Preparation and Crystal Structure of Carbonyltris(diethyldithiocarbamato)technetium(III): An Unexpected Source of Co-ordinated Carbon Monoxide

By **John Baldas, John Bonnyman, Peter M. Pojer,** and **Geoffrey A. Williams,** Australian Radiation Laboratory, Lower Plenty Road, Yallambie, Victoria 3085, Australia
Maureen F. Mackay, Department of Physical Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

The title compound $[Tc(S_2CNEt_2)_3(CO)]$ has been prepared by the reduction of $[NH_4][TcO_4]$ with aminoiminomethanesulphinic acid in the presence of $Na[S_2CNEt_2]$. It is suggested that the co-ordinated carbon monoxide is formed after co-ordination of aminoiminomethanesulphinic acid, or some decomposition product, with technetium. The crystal structure of $[Tc(S_2CNEt_2)_3(CO)]$ has been determined by single-crystal *X*-ray diffraction methods at 17 °C. Crystals are triclinic, space group $P\bar{1}$, with a = 9.510(1), b = 9.976(1), c = 14.637(3) Å, α = 103.79(1), β = 105.42(1), γ = 72.52(1)°, and Z = 2. Diffractometry has provided significant Bragg intensities for 2 045 independent reflections and the structure has been refined by full-matrix least-squares methods to R 0.049. The compound is isostructural with the rhenium analogue and consists of discrete $[Tc(S_2CNEt_2)_3(CO)]$ molecules, each containing a terminal 'linear' CO group. The technetium atom has a seven-co-ordinate environment which is best described as a distorted pentagonal bipyramid. The geometry of the Tc^{III}–C–O group [Tc–C 1.861(12), C–O 1.15(1) Å], by comparison with the Re^{III}–C–O case, indicates that technetium is a poorer π-donor than is rhenium.

THE chemistry of technetium has attracted increasing attention in recent years due to both the widespread use of the short-lived isomer, technetium-99m ($t_{\frac{1}{2}}$ 6 h) in diagnostic nuclear medicine,[1,2] and the greater availability of technetium-99 ($t_{\frac{1}{2}}$ 2.12×10^5 years). Tin(II) chloride is generally used to reduce the pertechnetate anion TcO_4^- to a lower oxidation state required for complex formation.

In 1977, Fritzberg *et al.*[3] proposed formamidinesulphinic acid [aminoiminomethanesulphinic acid, $NH_2(NH)CSO_2H$] as an alternative general reducing agent for the preparation of ^{99m}Tc radiopharmaceuticals. This new reducing agent avoids some of the problems associated with the tendency of tin(II) salts to hydrolysis and to oxidation.

We recently reported the biological behaviour of a highly lipophilic (dithiocarbamato)technetium-99m complex prepared by use of formamidinesulphinic acid as the reducing agent for pertechnetate.[4] In the present paper we report the isolation, characterisation, and *X*-ray crystal structure determination of carbonyltris(*NN*-diethyldithiocarbamato)technetium(III). This complex was prepared by the reduction of ammonium [^{99}Tc]-pertechnetate with formamidinesulphinic acid in the presence of sodium diethyldithiocarbamate. The formation of a carbonyl complex was unexpected but is of significance to any intended use of formamidinesulphinic acid as a reducing agent in the preparation of ^{99m}Tc radiopharmaceuticals.

EXPERIMENTAL

Ammonium [^{99}Tc]pertechnetate was supplied by The Radiochemical Centre, Amersham. Sodium [^{99m}Tc]pertechnetate (supplied by the Australian Atomic Energy Commission) was added to reaction mixtures to determine the yields of technetium-99 compounds. The gamma activity was measured in a Capintec CRC-2N ionisation chamber. Formamidinesulphinic acid was obtained from the Aldrich Chemical Co., Milwaukee, USA. Basic alumina (activity I), used for column chromatography, was supplied by E. Merck, Darmstadt, Germany.

