Valence delocalisation in a strongly coupled (K_c = 10^{14}) molecule-bridged cyanodiiron(III,II) species

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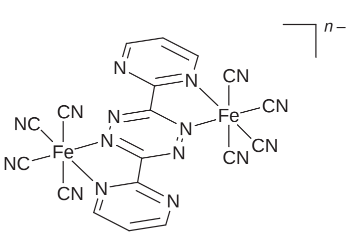
A hybrid between the Prussian Blue and Creutz–Taube mixed valent species is presented in the form of the bmtz-bridged bis[tetracyanoiron(+2.5)] complex 1^{3-} [bmtz = 3,6-bis(2-pyrimidyl)-1,2,4,5-tetrazine] which exhibits a very large comproportionation constant of 10^{14} and a delocalised structure, according to UV–VIS–NIR–IR spectroelectrochemistry in acetonitrile solution.

Mixed-valent compounds with electron transfer sites of similar or identical composition have become the focus of research for a number of reasons.[1–3] These include their function in biochemical systems,[1a] their model character for inner-sphere electron transfer,[1b,c] their special spectroscopic or other physical properties,[1d] their potential in 'molecular electronics'[1e] and their role as test systems for theory.[1d,f] Among the best known such mixed-valent coordination compounds are the cyanoferrate(III,II) species[2] Prussian Blue $Fe^{III}_4[Fe^{II}(CN)_6]_3$ and the molecule-bridged dinuclear Creutz–Taube ion $[(H_3N)_5Ru(\mu\text{-pz})Ru(NH_3)_5]^{5+}$ (pz = pyrazine) with delocalised valencies of +2.5 for the equivalent metal centres.[1b,c,3] Although molecule-bridged diiron(III,II) species have been reported with various comproportionation constants K_c,[4] cyanoiron compounds like $[(NC)_5Fe(\mu\text{-pz})Fe(CN)_5]^{5-}$ or $[(NC)_4Fe(\mu,\eta^4\text{-bpym})Fe(CN)_4]^{3-}$, bpym = 2,2′-bipyrimidine, showed only small values $K_c < 10^3$ in aqueous media and thus weak metal–metal interaction.[5]

$$K_c = 10^{\Delta E/59\,\text{mV}} = [M^{(n-1)}]^2/[M^n][M^{(n-2)}] \qquad (1)$$
$$M^n + M^{(n-2)} \rightleftharpoons 2\,M^{(n-1)}$$

In the course of exploring the potentially tetrafunctional ligand bmtz [3,6-bis(2-pyrimidyl)-1,2,4,5-tetrazine][6] we discovered that the ligand can serve as an efficient bridge for promoting metal–metal interactions. The diruthenium compound $[(bpy)_2Ru(\mu,\eta^4\text{-bmtz})Ru(bpy)_2]^{5+}$ [6] and the related $[(H_3N)_4Ru(\mu,\eta^4\text{-bptz})Ru(NH_3)_4]^{5+}$ [7] showed unusually large K_c values of $>10^{10}$ and $10^{15.0}$, respectively. Reacting bmtz with $FeCl_2$ and $[NEt_4]CN$‡,§ we have now found that the resulting redox system $[(NC)_4Fe(\mu,\eta^4\text{-bmtz})Fe(CN)_4]^{n-}$ 1^{n-} exhibits a diiron(III,II) state (n = 3) with an enormous stability constant K_c and delocalised vacancies.



In MeCN–0.1 M $[NBu_4]PF_6$ the redox system 1^{n-} exhibits four reversible one-electron waves between the n = 6 and n = 2 oxidation states at −1.92, −1.41, −0.32 and +0.52 V *vs.* Fc–Fc$^+$. The paramagnetic intermediate states with n = 3 ($K_c = 10^{14.1}$) and n = 5 ($K_c = 10^{8.7}$) could be characterised by EPR after *in situ* electrolytic generation from the diiron(II) precursor (n = 4).[8] Whereas the reduced form clearly shows a ligand-centered radical species at g = 1.998,[6–9] the oxidation produces an EPR signal with g components at 2.57, 2.44 and 1.78 in frozen acetonitrile solution. This result points to a metal-based oxidation process, implying the formation of a mixed-valent species.[1a,4] The corresponding data for the Creutz–Taube ion showed a similar splitting of g components at 2.799, 2.489 and 1.346,[10] the larger g anisotropy resulting from higher spin–orbit coupling effects from the heavier element (Ru *vs.* Fe).

Electronic absorption spectra of the n = 3, 4, 5 forms were obtained by spectroelectrochemistry in MeCN–0.1 M $[NBu_4]PF_6$, the isolated n = 4‡ and 3§ forms could also be studied separately. The intense (ε = 19 840 dm^3 mol^{-1} cm^{-1}) metal-to-ligand charge transfer (MLCT) band at 831 nm of the diiron(II) form is shifted to higher energy, both on reduction and oxidation (Fig. 1). Oxidation to the mixed-valent state produces an asymmetrical intervalence charge transfer (IVCT) transition at 2245 nm. While the corresponding energy of 4450 cm^{-1} suggests weaker metal–metal interaction than in the Creutz–Taube ion,[3] the low intensity at ε = 750 dm^3 mol^{-1} cm^{-1} reflects the bis-chelate nature of the system with a chelate-enforced orientation unfavourable for orbital overlap. It was shown previously[7,11] that the IVCT features in dinuclear complexes with related bis(bidentate) bridging ligands exhibit very low-intensity IVCT bands in spite of large comproportionation constants K_c.

