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Crystal structures of nitridotechnetium(V) complexes of amine oximes differing in carbon chain lengths

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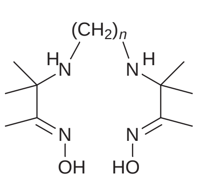
Structures of nitridotechnetium(V) amine oxime complexes, $[TcN(pnao)(H_2O)][BPh_4]$ **1**, $[TcN(bnao)(H_2O)][BPh_4]$ **2** and $[TcN(pentao)(H_2O)][BPh_4]$ **3** [Hpnao = $HON{=}CMeCMe_2NH(CH_2)_3NHCMe_2CMe{=}NOH$; Hbnao = $HON{=}CMeCMe_2NH(CH_2)_4NHCMe_2CMe{=}NOH$; Hpentao = $HON{=}CMeCMe_2NH(CH_2)_5NHCMe_2CMe{=}NOH$], differing in carbon chain length of the amine oxime ligands, were characterized by X-ray crystallography. These complexes are six-co-ordinated and distorted octahedral. Four nitrogen atoms of the amine oxime ligands are in the equatorial plane and both the nitrido and H_2O ligands in the apical positions. These complexes have an asymmetrical intramolecular hydrogen bond between the two oxime oxygen atoms. Their intramolecular O···O distances are 2.720 Å in **1**, 2.512 Å in **2** and 2.531 Å in **3**. The longest O···O distance in **1** is ascribed to a steric effect of the carbon chain length between the amine nitrogens. Namely, the shorter carbon chain of the pnao ligand causes strain on the co-ordinated pnao moiety, and the O···O distance in **1** is longer than that in **2** and **3** with longer carbon chains.

Introduction

A number of studies have been carried out on structures of amine oxime complexes of transition metals by X-ray and neutron diffraction crystallography.[1–10] Amine oxime complexes have an intramolecular hydrogen bond between the oxime oxygens, and the structural analysis gives a clue to an understanding of the nature of the hydrogen bonds. The intramolecular hydrogen bond distance (O···O) in amine oxime complexes depends on the size of the metal ions and the steric requirements of the amine oxime ligands in the square plane around the metal. For example, the O···O distance in the cobalt(III) complex of pnao (3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximate) is 2.432 Å,[5] while the same ligand gives a longer O···O distance (2.474 Å) in the rhodium(III) complex.[6] In amine oxime complexes of Ni^{II} with various carbon chain lengths between the amine nitrogens, the O···O distance (2.478 Å) in the enao (3,3,8,8-tetramethyl-4,7-diazadecane-2,9-dione dioximate) complex with the shortest carbon chain[7] is longer than those in the pnao (2.409 Å)[8] and bnao (3,3,10,10-tetramethyl-4,9-diazadodecane-2,11-dione dioximate) complexes (2.417 Å).[10] However, systematic studies on the relation between the O···O distance and the carbon chain length are limited. Although structures of the enao, pnao and bnao complexes of Rh^{III} and Cu^{II} have been studied,[6,9–11] those with enao and bnao are dinuclear, and the character of the intramolecular hydrogen bond in these complexes cannot be compared directly with that in mononuclear pnao complexes.



n = 2 Henao
3 Hpnao
4 Hbnao
5 Hpentao

We have recently determined the crystal structure of the pnao complex of nitridotechnetium(V), $[TcN(pnao)(H_2O)][BPh_4]$.[12] Its O···O distance [2.720(5) Å] of the intramolecular hydrogen bond is longer than those in pnao complexes of other transition metals.[12] The $[TcN(pnao)(H_2O)]^+$ complex has a nitrido (N^{3-}) ligand at the apical position, and electronic properties of the nitrido ligand would account for a longer O···O distance in $[TcN(pnao)(H_2O)]^+$ than that in pnao complexes without nitrido ligands.

