The Synthesis and Reactivity of a New Technetium(III) Precursor. The Crystal Structures of $[TcCl_3(MeCN)\{P(C_6H_4Me\text{-}3)_3\}_2]$ and $[Tc(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine)†

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The reduction of $[TcCl_4(PPh_3)_2]$ with zinc metal in acetonitrile in the presence of triphenylphosphine gives the orange crystalline technetium(III) complex $[TcCl_3(MeCN)(PPh_3)_2]$ **1** in good yield. Suitable crystals of **1** were grown, but the crystal structure could not be determined satisfactorily due to pseudo-symmetry in the crystal lattice. To overcome this problem the crystal and molecular structure of the tri-*m*-tolylphosphine analogue $[TcCl_3(MeCN)\{P(C_6H_4Me\text{-}3)_3\}_2]$ **1a** was determined. Crystals of **1a** are triclinic, space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions $a = 10.157(2)$, $b = 10.302(2)$, $c = 22.073(2)$ Å, $\alpha = 87.27(2)$, $\beta = 86.66(1)$ and $\gamma = 66.87(1)°$. The structure was refined based on 5636 reflections converging to $R = 0.039$. Complex **1a** exhibits a distorted pseudo-octahedral geometry with two *trans* $P(C_6H_4Me\text{-}3)_3$ groups, three meridionally disposed chloride groups, and a linear terminally N-bound acetonitrile ligand. The reaction of **1** with the aromatic imines 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), and 2,2′:6′2″-terpyridine (terpy) gives the blue-black technetium(II) dicationic complexes $[Tc(bipy)_3]^{2+}$, $[Tc(phen)_3]^{2+}$ and $[Tc(terpy)_2]^{2+}$ isolated as their $[BPh_4]^-$ or $[PF_6]^-$ salts. The crystal and molecular structure of one of these novel technetium(II) complexes, $[Tc(bipy)_3][PF_6]_2$ **2a**, has been determined. Crystals of **2a** are trigonal, space group $P\bar{3}c1$ (no. 165) with $Z = 2$ in a unit cell of dimensions $a = 10.847(2)$ and $c = 16.299(3)$ Å. The structure was refined based on 414 unique reflections converging to $R = 0.0525$. The monomeric complex **2a** exhibits exact D_3 symmetry with the Tc–N bonds [2.077(10) Å] equivalent by symmetry. The electrochemical behaviour of complexes **1**, **2** and **3** has been investigated.

The basic co-ordination chemistry of technetium has been increasingly studied in the past few years due to its importance in diagnostic nuclear medicine.[1,2] This work has mainly dealt with technetium complexes in higher oxidation states, particularly the +5 oxidation state. However, the chemistry of technetium in its lower oxidation states has proven to be a very important subject area, because apart from its intrinsic interest, it has led to the development of some new low-oxidation state technetium-containing radiopharmaceuticals.[3,4] The major obstacle to the study of technetium in oxidation states of +3 or lower is the lack of suitable technetium(III) starting materials.

In our initial investigations we desired to have at our means a suitably labile starting material which would be more reactive than either of the alternative technetium(III) complexes $[Tc(tu)_6]^{3+}$ (tu = thiourea) or $[TcCl_3(PMe_2Ph)_3]$ currently available.[5,6]

We describe here the synthesis of the new reactive technetium(III) complex $[TcCl_3(MeCN)(PPh_3)_2]$ **1** and report its reactions with the chelating aromatic imine ligands 2,2′-bipyridine, 1,10-phenanthroline, and 2,2′:6′,2″-terpyridine. A preliminary communication of this work has already appeared.[7] However, since the publication of this work a paper dealing with a preparation of **1** and its reactions with CO and NO has appeared.[8] We detail below our different synthetic method, which gives superior yields of this important new technetium(III) starting material, and the crystal and molecular structure of the tri-*m*-tolylphosphine analogue, $[TcCl_3(MeCN)\{P(C_6H_4\text{-}Me\text{-}3)_3\}_2]$ **1a**.

Results and Discussion

Preparation and Properties of $[TcCl_3(MeCN)(PPh_3)_2]$ **1**.—The orange crystalline complex $[TcCl_3(MeCN)(PPh_3)_2]$ **1** was synthesised by the reduction of $[TcCl_4(PPh_3)_2]$ with finely divided zinc metal, in degassed acetonitrile under reflux [equation (1)]. Complex **1** was obtained in pure form directly

$$[TcCl_4(PPh_3)_2] \xrightarrow[\text{reflux, 30 min}]{\text{MeCN,Zn,PPh}_3} [TcCl_3(MeCN)(PPh_3)_2] \quad (1)$$

from the cooled reaction mixture in yields ranging from 40 to 80%.

