Notes

Synthesis and Structure of a New Inorganic Dianionic Bis(dithiocarbonato)nitridotechnetate(V) Complex $K_2[TcN(S_2CO)_2]\cdot 2H_2O$ †

Roberto Rossi,* Andrea Marchi, and Luciano Magon*
Laboratorio di Chimica Nucleare ed Inorganica e Centro di Fotochimica del C.N.R., Dipartimento di Chimica, Università di Ferrara, Italy
Umberto Casellato
Istituto di Chimica e Technologia dei Radioelementi del C.N.R., Padova, Italy
Rodolfo Graziani
Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Padova, Italy

The nitrido compound $[TcNCl_2(PPh_3)_2]$ reacts with $K(S_2COEt)$ to give in aqueous medium the complex $K_2[TcN(S_2CO)_2]$. The crystal structure has been determined by *X*-ray crystallography: monoclinic, space group $P2_1/n$, with $a = 8.353(5)$, $b = 15.630(4)$, $c = 9.230(5)$ Å, and $\beta = 90.94(3)°$. The structure has been refined to a final R of 0.035 based on 2 803 observed reflections. The metal ion is five-co-ordinate in a distorted square-pyramidal arrangement. Selected bond distances (Å) are Tc–S 2.390 (mean), Tc–N 1.621(6), C–S 1.780 (mean), and C=O 1.207 Å (mean).

The recent surge in interest in technetium chemistry has been fueled by its widespread use in diagnostic nuclear medicine involving the imaging of internal organs by radioscintigraphic techniques.[1,2] In recent years it has been shown that ionic and neutral technetium complexes are of interest as potential tracers for myocardial and brain scintigraphy. Of particular importance are co-ordination compounds, the lipophilic and polar properties of which can be affected by simple substitutions in the molecular framework of the ligands to optimize the biodistribution of the potential radiopharmaceutical. For instance the diffusion of radiopharmaceuticals from the blood into the brain through an intact endothelial cell membrane requires that it be non-ionized and lipid soluble, whereas hydrophilic compounds are excluded from entering the normal brain by an intact blood–brain barrier, but under pathologic conditions the barrier is disrupted and the hydrophilic radiotracer can concentrate in the lesion and subsequently be identified.[3] The vast majority of the complexes which have potential as new clinical diagnostic agents involve technetium(V) $[TcO]^{3+}$, $[TcO_2]^+$, and, more recently, $[TcN]^{2+}$ cores, with co-ordinating chelating mixed-donor ligands.[4–8]

Crystal structures of a variety of Tc^V=O complexes have been reported.[9] Transition-metal nitrido-complexes are of interest because of the effects arising from the powerful *trans* influence and large steric requirements of the nitrido-ligand.[10,11] Recently we reported the synthesis and crystal structures of neutral and cationic technetium(V) nitrido complexes with a distorted octahedral geometry.[12,13] We report here the synthesis and crystal structure of a new inorganic dianionic square-pyramidal TcN complex, $K_2[TcN(S_2CO)_2]\cdot 2H_2O$ (**2**) obtained by hydrolysis of $[TcN(S_2COEt)_2]$ (**1**).

Experimental

Materials.—Technetium-99 is a β^- emitter ($t_{\frac{1}{2}} = 2.1 \times 10^5$ years). All manipulations of solutions and solids were performed in a laboratory approved for the handling of radioisotopes with monitored heads and glove-boxes. Ammonium [^{99}Tc]pertechnetate was supplied by Amersham International plc. The compound $[TcNCl_2(PPh_3)_2]$ was obtained by reaction of $[NH_4][TcO_4]$ with hydrazine dihydrochloride and triphenylphosphine.[14] The SC(OEt)SH ligand as its potassium salt was prepared by slow addition of CS_2 to an alcoholic solution of KOH. The product, recovered by filtration after cooling the solution, was treated with a small amount of EtOH, dried with Et_2O, and used without further purification.[15] Infrared spectra were recorded on a Perkin-Elmer spectrometer. Elemental analyses were performed on a Carlo Erba model 1106 elemental analyser.