The i.r. spectra were determined in KBr discs on a Perkin-Elmer 197 spectrophotometer. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

Formamidinesulphinic acid (3 g, 28 mmol) was added to distilled water (150 cm^3) and the pH was adjusted to 9 with 8 mol dm^{-3} NaOH. To this aqueous solution was added $Na[S_2CNEt_2]$ (3 g, 17.5 mmol) followed by ammonium [^{99}Tc]pertechnetate (80 mg, 0.44 mmol) containing 50 MBq of sodium [^{99m}Tc]pertechnetate. The mixture rapidly darkened and was stirred at 60 °C for 45 min. The precipitate, containing 98% of the radioactivity, was collected by filtration, dissolved in chloroform, dried over anhydrous sodium sulphate, and applied to an alumina column (2.5 cm diameter × 10 cm). Elution with chloroform gave an orange-brown fraction, 45% yield based on $[NH_4][TcO_4]$, and subsequent elution with methanol gave a dark brown fraction (45% yield) which could not be purified further. On concentration, the chloroform eluate deposited orange-brown crystals of carbonyltris(*NN*-diethyldithiocarbamato)-technetium(III) which were collected and recrystallised from a benzene–ethanol (1 : 1 v/v) mixture, m.p. 187—191 °C (decomp.) (Found: C, 33.7; H, 5.1; N, 7.2; S, 32.6. $C_{16}H_{30}N_3OS_6Tc$ requires C, 33.6; H, 5.3; N, 7.4; S, 33.6%). The i.r. spectrum showed peaks at 1 895vs, 1 496s, 1 432m, 1 273s, 1 212m, and 947m cm^{-1}.

Crystallography.—Single crystals suitable for *X*-ray diffraction studies were grown by slow evaporation of a benzene–ethanol (1 : 1 v/v) solution of $[Tc(S_2CNEt_2)_3(CO)]$ at room temperature. Oscillation and Weissenberg photographs showed the crystals to be triclinic, and the subsequent refinement of the structure confirmed the choice of the centrosymmetric space group $P\bar{1}$. Unit-cell parameters, together with their estimated standard deviations (e.s.d.s), were derived by least-squares methods from the 2θ values,

for 25 reflections well separated in angle, measured on a diffractometer at 17 °C with Cu-K_α radiation (λ = 1.5418 Å).

Crystal data. $C_{16}H_{30}N_3OS_6Tc$, M = 571.70, Triclinic, a = 9.510(1), b = 9.976(1), c = 14.637(3) Å, α = 103.79(1), β = 105.42(1), γ = 72.52(1)°, U = 1 257.7 Å^3, Z = 2, $F(000)$ = 588, D_c = 1.51 Mg m^{-3}, space group $P\bar{1}$, μ(Cu-K_α) = 9.07 mm^{-1}.[5]

TABLE 1

Final atomic positional co-ordinates for non-hydrogen atoms of [Tc(S_2CNEt_2)$_3$(CO)]

