Structure and Bonding

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Comparison of Cyanide and Carbon Monoxide as Ligands in Iron(II) Porphyrinates**

*Jianfeng Li, Bruce C. Noll, Charles E. Schulz, and W. Robert Scheidt**

Dedicated to Professor Martin Gouterman

Cyanide (CN^-) and carbon monoxide (CO) have long been of particular interest as classic inhibitors of respiration.[1] CO competes with oxygen, binding to reduced iron (Fe^{2+}) to form the stable low-spin hemoprotein carbonyl complexes, whereas CN^- inhibits O_2 reduction.[2] CN^- is isoelectronic and isosteric with CO; both are linearly bound to heme centers, and their complexes can often be found with the same symmetries.[3] Unlike CO and O_2, CN^- binds to both iron(II) and iron(III) hemoproteins, leading in most cases, but not all,[4] to low-spin states. The reaction of cyanide with ferrohemes has been relatively little-studied owing to the low stability of the complexes even at alkaline pH values (up to 9.4).[2] In most hemoproteins, only the kinetics of cyanide dissociation has been investigated as a transient species during reduction of the ferric cyanide complex.[5] The dissociation constants (K_{diss}) are of the order of $1\,mol\,L^{-1}$,[6,7] compared to 10^{-4}–$10^{-9}\,mol\,L^{-1}$ in ferrihemes.[8]

We recently reported the characterization of the first cyanoferroheme, five-coordinate [K(222)][Fe(tpp)CN].[4,9] The cyanide ligand field is insufficient to yield a completely low-spin complex; rather, the species is a $S=0 \rightleftharpoons S=2$ spin-crossover complex.[10] Herein we report a new polymorphic form of [K(222)][Fe(tpp)CN], which is also a spin-crossover complex.[12] More importantly, we also present examples of new six-coordinate cyanoferroheme species: bis(cyano) $[K(222)]_2[Fe(Por)(CN)_2]$, and mixed ligand [K(222)][Fe(tpp)CN(1-MeIm)], which are both low-spin.[11] Although a number of $[Fe^{III}(Por)(CN)_2]^-$ and $[Fe^{III}(Por)CN(L)]$ complexes have been well-studied,[13] no isolated six-coordinate (cyano)iron(II) porphyrinates or structures had been reported.

In thermodynamic and kinetic studies on the binding to hemoglobins, cyanide has some noteworthy properties compared to CO and O_2. For example, the geometric and electronic structure change induced by Fe–CN bonding may not trigger a cooperative process, unlike that of Fe–CO bonding.[14,15] The CN^- ligand in the iron(II) hemoproteins can be replaced upon exposure to CO.[2,16] It appears that a direct comparison between cyanide and carbon monoxide ligation in iron(II) porphyrinates will be fruitful.[14]

The reaction of [Fe(tpp)] with CN^- in chlorobenzene solution can be monitored by UV/Vis spectroscopy (see the Supporting Information), and suggests the presence of two cyano species, $[Fe(tpp)CN]^-$ and $[Fe(tpp)(CN)_2]^{2-}$. Binding constants for the mono- and bis(cyano) species can be determined from a least-squares analysis of the spectroscopic data.[17] The constants were determined to be $K_1 = 4.3\times10^5\,L\,mol^{-1}$ and $K_2 = 3.1\times10^3\,L\,mol^{-1}$, which are comparable to the values found by Goff and Morgan[18] for heme *c*, and also comparable to the binding constants found for the reaction of [Fe(oep)] with CO[19] ($K_1 = 3.3\times10^4\,L\,mol^{-1}$ and $K_2 = 2.3\times10^2\,L\,mol^{-1}$). As in the CO species,[20] both five-coordinate $[Fe(tpp)CN]^-$ and six-coordinate $[Fe(tpp)(CN)_2]^{2-}$ can be isolated.

