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Coordination Chemistry Reviews 250 (2006) 1653–1668

COORDINATION CHEMISTRY REVIEWS

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Review

# Tuning interaction in dinuclear ruthenium complexes: HOMO versus LUMO mediated superexchange through azole and azine bridges

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Received 9 September 2005; accepted 11 December 2005
Available online 3 February 2006

## Contents

## Abstract

In this review the interaction between metal centers in dinuclear complexes based on azole and azine containing bridging ligands is reviewed. The focus of the review is on the manner in which the interaction pathway can be manipulated by variations in the nature of both the direct bridging unit and the peripheral substituents. Ruthenium polypyridyl type complexes will form the basis of this overview with particular attention paid to the electrochemical and spectroelectrochemical investigation of mixed valence compounds.

*Keywords:* Mixed valence; Spectroelectrochemistry; Ruthenium; Azine; Azole

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doi:10.1016/j.ccr.2005.12.008

## 1. Introduction

Polypyridine complexes, in particular those of ruthenium, rhodium, osmium and iridium, are playing a key role in the development of multi-component (supramolecular) systems capable of performing photo- and/or redox-triggered useful functions [1] such as charge separation devices for photochemical solar energy conversion [2] and information storage devices [3]. With regard to the latter topic, species featuring photophysical properties and redox behavior, which can be switched or tuned, are of particular interest [3,4]. From the 10 nitrogen containing 5- and 6-membered heterocycles described in Fig. 1, a vast array of multinuclear transition metal based complexes have been prepared in which the ditopic nature of the heterocycles has been employed either to impart pH dependent properties to the complexes formed or to form a direct bridge between metal centers.

Interaction between metal centers by direct orbital overlap requires internuclear separation to be of the order of a few Angstroms, beyond this distance through space interactions are almost exclusively Coulombic (electrostatic). The use of bridging ligands to mediate interaction over much larger distances (~20 Å) [5] relies on effective overlap of ligand orbitals (e.g. $\pi$ or $\pi^*$ orbitals of the aromatic bridging heterocycle, Fig. 2) with those of the metal centers. Such overlap requires both spatial and energetic matching of orbitals.

In this review we address the importance of these parameters in determining the magnitude and nature of the ground state interaction between metal centers in dinuclear compounds. The review is based on observations made for electron ‘rich’ azole rings and electron ‘poor’ azine ligands. With bridging ligands based on these units the metal–metal distances will be very similar, therefore the effect of varying the electronic properties of the bridging ligand on the extent of interaction can be considered in detail. The influence of peripheral ligands (i.e. those ligands not forming a direct bridge between the metal centers) should not be forgotten, as it is these ligands, which determine [largely] the relative energies of the metal centered orbitals. Indeed, the use of environmentally sensitive ligands both as a direct bridge [6] and as peripheral ligands [7] enables the interaction between metal centers to be tuned post synthetically. Finally an important issue with regard to measuring interaction between metal centers electrochemically and spectroscopically presupposes that the bridging ligand is redox innocent, something which is not always the case [8,9].

## 2. Theoretical and experimental aspects in the study of internuclear interactions

Before reviewing the use of azole and azine bridging ligands in tuning interaction between metal centers it is pertinent

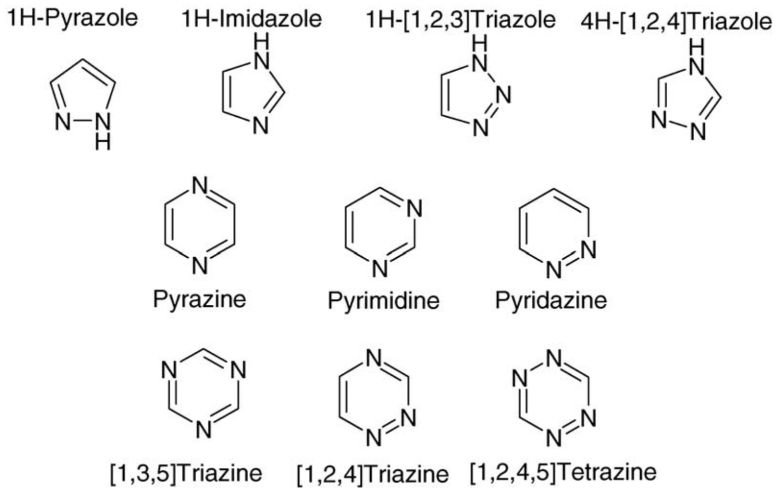


Fig. 1. Heterocycles used in the bridging ligands described in the text.

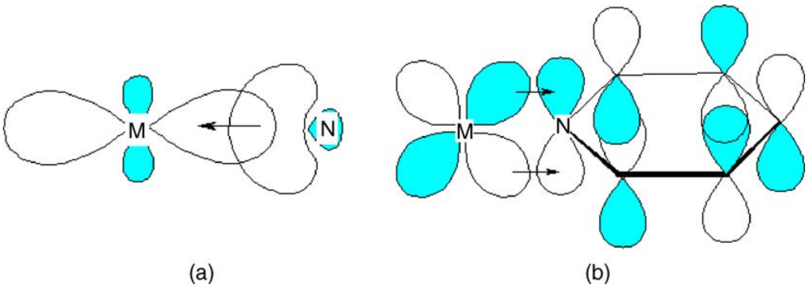


Fig. 2. Overlap between: (a) $\sigma$-donor bond of ligand and metal $d_{z^6}$ or $d_{x^2-y^2}$ orbital of the metal and (b) back donation or back bonding from metal to ligand via overlap of metal based $d_{xy}$, $d_{xz}$ or $d_{yz}$ orbital and ligand $\pi^*$ orbital.

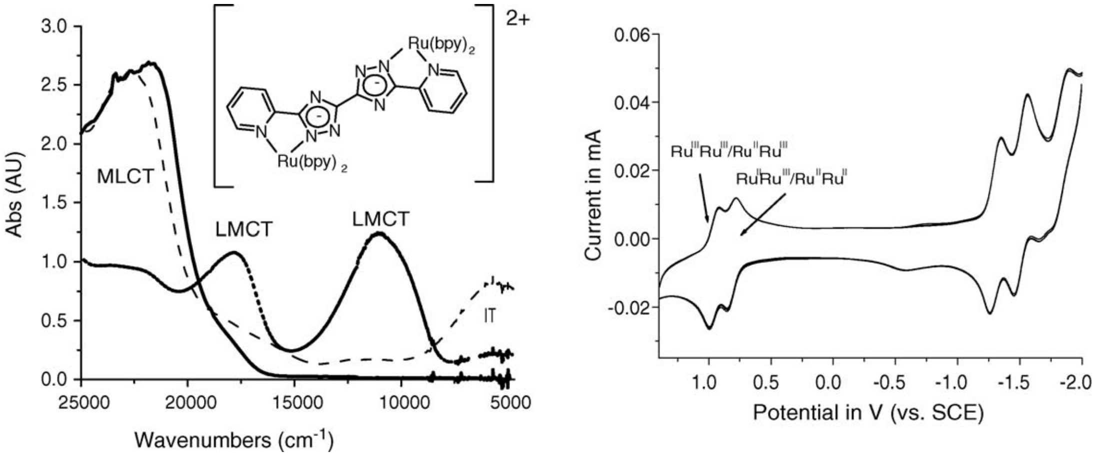


Fig. 3. Left: visible and near-IR absorption spectra of a binuclear ruthenium complex in acetonitrile (0.1 M TEAP) at 0.60 V (solid line), 1.00 V (dashed line), and 1.10 V (dotted line) vs. SCE. Right: cyclic voltammetry at 0.1 V s$^{-1}$. Reprinted with permission from [6d]. Copyright [2002] American Chemical Society Data.

to first consider what is meant by the term interaction. In the case of mixed valent systems there are four primary aspects to interaction of concern in the present review; the electrostatic interaction, the barrier to electron exchange in the mixed valent state, the coupling between the metal centers ($H_{ab}$) and the delocalization of the SOMO orbital in the mixed valent state ($\alpha^2$). Quantifying the strength of these interactions is at best difficult, however, the absolute values obtained using various approaches are very much of use for comparison between systems. Fortunately, the very early work of Hush, Robin and Day, later to be extended by many others, has provided a very practical method for ‘quantifying’ these various interaction concepts (vide infra).

