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Communications

Kinked Cyanide Binding to Iron in a Highly Hindered Dicyano-Iron(III)-Basket-Handle Porphyrin Complex

The cyanide ion is often used as a ligand in ferric heme proteins in order to prepare low-spin ($S = {}^1/_2$) ferric derivatives. These studies have raised questions about the geometry of the CN^- ligand when bound to iron in proteins. Crystallographic studies have shown that the geometry of the Fe–CN group in model ferric porphyrin systems is essentially linear,[1,2] whereas deviations from linearity are observed in the structures of several cyano–heme proteins.[3-6] Similar deviations from ideality have also been observed in carbon monoxide derivatives of ferrous heme proteins,[7-11] while the geometry of the CO group in model ferrous porphyrins appears to be linear.[12-14] The nonideal geometries of the coordinated CN^- and CO ligands in heme proteins are presumed to result from steric interactions with side arms of distal residues. Whether the apparent deviations from ideality of the Fe–CO and Fe–CN groups correspond to a bent, tilted, or kinked geometry is still uncertain. The recent high-resolution (1.5-Å) crystal structure of MbCO (Mb = myoglobin) shows that a bent Fe–CO geometry is more consistent with the electron density.[11] However, the Fe–CO angle is difficult to determine accurately, and at 1.5-Å resolution, X-ray diffraction alone cannot conclusively establish which model is better.[11] EXAFS data on MbCO have also been interpreted in terms of a bent structure.[15] Vibrational spectra of heme–CO complexes are more in favor of a concerted distortion model in which both tilting and bending of the Fe–CO group and a buckling of the porphyrin take place.[16]

As a part of our structural studies of cyanide and carbon monoxide binding in highly hindered iron porphyrins[14] we report here the synthesis and structure of a six-coordinate dicyano-iron(III)–bis(pyridine) basket-handle porphyrin with both faces hindered.[17]

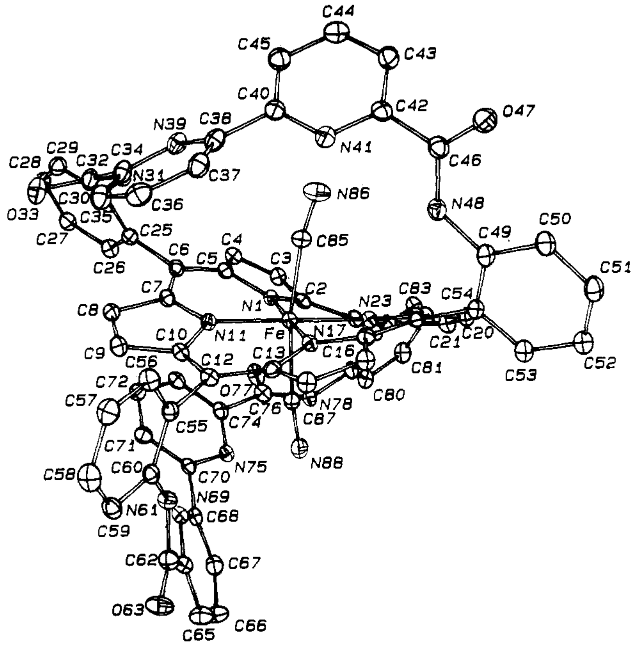

Figure 1. ORTEP plot of $[Fe(BH(Bipy)_2P)(CN)_2]^-$. Ellipsoids are scaled to enclose 30% of the electronic density. Hydrogen atoms are omitted.

The bis(6,6′-diphenylbipyridine) basket-handle porphyrin with both faces hindered, $BH(Bipy)_2P$, already briefly mentioned in the literature,[18] was synthesized by coupling $\alpha,\beta,\alpha,\beta$-5,10,15,20-tetrakis(*o*-aminophenyl)porphyrin with 2 equiv of 6,6′-bipyridine diacid chloride under high dilution conditions. The formation of this compound was followed by TLC on silica gel, the first moving product being the desired porphyrin. It was characterized by ^1H NMR spectroscopy (Bruker SY 200 spectrometer) in $CDCl_3$. The protons of the bipyridine moieties were found between 8.35 and 8.50 ppm. The pyrrole protons appeared at 7.90 ppm. The inner protons of the porphyrin exhibited chemical shifts of −3.50 ppm (vs TMS).

