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Review

Magnetic perturbation of the redox potentials of localized and delocalized mixed-valence complexes

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Abstract

The potential differences (ΔE) between the two one-electron events observed for symmetrical mixed-valence (MV) complexes is generally used as a measurement of the thermodynamic stability of the MV state and often extended to the evaluation of the strength of the coupling between the redox centers through the bridge. In this review article, selected examples illustrate how the ΔE values to assess the degree of electronic communication between metals must be approached very judiciously. The role of the magnetic exchange which can take place between the unpaired spins carried by the redox sites in the doubly oxidized complexes is emphasized.
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Keywords: Mixed-valence; Metal–metal coupling; Magnetic exchange; Comproportionation energy

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1. Introduction and background

In the emerging field of molecular electronics, polynuclear carbon-rich complexes featuring the electron-rich and redox-active organometallics endgroups [1–3] constitute very appealing materials for information storage and processing at the molecular level [4–18]. From this point of view the understanding of electron transfer over nanometric distances in a single molecule constitutes an important objective. Accordingly, this area is the center of active research from various groups involved in carbon-rich organometallics over the world [19–23]. Redox molecular wires with a symmetric bridge and two identical electroactive termini present a simple construction (see Fig. 1). When the remote ends possess different redox states (the donor and the acceptor sites), an odd electron-containing species or mixed-valence (MV) compound is generated

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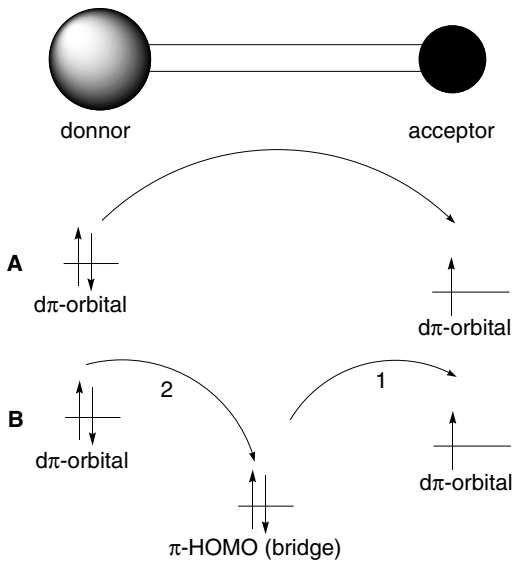


Fig. 1. Schematic representation of the two-level and three-level models for intramolecular ET.

and a wealth of information about through-bridge electron transfer can be gained by the study of such a species [24,25].

Such compounds were initially characterized experimentally by Creutz and Taube in 1969 [26]. They present an intervalence charge transfer (ICT) band characteristic of the optically induced intramolecular electron transfer in the NIR spectral domain which is absent in the spectra of the reduced and oxidized states [27,28]. Depending on the delocalization of the unpaired electron over both capping redox sites, a classification has been proposed by Robin and Day [29]. A MV compound belongs to class-I if the valence is totally localized, i.e. no through-bridge electron exchange between metal centers occurs and no ICT band can be observed. It belongs to class-III if the electron is fully delocalized, i.e. no available spectroscopy is able to discriminate the metal centers. Finally, it belongs to class-II in other cases, i.e. at least one spectroscopy is able to distinguish one site from the other while an ICT band is present [29–31]. In our work on dinuclear MV complexes where two "(η^2-dppe)(η^5-C_5Me_5)Fe–C≡C" units are connected by a carbon rich spacer, a high consistency of the experimental data justified *a posteriori* the use of the two-level model (mechanism **A**, Fig. 1) to interpret experimental data for both strongly coupled class III and weakly coupled class II complexes [32]. For other systems, the three-level model involving two sequential electron transfers proposed by Creutz, Newton and Sutin (often call the CNS model, mechanism B, Fig. 1) was found to be more powerful to rationalize the experimental data [33,34]. In the following, the so-called Hush model (or two-level model) will be applied.

Whatever the model, to evaluate the metal–metal coupling, an experimental measure of metal–metal coupling is needed. For a MV complex, this measure is provided by the free energy of comproportionation, ΔG_c, according to the comproportionation equilibrium, that also defines the comproportionation constant, K_c (Eq. (1)). ΔG_c may be determined electrochemically by using cyclic voltammetry, where the difference between metal centered redox couple potentials are E_1 and E_2 [30]. Often, cyclic voltammetry (CV) with the most stable redox state usually constitutes the easiest way to look at the electronic interaction between the remote electroactive termini. With symmetrical compounds, in the case of a sufficiently strong interaction, two one-electron events should be observed. The potential difference (ΔE) between the two waves is representative of the thermodynamic stability of the corresponding MV state relative to the other redox states and its comproportionation constant K_c can be computed using Eq. (2). Alternatively, when there is no, or negligible, communication, only a single redox event is observed. It is important to keep in mind that a single redox event which results from a small ΔE is not diagnostic of negligible communication. For example, recent some works has shown significant communication without a resolved separation between the redox processes [35,32]. In such cases, whenever possible, K_c has to be determined by other means, such as spectrometric titration [36,37]. In the case of a single two-electron wave, as observed for **12** (see below), the two standard potentials can also be derived from the location of the midpoint between the anodic and cathodic peaks and the distance between them (ΔE_p), provided the kinetics of the electron-transfer processes do not affect the cyclic voltammetric response [32]

