# Synthesis of Technetium Complexes with a P,N Bidentate Phosphine Amine Ligand. Crystal Structure of Bis[(*o*-amidophenyl)diphenylphosphine-κ*N*,*P*][(*o*-aminophenyl)-diphenylphosphine-κ*N*,*P*]technetium(III) Perchlorate†

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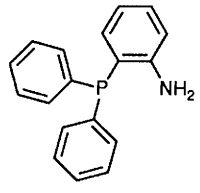
The reactions of (*o*-aminophenyl)diphenylphosphine (HL) with ammonium pertechnetate have been investigated. The complexes $[TcL_3]$ **1** and $[TcL_2(HL)]^+$ **2**, with $[TcO_4]^-$, $[ClO_4]^-$ and $[CF_3CO_2]^-$ as counter anions, were isolated from the reaction mixture depending on the pH. The transformation of **1** into **2**, and *vice versa*, was identified as an acid–base equilibrium by UV/VIS spectrophotometric measurements. The products have been characterized by means of the usual physicochemical determinations. Compound **2**, as its perchlorate salt, has been studied by means of X-ray analysis. It exhibits a distorted-octahedral configuration in a monoclinic crystal system: space group $P2_1/n$, $a$ = 11.009(2), $b$ = 19.361(3), $c$ = 24.473(3) Å, β = 100.76(1)° and $Z$ = 4. The structure was solved by Patterson and Fourier methods and refined by least-squares methods to $R$ = 0.052 using 5096 observed reflections. Relevant bond lengths and angles are: Tc–P(1) 2.483(2), Tc–P(2) 2.430(2), Tc–P(3) 2.436(2), Tc–N(1) 2.048(5), Tc–N(2) 1.948(5), Tc–N(3) 1.979(5) Å; P(2)–Tc–P(3) 160.2(1), P(1)–Tc–N(3) 164.3(2), N(1)–Tc–N(2) 163.6(2)°.

In an effort to increase the number of technetium complexes available as substrates for developing new radiopharmaceuticals, we have recently begun to explore the reactivity of functionalized phosphines towards technetium. In this context a remarkable property of phosphines is their ability to reduce pertechnetate which is the starting material for a $^{99m}$Tc-radiopharmaceutical synthesis. Functionalized phosphines contain phosphorus(III) atom(s) combined with one or more functional groups. Consequently, in reaction with pertechnetate this type of molecule works both as a reductant and as a co-ordinating ligand, providing clear advantages for the synthesis of a hypothetical radiopharmaceutical.

The bidentate functionalized phosphines were the first taken into consideration.[1,2] Due to the ability of the phosphine to stabilize transition metals in low oxidation states, complexes of $Tc^{IV}$ and $Tc^{III}$ were predicted. The choice of the functional groups was dictated by the scarce commercial availability of these ligands and by their available literature synthesis. Furthermore, owing to the high electrophilicity of the $Tc^{3+/4+}$ ions, functional groups amenable to bearing a negative charge were preferred. The first series of ligands extensively studied[2] were $Ph_2PRCO_2H$, where R = *o*-$C_6H_4$, $C_2H_4$ or $CH_2$. Pure, stable, neutral and lipophilic $[Tc^{III}L_3]$ complexes were readily obtained, thus giving us the impetus for furthering the research on other functional groups.

In this paper we report on the reactivity of the ligand $PPh_2(C_6H_4NH_2$-*o*) which contains a 'soft' phosphorus and a 'hard' primary aromatic amine as donors. Upon co-ordination the nitrogen group can act either as neutral (amino) or negatively charged (amido) by deprotonation, so providing a way of obtaining cationic technetium(III) complexes. To date




this ligand has been used only for complexation of late transition metals such as Pt and Rh, with particular regard to their possible catalytic activity.[3,4]

## Experimental

*Apparatus.*—**CAUTION:** Technetium-99 is a weak β-emitter ($E_{max}$ = 0.292 MeV, *ca.* 4.67 × $10^{-17}$ J) with $t_{\frac{1}{2}}$ = 2.12 × $10^5$ y. All manipulations were carried out in glove-boxes, in a laboratory approved for low-level radioactivity.

Microanalyses were carried out by the University of Ferrara on a model 1106 Carlo Erba elemental analyser. Infrared spectra were recorded in Nujol mulls using a Perkin-Elmer PE 580B spectrophotometer (4000–250 $cm^{-1}$), electronic absorption spectra in $CHCl_3$ on a Perkin-Elmer LAMBDA 15 spectrometer (750–220 nm). Magnetic susceptibility measurements in $CHCl_3$ solutions were carried out following the Evans method.[5] Proton and $^{31}$P NMR spectra were obtained on a Bruker AC-200 spectrometer using different solvents and $SiMe_4$ for proton and $PPh_3$ for phosphorus as internal references. Positive-ion fast atom bombardment (FAB) mass spectra were recorded on a VG 30-250 Masslab instrument. Xenon was used as the primary gas beam and the ion gun was operated at 7 keV (*ca.* 1.12 × $10^{-16}$ J) and 1 mA. Data were collected generally over the mass range 100–1000 at 0.7 s per scan and the matrix used was 3-nitrobenzyl alcohol. Unless otherwise stated,

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

conductivity measurements were carried out in MeCN at 293 K on a Metrohm Herison conductimeter, model E518.

