electron count is $N = 2T = 2 \times 161 = 322$. This is in agreement with the observed electron count of $N_{obs} = 10 \times 2$ (phosphine) $+ 25 \times 11$ (metal) $+ 2 \times 1$ (terminal Br) $+ 2 \times 3$ (doubly bridging Br) $+ 4 \times 5$ (triply bridging Br) $- 1$ (monocation) $= 322$.

While the agreement between theory and experiment is pleasingly good, it should be pointed out that the four triply bridging bromine ligands are highly asymmetric (see section III.D for a detailed discussion) and hence can also be considered as doubly bridging. The observed electron count for such a description (viz., with six doubly bridging and two terminal Br ligands) will become $N_{obs} = 322 - 4 \times 2 = 314$. This latter value is 8 electrons below that predicted by the C^2 model, but in good agreement with the shell model[16] of $N = 2T = 2(6G + K) = 2(6 \times 25 + 7) = 2 \times 157 = 314$, where G is the total number of atoms and K is the related to the B value of the "center" of the cluster.

We conclude that the "true" electron count for cluster **1** may lie somewhere between 314 and 322, with the former value representing a cluster with six doubly bridging halogens and the latter value corresponding to a cluster with two doubly bridging and four triply bridging halogen ligands. It should be emphasized, however, that the shell model, which is valid only for close-packed clusters, tends to give lower electron counts than the C^2 model.

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Supplementary Material Available: For $[(p\text{-Tol}_3P)_{10}Au_{13}Ag_{12}Br_8](PF_6)\cdot 10EtOH$, full listing of anisotropic thermal parameters (Table A), positional and thermal parameters with the refined occupancy factors for solvent atoms (Table B), interatomic distances (Table C), bond angles (Table D), least-squares planes (Table E), and intra- and intermolecular interactions (Table F) (29 pages); a listing of observed and calculated structure factors (Table G) (98 pages). Ordering information is given on any current masthead page.

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Synthesis of Technetium(V)–Nitrido Complexes with Chelating Amines: A Novel Class of Monocationic, Octahedral Complexes Containing the $[Tc{\equiv}N]^{2+}$ Core. Crystal Structures of $[TcN(en)_2Cl]^+$ (en = Ethylenediamine) and $[TcN(tad)Cl]^+$ (tad = 1,5,8,12-Tetraazadodecane)

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A novel class of monocationic complexes containing the $[Tc{\equiv}N]^{2+}$ functional moiety is reported. The complexes are prepared by substitution reactions on the starting compound $TcNCl_2(PPh_3)_2$ with neutral, bidentate, and tetradentate chelating amines or by reduction with KBH_4 of the complex $[TcNCl_4]^-$ in the presence of the same ligands. The complexes have been characterized by elemental analyses, IR and ^1H NMR spectroscopy, conductivity, and magnetic susceptibility measurements. All the complexes possess a distorted octahedral geometry and, thus, constitute the first homogeneous class of stable, octahedral technetium(V)–nitrido complexes having a sixth, charged ligand in a position trans to the $Tc{\equiv}N$ multiple bond. The crystal structures of two members of this class, namely the complexes $[TcN(en)_2Cl]^+$ (**1**) (en = ethylenediamine) and $[TcN(tad)Cl]^+$ (**2**) (tad = 1,5,8,12-tetraazadodecane), have been determined. The complexes have a distorted octahedral structure, with a Cl^- atom in a position trans to the $Tc{\equiv}N$ group and two bidentate en ligands in **1** or one tetradentate tad ligand in **2** in the plane normal to the $N{\equiv}Tc{-}Cl$ axis. Compound **1** crystallizes in the space group $P2_1/n$, with $a = 9.316$ (1) Å, $b = 12.404$ (1) Å, $c = 24.367$ (5) Å, $\beta = 93.76$ (1)°, and $V = 2809.7$ (7) Å^3 with $Z = 4$, for 4565 observed reflections with $I \geq 3\sigma(I)$; the $Tc{\equiv}N$ bond length is 1.603 (3) Å, while the length of the $Tc{-}Cl$ bond trans to $Tc{\equiv}N$ is 2.7320 (8) Å, which is the longest $Tc{-}Cl$ bond distance ever observed in technetium chemistry. Compound **2** crystallizes in space group $Pna2_1$ with $a = 9.966$ (2) Å, $b = 31.203$ (10) Å, $c = 9.706$ (4) Å, and $V = 3018$ (2) Å^3 with $Z = 4$, for 2991 observed reflections with $I \geq 3\sigma(I)$; the $Tc{\equiv}N$ bond length is 1.626 (6) Å, while the length of the $Tc{-}Cl$ bond trans to $Tc{\equiv}N$ is 2.663 (2) Å.

Introduction

In recent years, it was suggested by Deutsch that atomic or molecular species carrying a positive charge would have a preferential localization in myocardium tissues.[4] Following this hypothesis, a number of monocationic complexes of ^{99m}Tc have been prepared by different groups, with the aim to obtain a ^{99m}Tc-imaging agent for myocardial perfusion.

