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Axial $Mn-C_{CN}$ Bonds of Cyano Manganese(II) Porphyrin Complexes: Flexible and Weak?

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S Supporting Information

ABSTRACT: Three five-coordinate high-spin (cyano)manganese(II) complexes, utilized tetraphenylporphyrin (TPP), tetratolylporphyrin (TTP), and tetramesitylporphyrin (TMP) as ligands, are prepared and studied by single-crystal Xray, FT-IR, UV-vis, and EPR spectroscopies. The crystal structure studies revealed noteworthy structural features including unexpectedly wide tilting angles of the axial Mn- C_{CN} bonds, which is contrasted to the isoelectronic Fe(III)-



 C_{CN} bonds. Solid-state EPR measurements (90 K) and simulations are applied to obtain the ZFS parameters (*D*, *E*, and *E*/*D* (λ)), which are compared to Mn(II) porphyrin analogues of hemes to understand the ligand field of the cyanide. The solution EPR studies gave new insights into the chemical equilibrium of four- and five-coordinate species, which has been monitored by UV–vis spectroscopy.

INTRODUCTION

Although both iron¹ and manganese² porphyrin complexes have long been used as the models of cytochrome P-450 and hemoglobins, the reports on manganese(II) porphyrinates are much less as compared to the extensively studied iron(II,III) analogues. The first manganese(II) porphyrin structure [Mn-(TPP)(1-MeIm)]³ was reported by Scheidt and co-workers in 1977.⁴ The authors claimed that manganese(II) derivatives have a distinct preference for five coordination irrespective of the choice of axial ligand and when the $d_{x^2-y^2}$ orbital is populated, as the metal atom is too far out of plane to permit effective interaction with a sixth ligand. Only five-coordinate [Mn(II)(Porph)(L)] are isolated despite attempts to force sixcoordination with large excesses of a variety of ligands.⁵

Cyanide ion (CN⁻) has been widely investigated both as a classic inhibitor and as a ligand for exploring the properties of hemes and hemoproteins.⁶ The strong binding of cyanide to ferric hemoproteins has been long recognized, and cyanide is deeply entrenched as a strong-field ligand.⁷ All of the known cyano iron(III) porphyrinates, either bis(cyano) [Fe^{III}(Porph)- $(CN)_2$] or mixed-ligand [Fe^{III}(Porph)(CN)(L)], are sixcoordinated and low-spin.⁸ Recently, the first (cyano)iron(II) porphyrin complex, five-coordinate [K(222)][Fe^{II}(TPP)-(CN)], was isolated, which exhibited unusual temperaturedependent $S = 0 \rightleftharpoons S = 2$ spin crossover phenomena.⁹ [K(222)][Fe(TPP)(CN)] represents a case in which π backbonding should be maximized and the CN⁻ ligand should unequivocally lead to a LS species.¹⁰ The spin crossover behavior has been investigated using electronic structure methods.¹¹ The first cyano manganese(III) porphyrin complex $[Mn^{III}(TPP)(CN)]$ was reported to be a high-spin derivative.¹

In this Article, we report the synthesis and characterization of the first examples of five-coordinate (cyano)manganese(II) porphyrin derivatives: [K(222)][Mn(TPP)(CN)] (*Cc* and $P2_1/n$), [K(222)][Mn(TTP)(CN)], and [K(222)][Mn(TMP)-(CN)]. The single-crystal structures, UV–vis, FT-IR, and multitemperature EPR spectra in frozen solution and solid states are investigated.

EXPERIMENTAL SECTION

General Information. All experimental operations with Mn(II) complexes, including the reduction of Mn(III) complexes, were carried out using standard Schlenk ware and cannula techniques under an atmosphere of argon unless otherwise noted. Benzene (Sinopharm Chemical Reagent) was distilled over sodium/benzophenone, hexanes (Beijing Chemical Works) over potassium-sodium alloy, and chlorobenzene (Sinopharm Chemical Reagent) over P2O5 under nitrogen. 2,6-Dimethylpyridine and ethanethiol were purified by distilling before use. MnCl₂, dichloromethane, hydrochloric acid, acetone, methanol, DMF, and propionic acid were used as received. KCN was recrystallized and purified by a literature procedure. Krypotofix 222 (ACROS) was purified by vacuum sublimation. [K(222)(CN)] was prepared by the reaction of Krypotofix 222 with KCN (1:1) in THF, which was stirred overnight and evaporated to dryness. The porphyrin ligands H2TPP and H2TTP were prepared according to Adler et al.,¹⁴ and H₂TMP was made with a modified procedure published by Lindsey et al.¹⁵ UV-vis spectra were recorded on a PerkinElmer Lambda 25 UV-vis spectrometer. FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer as Nujol mulls.

Synthesis of [K(222)][Mn^{II}(Porph)(CN)]. Free-base porphyrin (1 g) and MnCl₂ (2 g, 14.7 mmol) were heated under reflux in DMF

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(500 mL) until the TLC showed the absence of free porphyrin red fluorescence.¹⁶ The cooled reaction mixture was poured into a flask containing 500 mL of water. The resulting green precipitate was collected by filtration and washed with 500 mL of H₂O. The solid was dissolved in dichloromethane, then vigorously shaken in 3 M solution of aqueous KOH. The dichloromethane layer was separated from the water layer, and the solvent was evaporated under vacuum. The residue was purified by column chromatography of silica gel with acetone, then eluted with methanol. Rotary evaporation of the solvent yielded a dark green solid, 0.73 g (73%) of [Mn(TPP)(OH)] (UV–vis (CH₂Cl₂): 374.5, 421.5, 472, 532, 578.5, and 616.5 nm), 0.68 g (68%) of [Mn(TTP)(OH)] (UV–vis (CH₂Cl₂): 378.5, 420, 470.5, 534, 582, and 622.5 nm), and 0.6 g (60%) of [Mn(TMP)(OH)] (UV–vis (CH₂Cl₂): 372, 397.5, 479, 534, 589, and 625 nm).