### 2.1. Measuring interaction strength

The most common techniques used in the investigation of internuclear interaction in multi-center systems are electrochemical. The first important observable is the redox behavior of the two metal centers. When two different redox potentials are observed a mixed valence compound may be formed after the first redox process. In extreme cases this mixed valence species may be considered as either valence localized ($M^{II}$–$M^{III}$) or valence delocalized ($M^{II_{1/2}}M^{II_{1/2}}$). To obtain further information about the extent of delocalization, frequently, spectroelectrochemical techniques are used. Against this background a theoretical basis for the study of the ground state interaction between metal centers in dinuclear compounds was developed by Hush [10] and by Robin and Day [11] and latter by Creutz, Meyer and others [12,13]. This analysis is based on the assumption that the best way to get information about interaction in dinuclear compounds is by detailed study of their mixed valence compounds.

### 2.2. The comproportionation constant: $K_c$

The stability of the intervalence compound can be determined from the comproportionation constant [14]:

$$\mathrm{Ru^{II}Ru^{II}} + \mathrm{Ru^{III}Ru^{III}} \overset{K_c}{\Leftrightarrow} 2\mathrm{Ru^{II}Ru^{III}} \qquad (1)$$

It is important to note that this constant does not necessarily yield information about electron delocalization but is indicative of the amount of electrostatic interaction and redox asymmetry between the metal centers. At the statistical level for a complex with equivalent redox sites, the value of $K_c$ should be equal to 4 [14], however, if the two metal centers interact either electrostatically, through delocalization or both then the stability of the mixed valence state increases dramatically.

Equilibrium constants such as $K_c$ may be related to other thermodynamic parameters and can therefore be obtained from the electrochemical data as shown in Eq. (2) (see also Fig. 3):

$$K_c = \exp\frac{RT\Delta E}{nF} = \exp\frac{\Delta E}{25.69} \quad \text{at } 298\,\mathrm{K} \qquad (2)$$

Thus the magnitude of $K_c$ may be determined directly from electrochemical measurements. It should be noted however that $K_c$ can be very medium dependent and is particularly sensitive to the donor and acceptor strengths of both the solvent and the supporting electrolyte [15]. A final comment regarding $K_c$ is that in systems where the redox centers are non-symmetric, i.e. each metal has a different coordination environment, then the asymmetry will contribute significantly the magnitude of $K_c$. These several contributions to $K_c$ make its use to estimate interaction through SOMO delocalization difficult, if not impossible, to determine interaction from electrochemical measurements alone:

$$K_c = \Sigma\{K_{c(\mathrm{electrostatic})} + K_{c(\mathrm{solvent\ \ DN/AN})} + K_{c(\mathrm{delocalization})} + K_{c(\mathrm{redox\ \ asymmetry})}\} \qquad (3)$$

### 2.3. Intervalence transitions (IT) and optical electron transfer [16]

Central to studying interaction between metal centres in the mixed valence state is the phenomenon of optical electron transfer. In Fig. 4 several electron transfer process are presented schematically, including (1) optical, (2, 3) photoinduced and (4) thermal electron transfer. Optical electron transfer (which is observed as an intervalence transition in mixed valence systems

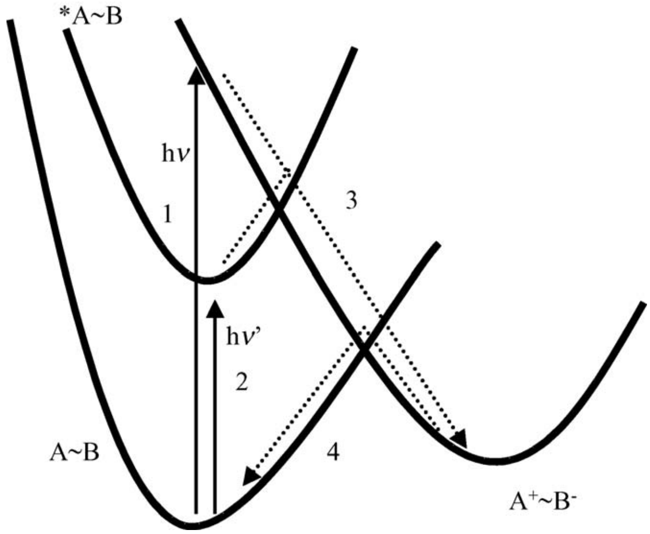


Fig. 4. Relationship between optical (1), photo-induced (2 and 3), and thermal back (4) electron transfer processes in supramolecular species.

such as those described below) uses EM radiation to move an electron spatially and is a temperature independent form of electron transfer (Eq. (4)). In contrast both thermal electron transfer processes (i.e. (2, 3) and (4)), thermal energy is required to transfer electronic charge (Eq. (5)).

$$A \sim B + h\nu \rightarrow A^{+} \sim B^{-} \tag{4}$$

$$A \sim B + h\nu \rightarrow A^{*} \sim B \rightarrow A^{+} \sim B^{-} \tag{5}$$

In order to glean information regarding electronic interaction in the mixed valent state, i.e. delocalized versus localized, we should consider the nature of the potential energy curves involved (Fig. 5) [16].

If the species ($M^{II}M^{III}$) and ($M^{III}M^{II}$) are considered as “electronic isomers” the equilibrium geometry of each species can be considered in terms of both inner sphere ($\lambda_i$) and outer sphere ($\lambda_o$) effects (vide infra). The inner sphere effects account for the differences in the metal–ligand bond lengths between the $M^{II}$ and $M^{III}$ states and the outer sphere effects refer to the difference in the solvation of the two “electronic isomers”. At the equilibrium geometry of each of the electronic states the other state can be considered as an electronically excited state and the possibility of an electronic transition between these states is present. The energy separation between these two states is called the reorganizational energy (λ) and is related to the intrinsic barrier to electron transfer (λ/4, i.e. the crossing point between the two potential wells: Fig. 5). At the crossing point there are no Frank–Condon [17] restrictions to electron exchange since both states have the same nuclear geometry and energy and hence thermal electron transfer is possible. If there is a large separation between the metal centers or if the bridge between the metal centers is insulating then the electronic interaction ($H_{ab}$) between the metal centers will be negligible and the system is best represented by Fig. 5(a). This in the Day nomenclature is called class I interaction type. For weakly interacting systems (Robin and Day Class II interaction) the electronic interaction is too small to affect the nuclear geometries of the metal centers (i.e., the difference in energy of the “electronic isomers” is much larger than $H$). However it does result in some mixing of the electronic states (Fig. 5(b)). In this situation the system retains the properties its individual components, but additional properties are observed, i.e. intervalence transitions. The probability of such a transition is dependent on the mixing between the two states and hence the larger the mixing the more intense the IT band. The thermal barrier to electron transfer is (when $H$ is small) only marginally less than λ/4. Finally when the electronic interaction is very strong (i.e. $H \approx \lambda$ Fig. 5(c)) the mixing between the two electronic states results in a single ground state minimum and the system is best described as valence delocalized ($M^{II_{1/2}}M^{II_{1/2}}$). In such systems the properties are usually completely different from those of its individual components and this interaction is classified as class III.

