present model compounds, the steric strain induced in the porphyrin cycle by the handle appears to be accommodated on several bonds by macrocycle deformations (ruffling and/or doming). Therefore, the near-constant values of CO dissociation rates is most probably due to these increased porphyrin distortions, which should energetically compensate the observed Fe—CO bond strengthening.

The oxygenated complexes of $\mathrm{Fe^{II}[(Piv)_2C_n](1MeIm)}$ provide a presently unique example of model compounds in which the ν(Fe—O$_2$) stretching mode occurs at such a low frequency (560–563 cm^{-1}). This effect is interpreted as reflecting antagonist effects between H-bonding at the O$_2$ moiety and deformation of the Fe–O–O angle. The nearly constant frequency of the ν(Fe—O$_2$) stretching mode shows that the decrease of O$_2$ off-rates upon handle shortening is not directly related to the Fe—O$_2$ bond strength. On the other hand, as in the case of carbonylated complexes, handle shortening of oxygenated complexes increases porphyrin deformations, but this effect has no compensation upon the Fe—O$_2$ bond strength. Therefore, the decrease of O$_2$ off-rates essentially originates in increased porphyrin distortions upon handle shortening.

The binding site of hemoproteins represents a way of preventing poisoning from CO produced by the cellular catabolism.[2c] Experimental support for this proposal has come from observations of tilted or bent Fe—CO structures in hemoproteins, as compared to the linear and perpendicular structures of model complexes.[3,4] The present data however suggest another mechanism by which hemoproteins may differentiate between O$_2$ and CO, the strong Fe—CO bond being destabilized by porphyrin deformations. Bringing some support to this proposal, the Raman-active, high-frequency modes of the O$_2$ and CO complexes of hemoglobin, myoglobin, and leghemoglobin exhibit some frequency dispersion,[38] suggesting variable deformation of the heme cycle. Unfortunately, however, Raman data are not yet available for imidazole–Fe(II)–protoporphyrin–ligand model compounds, which alone would allow such deformations to be unambiguously characterized. Yet, the present data point at the importance of the macrocycle structure and, hence, of the electron distribution over the porphyrin in this mechanism of ligand discrimination.

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Synthesis and Characterization of Technetium(V) Complexes with *N*-(Thiocarbamoyl)benzamidines. X-ray Crystal Structure of Bis[*N*-(*N*,*N*-diethylthiocarbamoyl)benzamidinato]oxotechnetium(V) Chloride, $\mathrm{[TcO(Et_2tcb)_2]Cl}$

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Technetium(V) complexes of the forms $\mathrm{TcNL_2}$ and $\mathrm{[TcOL_2]Cl}$ (L = Et$_2$tcb$^-$, morphtcb$^-$, piptcb$^-$) with *N*-(thiocarbamoyl)benzamidinato (tcb$^-$) ligands have been synthesized and characterized by elemental analysis and IR, ^{1}H NMR, and UV/vis spectroscopy. Selected compounds have been studied by EI and FAB mass spectrometry, including the MIKE technique. A single-crystal X-ray structure determination shows that the cation of bis[*N*-(*N*,*N*-diethylthiocarbamoyl)benzamidinato]oxotechnetium(V) chloride, formula weight 618.5, has a square-pyramidal structure with cis-coordinated ligands. This complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.87$ (2) Å, $b = 11.587$ (2) Å, $c = 12.374$ (2) Å, $\alpha = 91.94$ (2)°, $\beta = 106.04$ (2)°, $\gamma = 112.18$ (2)°, and $V = 1370.4$ (4) Å^3 with $Z = 2$ for 4723 independent observed reflections.

Introduction

The widespread use of complex compounds of the metastable nuclide ^{99m}Tc (γ-emitter with $E = 140$ keV and half-life $t_{1/2} = 6$ h) in diagnostic nuclear medicine[1-3] has resulted in a growing interest in the basic coordination chemistry of technetium,[4-6] which differs markedly from that of rhenium. This is mainly due to the different redox behaviors of these two group 7 elements.[6]

The further exploration of technetium chemistry is a main factor in the development of new Tc radiopharmaceuticals. In recent years cationic and neutral Tc complexes entered the center of interest as potential tracers for myocardial and brain scintigraphy. Of particular importance are coordination compounds, the lipophilic and polar properties of which can easily be varied by simple substitutions in the molecular framework of the ligands to optimize the biodistribution of the potential radiopharmaceutical preparations. This has been shown for various complex types including ditertiary phosphine,[7,8] alkyl isocyanide,[9] amino oxime,[10] amino

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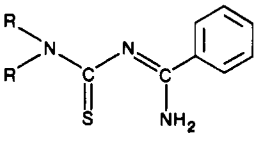
thiol,[11] dithiocarbamate,[12,13] and arene ligands,[14] respectively.

In this paper, we report the synthesis and characterization of a new class of technetium complexes with *N*-(*N*,*N*-dialkylthiocarbamoyl)benzamidines, HR_2tcb (I). The ligands coordinate bidentately, with single deprotonation of the NH_2 group, via S and N donors.[15] Substitutions in the molecular structure of the ligands are possible in the secondary amino group, in the phenyl group, and by replacement of one NH proton by (substituted) aryl substituents. So, a large number of stepwise varied ligands can be prepared, the ^{99m}Tc complexes of which should show a stepwise variation in their radiopharmaceutical properties.



I

Using the long-lived isotope ^{99}Tc (β^--emitter with $E_{max} = 0.3$ MeV and $t_{1/2} = 2.12 \times 10^5$ years), we synthesized R_2tcb complexes (R = ethyl, R_2 = piperidinyl, morpholinyl) of technetium(V) starting from $Tc^VOCl_4^-$ and $Tc^{VI}NCl_4^-$, which were shown to be convenient starting materials for the synthesis of Tc^V oxo and nitrido complexes, respectively.[4,16-18] The cationic TcO complex $[TcO(Et_2tcb)_2]Cl$ with the two benzamidinato ligands forming the basal plane of a square pyramid is the first transition-metal complex of this type in which cis arrangement of the two ligands can be found.

