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The 3-(3′-pyridyl)sydnone complex of pentacyanoferrate(II)

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Abstract

The 3-(3′-pyridyl)sydnone (3-PySd) complex of pentacyanoferrate(II) was prepared and characterized both in aqueous solution and in the isolated state. A comparison of ^{1}H NMR results between the free and the coordinated ligand indicates that the metal center is coordinated to the ligand through the pyridine nitrogen atom. A metal to ligand charge transfer band was observed at $\lambda_{max}=410$ nm and $\epsilon_{max}=3.20\times10^3$ M^{-1} cm^{-1}. The rate constants of formation and dissociation of the complex were measured; the k_f and k_d values at $\mu=0.10$ M(LiClO$_4$), pH=5 and $T=25$ °C are 5.62×10^2 M^{-1} s^{-1} and 3.23×10^{-3} s^{-1}, respectively. A cyclic voltammetric study of the complex has shown that the Fe^{II}–Fe^{III} oxidation is a reversible one-electron process with $E_{1/2}=0.54$ V versus NHE. The strong electron withdrawing power of the sydnone is demonstrated by both the spectral and the electrochemical properties of the title complex in comparison with those of the pyridine and 3-substituted pyridine complexes. This result is consistent with the assignment of the sydnones to the family of non-benzenoid aromatic compounds.

Introduction

The chemistry of sydnone compounds has been intensively studied since the initial report of the synthesis of 3-phenylsydnone [1, 2]. Interest in this class of compounds derives in part from their significant biological activity and pharmaceutical properties. The biological application of sydnone compounds has been reviewed in detail [3]. Inspection of the electronic arrangement of sydnone itself demonstrates that it is a non-benzenoid aromatic compound with a unique mesoionic character stabilized by the delocalization of six π-electrons within the ring [2]. Although significant effort has been devoted to the investigation of the aromaticity of the sydnones and their multiple binding sites available for metal coordination, no transition metal complex of sydnone or its derivatives has been reported.

The $Fe(CN)_5^{3-}$ moiety features a spin-paired, d^6 electronic configuration with filled orbitals of the appropriate symmetry for the interaction with low-lying unoccupied ligand π^* orbitals. Pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles have been prepared previously [4]; all exhibit interesting physical and spectral properties including intense metal-to-ligand charge transfer transitions ($\epsilon\sim10^3$ M^{-1} cm^{-1}) in the visible region. In view of our longstanding interest in the $Fe(CN)_5L^{2-/3-}$ complexes [5–8], we have undertaken studies on the complex $Fe(CN)_5(PySd)^{3-}$ (PySd = 3-(3′-pyridyl)sydnone). Our data demonstrate that in this complex the metal binds to the ligand through the pyridine nitrogen atom. Our interest is focused on the substituent effect of the sydnone ligand on the properties of complexes of this type. For comparative purposes, a series of $Fe(CN)_5(3\text{-Py-X})^{3-}$ (X = CH$_3$, Ph, NH$_2$, Cl, OH, CHO, CONH$_2$) complexes was prepared and characterized as well. Our results support the earlier assertion that the sydnone ring contains a strong π-electronic structure.

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Experimental

Materials

N-Methylpyrazinium iodide (MPzI) was prepared by the methylation of pyrazine [9]. 3-(3′-Pyridyl)sydnone was prepared according to the literature method [10, 11]. The crystal structure of this ligand has been determined [12]. Solutions of pentacyanoferrate(II) complexes were prepared by dissolving $Na_3Fe(CN)_5NH_3 \cdot 3H_2O$ [13, 14] in solutions containing a large excess of the ligands. The $Fe(CN)_5(PySd)^{3-}$ complex was isolated as a solid: 0.2 g $Na_3Fe(CN)_5NH_3 \cdot 3H_2O$ was added to a 10 ml predeaerated solution containing 0.16 g 3-(3′-pyridyl)sydnone. Nitrogen was bubbled through the resulting solution for 1 h in the absence of light. The resulting solution was cooled in ice and then filtered. Alcohol saturated with NaI (2 g) was added dropwise with constant stirring to the filtrate until a permanent turbidity was observed (~20 ml). After the solution was cooled in an ice bath for 2 h, the orange precipitate was filtered, washed with ethanol and ether, and dried in a vacuum desiccator. *Anal.* Calc. for $Na_3Fe(CN)_5C_7H_5N_3O_2 \cdot 4H_2O$: C, 29.4; H, 2.67; N, 22.9. Found: C, 29.4; H, 2.72; N, 23.0%. The formation of the Fe(II) complex was further demonstrated by the observation in the IR spectra of ν(CN) at 2045 cm^{-1} [15] and ν(CO) at 1780 cm^{-1}.