The yields were improved by adding 1 equivalent of PPh_3 to the reaction mixture and also by limiting the volume of acetonitrile solvent used. Typically, the preparation of **1** on a 500 mg scale was performed in no more than 10 cm³ of dry acetonitrile, the product **1** being sparingly soluble in this solvent. Attempts to obtain additional material from the filtered reaction solution have proved fruitless. The properties of **1** are similar to those of the previously described rhenium analogue, $[ReCl_3(MeCN)(PPh_3)_2]$.[9] Both are sparingly

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Final atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for complex **1a**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Tc	0.129 95(3)	0.282 92(3)	0.232 74(1)	C(36)	−0.238 4(5)	0.654 4(5)	0.362 9(2)
Cl(1)	0.225 6(1)	0.090 69(9)	0.300 30(4)	C(37)	−0.446 0(6)	0.850 9(6)	0.412 8(3)
Cl(2)	0.058 0(1)	0.486 45(9)	0.171 10(4)	C(41)	0.285 4(4)	−0.055 1(3)	0.150 3(2)
Cl(3)	−0.078 75(8)	0.239 28(9)	0.213 99(4)	C(42)	0.189 0(4)	−0.097 6(4)	0.183 3(2)
P(1)	0.003 38(9)	0.427 80(9)	0.321 60(4)	C(43)	0.201 6(4)	−0.235 6(4)	0.180 7(2)
P(2)	0.261 03(9)	0.130 89(9)	0.145 89(4)	C(44)	0.311 0(4)	−0.331 4(4)	0.146 0(2)
N	0.309 1(3)	0.323 7(3)	0.245 3(2)	C(45)	0.408 7(4)	−0.292 8(4)	0.113 9(2)
C(1)	0.409 6(4)	0.345 9(4)	0.249 7(2)	C(46)	0.395 3(4)	−0.153 6(4)	0.115 7(2)
C(2)	0.538 4(5)	0.373 4(6)	0.254 1(3)	C(47)	0.530 8(6)	−0.396 8(5)	0.076 1(3)
C(11)	−0.032 4(4)	0.331 0(4)	0.387 4(2)	C(51)	0.445 0(4)	0.117 3(4)	0.136 1(2)
C(12)	−0.014 8(5)	0.358 5(5)	0.446 6(2)	C(52)	0.538 9(4)	0.045 3(4)	0.180 0(2)
C(13)	−0.055 7(7)	0.288 3(5)	0.494 3(2)	C(53)	0.680 5(4)	0.029 8(4)	0.177 0(2)
C(14)	−0.110 7(6)	0.190 5(5)	0.483 3(2)	C(54)	0.724 9(5)	0.096 9(7)	0.131 0(3)
C(15)	−0.129 4(5)	0.162 0(5)	0.424 6(2)	C(55)	0.630 9(6)	0.173 2(9)	0.088 0(4)
C(16)	−0.090 2(4)	0.232 8(4)	0.377 2(2)	C(56)	0.491 9(6)	0.183 9(8)	0.090 5(3)
C(17)	−0.190 0(6)	0.054 3(6)	0.412 3(3)	C(57)	0.783 4(5)	−0.054 3(6)	0.225 5(3)
C(21)	0.111 3(4)	0.515 8(4)	0.348 3(2)	C(61)	0.183 8(4)	0.186 3(4)	0.071 7(2)
C(22)	0.085 3(5)	0.653 6(4)	0.330 8(2)	C(62A)	0.049 6(8)	0.276 7(7)	0.062 8(4)
C(23)	0.181 2(6)	0.713 2(5)	0.345 1(3)	C(62B)	0.093 7(7)	0.115 8(7)	0.052 7(4)
C(24)	0.300 2(5)	0.632 9(6)	0.376 4(3)	C(63A)	−0.004 6(8)	0.312 5(8)	0.004 4(4)
C(25)	0.328 9(5)	0.494 6(6)	0.395 0(3)	C(63B)	0.020 9(8)	0.156 8(8)	−0.000 3(4)
C(26)	0.234 1(4)	0.437 9(5)	0.379 5(2)	C(64)	0.060 7(7)	0.264 4(5)	−0.040 1(2)
C(27)	0.460 1(7)	0.412(1)	0.428 9(4)	C(65A)	0.228 5(8)	0.170 9(8)	−0.038 6(4)
C(31)	−0.174 6(4)	0.568 7(3)	0.314 0(2)	C(65B)	0.114 4(9)	0.338 3(9)	−0.014 9(4)
C(32)	−0.249 1(4)	0.586 8(4)	0.261 5(2)	C(66B)	0.183 8(8)	0.298 8(8)	0.039 8(4)
C(33)	−0.387 2(5)	0.689 3(5)	0.258 8(3)	C(66A)	0.281 0(8)	0.135 0(8)	0.019 3(4)
C(34)	−0.448 8(5)	0.772 4(5)	0.307 6(3)	C(67B)	−0.067 8(9)	0.081 0(9)	−0.020 3(4)
C(35)	−0.377 6(5)	0.758 3(4)	0.359 8(3)	C(67A)	−0.160(1)	0.409(1)	−0.002 5(5)

* Atoms labelled A or B correspond to the disordered phenyl group.

Table 2 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex **1a**

Tc–Cl(1)	2.3401(9)	Cl(1)–Tc–Cl(2)	171.64(4)
Tc–Cl(2)	2.3314(9)	Cl(1)–Tc–Cl(3)	95.16(4)
Tc–Cl(3)	2.395(1)	Cl(1)–Tc–P(1)	88.01(3)
Tc–P(1)	2.4920(9)	Cl(1)–Tc–P(2)	90.12(3)
Tc–P(2)	2.5013(9)	Cl(1)–Tc–N	86.80(9)
Tc–N	2.058(3)	Cl(2)–Tc–Cl(3)	92.88(4)
N–C(1)	1.141(6)	Cl(2)–Tc–P(1)	89.62(3)
P(1)–C(11)	1.824(4)	Cl(2)–Tc–P(2)	92.20(3)
P(1)–C(21)	1.812(5)	Cl(2)–Tc–N	85.21(9)
P(1)–C(31)	1.832(3)	Cl(3)–Tc–P(1)	92.58(3)
P(2)–C(41)	1.835(4)	Cl(3)–Tc–P(2)	89.75(3)
P(2)–C(51)	1.819(4)	Cl(3)–Tc–N	177.69(9)
P(2)–C(61)	1.825(4)		