 $[Mn^{II}(Porph)]$ was prepared by reduction of [Mn(Porph)(OH)] (0.03 mmol) with ethanethiol (1 mL) in benzene (10 mL) for 48 h. Vacuum evaporation of the solvent yielded a dark purple solid to which [K(222)(CN)] (12.6 mg, 0.03 mmol) in PhCl was added by cannula. The mixture was stirred overnight. X-ray quality crystals were obtained in 8 mm \times 500 mm sealed glass tubes by liquid diffusion using hexanes as nonsolvent.

[K(222)][Mn(TPP)(CN)] (*Cc* and *P2*₁/*n*). Two polymorphic crystals have been obtained in the preparation of [K(222)][Mn(TPP)(CN)], although the reactions have been conducted in the same manner. IR ν (C–N): 2198 cm⁻¹ (very weak) for [K(222)][Mn(TPP)(CN)] (*Cc*) and 2198 cm⁻¹ (very weak) for [K(222)][Mn(TPP)(CN)] (*P2*₁/*n*). UV–vis (PhCl) λ_{max} : 405, 420, 451, 516, 548, 583, and 626 nm.

[K(222)][Mn(TTP)(CN)]. IR ν (C–N): 2195 cm⁻¹ (very weak). UV–vis (PhCl) λ_{max} : 407, 420, 453, 521, 544, 585, and 627 nm.

[K(222)][Mn(TMP)(CN)]. IR ν (C–N): 2173 cm⁻¹ (very weak). UV–vis (PhCl) λ_{max} : 400, 416, 453, 513, 544, 588, and 628 nm.

X-ray Structure Determinations. Single-crystal experiments for [K(222)][Mn(TPP)(CN)] (Cc, $P2_1/n$) and [K(222)][Mn(TTP)-(CN)] were carried out on a Xcalibur, Eos, Gemini system and [K(222)][Mn(TMP)(CN)] on a Bruker ApexII system, with graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å). The crystalline samples were placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected at 150 or 100 K. The program SADABS¹⁷ was used to apply an absorption correction. The structures were solved by direct methods (SHELXS-97)¹⁸ and refined against F^2 using SHELXL-97.¹ Subsequent difference Fourier syntheses led to the location of all of the remaining non-hydrogen atoms. For the structure refinement, all data were used including negative intensities. All non-hydrogen atoms were refined anisotropically if not remarked otherwise below. Hydrogen atoms were added with the standard SHELXL-97 idealized methods.

[K(222)][Mn(TPP)(CN)] (Cc). A dark green crystal with dimensions of $0.86 \times 0.46 \times 0.25 \text{ mm}^3$ was used for the structure determination. The asymmetric unit contains one porphyrin complex and one potassium cation coordinated with Kryptofix 222.

[K(222)][Mn(TPP)(CN)] ($P2_1/n$). A dark green crystal with dimensions of 0.25 × 0.20 × 0.06 mm³ was used for the structure determination. The asymmetric unit contains one porphyrin complex and one potassium cation coordinated with Kryptofix 222. The C17 atom of the porphyrin phenyl group exhibited unusual thermal motions; thus the atom was restrained by the "ISOR" command.

[K(222)][Mn(TTP)(CN)]·PhCl. A dark green crystal with dimensions of $0.50 \times 0.39 \times 0.30 \text{ mm}^3$ was used for the structure determination. The asymmetric unit contains one porphyrin complex, one potassium cation coordinated with Kryptofix 222, and one chlorobenzene molecule. Three carbon atoms (C35, C41, C47) of Kryptofix 222 exhibited unusual thermal motions; thus the atoms were restrained by the "ISOR" command. Three components of 222 (O3 and C37, O4 and C39, N7 and C41) were restrained by "DELU" to constrain the anisotropic displacement parameters (ADPs).

[K(222)][Mn(TMP)(CN)]·**1.63PhCl.** A dark green crystal with dimensions of $0.34 \times 0.27 \times 0.16 \text{ mm}^3$ was used for the structure determination. The asymmetric unit contains one porphyrin complex,

one potassium cation coordinated with Kryptofix 222, one ordered chlorobenzene molecule, and one disordered chlorobenzene molecule. The disordered chlorobenzene was constrained by means of "DFIX" command, and the occupancy was found to be 0.63.

EPR. X-band continuous wave (cw) EPR measurements were carried out on a Bruker E500 EPR spectrometer at a microwave frequency of 9.45 GHz using a liquid nitrogen cooling system. The EPR spectra were measured at different temperatures between 4 and 100 K with a modulation amplitude 0.3 mT, a modulation frequency of 100 kHz, and a microwave power of 10.02 mW. EPR spectra of [K(222)][Mn(TPP)(CN)] were recorded on a powder sample, which was obtained by grinding a sufficient quantity of crystals, while [K(222)[Mn(TMP)(CN)] was recorded on both solid and solution states and the solution sample was prepared by mixing $[Mn^{II}(TMP)]$ with different equivalents of [K(222)(CN)] in chlorobenzene. The EPR spectra were simulated with the EasySpin package.²⁰

UV–Vis Titration. Aliquots of the benzene solution of [K(222)(CN)] (5.9 × 10⁻³ M) were added to a benzene solution of [MnII(TPP)] (5.0 × 10⁻⁵ M), and the mixture was subjected to UV–vis spectroscopy at 25 °C. The association constant K_a for the complex was derived by the nonlinear curve fitting based on the equations in the Supporting Information.²¹

Hirshfeld Surface Calculations. Hirshfeld surfaces, fingerprint plots, and void volumes of [K(222)][Mn(TPP)(CN)] (*Cc* and *P2*₁/*n*) were calculated using CrystalExplorer (version 3.1) software from the crystal structure coordinates supplied as CIF files.²² The Hirshfeld surface analysis is illustrated in the Supporting Information.²³ Hirshfeld surface was calculated at an isovalue of 0.5 e au⁻³. Void volumes were calculated using an isovalue of 0.002 e au^{-3,24}

RESULTS

The synthesis, UV–vis, IR, molecular structures, and EPR of several five-coordinate (cyano)manganese(II) porphyrinates are reported. The UV–vis spectrum of [Mn(TPP)(CN)] in chlorobenzene solution exhibits Soret bands at 405, 420, 451 nm and Q bands at 516, 548, 583, 626 nm (Figure S1). [Mn(TTP)(CN)] and [Mn(TMP)(CN)] show similar spectra with Soret bands at 407, 420, 453 nm and 401, 416, 453 nm (Figures S2 and S3). FT-IR spectra of these cyano complexes have been measured, and the spectra are found in Figure S4. The very weak C–N stretching bands ($\nu_{\rm CN}$) were observed at 2198, 2195, and 2173 cm⁻¹ for [(K222)][Mn(TPP)(CN)], [K(222)][Mn(TTP)(CN)], and [K(222)][Mn(TMP)(CN)], respectively.

