Structural Studies of Technetium Complexes. Part 4.[1] The Crystal Structure of *trans,trans*-Acetonitriledi-isothiocyanato(nitrido)bis-(triphenylphosphine)technetium(V)–Acetonitrile (1/0.5) †

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The title compound, $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]\cdot0.5CH_3CN$, has been prepared by substitution of $[TcNCl_2(PPh_3)_2]$ with NH_4NCS followed by the reaction of the $[TcN(NCS)_2(PPh_3)_2]$ complex with CH_3CN. The crystal structure of $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]\cdot0.5CH_3CN$ has been determined by single-crystal *X*-ray diffraction methods at 25 ± 2 °C. Crystals are monoclinic, space group $P2_1/c$, with $a = 9.296(3)$, $b = 18.614(5)$, $c = 23.307(6)$ Å, $\beta = 109.63(2)°$, and $Z = 4$. Diffractometry has provided significant Bragg intensities for 5 498 independent reflections and the structure has been refined by full-matrix least-squares methods to $R = 0.045$. The compound consists of discrete $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ molecules with CH_3CN of crystallisation also present in the crystal lattice. The technetium atom has a distorted octahedral environment with Tc–N–C angles of 177.1(4) and 166.7(4)° for the NCS ligands and 168.6(4)° for the CH_3CN ligand. The Tc≡N bond distance is 1.629(4) Å and the strong *trans* influence of the nitrido-group is evident in the exceptionally long Tc–N bond distance [2.491(4) Å] to the CH_3CN ligand.

The study of the co-ordination chemistry of technetium has grown rapidly in recent years,[2,3] due both to the widespread use of complexes of the short-lived isomer, technetium-99m ($t_{\frac{1}{2}} = 6$ h), in diagnostic nuclear medicine,[4] and to the greater availability of the long-lived technetium-99 ($t_{\frac{1}{2}} = 2.12 \times 10^5$ years). Single-crystal *X*-ray diffraction studies have played a major role in the structure determination of technetium-99 complexes and this topic has been recently comprehensively reviewed.[5]

The crystal structures of a variety of $Tc^V{=}O$ complexes have been reported.[5] These complexes are characterized by very short (1.61—1.67 Å) technetium–oxygen bonds. Structural studies of Tc≡N complexes are limited to our report of the crystal structure of $[TcN(S_2CNEt_2)_2]$.[6] The structure of transition-metal nitrido-complexes is of interest because of the effects arising from the powerful *trans* influence and large steric requirements of the nitrido-ligand.[7,8] We now report the synthesis and crystal structure of the first six-co-ordinate Tc≡N complex, *trans,trans*-acetonitriledi-isothiocyanato(nitrido)-bis(triphenylphosphine)technetium(V) hemiacetonitrile solvate, $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]\cdot0.5CH_3CN$. This complex was prepared by the reaction of $[TcNCl_2(PPh_3)_2]$ with thiocyanate ions followed by the reaction of the complex $[TcN(NCS)_2(PPh_3)_2]$ with acetonitrile.

Experimental

Ammonium [^{99}Tc]pertechnetate was supplied by Amersham International. All reagents and solvents used were of analytical grade. $[TcNCl_2(PPh_3)_2]$ was prepared from ammonium [^{99}Tc]pertechnetate as described by Kaden *et al.*[9] The i.r. spectra were determined in KBr discs on a Perkin-Elmer 197 spectrophotometer and the ^{1}H n.m.r. spectrum on a Varian EM360A spectrometer. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

