the five-coordinate form having heme methyls at ca. 50 ppm (Figure 1), while the six-coordinate form with imidazole coordination has no resonances below ca. 15 ppm (Figure 3) (extrapolated to 23 °C). Published spectra[20] for native HbM Iwate and HbM Boston in the state where only the mutated (tyrosine-containing) subunits are oxidized reveal a series of intense peaks in the region 30–45 ppm, consistent with their origin in heme methyls of high-spin ferric subunits. The unmutated reduced high-spin ferrous subunits are known not to exhibit hyperfine shifted peaks downfield of 25 ppm.[21] This suggests that the mutated $\alpha$ subunits of both HbM Iwate and HbM Boston are high-spin, and hence five-coordinate. The latter protein is known[3] to have a five-coordinate ferric $\alpha$ subunit, but the preliminary X-ray data have suggested[22] that the former has both tyrosinate and histidine coordination. In view of the fact that both phenoxide and imidazole coordination leads to a clear low-spin derivative with a characteristic NMR spectrum with heme methyls upfield of 30 ppm, we conclude that either the histidine E7 is not coordinated in the $\alpha$ chain of HbM Iwate in solution or the interaction is so weak as to leave the iron high-spin. ESR measurements also detect a high-spin species.[4]

The extreme low-field, nonexchangeable single-proton signals at 78, 91, and 122 ppm for HbM Iwate and at 80 and 105 ppm for HbM Boston (both at 35 °C) are very unlikely to arise from the ferric heme, but are consistent with assignments to the coordinated tyrosinate meta hydrogens and/or the two nonequivalent protons of the $p$-CH$_2$ ($\beta$-CH$_2$ in amino acid terminology). It is thus clear that the observations of several nonexchangeable single-proton peaks in the far downfield region of ferric heme systems can be used as strong indicators for tyrosinate coordination.

## Experimental Section

**Preparation of Samples.** The iron complexes, (PP)Fe$^{III}$(OAr),[4] (PP)Fe$^{III}$(SAr),[5] (TPP)Fe$^{III}$(OAr),[4] and (TPP)Fe$^{III}$(SAr),[5] were prepared by established routes. Because of the sensitivity of the thiolate complexes to moisture and dioxygen, all handling and measurements of these were performed under an atmosphere of purified dinitrogen.[5] The solvents for NMR measurements were distilled from phosphorus pentoxide (CDCl$_3$) or sodium (toluene-$d_8$) and stored over molecular sieves. The six-coordinate imidazole adduct was obtained by adding measured quantities of imidazole to the solution of (PP)Fe(OC$_6$H$_4$-$p$-NO$_2$) via a microliter syringe.

**NMR Measurements.** $^1$H NMR spectra were recorded on a Nicolet NT200 or GE QE300 FT NMR spectrometer operating in the quadrature mode ($^1$H frequencies 200 or 300 MHz). Typically, 1000 transients were accumulated by using a 7-$\mu$s 90° pulse and 8K data points. The peaks were referenced against tetramethylsilane. $T_1$ measurements were made by the standard inversion recovery technique.

**Acknowledgment.** We are indebted to A. Kabbani for experimental assistance and Professor L. Que for useful discussion. This research was supported by Grants HL-16087 and GM-26226 from the National Institutes of Health.

**Registry No.** (TPP)Fe$^{III}$(OC$_6$H$_5$), 76282-28-5; (PP)Fe$^{III}$(OC$_6$H$_3$-3,4-(CH$_3$)$_2$), 126460-00-2; (PP)Fe$^{III}$(OC$_6$H$_4$-$p$-NO$_2$), 54959-23-8; (PP)Fe$^{III}$(SC$_6$H$_4$-$p$-NO$_2$), 54959-22-7; (PP)Fe$^{III}$(OC$_6$H$_4$-$p$-NO$_2$)(Im), 126460-02-4; (PP)Fe$^{III}$(OC$_6$H$_4$-4-CH$_3$), 126460-03-5; (TPP)Fe$^{III}$(OC$_6$H$_4$-4-NO$_2$), 83486-39-9; (TPP)Fe$^{III}$(SC$_6$H$_4$-4-NO$_2$), 126460-04-6; (TPP)Fe$^{III}$(OC$_6$H$_4$-4-CH$_3$), 84893-13-0.

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# $\mu$-Oxo–Bis(oxo) Dinuclear Complexes of Technetium(V) with Amine Phenol Ligands: Syntheses, Characterization, and X-ray Crystal Structures

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Technetium(V) complexes of three amine phenol ligands prepared by reducing Schiff bases derived from salicylaldehyde and 1,3-diaminopropane, 2,2-dimethyl-1,3-diaminopropane, and 1,4-diaminobutane have been synthesized. $^1$H and proton-decoupled $^{13}$C nuclear magnetic resonance spectra of the complexes have been recorded and compared with those of the parent ligands. The complexes have been characterized by infrared spectroscopy, visible–UV spectrophotometry, and X-ray crystallography. X-ray crystal structures show all three complexes are dinuclear with a $\mu$-oxo-bis(oxo) (O=Tc—O—Tc=O) backbone. The distorted octahedral coordination of Tc(V) is completed by a tetradentate diamine diphenolate ligand. Neutrality of the complexes is achieved by deprotonation of the phenols and by terminal and bridging oxo ligands. The technetium complexes have either a true crystallographic center of symmetry or an approximate center at the bridging oxygen.

## Introduction

The widespread application of $^{99m}$Tc in nuclear medicine has initiated extensive studies on the coordination chemistry of this man-made element. This in turn has contributed to the development of a large number of custom-tailored ligands for possible application in such specialized areas of nuclear medicine as brain and heart perfusion studies. Fair et al.[1] and Jurisson et al.[2,3] have earlier reported the synthesis and characterization of several neutral, lipophilic $^{99}$Tc complexes of the amine oxime class of ligands. The $^{99m}$Tc complex of one such ligand, *dl*-HMPAO, is now widely used as an effective cerebral blood flow agent.[4-6] We have been continuing the search in this area for the development of more such neutral, lipophilic Tc complexes for likely application in nuclear medicine. Bandoli et al.[7] have reported the synthesis and crystal structure of Tc(V) complexes of tetradentate Schiff base ligands derived from salicylaldehyde and alkanediamines.

