

Osmium(IV) Complexes with 2,3-Diamino-2,3-dimethylbutane (tmen): Syntheses, Properties, and Structures†

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Received September 5, 1991

(NH₄)₂OsBr₆ reacts smoothly with an excess of 2,3-diamino-2,3-dimethylbutane (tmen) in water to give a brown Os(IV) tris-chelate complex which has lost two protons from two different ligands, [Os(tmen-H)₂tmen]²⁺. The same brown complex is also obtained when OsCl₃·3H₂O reacts with an excess of tmen in ethanol. In 6 M trifluoromethanesulfonic acid (Htfms), the brown complex accepts one proton and the monodeprotonated pale green [Os(tmen-H)(tmen)₂]³⁺ complex can be isolated. Its pK_a is 0.04. The pH dependence of the reduction potential of [Os(tmen-H)₂tmen]²⁺ determined by cyclic voltammetry shows that the reduction is accompanied by a gain of two protons, forming the fully protonated [Os(tmen)₃]³⁺ complex. In aerated aqueous acid, the [Os(tmen-H)₂tmen]²⁺ complex can be reduced using granulated Zn to give the fully protonated [Os(tmen)₃]³⁺ complex. The reduction potential of [Os(tmen)₃]^{3+/2+} occurs at -0.35 V (vs NHE). The solution structures of [Os(tmen-H)₂tmen]²⁺ and [Os(tmen-H)(tmen)₂]³⁺ have been determined by high-resolution ¹H and ¹³C 1D- and 2D-NMR spectroscopy in CD₃CN. Both ions show highly deshielded NH protons (δ = 13 and 30 ppm, respectively, relative to TMS) and slow exchange of NH and NH₂ protons. In [Os(tmen-H)₂tmen]²⁺, the two NH groups are in a cis arrangement both in solution and in the solid state, as shown by an X-ray structure determination at 100 K. Its toluenesulfonate salt crystallizes in the tetragonal space group P4₂1c with a = b = 13.310(2) Å, c = 23.607(4) Å, and Z = 4. The structure was refined to R = 0.037 (R_w = 0.046) for 1528 unique reflections with F_o > 6σ(F_o). Average Os–N distances are 2.15 Å (–NH₂) and 1.88 Å (–NH). The chemical shifts of the NH protons and the Os=N distances are both indicative of strong Os–N π-bonding.

Introduction

Diamagnetic Os(IV) complexes with singly and doubly deprotonated 1,2-ethanediamine (en) ligands were first reported by Dwyer and Hogarth.² Subsequent reinvestigation and a crystal structure determination of [Os(en-H)₂en]Br₂ by Sargeson et al.³ confirmed that these Os(IV) complexes are intermediates in the oxidative dehydrogenation reaction of the coordinated amine ligand leading to Os(II) imine and diimine complexes as the final products. Inhibition of this dehydrogenation reaction may be carried out by using the fully C-methylated 2,3-diamino-2,3-dimethylbutane (tmen) ligand known to stabilize high-oxidation-state Os-oxo complexes.^{4,5} This paper reports the syntheses and properties of [Os(tmen-H)₂tmen]²⁺ and [Os(tmen-H)(tmen)₂]³⁺, their solution structures as determined by ¹H and ¹³C NMR spectroscopy, and a crystal structure determination of [Os(tmen-H)₂tmen](C₇H₇SO₃)₂·2H₂O at 100 K.

† Abbreviations: tmen-H and en-H denote ligands which have lost one amine proton.

- (1) (a) Institut für Anorganische Chemie. (b) Laboratorium für Kristallographie. (c) Institut für Organische Chemie.
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- (3) Lay, P. A.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 6161–6164. The peaks were reported as being broad in D₂O, which may be indicative of the exchange of protons being on the NMR time scale. Recent NMR studies in CD₃CN (in the range 253–298 K) have shown resolved NH and NH₂ resonances, indicative of slow exchange of protons among the N sites. The spectra are very similar to those of the tmen complexes reported in this paper. Full details will be reported in a future communication.
- (4) Che, C.-M.; Hon-Wah Lam, M.; Wang, R.-J.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1990**, 820–821.
- (5) The effect of steric crowding by the 12 methyl groups has been investigated for [Co(tmen)₃]³⁺. In particular, the rates of racemization and hydrolysis in basic solution show half-lives of the order of milliseconds for [Co(tmen)₃]³⁺ as compared to the order of years for the parent [Co(en)₃]³⁺ complex.⁶
- (6) (a) Hendry, P.; Ludi, A. *Helv. Chim. Acta* **1988**, *77*, 1966–1970; *J. Chem. Soc., Chem. Commun.* **1987**, 891–892. (b) Diab, H.; Hendry, P.; Ludi, A.; Reddy, K. B.; Van Eldik, R. *Inorg. Chim. Acta* **1990**, *175*, 83–90.

Experimental Section

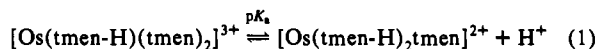
(A) Preparation of [Os(tmen-H)₂tmen]I₂·H₂O and Crystal Growth. (NH₄)₂OsBr₆ or (NH₄)₂OsCl₆ (0.5 g, Alfa) was added to a solution of tmen as free base⁷ in water (3 g in 15 mL). The solution was kept at 40 °C for 30 min. One gram of NaI was added, and the resulting brown solid was filtered off, washed with ice-cold water, ethanol, and ether, and recrystallized from water; yield 90%. Anal. Calcd for [Os(tmen-H)₂tmen]I₂·H₂O (C₁₈H₄₈N₆OI₂Os): C, 26.7; H, 5.9; N, 10.4; H₂O, 2.2; I, 31.4. Found: C, 27.0; H, 6.0; N, 10.4; H₂O, 2.5; I, 30.2.