Di-isothiocyanato(nitrido)bis(triphenylphosphine)technetium(V).—Ammonium thiocyanate (250 mg, 3.3 mmol) dissolved in water (1 cm^3) was added to a suspension of $[TcNCl_2(PPh_3)_2]$ (200 mg, 0.28 mmol) in ethanol (40 cm^3) and the mixture was heated under reflux for 30 min. The clear orange solution was cooled and the bulk of the ethanol removed by rotary evaporation. Water (25 cm^3) was added and the mixture extracted with 2 × 25 cm^3 of chloroform. The chloroform extracts were dried over anhydrous sodium sulphate, filtered, and evaporated to *ca.* 5 cm^3 in volume. Addition of diethyl ether resulted in the precipitation of fine yellow crystals of $[TcN(NCS)_2(PPh_3)_2]$ which were collected by filtration, yield 147 mg {69% based on $[TcNCl_2(PPh_3)_2]$}. Recrystallization from benzene gave yellow crystals, m.p. 230—234 °C (decomp.) (Found: C, 59.7; H, 4.2; N, 5.9; P, 8.6; S, 7.6. $C_{38}H_{30}N_3P_2S_2Tc$ requires C, 60.6; H, 4.0; N, 5.6; P, 8.2; S, 8.5%). The i.r. spectrum showed peaks at 2 070vs, 1 481s, 1 435vs, 1 099s, 1 087s, 742s, and 693vs cm^{-1}.

trans,trans-*Acetonitriledi-isothiocyanato(nitrido)bis(triphenylphosphine)technetium*(V).—A solution of $[TcN(NCS)_2(PPh_3)_2]$ (50 mg) in acetonitrile (5 cm^3) was heated under reflux for 10 min and then allowed to cool to room temperature. The orange-red crystals of $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ were collected by filtration and dried under vacuum; m.p. 230—233 °C (decomp.), yield 47 mg (89%) (Found: C, 59.9; H, 4.2; N, 7.2; P, 7.7; S, 8.2. $C_{40}H_{33}N_4P_2S_2Tc$ requires C, 60.4; H, 4.2; N, 7.05; P, 7.8; S, 8.1%). The i.r. spectrum showed peaks at 2 295vw, 2 265vw, 2 104s, 2 092vs, 2 060vs, 1 480s, 1 431s, 1 095s, 1 088s, 1 070m, 1 065m, 746s, 708s, and 694vs cm^{-1}. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed peaks at δ 7.5 (s, Ph) and 2.0 (s, CH_3).

Crystallography.—Single crystals suitable for *X*-ray diffraction studies were grown by slow evaporation of a benzene–acetonitrile (1 : 2 v/v) solution of $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ at room temperature. Oscillation and Weissenberg photographs showed the crystals to be monoclinic, of space group $P2_1/c$. Unit-cell parameters, together with their estimated standard deviations (e.s.d.s), were derived by a least-squares analysis of the setting angles, determined on a diffractometer at 25 ± 2 °C with Cu-K_α radiation ($\lambda = 1.5418$ Å), for 12 angularly well separated reflections each with $2\theta > 40°$.

Crystal data. $C_{41}H_{34.5}N_{4.5}P_2S_2Tc$, $M = 815.23$, Monoclinic, $a = 9.296(3)$, $b = 18.614(5)$, $c = 23.307(6)$ Å, $\beta =$

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† *Supplementary data available* (No. SUP 23847, 59 pp.): thermal parameters, observed and calculated structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii–xix.

