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EPR Evidence for Low-Lying MLCT States in Tetracyanoiron and -ruthenium Complexes with Strongly π-Accepting Chelate Ligands. Comparison with Isoelectronic Tetracarbonylmetal Species

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The complex ions $[(bpz)M(CN)_4]^{2-}$ (M = Fe, Ru) and $[(abpy)Fe(CN)_4]^{2-}$ with the strongly π-accepting chelate ligands 2,2′-bipyrazine (bpz) and 2,2′-azobis(pyridine) (abpy) were prepared as potassium or tetrabutylammonium salts and were characterized by IR and UV/vis absorption spectroscopy. Cyclic voltammetry in acetonitrile, DMF, or water revealed reversible one-electron oxidation processes, while the reduction waves showed reversibility only in aprotic solvents. EPR studies of the spectroelectrochemically generated (1−) and (3−) states confirm the MLCT formulation for the lowest excited states of the (2−) precursor complexes by showing typical low-spin Fe(III) signals of the oxidized species $[(abpy)Fe(CN)_4]^-$ and partially hyperfine-structured spectra for the reduced forms $[(bpz)M(CN)_4]^{3-}$. The latter are clearly tetracyanoiron(II) or -ruthenium(II) complexes of the corresponding anion radical acceptor ligands and are thus isoelectronic with monoanionic tetracarbonylchromium(0) or -molybdenum(0) radical complexes.

Although low-lying metal-to-ligand charge-transfer (MLCT) excited states of complexes between π acceptor ligands and electron-rich metal centers have frequently been invoked in order to interpret photochemical and photophysical properties,[1,2] the direct observation of such states by excited-state spectroscopy (UV/vis, resonance Raman) has not been all too common. One such reported[3] example has been $[(bpy)Fe(CN)_4]^{2-}$, which is also well-known for its pronounced solvatochromism.[4]

Indirect evidence for the presence of an MLCT state as lowest excited state can come from EPR spectroelectrochemistry. In a one-electron approximation, the singly oxidized form of an even-electron complex has the unpaired electron in the highest occupied molecular orbital (HOMO) of the precursor, i.e. the orbital from which the electron gets most easily excited, whereas the reduced form of the complex contains an electron in the lowest unoccupied MO (LUMO) of the precursor, i.e. the lowest-lying MO to which an excitation can occur. If reversible one-electron oxidation and reduction are possible and the EPR spectra of the paramagnetic neighboring ionization states reveal a metal oxidation and an acceptor ligand reduction, respectively, the existence of a low-lying MLCT excited state (MLCT1) is very likely. While this approach has often been used to study organometallic species[5,6] or (amine)ruthenium(II) complexes of α-diimines and similar π acceptor ligands,[7−9] we report here the first such study for iron(II) complexes $[(N^\frown N)Fe(CN)_4]^{2-}$. Equations 1−3 illustrate the optical and electrochemical electron transfer processes for the type of complex discussed in this work.

$$[(N^\frown N)M^{II}(CN)_4]^{2-} \xrightarrow[\text{MLCT1}]{h\nu} {}^*[(N^\frown N^{-I})M^{III}(CN)_4]^{2-} \quad (1)$$

$$[(N^\frown N)M^{II}(CN)_4]^{2-} \xrightarrow{-e^-} [(N^\frown N)M^{III}(CN)_4]^{-} \quad (2)$$

$$[(N^\frown N)M^{II}(CN)_4]^{2-} \xrightarrow{+e^-} [(N^\frown N^{-I})M^{II}(CN)_4]^{3-} \quad (3)$$

As acceptor ligands $N^\frown N$, we used 2,2′-bipyrazine (bpz)[10,11] and 2,2′-azobis(pyridine) (abpy)[12,13] which, in comparison to bpy, have lower lying π^* acceptor orbitals and higher orbital coefficients at the coordinating nitrogen centers. These ligand properties do not only serve to lower the MLCT excited state; they also ensure strong metal/ligand interaction and thus improve, *inter alia*, the resolution of the EPR spectra of reduced forms.[14,15] For comparison with the tetracyanoiron complexes, we also studied one ruthenium analogue, $[(bpz)Ru(CN)_4]^{2-}$; the dinuclear compound $\{(\mu\text{-abpy})[Fe(CN)_4]_2\}^{4-}$ could not be obtained in the absence of the mononuclear complex.

