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LETTER

Synthesis and crystal and molecular structure of a binuclear nitrido–technetium(VII)–hydrazido(2 –) complex, $[Tc_2N_2(NNPh_2)_2(2,4,6\text{-i-}Pr_3C_6H_2S)_4]\cdot 0.5(C_2H_5)_2O$

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The coordination chemistry of technetium continues to generate considerable contemporary interest by virtue of widespread use of Tc-99m in nuclear medicine [1]. One approach to tumor imagining [2–4] relies on the binding of Tc-99m to tumor localizing monoclonal and polyclonal antibodies. We have recently described a simple, efficient and general method for labelling proteins with this radioisotope which exploits bifunctional hydrazine reagents [5].

Although technetium has been shown to form multiple bonds with a variety of nitrogenous donor ligands, forming structurally characterized nitrido [6, 7] and nitrosyl species [8], the fundamental coordination chemistry with organohydrazine ligands is largely unexplored [9–12]. In this paper, we report the synthesis and structural characterization of $[Tc_2N_2(NNPh_2)_2(2,4,6\text{-i-}Pr_3C_6H_2S)_4]$, a species incorporating an unusual binuclear nitrido–technetium(VII)–hydrazido(2 –) core.

Experimental

Synthesis of $[Tc_2N_2(NNPh_2)_2(2,4,6\text{-i-}Pr_3C_6H_2S)_4]\cdot 0.5(C_2H_5)_2O$

To a solution of $(n\text{-}C_4H_9)_4N[TcOCl_4]$ (100 mg) in methylene chloride (2 ml) was added a solution of 1,1-diphenylhydrazine (110 mg) in CH_2Cl_2 (5 ml), yielding a homogeneous red–brown solution. To this solution, $2,4,6\text{-i-}Pr_3C_6H_2SH$ (TIPT, 100 mg) [13] in methanol (5 ml) was added, and the resultant red solution stirred at room temperature for 1 h. After concentration of the solution to 10 ml, followed by careful addition of 10 ml of ether/hexane (1:1, vol./vol.), bright yellow block-shaped crystals of $[Tc_2N_2(NNPh_2)_2(2,4,6\text{-i-}Pr_3C_6H_2S)_4]\cdot 0.5(C_2H_5)_2O$ were isolated in 45% yield. *Anal.* Calc. for $C_{86}H_{117}O_{0.5}N_6S_4Tc_2$: C, 65.9; H, 7.47; N, 5.36. Found: C, 65.8; H, 7.36; N, 5.42%. IR (KBr, pellet, cm^{-1}): 3060(w), 2960(s), 2866(s), 1593(m), 1486(m), 1460(s), 1361(s), 1309(m), 1261(w), 1102(w), 1059(s), 1027(w), 874(w), 804(m), 757(m), 693(m), 662(w), 554(m). UV–Vis [CH_2Cl_2; λ_{max} (nm) (ϵ (M^{-1} cm^{-1}))]: 420 (1.5×10^5), 240 (3.7×10^5).

X-ray crystallographic study of $[Tc_2N_2(NNPh_2)_2(2,4,6\text{-i-}Pr_3C_6H_2S)_4]\cdot 0.5(C_2H_5)_2O$

The crystal was mounted on a glass fiber and placed in a stream of N_2 at 233 K. Crystal data for $[Tc_2N_2(NNPh_2)_2(2,4,6\text{-i-}Pr_3C_6H_2S)_4]\cdot 0.5(C_2H_5)_2O$: triclinic space group $P\bar{1}$, $a = 14.422(3)$, $b = 16.049(5)$, $c = 18.918(8)$ Å, $\alpha = 81.89(2)$, $\beta = 73.60(2)$, $\gamma = 86.74(2)°$, $V = 4157.7(13)$ Å^3, $Z = 2$, $D_{calc} = 1.25$ g cm^{-3}. Structure solution and refinement based on 4376 reflections with $F_o \geqslant 6\sigma(F_o)$ (Mo Kα, $\lambda = 0.71073$ Å; 9421 collected) converged at a conventional discrepancy value (R) of 0.072.

