second negative group to the metal center to form $[Me_4Zn]^{2-}$ or $[Me_3Cu]^{2-}$, respectively, results in too great a coulombic repulsion and the reaction is thermodynamically unfavored. In the solid state, however, it appears that this coulombic repulsion may be overcome; $[Me_4Zn]Li_2$ has been isolated and structurally characterized by X-ray diffraction techniques.[5] The identity of the broad resonance at $\delta = -12$ is at this time unknown. On the basis of its chemical shift and broad appearance it could be similar to MeLi in structure, with the broadness of the peaks arising from unresolved coupling between ^{6}Li and ^{13}C. Our results do not contrast those obtained in the chemical reactivity studies for these systems.[1] Even though the ground-state structures of the "higher order" zincates and cuprates appear to be monoanionic, the reactive species could of course be the higher energy tetracoordinated zincate and tricoordinated cuprate.

Further studies involving the nature of the interaction of the anion and the Li^+ counterion and studies examining the interaction of **1**, **3**, and **4** with reactive substrates are currently underway.

Received: May 27, 1999 [Z13472IE]
German version: *Angew. Chem.* **1999**, *111*, 3256–3258

Keywords: NMR spectroscopy · organometallic compounds · structure elucidation · zinc

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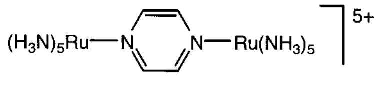
An Exceedingly Stable Diiron(II,III) Complex Ion $[(tz)\{Fe(CN)_5\}_2]^{5-}$ with Comproportionation Constants between 10^8 (in H_2O) and 10^{19} (in CH_3CN)

Markus Glöckle and Wolfgang Kaim*

Prussian Blue, formulated as cyanoiron compound $[Fe^{III}_4\{Fe^{II}(CN)_6\}_3]$ (**1**),[1] and the heterocycle-bridged Creutz–Taube ion $[(H_3N)_5Ru(\mu\text{-pz})Ru(NH_3)_5]^{5+}$ (**2**, pz = pyrazine) are textbook cases for mixed-valent compounds in coordination chemistry.[2] The equilibrium constant K_c for comproportionation, which measures the stability towards disproportionation [Eqs. (1), (2)] and thus specifies the range of existence of the mixed-valent state, is about 10^{12} for **1** in water[1b] and between $10^{6.8}$ and $10^{7.3}$ for **2**, depending on the solvent.[3]



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$$M^{n-} + M^{(n-2)-} \rightleftharpoons 2\,M^{(n-1)-} \tag{1}$$

$$K_c = \frac{[M^{(n-1)-}]^2}{[M^{n-}][M^{(n-2)-}]} = e^{\Delta EF/RT} \tag{2}$$

ΔE: redox potential difference

It was therefore disappointing when the bis(pentacyanoiron) complex $[(\mu\text{-pz})\{Fe(CN)_5\}_2]^{5-}$ ($\mathbf{3}^{5-}$) with bridging pyrazine was found to exhibit only a small K_c value of $10^{1.9}$ in water, signifying very little metal–metal interaction in $\mathbf{3}^{5-}$.[4] Recent experiments in aprotic polar media, however, showed that this value for $\mathbf{3}^{5-}$ can increase up to $10^{6.5}$,[5] illustrating the crucial role of the environment for the metal–metal coupling in such highly charged systems. Using the hitherto rather neglected[6] unsubstituted 1,2,4,5-tetrazine (tz) as an excellently π-accepting bridging ligand, we have now been able to extend the stability range of such simple diiron(II,III) systems to $10^{7.9}$ in water and to $10^{19.0}$ in acetonitrile, allowing for the isolation of the corresponding ion $[(\mu\text{-tz})\{Fe(CN)_5\}_2]^{5-}$ ($\mathbf{4}^{5-}$) as a stable pentakis(tetraethylammonium) salt.[7b]

