Tetrakis(cyclopentamethylenedithiocarbamate-*S*,*S*′)technetium(v) bromide, an unusual eight-coordinate complex of technetium(v)

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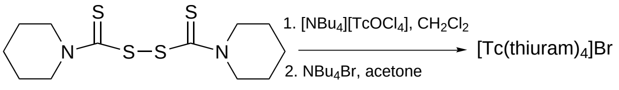
Reaction of the ligand dicyclopentamethylenethiuram disulfide with $[NBu_4][TcOCl_4]$ results in the formation of a unique eight-coordinate technetium(v) species.

The use of the metastable isotope of technetium (^{99m}Tc) in diagnostic imaging is well documented.[1] Technetium forms complexes in a variety of oxidation states, of which Tc^{V} is the best characterized. One of the reoccurring features of the Tc^{V} oxidation state is the stability of the TcO^{3+} unit, which can be transferred from compound to compound. We examined the reaction of $TcOCl_4^-$ anion with the ligand dicyclopentamethylenethiuram disulfide (Scheme 1) to determine if carbamates would be useful functional groups to include in a new class of technetium(v) chelants.

To our surprise the product was a stable eight co-ordinate cation **1** (Fig. 1) in which the oxygen had been removed from the technetium. Even more puzzling, the oxidation state of the metal had not changed. Four cyclopentamethylenedithiocarbamate groups from the cleaved ligand became bound, to give the large cation. Although eight coordination is known for rhenium(v),[2] eight-coordinate Tc^{V} is uncommon.[3,4]

The reaction of morpholine-*N*-carbodithioate anion with $[NBu_4][TcOCl_4]$ gives tetrakis(morpholine-*N*-carbodithioato-*S*,*S*′)technetium(iv).[4] The formation of this paramagnetic compound occurs by the ligand anion acting as a reducing agent and formation of the ligand disulfide. The compound was remarkably stable and attempts to oxidize it to a cation of Tc^{V}, of the type reported here, were unsuccessful. Under somewhat different conditions $TcOCl_4^-$ reacts with dialkyldithiocarbamates (dtc) to give the substitution, and hydrolysis products $[Tc_2O_3(dtc)_4]$.[5] Xanthate complexes of Tc^{III} are known in which the technetium is surrounded by three xanthate ligands and one triphenylphosphine.[6] Baldas *et al.*[7] synthesised a compound similar to the xanthate species, demonstrating that pertechnetate could be reduced in the presence of sodium diethyldithiocarbamate to give a tris(diethyldithiocarbamato)technetium(iii) species in which carbon monoxide is coordinated on the technetium. Until now there has been no solid evidence for eight-coordinate dithiocarbamatetechnetium(v) species.



Scheme 1 Synthesis of **1**

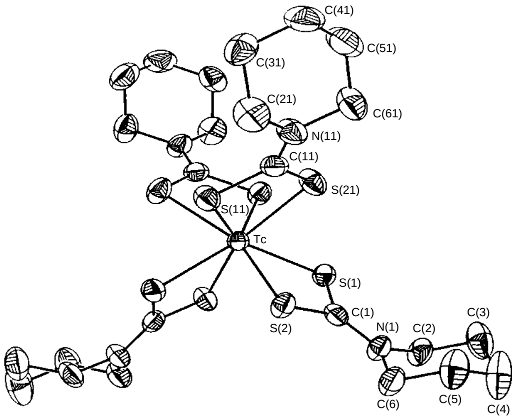


Fig. 1 50% thermal ellipsoid diagram of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Tc–S(1) 2.491(2), Tc–S(2) 2.463(2), Tc–S(21) 2.482(2), Tc–S(11) 2.494(2); S(2)–C(1)–S(1) 109.0(4), S(2)–Tc–S(1) 77.30(6), S(21)–C(11)–S(11) 109.3(4), S(21)–Tc–S(11) 79.57(7).

Compound **1** was obtained by addition of a dichloromethane solution of $[NBu_4][TcOCl_4]$[8] to a dichloromethane solution of the ligand. The product was crystallized from acetone as a bromide salt. Slow evaporation of the acetone solution of the bromide salt provided large, dark red X-ray quality crystals in reasonable yield (67%).[‡]

Compound **1** co-crystallized with its bromide counter ion, which was confirmed by neutron activation analysis, and a disordered acetone molecule. Its shape is a distorted square antiprism with Tc–S distances ranging between 2.463(2) and 2.494(2) Å which are consistent with other technetium thiocarbamates. The four S–Tc–S angles range between 77.30 and 79.57° and the S–Tc–S angles are all approximately 109°.

The electrospray mass spectrum of **1** contained the parent peak as well as fragmentation peaks which corresponded to sequential losses of carbamate groups. The ^{1}H and ^{13}C NMR spectra of compound **1** were relatively simple, with the ^{13}C NMR spectrum showing only four signals.

A possible mechanism for the formation of **1** is shown in Scheme 2. The driving force for this process is the formation of Tc–S bonds coupled with the cleavage of relatively weak S–S bonds by nucleophilic chloride ion. The first step of the proposed mechanism involves nucleophilic attack of the dithiocarbamate disulfide **2** on $TcOCl_4^-$. Because of the aprotic solvent nucleophilic chloride ion may react with the disulfide of intermediate **3** to give the technetium(v) species **4** and compound **5**; the cyano analogue of **5** has been reported.[9] Intermediate **4** converts to **6**, a typical reaction for dithiocarbamates. The sequence is repeated until species **7** is formed. We have prepared the rhenium analogue of **7** and observed that it equilibrates in solution to the cation **8**.[10] Intermediate **8** reacts with another dithocarbamate to form the neutral species **10** which converts to **11**. Because of the electron density supplied by the three dithiocarbamate ligands, the Tc–O bond should be sufficiently polarized to react with a molecule of the reactive species **5**. The resulting species **12** would then be susceptable to nucleophilic attack by another molecule of **2** to give the title compound **1**.