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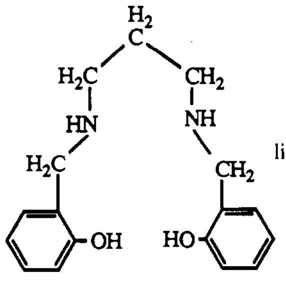
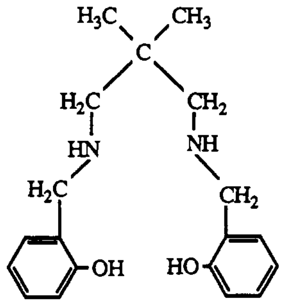
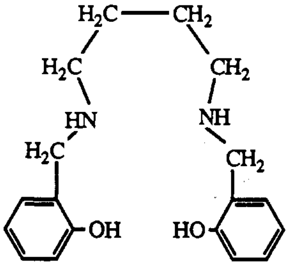


ligand 1: *N,N′*-bis(2-hydroxybenzyl)-1,3-diaminopropane



ligand 2: *N,N′*-bis(2-hydroxybenzyl)-2,2-dimethyl-1,3-diaminopropane



ligand 3: *N,N′*-bis(2-hydroxybenzyl)-1,4-diaminobutane

**Figure 1.** Ligands used for the preparation of Tc complexes.

It was observed earlier in this laboratory[8] and also reported by Williams et al.[9] that $^{99m}$Tc complexes of the amine oxime ligands are formed in much higher yield than the corresponding $^{99m}$Tc complexes of the imine oximes and that the resultant complexes are more lipophilic and stable. Hence we were interested in studying the behavior of amine phenol ligands vis-à-vis their corresponding imine phenols. We have synthesized a series of amine phenol ligands by reducing the Schiff bases of the type reported by Bandoli et al.[7] and investigated their $^{99m}$Tc complexes for possible application in nuclear medicine.[10,11] Due to the extremely low concentration of $^{99m}$Tc ($<10^{-8}$ M) used in such studies, there exists a good possibility of the complex being formed with an impurity present, at a much smaller concentration, rather than with the ligand itself. It has been our strategy to study the complexation chemistry at macroscopic scale and correlate it with the tracer-level experiments.[1-3,12] Hence we have prepared technetium complexes of three of those ligands (Figure 1) and characterized them by $^1$H and $^{13}$C NMR spectroscopy, UV-visible spectrophotometry, infrared spectroscopy, and X-ray crystallography.

Due to the short half-life of the often used $^{99m}$Tc isomer ($t_{1/2}$ = 6 h), most of the inorganic chemistry studies of this element have been done with the long-lived $^{99}$Tc isomer ($t_{1/2} = 2.12 \times 10^5$ years). Technetium-99 is a low-energy (0.292 MeV) $\beta$-particle emitter and can be handled in milligram quantities with little radiation hazard, as laboratory glassware provides adequate shielding. However, extreme care was taken to avoid possible contamination. Ligand 1 has a propane-1,3-diyl bridge, ligand 2, a 2,2-dimethylpropane-1,3-diyl bridge, and ligand 3, a butylene between the amine nitrogen atoms.

## Experimental Section

Technetium as $NH_4{}^{99}TcO_4$ (0.38 mmol/mL) was obtained from New England Nuclear Co. (division of Du Pont Chemical Co.). All common chemicals used were of reagent grade.

Synthesis and characterization of the ligands are described in detail elsewhere.[13] In brief, they were prepared by refluxing 2 equiv of salicylaldehyde (40 mmol) with 1 equiv (20 mmol) of 1,3-diaminopropane, 2,2-dimethyl-1,3-diaminopropane, or 1,4-diaminobutane in about 150 mL of ethanol for 24 h. The deep yellow solution of the product formed was evaporated, and the solid was recrystallized from hot ethanol.

About 10 mmol of the Schiff base was dissolved in 100 mL of ethanol and 2 g (52 mmol) of sodium borohydride added in two portions. The mixture was stirred for 2 h, and about 40 mL of double-distilled water was added to this. The product precipitated, was filtered out, and recrystallized from hot ethanol.

**Technetium Complexes.** Technetium complexes for all three ligands were prepared by a similar method. A typical preparation is given for $Tc_2C_{34}H_{40}N_4O_7{\cdot}2CHCl_3$, $[O{=}Tc(\text{ligand }1)]_2O$.

Ligand 1 (30 mg, 0.11 mmol) was dissolved in 3 mL of ethyl alcohol with slight heating. Saline (3 mL, 0.9%) solution and sodium bicarbonate buffer (0.5 mL, 0.5 M, pH 9) were added to this, followed by 0.3 mL (0.19 mCi, 0.11 mmol) of $NH_4TcO_4$. The mixture was stirred for 5 min. A slurry of stannous tartrate (60 mg, 0.22 mmol) in 6 mL of deionized water was added slowly to the mixture. A red-brown solution was formed, which was stirred for 1 h. At the end of this period the complex was extracted into 3 × 10 mL of $CHCl_3$. The first two $CHCl_3$ extracts were combined and left for slow evaporation in a hood, or the volume was reduced by rotary evaporation and left in a freezer. Brown crystals of the complex appeared, which were filtered and dried in air. The crystals were suitable for X-ray diffraction studies.

The complexes of ligands 2 and 3 were prepared similarly. Ligand 3 was less soluble and hence dissolved in 8 mL of ethyl alcohol instead of 3 mL.

The complex yields were estimated by spiking $^{99}$Tc with about 100 kBq of $^{99m}$Tc in independent experiments. The $CHCl_3$ extraction yields were estimated by measuring the activity of $^{99m}$Tc in both the aqueous and organic layer. The complex yields were 55, 35, and 40%, respectively, for the three complexes.

**Measurements.** $^1$H and proton-decoupled $^{13}$C NMR spectra were recorded on a JEOL FX 90Q or Nicolet NT 300 spectrometer using $CDCl_3$ as solvent. Visible-UV spectra were recorded at ambient temperature on a Perkin-Elmer 576 ST spectrophotometer using methanol as solvent. Infrared spectra were recorded as Nujol mulls between NaCl disks on a Nicolet 20 DXB Fourier transform infrared spectrometer. Visible-UV and infrared spectra were recorded for both complexes and free ligands.

**Collection and Reduction of X-ray Diffraction Data.** X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer at 22 (1) °C with the crystals lightly coated with epoxy to prevent chloroform loss. Graphite-monochromated Mo K$\alpha$ radiation was used for all work. Lattice constants were obtained by least-squares fits of the setting angles of 25 carefully centered reflections for each compound. The intensities of three standard reflections measured after every 7200 s of X-ray exposure were used to check for decomposition, which was significant for complex **2** (~35%) and complex **3** (~11%). Orientation was checked for every 200 reflections with the use of three standards. Recentering, using 25 reflections, was done if any of the three were found to be significantly off center.

**Solution and Refinement of the Structures.** The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares methods, which minimized $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = (\sigma^2(\text{counting}) + (0.04F_o)^2)/4F_o{}^2$. Atomic scattering factors were from ref 7 and included anomalous scattering contributions. All calculations were done on PDP11/24 and PDP11/34 computers with the Enraf-Nonius

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**Table I.** Crystal Data, Data Collection Parameters, and Refinement Parameters for Complexes **1–3**