*Materials.*—Technetium, as $[NH_4][TcO_4]$ in 0.1 mol $dm^{-3}$ ammonia solution, was supplied by the Radiochemical Centre, Amersham. Solid $[NH_4][TcO_4]$ was obtained by taking to dryness small aliquots of this solution. All common laboratory chemicals were of reagent grade. The ligand (*o*-aminophenyl)-diphenylphosphine (HL) was prepared according to the method reported by Cooper and Downes.[4]

$[TcL_3]$ **1**. The ligand (176 mg, 0.635 mmol) was added to $[NH_4][TcO_4]$ (23 mg, 0.127 mmol) suspended in EtOH (8 $cm^3$). After 5 min of stirring the ligand completely dissolved, while some solid $[NH_4][TcO_4]$ was still present. The solution was pale pink. The mixture was then taken to reflux; the colour became deep purple and a dark solid formed. After 4 h of refluxing the mixture was cooled and the compound precipitated was filtered off, washed with EtOH and dried by flowing, through the filter, a nitrogen stream.

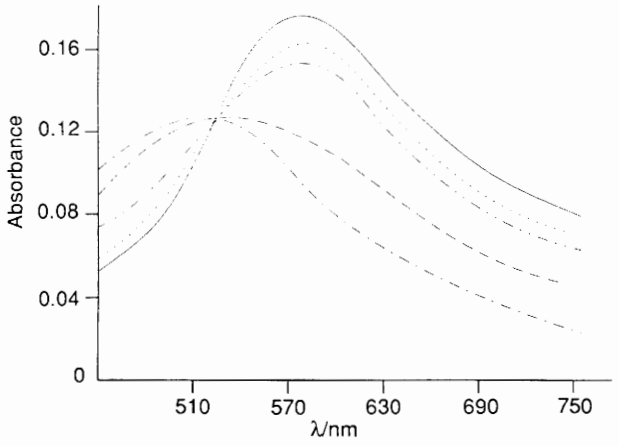



**Fig. 1** Variations of the UV/VIS spectrum of the technetium aminophosphine complexes with pH: 7 (——), 8 (• • • •), 9 (• • — • •), 10 (– – – –) and 11 (— • —)

The reaction leads to the same product even when carried out in basic medium, *i.e.* by adding 5% NaOH (0.5 $cm^3$) in water, $Et_3N$ (2 $cm^3$) or 0.75 mol $dm^{-3}$ sodium acetate (2 $cm^3$) (reaction volume 5 $cm^3$). Owing to the presence of a polymeric white solid, insoluble in the common solvents, the crude product was purified by direct dissolution on the filter with $CH_2Cl_2$ and further precipitation with EtOH (yield 100 mg, 85%) (Found: C, 69.4; H, 4.5; N, 4.3. $C_{54}H_{45}N_3P_3Tc$ requires C, 69.90; H, 4.90; N, 4.55%). The product is soluble in $CH_2Cl_2$, $CHCl_3$, benzene and toluene, slightly soluble in $Me_2CO$ and $Et_2O$, and insoluble in EtOH, MeOH, MeCN, dimethylformamide (dmf) and hydrocarbons. Molar conductivity in MeCN–$CH_2Cl_2$ (90:10 v/v), $\Lambda_M$ = 12 $ohm^{-1}$ $cm^2$ $mol^{-1}$. Magnetic moment at 293 K, $\mu$ = 2.49. FAB mass spectrum: *m/z* 928, $[M + H]^+$; 651, $[M^+ - HL]$. UV/VIS bands: 555 ($\varepsilon$ = 10 500 $dm^3$ $mol^{-1}$ $cm^{-1}$), 325 (sh) and 290 nm (sh).

$[TcL_2(HL)]X$ **2**. Slightly different procedures were used to prepare the cationic compounds depending on the counter anion.

X = $CF_3CO_2^-$. The ligand (183 mg, 0.663 mmol) was added to $[NH_4][TcO_4]$ (24 mg, 0.132 mmol) suspended in EtOH (5 $cm^3$). After 5 min of stirring, freshly prepared 0.13 mol $dm^{-3}$ $CF_3CO_2H$ (0.25 $cm^3$) in water was added. The initial pale red colour quickly turned to deep blue-violet. The mixture was refluxed for 30 min and the resulting blue-violet solution left to