X-ray structural characterization of bis(cyano)iron(II) porphyrinates reveals that cyanide can exhibit two different coordination modes. The cyanide ligands are either coordinated to the iron center without interaction with the K(222) cations, or with interaction with the cations to form Fe–CN–K bridges (Figure 1 a,b). Six-coordinate [K(222)][Fe(tpp)CN-(1-MeIm)] (Figure 1 c) can be prepared by addition of 1-methylimidazole to a solution of [K(222)][Fe(tpp)CN]. Careful control of imidazole concentration is important to yield the desired mixed-ligand complex. A number of structural features are illustrated in Figure 2, including iron atom displacements, ligand tilts, and equatorial Fe–N_p bond lengths. Structural parameters for the cyano complex are consistent with low-spin states for all derivatives. The corresponding parameters for three analogous carbonyl complexes are given in the right-hand column in Figure 2.

The axial Fe–CN bonds in the five-coordinate low-spin complex $[Fe(tpp)CN]^-$ (1.8783(10) Å for polymorph 1 and 1.869(2) Å for polymorph 2) are the shortest observed for all (porphinato)iron(II) cyanide complexes. This observation is consistent with a sole cyano axial ligand. As reported previously for polymorph form 1,[4] the Fe–CN bond lengthens to 2.108(3) Å as the complex undergoes a spin-state transition and becomes a high-spin species.[21] The addition of a second cyanide ligand to form the low-spin $[Fe(tpp)(CN)_2]^{2-}$ complex leads to an approximate 0.1 Å increase in the Fe–CN distance (two equal axial bonds) compared to the five-coordinate low-spin form. The interaction of the CN^- ligands

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[*] Dr. J. Li, Dr. B. C. Noll, Prof. W. R. Scheidt
Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, IN 46556 (USA)
Fax: (+1) 574-631-6652
E-mail: scheidt.1@nd.edu
Prof. C. E. Schulz
Department of Physics, Knox College
Galesburg, IL 61401 (USA)

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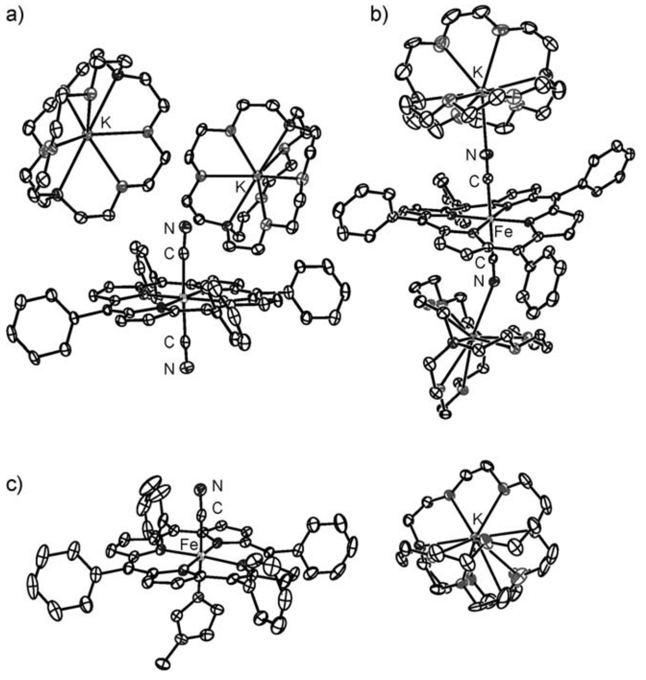

Figure 1. a,b) ORTEPs of two $[K(222)]_2[Fe(tpp)(CN)_2]$ structures, showing two different coordination modes: a) $[K(222)]_2[Fe(tpp)(CN)_2]$ 4PhCl and b) one of two $[K(222)]_2[Fe(tpp)(CN)_2]$ PhCl units. c) The structure of [K(222)][Fe(tpp)(CN)(1-MeIm)]. All three structures illustrated are at 100 K. Ellipsoids set at 50% probability, hydrogen atoms omitted for clarity.

