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Influence of peripheral ligands on the metal–metal interaction in dinuclear metal complexes with *N*-heterocyclic bridging ligands

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CONTENTS

ABSTRACT

Metal–metal interactions, as inferred from comproportionation constants calculated from electrochemical data, have been examined in more than 30 dinuclear metal complexes having *N*-heterocyclic bridging ligands. It is shown that the peripheral ligands strongly affect the metal–metal electronic coupling. A simple (intuitive) approach shows that the interaction proceeds via an electron or hole transfer mechanism depending on the electronic properties of both bridging and peripheral ligands. Although the proposed view is essentially qualitative, the results are of interest for the design of systems featuring switchable electron and energy transfer processes. Novel possibilities for controlling metal–metal interaction are also proposed.

1. INTRODUCTION

Metal–metal interactions in polynuclear metal complexes are a topic of great interest for both fundamental and application reasons. In fact, metal–metal interactions govern the rate of energy and electron transfer between metal units, the electrochemical properties of dinuclear species, the comproportionation constants and the intervalence transfer transitions in mixed-valence compounds [1–14]. Such

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properties are crucial for the design of photochemical and/or electrochemical molecular devices for energy conversion schemes, information recording, signal treatment, and other applications [14–20]. The degree of metal–metal interaction also controls the distinction between supramolecular polynuclear species (made of weakly interacting components which maintain most of their specific properties in the polynuclear species) and polynuclear single molecules (made of strongly interacting components which lose their specific properties in the assembly) [11,21].

The importance of the bridging ligand in determining the metal–metal interaction is well recognized [21–23]. Superexchange theory [24], providing a theoretical approach which considers overlap between orbitals of each metal, mediated by overlaps between the metal orbitals with those of the bridging ligand (through-bond interaction), is very useful in discussing the role played by the bridging ligands. Both bridge-mediated electron transfer (which takes advantage of the lowest unoccupied molecular orbitals (LUMOs) of the bridge) and hole transfer (which takes advantage of the highest occupied molecular orbitals (HOMOs) of the bridge) mechanisms may play a role in assuring the electronic interaction (Fig. 1). Furthermore, the bridging ligand plays an important role in electronic coupling via through-space interaction, by controlling distance and orientation of the metal-containing units. When suitably designed, bridging ligands may also be able to "read" environmental "information" (e.g. by protonation, replying to a pH change [25], or by alkali metal complexation, using designed molecular recognition abilities [26]) and transmit it to the metal–metal interaction. This may open the way to external control of electronic coupling between bridged units, an effect which can be exploited in a number of electronic and/or photochemical devices.

The importance of the nature of the peripheral ligands in determining the

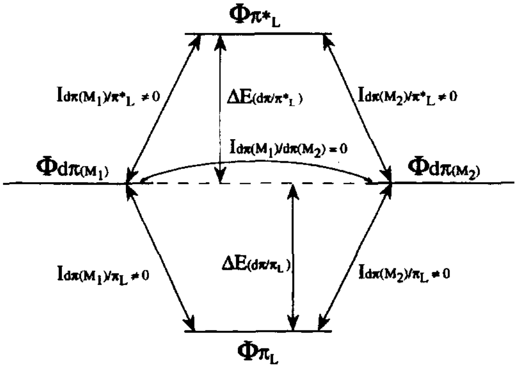

Fig. 1. Orbital diagram illustrating superexchange interaction between two metal ions through a simple bridging group L. $\Phi_{d\pi(M_1)}$, $\Phi_{d\pi(M_2)}$, $\Phi_{\pi*_L}$ and Φ_{π_L} represent metal (1) orbitals and metal (2) orbitals, bridge LUMO and bridge HOMO respectively. Ia/b is the interaction between a and b orbitals. In this approximation, through-space interactions (including the coulombic effect) are ignored for clarity, as well as "conduction pathways" of electronic communication within the bridging ligand structure (see later in the text).

degree of metal–metal electronic interaction is less investigated and not so well defined. To our knowledge, few reports deal with this matter [27] and no paper in the literature is focused explicitly on the influence of peripheral ligands on metal–metal interaction.