All solutions were prepared with deionized houseline distilled water which was further purified by passing it through an Osmonics Aris water purification system. The pK_a of the 3-(3′-pyridyl)sydnone was determined potentiometrically by titration of 50 ml containing 0.500 mmol sydnone solution with standardized 0.010 N HNO_3 [16]. The value was found to be 1.83.

Spectra

The ^1H NMR spectra were obtained on a Bruker Aspect-3000 spectrophotometer operating at a frequency of 300 MHz at ambient probe temperature. D_2O was used as solvent for both free and coordinated 3-(3′-pyridyl)sydnone with tetramethylsilane (TMS) as the internal standard. All chemical shifts are reported in δ units. The IR spectra were obtained from KBr pellets on a Jasco IR-100 spectrophotometer. The UV–Vis spectra were measured using a standard 1-cm quartz cell on a Hitachi U-2000 spectrophotometer.

Kinetic measurements

The rates of formation of the $Fe(CN)_5L^{3-}$ complexes were measured by mixing the freshly prepared $Fe(CN)_5OH_2^{3-}$ [6] with excess ligand in a Photal RA-401 stopped-flow instrument (Union Giken) interfaced with a NEC 9801 VX microcomputer for data treatment. The measurements were performed by following the absorbance increase at the band maxima of the complexes. The kinetic data for the dissociation of the complexes were measured by using MPz^+ as scavenger and following the formation of the $Fe(CN)_5(MPz)^{2-}$ complex at its maximum wavelength of absorption ($\lambda = 655$ nm) [4]. The measurements were carried out on a Hitachi U-2000 spectrophotometer. The pseudo-first-order rate constants were obtained from the slopes of the linear least-squares fits of $\ln(A_\infty - A_t)$ versus time plots. Temperatures of the experiments were controlled by a Hotech 631-D temperature bath.

Electrochemistry

Reduction potentials of the complexes were measured at room temperature on a Princeton Applied Research (PAR) cyclic voltammetry set up as described before [6]. Reversible behavior was found in all cases by an observation of peak-to-peak separation of 60–80 mV.

Results

^1H NMR spectra

The δ values for the ^1H NMR spectra of both the free and the coordinated 3-(3′-pyridyl)sydnone are tabulated in Table 1. As will be discussed in detail later, the four multiplets of the free ligand with relative intensities 1:1:1:1 appearing at δ 8.84, 8.15, 7.57 and 8.65 ppm can be assigned to protons on the pyridine ring at the C2, C4, C5 and C6 positions (see Fig. 3), respectively; the singlet at δ 7.28 ppm corresponds to the proton on C4′ of the sydnone ring. In the spectrum of the complex, a downfield shift of the hydrogens at the α positions and an upfield shift of the hydrogens at the β and γ positions with respect to the pyridine nitrogen were observed. The chemical shift of the sydnone proton is not significantly affected. Figure 1 shows the ^1H NMR spectra of aqueous solutions of both the free and complexed 3-(3′-pyridyl)sydnone ligand. The solution of the complex was prepared in D_2O at ~0.01 M by mixing the $Na_3Fe(CN)_5NH_3 \cdot 3H_2O$ and the ligand in a 1:1 molar ratio.