Metalation with iron was achieved with iron(II) acetate. Chromatography on an alumina column with dichloromethane/acetone (5/1) as eluent yielded the unreacted metal-free base as the first fraction (λ_{max} = 426, 510, 555, 593, 660 nm) and the hydroxo–iron(III) complex as the second fraction (λ_{max} = 426, 582, 623 nm). The dicyano–iron(III) complex was prepared by reaction of an excess of 222-cryptated potassium cyanide in fluorobenzene with the hydroxo–iron(III)–porphyrin derivative

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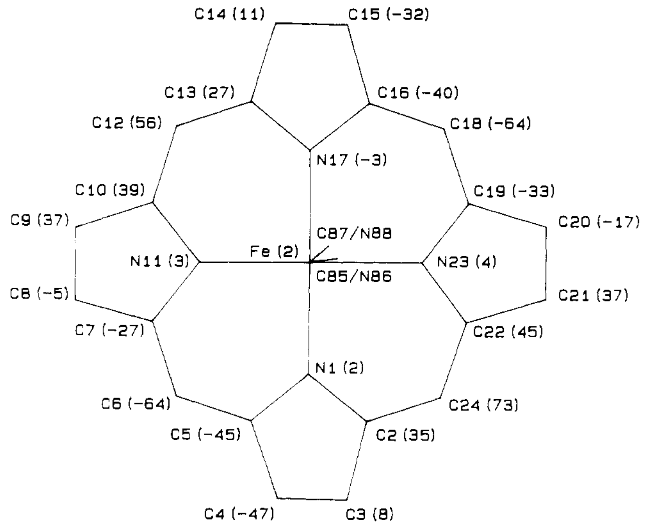

Figure 2. Diagram of the porphyrinato core in $[Fe(BH(Bipy)_2P)(CN)_2]^-$. The perpendicular displacements of each atom (in units of 0.01 Å) from the mean plane of the 24-atom core are displayed. The drawing also illustrates the distortion of the axial ligands from an ideal linear arrangement.

dissolved in fluorobenzene (λ_{max} = 452, 540 sh, 670 nm). Dark blue crystals of $[Fe(BH(Bipy)_2P)(CN)_2][K(\subset 222)](H_2O)_3 \cdot {}^1/_2C_6H_5F$ (**1**)[19] were obtained by slow diffusion of pentane into fluorobenzene solutions of the dicyano–iron(III) derivative.

An ORTEP representation of the porphyrinate anion $[Fe(BH(Bipy)_2P)(CN)_2]^-$ as it exists in the crystals of **1** is displayed in Figure 1. This figure also gives the labeling scheme used for most atoms.

The four Fe–N_p (N_p = porphyrinato nitrogen) bond distances range from 1.937 (4) to 1.969 (4) Å. Their mean value of 1.949 (14) Å appears to be shorter than the average values observed in the anionic complex $[Fe(TPP)(CN)_2]^-$ (2.000 (6) Å) and the neutral complex [Fe(TTP)(CN)(py)] (1.970 (14) Å). The reason for these short Fe–N_p bond distances observed in **1** is not clear yet[20] but is probably related to the very significant unsymmetrical ruffling of the porphyrin ring (Figure 2). This ruffling is probably mainly due to the presence of the two cyanide axial ligands and their steric interactions with the bipyridine handles. Due to these interactions the two handles are pushed toward the edge of the porphyrin ring (Figure 1).

Although the pyrrole rings are individually planar, the dihedral angles between their adjacent mean planes range from 24.0 (4) to 41.1 (3)°. The two nonequivalent Fe–C and C–N bond distances are not significantly different; the mean values of these bond lengths are respectively 1.949 (4) and 1.152 (9) Å. However, both Fe–CN groups are slightly bent; the corresponding bend angles are respectively θ(Fe–C85–N86) = 170.2 (5)° and θ(Fe–C87–N88) = 171.3 (5)°. Moreover, both Fe–C bonds are tilted off the normal to the 24-atom-core mean plane of the ring; the corresponding tilt angles are respectively φ(Fe–C85) = 5.3° and φ(Fe–C87) = 5.1°. The tilt angles with respect to the normal to the 4 N_p mean plane are respectively 5.9 (Fe–C85) and 4.0° (Fe–C87). The deviations of the two C–N vectors with respect to the planes defined by the normal to the 24-atom-core mean plane and the two Fe–C vectors are very small.