Table 1. Final atomic positional co-ordinates for non-hydrogen atoms of $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]\cdot0.5CH_3CN$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Tc	0.07165(3)	0.24095(2)	0.07952(1)
S(1)	0.5249(2)	0.0940(1)	0.1448(1)
S(2)	−0.1801(2)	0.4695(1)	0.0606(1)
P(1)	0.0882(1)	0.2522(1)	0.1882(1)
P(2)	0.0775(1)	0.2388(1)	−0.0280(1)
N(1)	0.2602(4)	0.1761(2)	0.1038(2)
N(2)	−0.0623(4)	0.3324(2)	0.0640(2)
N(3)	0.2626(4)	0.3384(2)	0.0900(2)
N(4)	−0.0631(4)	0.1810(2)	0.0668(2)
N(5)	0.4015(26)	0.9262(11)	0.0226(10)
C(1)	0.3699(6)	0.1406(3)	0.1201(2)
C(2)	−0.1116(5)	0.3899(2)	0.0628(2)
C(3)	0.3402(5)	0.3833(3)	0.0845(2)
C(4)	0.4441(1)	0.4390(3)	0.0790(3)
C(5)	0.1163(4)	0.1660(2)	0.2276(2)
C(6)	0.2490(5)	0.1262(2)	0.2346(2)
C(7)	0.2690(5)	0.0597(3)	0.2629(2)
C(8)	0.1625(6)	0.0328(3)	0.2851(2)
C(9)	0.0326(6)	0.0709(3)	0.2792(2)
C(10)	0.0079(5)	0.1378(3)	0.2504(2)
C(11)	0.2340(4)	0.3112(2)	0.2366(2)
C(12)	0.3392(5)	0.2893(2)	0.2923(2)
C(13)	0.4432(5)	0.3384(3)	0.3285(2)
C(14)	0.4419(5)	0.4087(3)	0.3107(2)
C(15)	0.3364(5)	0.4313(3)	0.2560(2)
C(16)	0.2339(5)	0.3833(2)	0.2187(2)
C(17)	−0.0879(4)	0.2863(2)	0.1962(2)
C(18)	−0.0858(5)	0.3337(2)	0.2426(2)
C(19)	−0.2227(5)	0.3557(2)	0.2491(2)
C(20)	−0.3589(6)	0.3307(3)	0.2100(2)
C(21)	−0.3618(6)	0.2837(3)	0.1644(2)
C(22)	−0.2270(5)	0.2617(2)	0.1566(2)
C(23)	0.0488(5)	0.1485(2)	−0.0608(2)
C(24)	0.1347(6)	0.1232(3)	−0.0943(2)
C(25)	0.1101(7)	0.0536(3)	−0.1190(3)
C(26)	−0.0005(6)	0.0114(3)	−0.1108(3)
C(27)	−0.0922(7)	0.0366(3)	−0.0795(3)
C(28)	−0.0668(6)	0.1058(3)	−0.0538(3)
C(29)	0.2564(4)	0.2692(2)	−0.0370(2)
C(30)	0.2617(5)	0.3255(2)	−0.0749(2)
C(31)	0.4017(6)	0.3476(3)	−0.0788(2)
C(32)	0.5347(6)	0.3131(3)	−0.0460(2)
C(33)	0.5292(6)	0.2554(3)	−0.0094(2)
C(34)	0.3914(5)	0.2336(3)	−0.0049(2)
C(35)	−0.0691(5)	0.2946(2)	−0.0809(2)
C(36)	−0.0712(5)	0.3680(2)	−0.0685(2)
C(37)	−0.1811(5)	0.4119(3)	−0.1078(2)
C(38)	−0.2888(6)	0.3830(3)	−0.1589(2)
C(39)	−0.2875(6)	0.3116(3)	−0.1712(2)
C(40)	−0.1780(5)	0.2666(2)	−0.1322(2)
C(41)	0.4701(21)	0.9734(9)	0.0108(8)
C(42)	0.5701(43)	1.0322(21)	−0.0017(18)

109.63(2)°, $U = 3\,798.6$ Å^3, $F(000) = 1\,668$, $Z = 4$, $D_c = 1.425$ Mg m^{-3}, space group $P2_1/c$, μ(Cu-K_α) = 4.967 mm^{-1}.[10]

Intensity data were recorded at 25 ± 2 °C on an automatic Siemens AED diffractometer with nickel-filtered Cu-K_α radiation. The crystal was cut from a long red needle, and it had well developed (100) and (010) faces with perpendicular distances between parallel faces of 0.14 and 0.12 mm respectively. Along the needle direction, the crystal was 0.39 mm in length. The crystal was aligned with the *c* (needle) axis approximately parallel to the diffractometer φ axis. Intensities were measured by the 'five-values' $\theta : 2\theta$ scan procedure detailed by Hoppe,[11] with a 2θ scan rate of 10° min^{-1}. A reference reflection, monitored every 20 reflections, showed no significant variation in intensity during data collection. A total of 7 635 different reflections in one quadrant was measured within the limit $(\sin\theta)/\lambda \leqslant 0.609$ Å^{-1}. Of these, 5 501 unique reflections 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.[10]

