Five Coordinate Complexes of Technetium(III) and (V) with Sterically Hindered Aryl Thiolate Ligands

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Although there has been considerable interest in the chemistry of oxotechnetium(V) complexes with multidentate sulfur donor ligands [1–5], there has been little work reported either for monodentate thiols or, except for hexakis(thiourea-*S*)technetium(III) trichloride [6], sulfur donors in lower oxidation states. Millar and Koch [7–10] have pioneered the use of sterically hindered, monodentate aromatic thiols to stabilize transition metals in a variety of oxidation states. These versatile ligands have been used to develop a rather extensive chemistry of rhenium in lower oxidation states [11–12]. The work described here shows that there is a corresponding series of technetium complexes that were initially synthesized from their oxotechnetium analogs.

The red oxotechnetium(V) complex, $Ph_4As[TcO(tmbt)_4]$ (Htmbt = 2,3,5,6-tetramethylbenzenethiol), is readily prepared from $Ph_4As[TcOCl_4]$ (IR: ν(TcO) = 933 cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} = 230**(100000); 282(56000); 440(7600); 530(2700). ^{1}H NMR: δ 2.03(s, 12H); 2.17(s, 24H); 2.35(s, 12H); 6.77(s, 4H); 7.61(d, 8H); 7.72(t, 8H); 7.80(t, 4H)).

The reaction of this complex with phosphines or alkyl isocyanides leads to loss of a thiolate ligand and reduction by oxygen abstraction. The resultant complexes are five coordinate, diamagnetic compounds which have three thiolate ligands. The reaction of $Ph_4As[TcO(tmbt)_4]$ with ^{i}PrNC gives the pink–purple *trans*-Tc(III)$(tmbt)_3(^iPrNC)_2$ (IR: ν(CN) = 2108 cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} = 232(57000); 334(68000); 560(2400). ^{1}H NMR: δ 0.40(d, 6H); 1.00(d, 6H); 2.15(s, 6H); 2.16(s, 6H); 2.20(s, 12H); 2.25(s, 6H); 2.28(s, 6H); 2.89(m, 1H); 3.65(m, 1H); 6.81(s, 2H); 6.93(s, 1H)).

Because the bulky isonitrile ligands (^{t}Bu, cyclohexyl, ^{i}Pr) are difficult to replace, the synthetically more useful complex, Tc(III)$(tmbt)_3(MeCN)_2$ (IR: ν(NC) = 2255 cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} = 230(50000); 328(40500); 648(1100). ^{1}H NMR: δ 1.12(s, 3H); 1.85(s, 3H); 2.09(s, 6H); 2.15(s, 6H); 2.19(s, 12H); 2.25(s, 6H); 2.28(s, 6H); 6.81(s, 2H); 6.94(s, 1H)), was prepared from $(NH_4)_2[TcCl_6]$ to give well formed blue crystals (MeCN/MeOH 1:1 ν/ν) in 70% yield. Zinc dust is added to the reaction mixture to facilitate the reduction of Tc(IV) to Tc(III) and to prevent contamination by the oxotechnetium(V) species. The X-ray crystal structure of Tc(III)$(tmbt)_3(MeCN)_2$ together with some relevant bond distances and angles is shown in Fig. 1. The donor set in the complex is a trigonal bipyramid with two inequivalent axial MeCN ligands. Two of the bulky aryl groups are equivalent and on the same side of the equatorial plane containing the sulfur atoms. This configuration is consistent with both the above NMR data and the structure proposed for the analogous rhenium complexes [12]. The bis-isopropylisocyanide complex has a similar NMR spectrum and must have the same disposition of the thiolate groups.

As with the analogous rhenium complexes, the acetonitrile ligands can be displaced by other donors, such as alkyl isocyanides, phosphines and carbon monoxide, to give a variety of five coordinate complexes in which the diamagnetic d^4 $Tc(SR)_3$ core is maintained.