Atom	X/a	Y/b	Z/c
Tc	0.202 78(10)	0.100 40(9)	0.241 12(6)
S(1)	0.404 3(3)	−0.118 0(3)	0.208 7(2)
S(2)	0.221 4(3)	0.041 9(3)	0.069 6(2)
S(3)	0.096 6(3)	0.259 6(3)	0.379 0(2)
S(4)	0.293 7(3)	−0.011 1(3)	0.387 8(2)
S(5)	0.396 5(3)	0.243 7(3)	0.287 3(2)
S(6)	0.088 4(3)	0.328 8(3)	0.185 8(2)
O	−0.056 5(9)	−0.038 0(9)	0.185 7(6)
N(1)	0.441 7(9)	−0.194 2(9)	0.025 6(6)
N(2)	0.191 0(9)	0.147 1(10)	0.542 8(6)
N(3)	0.270 9(9)	0.505 4(10)	0.244 8(6)
C(1)	0.366 4(11)	−0.105 9(11)	0.090 1(7)
C(2)	0.397 2(13)	−0.177 5(13)	−0.076 2(8)
C(3)	0.303 1(15)	−0.275 6(14)	−0.136 6(9)
C(4)	0.566 5(12)	−0.317 1(12)	0.052 7(8)
C(5)	0.715 6(14)	−0.282 6(15)	0.086 3(9)
C(6)	0.189 6(11)	0.135 3(12)	0.450 4(7)
C(7)	0.276 8(12)	0.032 4(13)	0.598 1(7)
C(8)	0.181 5(14)	−0.067 4(16)	0.594 8(9)
C(9)	0.106 1(14)	0.282 7(15)	0.595 0(9)
C(10)	0.198 4(16)	0.383 6(15)	0.644 8(11)
C(11)	0.256 2(11)	0.375 7(12)	0.240 0(7)
C(12)	0.409 0(14)	0.551 6(14)	0.299 7(10)
C(13)	0.394 7(18)	0.610 2(15)	0.404 5(11)
C(14)	0.151 6(12)	0.617 9(11)	0.202 7(8)
C(15)	0.151 1(14)	0.615 6(12)	0.098 8(9)
C(16)	0.041 9(11)	0.015 9(12)	0.205 1(8)

Intensity data were recorded at 17 °C on a Rigaku-AFC four-circle diffractometer with graphite-monochromatised Cu-K_α radiation. The crystal had well developed (100), (010), and (001) faces with perpendicular distances between parallel faces of 0.08, 0.12, and 0.05 mm respectively. The crystal was sealed in a thin-walled Lindemann glass tube and aligned with the b axis approximately parallel to the diffractometer Φ axis. Intensities were measured by an ω—2θ scan, with a 2θ scan rate of 2° min^{-1}, a scan range in ω of 1.2 + 0.5tanθ, and 10-s stationary background counts. Three reference reflections, monitored every 50 reflections, showed no significant variations in intensities during data collection. A total of 2 900 reflections, having non-zero intensities, were measured within the limit (sinθ)/λ ≤ 0.583 Å^{-1}. Of these, there were 2 740 unique data, of which 2 046 were considered observed [$I > 3\sigma(I)$] and were used for the structure analysis. The integrated intensities were corrected for Lorentz and polarisation effects, and for absorption.[5]

Structure determination and refinement. The structure was solved by the heavy-atom method. The position of the Tc atom was derived from a three-dimensional Patterson map, and subsequent difference-Fourier syntheses revealed the positions of all 27 non-hydrogen atoms. Full-matrix least-squares refinement, with data uncorrected for absorption and with anisotropic temperature factors assigned to all atoms, converged with a reliability index R = $\Sigma\Delta F/\Sigma|F_o|$ of 0.063 where $\Delta F = ||F_o| - |F_c||$. The function minimised was $\Sigma w(\Delta F)^2$, where w is the weight assigned to the $|F_o|$ values. After absorption corrections were applied to the intensity data, with transmission factors ranging between 0.50 and 0.66, the same refinement converged with R 0.056.

Difference syntheses yielded the sites of all hydrogen atoms, and these were included in the scattering model. The positions of the hydrogen atoms were not refined, and they were assigned a variable overall isotropic temperature factor B which, at convergence, had the value 8.1(7) Å^2. An examination of $|F_o|$ and $|F_c|$ values at this stage indicated that only the most intense reflection (101) was significantly affected by extinction and this was omitted from the refinement. Least-squares refinement {245 variables, 2 045 observations, $w = 1.165/[\sigma^2(F_o) + 0.0005(F_o^2)]$} converged with R 0.049 and $R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, 0.052. The maximum parameter shift-to-error ratios at convergence were 0.01 : 1 for the overall isotropic hydrogen-atom B value, and 0.003 : 1 for all other parameters. The largest peaks on a final difference synthesis were of heights 0.98 and −0.82 e Å^{-3} close to the Tc atom.