Discussion

Although reactions of metal–oxo species with organohydrazine ligands often proceed by condensation type reactions, resulting in the displacement of the oxo group as H_2O and the formation of the chemically robust metal–hydrazido, $M{=}NNR_2$, or metal–diazenido, $M{=}NNR$, unit [14–16], the hydrazine chemistry of the Tc–oxo group appears to be complicated by a tendency to promote N–N bond cleavage and subsequent formation of Tc–nitrido and Tc–imido species [17]. The reaction of $[TcOCl_4]^{1-}$ with 1,1-disubstituted organohydrazines initially yields a red–brown solution from which analytically pure products could not be isolated. Thin layer chromatography revealed the presence of three distinct products, while the infrared spectrum suggested the presence of hydrazido units (1550–1600 cm^{-1}, $\nu(N{=}N)$) and imido or nitrido moieties (1000–1050 cm^{-1}, $\nu(Tc{=}N)$). However, upon addition of 2,4,6-$\text{i-}Pr_3C_6H_2SH$ (TIPTH) a stable diamagnetic crystalline material, analyzing for $[TcN(NNPh_2)(TIPT)_2]_2\cdot 0.5(C_2H_5)_2O$ is isolated. The infrared spec-

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trum exhibits features at 1593 and 1059 cm^{-1} characteristic of ν(N=N) of the hydrazido ligand and ν(Tc=N) of the imido moiety, respectively.

The presence of the nitrido ligand was unexpected and must result from N–N bond cleavage of the organohydrazine reagent. In this regard, the chemistry of Tc–oxo species does not parallel that described for Mo=O and Re=O species, where condensation reactions are the rule. The difficulties encountered in our attempts to isolate complexes incorporating the [TcNNR] and [$TcNNR_2$] cores from Tc=O precursors reflect this tendency of the technetium hydrazide species to undergo N–N bond cleavage to give mixtures of species with Tc–nitrido, Tc–imido and/or Tc–hydrazido cores. Furthermore, the hydrazine acts as an oxidant in this reaction to yield a formally Tc(VII) core.

The structure of [$Tc_2N_2(NNPh_2)_2(TIPT)_4$], illustrated in Fig. 1, is seen to consist of discrete binuclear Tc(VII) units. The coordination geometry about each Tc center may best be described as distorted square pyramidal with the basal plane defined by the sulfur donors of the bridging thiolate ligands, the sulfur of the terminal thiolate and the α-nitrogen of the hydrazido(2−) ligand, while the apical position is occupied by the nitrido unit. As expected, the average Tc–S(bridging) distance of 2.470(7) Å is significantly longer than the average Tc–S(terminal) distance, 2.379(6) Å. The Tc–N(imido) distance, 1.64(1) Å av., is similar to those observed for [$TcN(SC_6HMe_4)_2(NHC(NMe_2)_2)_2$] [6] and [$TcN(S_2C_2O_2)_2]^{2-}$ [7].

The most unusual feature of the structure is the geometry of the [TcNN] unit of the technetium–organohydrazido fragment. The Tc–N distance, 1.88(1) Å av., is significantly longer (*c*. 0.10 Å) than corresponding distances in [$TcCl(PPh_3)_2(NNR)_2$ [9] and [$TcCl_2(PPh_3)_2(NNC_8H_5N_2)$ [12], where the Tc center is not additionally ligated to strong π-bonding groups, such as oxo or nitrido units. Comparison of the Tc–N(hydrazido) distance of the title complex to Re–N(hydrazido) distances in the [$ReCl_2(PPh_3)_2(NNR)$] and [$ReCl_2(PPh_3)_2(NNR)L$] classes of complexes [18] also indicates that this Tc–N distance is unusually long. Furthermore, the [Tc–N–N] angle of 141.0° deviates considerably from the linear limit of 180° consistent with the hydrazido(2−) description of the ligand moiety. However, it is instructive to compare the bonding of the Tc–hydrazido unit of the title complex with those reported for [$MoO(NNR_2)(SR)_3]^-$ [19] and [$ReO(NNR_2)(SR)_3$ [20], complexes which exhibit parallel ligation to that of [$Tc_2N_2(NNPh_2)_2(TIPT)_4$] in view of the presence of the strongly π-bonding oxo groups and thiolate ligands. The metal coordination geometry for both of these latter species is square pyramidal, with M–N(hydrazido) distances in the range 1.82–1.86 Å and N–N distances of 1.26–1.29 Å. Most significantly, the M–N–N angles are 145.6(10) and 152.5(10)° for [$ReO(NNR_2)(SR)_3$] and [$MoO(NNR_2)(SR)_3]^-$, respectively. The hydrazido(2−) description of the Tc–N–N unit is consistent with these arguments and with the oxidation state assignment. Furthermore, calculations indicate that the angle at the α-nitrogen in [M-NNR_2] species is an insensitive indicator of hybridization mode and cannot be used to infer charge distributions [21].