| | | | |
|---|---|---|---|
| formula | $Tc_2C_{34}H_{40}N_4O_7 \cdot 2CHCl_3$ | $Tc_2C_{38}H_{48}N_4O_7 \cdot CHCl_3$ | $Tc_2C_{36}H_{44}N_4O_7 \cdot 2CHCl_3$ |
| fw | 1051 | 988 | 1080 |
| space group | $P42_1c$ | $P2_1/n$ | $P2_1/c$ |
| $a$, Å | 29.505 (6) | 10.330 (3) | 17.201 (4) |
| $b$, Å | 29.505 (6) | 10.354 (3) | 15.098 (3) |
| $c$, Å | 9.544 (3) | 21.702 (5) | 17.388 (5) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 90 | 93.01 (2) | 110.63 (2) |
| $\delta$, deg | 90 | 90 | 90 |
| $V$, Å$^3$ | 8308 (2) | 2318.0 (8) | 4226 (1) |
| $Z$ | 8 | 2 | 4 |
| $\lambda$(Mo K$\alpha$), Å | 0.7107 | 0.7107 | 0.7107 |
| $d_{calcd}$, g/cm$^3$ | 1.681 (1) | 1.416 (1) | 1.697 (1) |
| cryst size, mm | 0.08 × 0.09 × 0.25 | 0.04 × 0.06 × 0.30 | 0.04 × 0.18 × 0.30 |
| $\mu$, cm$^{-1}$ | 10.9 | 8.0 | 10.7 |
| rel transm factors | <3% (no cor) | <3% (no cor) | emp $\Psi$ scan cor (87.6–99.8%) |
| scan method | $\theta$–$2\theta$ | $\theta$–$2\theta$ | $\theta$–$2\theta$ |
| scan range, deg | 0.75 + 0.35 tan $\theta$ | 1.00 + 0.35 tan $\theta$ | 1.00 + 0.35 tan $\theta$ |
| scan speed | to give 3% counting statistics up to a max of 90 s | to give 3% counting statistics up to a max of 90 s | to give 3% counting statistics up to a max of 90 s |
| $\theta$ range, deg | 2–22.5 | 2–22.5 | 2–20 |
| $hkl$ range collcd | $hkl$ (2–22.5), $\bar{h}\bar{k}\bar{l}$ (2–10) | $hkl$, $hk\bar{l}$ | $hkl$, $hk\bar{l}$ |
| no. of reflns measd | 6629 | 3318 | 4538 |
| no. of indep reflns | 3370 | 3223 | 4019 |
| no. of indep reflns above $2\sigma$ used in refinement | 1983 | 1595 | 3047 |
| no. of variables | 496 | 268 | 514 |
| $R(F)$ | 0.036 | 0.052 | 0.027 |
| $R_w(F)$ | 0.040 | 0.052 | 0.034 |
| max shift/error on last cycle | 0.16 | 0.01 | 0.01 |

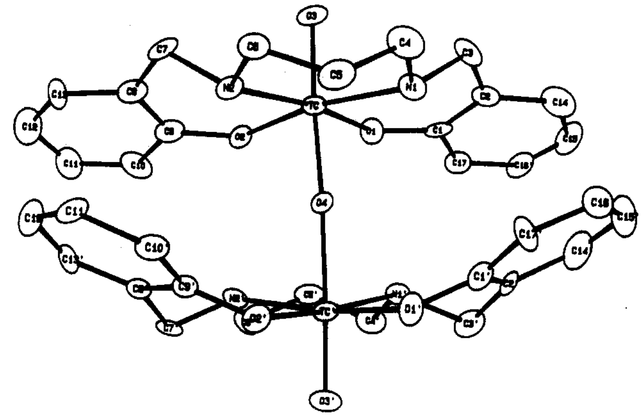


**Figure 2.** ORTEP diagram of Tc(V) complex of *N,N'*-bis(2-hydroxybenzyl)-1,3-diaminopropane (complex **1**).

SDP package. Maximum residual electron densities were in all cases less than 0.6 e/Å$^{3-}$, and the larger residuals were generally near the technetium atom positions. No extinction corrections were deemed necessary for any of the studies. Hydrogen atoms were located by difference Fourier methods or were placed in chemically reasonable positions (C–H ~ 0.95 Å) and were not refined ($B$ ~ 1.3 × $B$ of atom attached). Crystal data and data collection and refinement parameters are given in Table I.

## Results

The technetium(V) complexes were prepared by direct reduction of $TcO_4^-$ with stannous tartrate in the presence of ligand. The complexes formed are highly lipophilic, having $CHCl_3$/saline distribution ratios greater than 10, and can therefore be separated from unreduced $TcO_4^-$ and reduced hydrolyzed Tc by solvent extraction.[13] Technetium complexes with all three ligands were formed in yields greater than 35% in these studies. In another set of experiments with $10^{-4}$ mmol of ligand and technetium, the complex yields were 76, 63, and 63%, respectively, for the three ligands under identical conditions.

The proton NMR spectral parameters of the complexes (Figures 2–4) are given in Table II, and for the sake of comparison spectral parameters of the free ligands are given in Table III. The $^{13}C$ NMR chemical shifts of the complexes and ligands are given in Table IV.

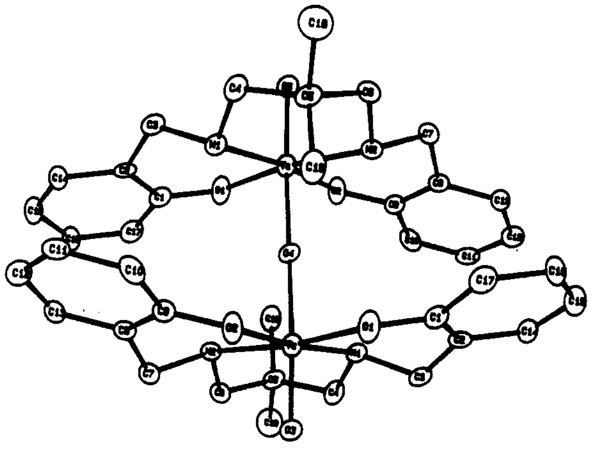


**Figure 3.** ORTEP diagram of Tc(V) complex of *N,N'*-bis(2-hydroxybenzyl)-2,2-dimethyl-1,3-diaminopropane (complex **2**).

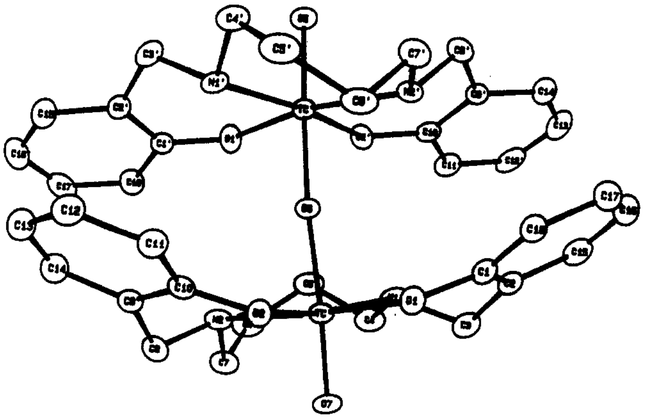
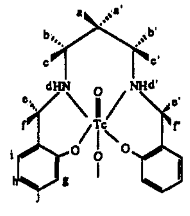


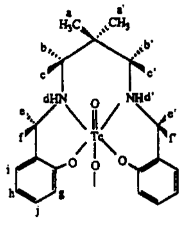
**Figure 4.** ORTEP diagram of Tc(V) complex of *N,N'*-bis(2-hydroxybenzyl)-1,4-diaminobutane (complex **3**).

