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Is Cyanide Really a Strong-Field Ligand?**

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chromium · crystal-field theory · cyanide · iron · spin states

Dedicated to Professor Michinori Oki

Spin states of transition-metal complexes are controlled by the number and nature of the ligands. In particular, first-row metal ions, such as Cr^{n+}, Mn^{n+}, Fe^{n+}, and Co^{n+}, adopt a variety of electronic structures, including high-spin, low-spin, and in some cases intermediate-spin states.[1] Furthermore, each spin state could have different electron configurations, as exemplified most explicitly in low-spin iron(III) porphyrins; they adopt either $(d_{xy})^2(d_{xz},d_{yz})^3$ or $(d_{xz},d_{yz})^4(d_{xy})^1$ configurations.[2] In octahedral complexes, strong-field ligands increase the magnitude of ligand field splitting (Δ_o) to the point that is larger than the electron pairing energy (PE). Consequently, they form low-spin complexes. In contrast, ligands for the case $\Delta_o < PE$ are known as weak-field ligands, and form high-spin complexes. Research has been carried out to determine the ligand field strengths. Among these studies, the spectrochemical series, which was developed by Tsuchida before the advent of crystal field theory, is most useful (Scheme 1).[3] It

$I^- < Br^- < S^{2-} < SCN^-$ (S-bonded) $< Cl^- < N_3^-, F^- < OH^- < O_2 < H_2O < NCS^-$ (N-bonded) $<$ py $< NH_3 <$ bpy $< NO_2^-$ (N-bonded) $< CH_3^- < CN^- <$ CO

Scheme 1. The spectrochemical series developed by Tsuchida.

identifies cyanide and carbon monoxide as two of the best strong-field ligands, which is understandable, as these ligands behave not only as strong σ donors but also as strong π acceptors.

In fact, the homoleptic cyano complexes $[M(CN)_6]^{n-}$ ($n = 2$–4) and $[M^{II}(CN)_5]^{3-}$ (M = Co, Ni) are known to adopt a low-spin ground state.[4] Thus cyanide and carbon monoxide have been deeply entrenched as being strong-field ligands.

In 2005, Miller et al. found that the low-spin ($S = 1$) tetraanionic $[Cr^{II}(CN)_6]^{4-}$ complex is structurally unstable if non-coordinating cations such as NEt_4^+ and less-polar acetonitrile instead of water are used in the synthesis. Instead, they obtained the high-spin ($S = 2$) trianionic $[Cr^{II}(CN)_5]^{3-}$ complex, which challenges the common notion that cyanide is a strong-field ligand and should always adopt a low-spin ground state.[5] The asymmetric unit cell of the crystal contains four $[Cr^{II}(CN)_5]^{3-}$ units. Each chromium(II) center is five-coordinate, with both square-pyramidal and distorted trigonal bipyramidal structures. The magnetic susceptibility of $[Cr^{II}(CN)_5]^{3-}$ was measured from 5 to 300 K. The complex shows an effective magnetic moment of $4.90\mu_B$ at room temperature, and which is invariant over the temperature range examined. This value is in excellent agreement with the expected spin-only value of $4.90\mu_B$ for $S = 2$ high-spin chromium(II).