Spectrophotometric titrations of the reaction of [Mn(TPP)] with [K(222)(CN)] were performed in benzene at room temperature, and the spectroscopic results are shown in Figure 1. On the basis of the change values of absorbance, the K_a of [K(222)][Mn^{II}(TPP)(CN)] was estimated to be $3.72(\pm 0.2) \times 10^4 \text{ M}^{-1}$, which is comparable to $1.9(\pm 0.3) \times 10^4 \text{ M}^{-1}$ of the cyano ferriprotoporphyrin IX.²⁵

The molecular structures of [K(222)][Mn(TPP)(CN)] (*Cc* and $P2_1/n$), [K(222)][Mn(TTP)(CN)]·PhCl, and [K(222)]-[Mn(TMP)(CN)]·1.63PhCl have been determined. A brief summary of the crystallographic data is given in Table 1. Two polymorphic forms of [K(222)][Mn(TPP)(CN)] in space groups of *Cc* and $P2_1/n$ have been characterized. Thermal ellipsoid plots of $[Mn(TPP)(CN)]^-$ (*Cc* and $P2_1/n$), $[Mn-(TTP)(CN)]^-$, and $[Mn(TMP)(CN)]^-$ are given in Figure 2. Formal diagrams showing the displacements of atoms (in units of 0.01 Å) from the 24-atom mean plane of the four complexes are given in Figure S5. The diagrams also display the average values for the bond distances and angles. Selected bond distances and angles of five-coordinated (cyano)manganese(II) porphyrinates and related complexes are given in Tables 2 and 3.



Figure 1. UV–vis spectral change (in benzene at 295 K) of 5×10^{-5} M solution of [Mn^{II}(TPP)] upon gradual addition of 0.1–5 equiv of [K(222)(CN)]. The enlarged spectra from 500 to 700 nm are measured in the 10 mm UV cell.

EPR spectra of [K(222)][Mn(TPP)(CN)] and [K(222)]-[Mn(TMP)(CN)] have been measured in solid and solution states at temperatures between 4 and 100 K. Computer simulation have been performed to assist in the analysis of the spectra. Both experimental and simulated spectra are given in Figures 4, 5, S10, and S11. The EPR parameters are summarized in Table 4.

DISCUSSION

Crystal Structures and IR Spectra. Until recently, only two manganese(II) porphyrin structures have been characterized, the low-spin nitrosyl $[Mn(TTP)(NO)]^{26}$ and the highspin [Mn(TPP)(1-MeIm)].⁴ Lately, we reported three fivecoordinate "picket fence" porphyrin complexes [Mn(TpivPP)-(R-Im)] (R-Im = 1-MeIm, 1-EtIm, and 2-MeHIm) and studied the EPR properties in both solution and solid states.²⁷ Here, three cyano Mn(II) porphyrin complexes are reported. The reactions of 1 equiv of $[Mn^{II}(Porph)]$ and [K(222)(CN)] yield the moderately air-stable products. Thermal ellipsoid diagrams of the four $[Mn(Porph)(CN)]^-$ structures are displayed in Figure 2, which shows the views parallel to the porphyrin planes. The top-down diagrams of these complexes will be found in Figures S6–S9. As can be seen, the new structures share some common features, which include near planar porphyrin macrocycles, more or less tilted $Mn-C_{CN}$ axial bonds, and significantly displaced high-spin Mn(II) atoms that induced noticeable porphyrin core doming and stretched $Mn-N_p$ bonds.

Key structural parameters of the four [Mn(Porph)(CN)] complexes are given in Table 2. Also given are the structural parameters of all known cyano Mn(III) and iron(II,III) porphyrin complexes. The Mn(II) atoms show significantly large out-of-plane displacements (Δ_{24} and Δ_4), which are consistent with the high-spin states and long Mn-N_p bonds. Only one cyano Mn(III) porphyrinate [Mn(TPP)(CN)] is high spin.¹² All of the cvano iron(III) porphyrinates, either bis(cyano) [Fe(Porph)(CN)₂] or mixed-ligand [Fe(Porph)-(CN)(L)], are six-coordinate and low spin. In these complexes, the iron(III) atoms rest in the porphyrin planes showing tiny out-of-plane displacements. The two five-coordinate cyano iron(II) complexes exhibit unusual temperature-dependent S = $0 \rightleftharpoons S = 2$ spin-crossover, which possess low-spin state in the temperature range of 2-100 K.9 Therefore, the metal out-ofplane displacements exhibit the sequence: HS Mn(II) > HSMn(III) > LS Fe(II) > LS Fe(III), which follows the same sequence of the metal ion radius.²⁸

The CN⁻ ligand bonds to heme complexes in a linear fashion, just as that of CO. The bending and tilting are key structural features of a (cylindrical) axial ligand; the strong bending sometimes, but not always, accompanies the strong tilting. The tilting angles (τ) of the four new structures are in an unexpectedly wide range of 2.6–11.2° (Table 2). Usually the σ -

Table 1. Complete Crystallographic Details for [K(222)][Mn(Porph)(CN)]