Visible–UV spectrophotometric parameters of the complexes and ligands are given in Table V. Two UV absorption peaks are seen for the free ligands, but on complexation a new charge-transfer band occurs as a shoulder in the UV spectrum. Visible

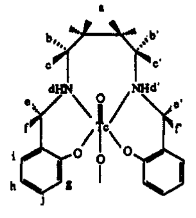
**Table II.** $^1$H Nuclear Magnetic Resonance Data for the Complexes (TMS Used as Reference)



1



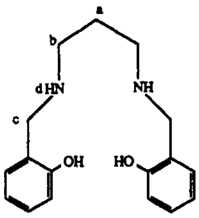
2



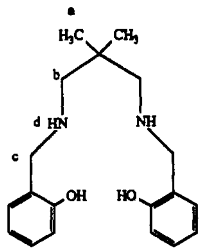
3

| proton | multiplicity | chem shift, ppm | no. of protons |
|---|---|---|---|
| | Complex 1 | | |
| a | triplet | 2.25 | 1 |
| a′ | multiplet | 1.25 | 1 |
| b,b′ | triplet | 2.9 | 2 |
| c | quartet | 2.7 | 1 |
| c′ | multiplet | 3.17 | 1 |
| d | multiplet | 3.25 | 1 |
| d′ | multiplet | 3.6 | 1 |
| e | multiplet | 3.21 | 1 |
| e′ | multiplet | 3.5 | 1 |
| f | triplet | 4.0 | 1 |
| f′ | multiplet | 3.22 | 1 |
| g | doublet | 6.35 | 2 |
| h | triplet | 6.6 | 2 |
| i | doublet | 7.1 | 2 |
| j | under $CHCl_3$ | 7.25 | 2 |
| | Complex 2 | | |
| a | singlet | 1.19 | 3 |
| a′ | singlet | 1.97 | 3 |
| b,b′,c,c′ | multiplet | 3-3.15 | 4 |
| d,d′ | multiplet, broad | 3.2 | 2 |
| e,e′ | doublet | 3.4 | 2 |
| f,f′ | triplet | 4.0 | 2 |
| g | doublet | 6.35 | 2 |
| h | triplet | 6.65 | 2 |
| i | doublet | 7.1 | 2 |
| j | under $CHCl_3$ | 7.25 | 2 |
| | Complex 3 | | |
| a | triplet | 1.2 | 4 |
| b,b′ | triplet | 2.35 | 2 |
| c | multiplet | 2.5 | 1 |
| c′ | multiplet, broad | 2.15 | 1 |
| d,d′ | multiplet | 3.7 | 2 |
| e | doublet | 3.1 | 1 |
| e′ | doublet, broad | 3.2 | 1 |
| f | triplet | 4.05 | 1 |
| f′ | multiplet, broad | 3.8 | 1 |
| g | doublet | 6.45 | 2 |
| h | triplet | 6.7 | 2 |
| i | doublet | 7.05 | 2 |
| j | under $CHCl_3$ | 7.25 | 2 |

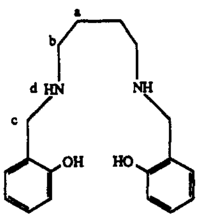
**Table III.** $^1$H Nuclear Magnetic Resonance Data for the Ligands (TMS Used as Reference)



1



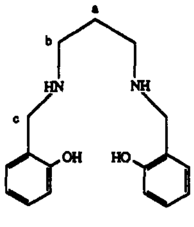
2



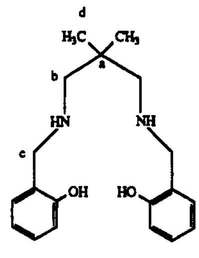
3

| proton | multiplicity | chem shift, ppm | no. of protons |
|---|---|---|---|
| | Ligand 1 | | |
| a | pentet | 1.6-1.9 | 2 |
| b | triplet | 2.6-2.8 | 4 |
| c | singlet | 4.0 | 4 |
| d | broad | 6.2 | 2 |
| aromatic | multiplet | 6.7-7.2 | 8 |
| | Ligand 2 | | |
| a | singlet | 1.0 | 6 |
| b | singlet | 2.5 | 4 |
| c | singlet | 4.0 | 4 |
| d | not seen | | |
| aromatic | multiplet | 6.7-7.3 | 8 |
| | Ligand 3 | | |
| a | multiplet | 1.4-1.8 | 4 |
| b | multiplet | 2.6-2.8 | 4 |
| c | singlet | 4.0 | 4 |
| d | broad | 6.0 | 2 |
| aromatic | multiplet | 6.7-7.3 | 8 |

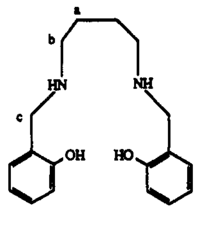
**Table IV.** $^{13}$C Nuclear Magnetic Resonance Data (ppm)



1



2



3

| | a | b | c | d | aromatic carbons |
|---|---|---|---|---|---|
| complex 1 | 26.91 | 57.11 | 58.76 | | 118.24, 118.59, 122.13, 129.43, 131.72, 165 |
| ligand 1 | 29.59 | 46.28 | 52.67 | | 116.27, 119.03, 122.34, 128.30, 128.68, 158.09 |
| complex 2 | 29.86 | 60.76 | 67.80 | 25.08 | 119.16, 121.56, 129.26, 132.22, 165.2 |
| ligand 2 | 34.47 | 53.27 | 57.22 | 24.28 | 116.22, 119.09, 122.5, 128.41, 128.79, 157.88 |
| complex 3 | 23.51 | 54.84 | 60.04 | | 118.36, 129.42, 131.7, 164.79 |
| ligand 3 | 27.15 | 48.34 | 52.67 | | 116.33, 118.98, 122.39, 128.24, 128.68, 158.20 |

absorption occurs between 397 and 424 nm in the complexes, while the free ligands do not show any absorption bands in the visible region. Infrared spectral parameters are given in Table VI. The stretching frequencies for Tc—O—Tc are seen between 664 and 674 cm$^{-1}$ and agree with the literature value for such a bridge.[7,14] Additional absorptions (absent for free ligands) are seen at 574 and 625, at 607 and 625, and at 613 cm$^{-1}$ for complexes **1**-**3**, respectively. For complexes **1** and **3** absorbances at 920 and 913 cm$^{-1}$, respectively, were seen, which correspond to the Tc═O stretching frequency. For complex **2** no absorption band could be identified in this region.

Some of the selected bond distances and bond angles from the X-ray studies are given in Table VII. Table VII also gives the bond distances and angles of the complex formed from the Schiff base analogue of ligand 1 from ref 7 for comparison.

All three Tc(V) complexes are dinuclear with an O═Tc—O—Tc═O backbone. The distorted octahedral coordination of Tc(V) is completed by a tetradentate diamine diphenolate ligand. The structure is very similar to the ($\mu$-oxo)bis(oxo)[*N*,*N*′-propane-1,3-diylbis(salicylidene)aminato)]technetium(V) complex reported by Bandoli et al.[7] Ligand 1 is the reduced analogue of the ligand used by them for making that complex.

The technetium complexes formed are neutral in all three cases, neutrality being achieved by deprotonation of the phenols and by terminal and bridging oxo ligands.

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(14) Clarke, M. J.; Kastner, M. E.; Podbielski, L. A.; Fackler, P. H.; Schreifels, G.; Meinken, G.; Srivastava, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 1818.

**Table V.** Visible–UV Spectrophotometric Parameters[a]

| | $\lambda_{max}$, nm | $10^{-3}\ \epsilon$, $M^{-1}\ cm^{-1}$ |
|---|---|---|
| complex **1** | 207 | 79 |
| | 225 (sh) | 45 |
| | 275 (sh) | 22 |
| | 406 | 19 |
| complex **2** | 212 | 68 |
| | 225 (sh) | 43 |
| | 265 (sh) | 28 |
| | 397 | 19 |
| complex **3** | 208 | 63 |
| | 230 (sh) | 53 |
| | 275 (sh) | 21 |
| | 424 | 12 |
| ligand 1 | 210 | |
| | 275 | |
| ligand 2 | 215 | |
| | 270 | |
| ligand 3 | 212 | |
| | 275 | |

[a] Solvent: methanol. sh = shoulder.