Deutsch and co-workers reported Tc^{3+} and Tc^+ complexes of the type $[Tc^{III}(dp)_2Cl_2]^+$ and $[Tc^I(dp)_3]^+$ (dp = bidentate diphosphine),[5] while Tc^+ complexes with substituted isocyanide (RCN), $[Tc(RCN)_6]^+$ were described by Davison and co-workers.[6]

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A Tc^+ complex of formula $\{Tc[P(OCH_3)_3]_6\}^+$ has been reported by Dean.[7]

Although many of these complexes showed a high degree of localization in the myocardium of some animal species, generally their uptake by human myocardium was negligible.[8] Only a few members of the class of isocyanide complexes showed pronounced myocardial uptake in both animals and humans to be useful as imaging agents.[9]

All the monocationic complexes cited above contain the technetium ion in a relatively low oxidation state (+3 or +1), and thus, their preparations require a convenient procedure to reduce the pertechnetate ion, $[TcO_4]^-$, to these lower oxidation numbers.[5a,6d] In such situations the choice of the ligands becomes crucial in order to stabilize the electronic configuration of the metal.

In higher oxidation states of technetium, the ligands play a less important role in stabilizing the metal electronic configuration. In fact, it has been observed that the chemistry of technetium in the +5 oxidation state is largely dominated by the properties and stabilities of monoxo, $[Tc{=}O]^{3+}$, and *trans*-dioxo, $[O{=}Tc{=}O]^+$, groups, and that the role of the ligands is only to determine the preference between these two cores.[10]

Only very few examples of monocationic Tc(V) complexes are presently known,[5d,10] the most important being the *trans*-dioxocomplexes $[TcO_2(en)_2]^+$ (en = ethylenediamine),[10h] $[TcO_2(DMPE)_2]^+$ [DMPE = 1,2-bis(dimethylphosphino)ethane],[5d] $[TcO_2(cyclam)]^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane),[10i] and $[TcO_2(py)_4]^+$.[10l]

These complexes did not show any myocardial uptake both in animals and in humans.[8a,11]

Table I. Crystallographic Data for $[TcN(en)_2Cl][B(C_6H_5)_4]$ (**1**) and $[TcN(tad)Cl][B(C_6H_5)_4]$ (**2**)

	1	2
formula	$[TcN_5C_{28}H_{36}BCl]$	$[TcN_5C_{32}H_{42}BCl]$
a, Å	9.316 (1)	9.966 (2)
b, Å	12.404 (1)	31.203 (10)
c, Å	24.367 (5)	9.706 (4)
β, deg	β = 93.76 (1)	
V, $Å^3$	2809.7 (7)	3018 (2)
Z	4	4
M	587.9	641.99
space group	$P2_1/n$	$Pna2_1$
T, °C	22	22
λ, Å	0.71069	0.71069
ρ_{obsd}, g cm^{-3}	1.38	1.42
ρ_{calcd} g cm^{-3}	1.39	1.41
μ, cm^{-1}	6.2	5.7
transm coeff		0.77-1.0
$R(F_o)$	0.028	0.050
$R_w(F_o^2)$	0.040	0.062

Recently, the advent of suitable synthetic procedures for the preparation of the nitrido complexes $[TcNCl_4]^-$ and $[TcNCl_2(PPh_3)_2]$[12] has allowed the investigation of the properties and stabilities of complexes containing the $[Tc^V{\equiv}N]^{2+}$ functional moiety, which can be thought as being formed through the bonding between the hard Tc^{5+} acid and what is considered the strongest known base, N^{3-}. The formation of the $[Tc{\equiv}N]^{2+}$ core may constitute an alternative route for the preparation of monocationic complexes of technetium in the +5 oxidation state.[12c]

In this paper, we will report the synthesis and characterization of a novel class of monocationic technetium(V)-nitrido complexes with chelating amines, and the crystal structures of two members of this class, namely $[TcN(en)_2Cl]^+$ (en = ethylenediamine) (**1**) and $[TcN(tad)Cl]^+$ (tad = 1,5,8,12-tetraazadodecane) (**2**). Previously, a technetium-nitrido complex with ethylenediamine has been prepared at the tracer level but characterized only by in vitro parameters.[12d] The present work represents, therefore, the first structural characterization of this type of complexes. On the basis of structural data, a comparison between the molecular geometry of the nitrido complexes and the analogous oxo and *trans*-dioxo complexes will be also given. Neutral and cationic technetium(V)-nitrido complexes with cyclam and cyclam-derived ligands will be described in a subsequent paper.[13]

Experimental Section

General Information. Unless otherwise noted, all chemicals were of reagent grade and were used without purification. Aqueous $NH_4[^{99}TcO_4]$ was obtained from Radiochemical Centre, Amersham, England. Solid samples were obtained by concentration and filtration of its ammonia solutions. ^{99}Tc is a weak β-emitter (0.292 keV; $t_{1/2} = 2.12 \times 10^5$ years). All manipulations were carried out in a laboratory approved for low-level radioactivity with a monitored hood and gloveboxes. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission, but normal radiation safety procedures must be used

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at all times to prevent contamination.

The complexes $[TcNCl_4]^-$ and $[TcNCl_2(PPh_3)_2]$ were prepared as reported in literature.[12a]

Ethylenediamine and 1,3-propanediamine were purchased from Fluka Chemie AG, while 1,5,8,12-tetraazadodecane was obtained from Strem Chemicals, Inc.

IR spectra were recorded on a Perkin-Elmer 599 grating spectrometer using KBr pellets. ^1H NMR spectra of CH_3CN solutions were collected on a Varian Gemini-300 spectrometer with $SiMe_4$ as the internal standard, while magnetic susceptibility measurements of CH_2Cl_2 solutions by the Evans method,[14] were obtained on the same apparatus. Elemental analyses were performed on a Carlo Erba elemental analyzer, Model 1106. The elemental analyses for the radioactive technetium were carried out on a Packard liquid-scintillation instrument, Model TRI-CARB 300 C, with Insta-gel as scintillator, after dissolution of the samples in hydrogen peroxide–nitric acid solutions. Conductivity measurements were performed in CH_3NO_2 solutions with use of an Amel Model 134 conductivity meter at $T = 20.5$ °C.