	[K(222)][Mn(TPP)(CN)] (Cc)	$ [K(222)][Mn(TPP)(CN)] (P2_1/n) $	[K(222)][Mn(TTP)(CN)]· PhCl	[K(222)][Mn(TMP)(CN)]· 1.63PhCl
chemical formula	C ₆₃ H ₆₄ MnKN ₇ O ₆	C ₆₃ H ₆₄ MnKN ₇ O ₆	C73H77ClMnKN7O6	C _{84.77} H _{96.15} MnKN ₇ O ₆ Cl _{1.63}
fw (amu)	1109.25	1109.25	1127.91	1461.05
a (Å)	14.1096(6)	13.2466(8)	11.7796(3)	13.2231(6)
b (Å)	20.8624(8)	25.3523(14)	14.8337(4)	24.3062(12)
c (Å)	20.7212(8)	17.9030(10)	20.0496(6)	24.7602(13)
α (deg)	90	90	81.690(2)	90
β (deg)	103.628(4)	109.549(6)	74.862(2)	90
γ (deg)	90	90	86.134(2)	90
V (Å ³)	5930.6(4)	5665.8(6)	3344.68(16)	7958.0(7)
space group	Сс	$P2_{1}/n$	$P\overline{1}$	$P2_{1}2_{1}2_{1}$
Ζ	4	4	2	4
cryst color	dark green	dark green	dark green	dark green
cryst dimensions (mm)	$0.86 \times 0.46 \times 0.25$	$0.25 \times 0.20 \times 0.06$	$0.50 \times 0.39 \times 0.30$	$0.34 \times 0.27 \times 0.16$
temp (K)	150	150	150	100
total data collected	11 644	23 619	40 103	139 376
unique data	7710 ($R_{\rm int} = 0.0324$)	11 091 ($R_{\rm int} = 0.0847$)	13 139 ($R_{\rm int} = 0.0276$)	17 528 ($R_{\rm int} = 0.0362$)
unique obsd data $[I > 2\sigma(I)]$	6732	5455	10 371	16 196
GOF (based on F ²)	1.050	0.894	1.039	1.109
$D_{\rm calcd}$, g cm ⁻³	1.242	1.300	1.269	1.219
μ , mm ⁻¹	0.348	0.365	0.357	0.329
final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0402, wR_2 = 0.0768$	$R_1 = 0.0607, wR_2 = 0.0781$	$R_1 = 0.0592, wR_2 = 0.1535$	$R_1 = 0.0494, wR_2 = 0.1449$
final R indices (all data)	$R_1 = 0.0501, wR_2 = 0.0811$	$R_1 = 0.1407, wR_2 = 0.1017$	$R_1 = 0.0767, wR_2 = 0.1667$	$R_1 = 0.0544, wR_2 = 0.1493$



Figure 2. Thermal ellipsoid plots of $[Mn(Porph)(CN)]^-$ with partial atom labeling scheme. The off-axis tilt of the axial ligand and the Mn– C–N angles are shown. The dashed line is the position of the normal to the porphyrin plane. Thermal ellipsoids are contoured at the 40% probability level. Hydrogen atoms have been omitted for clarity. (a) $[Mn(TPP)(CN)]^-$ (*Cc*). (b) $[Mn(TPP)(CN)]^-$ (*P*2₁/*n*). (c) $[Mn(TTP)(CN)]^-$. (d) $[Mn(TMP)(CN)]^-$.

interaction, which requires donations of lone-pair electrons from a ligand to the d_z^2 orbital of the metal center, is favored by "linear" coordination of the ligands. CN^- is a better σ -donor but a poorer π -acceptor; thus deviations from the linear conformation are more tolerated for the CN^- ligand. As a result, the bonding geometry of the cyanide is governed to a great extent by the environment of the heme center and varies considerably.³⁶ Here, we used the recently developed program of CrystalExplorer to do the Hirshfeld surface analysis,^{22,23,37} which provides the structural comparison by examining interactions of an individual molecule with its nearest neighbor molecules.

The two polymorphic structures $[Mn(TPP)(CN)]^-$ (*Cc* and $P2_1/n$) are picked as examples, and the Hirshfeld surfaces and fingerprint plots are presented in Figure 3. It is seen that the closest intermolecular contacts around the cyano group in [K(222)][Mn(TPP)(CN)] (*Cc*) are three N…H interactions of 2.492, 2.543, and 2.604 Å, from the surrounding porphyrin phenyl groups with a void volume of 1138.60 Å³. This is compared to the structure of [K(222)][Mn(TPP)(CN)] (*P*2₁/*n*), where the two closest N…H contacts, 2.571 and 2.717 Å, are from the $[K(222)]^+$ and phenyl groups with a void volume of 863.92 Å³. All of these distances are smaller than the sum of the van der Waals radii of H (1.20 Å) and N (1.55 Å) atoms,³⁸

and the contacts are illustrated at the bottom panels of Figure 3. The larger void volume in [K(222)][Mn(TPP)(CN)] (Cc) accompanies the shorter contacts, and the close proximity restricts further tilting of the CN ligand. In contrast, [K(222)][Mn(TPP)(CN)] (P2₁/n), with its larger room for the axial ligand, induces a larger tilting angle. These analyses are consistent with the void-volume percentage calculations. The smaller void-volume percentage of [K(222)][Mn(TPP)(CN)] $(P2_1/n)$, 15.25% versus 19.20%, is consistent with its more compact crystal lattice. Furthermore, a considerable number of points beyond 2.8 Å in the 2-D fingerprint plots of [K(222)][Mn(TPP)(CN)] (Cc) (left middle panel of Figure 3) is further evidence of "cavities" in the structure. Thus, the forces such as nonbonded interactions and/or crystal packing play important roles in the geometry of the Mn-C-N moieties.