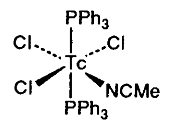

Fig. 1 The proposed structure of $[TcCl_3(MeCN)(PPh_3)_2]$

soluble with slow decomposition in acetonitrile, toluene, and acetone, and readily soluble in dichloromethane and chloroform. Solutions of **1** in CH_2Cl_2 or $CHCl_3$ are unstable with respect to aerial oxidation and decompose to give green solutions of what is presumed to be $[TcCl_4(PPh_3)_2]$. Similar behaviour was observed for $[ReCl_3(MeCN)(PPh_3)_2]$ in halogenated solvents.[9] As for $[ReCl_3(MeCN)(PPh_3)_2]$,[9a] the C≡N stretching mode of the co-ordinated acetonitrile molecule cannot be located in the solid-state infrared spectrum of complex **1**, the spectrum of which is unremarkable except for bands assigned to co-ordinated PPh_3. Suitable X-ray quality crystals of **1** were obtained and the structure determination was attempted. However, the structure did not refine well due to pseudo-symmetry in the crystal lattice. The phenyl rings of the two triphenylphosphine ligands could not be located satisfactorily.

The unit-cell dimensions* and preliminary structural information obtained are consistent with the proposed structure for **1** (Fig. 1), which is analogous to the structure of $[ReCl_3(MeCN)(PPh_3)_2]$.[9b] Accordingly, to overcome the problem of pseudo-symmetry, the tri-*m*-tolylphosphine analogue $[TcCl_3(MeCN)\{P(C_6H_4Me\text{-}3)_3\}_2]$ **1a** was synthesised and the structure determined.

Description of the Molecular Structure of Complex **1a**.—Final atomic coordinates and selected molecular dimensions are listed in Tables 1 and 2 respectively. Fig. 2 shows the molecular geometry of **1a** with associated atom numbering scheme. The structure consists of discrete molecules with no observable intermolecular interaction. The complex is pseudo-octahedral with *trans*-$P(C_6H_4Me\text{-}3)_3$ groups, as expected on steric grounds and the chlorine atoms are disposed meridionally. The structure confirms the presence of a normal N-bound acetonitrile ligand with a Tc–N bond distance of 2.058(3) Å. The Tc–Cl bond distances are 2.3401(9) and 2.3314(9) Å (*trans* to Cl) and 2.395(1) Å (*trans* to MeCN). The dimensions of the co-ordinated acetonitrile [N–C(1) 1.141(6) and C(1)–C(2) 1.453(7) Å] and the linearity of the Tc–N–C(1) linkage [177.1(3)°] are characteristic of acetonitrile functioning as a neutral two-electron donor ligand.[9b] The phenyl groups of the phosphine are twisted relative to one another by 120° and show no abnormal geometry. Of particular interest is the positioning of the acetonitrile moiety which lies sandwiched between two *m*-tolyl groups which themselves have their rings almost parallel.

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* The unit cell of **1** contains four molecules of **1** with a cell volume U = 3539.83 Å^3, a = 25.04, b = 10.03, c = 14.10 Å. The space group is $Pna2_1$. From ref. 9*b*, the unit-cell dimensions of $[ReCl_3(MeCN)(PPh_3)_2]$ are: U = 3560.28 Å^3, a = 10.036(8), b = 15.239(12), c = 23.280(17) Å. The space group was assigned as monoclinic $P2_1/n$.

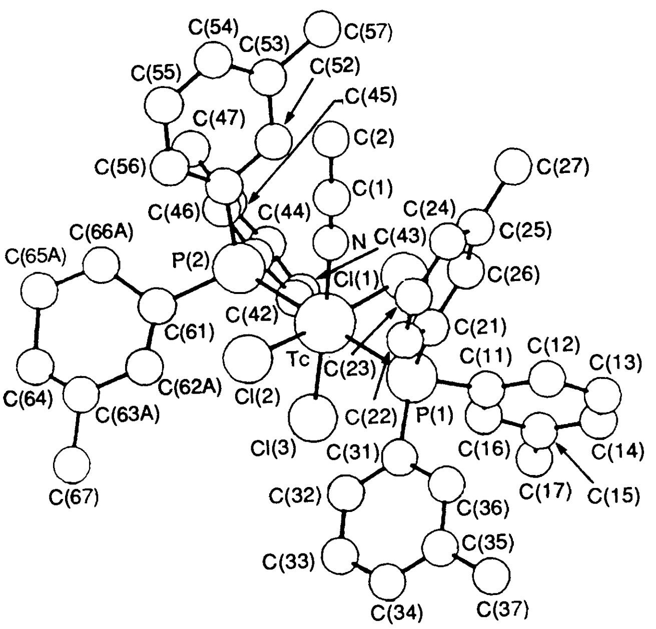

Fig. 2 A perspective view of the structure of $[\mathrm{TcCl_3(MeCN)\{P(C_6H_4\text{-}Me\text{-}3)_3\}_2}]$, showing the atom labelling scheme

