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Thiocarbonyl Complexes of Iron(II) Porphyrins. Formation by Thiophosgene Reduction

Sir:

Carbon monoxide is a widely used ligand of metalloporphyrins and hemoproteins.[1] Some transition metal complexes of its analogue, carbon monosulfide, have been described; this ligand is a better σ donor and π acceptor leading to stronger bonds with electron-rich metals.[2] However, no thiocarbonyl complexes of metalloporphyrin have yet been described, perhaps because of the great unstability of free CS contrary to CO.

Since iron(II) porphyrins are able to reduce various halogenated compounds[3] and to form CX_2 carbene complexes from polyhalogenated methanes CX_4 in the presence of an excess of reducing agent,[4-6] we tried to prepare thiocarbonyl-iron(II) porphyrin complexes by in situ reduction of thiophosgene. This paper reports the isolation and characterization of some $Fe^{II}(TPP)(CS)$[7] complexes and compares some of their properties with those of the corresponding $Fe^{II}(TPP)(CO)$ or -(carbene) complexes.

Addition of deaerated thiophosgene to a DMF[7] solution of $Fe^{II}(TPP)$ results in an immediate oxidation of the iron, giving $Fe^{III}(TPP)(Cl)$. When the same experiment is done in the presence of an excess of iron powder as a reducing agent, with vigorous stirring, there is formation of a new species[8] characterized in visible spectroscopy by peaks at 420 and 539 nm. In a preparative experiment, thiophosgene (1 mmol) is added to a stirred CH_2Cl_2-MeOH (20:1) solution of $Fe^{III}(TPP)(Cl)$ (0.5 mmol) and $(CH_3S)_2CS$[8] (3 mmol) in the presence of iron powder and under argon. After reaction for 1 h, followed by filtration, evaporation of solvents, and crystallization from CH_2Cl_2-EtOH, a crystalline purple complex **1** is obtained (yield 90%). All of its characteristics indicate the structure $Fe^{II}(TPP)(CS)(EtOH)$: elemental analysis (C, H, Cl, N, S) in agreement with $C_{47}H_{34}FeN_4OS$;[9] ¹H NMR δ (CDCl₃, Me₄Si,[7] ppm) 8.83 (s, 8 H), 8.11 (m, 8 H), 7.71 (m, 12 H) for the protons of the porphyrin ring, and 3.61 (q, J = 6.6 Hz, 2 H), 1.21 (t, J = 6.6 Hz, 3 H), 1.06 (s, 1 H) for the protons of EtOH; ¹³C NMR δ (CDCl₃, Me₄Si, ppm) 145.7, 141.7, 133.6, 132.5, 127.6, 126.7, 120.8 for the carbons of the porphyrin ring, 57.9 and 17.9 for the carbons of EtOH, and a sharp weak peak at 313.5. It is a low-spin iron(II) complex as indicated by its magnetic susceptibility (μ_{eff} = 0 at 33 °C, measured by the Evans method[10]), and by the positions and shapes of the signals of its ¹H and ¹³C NMR spectra. The NMR data are also indicative of an axial symmetry. Carbon monosulfide is one ligand of iron(II) as shown by the elemental analysis, the ¹³C NMR peak at 313.5 ppm, and the intense 1295-cm⁻¹ IR band (KBr pellet) of complex **1**. These two spectroscopic data ($\delta_{C=S}$ and $\nu_{C=S}$) are in good agreement with those reported for thiocarbonyl complexes of iron(II).[11] Furthermore, the mass spectrum (100 eV, 200 °C) of complex **1** exhibits a peak at m/e 712 corresponding to Fe(TPP)(CS).

In solution, complex **1** is in equilibrium with the pentacoordinated complex Fe(TPP)(CS) (**2**) and free EtOH. At 25 °C, this equilibrium, when established from pure complex **1**, is almost completely displaced toward complex **2**. Accordingly, the signals of EtOH in the ¹H NMR spectrum of complex **1** (10^{-2} M in CDCl₃ at 35 °C) are those of free EtOH. Lowering the temperature down to −60 °C causes a progressive upfield shift of the methylene quartet (~1.7 ppm) and the methyl triplet (~1 ppm) of EtOH, indicating that the equilibrium is progressively driven toward the hexacoordinated complex **1**, the exchange between bound and free EtOH remaining always fast on the NMR time scale. The equilibrium constant (K = 6 L mol⁻¹ at 25 °C) between the complexes **2**, λ 409 nm (ϵ 2.2 × 10⁵), 523 (17 × 10³), 550 (sh), and **1**, λ 419 nm (ϵ 2.3 × 10⁵), 535 (14 × 10³), has been calculated from the visible spectra of complex **1** in benzene containing increasing amounts of EtOH.