$$\{[M^{red}]\text{–B–}[M^{red}]\}^{n+} + \{[M^{ox}]\text{–B–}[M^{ox}]\}^{(n+2)+} \overset{K_c}{\rightleftharpoons} 2\{[M^{red}]\text{–B–}[M^{ox}]\}^{(n+1)+} \quad (1)$$

$$\Delta G_c = \Delta E = E_2 - E_1 = -(RT/F)\log K_c \quad (2)$$

The magnitude of K_c (and ΔG_c) is determined by the sum of all energetic factors relating to the stability of the reactant and product complexes. According to Sutton, Richarson and Taube, four distinct factors mainly contribute to the magnitude of ΔG_c [36,38,39,30]. Recently, in depth analysis of the energetic of mixed-valence systems has been reviewed [40].

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r \quad (3)$$

In Eq. (3), ΔG_s is the entropic factor which represents the statistical distribution of the comproportionation equilibrium ($\Delta G_s = 0.5RT\ln 1/4$), ΔG_e is the electrostatic force factor which reflects the repulsion between charged and linked redox centers, ΔG_i is an inductive factor dealing with the stabilization of the MV by electron polarization, back-bonding, etc, and ΔG_r accounts for the free energy of resonance exchange. This latter parameter is the only component of ΔG_c which is connected with the metal–metal coupling. In the case of class II MV, the term $\Delta G_r(\Delta G_r = H_{DA}^2/\lambda)$ is weak, but it become the dominant parameter for class III MV ($\Delta G_r = 1/2\ \nu_{max}$) [30].

Sutton and Crutchley recognized early the need for an additional term when magnetic exchange take place

between the unpaired electrons carried by the doubly oxidized complex (ΔG_{ST}) [34]. More recently, Geiger point out the role of ion-pairing (ΔG_{ip}) and electrolyte [41]

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r + \Delta G_{ST} + \Delta G_{ip} \quad (4)$$

The fifth term in Eq. (4), ΔG_{ST}, can play a decisive role. Its magnitude may be such that ignoring this parameter leads to inexact interpretation of ΔE and K_c. Note that ΔG_{ST} measures a stabilizing (or destabilizing) influence upon a reactant complex, and therefore its effect on the comproportionation equilibrium is opposite to that of the metal–metal coupling in the MV state represented by ΔG_r. The sign of ΔG_{ST} depends on the nature of the magnetic exchange. An antiferromagnetic coupling of the spins carried by the $\{[M^{ox}]–B–[M^{ox}]\}^{(n+2)+}$ complex yields a singlet ground state and will contribute to stabilize this species. The comproportionation equilibrium (Eq. (1)) will be displaced on the left hand side, while a ferromagnetic exchange which gives a triplet ground state will have an effect in the opposite direction.

For several years now, we have been investigating dinuclear organoiron complexes featuring various carbon-rich central spacers and possessing the electro-active terminal iron site "(η^5-C_5Me_5)(η_2-dppe)Fe–C≡C" [42,24]. The detailed synthesis and the properties of these compounds have already been presented elsewhere [43–54]. The one-electron oxidized complexes present a mixed-valence character and as monoradicals they are paramagnetic. The understanding of their magnetic properties is quite easy [55,24,25]. Their magnetic susceptibility obeys the Curie Law. In particular, it was shown that the product derived from one-electron oxidation of $\{(\eta^5\text{-}C_5Me_5)(\eta_2\text{-dppe})Fe–C{\equiv}C–C{\equiv}C\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ (**1**; Chart 1) also has a butadiyndiyl structure with the radical localized on the metal centers (structures **B**, **C**, Scheme 1). Further oxidation affords $\mathbf{[1]}^{2+}$, with a singlet state (D) and a triplet state

