction mixture was stirred for 17 h before the addition of NH_4PF_6. The complex was recrystallized by evaporation of an acetone/2 *N* HCl (1:1 v/v, the 2 *N* HCl was 0.04 *M* in dmtu) solution yielding bright red needles. MP 186–188 °C dec. *Anal.*: Calcd for $C_{18}H_{48}F_{18}N_{12}P_3S_6Tc$: C, 18.65; H, 4.18; N, 14.50; S, 16.59. Found: C, 18.59; H, 4.18; N, 14.33; S, 16.35. Optical spectrum (acetonitrile): 535(sh), 435 (4.4×10^3), 245 (7.3×10^4). IR spectrum (KBr): 3385(m), 3290(m), 2950(w), 1600(s), 1525(s), 1450(w), 1385(w), 1290(m), 1190(w), 1145(w), 1030(m), 1005(w), 840(s), 735(w), 555(s) cm^{-1}. Conductivity (acetonitrile, 10^{-3} M): $\Lambda_M = 418$ ohm^{-1} cm^2 mol^{-1}. Magnetic moment: μ_{eff} (308 °K) = 2.7 B.M. (Determined by the Evans NMR method in methanolic solution) [5].

Preparation of trans-dioxo(tetrapyridine)technetium(V)hexafluorophosphate

In a 100 ml beaker 0.13 g of $[TcO(tmtu)_4](PF_6)$ (0.12 mmol) was dissolved in acetone (40 ml). To the stirred, red solution pyridine (4.0 ml) was added dropwise, causing a color change to bright yellow. An aqueous solution (40 ml) of NH_4PF_6 (0.5 g) was then added and the reaction mixture allowed to slowly evaporate. Yellow needles of product formed which were isolated, washed with cold water (5 ml) and dried *in vacuo*. Yield of $[trans\text{-}TcO_2(py)_4]PF_6$, 0.06 g (0.10 mmol), 83% based on Tc; mp > 165 °C dec. *Anal.*: Calcd for $C_{20}H_{20}F_6N_4O_2PTc$: C, 40.55; H, 3.41; N, 9.46. Found: C, 40.38; H, 3.56; N, 9.36. This material has the same physical properties as the $[TcO_2(py)_4]^+$ species prepared from $[TcCl_6]^{-2}$ and pyridine [6].

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†Ref. [2] is the crystal structure of hexakis-(S–thiourea)-technetium trichloridetetrahydrate $[Tc(SC(NH_2)_6)]Cl_3{\cdot}4H_2O$.

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Preparation of Tetraphenylarsonium Oxo[N,N'-ethylenebis(2-mercaptoacetimido)technetate(V)(Ph$_4$-As[TcO(ema)])

To a solution of tetramethylthiourea (0.26 g, 1.95 mmol) in 2 *N* HCl (20 ml) was added 0.55 ml of 0.399 *M* NH_4TcO_4 (0.22 mmol). The deep red solution was stirred at room temperature for 2 h. This solution was added dropwise to a solution of N,N'-ethylenebis(2-mercaptoacetamide) [7] (0.24 g, 1.1 mmol) in 2 *N* NaOH (aq.)/ethanol (60 ml, 7:5 v/v) over 20 min. Additional ethanol (20 ml) was added to the golden yellow solution, followed by tetraphenylarsonium chloride monohydrate (0.25 g) in water (5.0 ml). The solution was allowed to slowly evaporate overnight depositing a golden yellow precipitate. This precipitate was dried *in vacuo* and recrystallized by slow evaporation of an acetone/water solution. Yield of $Ph_4As[TcO(ema)]$ 0.13 g (0.18 mmol), 82% based on Tc; mp 221–224 °C dec (lit. 219–221 °C [7]). The infrared (KBr) spectrum of this material was identical to that of a genuine sample of $Ph_4As[TcO(ema)]$.

Results and Discussion

In 2 *N* HCl the pertechnetate ion reacts with dmtu and tmtu to yield complexes of Tc(III) and Tc(V) respectively. The Tc(III) complex, $[Tc(dmtu)_6(PF_6)_3$, was isolated as bright red needles and characterized by elemental analysis, IR and optical spectroscopy, conductance and magnetic susceptibility. All of this data is consistent with the formulation of the cation as a dimethylthiourea analog of $[Tc(thiourea)_6]^{+3}$ [8, 9].

Tetramethylthiourea, however, does not form a simple hexacoordinate complex of Tc(III) under these conditions. Instead, an oxo species of Tc(V) was isolated, $[TcO(tmtu)_4](PF_6)_3$. This complex was characterized by elemental analysis, IR and optical spectroscopy, and conductance. Unlike the Tc(III) thiourea complexes discussed above, the infrared spectrum of this material has a strong band at 975 cm^{-1}, assignable to the Tc=O stretch. This difference in reactivity between the two substituted thioureas is probably due to the steric constraints imposed by the tmtu ligands.

The Tc(V) tmtu complex can be used as a precursor for other Tc(V) compounds. The complex reacts with pyridine in methanol to form the known cation, [*trans*-$TcO_2(py)_4]^+$ which can be isolated in high yield as its hexafluorophosphate salt. Also, the $[TcO(tmtu)_4]^{3+}$ ion (prepared *in situ* from $[TcO_4]^-$) reacts in ethanolic base with N,N'-ethylenebis(2-mercaptoacetamide) to form the $[TcO(ema)]^-$ anion which can be isolated as its tetraphenylarsonium salt in high yield.

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References

1 M. J. Abrams, A. Davison, J. W. Brodack, A. G. Jones, R. Faggiani and C. J. L. Lock, *J. Lab. Comp. Radiopharm.*, *14*, 1596 (1982).
2 M. J. Abrams, A. Davison, R. Faggiani, C. J. L. Lock and A. G. Jones, *Inorg. Chem.*, submitted.
3 A. Davison, C. Orvig, H. S. Trop, M. S. Sohn, B. V. DePamphilis and A. G. Jones, *Inorg. Chem.*, *19*, 1988 (1980).
4 F. A. Cotton, A. Davison, V. W. Day, L. D. Gage and H. S. Trop, *Inorg. Chem.*, *18*, 3024 (1979).
5 D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
6 A. F. Kuzina, A. A. Oblova and V. I. Spitsyn, *Russ. J. Inorg. Chem.*, *17*, 1377 (1972).
7 A. Davison, A. G. Jones, C. Orvig and M. Sohn, *Inorg. Chem.*, *20*, 1629 (1981).
8 W. J. Geary, *Coord. Chem. Rev.*, *7*, 81 (1971).
9 A. Earnshaw, 'Introduction to Magnetochemistry', Academic Press, New York, 1968.