More basic ligands such as pyridine or *N*-methylimidazole exhibit a greater affinity for complex **2**. For instance, binding of pyridine leads to the Fe(TPP)(CS)(pyridine) complex **3**, λ 424 nm (ϵ 2.25 × 10⁵), 543 (14 × 10³) nm in benzene, with

$$2 \qquad\qquad \underset{\underset{\textbf{3}\ L=Pyridine}{\textbf{1}\ L=EtOH}}{}$$
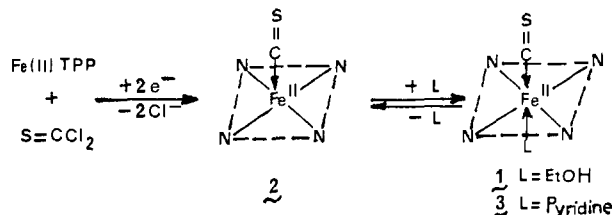
an equilibrium formation constant of 5600 L mol⁻¹ at 25 °C.

The Fe–CS bond in complexes **1**, **2**, or **3** is considerably stronger than the Fe–CO bond of known Fe(TPP)(CO)(L) complexes.[12] It is not dissociated upon dilution (2.10^{-8} M) or after heating complex **2** at 150 °C under 10^{-2} mmHg for 4 h. Moreover, solutions of complex **2** are remarkably stable to oxygen as shown by the lack of detectable oxidation after bubbling oxygen during 20 h. Complex **2** can thus be handled

in air and even purified without decomposition by silica gel column or thin layer chromatography. For comparison, Fe(TPP)(CO)(pyridine) or Fe^{II}(TPP) complexes known for their relative stability toward oxidation, like Fe(TPP)(CCl$_2$)[4] and Fe(TPP)(i-PrNO)(pyridine),[13] are oxidized irreversibly to the iron(III) state in aerated solvents (respective half-lives in benzene: 5 min, 4 h, and 5 h) and are destroyed during column or thin-layer chromatography.

The particular strength of the TPP Fe^{II}–CS bond is also emphasized by the stability of complex **3** in the presence of excess pyridine. After 24 h, <5% complex **3**, initially 6 × 10^{-5} M in benzene in the presence of 1 M pyridine at 25 °C, is transformed into Fe(TPP)(pyridine)$_2$, whereas Fe(TPP)(CCl$_2$) and Fe(TPP)(i-PrNO)(pyridine) are half-transformed into Fe(TPP)(pyridine)$_2$, respectively, within 1.5 and 6 h, under the same conditions. The differences between the strength of the TPP–Fe^{II} bonds with CS and CO are in agreement with the better σ-donor and π-acceptor ability of CS, previously reported for thiocarbonyl complexes in general.[2]

Thiocarbonyl complexes analogous to **1** are obtained from various iron(II) porphyrins like octaethylporphyrin, deuteroporphyrin dimethyl ester and protoporphyrin IX.[14]

We are currently trying to obtain thiocarbonyl complexes of hemoproteins and studying the chemical properties of CS bound to iron(II) porphyrins.

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(9) Actuallym, the crystals were found to retain CH$_2$Cl$_2$ (0.12 mol/mol of complex **1**, from ^{1}H NMR) even after 10-h heating at 50 °C under vacuum (10^{-6} mmHg). Anal. Calcd for TPPFe(CS)(EtOH)($^1/_8$CH$_2$Cl$_2$): C, 73.57; H, 4.49; Cl, 1.15; N, 7.28; S, 4.17. Found: C, 73.25; H, 4.47; Cl, 1.41; N, 7.24; S, 4.10.
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(14) Note Added in Proof. After acceptance of this communication, Professor J. W. Buchler told us that he independently obtained porphyrin iron(II) and osmium (II)(CS) complexes (paper in preparation), confirming the high stability of the Fe–CS bond in such complexes.