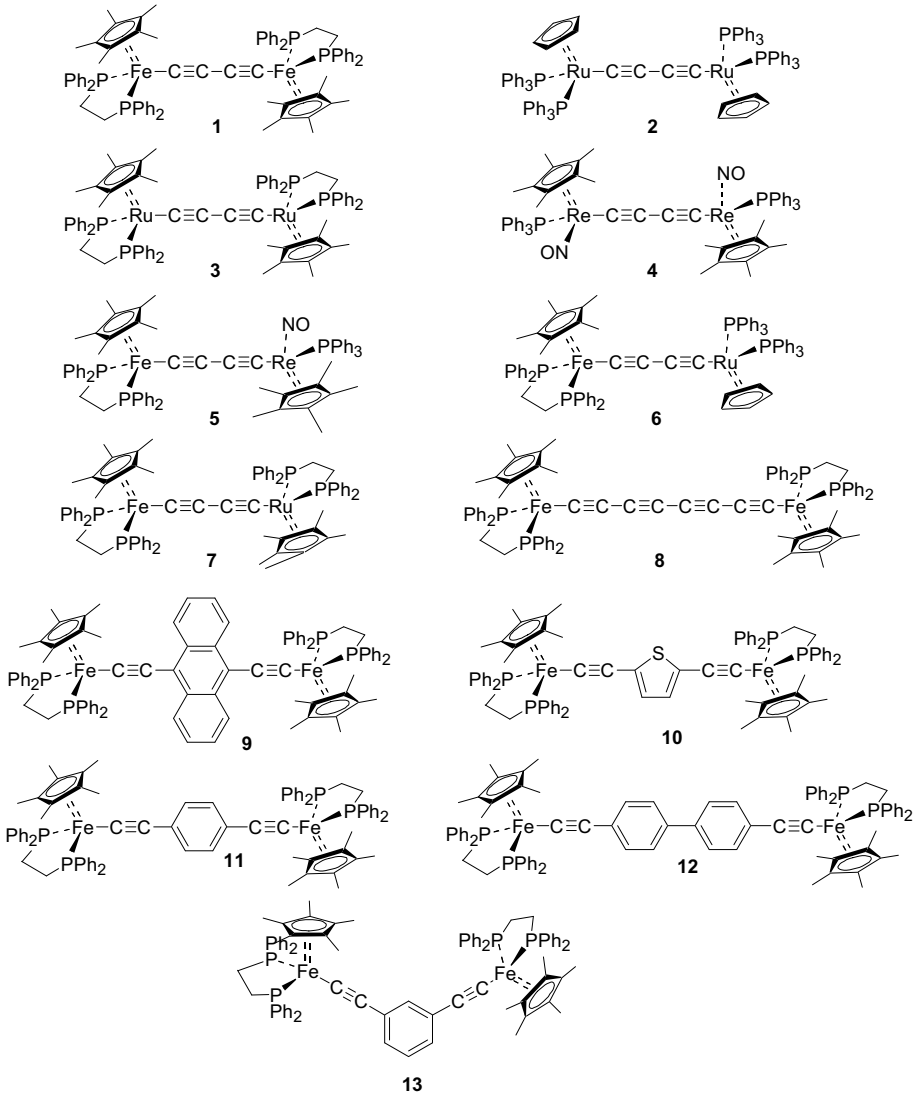
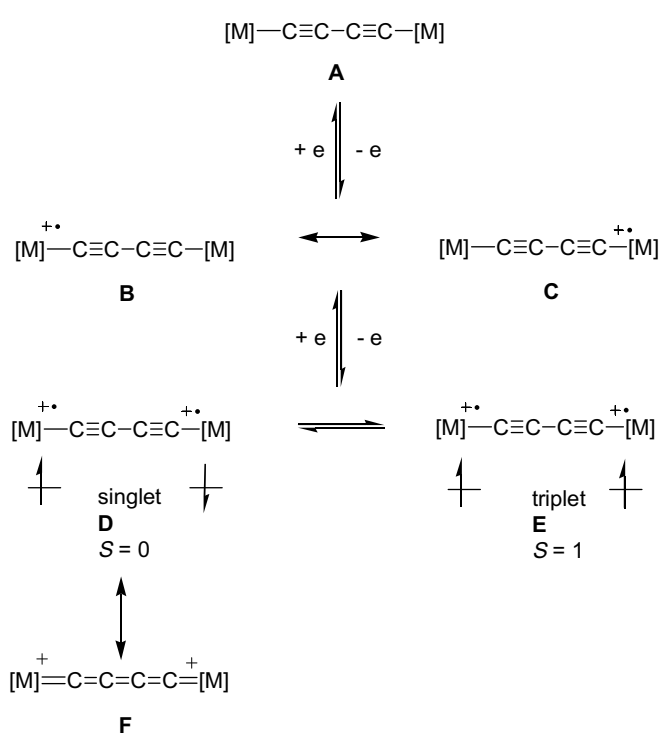


Chart 1. Selected examples containing the terminal iron group "(η^5-C_5Me_5)(η_2-dppe)Fe–C≡C".

(**E**). Early investigations on the diradical dication complexes deriving from two one-electron oxidations of the neutral species have revealed the magnetic properties of these species [56,25]. The energy gap between the two spin isomers **D** and **E** is sufficiently small ($\Delta G_{ST} = -18.2\ cm^{-1}$) for both states to be populated, even at liquid nitrogen temperatures [56]. A very weak contribution of the cumulenic resonance structure **F** contributes to stabilize the singlet state.

Various independent spectroscopic, structural and computational studies, reported by Bruce's group on the diruthenium complexes $\{Ru(PP)Cp'\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ ($Cp' = (\eta^5\text{-}C_5H_5)$, $PP = (PPh_3)_2$ **2**; $Cp' = (\eta^5\text{-}C_5Me_5)$, PP = dppe **3**) which can be readily oxidized to $[\mathbf{2}]^{n+}$ or $[\mathbf{3}]^{n+}$ ($n = 1$–4), have shown a smooth transition from the butadiyndiyl structure in the neutral compound to the cumulenic structure in the dications and eventually to the acetylide-bridged dicarbyne [57–60]. Similar observations have been previously made for the bis(rhenium) complexes $[\{Re(NO)(PPh_3)(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}C_4)]^{n+}$ ($n = 0$–2) [61]. In contrast to the iron species $[\mathbf{1}]^{2+}$, the dicationic ruthenium and rhenium complexes $[\mathbf{2}]^{2+}$, $[\mathbf{3}]^{2+}$ and $[\mathbf{4}]^{2+}$ have been reported to be diamagnetic between 80 and 300 K [61,57,58]. For these second and third row transition metal complexes, it seems that the stabilization of the singlet ground state by the cumulenic resonance structure **F** is strong enough to make the triplet excited state not thermally accessible.

