−78 °C and the evolved methane (0.07 mmol) Töpler pumped through a trap (at −196 °C) into the calibrated manometer. Steam-treated aluminum powder (10.0 g) was similarly titrated to yield 0.24 mmol of methane. Measurement of the surface area of the aluminum powder was not attempted.

Gas-Phase Deposition of Tetraneopentylzirconium onto Surface-Activated Aluminum. Tetraneopentylzirconium (ca. 150 mg) was placed in a small vial that was then attached to a cell containing an electrode-deposited quartz crystal held by spring clips (Figure 2). The cell was designed to allow separate evacuation of the reagent vessel and the one containing the crystal. The reagent vial was wrapped with heating tape and covered with glass wool and aluminum foil for insulation. The heated zone was warmed to 50–60 °C under vacuum; the temperature was monitored via a thermocouple or thermometer. After a short time (3–5 min), the vapor of the zirconium reagent was introduced into the crystal-containing chamber while the crystal frequency was monitored (ca. 0.5-Hz sampling rate). The crystal chamber was continuously evacuated by using the diffusion pump during and after exposure. The crystal frequency was periodically monitored, even after exposure, to ensure that mass changes observed were due to the deposition reaction and not to simple sublimation.

Deposition of Tetraneopentylzirconium from Solution onto Surface-Activated Aluminum. The crystal was clamped between two O-ring connectors under dry, oxygen-free N_2, and 1–2 mL dry *n*-pentane was placed on the crystal in order to eliminate mass changes due to solvent effects.[10] A 0.5-mL aliquot of 0.05 M $Zr(C_5H_{11})_4$ in pentane was added via syringe (see Figure 2). For depositions onto hydroxylated aluminum powder, solid $Zr(C_5H_{11})_4$ was mixed with the metal in a flask separated by a valve from a vial containing 5–10 mL of degassed pentane. The assembly was evacuated, and the valve was opened. Upon completion of this procedure, organic materials were distilled and the neopentane yield was measured (2.0 equiv).

Determination of Deuterium Incorporation in Evolved Neopentane. Neopentane-d_1 was collected from the reaction of neopentyllithium[11] (ca. 100 mg) with D_2O(g). GC/MS analysis (for neopentane minus methyl; molecular ion not observed) showed *m/z* 57:*m/z* 58 = 0.49:1. Neopentane evolved from deposition of $Zr(C_5H_{11})_4$ onto D_2O-steam-treated aluminum powder was collected and analyzed by GC/MS, which showed *m/z* 57:*m/z* 58 = 0.49:1. Thus, deuterium incorporation into evolved neopentane is ca. 100%.

Acknowledgment. We acknowledge generous support for this work from the National Science Foundation. We also thank Dr. Michael D. Ward, E. I. du Pont de Nemours & Co., for many helpful discussions.

Supplementary Material Available: Figures showing frequency vs time data for deposition of $Zr(C_5H_{11})_4$ onto surface-oxidized aluminum (4 pages). Ordering information is given on any current masthead page.

(10) Bruckenstein, S.; Shay, M. *Electrochim. Acta* **1985**, *30*, 1295.
(11) Zook, H. D.; March, J.; Smith, D. F. *J. Am. Chem. Soc.* **1958**, *81*, 1617.

Contribution from the Department of Chemistry,
University of Colorado at Colorado Springs,
Colorado Springs, Colorado 80933-7150

Synthesis and Characterization of Cyanoiron(II) Complexes Bound to the Bridging Ligand Tetrakis(2-pyridyl)-1,4-diazine (tpd)

Ronald R. Ruminski* and Jaqueline L. Kiplinger

Received February 20, 1990

Nitrogen aromatic heterocyclic ligands, such as 2,3-bis(2-pyridyl)pyrazine (dpp),[1-8] 2,3-bis(2-pyridyl)quinoxaline (dpq),[9,10] 2,2′-bipyrimidine (bpm),[10-17] and benzo[1,2-*b*:3,4-*b*′:5,6-*b*″]tripyrazine (hat),[10,18,19] have recently been used to prepare complexes with low-spin d^6 metals including Ru(II), Fe(II), Rh(III), and group 6 carbonyls. These complexes possess highly absorbing MLCT transitions in the visible–near-UV region of the spectrum, and good metal–metal electronic interaction in polymetallic systems has been observed.[20-22] Mono- and bimetallic d^6 complexes coordinated to this type ligand have thus been prepared and studied as models for photoinitiated excited-state energy-transfer reactions, photochemistry and photophysics of polymetallic complexes, and solvatochromic behavior.