Experimental Section

General Procedure. Due to the radioactivity of technetium some health precautions have been taken. All preparations have been carried out in a fume cupboard with gloves. Since ^{99}Tc is only a weak β^--emitter (specific activity of 17 μCi/mg), no further precautions are necessary provided some elementary steps are taken and no volatile compounds are being formed during the reaction. Normal glassware gives adequate protection against the weak β^--emission. Secondary X-rays (bremsstrahlung) become important only if ^{99}Tc is handled on a larger scale.

All common laboratory chemicals were of reagent grade. $Bu_4NTcOCl_4$ and $Bu_4NTcNCl_4$ were prepared as reported.[19,20] The R_2tcb ligands were synthesized from the corresponding *N*-(*N*,*N*-dialkylthiocarbamoyl)benzimide chlorides[21] and aqueous ammonia.[22] The ligands were twice recrystallized from ethanol and identified by their melting points and ^1H NMR spectra.

Synthesis of the Complexes. Bis[*N*-(*N*-morpholinylthiocarbonyl)-benzamidinato]oxotechnetium(V) Chloride, [TcO(morphtcb)$_2$]Cl. A 50-mg (0.1-mmol) amount of $Bu_4NTcOCl_4$ was stirred in a small amount of methanol (about 2 mL). Addition of 100 mg (0.4 mmol) of Hmorphtcb in 3 mL of methanol followed by 2 drops of triethylamine resulted in the precipitation of an orange-brown powder. The product was separated by suction filtration, washed with methanol and diethyl ether, and recrystallized from $CHCl_3$/2-propanol: yield 55 mg (85% based on Tc); mp 208–209 °C. Anal. Calcd for $C_{24}H_{28}N_6O_3S_2ClTc$: C, 44.50;, H, 4.37; N, 12.99; S, 9.91; Cl, 5.48; Tc, 15.30. Found: C, 42.59; H, 4.26; N, 12.49; S, 9.67; Cl, 5.24; Tc, 14.79.

Bis[*N*-(*N*,*N*-diethylthiocarbamoyl)benzamidinato]oxotechnetium(V) Chloride, [TcO(Et$_2$tcb)$_2$]Cl. Addition of 100 mg (0.4 mmol) of HEt_2tcb and 2 drops of triethylamine in 3 mL of methanol to 50 mg (0.1 mmol) of $Bu_4NTcOCl_4$ in 2 mL of methanol followed by stirring for 1 h at ambient temperature results in a deep brown solution, which was filtered. The solvent was removed in vacuo, leaving a brownish oil. This was dissolved in 3 mL of CH_2Cl_2. After addition of 3 mL of *n*-heptane and slow evaporation of the solvents red-brown crystals deposited. A small amount of a colorless solid (consisting of residual ligand, Bu_4NCl, and Et_3HNCl) could be removed by subsequent washing with water, 2-propanol, and diethyl ether: yield 43 mg (70% based on Tc); mp 198–201 °C. Anal. Calcd for $C_{24}H_{32}N_6OS_2ClTc$: C, 46.55; H, 5.22; N, 13.58; S, 10.36; Cl, 5.73; Tc, 15.99. Found: C, 46.54; H, 4.98; N, 13.18; S, 10.57; Cl, 5.01; Tc, 15.81.

Bis[*N*-(*N*-piperidinylthiocarbonyl)benzamidinato]oxotechnetium(V) Chloride, [TcO(piptcb)$_2$]Cl. The complex was prepared as outlined for [TcO(morphtcb)$_2$]Cl: yield 55 mg (85% based on Tc); mp 176 °C. Anal. Calcd for $C_{26}H_{32}N_6OS_2ClTc$: C, 48.50; H, 5.02; N, 13.07; S, 9.97; Cl, 5.51; Tc, 15.39. Found: C, 46.97; H, 5.03; N, 12.92; S, 9.37; Cl, 5.01; Tc, 15.21.

Bis[*N*-(*N*-morpholinylthiocarbonyl)benzamidinato]nitridotechnetium-(V), TcN(morphtcb)$_2$. (a) A 50-mg (0.1-mmol) amount of $Bu_4NTcNCl_4$ and 100 mg (0.4 mmol) of Hmorphtcb were dissolved in 5 mL of acetone. After 2 drops of triethylamine were added, the mixture was refluxed for 30 min, changing its color from red to yellow. The volume was reduced to about 1 mL, and 2 mL of methanol was added. When the mixture was cooled, yellow crystals deposited; yield 40 mg (60% based on Tc).

(b) A 71-mg (0.1-mmol) amount of $TcNCl_2(Ph_3P)_2$[23] and 200 mg (0.8 mmol) of Hmorphtcb were refluxed for 2 h in acetone. The clear solution was filtered and halved in volume. After 3 mL of methanol was added and the solution stood overnight in a refrigerator, the yellow crystals that deposited were collected and washed with water, methanol and diethyl ether: yield 58 mg (95% based on Tc); mp 287–288 °C. Anal. Calcd for $C_{24}H_{28}N_7O_2S_2Tc$: C, 47.27; H, 4.64; N, 16.08; S, 10.52; Tc, 16.24. Found: C, 46.81; H, 4.79; N, 16.21; S, 9.85; Tc, 15.88.