The same brown complex was obtained as the chloride salt when OsCl₃·3H₂O (0.5 g, Alfa) was reacted with tmen (3 g in 15 mL) in ethanol. The chloride salt precipitated from solution as the complex was formed; yield 90%. Anal. Calcd for C₁₈H₄₈N₆Cl₂Os: C, 35.6; H, 7.6; N, 13.8. Found: C, 35.8; H, 7.8; N, 13.4. An excess of sodium tosylate was added to a solution of the chloride salt, which upon slow evaporation at room temperature produced square platelike crystals suitable for X-ray analysis. Examination under polarized light showed them to be dichroic (E||c, brown; E⊥c, green).

[Os(tmen-H)(tmen)₂](CF₃SO₃)₂·0.5H₂O. [Os(tmen-H)₂tmen]Cl₂ was added to 10 mL of 6 M CF₃SO₃H (Htfms), and the mixture was stirred for 10–15 min. The brown complex became pale green with no apparent dissolution. It was filtered off and washed with ethanol and ether. Anal. Calcd for C₂₁H₄₇N₆O₉F₉S₃Os·0.5H₂O: C, 25.4; H, 4.9; N, 8.5; S, 9.7; F, 17.2; H₂O, 0.9. Found: C, 24.9; H, 4.7; N, 8.1; S, 10.2; F, 17.6; H₂O, 1.0.

[Os(en-H)₂en]I₂, [Os(en-H)(en)₂]I₃, and [Os(en)₃]I₃·2H₂O were prepared according to previously reported procedures.^{3,8}

(B) pK_a of [Os(tmen-H)(tmen)₂]³⁺. The pK_a of the tmen complex (eq 1) was determined spectrophotometrically at 25 °C by measuring the



absorption band of [Os(tmen-H)₂tmen]²⁺ at 486 nm (20 580 cm⁻¹) as a function of pH. Twelve solutions having identical concentrations of

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Table I. Crystal Data and Intensity Collection and Refinement Parameters for $[\text{Os}(\text{tmen-H})_2\text{tmen}](\text{C}_7\text{H}_7\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$

formula	$\text{C}_{32}\text{H}_{64}\text{O}_8\text{N}_6\text{S}_2\text{Os}$	Z	4
fw	915.3	D_{obs} , g/cm ³	1.40 (293 K)
space group	$P4_2/c$ (No. 114)	$D_{X\text{-ray}}$, g/cm ³	1.45 (100 K)
T	100K	λ , Å	0.710 69
a, Å	13.310 (2)	abs coeff, cm ⁻¹	31.95
c, Å	23.607 (4)	R	0.032 ^a
V, Å ³	4182 (1)	R _w	0.046 ^b

$${}^a R = \sum(|F_o| - |F_c|) / \sum|F_o|, {}^b R_w = [\sum w(F_o^2 - F_c^2) / \sum wF_o^2]^{1/2}.$$

$[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ (6×10^{-3} M) and concentrations of H_2SO_4 varying from 5×10^{-4} to 10 M were prepared by volumetric dilutions of stock solutions. A constant ionic strength was not maintained.

(C) **Cyclic Voltammetry.** In aqueous acid, carbon paste was used as the working electrode, and calomel and Pt wire were used as the reference and auxiliary electrodes, respectively. For the pH-dependence experiment, 20-mg samples of the doubly deprotonated complex were dissolved in 25-mL portions of solution containing various concentrations of H_2SO_4 (pH 0.5–3.5) and 0.25 M Na_2SO_4 .

(D) **Instrumentation.** Electronic spectra were recorded on a Hewlett Packard 8451A diode array spectrophotometer. ¹H and ¹³C NMR spectra were recorded in CD_3CN solution on a Bruker AM400 instrument, equipped with a standard 5-mm ¹H/¹³C dual probehead, an ASPECT 3000 computer, and a process controller.

(E) **Crystal Structure Analysis of $[\text{Os}(\text{tmen-H})_2\text{tmen}](\text{C}_7\text{H}_7\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$.** Unit cell parameters were refined with constrained parameters ($a = b$, $\alpha = \beta = \gamma = 90^\circ$) using 18 reflections in the 2θ range 22–23° at 100 K. Intensities were collected with a CAD-4F diffractometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.710$ 69 Å) and a low-temperature attachment. During data collection, the orientation was checked every 100 reflections and four reflections were used to monitor intensity changes. Intensity increased up to 104.4%, and data were accordingly corrected for time- and θ -dependent increase as well as for Lorentz and polarization effects. An empirical absorption correction was applied⁹ using transmission data from nine reflections. From preliminary precession photographs the space group was determined as $P4_2/c$. The agreement factor obtained for multiple measurements and equivalent reflections is $R(I) = 0.024$. Neutral-atom scattering factors¹⁰ included anomalous dispersion corrections for all non-hydrogen atoms. Further information concerning crystal data and intensity collection parameters is given in Table I. Data reduction was performed using the Enraf-Nonius structure determination package SDP¹¹ on a PDP 11/34 computer. Solution and refinement of the crystal structure were carried out with the NRCVAX program system¹² on a SUN 386i computer. Stereoscopic drawings of the unit cell were prepared with the ORTEP program of the XTAL¹³ package on an IBM 3090-28E computer. Stereoscopic drawings of the molecule were prepared with the PEANUT program¹⁴ on an Iris 3130 computer (Figure 6). Os and S atoms were found in a Patterson map. From subsequent difference Fourier maps all non-hydrogen atoms were located. A water molecule was found, which was disordered over three positions 1.2–1.3 Å apart from each other. Hydrogen positions were taken from a difference map (NH) or inserted at calculated positions (NH₂, CH₃; $d_{\text{N-H}} = 0.93$ Å, $d_{\text{C-H}} = 0.97$ Å) and were not refined. Non-hydrogen atoms were refined anisotropically, and for all hydrogen atoms, a fixed isotropic value ($U_{\text{iso}} = 0.055$ Å²) was used in least-squares refinements. A total of 240 parameters were refined on 1528 F_s ($>6\sigma(F)$).