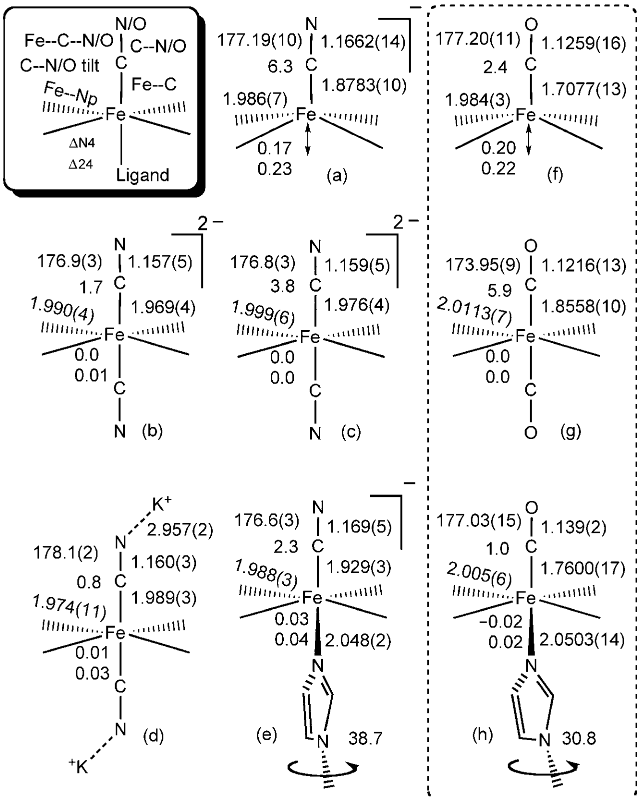

Figure 2. The coordination groups of a) [K(222)][Fe(tpp)(CN)] (polymorph 1), b) $[K(222)]_2[Fe(tpp)(CN)_2]$, c) $[K(222)]_2[Fe(ttp)(CN)_2]$, d) $[K(222)]_2[Fe(tpp)(CN)_2]$, and e) [K(222)][Fe(tpp)CN(1-MeIm)]. Structures of f) [Fe(oep)CO],[20] g) $[Fe(oep)(CO)_2]$,[20] and h) [Fe(tpp)CO(1-MeIm)][24] are also shown for comparison. The boxed key (upper left) indicates the structural parameters that are given for each structure. Δ_{N4} and Δ_{24} are the iron displacements from the four-nitrogen and 24-atom mean planes. The dihedral angle between the imidazole plane and the closest N_p-Fe-N_{ax} fragment are also shown for the imidazole derivatives. All the structures were obtained at 100 K.

with the $[K(222)]^+$ cations leads to a further small increase in the Fe−CN distance to 1.988(3) Å. It is presumed that the increases in the Fe−CN bond distances in the bis(cyano) complexes are the result of increased competition for bonding to the d^6 iron(II) center. The effect of binding an imidazole ligand, a weaker π-accepting ligand than the cyanide ion, leads to an increase of only about 0.05 Å in the Fe−CN bond length relative to the five-coordinate parent.

The Fe−CN bond distances show little variation with iron oxidation state change. The Fe−CN bond distance in bis(cyano)iron(III) derivatives range from 1.949(4) Å to 1.990(5) Å,[13,22] which form the limits for the range of values observed for the iron(II) species. Similarly, the Fe−CN bonds (1.918(2)–1.929(3) Å)[13,23] in the iron(III) derivatives [Fe(Por)CN(1-MeIm)] are equivalent to those observed in the iron(II) complex.

The changes in bond length in this series of cyano derivatives are strikingly similar to those of an analogous series of carbonyl complexes (Figure 2). As comparisons of CO and CN^- as ligands in coordination chemistry have long been of interest,[25] this similarity has lead us to examine the correspondence of properties of the cyano and carbonyl series. It should be noted that the longer Fe−C bond lengths in the cyano complexes is consistent with the idea that cyanide is a better σ donor but a poorer π acceptor than the carbonyl ligand.