The objective of the present review is to examine electrochemical data concerning a series of dinuclear metal complexes having *N*-heterocyclic bridging ligands and to discuss them in the framework of a simple intuitive approach that evidences the role played by peripheral ligands. Electrostatic effects and symmetry considerations would be useful in explaining the phenomena in further detail, but they are neglected in the present treatment for clarity. Because the most complete series of literature data concern d^6 Ru(II) and Os(II) complexes, we shall mainly make reference to these species. In principle, however, the present discussion can be considered of general validity. For simplicity reasons, we shall refer to "symmetric" dinuclear species, i.e. species made of two identical metal units.

We used the separation ΔE between the two metal-based oxidation potentials as the experimental parameter for obtaining information on metal–metal interaction. This is related to the comproportionation constant K_c, by the well-known relationship (at $T = 298$ K) [2e]

$$K_c = \exp\left(\frac{\Delta E(\mathrm{mV})}{25.69}\right) \tag{1}$$

Table 1 collects the data on some selected complexes. Figure 2 shows the structural formulae of the *N*-heterocyclic ligands. Although the discussion is essentially qualitative, it can give useful insights into the problem of metal–metal interaction.

2. MECHANISM OF METAL–METAL INTERACTION

The theory is based upon superexchange. Parameters which are effective to describe the through-bond interaction are the overlap between the frontier orbitals of the metal and bridging ligands and the electronic interactions between the atoms of the bridge that connect the frontier units to each other. "Atom pathways" (or "conduction pathways") connecting each metal to the other (Fig. 3) and the local electron density of the orbitals must therefore be considered, together with energy gap arguments. Within such an approach, the metal–metal interaction I may be approximately expressed as [24]

$$\begin{aligned} \mathrm{I} = & \sum_{\substack{\text{atom}\\ \text{pathways}}} \frac{(<\Phi_{\mathrm{d}\pi}|\mathscr{H}|\Phi_{\pi*_{\mathrm{L}}}>)^2 F_{\pi*(\mathrm{a,b})} F_{\pi*(\mathrm{b,c})} \cdots F_{\pi*(n-1,n)}}{|E_{\pi*_{\mathrm{L}}} - E_{\mathrm{d}\pi}|} \\ & + \sum_{\substack{\text{atom}\\ \text{pathways}}} \frac{(<\Phi_{\mathrm{d}\pi}|\mathscr{H}|\Phi_{\pi_{\mathrm{L}}}>)^2 F_{\pi(\mathrm{a,b})} F_{\pi(\mathrm{b,c})} \cdots F_{\pi(n-1,n)}}{|E_{\mathrm{d}\pi} - E_{\pi\mathrm{L}}|} + \mathrm{TS} \end{aligned} \tag{2}$$

TABLE 1

Electrochemical data with respect to a saturated calomel electrode, obtained from cyclic voltammetry and/or differential pulse voltammetry, and comproportionation constants of some selected dinuclear species with *N*-heterocyclic bridging ligands (the solvent is acetonitrile, unless otherwise stated; almost all the complexes reported exhibit two distinct oxidation potentials; complexes that exhibit one two-electron oxidation wave (typical of very weakly coupled systems) are reported only when they are necessary to the discussion or as representative examples; for such species, the limiting value of $\Delta E = 75$ mV is considered [2c])