Weights were chosen as $w = 1/[\sigma^2(F_o) + 0.0002F_o^2]$, and the function $\sum w(|F_o| - |F_c|)^2$ was minimized. The remaining difference electron densities were -1.46 e/Å³ (0.88 Å from Os) and 0.62 e/Å³ (1.48 Å from N1 and 2.4 Å from Os), respectively. An absolute structure would not be

Table II. Final Atomic Positional Parameters and B_{eq} Values, with Standard Deviations in Parentheses, for $[\text{Os}(\text{tmen-H})_2\text{tmen}](\text{C}_7\text{H}_7\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$

atom	x/a	y/b	z/c	B_{eq} , Å ²
Os	0	0	0.18864 (1)	2.067 (9)
N1	0.1143 (5)	-0.0004 (7)	0.1418 (2)	2.4 (1)
C1	0.1641 (8)	-0.0933 (6)	0.1237 (3)	2.7 (2)
C11	0.2009 (8)	-0.0800 (7)	0.0628 (4)	3.8 (2)
C12	0.2601 (8)	-0.1124 (7)	0.1600 (4)	3.6 (2)
N2	0.0273 (5)	-0.1584 (5)	0.1817 (3)	2.6 (1)
C2	0.0847 (8)	-0.1808 (6)	0.1287 (3)	3.0 (2)
C21	0.0149 (8)	-0.1803 (6)	0.0787 (3)	3.2 (2)
C22	0.1328 (7)	-0.2852 (7)	0.1340 (4)	3.1 (2)
N3	0.0986 (5)	-0.0039 (6)	0.2626 (2)	2.6 (1)
C3	0.0538 (8)	0.0221 (8)	0.3197 (4)	3.9 (2)
C31	0.1202 (8)	-0.0161 (8)	0.3664 (4)	3.9 (4)
C32	0.0499 (7)	0.1386 (6)	0.3235 (4)	3.3 (2)
S	0.2759 (2)	0.2094 (2)	0.1956 (1)	3.85 (5)
O1	0.3345 (5)	0.2879 (5)	0.2237 (2)	3.3 (1)
O2	0.2775 (5)	0.1158 (5)	0.2272 (3)	4.3 (1)
O3	0.1762 (5)	0.2450 (8)	0.1791 (3)	6.2 (2)
C4	0.3409 (7)	0.1861 (6)	0.1315 (4)	3.0 (2)
C5	0.3062 (6)	0.2222 (8)	0.0811 (4)	3.4 (2)
C6	0.3609 (7)	0.2125 (8)	0.0325 (4)	3.9 (2)
C7	0.4541 (7)	0.1628 (7)	0.0328 (4)	3.4 (2)
C8	0.4867 (7)	0.1253 (6)	0.0844 (4)	3.2 (2)
C9	0.4321 (8)	0.1379 (7)	0.1334 (4)	3.6 (2)
C10	0.5178 (8)	0.1503 (9)	-0.0194 (4)	5.0 (2)
O4	0.061 (2)	0.477 (2)	0.236 (1)	5.9 (7) ^b
O5	0.116 (2)	0.461 (2)	0.198 (1)	6.9 (7) ^b
O6	0.092 (2)	0.421 (2)	0.149 (1)	5.6 (5) ^b

^a $B_{\text{eq}} = 8\pi^2(u_{11} + u_{22} + u_{33})/3$. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter. ^b Population 0.333.

determined because the heaviest anomalous scatterer, Os, shows an exactly centrosymmetric arrangement. Final atomic positional parameters are given in Table II.

Results and Discussion

Reaction between Os(III) or Os(IV) halo complexes and tmen leads to the formation of the brown $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ complex, which is stable toward further reactions and differs from its en analogue, which undergoes oxidative dehydrogenation of the ligand. In strong acid, the complex is protonated to $[\text{Os}(\text{tmen-H})(\text{tmen})_2]^{3+}$. Zn/H⁺ reduction in air leads to the formation of the fully protonated $[\text{Os}(\text{tmen})_3]^{3+}$ complex, which is stable only in acidic solutions. In neutral or basic solution it disproportionates to Os(II) and Os(IV), resulting in a net oxidation to the brown $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ complex. The various tmen complexes of Os are summarized in Scheme I.¹⁵

The electronic spectra of the various Os(IV) en and tmen complexes are illustrated in Figure 1. The $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ complex shows a blue shift of about 3000 cm⁻¹. A slight increase in the extinction coefficient of the high-field band is also noticed.