Table 3 Fractional atomic coordinates with e.s.d.s in parentheses for complex **2a**

Atom	*x*	*y*	*z*
Tc	0.000 00	0.000 00	0.250 00
P	0.333 33	0.666 67	0.631 01(26)
F(1)	0.457 3(7)	0.681 5(8)	0.684 8(4)
F(2)	0.205 2(9)	0.644 5(10)	0.576 9(4)
C(1)	0.058 5(9)	−0.168 8(9)	0.380 0(5)
C(2)	0.139 1(9)	−0.209 7(9)	0.425 7(5)
C(3)	0.276 3(11)	−0.164 1(10)	0.400 2(6)
C(4)	0.328 7(11)	−0.081 6(10)	0.329 1(6)
C(5)	0.242 5(8)	−0.044 8(8)	0.287 4(5)
N	0.109 2(8)	−0.082 9(8)	0.312 4(4)

This places the MeCN ligand in a relatively protected environment. One of the aromatic rings of a tri-*m*-tolylphosphine ligand exhibits quite severe disorder. A consequence of this is the larger thermal parameters exhibited for this disordered aromatic ring than for the other phenyl rings in the structure. The alternative position is where the disordered aromatic ring rotates along its axis [C(61), C(64)] by about 160°. This disorder appears to be a function of packing considerations as there are little or no intermolecular interactions.

Reactions of Complex **1** *with Aromatic Imines.*—Complex **1** has been found to be a suitably reactive starting material for the synthesis of other lower-valent technetium species. Reaction of **1** with an excess of 2,2′-bipyridine (bipy) in dry methanol under reflux gives the cation $[\mathrm{Tc^{II}(bipy)_3}]^{2+}$. This deep blue compound has been isolated from reactions using absolute ethanol, acetonitrile, or reagent grade methanol. We have found that the synthesis of $[\mathrm{Tc(bipy)_3}]^{2+}$ salts can also be prepared equally well without the exclusion of air. The reaction of **1** with 1,10-phenanthroline (phen) or 2,2′:6′,2″-terpyridine (terpy) under similar conditions yields the analogous cations $[\mathrm{Tc(phen)_3}]^{2+}$ and $[\mathrm{Tc(terpy)_2}]^{2+}$. All of these technetium(II) complexes can be isolated in good yield as either their $[\mathrm{BPh_4}]^-$ or $[\mathrm{PF_6}]^-$ salts, and they are quite soluble in $\mathrm{CH_2Cl_2}$, acetone, dimethylformamide (dmf), and dimethyl sulfoxide (dmso).

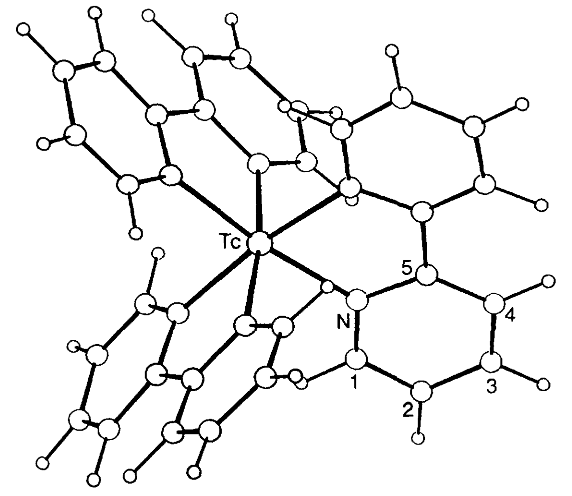

Fig. 3 A perspective view of the structure of the $[\mathrm{Tc(bipy)_3}]^{2+}$ cation showing the atom labelling scheme

Table 4 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex **2a**

Tc–N	2.077(10)	N(11)–Tc–N(21)*	98.0(3)
C(1)–N	1.368(11)	N(11)–Tc–N(51)*	88.2(4)
C(3)–C(4)	1.399(13)	N(11)–Tc–N(31)*	98.0(3)
C(5)–N	1.353(13)	N(61)–Tc–N(11)*	76.2(4)
C(1)–C(2)	1.379(16)	C(1)–N–Tc	124.6(7)
C(2)–C(3)	1.378(15)	C(5)–N–Tc	117.1(9)
C(4)–C(5)	1.366(16)		
C(5)–C(5)	1.482(16)		

* The first digit refers to the symmetry operation shown in Fig. 4.

A single-crystal X-ray structural determination was undertaken on a suitable crystal of the hexafluorophosphate salt $[\mathrm{Tc(bipy)_3}][\mathrm{PF_6}]_2$ **2a** obtained from dmf–EtOH.

Description of the Molecular Structure of Complex **2a**.—The X-ray structural analysis confirms the formulated stoichiometry of the dicationic bipyridyl tris-chelate $[\mathrm{Tc(bipy)_3}]^{2+}$, with two $[\mathrm{PF_6}]^-$ counter ions. There is no evidence for the presence of lattice solvent molecules. Both optical isomers of the complex dication are present in the crystal structure. The molecular geometry of the Δ isomer of $[\mathrm{Tc(bipy)_3}]^{2+}$ is shown in Fig. 3 with the associated numbering scheme used in the structure analysis shown.

A perspective view of the arrangement of a dication and three symmetry related $[\mathrm{PF_6}]^-$ counter ions is shown in Fig. 4. The final atomic coordinates and the principal molecular dimensions of **2a** are listed in Tables 3 and 4 respectively.