In this paper, selected examples (Chart 1) of homo- and hetero-binuclear systems with delocalized and localized MV states have been chosen in the literature to illustrate how the ΔE (ΔG_c) values to assess the degree of electronic communication between metals must be approach very judiciously. The contribution of the magnetic exchange which can take place between the unpaired spins carried by the redox sites in the di-oxidized complexes on the ΔE (ΔG_c) values is discussed.



Scheme 1. Various valence bond descriptions which may be used to describe the oxidation of homobinuclear C_4-bridged complexes.

2. Heterobinuclear Fe–Ru and Fe–Re C_4-bridged systems

Considering the different magnetic properties of the homobinuclear dication Fe–Fe complexes on one side and the Re–Re and Ru–Ru on the other side, it was of interest to examine the properties of the Fe–Re and Fe–Ru dications. Efforts to explore further these structure/properties relationships have resulted in the preparation of the heterometallic species $\{(\eta^5\text{-}C_5Me_5)(Ph_3P)(NO)Re\}(C{\equiv}C\text{–}C{\equiv}C)\{Fe(dppe)(\eta^5\text{-}C_5Me_5)\}$ (**5**) [62]. The neutral complex **5** is well described by the butadiynyl representation (**A**) and can be oxidized to a monocation which exists in the ground state as a Fe-centered radical. Further oxidation gives the dication, which shows a singlet/triplet energy gap (**D**, **E**, $\Delta G_{ST} = -175\ cm^{-1}$), the occupation of each state being 37/63 at 300 K. However, as a result of the different electron counts and ancillary ligands on Re and Fe, the end-caps are different, which prevents a clear examination of the respective roles of the metal and ligands in determining the properties of this system.

Thus, the properties of mixed Fe–Ru diynyl complexes $\{(\eta^5\text{-}C_5H_5)(Ph_3P)_2Ru\}(C{\equiv}C\text{–}C{\equiv}C)\{Fe(dppe)(\eta^5\text{-}C_5Me_5)\}$ (**6**) and $\{(\eta^5\text{-}C_5Me_5)(dppe)Ru\}(C{\equiv}C\text{–}C{\equiv}C)\{Fe(dppe)(\eta^5\text{-}C_5Me_5)\}$ (**7**), which might be expected to exhibit behavior intermediate between those of the homobinuclear Fe–Fe and Ru–Ru systems, were examined [63]. The expected diynyl nature of the carbon bridge was confirmed with $\nu_{C\equiv C}$ bands at ca. 1966 cm^{-1} in the Nujol mull spectra of the neutral complexes **6** and **7**.

The IR spectra of the cationic complexes $\mathbf{6}^{n+}$ and $\mathbf{7}^{n+}$ show two $\nu_{C\equiv C}$ bands, suggesting that the symmetry of the complexes decreases as the oxidation proceeds (Fig. 2). The frequencies decrease with oxidation, consistent with a gradual reduction in C≡C bond order. The two vibrational modes observed in $\mathbf{6}^{n+}$ and $\mathbf{7}^{n+}$ ($n = 1, 2$) were assigned to Ru–CC and Fe–CC stretching modes. The Mössbauer spectroscopy analysis of the complexes $\mathbf{6}^{n+}$ and $\mathbf{7}^{n+}$ ($n = 0, 1, 2$) established that the first oxidation was mainly iron centered while the iron nucleus remained almost unchanged by the second oxidation. Consequently, it was possible to assign the low energy $\nu_{C\equiv C}$ band at the $\nu_{FeC\equiv C}$ stretch, while the band at higher energy was attributed to the $\nu_{RuC\equiv C}$ stretch in the monocation. In the dication, the opposite situation was found. The $\nu_{RuC\equiv C}$ and $\nu_{FeC\equiv C}$ stretches were assigned to the low and high energy bands of the 1600–2100 cm^{-1} IR range, respectively. Moreover, the X-ray data, the Mössbauer and IR spectra and the theoretical (DF) computations have suggested that the carbon chain structures in these dicationic Fe–Ru

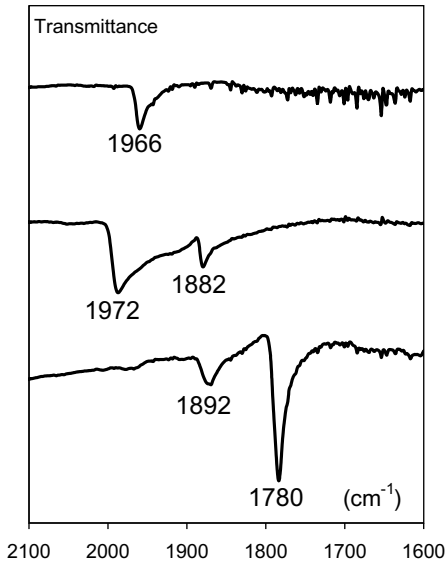


Fig. 2. Nujol mull IR spectra of $\mathbf{7}^{n+}$ $n[PF_6]$ (top, $n = 0$; middle, $n = 1$, bottom, $n = 2$).

complexes lie between the diynediyl and cumulenic structures [63].