Due to these distortions from ideal geometry, the cyano carbon atoms C85 and C87 are displaced respectively by 0.18 and 0.17 Å away from the normal to the 24-atom-core mean plane while the cyano nitrogen atoms are displaced respectively by 0.48 and 0.45 Å from this normal. The observed distortions of the Fe–CN groups in **1** are similar to those observed in the crystal structure of $[Mn^{III}(TPP)CN]CHCl_3$.[3] However, whereas in the manganese(III) complex they result only from intermolecular packing interactions, in **1** they are due mainly to intramolecular steric interactions of the cyano nitrogens N86 and N88 with the bipyridine handles. The closest contacts are N86···C40 (3.00 Å), N86···N41 (3.04 Å), N88···C68 (3.18 Å), and N88···N75 (3.22 Å). However, for N88 a strong hydrogen bond with the water molecule OW_1 occurs also; the corresponding N88···OW_1 distance is 2.82 Å.

The two bipyridine handles are in a nonplanar trans conformation. The dihedral angles between the mean planes of the pyridine moieties are respectively 39.2 (2) and 43.7 (2)° in the two bipyridine groups. Due to the steric constraints introduced by the two cyano groups, the handles are pushed toward the edge of the porphyrin ring and the mean planes of the bipyridine groups are almost perpendicular to the 24-atom-core mean plane (Figure 1). The very pronounced unsymmetrical ruffling of the porphyrinato core is probably related to these unsymmetrical orientations of the two handles relative to the normal of the 24-atom-core mean plane of the porphyrin.[21]

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Supplementary Material Available: Non-hydrogen atom coordinates (Table S1), anisotropic thermal parameters (Table S2), hydrogen atom coordinates (Table S3), and a complete set of bond lengths (Table S4) and bond angles (Table S5) (19 pages); observed and calculated structure factor amplitudes for all observed reflections (Table S6) (22 pages). Ordering information is given on any current masthead page.

Institut Le Bel[22]
Université Louis Pasteur
4, rue Blaise Pascal
67070 Strasbourg Cedex, France

Michèle Schappacher
Jean Fischer
Raymond Weiss*

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(19) $[Fe(CN)_2BH(Bipy)_2P][K(\subset 222)](H_2O)_3 \cdot {}^1/_2C_6H_5F$: M_r = 1714.7, space group $P2_1/c$, a = 14.089 (2) Å, b = 24.161 (4) Å, c = 25.525 (4) Å, β = 105.05 (2)°, V = 8390.7 Å^3, Z = 4, D_c = 1.35 g cm^{-3}. Data were collected on a Philips PW1100/16 automatic diffractometer in the range 4° < θ < 57° at −100 °C using a single crystal of dimensions 0.20 × 0.28 × 0.32 mm^3. The 9120 measured reflections yielded 5502 observations with $I > 3\sigma(I)$. The full-matrix refinement conducted using these reflections and the coordinates obtained from Patterson and Fourier syntheses yielded agreement factors for R_1 = 0.049 and R_2 = 0.071 (GOF = 1.43). Hydrogen atoms were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors such as B(H) = 1.3[B(X)] but not refined. Fluorobenzene and water hydrogens were omitted.

(20) The electronic structure of this ferric porphyrin is presently under study by EPR and Mössbauer spectroscopy.

(21) In $[Zn(BH(Bipy)_2P)]$, the two bipyridine handles present a quasi-planar trans conformation and lie almost parallel to the 24-atom-core mean plane of the porphyrin ring. The ruffling of the porphyrin is much less important than in the iron derivative. The dihedral angles between the adjacent mean planes of the pyrrole rings range from 9.1 to 11.8° (average ≃10.6°). The Zn–N_p distances have the normal expected values (average Zn–N_p 2.030 (14) Å). Schappacher, M.; Fischer, J.; Doppelt, P.; Weiss, R. To be submitted for publication.

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Identification of a Soluble Form of Colloidal Manganese(IV)

For several decades it has been known that many permanganate reactions carried out in both aqueous[1] and organic media[2] lead to the formation of a soluble brown-yellow manganese species whose UV–vis spectrum shows a broad band with absorbance uniformly decreasing as wavelength increases. Despite its extensive occurrence, identification of this species has not been so far possible, and a survey of the permanganate literature reveals that what appears to be the same species (from both aspect and the

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