As given in Table 2, a total of 17 cyano iron(III) porphyrin structures have been reported. For such a large number of structures, the τ angles of the cyanide are in a small range of 1.6–8.6°. For example, the basket-handle porphyrin complex [K(222)][Fe(BH(Bipy)_2P)(CN)_2] has two kinked cyanide ligands bonding to the iron(III) center.³³ The extremely strong hindrance to the axial ligands induces a very large bending Fe–C–N angle of 170.8(5)° (average value of two cyanide ligands as reported), similar to 171.3(4)° in [Mn(TPP)(CN)]⁻ (P2₁/n). However, the strong bending does not lead to the strong tilting, as [Fe(BH(Bipy)_2P)(CN)_2]⁻ shows much less tilting angle than that of [Mn(TPP)(CN)]⁻ (P2₁/n) (5.2° vs 11.2°). This difference led us to inspect the isoelectronic Fe^{III}–C_{CN} and Mn^{II}–C_{CN} bonds: Is the Mn^{II}–C_{CN} bond more flexible to tilt?

Apparently, the significantly out-of-plane high-spin Mn(II) atom is more able to cause a tilted axial bond than the low-spin iron(III) atom, which deeply rests in the porphyrin plane. However, more insights are provided by the vibrational properties of the cyanide ligand, which are available in Table 2. Cyano Mn(II) complexes shows 40–90 cm⁻¹ higher C–N stretches than the Fe(III) analogues. It has been agreed that the σ -donation has the effect of increasing C-N stretching frequency, while the π -back-bonding tends to decrease the value of $\nu_{\rm CN}$. ^{8b,39} Thus, the higher $\nu_{\rm CN}$ of the Mn(II)–C_{CN}. bonds suggests they are more dominated by σ -bonding than the $Fe(III)-C_{CN}$ bonds. This suggestion is in agreement with their wider range of tilting angles (and flexibility). Among the four new complexes, a decreased $\nu_{\rm CN}$ sequence is seen with the increase of electron-donating substituents at the meso-phenyl groups of the porphyrins. The increase of electron-donation of porphyrin substituents will in turn increase the π donation of the Mn(II) atom to the cyanide ligands, which has the effect of decreasing the $\nu_{\rm CN}$. As a consequence, a decreasing $\nu_{\rm CN}$ was observed from $[Mn(TPP)(CN)]^-$ (2198 cm⁻¹) to $[Mn(TTP)^ (CN)^{-}$ (2195 cm⁻¹) and $[Mn(TMP)(CN)]^{-}$ (2173 cm⁻¹).

Table 3 gives the structural parameters of all known fivecoordinate Mn(II) porphyrin complexes. All of the complexes are high spin except [Mn(TTP)(NO)]. The cyanide, imidazole, and chloride, three types of derivatives, are seen. In each type, the complexes show consonant structural parameters. Cyano complexes show the largest metal out-of-plane displacements and the longest $Mn-N_p$ distances, while the chloride complexes show the longest axial distance of the Mn-Cl bonds. It is probably surprising to see that the axial $Mn-C_{CN}$ bond is slightly longer than the $Mn-N_{Im}$ bond, because the cyanide has been known to be a stronger ligand than the

complex	$\Delta_{24}^{\ a,b}$	$\Delta_4^{a,c}$	$(M-N_p)_{av}^a$	M-C _{CN} ^a	$C-N^{a}$	M-C-N ^d	$\tau^{q,e}$	$\nu_{\rm CN}^{f}$	ref ^g
				Manganese(II)					
[K(222)][Mn(TTP)(CN)]	0.83	0.70	2.173(6)	2.210(3)	1.114(4)	177.1(3)	2.6	2195	tw
[K(222)][Mn(TMP)(CN)]	0.81	0.70	2.167(5)	2.245(4)	1.088(6)	174.0(4)	5.7	2173	tw
[K(222)][Mn(TPP)(CN)] (Cc)	0.70	0.63	2.163(9)	2.220(4)	1.036(5)	176.8(4)	8.1	2198	tw
[K(222)][Mn(TPP)(CN)] (P2 ₁ /n)	0.81	0.66	2.176(4)	2.193(4)	1.150(5)	171.3(4)	11.2	2198	tw
				Manganese(III)					
[Mn(TPP)(CN)]	0.25	0.25	2.008(8)	2.166(6)	1.132(6)	172.1(5)	5.8	2120	12
				Iron(II)					
[K(222)][Fe(TPP)(CN)] (LS)	0.23	0.17	1.986(7)	1.8783(10)	1.1662(14)	177.19(10)	6.3	2070	6
[K(222)][Fe(TPP)(CN)] (HS)	0.54	0.45	2.089(8)	2.108(3)	1.122(3)	175.8(2)	7.4	2105	6
[K(222)][Fe(TPP)(CN)] (LS)	0.22	0.16	1.984(8)	1.869(2)	1.152(3)	178.1(2)	3.1	2072	8a
[K(222)][Fe(TPP)(CN)] (HS)	0.50	0.42	2.070(9)	2.068(4)	1.099(4)	176.5(4)	2.8	2106	8a
				Iron(III)					
$[K(18-C-6)][Fe(TPP)(CN)_2]^{hj}$ (block)	0	0	2.002(4), 2.003(10)	1.9808(19), 1.977(2)	1.158(3), 1.154(3)	176.6(2), 176.7(2)	2.5 3.9	2115	29
$[K(18-C-6)][Fe(TPP)(CN)_2]^i$ (needle)	0	0	2.000(9)	1.978(3), 1.988(3)	1.162(4), 1.152(4)	177.0(3), 175.4(3)	6.0 7.5	2114	29
$[K(222)][Fe(TPP)(CN)_2]$	0.02	0.01	1.995(4)	$1.981(6)^{1}$	1.148(3)	$176.4(14)^{j}$	2.8	2114	29
$[K(222)][Fe(TPP)(CN)_2]^h$	0	0	1.998(4)	1.9762(14)	1.151(2)	173.34(13)	7.6	2113	29
$[K((CH_3)_2CO)_2][Fe(TPP)(CN)_2]^h$	0	0	2.000(6)	1.975(2)	1.147(3)	177.8(3)	1.6	2120	30
$[\mathrm{Et_4N}][\mathrm{Fe}(\mathrm{TPP})(\mathrm{CN})_2]^h$	0	0	1.9990(14)	1.978 (6)	1.1555(7)	178.3(15)	2.4		31
$[K(222)][Fe(TTP)(CN)_2]^h$	0	0	2.007(8)	1.985(2)	1.142(3)	174.9(2)	8.6	2110	29
$[\mathrm{K}(222)][\mathrm{Fe}(\mathrm{TMP})(\mathrm{CN})_2]^{h,k}$	0	0	1.9997(10)	1.985(11)	1.154(4)	175.1(3)	5.7	2113	29
$[K(18-C-6)][Fe(TMP)(CN)_2]^{i,k}$	-0.03	0	1.973(5)	1.970(4), 1.986(6)	1.158(1), 1.159(2)	175.3(12), 172.8(14)	3.8 5.2	2111	8b
$[Fe(OEOP)(CN)_2]^h$	0		1.966(9)	1.969(10)	1.128(14)	177.4(11)			32
$[K(222)][Fe(BH(Bipy)_2P)(CN)_2]$	0.02	0.01	1.949(14)	$1.949(4)^{j}$	$1.152(9)^{1}$	$170.8(5)^{j}$	5.2		33
[Fe(TPP)(CN) (Py)]	0.02	0.02	1.977(10)	1.927(3)	1.157(3)	176.4(2)	3.1	2130	8b
[Fe(TPP)(CN) (Py)]	0.03	0.02	1.970(14)	1.908(4)	1.152(4)	176.8(3)	3.2	2130	12
[Fe(OEP)(CN) (Py)]	0.05	0.02	1.980(4)	1.934(4)	1.140	179.1(1)	1.8		34
[Fe(TPP)(CN)(1-MeIm)]	-0.06	-0.02	1.993(3)	1.9179(15)	1.1616(19)	177.18(13)	2.2	2130	8b
[Fe(TMP)(CN)(1-MeIm)]	0.01	0.01	1.982(8)	1.929(3)	1.155(4)	176.2(3)	3.2	2125	8b
[Fe(OEP)(CN)(1-MeIm)]	-0.01	-0.01	1.994(7)	1.927(8)	1.15(1)	175.6(5)	2.6	2115	35
^{<i>a</i>} Values in angstroms. ^{<i>b</i>} Displacement of m. of the four pyrrole nitrogen atoms. The po in cm ⁻¹ . ^{<i>B</i>} tw = this work. ^{<i>h</i>} These structure coordinated with K or H atoms. ^{<i>J</i>} Averase	etal atom fror sitive number es all have cry; e values for th	n the 24-ator s indicate a c stallographic e two cvanic	m mean plane. The posit displacement toward the ally required inversion s de grouns. ^k Average val	ive numbers indicate a dis C-N. ^d Values in degrees. ymmetry. ⁱ Top line is for ⁱ ues for the two or three u	placement toward the C- e The tilt of the M- C_{CN} the simpler cyanide ligan mique porphyrin units.	 -N. ^cDisplacement of man, vector from the normal to ud/porphyrin unit, while th 	ganese atom fr the 24-atom n e bottom line	om the mea nean plane. ⁻ has cyanide	n plane ⁶ Stretch further
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Table 3. Selected Structural Parameters for [Mn^{II}(Porph)(L)]^a