In contrast with the complex $\mathbf{5}^{2+}$ which displayed well-resolved ESR spectra in the range 4–77 K with a sharp half-field signal ($g = 4.3046$) characteristic of the triplet states the complexes $\mathbf{6}^{2+}$ and $\mathbf{7}^{2+}$ were not ESR active in the same temperature range [62,63]. The strong antiferromagnetic interaction, which precluded recording their ESR spectra, favored observation of well-resolved NMR spectra of the dication $\mathbf{6}^{2+}[PF_6]_2$ and $\mathbf{7}^{2+}[PF_6]_2$ (Fig. 3). In accord with the paramagnetic nature of these compounds, the resonances are shifted with respect to those of the corresponding neutral complexes. Variable-temperature ^{1}H NMR spectra were run for $\mathbf{6}^{2+}[PF_6]_2$ and $\mathbf{7}^{2+}[PF_6]_2$ and it was found that the chemical shifts moved toward the positions usually found in diamagnetic compounds as the temperature decreased. Plots of the experimental chemical shifts against $1/T$ all display deviation from linearity and the Van Vleck equation (Eq. (5)) allowed the determination of the energy difference between the singlet ground state and triplet excited states (according to Eq. (5) $\Delta G_{ST} = 2J$) [64]

$$\chi = C/T[3 + \exp(-2J/kT)] \quad (5)$$

The energy gap (ΔG_{ST}) decreased from $-350\ cm^{-1}$ for $\mathbf{6}^{2+}[PF_6]_2$ to $-500\ cm^{-1}$ for $\mathbf{7}^{2+}[PF_6]_2$ [63]. It is noteworthy that substitution of one Fe atom by a Ru atom in $\mathbf{1}^{2+}$ increases the gap by almost $500\ cm^{-1}$. In other words, at 293 K samples of $\mathbf{1}^{2+}[PF_6]_2$, $\mathbf{6}^{2+}[PF_6]_2$ and $\mathbf{7}^{2+}[PF_6]_2$ contain 75%, 35%, and 20% of molecules in the triplet excited state, respectively.

3. Homobinuclear Fe–Fe, Ru–Ru and Re–Re C_4-bridged systems with delocalized MV states

In the light of the results obtained for the heterobinuclear complexes, it was decided to reinvestigate the magnetic properties of the apparently diamagnetic $\{(\eta^5\text{-}C_5Me_5)(dppe)Ru\}(C{\equiv}C{-}C{\equiv}C)\{Ru(dppe)(\eta^5\text{-}C_5Me_5)\}[PF_6]_2$ ($\mathbf{3}^{2+}[PF_6]_2$) complex by ^{1}H and ^{31}P NMR in the range 193–300 K in solution. A small, but significant curvature of the chemical shifts versus $1/T$ was found and the best fit of the experimental data were found for $\Delta G_{ST} = -850\ cm^{-1}$. This result established that the dication $\mathbf{3}^{2+}[PF_6]_2$ is present as a mixture of singlet and triplet states, the two-spin isomers being in equilibrium in the 91/9 ratio at 293 K [63].

The key parameters of free energies of comproportionation (Eq. (4)) are listed in Table 1 for the homobinuclear complexes $\mathbf{1}^{n+}$ and $\mathbf{3}^{n+}$. Comparison of the comproportionation constant (K_c) clearly indicates that the MV complex is more stable in the iron series by almost two orders of magnitude. However, the energy of resonance ΔG_r which is directly connected with the metal–metal coupling through the carbon bridge is much larger in the case of ruthenium. This example emphasizes dramatically how

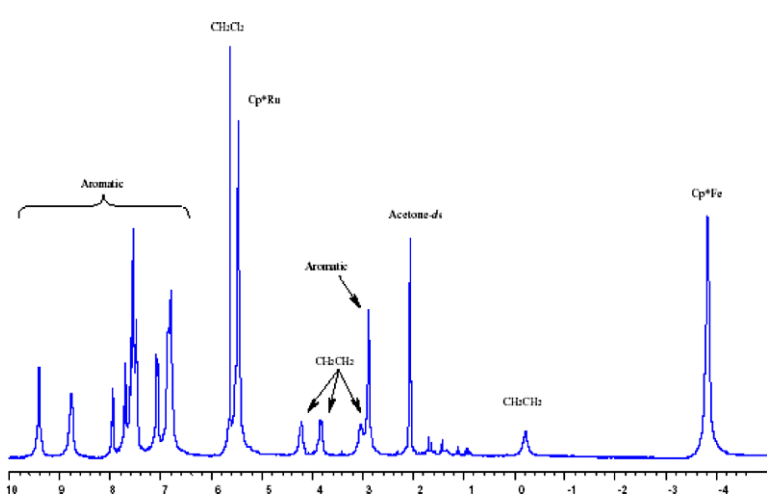


Fig. 3. Paramagnetic ^{1}H NMR spectrum of $\mathbf{7}^{2+}[PF_6]_2$ in acetone-d_6.

Table 1
Key parameters for the free energy of comproportionation of the homobimetallic systems $\mathbf{1}^{n+}$ and $\mathbf{3}^{n+}$

Compound	M	ΔE_1 (V/ecs)	ΔE_2 (V/ecs)	ΔE (V)	K_c	ΔG_c (cm^{-1})[b]	ΔG_r^a (cm^{-1})	ΔG_{ST} (cm^{-1})	Refs.
1	Fe	−0.67	0.05	0.72	1.6×10^{12}	5807	3700	−18	[46,56]
3	Ru	−0.43	0.22	0.65	9.7×10^{10}	5242	5100	−850	[58]

[a] For a class III MV, $\Delta G_r = 1/2\ \nu_{max}$.
[b] 1 V = 8065 cm^{-1}.

the use of ΔE and K_c values to assess the degree of electronic communication between metals must be approached very judiciously.