Preparation of $[TcN(L)_2Cl][B(C_6H_5)_4]$ [L = Ethylenediamine (en), 1,3-Propanediamine (pn)] and $[TcN(tad)Cl][B(C_6H_5)_4]$ (tad = 1,5,8,12-Tetraazadodecane). All of the complexes were prepared with the same general procedure. A 0.2-g sample of $[TcNCl_2(PPh_3)_2]$ (0.28 mmol) was dissolved in 40 mL of a CH_2Cl_2/EtOH (3:1) mixture, and the resulting pink solution was slightly heated until the temperature was 40 °C. Then, 0.4 mL of a 1.6 M solution of the appropriate ligand in EtOH (0.64 mmol) was added dropwise to the reaction solution until its color became light yellow. The heating was then turned off, and an ethanolic solution (5 mL) containing 0.1 g of $NaB(C_6H_5)_4$ was added. Cooling the resulting solution caused the precipitation of light yellow crystals of the final product, which were washed with EtOH and Et_2O. (Yield = 90%.) Recrystallization was carried out from CH_2Cl_2/EtOH.

If the reaction solution was left to evaporate in air, without adding $NaB(C_6H_5)_4$, the corresponding chloride salts $[TcN(L)_2Cl]Cl$ and $[TcN(tad)Cl]Cl$ were isolated as thin, tiny crystals, but were unsuitable for X-ray diffraction.

The same complexes were also obtained, as chloride salts, by starting with an ethanolic solution (40 mL) of the complex $[TcNCl_4][As(C_6H_5)_4]$ (0.6 g, 0.93 mmol) and following the same procedure described above, but without adding $NaB(C_6H_5)_4$. The yield (5%) for all the final complexes was, however, lower than that obtained with the previously described method. The addition to the reaction solution of 0.2 g of KBH_4 dissolved in 10 mL of H_2O increased the yield up to 50%. All of the complexes are stable in the solid state.

The tetraphenylborate salts of the complexes are soluble in CH_2Cl_2, $CHCl_3$, CH_3CN, and acetone, slightly soluble in EtOH, MeOH, and H_2O, and insoluble in Et_2O, pentane, benzene, and CCl_4. The chloride salts are soluble in H_2O and in common polar organic solvents and insoluble in pentane, benzene, and CCl_4.

Collection of X-ray Data. Intensity data for the complexes $[TcN(en)_2Cl][B(C_6H_5)_4]$ (**1**) and $[TcN(tad)Cl][B(C_6H_5)_4]$ (**2**) were collected on an Enraf-Nonius CAD4 diffractometer with monochromated Mo Kα radiation and $\omega/2\theta$ scan technique, using prismatic crystals of dimensions 0.24 × 0.33 × 0.36 mm for **1** and prismatic crystals of dimensions 0.26 × 0.44 × 0.50 mm for **2**. Cell parameters were obtained from least-squares refinement of the setting angles of 25 centered reflections in the range $9 \leq \theta \leq 15°$. Crystal data are given in Table I. Intensities were corrected for Lorentz and polarization for both compounds and for absorption for compound **2** (transmission factor in the range 0.77–1). Scattering factors and anomalous dispersion parameters were taken from ref 24.

Table II. Positional (×10^4; ×10^3 for H Atoms) and Thermal (Å^2) Parameters with Esd's in Parentheses for the Cation of Compound **1**

	x	y	z	B_{eq}
Tc	1577.9 (2)	986.1 (2)	1060.9 (1)	2.705 (3)
Cl	−981.6 (7)	990.8 (6)	445.7 (3)	3.76 (1)
N(1)	3097 (3)	1002 (2)	1410 (1)	4.33 (5)
N(2)	1251 (3)	2714 (2)	1023 (1)	3.99 (5)
N(3)	2339 (2)	1341 (2)	262.8 (9)	3.91 (5)
N(4)	199 (2)	587 (2)	1705.4 (8)	3.33 (4)
N(5)	1352 (2)	−723 (2)	942.0 (9)	3.51 (5)
C(1)	2182 (4)	3166 (3)	605 (1)	5.18 (8)
C(2)	2030 (4)	2480 (3)	99 (1)	5.18 (7)
C(3)	−396 (3)	−506 (3)	1628 (1)	4.30 (6)
C(4)	715 (4)	−1230 (3)	1418 (1)	4.79 (7)
H(21N)	38 (3)	280 (3)	94 (1)	6.0 (8)
H(22N)	148 (4)	310 (3)	133 (1)	7.3 (9)
H(31N)	327 (3)	121 (2)	27 (1)	3.8 (6)
H(32N)	201 (3)	94 (2)	3 (1)	4.5 (7)
H(41N)	64 (3)	63 (2)	203 (1)	3.5 (6)
H(42N)	−50 (3)	104 (2)	171 (1)	4.6 (7)
H(51N)	211 (3)	−102 (2)	89 (1)	4.9 (7)
H(52N)	90 (3)	−80 (2)	66 (1)	2.7 (5)
H(11C)	316 (4)	317 (3)	74 (1)	7.2 (9)
H(12C)	198 (3)	395 (2)	54 (1)	5.2 (8)
H(21C)	266 (3)	267 (2)	−14 (1)	6.0 (8)
H(22C)	91 (4)	251 (3)	−7 (1)	8 (1)
H(31C)	−78 (3)	−79 (2)	198 (1)	4.7 (7)
H(32C)	−122 (4)	−44 (3)	134 (1)	6.5 (8)
H(41C)	29 (3)	−187 (3)	127 (1)	5.9 (8)
H(42C)	145 (4)	−137 (3)	171 (2)	8 (1)