The nature of the intervalence transition is best described as a optical electron transfer process. Optical electron transfer (which is observed as an intervalence transition in mixed valence systems such as those described above) uses electromagnetic radiation to move an electron spatially from one metal center to another and is a temperature independent form of electron transfer (Eq. (4)). For optical electron transfer to take place the transition must be vertical (Frank–Condon principle) with

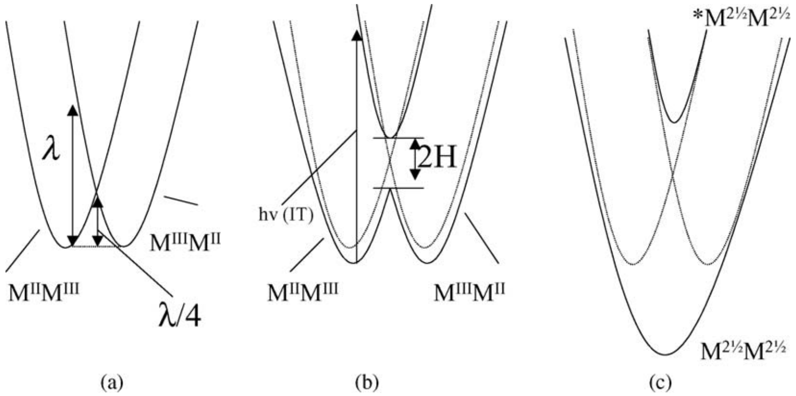


Fig. 5. Potential energy curves for a symmetric mixed valence compound showing: (a) negligible, (b) weak, and (c) strong electronic coupling. In the case of (b) and (c) the dashed lines represent the zero order states [76].

$E_{\text{op}}$ being the energy of the transition. For symmetric systems the value of $\Delta G^{\text{o}}$ is zero (where $\Delta G^{\text{o}}$ is the energy difference between the two potential curve minima) and hence Eq. (6) becomes $E_{\text{op}} = \lambda$ [18]:

$$E_{\text{op}} = \lambda + \Delta G^{\text{o}} \qquad (6)$$

### 2.4. The application of spectro-electrochemistry

As noted above, information can be obtained from the investigation of the compounds using spectroelectrochemical techniques to study the mixed valence compounds (see Fig. 3). Of particular interest are the spectroscopic features of the intervalence band of the mixed valence species, which allow for the estimate of the delocalization parameter ($\alpha^2$) and the coupling constant $H_{\text{ab}}$ as in Eqs. (7) and (8).

$$\alpha^2 = \frac{(4.2 \times 10^{-4})\varepsilon_{\max}\Delta\nu_{1/2}}{d^2 E_{\text{op}}} \qquad (7)$$

$$H_{\text{ab}} = [\alpha^2 E_{\text{op}}^2]^{1/2} \qquad (8)$$

where $\Delta\nu_{1/2}$ is its peak width at half height (in $\text{cm}^{-1}$), $d$ the inter component distance in Å and $E_{\text{op}}$ is the energy of the absorption maximum of the intervalence band (in $\text{cm}^{-1}$). These parameters provide the most direct indication for the importance of charge delocalization in the system. Additional information can be obtained by estimating the theoretical peak width at half height, $\Delta\nu_{1/2\text{calc}}$ using Eq. (9).

$$\Delta\nu_{1/2\text{calc}} = [2310(E_{\text{op}} - \Delta E)]^{1/2} \qquad (9)$$

If the value of $\Delta\nu_{1/2}$ obtained from this equation correlates well with the value found from direct measurement than the system can be described as valence localized $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$, i.e. Type II. If the IT band is narrower then the system is better described as Type III (valence delocalized). In addition the solvatochromic behavior of the intervalence band can be used. Type II can be identified by the large solvent dependence of the IT band. A complication arises, in the case of Type II/III systems [12], the properties of the IT band may suggest Type II and Type III interaction, in that a strong solvatochromic effect (indicating Type II) may be observed despite the band being very narrow (indicating Type III).

### 2.5. HOMO versus LUMO mediated superexchange interaction

Interaction in terms of ligand mediated superexchange can be viewed as coupling through either $\pi$ or $\pi^*$ orbitals of the bridging ligand (Fig. 6). In both cases the ligand orbitals are [transiently] either oxidised (HOMO mediated) or reduced (LUMO mediated) during the electron exchange process. Hence, since HOMO mediated superexchange requires initial oxidation of the bridging ligand and reduction of one of the metal centers, the electron rich bridging ligands such as triazoles and a electron deficient metals (i.e. more anodic metal oxidation potential) encourage interaction (and vice versa).

## 3. Azole bridges

Azole based bridging ligands containing imidazole, triazoles, tetrazoles and pyrazole, units have seen widespread application in multinuclear complexes. The different types of azole based ligands show considerable differences in the geometry of the two metal centers. Pyrazole ligands allow for a much closer spatial orientation of the two metal centers than imidazole ligands (see Fig. 7). Triazoles and tetrazoles, by contrast, allow for coordination in a similar mode to both pyrazoles and imidazoles. The azole ligands are typically strong σ-donors and weak π-acceptor ligands by virtue of the electron rich nature of the five-membered aromatic ring. This feature allows stabilization of higher oxidation states and large ligand field stabilization. As a result, these ligands have seen widespread application in 1st row transition metal complexes, in particular in spin cross-over complexes and structural models for many metalloenzymes [19]. Results obtained for the application of these units in a range of bridging ligands are discussed below.

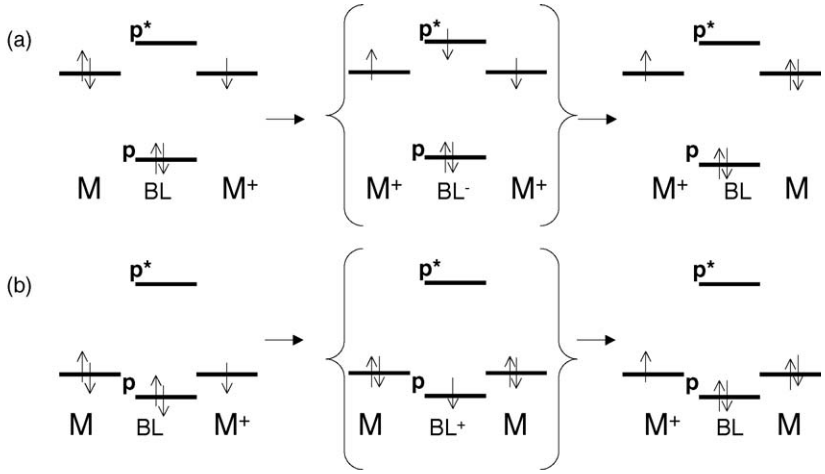


Fig. 6. (a) LUMO and (b) HOMO bridging ligand mediated superexchange.

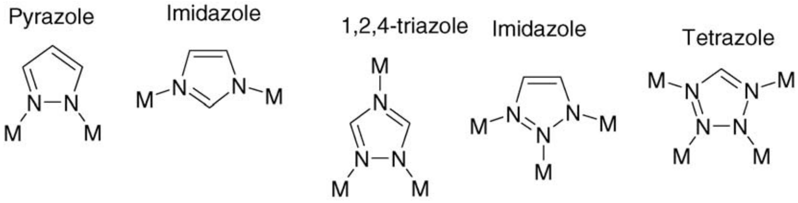


Fig. 7. Separation of metal centers for pyrazole, imidazole, triazole and tetrazole anionic ligands.