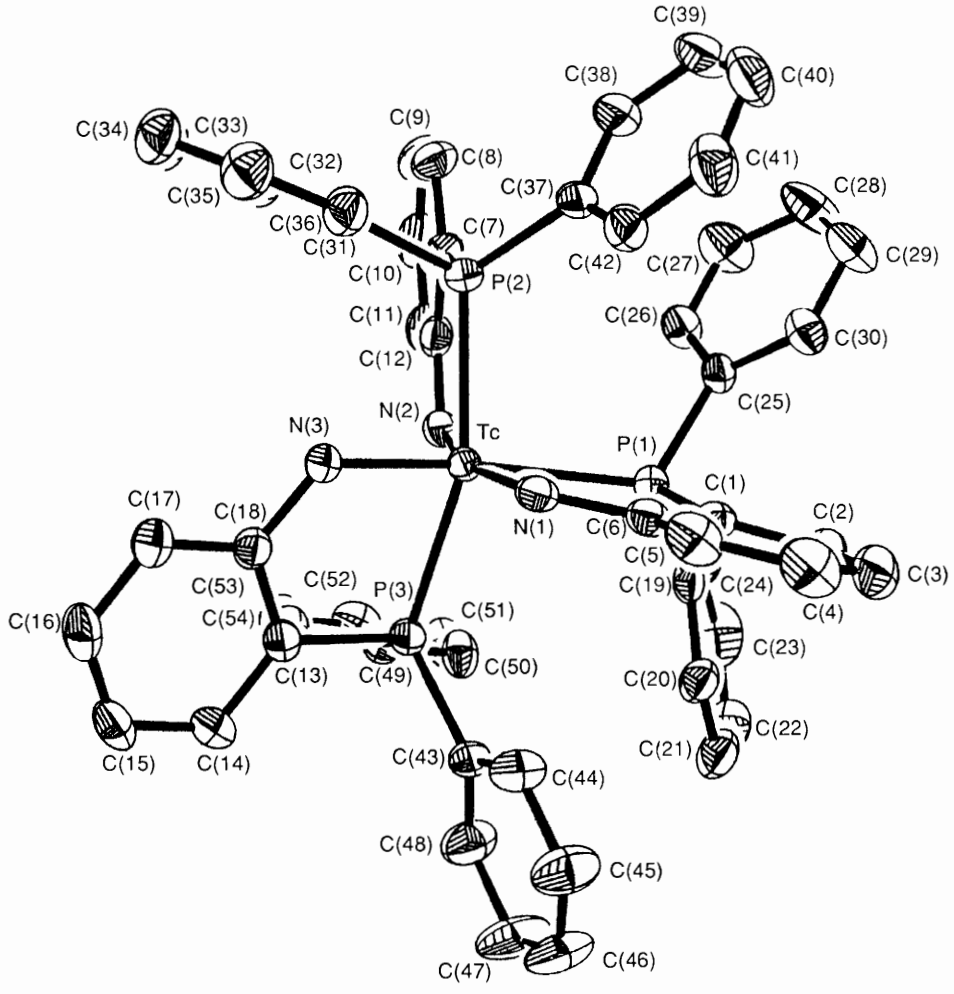



**Fig. 2** An ORTEP[8] view of complex **2**, showing the atom labelling, with thermal ellipsoids at the 50% probability level

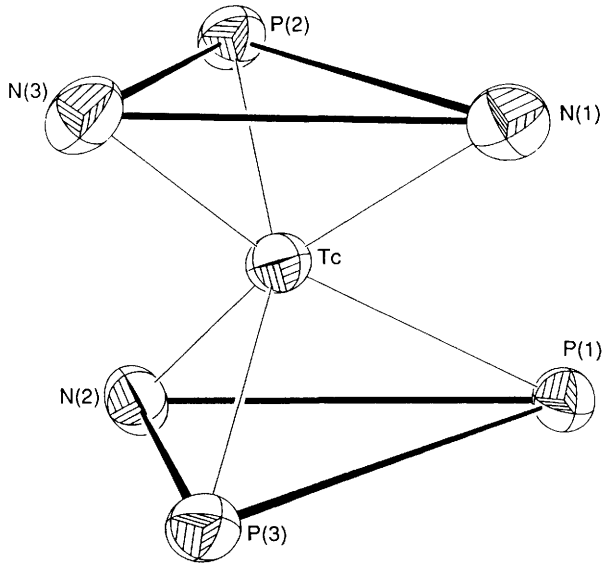



**Fig. 3** The octahedral environment about the Tc atom; the angle between the two trigonal planes illustrated is 3.3°

cool. Upon standing overnight blue crystals separated; they were washed with a small amount of EtOH and dried with a nitrogen stream (yield 86 mg, 63%) (Found: 63.2; H, 4.5; N, 3.7. $C_{56}H_{46}F_3N_3O_2P_3Tc{\cdot}C_2H_5OH$ requires C, 64.00; H, 4.80; N, 3.85%). The crystals are soluble in $CH_2Cl_2$, $CHCl_3$, MeCN, dmf, $Me_2CO$ and MeOH, slightly soluble in EtOH and $Et_2O$ and insoluble in hydrocarbons. Conductivity, $\Lambda_M$ = 128 ohm$^{-1}$ cm$^2$ mol$^{-1}$. Magnetic moment at 293 K, $\mu$ = 2.46. FAB mass spectrum (major peaks); *m/z* 928, $M^+$: 651 [$M^+$ − HL], and 374, [$M^+$ − 2HL]. UV/VIS bands: 586 nm ($\varepsilon$ = 11 000 dm$^3$ mol$^{-1}$ cm$^{-1}$), 390 (sh), 340 (sh), and 222 (sh) nm.

