

Figure 5. Changes in S 2p signals by reduction and oxidation for the following samples: (a-1) Fe(OH)₃ treated by a few torr of H₂S at 500 °C; (a-2) sample a-1 oxidized in situ by a few torr of O₂ at 500 °C; (b-1) AS/Fe(OH)₃ calcined at 500 °C, followed by evacuation in situ at 500 °C; (b-2) sample b-1 reduced in situ by a few torr of H₂ at 450 °C; (b-3) sample b-1 oxidized in situ by a few torr of O₂ at 300 °C.

can be oxidized to the >SO₂ state.

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Registry No. S, 7704-34-9; H₂S, 7783-06-4; SO₂, 7446-09-5; (NH₄)₂SO₄, 7783-20-2; Fe(OH)₃, 1309-33-7; Fe₂O₃, 1309-37-1.

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N-Acyl Isocyanide Complexes of Iron(II) Porphyrins. Access to Mixed-Ligand Species Using a Substitute for Carbon Monoxide

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Although isocyanides (CNR) are not natural substrates in biological systems, their interactions with hemoproteins have been extensively studied.¹ The interest in isocyanides derives from a possible understanding of the steric effect of R on rates and equilibria of binding in human hemoglobin. Particularly significant results have recently been reported for both the protein² and porphyrin models³ using classical alkyl isocyanides

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Scheme I

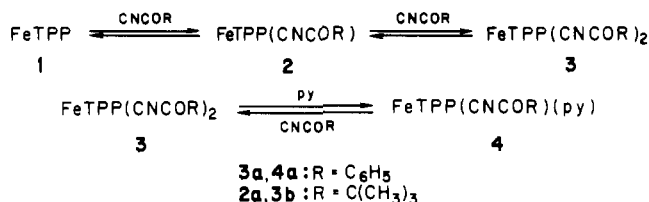


Table I. Carbonyl and Isocyanide Stretching Frequencies of FeTPP Complexes^a

L	free ligand	FeTPP(L) ₂	FeTPP(L)	FeTPP(L)(py)
ν(CO)	2143	2042 ^b	1973 ^b	1980 ^c
ν(CNCOC ₆ H ₅)	2100 ^d	2040		1980
ν(CNCOC(CH ₃) ₃)	2100 ^d	2045	1970	
ν(CNC(CH ₃) ₃)	2130	2129 ^e		

^a Nujol. ^b From ref 6. ^c From ref 14. ^d From ref 9. ^e From ref 7.

Table II. Mössbauer Data for Substituted Iron(II) Tetraphenylporphyrins at 298 K

compd	δ ^a	ΔE _Q ^b	Γ ^c
FeTPP(CNCOC ₆ H ₅) ₂	0.16	0.26	0.26
FeTPP(CO) ₂ ^d	0.19	0.27	0.26
FeTPP(CNCOPh)(py)	0.19	0.58	0.25
FeTPP(CO)(pip) ^e	0.18	0.53	0.24

^a Isomer shift in mm/s relative to iron; ±0.01 mm/s.

^b Quadrupole splitting; ±0.02 mm/s. ^c Line width in mm/s at half-maximum. ^d Reference 15. ^e Reference 16.

in solution. Previously, we described *N*-acyl isocyanide complexes of chromium(0).⁴ The synthetic and spectroscopic results observed with electron-deficient isocyanides revealed ligand properties similar to those of carbon monoxide. This behavior prompts us to consider the application of the CNCOR group as a substrate in porphyrin chemistry. We report here the preparation of FeTPP(CNCOR), FeTPP(CNCOR)₂, and FeTPP(CNCOR)(base) (R = C₆H₅, (CH₃)₃C; base = pyridine, 1-methylimidazole, 4-cyanopyridine).⁵ The spectral properties of these new complexes are discussed in comparison with those of carbon monoxide⁶ and alkyl isocyanide adducts.⁷

Results and Discussion

Our results are summarized in Scheme I. Treating FeTPP (1)⁸ with 2 equiv of *N*-benzoyl isocyanide⁹ in CH₂Cl₂ at -40 °C followed by addition of methanol yields the purple crystalline complex 3a in 85% yield. The position and shape of the signals in its ¹H NMR spectrum (-40 °C, CDCl₃, SiMe₄), 8.78 (s, 8 H), 7.97 (m, 8 H), and 7.43 ppm (m, 12 H) for the protons of the porphyrin ring and 7.15 (m, 4 H) and 6.81 ppm (m, 6 H) for the protons of CNCOC₆H₅, are indicative of low-spin iron(II). The electronic spectrum of this new derivative exhibits λ_{max} at 428 nm (ε 4.30 × 10⁵), 553 nm (ε 1.07 × 10⁴), and 593 nm (ε 6.16 × 10³) in toluene. Mössbauer and IR spectra confirm the structure (see Tables I and II). Moreover, it is interesting to note that, by use of *N*-pivaloyl