### 3.1. Pyrazoles and imidazoles

Ruthenium polypyridyl complexes of mixed 3,5-dicarboxypyrazole ($H_3$pzdc) [20], pyrazole-benzimidazole ($H_3$pzbzim) [21] and pyrazole-benzothiazole (Hpzbzth) [22] type ligands have been reported by Nag and co-workers (Fig. 8). The structural features of the dinuclear Ru(II)(bpy)$_2$ complex of the benzimidazole analogue is reported, together with the separation of its optical isomers. The dinuclear compound shows well-behaved electrochemistry with two metal-based oxidations at 1.01 and 1.23 V versus SCE ($\Delta E = 220$ mV). Upon deprotonation of the imidazole moieties these redox processes move to less anodic potentials (0.63 and 0.96 V, $\Delta E$ is 330 mV) as expected by the increased $\sigma$-donor properties of the ligand. This is a considerable increase compared to the value obtained for the compound containing the neutral imidazole units and indicates that the stability of the intervalence compound is increased for the deprotonated compound, with an increase in $K_c$ by two orders of magnitude from $\sim 5 \times 10^3$ to $4 \times 10^5$. Detailed acid–base studies are reported for the dinuclear compounds. In these studies the two-step acidity of the imidazole NH protons was considered. Interestingly the values obtained for the intervalence compound are a combination of those found for the Ru(II) and Ru(III) centers. For the Ru(II) complex two values of pH 7.7 and 9.8 were obtained, while for the Ru(III) complex the values obtained are pH 1.4 and 3.5. For the mixed valence compound values of pH 3.5 and 8.6 were obtained. Although, there is a significant interaction between the metal centers (i.e., $\Delta E$) the authors postulate that since two very different values are obtained for each deprotonation step of the mixed valence compound, it is valence trapped and no intervalence transition is reported for the complex. In an analogous compound a thiazole ring replaces the imidazole moiety. For the Ru(II)(bpy)$_2$ complex of this ligand a $\Delta E$ value of 260 mV is obtained. A weak intervalence band is reported at 950 mV. This band is observed as a shoulder on the LMCT bands and the compound is described as a Class II compound with a value of $H_{ab} \approx 335\ \mathrm{cm}^{-1}$. Meyer and co-workers reported the synthesis and electrochemical properties of a dinuclear Ru(II)(bpy)$_2$ complex containing two deprotonated pyrazolato groups as a double bridge [23]. The compound exhibits two well-separated metal-based oxidations with potentials of 0.83 and 1.21 V ($\Delta E$ 360 mV). However, the intervalence compound is unstable and undergoes asymmetric cleavage of the complex to give the mononuclear complex $[\mathrm{Ru(bpy)_2(pz)_2}]^{2+}$.

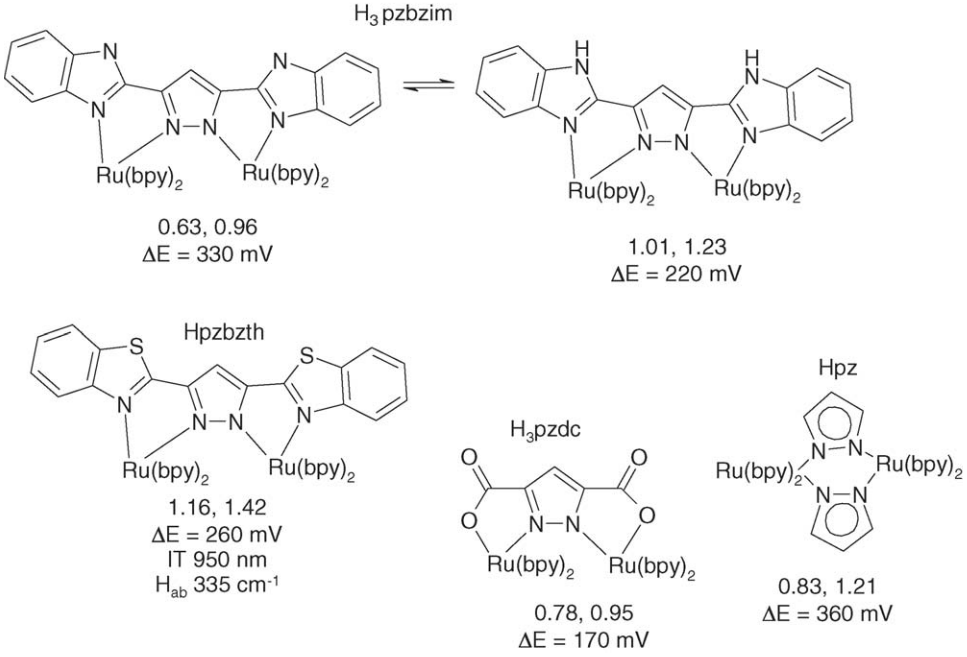


Fig. 8. Structures and electrochemical data for binuclear ruthenium pyrazole bridged complexes described in the text.

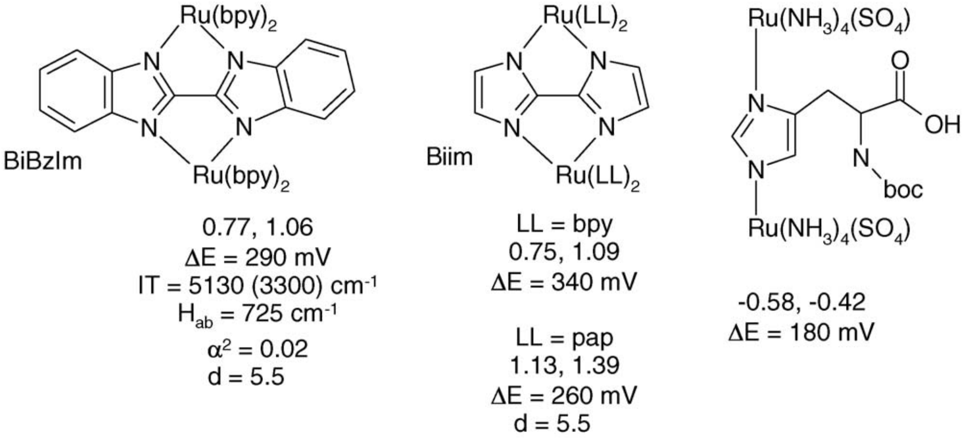


Fig. 9. Structures and electrochemical data for binuclear ruthenium imidazole bridged complexes described in the text.

Haga and co-workers have carried out a wide range of studies on dinuclear Ru(II)(bpy)$_2$ complexes of benzimidazole type bridging ligands. Of relevance to the present review are the bis-benzimidazole type ligands (Fig. 9) [24,25]. The homonuclear Ru(bpy)$_2$–BiBzim–Ru(bpy)$_2$ compound shows two metal based oxidation potentials at 0.77 and 1.06 V versus SCE ($\Delta E$ 290 mV). Interestingly the intervalence compound shows two intervalence bands at 1060 and 1950 nm. Although the presence of more than one intervalence band is common for osmium complexes, the presence of two intervalence bands is unusual for ruthenium-based complexes. As for the osmium compounds this observation is most probably related to the presence of spin–orbit coupling. For the related bisimidazole complex reported by Rillema et al., a $\Delta E$ 340 mV is observed with oxidation potentials of Ru(II)/(III) and Ru(III)/Ru(III) of 0.75 and 1.09 V versus SCE [26]. Majumdar et al. have reported the bi- and tri-nuclear bisimidazole bridged complexes incorporating Ru(pap)$_2$-, where pap = 2-(phenylazo)pyridine, in place of the more usual Ru(bpy)$_2$ unit [27,28]. The good π-acceptor pap ligands allow for the formation of stable multinuclear complexes bridged by the bisimidazolato dianion, however, the mixed valence state was found to be unstable towards dissociation to mononuclear complexes. The pap ligand results in an anodic shift in the metal oxidation processes of approximately 380 mV (i.e., to 1.13 and 1.39, $\Delta E = 260$ mV). For the asymmetric complexes $[\mathrm{Ru(pap)_2(Biim)Ru(bpy)_2}]^{2+}$ the value of $\Delta E$ increases due to the redox asymmetry to 390 mV. However, the increase is not as much as would be expected ($\Delta E = 640$ mV), due to the much weaker π-acceptor properties of bpy relative to pap, which in turn affects the donor strength of the bisimidazolato ligand. This highlights the influence of non-bridging ligands on the properties of the bridging ligand. Several complexes incorporating a single imidazole ring as bridging ligand have been reported also. Gulka and Isied have reported the imidazole bridged complex *trans*-$[\mathrm{SO_4(NH_3)_4Ru^{III}(His\text{-}NBOC)Ru^{III}(NH_3)_4SO_4]BF_4}$, which shows two metal centered redox processes at −0.42 and −0.58 V ($\Delta E = 160$ mV) [29]. Toma and co-workers have reported the imidazole bridged complexes *cis*,*cis*-$[\mathrm{(bpy)_2ClRu(\mu\text{-}bim)RuCl(bpy)_2}]^{n+}$ (bim = benzimidazolate) [30]. The mixed-valent species shows type II coupling.