The magnetic exchange interaction (ΔG_{ST}) plays a decisive role on the difference of comproportionation free energy between these two compounds. Indeed, the substitution of the iron atoms by ruthenium produces an increase of ΔG_r by almost 40% while the magnitude of ΔG_{ST} is multiplied by ca. 50. As a result, the stabilization of one of the reactants is much larger than the stabilization of the product and the equilibrium of Eq. (1) is displaced towards the left hand side.

It is also interesting to examine the case of the homobimetallic rhenium system $[\{Re(NO)(PPh_3)(\eta^5\text{-}C_5Me_5)\}_2\text{-}(\mu\text{-}C_4)]^{n+}$ ($\mathbf{4}^{n+}$) [61]. In these series, the rhenium is chiral and the binuclear complexes $\mathbf{4}^{n+}$ were isolated and characterized as a mixture of two diastereoisomers. The low temperature ^{1}H NMR spectra of **4** and $\mathbf{4}^{2+}$ as well, displayed complicated patterns [61] which probably resulted from a rotation barriers along the Re–C_4–Re axis (also observed for the Fe–C_4–Fe [65]). As a consequence, the resolution of the spectra was not good enough in a large enough range of temperature to permit the evaluation of the singlet to triplet states energy gap by NMR in solution [66]. In the dication series $\mathbf{1}^{2+}$–$\mathbf{7}^{2+}$, a very good linear relationship ($R = 0.99$, Fig. 4) was found between the experimental singlet/triplet states energy gaps and the spin densities on the metal atoms calculated by DFT methods [63]. While this empirical correlation is not supported theoretically, it clearly shown that for the series of dications $\mathbf{1}^{2+}$, $\mathbf{3}^{2+}$, $\mathbf{5}^{2+}$, $\mathbf{6}^{2+}$, $\mathbf{7}^{2+}$, the singlet/triplet energy differences increase linearly as the spin densities on the metal atoms decrease.

Assuming that the dication $\mathbf{4}^{2+}$ might also obey this empiric law it appears possible to obtain a graphic estimate of the singlet/triplet state energy gap for the bis(rhenium) dication from the computed spin density on the two rhenium atoms. The spin density on the rhenium atoms was computed to be 0.82 [68] allowing the graphic determination of ΔG_{ST} for $\mathbf{4}^{2+}$ ($\Delta G_{ST} = 750 \pm 50$ cm^{-1}). Note that this value is very close to the value obtained for the bis(ruthenium) dication $\mathbf{3}^{2+}$. These data provide a self consistency for the analysis of the properties of the dications in the Fe, Ru and Re series, but the results must be considered with caution and it should not be forgotten that the variation of the magnetic susceptibility with temperature was measured for a powdered sample of $\mathbf{4}^{2+}$. The experimental data established that the dependence of the magnetic susceptibility was inconsistent with a thermally populated triplet excited state [61]. However, when the gap is high and the sample contains small traces of magnetic impurities the fit of the experimental magnetic susceptibility could be a hard task.

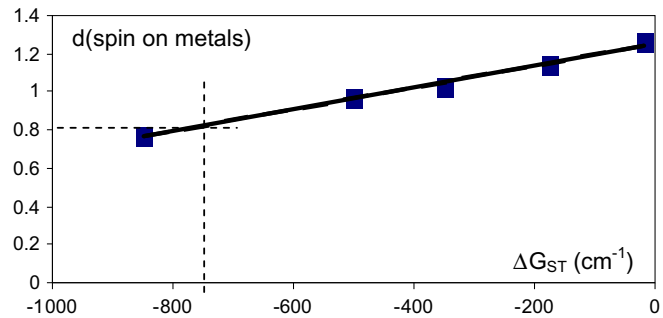


Fig. 4. Plot of the ST energy gap (cm^{-1}) vs computed spin densities on the metal atoms for compounds $\mathbf{1}^{2+}$, $\mathbf{3}^{2+}$, $\mathbf{5}^{2+}$, $\mathbf{6}^{2+}$, $\mathbf{7}^{2+}$ [67]. The dashed line represents the extrapolation of ΔG_{ST} for $\mathbf{4}^{2+}$.

4. Bis(iron) systems connected through nine-bond bridges with delocalized MV states

Comparison of the thermodynamic parameters for a family of compounds with the same terminal ends, namely the electro-active terminal iron site "$(\eta^5\text{-}C_5Me_5)\text{-}(\eta^2\text{-dppe})Fe$" connected with carbon bridges of similar distances and containing all nine bonds between the remote metal centers is also of interest. The bis(iron) derivatives bridged by various linkers such as –C_8– elemental carbon chain (**8**), 9,10-bis(ethynyl)anthracene (**9**), 2,5-bis(ethynyl)thiophene (**10**) and a 1,4-bis(ethynyl)phenyl (**11**) were prepared and characterized. Their corresponding MV complexes were also prepared by a one-electron oxidation of the parent neutral complex, isolated and characterized by various spectroscopic means. They all belong to class III, except compound **11** which was recognized as a border-line class II/III MV complex.

