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LETTER

Synthesis and Structural Characterization of a Technetium(V)–Diazene Complex, [Tc(HNNCSC$_6$H$_5$)$_2$(S$_2$CC$_6$H$_5$)]·(n-C$_4$H$_9$)$_4$NCl

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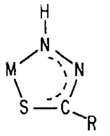
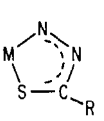
The coordination chemistry of technetium continues to be of significant interest by virtue of the widespread use of technetium complexes in diagnostic nuclear medicine [1–3]. A ligand type of potential utility as a linker for incorporating Tc into antibody complexes is the versatile organohydrazine species. Although the chemistry of organohydrazines with Re, the Group VIIa congener of technetium, has been extensively studied [4], Tc–hydrazine coordination remains undeveloped**.

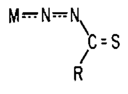
The thiobenzoylhydrazine ligand, specifically, exhibits considerable geometric versatility in its coordination chemistry, adopting the chelating diazene **I**, the chelating diazenido **II**, and the unidentate diazenido coordination modes **III** [6, 7]. In this paper we report the synthesis and structure of [Tc(HNNCSC$_6$H$_5$)$_2$(S$_2$CC$_6$H$_5$)]·n-Bu$_4$NCl, the first example of a technetium–diazene complex.



I



II



III

The reaction of a methanolic solution of thiobenzoylhydrazine, H$_2$NNHC(S)C$_6$H$_5$ [8], with [(n-C$_4$H$_9$)$_4$N][TcOCl$_4$] yields, after addition of diethyl ether, lustrous red crystals of [Tc(HNNCSC$_6$H$_5$)$_2$(S$_2$CC$_6$H$_5$)]·n-Bu$_4$NCl in 45% yield. IR (KBr pellet, cm^{-1}): 3060(m), 2940(s), 2880(s), 1610(m), 1481(m), 1467(s), 1455(m), 1382(m), 1268(m), 1880(m), 936(w), 880(w), 768(m), 688(m), 311(s). Crystal data: monoclinic $P2_1/c$; $a = 11.576(4)$, $b =$

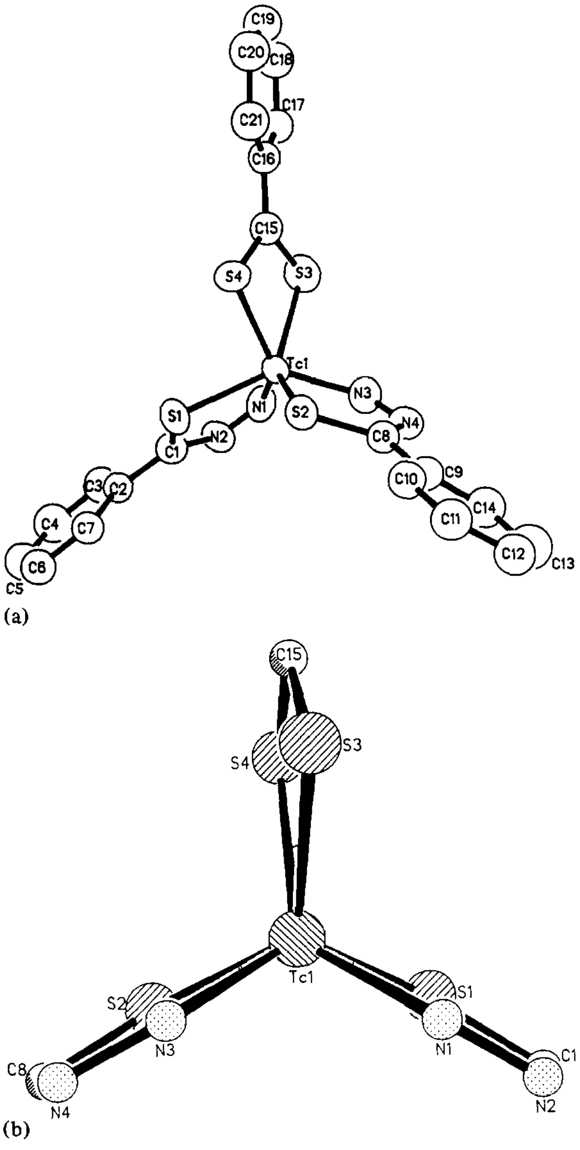


Fig. 1. (a) ORTEP view of the structure of [Tc(HNNCSC$_6$H$_5$)$_2$(S$_2$CC$_6$H$_5$)] showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Tc–S1, 2.312(3); Tc–S2, 2.321(2); Tc–S3, 2.415(3); Tc–S4, 2.403(3); Tc–N1, 1.980(7); Tc–N3, 1.969(7); N1–N2, 1.26(1); N3–N4, 1.28(1); S1–Tc–N1, 78.0(2); S2–Tc–N3, 77.4(2); S3–Tc–S4, 69.7(1); S1–Tc–N3, 139.1(2); S2–Tc–N1, 135.7(2). (b) Schematic representation of the chelate ring geometry about the [TcS$_4$N$_2$] core, illustrating the trigonal prismatic coordination geometry.