Bis[*N*-(*N*,*N*-diethylthiocarbamoyl)benzamidinato]nitridotechnetium-(V), TcN(Et$_2$tcb)$_2$. The complex was synthesized as outlined for TcN-(morphtcb)$_2$: yields 30 mg (50% based on Tc) via $TcNCl_4^-$ and 43 mg (70%) via $TcNCl_2(Ph_3P)_2$; mp 230–233 °C. Anal. Calcd for $C_{24}H_{32}N_7S_2Tc$: C, 49.55; H, 5.56; N, 16.86; S, 11.02; Tc, 17.02. Found: C, 49.46; H, 5.61; N, 16.18; S, 10.86; Tc, 16.94.

Bis[*N*-(*N*-piperidinylthiocarbonyl)benzamidinato]nitridotechnetium-(V), TcN(piptcb)$_2$. The synthesis was carried out as outlined above: yield 36 mg (60% based on Tc) via $TcNCl_4^-$ and 48 mg (80%) via $TcNCl_2(Ph_3P)_2$; mp 242–243 °C. Anal. Calcd for $C_{26}H_{32}N_7S_2Tc$: C, 51.55; H, 5.34; N, 16.19; S, 10.58; Tc, 16.34. Found: C, 50.12; H, 5.03; N, 14.97; S, 9.32; Tc, 16.12.

Physical Measurements. UV/visible spectra were recorded at ambient temperature on a Specord M 40 (Carl-Zeiss-Jena, Jena, GDR). IR measurements were carried out for KBr pellets on a UR 20 instrument. The ^1H NMR spectra were recorded on a Bruker WX 90 DS spectrometer. EPR spectra were recorded at $T = 295$ K in the X-band on a E-112 spectrometer (Varian).

Mass spectra were recorded on a VG ZAB-HSQ spectrometer. For FAB measurements argon was used as the primary beam gas. The ion gun was operated at 8 kV and 100 μA. Glycerol and thioglycerol were used as matrices. CID spectra could be obtained with argon as the collision gas.

The technetium contents of the complexes were determined by liquid-scintillation measurements.

X-ray Structure Determination of Bis[*N*-(*N*,*N*-diethylthiocarbamoyl)benzamidinato]oxotechnetium(V) Chloride, [TcO(Et$_2$tcb)$_2$]Cl. Crystals suitable for X-ray diffraction analysis were obtained from slow evaporation of a $CHCl_3$/*n*-heptane solution. A crystal of approximate dimensions 0.23 × 0.23 × 0.18 mm^3 was used during the measurements. The structure determination was carried out at $T = 295$ K. Throughout the experiment Cu Kα radiation was used with a graphite crystal monochromator on a Nonius CAD4 single-crystal diffractometer (λ = 1.541 84 Å). The unit cell dimensions were determined from the angular settings of 25 reflections with $21° < \theta > 41°$: a = 10.872 (2) Å, b = 11.587 (2) Å, c = 12.374 (2) Å, α = 91.94 (2)°, β = 106.04 (2)°, γ = 112.18 (2)°. The space group was determined to be triclinic; $P\bar{1}$ was

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Table I. UV/Vis and IR Spectral Parameters for *N*-(*N*,*N*-Dialkylthiocarbamoyl)benzamidinato Complexes of Technetium[a]

complex	λ_{max}	ν(Tc=O)	ν(Tc≡N)
[TcO(morphtcb)$_2$]Cl	494 (2.5), 364 (3.0), 281 (4.5)	981	
[TcO(Et$_2$tcb)$_2$]Cl	386 (4.0), 272 (4.6)	978	
[TcO(piptcb)$_2$]Cl	359 (3.8), 276 (4.2)	984	
TcN(morphtcb)$_2$	455 sh (2.6), 314 (4.4), 253 (4.6)		1065
TcN(Et$_2$tcb)$_2$	419 (2.7), 310 (4.4), 248 (4.5)		1071
TcN(piptcb)$_2$	451 (2.7), 313 (4.3), 251 (4.4)		1073

[a] λ_{max} in nm; ϵ in M^{-1} cm^{-1}; ν in cm^{-1}. [b] Chloroform solutions.

established by the structure determination. The intensity data of 5456 reflections (*hkl* half a sphere up to $\theta = 70°$) were measured by using the ω–2θ scan technique with a scan angle of 1.50° in ω and a variable scan rate with a maximum scan time of 20 s/reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three reference reflections every 30 min. The final drift correction factors were between 0.98 and 1.03. A smooth curve based on the reference reflections was used to correct for this drift. For all reflections a profile analysis was performed;[24,25] empirical absorption correction was applied, by using ψ-scan data[26] (μ(Cu Kα) = 68.4 cm^{-1}; correction factor in the range 0.64–1.0). Symmetry-equivalent reflections were averaged (one layer only), $R_{mer} = \sum(F_o - \langle F_o \rangle)/\sum F_o = 0.017$ resulting in 5165 unique reflections, of which 4723 were observed with $F_o > 6\sigma(F_o)$. Lorentz and polarization corrections were applied.

The structure was solved with the Patterson method using the automated program system PATSYS,[27] which combines SHELX86[28] and DIRDIF.[29] All non-hydrogen atoms were obtained in a single automatic run. The structure was refined by blocked full-matrix least-squares methods on $|F_o|$ values using SHELX.[30] Scattering factors were taken from ref 31. Isotropic refinement converged to $R = 0.117$. An attempt to refine the structure in the related acentric space group $P\bar{1}$ showed strong correlations between related parameters. No deviations from the centricity could be recognized. At this stage an additional empirical absorption correction was applied,[32] resulting in a further decrease of R to 0.062 (correction factors were in the range 0.80–1.67).