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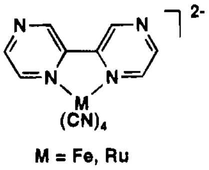

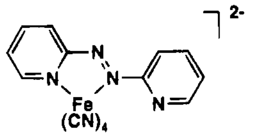

Considering the isoelectronic relation between complex fragments $[M(CN)_4]^{2-}$ (M = Fe, Ru) and $M(CO)_4$ (M = Cr, Mo), we shall compare the results obtained here with the observations reported for corresponding tetracarbonylmetal(0) systems.[11,13,16]

Experimental Section

Materials. Aprotic solvents were rigorously dried and freshly distilled before use. The commercially not available ligand abpy was prepared according to published procedures.[13]

Syntheses. The tetracyanoiron complexes were obtained via a modification of an established route[17] by reacting equimolar amounts of $FeCl_2$ and the chelate ligand under an argon atmosphere in methanol/water (1/1) for about 1 h. After addition of 4 equiv of KCN the mixture is refluxed for 8 h and filtered, and most of the methanol solvent is evaporated from the filtrate. From the clear solution the product is first precipitated with acetone and filtered and then redissolved in water, reprecipitated with ethanol, and dried under vacuum. The complexes gave satisfactory analyses (C, H, N) and were characterized by cyanide stretching bands in the IR (KBr pellets): 2094 (m), 2073 (s), 2065 (s), 2026 (w) cm^{-1} for $K_2[(bpz)Fe(CN)_4]$;[17] 2089 (vs) cm^{-1} for $K_2[(abpy)Fe(CN)_4]$. The latter complex showed ν(CN) 2092 cm^{-1} in acetonitrile/18-crown-6 solution. Ion-exchange with tetrakis(*n*-butyl)ammonium chloride in water on SP-Sephadex C-25 yields the corresponding salts $(Bu_4N)_2[(N^\frown N)Fe(CN)_4]$.

The ruthenium(II) analogue $(Bu_4N)_2[(bpz)Ru(CN)_4]$ was prepared as described in ref 18. IR (KBr): 2101 (m), 2072 (s), 2060 (s), 2050 (w, sh) cm^{-1}.

Instrumentation. EPR spectra were recorded in the X band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. Infrared spectra were obtained using Perkin-Elmer 983 G and 684 instruments. UV/vis/near-IR absorption spectra were recorded on Shimadzu UV160 and Bruins Instruments Omega 10 spectrophotometers. Cyclic voltammetry was carried out in 1,2-dichloroethane/0.1 M Bu_4NPF_6 using a three-electrode configuration (glassy carbon working electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. EPR spectroelectrochemical measurements were performed using a two-electrode capillary.[8]

Results and Discussion

The mononuclear complexes were obtained as potassium salts which were soluble in water and could be solubilized in DMF for measurements by adding the K^+-complexing crown ether 18-crown-6. Typically, the abpy ligand produced predominantly the mononuclear complex because the dinuclear abpy complex would involve rotation of the noncoordinated 2-pyridyl ring into a very unfavorable conformation.[13,16]

While both bpz complexes exhibit the expected four IR-active cyanide stretching bands, if only split by about 60 cm^{-1}, the tetracyanoiron(II) complex of abpy shows only one such band in KBr (see Experimental Section). This result indicates a virtual coincidence of the four bands expected from formal symmetry considerations, suggesting practically equivalent ligand effects from the cyanide ions and the η^2-abpy ligand and thus "spectroscopic O_h symmetry". This result stands in contrast to the observations made for corresponding tetracarbonylmetal complexes where such effects are not nearly as pronounced.[13]

Table 1. Spectroscopic[a] and Electrochemical Data[b] for Isoelectronic Complexes of 2,2′-Bipyrazine

	$[(bpz)M(CN)_4]^{2-}$ [d]		$(bpz)M(CO)_4$ [d,e]	
	M = Fe	M = Ru	M = Cr	M = Mo
λ_{max}(MLCT1)	736 (580[c])	601 (554[c])	549	509
λ_{max}(MLCT2)	506 (413[c])	433 (405[c])	390 (in THF)	378 (in THF)
E_{red}	−1.54	−1.48	−1.09	−0.89
E_{ox}	+0.13	+0.50	+0.68	+0.90 (pa)
$\Delta E = E_{ox} - E_{red}$	1.67	1.98	1.77	

[a] Wavelengths λ in nm at the absorption maxima. [b] Potentials in V vs Ag/AgCl (cyanides) or SCE (carbonyl complexes) from cyclic voltammetry at 100 mV/s scan rate. The SCE reference has a value of +0.02 V vs the Ag/AgCl electrode. pa: anodic peak potential for an irreversible process. [c] In acetonitrile. [d] In DMF. [e] From refs 11 and 19a.