The question of localisation or delocalisation in mixed-valent complexes in solution may be most elegantly answered by vibrational spectroscopy.[12,13] On the corresponding time scale of about 10^{-12} s the appearance of averaged bands in relation to the neighbouring oxidation states suggests delocalisation whereas the appearance of separate or broadened features indicates localisation. The redox system 1^{n-} was thus studied in the cyanide stretching region for n = 3, 4 and 5 (Fig. 2). The direction of shifts of the typically single band (very close A_1, B_1 and B_2 features) corresponds to charge alteration,[11–13] however, the oxidation to a metal-based mixed-valent species and the

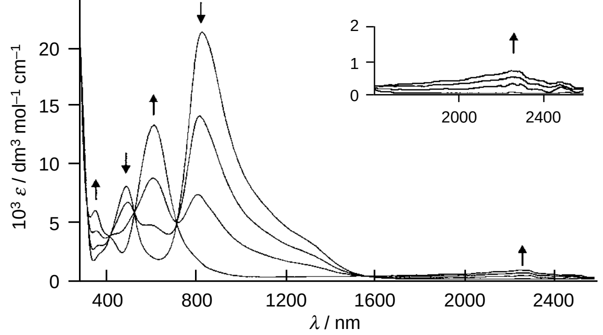


Fig. 1 UV–VIS–NIR spectroelectrochemical response of the 1^{4-} ion (831 and 489 nm) on one-electron oxidation (2245, 613 and 354 nm) in MeCN–0.1 M $[NBu_4]PF_6$

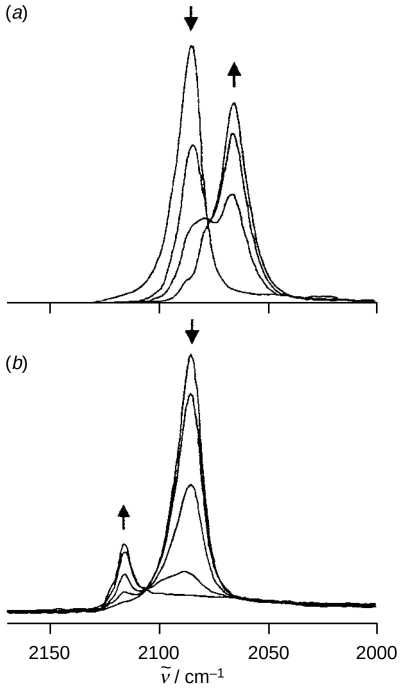


Fig. 2 IR-spectroelectrochemical response of the $\mathbf{1}^{4-}$ ion (ν_{CN} = 2085 cm^{-1}) on one-electron reduction (*a*) (2064 cm^{-1}) and oxidation (*b*) (2116 cm^{-1}) in MeCN–0.1 M $[NBu_4]PF_6$

reduction to a ligand-centered radical complex produce rather similar amounts of high- and low-energy shifts, respectively. As noted previously,[11] such band energy differences are thus not suitable to unambiguously clarify the site of electron addition or removal. However, the appearance of only one albeit intensity-diminished CN stretching band at an intermediate value after one-electron oxidation clearly confirms the delocalised nature of the mixed-valent $Fe_2^{2,5}$ species $\mathbf{1}^{3-}$ in agreement with the very large K_c value and the relatively narrow IVCT band ($\Delta\nu_{\frac{1}{2}}$ = 1200 cm^{-1}). Further studies of this and related systems will also focus on the solid state properties of such materials.

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Notes and References

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‡ A solution of 940 mg (6.0 mmol) $[NEt_4]CN$ in 50 ml MeOH was slowly added to a mixture containing 60 mg (0.25 mmol) bmtz[6] and 190 mg (1.5 mmol) $FeCl_2$ in 50 ml MeOH. After completion of the reaction the green solution was concentrated and the product precipitated by adding acetone and diethyl ether. Recrystallization from EtOH–Et_2O–acetone (1 : 6 : 3) yielded 35% of $[NEt_4{}^+]_4$ $[\mathbf{1}^{4-}]$ as black microcrystals. Correct C, H, N analysis; ^{1}H NMR (CD_3OD): δ 9.67 (dd, H^4), 7.56 (dd, H^5), 8.93 (dd, H^6). UV–VIS (MeCN): λ_{max} = 831 nm (ε = 19 840 dm^3 mol^{-1} cm^{-1}).

§ 50 mg (0.05 mmol) of $[NEt_4{}^+]_4[\mathbf{1}^{4-}]$ were oxidized electrolytically at a platinum electrode in MeCN–0.1 M $[NBu_4]PF_6$. The reaction was monitored by UV–VIS spectroscopy. Precipitation with diethyl ether and washing twice with THF yielded 10 mg (12%) of deep blue $[NBu_4{}^+]_3[\mathbf{1}^{3-}]$, identified *via* EPR, IR and UV–VIS–NIR spectroscopy.

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