Synthesis of an Iron(IV) Cyanide Complex That Contains the Triamido Amine Ligand [(*t*-BuMe₂SiNCH₂CH₂)₃N]³⁻

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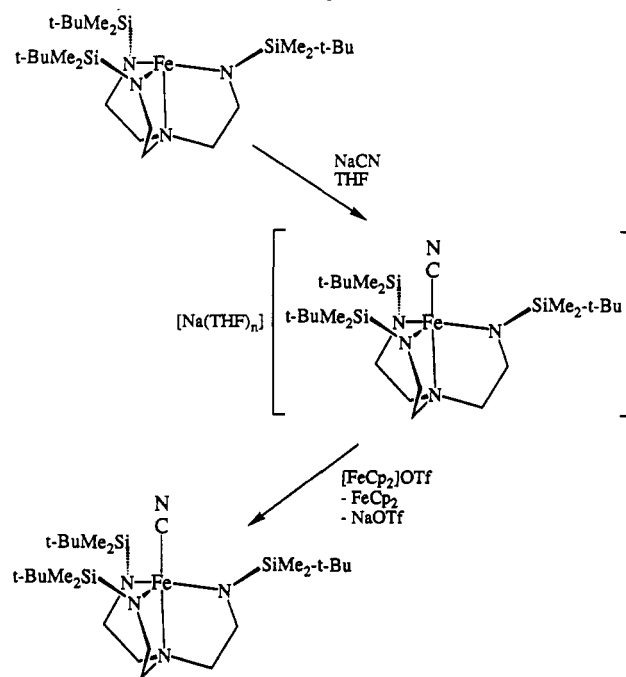
Introduction

Iron(IV) is believed to be present in biological porphyrin-containing systems such as horseradish peroxidase and cytochrome P-450.[1] However, well-characterized Fe(IV) complexes are relatively rare.[2] A typical iron(IV) porphyrin complex is Fe-(TMP)(OCH₃)₂, where TMP = *meso*-tetramesitylporphyrin.[2] Several other known iron(IV) complexes are octahedral and cationic with donor ligands that include halide, phosphine, arsine, and dithiocarbamate.[2] These complexes appear to be of limited thermal stability. Iron(IV) complexes have been prepared that contain ligands that resist oxidative degradation.[3] To date, however, the only diamagnetic iron(IV) complex to our knowledge is purple Fe(1-norbornyl)₄.[4]

We reported recently that trigonal-monopyramidal M(III) complexes (M = Ti, V, Cr, Mn, Fe) can be prepared that contain a trianionic triamido amine ligand, [(*t*-BuMe₂SiNCH₂CH₂)₃N]³⁻.[5] Titanium, vanadium, and tantalum species that contain unusual ligands in the apical position in related trigonal-bipyramidal complexes (e.g., Ti—H,[6] V=NH,[7] or Ta=PR[8]) have been prepared that illustrate that the "pocket" formed by the three bulky amido substituents provides a considerable amount of steric protection for relatively reactive functionalities in the apical site. (Other triamido amine complexes that contain Ti, V, and Mo were also reported recently.[9-11]) We decided to try to prepare an iron(IV) derivative in order to test whether the triamido amine ligand system would stabilize a complex that contains such an "unstable" oxidation state. We describe here the synthesis and characterization of [N₃N']FeCN ([N₃N']³⁻ = [(*t*-BuMe₂SiNCH₂-CH₂)₃N)]³⁻), a diamagnetic trigonal-bipyramidal coordination complex of iron(IV).

Results and Discussion

Addition of ~2 equiv of sodium cyanide to a brown solution of Fe[N₃N']⁵ in tetrahydrofuran caused the solution to change to deep purple-red over a period of 3 h. We presume that the resulting solution contains the anionic cyanide complex of iron(III), as depicted in Scheme 1. The slow reaction most likely can be ascribed to the low solubility of sodium cyanide in tetrahydrofuran, although we cannot exclude the possibility that the apical nitrogen donor atom is *not* coordinated to the metal in the anionic product, i.e., that dissociation of the apical nitrogen atom

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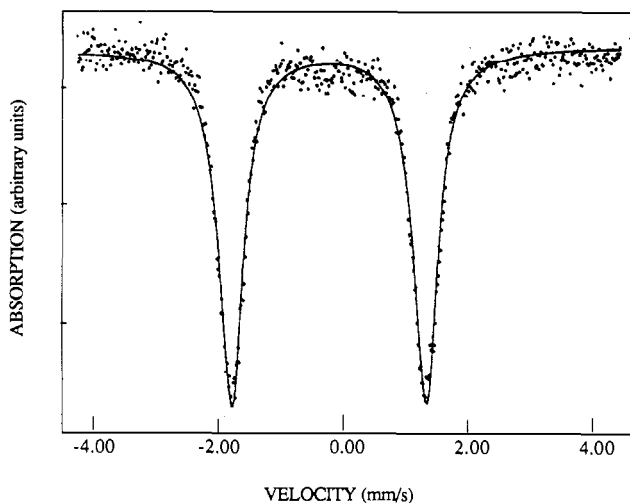(11) Plass, W.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 3762.

