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Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Department of Radiology, Harvard Medical School and Brigham and Women's Hospital, Boston, Massachusetts 02115

Technetium(I) Isocyanide Complexes with Bidentate Aromatic Amine Ligands: Structural Characterization of $[Tc(CNtBu)_4(bpy)]PF_6$, a Complex with "Tc(III) Character"

Lynne A. O'Connell,[1a] John Dewan,[1b] Alun G. Jones,[1c] and Alan Davison*,[1a]

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A series of compounds of the type $[Tc(CNR)_4(NN)]PF_6$ (NN = bidentate aromatic amine) is synthesized by one of two methods: photolysis of $[Tc(CNR)_6]PF_6$ in the presence of excess ligand, NN, or reduction of $NH_4[TcO_4]$ in the presence of excess ligand, NN, and 4 mol of isocyanide. A single-crystal X-ray structure determination was carried out on the compound $[Tc(CNtBu)_4(bpy)]PF_6$ (crystal data: orthorhombic, a = 25.060 (8) Å, b = 18.717 (3) Å, c = 15.769 (8) Å, space group = $Pbca$, Z = 8, final R = 0.072). The coordination sphere is an octahedron, and a deviation from linearity in one of the isonitrile ligands is present at the nitrogen atom, where the C-N-C angle is 148°. The structural features along with the infrared and ^{99}Tc NMR spectral data suggest that the bent isocyanide is the result of a "pseudo" internal oxidation from Tc(I) to Tc(III). Protonation of the bent isocyanide ligand produces an unstable aminocarbyne complex, which deprotonates to re-form the starting material. The spectrochemical dependence of the ^{99}Tc NMR chemical shifts of the series of compounds is also discussed.

Introduction

In 1983, a class of technetium compounds, the hexakis(isocyanide)monocations, was discovered.[2] Some of these compounds were found to have good heart uptake and produced clear pictures of this organ with the γ-camera in diagnostic imaging studies.[3] While a wide variety of biological and radiopharmaceutical investigations were carried out on these compounds, the chemistry of low-oxidation-state technetium isocyanide complexes was left largely unexplored with the following exceptions. The reaction of the hexakis(*tert*-butyl isocyanide)technetium(I) compound with either chlorine or bromine has been shown to oxidize the technetium from the +1 to the +3 state and produces a seven-coordinate compound $[Tc(CNtBu)_6X]^{2+}$ (X = Cl, Br).[4] Further reaction of this latter compound with an excess of 2,2'-bipyridine (bpy) accompanied by heating led to a dealkylation of one of the isonitrile ligands. Linder et al.[5] reported the synthesis of the nitrosyl compound $[Tc(NO)(CNtBu)_5](PF_6)_2$ by the reaction of $[Tc(CNtBu)_6]PF_6$ under highly oxidizing conditions (HNO_3/HOAc or $NOPF_6$).

The hexakis(isocyanide)technetium(I) monocations are prepared via a reduction of pertechnetate with sodium dithionite in the presence of a large excess of isonitrile.[2] Although the ease of preparation of the hexakis(*tert*-butyl isocyanide)technetium(I) monocationic complex makes it a potentially useful starting material for the preparation of low-oxidation-state technetium compounds, its inherent kinetic inertness diminishes this potential somewhat. Two routes into mixed-ligand compounds of technetium in low oxidation states that contain both isonitrile and bidentate aromatic amine (NN) ligands are discussed. A series of compounds of the type $Tc(CNR)_4(NN)^+$ was synthesized with the use of these methods and characterized both spectroscopically and by X-ray crystallography.

Experimental Section

Caution! Technetium-99 is a weak β^- emitter (E = 0.292 MeV, $t_{1/2}$ = 2.12×10^5 years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[6]

Materials. Ammonium pertechnetate was supplied as a gift by DuPont/Biomedical Products. The compounds $[Tc(CNtBu)_6]PF_6$ and $[Tc(CNMe)_6]PF_6$ were prepared by the method of Abrams et al.[2] The reagents 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (Me_2bpy), and $HBF_4 \cdot Et_2O$ were obtained from Aldrich Chemicals; 1,10-phenanthroline (phen), *tert*-butyl isocyanide, and 2,6-dimethylphenyl isocyanide (CNmXyl) were obtained from Fluka Chemicals; 5-nitro-1,10-phenanthroline (NO_2phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen), and 4-methyl-1,10-phenanthroline (Me-phen) were obtained from GFS Chemicals. The methyl isonitrile was provided by Nadine deVries.[7] The solvents and reagents were used as received. Column chromatography was performed by using TLC grade silica gel 60H (EM Science). The ultraviolet lamp contained two 15-W self-filtering black light blue tubes producing a 108° beam of 365-nm radiation, 1600 $\mu W/cm^2$ at 12 in. (VWR).

Measurements. The ^{1}H NMR spectra were recorded on a Varian XL-300 spectrometer using the residual proton signal from the solvent as a reference. All ^{99}Tc NMR spectra were recorded on a Varian XL-300 spectrometer with $CDCl_3$ as solvent. The ^{99}Tc signals are reported with respect to $(NH_4)[TcO_4]$ and were referenced to $[Tc(CNtBu)_6]PF_6$ which was present as a secondary, internal standard. The primary reference ($(NH_4)[^{99}TcO_4]$ in D_2O = 0 ppm) resonates at 67.516 MHz in this spectrometer. The pulse width necessary to obtain a 90° tip angle was determined for an aqueous solution of $(NH_4)[TcO_4]$. No relaxation delay in addition to the acquisition time was employed. Fourier transform infrared spectra were measured from 4000 to 400 cm^{-1} on either an IBM System 9000 spectrometer or a Mattson Cygnus 100 spectrometer using a 2-cm^{-1} bandwidth. UV-visible spectra were recorded by using a Hewlett-Packard 8451A photodiode array spectrophotometer. Fast atom bombardment mass spectra (FABMS) of samples dissolved in a p-nitrobenzyl alcohol matrix were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun and operating at an accelerating voltage of 8 kV. The FAB gun produced a beam of 6-8-keV xenon neutrals. Electrochemical measurements were performed on N_2-purged acetonitrile solutions of the metal complexes with 0.1 M tetrabutylammonium perchlorate (TBAP, GFS Chemicals) as supporting electrolyte. The acetonitrile was of spectrophotometric grade and was kept over 3 Å sieves to remove water. Experiments were conducted by using a one-compartment cell with a Pt disk as the working electrode, a Pt wire as the auxiliary electrode, and an SCE (Fisher) as the reference. The $E_{1/2}$ values were calculated as the average of the E_{peak} values for the anodic and cathodic waves from cyclic voltammetry. $E_{1/2}$ values are measured relative to SCE and are uncorrected for junction potentials; however, the potential of the ferrocenium/ferrocene couple occurs at 0.39 V for this setup and can be used as a secondary reference.[8] The potentiostat employed was a PAR Model 174 polarographic analyzer, and the data were plotted with a Hewlett Packard 7044AXY recorder. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Preparation of $[Tc(CNtBu)_4(bpy)]PF_6$. Method 1. A sample of $[Tc(CNtBu)_6]PF_6$ (0.136 g, 0.184 mmol) was dissolved in 20 mL of CH_3CN, 0.28 g of 2,2'-bipyridine was added, and the flask was stoppered with a rubber septum. The clear, colorless solution was placed under an ultraviolet lamp for 4 days during which time the solution turned a deep red. The CH_3CN was removed under reduced pressure, and the residue

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was dissolved in CH_2Cl_2 and loaded onto a silica gel column followed by elution with CH_2Cl_2. The eluant was an orange solution, which contained both unreacted $[Tc(CNtBu)_6]PF_6$ and $[Tc(CNtBu)_4(bpy)]PF_6$, while brown, presumably, polymeric, material remained at the top of the column. To the eluant was added silica gel, and the solvent was again removed under reduced pressure. The gel with the adsorbed material was slurried with ether and loaded onto a silica column, which was eluted with a 10% CH_2Cl_2/Et_2O mixture. The orange eluant was collected, and the solvent was removed under reduced pressure. The oil was dissolved in acetone, and water was added to precipitate a red-orange solid, which was washed with water followed by diethyl ether and dried in vacuo. Yield: 0.0073 g, 0.01 mmol, 6%. Anal. Calcd for $C_{30}H_{44}F_6N_6PTc\cdot1.5H_2O$: C, 47.47; H, 6.24; N, 11.07. Found: C, 47.42; H, 5.99; N, 11.02.

Method 2. A 0.3-mL aliquot of an aqueous, 0.350 M solution of $NH_4[TcO_4]$ was added to a mixture containing 5 mL of ethanol and 5 mL of aqueous NaOH solution at pH 12. To this solution was added 0.16 g of 2,2'-bipyridine and 47 μL of *tert*-butyl isocyanide, and the mixture was stirred and heated to reflux. A solution of 0.05 g of $Na_2S_2O_4$ in 5 mL of aqueous NaOH (pH 12) was added dropwise to the refluxing reaction mixture, which caused the solution to turn deep red. Refluxing continued for 1.25 h, and the solution was then allowed to cool to room temperature. A solution of 0.08 g of $[NH_4]PF_6$ in 5 mL of water was added, followed by additional water until the solution became cloudy. Solvent was removed under reduced pressure until a red-orange solid appeared, which was then collected and washed with water followed by diethyl ether. The product was recrystallized from acetone and water and dried in vacuo. Yield: 0.018 g, 0.025 mmol, 25%. The compound was spectroscopically identical with the product analyzed above.