Table III. Positional (×10^4) and Thermal (Å^2) Parameters with Esd's in Parentheses for the Cation of Compound **2**

	x	y	z	B_{eq}
Tc	2449.3 (5)	1294.7 (1)	0	2.992 (7)
Cl	4034 (2)	1793.5 (6)	1520 (2)	4.31 (4)
N(1)	1561 (6)	976 (2)	−962 (6)	3.8 (1)
N(2)	4326 (6)	984 (2)	−478 (8)	4.7 (1)
N(3)	2288 (5)	957 (2)	1924 (6)	3.2 (1)
N(4)	774 (5)	1641 (2)	864 (6)	3.2 (1)
N(5)	2840 (7)	1790 (2)	−1511 (7)	5.6 (2)
C(1)	4411 (7)	530 (3)	−37 (14)	7.2 (2)
C(2)	4165 (8)	460 (3)	1499 (13)	6.1 (2)
C(3)	2735 (8)	512 (2)	1974 (10)	4.8 (2)
C(4)	914 (7)	1031 (3)	2428 (8)	4.0 (1)
C(5)	624 (6)	1505 (2)	2344 (7)	3.7 (1)
C(6)	694 (7)	2105 (2)	696 (9)	4.0 (2)
C(7)	909 (7)	2246 (2)	−755 (9)	4.3 (2)
C(8)	2329 (8)	2230 (2)	−1282 (10)	5.0 (2)

Solution and Refinement of the Structures. In both structures, the positions of the Tc atom were located from Patterson synthesis. All other non-H atoms were located in the subsequent Fourier maps. H atoms of the cation of compound **1** were found in difference maps calculated after few cycles of isotropic refinement. All H atoms of compound **2** and H atoms of the anion of compound **1** were given calculated positions with C–H bond distances of 0.95 Å and fixed isotropic B's of 5.0 Å^2. Finally, the structures were refined by full-matrix least-squares techniques using anisotropic temperature factors for all non-H atoms and isotropic ones for the hydrogens of the cation in compound **1**.

Weights were applied according to the scheme given in Table I. Final positional and equivalent isotropic vibrational parameters are reported in Tables II and III for compounds **1** and **2** respectively. All calculations were done using the SDP and PARST systems of programs.[25,26]

Results

Synthesis and Properties. The complexes $[TcN(L)_2Cl][B(C_6H_5)_4]$ [L = ethylenediamine (en), 1,3-propanediamine (pn)] and $[TcN(tad)Cl][B(C_6H_5)_4]$ (tad = 1,5,8,12-tetraazadodecane) are easily prepared from the starting square-pyramidal complex

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Table IV. Bond Distances (Å) and Interatomic Angles (deg) for the $[\mathrm{TcN(en)_2Cl}]^+$ Cation with Esd's in Parentheses

Tc–Cl	2.7320 (8)	N(2)–C(1)	1.490 (4)
Tc–N(1)	1.603 (3)	N(3)–C(2)	1.491 (4)
Tc–N(2)	2.166 (2)	N(4)–C(3)	1.472 (4)
Tc–N(3)	2.159 (2)	N(5)–C(4)	1.478 (4)
Tc–N(4)	2.151 (2)	C(1)–C(2)	1.497 (4)
Tc–N(5)	2.148 (2)	C(3)–C(4)	1.486 (5)
N–H (av)	0.84 [4]	C–H (av)	0.98 [6]
Cl–Tc–N(1)	178.53 (9)	N(3)–Tc–N(4)	162.2 (1)
Cl–Tc–N(2)	81.91 (7)	N(3)–Tc–N(5)	96.6 (1)
Cl–Tc–N(3)	80.31 (6)	N(4)–Tc–N(5)	79.2 (1)
Cl–Tc–N(4)	81.93 (5)	Tc–N(2)–C(1)	108.4 (2)
Cl–Tc–N(5)	81.60 (6)	Tc–N(3)–C(2)	111.4 (2)
N(1)–Tc–N(2)	97.3 (1)	Tc–N(4)–C(3)	110.9 (2)
N(1)–Tc–N(3)	98.3 (1)	Tc–N(5)–C(4)	110.8 (2)
N(1)–Tc–N(4)	99.4 (1)	N(2)–C(1)–C(2)	108.7 (3)
N(1)–Tc–N(5)	99.2 (1)	N(3)–C(2)–C(1)	108.2 (2)
N(2)–Tc–N(3)	79.2 (1)	N(4)–C(3)–C(4)	109.6 (3)
N(2)–Tc–N(4)	99.8 (1)	N(5)–C(4)–C(3)	109.7 (2)
N(2)–Tc–N(5)	163.4 (1)		

Table V. Bond Distances (Å) and Interatomic Angles (deg) with Esd's in Parentheses for the $[\mathrm{TcN(tad)Cl}]^+$ Cation