**Table VI.** Infrared Spectral Parameters[a] ($cm^{-1}$)

| complex | Tc—O—Tc | Tc=O |
|---|---|---|
| **1** | 674 (s) | 920 (w) |
| **2** | 670 (s) | cannot be identified |
| **3** | 664 (s) | 913 (w) |

[a] Spectra taken as Nujol mulls between NaCl disks.

**Table VII.** Comparison of Technetium Coordination (Average)[a]

| | complex | | | Schiff base[b] |
|---|---|---|---|---|
| | **1** | **2** | **3** | |
| $Tc{=}O_t$ | 1.677 (1) | 1.665 (6) | 1.672 (3) | 1.68 (1) |
| $Tc—O_b$(bridge) | 1.917 (27) | 1.918 (1) | 1.922 (12) | 1.90 (1) |
| $Tc—O_p$(phenol) | 1.99 (1) | 1.985 (10) | 1.991 (4) | 2.01 (1) |
| Tc—N | 2.17 (3) | 2.182 (13) | 2.228 (20) | 2.12 (1) |
| $O_p—Tc—O_b$ | 164.4 (1) | 163.7 (2) | 163.0 (1) | 166.3 (8) |
| $Tc—O_b—Tc$ | 166.5 (5) | 180 | 169.6 (1) | 180 |
| $O_t—Tc—N$ | 86.9 (5) | 85.0 (1) | 85.4 (1.2) | 88.4 (9) |
| $O_t—Tc—O_p$ | 100.6 (1) | 100.8 (7) | 100.7 (9) | 98.9 (7) |
| $O_b—Tc—N$ | 82.7 (9) | 83.6 (6) | 84.0 (1) | 82.4 (1.2) |
| $O_b—Tc—O_p$ | 91.2 (5) | 91.4 (4) | 91.8 (9) | 91.2 (8) |
| $N—Tc—O_p$(trans) | 170.9 (1) | 172.8 (6) | 169.4 (1.8) | 170.9 (5) |
| $N—Tc—O_p$(cis) | 90.4 (1) | 92.5 (3) | 89.5 (1.1) | 90.7 (5) |
| N—Tc—N | 95.5 (2) | 92.1 (3) | 99.6 (1.3) | 94.7 (8) |
| $O_p—Tc—O_p$ | 83.1 (2) | 82.3 (3) | 81.0 (4) | 83.2 (7) |

[a] Distances in angstroms; angles in degrees. [b] Values from ref 7.

Although only complex **2** has a crystallographic center of symmetry, all three dinuclear complexes are approximately centrosymmetric. Complexes **1** and **3** are slightly puckered at the bridging oxygen in contrast to complex **2** and the Schiff base complex.[7] In all cases, there is significant deviation from linearity in the O=Tc—O(bridging) angle (164.4, 163.7, 163.0°).

Positional parameters and their estimated standard deviations for complexes **1**–**3** are given in Tables VIII–X, respectively. ORTEP drawings of the Tc complexes are given in Figures 2–4. Parameters for hydrogen atoms, complete bond distances, complete bond angles, thermal parameters, least-squares planes, and $F_o/F_c$ tables are available as supplementary material.

## Discussion

The ($\mu$-oxo)bis(oxo)technetium(V) complexes formed in these studies are very similar to ($\mu$-oxo)bis(oxo)[*N*,*N*′-propane-1,3-diylbis(salicylidineaminato)]technetium(V) reported in ref 7. Attempts by those authors to produce a technetium complex with the corresponding four-carbon backbone salicylidineaminato ligand resulted in "half-coordinated" complexes wherein the ligand was bidentate. We find no evidence for a complex of this nature with these ligands with either $^{99}$Tc or $^{99m}$Tc.

**Table VIII.** Positional Parameters and Their Estimated Standard Deviations for Complex **1**

| atom | *x* | *y* | *z* | *B*,[a] Å$^2$ |
|---|---|---|---|---|
| Tc | 0.74946 (4) | −0.01222 (3) | 0.08914 (9) | 3.14 (2) |
| Tc′ | 0.74841 (4) | 0.03126 (3) | 0.46456 (9) | 3.07 (2) |
| Cl1 | 0.7087 (2) | 0.2028 (2) | −0.4711 (8) | 13.4 (2) |
| Cl2 | 0.7997 (2) | 0.2001 (2) | −0.5427 (9) | 21.0 (3) |
| Cl3 | 0.7693 (3) | 0.1590 (3) | −0.3065 (6) | 18.8 (3) |
| Cl4 | 0.3619 (3) | 0.1957 (3) | 0.3803 (7) | 17.0 (3) |
| Cl5 | 0.3201 (2) | 0.2307 (4) | 0.6139 (8) | 19.7 (3) |
| Cl6 | 0.3491 (3) | 0.2880 (2) | 0.4021 (8) | 17.9 (3) |
| O1 | 0.7891 (3) | −0.0623 (3) | 0.1592 (9) | 4.5 (2) |
| O1′ | 0.7968 (3) | 0.0770 (3) | 0.4374 (8) | 4.7 (2) |
| O2 | 0.7000 (3) | −0.0537 (3) | 0.1508 (8) | 3.8 (2) |
| O2′ | 0.7077 (3) | 0.0838 (2) | 0.4304 (8) | 3.8 (2) |
| O3 | 0.7517 (3) | −0.0242 (2) | −0.0826 (7) | 4.4 (2) |
| O3′ | 0.7454 (3) | 0.0279 (2) | 0.6396 (7) | 4.4 (2) |
| O4 | 0.7504 (3) | 0.0163 (2) | 0.2664 (6) | 3.4 (2) |
| N1 | 0.8085 (3) | 0.0290 (3) | 0.0588 (9) | 4.1 (3) |
| N1′ | 0.7983 (3) | −0.0231 (3) | 0.479 (1) | 3.5 (2) |
| N2 | 0.6989 (3) | 0.0390 (3) | 0.0374 (9) | 3.3 (2) |
| N2′ | 0.6915 (3) | −0.0154 (3) | 0.4593 (9) | 3.4 (2) |
| C1 | 0.8350 (4) | −0.0634 (4) | 0.166 (1) | 4.0 (3) |
| C1′ | 0.8388 (4) | 0.0692 (5) | 0.393 (1) | 5.2 (4) |
| C2 | 0.8635 (4) | −0.0353 (5) | 0.097 (1) | 5.3 (3) |
| C2′ | 0.8624 (4) | 0.0310 (5) | 0.436 (1) | 4.7 (3) |
| C3 | 0.8473 (4) | 0.0018 (5) | 0.006 (2) | 5.5 (4) |
| C3′ | 0.8420 (4) | −0.0038 (5) | 0.534 (1) | 6.3 (4) |
| C4 | 0.8013 (5) | 0.0711 (4) | −0.024 (2) | 5.6 (4) |
| C4′ | 0.7822 (5) | −0.0639 (4) | 0.560 (1) | 4.8 (3) |
| C5 | 0.7601 (5) | 0.0972 (4) | 0.020 (1) | 4.8 (3) |
| C5′ | 0.7402 (5) | −0.0836 (4) | 0.508 (1) | 4.6 (3) |
| C6 | 0.7156 (4) | 0.0800 (4) | −0.034 (1) | 4.2 (3) |
| C6′ | 0.6960 (4) | −0.0583 (4) | 0.542 (1) | 4.4 (3) |
| C7 | 0.6586 (5) | 0.0179 (5) | −0.038 (1) | 4.8 (3) |
| C7′ | 0.6493 (4) | 0.0073 (4) | 0.494 (1) | 3.5 (3) |
| C8 | 0.6344 (4) | −0.0161 (4) | 0.041 (1) | 4.2 (3) |
| C8′ | 0.6371 (4) | 0.0455 (4) | 0.389 (1) | 3.1 (3) |
| C9 | 0.6535 (4) | −0.0462 (4) | 0.128 (1) | 4.3 (3) |
| C9′ | 0.6681 (4) | 0.0808 (4) | 0.368 (1) | 3.2 (3) |
| C10 | 0.6257 (5) | −0.0783 (4) | 0.203 (1) | 5.1 (3) |
| C10′ | 0.6550 (4) | 0.1156 (4) | 0.278 (1) | 3.9 (3) |
| C11 | 0.5793 (5) | −0.0775 (5) | 0.189 (1) | 6.6 (4) |
| C11′ | 0.6139 (5) | 0.1151 (4) | 0.209 (1) | 4.1 (3) |
| C12 | 0.5604 (5) | −0.0442 (5) | 0.100 (2) | 7.4 (4) |
| C12′ | 0.5840 (4) | 0.0801 (5) | 0.231 (1) | 5.5 (4) |
| C13 | 0.5869 (4) | −0.0150 (5) | 0.036 (1) | 5.0 (3) |
| C13′ | 0.5965 (4) | 0.0461 (5) | 0.325 (1) | 4.2 (3) |
| C14 | 0.9127 (5) | −0.0405 (6) | 0.120 (2) | 8.4 (5) |
| C14′ | 0.9070 (5) | 0.0247 (6) | 0.387 (2) | 8.9 (5) |
| C15 | 0.9271 (5) | −0.0753 (5) | 0.206 (2) | 7.5 (4) |
| C15′ | 0.9276 (5) | 0.0541 (6) | 0.312 (2) | 7.7 (5) |
| C16 | 0.9024 (5) | 0.0931 (5) | 0.264 (1) | 6.7 (4) |
| C16′ | 0.8975 (5) | −0.1011 (6) | 0.265 (1) | 7.1 (4) |
| C17 | 0.8523 (5) | −0.0985 (5) | 0.250 (1) | 4.9 (3) |
| C17′ | 0.8603 (4) | 0.0997 (5) | 0.306 (1) | 6.0 (4) |
| C18 | 0.7581 (5) | 0.1720 (5) | −0.473 (1) | 6.1 (4) |
| C19 | 0.3587 (4) | 0.2390 (6) | 0.492 (1) | 6.7 (4) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