The dication has exact D_3 symmetry, consequently the three chelating ligands are related by a C_3 axis, and there are three C_2 axes perpendicular to the C_3 axis and passing through the centre of the bond linking the two halves of each bipyridyl ligand [*e.g.* C(15)–C(65)] and the technetium atom. The numbering scheme of the six symmetry related ($\mathrm{C_5N}$) rings of **2a** is given in Fig. 4.*

The Tc–N bonds for $[\mathrm{Tc(bipy)_3}]^{2+}$ are equivalent by symmetry and their length of 2.077(10) Å is shorter than any of the Tc–N(bipyridyl) bonds in the two independent cations of the recently characterised nitrido-complex $[\mathrm{Tc(N)Br(bipy)_2}]_2$-$[\mathrm{TcBr_4}]$ which are in the range 2.11(2)–2.42(2) Å.[10] This difference is in part due to the strong *trans*-influence of nitride present in the monocationic complex, and also to the doubly

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* These numbers are for convenience of identification of the individual atoms in Table 4 and were not required in the structure analysis.

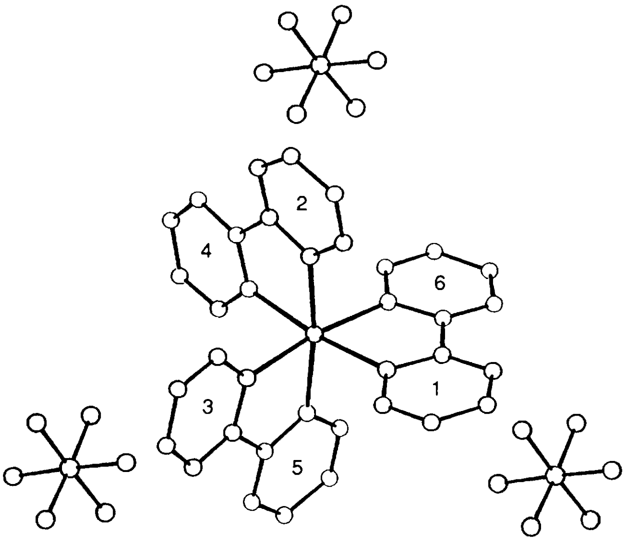

Fig. 4 A perspective view of the $[Tc(bipy)_3]^{2+}$ cation with three symmetry related $[PF_6]^-$ anions, showing the symmetry labels used for the aromatic rings

positive nuclear charge of the tris-chelate which would be expected to produce a shortening of the Tc–N bond, as well as the greater Tc–N π-back bonding interactions expected in the lower oxidation state complex. The Tc–N bond length determined here also compares reasonably well with the Tc–N bond distances found for the recently determined structures of some mixed-ligand technetium(III)–imine monocationic complexes: $[TcCl_2(PMe_2Ph)_2(bipy)]^+$ [2.058(12) Å], $[TcCl_2(PEtPh_2)_2(bipy)]^+$ [2.115(8) Å], $[TcCl_2(PMe_2Ph)_2(phen)]^+$ [2.109(3) Å][11a] and some mixed ligand technetium(II)–imine complexes: $[TcCl_2(PMe_2Ph)(phen)]$ [2.086(7) Å] and $[TcBr(PMe_2Ph)_2(terpy)]^+$ [2.097(9) Å, terminal N].[11b] The most interesting structural feature of $[Tc(bipy)_3][PF_6]_2$ is its similarity to those of $[Ru(bipy)_3][PF_6]_2$[12] and the more recently characterised $[Os(bipy)_3][PF_6]_2$,[13] both of which are isomorphous to the technetium complex. The situation has been slightly confused by the erroneous assignment of the space group for $[Ru(bipy)_3][PF_6]_2$ as hexagonal[12] whereas *P*3*c* is in fact trigonal. The unit-cell dimensions for the ruthenium complex[12] [a = 10.760(1) and c = 16.391(3) Å] and the closely related osmium complex[13] [a = 10.772(1) and c = 16.342(1) Å] are both closely similar to those of **2a**. The M–N bond distances in these and other structurally characterised second-and third-row transition-metal $[M(bipy)_3]^{n+}$ complexes: $[Ru(bipy)_3]^{2+}$ [2.056(6) Å];[12] $[Os(bipy)_3]^{2+}$ [2.056(8) Å];[13] $[Rh(bipy)_3]^{3+}$ [2.031–2.039 Å];[14] $[Ir(bipy)_3]^{3+}$[2.00(2)–2.02(2) Å][15] are reasonably similar to those determined here for $[Tc(bipy)_3]^{2+}$ [2.077(10) Å]. The main distortions from regular octahedral co-ordination are a result of the small bite of the bipyridyl ligand, and the N–Tc–N bite angle in the chelate ring of 76.2(4)° is only slightly less than the corresponding angles observed in $[Ru(bipy)_3]^{2+}$ (78.7°),[12] $[Os(bipy)_3]^{2+}$ [77.8(4)°],[13] $[Rh(bipy)_3]^{3+}$ (80.1–80.6°),[14] and $[Ir(bipy)_3]^{3+}$ (78.5–79.1°).[15]