Structure determination and refinement. The structure was solved by the heavy-atom method. The position of the technetium atom was derived from a three-dimensional Patterson map, and subsequent difference-Fourier syntheses revealed the positions of all 49 non-hydrogen atoms of the complex. An acetonitrile solvent molecule was located close to the special position ($\frac{1}{2}$, 0, 0), precluding the possibility of one solvent molecule per metal complex since this would place two centrosymmetrically related acetonitrile molecules at an unrealistically short distance from each other. The acetonitrile solvent atoms were accordingly each given an occupancy factor of 0.5 with the solvent molecule being assumed disordered between its two centrosymmetrically related positions. The relative peak heights of these atoms in the electron-density maps also suggested disorder.

Full-matrix least-squares refinement, with data uncorrected for absorption and with anisotropic temperature factors assigned to all but the 36 phenyl carbon atoms and the three carbon and nitrogen solvent atoms, converged (274 variables) with a reliability index $R = \Sigma\Delta F/\Sigma|F_o|$ of 0.055 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 0.34 and 0.62, the same refinement converged with $R = 0.054$.

All hydrogen atoms were then included in the scattering model in idealised positions (C–H 1.08 Å). The 30 phenyl hydrogen atoms were given a common isotropic temperature factor B which, at convergence, had the value 6.4(3) Å^2, and the methyl groups on the co-ordinated and solvent acetonitrile molecules were refined as idealised rigid groups each with common isotropic temperature factors which refined to $B = 12(1)$ and 22(8) Å^2 respectively. An examination of $|F_o|$ and $|F_c|$ values at this stage indicated that the three most intense reflections were significantly affected by extinction and these were omitted from the refinement. Least-squares refinement, with anisotropic temperature factors assigned to 13 atoms of the metal complex, and isotropic temperature factors assigned to the remaining 36 phenyl carbon atoms and three carbon and nitrogen atoms of the solvent molecule, converged {NV = 283 variables, NO = 5 498 observations, $w = [\sigma^2(F_o) + 0.0001(F_o^2)]^{-1}$} with $R = 0.045$, $R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}} = 0.049$, and $\chi = [\Sigma w(\Delta F)^2/(\text{NO}-\text{NV})]^{\frac{1}{2}} = 2.54$. The maximum parameter shift-to-error ratios at convergence were 0.26 : 1 for the X/a positional co-ordinate of the solvent nitrogen atom and 0.2 : 1 for the Z/c and U_{23} parameters of the methyl carbon atom [C(4)] of the co-ordinated acetonitrile molecule. All other shift-to-error ratios for non-hydrogen atoms of the metal complex were <0.08 : 1. The largest peaks on a final difference synthesis were of heights ±0.62 e Å^{-3}.

Final atomic positional co-ordinates, with e.s.d.s in parentheses, are listed in Table 1.

Neutral atom scattering-factor curves for C, N, P, and S were taken from ref. 12, that for neutral Tc was from ref. 13, and that for H was from ref. 14. Real and imaginary anomalous dispersion corrections [10] were applied to the non-hydro-

Table 2. Interatomic bond distances (Å) in $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]{\cdot}0.5CH_3CN$