Complex	$E_{\mathrm{red(BL)}}$, (V)	E_{ox} (1) (V)	E_{ox} (2) (V)	ΔE (mV)	K_c	Reference
1 $[(bpy)_2Ru(bpym)Ru(bpy)_2]^{4+}$	−0.41	+1.53	+1.65	120	1.1×10^2	[28]
2 $[(bpy)_2Ru(2,3\text{-}dpp)Ru(bpy)_2]^{4+}$	−0.67	+1.38	+1.55	170	7.5×10^2	[29][a]
3 $[(biq)_2Ru(2,3\text{-}dpp)Ru(biq)_2]^{4+}$	−0.45	+1.57[b]		<75	<18	[29]
4 $[(phen)_2Ru(2,3\text{-}dpp)Ru(phen)_2]^{4+}$	−0.64	+1.44	+1.65	210	3.5×10^3	[32]
5 $[(bpy)_2Os(2,3\text{-}dpp)Os(bpy)_2]^{4+}$	−0.68	+0.90	+1.20	300	1.2×10^5	[33][c]
6 $[(bpy)_2Ru(dpq)Ru(bpy)_2]^{4+}$	−0.37	+1.47	+1.62	150	3.4×10^2	[35]
7 $[(phen)_2Ru(dpq)Ru(phen)_2]^{4+}$	−0.40	+1.48	+1.64	160	5.1×10^2	[32]
8 $[(bpy)_2Ru(ppz)Ru(bpy)_2]^{4+}$	−0.60	+1.35	+1.55	200	2.5×10^3	[36]
9 $[(bpy)_2Ru(HAT)Ru(bpy)_2]^{4+}$	−0.49	+1.53	+1.78	250	1.8×10^4	[37]
10 $[(bpy)_2Ru(2,5\text{-}dpp)Ru(bpy)_2]^{4+}$	−0.53	+1.37	+1.54	170	7.5×10^2	[29][d]
11 $[(biq)_2Ru(2,5\text{-}dpp)Ru(biq)_2]^{4+}$	−0.45	+1.48[b]		<75	<18	[29]
12 $[(bpy)_2Os(2,5\text{-}dpp)Os(bpy)_2]^{4+}$	−0.56	+0.92	+1.22	300	1.2×10^5	[33]
13 $[(bpy)_2Ru(bptz)Ru(bpy)_2]^{4+}$	[e]	+1.52	+2.02	500	3.1×10^8	[38]
14 $[(bpy)_2Ru(abpy)Ru(bpy)_2]^{4+}$	[e]	+1.67	+2.22	550	2.2×10^9	[38]
15 $[(terpy)Ru(tpp)Ru(terpy)]^{4+}$	−0.34	+1.43	+1.72	290	8.0×10^4	[39]
16 $[(terpy)Ru(bterpy)Ru(terpy)]^{4+}$	−0.96	+1.36[b]		<75	<18	[40]
17 $[(Cl)_2(CO)_2Ru(2,3\text{-}dpp)Ru(CO)_2(Cl)_2]$	−0.62	+1.90[b]		<75	<18	[41]
18 $[(Cl)_2(CO)_2Ru(2,5\text{-}dpp)Ru(CO)_2(Cl)_2]$	−0.38	+1.92[b]		<75	<18	[41]
19 $[(bpy)_2Ru(bpt)Ru(bpy)_2]^{3+}$	< −1.40[f]	+1.04	+1.34	300	1.2×10^5	[42]
20 $[(bpy)_2Os(bpt)Os(bpy)_2]^{3+}$	< −1.34[f]	+0.64	+0.85	210	3.5×10^3	[43]
21 $[(ppy)_2Rh(bpt)Rh(ppy)_2]^{+}$	−1.92	+1.36	+1.83	470	8.8×10^7	[44]

22 $[(ppy)_2Ir(bpt)Ir(ppy)_2]^{+}$	−1.80	+1.13	+1.30	170	7.5×10^{2}	[44]
23 $[(bpy)_2Ru(bpzt)Ru(bpy)_2]^{3+}$	< −1.26[f]	+1.16	+1.46	300	1.2×10^{5}	[45]
24 $[(bpy)_2Ru(bii)Ru(bpy)_2]^{2+}$	< −1.54[f]	+0.75	+1.09	340	5.6×10^{5}	[46]
25 $[(bpy)_2Ru(bzim)Ru(bpy)_2]^{2+}$	< −1.49[f]	+0.76	+1.04	280	5.4×10^{4}	[47]
26 $[(bpy)_2Os(bzim)Os(bpy)_2]^{2+}$	< −1.47[f]	+0.37	+0.56	190	1.6×10^{3}	[48]
27 $[(bpy)_2Ru(qpy)Ru(bpy)_2]^{4+}$	−1.10	+1.24[b]		<75	<18	[49]
28 $[Cl(bpy)_2Ru(pz)Ru(bpy)_2Cl]^{2+}$	[e]	+0.89	+1.02	130	1.6×10^{2}	[50]
29 $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{4+}$ [g]	[e]	+0.37	+0.76	390	4.2×10^{6}	[51]
30 $[(NH_3)_5Ru(4,4'\text{-}bpy)Ru(NH_3)_5]^{4+}$	[e]	+0.33	+0.41	80	20[h]	[52]
31 $[(NH_3)_5Ru(4,4'\text{-}Mbpy)Ru(NH_3)_5]^{4+}$	[e]	+0.31	+0.37	60	10[h]	[52]
32 $[(NH_3)_4Ru(2,3\text{-}dpp)Ru(NH_3)_4]^{4+}$	[e]	+0.90	+1.29	390	4.2×10^{6}	[53]
33 $[(NH_3)_4Ru(bpym)Ru(NH_3)_4]^{4+}$ [g]	[e]	+0.83	+1.02	190	1.6×10^{3}	[54]
34 $[(NH_3)_3Ru(tpp)Ru(NH_3)]^{4+}$ [i]	[e]	+0.81	+1.31	500	3.1×10^{8}	[55]
35 $[(terpy)Os(tpp)Os(terpy)]^{4+}$	−0.39	+0.97	+1.44	470	9.7×10^{7}	[56]
36 $[(tpp)Ru(tpp)Ru(tpp)]^{4+}$	−0.29	+0.99	+1.53	540	1.5×10^{9}	[56]
37 $[(tpp)Os(tpp)Os(tpp)]^{4+}$	−0.29	+1.18	+1.58	400	6.2×10^{6}	[56]