Preparation of the Bis(dithiocarbonato)nitridotechnetate(V) *Complex*, $K_2[TcN(S_2CO)_2]$.—A three-fold molar excess of $K(S_2COEt)$ dissolved in methanol was added to a solution of $[TcNCl_2(PPh_3)_2]$ (0.162 mmol) in dichloromethane–benzene (1:3). The solution immediately turned pale yellow and was gently warmed for a few minutes. A pale yellow solid formed when the solution was concentrated. It was removed by filtration, washed with a small amount of EtOH, and dried with Et_2O. Slow evaporation of a water–ethanol (1:3) solution of the solid yielded the dithiocarbonate compound as suitable crystals for *X*-ray determination. Yield 40% (Found: C, 6.8; N, 3.2; S, 33.2. Calc. for $C_2K_2NO_2S_4Tc$: C, 6.4; N, 3.7; S, 34.2%). I.r. (Nujol): ν(C=O) 1 710, ν(Tc≡N) 1 060 cm^{-1}.

Crystallography.—A crystal of maximum dimensions 0.2 mm was used for the *X*-ray measurements on a Philips diffractometer with Mo-K_α radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings.

Crystal data. $C_2K_2NO_2S_4Tc\cdot 2H_2O$, $M = 411.3$, monoclinic, space group $P2_1/n$, $a = 8.353(5)$, $b = 15.630(4)$, $c = 9.230(5)$ Å, $\beta = 90.94(3)°$, $U = 1\,204.9$ Å^3, $D_c = 2.09$ g cm^{-3}, $Z = 4$, $F(000) = 800$, μ(Mo-K_α) = 23.5 cm^{-1}, λ(Mo-K_α) = 0.7107 Å.

The crystal is stable under irradiation. Of a total of 3 835 reflections recorded, whose intensities were corrected for Lorentz polarization and absorption[16] (transmission range

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Fractional co-ordinates of $K_2[TcN(S_2CO)_2]\cdot 2H_2O$

Atom	*x*	*y*	*z*
Tc	0.225 01(6)	0.180 48(3)	0.290 16(5)
N	0.359 4(6)	0.179 5(4)	0.165 4(6)
S(1)	0.286 9(2)	0.064 1(1)	0.449 7(2)
S(2)	0.035 4(2)	0.070 6(1)	0.234 8(2)
C(1)	0.134 2(8)	0.002 2(4)	0.363 2(8)
O(1)	0.101 4(7)	−0.071 9(3)	0.387 8(6)
S(3)	0.297 7(2)	0.292 4(1)	0.455 3(2)
S(4)	0.045 0(2)	0.296 2(1)	0.240 6(2)
C(2)	0.144 9(9)	0.357 5(4)	0.378 5(8)
O(2)	0.110 3(8)	0.428 4(4)	0.417 5(7)
K(1)	0.108 0(2)	0.192 5(1)	−0.284 5(2)
K(2)	0.399 6(2)	0.962 3(1)	0.776 2(2)
O(3)	0.217 0(7)	0.082 1(4)	0.909 3(6)
O(4)	0.196 5(8)	0.327 8(4)	0.898 5(7)

Table 2. Bond distances (Å) and angles (°)