X = $TcO_4^-$. When the reaction was carried out in MeOH or MeCN, in presence of $CF_3SO_3H$, the product obtained was still a blue solid, but with some slight differences in solubility, being slightly soluble in MeOH and MeCN. Average yield 46% (Found: C, 58.6; H, 4.1; N, 3.6. $C_{54}H_{46}N_3O_4P_3Tc_2$ requires C, 59.40; H, 4.25; N, 3.85%) and the presence in the IR spectrum of a stretching vibration at 900 cm$^{-1}$ attributable to ν(Tc=O), supporting the formulation with $[TcO_4]^-$ as counter ion.

X = $ClO_4^-$. Solutions in MeOH of the above blue solids, treated with a saturated MeOH solution of $NaClO_4$, gave, after slow evaporation, nice blue crystals, used for X-ray crystal-structure determination, containing $[ClO_4]^-$ as counter anion.

*Crystallography.*—A crystal grown as above was used for data collection. Details of the crystal data, measurement of intensity, and data processing are summarized in Table 1. The perchlorate ion is disordered as shown by the high thermal parameters, values of up to 0.172 Å$^2$ being observed. In the final refinement the oxygen atoms were fixed at the positions derived from the $\Delta F$ map as the highest peaks, although other relevant maxima in the vicinity were detectable. Further attempts to refine the disordered ion were unsuccessful. Hydrogen atoms were introduced at the expected positions with a common $U$ value of 0.08 Å$^2$, but they were not refined.

Fractional atomic coordinates are given in Table 2, selected bond lengths and angles in Table 3.

Additional data available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## Results

*Synthesis.*—(*o*-Aminophenyl)diphenylphosphine (HL) reacts with pertechnetate producing technetium(III) complexes, the products being strictly dependent on the pH of the reaction medium. By refluxing pertechnetate and excess of HL (at least

**Table 1** Structure determination summary

| | |
|---|---|
| Crystal data | |
| Empirical formula | $C_{54}H_{46}ClN_3O_4P_3Tc$ |
| Colour, habit | Dark blue-violet, cubic |
| Crystal size/mm | 0.38 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| Unit-cell dimensions | $a$ = 11.009(2), $b$ = 19.361(3), $c$ = 24.473(3) Å, β = 100.76(1)° |
| $U$/Å$^3$ | 5124.3 |
| $Z$ | 4 |
| Formula weight | 1028.3 |
| $D_c$/Mg m$^{-3}$ | 1.33 |
| μ/mm$^{-1}$ | 0.46 |
| $F$(000) | 2112 |
| Data collection | |
| Diffractometer | Siemens R3m/V |
| Radiation | Mo-Kα (λ = 0.710 73 Å) |
| $T$/K | 294 |
| Monochromator | Highly oriented graphite crystal |
| 2θ/° | 3.0–50.0 |
| Scan type, speed and range | ω, Variable (3–15° min$^{-1}$), 1.20° |
| Background measurement | Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time |
| Standard reflections | 2 every 100 |
| Index ranges | $-14 < h < 14$, $0 < k < 24$, $0 < l < 30$ |
| Independent reflections | 8680 |
| Observed reflections | 5096 [$F > 3.0\sigma(F)$] |
| Absorption correction | Empirical; ψ-scan method for 4 reflections at χ = 90°; 0.46 < transmission factor < 1.00 |
| Solution and refinement | |
| System used | Siemens SHELXTL PLUS (MicroVAX 3300)* |
| Solution | Heavy-atom methods |
| Refinement method | Full-matrix least-squares |
| Quantity mimimized; weighting scheme | $\Sigma w(\|F_o\| - \|F_c\|)^2$; $w^{-1} = \sigma^2(F) + 0.001\,55F^2$ |
| Hydrogen atoms | Riding model, fixed isotropic $U$ |
| Thermal parameters | Anisotropic |
| Final $R$ indices (obs. data) | $R$ = 0.052, $R'$ = 0.069 |
| Goodness-of-fit | 1.43 |
| Data-to parameter ratio | 9:1 |
| Largest difference peak | 0.91 e Å$^{-3}$ (near $ClO_4^-$) |
| Largest difference hole | −0.67 e Å$^{-3}$ |

* Ref. 6.

1:5) in acetonitrile or methanol, the complex $[TcL_2(HL)]^+$ **2** is obtained. The reaction involves reduction of $Tc^{VII}$ to $Tc^{III}$ by the phosphorus(III) atom of the ligand which helps the extraction of oxygen atoms from pertechnetate as phosphine oxide, which, actually, is collected from the reaction mixture. Complex **2** is obtained as the pertechnetate salt according to equation (1).

$$2[TcO_4]^- + 5HL \rightleftharpoons [TcL_2(HL)][TcO_4] + 2O(HL) + 2OH^- \quad (1)$$

The reaction yield is improved by adding a non-co-ordinating acid such as $CF_3CO_2H$ or $CF_3SO_3H$; in these cases the collected compound contains the specific counter ion only when the salt solubility is lower than that of the pertechnetate. For instance the $CF_3SO_3$ salt was never recovered. When the reaction is performed by refluxing pertechnetate and the ligand in ethanol or other solvents in which a base (*i.e.* NaOH, $Et_3N$ or sodium acetate) is added the product $[TcL_3]$ **1** is obtained.