The proton NMR spectra of the ligands are straightforward, and there are no particularly unusual features. However, the corresponding spectra of the Tc(V) complexes are more complicated and interesting. The simplest spectrum is that of complex **2**, which suggests only half of the ligand being independent, but methylene protons on the same carbon atom as well as the two methylene groups are nonequivalent because of the puckering of the chelate rings. Complexes **1** and **3** apparently involve a conformation that results in nonequivalence of the halves of each ligand or nonequivalence of the corresponding groups on the two separate ligands. The former is assumed in assigning the spectra. For example, nonequivalence of methyl protons c and c′ results in chemical shift differences of 0.35–0.47 ppm in these two complexes. The nonequivalence found above was surprising and might result from the hindered rotation effects about the Tc–O–Tc bond. It should be noted that only compound **2** has a true center

**Table IX.** Positional Parameters and Their Estimated Standard Deviations for Complex **2**

| atom | *x* | *y* | *z* | *B*,[a] Å$^2$ |
|---|---|---|---|---|
| Tc | 0.13954 (8) | 0.12197 (9) | −0.00169 (4) | 3.15 (2) |
| Cl1 | 0.5729 (4) | −0.3335 (4) | −0.1185 (2) | 8.3 (1) |
| Cl2 | 0.7840 (4) | −0.4195 (4) | −0.1853 (2) | 9.4 (1) |
| Cl3 | 0.6582 (5) | −0.1871 (4) | −0.2201 (2) | 9.6 (1) |
| O1 | 0.2239 (6) | 0.0450 (7) | 0.0735 (3) | 4.3 (2) |
| O2 | 0.0580 (6) | 0.2349 (7) | 0.0599 (3) | 4.2 (2) |
| O3 | 0.2550 (6) | 0.2204 (7) | −0.0246 (3) | 4.1 (2) |
| O4 | 0.000 | 0.000 | 0.000 | 3.3 (2) |
| N1 | 0.2270 (7) | −0.0208 (8) | −0.0616 (4) | 3.0 (2) |
| N2 | 0.0225 (7) | 0.2027 (8) | −0.0781 (4) | 3.0 (2) |
| C1 | 0.2963 (9) | −0.065 (1) | 0.0787 (5) | 3.4 (2) |
| C2 | 0.3555 (8) | −0.122 (1) | 0.0298 (4) | 3.4 (2) |
| C3 | 0.3533 (9) | −0.066 (1) | −0.0331 (5) | 3.9 (3) |
| C4 | 0.2490 (9) | 0.024 (1) | −0.1249 (5) | 3.9 (3) |
| C5 | 0.1340 (9) | 0.080 (1) | −0.1628 (5) | 3.7 (3) |
| C6 | 0.0838 (9) | 0.207 (1) | −0.1382 (5) | 3.7 (3) |
| C7 | −0.0202 (9) | 0.3386 (9) | −0.0639 (5) | 3.7 (3) |
| C8 | −0.0927 (8) | 0.3517 (9) | −0.0063 (5) | 3.0 (2) |
| C9 | −0.0493 (9) | 0.3062 (9) | 0.0510 (5) | 3.1 (2) |
| C10 | −0.118 (1) | 0.334 (1) | 0.1022 (5) | 4.3 (3) |
| C11 | −0.232 (1) | 0.409 (1) | 0.0974 (5) | 4.4 (3) |
| C12 | −0.274 (1) | 0.458 (1) | 0.0415 (5) | 4.6 (3) |
| C13 | −0.2061 (9) | 0.429 (1) | −0.0094 (5) | 3.8 (3) |
| C14 | 0.4346 (9) | −0.231 (1) | 0.0423 (5) | 4.0 (3) |
| C15 | 0.452 (1) | −0.279 (1) | 0.1003 (6) | 4.8 (3) |
| C16 | 0.386 (1) | −0.228 (1) | 0.1491 (5) | 4.2 (3) |
| C17 | 0.3091 (9) | −0.121 (1) | 0.1371 (5) | 4.5 (3) |
| C18 | 0.189 (1) | 0.110 (1) | −0.2257 (5) | 6.5 (3) |
| C19 | 0.025 (1) | −0.018 (1) | −0.1730 (5) | 4.9 (3) |
| C20 | 0.704 (1) | −0.286 (1) | −0.1581 (5) | 5.0 (3) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