Our research group has been interested in the design and characterization of low-spin d^6 transition-metal complexes bound through the bis-tridentate ligand tetrakis(2-pyridyl)-1,4-diazine (tpd), for potential use in photo-capture/excited-state energy-transfer processes. Bimetallic complexes with tpd have only recently prepared with Ru(II)[23,24] and Rh(III)[25] centers. We report the preparation and characterization of the first cyanoiron(II) complexes bound with tpd.

Experimental Section

Materials. Analytical reagent grade solvents and compounds were used for preparations and experiments described in this work. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA.

Instrumentation. Electronic absorption spectra were recorded on a Varian DMS 300 spectrophotometer with matching quartz cells. Cyclic voltammograms were recorded on a Bio Analytic Systems CV-1B cyclic voltammograph with a Princeton Applied Research Model 0074 X-Y recorder. Cyclic voltammograms were recorded in distilled H_2O with 0.10 M KCl and in DMF with 0.10 M tetrabutylammonium perchlorate as supporting electrolyte. A Pt working electrode (2.0-mm diameter) and an Ag/AgCl (3 M KCl nominally −0.44 V vs SCE) reference electrode were used. All potentials are reported vs SCE and are uncorrected for junction potentials. Infrared spectra were recorded as solid KBr samples on a Nicolet Model 20DX FTIR spectrometer from 4000 to 400 cm^{-1} using 2-cm^{-1} resolution. ^1H NMR spectra were obtained on a Bruker Model AC 300 Fourier Transform NMR instrument operating at 300.1 MHz. Samples were run in a 10.0-mm probe with D_2O as the solvent and internal lock. The reference was $(CH_3)_3SiC_3H_5SO_3^-Na^+$ ($\delta = 0.015$ ppm vs TMS).

Synthesis. The tpd ligand was prepared according to the literature without difficulty.[26] The $Na[Fe(CN)_3(tpd)]$ complex was prepared by

---

(1) Braunstein, C. H.; Baker, A. D.; Strekas, T. C.; Gafney, H. D. *Inorg. Chem.* **1984**, *23*, 857.
(2) Brewer, K. J.; Murphy, W. R., Jr.; Spurlin, S. R.; Petersen, J. D. *Inorg. Chem.* **1986**, *25*, 882.
(3) Ruminski, R. R.; Cockroft, T.; Shoup, M. *Inorg. Chem.* **1988**, *27*, 4026.
(4) Brewer, K. J.; Murphy, W. R., Jr.; Petersen, J. D. *Inorg. Chem.* **1987**, *26*, 3376.
(5) Ruminski, R. R.; Johnson, J. O. *Inorg. Chem.* **1987**, *26*, 210.
(6) Shoup, M.; Hall, B.; Ruminski, R. R. *Inorg. Chem.* **1988**, *27*, 200.
(7) Wallace, I.; Ruminski, R. R. *Polyhedron* **1987**, *6* (8), 1673.
(8) Ruminski, R. R.; Cambron, R. T. *Inorg. Chem.* **1990**, *29*, 1575.
(9) Rillema, D. P.; Taghdiri, D. G.; Jones, D. S.; Keller, C. D.; Worl, L. A.; Meyer, T. J.; Levy, H. A. *Inorg. Chem.* **1987**, *26*, 578.
(10) Sahai, R.; Morgan, L.; Rillema, D. P. *Inorg. Chem.* **1988**, *27*, 3495.
(11) Ruminski, R. R.; Petersen, J. D. *Inorg. Chem.* **1982**, *21*, 3706.
(12) Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660.
(13) Hunziker, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7370.
(14) Overton, C.; Connor, J. A. *Polyhedron* **1982**, *1*, 53.
(15) Petersen, J. D.; Murphy, W. R., Jr.; Sahai, R.; Brewer, K. J.; Ruminski, R. R. *Coord. Chem. Rev.* **1985**, *64*, 261.
(16) Jaradat, Q.; Barqawi, K.; Akasheh, T. S. *Inorg. Chim. Acta* **1986**, *116*, 63.
(17) Ruminski, R. R.; Van Tassel, K. D.; Petersen, J. D. *Inorg. Chem.* **1984**, *23*, 4380.
(18) Nasielski-Hinkens, R.; Benedek-Vamos, M.; Maetens, D.; Nasielski, J. *J. Organomet. Chem.* **1981**, *217*, 79.
(19) Masschelein, A.; Kirsch-De Mesmaeker, A.; Verhoeven, C.; Nasielski-Hinkens, R. *Inorg. Chim. Acta* **1987**, *129*, L13.
(20) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.
(21) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289.
(22) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.
(23) Thummel, R. P.; Chirayil, S. *Inorg. Chim. Acta* **1988**, *154*, 77.
(24) Ruminski, R. R.; Kiplinger, J.; Cockroft, T.; Chase, C. *Inorg. Chem.* **1989**, *28*, 370.
(25) Ruminski, R. R.; Letner, C. *Inorg. Chim. Acta* **1989**, *162*, 175.
(26) Goodwin, H. A.; Lyons, F. *J. Am. Chem. Soc.* **1959**, *81*, 6415.