Tc–P(1)	2.494(1)	P(1)–C(17)	1.823(4)	C(15)–C(16)	1.381(6)	C(29)–C(30)	1.382(6)
Tc–P(2)	2.524(1)	P(2)–C(23)	1.830(4)	C(11)–C(16)	1.404(5)	C(30)–C(31)	1.397(6)
Tc–N(1)	2.045(4)	P(2)–C(29)	1.834(4)	C(17)–C(18)	1.391(6)	C(31)–C(32)	1.375(7)
Tc–N(2)	2.068(3)	P(2)–C(35)	1.824(4)	C(18)–C(19)	1.393(6)	C(32)–C(33)	1.382(7)
Tc–N(3)	2.491(4)	C(5)–C(6)	1.400(5)	C(19)–C(20)	1.370(6)	C(33)–C(34)	1.381(6)
Tc–N(4)	1.629(4)	C(6)–C(7)	1.387(6)	C(20)–C(21)	1.368(6)	C(29)–C(34)	1.393(6)
N(1)–C(1)	1.167(6)	C(7)–C(8)	1.357(6)	C(21)–C(22)	1.388(6)	C(35)–C(36)	1.397(5)
N(2)–C(2)	1.160(5)	C(8)–C(9)	1.367(6)	C(17)–C(22)	1.389(6)	C(36)–C(37)	1.386(6)
N(3)–C(3)	1.139(6)	C(9)–C(10)	1.397(7)	C(23)–C(24)	1.374(6)	C(37)–C(38)	1.382(6)
C(1)–S(1)	1.613(5)	C(5)–C(10)	1.390(6)	C(24)–C(25)	1.404(7)	C(38)–C(39)	1.360(6)
C(2)–S(2)	1.607(4)	C(11)–C(12)	1.400(6)	C(25)–C(26)	1.358(7)	C(39)–C(40)	1.393(6)
C(3)–C(4)	1.453(7)	C(12)–C(13)	1.391(6)	C(26)–C(27)	1.378(8)	C(35)–C(40)	1.383(6)
P(1)–C(5)	1.824(4)	C(13)–C(14)	1.373(6)	C(27)–C(28)	1.407(8)	N(5)–C(41)	1.170(27)
P(1)–C(11)	1.814(4)	C(14)–C(15)	1.387(6)	C(23)–C(28)	1.389(6)	C(41)–C(42)	1.527(27)

Table 3. Selected bond angles (°) in $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]{\cdot}0.5CH_3CN$

P(1)–Tc–P(2)	174.0(1)	N(2)–Tc–N(4)	98.7(2)	N(3)–C(3)–C(4)	177.8(5)	C(22)–C(17)–P(1)	119.0(3)
P(1)–Tc–N(1)	90.8(1)	N(3)–Tc–N(4)	174.6(2)	N(5)–C(41)–C(42)	175.9(20)	C(24)–C(23)–P(2)	121.5(3)
P(1)–Tc–N(2)	86.3(1)	Tc–P(1)–C(5)	112.8(1)	C(5)–P(1)–C(11)	105.6(2)	C(28)–C(23)–P(2)	119.1(4)
P(1)–Tc–N(3)	92.3(1)	Tc–P(1)–C(11)	117.4(1)	C(5)–P(1)–C(17)	103.7(2)	C(30)–C(29)–P(2)	122.3(3)
P(1)–Tc–N(4)	91.4(1)	Tc–P(1)–C(17)	112.5(1)	C(11)–P(1)–C(17)	103.6(2)	C(34)–C(29)–P(2)	118.7(3)
P(2)–Tc–N(1)	87.9(1)	Tc–P(2)–C(23)	112.4(1)	C(23)–P(2)–C(29)	104.2(2)	C(36)–C(35)–P(2)	118.4(3)
P(2)–Tc–N(2)	93.0(1)	Tc–P(2)–C(29)	115.6(1)	C(23)–P(2)–C(35)	105.6(2)	C(40)–C(35)–P(2)	122.3(3)
P(2)–Tc–N(3)	81.8(1)	Tc–P(2)–C(35)	113.7(1)	C(29)–P(2)–C(35)	104.3(2)	C(6)–C(5)–C(10)	118.7(4)
P(2)–Tc–N(4)	94.6(1)	Tc–N(1)–C(1)	177.1(4)	C(6)–C(5)–P(1)	119.7(3)	C(12)–C(11)–C(16)	119.0(4)
N(1)–Tc–N(2)	160.7(2)	Tc–N(2)–C(2)	166.7(4)	C(10)–C(5)–P(1)	121.6(3)	C(18)–C(17)–C(22)	119.5(4)
N(1)–Tc–N(3)	83.5(1)	Tc–N(3)–C(3)	168.6(4)	C(12)–C(11)–P(1)	122.9(3)	C(24)–C(23)–C(28)	119.4(4)
N(1)–Tc–N(4)	100.4(2)	N(1)–C(1)–S(1)	177.6(5)	C(16)–C(11)–P(1)	118.0(3)	C(30)–C(29)–C(34)	119.0(4)
N(2)–Tc–N(3)	77.6(1)	N(2)–C(2)–S(2)	179.7(3)	C(18)–C(17)–P(1)	121.5(3)	C(36)–C(35)–C(40)	119.3(4)

gen atoms. Structure determination and refinement were performed with the SHELX 76 program system [15] on the Commonwealth Department of Health IBM 370/168 computer.