Compounds $(NEt_4)_6$(**4**) (Fe^{II}(tz)Fe^{II}) and $(NEt_4)_5$(**4**) ($Fe^{2.5}$(tz)$Fe^{2.5}$) were isolated[7a,b] and characterized spectroscopically and electrochemically (Figure 1, Table 1). The neighbor-

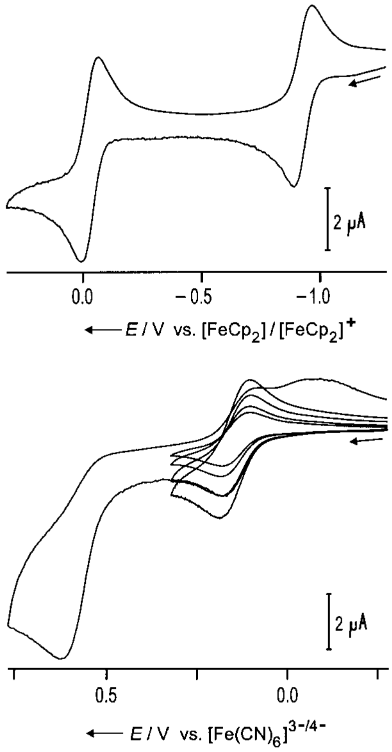

Figure 1. Cyclic voltammograms of $(NEt_4)_6(\mathbf{4})\cdot 2H_2O$ in CH_3CN/0.1 M NBu_4PF_6 at −35 °C (50 mV s^{-1}; top) and in H_2O/0.25 M Na_2SO_4 at room temperature (50 mV s^{-1} for full-scale voltammogram and 100, 50, 25, and 15 mV s^{-1} for the first oxidation wave; bottom).

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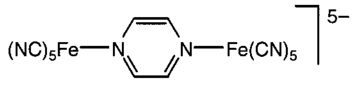
Table 1. Electrochemical and spectroscopic data of pentacyanoiron complexes

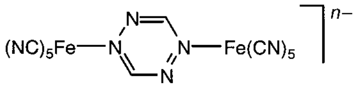
Complex	E_{ox2}[a]	E_{ox1}[a]	K_c	$\lambda_{IVCT}(\varepsilon)$[b]	λ (ε)[b]	$\tilde{\nu}_{CN}$[c]	Solvent[d]	Temp.[e]
3^{6-}	0.62[f]	0.51[f]	$10^{1.9}$	–	505 (13180)		H_2O	298[4c]
3^{6-}	– 0.60	– 0.92	$10^{6.5}$	–	599 (17400), 406 (3400)		CH_3CN	248[5]
3^{5-}				1205 (2200) $\Delta\tilde{\nu}_{1/2}$ 4800 cm^{-1}	n.o.	n.o.	H_2O	298[4]
3^{5-}				2475 (3900) $\Delta\tilde{\nu}_{1/2}$ 1500 cm^{-1}	745 (8000), 599 (7300), 406 (4400)	2070 br, 2112 w	CH_3CN	–/298/298[5]
4^{6-}	0.64[g, h]	0.14[h]	$10^{7.9}$	–	848 (22000), 452 (1300), 395 sh	n.o.	H_2O	293/298/–;
	0.00	– 0.85	$10^{17.8}$	–	1014[i]	n.o.	CH_2Cl_2	233/240/–
	– 0.03	– 0.93	$10^{19.0}$	–	1021 (21670), 543 sh, 520 (1620), 353	2087 sh, 2067 vs	CH_3CN	238/233/242
4^{5-}				2250(2820) $\Delta\tilde{\nu}_{1/2}$ 970 cm^{-1}	744 (15060), 439 sh, 402 (1420)	n.o.	D_2O	298
				2520 (1150) $\Delta\tilde{\nu}_{1/2}$ 860 cm^{-1}	678 (13070), 345 (3710)	2110s, 2101s	CH_3CN	298
4^{4-}				–	630 (6190), 414 (2020)	2123 sh, 2117 w	CH_3CN	–/238/242
5	–	0.37h	–	–	685 (7830), 423 (1050)	n.o.	H_2O	293/298/–
	–	– 0.32	–	–	690 (7180)	2106 sh, 2097 m, 2082 s	CH_3CN	243/298/298