The nitrido ligand is a strong π electron donor, and weakens a bond in the *trans* position to itself by the *trans* influence.[13] Lengthening of a bond between the central metal and the *trans* ligand is almost invariably accompanied by bending of *cis* ligands away from the nitrido ligand.[13] In $[TcN(pnao)(H_2O)]^+$ two structural features of the *trans* influence are observed; the bond length between the technetium and the oxygen atom of an aqua ligand in the *trans* position to the nitrido ligand is fairly long (2.481 Å) and the nitrido–technetium–*cis* ligand angles are about 100°.[12] An electron donation of the nitrido ligand and bending of the *cis* ligands would weaken the bond between the technetium and the *cis* nitrogen atoms. The weakening of technetium–*cis* nitrogen bonds results in a longer distance between the oxime nitrogens, and the O···O distance in $[TcN(pnao)(H_2O)]^+$ becomes long.

In addition to electronic factors, it is essential to examine a steric factor associated with the length of amine oxime ligands. In this respect, we have synthesized amine oxime complexes of nitridotechnetium(V) with longer carbon chains such as bnao and pentao. This paper reports the structures of these complexes determined by X-ray crystallography, and discusses the structural features of $[TcN(pnao)(H_2O)][BPh_4]$ **1**, $[TcN(bnao)(H_2O)][BPh_4]$ **2** and $[TcN(pentao)(H_2O)][BPh_4]$ **3**, focusing on the intramolecular hydrogen bond.

Results and discussion

The nitridotechnetium(V) amine oxime complexes **1**–**3** were synthesized by ligand exchange reaction of $[TcNCl_2(PPh_3)_2]$ with each amine oxime ligand. The ^1H NMR results for the methyl protons of **1**–**3** are listed in Table 1. The two methyl groups **a** and **b** adjacent to the amine nitrogens give two singlet peaks; the peak of the methyl group **a** near the $Tc–N_{nitrido}$ bond is downfield from that of the methyl group **b**. The $Tc–N_{nitrido}$

Table 1 Proton NMR data[a] for the methyl protons of nitridotechnetium–amine oxime complexes

Complex	n[b]	a	b	c
1 $[TcN(pnao)(H_2O)][BPh_4]$	3	1.648	1.524	2.150
2 $[TcN(bnao)(H_2O)][BPh_4]$	4	1.606	1.487	2.153
3 $[TcN(pentao)(H_2O)][BPh_4]$	5	1.602	1.525	2.158

[a] δ in ppm, $SiMe_4$ reference. In CD_3CN. [b] The number of carbons between amine nitrogens.

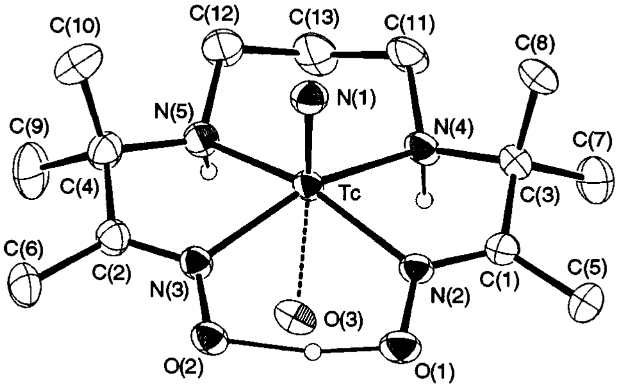


Fig. 1 An ORTEP drawing of the complex cation $[TcN(pnao)(H_2O)]^+$ **1**.

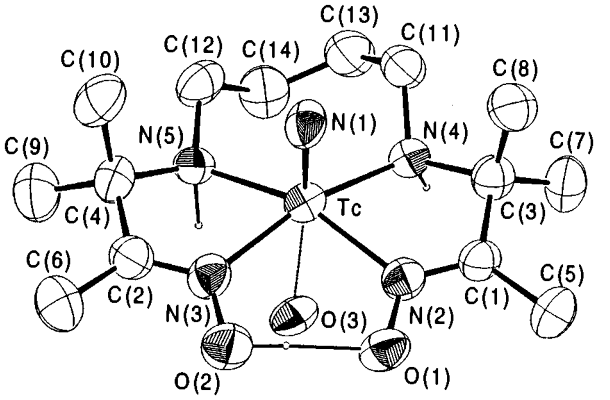
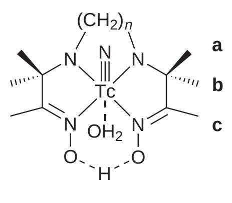


Fig. 2 An ORTEP drawing of the complex cation $[TcN(bnao)(H_2O)]^+$ **2**.

triple bond is known to generate a downfield environment,[14] and the signal of the methyl group near the Tc–$N_{nitrido}$ bond is more deshielded to shift downfield.