The spectrophotometrically determined pK_a of $[\text{Os}(\text{tmen-H})(\text{tmen})_2]^{3+}$ is 0.04 ($I = 0.25$ M), significantly smaller than the value of 5.2 ($I = 0.15$ M) found for the corresponding en complex. This difference is in agreement with the observed pH dependence of the irreversible reduction potential of both $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ and $[\text{Os}(\text{en-H})_2\text{en}]^{2+}$ (Figure 2). From the slope of the graph of E_p (for the Os(IV) → Os(II) reduction at 500 mV s⁻¹) vs pH, the number of protons involved in the reduction is found to be 2.0 or 1, respectively in the pH range 0.5–3.5. The value of 2 implies that, upon reduction, the tmen complex takes up two protons; this is consistent with the low pK_a , which requires $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ as the main species present under the con-

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(15) The ¹H NMR spectra of $[\text{Os}(\text{tmen})_3]^{3+}$ in D₂O and CD₃CN are characterized by the absence of any resonances arising from the ligand due to the paramagnetic effects (shifts or broadening) of Os(III). Details of the chemistry of $[\text{Os}(\text{tmen})_3]^{3+}$ and its X-ray structure will be reported in a separate communication.

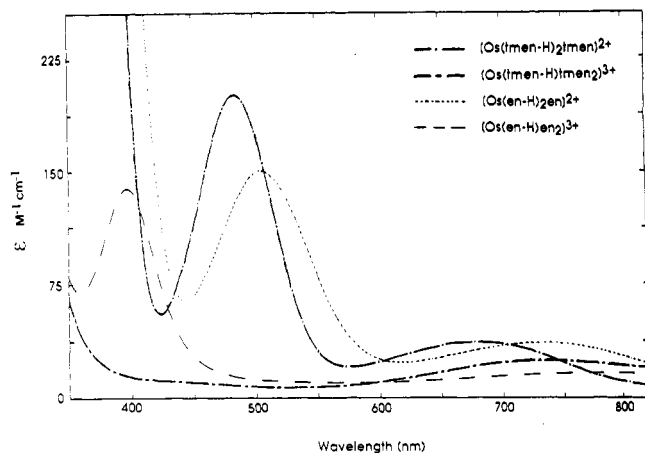
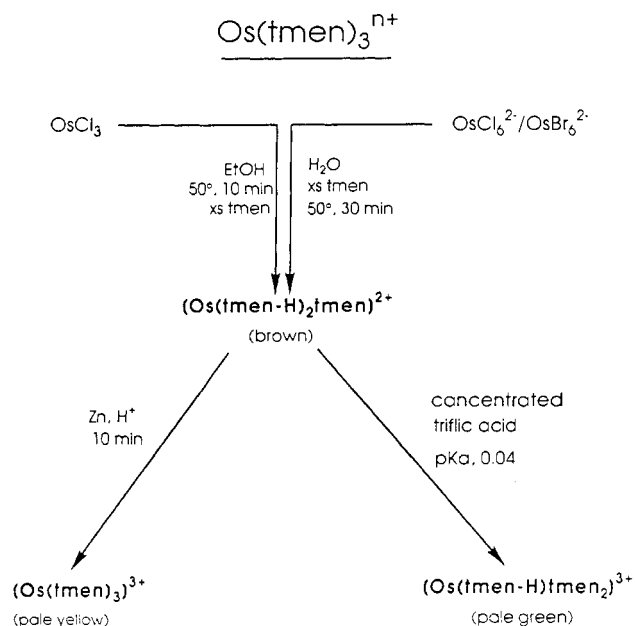


Figure 1. Electronic spectra of $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ (in water), $[\text{Os}(\text{tmen-H})(\text{tmen})_2]^{3+}$ (in 6 M H_2SO_4), $[\text{Os}(\text{en-H})_2\text{en}]^{2+}$ (in water), and $[\text{Os}(\text{en-H})(\text{en})_2]^{3+}$ (in 1 M H_2SO_4). Concentration of complex = 5×10^{-3} M.

Scheme I. Preparative Routes to Osmium tmen Complexes



ditions of the electrochemical experiment. Similarly, the value of 1 found for the en complex is consistent with its much higher pK_a , since during reduction the monodeprotonated ion $[\text{Os}(\text{en-H})(\text{en})_2]^{3+}$, which gains only one proton, is the main species in solution. The pH dependence is only observed upon reduction of the doubly deprotonated complexes at relatively fast scan rates (500 mV/s), and it is only the first scan that shows the irreversible $2e^-$ reduction of Os(IV). Subsequent scans show that the irreversible $2e^-$ wave is replaced by the reversible $1e^-$ Os(III/II) redox couple, which is pH independent. Cyclic voltammetry with authentic $[\text{Os}(\text{tmen})_3]^{3+}$ in acid solution only shows the reversible Os(III/II) redox couple.

Solution NMR studies on $[\text{Os}(\text{en-H})_2\text{en}]^{2+}$ in D_2O at ambient temperature showed a ^{13}C spectrum consistent with equivalent C atoms on the NMR time scale and rapid exchange of protons among the N sites.³ In contrast, the NMR evidence for both singly and doubly deprotonated tmen complexes is consistent with a slow exchange of protons among the different N atoms. For the $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ complex, ^1H NMR spectra (recorded in the range 25–95 °C) and ^{13}C NMR spectra (in D_2O and CD_3CN) show six nonequivalent methyl resonances centered at 1.2 ppm (^1H) and 26 ppm (^{13}C), respectively, and three additional ^{13}C resonances in the range 78–62 ppm attributed to the three pairs of equivalent quaternary carbons. The NH protons appear