**Table X.** Positional Parameters and Their Estimated Standard Deviations for Complex **3**

| atom | *x* | *y* | *z* | *B*,[a] Å$^2$ |
|---|---|---|---|---|
| Tc | 0.83997 (2) | −0.07316 (3) | 0.83064 (2) | 2.886 (9) |
| Tc′ | 0.67531 (2) | 0.06365 (2) | 0.66774 (2) | 2.761 (9) |
| Cl1 | 0.7311 (1) | −0.1018 (1) | 1.3368 (1) | 6.68 (4) |
| Cl2 | 0.7222 (1) | −0.1083 (1) | 1.16946 (9) | 6.22 (4) |
| Cl3 | 0.8803 (1) | −0.1219 (1) | 1.3015 (1) | 7.44 (5) |
| Cl4 | 0.82859 (9) | 0.3815 (1) | 0.7741 (1) | 6.50 (5) |
| Cl5 | 0.6594 (1) | 0.3821 (1) | 0.7635 (1) | 7.76 (5) |
| Cl6 | 0.6971 (2) | 0.3629 (1) | 0.6172 (1) | 9.44 (7) |
| O1 | 0.7582 (2) | −0.1613 (2) | 0.8417 (2) | 3.67 (8) |
| O1′ | 0.7619 (2) | 0.1498 (2) | 0.6662 (2) | 3.95 (8) |
| O2 | 0.8512 (2) | −0.1653 (2) | 0.7535 (2) | 3.48 (7) |
| O2′ | 0.6723 (2) | 0.1423 (2) | 0.7588 (2) | 3.63 (8) |
| O5 | 0.5924 (2) | 0.1030 (2) | 0.5919 (2) | 3.94 (8) |
| O6 | 0.7569 (2) | −0.0121 (2) | 0.7412 (2) | 2.88 (7) |
| O7 | 0.9212 (2) | −0.0951 (2) | 0.9157 (2) | 3.95 (8) |
| N1 | 0.7998 (2) | 0.0209 (3) | 0.9062 (2) | 3.5 (1) |
| N1′ | 0.6959 (2) | −0.0138 (3) | 0.5662 (2) | 3.4 (1) |
| N2 | 0.9293 (2) | 0.0157 (3) | 0.7992 (2) | 3.7 (1) |
| N2′ | 0.5875 (2) | −0.0238 (3) | 0.6986 (2) | 3.3 (1) |
| C1 | 0.6946 (3) | −0.1470 (3) | 0.8688 (3) | 3.6 (1) |
| C1′ | 0.8112 (3) | 0.1508 (3) | 0.6212 (3) | 3.6 (1) |
| C2 | 0.6983 (3) | −0.0830 (3) | 0.9285 (3) | 3.8 (1) |
| C2′ | 0.7933 (3) | 0.1036 (3) | 0.5476 (3) | 4.0 (1) |
| C3 | 0.7746 (3) | −0.0282 (4) | 0.9675 (3) | 4.6 (1) |
| C3′ | 0.7164 (3) | 0.0499 (4) | 0.5107 (3) | 4.6 (1) |
| C4 | 0.8551 (3) | 0.0969 (4) | 0.9466 (3) | 4.7 (1) |
| C4′ | 0.6257 (3) | −0.0697 (4) | 0.5141 (3) | 4.5 (1) |
| C5 | 0.8683 (3) | 0.1594 (3) | 0.8831 (3) | 4.6 (1) |
| C5′ | 0.6182 (3) | −0.1606 (4) | 0.5478 (4) | 5.1 (2) |
| C6 | 0.9556 (4) | 0.1594 (4) | 0.8807 (4) | 5.7 (2) |
| C6′ | 0.6172 (3) | −0.1620 (3) | 0.6345 (3) | 4.3 (1) |
| C7 | 0.9883 (3) | 0.0688 (4) | 0.8690 (3) | 4.7 (1) |
| C7′ | 0.5503 (3) | −0.1017 (4) | 0.6456 (3) | 4.5 (1) |
| C8 | 0.9803 (3) | −0.0388 (4) | 0.7640 (3) | 4.5 (1) |
| C8′ | 0.5201 (3) | 0.0298 (4) | 0.7102 (3) | 4.3 (1) |
| C9 | 0.9311 (3) | −0.0873 (3) | 0.6867 (3) | 3.6 (1) |
| C9′ | 0.5498 (3) | 0.0897 (4) | 0.7839 (3) | 3.7 (1) |
| C10 | 0.8726 (3) | −0.1508 (3) | 0.6872 (3) | 3.4 (1) |
| C10′ | 0.6220 (3) | 0.1407 (3) | 0.8037 (3) | 3.7 (1) |
| C11 | 0.8346 (3) | −0.2015 (3) | 0.6174 (3) | 4.2 (1) |
| C11′ | 0.6462 (3) | 0.1947 (4) | 0.8732 (3) | 4.6 (1) |
| C12 | 0.8515 (3) | −0.1861 (4) | 0.5461 (3) | 5.1 (1) |
| C12′ | 0.5962 (4) | 0.2007 (4) | 0.9216 (3) | 5.8 (2) |
| C13 | 0.9062 (3) | −0.1197 (4) | 0.5448 (3) | 5.5 (1) |
| C13′ | 0.5244 (3) | 0.1511 (4) | 0.9019 (3) | 6.1 (2) |
| C14 | 0.9450 (3) | −0.0714 (4) | 0.6136 (3) | 4.9 (1) |
| C14′ | 0.5019 (3) | 0.0965 (4) | 0.8336 (3) | 5.1 (1) |
| C15 | 0.6290 (3) | −0.0706 (4) | 0.9505 (3) | 5.1 (1) |
| C15′ | 0.8469 (3) | 0.1099 (4) | 0.5038 (3) | 5.5 (1) |
| C16 | 0.5582 (3) | −0.1211 (4) | 0.9168 (3) | 5.6 (2) |
| C16′ | 0.9164 (3) | 0.1641 (4) | 0.5307 (4) | 6.5 (2) |
| C17 | 0.5561 (3) | −0.1856 (4) | 0.8605 (3) | 5.3 (1) |
| C17′ | 0.9341 (3) | 0.2113 (4) | 0.6028 (4) | 5.8 (2) |
| C18 | 0.6236 (3) | −0.1983 (3) | 0.8362 (3) | 4.2 (1) |
| C18′ | 0.8821 (3) | 0.2041 (4) | 0.6495 (3) | 4.8 (1) |
| C19 | 0.7745 (3) | −0.1476 (3) | 1.2684 (3) | 4.4 (1) |
| C20 | 0.7307 (3) | 0.3392 (3) | 0.7216 (3) | 4.9 (1) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

of symmetry at the bridging oxygen atom in the crystal structure. There is asymmetric overlap on the aromatic ring in both complexes **1** and **3**. One would expect that this would not remain in solution, but if it did, it might account for the nonequivalence of protons observed here. An $^1$H NMR temperature dependence study (−50 to +40 °C) was done for compound **1** to check for sharpening, broadening, and/or disappearance of the nonequivalence discussed above. Although there were some slight shifts in relative intensities, there was no other significant change in the overall spectral parameters.

Significant changes in chemical shifts were noticed for the aliphatic carbon atoms in $^{13}$C NMR spectra of the complexes compared with those of the ligands. The resonances of the carbon atoms adjacent to the nitrogen atoms shift downfield whereas the resonances of the methylene carbons shift upfield in all three complexes compared to those of the ligands. The independent carbon atoms in all three complexes are restricted to half of one ligand.