A detailed computational study of $[Cr^{II}(CN)_5]^{3-}$ and $[Cr^{II}(CN)_6]^{4-}$, using both qualitative ligand field theory (LFT) and quantitative density functional theory (DFT), has been carried out by Deeth.[6] The aim of this study was to reveal why $[Cr^{II}(CN)_5]^{3-}$ displays a high-spin state despite the presence of a strong-field ligand, and why the change in medium from water to acetonitrile causes the reaction to stop at coordination number five. The calculations suggest that the ligand field splitting is larger than the spin-paring energy for octahedral $[Cr^{II}(CN)_6]^{4-}$, whereas the reverse is the case in $[Cr^{II}(CN)_5]^{3-}$. Furthermore, a strong repulsive interaction occurs between trianionic $[Cr^{II}(CN)_5]^{3-}$ and cyanide in less polar acetonitrile solution, thus preventing the formation of tetraanionic $[Cr^{II}(CN)_6]^{4-}$. Therefore, the calculation shows that the lack of solvation is the reason for high-spin state in $[Cr^{II}(CN)_5]^{3-}$, and that cyanide behaves as a strong σ donor and π acceptor in both complexes. Lord and Baik have also used DFT coupled to a continuum solvation model, and have examined the relative stability of high-spin and low-spin $[Cr^{II}(CN)_5]^{3-}$.[7] They also concluded that cyanide behaves as a strong-field ligand electronically because the orbital interaction is energetically more favorable in the low-spin than in the corresponding high-spin configuration. The Coulombic repulsion between the anionic cyanide ligands in $[Cr^{II}(CN)_5]^{3-}$, however, dominates the overall energetics and ultimately gives preference to the high-spin complex, in which the ligand–ligand separation is larger owing to the longer Cr–CN bonds. Lord and Baik emphasize the importance of ligand–ligand electrostatic interactions along with the classical ligand-field arguments based on M–L orbital interaction for a quantitative understanding of spin-state energetic ordering. Prior to this work, some calculations on the ligand field strengths of strong-field ligands had been reported.[8,9]

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Gray et al. compared the field strengths of the ligands CO, CNH, and CN^- in a wide variety of $[ML_6]^{n\pm}$ complexes by means of DFT calculations. They confirmed that ligand field splitting falls in the order $CO > CNH > CN^-$. The smaller ligand field splitting in CN^- relative to CO is ascribed to the decrease in metal-to-ligand π* backbonding owing to the net negative charge present on cyanide ligands.[9]

More recently, Scheidt et al. reported a complex containing five-coordinate iron that strongly demonstrates the weaker-field nature of cyanide.[10] The complex in question is [K(222)][Fe(tpp)(CN)], which is the first monocyano complex of an iron(II) porphyrin.[11] Structural analysis at 100 K reveals that the average Fe–N_p and Fe–C bond lengths are 1.986(7) and 1.8783(10) Å, respectively, which are consistent with a low-spin state. However, the Mössbauer parameters show a large temperature dependence. As shown in Figure 1, the quadrupole splitting value decreases from

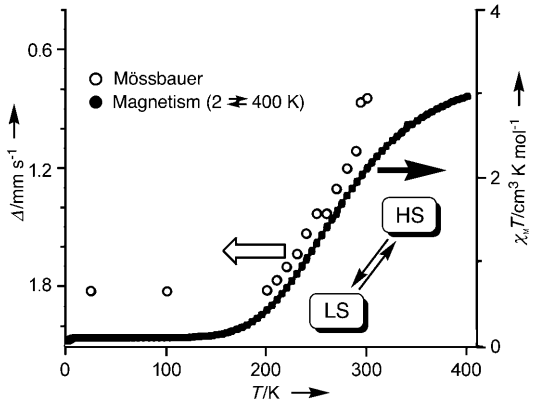

Figure 1. $\chi_m T$ versus T plots for [K(222)][Fe(tpp)(CN)] at an applied field of 2 T. The Mössbauer quadrupole splitting values are also presented for comparison. Adapted from Ref. [10].

1.827 mm s^{-1} at 25 K to 0.85 mm s^{-1} at 300 K. This phenomenon can be best interpreted as a thermally induced spin crossover from low-spin ($S=0$) to high-spin ($S=2$) state, the interconversion of which is rapid on the Mössbauer timescale (10^{-8} s).[1a,12] The temperature dependence of the magnetic susceptibility given in Figure 1 provides direct evidence for the spin crossover. The $\chi_M T$ value reaches 2.96 cm^3 K mol^{-1} (4.87 μ_B) at 400 K, which is close to that expected for $S=2$. However, the spin transition is not complete even at 400 K, as the plots in Figure 1 do not exhibit any significant plateaus. Additional evidence for the spin crossover comes from temperature-dependent IR spectra, which have the advantage of a shorter timescale (10^{-13} s), and thus can detect both spin isomers.[13] Two bands, observed at 2070 and 2105 cm^{-1} at 296 K, are assigned to the C–N stretching band of the low-spin and high-spin complex, respectively. The intensity of the former band increases whereas that of the latter decreases as the temperature is lowered, which is consistent with the magnetic data. The temperature-dependent structural change has also been examined. Both the Fe–C distance and the displacement of the iron atom from the mean N_4 plane increase, by 0.23 and 0.28 Å, respectively, as the temperature is raised from 100 to 400 K, which is in complete agreement with the spin crossover from $S=0$ to $S=2$.