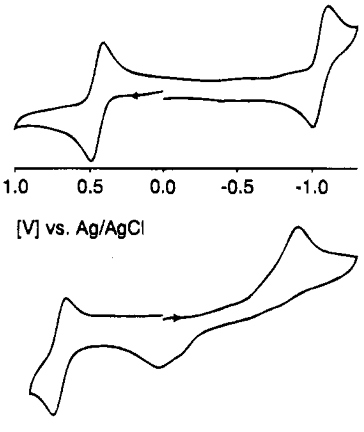

Figure 1. Cyclic voltammograms of $K_2[(abpy)Fe(CN)_4]$ at 100 mV/s scane rate: (Top) in DMF/0.1 M Bu_4NPF_6, potentials at +0.46 V (oxidation) and −1.06 V (reduction) vs Ag/AgCl; (bottom) in water at pH 6.82 (phosphate buffer), oxidation at +0.70 V.

In addition to the characteristic ν(CN) bands in the vibrational spectra the compounds show intense and very solvatochromic[3,4] long-wavelength absorptions in the visible region (Table 1). The absorption maxima are similar to those of corresponding complexes with $M(CO)_4$ (M = Cr, Mo)[11,13,19a] or $[Ru(bpy)_2]^{2+}$,[19b] which further indicates the MLCT nature of the responsible transitions. The complex ion $[(abpy)Fe(CN)_4]^{2-}$ has λ_{max} 590 nm (in acetonitrile) or 575 nm (in water); for complexes $[(bpz)M(CN)_4]^{2-}$ which display two MLCT transitions to the π_1*(LUMO) and π_2*(SLUMO) orbitals of bpz in the visible, see Table 1.

In comparison to the iron analogue the complex $[(bpz)Ru(CN)_4]^{2-}$ exhibits an MLCT absorption at shorter wavelengths (Table 1) which is interpreted as an effect of the stabilized d(t_{2g}) orbital set; electrochemical results in comparison with data for isoelectronic tetracarbonylmetal analogues confirm this notion.

Cyclic Voltammetry. In aprotic media the complexes $[(bpz)M(CN)_4]^{2-}$ (M = Fe, Ru) and $[(abpy)Fe(CN)_4]^{2-}$ exhibit reversible oxidation and reduction waves (Figure 1; Table 1).

Whereas the oxidation processes for the iron(II) complexes occur at rather low potentials, the negative charge of the compounds causes a considerable cathodic shift of the reduction potentials which thus lie close to the values of the corresponding free ligands.[11,13] In aqueous solutions it is only possible to observe oxidations as reversible processes; the reduction shows the typical strong shift of the anodic wave ($\overrightarrow{E}C\overleftarrow{E}$ process,

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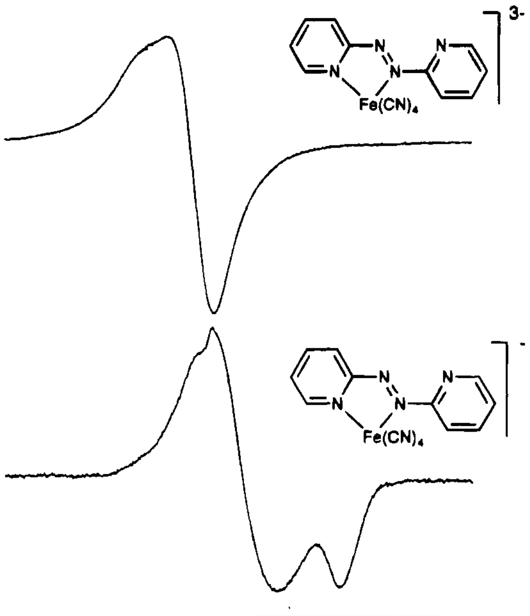

Figure 2. EPR spectra in glassy frozen solutions (110 K) of electrogenerated $[(\text{abpy})\text{Fe}(\text{CN})_4]^{n-}$ in DMF/0.1 Bu_4NPF_6: (Top) n = 3; g components at 2.016 ($g_\|$) and 2.0047 ($g_\perp$); (bottom) n = 1; g components at 2.002, 1.9925, and 1.9680.