Preparation of $[Tc(CNtBu)_4(Me_4phen)]PF_6$. A sample of $[Tc(CNtBu)_6]PF_6$ (0.112 g, 0.151 mmol) was dissolved in 20 mL of CH_3CN, 0.10 g of Me_4phen was added, and the flask was stoppered. The solution was placed under an ultraviolet lamp for 8 days during which time the solution turned orange. The CH_3CN was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and loaded onto a silica gel column followed by elution with CH_2Cl_2. An orange band was collected, the solvent was removed under reduced pressure, and the oil was dissolved in acetone. Water was added to the solution, and on the following day, the orange crystalline solid was collected and washed with water and dried in vacuo. The solid obtained weighed 0.0560 g and was 91% $[Tc(CNtBu)_6]PF_6$ and 9% $[Tc(CNtBu)_4(Me_4phen)]PF_6$ as determined from ^{1}H NMR integrals (the estimated error associated with these percentages is ±2%). Further chromatography with diethyl ether and Et_2O/CH_2Cl_2 as eluants failed to remove the remainder of starting material, which was evident in the analytical and spectroscopic results. Yield: 0.0560 g, 0.0748 mmol (91% of which is $[Tc(CNtBu)_6]PF_6$), 4.5%. Anal. Calcd for 91% $C_{30}H_{54}F_6N_6PTc$ and 9% $C_{36}H_{52}F_6N_6PTc$: C, 48.97; H, 7.24; N, 11.22. Found: C, 49.06; H, 7.31; N, 11.24.

Preparation of $[Tc(CNtBu)_4(Me_2bpy)]PF_6$. Method 1. The complex was prepared similarly to $[Tc(CNtBu)_4(Me_4phen)]PF_6$ with Me_2bpy used as the added ligand. The product obtained was also contaminated with the starting material, and the yield was approximately 5%. The compound was spectroscopically identical with the product analyzed below.

Method 2. A 0.3-mL aliquot of an aqueous, 0.350 M solution of $NH_4[TcO_4]$ was added to a mixture of 5 mL of ethanol and 5 mL of aqueous NaOH solution of pH 12. To this solution was added 0.11 g of 4,4'-dimethyl-2,2'-bipyridine and 47 μL of *tert*-butyl isocyanide, and the mixture was stirred and heated to reflux. Note: some of the 4,4'-dimethyl-2,2'-bipyridine remained undissolved. A solution of 0.05 g of $Na_2S_2O_4$ in 5 mL of aqueous NaOH (pH 12) was added dropwise to the refluxing reaction mixture, which caused the solution to turn dark orange. Refluxing continued for 1.25 h, and the solution was then allowed to cool to room temperature and was filtered to remove the undissolved excess of 4,4'-dimethyl-2,2'-bipyridine. A solution of 0.10 g of $[NH_4]PF_6$ in 5 mL of water was added, followed by additional water, until the solution became cloudy. An orange precipitate appeared after several hours, which was collected and contained both the product and the remaining 4,4'-dimethyl-2,2'-bipyridine. It was dissolved in CH_2Cl_2 and washed three times with aqueous HCl, three times with water, and one time with a saturated aqueous NaCl solution. The CH_2Cl_2 was removed under reduced pressure, the orange oil was dissolved in acetone, and water was added to cause the orange product to precipitate. This orange solid contained $[Tc(CNtBu)_6]PF_6$ (24%) as well as the desired product (76%) as evidenced by ^{1}H NMR integral areas. While the product is soluble in diethyl ether, filtration in diethyl ether, as well as silica gel column chromatography with diethyl ether eluant, failed to remove the $[Tc(CNtBu)_6]PF_6$. This impurity therefore appears in all analytical and spectroscopic results. The precipitate was washed with water. The product was recrystallized from acetone and water and was dried in vacuo. Yield: 0.0220 g, 0.029 mmol (24% of which is $[Tc(CNtBu)_6]PF_6$), 21%. Anal. Calcd for 76% $C_{32}H_{48}F_6N_6PTc$ and 24% $C_{30}H_{54}F_6N_6PTc$: C, 50.08; H, 6.59; N, 11.12. Found: C, 50.08; H, 6.50; N, 11.02.

Preparation of $[Tc(CNtBu)_4(phen)]PF_6$. Method 1. The complex was prepared similarly to $[Tc(CNtBu)_4(Me_4phen)]PF_6$ by using phen as the added ligand. The product obtained was also contaminated with the starting material, and the yield was approximately 5%. The compound is spectroscopically identical with the product analyzed below.

Method 2. A 0.3 mL aliquot of an aqueous, 0.350 M solution of $[NH_4]TcO_4$ was added to a mixture of 5 mL of ethanol and 5 mL of aqueous NaOH solution of pH 12. To this solution was added 0.10 g of 1,10-phenanthroline and 47 μL of *tert*-butylisocyanide, and the mixture was stirred and heated to reflux. A solution of 0.05 g of $Na_2S_2O_4$ in 5 mL of aqueous NaOH (pH 12) was added dropwise to the refluxing reaction mixture, which caused the solution to turn dark orange. Refluxing continued for 1.5 h, and the solution was then allowed to cool to room temperature. A solution of 0.15 g of $[NH_4]PF_6$ in 5 mL of water was added followed by additional water until the solution became cloudy. A dark brown precipitate appeared in the solution after several hours, which was then collected and washed with water followed by diethyl ether. The product was recrystallized from acetone and water and was dried in vacuo. Yield: 0.0196 g, 0.026 mmol, 25%. Anal. Calcd for $C_{32}H_{44}F_6N_6PTc$: C, 50.84; H, 5.87; N, 11.12. Found: C, 50.98; H, 5.77; N, 11.24.

Preparation of $[Tc(CNtBu)_4(NO_2phen)]PF_6$. The complex was prepared similarly to $[Tc(CNtBu)_4(Me_4phen)]PF_6$ with NO_2phen used as the added ligand. The chromatography produced a purple band, corresponding to the desired product, immediately followed by a yellow band, corresponding to excess NO_2phen ligand. The eluant that was collected therefore contained these two compounds along with $[Tc(CNtBu)_6]PF_6$, and repeated attempts to remove the two impurities by either chromatographic or recrystallization techniques failed to produce pure $[Tc(CNtBu)_4(NO_2phen)]PF_6$. In addition, the yield of the product is quite low (less than 5%). The spectral evidence for the presence of this compound is provided in the results and discussion of the $Tc(CNR)_4(NN)^+$ compounds, vide infra; however, due to the inadequate purification, extinction coefficients, analytical, electrochemical, and infrared data, and some ^{1}H NMR chemical shifts were not obtained.

Preparation of $[Tc(CNmXyl)_6]PF_6$. A 0.47-mL aliquot of a 0.433 M solution of $NH_4[TcO_4]$ and 0.3 g of 2,6-dimethylphenyl isocyanide were added to 10 mL of aqueous NaOH solution of pH 12 and 15 mL of ethanol. The solution was heated to reflux with stirring, and a solution of 0.08 g of $Na_2S_2O_4$ in 5 mL of aqueous NaOH (pH 12) was added dropwise, which turned the solution orange. The reaction was refluxed for 30 min at which point another solution of 0.08 g of $Na_2S_2O_4$ in 5 mL of aqueous NaOH (pH 12) was added. The refluxing was stopped after 30 min, and the solution was allowed to cool to room temperature. A solution of 0.15 g of $[NH_4]PF_6$ in 5 mL of water was added to the reaction mixture, and the solvent was removed under reduced pressure. The residue was dissolved in 20 mL of CH_3CN and filtered. Water was added to the filtrate (~7 mL), and pale yellow needles crystallized overnight. The solid was collected and washed with water and dried in vacuo. Yield: 0.073 g, 0.071 mmol, 36%. Anal. Calcd for $C_{54}H_{54}F_6N_6PTc$: C, 62.91; H, 5.28; N, 8.15. Found: C, 62.68; H, 5.32; N, 7.91. IR (KBr): ν_{CN} 2075 s, 2000 sh cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (ϵ) 236 nm (52000 L mol^{-1} cm^{-1}), 302 nm (67000). ^{1}H NMR ($CDCl_3$): δ 2.42 (s, 36 H, CH_3); 7.12 (m, 18 H, Ar*H*). ^{99}Tc NMR ($CDCl_3$): δ −1924 (30 Hz). $E_{1/2}$ (CH_3CN): 1.17 V vs SCE (1e, rev). FABMS(+): *m/z* 885 $(M)^+$; 754 $(M - CNmXyl)^+$; 623 $(M - 2CNmXyl)^+$; 492 $(M - 3CNmXyl)^+$.

Preparation of $[Tc(CNmXyl)_4(bpy)]PF_6$. A sample of $[Tc(CNmXyl)_6]PF_6$ (0.480 g, 0.0466 mmol) was dissolved in 20 mL of CH_3CN, 0.10 g of 2,2'-bipyridine was added, and the flask was stoppered with a rubber septum. The solution was placed under an ultraviolet lamp for 4 days, during which time the solution turned orange. The CH_3CN was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and loaded onto a silica gel column followed by elution with CH_2Cl_2. A red band was collected, leaving brown material on the top of the column. The orange CH_2Cl_2 solution was washed three times with aqueous HCl, three times with water, and one time with saturated aqueous NaCl solution. The CH_2Cl_2 was removed under reduced pressure, and the residue was dissolved in acetone. Water was added to the solution, and on the following day, orange crystalline solid was collected, washed with water, and dried in vacuo. Yield: 0.0138 g, 0.0149 mmol, 15%. Anal. Calcd for $C_{46}H_{44}F_6N_6PTc$: C, 59.80; H, 4.80; N, 9.10. Found: C, 59.74; H, 4.97; N, 8.87.