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[a] Data on this complex can also be found in refs. 30 and 31.

[b] This value refers to a two-electron peak.

[c] Data on this complex can also be found in ref. 34.

[d] Data on this complex can also be found in ref. 38.

[e] Reduction potential not reported.

[f] The first reduction process of this complex is peripheral ligand centered.

[g] Data obtained in H_2O.

[h] Data for this species are calculated by spectrophotometric titration (see original reference).

[i] Data obtained in *N,N*-dimethylformamide.

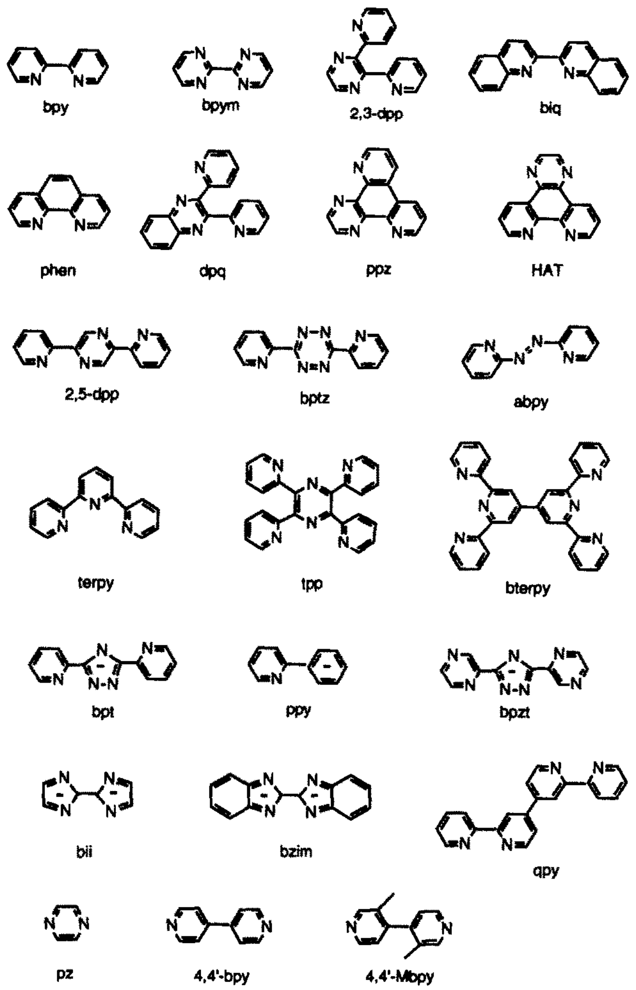

Fig. 2. Structural formulae of the *N*-heterocyclic ligands.

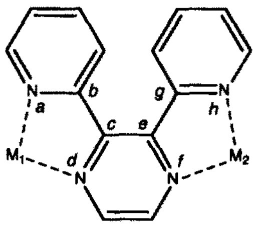

Fig. 3. Atom labelling of the 2,3-dpp bridge. The sequences a→b→c→e→f and d→c→e→g→h identify two atom pathways connecting the metal ions M_1 and M_2.

where $\Phi_{d\pi}$, $\Phi_{\pi*_L}$, and Φ_{π_L} are the metal-centered molecular orbital, bridge LUMO(s), and bridge HOMO(s) respectively, $\mathscr{H}$ is the coupling operator, a, b, ..., n are the atoms of the bridge connecting the metal ions (e.g. a sequence of proximate bridge atoms connecting the metal ions identifies an "atom pathway"; see Fig. 3) and $F_{\pi*(i,j)}$ and $F_{\pi(i,j)}$ terms are "transmission coefficients" of metal–metal interaction through the atoms of the pathway, and are functions of electronic density of the π^* and π orbitals at the ith atom [57]. The first term of I is the electron transfer interaction and the second term is the hole transfer contribution, while TS takes into account the through-space coupling, including the Coulombic interaction [58].