TABLE 1. ^1H NMR spectra of the $Fe(CN)_5L^{3-}$ (L = 3-(3′-pyridyl)sydnone) complex

Position	δ[a] (ppm)		$\Delta\delta$
	L	$Fe(CN)_5L^{3-}$	
H2	8.84	9.23	+0.39
H4	8.15	7.97	−0.18
H5	7.57	7.29	−0.28
H6	8.65	9.06	+0.41
H4′	7.28	7.35	−0.07

[a] TMS as internal standard.

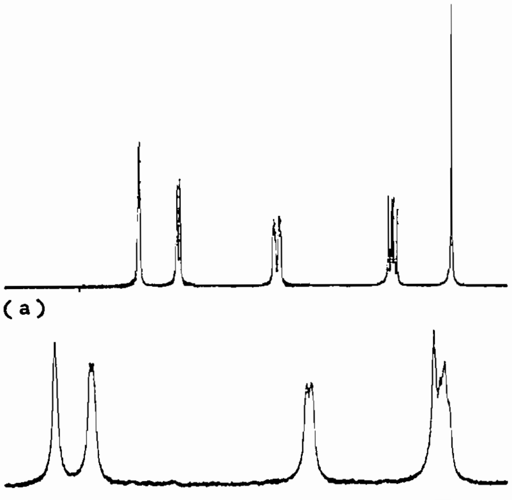

Fig. 1. ^{1}H NMR spectra of 3-(3′-pyridyl)sydnone and its pentacyanoferrate(II) complex: (a) free ligand; (b) $Fe(CN)_5(PySd)^{3-}$ complex.

TABLE 2. Absorption spectra of $Fe(CN)_5(3\text{-}PyX)^{3-}$

X	λ_{max} (nm) (10^3 ϵ_{max})	σ_m[a]	Reference
Sydnone	410 (3.20)	3.38	this work
H	362 (3.72)	0	4
CH_3	361 (3.65)	−0.31	this work
Ph	363 (4.45)	0.41	this work
NH_2	362 (4.42)	−0.82	6
Cl	387 (3.93)	2.37	this work
OH	367 (3.72)	0.11	this work
CHO	369sh (2.82)	1.51	this work
	372		17
$CoNH_2$	398 (3.29)	1.86	this work
CN	415 (3.29)	3.82	18

[a] The σ_m values were calculated from $\sigma_m = \log(K_X/K_H)$, where K_H and K_X were obtained from the pK_a of pyridine and the corresponding 3-PyX. See ref. 19 for the pK_a values of 3-PyX, with the exception of 3-(3′-pyridyl)sydnone.

UV–Vis absorption spectra

The $Fe(CN)_5(PySd)^{3-}$ complex absorbs light strongly, exhibiting a metal to ligand charge transfer (MLCT) band at $\lambda_{max} = 410$ nm, $\epsilon_{max} = 3.20 \times 10^3$ M^{-1} cm^{-1}. In comparison with the $Fe(CN)_5Py^{3-}$ complex, the presence of the sydnone group on the pyridine ring stabilizes the backbonding transition of the complexes. Table 2 summarizes the results of the electronic absorption spectra for a series of 3-substituted pyridine complexes of the pentacyanoferrate(II).

Kinetics of formation and dissociation

Rate constants for the substitution reactions (eqn. (1)) were measured spectrophotometrically. The pseudo-first-order rate constants at various ligand concentrations are shown in Table 3. The second-order rate constants as obtained from the slopes of plots of k_{obs} versus [L] are listed in column 2 of Table 4. Typical plots of k_{obs} versus [L] for the $Fe(CN)_5(PySd)^{3-}$ complex at different temperatures are shown in Fig. 2. In the dissociation reactions the observed first-order rate constants were independent of the concentration of the scavenger and, therefore, can be identified as the k_d for the reaction in eqn. (1). The results are indicated in column 3 of Table 4.

$$Fe(CN)_5OH_2^{3-} + L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} Fe(CN)_5L^{3-} + H_2O \qquad (1)$$