Preparation of $[Tc(CNMe)_4(bpy)]PF_6$. Method 1. The complex was prepared similarly to $[Tc(CNmXyl)_4(bpy)]PF_6$ by reacting $[Tc(CNMe)_6]PF_6$ with an excess of 2,2'-bipyridine. The yield of product from this reaction is negligible (<5%); however, it is spectroscopically

Table I. X-ray Data for the Structure Determination of $[Tc(CNtBu)_4(bpy)]PF_6$

$C_{30}H_{44}N_6TcPF_6$	$T = 23$ °C
fw = 732.04	$\lambda = 0.71069$ Å, graphite monochromated
space group = *Pbca*	$\rho_{calcd} = 1.31$ g/cm^3
$a = 25.060$ (8) Å	$\mu = 4.81$ cm^{-1}
$b = 18.717$ (3) Å	transm coeff = 0.65–1.37
$c = 15.769$ (8) Å	$R = 0.072$
$V = 7396$ (8) Å^3	$R_w = 0.075$
$Z = 8$	

identical with the product analyzed below.

Method 2. A 0.75-mL aliquot of an aqueous, 0.408 M solution of $NH_4[TcO_4]$ was added to a mixture of 15 mL of ethanol and 15 mL of aqueous NaOH solution of pH 12. To this solution was added 0.30 g of 2,2'-bipyridine and 66 μL of methyl isocyanide, and the mixture was stirred and heated to reflux. A solution of 0.15 g of $Na_2S_2O_4$ in 10 mL of aqueous NaOH (pH 12) was added dropwise to the refluxing reaction mixture, which caused the solution to turn deep red. Refluxing continued for 1.25 h, and the solution was then allowed to cool to room temperature. The solution was filtered, and a solution of 0.18 g of $[NH_4]PF_6$ in 5 mL of water was added followed by additional water until it became cloudy. A dark red precipitate appeared after several hours, which was collected and washed with water followed by diethyl ether. The product was recrystallized from acetone and water and dried in vacuo. Yield: 0.032 g, 0.056 mmol, 19%. Anal. Calcd for $C_{18}H_{20}F_6N_6PTc$: C, 38.35; H, 3.58; N, 14.91. Found: C, 38.22; H, 3.51; N, 14.82.

Protonation Reactions. (a) The following procedure, which describes the protonation of $[Tc(CNtBu)_4(Me_2bpy)]PF_6$, is a general method to form aminocarbyne complexes of the type $Tc(CN(H)R)(CNR)_3(NN)^{2+}$. A sample of $[Tc(CNtBu)_4(Me_2bpy)]PF_6$ (0.012 g) was dissolved in ~5 mL of CH_2Cl_2, which produced an orange solution. Two drops of $HBF_4{\cdot}Et_2O$ were added under a stream of N_2, which immediately turned the solution bright yellow. The solution was stoppered and allowed to sit at 0 °C. Yellow needles crystallized overnight, which were collected by filtration and turned orange over the course of 10 min.

(b) A FAB(+) mass spectrum of the product from the following procedure was obtained. A sample of $[Tc(CNtBu)_4(Me_2bpy)]PF_6$ (0.0048 g) was dissolved in CH_2Cl_2, and 3 drops of an aqueous solution of HPF_6 (60% by weight) were added. The solution turned yellow after 1 day. The organic phase was separated from the aqueous phase, diethyl ether was added to it, and the solution was stoppered and allowed to sit at 0 °C overnight. The flocculent, yellow solid was collected.

Preparation of $[Tc(CNtBu)_4(Me\text{-}phen)]PF_6$. A 0.52-mL aliquot of an aqueous, 0.384 M solution of $(NH_4)[TcO_4]$ was added to a mixture of 15 mL of ethanol and 10 mL of aqueous NaOH solution of pH 12. To this solution was added 0.11 g of 4-methyl-1,10-phenanthroline (Me-phen) and 90 μL of *tert*-butyl isocyanide, and the mixture was stirred and heated to reflux. A solution of 0.1 g of $Na_2S_2O_4$ in 5 mL of aqueous NaOH (pH 12) was added dropwise to the refluxing reaction mixture, which caused the colorless solution to turn orange. Refluxing continued for 1.75 h, and the solution was then allowed to cool to room temperature. A solution of 0.1 g of $[NH_4]PF_6$ in 5 mL of water was added and the mixture allowed to sit overnight. An orange precipitate was collected. The solid was dissolved in CH_2Cl_2, loaded onto a silica gel column, and eluted with CH_2Cl_2, which produced a dark orange solution. The solvent was removed under reduced pressure, and the orange oil was dissolved in acetone. The addition of water precipitated an orange solid, which was collected, washed with water, and dried in vacuo. The product was characterized by ^1H NMR spectroscopy in $CDCl_3$. From the integrals, it was found that 8% of the product was $[Tc(CNtBu)_6]PF_6$, which could not be removed from the desired compound. Yield: 0.035 g, 0.046 mmol (8% of which is $[Tc(CNtBu)_6]PF_6$), 21%. Anal. Calcd for 92% $C_{33}H_{45}F_6N_6PTc$ and 8% $C_{30}H_{54}F_6N_6PTc$: C, 51.24; H, 6.00; N, 10.94. Found: C, 51.00; H, 5.87; N, 10.79.

X-ray Crystal Structure of $[Tc(CNtBu)_4(bpy)]PF_6$. Red needle-shaped crystals were obtained by slow evaporation of a solution of $[Tc(CNtBu)_4(bpy)]PF_6$ in acetonitrile/water at room temperature. The crystal selected measured approximately 0.05 × 0.40 mm. X-ray diffraction data were collected at a temperature of 23 °C on a Rigaku AFC-6R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and a 12-kW rotating-anode generator. The unit cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections in the range $21° < 2\theta < 30°$, and the scan mode used was ω–2θ with a maximum 2θ of 45.1°. The crystal system is orthorhombic, space group *Pbca*. An octant of data was collected (+*h*,+*k*,–*l*) giving a total of 5385 reflections, and of those, 1948 with $I > 2\sigma(I)$ were used in the final structure refinement. The crystal exhibited no significant decay under X-ray irradiation. Crystal data and experimental details of the structure determination are given in Table I.

Table II. Atomic Positional Parameters and *B*(eq) for $[Tc(CNtBu)_4(bpy)]PF_6$

atom	*x*	*y*	*z*	*B*(eq), Å^2
Tc1	0.14430 (5)	0.07960 (7)	0.12322 (9)	1.90 (5)
P1	0.5410 (2)	0.7899 (4)	0.1512 (4)	5.3 (4)
F1	0.5877 (8)	0.748 (1)	0.155 (2)	19 (2)
F2	0.5773 (9)	0.854 (1)	0.176 (1)	15 (2)
F3	0.501 (1)	0.853 (1)	0.139 (3)	22 (2)
F4	0.5032 (9)	0.733 (1)	0.130 (2)	22 (2)
F5	0.526 (1)	0.784 (1)	0.241 (1)	19 (2)
F6	0.550 (1)	0.800 (2)	0.059 (1)	17 (2)
N11	0.1294 (5)	−0.0323 (7)	0.1019 (8)	2.1 (8)
N12	0.0896 (4)	0.075 (1)	0.0167 (8)	2.0 (7)
N21	0.2443 (6)	0.0901 (8)	0.0038 (9)	3.0 (8)
N31	0.2306 (6)	0.0677 (9)	0.268 (1)	3.6 (9)
N41	0.1545 (5)	0.2449 (9)	0.132 (1)	4.1 (8)
N51	0.0545 (5)	0.082 (1)	0.265 (1)	3.5 (8)
C11	0.1472 (8)	−0.085 (1)	0.148 (1)	4 (1)
C12	0.1355 (8)	−0.157 (1)	0.134 (2)	4 (1)
C13	0.1060 (9)	−0.172 (1)	0.068 (2)	6 (1)
C14	0.0866 (7)	−0.121 (1)	0.015 (1)	4 (1)
C15	0.0996 (7)	−0.050 (1)	0.032 (1)	2.4 (9)
C16	0.0777 (6)	0.011 (1)	−0.015 (1)	2 (1)
C17	0.0468 (8)	0.004 (1)	−0.088 (2)	5 (1)
C18	0.0270 (7)	0.063 (1)	−0.130 (1)	5 (1)
C19	0.0383 (8)	0.130 (1)	−0.097 (1)	4 (1)
C110	0.0687 (8)	0.132 (1)	−0.027 (1)	4 (1)
C21	0.2068 (6)	0.083 (1)	0.045 (1)	1.9 (8)
C22	0.2946 (8)	0.115 (1)	−0.035 (1)	4 (1)
C23	0.287 (1)	0.115 (2)	−0.120 (2)	14 (2)
C24	0.339 (1)	0.069 (2)	−0.001 (3)	18 (3)
C25	0.300 (1)	0.191 (2)	−0.008 (2)	11 (2)
C31	0.1949 (8)	0.073 (1)	0.212 (1)	3 (1)
C32	0.2743 (8)	0.100 (1)	0.309 (1)	4 (1)
C33	0.263 (1)	0.108 (2)	0.401 (2)	10 (2)
C34	0.323 (1)	0.051 (2)	0.303 (2)	12 (2)
C35	0.287 (1)	0.170 (1)	0.271 (2)	9 (2)
C41	0.1510 (7)	0.1838 (9)	0.133 (1)	2.5 (9)
C42	0.1568 (7)	0.320 (1)	0.151 (1)	3 (1)
C43	0.2153 (8)	0.342 (1)	0.147 (1)	6 (1)
C44	0.128 (1)	0.357 (1)	0.077 (2)	12 (2)
C45	0.137 (1)	0.335 (1)	0.237 (2)	10 (2)
C51	0.0848 (6)	0.083 (1)	0.211 (1)	2.4 (9)
C52	0.0252 (8)	0.092 (1)	0.343 (1)	4 (1)
C53	0.032 (1)	0.166 (1)	0.371 (2)	8 (2)
C54	−0.033 (1)	0.080 (2)	0.326 (2)	11 (2)
C55	0.046 (1)	0.041 (1)	0.409 (1)	9 (2)