It is interesting to note the borderline behaviour of methanol and ethanol, the difference in acidity between which is sufficient

**Table 2** Atomic coordinates ( $\times 10^5$ for Tc and P, $\times 10^4$ for other atoms) for $[TcL_2(HL)][ClO_4]$

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Tc | 17 158(4) | 80 239(2) | 8 732(2) | C(27) | −2 289(7) | 6 396(5) | 790(4) |
| P(1) | 13 865(14) | 68 387(7) | 12 054(7) | C(28) | −2 310(8) | 5 788(5) | 493(4) |
| P(2) | 524(14) | 80 013(8) | 665(7) | C(29) | −1 237(7) | 5 505(4) | 399(4) |
| P(3) | 31 220(14) | 84 519(8) | 16 915(7) | C(30) | −112(6) | 5 804(3) | 613(3) |
| N(1) | 2 953(4) | 7 438(3) | 545(2) | C(31) | 199(6) | 8 655(3) | −460(3) |
| N(2) | 328(4) | 8 323(3) | 205(2) | C(32) | −414(7) | 9 278(3) | −488(3) |
| N(3) | 2 380(5) | 8 848(3) | 552(2) | C(33) | −193(9) | 9 786(4) | −862(4) |
| C(1) | 2 561(5) | 6 358(3) | 952(2) | C(34) | 620(9) | 9 671(4) | −1 205(3) |
| C(2) | 2 861(6) | 5 666(3) | 1 067(3) | C(35) | 1 249(8) | 9 056(4) | −1 182(3) |
| C(3) | 3 741(7) | 5 345(4) | 814(4) | C(36) | 1 029(7) | 8 544(4) | −804(3) |
| C(4) | 4 341(7) | 5 718(5) | 472(4) | C(37) | −337(7) | 7 226(3) | −349(3) |
| C(5) | 4 090(7) | 6 407(4) | 366(3) | C(38) | −1 541(7) | 6 996(4) | −533(3) |
| C(6) | 3 221(5) | 6737(3) | 617(3) | C(39) | −1 747(10) | 6 417(6) | −870(4) |
| C(7) | −1 228(6) | 8 270(3) | 376(3) | C(40) | −789(13) | 6 083(5) | −1 036(4) |
| C(8) | −2 468(7) | 8 374(4) | 114(3) | C(41) | 403(10) | 6 293(4) | −852(4) |
| C(9) | −3 361(7) | 8 561(5) | 411(4) | C(42) | 639(7) | 6 857(3) | −503(3) |
| C(10) | −3 033(7) | 8 668(4) | 974(4) | C(43) | 4 482(6) | 8 010(3) | 2 068(3) |
| C(11) | −1 814(7) | 8 580(4) | 1 252(3) | C(44) | 5 168(6) | 7 612(4) | 1 765(3) |
| C(12) | −914(6) | 8 394(3) | 950(3) | C(45) | 6 238(8) | 7 291(5) | 2 029(4) |
| C(13) | 3 761(6) | 9 184(3) | 1 387(3) | C(46) | 6 643(9) | 7 379(6) | 2 583(4) |
| C(14) | 4 685(6) | 9 618(4) | 1 673(3) | C(47) | 5 979(9) | 7 753(6) | 2 885(3) |
| C(15) | 5 141(6) | 10 151(4) | 1 388(4) | C(48) | 4 881(8) | 8 078(4) | 2 632(3) |
| C(16) | 4 679(7) | 10 256(3) | 828(4) | C(49) | 2 293(6) | 8 782(3) | 2 215(3) |
| C(17) | 3 774(6) | 9 825(3) | 545(3) | C(50) | 1 821(7) | 8 313(3) | 2 547(3) |
| C(18) | 3 304(6) | 9 291(3) | 823(3) | C(51) | 994(8) | 8 528(4) | 2 883(3) |
| C(19) | 1 636(6) | 6 643(3) | 1 957(3) | C(52) | 655(8) | 9 213(5) | 2 885(3) |
| C(20) | 2 836(7) | 6 565(3) | 2 241(3) | C(53) | 1 161(8) | 9 678(4) | 2 571(4) |
| C(21) | 3 070(9) | 6 475(4) | 2 824(4) | C(54) | 1 971(7) | 9 474(3) | 2 232(3) |
| C(22) | 2 111(12) | 6 455(5) | 3 100(3) | Cl | −767(2) | 7 345(2) | 4 095(1) |
| C(23) | 937(11) | 6 525(5) | 2 825(4) | O(1) | −892 | 6 977 | 4 600 |
| C(24) | 686(7) | 6 629(4) | 2 251(3) | O(2) | −1 656 | 7 898 | 4 044 |
| C(25) | −79(5) | 6 404(3) | 929(3) | O(3) | −1 119 | 6 880 | 4 634 |
| C(26) | −1 180(6) | 6 692(3) | 1 003(3) | O(4) | 428 | 7 591 | 4 136 |