0020-1669/90/1329-4581$02.50/0

Table I. Aqueous[a] Electronic Absorption and Electrochemical[b] Data for Cyanoiron(II) Complexes[a]

complex ion	λ_{max}, nm $10^3(\epsilon$, M^{-1} $cm^{-1})$	assgnt	oxidn $E_{1/2}(1,2)$, V	redn $E_{1/2}$, V
$[Fe(CN)_3(tpd)]^-$	580 (sh) (4.5)	MLCT	+0.66 (H_2O)	
	532 (6.2)	MLCT	+0.54 (DMF)	−1.29 (DMF)
	375 (sh) (4.7)	MLCT		
	333 (32.0)	$\pi \rightarrow \pi^*$		
$[(Fe(CN)_3)_2(tpd)]^-$	750 (3)	MLCT	+0.60, +0.85 (H_2O)	
	605 (17.5)	MLCT	+0.41, +0.90 (DMF)	−0.94 (DMF)
	420 (sh) (5)	MLCT		
	375 (sh) (30)	MLCT		
	359 (34)	$\pi \rightarrow \pi^*$		

[a] MLCT energies in other solvents noted in Table II. [b] Electrochemical conditions noted in the Experimental Section.

Table II. MLCT Absorption ν_{max} (10^3 cm^{-1}) of $[(Fe(CN)_3)_{1,2}(tpd)]^{-,2-}$ Complexes in Different Solvents[a,b]

solvent	E^*_{MLCT}	Gutmann AN	ν for $[Fe(CN)_3(tpd)]^-$				ν for $[(Fe(CN)_3)_2(tpd)]^{2-}$				
H_2O		54.8	(17.2)	18.8	(26.7)	30.0	16.5	(23.8)	(26.7)		27.8
DMSO	1.00	19.3	(14.8)	16.9	23.95	29.6	14.1	20.5	23.5	(26)	27.5
CH_3CN	0.98	19.3	(14.8)	17.0	24.1	29.8	14.2	20.9	23.4	(26)	27.7
DMF	0.95	16.0	(14.4)	16.7	23.6	29.8	14.0	(20.2)	23.0	(26)	27.5
DMA	0.93	13.6	(14.2)	16.6	23.5	29.8	13.9	(20.2)	22.8	(26)	27.5
methanol	0.73	41.3	(16.4)	18.0	25.6	30.0	15.4	(26)	(26)		27.8
ethanol	0.69	37.1	(16.0)	17.8	25.3	29.8	15.1	(26)	(26)		27.8
1-butanol	0.55		(15.6)	17.6	25.0	29.8	15.0	(26)	(26)		27.7
2-propanol	0.46	33.5	(15.4)	17.5	24.9	29.8	14.9	(26)	(26)		27.7

[a] E^*_{MLCT} solvent parameters taken from ref 30. [b] Gutmann AN taken from ref 31.

dissolution of 0.207 g (1.70×10^{-4} mol) of the previously prepared $[Fe(tpd)_3](I)_2$ complex[26] in 200 mL of hot water in a round-bottom flask fitted with a condenser (top closed with a septum and an Ar inlet needle). A solid sample of 0.263 g (5.36×10^{-4} mol) of NaCN was added, and the solution was kept hot under Ar for 5 h. After cooling to room temperature, the purple solution was filtered to remove the displaced tpd, the filtrate was eluted down a Sephadex C-25 cation-exchange resin with water, and the eluent was rotary-evaporated to dryness. The product was dissolved in methanol, the solution was filtered, and the product was reprecipitated by addition of diethyl ether. The collected product was washed with acetone to remove any possible NaI and air-dried. Yield of $Na[Fe(CN)_3(tpd)]\cdot 3H_2O$: 0.082 g ($1.37 \times 10^{-4}$ mol), 76%. Anal. Calcd for $C_{27}H_{22}N_9O_3FeNa$ (molecular mass 599.4): C, 54.09; H, 3.71; N, 21.04. Found: C, 53.88; H, 3.77; N, 20.99. IR: ν_{CN} 2081 cm^{-1}.