Table III. Selected Bond Angles (deg) for $[Tc(CNtBu)_4(bpy)]PF_6$

C31–Tc1–C41	87.4 (8)	C21–N21–C22	165 (2)
C31–Tc1–C21	86.1 (6)	C31–N31–C32	148 (2)
C31–Tc1–C51	89.3 (6)	C41–N41–C42	168 (3)
C31–Tc1–N11	99.4 (7)	C51–N51–C52	167 (2)
C31–Tc1–N12	173.2 (8)	N21–C21–Tc1	175 (2)
C41–Tc1–C21	86.9 (8)	N31–C31–Tc1	176 (1)
C41–Tc1–C51	88.7 (8)	N41–C41–Tc1	175 (2)
C41–Tc1–N11	173.2 (7)	N51–C51–Tc1	174 (2)
C41–Tc1–N12	98.7 (7)	N31–C32–C35	111 (2)
C21–Tc1–C51	173.8 (7)	N31–C32–C33	110 (2)
C21–Tc1–N11	94.2 (6)	N31–C32–C34	109 (2)
C21–Tc1–N12	91.2 (5)	C35–C32–C33	111 (2)
C51–Tc1–N11	90.6 (7)	C35–C32–C34	110 (2)
C51–Tc1–N12	93.8 (5)	C33–C32–C34	106 (2)
N11–Tc1–N12	74.5 (6)		

The structure was solved by direct methods. Neutral-atom scattering factors were taken from Cromer and Waber.[9a] All calculations were performed by using the TEXSAN crystallographic software package of the Molecular Structure Corp. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction[9b] was applied. The non-hydrogen atoms were refined anisotropically, and their atomic parameters are listed in Table II. Hydrogen atoms were placed in idealized positions. The shortest intermolecular distance involving a fluorine atom and a hydrogen atom is 2.471 Å, thus indicating that there

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(9) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. (b) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

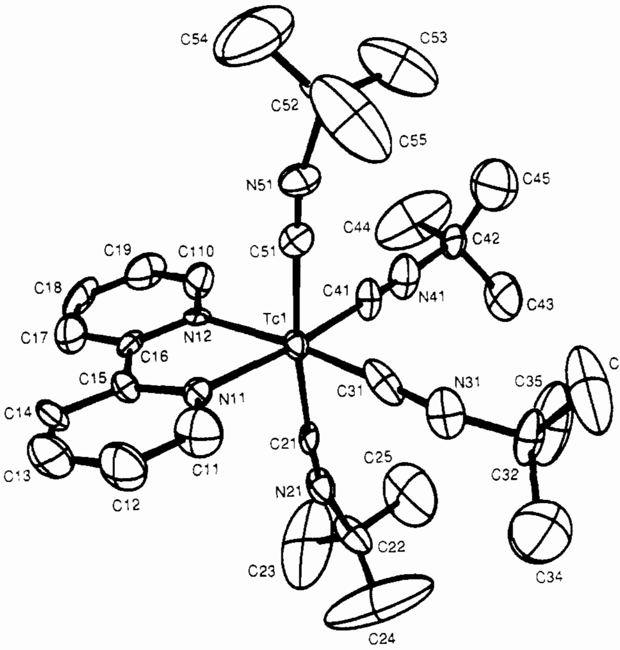

Figure 1. ORTEP diagram of [Tc(CNtBu)$_4$(bpy)]PF$_6$ showing the atom-labeling scheme and 30% probability thermal ellipsoids.

Table IV. Selected Bond Distances (Å) for [Tc(CNtBu)$_4$(bpy)]PF$_6$

Tc1-C21	1.99 (2)	N31-C32	1.42 (2)
Tc1-C31	1.90 (2)	N41-C41	1.15 (2)
Tc1-C41	1.96 (2)	N41-C42	1.43 (2)
Tc1-C51	2.04 (2)	N51-C51	1.14 (2)
Tc1-N11	2.15 (1)	N51-C52	1.44 (2)
Tc1-N12	2.17 (1)	C32-C35	1.47 (3)
N21-C21	1.15 (2)	C32-C33	1.47 (3)
N21-C22	1.48 (2)	C32-C34	1.53 (3)
N31-C31	1.25 (2)		

are no unusually close contacts between the anion and cation. An ORTEP drawing of the compound is shown in Figure 1, and selected bond angles and distances are listed in Tables III and IV, respectively. Full tables of X-ray data, bond lengths and angles, anisotropic temperature factors, hydrogen atom positions, and calculated and observed structure factors are available as supplementary material.

Results and Discussion

Syntheses of [Tc(CNR)$_4$(NN)]PF$_6$ Compounds. Irradiation with ultraviolet light photolabilizes the isocyanide ligands of the hexakis(isocyanide)technetium(I) monocation, allowing for substitution of two of the isocyanides by a bidentate nitrogen-donating ligand. The electronic absorption spectrum of Tc(CNtBu)$_6^+$ displays strong charge-transfer absorptions in the ultraviolet region at 235 nm.[2] Excitation of a metal-to-ligand charge-transfer band could result in an associative process for this substitution reaction.[10] On the other hand, a ligand field excitation from a $t_{2g}(\pi)$ to an $e_g(\sigma^*)$ orbital would result in a dissociative mechanism. It is possible that a d–d transition absorption is hidden by the tail of the intense charge-transfer band,[11] so that the actual mechanism occurring in this reaction is unknown. The reaction is limited to the removal of two isocyanide ligands. Attempts were made to carry out the reaction in a 2,2'-bipyridine melt, which produced only Tc(CNtBu)$_4$(bpy)$^+$, and neither the bis- nor tris(bipyridine) compound was detected.

A variety of bidentate aromatic amine ligands were used, while keeping the *tert*-butyl isocyanide ligand constant, in order to synthesize compounds of the type Tc(CNtBu)$_4$(NN)$^+$ (NN = bpy, Me$_2$bpy, phen, Me$_4$phen, NO$_2$phen). Similarly, the isocyanide ligand was also varied, while the amine ligand remained constant as 2,2'-bipyridine, in order to synthesize Tc(CNR)$_4$(bpy)$^+$ compounds (R = tBu, Me, mXyl). The yields obtained from the aryl isocyanide starting material were the highest of the Tc(CNR)$_4$(NN)$^+$ series. The ease of this reaction is probably related to the excitation energy required to photolabilize the isonitrile ligands. The presence of the aromatic ring lowers the energy of the π^* orbital, which in turn lowers the electronic transition energy.[10] The λ_{max} values (nm), in CH$_3$CN, for the three starting materials used in the syntheses of these compounds are as follows: [Tc(CNMe)$_6$]PF$_6$, 229 (73 000 L mol^{-1} cm^{-1}), 263 (41 000);[2] [Tc(CNtBu)$_6$]PF$_6$, 235 (80 000), 260 sh;[2] [Tc(CNmXyl)$_6$]PF$_6$, 236 (52 000), 302 (67 000). The black light produces radiation with a 365-nm wavelength, which is closest to the strongest absorption found in the spectrum of Tc(CNmXyl)$_6^+$ at 302 nm. On the other hand, the yield for the reaction of Tc(CNMe)$_6^+$ with bipyridine is extremely low, probably because its strong absorption at 229 nm is the highest in energy of the three compounds. The yields of all of the reactions are low, and the majority of the technetium is present as unreacted starting material. The low yields, along with the necessary purification methods and extent of time required for this photochemical method of preparation, preclude its use as a viable synthetic route to aromatic amine tetrakis(isocyanide)technetium(I) compounds.

A more viable preparation of these complexes uses a method based on the synthesis of the hexakis(isocyanide)technetium(I) compounds. Refluxing a mixture of pertechnetate, an excess of the N-donor ligand, and 4 mol of the isocyanide with concurrent reduction by sodium dithionite yields the desired compound. This method works well if R is either a *tert*-butyl or methyl group and NN is bpy, phen, or Me$_2$bpy. When R is the aryl group mXyl, the reaction produces a mixture of several brown and orange products, which were not identified but do not have the spectral characteristics expected for Tc(CNmXyl)$_4$bpy$^+$. The ligands Me$_4$phen and NO$_2$phen are insufficiently soluble in the preferred solvent system (EtOH/aqueous NaOH) to react, and reactions carried out in acetonitrile produced a mixture of compounds without yielding the desired product in any significant amount. This mode of preparation is superior to the photochemical means of synthesis for the following reasons: (a) the compounds are produced in higher yields, for example, a 25% yield for Tc(CNtBu)$_4$bpy$^+$ versus the 6% obtained with the photolysis reaction, (b) the compounds precipitate out of solution in a purer form and do not require chromatographic purification techniques if the stoichiometry is carefully controlled, and (c) the pertechnetate starting material is readily available, in contrast to the hexakis(isocyanide) monocationic complexes, which must be synthesized prior to the photochemical reaction with the N-donor ligand.

A significant obstacle was encountered in trying to purify these compounds in that separation of the product from the hexakis(isocyanide)technetium(I) material proved to be quite difficult. Both silica gel and alumina columns were tested with a variety of solvent gradients, and attempts at purification were made by using both preparative HPLC and TLC. The result was that the compounds [Tc(CNtBu)$_4$(bpy)]PF$_6$, [Tc(CNtBu)$_4$(phen)]PF$_6$, [Tc(CNmXyl)$_4$(bpy)]PF$_6$, and [Tc(CNMe)$_4$(bpy)]PF$_6$ could be obtained in analytically pure form by using one of the two synthetic methods described, while the 4,4'-dimethyl-2,2'-bipyridine (Me$_2$bpy) and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me$_4$phen) complexes with technetium could not be separated from the remaining [Tc(CNtBu)$_6$]PF$_6$, and this impurity is evident in both the analytical and spectroscopic results. The very low yields of the 5-nitro-1,10-phenanthroline (NO$_2$phen) technetium compound in conjunction with the difficulty encountered in separating the product from the starting materials precluded it also from being obtained in an analytically pure form. The identities of the latter three compounds were corroborated by their spectroscopic properties (vide infra) and are thus included in the discussion of the complete series of compounds despite their lack of purity.