Tc–Cl	2.663 (2)	N(4)–C(5)	1.505 (9)
Tc–N(1)	1.626 (6)	N(4)–C(6)	1.459 (9)
Tc–N(2)	2.157 (6)	N(5)–C(8)	1.481 (9)
Tc–N(3)	2.150 (6)	C(1)–C(2)	1.527 (18)
Tc–N(4)	2.158 (6)	C(2)–C(3)	1.507 (12)
Tc–N(5)	2.166 (7)	C(4)–C(5)	1.509 (11)
N(2)–C(1)	1.482 (12)	C(6)–C(7)	1.491 (12)
N(3)–C(3)	1.459 (9)	C(7)–C(8)	1.506 (11)
N(3)–C(4)	1.472 (9)		
Cl–Tc–N(1)	176.6 (2)	Tc–N(3)–C(3)	118.2 (5)
Cl–Tc–N(2)	82.4 (2)	Tc–N(3)–C(4)	106.3 (4)
Cl–Tc–N(3)	81.4 (2)	C(3)–N(3)–C(4)	115.0 (6)
Cl–Tc–N(4)	87.2 (2)	Tc–N(4)–C(5)	107.8 (4)
Cl–Tc–N(5)	81.5 (2)	Tc–N(4)–C(6)	119.7 (4)
N(1)–Tc–N(2)	94.2 (3)	C(5)–N(4)–C(6)	112.4 (5)
N(1)–Tc–N(3)	99.1 (3)	Tc–N(5)–C(8)	119.9 (5)
N(1)–Tc–N(4)	96.2 (2)	N(2)–C(1)–C(2)	114.2 (8)
N(1)–Tc–N(5)	98.4 (3)	C(1)–C(2)–C(3)	115.8 (9)
N(2)–Tc–N(3)	91.8 (2)	N(3)–C(3)–C(2)	112.4 (6)
N(2)–Tc–N(4)	168.3 (2)	N(3)–C(4)–C(5)	108.3 (6)
N(2)–Tc–N(5)	91.1 (3)	N(4)–C(5)–C(4)	108.0 (6)
N(3)–Tc–N(4)	81.4 (2)	N(4)–C(6)–C(7)	113.0 (6)
N(3)–Tc–N(5)	162.0 (2)	C(6)–C(7)–C(8)	116.5 (7)
N(4)–Tc–N(5)	92.6 (2)	N(5)–C(8)–C(7)	113.9 (5)
Tc–N(2)–C(1)	114.6 (5)		

$[\mathrm{Tc^{V}NCl_2(PPh_3)_2}]$, by simple substitution reactions in $\mathrm{CH_2Cl_2/EtOH}$ solutions, in the presence of $\mathrm{NaB(C_6H_5)_4}$.

When no counterion is added, the corresponding chloride salts $[\mathrm{TcN(L)_2Cl}]\mathrm{Cl}$ and $[\mathrm{TcN(tad)Cl}]\mathrm{Cl}$ are isolated. Since no excess chloride is added to the preparation, the reaction is formally stoichiometric and the isolation of 6-coordinate, trans-Cl complexes implies that in this system the 6-coordinate species is much more stable than the 5-coordinate species.

A related synthetic route uses the complex $[\mathrm{Tc^{VI}NCl_4}]^-$ as the starting reagent. With this latter method, the yields in the final complexes are very low (5%) as compared to those obtained with the former method (90%). This indicates that reduction of the $[\mathrm{Tc^{VI}}{\equiv}\mathrm{N}]^{3+}$ core to the $[\mathrm{Tc^{V}}{\equiv}\mathrm{N}]^{2+}$ core[12a,15] is a preliminary condition in order to obtain the final complexes. Addition of $\mathrm{KBH_4}$, in fact, drastically increases the yield for the products up to 50%, as a result of the more efficient reduction of the complex $[\mathrm{TcCl_4}]^-$.

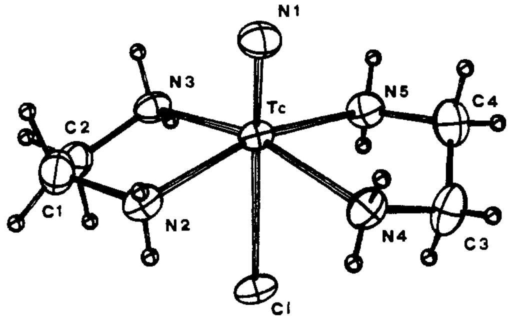

Figure 1. ORTEP[27] view of the $[\mathrm{TcN(en)_2Cl}]^+$ cation showing the thermal ellipsoids at 30% probability.

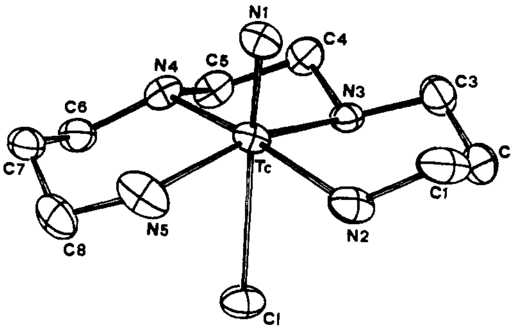

Figure 2. ORTEP[27] view of the $[\mathrm{TcN(tad)Cl}]^+$ cation showing the thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity.

The formulation of the complexes is supported by elemental analyses, conductivity, and magnetic susceptibility measurements, IR and ^{1}H NMR spectra (Table VI).