## 3.2. Triazoles

### 3.2.1. 1,2,3-Triazoles

Toma and co-workers reported 1,2,3-triazole bridged (edta)Ru(II)- and Ru(II)(bpy)$_2$-binuclear complexes [31]. For the Ru(bpy)$_2$ based benzo-1,2,3-triazole complex the mixed valence complex ($\mathrm{Ru^{II}Ru^{III}}$) has been assigned as Type II or valence-trapped based on analysis of the IT band. For the related edta complex, a distinct pH dependence of the interaction in the mixed valence state was observed [32]. Depending on the proton concentration, the electronic coupling and delocalization can be tuned between class III (deprotonated bridging ligand), class II (protonated), or even a borderline class II/class III system.

### 3.2.2. 1,2,4-Triazole based compounds

Of the azole family of bridging ligands perhaps, 1,2,4-triazole based ligands have received the most attention both in terms of forming a direct bridge with a wide range of metal centers [33] and as components in more extended systems [34,35]. Indeed, the large number of complexes reported has ensured that this ligand unit has played a prominent role in the investigation of intercomponent interactions. Their synthetic flexibility allows for systematic tuning of their electronic, electrochemical and acid–base behavior. Some triazole bridging ligands are outlined in Fig. 10.

Triazoles are of interest in the investigation of intercomponent interaction since deprotonation of the triazole ring occurs upon coordination. The first compounds studied were based on 1,2,4-triazole ring substituted with two pyridine (L1) [34] and pyrazine (L2) moieties [35] (Fig. 10).

Homo and hetero-dinuclear Ru(bpy)$_2$- and Os(bpy)$_2$-complexes have been described and the electrochemical properties of these compounds and of their intervalence compounds have been reported [34]. Interaction between the two metal centers is evident from the fact that two separate metal-based oxidations are obtained for all compounds. For RuL1Ru the redox

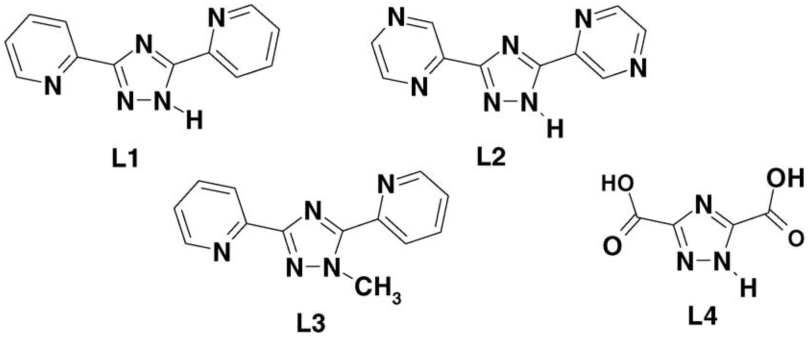


Fig. 10. Structures of triazole type ligands discussed in the text.

processes are observed at 1.04 and 1.34 V ($\Delta E = 300$ mV). For OsL1Os the difference is somewhat smaller at 0.64 and 0.85 V ($\Delta E = 210$ mV), while as expected for the mixed metal complexes values of about 450 mV are observed for $\Delta E$ [36]. For all compounds well-defined intervalence bands are observed. The relevant spectroelectrochemical data observed for the compounds RuL1Ru and RuL2Ru are shown in Table 1.

The magnitude of $H_{ab}$ (700 cm$^{-1}$) suggests that the interaction in the mixed valence state is best described as Class II. Although the situation in the case for the Os containing compounds is more complicated, due to stronger spin–orbit coupling three intervalence bands are observed, overall, similar results are obtained. The importance of the negative charge can be established by comparing RuL1Ru ($\Delta E = 300$) with the value obtained for a related ligand L3 where the free nitrogen is methylated [37]. For the dinuclear ruthenium complex RuL3Ru ($\Delta E = 160$ mV) metal-based oxidation processes were observed at 1.39 and 1.55 V. The substantial increase in redox potentials observed for this compound can be explained by the presence of the methyl group, which ensures that the triazole is no longer anionic.

Replacement of the pyridine rings of L1 for pyrazine rings (L2) results in a modest increase in redox potentials of the metal centers due to the greater π-acceptor properties of pyrazine [34]. For this compound two metal-based oxidations are observed at 1.16 and 1.46 V, however, $\Delta E$ is identical to that found for the L1 bridged complex. In addition, the intervalence parameters of the compound are very similar also (see Table 1). This suggests that the interaction between the metal centers is not significantly affected by the nature of non-bridging components of the bridging ligand and the ground state interaction is dependent predominantly on the triazolato ring. This contrasts with the effect of methylation of the triazole ring and supports the assignment of a HOMO rather than LUMO mediated superexchange. Further support for HOMO mediated superexchange is found in the related ligand, 3,5-dicarboxytriazole (L4) reported by Nag and co-workers. The dinuclear Ru(II)(bpy)$_2$ complex based on this ligand has two metal-based oxidations at 0.75 and 0.92 V ($\Delta E = 170$) [21b]. This value is similar to that for the L3 complex and reflects the electron withdrawing properties of the carboxylic acid groups, which reduce the electron density of the bridging triazole ring, stabilizing the triazole HOMO orbitals.

In contrast to the imidazole, pyrazole and 1,2,3-triazole based complexes, the two metal centers bridged by the 1,2,4-triazole unit are inherently asymmetric due to the difference of the N2 and N4 nitrogen atoms. Hence, the difference in redox potentials of the metal centers coordinated to the N2 and N4 nitrogen atoms will add to the magnitude of $K_c$. Nevertheless, the relatively large value of $K_c$ for the L1 and L2 bridged complexes in comparison with the L3 and L4 bridged complexes confirm the presence of contributions to $K_c$ from HOMO mediated superexchange interactions.

## 4. Azine bridges

In contrast to the five membered heterocyclic ligands, the six membered heterocyclic ligands are electron deficient and, hence, are weak σ-donors and strong π-acceptors. The majority of [directly] azine-bridged binuclear complexes are based on the pyrazine heterocycle, the most famous of which is undoubtedly the Creutz–Taube ion (CT ion) [38]. Nevertheless, binuclear complexes based on other pyrimidine and pyridazine have been reported and in recent years triazines and tetrazines have been employed.

Table 1
Spectroelectrochemical data for complexes discussed in text

| | $H_{ab}$ (cm$^{-1}$) | $\alpha^{2}$[a] | $\Delta E$ (±10 mV) | $K_c$ | $\Delta\nu_{1/2calc}$ (cm$^{-1}$) | $\Delta\nu_{1/2}$ (cm$^{-1}$)[b] | $\varepsilon_{max}$ (M$^{-1}$ cm$^{-1}$) ±20% | $E_{op}$ (cm$^{-1}$) ±100 cm$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| $[(Ru(bpy)_2)_2L1]^{3+}$[c] | 700 | 0.016 | 300 | 117910 | 3341 | 3300 | 2400 | 5556 |
| $[(Ru(bpy)_2)_2L2]^{2+}$[c] | 745 | 0.019 | 300 | 117910 | 3260 | 4200 | 2200 | 5405 |

[a] Extent of electronic delocalisation.

[b] Taken as double the width at half maximum of the high energy side of the absorption band.

[c] From Refs. [34,35].