reduction–chemical step–oxidation; see Figure 1) which results from protonation of electrogenerated ligand-reduced forms by the solvent.[20]

It is not surprising that the mononuclear complex $[(\text{abpy})\text{Fe}(\text{CN})_4]^{2-}$ with the better π-accepting ligand abpy shows a less negative reduction potential and a more positive oxidation potential than the analogous complex of bpz (Figure 1; Table 1). Within the series of complexes $[(\text{bpz})\text{M}(\text{CN})_4]^{2-}$, the ruthenium analogue of the iron complex is slightly easier to reduce but distinctly harder to oxidize which produces a larger difference ΔE between the potentials of reversible oxidation and reduction. Those differences ΔE (in V) correspond to the energies (in eV) of the long-wavelength MLCT bands according to the relation (4), in which the values χ represent the combined contributions from intra- and intermolecular reorganization energies.[11,21,22]

$$E_{\text{op}}(\text{MLCT1})\ (\text{eV}) = \Delta E\ (\text{V}) + \chi \tag{4}$$

In comparison with the neutral tetracarbonylmetal complexes, the isoelectronic but dianionic tetracyanometal species are easier to oxidize but harder to reduce. Since both effects amount to approximately 0.5 V, the results are little changed ΔE values and quite similar absorption energies (Table 1).

EPR Spectroscopy. Figure 2 shows the EPR spectra of the one-electron oxidized and reduced forms of $[(\text{abpy})\text{Fe}(\text{CN})_4]^{2-}$. While there is no ligand hyperfine structure visible at room temperature for the (3−) ion, the g factor of 2.0085 and its small axial anisotropy in glassy frozen solution clearly indicate π ligand-centered spin, i.e. an anion radical complex[23] according to (3). The (1−) ion, on the other hand, shows a greater (rhombic) g anisotropy (Figure 2) with an average g < 2 which is typical for low-spin Fe(III).[24]

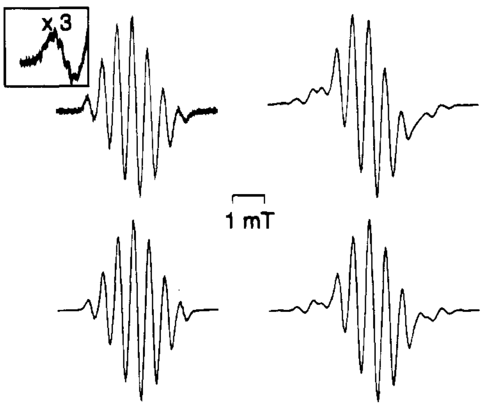

Figure 3. EPR spectra of electrogenerated radical complexes $[(\text{bpz})\text{M}(\text{CN})_4]^{3-}$, M = Fe (top left, with enlarged last line at high resolution) and M = Ru (top right) with respective computer simulations (bottom left and right). Room-temperature spectra were measured in MeCN/0.1 M Bu_4NPF_6.

Table 2. EPR Data for the 2,2′-Bipyrazine Radical Anion and Its Isoelectronic Complexes

	$[(\text{bpz})\text{M}(\text{CN})_4]^{3-}$		$[(\text{bpz})\text{M}(\text{CO})_4]-$ [b]		
	M = Fe	M = Ru	M = Cr	M = Mo	$\text{bpz}^{-\bullet}$ [b]
g	1.9965	1.9934	2.0024	2.0026	2.0033
a_M	n.o.	0.514 (^{101}Ru)[c] 0.458 (^{99}Ru)	n.o.	0.22 (^{95,97}Mo)[d]	
a_M/A_iso[e]		0.0074		0.0030	
$a_\text{N}(\text{N}^{1,1'})$	0.51	0.49	0.482	0.468	0.370
$a_\text{H}(\text{H}^{3,3'})$	0.06	n.o.	0.044	0.033	0.012
$a_\text{N}(\text{N}^{4,4'})$	0.06	n.o.	0.093	0.101	0.100
$a_\text{H}(\text{H}^{5,5'})$	0.43	0.49	0.469	0.452	0.480
$a_\text{H}(\text{H}^{6,6'})$	0.06	n.o.	0.020	0.016	0.020

[a] Coupling constants a in mT. [b] From ref 15. [c] ^{99}Ru: 12.8% natural abundance, $I = {}^5/_2$. ^{101}Ru: 17.0%, $I = {}^5/_2$. [d] ^{95}Mo: 15.8% natural abundance, $I = {}^5/_2$. ^{97}Mo: 9.6%, $I = {}^5/_2$. [e] A_iso values from ref 24.