Comparisons of changes in the stretching frequency of the two diatomic ligands and variation in the Mössbauer parameters should provide further enlightenment. Values of ν_{CN} and ν_{CO} are given in Table 1: there are large variations in the patterns of CN^- and CO frequency changes across the series. The change in ν_{CO} between the five-coordinate complex (1944–1948 cm^{-1}) and the bis(carbonyl) complex (2021 cm^{-1}) is about 77 cm^{-1}. This large difference strongly suggests a significant competition for π donation by the two carbonyl ligands from the d^6 iron center in the bis complex. However the difference in the cyanide stretching frequency in the analogous pairs of cyanide complexes is virtually zero, with the differences between the five-coordinate species and the various bis(cyano) complexes ranging from 1 to 14 cm^{-1}. The absence of significant variation in ν_{CN} between the mono and bis species suggests that change in the π bonding are much smaller in the cyano complexes. As shown in Table 1, the addition of a neutral nitrogen donor (imidazole) to the cyano complex has a modest effect; the same transformation in the carbonyl complexes leads to much larger changes with both increased and decreased shifts in ν_{CO} relative to the five-coordinate species.[24] The large variation in ν_{CO} in the six-coordinate mixed ligand species reflects the sensitivity of the vibration to its immediate environment.[24] We were thus

Table 1: Multi-temperature Mössbauer data and C–N/O stretching frequencies for iron porphyrinato complexes.[a]

Complex	T [K]	ΔE_Q	δ	Complex	T [K]	ΔE_Q	δ
$[Fe(tpp)CN]^-$	25	1.83	0.37	[Fe(oep)CO]	25	1.84	0.23
$\nu = 2070\ cm^{-1}$	100	1.83	0.36	$\nu = 1948\ cm^{-1}$	100	1.84	0.23
	300	0.85	0.47		298	1.81	0.14
$[Fe(tpp)(CN)_2]^{2-}$	20	0.27	0.31	$[Fe(oep)(CO)_2]$	15	0.09	0.28
$\nu = 2069\ cm^{-1}$	100	0.24	0.31	$\nu = 2021\ cm^{-1}$	100	0.10	0.28
	296	0.13	0.22		298	0.18	0.18
$[Fe(ttp)(CN)_2]^{2-}$	15	0.15	0.29				
$\nu = 2056\ cm^{-1}$	100	0.13	0.29				
	298	0.07	0.22				
$[Fe(tpp)\{CN{-}K(222)\}_2]^{2-}$				[Fe(oep)CO-(1-MeIm)]	15	0.34	0.24
$\nu = 2069\ cm^{-1}$				$\nu = 1980\ cm^{-1}$	100	0.37	0.23
					293	0.40	0.18
$[Fe(tpp)CN(1\text{-}MeIm)]^-$	16	0.60	0.39	[Fe(tpp)CO-(1-MeIm)]	15	0.30	0.26
$\nu = 2076\ cm^{-1}$	100	0.61	0.37	$\nu = 1968\ cm^{-1}$	100	0.32	0.25
	298	0.62	0.26		293	0.35	0.16

[a] [Fe(oep)CO], $[Fe(oep)(CO)_2]$: Ref. [20]; [Fe(oep)(CO)(1-MeIm)], [Fe(tpp)(CO)(1-MeIm)]: Ref. [24]. Mössbauer data: ΔE_q and δ values in $mm\,s^{-1}$.

surprised that the cyano derivative with ion-pair interactions to the terminal cyanide nitrogen atoms had no effect on the CN^- frequency.