The temperature dependence of the formation and dissociation rate constants were also studied for the $Fe(CN)_5(PySd)^{3-}$ complex, and the results are shown in Table 5. The plots of $\ln(k/T)$ versus $1/T$ show a linear relationship yielding $\Delta H_f^{\ddagger} = 13.4 \pm 0.5$ kcal mol^{-1}, $\Delta S_f^{\ddagger} = -0.9 \pm 0.1$ cal deg^{-1} mol^{-1}, and $\Delta H_d^{\ddagger} = 23.8 \pm 1.0$ kcal mol^{-1}, $\Delta S_d^{\ddagger} = 9.9 \pm 0.5$ cal deg^{-1} mol^{-1}, for the formation and dissociation reactions, respectively, at $\mu = 0.10$ M $LiClO_4$ and pH = 5.

Electrochemistry

The reduction potentials for a series of $Fe(CN)_5L^{2-/3-}$ complexes are listed in Table 6. The concentrations of the complexes were kept at $\sim 1 \times 10^{-3}$ M. The reduction potential for the $Fe(CN)_5OH_2^{2-/3-}$ couple has been reported as 0.39 V [20]. The equilibrium

TABLE 3. Pseudo-first-order rate constants of formation of the $Fe(CN)_5(3\text{-}PyX)^{3-}$ complexes[a]

X	$10^3 \times$ [L] (M)	k_{obs} (s^{-1})	X	$10^3 \times$ [L] (M)	k_{obs} (s^{-1})
Sydnone	1.02	0.535	OH	0.528	0.807
	3.42	1.78		1.01	1.61
	5.32	2.98		2.02	3.19
	6.06	3.37		2.89	4.95
	7.18	4.15		4.05	6.80
CH_3	1.00	0.0654	CHO	1.00	0.357
	3.00	0.166		3.00	1.17
	5.00	0.290		5.00	1.88
	8.00	0.485		8.00	3.06
				12.0	4.62
Ph	0.500	0.0933	$CONH_2$	1.06	0.398
	1.00	0.168		3.05	0.872
	3.00	0.487		5.10	1.81
	5.00	0.822		7.24	2.58
				9.05	3.28
Cl	1.00	0.523			
	3.00	1.67			
	5.00	2.60			
	8.00	4.05			

[a] $\mu = 0.10$ M $LiClO_4$, pH = 5 (acetate), $T = 25$ °C.

TABLE 4. Rate constants of formation and dissociation of the $Fe(CN)_5(3\text{-}PyX)^{3-}$ complexes[a]

X	$10^{-2}\times k_f$ (M^{-1} s^{-1})	$10^3\times k_d$ (s^{-1})	K_{II} (M^{-1})[e]	K_{III} (M^{-1})
H[b]	3.65	1.10	3.32×10^5	1.5×10^4
Sydnone	5.62+0.07	3.23+0.008	1.74×10^5	5.0×10^2
CH_3	0.595+0.009	1.56+0.001	3.81×10^4	8.0×10^3
Ph	1.64+0.01	1.11+0.006	1.48×10^5	3.1×10^4
NH_2[c]	3.10	1.84	1.68×10^5	3.5×10^4
Cl	5.15+0.07	2.48+0.006	2.08×10^5	4.2×10^4
OH	3.25+0.05	2.59+0.04	1.25×10^5	1.2×10^4
CHO	3.84+0.02	1.56+0.006	2.46×10^5	2.3×10^4
$CONH_2$	3.59+0.02	1.36+0.002	2.64×10^5	5.3×10^4
CN[d]	4.13	2.80	1.48×10^5	6.3×10^2

[a] $Fe(CN)_5OH_2^{3-} + \rightleftharpoons Fe(CN)_5L^{3-} + H_2O$. $\mu=0.10$ M $LiClO_4$, pH=5 (acetate), $T=25$ °C. [b] Ref. 20. [c] Ref. 6. [d] Ref. 18. [e] Obtained from k_f/k_d.