Molecular Structure of [Tc(CNtBu)$_4$(bpy)]PF$_6$. The structure of [Tc(CNtBu)$_4$(bpy)]PF$_6$, as established by X-ray crystallography, reveals that the TcC$_4$N$_2$ core is slightly distorted from a perfect octahedron (see ORTEP drawing in Figure 1 and selected bond angles in Table III). The Tc–N bond distances (see Table

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(10) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; pp 258–276.

(11) Mann, K. R.; Cimolino, M.; Geoffroy, G. L.; Hammond, G. S.; Orio, A. A.; Albertin, G.; Gray, H. B. *Inorg. Chim. Acta* **1976**, *16*, 97.

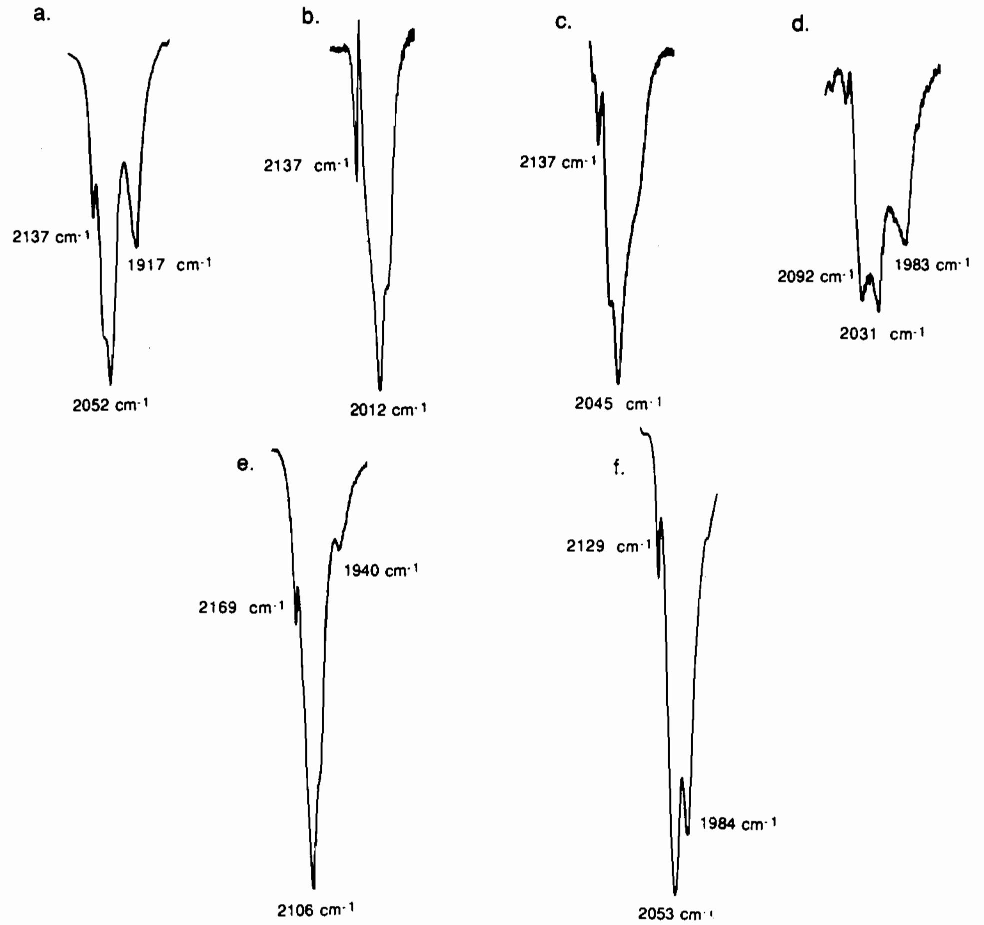
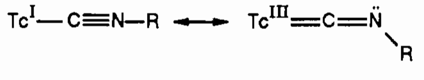


Figure 2. $\nu_{C\equiv N}$ stretching regions of the infrared spectra of the compounds (a) $[Tc(CNtBu)_4(bpy)]PF_6$, (b) $[Tc(CNtBu)_4(Me_2bpy)]PF_6$, (c) $[Tc(CNtBu)_4(phen)]PF_6$, (d) $[Tc(CNtBu)_4(Me_4phen)]PF_6$, (e) $[Tc(CNMe)_4(bpy)]PF_6$, and (f) $[Tc(CNmXyl)_4(bpy)]PF_6$.

IV) are not significantly different from bond lengths that have been reported previously for Tc(III) complexes with amine-type ligands.[12] The most prominent feature of this structure is that one of the isocyanides that is trans to the bipyridine is significantly bent at the nitrogen atom, having a C–N–C angle of 148°. In addition, there is a significant difference in the metal-to-ligand bond length of this isocyanide when compared to those for the coordinated ligands in $Tc(CNtBu)_6^+$. The Tc–C_{31} bond distance of 1.90 (2) Å in this compound is shorter than the reported Tc–C distances of 2.029 (5) Å in the hexakis(*tert*-butyl isocyanide)technetium(I) compound.[13]

A number of bent isocyanide ligands have been reported in the literature and can be explained by considering valence bond theory.[14] The following two resonance forms can be drawn for a coordinated isonitrile:


$$Tc^{I}—C\equiv N—R \longleftrightarrow Tc^{III}=C=\ddot{N}\diagdown R$$

Presumably, the σ-donating property of the bipyridine ligand causes the electron density at the technetium center to increase. This effect in turn allows the technetium to donate electron density into the Tc–C bond, which causes the bend at the nitrogen atom. The overall result is an internal oxidation giving the formally Tc(I) compound what can be referred to as "Tc(III) character". The inability of the reaction to proceed to further substitution of the remaining isocyanides is a reflection of the strengthening of the Tc–C bonds.

Spectral Characterization of $[Tc(CNR)_4(NN)]PF_6$ Compounds. The CN stretching regions of the infrared spectra of the $Tc(CNR)_4(NN)^+$ series are shown in Figure 2. [Note: the spectra of the compounds that could not be separated from the hexakis(isocyanide)technetium starting material were obtained with the use of a subtraction program that eliminated the peaks arising from this impurity. The spectrum of the compound $[Tc(CNtBu)_4(NO_2phen)]PF_6$ obtained in this manner was unreliable due to the extremely large excess of both the technetium and ligand starting materials.] The lowering of symmetry from local O_h to approximate C_{2v} should result in a maximum of three bands for these compounds. Three distinct stretches in this region are apparent in the spectrum of $Tc(CNtBu)_4(bpy)^+$ with a shoulder on the band at 2052 cm^{-1}. The additional stretch can be accounted for by a lowering of symmetry in the solid state due to the varying degrees of bending that the isocyanide ligands take on, as has been seen in the crystal structure. The strongest band in each of the six spectra occurs at a lower frequency than is found for the technetium starting materials, $Tc(CNtBu)_6^+$, $Tc(CNmXyl)_6^+$, and $Tc(CNMe)_6^+$, which have strong bands in their IR (KBr) spectra that occur at 2097, 2075 and 2130 cm^{-1}, respectively. In addition, bands or shoulders can be discerned in each case at frequencies below 2000 cm^{-1}. These low values for the C≡N stretching frequencies imply that a lowering of the carbon–nitrogen bond order is occurring.

The chemical shifts of the ^1H NMR resonances for these compounds are listed in Table V, and all of the spectra for the $Tc(CNR)_4(NN)^+$ compounds display two distinct resonances of equal area in their alkyl regions corresponding to the alkyl groups

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[12] (a) Melník, M.; van Lier, J. E. *Coord. Chem. Rev.* **1987**, *77*, 275. (b) Wilcox, B. E.; Ho, D. M.; Deutsch, E. *Inorg. Chem.* **1989**, *28*, 1743. (c) Breikss, A. I.; Nicholson, T.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1990**, *29*, 640.

[13] Tulip, T. H.; Calabrese, J.; Kronauge, J. F.; Davison, A.; Jones, A. G. In *Technetium in Chemistry and Nuclear Medicine*, Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Raven Press: New York, 1986; p 119.

[14] (a) Chatt, J.; Pombeiro, A. J. L.; Richards, R. L.; Royston, G. H. D.; Muir, K. W.; Walker, R. *J. Chem. Soc., Chem. Commun.* **1975**, 708. (b) Barker, G. K.; Galas, A. M. R.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Turney, T. W.; Welch, A. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1977**, 256. (c) Chiu, K. W.; Howard, C. G.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 803. (d) Jones, W. D.; Foster, G. P.; Putinas, J. M. *Inorg. Chem.* **1987**, *26*, 2120. (e) Warner, S.; Lippard, S. J. *Organometallics* **1989**, *8*, 228.