The $Na_2[(Fe(CN)_3)_2(tpd)]$ complex was prepared by dissolution of 0.296 g (1.49×10^{-3} mol) of $FeCl_2\cdot 4H_2O$ in 100 mL of methanol in a two-neck round-bottom flask, which was fitted with a condenser (top closed with a septum and Ar inlet needle) and an addition side funnel. To the yellow solution was added through the addition funnel a suspension of 0.288 g (7.42×10^{-4} mol) of tpd in methanol, producing a purple solution as the bimetallic framework was formed. After complete dissolution of the tpd, 0.229 g (4.68×10^{-3} mol) of NaCN was dissolved in a minimum of methanol and the resulting solution was added through the addition funnel. The color of the mixture progressed from purple through blue to a distinct green while with heating at reflux over a period of 4 h. After cooling to room temperature, the green solution was filtered to remove insoluble material, and diethyl ether was added to precipitate the crude product. The product was then dissolved in a minimum amount of water, the solution was filtered, and the filtrate was loaded onto a Sephadex A-25 anion-exchange resin. The resin passed a blue-green neutral or cationic species with H_2O, and that was discarded. A solution of 4 g of NaI/400 mL of H_2O was used to remove the purple monometallic $[Fe(CN)_3(tpd)]^-$ complex, followed by a solution of 10 g of NaI/400 mL of H_2O to remove the blue bimetallic complex. The eluent was collected and rotary-evaporated to complete dryness. The dried product (still in the round-bottom flask) was soaked in 400 mL of acetone for 12 h to remove large amounts of excess NaI. The remaining solid was then placed in a Soxhlet extractor and washed with acetone for 48 h to remove trace amounts of excess NaI. The product was removed and vacuum-dried. Yield of $Na_2[(Fe(CN)_3)_2(tpd)]\cdot 6H_2O$: 10%. Anal. Calcd for $C_{30}H_{28}N_{12}O_6Fe_2Na_2$: C, 44.5; H, 3.5; N, 20.7. Found: C, 44.1; H, 3.8; N, 20.3. IR: ν_{CN} 2081 cm^{-1}.

Results and Discussion

The syntheses of $Na_{1,2}[(Fe(CN)_3)_{1,2}(tpd)]$ complexes are based on previously reported preparations of cyanoiron(II) complexes with bpm and dpp.[4,17] The monometallic complex is formed by replacement of a tpd ligand from $[Fe(tpd)_2]^{2+}$ with three CN^-. The bimetallic complex was prepared by the initial formation of a Fe(tpd)Fe framework, followed by addition of CN^-. After chromatography and washing, the products were identified as $Na_{1,2}[(Fe(CN)_3)_{1,2}(tpd)]$ by percent C, H, and N analyses and the C/N ratio. The purity of each complex was further verified by clarity of cyclic voltammograms and characteristics of the Ce(IV) titrations.

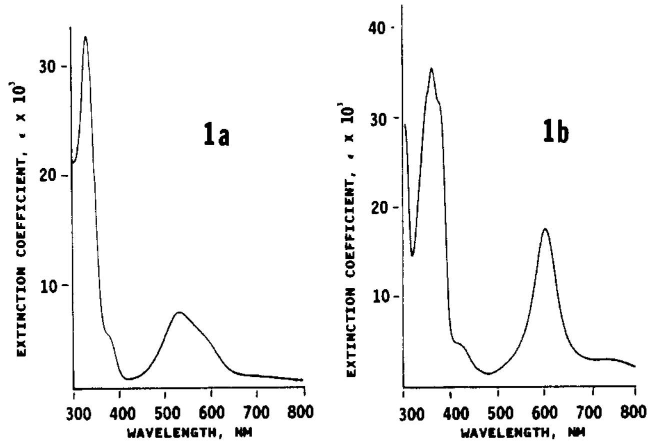
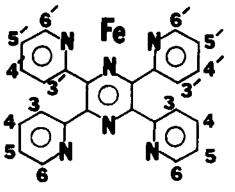


Figure 1. Aqueous electronic absorption spectra for (a) $[Fe(CN)_3(tpd)]^-$ and (b) $[(Fe(CN)_3)_2(tpd)]^{2-}$.