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**For a recent example of a diazenido complex, see ref. 5.

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15.698(5), $c = 22.718(6)$ Å; $\beta = 94.93(2)^\circ$, $V = 4113.2(12)$ Å^3, $Z = 4$, $D_{\mathrm{calc}} = 1.34$ g cm^{-3}. Structure solution and refinement based on 3703 reflections with $F_o \geqslant 6\sigma(F_o)$ (Mo Kα, $\lambda = 0.71073$ Å) converged at $R = 0.0587$.

The reaction of $[\mathrm{TcOCl_4}]^{1-}$ with thiobenzoylhydrazine proceeds by the usual condensation-type reaction to abstract the oxo group and by substitution of the chloride ligands by the N and S donors of the chelating groups. The presence of the dithioacid ligand moiety is a consequence of the method used in the synthesis of the thiobenzoylhydrazine. The immediate precursor to the ligand is a carboxymethyldithioate, $\mathrm{C_6H_5C(S)SCH_2CO_2H}$, which remains as a persistent contaminant in the preparations of $\mathrm{C_6H_5C(S)NHNH_2}$. Upon acidification, S–C bond rupture of the carboxymethyldithioate yields the dithioacid $\mathrm{C_6H_5CS_2H}$ which is then available for coordination to the Tc. The absence of bands attributable to ν(Tc=O) in the 900–1000 cm^{-1} range of the infrared confirmed the displacement of the oxo group, while the feature at 1610 cm^{-1} indicated the presence of the delocalized [Tc–N–N] moiety. That the thiobenzoylhydrazine-derived ligand is present in the diazene form is suggested by the band at 3060 cm^{-1}, which is attributed to ν(N–H). The strong band at 310 cm^{-1} is assigned to ν(Tc–S).

The structure of $[\mathrm{Tc(HNNCSC_6H_5)_2(S_2CC_6H_5)}]\cdot$n-$\mathrm{Bu_4NCl}$ is shown in Fig. 1 and relevant bond lengths and angles are presented in the caption. The Tc center exhibits distorted trigonal prismatic geometry through ligation to the S donors of the bidentate dithioacid group and the N$_\alpha$ and S donors of the chelating diazene ligands. The formulation of the hydrazine ligand as the diazene type is consistent with the charge requirements of the complex as a formally Tc(V) species and the structural parameters associated with the [Tc–NNCS] chelate rings. A comparison with Mo–diazene and Mo–diazenido ring parameters, shown in Fig. 2, establishes the diazene formalism with the metal-bound nitrogen N$_\alpha$ as the protonation site.

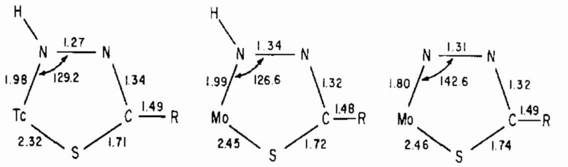

Fig. 2. Schematic representations of the diazene chelate geometries observed for $[\mathrm{Tc(HNNCSC_6H_5)_2(S_2CC_6H_5)}]$ and related Mo complexes and of the diazenido chelate ring parameters observed for representative Mo complexes. Metric parameters for the Mo structures are found in ref. 7.

The tristhiobenzoyldiazene complex $[(\mathrm{n\text{-}C_4H_9})_4\mathrm{N}][\mathrm{Tc(HNNCSC_6H_5)_3}]$ may be prepared from the reaction of $[(\mathrm{n\text{-}C_4H_9})_4\mathrm{N}][\mathrm{TcOCl_4}]$ with a preparation of carefully recrystallized $\mathrm{H_2NNHC(S)C_6H_5}$. The complex is a deep green diamagnetic Tc(V) species which most likely exhibits the trigonal prismatic geometry common to the $[\mathrm{M(HNNCXC_6H_4R)_3}]^{n-}$ class of complexes.

References

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