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Preparation and Structure of $[Tc_2(SC_6H_4S)_4]\cdot CHCl_3$, a Technetium–Dithiolate Dimer of Novel Trigonal Prismatic Geometry

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Reaction of benzene-1,2-dithiol with NH_4TcO_4 yields, from chloroform, the dimeric complex $[Tc_2(bdt)_4]\cdot CHCl_3$ (bdt = benzene-1,2-dithiolate) (**1**) which has a new co-ordination geometry with a Tc_2S_8 core consisting of two trigonal prisms joined by a quadrilateral face.

The reaction of technetium with dithiols has been extensively studied in recent years.[1] The Tc^{V} complexes $[AsPh_4][TcO(edt)_2]$[2] and $[(TcO)_2(edt)_3]$[3] (edt = ethane-1,2-dithiolate) have been structurally characterised and shown to contain the technetium in a square-pyramidal co-ordination. Toluene-3,4-dithiol ($tdtH_2$) has been used for the spectrophotometric determination of technetium,[4] and the preparation of $[Tc^{VI}(tdt)_3]$[5] (tdt = toluene-3,4-dithiolate) has been reported but this complex has not been structurally characterised. We now report the preparation and structure of $[Tc_2(bdt)_4]\cdot CHCl_3$ (**1**) (bdt = benzene-1,2-dithiolate), a complex with novel trigonal-prismatic geometry which we believe has not been observed in any other co-ordination complex. The complex (**1**) also represents the first characterised example of a Tc^{IV} dithiolate complex.

Hydrochloric acid (12 M) was added dropwise to an ethanolic solution of benzene-1,2-dithiol (480 μmol) and ammonium [^{99}Tc] pertechnetate (160 μmol) and the mixture was allowed to stand for several days. The mixture was extracted with chloroform and the extracts applied to a silica-gel column. Elution with chloroform gave a deep wine-red fraction which upon slow evaporation gave crystals of (**1**) (16% yield based on Tc) suitable for *X*-ray studies.†

The structure of (**1**) is shown in Figure 1. Each technetium atom is co-ordinated to a trigonal-prismatic array of six sulphur ligand atoms. These arrays share a common face, defined by four μ_2-sulphur atoms S(3,4,3′,4′) of two benzene-1,2-dithiolate ligands defining a Tc_2S_8 core of pseudo-D_{2h} point symmetry. The complex molecules lie at inversion centres and thus have exact C_i point symmetry. A Tc–Tc bond [2.591(3) Å] passes through the shared face of the trigonal prisms, thus the geometry around the technetium atoms can also be described in terms of capped trigonal prisms. The Tc–S bond of the terminal ligands are significantly shorter [mean $Tc\text{–}S_{term.}$ = 2.295(7) Å] than those of the bridging ligands [mean $Tc\text{–}S_{br.}$ = 2.408(6) Å]. A similar bonding pattern has

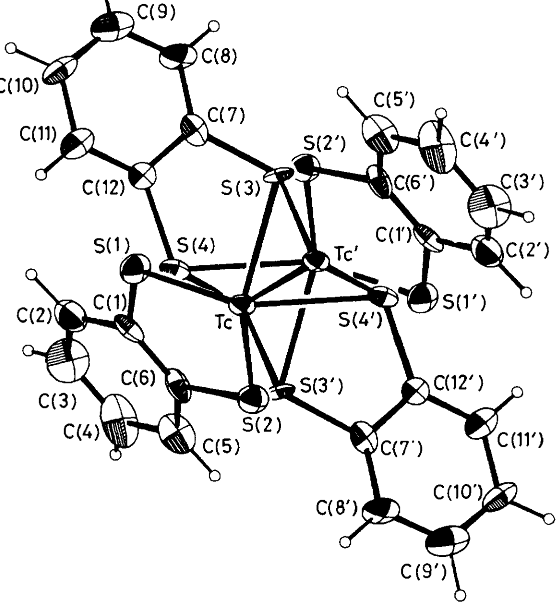

Figure 1. ORTEP diagram for $[Tc(bdt)_4]$ showing the 40% probability thermal ellipsoids.