The $[Fe(CN)_3(tpd)]^-$ ion exhibits intense solvent-dependent electronic transitions between 800 and 300 nm (Tables I and II, Figure 1a). All absorptions except the 333-nm peak are solvent sensitive, and the 375-nm shoulder (in H_2O) is red-shifted in other solvents and appears as a distinct peak. On the basis of the solvatochromic behavior of the absorptions and the similarity with previously reported spectra for $[Fe(CN)_4(LL)]^{2-}$ (where LL = dpp and bpm)[4,17] and Ru^{II}(tpd) complexes,[23,24] the monometallic absorptions in aqueous solution at 580 (sh), 532, and 375 (sh) nm are assigned as Fe d$\pi \rightarrow$ tpd pπ^* MLCT transitions, while the 333-nm peak is assigned as a tpd intraligand p$\pi \rightarrow$ pπ^* transition. The low-energy MLCT shoulder on the lowest energy MLCT peak has also been reported for Ru^{II}(tpd)[23,24] and Rh(tpd)[25] complexes and may be due to distinct M d$\pi \rightarrow$ tpd pπ^* transitions into the pz and py rings. The $[(Fe(CN)_3)_2(tpd)]^{2-}$ ion also exhibits intense solvent-dependent absorptions in the visible spectrum (Tables I and II, Figure 1b). All lower energy absorptions are solvatochromic, and the shoulders at 420 and 375 nm (in H_2O) appear as distinct peaks in nonaqueous solvents, while the 359-nm transition is not solvent sensitive. Again, on the basis of solvent sensitivity and similarity to previously reported com-

Table III. Proton NMR Resonances (ppm) for tpd, $[Fe(CN)_3(tpd)]^-$, and $[(Fe(CN)_3)_2(tpd)]^{2-}$



complex	H_3	H_4	H_5	H_6	$H_{3'}$	$H_{4'}$	$H_{5'}$	$H_{6'}$
tpd[a]	8.05	7.80	7.23	8.38				
$[Fe(CN)_3(tpd)]^-$	8.74 D[b]	8.21 T	7.76 T	8.82 D	6.98 D	7.75 T	7.40 T	8.04 D
$[(Fe(CN)_3)_2(tpd)]^{2-}$					8.66 D	7.92 T	7.54 T	8.95 D
$[Ru(tpy)(tpd)]^{2+}$[a]	8.39	8.24	7.74	8.73	7.64	7.65	7.22	7.57
$[(Ru(tpy))_2(tpd)]^{4+}$[a]					8.95	7.93	7.30	7.70

[a] Reference 23; recorded in CD_3CN. [b] T and D refer to triplet and doublet resonances. Primed protons refer to coordinated protons, and unprimed protons refer to uncoordinated protons.

plexes, the bimetallic absorptions in aqueous solution at 750 (sh), 650, 420 (sh), and 375 (sh) nm are assigned as MLCT transitions, while the 359-nm absorption is assigned as a tpd intraligand $p\pi \rightarrow p\pi^*$ transition. The lowest energy MLCT peak for the $[(Fe(CN)_3)_2(tpd)]^{2-}$ ion is lower in energy than that for the analogous $[Fe(CN)_3(tpd)]^-$ ion. The lower energy MLCT value for the bi- vs monometallic complex is expected, since the addition of π-electron-withdrawing $Fe(CN)_3$ fragments on the opposite side of the tpd ligand stabilizes the tpd π system. Electrochemical measurements (Table I) verify the tpd $p\pi^*$ LUMO in the bimetallic complex is 0.35 V (in DMF) more easily reduced (stabilized) than that in the monometallic complex, resulting in the observed lower energy bimetallic $d\pi \rightarrow p\pi^*$ transition.

Cyclic voltammograms of $[(Fe(CN)_3)_{1,2}(tpd)]^{-,2-}$ were recorded in H_2O and DMF (Figure 2, Table I). The monometallic complex exhibits a reversible redox wave associated with the Fe(II)/Fe(III) couple at +0.66 V when scanned in a positive direction, while the bimetallic complex shows two well-resolved waves with $E_{1/2}(1) = +0.60$ and $E_{1/2}(2) = +0.85$ V. The $E_{1/2}(1)$ value for the bimetallic complex is less positive than $E_{1/2}$ for the monometallic species, and this is similar to the cases of previously reported cyanoiron(II) complexes.[4,17] The more easily oxidized bimetallic vs monometallic complex has been rationalized by the addition of the anionic cyanoiron(II) fragment to the already anionic monometallic complex, thus increasing the overall electrostatic repulsions. Metal–metal communication through tpd was evaluated electrochemically for the bimetallic $[(Fe(CN)_3)_2(tpd)]^{2-}$ complex as $E_{1/2}(2) - E_{1/2}(1) = \Delta E_{1/2} = 250$ mV. The π-withdrawing CN^- ligands on the metal centers could be expected to minimize π electron interaction through the metal $d\pi$–bridging ligand–metal $d\pi$ moiety, as has been reported in the comparison of NH_3 vs CN^- and bpy Ru(II) complexes.[27] Thus, the large $\Delta E_{1/2}$ value for $[(Fe(CN)_3)_2(tpd)]^{2-}$ is attributed to good communicative ability of tpd, even in the presence of competitive π-withdrawing CN^- ligands. The reduction couples associated with tpd were recorded only in DMF due to the solvent window. The most positive tpd reduction potential for $[(Fe(CN)_3)_2(tpd)]^{2-}$ at −0.94 V vs −1.29 V for $[(Fe(CN)_3)(tpd)]^-$ indicates the π-withdrawing effects of the cyanoiron(II) fragment on the tpd π system, making ligand reduction more favorable.