The dependence of the metal–metal interaction on the energy gap between the d_π-metal and LUMO–HOMO bridging ligand orbitals has interesting consequences; different metals would experience different degrees of metal–metal interaction in dinuclear species having the same ligands, even if it is assumed that the orbital energies of the bridge are not significantly affected by substitution of the metals. This is exemplified by comparing the ruthenium dimers $[(bpy)_2Ru(2,3\text{-}dpp)Ru(bpy)_2]^{4+}$ (**2**) and $[(bpy)_2Ru(2,5\text{-}dpp)Ru(bpy)_2]^{4+}$ (**10**) with the osmium dimers $[(bpy)_2Os(2,3\text{-}dpp)Os(bpy)_2]^{4+}$ (**5**) and $[(bpy)_2Os(2,5\text{-}dpp)Os(bpy)_2]^{4+}$ (**12**) respectively (see Table 1). In these complexes, the difference ΔE between first and second oxidation potentials, which is indicative of the degree of metal–metal electronic coupling, changes from 170 mV for both Ru dimers to 300 mV for both Os species (Table 1). The greater degree of metal–metal interaction for the osmium species with respect to the ruthenium species can be attributed to a more efficient mixing of the higher energy d_π orbitals of the osmium centers with the π^* orbitals of the bridge, π^*_{BL}, justified by a smaller energy gap between d_π and π^*_{BL} in the osmium complexes. Thus the dominant mechanism for metal–metal interaction in these complexes is bridge-assisted coupling via electron transfer. The situation is exemplified in Fig. 4, mechanism a.

Interestingly, the opposite order of metal–metal interaction occurs for Os and Ru species when low-lying π^* orbital bridges are replaced by electron-rich high-lying π^* orbital bridges, such as in the *N*-donor bis(pyridyl)triazolate anion bpt [42–44,59] (see Fig. 2 and Table 1, complexes $[(bpy)_2Ru(bpt)Ru(bpy)_2]^{3+}$ (**19**) and $[(bpy)_2Os(bpt)Os(bpy)_2]^{3+}$ (**20**)). In these systems, the ruthenium dimers exhibit a larger degree of metal–metal interaction than do the osmium centers (compare the ΔE value of the Ru species, 300 mV, and that of the Os dimer, 210 mV). The metal–metal interaction in these systems occurs following a hole transfer mechanism [44–46,59]. Within such a hypothesis, the decisive factor for the coupling is the energy gap between the HOMO of the bridge (the occupied π bridge orbital(s)) and the d_π orbitals. This energy gap is smaller for the more stabilized ruthenium centers. The situation is represented in Fig. 4, mechanism b. This explanation is also confirmed by the results obtained from the couple of complexes $[(bpy)_2Ru(bzim)Ru(bpy)_2]^{2+}$ (**25**) and $[(bpy)_2Os(bzim)Os(bpy)_2]^{2+}$ (**26**), having as bridging ligand another *N*-heterocyclic anion (ΔE of **25**, the Ru dimer, is 280 mV; ΔE of **26**,