The ORTEP[15] drawings of the complex cations $[TcN(pnao)(H_2O)]^+$, $[TcN(bnao)(H_2O)]^+$ and $[TcN(pentao)(H_2O)]^+$ are shown in Figs. 1–3. Selected interatomic distances and angles of these complexes are listed in Table 2.

The cations in the nitridotechnetium(v) amine oxime complexes **1**-**3** are six-co-ordinated and distorted octahedral; *i.e.* four nitrogen atoms of the amine oxime ligands are in the equatorial plane and both the nitrido and H_2O ligands are at the apical positions. The Tc–N(1) distances in **1**–**3** (*ca.* 1.6 Å) are comparable with the Tc≡N triple-bond distance in other nitridotechnetium(v) complexes (1.59–1.63 Å).[16] The Tc–O(3) distance is 2.481(4) Å in **1**, 2.472(3) Å in **2** and 2.390(3) Å in **3**. The fairly long Tc–O(3) bond length is ascribed to the strong *trans* influence of the nitrido ligand. The technetium atom is not on the least-squares plane defined by the four nitrogen atoms of the amine oxime ligands. The deviation of the technetium atom from the plane toward the nitrido ligand is 0.399 Å in **1**, 0.344 Å in **2** and 0.315 Å in **3**. The complex with larger deviation of the Tc atom has a longer Tc–O(3) distance.

Table 2 Selected interatomic distances (Å) and angles (°) for $[TcN(pnao)(H_2O)][BPh_4]$ **1**, $[TcN(bnao)(H_2O)][BPh_4]$ **2** and $[TcN(pentao)(H_2O)][BPh_4]$ **3**

	1	**2**	**3**
Tc–N(1)	1.610(5)	1.604(4)	1.610(3)
Tc–N(2)	2.055(3)	2.062(4)	2.077(3)
Tc–N(3)	2.065(4)	2.064(4)	2.075(3)
Tc–N(4)	2.094(4)	2.144(3)	2.182(3)
Tc–N(5)	2.113(4)	2.146(4)	2.164(3)
Tc–O(3)	2.481(4)	2.472(3)	2.390(3)
N(2)–C(1)	1.292(7)	1.262(5)	1.278(4)
N(2)–O(1)	1.363(5)	1.362(4)	1.382(3)
N(3)–C(2)	1.287(6)	1.269(5)	1.292(5)
N(3)–O(2)	1.390(5)	1.387(5)	1.357(4)
N(4)–C(3)	1.518(7)	1.533(5)	1.528(4)
N(4)–C(11)	1.492(6)	1.508(6)	1.512(4)
N(5)–C(4)	1.518(6)	1.511(6)	1.520(5)
N(5)–C(12)	1.496(7)	1.498(6)	1.512(5)
C(1)–C(3)	1.552(7)	1.523(6)	1.523(5)
C(2)–C(4)	1.542(6)	1.528(6)	1.518(6)
O(1)···O(2)	2.720(5)	2.512(4)	2.531(3)
N(1)–Tc–N(2)	101.9(2)	103.9(2)	100.9(1)
N(1)–Tc–N(3)	102.8(2)	100.7(2)	100.4(1)
N(1)–Tc–N(4)	98.9(2)	95.8(2)	96.8(1)
N(1)–Tc–N(5)	100.5(2)	97.7(2)	96.5(1)
N(2)–Tc–N(3)	99.4(2)	96.4(2)	95.7(1)
N(4)–Tc–N(5)	97.2(2)	105.2(1)	107.1(1)
Tc–N(2)–O(1)	120.5(3)	118.4(3)	121.5(2)
Tc–N(2)–C(1)	118.0(3)	120.6(3)	121.4(2)
Tc–N(3)–O(2)	122.0(3)	121.2(3)	119.7(2)
Tc–N(3)–C(2)	120.0(3)	121.4(3)	119.4(3)
Tc–N(4)–C(3)	111.6(3)	109.1(2)	109.8(2)
Tc–N(4)–C(11)	112.9(3)	115.2(3)	116.7(2)
Tc–N(5)–C(4)	110.9(3)	110.6(3)	109.7(2)
Tc–N(5)–C(12)	111.9(3)	115.8(3)	118.8(2)