[a] Potentials in V vs. ferrocene$^{+/o}$ (aprotic media) from cyclic voltammetry at 50 mV s^{-1} scan rate (30 mV s^{-1} in CH_2Cl_2). Values from aqueous solution were measured vs. $[Fe(CN)_6]^{3-/4-}$. [b] Wavelengths in nm, molar extinction coefficients in M^{-1} cm^{-1}. n.o. = not observed. [c] CN stretching frequencies in cm^{-1} (solution studies). [d] Electrolyte solutions for cyclic voltammetry: H_2O/0.25 M Na_2SO_4, CH_3CN/0.1 M Bu_4NPF_6, CH_2Cl_2/0.2 M Bu_4NPF_6. [e] In K, for cyclic voltammetry/absorption spectroscopy/IR spectroscopy. [f] Values vs. NHE in H_2O/1 M KCl, from ref. [4c]. [g] Anodic peak potential (irreversible wave due to adsorption); K_c calculated from peak potential difference. [h] Potentials vs. $[Fe(CN)_6]^{3-/4-}$. $E_{1/2}([Fe(CN)_6]^{3-/4-})$ = 0.17 V vs. SCE; $E_{1/2}$(ferrocene$^{+/0}$) = 0.16 V vs. SCE. [i] Poor solubility in electrolyte-free CH_2Cl_2.

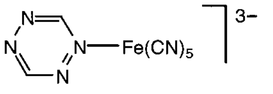
ing, more labile oxidation state **4**$^{4-}$ (Fe^{III}(tz)Fe^{III}) was studied after chemical oxidation.[7c] For comparison the mononuclear complex $(NEt_4)_3[(tz)Fe(CN)_5]$ (**5**) was also prepared and characterized.[8]



3^{5-}



4^{n-}



5^{3-}

The first remarkable result of these studies is the chemical stability of the mixed-valent complex $(NEt_4)_5$(**4**) in comparison to both the Fe^{II}(tz)Fe^{II} form (labile in aprotic media[7a]) and the Fe^{III}(tz)Fe^{III} form. The facile synthesis, high stability, and easy handling correlate with the enormous increase in K_c on going from the pz- to the tz-bridged system, that is, from $10^{1.9}$ to $10^{7.9}$ in water and from $10^{6.5}$ to $10^{19.0}$ in acetonitrile. Both the absolute values for K_c and the solvent dependence of K_c are extraordinary (Table 1); apparently, the presence of electrophilic (protic) components in corresponding solvents attenuates the capability of the strong π acceptor 1,2,4,5-tetrazine to mediate the iron–iron interaction over a distance of about 6.8 Å.[9] Hydrogen bonding to the "free" nitrogen atoms of the tetrazine and of the cyanide ligands is presumably responsible for this unusually strong effect. The additional factor of 10^5 in comparison to bis(tetracyanoiron) complexes of bis(chelating) tetrazine ligands[5, 10] is attributed to the lower charge and restricted orientation of the cyanometal moieties in the latter systems.

In the absorption spectra the iron(II)-containing tetrazine complexes exhibit intense metal-to-ligand charge transfer (MLCT) bands in the long-wavelength region. The intervalence charge transfer (IVCT) feature expected for a mixed-valent state occurs in the near IR range at 2520 nm in acetonitrile and at 2250 nm in aqueous solution (Figure 2).