The O=Tc—O—Tc=O core is analogous to that established much earlier for Re(V) complexes. The structure of $Re_2O_3(S_2CN(C_2H_5)_2)_4$ was reported by Fletcher et al.,[15] and that of $[Re_2O_3(CN)_8]^{4-}$, by Shandles et al.[16] In these structures, the Re=O distances seem to depend on the ligands in the square plane, being 1.734 (4) Å in the former and 1.698 (7) Å in the latter. The bridging Re–O distance is less sensitive, being 1.910 (10) Å in the former and 1.9149 (4) Å in the latter. In the present Tc(V) complexes, both of these distances are fairly constant, averaging 1.671 (6) and 1.919 (3) Å. These are very similar to the values observed for the Schiff base analogue of compound **2** (1.68 (1) and 1.90 (1) Å), as might be expected for comparable ligands in the square plane. The Tc=O bond in these complexes is essentially the same as that (1.675 (2) Å) in the five-coordinate $TcOEn(AO)_2$ complex, but much shorter than that (1.744 (2) Å) in the six-coordinate $TcO_2Pent(AO)_2$ complex.[2]

The average Tc–N(amine) distances (2.17 (3), 2.182 (13), 2.228 (20) Å) observed in this work are similar to the one reported for $TcO_2Pent(AO)_2$ (2.219 (15) a).[3] These are all, not surprisingly, longer than that (2.12 (1) Å) for the imine nitrogen of the Schiff base analogue.[7] The longer bond distance for compound **3** may be related to the steric unfavorability of the seven-membered ring formed due to the four-carbon backbone. This complex has a lower energy visible absorption maximum (424 nm) than the other two complexes (average 401 nm), suggesting a weak crystal field, in keeping with the longer Tc–N bond length. The N–Tc–N angle

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opens to 99.6 (1.3)° in complex **3**, which is higher than that for complexes **1** and **2** and also larger than that for the Schiff base analogue. In that case the Tc–O(phenol) distance (2.01 (1) Å) appears to be slightly longer than that observed here (1.99 (1) Å).

The least-squares planes (supplementary material) show the Tc atom to be approximately 0.1 Å out of the plane defined by the coordinated atoms of the tetradentate ligand toward the terminal oxygen atoms. The chloroform molecules present in all three crystal structures are not especially close to any of the Tc complex atoms (closest contacts: compound **1**, O1–C18 = 3.15 Å, O1–C19 = 3.19 Å; compound **2**, O1–C20 = 3.16 Å, O2–C20 = 3.21 Å; compound **3**, O1–C20 = 3.12 Å, O2–C20 = 3.27 Å). Within the dimers, the aromatic rings bend away from the terminal oxygen atoms. This results in rather close contact between portions of these rings (e.g.: in compound **1**, C14---C14′ = 3.19 Å, C13---C13′ = 3.31 Å; in compound **2**, C13---C14 = 3.18 Å, C12---C14 = 3.36a; in compound **3**, C14---C15′ = 3.42 Å, C14′---C15 = 3.49 Å).

The behavior of the complexes of the $^{99m}$Tc isomer has also been investigated.[13] These complexes are formed in very dilute solutions in greater than 95% yield, are stable in vitro, and are readily extracted into $CHCl_3$ or 1-octanol. These observations suggest that derivatives of these ligands as bifunctional chelating agents for technetium might be useful for protein labeling. Studies of the biodistribution in rats of the $^{99m}$Tc complexes[11] showed a very slow clearance from the blood. Further studies showed that white blood cells could be labeled in 30–70% yield after 30-min reaction with the complex. However, radioactivity was released from the cells at 37 °C at a rate of ~30%/h. Because of this high rate of release, the complexes described in this work are probably not directly suited for cell labeling, but it may be possible to prepare derivatives with higher retention.

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**Supplementary Material Available:** Tables of anisotropic displacement parameters, least-squares planes, bond distances and angles, and hydrogen atom positional parameters for complexes **1–3** (27 pages); tables of observed and calculated structure factors for complexes **1–3** (46 pages). Ordering information is given on any current masthead page.

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# Indole Nitrogen–Palladium(II) Bonding. Chemical and Structural Characterization of Palladium(II) Complexes of Alkylindoles and Intermediacy of the 3*H*-Indole Ring

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The first palladium(II) complexes of alkylindoles (2-methylindole (MI) and 2,5-dimethylindole (DMI)) coordinating through the nitrogen atom in the 3*H*-indole form have been isolated and characterized by X-ray crystal structure analysis and spectroscopic methods. The complexes $[Pd(MI)_2Cl_2]$ (**1**) and $[Pd(DMI)_2Cl_2]$ (**2**) were obtained as pale brown crystals from methanol solutions. Both complexes crystallized in the monoclinic space group $P2_1/c$ with $Z = 2$. They have a square-planar structure with two indole molecules coordinating to Pd(II) in the trans geometry with two chloride ions occupying the remaining positions. The indole ring is bound to Pd(II) through the $sp^2$ nitrogen atom (N(1)) and is nearly perpendicular to the Pd(II) coordination plane. The N(1)–C(2) bond length (1.305 (12) Å) in **1** is much shorter than that found for 2,3-diphenylindole (1.392 (2) Å), and the C(2)–C(3) (1.516 (12) Å) and C(3)–C(3a) (1.469 (15) Å) bonds are nearly equal to single bonds, indicating that the indole ring assumes the 3*H*-indole form. The $^1H$ NMR spectra of **1** in $CDCl_3$ exhibited $CH_2$ signals at ~3.9 ppm but no C(3) and N(1) proton signals observed for MI, which is in accord with the 3*H*-indole structure. The $^{13}C$ NMR spectra in solution and in the solid state further confirmed that the 3*H*-indole structure with the $sp^3$-like C(3) is maintained under both conditions. The results establish the coordination of the indole ring through the "pyridine-like" nitrogen and the intermediacy of the 3*H*-indole structure in the course of reactions catalyzed, e.g., by metal ions having strong affinity toward nitrogen donors.

## Introduction

Indole is an electron-rich aromatic ring showing characteristic chemical reactivities and serving as an important constituent of tryptophan and ergot alkaloids and other pharmacologically active natural compounds.[2] It has the greatest hydrophobicity among amino acid side chains,[3] which is suitable for constituting a hydrophobic environment in proteins. Some oligopeptides with a tryptophyl residue recognize apurinic sites in DNA or intercalate into the base pairs by this residue.[4] Because of the enamine nature of the indole ring, 3*H*-indole forms are often assumed as intermediates in the reactions with electrophiles.[2] While alkali-metal and Grignard derivatives are known to involve essentially ionic metal–nitrogen bonds,[5] the bonding with transition-metal ions is usually achieved by side-chain donor groups such as the amino and carboxylate groups of tryptophan typically exemplified by the structure of a ternary copper(II) complex [Cu(phen)(L-Trp)]$^+$ (phen = 1,10-phenanthroline; Trp = tryptophan).[6] A bidentate bonding with Pd(II) through the nitrogen (N(1)) and carbon (C(2)) has been reported for binuclear complexes with N,C-bridging indole or 3-methylindole, where the N(1)–C(2) double bond with protonation at C(3) has been concluded from $^1H$ NMR spectra.[7] In the course of the studies on the aromatic ring stacking

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