Final atomic positional co-ordinates, with e.s.d.s in parentheses, are listed in Table 1. Isotropic and anisotropic atomic thermal parameters, and observed and calculated structure factors, are listed in Supplementary Publication No. SUP 23219 (25 pp.).*

Neutral atom scattering-factor curves for C, N, O, and S were taken from ref. 6, that for neutral Tc was from ref. 7, and that for H was from ref. 8. Real and imaginary anomalous dispersion corrections [5] were applied to the non-hydrogen atoms. Structure determination and refinement were performed with the SHELX 76 program system [9] on a VAX11/780 computer at the La Trobe University Computer Centre.

TABLE 2

Interatomic bond distances (Å) in [Tc(S_2CNEt_2)$_3$(CO)]

Tc–S(1)	2.475(3)	N(1)–C(4)	1.48(1)
Tc–S(2)	2.480(3)	N(2)–C(6)	1.33(1)
Tc–S(3)	2.491(3)	N(2)–C(7)	1.47(1)
Tc–S(4)	2.483(3)	N(2)–C(9)	1.50(1)
Tc–S(5)	2.520(3)	N(3)–C(11)	1.33(1)
Tc–S(6)	2.440(3)	N(3)–C(12)	1.49(1)
Tc–C(16)	1.861(12)	N(3)–C(14)	1.46(1)
S(1)–C(1)	1.704(10)	C(2)–C(3)	1.49(2)
S(2)–C(1)	1.713(9)	C(4)–C(5)	1.49(2)
S(3)–C(6)	1.696(11)	C(7)–C(8)	1.52(2)
S(4)–C(6)	1.711(10)	C(9)–C(10)	1.47(2)
S(5)–C(11)	1.698(11)	C(12)–C(13)	1.53(2)
S(6)–C(11)	1.730(11)	C(14)–C(15)	1.51(2)
N(1)–C(1)	1.33(1)	C(16)–O	1.15(1)
N(1)–C(2)	1.47(1)		

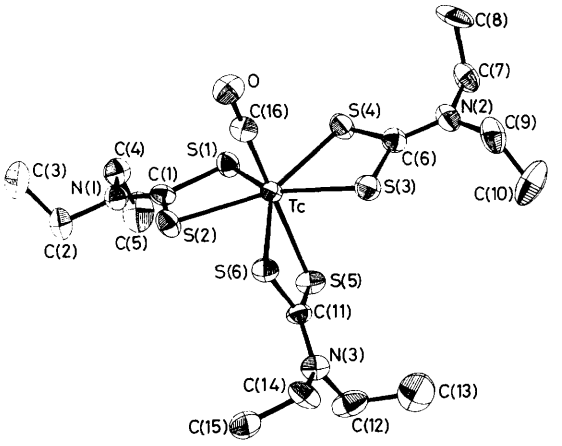
RESULTS AND DISCUSSION

The molecular geometry and atom numbering of the [Tc(S_2CNEt_2)$_3$(CO)] molecule are shown in the Figure. Interatomic bond distances and angles, with estimated standard deviations derived from the refinement, are given in Tables 2 and 3. Intramolecular and intermolecular contact distances are given in Table 4.

The structure consists of discrete molecules of [Tc(S_2CNEt_2)$_3$(CO)], each containing a terminal 'linear' CO group [Tc–C–O 178(1)°]. The compound is isostructural with the rhenium analogue [Re(S_2CNEt_2)$_3$-

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

(CO)],[10] with a seven-co-ordinate distorted pentagonal-bipyramidal environment about the technetium(III) atom. Two of the S_2CNEt_2 ligands occupy equatorial positions, while the third spans an equatorial and an axial site. The remaining axial site is occupied by the carbonyl group.