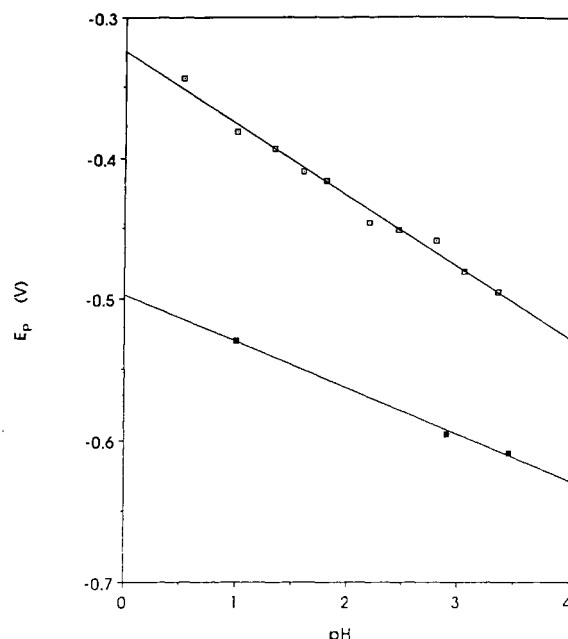


Figure 2. pH dependence of the irreversible reduction potentials exhibited by $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ (\square) and $[\text{Os}(\text{en-H})_2\text{en}]^{2+}$ (\blacksquare) as measured by cyclic voltammetry.

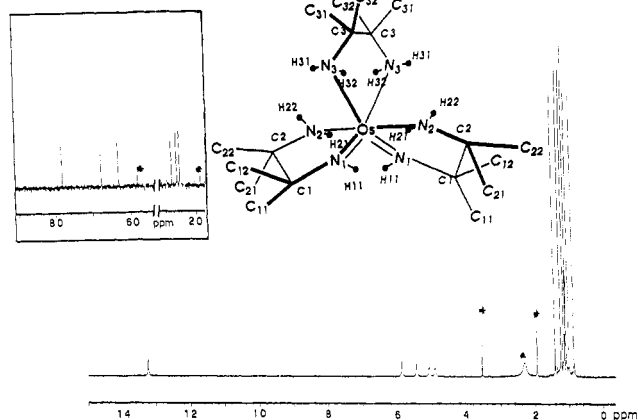


Figure 3. ^1H and ^{13}C (inset) NMR spectra of $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ in CD_3CN , at 298 K. Amine protons: H11, 13.2; H31, 5.9; H21, 5.4; H22, 5.1; H32, 4.9 ppm. Methyl protons: C22, 1.40; C31, 1.23; C11, 1.14; C12, 1.08; C32, 1.00; C21, 0.85 ppm. Quaternary carbons: C1, 77.9; C2, 67.4; C3, 62.9 ppm. Methyl carbons: C31, 26.2; C21, 25.0; C11, 24.8; C22, 24.2; C32, 24.1; C12, 24.0 ppm. Asterisks denote resonances due to ethanol impurity, H_2O , and partially deuterated CH_3CN present in the solvent.

as a singlet at 13.2 ppm and the NH_2 protons as doublets between 4.8 and 6 ppm (Figure 3). The number of resonances indicates a 2-fold symmetry of the complex in solution. Upon protonation of the doubly deprotonated to the singly deprotonated complex, this symmetry is lost. In both neat triflic acid (Htms, 11.15 M H^+) and CD_3CN (1 mL of solvent with two drops of neat Htms from a dropping pipet, ca. 0.5 M H^+), the NMR spectra of $[\text{Os}(\text{tmen-H})(\text{tmen})_2]^{3+}$ reveal 12 different methyl resonances centered at 0.7 ppm (^1H) and 24 ppm (^{13}C), respectively, and 6 additional ^{13}C resonances in the range 101–66 ppm attributed to the six nonequivalent quaternary carbons. Furthermore they reveal 11 resonances (10 doublets, 5–9 ppm and a singlet at 30 ppm) accounting for the amine protons (Figure 5).

Solution Structure of $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ Determined by NMR Spectroscopy. Because of fast exchange of protons among the N sites in $[\text{Os}(\text{en-H})_2\text{en}]^{2+}$ in water at 298 K, the structure in solution was not determined.³ On the basis of several factors, including electronic and angular strain, it was proposed that, of the five possible structures in Chart I, either one of structures 1