Results and Discussion

Nitrido-complexes are known for many transition metals but appear to be most readily formed by molybdenum, tungsten, rhenium, ruthenium, and osmium.[7,8] Technetium will undoubtedly be added to this list as the chemistry of this element is further investigated.

The molecular geometry and atom numbering of the $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ molecule are shown in the Figure. Interatomic bond distances and angles, with e.s.d.s derived from the refinement, are given in Tables 2 and 3. Intra- and inter-molecular contact distances are given in Table 4. The structure consists of discrete molecules of $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$, each containing a terminal nitrido-ligand and one co-ordinated acetonitrile molecule. Acetonitrile of crystallization [N(5), C(41), C(42)] is also present in the lattice. The technetium co-ordination environment is distorted octahedral.

The $Tc^{V}{\equiv}N$ bond distance in $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ is 1.629(4) Å, somewhat longer than that in $[TcN(S_2CNEt_2)_2]$ [1.604(6) Å].[6] Comparisons of M≡N bond distances must take into account the co-ordination number and the nature of the ligands. A wide variation of the Re≡N bond distance has been reported and it has been proposed that this variation is steric in origin.[7,16] This view is supported by the comparison of the $Re^{V}{\equiv}N$ bond distance of 1.602(9) Å in the five-co-ordinated $[ReNCl_2(PPh_3)_2]$ [17] with that of 1.788(11) Å in the six-co-ordinated *mer*-$[ReNCl_2(PEt_2Ph)_3]$ which contains three bulky phosphine ligands.[18] The $Re^{VI}{\equiv}N$ bond distance in $[AsPh_4][ReNCl_4]$ is 1.619(10) Å [19] and in $[AsPh_4]_2[ReN(NCS)_5]$ it is 1.657(12) Å.[20] It will be of interest to determine whether a similar variation exists in Tc≡N bond distances.

The solid-state i.r. spectra of $[TcN(NCS)_2(PPh_3)_2]$ and $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ show absorptions at 1 087 and 1 088 cm^{-1} respectively, which are assigned to the Tc≡N stretching frequency. Absorption in the region 1 000—1 100 cm^{-1} is characteristic of terminal M≡N groups.[8]

The bonding of the thiocyanato-groups of $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ is through the nitrogen atoms. Bonding *via* nitrogen has been found to be the case for the other technetium thiocyanato-structures reported to date.[21–23] The Tc^{V}–N single-bond distances in $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ [2.045(4), 2.068(3) Å] are similar to the Tc^{III}–N bond distances in $[NBu^n_4]_3[Tc(NCS)_6]$ [2.04(2), 2.05(2) Å].[21] The crystal structures of $[NMe_4]_2[Tc^{IV}(NCS)_6]$ [22] and $[NMe_4][Tc^{V}(NCS)_6]$ [23] have been reported but the Tc–N bond distances are not given. Both NCS groups of $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ are linear with N–C–S angles of 177.6(5) and 179.7(3)°. However, the Tc–N–C angles differ markedly with Tc–N(1)–C(1) being 177.1(4) and Tc–N(2)–C(2) 166.7(4)°. It is likely that the deviation from linearity of Tc–N(2)–C(2) results from intramolecular steric constraints within the co-ordination sphere. In this regard, it is seen (Table 4) that N(2) in general has closer contacts with the other co-ordinated atoms than does N(1). There is also a short S(2) · · · H intermolecular contact distance of 2.747 Å, which suggests that packing forces within the crystal lattice contribute to the overall Tc–NCS geometry. The average Tc–N–C bond angle in $[NBu^n_4]_3[Tc(NCS)_6]$ is 173(2)°,[21] while in $[AsPh_4]_2[ReN(NCS)_5]$ the Re–N–C angles vary from 169.5(10) to 174.5(10)°.[20] Hazell [24] noted from a study of the crystallographic data for isothiocyanato-complexes that an increase in the M–N–C angle from *ca.* 120 to 180° is generally associated with a decrease in the N–C bond distance and an increase in the C–S bond distance.