The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. From a difference Fourier map all hydrogen atoms could be located except those atoms that belong to the methyl groups in the structure. During the final stages of the refinement the positional and anisotropic thermal parameters of the non-hydrogen atoms, the positional and isotropic thermal parameters of the non-methyl hydrogen atoms, and the overall isotropic thermal parameters of calculated methyl hydrogen atoms with a fixed C–H distance of 1.0 Å were refined. The final conventional agreement factors were $R = 0.044$ and $R_w = 0.058$ for the 4723 "observed" reflections and 416 variables. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/(\sigma^2(F_o) + 0.00010F_o^2)$ and $\sigma(F_o)$ taken from counting statistics. Full-matrix least-squares refinement was performed in two alternating blocks, one block containing scale atoms C(12)–C(24) and attached hydrogen atoms and the second block containing scale and all other atoms. The maximum shift to error ratio in the last cycle was less than 0.1. The final difference Fourier map still showed peaks of maximum 1.1 and minimum −1.0 e/Å^3 close to the chloride ion.

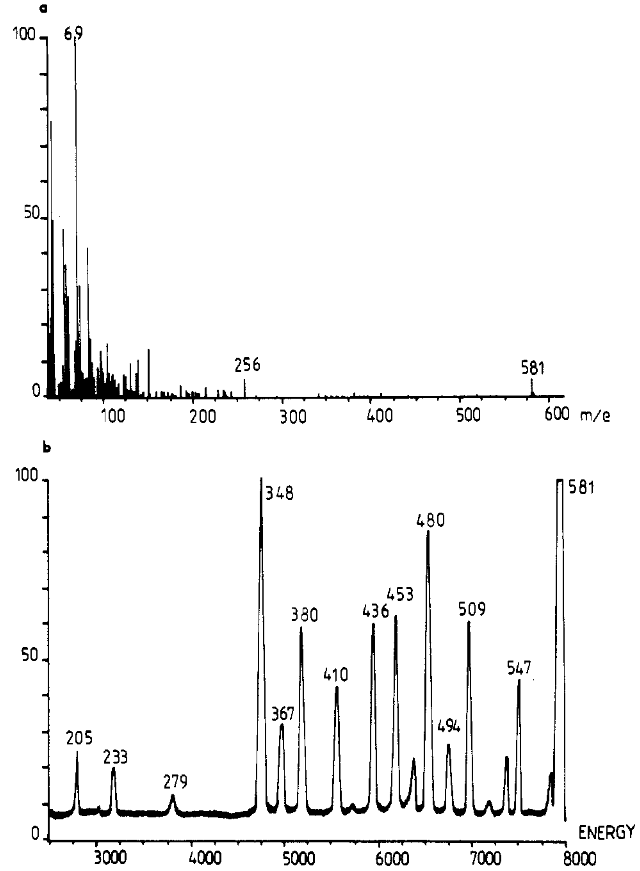

Figure 1. (a) EI$^+$ mass spectrum of TcN(Et$_2$tcb)$_2$ and (b) MIKE spectrum of mass-selected [TcN(Et$_2$tcb)$_2$]$^+$ ions (50% main beam reduction, collision gas Ar).

Results

Synthesis and Characterization. The utility of TcOCl$_4^-$ and TcNCl$_4^-$, respectively, as starting materials for the preparation of Tc(V) complexes with TcO and TcN moieties has been demonstrated previously for a great number of ligands.[4,16–18,33,34] In this study the products were readily obtained by displacement of the halide ligands in methanol or acetone with R$_2$tcb$^-$ ligands. The resulting oxo complexes of Tc(V) are cations of the general formula [TcO(R$_2$tcb)$_2$]$^+$ whereas the corresponding nitrido compounds, TcN(R$_2$tcb)$_2$, are neutral. Generally the compounds are soluble in dimethyl sulfoxide (dmso).

Table I lists the UV/vis and IR spectral parameters for the R$_2$tcb complexes under study. The UV/vis spectra of the TcO and TcN compounds are not significantly influenced by changes in the equatorial ligands. The same holds true for the salient infrared parameters of the compounds. The strong absorption between 965 and 990 cm^{-1} is assignable to the Tc=O stretch of the TcO^{3+} core,[33,34] and the strong band between 1060 and 1080 cm^{-1} reflects the Tc≡N stretch of the TcN^{2+} core.[35]

The Tc center of the TcNCl$_4^-$ starting complex is reduced during the reaction. This reduction takes place via an intermediate Tc(VI) complex as suggested by an intense blue-green color of the reaction mixture at the beginning of the reaction. UV/vis spectra recorded during the reaction are characterized by an intermediate absorption at 580 nm (attributable to the Tc(VI) intermediate) and an isosbestic point at 510 nm. A very suitable method for the detection of intermediate Tc(VI) complexes is given by EPR spectroscopy, as has been shown for some Tc(VI) nitrido[17,36–38] and oxo complexes.[39] EPR detection of the reduction

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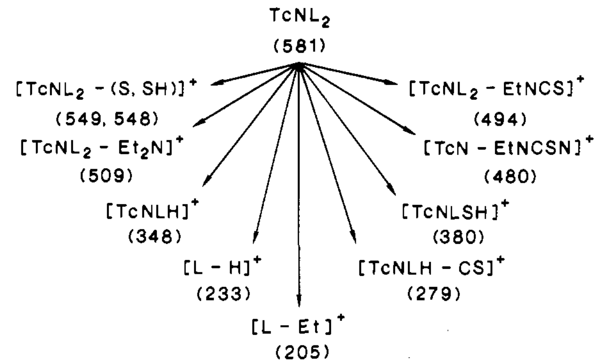
Table II. ^{1}H NMR Spectra of the Tc(V) Complexes and the Corresponding Ligands[a]