complex	$\Delta_{24}^{\ b}$	$\Delta_4^{\ b}$	$(Mn-N_p)_{av}$	Mn-L	$(Mn-L)_{av}^{c}$	ref ^d
[K(222)][Mn(TPP)(CN)] (Cc)	0.70	0.63	2.163(9)	2.220(4)	2.217(22)	tw
$[K(222)][Mn(TPP)(CN)](P2_1/n)$	0.81	0.66	2.176(4)	2.193(4)		tw
[K(222)][Mn(TTP)(CN)]	0.83	0.70	2.173(6)	2.210(3)		tw
[K(222)][Mn(TMP)(CN)]	0.81	0.70	2.167(5)	2.245(4)		tw
[Mn(TPP)(1-MeIm)]	0.56	0.51	2.128(7)	2.192(2)	2.177(11)	4
[Mn(TpivPP)(1-MeIm)]	0.56	0.50	2.1285(6)	2.168(5)		27
[Mn(TpivPP)(1-EtIm)]	0.54	0.49	2.122(3)	2.17(7)		27
[Mn(TpivPP)(2-MeHIm)]	0.60	0.54	2.129(3)	2.177(9)		27
[K(222)][Mn(TPP)Cl]	0.74	0.64	2.160(10)	2.364(2)	2.367(5)	40
[K(222)][Mn(TpivPP)Cl]	0.70	0.63	2.152(4)	2.3704(6)		41
[Mn(TTP)(NO)](LS)	0.40		2.004(4)	1.641(2)		26

^aValues in angstroms. ^bDisplacement of manganese atom from the 24-atom mean plane (Δ_{24}) or the mean plane of the four pyrrole nitrogen atoms (Δ_4). The positive values are toward the axial ligand. ^cAveraged values of Mn–L distances. ^dtw = this work.

Table 4. EPR Parameters of High-Spin Five-Coordinate Manganese(II) Porphyrin Complexes