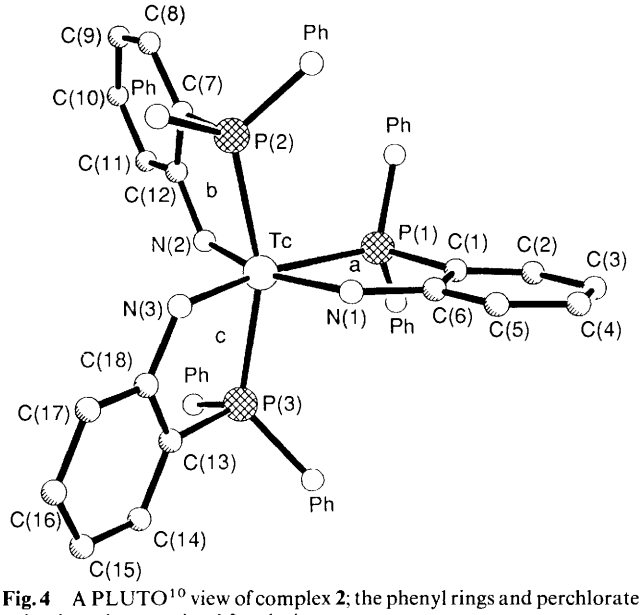



**Fig. 4** A PLUTO[10] view of complex **2**; the phenyl rings and perchlorate anion have been omitted for clarity

to allow recovery of the cationic and the neutral compounds, respectively.

The following experiment was carried out to verify the acid–base equilibrium. Five water–MeCN (50:50 v/v) solutions were prepared, each differing by one pH unit, in the range 7–11, using $CO_2$–$HCO_3^-$–$CO_3^{2-}$ buffer solution. An aliquot (2.5 $cm^3$) of each solution was treated, immediately before the spectrophotometric measurement, with a MeCN solution (0.5 $cm^3$, 5 mmol) of the blue product. The pH was measured upon addition of the compound, and the UV/VIS spectra recorded 2 min after the preparation of the solutions (Fig. 1). An isosbestic point was found at 523 nm, and its maintenance up to pH 11 indicates that the acid–base equilibrium is the only reaction operating at the considered pH range.

An analogous experiment was performed to calculate the equilibrium constant of the acid–base reaction (2). Nine

$$[TcL_2(HL)]^+ \rightleftharpoons [TcL_3] + H^+ \qquad (2)$$

solutions prepared as above, each differering by 0.5 pH unit in the range 7–11, were measured at $\lambda = 630$ nm, where the absorbance variation between the neutral and the charged complex is highest. Values of absorbance were plotted *vs.* pH and the resulting curve showed an inflection at pH 9.1 ± 0.2 (three measurements), which can be considered as the p*K* value of the acid–base equilibrium.

At pH > 11 another reaction different from the acid–base one takes place. The same reaction occurs also at lower pH, but slowly enough to allow the recording of the electronic spectra. On performing the reaction at pH ≥ 11, on a preparative scale, an oxotechnetium(v) complex was obtained with ν(Tc=O) at 878 $cm^{-1}$, whose elemental analysis supports the presence of two ligands per technetium.[7]

*Crystal Structure of* $[TcL_2(HL)][ClO_4]$ **2**.—Fig. 2 illustrates the geometry of the compound and atom numbering scheme used. The complex is built up by the juxtaposition at van der Waals distances of well separated technetium(III) monocations and perchlorate counter anions. The co-ordination geometry about the Tc is distorted octahedral (Fig. 3); the P atoms are arranged in the *meridional* manner, so that two adopt the *trans* axial configuration and the equatorial plane is generated by the remaining P atom and the N donors of the three ligands. In the $P_3N_3$ co-ordination polyhedron the Tc atom is 0.07 Å from the $N_3$ plane, 0.23 Å from the $P_3$ plane. The P(2)–Tc–P(3),