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isocyanide (CNCOC(CH₃)₃)⁹ instead of benzoyl isocyanide, the monoadduct **2b** is also formed (IR (Nujol) $\nu(\text{C}\equiv\text{N})$ 1970 cm⁻¹, $\nu(\text{C}=\text{O})$ 1720 cm⁻¹) together with the bis adduct **3b** (IR (Nujol) $\nu(\text{C}\equiv\text{N})$ 2045 cm⁻¹, $\nu(\text{C}=\text{O})$ 1745 cm⁻¹).¹⁰ This behavior parallels nicely that of CO complexation to Fe^{II}TPP.⁶

Reaction between **3a** and 1 equiv of pyridine in CH₂Cl₂ (20 °C) gives **4a**, which has been crystallized by CH₃OH addition as a red-purple solid whose elemental analysis and mass spectrum¹¹ agree with the formula C₅₇H₃₈N₆OFe (electronic spectrum (toluene) λ_{max} 424 nm (ϵ 4.3 × 10⁵), 534 nm (ϵ 1 × 10⁴)). The ¹³C NMR spectrum of **4a** (CD₂Cl₂, 20 °C, SiMe₄) exhibits a sharp peak at 186 ppm, which can only be observed when the compound is prepared from ¹³CNCOC₆H₅ (porphyrin ring 145, 142.6, 134.7, 134.1, 127.1, 126.9, 121.7 ppm; pyridine 146.1, 133.8, 120 ppm; CN¹³COC₆H₅ 150.07 ppm; free C¹³NCOPh 165 ppm⁹). In deoxygenated solvents like C₆H₆ or C₆H₅CH₃, complex **4a** is stable indefinitely and is slowly transformed into the known FeTPP(py)₂ only by further addition of a large excess of pyridine. However, in aerated solution, the FeTPP(CNCOC₆H₅)(py) is irreversibly oxidized to the μ -oxo dimer (FeTPP)₂O (10⁻⁴ M, benzene, 8% after 24 h). In comparison FeTPP(py)(CO) is more sensitive to dioxygen under identical conditions ($t_{1/2}$ = 0.5 h).¹² The preparation of other mixed hexacoordinated complexes can be realized similarly with 1-methylimidazole (electronic spectrum (toluene) λ_{max} 428 nm (ϵ 4 × 10⁵), 539 nm (ϵ 1.05 × 10⁴); IR (Nujol) $\nu(\text{C}\equiv\text{N})$ 1980 cm⁻¹, $\nu(\text{C}=\text{O})$ 1690 cm⁻¹) and 4-cyanopyridine (electronic spectrum (toluene) λ_{max} 424 nm (ϵ 4.1 × 10⁵), 532 nm (ϵ 1.1 × 10⁴); IR (Nujol) $\nu(\text{C}\equiv\text{N})$ 2020 cm⁻¹, $\nu(\text{C}=\text{O})$ 1700 cm⁻¹), thus providing models for isocyanide binding to myoglobin.¹³

Determination of the isocyanide stretching frequencies in heme isocyanides provides an opportunity to demonstrate clearly the sensitivity of ligand binding to the electronic properties of the second axial ligand and the porphyrin. For example, the data in Table I demonstrate that the *N*-acyl isocyanide group is more sensitive than alkyl isocyanide ligands to changes in the electronic environment. Reduction of the C≡N stretching frequency relative to the free ligand value is $\Delta\nu$ = 60 cm⁻¹ for **3a**, while the CN-C(CH₃)₃ frequency does not show a significant shift upon complexation to form [Fe^{II}TPP(CNC(CH₃)₃)₂].⁷ The $\nu(\text{C}\equiv\text{N})$ shift indicates that the bond order of the C-N bond decreases in CNCOC₆H₅. This is consistent with a greater π -acceptor ability of the *N*-acyl isocyanide group compared with that of the CNC(C-H₃)₃ ligand and with a concomitant increase in back- π -bonding from iron to the C≡N bond.