### 4.1. Pyrazine and Pyrimidine bridged binuclear complexes

The Creutz–Taube (CT) ion $\{[(NH_3)_5Ru–(\mu\text{-pyrazine})–Ru(NH_3)_5]^{4+}\}$ reported by Creutz and Taube in 1969 [38] is, arguably, the archetypal binuclear azine bridged complex and both itself and similar pyrazine bridged multinuclear systems remain the focus of considerable attention. A key feature of the CT ion is the large separation between the first and second metal oxidation steps at 0.4 and 0.76 V ($\Delta E = 360$ mV), despite the structural equivalence of both metal centers. In addition, for the mixed valence species (Ru(II)–Ru(III)) a band in the visible region at 565 nm (the fully reduced species shows an absorption at 547 nm) and a distinct band, assigned as the intervalence transition, at 1570 nm are observed.

In view of the relatively large distance between the metal centers and low $\pi$–$\pi^*$ gap of the pyrazine bridge, the mechanism for the interaction between the metal centers in pyrazine-bridged binuclear complexes is generally agreed to be via a bridge mediated superexchange process rather than by direct overlap of metal based orbitals [39]. What is less clear is whether the superexchange is via hole or electron transfer (vide supra). In order to determine this the relative energies of both the bridging ligand and the metal centers must be varied and the effect of this variation on the strength of the interaction examined. Since the first report on the paradigm pyrazine (pz) bridged binuclear ruthenium(II) complex ($[(NH_3)_5Ru)_2pz]^{2+}$), by Creutz and Taube [38], pyrazine bridged multinuclear complexes have received considerable attention [40], and the family of pyrazine-bridged analogues of the CT ion has been reviewed recently by Kaim et al. [41] Investigations have focused predominantly on the electrochemical and spectroelectrochemical properties of these complexes, in particular towards the measurement of the degree of delocalization in the mixed valence ($Ru^{II}Ru^{III}$) species [42]. The many structural analogues of the Creutz–Taube (CT) ion involving substitution of the monodentate amine groups with pyridyl, bipyridyl, chloro, and/or aquo groups, have provided considerable insight into the factors that control internuclear interaction in the Ru(II)Ru(III) state [43,44].

The effect of substitution of peripheral ligands (i.e., $NH_3$) (Fig. 11) provided invaluable information as to the nature of the interaction between the two metal centers. Substitution of one $NH_3$ for $H_2O$ resulted in a very slight shift in the $\lambda_{max}$ of the IT band (to 1530 nm). However, substitution with a chloride anion or pyrazine resulted in a large blue shift in the $\lambda_{max}$ of the IT band to 1450 and 1160 nm, respectively. The changes in the energy of the IT band have been interpreted on the basis of the effect of substitution on the barrier to electron transfer, as the reduction of electron density on the substituted metal center makes that same center more difficult to oxidize. Increasing the asymmetry in the complex by replacement of one of $Ru(NH_3)_5$ moieties by $RuCl(bpy)_2$ (960 nm), $Ru(NO_2)(bpy)_2$ (790 nm) or $Ru(CH_3CN)(bpy)_2$ (750 nm) results in a further blue-shift of the IT band [43a,b]. Similar studies on the 4,4′-bipyridine bridged analogue of the CT ion have been reported also and show a much reduced level of interaction for symmetric systems with increasing oxidation potential of the ruthenium centers (based on electrochemistry) [45].

Meyer and co-workers have examined the intervalence properties of the CT ion analogues $[(bpy)_2ClM–(\mu\text{-pyrazine})–MCl(bpy)_2]^{2+}$ (where M = Ru or Os) [44]. In these ions the extent of electron delocalization in the mixed valence state is very small. The difference between successive metal oxidation waves ($\Delta E$) for the ruthenium dimer is 120 mV and an intervalence transition at 1300 nm ($\varepsilon = 455\ M^{-1}\ cm^{-1}$) is observed for this ion. Importantly the mixed valence and fully oxidized species show some instability, which prevented their observation initially [46]. Similarly, for the osmium complexes only weak absorptions were observed for the mixed valance species.

For the related complex $\{[(bpy)_2ClRu–\text{pyrimidine}–RuCl(bpy)_2]^{2+}$ the interaction observed electrochemically ($\Delta E = 120$ mV) is equal to that observed for the pyrazine-bridged complex. However, despite the direct separation between the metal centers being less for the pyrimidine compared to the pyridine complex a considerably reduced interaction is present with an IT band observed at 1360 nm ($\varepsilon = 34\ M^{-1}\ cm^{-1}$) and a calculated delocalization parameter ($\alpha^2$) an order of magnitude lower than for the pyrazine bridged dimmer [47]. Again the stability of the mixed valence and fully oxidized species is poor and decomposition is observed. Pavinato et al. [48] have reported a similar metal–metal interaction strengths for systems based on $Ru(bpy)_2$bipyrimidine- and Phillips and Steel, for systems based on the ditopic ligand 4,6-di(2-pyridyl)pyrimidine [49].

Meyers and Powers [47] have proposed, on the basis of molecular orbital (CNDO, INDO) calculations on the free ligands, that the disparity in interaction strength comparing pyrazine to pyrimidine is due to the lower $\pi^*$ level and the higher atomic coefficients at the nitrogen atoms of the pyrazine ligand. Thus, it is apparent that over the same internuclear separation and using the same bridging ligand, there is a very large range of interaction strengths which may be accessed by varying both the metal centers employed and the peripheral ligands, from the type III interaction of the CT ion [38] to the Type I strength interaction of the bis(allyl)based Ru(II)/Ru(IV) complex $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\mu\text{-pyrazine})Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)Cl_2]$ [50].

Although the majority of studies of CT analogues involve substitution of the non-bridging ligands, an alternative approach to tuning the internuclear interaction in pyrazine bridged binuclear complexes such as the CT ion is to modify the bridging pyrazine unit by substitution in the 2,3-, 2,5- or 2,3,5,6-positions [51]. Indeed, many of the complexes prepared from modified pyrazine ligands have proven to be well suited to investigation by techniques such as electrochemistry, spectro-electrochemistry [52], Infrared [53], Mössbauer [54], and UV–vis absorption spectroscopy. The majority of these studies have focused on the relative delocalization of the singly occupied molecular orbital of the mixed valence state, e.g. Ru(II)–pz–Ru(III), where the mechanism for interaction cannot involve direct overlap of the metal orbitals (i.e. superexchange processes mediated via either the ‘HOMO’ or ‘LUMO’ of the bridging ligand).

Multinuclear complexes employing ligands based on 2,3-(dipyrid-2′-yl)-pyrazine have been reported by several groups [55]. IT absorption bands at between 5000 and 8000 $cm^{-1}$

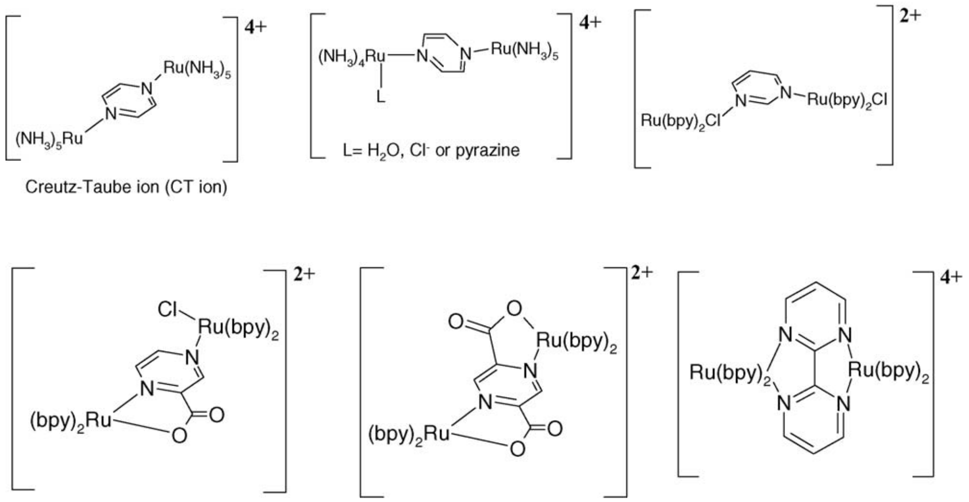


Fig. 11. CT ion and related complexes discussed in the text.

are typical of these classes of complex and the interaction in most cases has been classified as Type II [56–59]. There are some examples of Type III interactions, however. For the Ru(L)Cl-based binuclear complex of tppz (Fig. 12) (where $L = 2,2'$-dipyridylamine) a strong interaction was observed both electrochemically ($\Delta E = 380$ mV) and spectroscopically, with a narrow intervalence band at 1700 nm ($H_{ab} = 2940\ \mathrm{cm}^{-1}$) [60]. In this case the lowering of the redox potential of the complex through the use of chloro ligands facilitates the LUMO mediated superexchange.