The addition of pyridine-*N*-oxide to a refluxing methanolic solution of $Tc(tmbt)_3(MeCN)_2$ in the presence of excess Htmbt gives $Ph_4As[TcO(tmbt)_4]$ in 60% yield. Without the added thiol the oxidation

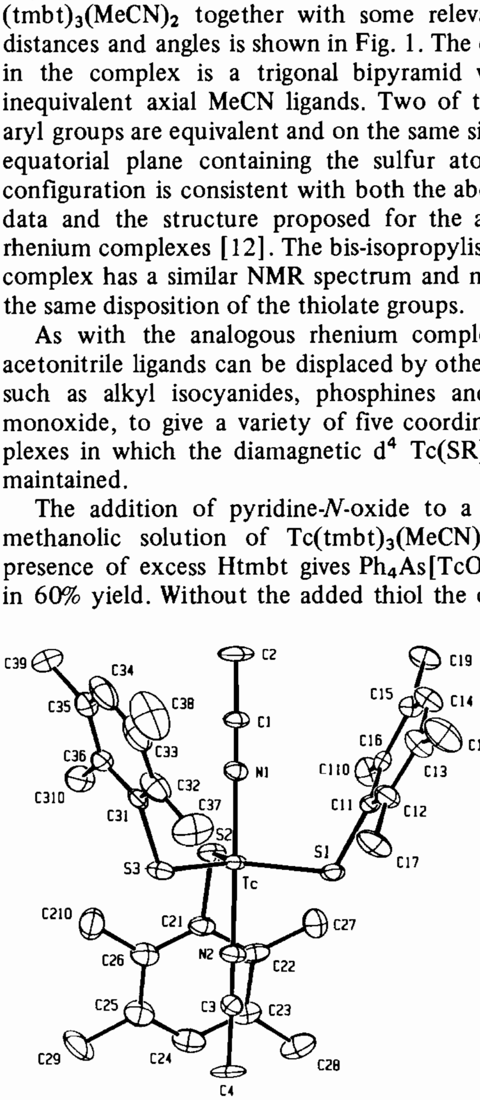

Fig. 1. An ORTEP representation of the structure of Tc$(tmbt)_3(MeCN)_2$ showing the atom labelling scheme and 30% probability ellipsoids. Selected bond lengths (Å) and angles (°): Tc–S1, 2.255(3); Tc–S2, 2.246(3); Tc–S3, 2.245(3); Tc–N1, 2.042(8); Tc–N2, 2.043(8); S1–C11, 1.789(10); S2–C21, 1.797(10); S3–C31, 1.819(10); N1–C1, 1.148(11); N2–C3, 1.145(12); N1–Tc–N2, 178.8(3); N1–Tc–S1, 95.0(2); N1–Tc–S2, 86.2(2); N1–Tc–S3, 93.7(2); N2–Tc–S1, 86.0(2); N2–Tc–S2, 92.8(2); N2–Tc–S3, 86.2(3); Tc–S1–C11, 114.6(3); Tc–S2–C21, 109.2(3); Tc–S3–C31, 113.0(3); Tc–N1–C1, 175.4(8); Tc–N2–C3, 179.6(7).

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**nm throughout, value in parentheses is ϵ(l mol^{-1} cm^{-1}) throughout.

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gives a neutral dimeric material, $(TcO)_2(tmbt)_6$ (IR: $\nu(TcO) = 934\ cm^{-1}$. UV–Vis (CH_2Cl_2): λ_{max} = 230(98000), 260(44000), 290(47000), 410(8500). FABMS(+): $m/z = 1220$ (M^+)), that is similar to the analogous compound $(TcO)_2(SCH_2CH_2S)_3$ which contains two sulfur bridges [13]. The bridging of two metal centers by such sterically hindered thiolates was unexpected. Attempts to prepare the tmbt directly from TBA[$TcOCl_4$] have only produced polymeric materials.

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