Electrochemical Investigations of Complexes 1, 2 *and* 3.—The electrochemical behaviour of the neutral technetium(III) acetonitrile complex **1** was investigated at a platinium wire electrode in MeCN–CH_2Cl_2 (1 : 1) containing 0.2 mol dm^{-3} $[NBu_4][BF_4]$ under an atmosphere of dinitrogen gas. The redox behaviour of the technetium complex was compared with that of the rhenium congener $[ReCl_3(MeCN)(PPh_3)_2]$ under closely similar conditions. The analogous complexes of Tc and Re yield qualitatively similar cyclic voltammograms in MeCN–CH_2Cl_2 solution at 3 mmol dm^{-3} concentration. Both complexes undergo a reversible one-electron oxidation wave and a reversible one-electron reduction wave. The reversibility of the redox couples was confirmed by the usual criteria. Peak separations observed were close to the ideal behaviour of 59 mV. The $E_{\frac{1}{2}}$ values [*versus* the saturated calomel electrode (SCE)] for the oxidation and reduction processes are + 1.05 and − 0.34 V for $[TcCl_3(MeCN)(PPh_3)_2]$ and + 0.93 and − 0.54 V for $[ReCl_3(MeCN)(PPh_3)_2]$ respectively under the conditions stated. The data confirm the fact that the technetium complex is easier to reduce and harder to oxidise than the rhenium complex. Convolution analysis indicates the technetium reduction process to be less reversible than the corresponding process for rhenium. The redox behaviour of $[Tc(bipy)_3][BPh_4]_2$ **2** was investigated at a platinum wire electrode in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–MeCN under dinitrogen. The cyclic voltammogram indicated three diffusion-controlled reversible one-electron reduction processes for $[Tc(bipy)_3]^{2+}$ at $E_{\frac{1}{2}}$ values of − 0.34, − 1.36 and − 1.70 V *versus* SCE for each couple respectively. Convolution analysis for each process indicates that one electron is involved and that little chemical decomposition occurs throughout the entire sequence. The complex $[Tc(bipy)_3]^{2+}$ is therefore reduced in a succession of one-electron steps formally from Tc^{II} to Tc^{-I}. The reversibility of the voltammograms suggests that the reductions proceed essentially without any change in the configuration of the complex or accompanying chemical reactions.

Attempted electrochemical investigation of $[Tc(phen)_3][BPh_4]_2$ **3** under similar conditions to **2** at a platinum wire in MeCN was not successful due to severe adsorption problems on the electrode. Consequently, the redox behaviour of **3** was studied in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–dmf using a vitreous carbon working electrode. The redox behaviour of **3** is qualitatively the same as for **2**, three one-electron reductive couples being observed. The first two reduction waves are reversible with $E_{\frac{1}{2}}$ values of − 0.35 and − 1.26 V respectively. Convolution analysis for each couple indicated some chemical processes accompany electron transfer. More Nernstian behaviour is observed at faster scan rates. The final couple, E = − 1.82 V, is irreversible and convolution analysis indicates a gross amount of chemical decomposition.

Conclusion

We have found the new technetium(III) acetonitrile complex **1** to be an excellent starting material for the facile synthesis of other lower-valent technetium complexes. The EPR and electrochemistry of the complexes presented here and the synthesis of a wide variety of other low-valent technetium species will be reported at a later date.

Experimental

CAUTION: technetium-99 is a low energy β^--particle emitter [292 keV ($\simeq$4.67 × 10^{-14} J), $t_{\frac{1}{2}}$ = 2.14 × 10^5 years]. Normal radiation safety procedures were followed at all times. All manipulations of solutions and solids were performed in an efficient fumehood to prevent contamination and inadvertent inhalation. When handled in milligram quantities ^{99}Tc compounds do not present a serious health hazard since common laboratory glassware provides adequate shielding. Bremmsstrahlung radiation is not a significant problem due to the low energy of the β^--particle emission. All preparations were performed under an atmosphere of purified dinitrogen using pre-dried distilled solvents[16] unless otherwise stated. Solutions of $[NH_4][TcO_4]$ in 0.1 molar ammonia were kindly supplied by Amersham International plc. Triphenylphosphine, tri-*m*-tolylphosphine, 2,2′-bipyridine, 1,10-phenanthroline, and 2,2′:6′,2″-terpyridine (Aldrich) were used as received. The complex $[TcCl_4(PPh_3)_2]$ was prepared according to the literature procedure.[17] The complex $[TcCl_4\{P(C_6H_4Me\text{-}3)_3\}_2]$ was similarly prepared using tri-*m*-tolylphosphine. Infrared spectra were measured on a Perkin Elmer 257 infrared spectrophotometer. Elemental analysis was performed by Butterworths Ltd, Teddington, England.

Electrochemical Measurements.—Cyclic voltammetry measurements were made using an EG and G PAR model 362 scanning potentiostat. The current and potential responses were stored on a floppy disk *via* an EG and G twin channel 12-bit analogue-to-digital converter (650 μs conversion time). Data were manipulated on an Opus microcomputer using EG and G's CONDECON 300 (TM) software, version 1.1. Typically 1000 data points were collected and where appropriate, background data were subtracted from sample data. Internal cell resistance was minimised using positive feedback *via* the potentiostat. Cyclic voltammetry experiments were typically carried out in 0.2 mol dm^{-3} solutions of $[NBu_4][BF_4]$ as supporting electrolyte in carefully purified MeCN, CH_2Cl_2 or dmf under N_2 at room temperature using a three electrode cell configuration. The working electrode was normally a platinum wire or vitreous graphite disc. A platinum wire secondary electrode was included together with a silver wire pseudo-reference electrode arranged such that a Luggin capillary was in close proximity to the working electrode; $E_{\frac{1}{2}}$ values are quoted *versus* the saturated calomel electrode (SCE), against which the ferrocene–ferrocenium couple has an $E_{\frac{1}{2}}$ value of +0.54 V in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$.