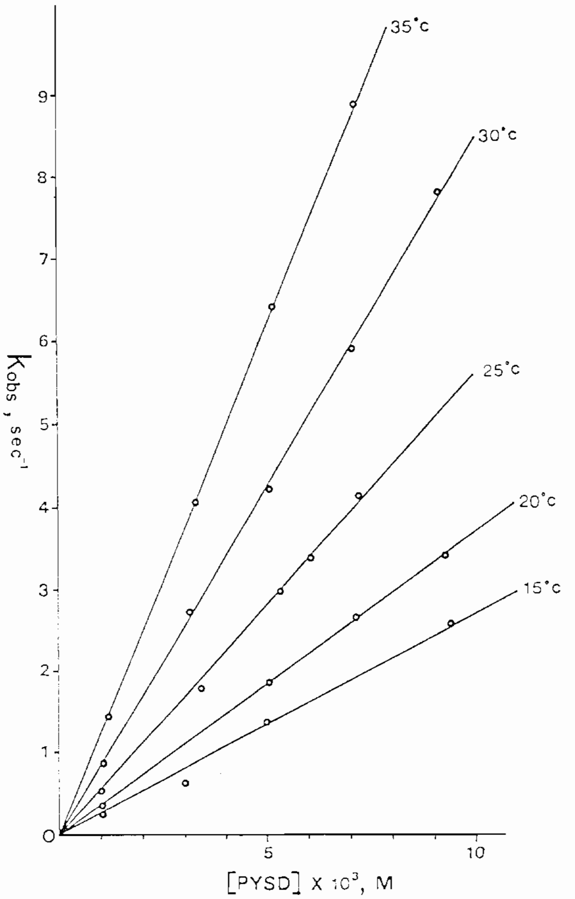

Fig. 2. k_{obs} vs. [PySd] plots at various temperatures.

constants (K_{III}) governing the affinities of $Fe(CN)_5OH_2^{2-}$ and L (eqn. (2)) can be obtained from the electrochemical data and the equilibrium quotients for the reactions according to eqn. (1). The results are indicated in column 5 of Table 4.

$$Fe(CN)_5OH_2^{2-} + L \xrightleftharpoons{K_{III}} Fe(CN)_5L^{2-} + H_2O \qquad (2)$$

TABLE 5. Temperature dependence of formation and dissociation for the $Fe(CN)_5(PySd)^{3-}$ complex[a]

T (°C)	$10^{-2}\times k_f$ (M^{-1} s^{-1})	$10^3\times k_d$ (s^{-1})
15.0	2.71+0.09	0.771+0.001
20.0	3.71+0.02	1.53+0.01
25.0	5.62+0.07	3.23+0.01
30.0	8.47+0.08	6.06+0.03
35.0	12.5+0.1	11.0+0.05

[a] $\mu=0.10$ M $LiClO_4$, pH=5 (acetate).

TABLE 6. Reduction potentials of the $Fe(CN)_5(3\text{-}PyX)^{3-}$ complexes[a]

X	$E_{1/2}$ (V) (vs. NHE)	X	$E_{1/2}$ (V) (vs. NHE)
H[b]	0.47	Cl	0.49
Sydnone	0.54	OH	0.45
CH_3	0.43	CHO	0.51
Ph	0.43	$CONH_2$	0.49
NH_2[c]	0.43	CN[d]	0.53

[a] $\mu=0.10$ M $LiClO_4$, pH=5 (acetate), $T=25$ °C. [b] Ref. 20. [c] Ref. 6. [d] Ref. 8.