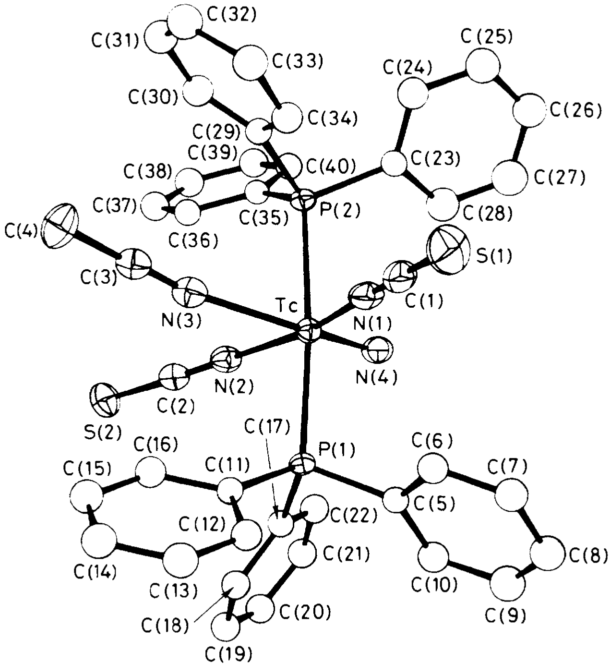

Figure. ORTEP drawing of the $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ molecule. The thermal ellipsoids, and spheres for the carbon atoms with isotropic temperature factors, are drawn at the 30% probability level

Table 4. Selected intramolecular and intermolecular contact distances * (Å) in $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]\cdot 0.5CH_3CN$

Tc · · · C(1)	3.211	S(1) · · · $C(14^{I})$	3.583
Tc · · · C(2)	3.208	S(1) · · · $H(14^{I})$	2.825
Tc · · · C(3)	3.615	S(1) · · · $H(42B^{II})$	3.159
N(3) · · · N(1)	3.038	S(2) · · · $H(4A^{III})$	2.747
N(3) · · · N(2)	2.876	N(4) · · · $H(26^{IV})$	2.928
N(3) · · · P(1)	3.595	N(5) · · · $H(27^{III})$	2.995
N(3) · · · P(2)	3.282	N(5) · · · $H(28^{III})$	2.689
N(4) · · · N(1)	2.836	N(5) · · · $H(33^{II})$	2.980
N(4) · · · N(2)	2.820	C(19) · · · $H(8^{V})$	2.772
N(4) · · · P(1)	3.011	C(19) · · · $H(40^{VI})$	2.720
N(4) · · · P(2)	3.111	H(15) · · · $H(38^{III})$	2.275
P(1) · · · N(1)	3.247		
P(1) · · · N(2)	3.137		
P(2) · · · N(1)	3.190		
P(2) · · · N(2)	3.345		

Roman numeral superscripts refer to the following co-ordinate transformations: I $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; II $1 - x, 1 - y, -z$; III $-x, 1 - y, -z$; IV $-x, -y, -z$; V $-x, \frac{1}{2} + y, \frac{1}{2} - z$; VI $x, \frac{1}{2} - y, \frac{1}{2} + z$

* Hydrogen atoms, in idealised positions (C–H 1.08 Å), are given the same number as the C atom to which they are bonded. All intermolecular contacts are given within the limits of the contact radii: Tc, 2.5; P and S, 2.0; N, 1.8; C, 1.7; H, 1.2 Å.

In the case of $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ the two N–C distances [1.167(6), 1.160(5) Å] and the two C–S distances [1.613(5), 1.607(4) Å] do not differ significantly. However, the Tc–N distance in the nearly linear Tc–N–C group is significantly shorter than that in the bent grouping.