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†*Crystal data* for (**1**): $C_{25}H_{17}Cl_3S_8Tc_2$, M = 878.04, triclinic, space group $P\bar{1}$, a = 8.534(1), b = 8.842(2), c = 11.192(3) Å, α = 107.02(2), β = 98.13(1), γ = 100.60(2)°, U = 776.5(3) Å^3, D_m = 1.89(1), D_c = 1.88 g cm^{-3}, Z = 1. Intensity data were measured at 288(1) K with Cu-K_α radiation (graphite-crystal) monochromator, (λ = 1.5418 Å) on a Rigaku-AFC four-circle diffractometer. The structure was solved by the heavy-atom method, and full-matrix least-squares refinement with SHELX-76 converged at R = 0.082 and R_w = 0.081 for 1524 observed terms [$I \geqslant 3\sigma(I)$]. The chloroform molecules which lie at inversion centres are disordered throughout the structure. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

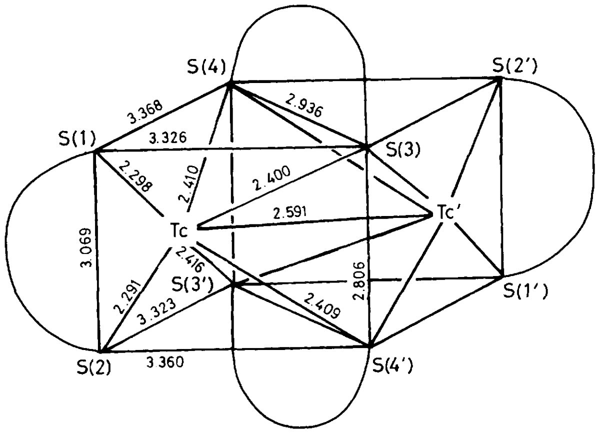

Figure 2. Distances (Å) in the Tc_2S_8 core. E.s.d.s for the Tc–Tc, Tc . . . S, and S . . . S distances are 0.003, 0.006 (mean), and 0.008 (mean) Å respectively. Angles (°): S(1)–Tc–S(2) 83.9(2), S(3)–Tc–S(4) 75.2(2), S(3')–Tc–S(4') 75.0(2), S(3)–S(1)–S(4) 52.0(2), S(1)–S(3)–S(4) 64.7(2), S(3')–S(2)–S(4') 52.1(2), and S(2)–S(4')–S(3') 63.3(2).

been reported in $[M_2(edt)_4]^{2-}$ (M = Mn, Fe, V) but these complexes have different co-ordination geometries. The Mn[6] and Fe[7] structures have five-co-ordinate geometries which are best described as distorted trigonal pyramidal about each metal atom. The co-ordination sphere of $[V_2(edt)_4]^{2-}$ is similar to that of (**1**) with the two V atoms quadruply bridged by the four μ_2-sulphur atoms of two thiolate groups and each V atom is co-ordinated by a terminal dithiol group.[8] The V–V bond distance of 2.600 (2) Å in $[V_2(edt)_4]^{2-}$ is almost identical to the Tc–Tc distance of 2.591(3) Å in (**1**).

The description of (**1**) as two trigonal prisms sharing a face is clearly seen in the Tc_2S_8 core shown in Figure 2. The near perfect trigonal-prismatic geometry of (**1**) is emphasised by the parallel nature of the triangular faces [dihedral angle 5.0(3)°], the chelate twist angle of 1.2°, and the regularity of the S · · · S bond distances. The two terminal S–Tc–S planes are coplanar since the molecules of (**1**) lie at inversion centres. In contrast, the orientation of the two terminal S–V–S planes of the $[V_2(edt)_4]^{2-}$ anion are staggered with a dihedral angle of 102.0°. The geometry of the $[V_2(edt)_4]^{2-}$ anion is severely distorted from octahedral and trigonal-prismatic and is best described as square-prismatic (cubic with four vacant terminal positions).[8]

It is of interest to note that the dithiolate ligands of (**1**) do not radiate from the metal in a 'paddle-wheel' arrangement (Figure 2) as has been found in other trigonal-prismatic complexes containing 1,2-dithiols.[9] Dimers where two trigonal prisms share either a quadrilateral or trigonal face edge have been reported,[10] but (**1**) represents two trigonal prisms joined by a face to give an S_8 core which closely delineates a rhombohedral prism.

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