Discussion

The assignments of the ring protons in free 3-(3′-pyridyl)sydnone were made on the basis of the coupling constants (J_{HH}) and the observation that in pyridine the chemical shifts of α-protons are more downfield than β- and γ-protons [21–24]. As shown in Fig. 1, the spectrum of free 3-(3′-pyridyl)sydnone consists of one doublet of doublets, three doublets and one singlet. Apparently, the doublet of doublets at 7.57 ppm arises from H5, coupled with H4 and H6. The doublets at 8.15 and 8.65 ppm correspond to H4 and H6, respectively, since H6 (α to the pyridine nitrogen) is expected to be more downfield than H4 (γ to N). The other downfield doublet (8.84 ppm) can be assigned to H2

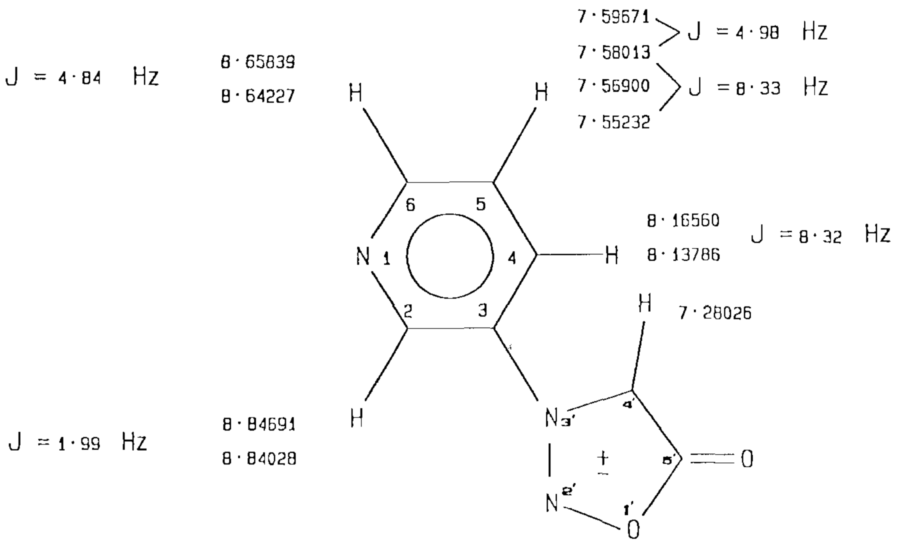

Fig. 3. The chemical shifts and coupling constants for protons of the 3-(3′-pyridyl)sydnone.

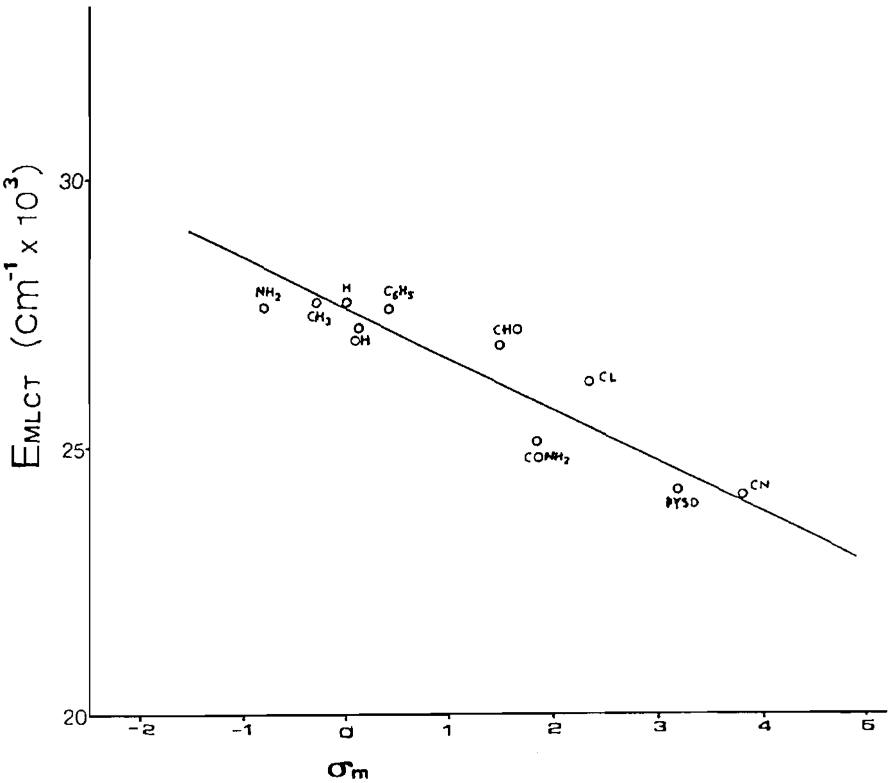

Fig. 4. E_{MLCT} vs. Hammett's σ_m plots for 3-substituted pyridines in $Fe(CN)_5L^{3-}$ complexes.