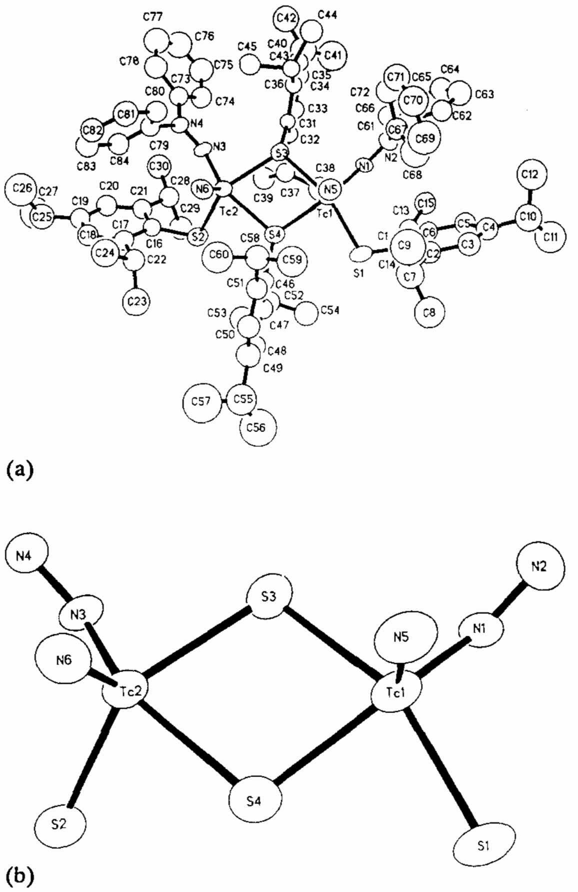

Fig. 1. (a) ORTEP view of the structure of [$Tc_2N_2(NNPh_2)_2(2,4,6\text{-i-}Pr_3C_6H_2S)_4$], showing the atom labelling scheme. (b) A view of the Tc coordination geometry. Selected bond lengths (Å) and angles (°): Tc1–S1, 2.389(4); Tc1–S3, 2.458(5); Tc1–S4, 2.484(5); Tc(1)–N(5), 1.64(1); Tc1–N1, 1.87(1); N1–N2, 1.25(1); Tc2–S2, 2.368(5); Tc2–S3, 2.463(4); Tc2–S4, 2.476(5); Tc2–N6, 1.64(1); Tc2–N3, 1.89(1); N3–N4, 1.24(2); S1–Tc1–S3, 152.1(2); S1–Tc1–S4, 83.5(2); S4–Tc1–N1, 140.4(4); S2–Tc2–S3, 143.8(1); S2–Tc2–S4, 82.7(2); S4–Tc2–N3, 147.3(4); Tc–N1–N2, 141.7(11); Tc–N3–N4, 140.2(11).

The isolation of [$Tc_2N_2(NNPh_2)_2(TIPT)_4$] under conditions which resulted in mononuclear oxo–hydrazido(2−) species with Mo and Re demonstrates that the hydrazido chemistry of Tc is not strictly analogous to that of Mo and Re. Technetium–oxo precursors do not appear to undergo exclusively simple condensation reactions with organohydrazines, but rather display more complicated chemistry as a consequence of N–N bond cleavage, resulting in Tc–imido and Tc–nitrido species and concomitant oxidation of the Tc core. The resultant structural types may be unprecedented in the Mo and Re chemistries.

Supplementary material

Tables of fractional coordinates, thermal parameters, interatomic bond distances and angles, and calculated and observed structure factors are available from J.Z.

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