The mono-, bis- and tri-nuclear Ru(II)(bpy)$_2$-complexes of the ligand 1,4,5,8,9,12-hexaazatriphenylene (HAT) have been reported by Kirsch-de Mesmaeker and co-workers [61]. Increasing the number of Ru(bpy)$_2$ units coordinated to the HAT ligand from 2 and 3 results in an anodic shift of the 1st and 2nd metal oxidation step from 1.53 V (versus SCE) to 1.61 and 1.78 V (versus SCE) to 1.87 V, reflecting the reduction in electron density of the HAT ligand with increasing nuclearity. Despite this change in the electron density of the ligand the separation of the 1st and 2nd redox waves are approximately equal ($\Delta E = 250$ for Ru$_2$ and $\Delta E_1 = 260$ mV for Ru$_3$). Indeed the separation between the 2nd and 3rd oxidation steps for the trinuclear complex is also 250 mV ($\Delta E_2$). The lack of sensitivity to changes in bridging ligand electron density and the similarity of the magnitude of $\Delta E_1$ and $\Delta E_2$ suggests that the major contribution to the separation is electrostatic rather than delocalization. However, recent examination of the UV–vis NIR spectra (at <0 °C) of the intervalence complexes of both Ru$_2$ and Ru$_3$ by D'Alessandro and Keene [62], indicate that the complexes lie in the boundary Type II/III classification of interaction.

For pyrazine carboxylate bridged systems such as those shown in Fig. 11 [63], the differences in redox potentials of the 1st and 2nd metal oxidation process are similar to those found for the pyrazine and pyrimidine bridged binuclear complexes described above. It is clear that the interaction between the metal centers in terms of the IT band is dependent on the nature of the non-bridging moieties of the complex, whilst the value of $\Delta E$ from electrochemical analysis is less so. Toma et al. have reported tetra- and hepta-nuclear complexes based around a central [Ru(bpz)$_3$]$^{2+}$ moieties with the remaining centers being Ru(II) penta-amine groups [64]. In these systems no IT bands were observed, however the low energy absorption bands of the

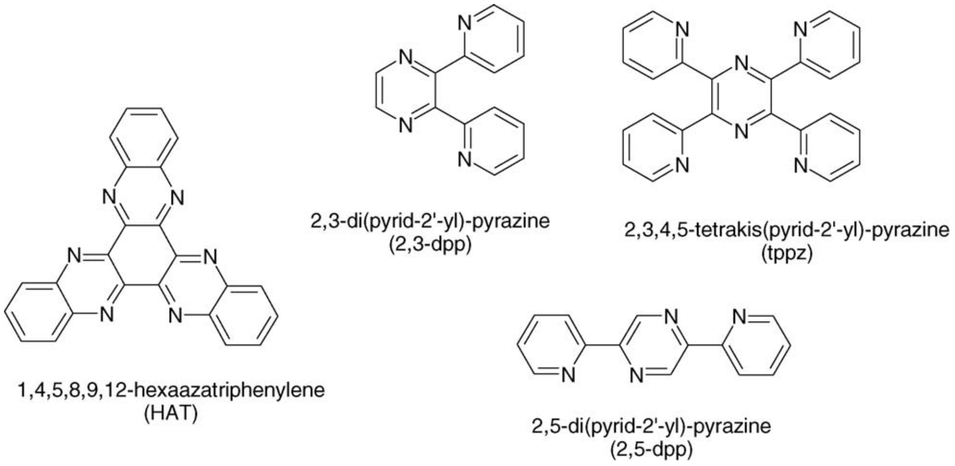
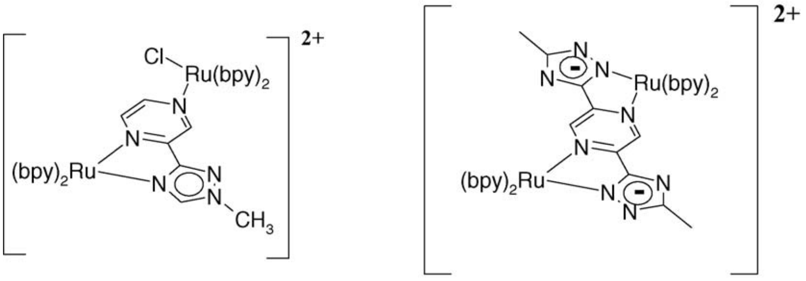


Fig. 12. Pyrazine based bridging ligands discussed.



$[(Ru(bpy)_2)(2\text{-Metrpz})(Ru(bpy)_2Cl)]^{2+}$ $[(Ru(bpy)_2)_2((5\text{-Metr})_2pz)]^{2+}$

Fig. 13. Structure of pyrazine-triazole bridged complex.

mixed valence species and the very low values of $\varepsilon$ expected may result in the IT band being unobservable due to the overlap with other bands.

Hage et al. have reported asymmetric pyrazine bridged homo- and hetero-binuclear complexes, Fig. 13, left [65]. Due the inherent differences in the oxidation potentials of the mononuclear analogues $[Ru(bpy)_2(pz)Cl]^+$ and $[Ru(bpy)_2$(1-methyl-3-(pyrazin-2′-yl)-1,2,4-triazole)$]^+$, a large separation ($\Delta E$) between the 1st and 2nd oxidation waves (490 mV) is expected. As for the 2-pyrazine-carboxylic acid bridged dimer described above an IT band is observed for the ruthenium based dimer at 962 nm ($\varepsilon = 480\,M^{-1}\,cm^{-1}$) and for the ruthenium/osmium based dimers at around 1300–1600 nm ($\varepsilon \sim 800\,M^{-1}\,cm^{-1}$).

$H_2$(5-Metr)$_2$pz, Fig. 13 [7] is a variation on L2, however the units involved in the bridging ligands have been rearranged. Of interest is how this rearrangement affects the interaction between two metal centers. If the connectivity of the components of the bridging ligand would be of minor importance then it was anticipated that due to the presence of two triazole moieties a stronger interaction would be obtained than observed for L2. However, the separation between the metal-based oxidation is only 170 mV, comparable with that obtained for L3. It was also observed that protonation of the triazolato groups in the complex leads as expected to a shift of these oxidations to higher potentials but the $\Delta E$ value obtained is not affected. This latter observation is important since it rules out HOMO mediated superexchange as a possible mechanism for metal–metal interaction. Instead a LUMO based superexchange mechanism is proposed in line with that observed form the Creutz–Taube ion and other pyrazine bridged ruthenium based polypyridyl complexes. The results obtained suggest that part of the bridging ligand which can mediate direct contact between the metal centers, i.e. pyrazine for $H_2$(5-Metr)$_2$pz complexes and triazole in L1 and L2 complexes plays a crucial role in determining the mechanism of interaction between the metal centers in the dinuclear molecule.

### 4.2. Intercomponent interactions—information from peripheral ligand reductions

Although the role of bridging ligands in mediating intercomponent interaction in multinuclear complex is usually concerned with metal-centered oxidations, the binuclear complexes based on the ligands (5-Metr)$_2$pz$^{2-}$ (Fig. 13), 2,3- and 2,5-dppz, highlight the importance of the redox state of the bridging ligand in considering intercomponent interactions.