Temperature-dependent Mössbauer spectroscopy values are also shown in Table 1. Mössbauer spectra of many mixed-ligand, six-coordinate carbonyl complexes have been measured. Typical features are 1) the relatively low value of the isomer shift, which is lower than typical for a formally iron(II) state and consistent with strong π back-donation from iron to CO,[26] and 2) the small value of the quadrupole splitting that is consistent with a nearly symmetric electron distribution at iron. The analogous cyano imidazole derivative shows interesting differences. The larger value of the isomer shift δ (0.39 vs. $0.26\ mm\,s^{-1}$) is consistent with the expected lowered π acceptance by cyanide and the larger value of the quadrupole splitting ΔE_Q (0.60 vs. $0.30\ mm\,s^{-1}$) is that expected for greater σ donation to iron. As expected, the five-coordinate species yield larger values of the quadrupole splitting. Again, the differences in the isomer shift values are consistent with the differences in the π-bonding characteristics of CN^- and CO. The large change in the temperature-dependent quadrupole splitting values for the five-coordinate cyanide is the result of a LS$\rightleftharpoons$HS spin-crossover. No evidence for a higher spin state in the five-coordinate CO complex is seen, which is consistent with its stronger ligand-field character.

The cyano and carbonyl types of bis-ligated species also show many (and unexpected) similarities. First, the isomer shift values are more similar; the bis(cyano) derivatives have isomer shifts that are smaller than the other groups of cyanoiron(II), whereas the bis(carbonyl) derivative shows a modest increase in the isomer shift relative to other carbonyl species. Clearly for the bis-ligated species, relative to all other species, the iron s-electron density is at a minimum, and in the bis(carbonyl) derivative, iron π donation must be at a maximum. Second, the quadrupole splitting values are all near zero and are the smallest for any of the members of the cyano or the carbonyl systems, which is consistent with a near spherical distribution of d-electron density. Third, the ΔE_q values show substantial temperature dependencies (Table 1). Interestingly, the direction of the change is opposite in the cyano and carbonyl species. A large temperature dependence for ΔE_q is usually considered to be the result of low-lying excited state(s), which in this case must be true for both classes. In view of the differing directions of change, it is most likely that the ΔE_q signs are opposite. Obtaining the sign of ΔE_q is difficult when the magnitude is small as in these cases,[27] and the signs have not yet been determined.

In summary, we have presented the synthesis, molecular structures, and Mössbauer and vibrational spectroscopy of new six-coordinate cyano-ligated iron(II) porphyrinates. The invariant bond distances of the analogous iron(II) and iron(III) porphyrinates are consistent with little π back-bonding between iron and cyanide. This conclusion is strengthened by the comparison with analogous carbonyl complexes. Clearly cyanide is a weaker field ligand than CO in iron(II) porphyrinates.

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[9] Abbreviations: Por = generalized porphyrin dianion, N_p = porphyrinato nitrogen, N_{ax} = axial nitrogen, tpp = dianion of *meso*-tetraphenylporphyrin, ttp = *meso*-tetra-*p*-tolylporphyrin, oep = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin, 1-MeIm = 1-methylimidazole, kryptofix-222 or 222 = 4,7,13,16,21,24-hexaoxo-1,10-diazabicyclo[8.8.8]hexacosane.

[10] The unexpectedly lower ligand field strength of cyanide in this complex has been highlighted: M. Nakamura, *Angew. Chem.* **2009**, *121*, 2676; *Angew. Chem. Int. Ed.* **2009**, *48*, 2638.

[11] CCDC 723540, 723541, 723542, and 723543 ([K(222)][Fe(tpp)CN] at 100, 296, 325, and 400 K), 723544 $[K(222)]_2[Fe(tpp)(CN)_2]\cdot PhCl$, 723545 $[K(222)]_2[Fe(tpp)(CN)_2]\cdot 4\,PhCl$, 723546 $[K(222)]_2[Fe(ttp)(CN)_2]$, and 723547 [K(222)][Fe(tpp)CN(1-MeIm)] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] Comparisons of the structures of the two spin-crossover polymorphic forms at four temperatures between 100 and 400 K is given in the Supporting Information.

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