compd	NH	Ph	CH_2O	CH_2N
Hmorphtcb	9.01 s (2 H)	7.92 + 7.31 m (5 H)	4.07 m (4 H)	3.62 m (4 H)
[TcO(morphtcb)$_2$]Cl	11.29 s (1 H)	7.74 ± 7.36 m (5 H)	3.92 m (4 H)	3.45 m (4 H)
TcN(morphtcb)$_2$	8.72 s (1 H)	8.02 + 7.49 m (5 H)	4.26 m (4 H)	3.77 m (4 H)
compd	NH	Ph	CH_2[b]	CH_3[b]
HEt$_2$tcb	8.82 s (2 H)	7.93 + 7.50 m (5 H)	3.79 (4 H)	1.15 (6 H)
[TcO(Et$_2$tcb)$_2$]Cl	11.40 s (1 H)	8.06 + 7.62 m (5 H)	4.02 (4 H)	1.33 (6 H)
TcN(Et$_2$tcb)$_2$	7.02 s (1 H)	7.87 + 7.46 m (5 H)	3.93 (4 H)	1.34 (6 H)
compd	NH	Ph	C–CH$_2$–C	C–CH$_2$–N
Hpiptcb	8.33 s (2 H)	7.80 + 7.44 m (5 H)	4.12 m (4 H)	1.68 s (6 H)
[TcO(piptcb)$_2$]Cl	13.04 s (1 H)	8.40 + 7.49 m (5 H)	4.19 m (4 H)	1.78 s (6 H)
TcN(piptcb)$_2$	7.10 s (1 H)	7.85 + 7.43 m (5 H)	4.20 m (4 H)	1.69 s (6 H)

[a] Ligands and nitrido complexes in chloroform, oxo complexes in dmso solutions; chemical shift (in ppm) relative to TMS. [b] Multiplets due to hindered rotation.

Scheme I



under study results in the observation of the signals of *one* intermediate product, the parameters of which ($g_0 = 2.015 \pm 0.005$; $a_0^{Tc} = (170 \pm 5) \times 10^{-4}$ cm^{-1}) come close to those obtained for the intermediate which is detectable at the "reversed" reaction, the oxidation of TcN(Et$_2$tcb)$_2$ by elemental chlorine. The intensity of the intermediate signals decreases with time. They can clearly be distinguished from those of $TcCl_4^-$, the parameters of which are well-known ($g_0 = 2.006 \pm 0.003$; $a_0^{Tc} = (188.0 \pm 3.0) \times 10^{-4}$ cm^{-1}).[37]

The results of the ^{1}H NMR measurements on the resulting Tc(V) complexes are summarized in Table II. Whereas the chemical shifts of the phenyl and amino group protons of the complexes show no changes with respect to those of the uncoordinated ligands, the chelate ring proton NMR signals are markedly shifted.

Mass spectra were recorded for TcN(morphtcb)$_2$, TcN(Et$_2$tcb)$_2$, and [TcO(Et$_2$tcb)$_2$]Cl with use of electron impact ionization for the neutral nitrido complexes and fast atom bombardment for the cationic oxo complexes. Besides the molecular ions ([TcN(morphtcb)$_2$]$^+$, $m/e = 609$ (1.8% *B*); [TcN(Et$_2$tcb)$_2$]$^+$, $m/e = 581$ (3.7% *B*)), the mass spectra of the nitrido compounds are dominated by numerous ligand fragments. Peaks due to metal-containing fragments have very low intensity, preventing a detailed structural characterization of the complexes (Figure 1a). More detailed information could be derived from the MIKE spectra obtained by mass selection of the molecular ions. The metastable decomposition of the mass-selected ions yields a large number of metal-containing daughter ions, the intensity of which could be increased by collision activation.[40] The MIKE spectrum of [TcN(Et$_2$tcb)$_2$]$^+$ is shown in Figure 1b. Some of the most important unimolecular reaction products are summarized in Scheme I (*m/e* values are shown in parentheses). The MIKE spectrum obtained for [TcN(morphtcb)$_2$]$^+$ ions yields fragments similar to those observed for [TcN(Et$_2$tcb)$_2$]$^+$. Differences are due to the presence of the morpholine substituents instead of the Et$_2$N groups in the chelate rings.

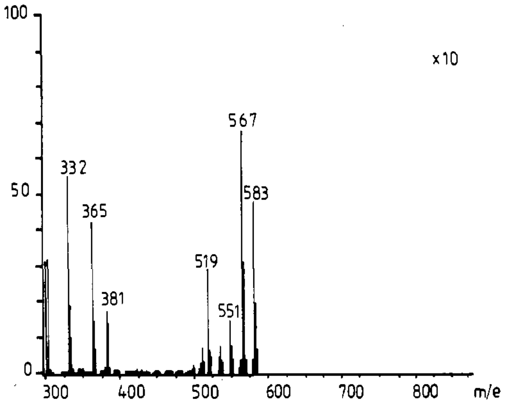


Figure 2. Portion of the FAB$^+$ spectrum of [TcO(Et$_2$tcb)$_2$]Cl.

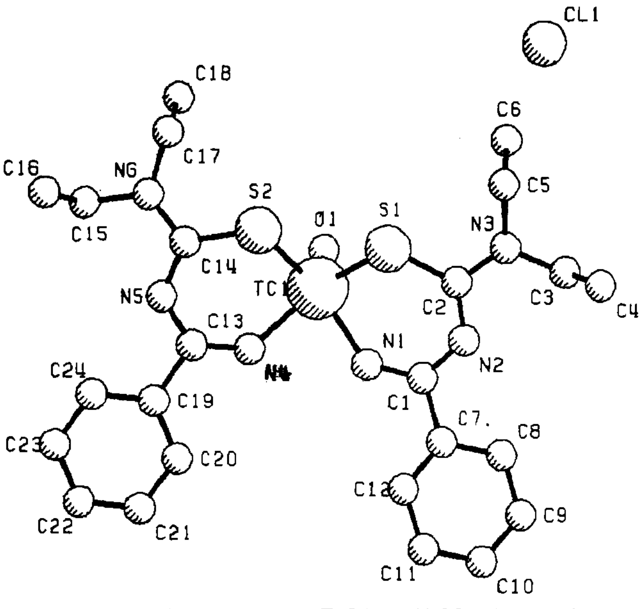


Figure 3. Molecular structure of [TcO(Et$_2$tcb)$_2$]Cl with atomic numbering scheme.