From the separation of $E_{1/2}(2) - E_{1/2}(1) = \Delta E_{1/2}$, the comproportionation constant, $K_c = \exp(\Delta E_{1/2}/25.69)$, where $E_{1/2}$ is in millivolts and $T = 25$ °C, for the reaction of the bimetallic complex

$$\mathrm{Fe(II)–Fe(II)} + \mathrm{Fe(III)–Fe(III)} \rightarrow 2(\mathrm{Fe(II)–Fe(III)})$$

is calculated as 1.68×10^4.[28] This value, and that previously reported for the tpd-bridged ruthenium(II) ammine complex,[24] suggests the two metal centers are much more effectively coupled than in the cyanoiron(II) bpm- and dpp-bridged systems.[4,17] The stability of the mixed-valent $Fe^{III}(tpd)Fe^{II}$ system calculated[20] by $\Delta G_{MV} = 0.5RT \ln (K_c/4)$ is 2.47 kcal, compared with 1.32 kcal for dpp-bridged and 1.21 kcal for bpm-bridged cyanoiron(II) complexes. Titration of the tpd-bridged Fe(II)–Fe(II) complex with Ce(IV) produced a decrease and broadening of the characteristic MLCT transitions with isosbestic points at 620 and 700 nm, without an observable intervalence transition (IT) band between 700 and 1300 nm. Additional Ce(IV) to produce the Fe(III)–Fe(III) species resulted in loss of the isosbestic points. Rereduction of Fe(II)–Fe(III) or Fe(III)–Fe(III) with Sn(II) produced a duplication of the original absorption spectrum, further verifying the electrochemical reversibility observations. While the IT band for $[Fe(CN)_5(pz)Fe(CN)_5]^{5-}$ has been reported to be 1200–1300 nm,[29] the absence of an IT band in mixed-ligand complexes has been attributed to the competitive CN^- groups reducing the metal $d\pi$ orbital radial extension and ultimately the direct metal–BL–metal π interaction.[27] Increased Fe(tpd)Fe vs Fe(pz)Fe π interaction is assessed by comparative $\Delta E_{1/2}$ values of 250 and 100 mV, respectively, and suggests that tpd more effectively competes for electron density in $[(CN)_3Fe(tpd)Fe(CN)_3]^-$, than does pz in $[(CN)_5Fe(pz)Fe(CN)_5]^{5-}$. It is possible that the IT band for $[(CN)_3Fe(tpd)Fe(CN)_3]^{2-}$ is outside the low end of the solvent window.

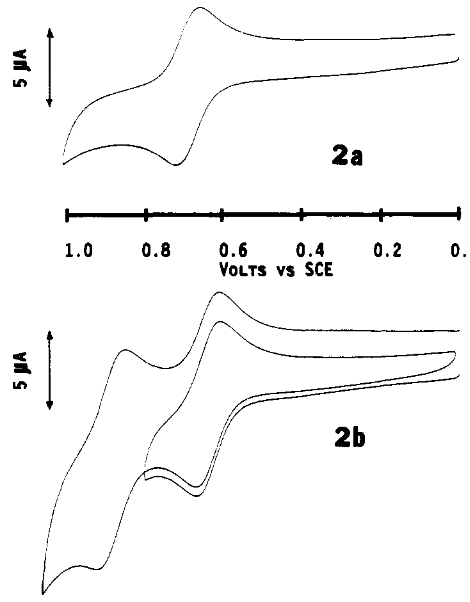


Figure 2. Cyclic voltammograms of (a) $[Fe(CN)_3(tpd)]^-$ and (b) $[(Fe(CN)_3)_2(tpd)]^{2-}$ in aqueous solution/0.10 M KCl at a Pt working electrode vs SCE.