Scheme 1. Synthesis of [N₃N']FeCN

must precede coordination of the cyanide. After 2 days, the excess sodium cyanide was removed by filtration and the solution was chilled to -35 °C prior to addition of 1 equiv of ferrocenium triflate. Oxidation of {[N₃N']FeCN}⁻ to what we propose is [N₃N']FeCN is rapid; a deep purple color develops as the ferrocenium salt dissolves. We can confirm by proton NMR examination of crude reaction mixtures that diamagnetic [N₃N']-FeCN and ferrocene are produced in equal amounts. The ferrocene is readily separated from [N₃N']FeCN by adding pentane, since only ferrocene has a significant solubility in pentane. Purple [N₃N']FeCN dissolves readily in benzene, in which it is thermally stable (25 °C) for up to 3 h under dinitrogen. However, extensive decomposition (>50%) is observed in solution at 25 °C after 12 h. Spectral features characteristic of paramagnetic Fe-[N₃N']⁵ appear during this time. Therefore, it seems likely that homolytic Fe–C bond cleavage is a mechanism of decomposition of [N₃N']FeCN.

The low-spin configuration of [N₃N']FeCN contrasts markedly with the high-spin configuration of Fe[N₃N'].[5] The [N₃N']³⁻ ligand can be viewed as being a 12-electron donor if the axial nitrogen donor in the [N₃N'] ligand is bound to the metal, since one of the three MO's formed from the three in-plane p orbitals on the equatorial nitrogen atoms has a symmetry that is not matched by an orbital on the metal and therefore constitutes a ligand-centered nonbonding orbital. Thus, [N₃N']FeCN can be viewed as an 18-electron complex, if the nitrogen donor atom is bound to the metal and two π bonds are formed that involve the equatorial nitrogen atoms. If π bonding is not significant, the trianionic ligand can be regarded as contributing as few as 8 electrons. It is most likely that in this circumstance the d_{xz} and d_{yz} orbitals (assuming the trigonal axis to be the z axis) contain the four paired electrons. The d_{xz} and d_{yz} orbitals could be regarded as degenerate in energy and nonbonding, or one or both could be involved in π bonding to the cyanide ligand. In any case, [N₃N']FeCN is best described as having a low-spin (d_{xz}^2,d_{yz}^2) ground-state configuration.

Both NMR and IR spectra fully support the presence of a cyanide ligand in [N₃N']FeCN. The proton NMR spectrum exhibits four resonances characteristic of 3-fold-symmetric, diamagnetic complexes that contain the [N₃N']³⁻ ligand.[6-8] Characteristic resonances for the N₃N ligand are also observed

Figure 1. Mössbauer spectrum at 180 K with least-squares fit for [N₃N']-FeCN. δ = –0.22 mm/s; ΔE_q = 3.28 mm/s.

in the ¹³C NMR spectrum of [N₃N']FeCN, but a singlet resonance for the cyano carbon atom could be observed readily only in [N₃N']Fe(¹³CN) at δ 128.92 (in C₆D₆) or 131.04 (in CDCl₃). The IR spectrum contains a medium-intensity, somewhat broad peak at 2059 cm⁻¹, consistent with a ν_{CN} stretch. Unfortunately, we have not yet been able to obtain satisfactory elemental analytical data for [N₃N']FeCN, possibly because of sample decomposition, or crystals suitable for X-ray studies.

Further evidence confirming the identity of [N₃N']FeCN as a coordination complex of iron(IV) was obtained via Mössbauer spectroscopy. Mössbauer spectra were obtained at three temperatures (250, 115, and 180 K) in the absence of an applied magnetic field (Figure 2). Little dependence upon the temperature was observed, as expected for the proposed mononuclear complex. A least-squares fit of the data obtained at 180 K (Figure 1) gave an isomer shift δ = –0.22 mm/s and a quadrupole splitting ΔE_q = 3.28 mm/s. Small negative values of the isomer shift are considered diagnostic of iron(IV), and large quadrupole splittings such as that we observe are entirely consistent with this formulation.[2]

One might imagine that iron(IV) complexes other than the cyanide derivative reported here should be stable. However, although the reaction of Fe[N₃N'] with lithium phenylacetylide or sodium azide in tetrahydrofuran led to color changes indicative of formation of an "ate" complex of iron(III), and subsequent oxidation of these solutions with ferrocenium triflate gave purple solutions (and ferrocene) at –40 °C, these reaction mixtures became brown and Fe[N₃N'] was at least partially regenerated when the solutions were warmed to 25 °C.