The experimental data given above clearly indicate that $[Fe(tpp)(CN)]^-$ adopts the high-spin state at ambient temperature, which strongly suggests a weaker-field nature of cyanide. The validity of using five-coordinate iron(II) porphyrins, $[Fe^{II}(tpp)L]$, to determine the order of ligand field strengths may be debatable. However, some of the $[Fe^{II}(tpp)L]$ complexes certainly exhibit the low-spin state if L is a ligand such as CO, NO, or NO_2^- with strong σ-donating and π-accepting ability.[14] It should rather be emphasized that $[Fe^{II}(tpp)L]$ serves as an idealized framework to evaluate the ligand field strengths of strong-field ligands mentioned above, as the coulombic repulsion among intramolecular ligands observed in $[Cr(CN)_5]^{3-}$ should be minimized. In fact, Reed et al. ranked the ligand field strength of a large number of weakly binding anions X^-, such as SbF_5^-, ClO_4^-, $CF_3SO_3^-$, on the basis of the pyrrole hydrogen chemical shifts in $[Fe^{III}(tpp)X]$ and called the hierarchy a magnetochemical series.[15] Ranking is possible because the pure intermediate-spin complex exhibits the pyrrole hydrogen signal at about $\delta = -60$ ppm, whereas the pure high-spin complex exhibits it at circa $\delta = +80$ ppm, as shown in Figure 2. The field strengths

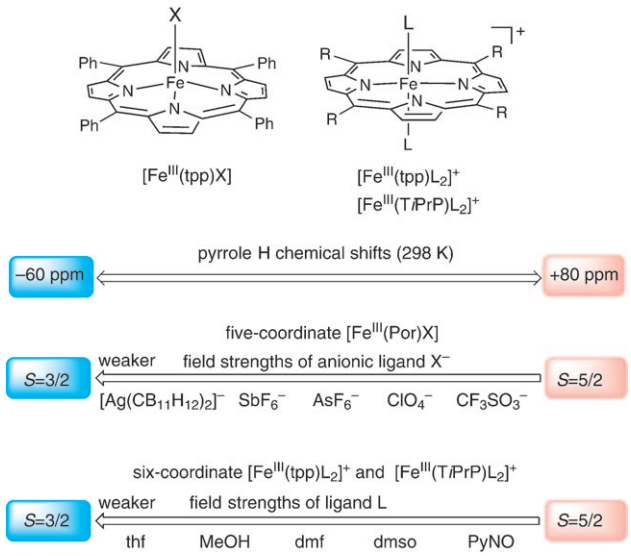

Figure 2. Field strengths of weak anionic ligands X^- in $[Fe^{III}(tpp)X]$ and weak oxygen-donor ligands L in $[Fe^{III}(tpp)L_2]^+$ and $[Fe^{III}(TiPrP)L_2]^+$ ranked on the basis of the pyrrole hydrogen chemical shifts.

of weak neutral oxygen-donor ligands, such as pyridine *N*-oxide, DMSO, and THF, which are otherwise difficult to determine, are ranked similarly on the basis of the pyrrole hydrogen chemical shifts of six-coordinate iron(III) porphyrin complexes such as $[Fe^{III}(tpp)L_2]^+$ and $[Fe(TiPrP)L_2]^+$.[16] Thus, it is important to reevaluate the rank of biologically important strong-field ligands, such as CO, NO, NO_2^-, and CN^-, on the basis of the spin state of a series of $[Fe^{II}(porphyrin)L]$ complexes.

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[11] Abbreviations: tpp = *meso*-tetraphenylporphinate, T*i*PrP = *meso*-tetraisopropylporphinate, K(222) = kryptofix 222.

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