The solid-state i.r. spectrum of $[TcN(NCS)_2(PPh_3)_2]$ showed a single intense peak at 2 070 cm^{-1} due to the NCS ligands. For $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ three NCS absorption bands were present, at 2 104, 2 092, and 2 060 cm^{-1}. The multiplicity of NCS absorption in the acetonitrile adduct is indicative of the lower symmetry of this complex.

The two *trans* triphenylphosphine ligands are bonded to technetium in an approximately linear fashion with a P–Tc–P angle of 174.0(1)°. The Tc–P bond distances, 2.494(1) and 2.524(1) Å, fall in the range (2.42—2.47 Å) of Tc^{III}–P distances observed in six- and seven-co-ordinate tertiary phosphine complexes[5] and the Tc^{IV}–P bond distance [2.57(1) Å] in $[PPh_3R][TcCl_5(PPh_3)]$ (R = 1,1-dimethyl-3-oxobutyl).[25] Bond distances and angles in the phenyl groups are as expected.

The exceptionally long Tc–N bond distance of 2.491(4) Å for the co-ordinated acetonitrile group is a result of the powerful *trans* influence of the nitrido-ligand which apart from the carbyne ligand, is the strongest known π-electron donor.[8] The Re–N bond distance in six-co-ordinate acetonitrile complexes of rhenium varies widely as a consequence of the influence of the *trans* group. In $[ReCl_3(NO)_2(CH_3CN)]$ [26] and $[ReCl_3(PPh_3)_2(CH_3CN)]$,[27] where the acetonitrile ligand is *trans* to chlorine, the Re–N bond distances are 1.95(6) and 2.05 Å respectively. The Re–N bond distance increases to an average of 2.13 Å in *fac*-$[Re(CH_3CN)_3(CO)_3][BF_4]$,[28] 2.153(11) Å in *trans*-$[NEt_4][Re(NO)Br_4(CH_3CN)]$,[29] and to 2.31(6) Å in *trans*-$[AsPh_4][Re(O)Br_4(CH_3CN)]$.[30] The long Tc–$NCCH_3$ bond distance in $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ is manifested by the ease with which the co-ordinated acetonitrile molecule may be displaced. Dissolution of crystalline $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ in chloroform and evaporation to dryness at room temperature resulted in the complete loss of the co-ordinated acetonitrile and the formation of $[TcN(NCS)_2(PPh_3)_2]$.

The acetonitrile ligand in $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ is essentially linear with a N–C–C angle of 177.8(5)°. However, the acetonitrile is bonded to technetium in a distinctly bent fashion with the Tc–N–C angle of 168.6(4)°. Non-linear metal–acetonitrile linkages have been reported, the Re–N–C angle in $[Re(O)Br_4(CH_3CN)]$ is 170(4)°,[30] and angles of 165(4) and 158.8(13)° have been found in two copper complexes.[31]

The solid-state i.r. spectrum of $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ showed only two very weak peaks attributable to acetonitrile, at 2 295 and 2 265 cm^{-1}, in the absorption region 2 400—2 200 cm^{-1}. The absence of C≡N stretching absorptions has been noted in the i.r. spectra of $[ReX_3(RCN)(PPh_3)_2]$ (R = alkyl, X = Cl or Br) complexes.[32]

A consequence of the large steric requirement of oxo-ligands in six-co-ordinated Tc=O complexes is the displacement of the *cis* ligands to angles of greater than 90° from the Tc=O axis.[5] This effect is clearly evident in $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ where the two N≡Tc–P angles are 91.4(1) and 94.6(1)° and the two N≡Tc–NCS angles are 98.7(2) and 100.4(2)°. The lesser displacement of the phosphine ligands has also been found in $[ReNCl_2(PEt_2Ph)_3]$ where the *cis*-N≡Re–Cl angle is 99.2(4)° and the three *cis*-N≡Re–PEt_2Ph angles are 91.8(4), 95.6(4), and 89.1(4)°.[18]

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