A two-electron oxidation of the neutral parents or a one-electron oxidation of the MV complexes also allowed the isolation and study of the corresponding dications except in the case of the binuclear compound bridged by the –C_8– all-carbon bridge for which the dication could never be isolated as a pure salt [45,47,54,65,69,70,32].

From the data listed Table 2, it is apparent that the larger comproportionation constant was obtained for the compounds $\mathbf{8}^{n+}$ which contain the all-carbon bridge and decrease according to the sequence $\mathbf{8}^{n+}$, $\mathbf{9}^{n+}$, $\mathbf{10}^{n+}$, and

Table 2
Key parameters for the free energy of comproportionation of the bis(iron) systems $\mathbf{8}^{n+}$, $\mathbf{9}^{n+}$, $\mathbf{10}^{n+}$, and $\mathbf{11}^{n+}$

Compound	ΔE_1 (V/ecs)	ΔE_2 (V/ecs)	K_c	ΔG_c (cm^{-1})[b]	ΔG_r^a (cm^{-1})	ΔG_{ST} (cm^{-1})	d_{FeFe} (Å)	Refs.
8	−0.23	0.20	2.0×10^7	3470	2500	Not available[c]	12.6	[47,65]
9	−0.40	−0.04	1.3×10^6	2900	2500	[d]	11.8	[70]
10	−0.39	−0.05	5.8×10^5	2740	2500	−300	11.6	[54,69]
11	−0.31	−0.05	2.6×10^4	2100	⩽2000	−400	11.6	[45,32,71]

[a] For a class III MV, $\Delta G_r = 1/2\nu_{max}$.
[b] 1 V = 8065 cm^{-1}.
[c] The dication $\mathbf{8}^{2+}$ could not be isolated.
[d] The triplet state contribution could not be detected in the range 4–300 K.

$\mathbf{11}^{n+}$. Again the use of ΔE^0 and K_c values to assess the degree of electronic communication between metals must be approached very judiciously. Indeed, the degree of electronic communication represented by the free energy of resonance and determined by a careful analysis of the absorption spectra in the NIR range established that the MV complexes $\mathbf{8}^+$, $\mathbf{9}^+$, $\mathbf{10}^+$ possess the same resonance energy (ΔG_r). As a consequence, the differences observed for the corresponding ΔE^0 and K_c values which were all determined in the same conditions, come from other contributions like ΔG_i, the inductive factor or ΔG_{ST}, the magnetic exchange in the dications. The energy gaps were measured for $\mathbf{9}^{2+}$, $\mathbf{10}^{2+}$, and $\mathbf{11}^{2+}$ by various means including magnetic susceptibility measurements, ^{57}Fe Mössbauer spectroscopy on powdered samples and NMR in solution. This determination is not always easy, in particular when the magnetic susceptibility contains an important contribution independent of the temperature due to the presence of very small traces (too small to be detected by spectroscopic or elemental analyses) of paramagnetic inorganic iron. In particular, in the case of complex $\mathbf{11}^{2+}$, a very small magnetic exchange was previously determined [56]. Recently, new measurements on magnetically purer sample showed that this value was not correct (see Table 2) [71]. The dication $\mathbf{10}^{2+}$ and $\mathbf{11}^{2+}$ possess a singlet ground state and a triplet exited state with energy gaps of the same magnitude. In contrast, the magnetic behavior of the dication $\mathbf{9}^{2+}$ is unique in the iron series. The ^{1}H, ^{31}P and ^{13}C NMR in solution suggest that this compound is diamagnetic. Its diamagnetic character was also probed by the determination of the magnetic moment in solution by the Evans method and the variation of the magnetic susceptibility with temperature by SQUID measurements on a powdered sample in the 4–300 K range.

The observation of exactly the same resonance energy, or in other words the same iron–iron coupling through three different carbon bridges, for the three class III MV complexes $\mathbf{8}^+$, $\mathbf{9}^+$, $\mathbf{10}^+$ was unexpected. It is important to note that such a conclusion cannot be drawn from analysis of the free energy of comproportionation constant values. Despite the fact that the spin density is symmetrically distributed between the two metal centers and the carbon-rich bridges which contain the same number of carbon between the iron atoms, this is probably fortuitous. It is difficult to say how an important role the magnetic exchange interaction can play in the variation of ΔG_c°. However the term ΔG_{ST} represents 10–20% of the total free energy ΔG_c°, and this contribution is clearly large enough for not to be neglected in discussing about the metal–metal couplings.

5. Bis(iron) systems with localized MV states

Bis(organoiron) class II MV complexes featuring the "(η^5-C_5Me_5)(η^2-dppe)Fe" end groups can also be designed by insertion of two 1,4-phenylene units ($\mathbf{12}^+$) or one single 1,3-phenylene fragment in the butadiyne-diyl bridge ($\mathbf{13}^+$) [72,32]. For these compounds the electron transfer is slow and in contrast with the MV compounds $\mathbf{8}^+$–$\mathbf{11}^+$, the metal sites are not spectroscopically and crystallographically equivalent. X-ray analyses and spectroscopic measurements allowed the observation of a distinct reduced Fe(II) metal site and an oxidized Fe(III) center. In particular, the ^{57}Fe Mössbauer spectra of these MV complexes which allows the direct observation of the iron nuclei, displayed two well-resolved doublets with relative spectral absorption areas in 1:1 ratio as illustrated in Fig. 5 for $\mathbf{13}^+[PF_6]$. The spectroscopic characteristics of these doublets are very close to those obtained for mononuclear Fe(II) and Fe(III) complexes indicating the localization of the electronic spin on the slow time scale of Mössbauer spectroscopy [73].