The charge on the mono- and bimetallic complexes prohibited dissolution in many solvents of lower polarity. Plots of ν_{max} values

---

(27) Hendersen, W. W.; Shepherd, R. R. *Inorg. Chem.* **1985**, *24*, 2398.

(28) Richardson, D.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(29) Felix, F.; Ludi, A. *Inorg. Chem.* **1978**, *17*, 1782.

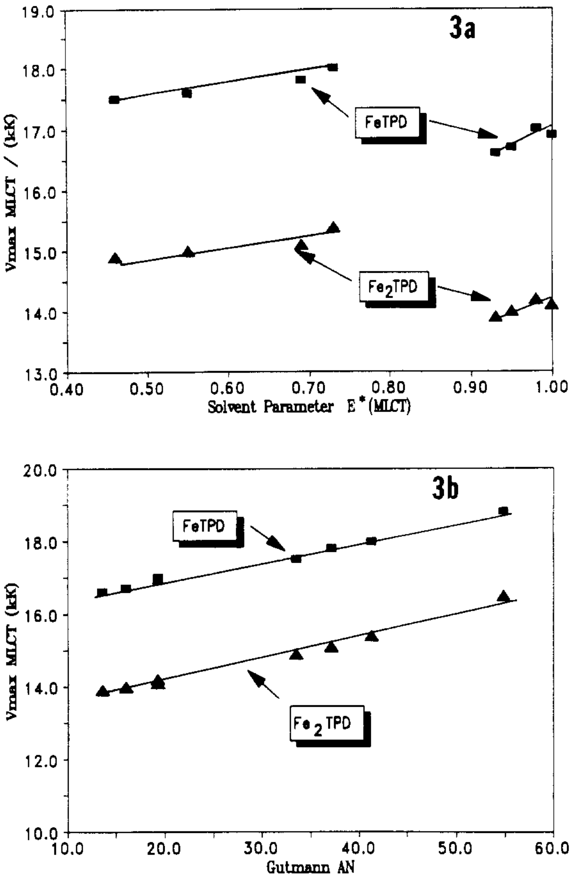


Figure 3. Plots of ν_{max} (kK = 10^3 cm^{-1}) for the lowest energy MLCT peak of $[Fe(CN)_3(tpd)]^-$ (■) and $[(Fe(CN)_3)_2(tpd)]^{2-}$ (▲) ions in various solvents vs (a) E^*_{MLCT} solvent parameter and (b) Gutmann AN.

of the lowest energy MLCT peaks for $[(Fe(CN)_3)_{1,2}(tpd)]^{-,2-}$ vs the E^*_{MLCT} solvent parameters[30] for combined alcoholic and aliphatic solvents are nonlinear (Figure 3a). Separation of solvents produces two distinct linear solvatochromic behaviors for both mono- and bimetallic complexes. The discontinuity of $[Fe(CN)_3(tpd)]^-$ and $[(Fe(CN)_3)_2(tpd)]^{2-}$ plots may result from the fact that the E^*_{MLCT} solvent parameter was derived from solvent effects on neutral complexes and does not compensate for enhanced ground-state stabilization due to the polarizability of anionic metal complexes by the very polarizing alcoholic protons. The Gutmann acceptor number, a solvent parameter based on the hardness of the solvent in donor-acceptor interactions,[31] appears to be a more appropriate model for the $[(Fe(CN)_3)_{1,2}(tpd)]^{-,2-}$ complexes. A plot of ν_{max} MLCT vs Gutmann AN (Figure 3b) is linear, suggesting that molecular polarizability of the metal complex plays an important role in solvatochromic behavior.[32]