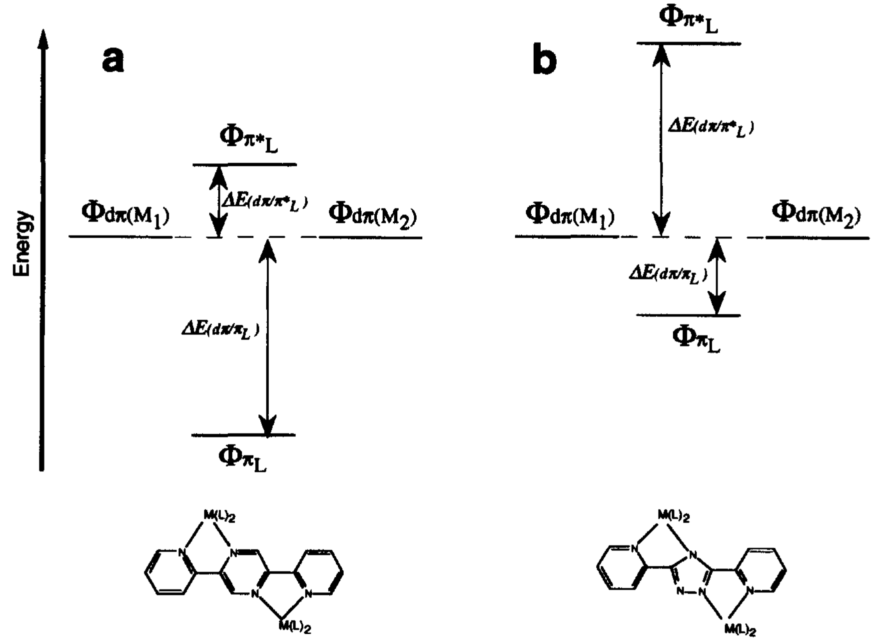

Fig. 4. Schematic representation of the energy- level diagrams suitable for metal–metal interaction dominated by superexchange-assisted electronic coupling via an electron transfer mechanism a or a hole transfer mechanism b. The bridging ligands are 2,5-bis(pyridyl)pyrazine (2,5-dpp) in mechanism a and a bis(pyridyl)triazolate anion (bpt) in mechanism b.

the Os analogue, is 190 mV; see Table 1). This behavior is not peculiar to the Ru–Os couple but is of general validity, as demonstrated by the complexes $[(ppy)_2Rh(bpt)Rh(ppy)_2]^+$ (**21**) and $[(ppy)_2Ir(bpt)Ir(ppy)_2]^+$ (**22**); in **21**, a rhodium species, ΔE is 470 mV, and it is only 170 mV in the iridium complex **22**, in agreement with expectation.

In a pictorial way, in which π back bonding is over estimated with respect to σ donation, for clarity, the difference between the successive oxidations of the two metal ions in weakly coupled dinuclear species may be described as follows, with the assumption, for example, that a bridge-mediated electron transfer mechanism across low-lying π^*_{BL} orbitals (i.e. the first term in eqn. (2)) is the dominant mechanism for electronic coupling. As a consequence of the stabilization of the d_π orbital of the oxidized metal, it cannot back bond to the π* orbital of the bridging ligand. The π* orbital of the bridge therefore couples more efficiently with the d_π orbital of the other (not yet oxidized) metal and is available to receive more electron charge via enhanced back bonding from the second metal. Therefore the d_π orbital of the second metal is stabilized following oxidation of the first metal ion. The more the bridging ligand is involved in back bonding with the metals, the larger is the bridge-mediated metal–metal interaction. A similar view can describe the hole transfer interaction mechanism.

3. PERIPHERAL LIGANDS AND METAL–METAL INTERACTION

Let us now consider the complexes $[(bpy)_2Ru(2,3\text{-dpp})Ru(bpy)_2]^{4+}$ (**2**), $[(biq)_2Ru(2,3\text{-dpp})Ru(biq)_2]^{4+}$ (**3**), $[(Cl)_2(CO)_2Ru(2,3\text{-dpp})Ru(CO)_2(Cl)_2]$ (**17**) and $[(NH_3)_4Ru(2,3\text{-dpp})Ru(NH_3)_4]^{4+}$ (**32**) of Table 1. The same bridging ligand, 2,3-dpp (Fig. 2), and metal ions, Ru(II), are present in all the complexes, but different peripheral ligands are bound to the metals. Quite different comproportionation constants characterize the complexes; this indicates that very different degrees of metal–metal interaction occur in the complexes, as a function of the peripheral ligands. The effect of the peripheral ligands is easy to understand when one considers that such ligands directly interact with the metals and therefore affect the d_π metal orbital energy [60]. This has a dramatic effect on metal–bridging ligand orbital overlap. For example, biq ligands are a better π acceptor than bpy ligands. Ru(II) metal ions bound to biq peripheral ligands are more stabilized (by enhanced metal back bonding to the peripheral ligands) than Ru(II) metals with bpy peripheral ligands. As a consequence, the energy gap between d_π metal orbitals and π^* bridging ligand orbitals is larger in the biq case than in the bpy case, so justifying the difference in K_c (7×10^2 versus less than 18; see Table 1). Similar arguments explain the behavior of the complex **32**, having NH_3 groups as peripheral ligands. In fact, NH_3 groups are not electron acceptors and, as a consequence, d_π orbitals are raised in energy, so decreasing the gap from the $\pi^*_{(BL)}$ orbitals. The resulting effect is $K_c = 4.2 \times 10^6$ for this complex, a value that indicates a noticeable communication between the metals. The opposite behavior, as expected, is exhibited by the complex **17**, having strong π^* acceptor CO ligands (see Table 1). The same considerations also account for the variation of the extent of metal–metal interaction in the series of complexes $[(bpy)_2Ru(2,5\text{-dpp})Ru(bpy)_2]^{4+}$ (**10**), $[(biq)_2Ru(2,5\text{-dpp})Ru(biq)_2]^{4+}$ (**11**) and $[(Cl)_2(CO)_2Ru(2,5\text{-dpp})Ru(CO)_2(Cl)_2]$ (**18**), in the complexes $[(bpy)_2Ru(bpym)Ru(bpy)_2]^{4+}$ (**1**) and $[(NH_3)_4Ru(bpym)Ru(NH_3)_4]^{4+}$ (**33**), and in the couple $[Cl(bpy)_2Ru(pz)Ru(bpy)_2Cl]^{2+}$ (**28**) and $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{4+}$ (**29**) (see Table 1).