ORTEP drawing of the $[Tc(S_2CNEt_2)_3(CO)]$ molecule. The thermal ellipsoids are constructed at the 40% probability level

The $[Tc(S_2CNEt_2)_3(CO)]$ molecules pack in the unit cell in an analogous fashion to the isostructural $[Re(S_2CNEt_2)_3(CO)]$.[10] There are no contacts of significance between neighbouring molecules (Table 4). The dithiocarbamato-ligands adopt the usual geometry with planar S_2CNC_2 segments (Table 5). The largest deviations from planarity (ignoring the terminal methyl groups) occur in the dithiocarbamato-ligand which spans an equatorial and an axial site. As in the case of $[Re(S_2CNEt_2)_3(CO)]$, the metal atom is *ca.* 0.3 Å out of this dithiocarbamato-plane whereas it is almost coplanar with the two equatorial dithiocarbamato-ligands. In the equatorial ' plane ', the technetium and four sulphur atoms of the equatorial dithiocarbamato-ligands are nearly coplanar (Table 5). However, the ' equatorial ' sulphur atom S(6) of the remaining dithiocarbamato-ligand is significantly displaced [0.684(3) Å] from this mean TcS_4 plane, a result imposed by the restricted bite of the bidentate ligand [S(5) · · · S(6) 2.88 Å].

The $[Tc(S_2CNEt_2)_3(CO)]$ structure can be compared with that of another seven-co-ordinate complex of technetium, $[TcCl_3(PMe_2Ph)_3(CO)]$.[11] In this case the co-ordination polyhedron around the technetium(III) atom is a distorted capped octahedron. The geometry of the Tc–C–O group in this phosphine complex [Tc^{III}–C 1.86(2), C–O 1.12(3) Å; Tc–C–O 178(2)°] is in excellent agreement with that found in $[Tc(S_2CNEt_2)_3(CO)]$ (Tables 2 and 3).

The isostructural complexes $[Tc^{III}(S_2CNEt_2)_3(CO)]$ and $[Re^{III}(S_2CNEt_2)_3(CO)]$, together with the two isostructural nitrido-complexes $[M^{V}(S_2CNEt_2)_2N]$, where M = Tc,[12] or Re,[13] provide an opportunity to compare bonding to technetium and rhenium in the two oxidation states. Relevant mean bond distances in these compounds are presented in Table 6. In each case the mean M^{V}–S bond distance is less than the M^{III}–S distance, consistent with the different oxidation state and co-ordination number of the metal. For technetium and rhenium in the same oxidation state, there is little difference in the M–S bond distances. Presumably the ability of the dithiocarbamato-sulphur atoms to compete for the available *s*, *p*, *d*, and *f* valence orbitals of the metal atoms is affected by both the radial extents of the orbitals and by the steric constraints imposed by the bidentate ligands. The similarity in Tc–S and Re–S bond lengths is also consistent with the lanthanide contraction.

However, the $Tc^{V}{\equiv}N$ bond is significantly shorter [1.604(6) Å] than the $Re^{V}{\equiv}N$ bond [1.656(8) Å], and this suggests a greater affinity of technetium(V) over rhenium(V) for strong π-donor ligands such as N^{3-}. On the other hand, the $Tc^{III}{=}CO$ and $Re^{III}{=}CO$ bond distances [1.861(12) and 1.852(8) Å respectively] show a trend in the reverse direction and indicate that technetium(III) is