**Table 3** Selected bond lengths (Å) and angles (°)

| | | | |
|---|---|---|---|
| Tc–P(1) | 2.483(2) | Tc–P(2) | 2.430(2) |
| Tc–P(3) | 2.436(2) | Tc–N(1) | 2.048(5) |
| Tc–N(2) | 1.948(5) | Tc–N(3) | 1.979(5) |
| P(1)–C(1) | 1.795(6) | P(1)–C(19) | 1.848(7) |
| P(1)–C(25) | 1.833(6) | P(2)–C(7) | 1.797(7) |
| P(2)–C(31) | 1.835(7) | P(2)–C(37) | 1.819(7) |
| P(3)–C(13) | 1.804(6) | P(3)–C(43) | 1.819(6) |
| P(3)–C(49) | 1.822(7) | N(1)–C(6) | 1.392(8) |
| N(2)–C(12) | 1.400(8) | N(3)–C(18) | 1.399(7) |
| C(1)–C(6) | 1.401(9) | C(7)–C(12) | 1.404(10) |
| C(13)–C(18) | 1.393(9) | | |
| P(1)–Tc–P(2) | 96.6(1) | P(1)–Tc–P(3) | 98.9(1) |
| P(2)–Tc–P(3) | 160.2(1) | P(1)–Tc–N(1) | 76.4(1) |
| P(2)–Tc–N(1) | 97.3(1) | P(3)–Tc–N(1) | 98.3(1) |
| P(1)–Tc–N(2) | 88.0(2) | P(2)–Tc–N(2) | 79.2(1) |
| P(3)–Tc–N(2) | 89.1(1) | N(1)–Tc–N(2) | 163.6(2) |
| P(1)–Tc–N(3) | 164.3(2) | P(2)–Tc–N(3) | 88.3(1) |
| P(3)–Tc–N(3) | 80.0(1) | N(1)–Tc–N(3) | 88.2(2) |
| N(2)–Tc–N(3) | 107.6(2) | Tc–P(1)–C(1) | 102.0(2) |
| Tc–P(1)–C(19) | 120.8(2) | C(1)–P(1)–C(19) | 104.7(3) |
| Tc–P(1)–C(25) | 118.4(2) | C(1)–P(1)–C(25) | 106.0(3) |
| C(19)–P(1)–C(25) | 103.3(3) | Tc–P(2)–C(7) | 100.6(2) |
| Tc–P(2)–C(31) | 114.0(2) | C(7)–P(2)–C(31) | 105.9(3) |
| Tc–P(2)–C(37) | 122.2(2) | C(7)–P(2)–C(37) | 110.7(3) |
| C(31)–P(2)–C(37) | 102.7(3) | Tc–P(3)–C(13) | 99.5(2) |
| Tc–P(3)–C(43) | 126.3(2) | C(13)–P(3)–C(43) | 103.4(3) |
| Tc–P(3)–C(49) | 111.8(2) | C(13)–P(3)–C(49) | 107.5(3) |
| C(43)–P(3)–C(49) | 106.4(3) | Tc–N(1)–C(6) | 129.1(4) |
| Tc–N(2)–C(12) | 128.3(4) | Tc–N(3)–C(18) | 126.6(4) |
| P(1)–C(1)–C(2) | 125.9(5) | P(1)–C(1)–C(6) | 114.6(4) |
| N(1)–C(6)–C(1) | 117.7(6) | N(1)–C(6)–C(5) | 122.7(6) |
| P(2)–C(7)–C(8) | 128.2(6) | P(2)–C(7)–C(12) | 113.9(5) |
| N(2)–C(12)–C(7) | 117.8(6) | N(2)–C(12)–C(11) | 121.5(6) |
| P(3)–C(13)–C(14) | 124.6(5) | P(3)–C(13)–C(18) | 115.4(4) |
| N(3)–C(18)–C(13) | 118.3(6) | N(3)–C(18)–C(17) | 121.9(6) |
| P(1)–C(19)–C(20) | 118.3(6) | P(1)–C(19)–C(24) | 122.5(5) |
| P(1)–C(25)–C(26) | 120.1(5) | P(1)–C(25)–C(30) | 121.2(5) |
| P(1)–C(31)–C(32) | 122.2(6) | P(2)–C(31)–C(36) | 118.6(5) |
| P(2)–C(37)–C(38) | 123.8(6) | P(2)–C(37)–C(42) | 117.3(5) |
| P(3)–C(43)–C(44) | 118.1(5) | P(3)–C(43)–C(48) | 122.8(6) |
| P(3)–C(49)–C(50) | 118.4(5) | P(3)–C(49)–C(54) | 121.6(5) |

N(1)–Tc–N(2) and P(1)–Tc–N(3) angles are only 160.2(1), 163.6(2) and 164.3(2)° respectively, and the 'twist angles',[9] which define the relative orientation of the two triangular faces, are 21.7, 11.4 and 75.8° for the three ligands (a,b,c of Fig. 4), *cf.* 60° for the ideal octahedron. The complex is interesting in that it contains one bidentate neutral ligand with a protonated arm (a) different from the other two with deprotonated ones (b and c). This difference is mainly evidenced by the elongation of Tc–N(1) distance and by the decrease in the P(1)–Tc–N(1) angle [76.4(1)°], in comparison with P(2)–Tc–N(2) and P(3)–Tc–N(3) [79.2(1) and 80.0(1)°]. In effect the complex seems to show three types of Tc–N distance: (*i*) Tc–N(1)$H_2$ [2.048(5) Å] shorter when compared to the range 2.086–2.259 Å for typical Tc–$N_{amine}$ single bonds;[11] (*ii*) Tc–N(2)H [1.948(5) Å], intermediate between Tc–$N_{amide}$ in oxo[3,3′-(1,3-propanediyldiimino)bis(3-methyl-2-butanoneoximato)(3−)]technetium(v)[12] (1.91 Å) and Tc–NH in $[Tc(NHC_6H_4S)_3]^+$ (1.99 Å);[13] (*iii*) Tc–N(3)H [1.979(5) Å], longer than the amide bond Tc–N(2)H probably owing to the strong *trans* effect of the phosphine relative to that of the amine *trans* to N(2). The difference in bond lengths of Tc–N(2)H and Tc–N(3)H is not as great as that found for Tc–N bonds in $[TcCl_3(PPh_3)(bipy)]$[14] (bipy = 2,2′-bipyridine) for which the corresponding *trans* ligands are $PPh_3$ and Cl.

The Tc–P bond lengths are typical of those for technetium(III) complexes[15,16] and the three five-membered chelate rings are essentially planar, with torsion angles in the range −5.3 to 4.1 .

Distances within the organic moiety are normal and all angles lie within the ranges of related angles in similar compounds.