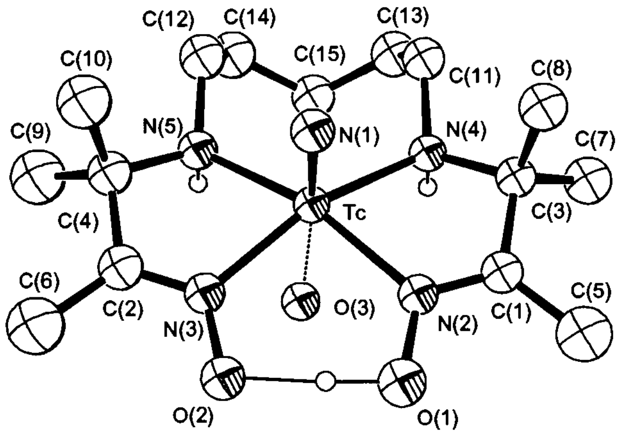


Fig. 3 An ORTEP drawing of the complex cation $[TcN(pentao)(H_2O)]^+$ **3**.

The Tc–N_{amine} and Tc–N_{oxime} distances in complexes **1**–**3** are summarized in Table 3, together with those in amine oxime complexes of other transition metals. The Tc–N_{amine} distances are in the order of **1** < **2** < **3**, while the Tc–N_{oxime} distances are nearly the same for **1**–**3**. The Tc–N_{amine} distance in **1** with the pnao ligand is longer than that in the analogous oxotechnetium(v) pnao complex [1.908(3) and 1.917(3) Å][17] in which the two amine protons of the pnao ligand are lost on co-ordination to Tc. The long distance in **1** would imply a weaker interaction between the Tc and N_{amine} than the Tc and N_{amide} in the oxo-

Table 3 Selected intramolecular distances (Å) in amine oxime complexes of nitridotechnetium(v) and other transition metals without nitrido ligands

Complex	M–N_{amine}	M–N_{oxime}	$N_{oxime} \cdots N_{oxime}$	O···O	Ref.
1 [TcN(pnao)(H_2O)][BPh_4]	2.10	2.06	3.14	2.720(5)	This work
2 [TcN(bnao)(H_2O)][BPh_4]	2.15	2.06	3.08	2.512(4)	This work
3 [TcN(pentao)(H_2O)][BPh_4]	2.17	2.08	3.08	2.531(3)	This work
[Co(pnao)(NO_2)$_2$]	1.98	1.90	2.88	2.432(3)	5
[Pd(pnao)]NO_3	2.04	1.97	2.96	2.474(5)	3
[Cu(pnao)(CN)]	2.04	1.98	2.90	2.475(4)	4
[Rh(pnao)Cl_2]	2.06	1.99	3.02	2.474(7)	6
[Ni(bnao)]I	1.92	1.86	2.86	2.417(7)	10
[Cu(bnao)(H_2O)]ClO_4	2.04	1.97	2.89	2.421(5)	10

technetium complex. On the other hand, the Tc–N_{amine} and Tc–N_{oxime} distances in **1**–**3** are longer than those in amine oxime complexes of other transition metals without nitrido ligands. Strong π donation of the nitrido ligand at the apical position in **1**–**3** would account for long Tc–N_{amine} and Tc–N_{oxime} distances in the nitridotechnetium complexes, because the strong Tc≡N bonding weakens the Tc–N_{amine} and Tc–N_{oxime} bonds.

The complexes **1**–**3** have an intramolecular hydrogen bond between the two oxime oxygen atoms. The hydrogen bond O(1)···O(2) distance is 2.720(5) Å in **1**, 2.512(4) Å in **2** and 2.531(3) Å in **3**. These O···O distances are longer than those in amine oxime complexes of Co^{II}, Pd^{II}, Cu^{II}, Ni^{II} and Rh^{III} as seen in Table 3. The long O···O distance in **1**–**3** should also be attributed to strong π donation of the nitrido ligand. Longer Tc–N_{oxime} distances give longer $N_{oxime} \cdots N_{oxime}$ distances, and the intramolecular O···O distances in **1**–**3** become longer.