TABLE 3

Bond angles (°) in $[Tc(S_2CNEt_2)_3(CO)]$

S(1)–Tc–S(2)	68.2(1)	Tc–S(6)–C(11)	88.1(4)
S(3)–Tc–S(4)	68.4(1)	C(1)–N(1)–C(2)	121.0(9)
S(5)–Tc–S(6)	71.0(1)	C(1)–N(1)–C(4)	121.0(9)
S(1)–Tc–S(4)	72.4(1)	C(2)–N(1)–C(4)	117.9(8)
S(2)–Tc–S(6)	76.8(1)	C(6)–N(2)–C(7)	122.4(9)
S(3)–Tc–S(6)	76.2(1)	C(6)–N(2)–C(9)	119.9(9)
S(1)–Tc–S(3)	139.7(1)	C(7)–N(2)–C(9)	117.7(9)
S(1)–Tc–S(6)	138.6(1)	C(11)–N(3)–C(12)	122.4(9)
S(2)–Tc–S(3)	151.9(1)	C(11)–N(3)–C(14)	123.7(9)
S(2)–Tc–S(4)	139.6(1)	C(12)–N(3)–C(14)	113.8(9)
S(4)–Tc–S(6)	142.9(1)	S(1)–C(1)–S(2)	108.8(5)
S(1)–Tc–S(5)	89.0(1)	S(1)–C(1)–N(1)	125.0(8)
S(2)–Tc–S(5)	92.8(1)	S(2)–C(1)–N(1)	126.2(8)
S(3)–Tc–S(5)	85.7(1)	N(1)–C(2)–C(3)	112.6(10)
S(4)–Tc–S(5)	95.0(1)	N(1)–C(4)–C(5)	113.1(10)
S(1)–Tc–C(16)	97.8(3)	S(3)–C(6)–S(4)	110.3(6)
S(2)–Tc–C(16)	87.6(3)	S(3)–C(6)–N(2)	127.0(8)
S(3)–Tc–C(16)	90.6(3)	S(4)–C(6)–N(2)	122.7(9)
S(4)–Tc–C(16)	89.2(3)	N(2)–C(7)–C(8)	111.3(9)
S(5)–Tc–C(16)	172.9(3)	N(2)–C(9)–C(10)	113.6(10)
S(6)–Tc–C(16)	102.2(3)	S(5)–C(11)–S(6)	114.4(7)
Tc–S(1)–C(1)	91.7(3)	S(5)–C(11)–N(3)	123.7(8)
Tc–S(2)–C(1)	91.3(3)	S(6)–C(11)–N(3)	121.9(8)
Tc–S(3)–C(6)	90.7(3)	N(3)–C(12)–C(13)	109.2(11)
Tc–S(4)–C(6)	90.6(4)	N(3)–C(14)–C(15)	113.1(9)
Tc–S(5)–C(11)	86.2(4)	Tc–C(16)–O	177.8(10)

TABLE 4

Selected intramolecular and intermolecular contact distances (Å) in $[Tc(S_2CNEt_2)_3(CO)]$ *

Tc · · · C(1)	3.05	S(5) · · · S(6)	2.88
Tc · · · C(6)	3.03	S(1) · · · S(4)	2.93
Tc · · · C(11)	2.94	S(2) · · · S(6)	3.05
Tc · · · O	3.02	S(3) · · · S(6)	3.04
C(16) · · · S(1)	3.29	C(7) · · · $S(1^{I})$	3.71
C(16) · · · S(2)	3.04	O · · · $S(2^{II})$	3.64
C(16) · · · S(3)	3.12	C(13) · · · $S(4^{III})$	3.66
C(16) · · · S(4)	3.08	C(7) · · · $S(5^{I})$	3.79
C(16) · · · S(6)	3.37	C(3) · · · $S(6^{II})$	3.77
S(1) · · · S(2)	2.78	C(3) · · · $O^{(II)}$	3.40
S(3) · · · S(4)	2.80		

Roman numeral superscripts refer to the following co-ordinate transformations: I $1-x, -y, 1-z$; II $-x, -y, -z$; III $x, 1+y, z$

* Data given within the limits of the contact radii: Tc 2.5; S 2.1; O,N,C 1.7 Å.

TABLE 5

Planarity of groups of atoms within the $[Tc(S_2CNEt_2)_3(CO)]$ molecule and distances from least-squares planes

Atoms defining plane	Mean deviation of atoms in plane (Å)	Maximum deviation of atoms in plane (Å)	Atom out of the plane	Perpendicular distance from the plane (Å)
S(1),S(2),S(3),S(4),Tc	0.106	0.165(3)	S(5)	−2.514(3)
			S(6)	−0.684(3)
			C(16)	1.860(11)
S(1),S(2),C(1),N(1),C(2),C(4)	0.016	0.023(13)	Tc	−0.016(1)
			C(3)	1.394(15)
			C(5)	−1.376(14)
S(3),S(4),C(6),N(2),C(7),C(9)	0.023	0.035(14)	Tc	−0.046(1)
			C(8)	1.433(15)
			C(10)	−1.395(16)
S(5),S(6),C(11),N(3),C(12),C(14)	0.036	0.060(14)	Tc	−0.266(1)
			C(13)	−1.534(16)
			C(15)	1.431(13)

a poorer π-donor to the π-acceptor carbonyl ligand than is rhenium(III). This is supported by the C–O bond lengths of 1.154(12) and 1.171(10) Å respectively in the technetium and rhenium complexes. Thus the weaker Tc^{III}=CO bonding is associated with a stronger CO bond.