*Characterization.*—Complexes **1** and **2** were characterized by elemental analysis, infrared, utraviolet–visible spectroscopy and conductivity and magnetic susceptibility measurements.

Complex **1** was formulated from the results of elemental analyses and from positive-ion FAB mass spectrometry, showing a parent ion at *m/z* 928. The compound is non-conducting in MeCN–$CH_2Cl_2$ (90:10 v/v). Magnetic susceptibility measurements gave a $\mu_{eff}$ of 2.49, which indicates a 3+ oxidation state of technetium in a $d^4$ octahedral environment. The complex is not very stable in solution owing to its tendency to transform to the charged form **2** at acid or neutral pH and/or to oxidize to $Tc^V$ in basic media. The IR spectrum is consistent with the presence of the L ligands, showing the same fingerprinting as for the cationic compound, and with only a sharp band at 3303 $cm^{-1}$ in the ν(N–H) region. The UV/VIS spectrum shows a charge-transfer band at 555 nm with ε = 10 500 $dm^{-3}$ $mol^{-1}$ $cm^{-1}$.

Due to their paramagnetism, proton NMR spectra of both species **1** and **2** show only an unresolved multiplet centred in the aromatic region (δ 6–8) while other peaks are broadened on the baseline. In the δ 30 to −15 region, even cooling to −40 °C resulted in no appreciable improvement, the only observable signal being a broad one centred at δ −11.50 impossible to attribute. Attempts to record $^{31}P$ NMR signals also failed.

The $[TcL_2(HL)]^+$ complex, prepared with different counter anions ($TcO_4^-$, $ClO_4^-$ and $CF_3CO_2^-$), showed elemental analysis consistent with the formulation. Positive-ion FAB mass spectrometery shows the molecular cation at *m/z* 928 and other fragmentation peaks at 651 ($M^+$ − HL) and 374 ($M^+$ − 2HL). The conductivity measurements support the 1:1 electrolytic character of the compounds, $\Lambda_M$ = 128–135 $ohm^{-1}$ $cm^2$ $mol^{-1}$, Infrared spectra of the complexes confirm the presence of the counter ions, showing ν(Tc=O) at 900 $cm^{-1}$ when $TcO_4^-$ is the counter anion, a characteristic strong and broad band at 1096 $cm^{-1}$ when perchlorate is present, and ν(C=O) stretches at 1665(br) $cm^{-1}$ when the trifluoroacetic salt precipitates; no $CF_3SO_3^-$ salt was recovered. In the ν(N–H) region bands at 3390(br), 3286 and 3262 $cm^{-1}$ are present. The UV/VIS spectra show always the maximum at 586 nm with an absorption coefficient ε = 11 000 $dm^3$ $mol^{-1}$ $cm^{-1}$, responsible for the intense blue colour and attributable to a charge-transfer band.

## Discussion

Phosphorus(III)-based ligands have already been studied as reducing agents for pertechnetate anion.[16,17] These ligands can reduce $Tc^{VII}$ to $Tc^V$, $Tc^{IV}$, $Tc^{III}$, $Tc^{II}$ and $Tc^I$, promoting a large series of complexes which can be studied from the point of view of stability and reactivity. The oxidation states V, IV and III can be reached only if other nucleophilic groups are present and the ligands are used in stoichiometric amount. In particular, the use of monotertiary phosphines in the presence of HCl yields complexes of $Tc^{IV}$ and $Tc^{III}$.[14]

The use of bidentate functionalized phosphines in direct reaction with $TcO_4^-$ can produce the technetium(III) oxidation state when the phosphine is used in excess and the only nucleophilic groups are those functionalizing the phosphines themselves.

While $Ph_2PRCO_2H$ ligands,[2] reacting with technetium, prduce only complexes with the three nucleophilic groups deprotonated, the $PPh_2(C_6H_4NH_2$-*o*) ligand leads to stable complexes with only two amine groups deprotonated. This can be explained in terms of basicity. Carboxylate groups are less basic than amide ones, so that, to satisfy the electron density of $TcP_3^{3+}$ core, three carboxylates or only two amide and an amine group are necessary. The complex $[TcL_3]$, which lives long enough to be collected, is stable in the solid state, but, because of

the excess of electron density on technetium, it easily oxidizes to $Tc^{V}$ in solution.

Complex **2** shows three different Tc–N bond lengths and the protonated nitrogen was found as the one of the two *trans* nitrogens and precisely that belonging to the ligand presenting a phosphorus *trans* to another one. Thus, the acid proton is not delocalized among the three nitrogen atoms but stays only on the nitrogen in which there is the highest electron density. This is confirmed by the fact that the acid–base equilibrium is reversible and always leads to the same characterized blue product and not to different isomers.

Finally the shortest Tc–N bond length of 1.948 Å can be rationalized on the basis of the 18-electron rule. For 18 electrons in the valence shell, one of the nitrogens, must formally contribute four electrons and can do so by donating a lone pair to the metal, thus giving rise to the short Tc–N distance which indicates considerable multiple-bond character. This could also lead to further deprotonation of the NH group to give an imide ligand, as reported for other technetium complexes,[18] but presumably in this case the resulting M=N–C system would be bent, and this is not the favoured configuration.

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