for the same reason. The slightly further downfield shift for H2 than for H6 may be caused by the electron withdrawing effect of the sydnone group. The remaining singlet at 7.28 ppm therefore belongs to the sydnone proton (H4′). The pyridine proton assignments can further be confirmed by the corresponding coupling constants. The chemical shifts and coupling constants of the protons of 3-(3′-pyridyl)sydnone are shown in Fig. 3. The J_{HH} on H5, 8.33 and 4.98 Hz, agree with the observed values of J_{45} (8.32 Hz) and J_{56} (4.84 Hz). The small J_{HH} value (1.99 Hz) for H2 may arise from long-range coupling rather than a vicinal coupling.

The previous ^1H NMR work [21] on the pyridine-pentacyanoferrate(II) complex has shown that the influence of the $Fe(CN)_5^{3-}$ moiety on the chemical shifts of the coordinated pyridine relative to the free ligand is to shift the α-positions to lower field and the β- and γ-positions to higher field. As shown in Table 1, our results for the $Fe(CN)_5(PySd)^{3-}$ complex are consistent with this observation, and suggest that the Fe(II) center coordinates through the pyridine nitrogen atom of the ligand. The possibility of the Fe binding at N2′ of the sydnone ring can be rejected. If this is the case, the chemical shift of the proton on the sydnone would be more strongly affected than those of the pyridine protons. However, H4′ in the complex is shifted only slightly (downfield) relative to the free ligand. Moreover, the ^1H NMR spectrum of the 3-cyclohexylsydnone complex of pentacyanoferrate(II), where the only available coordination site is N2′, shows a significant upfield shift of H4′ from 6.72 ppm for the free ligand to 4.86 ppm for the complex [25].

The charge transfer band of the $Fe(CN)_5(PySd)^{3-}$ complex is found at much lower energy than that of the pyridine complex, (Table 2). Evidently, the sydnone group on the pyridine ring lowers the transition energy E_{MLCT} by increasing the electron affinity of the ligand even though the substituent is in the *meta*-position. We have correlated the absorption spectra with the Hammett σ_m values for the pentacyanoferrate(II) complexes; the results are shown in Table 2. A plot of E_{MLCT} versus σ_m values is indicated in Fig. 4. For those electron withdrawing substituents, such as CH_3 or Cl^-, the absorption spectra vary only slightly from that of the pyridine complex. The electrochemical results are consistent with the spectral data. The reduction potential of 0.54 V for the $Fe(CN)_5(PySd)^{2-/3-}$ couple relative to 0.47 V for the $Fe(CN)_5Py^{2-/3-}$ couple indicates that significant backbonding stabilization arises from the sydnone substituent on the complex.

Finally, the contribution of π-stabilization by the sydnone groups to the pyridine complex of Fe(II) can be seen by comparing the equilibrium constants for the formation of iron(II) and iron(III) complexes. The K_{II}/K_{III} ratios for 3-(3′-pyridyl)sydnone and 3-cyanopyridine complexes are 3.5×10^2 and 2.4×10^2, respectively, as compared to the pyridine complex of 24. The K_{II}/K_{III} ratios for other 3-substituted pyridine complexes are comparable to that of the pyridine complex. Since Fe(III) is a stronger σ acid than the Fe(II), an increase in complex stability on going from Fe(III) to Fe(II) reflects an increase in dπ–pπ donation of the corresponding Fe(II) complex relative to that of the Fe(III).

Acknowledgements

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