The FAB$^+$ mass spectrum of [TcO(Et$_2$tcb)$_2$]Cl shows both a molecular ion at $m/e = 583$ (4.8% *B*) and a less intense protonated molecular ion, which is evident from the isotope peak $m/e = 584$ having an intensity of 39% (calculated 28.5%) with respect to $m/e = 583$. The molecular ion region of the spectrum is shown in Figure 2. In contrast to the EI$^+$ spectra recorded for the nitrido complexes metal-containing fragments have a much larger intensity in the FAB$^+$ spectrum of [TcO(Et$_2$tcb)$_2$]Cl. They are caused by loss of one oxygen ($m/e = 567$ (6.8% *B*)) and sulfur

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(37) Kirmse, R.; Stach, J.; Abram, U. *Polyhedron* **1985**, *4*, 1405.
(38) Kirmse, R.; Stach, J.; Abram, U. *Inorg. Chim. Acta* **1986**, *117*, 117.
(39) Abram, U.; Abram, S.; Kirmse, R.; Stach, J. *J. Radioanal. Nucl. Chem.* **1986**, *100*, 325.
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Table III. Fractional Positional and Thermal Parameters (with Esd's) for $[TcO(Et_2tcb)_2]Cl$

atom	*x*	*y*	*z*	$100U_{eq}$,[a] Å^2
Tc1	0.14306 (3)	0.17053 (3)	0.39470 (3)	3.30 (1)
Cl1	0.83722 (14)	0.27429 (12)	0.17111 (9)	5.29 (5)
S1	0.18753 (12)	−0.00979 (10)	0.40221 (9)	4.29 (4)
S2	0.21493 (14)	0.16835 (11)	0.58922 (9)	4.99 (5)
O1	0.2728 (3)	0.2812 (3)	0.3647 (3)	5.04 (13)
N1	−0.0141 (4)	0.0824 (3)	0.2492 (3)	3.96 (13)
N2	0.0236 (4)	−0.0923 (3)	0.1794 (3)	3.78 (13)
N3	0.2140 (4)	−0.1392 (3)	0.2357 (3)	4.01 (13)
N4	0.0070 (4)	0.2415 (3)	0.41962 (28)	3.65 (13)
N5	0.0874 (4)	0.3250 (3)	0.61645 (28)	4.05 (13)
N6	0.3009 (4)	0.3693 (3)	0.7448 (3)	4.64 (14)
C1	−0.0500 (4)	−0.0239 (4)	0.1794 (3)	3.45 (14)
C2	0.1374 (4)	−0.0823 (4)	0.2610 (3)	3.66 (14)
C3	0.1779 (6)	−0.2023 (5)	0.1180 (4)	5.15 (18)
C4	0.1132 (10)	−0.3396 (6)	0.1072 (6)	11.6 (3)
C5	0.3353 (5)	−0.1469 (5)	0.3199 (4)	4.85 (18)
C6	0.4702 (6)	−0.0481 (8)	0.3138 (7)	10.73 (27)
C7	−0.1861 (4)	−0.0710 (4)	0.0863 (3)	3.65 (14)
C8	−0.1971 (5)	−0.1312 (4)	−0.0182 (4)	4.72 (17)
C9	−0.3246 (6)	−0.1788 (5)	−0.1045 (4)	5.79 (19)
C10	−0.4414 (5)	−0.1726 (5)	−0.0871 (4)	5.61 (18)
C11	−0.4318 (5)	−0.1145 (5)	0.0159 (4)	5.29 (18)
C12	−0.3030 (5)	−0.0623 (5)	0.1022 (4)	4.66 (17)
C13	−0.0029 (4)	0.2925 (4)	0.5132 (3)	3.70 (14)
C14	0.1993 (5)	0.2985 (4)	0.6512 (3)	4.10 (16)
C15	0.2892 (7)	0.4765 (5)	0.8041 (4)	6.10 (20)
C16	0.2699 (10)	0.4507 (9)	0.9144 (6)	12.1 (3)
C17	0.4320 (6)	0.3546 (5)	0.7907 (4)	5.74 (19)
C18	0.5505 (7)	0.4476 (8)	0.7572 (6)	9.9 (3)
C19	−0.1252 (5)	0.3253 (4)	0.5033 (4)	3.96 (16)
C20	−0.2524 (5)	0.2644 (5)	0.4182 (4)	4.96 (18)
C21	−0.3625 (6)	0.2982 (6)	0.4138 (5)	6.27 (21)
C22	−0.3480 (7)	0.3927 (6)	0.4930 (5)	6.47 (22)
C23	−0.2231 (7)	0.4544 (5)	0.5777 (5)	5.90 (21)
C24	−0.1117 (5)	0.4218 (4)	0.5835 (4)	4.75 (17)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j a_i^* a_j^* a_i a_j U_{ij}$.

Table IV. Selected Bond Lengths (Å) and Angles (deg) of $[TcO(Et_2tcb)_2]Cl$ with Esd's