The series of complexes $[(terpy)Ru(tpp)Ru(terpy)]^{4+}$ (**15**), $[(NH_3)_3Ru(tpp)Ru(NH_3)]^{4+}$ (**34**) and $[(tpp)Ru(tpp)Ru(tpp)]^{4+}$ (**36**) deserves particular attention. In these complexes, the bridge is a terdentate ligand tpp (see Table 1 and Fig. 2), and peripheral ligands are NH_3 groups (**34**), or the bpy terdentate analogue terpy (**15**), or other tpp ligands (**36**). The degree of metal–metal interaction strongly decreases on passing from **34** to **15** (K_c passes from 3.1×10^8 to 8.0×10^4; see Table 1), as expected on replacing the NH_3 ligands with the good π acceptor terpy ligands; however, when the peripheral ligands are the better π acceptor tpp ligands, the quite unexpected value of K_c 1.5×10^9 is obtained, indicating a large increase in metal–

metal interaction. The presence of tpp as a peripheral ligand also leads to apparently anomalous results in comparing the Ru–Os pair $[(terpy)Os(tpp)Os(terpy)]^{4+}$ (**15**) and $[(terpy)Os(tpp)Os(terpy)]^{4+}$ (**35**) with the Ru–Os pair $[(tpp)Os(tpp)Os(tpp)]^{4+}$ (**36**) and $[(tpp)Os(tpp)Os(tpp)]^{4+}$ (**37**). In the former pair (tpp bridge; terpy peripheral ligands; Ru versus Os), the metal–metal interaction is larger for the Os species than for the Ru species, as expected for superexchange-assisted coupling via an electron transfer mechanism. On the contrary, in the latter couple (tpp bridge; tpp peripheral ligands; Ru versus Os), communication is larger for the Ru dimer (K_c changes from 6.2×10^6 for the Os species to 1.5×10^9 for the Ru compound). Therefore, even if the bridge remains the same, in changing the peripheral ligands a qualitatively different effect on the extent of metal–metal communication is observed by replacing Ru with Os [56]. The latter feature, as well as the above-mentioned "strange" behavior of the series **34**–**15**–**36**, can be rationalized by considering that the strong electron acceptor ability of peripheral tpp ligands may stabilize the $d\pi$ metal orbitals in such a way as to enhance effectively the coupling of these orbitals with the proximate-lying π_{BL} (i.e. the HOMOs) orbitals of the bridge. If this is the case, superexchange-assisted coupling via the hole transfer mechanism may effectively contribute to the metal–metal coupling and can also assume the role of the dominant mechanism for the interaction [61]. In conclusion, we would like to stress that it appears that peripheral ligands, beside affecting the degree of metal–metal coupling, can even play a role in determining the nature of the dominant mechanism for the interaction.