complex	g_1	g_2	g_3	g_4	<i>g</i> ₅	T^{a}	phase	$D^{\boldsymbol{b}}$	E ^b	λ^{c}	ref ^d
$[K(222)][Mn(TPP)(CN)]^e$	5.95	2.00				4	powder	0.53	0.0026	5	tw
	5.95	2.00				20	powder	0.53	0.0026	5	tw
	5.95	2.00				50	powder	0.53	0.0026	5	tw
	5.95	2.00				100	powder	0.53	0.0026	5	tw
$[K(222)][Mn(TMP)(CN)]^e$	5.95	2.00				90	powder	0.53	0.0026	5	tw
$[K(222)][Mn(TMP)(CN)]^{e,f}$	5.95	2.00				90	solution	0.67			tw
$[Mn(TMP)]^{e,f}$	5.95	2.00				90	solution	0			tw
$[Mn(TPP)]^g$		2.0				50	powder	0.79			50
[Mn(TpivPP)(1-MeIm)]	5.94	1.98	1.24	0.78	0.55	90	powder	0.68	0.0034	5	41
[Mn(TpivPP)(2-MeHIm)]	5.95	2.00	1.23	0.77	0.54	90	powder	0.69	0.0035	5	41
	5.97	1.99	1.24	0.77	0.55	90	solution	0.67	0.0034	5	41
[Mn(TPP)(Py)]	5.96	2.0				77	solution	>0.3			51
Mn-CCP ^h	5.9	2.0	1.21	0.77		77	solution	0.56		~ 20	52
Mn-Hb ^h	5.9	2.0				77	solution	0.54		10	52
Mn-HRP ^h	5.9	2.0				77	solution	0.5		<2	52
Mn-Mb ^h	5.9	2.0				77	solution	0.56		<5	52
Mn(II)·S		2.0				2	solution	~0.03			53
Mn(II)·Pf		2.0				2	solution	~0.03			53
Mn(II)·PO ₄		2.0				2	solution	~0.03			53
$E \cdot Mn(II)$		2.0				2	solution	0.105	0.020		53
E·Mn(II)·PO ₄		2.0				2	solution	0.105	0.020		53
E·Mn(II)·Pf		2.0				2	solution	0.090	0.003		53
E·Mn(II)·S		2.0				2	solution	0.235	0.022		53

^{*a*}Values in K. ^{*b*}Values in cm⁻¹. ^{*c*}Values in ×10⁻³. ^{*d*}tw = this work. ^{*c*}D, E were estimated from EasySpin simulation. ^{*f*}The computer simulations are given in Figure S11. ^{*g*}ZFS was determined by inelastic neutron scattering (INS). ^{*h*}D was estimated from positions of X- and K-band transitions at 77 K; λ was estimated from the number and line shape of hyperfine lines in the X-band transitions at $g_{\perp} = 5.9$.

imidazoles. This has aroused our interest to study the complexes by means of EPR, which may give new insights into this issue.

EPR Spectroscopy. EPR measurements have been performed on [K(222)][Mn(TPP)(CN)] (powder) and [K(222)][Mn(TMP)(CN)] (powder and solution) at multiple temperatures between 4 and 100 K. The powder spectra of [K(222)][Mn(TPP)(CN)] and [K(222)][Mn(TMP)(CN)] and the simulations are given in Figure 4. Two features are noted on the experimental spectra. The characteristic signals at $g_{\perp} \approx 5.9$ and $g_{\parallel} \approx 2.0$ are typical of a high-spin (S = 5/2) d⁵ system, for example, high-spin Fe(III) porphyrin complexes,⁴² and suggest the strong tetragonal field and transitions within the lowest lying Kramers doublet $(|\pm 1/2\rangle)$.⁴³ The spectra also appear highly complicated and spread over the full field range of the electromagnet (0-1.5 T). This is evidence for the zero-

field splitting (D) being comparable to, or larger than, $h\nu$ at this frequency.⁴⁴ The manganese(II) ion has the electron configuration of high-spin 3d⁵; in general, there are six spin levels $(M_{\rm S} = \pm 5/2, \pm 3/2, \pm 1/2)$ between which a maximum of five allowed transitions are possible according to the selection rule $\Delta M_{\rm S} = \pm 1$. When the magnitude of *D* is comparable to, or larger than, the energy of the microwave quantum $(h\nu)$, the magnetic $M_{\rm S}$ levels are significantly mixed and $M_{\rm S}$ is not a strictly good quantum number.45 In such instances, besides the usual Kramers doublet transitions, the interdoublet transitions also contribute significantly to resonances in the magnetic field range.^{44,46} Therefore, the spectra are complicated by resonances from multiple overlapping transitions and offprinciple-axis signals (looping transition).⁴⁷ Temperaturedependent measurements from 4 to 100 K have also been performed on the powder [K(222)][Mn(TPP)(CN)], and the



Figure 3. Hirshfeld surface (top-down view, the top panels) of [K(222)][Mn(TPP)(CN)] (*Cc*, left and $P2_1/n$, right) showing normalized close distance of the promolecule, 2D fingerprint plots (the middle panels), and the distances of the N···H contacts (the bottom panels) for the two structures. Highlighted regions on the Hirshfeld surface indicate the intermolecular contacts (N···H) around the cyan group (yellow for H atoms of the phenyl to N_{CN} and black for H atom of $[K(222)]^+$ to N_{CN}).



Figure 4. X-band EPR spectra of powder [K(222)][Mn(TPP)(CN)](a) and [K(222)][Mn(TMP)(CN)] (b) at 90 K (black lines) and their simulations (red lines). EPR simulation conditions: D = 0.53 cm⁻¹, E = 0.0026 cm⁻¹.

spectra are given in Figure S10. The very similar spectra suggest a stable molecular structure in the temperature range.

Computer simulations on the experimental spectra have been performed to give the spin Hamiltonian parameters. The resulting *D*, *E*, and the ratio of $E/D(\lambda)$ are given in Table 4. Also given are the parameters of all known manganese(II) heme complexes. It is seen the two cyano complexes ([K(222)][Mn(TPP)(CN)] and [K(222)][Mn(TMP)(CN)]) show consonant *D* and *E* values (D = 0.53, E = 0.0026 cm⁻¹), both of which are smaller than those of the imidazole derivatives [Mn(TpivPP)(1-MeIm)] (D = 0.68, E = 0.0034cm⁻¹) and [Mn(TpivPP)(2-MeHIm)] (D = 0.69, E = 0.0035cm⁻¹). It has been shown that *D* is inversely proportional to the energy difference between the ground and the excited states.⁴⁸ For such a case of 5-coordinate square pyramidal, high-spin d⁵ complex, the smaller *D* of the cyanide suggests its stronger field than the imidazole ligand. In an elegant research of high-spin iron(III) porphyrin halides, the trend of the increased *D* was reported from ligand = F, Cl, Br to I.⁴⁹

Now we consider the EPR spectra in the glassy solution state. Four-coordinate [Mn(TMP)] and the mixture of [Mn(TMP)] with equivalents of [K(222)(CN)] in chlorobenzene have been measured at 90 K, and the spectra are given in Figure 5. The