	Bond Lengths		
Tc1–S1	2.315 (1)	N1–C1	1.340 (6)
Tc1–S2	2.321 (1)	N2–C1	1.321 (7)
Tc1–O1	1.651 (3)	N2–C2	1.326 (5)
Tc1–N1	2.015 (3)	N3–C2	1.331 (7)
Tc1–N4	2.027 (5)	N4–C13	1.332 (6)
S2–C14	1.755 (5)	N5–C14	1.327 (7)
	Bond Angles		
S1–Tc1–S2	78.1 (0)	C14–N6–C15	120.2 (5)
S1–Tc1–O1	107.8 (1)	C14–N6–C17	123.9 (5)
S2–Tc1–O1	107.5 (1)	C15–N6–C17	115.7 (4)
S1–Tc1–N1	88.3 (1)	N1–C1–N2	127.9 (3)
S2–Tc1–N1	143.3 (1)	N1–C1–C7	117.9 (4)
S1–Tc1–N4	142.1 (1)	S1–C2–N2	125.0 (4)
S2–Tc1–N4	88.1 (1)	S1–C2–N3	117.6 (3)
O1–Tc1–N4	110.0 (2)	N2–C2–N3	117.3 (4)
N1–Tc1–N4	82.1 (2)	N3–C3–C4	112.4 (5)
Tc1–S1–C2	106.9 (2)	N3–C5–C6	111.1 (5)
Tc1–S2–C14	105.0 (1)	N4–C13–N5	127.9 (5)
Tc1–N1–C1	132.6 (3)	N4–C13–C19	118.5 (4)
C1–N2–C2	126.3 (4)	N5–C13C19	113.5 (4)
C2–N3–C3	120.5 (4)	S2–C14–N5	124.0 (3)
C2–N3–C5	123.6 (4)	S2–C14–N6	118.1 (4)
C3–N3–C5	115.9 (5)	N5–C14–N6	117.6 (5)
Tc1–N4–C13	132.1 (3)	N6–C15–C16	111.2 (6)
C13–N5–C14	126.1 (4)	N6–C17–C18	113.0 (5)

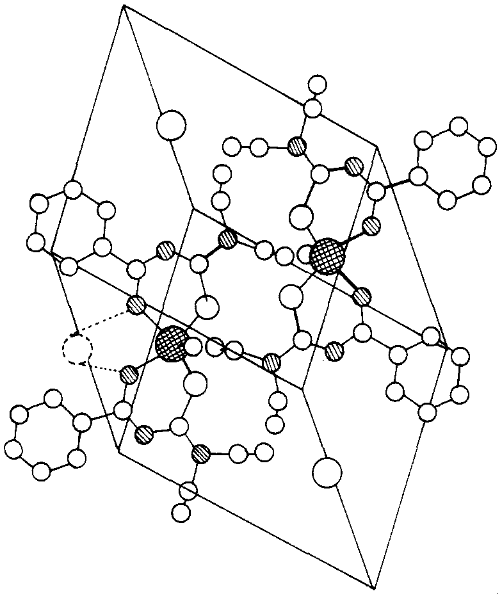

Figure 4. Unit cell plot of $[TcO(Et_2tcb)_2]Cl$. The broken line illustrates the relatively small intermolecular distances between the chelate ring N atoms and the Cl^- of the neighboring unit cell (distances: N(1)- - -Cl = 3.239 (5) Å; N(4)- - -Cl = 3.238 (4) Å).

(*m*/*e* = 551 (1.4% *B*), 519). Other principal fragments appear from the additional loss of one ligand (*m*/*e* = 381 (1.8% *B*), 365 (4.1 *B*), 332 (5.5% *B*)).

Crystal Structure of Bis[*N*-(*N*,*N*-diethylthiocarbamoyl)benzamidinato]oxotechnetium(V) Chloride, $[TcO(Et_2tcb)_2]Cl$. Final positional parameters are given in Table III. Selected interatomic distances and angles are collected in Table IV. Fractional positional parameters of the hydrogen atoms, anisotropic temperature factors, all bond lengths and angles, and the observed and calculated structure factors are contained in Tables A–D.[41] The molecular structure together with the crystallographic numbering scheme is given in Figure 3; a unit cell plot is given in Figure 4. Plots were made with PLUTO.[42]

Discussion

Synthesis and Characterization. A new class of cationic technetium(V) complexes of the general formula $[TcOL_2]Cl$ (L = *N*-(*N*,*N*-dialkylthiocarbamoyl)benzamidinate) can be synthesized by simple substitution of the benzamidinato ligands onto $TcOCl_4^-$ in methanol. This class of complexes is characterized by elemental analysis, IR, UV/vis, ^1H NMR, and mass spectra, and single-crystal X-ray analysis of $[TcO(Et_2tcb)_2]Cl$.

Evidence for the central Tc=O unit is given by strong infrared absorptions in the 965–990-cm^{-1} region. These frequencies are increased with respect to those of other square-pyramidal oxo Tc(V) complexes with dithiolato ligands (saturated ligands, 940–955 cm^{-1}; olefinic ligands with electron-withdrawing substituents, 960–970 cm^{-1}; aromatic ligands, 930–940 cm^{-1}),[43] dimercapto diamide ligands (940–960 cm^{-1})[44] and tetradentate amino oxime ligands (911–925 cm^{-1}).[10] This indicates a considerable electron withdrawal by the benzamidinato ligands.

During the reaction of the benzamidinates under study with the paramagnetic $Tc^{VI}NCl_4^-$, reduction takes place to yield diamagnetic, neutral Tc(V) complexes of the general formula $TcNL_2$. The reduction of the metal center most probably occurs via a Tc(VI) intermediate with coordinated organic ligands. This is suggested by UV/vis studies showing the spectrum of one intermediate product and an isosbestic point at 510 nm. This is in contrast to the analogous ligand-exchange reaction with NCS^- yielding different Tc(VI) mixed-ligand intermediates, as could be verified by use of UV/vis and EPR spectroscopy.[17,18]

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(41) All tables with letter designations have been deposited as supplementary material.

(42) Motherwell, W. D. S. "PLUTO, a program for plotting molecular and crystal structures"; University Chemical Laboratory: Cambridge, England, 1976. Some anisotropy is shown for the outer carbon, which is not of basic interest for inorganic chemists. For the central part of the molecule, all atoms are isotropic within the accuracy of the determination of the thermal parameters.

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(44) Davison, A.; Jones, A. G.; Orvig, C.; Sohn, M. *Inorg. Chem.* **1981**, *20*, 1629.