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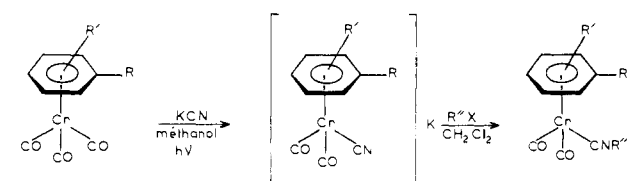
Received March 29, 1978

Structural and Chemical Aspects of Metal Stabilized *N*-Acyl Isocyanide Groups (MCNCOR)

Sir:

As extensively exemplified in metal–carbene chemistry, very reactive intermediates that are incapable of existence or iso-

Scheme I

lation in the free state may be studied and utilized after syntheses on a protecting metal.[1] Similar behavior might be anticipated for the potentially highly reactive *N*-acyl isocyanides series (:CNCOR).[2] Since alkylation of cyanide complexes has been used to synthesize alkyl or aryl isocyanides[3] on a metal atom, we considered the possible formation of N-α-functionalized isocyanides via electrophilic attack of acyl halides on metal cyanide ions. We report here the synthesis and the structural and chemical properties of arenechromium dicarbonyl *N*-benzoyl isocyanide derivatives prepared in this manner.

Scheme I outlines the general preparation of η^6-(arene)-Cr(CO)$_2$CNR derivatives starting from the readily available η^6-(arene)Cr(CO)$_3$ complexes.[4] The air-sensitive monocyanide intermediates, generated by UV irradiation in presence of KCN, were treated with various electrophiles at room temperature. The overall yields, based on isolated products, were usually 65–80%.[5]

In a typical experiment 2 g of (methyl benzoate)Cr(CO)$_3$ (7.35 × 10^{-3} M) and 1 g of KCN (1.54 10^{-2} M) in 200 mL of deoxygenated methanol were irradiated (Lamp HANAU TQ 150) under nitrogen for 3 h. After vacuum evaporation of the solvent, the anion (C$_6$H$_5$CO$_2$CH$_3$)Cr(CO)$_2$CN$^-$ (IR frequencies ν_{CO} (CH$_2$Cl$_2$) 1910, 1830 cm^{-1}; NMR (CD$_3$COCD$_3$) $\delta_{C_6H_5Cr}$ 5.82 (m, 2), 5.12 (m, 1), 4.84 (m, 2), and δ_{OCH_3} 3.47 (s, 3) ppm) was allowed to react with 1 g of C$_6$H$_5$COCl (7.1 × 10^{-3} M) followed by immediate addition of 20 mL of CH$_2$Cl$_2$. After TLC purification (silica gel, eluent; ether–petroleum ether, 1:4), a 2.26-g sample of η^6-(C$_6$H$_5$CO$_2$CH$_3$)Cr(CO)$_2$(CNCOC$_6$H$_5$) was isolated (yield 81%; mp 78 °C; NMR (CDCl$_3$) $\delta_{C_6H_5}$ 8.45 (m, 2), 7.90 (m, 3), $\delta_{C_6H_5Cr}$ 6.45 (m, 2), 5.65 (m, 3), and δ_{OCH_3} 4.05 (s, 3); mass spectrum *m/e* 375.0200 (calcd 375.019879).

To prove the structure of (C$_6$H$_5$CO$_2$CH$_3$)Cr(CO)$_2$-(CNCOC$_6$H$_5$), an x-ray crystal structure analysis was carried out. Red crystals exhibiting two different morphologies were obtained by slow recrystallization from pentane. Although the poor diffractive properties of the crystals resulted in a low yield of data, it was possible to obtain, for both crystal forms, data of sufficiently high quality to allow a reasonably precise description of the solid-state structure.[6]

The structural analysis reveals that the stereochemistry of the molecular complex (Figures 1 and 2) is approximately the same in both crystal forms. Salient structural features include (i) a bent two-electron donating N-α-functionalized isocyanide ligand (C–N–C angle of 168 (1)°) coordinated in a linear fashion to the chromium atom (Cr–C(3)–N angle of 178.8 (9)°, average length of Cr–C(3) bond 1.85 (1) Å); (ii) a disparity in the Cr–C(arene) bonds arising in both forms from a significant lengthening of most of the Cr–C bonds (average length 2.24 (1) Å) compared with the short Cr–C(6) bonds in forms A and B plus the Cr–C(7) bond in form B (average length 2.20 (1) Å); (iii) an unusual staggered configuration of the C(1), C(2), and C(3) atoms of the Cr(CO)$_2$CNCOC$_6$H$_5$ which is tripod with respect to the C(5), C(7), and C(9) atoms of the arene ligand.[7]

Also of interest is the possibility of the occurrence of an intramolecular interaction considering (a) the geometry of the Cr–CN–CO– group in which N⋯O(3) distance is only 2.26 (1)