When features of intramolecular hydrogen bonding are compared among the nitridotechnetium complexes **1**–**3**, the O···O distance in **1** with the shortest carbon chain (propylene) is the longest. This fact suggests that a steric factor arising from the carbon chain length also plays a role in determining the O···O distance. In the complex **1** with the shortest carbon chain the N(4)–Tc–N(5) angle is the smallest of the three complexes examined here; *i.e.* 97.2(2)° in **1**, 105.2(1)° in **2** and 107.1(1)° in **3**, as listed in Table 2. On the contrary, the N(2)–Tc–N(3) angle, on the opposite side of the carbon chain, is the largest in **1**; *i.e.* 99.4(2)° in **1**, 96.4(2)° in **2** and 95.7(1)° in **3**. Thus these angles depend on the length of the carbon chains of the ligands. The shorter the carbon chain the wider is the N(2)–Tc–N(3) angle. Thus a shorter carbon chain affords a longer intramolecular hydrogen bond distance, O(1)···O(2), as a result of the elongation of the N(2)···N(3) distance.

It is also instructive that deviation of the Tc atom from the least-squares plane in **1** is the largest of the three complexes and that the C–C distances in the ligand moieties are longer in **1** than in **2** and **3**. These facts reveal that there should be strong strain on the pnao ligand in **1**, leading to elongation of the O···O distance in **1**. In **2** and **3** with longer carbon chains the strain on the ligand moieties would not be so strong as in **1**. Consequently, the O(1)···O(2) distances in **2** and **3** are shorter than that in **1**.

The O···O distances in complexes **1**–**3** are as long as 2.51–2.72 Å. This fact suggests that the intramolecular hydrogen bond in these complexes is asymmetrical in the crystalline state. Experiments as well as theories have shown that the O–H···O hydrogen bonds with O···O distances longer than 2.5 Å are asymmetrical.[18] A significant difference between the N(2)–O(1) and N(3)–O(2) distances in **1**–**3** manifests the asymmetrical hydrogen bond.[19] Furthermore, the position of hydrogen in the intramolecular hydrogen bond in **1**–**3** must be restricted by the formation of an intermolecular hydrogen bond between one of the oxime oxygen atoms and the oxygen atom in another molecule in the crystal. In fact, this hydrogen bond is formed between O(1) of the oxime and O(5) of ethanol in **1**, O(1) of the oxime and O(3) of an aqua ligand in the neighboring complex cation in **2** and O(2) of the oxime and O(3) of an aqua ligand in the neighboring complex cation in **3**. The electron density of this oxime oxygen should be reduced, so that the intramolecular hydrogen bond in **1**–**3** becomes asymmetrical.

Conclusion

Structures of amine oxime complexes of nitridotechnetium(v), [TcN(pnao)(H_2O)][BPh_4] **1**, [TcN(bnao)(H_2O)][BPh_4] **2** and [TcN(pentao)(H_2O)][BPh_4] **3**, were determined by X-ray crystallography. These complexes have an asymmetrical intramolecular hydrogen bond between the oxime oxygen atoms. The intramolecular O···O distances determined are 2.720 Å in **1**, 2.512 Å in **2** and 2.531 Å in **3**. These distances are longer than those in pnao complexes of Co^{III}, Cu^{II}, Pd^{II} and Rh^{III} (2.43–2.48 Å) as well as in bnao complexes of Ni^{II} and Cu^{II} (*ca.* 2.42 Å). The presence of a nitrido ligand would contribute to the formation of a longer intramolecular hydrogen bond, because the strong π donation weakens the technetium–amine nitrogen bonding in the complexes. Of these three nitridotechnetium complexes differing in the carbon chain length of the ligands, the pnao complex with the shortest carbon chain has the longest intramolecular O···O distance. This is explained in terms of strain on the pnao moiety in the complex caused by the relatively short propylene chain. The strain would be rather small in the bnao and pentao complexes.