The reduced forms of both bpz complexes presented here are clearly anion radical complexes[23] according to (3), as evident from high spectral resolution at room temperature in solution (Figure 3), ligand-based hyperfine splitting, small metal isotope coupling, and g factors close to the free electron value of 2.0023. Computer-simulated spectra are shown in Figure 3; Table 2 summarizes the data and puts them in comparison to those of isoelectronic anion radical complexes $[(\text{bpz})\text{M}(\text{CO})_4]^-$ (M = Cr, Mo).[14]

The typical presence of only two large coupling constants at $\text{N}^{1,1'}$ and $\text{H}^{5,5'}$ favors the EPR resolution of $\text{bpz}^{-\bullet}$ and its complexes;[14] furthermore, the large π spin population at the coordinating nitrogen centers allows for relatively large metal isotope hyperfine splitting.[14,15] In fact, the EPR spectrum (Figure 3) of electrogenerated $[(\text{bpz})\text{Ru}(\text{CN})_4]^{3-}$ shows clear coupling from the ^{99,101}Ru isotopes ($I = {}^5/_2$) in natural abundance (Table 2) while the magnetic moment and natural abundance (2.2%) of ^{57}Fe ($I = {}^1/_2$) are too low to detect a metal isotope coupling.[25] However, the iron(II) radical complex shows better resolved lines which allowed us to observe coupling with the centers $\text{H}^{3,3'}$, $\text{N}^{4,4'}$, and $\text{H}^{6,6'}$ in the expected range.[14] Additional hyperfine splitting due to the ^{14}N nuclei in the axial or equatorial cyano ligands is not observed and must be smaller than 0.02 mT.

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While the ^1H and ^{14}N hyperfine data in Table 2 clearly show that the π^* orbital of bpz is primarily occupied in all four complexes with little spin delocalization to the ancillary cyano ligands, the characteristic deviations of the g factors and the available metal isotope splitting parameters for the 4d species allowed us to gain further insight into the electronic structures. In relation to the isotropic hyperfine coupling constant A_{iso},[24] the observed ruthenium coupling is much larger than the molybdenum satellite splitting in $[(bpz)Mo(CO)_4]^{-\bullet}$. This result probably reflects a higher degree of metal/ligand orbital mixing ($4d/\pi^*$) for the complex with the higher valent metal. Similarly, the decrease of g from the value of 2.0033 for the free ligand radical anion is far greater for the tetracyanometalate complexes than for both tetracarbonylmetal(0) compounds. Again, the largest such deviation for the Ru(II) complex reflects considerable orbital mixing; similar effects were noted previously e.g. for $[(bpz)Ru(bpy)_2]^+$ ($g = 1.9910$)[8] because of the high atomic orbital coefficients at the chelating nitrogen atoms in that particular π^*(bpz) orbital.[8,11,14] These results thus add to the available EPR evidence[7,8,9,20,26] for a particular strong interaction between Ru(II) d orbitals and π^* MOs of unsaturated N-heterocyclic acceptor ligands.

The direction of the deviation of g to lower values $g < 2.00$ for both tetracyanometalate radical complexes reveals contributions from low-lying excited states with nonzero angular orbital momentum. Such states could involve the cyanide ligands or simply ligand-field (d−d) excited configurations.[27] In view of the much larger spin−orbit coupling constant of Ru(II) (990 cm^{-1}) relative to Fe(II) (400 cm^{-1})[24] the low g factor of $[(bpz)Fe(CN)_4]^{3-}$ suggests particularly close-lying such levels which supports the notion of low-lying non-charge-transfer excited states for α-diimine complexes of iron(II).[3,28,29]

In contrast to the complexes of $bpz^{-\bullet}$ the trianion $[(abpy)Fe(CN)_4]^{3-}$ ($g = 2.0038$) does not exhibit a lowered g factor. In agreement with MO calculations,[13] measured redox potentials (Figure 1; Table 1) and previous observations on $bpz^{-\bullet}$ and $abpy^{-\bullet}$ complexes with the $[Ru(bpy)_2]^{2+}$ fragment[2,8] this effect is due to a much lowered π^* orbital of the abpy ligand which stabilizes the reduced state and thus moves it away from excited states which involve e.g. the $d(e_g)$ orbitals.

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