The results reported here were somewhat surprising, since the [N₃N']³⁻ ligand system would not appear to fall in the general category of "oxidatively-stable" ligands that are analogous to those that other researchers have employed to prepare some iron(IV) species. What these results do suggest to us is that the triamido amine ligand system may stabilize complexes in which the metal is in a relatively high oxidation state for more than steric reasons, which up to this point has been our main focus.

Experimental Section

General procedures can be found in elsewhere.[7]

Preparation of [N₃N']FeCN. Sodium cyanide (110 mg, 2.22 mmol) was added to a solution of Fe[N₃N'][5] (500 mg, 920 μmol) in tetrahy-

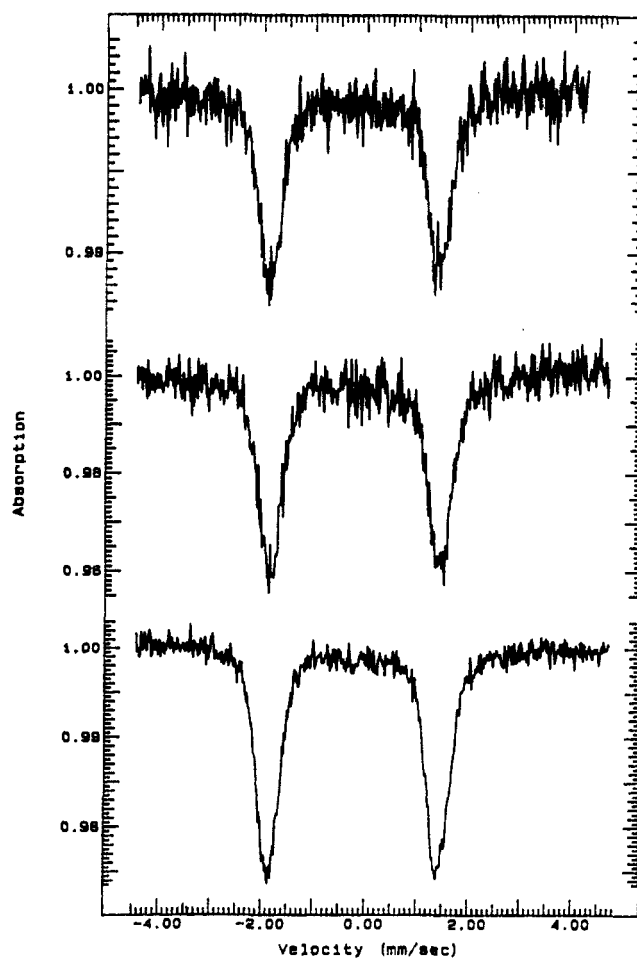**Figure 2.** Mössbauer spectra at 250 K (top), 115 K (center), and 180 K (bottom) for [N₃N']FeCN.

drofuran (4 g), and the solution was stirred at 25 °C. After 3 h, the color of the mixture changed to deep red-purple. After 48 h, the excess sodium cyanide was removed by filtration, and the solution was chilled to –35 °C. [FeCp₂][O₃SCF₃] (310 mg, 920 μmol) was added and the solution stirred. After 1 h, the tetrahydrofuran was removed in vacuo from the inky purple solution. The crystalline residue was extracted with ether until the washings were pale, the filtered extract was concentrated in vacuo, and pentane was added to afford 266 mg of dark purple microcrystals (470 μmol, 51% yield). The product crystallizes readily from cold toluene, and any residual FeCp₂ is removed easily by washing a solid mixture with pentane at 25 °C.

The ¹³C-labeled derivative was prepared similarly using K¹³CN (Aldrich, 99 atom % ¹³C) instead of NaCN: ¹H NMR (C₆D₆) δ 2.950 (t, CH₂), 1.305 (t, CH₂), 1.182 (s, *t*-Bu), 0.542 (s, SiMe₂); ¹H NMR (CDCl₃) δ 3.323 (t, CH₂), 2.037 (t, CH₂), 1.006 (s, *t*-Bu), 0.346 (s, SiMe₂); ¹³C NMR (C₆D₆) δ 128.92 (s, Fe¹³CN), 64.62 (t, $^1J_{CH}$ = 136 Hz, CH₂), 57.00 (t, $^1J_{CH}$ = 136 Hz, CH₂), 28.41 (q, $^1J_{CH}$ = 126 Hz, C(*CH₃*)₃), 21.71 (s, C(CH₃)₃), 0.27 (q, $^1J_{CH}$ = 120 Hz, SiMe₂); ¹³C NMR (CDCl₃) δ 131.04 (s, Fe¹³CN), 64.46 (CH₂), 57.34 (CH₂), 27.93 (C(CH₃)₃), 21.34 (C(*CH₃*)₃), –0.23 (SiMe₂); IR (toluene) 2059 cm⁻¹ (broad, ν_{CN}).