Conductivity data show that all the complexes carry a positive charge,[16] while magnetic susceptibility data reveal that they are diamagnetic, supporting the conclusion that the technetium atom is in a d^2 closed-shell configuration characteristic of the $[\mathrm{Tc^{V}}{\equiv}\mathrm{N}]^{2+}$ core.[17]

IR spectra (Table VI) are similar to those reported for other amine complexes,[10h,18] and show the stretching of the N–H bond in the interval 3100–3300 cm^{-1}. The $\nu(\mathrm{Tc{\equiv}N})$ is found in the range 1085–1080 cm^{-1} for all the complexes. This frequency is comparable with those recently reported for other technetium(V)-nitrido complexes.[15] No $\nu(\mathrm{Tc{-}Cl})$ stretchings were observed in the 350–250-cm^{-1} region, and this is consistent with the very long Tc–Cl bond distance found in these complexes (see below).

^{1}H NMR spectra of the complexes are difficult to interpret due to the presence of poorly resolved multiplets. Attributions were given only for the complex $[\mathrm{TcN(en)_2Cl}][\mathrm{B(C_6H_5)_4}]$, and these are shown in Table VI.

Crystal Structures of $[\mathrm{TcN(en)_2Cl}]^+$ (1) and $[\mathrm{TcN(tad)Cl}]^+$ (2). Bond distances and angles for the cations of the two structures are given in Table IV and V, for compounds **1** and **2**, respectively,

Table VI. Elemental Analyses[a] and IR, ^{1}H NMR, Magnetic Susceptibility,[b] and Conductivity Data for the Complexes[c]

complex[d]	% C	% H	% N	% Tc	ν(N—H)	ν(C—N)	ν(Tc≡N)	δ(NH)[e]	$\delta(\mathrm{CH_2})$[e]	Λ (concn)
$[\mathrm{TcN(en)_2Cl}][\mathrm{B(C_6H_5)_4}]$	57.6	6.2	11.8	17.4	3240	1070	1085	3.3 (b)	3.0 (m)	99.16 (1.20×10^{-4})
	(57.2)	(6.2)	(11.9)	(16.8)	3280			3.8 (b)		137.32 (6.19×10^{-5})
$[\mathrm{TcN(pn)_2Cl}][\mathrm{B(C_6H_5)_4}]$	58.0	6.7	11.3	17.1	3235	1070	1080			95.30 (1.47×10^{-4})
	(58.4)	(6.5)	(11.4)	(16.1)	3280					136.40 (7.36×10^{-5})
$[\mathrm{TcN(tad)Cl}][\mathrm{B(C_6H_5)_4}]$	60.6	7.2	11.0	16.3	3240	1060	1085			104.83 (1.45×10^{-4})
	(60.0)	(6.9)	(10.9)	(15.5)						134.72 (7.20×10^{-5})

[a] Calculated values are in parentheses. [b] All of the complexes in the table are diamagnetic. [c] IR frequencies in cm^{-1}; ^{1}H NMR shifts relative to $\mathrm{Si(CH_3)_4}$; conductivity values in Ω^{-1} cm^2 mol^{-1}, at 20.5 °C in nitromethane solutions (molar concentrations given in parentheses). [d] Ligand abbreviations are defined in the text. [e] b = broad; m = multiplet.

Table VII. Puckering Coordinates According to Cremer and Pople[28]

ring	φ, deg	θ, deg	Q, Å	conformn
	Compound **1**			
R_1: Tc–N(2)–C(1)–C(2)–N(3)	78.1 (3)		0.452 (3)	$^3E/^3T_4$
R_2: Tc–N(4)–C(3)–C(4)–N(5)	89.6 (3)		0.402 (3)	$^3T_4$
	Compound **2**			
R_1: Tc–N(2)–C(1)–C(2)–C(3)–N(3)	−8 (4)	169.7 (7)	0.578 (9)	$^4C_1$
R_2: Tc–N(3)–C(4)–C(5)–N(4)	−100.1 (6)		0.487 (7)	E_3
R_3: Tc–N(4)–C(6)–C(7)–C(8)–N(5)	174 (2)	31.5 (7)	0.518 (8)	$^1C_4$

and ORTEP[27] views of the two structures with the atom-labeling scheme are shown in Figures 1 and 2.

Compound 1. The crystal structure consists of couples of independent *trans*-$[Tc^VN(en)_2Cl]^+$ cations and $[B(C_6H_5)_4]^-$ anions. The coordination around the Tc atom is approximately octahedral with two molecules of ethylenediamine on the basal plane and a Cl^- ligand at the apical position trans to the nitrido group. The four basal N atoms lie approximately on a plane, and the Tc atom is displaced from this plane by 0.3231 (3) Å toward the N(1) atom.