Tc–N	1.621(6)	Tc–S(1)	2.392(2)
Tc–S(2)	2.386(2)	Tc–S(3)	2.392(2)
Tc–S(4)	2.391(2)	S(1)–C(1)	1.779(7)
S(2)–C(1)	1.788(7)	C(1)–O(1)	1.213(8)
S(3)–C(2)	1.771(7)	S(4)–C(2)	1.789(7)
C(2)–O(2)	1.202(9)		
S(3)–Tc–S(4)	73.82(7)	S(2)–Tc–S(4)	95.16(7)
S(2)–Tc–S(3)	145.44(8)	S(1)–Tc–S(4)	145.27(8)
S(1)–Tc–S(3)	96.52(7)	S(1)–Tc–S(2)	73.78(7)
N–Tc–S(4)	108.2(2)	N–Tc–S(3)	106.8(2)
N–Tc–S(2)	107.8(2)	N–Tc–S(1)	106.5(2)
Tc–S(1)–C(1)	89.5(2)	Tc–S(2)–C(1)	89.4(2)
S(1)–C(1)–S(2)	107.0(4)	S(2)–C(1)–O(1)	126.3(6)
S(1)–C(1)–O(1)	126.7(6)	Tc–S(3)–C(2)	89.5(2)
Tc–S(4)–C(2)	89.1(2)	S(3)–C(2)–S(4)	107.5(4)
S(4)–C(2)–O(2)	126.5(6)	S(3)–C(2)–O(2)	125.8(6)
Contact distances			
$K(1^{I})\cdots N$	2.92	$K(2^{III})\cdots O(2^{IV})$	2.88
$K(1^{I})\cdots O(1^{II})$	2.73	$K(2^{III})\cdots O(2^{V})$	2.76
$K(1^{I})\cdots O(3^{I})$	2.64	$K(2^{III})\cdots O(3^{VI})$	2.72
$K(1^{I})\cdots O(4^{I})$	2.80	$K(2^{III})\cdots O(4^{IV})$	2.76

I $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; II $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; III $1 - x, 1 - y, 1 - z$; IV $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; V $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; VI $1 - x, \bar{y}, 1 - z$.

0.92—1.00), 2 803 with $I > 3\sigma(I)$ were considered as observed and used in subsequent calculations.

Solution of the structure was achieved by Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters. At convergence the conventional residual factor *R* was 0.035, based on the observed reflections. No significant electronic density was observed in the final Fourier-difference map. The function minimized was $\Sigma w(\Delta F)^2$ with $w = 1$. Calculations were done using the SHELX program package.[17] Scattering factors for neutral atoms were taken from ref. 18, and those of Tc were corrected for the anomalous dispersion.[19] Final atomic parameters are listed in Table 1, bond lengths and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results and Discussion

Interaction of the nitrido compound $[TcNCl_2(PPh_3)_2]$ with the $K(S_2COEt)$ ligand in CH_2Cl_2–C_6H_6 gives a pale yellow product (**1**) which when treated with a water–ethanol mixture forms a crystalline complex of analytical composition $K_2[TcN(S_2CO)_2]$ (**2**). The i.r. spectra of the two complexes are different. The first shows many strong absorptions in the region 1 240—1 000 cm^{-1} due to vibrations arising from the dithiocarbonate ligand,[20] the Tc≡N group (1 100—1 050 cm^{-1}),[8] and the PPh_3 group.[21] In the second spectrum only one band is observed in the same region at 1 060 cm^{-1} due to the Tc≡N group. In addition two absorptions are found at *ca.* 1 710 and 860 cm^{-1}, due to the C=O and C–S groups respectively. The i.r. data and the elemental analyses suggest that the co-ordinated *O*-ethyl dithiocarbonate ligand evolves in aqueous solution to give the dithiocarbonate derivative.

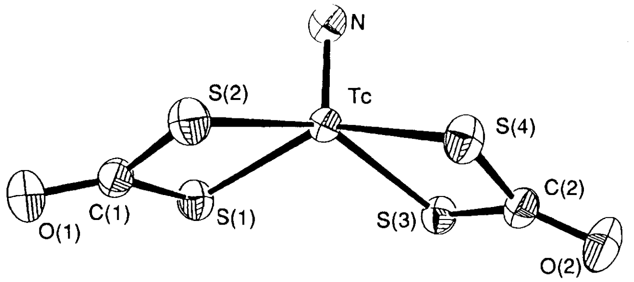
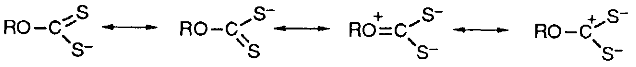