In the pictorial representation, for the through-bond mechanism via an electron transfer pathway, strong π^* acceptor peripheral ligands compete with π^* bridging ligand orbital(s) for back bonding from the metal. As a consequence, the extent of back bonding from the metal to π^* bridging ligand orbital depends on the peripheral ligands. When a metal is oxidized, the lack of back bonding from that metal is divided among all the ligands. Therefore the effect of the oxidation in decreasing the energy of the π^* bridging ligand orbital level is reduced in dinuclear complexes with strong π^* acceptor peripheral ligands because of the competition between all the ligands for back bonding. This results in a reduced metal–metal interaction. Once again, a similar picture can be drawn for the hole transfer pathway.

The realization that metal–metal interactions in dinuclear bridged systems can be strongly modified by variation in the peripheral ligands may have important consequences, for example, for controlling metal–metal interaction in multinuclear compounds and for the design of systems featuring switchable electron and energy transfer processes. For example, one could design peripheral ligands coupled with cryptands suitable for hosting ions and/or molecules and, as a consequence, for modifying the electron density on the ligand (and on the coordinated metal). External control of the concentration of such ions and/or molecules could dramatically influence metal–metal interaction and switch on and off electron and energy transfer processes. Ligands with pH- and conformation-controlled intercomponent transfer abilities may also play the role of peripheral ligands. If one considers that peripheral ligands are usually more versatile than bridging ligands from a synthetic point of view, novel possibilities for the design of effective molecular devices based on electron and/or energy transfer can emerge.

4. PERIPHERAL LIGANDS AND METAL-TO-BRIDGING-LIGAND CHARGE TRANSFER TRANSITIONS

The influence of peripheral ligands on the energy of metal orbitals is also reflected in the energy and intensity of the metal-to-bridging-ligand charge transfer (MBCT) transition. For example, by comparing the absorption spectra in acetonitrile solution of $[(NH_3)_4Ru(2,3\text{-dpp})Ru(NH_3)_4]^{4+}$ (**32**), $[(bpy)_2Ru(2,3\text{-dpp})Ru(bpy)_2]^{4+}$ (**2**), and $[(Cl)_2(CO)_2Ru(2,3\text{-dpp})Ru(CO)_2(Cl)_2]$ (**17**), one can note that the maximum of the MBCT band moves from 558 nm ($\varepsilon = 19000\ M^{-1}\ cm^{-1}$) [53] to 527 nm ($\varepsilon = 24200\ M^{-1}\ cm^{-1}$) [29] and to 410 nm ($\varepsilon = 4500\ M^{-1}\ cm^{-1}$) [41] respectively. The same trend is exhibited by the couple of compounds $[(bpy)_2Ru(2,5\text{-dpp})Ru(bpy)_2]^{4+}$ (**10**) and $[(Cl)_2(CO)_2Ru(2,5\text{-dpp})Ru(CO)_2(Cl)_2]$ (**18**), where the maxima of the MBCT bands are at 585 nm ($\varepsilon = 15900\ M^{-1}\ cm^{-1}$) [29] and 448 nm ($\varepsilon = 4600\ M^{-1}\ cm^{-1}$) [41] respectively. The reason for such a behavior is well understood when one considers that the MBCT transition energy is strongly dependent on the potential of metal oxidation, which is related to the energy level of the HOMO metal orbitals. Peripheral ligands with better electron acceptor ability stabilize metal orbitals, so increasing MBCT transition energies. Of course, peripheral ligands also modify the energy of the LUMO of the bridge, but by a second-order effect. The possibility of tuning the MBCT excited-state energy by peripheral ligands has interesting consequences on the design of (i) luminescent dinuclear (or multinuclear) compounds having the desired excited state energy and (ii) "asymmetric" dinuclear (or multinuclear) homometallic systems featuring vectorial excited-state energy transfer [62].

The influence of peripheral ligands on the intensity of the MBCT transitions is less clear. The intensity depends on the transition moment *M* between the states involved. In its turn, *M* depends on the mixing between the states. Leaving aside symmetry considerations, enhanced mixing between metal and bridging ligand orbitals should lead, to a first approximation, to a better mixing between the states involved in the charge transfer process and to a higher probability of the transition. A crude comparison of the extinction coefficients ε of the MBCT bands between **2** and **17** and between **10** and **18** (see above) seems to confirm this expectation. Failures of this crude relationship may often occur because of the influence of other factors, including broadening of MBCT bands and overlapping with other charge transfer bands which can make it difficult to evaluate the area of the MBCT absorption.

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