The intense i.r. absorption at 1 895 cm^{-1} in $[Tc(S_2CNEt_2)_3(CO)]$ is assigned to the carbonyl stretching frequency. By analogy, the carbonyl stretching frequency in $[Re(S_2CNEt_2)_3(CO)]$ occurs at 1 870 cm^{-1} {in the original report of this compound,[14] it was incorrectly formulated as $[Re(S_2CNEt_2)_3(CO)_2]$}. These carbonyl stretching frequency values are in agreement with a greater CO bond order, and hence weaker metal–carbonyl bonding, in the technetium case.

TABLE 6

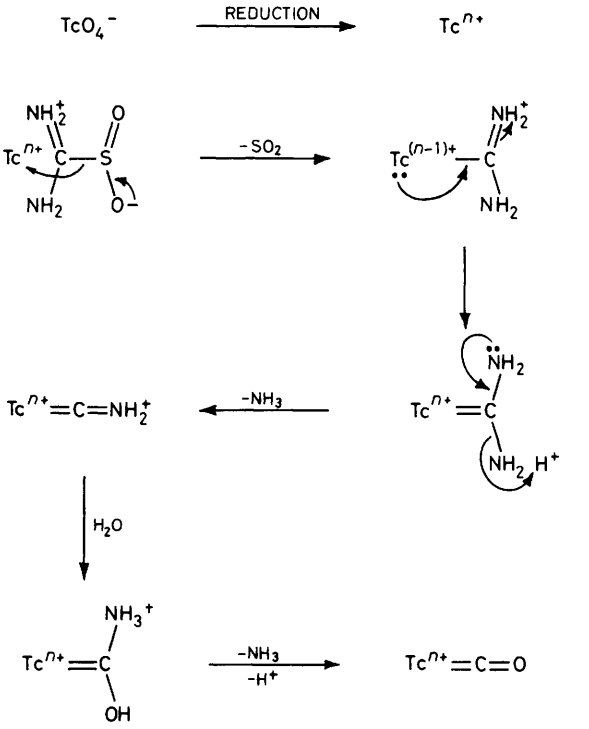
Mean bond distances (Å) in two isostructural pairs of technetium and rhenium complexes

Complex	M–S	M=CO	M≡N
$[Tc^{III}(S_2CNEt_2)_3(CO)]$	2.482	1.861(12)	
$[Re^{III}(S_2CNEt_2)_3(CO)]$	2.480	1.852(8)	
$[Tc^{V}(S_2CNEt_2)_2N]$	2.401		1.604(6)
$[Re^{V}(S_2CNEt_2)_2N]$	2.388		1.656(8)

The suggestion that technetium is a poorer π-donor than rhenium is supported by the bond distances in the isostructural metal(I) complexes $[\{Tc(CO)_3\}_2(tpp)]$ and $[\{Re(CO)_3\}_2(tpp)]$ (tpp = *meso*-tetraphenylporphinate).[15] The average Tc=CO [1.892(17) Å] and Re=CO [1.855(13) Å] bond distances in these compounds indicate that the technetium–carbonyl bond is the weaker. Again, the average CO bond distances in the technetium [1.46(2) Å] and rhenium [1.162(9) Å] complexes are in agreement with this view of the metal–carbonyl bonding. It therefore appears that complexes of technetium containing the π-acceptor dinitrogen ligand will be considerably less stable than the rhenium analogues.