Syntheses.—$[TcCl_3(MeCN)(PPh_3)_2]$ **1**. The complex $[TcCl_4(PPh_3)_2]$ (0.500 g, 0.65 mmol), PPh_3 (0.210 g, 0.79 mmol) and zinc powder (0.022 g, 0.34 mmol) in acetonitrile (10 cm^3) were heated under reflux for 1 h. The colour of the reaction mixture changed from green to orange. The reaction mixture was cooled to room temperature. The bright orange precipitate was collected by filtration, washed with ethanol and diethyl ether and dried *in vacuo* at room temperature to give **1**, yield 0.360 g, 0.47 mmol, 72% (Found: C, 58.35; H, 4.30; Cl, 13.65; N, 1.35. $C_{38}H_{33}Cl_3NP_2Tc$ requires C, 59.20; H, 4.30; Cl, 13.80; N, 1.80%).

$[TcCl_3(MeCN)\{P(C_6H_4Me\text{-}3)_3\}_2]$ **1a**. Complex **1a** was prepared in the same way as for **1** from $[TcCl_4\{P(C_6H_4Me\text{-}3)_3\}_2]$ (0.131 g, 0.15 mmol), $P(C_6H_4Me\text{-}3)_3$ (0.05 g, 0.16 mmol) and zinc powder (0.05 g, 0.076 mmol) in acetonitrile (4 cm^3) to give the bright orange product **1a**, yield 0.048 g, 37% (Found: C, 61.40; H, 5.20; Cl, 12.70; N, 1.90. $C_{44}H_{45}Cl_3NP_2Tc$ requires C, 61.80; H, 5.30; Cl, 12.45; N, 1.65%). Complex **1a** was suitably recrystallised for X-ray crystallography as deep-red plates by slow cooling of a hot saturated acetonitrile solution.

$[Tc(bipy)_3][BPh_4]_2$ **2**. Complex **1** (0.160 g, 0.20 mmol) and 2,2′-bipyridine (0.116 g, 0.74 mmol) in methanol (5 cm^3) were heated under reflux for 30 min. As the reaction proceeded the initial orange suspension became a dark blue-purple solution. The reaction mixture was cooled to room temperature and filtered to remove a small amount of pale green solid precipitate. An excess of solid $Na[BPh_4]$ was then added to the stirred solution. After 30 min the dark blue solid which had precipitated was collected by filtration, washed with ethanol and diethyl ether and dried *in vacuo* to give **2**, yield 0.149 g, 0.12 mmol, 62%. The product could be recrystallised from dmf–EtOH to give dark blue-black needles (Found: C, 78.40; H, 5.50; N, 7.25. $C_{78}H_{64}B_2N_6Tc$ requires C, 78.45; H, 5.40; N, 7.05%).

$[Tc(bipy)_3][PF_6]_2$ **2a**. Complex **2a** was prepared in the same way as for **2** from **1** (0.172 g, 0.22 mmol) and 2,2′-bipyridine (0.176 g, 1.13 mmol) except that solid $[NH_4][PF_6]$ (0.168 g, 1.03 mmol) was added to precipitate the cation, yield 0.120 g, 0.14 mmol, 64%. This complex can be recrystallised from dmf–EtOH (Found, C, 41.75; H, 2.65; N, 9.90. $C_{30}H_{24}F_{12}N_6P_2Tc$ requires C, 42.05; H, 2.80; N, 9.80%). These crystals were also found to be suitable for an X-ray structure determination.

$[Tc(phen)_3][BPh_4]_2$ **3**. Complex **3** was prepared as for **2** using **1** (0.060 g, 0.08 mmol) and 1,10-phenanthroline (0.070 g, 0.39 mmol). The dark blue complex was isolated as its $[BPh_4]^-$ salt, yield 0.069 g, 0.05 mmol, 69%. The product was recrystallised from dmf–EtOH (Found: C, 78.95; H, 5.10; N, 6.80. $C_{82}H_{64}B_2N_6Tc$ requires C, 78.55; H, 5.15; N, 6.70%).

$[Tc(terpy)_2][BPh_4]_2\cdot H_2O$ **4**. Complex **4** was prepared from **1** (0.218 g, 0.283 mmol) and 2,2′:6′,2″-terpyridine (0.200 g, 0.861 mmol). The black complex was isolated as its $[BPh_4]^-$ salt, yield 0.233 g, 0.194 mmol, 68%. The product was recrystallised from dmf–EtOH (Found: C, 76.10; H, 5.15; N, 6.55. $C_{78}H_{62}B_2N_6Tc\cdot H_2O$ requires C, 76.65; H, 5.25; N, 6.90%).

X-Ray Crystal Structure Determination of Complex **1a**.—*Crystal data*. $C_{44}H_{45}Cl_3NP_2Tc$, M = 854.15, triclinic, space group $P\bar{1}$, a = 10.157(2), b = 10.320(2), c = 22.073(2) Å, α = 87.27(2), β = 86.66(1), γ = 66.87(1)°, U = 2123(3) Å^3, $F(000)$ = 880, μ(Mo-Kα) = 6.2 cm^{-1}, Z = 2, D_c = 1.336 g cm^{-3}.