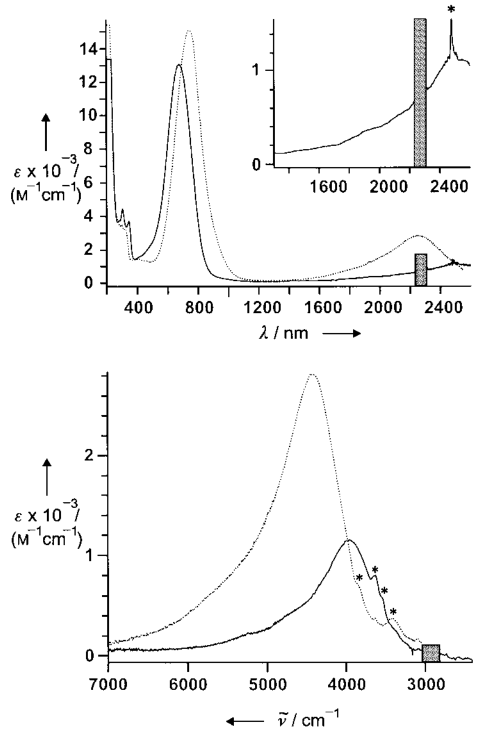


Figure 2. Absorption spectra of $(NEt_4)_5(\mathbf{4}) \cdot 2H_2O$ in CH_3CN (——) and in D_2O (••••). Solvent absorptions are marked (* and bars).

Remarkably, the intensity of the IVCT band is more than twice as large in D_2O (Table 1), while the bandwidth at half height remains virtually unchanged at about 900 cm^{-1}. This value is thus well below that of approximately 3200 cm^{-1} calculated by the Hush formula[11a,b] for weakly coupled mixed-valent centers. In other words, **4**$^{5-}$ is a strongly coupled mixed-valent system belonging to class III according to the classification of Robin and Day;[11c] the electronic interaction constant V_{AB} may thus be estimated[11b] at $\nu_{IVCT}/2 = 2220$ (D_2O) or 1980 cm^{-1} (CH_3CN).

The IR spectra exhibit only a limited number of discernible cyanide stretching features because of band overlap.[4, 5] The high-energy shift from **4**$^{6-}$ via **4**$^{5-}$ to **4**$^{4-}$ is as expected; the resolved band splitting of 9 cm^{-1} for the mixed-valent system does not signify valence localization but occurs similarly for the mononuclear iron(II) complex **5** (Table 1). Most importantly, there is no specific aromatic ring vibration band visible in the IR spectrum between 1500 and 1700 cm^{-1} for the mixed-valent state. This would indicate loss of inversion symmetry (nonzero dipole moment) and thus (partial) valence localization, as has been observed for pyrazine-bridged analogues.[5, 12]

The *g* factor component pattern of $(NEt_4)_5(\mathbf{4})$ in the EPR spectrum at $g = 2.531$, 2.422, and 1.794 is similar to the results observed for other $Fe^{II}(L)Fe^{III}$ systems.[5, 10, 13] This supports the formulation of a mixed-valent diiron complex with little direct participation of the ligands in the spin distribution.

By using 1,2,4,5-tetrazine as a superior π-acceptor bridging ligand, we have been able to obtain an unprecedentedly stable new cyanodiiron(2.5) coordination compound with an extraordinary solvent dependence[14]—a link between the numerous well-known ammineruthenium complexes[11b] and Prussian Blue.[1]

Received: May 11, 1999 [Z13405IE]
German version: *Angew. Chem.* **1999**, *111*, 3262–3264