EPR detection of the Tc(VI) intermediate with an organic ligand during the reaction confirms the results of the UV/vis spectroscopic studies. From the EPR parameters the composition of the intermediate is suggested to be $TcNCl_2L$.[45] This proposal is confirmed by the detection of the same product in the oxidation reaction of $TcN(Et_2tcb)_2$ with elemental chlorine.

Synthesis of the $TcN(R_2tcb)_2$ complexes can be carried out also by starting from $TcNCl_2(Ph_3P)_2$, which has been shown to be a convenient precursor for the preparation of other Tc(V) nitrido compounds. The yields from this synthetic route are always high, but the crude products are contaminated with Ph_3P and must be purified by repeated recrystallization.

A comparison of the spectroscopic data of the TcN and the TcO complexes shows a general bathochromic shift of the UV/vis bands of the TcO complexes with respect to those of the TcN ones. Infrared bands observed for the $\mathrm{C}\underset{\cdots}{-}\mathrm{N}$ frequencies of the coordinated ligands (for the TcN complexes, bathochromic shifts up to 35 cm^{-1}) indicate a greater extent of electron delocalization inside the chelate rings of the TcN complexes. The ^1H NMR spectral results reveal the NH proton signal in the oxo complexes to be shifted more downfield. The latter fact also confirms the assumption of slight interactions between the NH protons and the Cl anion, as will be discussed in the section on the crystal structure.

Further evidence for the structure of the complexes under study is given by their mass spectra. It has been shown that the MIKE technique is a valuable support for the evaluation of fragmentation of metal complexes whose EI^+ spectra exhibit only a few peaks arising from metal-containing fragments. For the cationic technetium chelates fast atom bombardment ionization is the method of choice, which allows the observation of metal-containing fragments.

Despite the fact that different ionization techniques have been used, a significant difference in the fragmentation of the TcN and the TcO complexes has been found: whereas the loss of the oxo oxygen for $[TcO(Et_2tcb)_2]^+$ represents a main fragmentation pathway, for the nitrido complexes no metal-containing fragments without the TcN group could be detected.

Crystal Structure of Bis[*N*-(*N*,*N*-diethylthiocarbamoyl)benzamidinato]oxotechnetium(V) Chloride, $[TcO(Et_2tcb)_2]Cl$. The structure of $[TcO(Et_2tcb)_2]Cl$ contains complex cations and chloride anions. The geometry of the cation is illustrated in Figure 3 and shows a cis arrangement of the two Et_2tcb^- ligands with respect to their donor atoms S and N, resulting in a distorted-pyramidal coordination geometry of the $TcON_2S_2$ unit. It is interesting to note that a structural study of a Ni(II) complex of Et_2tcb^-, $Ni(Et_2tcb)_2$,[46] shows a trans arrangement of the ligands. Possibly the formation of hydrogen bonds of the NH protons to the Cl^- anion plays an important role for the cis configuration observed for the Tc complex and its stability. Such hydrogen bonds cannot be formed for the analogous bromide $[TcO(Et_2tcb)_2]Br$, which may be the reason that it is impossible to prepare the latter as a defined compound; only oligomeric products can be obtained. A cis arrangement of the ligands has been observed also for some Cu(II) and Ni(II) complexes with monothio-β-diketonates and the analogous benzoylthiourea ligands,[47] and a relatively short interligand S–S distance (<3 Å) has been discussed as being responsible for the cis coordination due to some residual S–S interaction. Such effects cannot be ruled out for the compound under study (interligand S–S distance 2.922 (2) Å).

There is no significant difference between the Tc–S1 and Tc–S2 bond lengths of 2.315 (1) and 2.321 (1) Å, respectively. The same holds true for the Tc–N1 and Tc–N4 bond lengths: 2.015 (3) and 2.027 (5) Å. The values of the C–S bond lengths correspond to values lying between single- and double-bond character. Interestingly, almost equal bond lengths (~1.33 Å) are observed for all C–N bonds in the chelate ring system. This includes also the C–N bonds between the diethylamino substituents and the chelate rings, indicating a noticeable deviation from a normal single C–N bond length of the latter and the presence of an extended conjugated π-system. The Tc–O1 distance of 1.651 (3) Å indicates multiple-bond character and is typical of Tc=O lengths in complexes where only one such linkage is present.[48]

There are only two other structural studies[49,50] on $TcON_2S_2$ complexes that should be used for comparison purposes, both made on quadridentate [*N*,*N*′-ethylenebis(2-mercaptoacetamidato)]-oxotechnetate(V) and neutral [*N*,*N*′-ethylenebis(2-mercaptoacetaminato)]oxotechnetium(V) complexes. In both cases, however, only very few data concerning bond lengths and angles are given: Tc=O bond lengths, 1.68–1.69 Å; Tc—N, 2.05 Å (averaged). Data on Tc–S bond lengths were not indicated.

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Registry No. $[TcO(Et_2tcb)_2]Cl$, 118335-40-3; $[TcO(morphtcb)_2]Cl$, 118335-39-0; $[TcO(piptcb)_2]Cl$, 118335-41-4; $TcN(morphtcb)_2$, 114056-23-4; $TcN(Et_2tcb)_2$, 118335-42-5; $TcN(piptcb)_2$, 118335-43-6; $Bu_4NTcOCl_4$, 92622-25-8; $Bu_4NTcNCl_4$, 95012-26-3; $TcNCl_2(Ph_3P)_2$, 113945-92-9.

Supplementary Material Available: Tables of hydrogen positional parameters (Table A), anisotropic temperature factors (Table B), and bond lengths and angles (Table C) for $[TcO(C_{12}H_{16}N_3OS)_2]Cl$ (4 pages); a table of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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(45) A nearly linear dependence of the *g* values and the ^{99}Tc hyperfine interactions a_0^{Tc} on the composition of the first coordination sphere has been shown for a number TcN complexes.[17,36,38]

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