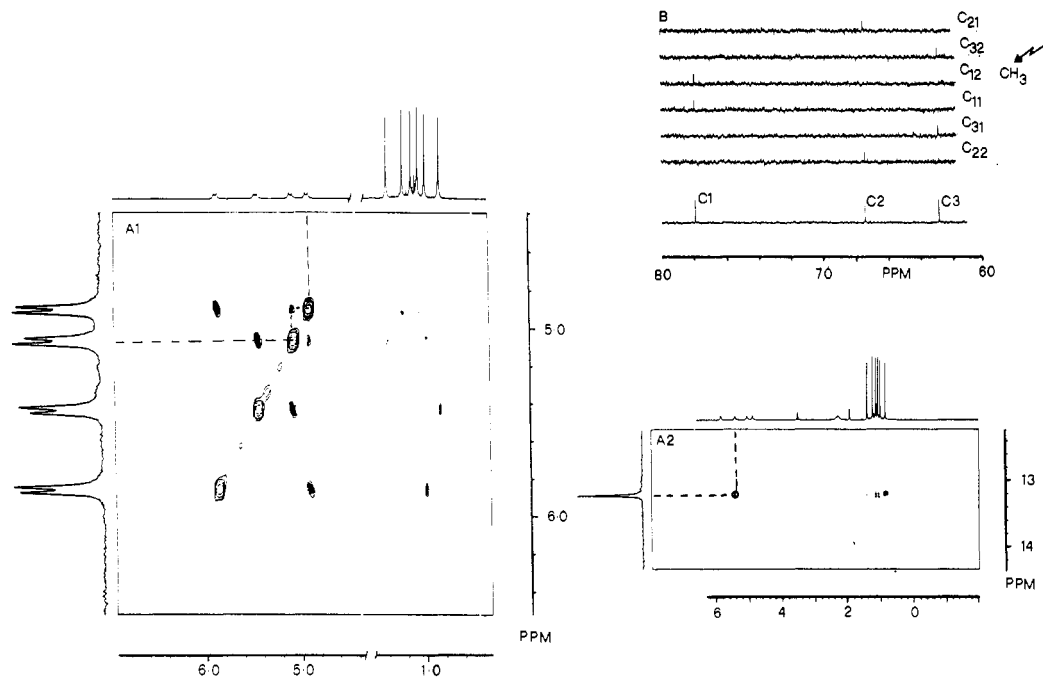


Figure 4. 2D NOESY (A1, A2) and heteronuclear 1D NOE (B) spectra of $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ in CD_3CN (298 K): (A1) between NH_2 protons and amine and methyl protons; (A2) between NH protons and amine and methyl protons; (B) between quaternary carbons and methyl protons.

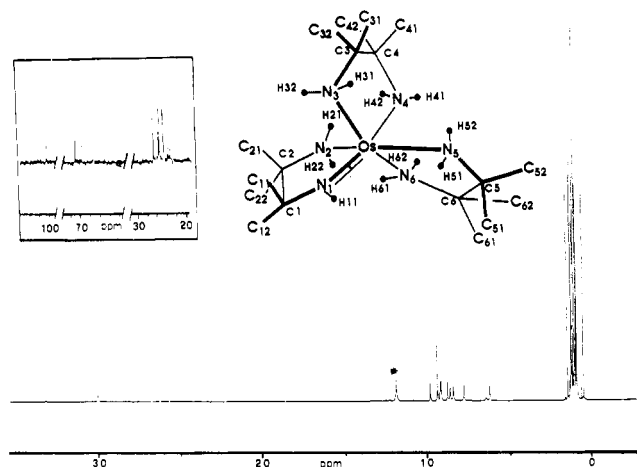
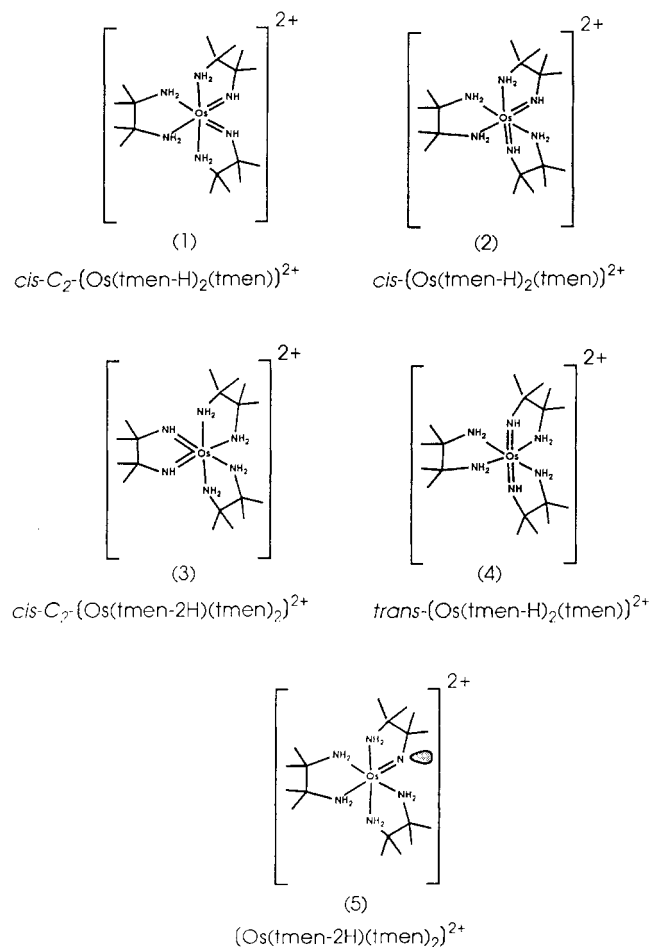


Figure 5. ¹H and ¹³C (inset) NMR spectra of $[\text{Os}(\text{tmen-H})(\text{tmen})_2]^{3+}$ in CD_3CN , 0.3 M Htms, at 298 K. Amine protons: H11, 30.2; H51, 9.8; H21, H22, 9.4; H52, 9.2; H42, 9.1; H41, 8.8; H31, 8.6; H32, 8.4; H61, 7.7; H62, 6.2 ppm. Methyl protons: C₂₁, 1.33; C₅₁, 1.13; C₆₂, 1.11; C₁₂, 1.09; C₅₂, 1.01; C₄₂, 0.94; C₁₁, 0.92; C₂₂, C₄₁, 0.85; C₃₂, 0.79; C₃₁, 0.75; C₆₁, 0.36 ppm. Methyl carbons: C₂₂, 26.4; C₄₂, 26.3; C₁₂, 25.8; C₃₁, 25.4; C₁₁, 25.3; C₃₂, 25.1; C₅₂, 25.0; C₂₁, 24.4; C₄₁, C₅₁, 24.2; C₆₂, 23.4; C₆₁, 22.9 ppm. Quaternary carbons: C₁, 100.2; C₂, 71.0; C₅, 70.8; C₆, 70.0; C₃, 69.5; C₄, 67.2 ppm. The asterisk denotes the proton resonance from Htms.