The conformations of the two bonded ethylenediamine molecules are slightly different and can be described by using the puckering parameters[28,29] of the two five-membered rings R_1 = [Tc, N(2), C(1), C(2), N(3)] and R_2 = [Tc, N(4), C(3), C(4), N(5)], reported in Table VII. They indicate that R_1 cycle adopts a mixed $^3E/^3T_4$ envelope/twisted conformation, while R_2 cycle adopts an almost perfect $^3T_4$ twisted conformation (Table VII). Such a conformational differences are not uncommon; they have been found, for instance, in the *trans*-$[Tc^VO_2(en)_2]^+$ compound.[10h]

Compound 2. The crystal is built up of discrete $[Tc^VN(tad)Cl]^+$ and $[B(C_6H_5)_4]^-$ units packed together by means of van der Waals interactions. The coordination around the central Tc atom is distorted octahedral, with the four N atoms of the tad ligand in the equatorial plane and the nitrido and Cl^- anions at the apical positions. The Tc atom is displaced from the least-squares plane defined by the four N basal atoms by 0.2163 (6) Å toward the nitrido group. The analysis of the conformations of the R_1 = [Tc, N(2), C(1), C(2), C(3), N(3)], R_2 = [Tc, N(3), C(4), C(5), N(4)], and R_3 = [Tc, N(4), C(6), C(7), C(8), N(5)] rings in terms of puckering coordinates (Table VII) has led to the following results: the R_1 and R_3 cycles adopt $^4C_1$ and $^1C_4$ "chair" conformations, that is the most stable spatial arrangement for six-membered rings, while the R_2 ring conformation is envelope E_3.

Discussion

The synthesis of the $Tc\equiv N$ multiple bond has been obtained with the two metal oxidation states +6 and +5, corresponding to the formation of the $[Tc^{VI}\equiv N]^{3+}$ and $[Tc^V\equiv N]^{2+}$ functional groups.[12] It has been found that the $[Tc^{VI}\equiv N]^{3+}$ core is stabilized by negatively charged "hard" bases like Cl^- and Br^-,[12b] while the $[Tc^V\equiv N]^{2+}$ core prefers to bound "soft" bases like phosphines and arsines,[19] dichalcogeno ligands,[20] Schiff bases,[15] 8-quinolinethiol,[12a] dithiocarbamates,[21] and NCS^-.[12a,22] The chelating amine ligands used in this study react easily with the complex $[Tc^VNCl_2(PPh_3)_2]$, to form the final Tc^VN–amine complexes. However, the reactions of these ligands with the complex $[Tc^{VI}NCl_4]^-$, did not lead to the isolation of the corresponding $Tc^{VI}N$–amine complexes.

These results indicate that, although such ligands can be classified as "hard" bases, their neutral character prevents the stabilization of the $[Tc^{VI}\equiv N]^{3+}$ core. At the same time, the lower reducing power of the amine ligands, as compared to that of phosphines or thiols, does not permit a quantitative reduction of the $[Tc\equiv N]^{3+}$ core to the $[Tc\equiv N]^{2+}$ core. These considerations may explain the very low yields observed in the reactions where $[TcNCl_4]^-$ was the starting reagent. Preliminary reduction of the Tc^{6+} ion must be accomplished before obtaining the final complexes.

Table VIII. Tc–Cl Bond Distances (Å) in Octahedral Oxo and Nitrido Complexes of Tc(V)

	Tc–Cl			
compd[a]	cis to O_{oxo}	trans to O_{oxo}	trans to $N_{nitrido}$	ref
$TcOCl(phsal)_2$	2.38 (1)			32
$TcOCl(oxMe)_2$	2.360 (1)			33
$TcOCl_2(HbPz_3)$	2.332 (1)			
	2.324 (1)			34
$[TcOCl_3(hbt)]^-$	2.413 (2)			
	2.370 (2)			
	2.363 (2)			35
$TcOCl[(sal)_2en]$		2.527 (4)		36
$TcOCl(salpd)$		2.44 (1)		37
$[TcN(en)_2Cl]^+$			2.7320 (8)	*b*
$[TcN(tad)Cl]^+$			2.663 (2)	*b*
	2.36 [3] (av)	2.48 [6] (av)	2.70 [5] (av)	

[a] phsal = *N*-phenylsalicylideneaminato; oxMe = 2-methyl-8-quinolinolato; $HBPz_3$ = hydrotris(1-pyrazolyl)borato; hbt = 2-(2-hydroxyphenyl)benzothiazolato; $(sal)_2en$ = *N,N'*-ethylenebis(salicylideneaminato); salpd = *N,N'*-propane-1,3-diylbis(salicylideneaminato). [b] This work.

The neutral character of the chelating amine ligands, together with the requirement of neutralization of the residual charge on the technetium ion, may be used to account, in a qualitative way, for the particular structural properties of the cationic complexes prepared here.

The chemistry of the $Tc\equiv N$ bond is characterized by the formation of square-pyramidal complexes having an apical technetium–nitrido multiple bond. The $Tc\equiv N$ bond distances of 1.603 (3) and 1.626 (6) Å for compounds **1** and **2**, respectively, are consistent with the triple-bond TcN distances found in all Tc(V)–nitrido complexes structurally characterized.[12,15,19–22] Among these structures, only that of the complex $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ shows the Tc atom in an octahedral coordination,[22] the others being square pyramidal.

In this context, the technetium(V)–nitrido complexes described here constitute the first examples of an homogeneous class of distorted pseudooctahedral TcN complexes having a sixth, negatively charged ligand in the trans position to the $Tc\equiv N$ bond. Such geometrical preference can be interpreted in terms of a balancing between the strong trans influence of the nitrido group, which makes the octahedral coordination less stable, and the demand of neutralization of the excess of positive charge on the metallic ion. The neutral character of the ligands used here does not produce an effective neutralization of the residual charge on the $[Tc\equiv N]^{2+}$ group. This is partially obtained through the coordination of a sixth Cl^- ligand in the trans position to the $Tc\equiv N$ multiple bond. However, the strong trans influence and large steric requirements of the nitrido ligand[23] cause an extreme lengthening of the $Tc–Cl_{trans}$ bond distances in these complexes, which are the longest Tc–Cl bond distances ever observed in other technetium complexes [2.7320 (8) Å in compound **1** and 2.663 (2) Å in compound **2**].