Figure 5. X-band EPR spectra of $[Mn^{II}(TMP)]$ with different equivalents of [K(222)(CN)] in chlorobenzene at 90 K. (a) $[Mn^{II}(TMP)]$ only. (b) 0.5 equiv of [K(222)(CN)]. (c) 1 equiv of [K(222)(CN)]. (d) 3 equiv of [K(222)(CN)]. (e) [K(222)(CN)] saturated.

sample of four-coordinate [Mn(TMP)], without any addition of cyanide ligand, shows a distinct resonance at g = 2.0 (Figure 5a). This is an idealized case of pure axial distortion, D = 0. Each transition satisfies the selection rule $\Delta M_{\rm S} = \pm 1$, and the levels are equally separated at all values of H_0 .⁵⁴ Upon the addition of [K(222)(CN)], the resonance at 5.95 increases gradually, suggesting the increase of five-coordinate species $[Mn(TMP)(CN)]^{-}$ (Figure 5b-e). Hyperfine splitting from the Mn nucleus (I = 5/2) also emerges gradually at both positions of 5.9 and 2.0. The much stronger resonance at 2.0 from the beginning to the last measurement where the solution was saturated with [K(222)(CN)] (Figure 5e) suggests the existence of four-coordinate [Mn(TMP)] because of the chemical equilibrium. This equilibrium has been monitored by the UV-vis spectra of the [Mn(TPP)] solution, which was titrated by [K(222)(CN)], and the resulting spectra are available in Figure 1. Hence, two Mn(II) nuclei, four- and five-coordinate, with different ZFS parameters (D = 0 and 0.67 cm⁻¹) are combined in the computer simulations, and the resulting data are given in Table 4 and Figure S11. Such apparent coexistence of four- and five-coordinate species is contrasted to the imidazole derivatives where the four-coordinate species is undetectable by the EPR spectra of [Mn(TpivPP)(2-MeHIm)] (CH₂Cl₂ solution).²⁷

CONCLUSIONS

Three, five-coordinate cyano manganese(II) porphyrinates have been investigated by single-crystal X-ray, FT-IR, UV–vis, and multitemperature EPR spectroscopies, all of which are consistent with the high-spin state of the metal centers. Although the axial Mn– $C_{\rm CN}$ bonds appear flexible and weak for the unexpectedly wide tilting angles and relatively longer bond distances, the ZFS parameters presented by the solid-state EPR investigations are consistent with the stronger field of the cyanide. The strong coexistence of four- and five-coordinate species even in saturated solutions is revealed by EPR and UV–vis experiments. The research sheds new light on the nature of the cyanide ligand.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00173.

UV-vis and FT-IR spectra (Figures S1-S4), formal diagrams of the porphyrin cores (Figure S5), figures with ORTEP diagrams (Figures S6-S9), EPR spectra of [K(222)][Mn(TPP)(CN)] for crystalline powder at different temperature (Figure S10), EPR spectra of [Mn(TMP)] with different equivalents of [K(222)(CN)] at 90 K and their simulations (Figure S11), Hirshfeld surface (down-top and edge-on) of [K(222)][Mn(TPP)(CN)] (*Cc* and $P2_1/n$) (Figure S12), equation for association constants K_a , and Hirshfeld surface analysis PDF)

X-ray data for compound [K(222)][Mn(TMP)(CN)]-1.63PhCl (CIF)

X-ray data for compound [K(222)][Mn(TPP)(CN)] (Cc) (CIF)

X-ray data for compound [K(222)][Mn(TPP)(CN)](P2₁/n) (CIF)

X-ray data for compound [K(222)][Mn(TTP)(CN)]· PhCl (CIF)

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Notes

The authors declare no competing financial interest.

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(3) Abbreviations: Porph, generalized porphyrin dianion; TPP, mesotetraphenylporphyrin dianion; TTP, meso-tetratolylporphyrin dianion; TMP, meso-tetramesitylporphyrin dianion; TpivPP, $\alpha, \alpha, \alpha, \alpha$ -tetrakis(opivalamidophenyl)porphyrin dianion: OEOP, octaethyloxoporphyrin dianion; BH(Bipy)₂P, bis(6,6'-diphenylbipyridine) basket-handle porphyrin dianion; OEP, 2,3,7,8,12,13,17,18-octaethylporphyrin dianion; 1-MeIm, 1-methylimidazole; 1-EtIm, 1-ethylimidazole; 2-MeHIm, 2-methylimidazole; Py, pyridine; 18-C-6, 1,4,7,10,13,16hexaoxacyclooctadecane; 222 or Krypotofix 222, 4,7,13,16,21,24hexaoxo-1,10-diazabicyclo [8.8.8] hexacosane; Nn, porphyrinato nitrogen; N_{Im}, nitrogen of imidazole ring; C_{CN}, carbon of cyanide; ZFS, zero field splitting; PhCl, chlorobenzene; DMF, N,N-dimethylformamide; THF, tetrahydrofuran; DCM, dichloromethane; UV-vis, ultraviolet-visible; TLC, thin layer chromatography; EPR, electron paramagnetic resonance; CCP, cytochrome c peroxidase; Hb, hemoglobin; HRP, horseradish peroxidase; Mb, myoglobin; Mn(II). X, is frozen aqueous $MnCl_2$ solutions, where X = S (fosfomycin), Pf (phosphonoformate), PO₄ (in phosphate buffer); E·Mn(II)·X, without indication of the enzymes' origin, is genomically encoded FosA (PA1129) from P. aeruginosa, where X = S, Pf, PO₄.

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 $F_c || / \sum |F_o|$ and $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^4]\}^{1/2}$. The conventional *R*-factors R_1 are based on *F*, with *F* set to zero for negative F^2 . The criterion of $F^2 > 2\sigma(F^2)$ was used only for calculating R_1 . *R*-factors based on $F^2(wR_2)$ are statistically about twice as large as those based on *F*, and *R*-factors based on all data will be even larger. (20) EasySpin is a numerical EPR toolbox for MATLAB available at http://www.esr.ethz.ch (accessed Jan 2014).

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