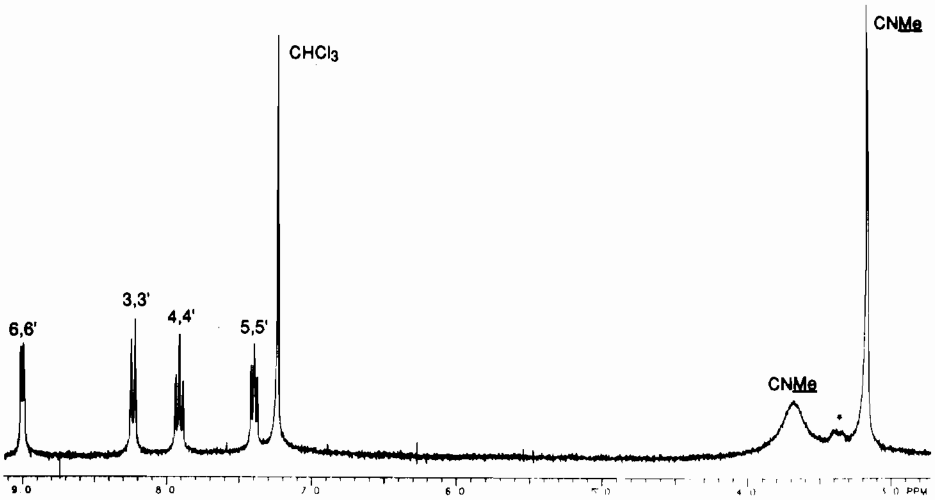

Figure 3. ^{1}H NMR spectrum of [Tc(CNMe)$_4$(bpy)]PF$_6$, which shows ^{99}Tc–^{1}H coupling effects. An asterisk indicates resonance due to [Tc(CNMe)$_6$]PF$_6$.

Table V. The ^{1}H NMR Data for the [Tc(CNR)$_4$(NN)]PF$_6$ Series and Assignment of the Resonances

compd	δ, ppm	assignt
Tc(CNtBu)$_4$(Me$_4$phen)$^+$	1.14 s (18 H)	$C(CH_3)_3$
	1.54 s (18 H)	$C(CH_3)_3$
	2.57 s (6 H)	CH_3
	2.76 s (6 H)	CH_3
	8.15 s (2 H)	5,6
	8.98 s (2 H)	2,9
Tc(CNtBu)$_4$(Me$_2$bpy)$^+$	1.20 s (18 H)	$C(CH_3)_3$
	1.48 s (18 H)	$C(CH_3)_3$
	2.53 s (6 H)	CH_3
	7.14 d (2 H)	5,5′
	8.16 s (2 H)	3,3′
	8.71 d (2 H)	6,6′
Tc(CNtBu)$_4$(bpy)$^+$	1.20 s (18 H)	$C(CH_3)_3$
	1.49 s (18 H)	$C(CH_3)_3$
	7.37 t (2 H)	5,5′
	7.95 t (2 H)	4,4′
	8.30 d (2 H)	3,3′
	8.92 d (2 H)	6,6′
Tc(CNtBu)$_4$(phen)$^+$	1.13 s (18 H)	$C(CH_3)_3$
	1.54 s (18 H)	$C(CH_3)_3$
	7.81 m (2 H)	3,8
	8.00 s (2 H)	5,6
	8.43 d (2 H)	4,7
	9.29 d (2 H)	2,9
Tc(CNtBu)$_4$(NO$_2$phen)$^+$	1.18 s (18 H)	$C(CH_3)_3$
	1.54 s (18 H)	$C(CH_3)_3$
	7.55 m (2 H)	3,8
	8.48 d (1 H)	*b*
	9.08 m (2 H)	2,9
Tc(CNmXyl)$_4$(bpy)$^+$	2.01 s (12 H)	CH_3
	2.46 s (12 H)	CH_3
	7.00 m (12 H)	ArH
	7.48 m (2 H)	5,5′
	8.14 t (2 H)	4,4′
	8.67 d (2 H)	3,3′
	9.18 d (2 H)	6,6′
Tc(CNMe)$_4$(bpy)$^+$	3.17 s (6 H)	CH_3
	3.6 br (6 H)	CH_3
	7.40 t (2 H)	5,5′
	7.92 t (2 H)	4,4′
	8.22 d (2 H)	3,3′
	9.01 d (2 H)	6,6′

[a] All spectra were obtained with CDCl$_3$ as the solvent. [b] This resonance could not be assigned. Other resonances for NO$_2$phen are obscured by the remaining free ligand, which could not be removed.

Table VI. Cyclic Voltammetry Results and Electronic Absorption Spectral Data for the [Tc(CNR)$_4$(NN)]PF$_6$ Series

compd	$E_{1/2}$, V	E^0 of Fe(NN)$_3$SO$_4$, V[16]	λ_{max}, nm	ε, L mol^{-1} cm^{-1}
Tc(CNtBu)$_4$(Me$_4$phen)$^+$	+0.40	+0.81	464	9300
Tc(CNtBu)$_4$(Me$_2$bpy)$^+$	+0.41	+0.95	492	4400
Tc(CNtBu)$_4$(bpy)$^+$	+0.42	+0.97	508	6200
Tc(CNtBu)$_4$(phen)$^+$	+0.44	+1.06	498	10300
Tc(CNtBu)$_4$(NO$_2$phen)$^+$	*a*	+1.25	520	*a*
Tc(CNMe)$_4$(bpy)$^+$	+0.38		504	4700
Tc(CNmXyl)$_4$(bpy)$^+$	+0.74		474	5900

[a] Could not be obtained.

on the isocyanide ligands. The presence of only two peaks in this region indicates that the electronic effect that causes the isocyanides to be bent is delocalized in solution, in contrast to the localized bends seen in the crystal structure. A comparison of the spectra for the Tc(CNtBu)$_4$(NN)$^+$ series enabled the resonances for the protons on the aromatic amine ligands to be assigned as shown in the table. The aromatic amine signals reported for Tc(CNtBu)$_4$(NO$_2$phen)$^+$ are assigned on the basis of similarities of splitting patterns to those of the free ligand. The remaining unreported resonances are obscured by those of the free ligand, which could not be separated from the product.

The breadth of the peak at 3.6 ppm found in the spectrum of Tc(CNMe)$_4$(bpy)$^+$ (see Figure 3) is due to long-range coupling of the proton with the ^{99}Tc nucleus as has been observed in the ^{1}H NMR spectrum for Tc(CNMe)$_6{}^+$.[15] It is obvious that the protons on two of the isonitriles are more strongly coupled to the ^{99}Tc nucleus since one of these resonances is much broader (60 Hz) than the other (4 Hz). In order to determine which protons are the more strongly coupled—those contained in the equatorial or axial ligands—the compound Tc(CNtBu)$_4$(Me-phen)$^+$ was synthesized via method 2. The presence of the asymmetric aromatic amine ligand should result in the appearance of two resonances for the equatorial isocyanide protons and only one for the axial. The spectrum shown in Figure 4a was obtained by using CDCl$_3$ as the solvent, and it appears that one of the signals for the equatorial protons is obscured by the water resonance at 1.5 ppm. Spectra obtained with other solvents displayed only one resonance for these protons; however, in the case where CD$_3$CN was employed, the downfield resonance is broadened (see Figure 4b). These two spectra provide sufficient evidence to conclude that the resonant frequency for the equatorial protons occurs downfield from that of the axial protons. It then follows, from the spectrum of Tc(CNMe)$_4$(bpy)$^+$, that it is the equatorial protons which are more strongly coupled. These ligands, trans to the 2,2′-bipyridine, would have the shorter Tc–C bonds, as seen in the structure of Tc(CNtBu)$_4$(bpy)$^+$, which is presumably the reason that they couple to the technetium to a greater extent.

The compounds of this series all exhibit what appear to be one-electron reversible oxidation waves that have similar $E_{1/2}$ values. These values can be used as a reflection of the elec-

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(15) O'Connell, L. A.; Pearlstein, R. M.; Davison, A.; Thornback, J. R.; Kronauge, J. F.; Jones, A. G. *Inorg. Chim. Acta* **1989**, *161*, 39.

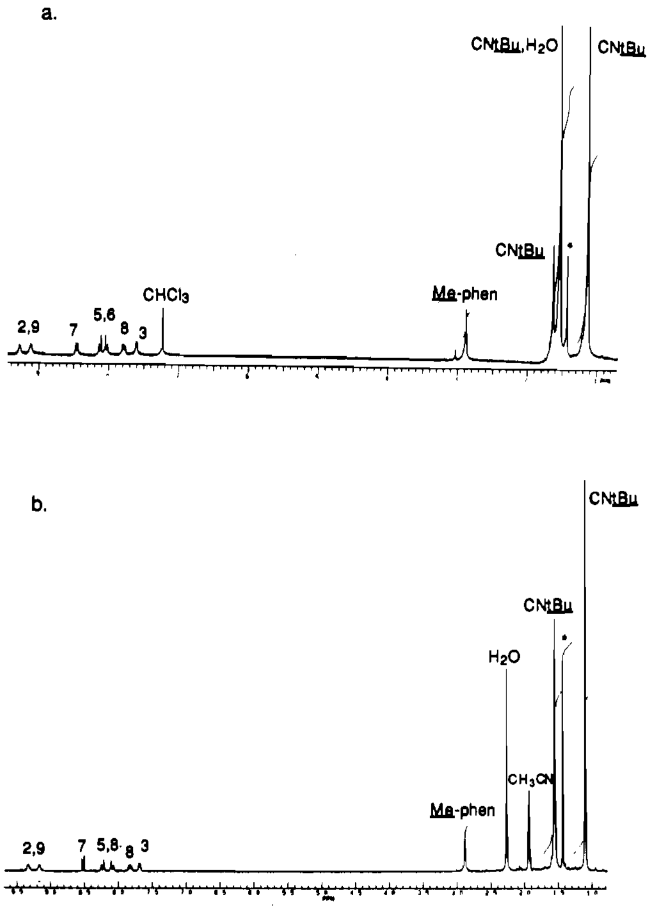

Figure 4. ^{1}H NMR spectrum of $[Tc(CNtBu)_4(Me\text{-}phen)]PF_6$ in (a) $CDCl_3$ and (b) CD_3CN. An asterisk indicates resonance due to $[Tc(CNtBu)_6]PF_6$.

tron-donating or -withdrawing capability of the ligands, where the most electron-donating ligand stabilizes the higher oxidation state and produces the least positive oxidation potential. In Table VI, the $E_{1/2}$ values of the $Tc(CNtBu)_4(NN)^+$ compounds are compared to those of $[Fe(NN)_3]SO_4$.[16] While the differences between the potentials for the technetium compounds are smaller than for the iron complexes, the ordering is the same. Similarly, the $E_{1/2}$ values of the $Tc(CNR)_4(bpy)^+$ compounds should reflect the electron-withdrawing capabilities of the R group on the isonitrile ligand. Such is the case for the aryl isocyanide ligand, which produces an oxidation wave for $Tc(CNmXyl)_4(bpy)^+$ with a more positive potential than that of $Tc(CNtBu)_4(bpy)^+$; however, in the case of the methyl isocyanide complex, the $E_{1/2}$ value is unexpectedly smaller than that of $Tc(CNtBu)_4(bpy)^+$. An explanation for this anomaly has not yet been determined.