The situation is quite similar to that observed with the isoelectronic $[Tc=O]^{3+}$ core. Also in that case, σ-donor ligands favor the bonding of a negatively charged group in the trans position to the Tc=O bond, with the consequent formation of pseudooc-

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tahedral species.[10a] In the limit of "hard" neutral ligands, the substituent in the trans position to the Tc=O is a second oxo group, O^{2-}, leading to the formation of the *trans*-$[O{=}Tc{=}O]^+$ group and to nearly regular octahedral structures (the Tc atom lying on the same plane of the ligands cis to the Tc=O).[10,30]

Apart from the carbyne ligand, the N^{3-} group is considered the strongest known π-electron donor, and thus it is likely that its trans influence should be greater than that of the oxo group. This should cause a more remarkable lengthening of the metal-ligand bond distance of the substituent trans to the nitrido group. To give support to such an idea, all the Tc-Cl bond distances found in octahedral Tc(V)-oxo and Tc(V)-nitrido complexes have been collected in Table VIII. The analysis of the structural data suggests that the trans influence exerted on the Cl^- group by the $Tc{\equiv}N$ multiple bond (of the order of magnitude of some 0.34 Å) is much greater than that exerted by the isoelectronic Tc=O group, in agreement with experimental data as well as theoretical arguments.[31]

Even though in both the compounds **1** and **2** the Tc-Cl bond distances are abnormally long, it is interesting to notice that the lengths of the $Tc{\equiv}N$ and Tc—Cl bonds are inversely related, suggesting an incipient transition from square-pyramidal to octahedral geometry of the coordination around the $[Tc{\equiv}N]^{2+}$ moiety. The observed differences in Tc—Cl and $Tc{\equiv}N$ distances in the structures reported here might be ascribed to the different strain effects arising from the coordination of the two neutral ligands, although the analysis of the rings puckering and of the Tc—N bond distances has not shown any particular evidence for it.

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Supplementary Material Available: Tables of anisotropic thermal parameters, positional parameters for the anions, calculated hydrogen atom parameters, and crystal data for both compounds and ORTEP views of the anions for both compounds (10 pages); tables of structure factor amplitudes for both compounds (76 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Head-to-Head Bis(μ-α-pyridonato-*N*,*O*)bis[(ethylenediamine)palladium] Nitrate, $[Pd_2(en)_2(C_5H_4NO)_2](NO_3)_2$, and ^{13}C and ^1H-^{13}C COSY NMR Study of Head-to-Head to Head-to-Tail Isomerization in Solution

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Binuclear head-to-head $[Pd_2(en)_2(\alpha\text{-pyridonato})_2](NO_3)_2$ has been synthesized, and the crystal structure has been solved with a single-crystal X-ray diffraction technique. The crystal is monoclinic, space group $P2_1/a$, with a = 17.201 (8) Å, b = 10.879 (1) Å, c = 12.175 (3) Å, β = 102.96 (3)°, and Z = 4. The binuclear complex cation has head-to-head geometry with a Pd-Pd distance of 2.981 (1) Å. Two binuclear cations are arranged in the crystal as if to form a zigzag chain of four palladium atoms with an inversion center at the midpoint of the central Pd-Pd vector between the two dimers. However, the central Pd-Pd distance is 3.220 (1) Å and is not a Pd-Pd bonding. The ^{13}C NMR spectrum of the compound shows two very close signals for every carbon resonance in both D_2O and DMF, which indicates the existence of head-to-head (HH) and head-to-tail (HT) isomers. Although the isolated complex is pure HH complex, which was confirmed with powder X-ray diffraction, the isomerization to the HT isomer after dissolution is very rapid and the equilibrium is established almost instantaneously after dissolution. The present complex is the first example of HH to HT isomerization of a binuclear palladium(II) complex in solution.

Introduction

We have studied the syntheses and chemical properties of amidate-bridged tetranuclear platinum complexes containing Pt(II) and Pt(III), so-called "platinum blues", with the general formula $[Pt_4A_8L_4]^{5+}$ (A is amine ligand, L is deprotonated amide ligand)[2] and revealed their novel redox behavior, i.e., reduction to $[Pt^{II}{}_2A_4L_2]^{2+}$ by OH^-[3,4] or oxidation to $[Pt^{III}{}_4A_8L_4]^{n+}$ (n = 6, 8) by dioxygen or persulfate.[5] In a parallel experiment attempting to synthesize "palladium blues", the palladium analogues of platinum blues, it would be reasonable first to synthesize a Pd(II) dimer of the type $[Pd_2A_4L_2]^{2+}$ and examine its oxidizability to binuclear $[Pd^{III}{}_2A_4L_2L'_2]^{4+}$ (L' is the axial ligand) or to a tetranuclear palladium blue $[Pd^{III}Pd^{II}{}_3A_8L_4]^{5+}$, similar to the syntheses of amidate-bridged Pt(III) dimer complexes[6] or platinum blues[6b] from amidate-bridged Pt(II) dimers. Dimer complexes containing Pd(III) have so far been little reported with any bridging ligand. $[Pd_2(\text{form})_4]$ (form is *N*,*N'*-di-*p*-tolylformamidinato), which is reversibly oxidized to $[Pd(\text{form})_4]^{n+}$ (n = 1, 2),[7] is the only example so far as we know. Therefore, it would

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