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The Chemistry of Rhenium and Technetium.
Part IV. Facile Cleavage of the Tc=O Bond in the Oxotetrachlorotechnetium(V) Anion by Morpholine-N-carbodithioate to Yield the Eight-coordinate Monomeric Tetracarbodithioatetechnetium(IV) Complex

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Transition metal and main-group element dithiocarbamate complexes have been extensively investigated and are of interest in many fields [1–4]. Our interest in dithiocarbamate complexes arises from the fact that the sulfur atoms in these ligands have the ability to participate in π-bonding in addition to σ-donation, which allows for the stabilisation of metal ions in unusually high oxidation states. We were particularly interested in the reactions of these type of ligands with the $TcOCl_4^-$ anion in order to investigate the electronic factors which influence the lability of the oxo group in these species.

Previously reported technetium complexes in which dithiocarbamates have been used as ligands were $Tc(S_2CNEt_2)_3(CO)$ [5], $TcN(S_2CNEt_2)_2$ [6] and the oxygen-bridged dimer $Tc_2O_3(S_2CNEt_2)_4$ [7], which was prepared from the reaction of $NaEt_2NCS_2$ with $TcOCl_4^-$. Although reactions of $TcOCl_4^-$ with neutral ligands to give $TcOCl_3L$ and $TcOCl_3L_2$ and with dianionic ligands L to give $TcOL_2^-$ are well known [8, 9], no complexes have been reported in which the oxo-group has been replaced in substitution reactions of $TcOCl_4^-$. Here we report the synthesis and characterisation of the $Tc(mdtc)_4$ complex formed by the facile cleavage of the Tc=O bond in $TcOCl_4^-$ by morpholine-N-carbodithioate (mdtc).

Experimental

Technetium (as $NH_4{}^{99}TcO_4$) was obtained from the Oak Ridge National Laboratory, Tenn. n-$Bu_4NTcOCl_4$ [10] and morpholinium morpholine-N-carbodithioate [11] were prepared by literature methods. All other chemicals were used without further purification unless otherwise specified.

Physical measurements were obtained as previously described [12].

Preparation of $Tc(mdtc)_4(H_2O)$

To a solution of 50 mg of $Bu_4NTcOCl_4$ (0.1 mmol) in dried methanol (5 cm^3) was added 0.15 g morpholinium morpholine-N-carbodithioate (0.6 mmol) in 15 cm^3 dried acetone at room temperature. The solution first turned brown, and after about 1 min the solution acquired a dark purple colour. After stirring for 5 min, the purple solution was filtered, and distilled water was added to precipitate a purple crystalline powder. This precipitate was filtered, washed with water and dried in vacuuum for 24 h. Yield = 67 mg, 87% based on Tc. *Anal.* Calcd. for $C_{20}H_{34}N_4O_5S_8Tc$: C, 31.36; H, 4.47; N, 7.31. Found: C, 31.18; H, 4.64; N, 7.47. Conductivity (10^{-3} M, DMF): $\Lambda_M = 0.64$ $\mu S\ cm^{-1}$. Optical spectrum ($CHCl_3$): 522 (2950), 425sh, 325sh, 318sh, 312sh, 307sh, 279nm (32000).

Results and Discussion

The purple crystalline complex $Tc(mdtc)_4(H_2O)$ was obtained under aerobic conditions at room temperature by treating $Bu_4NTcOCl_4$ in methanol with an acetone solution of morpholinium morpholine-N-carbodithioate. $Tc(mdtc)_4(H_2O)$ appears to be indefinitely stable in the solid state, and is a non-electrolyte in DMF solution. It is practically insoluble in polar solvents such as water, and is slightly soluble in non-polar or weakly polar organic solvents such as acetone, benzene, chloroform and methylene chloride. Thermal and elemental analyses of the complex suggest a hydrate, with a water molecule (2.35% of the molecular mass) being removed at 120 °C. The magnetic moment of this complex was found to be 3.73 B.M., which is indicative of a d^3 (t_{2g}^3) configuration. The technetium in this complex then appears to be in the +4 oxidation state. Molecular weight data (osmometric) are rather inaccurate due to the low solubilities; however, they clearly suggest a monomeric species for this complex.

A ^1H NMR spectrum of $Tc(mdtc)_4$ in $CDCl_3$ proved to be very informative in suggesting the structure of this compound. The fact that an NMR spectrum was obtainable suggested either a Tc(IV) monomer or a Tc–Tc dimer as the structure of this molecule. Resonance lines representing the α- and β-protons of the morpholine ring were detected at 9.16 and 8.99 ppm (referenced to Me_4Si), respectively, showing clearly the upfield shifts due to the paramagnetism of the compound.