Figure 1. ORTEP plot and numbering scheme for the $[TcN(S_2CO)_2]^{2-}$ anion

Dithiocarbonate complexes generally cannot be obtained directly from the ligand because of its instability to disproportionation; therefore hydrolysis of the dithiocarbonate ester complexes is a useful method to obtain them. Nucleophilic attack of amines and phosphines on the carbon atom of the CS_2 moiety of the ester ligand suggests a significant contribution of resonance structure (**IV**) to the total structure of this group in



(I) (II) (III) (IV)

these complexes.[22] This reaction shows that the neutral ester compound can be transformed in aqueous medium into a dianionic complex, so affecting the biodistribution of the eventual radiopharmaceutical compound.[23]

Description of the Crystal Structure.—The technetium(v) metal ion is five-co-ordinate in a distorted square-pyramidal arrangement, being directly bonded to two chelated dithiocarbonato anions and to the apical nitrogen (Figure 1). As expected, owing to the constraints imposed by the geometry of the ligands, the base of the co-ordination pyramid is rectangular, with internal S···S bites of 2.87 Å and external S···S contacts of 3.57 and 3.53 Å, the metal ion being displaced by 0.71 Å from the (mean) base plane of the four S atoms. The planes of the bidentate anions are inclined by 16.3 and 21.6° with respect to the base plane and by only 5.5 and 0.3° with respect to the corresponding TcS_2 planes. Structural details of these groups compare well. The C=O group is ketonic (mean 1.207 Å) while the C–S bonds (1.77—1.79 Å) can be considered single. Accordingly, the O–C–S angles are significantly larger (mean 126.3°) than the S–C–S ones (mean 107.3°). All Tc–S–C angles are essentially right (89.1—89.5°); the Tc–S bonds (2.39 Å) are somewhat longer than the sums of the covalent and atomic radii (2.29 and 2.35 Å, respectively), their lengths being probably determined also by the geometry of the chelating groups. The formal triple Tc≡N bond [1.621(6) Å] compares well with values found in other technetium(v) nitrido complexes in which Tc is five-co-ordinated.[8,21]

Each of the two K^+ ions is surrounded in a rather irregular tetrahedral arrangement by oxygen or nitrogen atoms, with

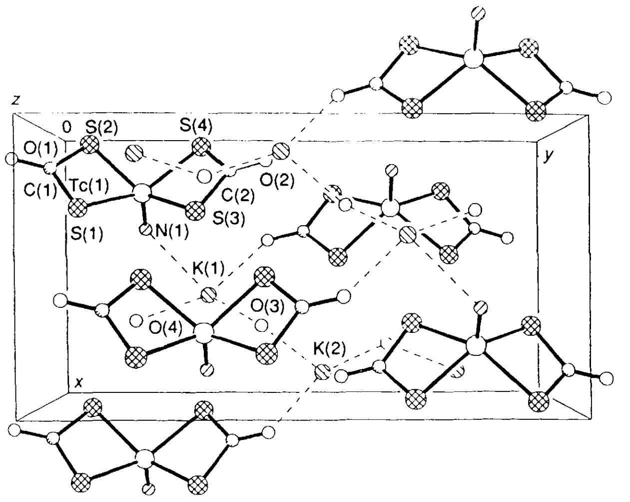


Figure 2. Packing diagram of $K_2[TcN(S_2CO)_2]\cdot 2H_2O$. The broken lines indicate the interactions with K^+

distances ranging from 2.64 to 2.88 Å for the water and dithiocarbonato oxygens and with a relatively longer K(1)···N contact of 2.92 Å. Linking of adjacent complex anions through the K^+ ions and the water molecules produces a rather complicated network of ionic interactions which provides compactness to the crystal packing (Figure 2).

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Received 7th February 1990; *Paper* 0/00552E