Mössbauer results reported in Table II provide further evidence for the analogy between CO and CNCOR. Trends in both isomer shift δ and quadrupole splitting ΔE_Q in FeTPP-(CNCOC₆H₅)₂ and FeTPP(CNCOC₆H₅)(py) parallel those found in the corresponding CO adducts:^{15,16} *N*-acyl isocyanide

like carbon monoxide significantly reduces the observed splitting relative to the ferroporphyrin bis(amine).¹⁶

We are currently studying the chemical properties of *N*-acyl isocyanides bound to hemoproteins.

Experimental Section

5,10,15,20-Tetraphenylporphyrin, TPPH₂, was prepared by the standard procedure from benzaldehyde and pyrrole in refluxing propionic acid.¹⁷ The iron complex FeTPP(Cl) was prepared from FeCl₂·4H₂O and tetraphenylporphyrin in DMF.¹⁸

FeTPP(CNCOC₆H₅)₂ (3a). In a typical experiment, a solution of **1** (0.2 g, 0.29 mmol) in CH₂Cl₂ (20 mL) was treated under argon with 2 equiv of CNCOC₆H₅ (0.08 g, 0.6 mmol) in 2 mL of CH₂Cl₂ (-40 °C). The reaction was stirred for 10 min. After addition of 70 mL of CH₃OH, purple crystals of **3a** formed, which after 24 h at -40 °C were collected by filtration and vacuum-dried (0.23 g, 85%). Anal. Calcd for C₆₀H₃₈N₆O₂Fe: C, 77.41; H, 4.09; N, 9.03. Found: C, 77.82; H, 4.35; N, 8.71.

FeTPP(CNCOC(CH₃)₃)₂ (3b). The reaction of **1** with a large excess of CNCOC(CH₃)₃ yields pure **3b** in 78% yield. ¹H NMR (-40 °C, CDCl₃, SiMe₄): 8.76 (s, 8 H), 8.15 (m, 8 H), 7.8 (m, 12 H), -0.45 (s, 18 H) ppm. Mass spectrum: *m/e* 668 (FeTPP)⁺, 111 (CNCOC(CH₃)₃)⁺. Electronic spectrum (toluene): λ_{max} 430 nm (ϵ 4.05 × 10⁵), 552 nm (ϵ 1.1 × 10⁴), 593 nm (ϵ 6.5 × 10³).

FeTPP(CNCOC₆H₅)(py) (4a). A 150-mL Schlenk flask was charged with 0.2 g (0.21 mmol) of **3**, 20 mL of CH₂Cl₂, and a stir bar under argon (20 °C). Then 1 equiv of pyridine (0.016 g) in 5 mL of CH₂Cl₂ was added and the reaction mixture stirred for 5 min, after which 80 mL of CH₃OH was added and the resulting solution filtered, giving red-purple crystals in 92% yield (0.17 g). Anal. Calcd for C₅₇H₃₈N₆OFe: C, 77.97; H, 4.33; N, 9.57. Found: C, 77.31; H, 4.21; N, 9.10.

Instrumentation. Infrared spectra were recorded on a Unicam SP 1100 spectrophotometer. Mössbauer spectra were recorded with a ⁵⁷Co(Rh) source. Mass spectra were recorded by using a Varian MAT 311 spectrometer. ¹H NMR spectra were obtained at 80 MHz and proton-decoupled ¹³C NMR spectra were obtained at 20 MHz in the pulse-Fourier-transform mode with a Bruker WT 80 DS spectrometer. Ultraviolet spectra were recorded with a Jobin Yvon Hitachi spectrophotometer.

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Registry No. **1**, 16591-56-3; **2b**, 92958-46-8; **3a**, 92958-47-9; **3b**, 92958-48-0; **4a**, 92958-49-1; FeTPP(CNCOC(CH₃)₃)(B) (B = 1-methylimidazole), 92958-50-4; FeTPP(CNCOC(CH₃)₃)(B) (B = 4-cyanopyridine), 92958-51-5.

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Kinetics and Mechanism of the Reactions of Sulfito Complexes in Aqueous Solution. 6. Formation, Aquation, and Intramolecular Electron Transfer of the *cis*-Aquo(sulfito-*O*)bis(ethylenediamine)cobalt(III) Ion¹

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In previous studies it has been shown that aquopentaammine,² aquo(tetraethylenepentamine)³ ("tetren"),

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(11) Upon direct introduction of the complex at 65 °C, we never observed the molecular peak corresponding to FeTPP(CNCOC₆H₅)(py) but rather observed the progressive appearance of the two axial ligands, pyridine and CNCOC₆H₅, and FeTPP when the temperature reached 190 °C.

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