For these weakly coupled MV complexes, the separation of two one-electron processes is small, sometimes below the limit of the resolution of the CV as found for **12**. In the

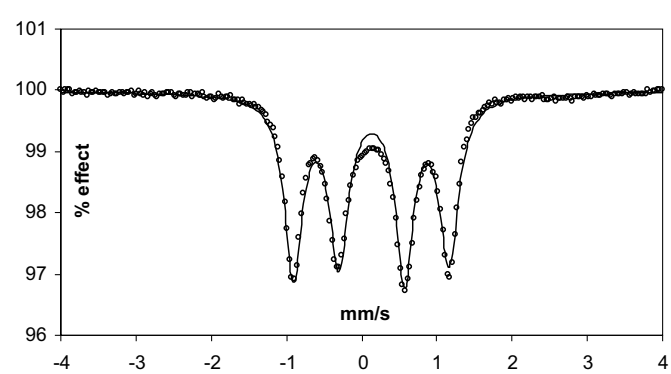


Fig. 5. ^{57}Fe Mössbauer spectrum of a powder sample of $\mathbf{13}^+[PF_6]$ recorded at 77 K (experimental data, open circle and best computed fit, solid line) showing the Fe(II) (the two external absorption bands) and Fe(III) (two central bands) doublets.

Table 3
Key parameters for the free energy of comproportionation of the bis(iron) systems $\mathbf{12}^{n+}$, $\mathbf{13}^{n+}$

Compound	ΔE_1 (V/ecs)	ΔE_2 (V/ecs)	K_c	ΔG_c (cm^{-1})[b]	ΔG_r^a (cm^{-1})	ΔG_{ST} (cm^{-1})	Refs.
12	−017	0.11	11	500	3.6	~0	[32]
13	−0.23	−0.10	130	1008	4.6	130	[72]

[a] For class II MV, $\Delta G^r = H_{DA}^2/\lambda$.
[b] 1 V = 8065 cm^{-1}.

favorable case of the complex **13**, it is possible to directly access to the potentials of the redox couples and the free energy of comproportionation. For all these compounds, the ΔG_c values are small and range between few hundreds and one thousand of wave numbers (Table 3). In these weakly coupled class II complexes, the energy of resonance ΔG_r is very weak and cannot be regarded as a significant contribution to ΔG_c [30]. In particular, comparison of metal–metal couplings between different class II complexes based on ΔG_c (or K_c) values does not make sense. Accurate determination of the H_{DA} and λ parameters from the IVCT band constitutes the unique method to evaluate the metal–metal coupling between donor and acceptor centers connected through a linker with multiple bonds.

In the particular cases of the MV complexes $\mathbf{12}^+$ and $\mathbf{13}^+$, the resonance energies are small and very similar. Probably, the difference observed in their free energies of comproportionation comes from their different magnetic properties. Indeed, while an antiferromagnetic coupling between unpaired electrons is expected for $\mathbf{12}^{2+}$ according to Ovchinnikov's rule or molecular orbital considerations, ferromagnetic exchange should take place between the spins carried by the iron(III) centers of $\mathbf{13}^{2+}$ [74,25]. Experimental measurements have shown that $\mathbf{12}^{2+}$ behaves as an unpaired biradical in solution at ambient temperature in line with no or weak antiferromagnetic coupling between the unpaired spins through the 4,4′-bis(ethynyl)-(1,1′-biphenyl) spacer [32]. In contrast, the existence of a ferromagnetic coupling between the metal centered spins through the 1,3-bis(ethynyl)phenyl connector was previously firmly established for $\mathbf{13}^{2+}$ by the measurement of the variation of the magnetic susceptibility on a powdered sample in the 4–300 K range of temperature [75]. The energy of the magnetic exchange (ΔG_{ST}) was found to be many times larger than the energy of resonance (ΔG_r). In the case of a triplet ground state, the value of ΔG_{ST} is positive and contributes to increase ΔG_c (K_c and ΔE as well) and the equilibrium of comproportionation (Eq. (1)) is displaced on the right hand side providing the intuitive, but false idea, that the MV complex $\mathbf{13}^+$ might be more stabilized than $\mathbf{12}^+$ by a better metal–metal coupling through the bridge.

6. Conclusion

As several times mentioned in this paper, the use of ΔE and K_c values to assess the degree of electronic communication between metals in MV systems must be approached very judiciously. Indeed, the variation of the thermodynamic parameter ΔG_c (and the related terms ΔE and K_c) from one MV complex to another, might reflect the variation of the through bridge metal–metal coupling (often called the electronic communication), but it is also possible that MV complexes with the same energy of resonance (ΔG_r) possess different ΔG_c values. Furthermore, it cannot be excluded that MV compounds possess stronger through bridge metal–metal couplings despite smaller ΔG_c values. In the particular case of class II MV, the term ΔG_r is always weak whereas the absolute value of ΔG_{ST} might be larger by several orders of magnitude.

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