As with other metal complexes that contain either bipyridine or other aromatic amine ligands, these complexes are intensely colored.[17] Each exhibits an absorption in the visible region that results in either an orange $\{Tc(CNtBu)_4(Me_4phen)^+$, $Tc(CNtBu)_4(Me_2bpy)^+$, $Tc(CNtBu)_4(phen)^+$, $Tc(CNmXyl)_4(bpy)^+\}$, a red $\{Tc(CNtBu)_4(bpy)^+$, $Tc(CNMe)_4(bpy)^+\}$, or a purple-red $\{Tc(CNtBu)_4(NO_2phen)^+\}$ color, and these λ_{max} and ϵ values are listed in Table VI. Similar to other bipyridine compounds, this band is attributed to $\pi^*(bpy) \leftarrow d\pi(Tc(I))$ metal-to-ligand charge-transfer (MLCT) transitions.[18] The λ_{max} of this absorption shifts when the spectra are obtained in different solvents, as evidenced for the bipyridine complex which has λ_{max} values of 508 and 492 nm in methylene chloride and methanol, respectively.

Table VII. Mass Spectral Data for the $[Tc(CNR)_4(NN)]PF_6$ Series and Fragment Assignments

compd	m/z	fragment
$Tc(CNtBu)_4(Me_4phen)^+$	667	M^+
	584	$(M - CNtBu)^+$
	431	$(M - Me_4phen)^+$
$Tc(CNtBu)_4(Me_2bpy)^+$	615	M^+
	600	$(M - Me)^+$
	532	$(M - CNtBu)^+$
	431	$(M - Me_2bpy)^+$
$Tc(CNtBu)_4(bpy)^+$	587	M^+
	530	$(M - tBu)^+$
	504	$(M - CNtBu)^+$
	431	$(M - bpy)^+$
$Tc(CNtBu)_4(phen)^+$	611	M^+
	528	$(M - CNtBu)^+$
	431	$(M - phen)^+$
$Tc(CNtBu)_4(NO_2phen)^+$	656	M^+
	573	$(M - CNtBu)^+$
	431	$(M - NO_2phen)^+$
$Tc(CNMe)_4(bpy)^+$	419	M^+
	378	$(M - CNMe)^+$
$Tc(CNmXyl)_4(bpy)^+$	779	M^+
	648	$(M - CNmXyl)^+$

Qualitative relationships between electronic absorption spectra and electrochemical potentials for series of compounds have been investigated in the past, and linear correlations have been found where an increase in the $E_{1/2}$ to a more positive value follows an increase in the energy of the lowest energy CT transition.[19] For the aryl isocyanide compound, it is evident that the $E_{1/2}$ value correlates with the λ_{max} value as expected when compared to those of the *tert*-butyl isocyanide complex; that is, the oxidation potential is more positive and the transition energy is higher for the aryl isocyanide compound. The same correlation does not hold true for the methyl isocyanide complex; however, the $\pi^*(bpy) \leftarrow d\pi(Tc(I))$ transition energy in this case is slightly higher than that of the *tert*-butyl isocyanide compound, as would be expected. In the case where the chromophoric ligand is varied, as with the $Tc(CNtBu)_4(NN)^+$ series, the increase in the transition energy actually correlates with an increase in the difference between the potential of the metal-based, $M(n + 1/n)$, couple and the potential of the ligand-based, $NN(0/-)$, couple:

$$\Delta E_{1/2} = E_{1/2}(M^{n+1/n}) - E_{1/2}(NN^{0/-})^{19b-d}$$

The cyclic voltammograms of the $Tc(CNtBu)_4(NN)^+$ compounds exhibit only a metal-based oxidation wave, and no wave is seen for the ligand reduction within the accessible potential range; therefore, a clear relationship between the electrochemical potentials and the electronic absorption spectra is not found with these molecules.

The FAB(+) mass spectra of the compounds all exhibit molecular ion peaks for the cationic species (see Table VII). In addition, several fragment peaks are seen that correspond to losses of isocyanide or aromatic amine ligands. The peak with a m/z value of 530 in the spectrum of $Tc(CNtBu)_4(bpy)^+$ corresponds to a fragment that arises from the dealkylation of an isocyanide and is typical for FAB(+) mass spectra of technetium (I) alkyl isocyanide cations.[20] It should be noted that this pattern does not occur in the case where aryl isocyanide ligands are present, as demonstrated by the spectrum of $Tc(CNmXyl)_6^+$, which does not contain peaks due to loss of the aryl group.

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Table VIII. ^{99}Tc NMR Chemical Shifts and Line Widths for the $[Tc(CNR)_4(NN)]PF_6$ Series

compd	δ, ppm	line width, Hz
$Tc(CNtBu)_4(Me_4phen)^+$	−884	3000
$Tc(CNtBu)_4(Me_2bpy)^+$	−869	2500
$Tc(CNtBu)_4(bpy)^+$	−856	2000
$Tc(CNtBu)_4(phen)^+$	−864	2000
$Tc(CNtBu)_4(NO_2phen)^+$	−829	2500
$Tc(CNMe)_4(bpy)^+$	−836	2500
$Tc(CNmXyl)_4(bpy)^+$	−872	2500

Protonation Reactions. Attempts were made to protonate the bent isocyanide ligand with strong acids such as HBF_4 and HPF_6 since the formation of aminocarbyne ligands has been achieved in this way for several metal complexes.[14a,c,e,21] Each of the compounds in the series $Tc(CNR)_4(NN)^+$, with one exception, turns from orange or red to bright yellow in CH_2Cl_2 solution when the acid is added, and a yellow solid precipitates out of solution with the addition of diethyl ether. Efforts to protonate the aryl isocyanide ligand produced an intractable, brown material. The yellow products appear to be unstable, since both the solutions and solid materials turn orange over time when exposed to air. Infrared and ^{1}H NMR evidence indicate that the orange color is due to starting material; therefore, if protonation is occurring, the process is reversible. Although many of the aminocarbyne complexes that have been reported decompose to form metal hydride bonds,[21] there is one instance where the protonation/deprotonation has been shown to be an equilibrium process. Warner and Lippard found that repeated recrystallizations of $[ReCl(CNHMe)(CNMe)_2(PMePh_2)_2]SbF_6$ from THF will produce $[ReCl(CNMe)_3(PMePh_2)_2]$, which is an intermediate in the formation of the aminocarbyne complex from $[ReCl_2(CNMe)_3(PMePh_2)_2]^+$ under reductive-coupling reaction conditions.[14e] Attempts to alkylate the isocyanides with $Et_3O{\cdot}BF_4$ or $Me_3O{\cdot}BF_4$ resulted only in the recovery of starting material.

The products that result from the protonation reactions of the compounds $Tc(CNtBu)_4(phen)^+$, $Tc(CNtBu)_4(Me_4phen)^+$, $Tc(CNtBu)_4(NO_2phen)^+$, and $Tc(CNMe)_4(bpy)^+$ appear to be the most acidic of the series as they readily deprotonate during isolation procedures. In contrast, the isolated products that result from reactions with $Tc(CNtBu)_4(bpy)^+$ and $Tc(CNtBu)_4(Me_2bpy)^+$ remain yellow for several minutes, and the solid obtained from the reaction of $Tc(CNtBu)_4(Me_2bpy)^+$ with HPF_6 turns orange over the course of 1–2 days. For this reason, only spectral characterization of the products from the reactions of these latter two compounds were carried out. The ^{1}H NMR spectra display very broad resonances (on the order of 100 Hz) extending over larger than normal chemical shift ranges (+16 ppm to −1 ppm), which indicates that the compounds are paramagnetic, as would be expected for a Tc(III), d^4, octahedral complex. The IR spectrum of the product from the reaction with the Me_2bpy compound displays several new bands in the C≡N stretching region at 2233, 2200, and 2140 cm^{-1}. If protonation is occurring, the increase in the number of stretches reflects the lower symmetry of the molecule. In addition, the higher frequencies correlate to a higher oxidation state of the technetium, which results in less back-bonding between the metal and the isonitrile.[22] Some new bands are also seen that correspond to C=N stretches and appear at 1617 cm^{-1}, in the case of the Me_2bpy product, and 1635 cm^{-1} for the bpy product. No obvious bands appear in the ν_{NH} stretching region, although a broad shoulder shows up on the water peak in the spectrum of the bpy product at 3250 cm^{-1}. The mass spectrum of the Me_2bpy product displays a peak at *m/z* 615, which corresponds to $[Tc(CNtBu)_4(Me_2bpy)]^+$, as well as a peak at *m/z* 616, which has a relative intensity that is 95% that of $[Tc(CNtBu)_4(Me_2bpy)]^+$. The appearance of this singly charged species, $[Tc(CN(H)tBu)(CNtBu)_3(Me_2bpy)]^+$, seems to indicate that the protonated product is reduced in the *p*-nitrobenzyl alcohol matrix.