and **2** or both are the probable species in solution,¹⁶ although it was argued that structure **1** is likely to be the more stable. In the corresponding tmen complex, the 2-fold symmetry required by the spectral evidence is consistent with structures **1**, **3**, and **4** in Chart I. Since exchange of protons among the N sites is slow on the NMR time scale, a full determination of the structure in solution has been undertaken. Carbon and proton chemical shifts were correlated through $^1J_{\text{CH}}$ and $^nJ_{\text{CH}}$ ($n = 2, 3$) coupling interactions using the standard heteronuclear 2D and the FLOCK¹⁷ techniques, respectively. 2D NOESY and heteronuclear 1D NOE experiments were used to detect spatial proxim-

Chart I. Possible Structures of $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ in Solution



ities between amine and methyl protons and between quaternary carbon and methyl or amine protons, respectively (Figure 4). From these experiments, ¹H and ¹³C resonances of the symmetric ligand $[(\text{H}_2\text{NC}(\text{CH}_3)_2)_2]$ could be identified and the signals of the nonsymmetric ligand $[\text{H}_2\text{NC}(\text{CH}_3)_2\text{-C}(\text{CH}_3)_2\text{NH}]$ could be

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(17) Reynolds, W. F.; McLean, S.; Perpich-Dumont, M.; Enriquez, R. G. *Magn. Reson. Chem.* **1989**, *27*, 162.

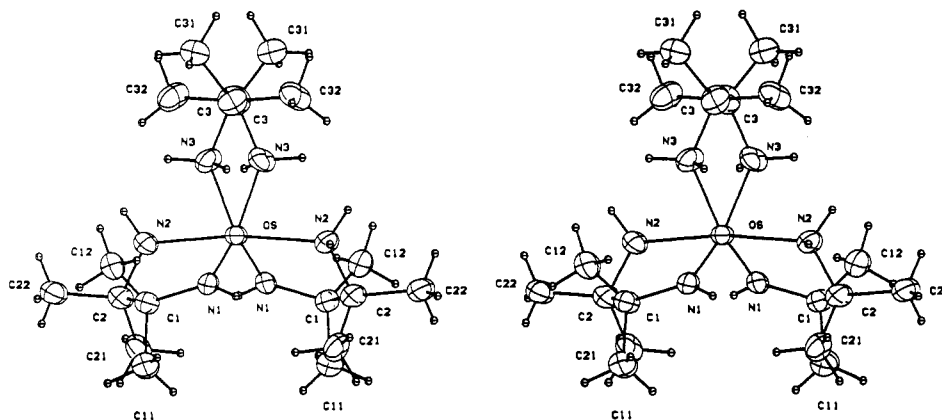


Figure 6. Stereoscopic view of $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$, showing atomic labeling, 2-fold symmetry of the cation, and root-mean-square displacement surfaces (scale 1.54, drawn with the program PEANUT¹⁴). Note that one H bonded to N2 is obscured in the left-hand side of the molecule.

grouped according to the two halves of this ligand. Furthermore, homonuclear NOE's observed between the protons within the same ligand allowed pairs of closely spaced methyl and NH_2 protons to be connected in both types of ligands. On the basis of these data, structure 3 in Chart I could be excluded. NOE's measured between protons of different ligands, i.e. between H21(NH_2) and H11(NH) as well as between H32(NH_2) and H22(NH_2), finally allowed us to exclude structure 4 and assign structure 1 (Chart I) as the only species present in solution (>95%) under the conditions of the NMR experiments. The same structure was found in the solid state (see below).

Solution Structure of $[\text{Os}(\text{tmen-H})(\text{tmen})_2]^{3+}$ Determined by NMR Spectroscopy. The unusual chemical shift of the NH proton ($\delta = 30$ ppm, Figure 5) in the monodeprotonated complex was the experimental starting point to determine its solution structure. The NMR experiments were more difficult than for $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ due to lower solubility and sample instability. Both 1D and 2D NOE results show no evidence of exchange in CD_3CN solution. Geminal exchange between NH_2 protons was seen when neat H_2fms was used as solvent.

By using heteronuclear 2D experiments optimized for the detection of $^1J_{\text{CH}}$ coupling interactions, the shifts of directly bound methyl protons and carbons could be correlated. Experiments optimized to selectively detect $^nJ_{\text{CH}}$ coupling interactions (FLOCK) allowed us to identify pairs of geminal methyl groups. Three groups of four methyl proton signals, attributed to the three non-equivalent ligands, could be correlated through long-range coupling interactions involving three pairs of quaternary carbon signals.

On the basis of the NOE results, the NH and NH_2 's were linked to the corresponding pairs of neighboring CH_3 's. The relative disposition of ligands about Os(IV) was determined primarily by NOE's between H51, C(61) H_3 , and H11 and between H42 and H62, as well as between H32 and H21. Almost all of the remaining NOE's were compatible with the detailed assignment given in Figure 5 and the caption to Figure 5.

In summary, the number of NMR signals and the observed couplings and NOE's show that protonation of $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ in solution leads to N-protonated $[\text{Os}(\text{tmen-H})(\text{tmen})_2]^{3+}$, as shown in Figure 5.