It is apparent that both technetium and rhenium favour the odd-numbered oxidation states +III and +V in these dithiocarbamato-complexes. By considering the structures of the carbonyl and nitrido-complexes, it appears that steric factors have little influence on whether two or three dithiocarbamato-ligands are present. In the case of $[Tc(S_2CNEt_2)_3(CO)]$, with the strong π-acceptor carbonyl ligand, the presence of three dithiocarbamato-groups, which are themselves good electron donors,[16] is preferred.

Origin of the Carbonyl Ligand.—In the formation of $[Tc(S_2CNEt_2)_3(CO)]$, the formamidinesulphinic acid acts both as a reducing agent and as a source of the carbonyl ligand. The use of reducing agents other than $NH_2(NH)CSO_2H$ for the preparation of dithiocarbamato-complexes of technetium resulted in products which did not exhibit carbonyl absorptions in the i.r. spectra.[17] A satisfactory mechanism for the formation of carbon monoxide by the decomposition of $NH_2(NH)CSO_2H$ in aqueous solution is difficult to envisage. It is probable that the CO group is formed after co-ordination by $NH_2(NH)CSO_2H$, or some decomposition product, has occurred to technetium. This suggestion is supported



SCHEME Suggested mechanism for the formation of co-ordinated carbon monoxide from formamidinesulphinic acid

by our earlier work which showed that the reduction of [^{99m}Tc]pertechnetate in the presence of only $NH_2(NH)CSO_2H$ resulted in complex formation.[18] The impure methanol eluate, separated from the reaction mixture which yielded $[Tc(S_2CNEt_2)_3(CO)]$, showed peaks in the i.r. spectrum characteristic of the S_2CNEt_2 ligand. On standing, this material gradually developed a peak at 2 065 cm^{-1} in the i.r. spectrum. This supports the contention that the carbonyl ligand is formed from a co-ordinated species. A mechanism consistent with these observations is given in the Scheme.

[1/1070 *Received*, 7*th July*, 1981]

REFERENCES

[1] ' Radiopharmaceuticals,' eds. G. Subramanian, B. A. Rhodes, J. F. Cooper, and V. J. Sodd, The Society of Nuclear Medicine, Inc., New York, 1975.
[2] ' Radiopharmaceuticals II,' *Proc. 2nd Int. Symp. Radiopharmaceuticals*, The Society of Nuclear Medicine, Inc., New York, 1979.
[3] A. R. Fritzberg, D. M. Lyster, and D. H. Dolphin, *J. Nucl. Med.*, 1977, **18**, 553.
[4] P. M. Pojer and J. Baldas, *Int. J. Nucl. Med. Biol.*, 1981, **8**, 112.
[5] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
[6] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
[7] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 100.
[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
[9] G. M. Sheldrick, SHELX 76 Program for Crystal Structure Determination, University of Cambridge, 1976.
[10] S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1974, 486.
[11] G. Bandoli, D. A. Clemente, and U. Mazzi, *J. Chem. Soc., Dalton Trans.*, 1978, 373.
[12] J. Baldas, J. Bonnyman, P. M. Pojer, G. A. Williams, and M. F. Mackay, *J. Chem. Soc., Dalton Trans.*, 1981, 1798.
[13] S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1972, 1079.
[14] J. F. Rowbottom and G. Wilkinson, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 675.
[15] M. Tsutsui, C. P. Hrung, D. Ostfeld, T. S. Srivastava, D. L. Cullen, and E. F. Meyer, *J. Am. Chem. Soc.*, 1975, **97**, 3952.
[16] J. Willemse, J. A. Cras, J. J. Steggerda, and C. P. Keijzers, *Struct. Bonding (Berlin)*, 1976, **28**, 83.
[17] J. Baldas, J. Bonnyman, P. M. Pojer, and G. A. Williams, *Eur. J. Nucl. Med.*, in the press.
[18] J. Baldas and P. M. Pojer, *Int. J. Nucl. Med. Biol.*, 1981, **8**, 110.