Experimental

Materials

Potassium pertechnetate-^{99}Tc from Radiochemical Centre Amersham was dissolved in an aqueous ammonium solution. The ligands Hpnao, Hbnao and Hpentao were prepared as reported in the literature.[20,21]

Physical measurements

Elemental analyses for carbon, hydrogen and nitrogen were made with a Yanaco CHN CORDER MT-3 analyzer. Technetium contents were determined by radioactivity measurements with a liquid scintillation counter (Aloka LSC-5100). Infrared spectra were taken with a Shimadzu IR-470 spectrophotometer using KBr pellets, ^{1}H and ^{13}C NMR spectra by a JEOL GX 400 with acetonitrile-d_3 solution.

Preparation of complexes

[TcN(pnao)(H_2O)][BPh_4] 1. The starting material [TcNCl_2(PPh_3)$_2$] (70 mg, 0.099 mmol), prepared as described,[22] was dissolved in a mixture (20 cm^3) of CH_2Cl_2 and ethanol (3:1). The pink solution was gently heated to 40 °C, and then 40 mg of Hpnao (0.15 mmol) in 10 cm^3 of ethanol were added. The solution was stirred for 30 min until it turned yellow, and then evaporated to dryness with a rotary evaporator. The residue was dissolved in water to remove PPh_3. Addition of an aqueous $NaBPh_4$ solution gave a yellow precipitate which was filtered

Table 4 Crystallographic data for [TcN(bnao)(H_2O)][BPh_4] **2** and [TcN(pentao)(H_2O)][BPh_4] **3**

	2	**3**·$(CH_3)_2CO$
Formula	$C_{38}H_{51}BN_5O_3Tc$	$C_{39}H_{53}BN_5O_3Tc\cdot(CH_3)_2CO$
M	733.66	805.77
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	9.683(3)	9.986(5)
b/Å	24.944(6)	30.636(2)
c/Å	15.149(2)	13.967(3)
β/°	97.39(3)	95.24(3)
V/Å^3	3628(1)	4254(2)
Z	4	4
μ/cm^{-1}	35.29 (Cu-Kα)	3.80 (Mo-Kα)
No. reflections measured	6397	10499
No. unique data	6154 ($R_{int} = 0.046$)	9946 ($R_{int} = 0.036$)
No. data used with $I > n\sigma(I)$	4211 ($n = 3$)	5599 ($n = 4$)
R	0.046	0.034
R'	0.042	0.036

off and washed with water and ethanol. Recrystallization from an acetone–ethanol solution gave yellow crystals of [TcN(pnao)(H_2O)][BPh_4] **1** (53 mg, 74%) (Found: C, 61.6; H, 7.10; N, 9.75; Tc, 13.9. $C_{37}H_{49}BN_5O_3Tc$ requires C, 61.6; H, 6.84; N, 9.71; Tc, 13.7%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 2315 (OH), 1576 (C=N) and 1061 ($Tc{\equiv}N$). δ_H(CD_3CN) 19.6 (br, O–H···O), 3.70 (2 H, dd, CH_2), 2.967 (2 H, qd, CH_2), 2.37 (2 H, m, CH_2), 2.150 (6 H, s, $2CH_3$), 1.648 (6 H, s, $2CH_3$) and 1.524 (6 H, s, $2CH_3$). δ_C(CD_3CN) 50.670 (CH_2), 30.421 (CH_2), 24.512 (CH_3), 19.333 (CH_3) and 12.555 (N=C–*C*H_3).

[TcN(bnao)(H_2O)][BPh_4] 2. A mixture of [$TcNCl_2(PPh_3)_2$] (73 mg, 0.10 mmol) and Hbnao (40 mg, 0.15 mmol) in CH_2Cl_2–ethanol (3 : 1) was stirred at 40 °C for 30 min until it turned yellow, then evaporated to dryness with a rotary evaporator. The residue was dissolved in water to remove PPh_3. The yellow precipitate given by addition of an aqueous solution of $NaBPh_4$ was filtered off and washed with water and ethanol. Crystals of [TcN(bnao)(H_2O)][BPh_4] **2** were obtained by recrystallization from an acetone solution (59 mg, 79%) (Found: C, 62.1; H, 7.19; N, 9.37; Tc, 13.2. $C_{38}H_{51}BN_5O_3Tc$ requires C, 62.0; H, 6.99; N, 9.52; Tc, 13.5%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1758 (OH), 1577 (C=N) and 1048 ($Tc{\equiv}N$). δ_H(CD_3CN) 19.3 (br, O–H···O), 3.52 (4H, m, $2CH_2$), 2.153 (6 H, s, $2CH_3$), 1.71 (2 H, m, CH_2), 1.606 (6 H, s, $2CH_3$), 1.487 (6 H, s, $2CH_3$) and 1.45 (2 H, m, CH_2). δ_C(CD_3CN) 50.002 (CH_2), 26.854 (CH_2), 23.742 (CH_3), 19.439 (CH_3) and 12.912 (N=C–*C*H_3).