Keywords: iron · mixed-valent compounds · N ligands · oxidation states

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[7] All synthetic operations were carried out under argon. a) $(NEt_4)_6(\mathbf{4})\cdot 2H_2O$: An aqueous solution of $Na_3[Fe(NH_3)(CN)_5]\cdot 3H_2O$ (536 mg, 1.64 mmol) was passed through a Dowex W50 column charged with NEt_4Cl. The eluate (ca. 100 mL) was added to a solution of 1,2,4,5-tetrazine (94 mg, 1.15 mmol) in water (30 mL). After 10 h at ambient temperature the solvent was removed and the residue purified by repeated chromatography (Sephadex LH 20, H_2O). The dark green solid obtained after removal of water was treated with acetone (25 mL) for 5 min in an ultrasonic bath. The undissolved solid was collected and dried under vacuum (230 mg, 18% $(NEt_4)_6(\mathbf{4})\cdot 2H_2O$). Elemental analysis calcd for $C_{60}H_{126}Fe_2N_{20}O_2$ (1271.51 $g\,mol^{-1}$): C 56.68, H 9.99, N 22.03; found: C 56.74, H 10.01, N 21.95%. The complex is stable in water but dissociates above −25°C in CH_3CN or CH_2Cl_2. ^1H NMR (D_2O): $\delta = 9.55$ (s); b) $(NEt_4)_5(\mathbf{4})\cdot 2H_2O$: $(NEt_4)_6(\mathbf{4})\cdot 2H_2O$ (50 mg, 0.039 mmol) was dissolved at −36°C in acetonitrile (50 mL). A solution of *p*-(*N*,*N*-dimethylamino)benzenediazonium hexafluorophosphate (12.7 mg, 0.043 mmol) in cold acetonitrile (−30°C, 20 mL) was added, and the resulting mixture stirred for 15 min at −36°C. After removal of the solvent the residue was treated with acetone (20 mL) in an ultrasonic bath at room temperature. The solid residue was treated once more with acetone (20 mL) to yield a colorless solution and a dark blue residue, which was collected and dried under vacuum (40 mg, 90% $(NEt_4)_5(\mathbf{4})\cdot 2H_2O$). Elemental analysis calcd for $C_{52}H_{106}Fe_2N_{19}O_2$ (1141.25 $g\,mol^{-1}$): C 54.73, H 9.36, N 23.32; found: C 54.33, H 9.22, N 23.13%. The complex is stable in air as a solid and in solution, both in water and aprotic solvents. EPR (CH_3CN, 4 K): $g_1 = 2.531$, $g_2 = 2.422$, $g_3 = 1.794$. c) $(NEt_4)_4(\mathbf{4})$: $(NEt_4)_6(\mathbf{4})\cdot 2H_2O$ (6.1 mg, 4.8 μmol) was dissolved at −36°C in acetonitrile (5 mL). A solution of *p*-fluorobenzenediazonium hexafluorophosphate (3.6 mg, 13.4 μmol) in cold acetonitrile (−30°C, 1.1 mL) was added. This mixture was then rapidly transferred to a cooled (−42°C) cuvette for spectroscopic measurement. Temperatures higher than −30°C resulted in dissociation with formation of free tetrazine.

[8] $(NEt_4)_3(\mathbf{5})\cdot 2H_2O$: $(NEt_4)_6(\mathbf{4})\cdot 2H_2O$ (50 mg, 0.039 mmol) dissolved under dissociation in acetonitrile (60 mL). Addition of solid NEt_4CN (10 mg, 0.064 mmol), removal of the solvent, and repeated chromatography on Sephadex LH20 in water yielded a dark blue powder which was treated with acetone (10 mL) in an ultrasonic bath at room temperature. The solid residue was dried under vacuum (8 mg, 30% $(NEt_4)_3(\mathbf{5})\cdot 2H_2O$). Elemental analysis calcd for $C_{31}H_{66}FeN_{12}O_2$ (694.80 $g\,mol^{-1}$): C 53.59, H 9.58, N 24.19; found: C 53.28, H 9.28, N 23.04%. The complex is stable in air as a solid and in solution, both in water and aprotic solvents. ^1H NMR (D_2O): $\delta = 10.25$ (d, 1H), 9.18 (d, 1H); $J = 2.6$ Hz.

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Conversion of Molecular Oxygen into a Hydroperoxo Species by Ring-Opening Protonation of a Cyclic η^2-Peroxo Intermediate: Characterization of the η^2-Peroxo and Hydroperoxo Complexes[**]

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Transition metal–dioxygen species are key intermediates in catalytic oxygenation reactions such as synthetic and metabolic transformations.[1] Since the oxygen atoms of cyclic

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[**] We are grateful to the Ministry of Education, Science, Sports, and Culture of the Japanese Government for financial support of this research (Grant-in Aid for Scientific Research).