Footnotes

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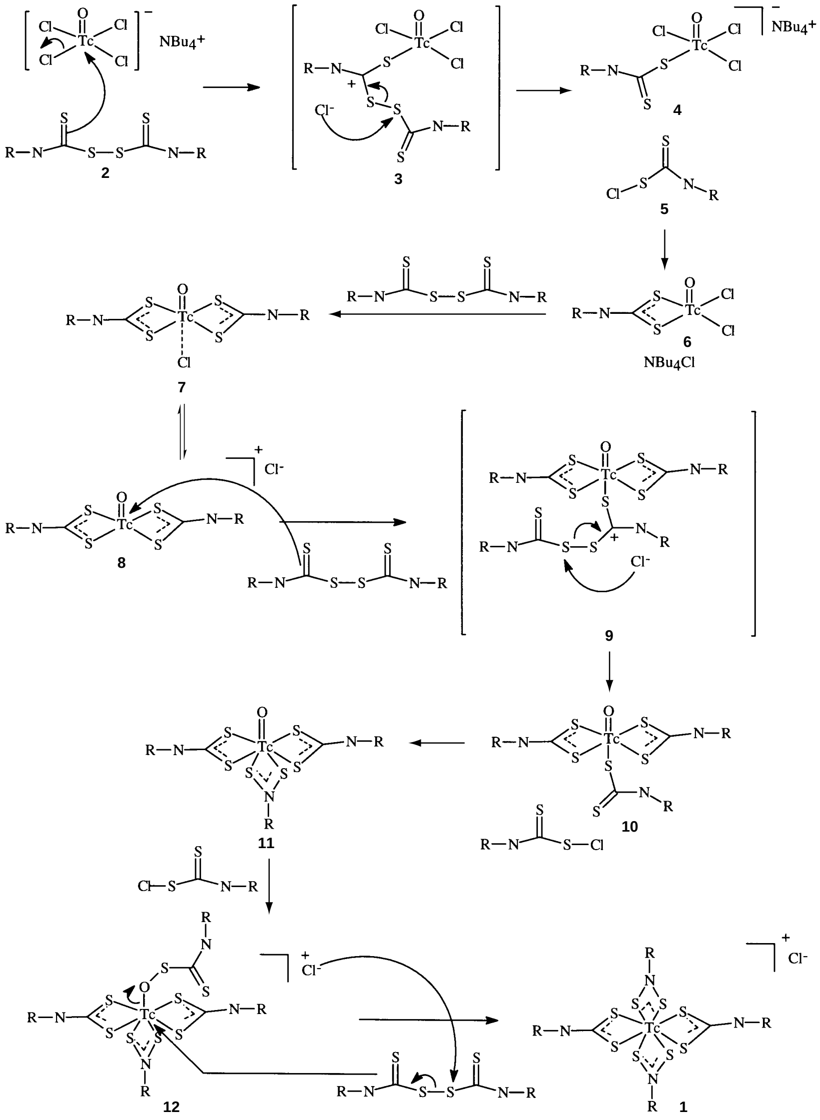
[‡] *Crystal data for* **1**: $[Tc(C_6H_{10}NS_2)_4]Br\cdot C_3H_6O$, M = 877.07, monoclinic, space group $C2/c$, a = 12.343(2), b = 20.557(3), c = 15.133(2) Å, β = 103.42(1)°, U = 3735(1) Å^3, Z = 4, D_c = 1.56 g cm^{-3}, $F(000)$ = 1808, μ(Mo-Kα) = 1.931 mm^{-1}, 4012 reflections collected in the range $1.96 < \theta < 25.00°$; of these 3279 were unique, R = 0.0919,



Scheme 2 Proposed mechanism for the formation of **1**

R_w = 0.1320 for 188 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/375.

§ *Preparation* of **1**. $[NBu_4][TcOCl_4]$ (50 mg, 0.10 mmol) in dichloromethane (2 ml) was added to dicyclopentamethylenethiuram disulfide (0.128 g, 0.4 mmol) in dichloromethane (4 ml) with stirring. After 2 h at room temp., acetone (4 ml) was added and the whole filtered after a further 2 h with an acetone wash (10 ml). $[NBu_4][Br]$ (65 mg, 0.20 mmol) was added to the filtrate giving **1** as deep red crystals (48 mg, 67%). Mp 188 °C (decomp.); ^1H NMR (CD_3OD) δ 3.752–3.715 (m, 4 H, *o*-H), 1.796–1.781 (m, 2 H, *p*-H), 1.680–1.663 (m, 4 H, *m*-H); ^{13}C NMR (CD_3OD) δ 195.96 (CS_2), 47.31 (C_α), 26.34 (C_β), 24.99 (C_γ); ESIMS (+ve ion) *m/z* (%), 739 {55, $[Tc\{S_2CN(CH_2)_5\}_4]^+$}, 579 {100, $[Tc\{S_2CN(CH_2)_5\}_3]^+$}, 517 {4, $[Tc\{HO_3SCSN(CH_2)_5\}_2]^+$}, 435 {18, $[TcO\{S_2CN(CH_2)_5\}_2]^+$}, 210 {3, $[(CH_2)_5NCSSO_3H_2]^+$}.

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