Chemical Shifts. Further support for the structural assignments derives from a number of trends observed in the chemical shifts of the amine protons and the quaternary carbons. Upon protonation, the NH(11) singlet shifts from 13.2 ppm to the very high value of 30 ppm. At the same time, the quaternary C(1) next to NH(11) shifts from 77.9 to 100.2 ppm. Note also, that the quaternary carbons with the smallest chemical shift C(3) (Figure 2) and C(4) (Figure 6), respectively, are attached to the nitrogens trans to the deprotonated N(1)H groups. The high values of the chemical shifts mentioned above and their change upon protonation are interpreted as a consequence of π -bonding

Table III. Important Interatomic Distances and Angles for $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ and $[\text{Os}(\text{en-H})_2\text{en}]^{2+}$ ^a

	osmium coordination environment	
	$[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ ($\text{C}_7\text{H}_7\text{SO}_3$) ₂ ·2H ₂ O	$[\text{Os}(\text{en-H})_2\text{en}]^{2+}\text{Br}_2^b$
	Distances (Å)	
Os–N1	1.880 (6)	1.896 (7)
Os–N2	2.146 (6)	2.113 (9)
Os–N3	2.186 (6)	2.194 (7)
	Angles (deg)	
N1–Os–N1	108.3 (6)	110.0 (3)
N1–Os–N2	95.5 (3)	94.6 (3)
N1–Os–N3	79.4 (3)	81.0 (4)
N1–Os–N3	89.1 (2)	87.4 (3)
N1–Os–N3	162.9 (2)	161.7 (3)
N2–Os–N2	171.3 (2)	172.5 (3)
N2–Os–N3	86.3 (3)	93.5 (3)
N3–Os–N2	100.7 (3)	92.5 (3)
N3–Os–N3	73.9 (2)	76.0 (3)
Os–N1–C1	122.6 (6)	118.6 (7)
Os–N3–C3	118.0 (5)	112.3 (5)
Os–N2–C2	110.2 (5)	106.3 (7)
N2–C2–C1	104.9 (6)	108.0 (9)
N1–C1–C2	107.3 (8)	107.2 (6)
N3–C3–C3	106.1 (7)	106.8 (9)

^a For numbering scheme, see Figure 3. Atoms in italics: $-x, -y, z$ (right half of molecule). ^b Reference 3.

between the p-type lone pair on the $-\text{NH}$ nitrogen and the empty t_{2g} -like d orbital on Os(IV). In $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$, two $-\text{NH}$ groups are available for such dative bonding (Figures 3 and 6); in $[\text{Os}(\text{tmen-H})(\text{tmen})_2]^{3+}$, there is only one. Thus, the deshielding of NH(11) and C(1) increases drastically upon protonation.

The X-ray structure of $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ confirms several of the interpretations given above. In the solid state, isomer 1 (Chart I) is observed, with deprotonated nitrogens on different ligands, in agreement with solution NMR data and as for the en complex. The cation shows crystallographic 2-fold symmetry. The important interatomic distances for the tmen and en complexes are highlighted in Table II. The Os–NH distances are 0.3 Å shorter than the average Os– NH_2 distances, i.e. indicative of the Os=NH π -bonding invoked to interpret the chemical shift data.

Comparison of the structural data of $[\text{Os}(\text{tmen-H})_2\text{tmen}]^{2+}$ with those of $[\text{Os}(\text{en-H})_2\text{en}]^{2+}$ (Table III) shows the same average Os–N distance of 2.07 Å for both. Os–N(1) and Os–N(3) are shorter by ca. 0.01 Å in the tmen than in the en complex. Os–N(2) is correspondingly longer by 0.03 Å. The shortening of the Os=N(1)H distance is consistent with an increased charge transfer from NH- to Os(IV), a consequent decrease in nucleophilicity of NH-, and a lowering of the pK_a (5.2 vs 8.2).

The structure also highlights the effect of the trans influence

on Os–N bond lengths.¹⁶ The two Os–N bonds trans to the Os=N bonds are elongated by 0.04 Å in the tmen complex and by 0.08 Å in the en complex relative to the cis Os–N bonds. Another feature apparent from the crystal structure is the repulsion of the Os=N double bonds, causing an N=Os=N angle of 108° in the tmen complex and 110° in the en complex.

Methyl substitution affects the geometry at N(2) in particular. Its distance to Os increases by 0.03 Å compared to the analogous distance in the en complex, probably due to repulsion between C(21)H₃ and N(1)H (Figure 6). The N(2)–N(2) axis tilts significantly, approximately toward the bisector of the angle N(1)–Os–N(3). The tilt of the N(2)–N(2) axis is around 12° in the tmen complex and around 5° in the en complex. This distortion releases repulsion between C(32)H₃ and N(2)H₂ and between N(1)H and C(21)H₃. The analogous interaction between C(12)H₃ and N(3)H₂ seems responsible for the smaller torsion angles N(1)C(1)C(2)N(2) (–39°) and OsN(1)C(1)C(2) (22°) compared to N(3)C(3)C(3)N(3) (–44°) and OsN(3)C(3)C(3) (37°). The only other effect of the additional methyl groups is to lengthen the ligand C–C bonds (1.51 Å to 1.55 Å) and to decrease the ligand bite size somewhat (ca. 2°). In all other structural parameters, the tmen and en complexes are very similar.

Conclusion

The fully C-methylated complex [Os(tmen-H)₂tmen]²⁺ and its parent en complex have remarkably different chemical and physical properties in solution. The most notable difference is the ability of the tmen ligand to completely inhibit further oxidative dehydrogenation of the ligand and retard the proton exchange among the N atoms substantially. The differences between the solid-state structures of the two complexes are small but consistent with the difference in solution properties.

Acknowledgment. We wish to thank Professor A. Sargeson and Dr. P. Bernhard for stimulating discussions and Ciba-Geigy for continued support with elemental analysis and a supply of tmen. Financial support from the Swiss National Science Foundation (Grant No. 20-29585-90) is gratefully acknowledged.

Supplementary Material Available: Tables S1 and S2, listing positional parameters and anisotropic displacement and thermal parameters, Tables S4 and S5, giving bond distances, bond angles, and full crystal data, and a stereoscopic view of the unit cell (10 pages); Table S3, listing observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.