Data collection. All data were collected on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation (Philips fine-focus X-ray tube, 50 kV, 26 mA). This cell was refined using the conventional least-squares procedure by selecting the θ values of a set of reflections in the range $13 < \theta < 15°$ from a preliminary fast data connection (20° min^{-1} scan speed). The intensity data were collected from a crystal of dimensions 0.50 × 0.40 × 0.15 mm. A total of 7069 reflections were measured to θ_{max} = 24°; 5636 (85%) having $I < 3\sigma(I)$. The scan speed was 3.3° min^{-1} in θ to a maximum count time of 90 s.

The data were corrected for Lorentz-polarisation effects but a decay correction was not applied, the monitoring of a standard indicating no significant decay had taken place. An empirical absorption correction was applied to the data (ψ-scans) and the symmetry-equivalent reflections measured as part of the data collection process ($0\bar{k}l$ and $0\bar{k}\bar{l}$) were rejected.

Structure analysis and refinement. The calculated density based on two molecules in the unit cell (1.34 g cm^{-3}) together with an $N(Z)$ test confirmed the space group as $P\bar{1}$. A Patterson synthesis was calculated and the heaviest peak determined to be the Tc–Tc vector. However, apart from this, five further peaks were observed all about 2.3 Å from the origin. These were felt to correspond to either Tc–P or Tc–Cl vectors and the corresponding positions of these further three atoms were derived, based on the Tc position obtained from the Tc–Tc vector. These six positions were refined by isotropic least squares to R = 0.325. A resultant Fourier map allowed three complete phenyl rings to be constructed together with fragments of a fourth. Further refinement using anisotropic thermal parameters for Tc reduced R to 0.214. A further Fourier revealed all the expected remaining atoms which were now refined using anisotropic thermal parameters for all the heavy atoms to R = 0.144. A Fourier difference map was calculated to look for possible solvent molecules and revealed an interesting feature. Five peaks were observed around one of the phenyl groups [C(61)–C(67)] which corresponded to an alternative arrangement of this group and resulted from a rotation about C(61)–C(64). This order was treated by fixing the occupancies of the disordered atoms at 0.5 and refining these atoms isotropically. An agreement analysis of the data allowed a suitable weighting scheme to be derived. After subsequent refinement and the calculation of hydrogen atom positions from geometric criteria (except for the disordered phenyl group) a DIFABS correction was applied. Final full-matrix refinement with all atoms anisotropic (except those which were disordered) and including a fixed contribution from the hydrogen atoms reduced R to its final value of 0.039; R' = 0.062 with the value of the estimated standard deviation of an observation of unit weight = 1.173. A final Fourier difference calculation showed residual electron density in the range 0.3–0.5 e Å^{-3}. Atomic scattering factors and corrections for anomalous dispersion were taken from ref. 18. Calculations were performed using the Enraf–Nonius Structure Determinations Package (SPD version 3.0) on a DEC Microvax II computer.

X-Ray Crystal Structure Determination of Complex **2a**.—*Crystal data*. $C_{30}H_{24}F_{12}N_6P_2Tc$, M = 857.394, trigonal, space group $P\bar{3}c1$ (no. 165), a = 10.847(2), c = 16.299(3) Å, U =

1660.77 Å^3, $F(000) = 854$, μ(Mo-Kα) = 5.47 cm^{-1}, $Z = 2$, $D_c = 1.714$ g cm^{-3}.

Data collection. Data were collected using a crystal of dimensions 0.36 × 0.09 × 0.05 mm on a Philips PW1100 diffractometer with a constant scan width of 0.90° in the θ range 3–25°, using graphite crystal monochromated Mo-K radiation. A θ–2θ scan mode was used, and during data collection no significant change in intensity occurred in three reference reflections which were checked every 5 h. Lorentz-polarisation corrections were applied to the data and equivalent reflections were merged to give a total of 414 unique reflections with $I/\sigma(I) > 3.0$.

Structure analysis and refinement. The Laue symmetry and the systematic absences in the data (hkl, $l = 2n + 1$) indicated that the space group was either $P31c$ (no. 158) or $P\bar{3}c1$ (no. 165). The positions of the technetium atom and the two phosphorus atoms of the counter anions were deduced from a Patterson synthesis and satisfactory refinement was obtained in the centrosymmetric space group $P\bar{3}c1$. The positions of the remaining non-hydrogen atoms were located from subsequent Fourier difference syntheses, and the hydrogen atoms of the bipyridyl rings were included at calculated positions. After four cycles of full-matrix refinement of the atomic parameters using isotropic thermal parameters absorption corrections were applied to the data using the empirical method of Walker and Stuart.[19] Anisotropic thermal parameters were assigned to the metal in the final cycles of refinement, and the H-atoms were assigned a common isotropic thermal parameter which refined to a final value 0.14 Å^2. Weights were applied to the individual reflections as $1/\sigma^2(F)$ and refinement converged at $R = 0.0525$ and $R' = 0.0475$. Neutral scattering factors, corrected for the real and imaginary parts of the anomalous scattering, were used for all atoms and were taken from ref. 18.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles for both **1a** and **2a**.

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