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The infrared spectrum of Tc(mdtc)$_4$ exhibits absorptions typical of bidentate dithiocarbamate coordination, and there are no bands in the 1460–1470 cm^{-1} region characteristic of monodentate dithiocarbamate ligands [13]. There is a single strong absorption at 1026 cm^{-1} and at 395 cm^{-1}, which we assign to the $\nu(CS_2)$ and ν(Tc–S) vibrations, respectively, and there are no absorptions due to ν(Tc=O) in the 900–970 cm^{-1} region and no absorptions which could be assigned to Tc–Cl vibrations. It is thus evident that in this reaction all of the Tc–Cl bonds as well as the terminal Tc=O bond have been cleaved.

The stoichiometry of this compound is unusual since eight-coordinate monomeric complexes of Tc(IV) are unknown, while only one eight-coordinate complex of Tc(V) has been reported [14]. However, the conditions under which this compound is stable is remarkable, since with previous reactions of $TcOCl_4^-$ with dialkyldithiocarbamates under these conditions, a $Tc_2O_3^{4+}$ core has resulted [7]. The apparent product of the reducing agent is likely the disulfide derived from two morpholine-N-carbodithioate ligands.

The fate of the oxygen atom on the technetium(V) unit is unknown. In our view it is possible that the π-structure of the four-membered TcS_2C chelate ring is very important in the cleavage of the Tc=O bond, as it can remove π-density from the Tc=O unit to such an extent that the Tc=O bond becomes labile. It may also be that chemical reduction occurs first ($TcO^{3+} \rightarrow TcO^{2+}$), followed by the oxygen labilisation since Tc^{IV}=O species are not as common as the Tc^{V}=O unit.

The electronic spectrum of Tc(mdtc)$_4$ was complex, showing at least six bands in the optical region. Even though a spectrum of this complexity could not be interpreted, the single band at 279 nm should be assigned to a charge-transfer transition by virtue of its intensity (ϵ = 32000 dm^3 mol^{-1} cm^{-1}), and can therefore be associated with a charge transfer mainly between the sulfur donor atoms and the technetium(IV) ion.

In conclusion, it could be stated that under selective conditions of special ligands, eight-coordinate technetium(IV) complexes can be prepared from $TcOCl_4^-$ in which all the Tc–Cl bonds as well as the terminal Tc=O have been cleaved. It seems that such reactions would inevitably lead to the reduction of Tc(V) to Tc(IV), since all attempts to synthesize Tc(mdtc)$_4^+$, analogous to $Re(S_2CNEt_2)_4^+$ [15], were unsuccessful.

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References

1 A. Cristini, G. Ponticelli and C. Preti, *J. Inorg. Nucl. Chem., 36,* 2473 (1974).
2 G. E. Coates and D. Ridley, *J. Chem. Soc.,* 166 (1964).
3 R. J. H. Clark and C. S. Williams, *Inorg. Chem., 4,* 350 (1965).
4 E. J. Duff and M. N. Hughes, *J. Chem. Soc. A:,* 477 (1969).
5 J. Baldas, J. Bonnyman, P. M. Pojer, G. A. Williams and M. F. Mackay, *J. Chem. Soc., Dalton Trans.,* 451 (1982).
6 J. Baldas, J. Bonnyman, P. M. Pojer and G. A. Williams, 'Technical Report, ARL/TR 3630', 1981, *Chem. Abstr.,* 95, 54003 (1981).
7 H. S. Trop, *Ph.D. Thesis,* Massachusetts Institute of Technology, 1979.
8 A. Davison, A. G. Jones and M. J. Abrams, *Inorg. Chem., 20,* 4300 (1981).
9 A. Davison, C. Orvig, H. S. Trop, M. Sohn and B. V. DePhamphilis, *Inorg. Chem., 19,* 1988 (1980).
10 F. A. Cotton, A. Davison, V. W. Day, L. D. Gage and H. S. Trop, *Inorg. Chem., 18,* 3024 (1979).
11 G. Aravamudan, D. H. Brown and D. Venkappayya, *J. Chem. Soc. A:,* 2744 (1971).
12 J. G. H. du Preez, T. I. A. Gerber, P. J. Fourie and A. J. van Wyk, *J. Coord. Chem., 13,* 173 (1984).
13 A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader and L. M. Venanzi, *Chem. Commun.,* 476 (1966).
14 K. A. Glavan, R. Whittle, J. F. Johnson, R. C. Elder and E. Deutsch, *J. Am. Chem. Soc., 102,* 2103 (1980).
15 J. F. Rawbottom and G. Wilkinson, *Inorg. Nucl. Chem. Lett., 9,* 675 (1973).