[TcN(pentao)(H_2O)][BPh_4]·$(CH_3)_2CO$ 3·$(CH_3)_2CO$. A mixture of [$TcNCl_2(PPh_3)_2$] (97 mg, 0.14 mmol) and Hpentao (0.21 mmol) in CH_2Cl_2–ethanol (3 : 1) was stirred at 40 °C for 2 h until it turned yellow, and then evaporated to dryness. The residue was dissolved in water, and the yellow solution charged on a cation exchange column (Sephadex C-25). An aqueous solution of $NaBPh_4$ was added to the yellow fraction eluted with 0.1 mol dm^{-3} NaCl solution. The yellow precipitate was filtered off and washed with water and ethanol. Crystals of [TcN(pentao)(H_2O)][BPh_4]·$(CH_3)_2CO$ were obtained by recrystallization from an acetone solution (34 mg, 31%) (Found: C, 62.4; H, 7.36; N, 8.62; Tc, 12.5. $C_{42}H_{59}BN_5O_4Tc$ requires C, 62.5; H, 7.36; N, 8.67; Tc, 12.3%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1770 (OH), 1578 (C=N) and 1055 ($Tc{\equiv}N$). δ_H(CD_3CN) 19.4 (br, O–H···O), 3.581 (2 H, m, CH_2), 3.367 (2 H, m, CH_2), 2.158 (6 H, s, $2CH_3$), 1.954 (2 H, m, CH_2), 1.756 (2 H, m, CH_2), 1.602 (6 H, s, $2CH_3$), 1.57 (2 H, m, CH_2) and 1.525 (6 H, s, $2CH_3$). δ_C(CD_3CN) 51.770 (CH_2), 30.087 (CH_2), 23.636 (CH_3), 19.075 (CH_3), 18.908 (CH_2) and 13.011 (N=C–*C*H_3).

Crystal structure determination

The crystal structure determination of [TcN(pnao)(H_2O)][BPh_4]·$2C_2H_5OH$ **1**·$2C_2H_5OH$ has been previously reported.[12]

[TcN(bnao)(H_2O)][BPh_4] and [TcN(pentao)(H_2O)][BPh_4]·$(CH_3)_2CO$. Single crystals of [TcN(bnao)(H_2O)][BPh_4] **2** and [TcN(pentao)(H_2O)][BPh_4]·$(CH_3)_2CO$ **3**·$(CH_3)_2CO$ suitable for X-ray analysis were grown by slow evaporation of acetone solutions. The X-ray diffraction data were measured on a Rigaku AFC5R diffractometer with graphite-monochromated Cu-Kα radiation ($\lambda = 1.54178$ Å) for **2** and Mo-Kα radiation ($\lambda = 0.71069$ Å) for **3**. The data were collected at 13 ± 1 °C using the ω–2θ scan technique to the maximum 2θ values of 126.2° for **2** and 55.0° for **3**. The crystallographic data are listed in Table 4.

The structures of these two complexes were solved by the direct method (SIR 92) and the expanded using the Fourier technique (DIRDIF 94). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined for **3**. The neutral atom scattering factors were taken from ref. 25. Anomalous dispersion effects were included in F_c;[26] the values for $\Delta f'$ and $\Delta f''$ were those of ref. 27. All of the calculations were made using the TEXSAN[28] crystallographic software package.

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See http://www.rsc.org/suppdata/dt/1999/209/ for crystallographic files in .cif format.

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