Proton NMR spectra of $[(Fe(CN)_3)_{1,2}(tpd)]^{-,2-}$ were recorded in D_2O (Table III). The bimetallic complex spectrum shows two doublets and two triplets, as expected from the symmetrically coordinated tpd ligand. The two sets farthest downfield at 8.95 and 8.66 ppm are doublets that must be assigned to $H_{6'}$ and $H_{3'}$ on coordinated pyridine rings. In accordance with previous assignments for cyanoiron(II) complexation to pyridine,[33] and tpd when symmetrically coordinated to two metals,[24] the doublet at 8.95 ppm is assigned to $H_{6'}$ and the 8.66 ppm doublet to $H_{3'}$. The triplets at 7.92 and 7.54 ppm are assigned to $H_{4'}$ and $H_{5'}$, respectively, also in agreement with previous assignments. It is of interest to note that, for the $[(Fe(CN)_3)_2(tpd)]^{2-}$ ion, the $H_{3'}$ doublet is shifted downfield with respect to the $H_{4'}$ and $H_{5'}$ triplets, in contrast with the previously reported $[(Ru(tpy))_2(tpd)]^{4+}$ ion, where $H_{3'}$ reported further upfield from $H_{4'}$ and $H_{5'}$ triplets. The downfield shift observed for $H_{3'}$ in the bimetallic cyanoiron(II) complex must be due to increased π-withdrawing effects of the CN^- vs tpy ligand on the metal center. The monometallic complex displays four sets of doublets and four sets of triplets, as expected from protons on the coordinated and noncoordinated rings. Two sets of doublets at 8.82 and 8.74 ppm are assigned to the protons in the coordinated rings as $H_{6'}$ and $H_{3'}$. Doublets at 8.04 and 6.98 ppm are assigned to H_6 and H_3 on the uncoordinated rings. As previously noted for the monometallic ruthenium complex,[23] when the coordinated pyridine and diazine rings are held coplanar, the uncoordinated pyridine ring presumedly rotates out of plane, resulting in an upfield shift of the uncoordinated protons. The observation of H_3 in the $[Fe(CN)_3(tpd)]^-$ complex to be shifted upfield to 6.98 ppm appears to support the previous rationale.

Acknowledgment. We acknowledge the generous financial support of this work through a Bristol-Myers Co. Grant of the Research Corp. R.R.R. thanks Jeff Boone at the Frank Seiler Laboratories, USAFA, Colorado Springs, CO, for NMR data.

---

(30) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 3825.
(31) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.
(32) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3306.
(33) Malin, J. M.; Schmidt, C. F.; Toma, H. E. *Inorg. Chem.* **1975**, *14*, 2924.

Contribution from the Department of Chemistry,
Georgetown University, Washington, D.C. 20057

Reformulation of the Hexafluorooctadecatungstate Anion as a Heteropoly Sodate Complex: $[H_2F_6NaW_{18}O_{56}]^{7-}$[†]

Thomas L. Jorris, Mariusz Kozik,[‡] and Louis C. W. Baker*

Received June 5, 1990

Chauveau, Doppelt, Lefebvre, et al.[1-11] published an elegant and valuable series of papers (1974-1983) on fluoroisopolytungstate complexes, chiefly derivatives of the metatungstate ($[H_2W_{12}O_{40}]^{6-}$) structure, wherein F^- ions replaced various interior isoelectronic O^{2-} ions. In the course of that work they reported[4] the preparation and structure of "$[H_2F_6W_{18}O_{56}]^{8-}$", which is grossly isostructural with the well-known Wells-Dawson[12-14] species α-$[P_2W_{18}O_{62}]^{6-}$ but wherein the P atoms have been replaced by H's and the six most central O atoms have been replaced by F atoms. Their structure proof was based on chemical analyses, similarities of X-ray powder patterns and CV data with those of known Wells-Dawson derivatives, ultracentrifugation, and especially ^{1}H and ^{19}F NMR spectroscopy.

The present paper modifies their conclusion by showing that a nonexchanging Na^+ ion is enclosed at the very center of the complex, in trigonal-prismatic coordination to its six nearest-neighbor F atoms. (See Figure 1.) So far as we are aware, this is the first case of trigonal-prismatic coordination by hard ligands. We have been unable to form the complex in the absence of Na^+.

In 1973 our laboratory reported[15] the first polytungstate complexes containing fluoride ions substituted for oxide ions. We subsequently unequivocally established[16-18] those complexes and others as comprising a series of isomorphous heteropoly *d,l*-α_1-aquometalloheptadecatungstopolyfluorosodates, *d,l*-α_1-$[(H_2O)M^{n+}O_5H_2F_6NaW_{17}O_{50}]^{(11-n)-}$, wherein M^{n+} = Co^{2+}, Co^{3+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, or Mn^{3+}. The detailed structure proof was based primarily on ^{23}Na, ^{19}F, ^{1}H, and ^{183}W NMR spectroscopy, a complete X-ray structure, and isotope-exchange studies. That proof is contained in a dissertation[16] and has been presented at an international heteropoly symposium.[18] It will be the subject of a forthcoming detailed major paper. The 18-tungstohexafluorosodate complex which is the subject of this paper turned out to be an isomorph of the α_1-aquometalloheptadecatungsto-

---

[†] Abstracted from a portion of the Ph.D. dissertation of Thomas L. Jorris, Georgetown University, 1987.

[‡] Present address: Department of Chemistry, Canisius College, Buffalo, NY.

0020-1669/90/1329-4584$02.50/0