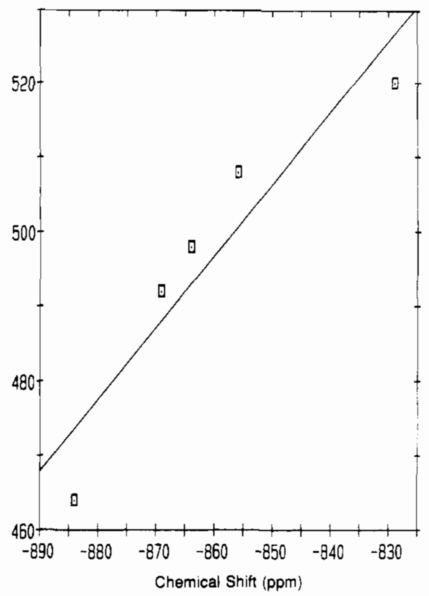

Figure 5. λ_{max} values of the lowest energy electronic transition for the $[Tc(CNtBu)_4(NN)]PF_6$ series plotted as a function of the ^{99}Tc NMR chemical shifts for the compounds.

^{99}Tc NMR Spectral Results. The ^{99}Tc NMR chemical shifts for the series $Tc(CNR)_4(NN)^+$ are listed in Table VIII along with their line widths. We have recently reported that a correlation exists between the ^{99}Tc NMR chemical shift and the oxidation state of the technetium.[15] The values found in Table VIII fall outside of the realm of the Tc(I) region, which ranges from −3517 to −1460 ppm, and appear within the Tc(III) region, which ranges from −1329 to −78 ppm. This result correlates well with both the infrared and X-ray crystallographic data for these compounds (vide supra), which indicate that there is a significant contribution from the resonance form where technetium is in the +3 oxidation state.

The ordering of the chemical shifts for the $Tc(CNtBu)_4(NN)^+$ compounds is accounted for by the paramagnetic shielding term, σ_p. Molecular orbital theory invokes the relationship

$$\sigma_p \propto -1/\Delta E$$

where ΔE is the energy of the lowest energy electronic transition, or the HOMO–LUMO gap.[23] Keeping in mind that the chemical shift is related to the shielding term by a negative sign ($\delta = \sigma_{ref} - \sigma_{sample}$), one can determine a relationship between the chemical shift and the wavelength of the lowest energy electronic transition. As the value for the wavelength increases, which decreases ΔE, the σ_p term takes on a higher negative value and the chemical shift becomes more positive. A plot of the ^{99}Tc shifts and the λ_{max} values for the $Tc(CNtBu)_4(NN)^+$ compounds is shown in Figure 5. This spectrochemical dependence of the NMR chemical shift of a quadrupolar nucleus has been seen for other nuclei[24] and is usually found when low-lying excited states dominate the σ_p term. While the ^{99}Tc NMR shift of the aryl compound also follows this observed trend (that is, a decrease in its λ_{max}, as compared to that of $Tc(CNtBu)_4(bpy)^+$, corresponds to a more negative chemical shift value) the $Tc(CNMe)_4(bpy)^+$ compound appears to be an anomaly in terms of this spectrochemical dependence (its λ_{max} value is also less than that of $Tc(CNtBu)_4(bpy)^+$, but its shift value is more positive). A possible explanation for this exception is that the lack of steric hindrance associated with the methyl isocyanide ligand enables it to achieve a greater degree of bending at the nitrogen atom. A larger deviation from linearity implies more

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Tc(III) character, and thus its signal appears farther away from the Tc(I) region and further into the Tc(III) region.

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Supplementary Material Available: Tables SI–SV, listing respectively complete X-ray data, hydrogen atom positional parameters, intramolecular atomic distances involving the non-hydrogen atoms, intramolecular bond angles, and anisotropic thermal parameters (8 pages); Table SVI, listing calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, D-006, University of California at San Diego,
La Jolla, California 92093-0506, Microcalorimetry Research Center, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan, Department of Chemistry, University of Louisville, Louisville, Kentucky 40292,
Department of Chemistry, University of Delaware, Newark, Delaware 19716,
and School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Effect of Quenched Disorder on Phase Transitions in the Mixed-Valence Solid Solution $[\mathrm{Fe^{III}{}_2Fe^{II}{}_{1-x}Co^{II}{}_xO(O_2CCH_3)_6(py)_3](py)}$[†]

Ho G. Jang,[1] Kazutoshi Kaji,[2] Michio Sorai,*,[2] Richard J. Wittebort,*,[3] Steven J. Geib,[4]
Arnold L. Rheingold,[4] and David N. Hendrickson*,[5]

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The effect of adding permanently distorted $[\mathrm{Fe^{III}{}_2Co^{II}O(O_2CCH_3)_6(py)_3](py)}$ (**2**) complexes to the lattice of the isostructural mixed-valence $\mathrm{Fe^{III}{}_2Fe^{II}O}$ complex **1** to form solid solutions of $[\mathrm{Fe^{III}{}_2Fe^{II}{}_{1-x}Co^{II}{}_xO(O_2CCH_3)_6(py)_3](py)}$ is examined. Single-crystal 298 K X-ray structures are presented for $[\mathrm{Fe_3O(O_2CCH_3)_6(py)_3](py)}$ (**1**) and $\mathrm{Fe^{III}{}_2Co^{II}O}$ complex **2**. Both complexes crystallize in the rhombohedral space group $R32$. Complex **1** has a unit cell with $a = 17.558$ (7) Å and $c = 11.074$ (4) Å, where $Z = 3$. Complex **2** crystallizes with a unit cell of $a = 17.583$ (6) Å and $c = 11.074$ (3) Å, with $Z = 3$. Complex **2** is statically disordered, whereas complex **1** is dynamically disordered at 298 K. In both cases $\mathrm{Fe_2MO}$ (M = Fe, Co) complexes and pyridine solvate molecules are alternatively stacked along the crystallographic C_3 axis. Each $\mathrm{Fe_2MO}$ and pyridine solvate molecule is at a 32 symmetry site, when the effects of the disorder are considered. Powder XRD data for **1**, **2**, and the $x = 0.5$ solid solution (complex **3**) show that complex **3** is indeed a solid solution and not just a mixture of crystals of **1** and **2**. Adiabatic calorimetry was used to measure the heat capacity at constant pressure, C_P, in the 12–300 K range for a 17.4981-g sample of complex **2** and a 13.6562-g sample of complex **3**. For the $x = 0.5$ solid solution complex **3** three C_P peaks were seen at 84.5, 148.0, and 168.8 K. A single broad C_P peak was seen at 148.5 K for $\mathrm{Fe^{III}{}_2Co^{II}}$ complex **2**. This one broad peak gave a total entropy gain for the phase transition of 10.32 J $\mathrm{K^{-1}\,mol^{-1}}$, which is close to a value of $\Delta S = R \ln 3 = 9.13$ J $\mathrm{K^{-1}\,mol^{-1}}$. Solid-state ^{2}H NMR results for randomly oriented polycrystalline and magnetically oriented microcrystalline samples of **2** confirmed that the 148.5 K phase transition for $\mathrm{Fe^{III}{}_2Co^{II}}$ complex **2** is due only to a cooperative onset of motion of the pyridine solvate molecules. The total entropy gain for the $x = 0.5$ solid solution was calculated to be $\Delta S = 19.74$ J $\mathrm{K^{-1}\,mol^{-1}}$. This ΔS value is rationalized in terms of the onset of valence detrapping in the $\mathrm{Fe_2O}$ complexes and pyridine solvate molecules in the solid-solution complex **3**. In agreement with the heat capacity results, ^{57}Fe Mössbauer data for $[\mathrm{Fe^{III}{}_2Fe^{II}{}_{1-x}Co^{II}{}_xO(O_2CCH_3)_6(py)_3](py)}$ show that this solid solution converts from a ferrodistortive phase to a antiferrodistortive phase at ~85 K, finally to be completely valence detrapped and dynamic in a paradistortive phase at ~175 K. The $\mathrm{Fe^{III}{}_2Co^{II}O}$ complexes in the solid-solution complex **3** behave as an unusual type of quenched disorder. They do not serve simply as lattice sites missing a mixed-valence $\mathrm{Fe_3O}$ complex. Each $\mathrm{Fe^{III}{}_2Co^{II}O}$ complex is permanently distorted, and due to py···py contacts with neighboring trinuclear complexes it acts as an unusual element of disorder that appears to prohibit the appearance of an ordered state at a concentration of $\mathrm{Fe^{III}{}_2Co^{II}O}$ complex below that predicted by percolation theory.

Introduction

In the solid state several mixed-valence complexes have been shown to convert from being valence trapped at low temperatures to valence detrapped at high temperatures. A valence-detrapped complex is rapidly interconverting between the different minima on its ground-state potential-energy surface. Mixed-valence biferrocenes[6] and trinuclear iron acetates[7] of the composition $[\mathrm{Fe^{III}{}_2Fe^{II}O(O_2CCH_3)_6(L)_3]S}$, where L is a ligand and S is a solvate molecule, are some of the best studied complexes that valence detrap in the solid state. Valence detrapping of biferrocenium triiodide has been shown[8] to occur cooperatively in a phase transition by means of heat capacity measurements. The presence of valence-detrapping phase transitions has also been established with this same technique for several $[\mathrm{Fe^{III}{}_2Fe^{II}O(O_2CCH_3)_6(L)_3]S}$ complexes.[7a,b,g,h] Intermolecular interactions are present between pairs of $\mathrm{Fe_3O}$ complexes due to the overlap of two L = pyridine ligands. As a result, long-range order develops and valence detrapping occurs cooperatively in large regions (domains) of each crystal.

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(1) University of Illinois.

(2) Osaka University.

(3) University of Louisville.

(4) University of Delaware.

(5) University of California at San Diego.

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