The reductive electrochemistry of the complexes $[(Ru(bpy)_2)_2(2,3\text{-dpp})]^{4+}$ and $[(Ru(bpy)_2)_2(2,5\text{-dpp})]^{4+}$ is shown in Fig. 14. The first two reduction (I, II) processes for both com-

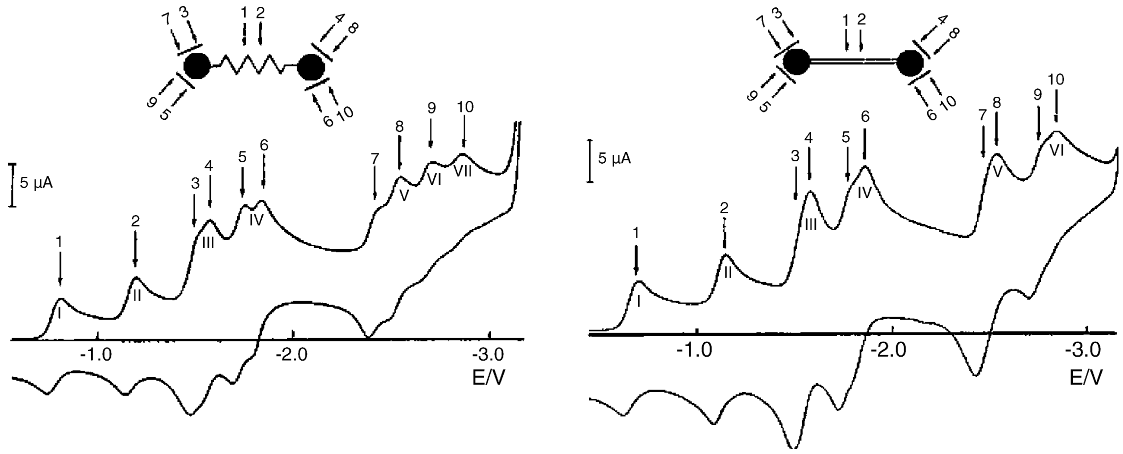


Fig. 14. Cyclic voltammetry of left: $[(Ru(bpy)_2)_2(2,3\text{-dpp})]^{4+}$ and right: $[(Ru(bpy)_2)_2(2,5\text{-dpp})]^{4+}$ in DMF. Reprinted with permission from [59]. Copyright [2002] American Chemical Society Data.

plexes are assigned as bridging ligand reductions. The 2 two-electron reduction processes (III, IV) are assigned to reduction of the bpy ligands. The separation of waves III and IV is as expected for sequential reduction of the two bpy ligands of each metal center. The splitting of the two one-electron processes within each two-electron peak confirms that the $Ru(bpy)_2$ groups are not being reduced independently. This is further supported by the larger splitting observed in the second peak (IV) than the first peak (III). The difference in splitting between the two complexes indicates that 2,3-dpp allows for more effective interaction than 2,5-dpp. Similar effects are observed for the $(5\text{-Metr})_2pz^{2-}$ bridged complexes [7].

### 4.3. Pyridazine bridged binuclear complexes

In contrast to pyrazine, pyridazine has received relatively little attention as a bridging ligand in part due to the steric constraints imposed by the ligand. Nevertheless, as for pyrazole, pyridazine allows for two metal centers to be brought very close together opening the possibility of direct metal–metal interactions. Ghumaan et al. [66] have reported two binuclear complexes based on the ligand 3,6-bis(2′-pyridyl)pyridazine and the metal units $(acac)_2Ru$- and $(bpy)_2Ru$-, however, although the first metal center coordinates via N1 of the pyridine ring and N2 of the pyridazine ring the second metal center coordinates through cyclo-metallation at the C5 carbon of the pyridazine ring rather than the sterically crowded N1. Hence, both binuclear complexes can be viewed as analogues of the CT ion. Interestingly, the complex $[((acac)_2Ru)_2\{3,6\text{-bis}(2'\text{-pyridyl})\text{pyridazine}\}]^+$ where the ruthenium centers are in the Ru(III) oxidation state, allows for the use of magnetic susceptibility to probe the internuclear interaction, which was found to show anti-ferromagnetic coupling of the centers ($J = -11.5\,\text{cm}^{-1}$). Despite the markedly different stabilization of the metal orbitals of the acac and bpy based complexes the separation or the II, II/II, III and II, III/III, III redox states is approximately equal (~490 mV), however, as the separation of the III, III/III, IV and III, IV/IV, IV redox process for the $(acac)_2$ based complex is 390 mV, suggests that the asymmetry of the two redox sites is responsible primarily for the large $K_c$ values. This assignment is supported by EPR spectra of the mixed valent species. Hence, while for the $Ru^{III}Ru^{III}$ state of the acac based complex, a strong interaction between the metal centers is observed by EPR and magnetic susceptibility, for the mixed valence complexes the interaction although present is much weaker than the large values of $K_c$ would presuppose.

### 4.4. Triazines

In contrast to pyrazine, triazines (both 1,2,4- and 1,3,5-triazines) have received relatively little attention despite the possibility of coordination of up to three metal centers simultaneously, and its use in mononuclear complexes. Nevertheless, recently several studies employing triazines have been reported, including Re(I) [67], Ru(II) [68] and Os(II) [69] based binuclear systems. A particular feature of 1,3,5-trazines is their susceptibility to methoxylation and hydroxylation of the triazine carbon atoms.

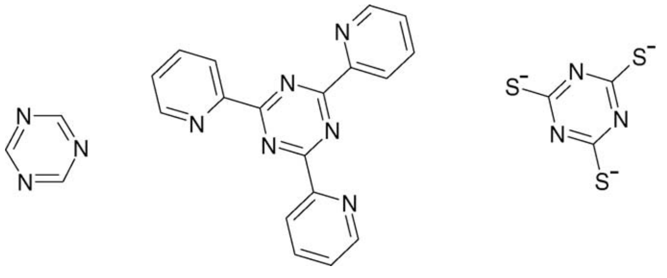


Fig. 15. Triazine based bridging ligands.

Lahiri and co-workers have reported a trinuclear 1,3,5-triazine bridged Ru(II) complex (i.e., $[\{(\text{arylazopyridine})_2\text{-}Ru^{II}\}_3(L)]^{3+}$, $[\{(bpy)_2Ru^{II}\}_3(L)]^{3+}$ and $[\{(phen)_2Ru^{II}\}_3L]^{3+}$, where L3 = 1,3,5-triazine-2,4,6-trithiol) [70,71]. These complexes are of particular interest as it allows for the generation of two distinct mixed valent states i.e. $Ru(II)_2Ru(III)$ and $Ru(II)Ru(III)_2$, with the separation between successive oxidation steps being between 190 and 250 mV. For the $Ru(bpy)_2$ complexes, both states exhibit weak IT bands in the near-IR spectrum (~1900 nm) characteristic of type II behaviour ($H_{ab} \sim 560\,\text{cm}^{-1}$). Complexes based on tris(pyrid-2′-yl)-1,3,5-triazine (tpt) have been reported by Chirayil et al. [71] and Berger and Ellis [72]. Berger have reported the oxidation potentials of the binuclear complex $[(Ru(bpy)_2)_2tpt]^{4+}$ (1.10 and 1.50, $\Delta E = 400$ mV) (Fig. 15).

### 4.5. Tetrazines

The π-electron rich six-membered tetrazine rings allow for an increased number of bridging modes to be accessed than can be for pyrazine, however, despite this tetrazine has received little attention. Nevertheless, the number of binuclear tetrazine bridged ligands in increasing steadily and, indeed, the use tetrazines as bridging ligands has been the focus of a recent review by Kaim [73].

Sarkar and co-workers have reported tetrazine bridged binuclear ruthenium polypyridyl complexes (see Fig. 16), which show tunable interaction between the two metal centers [74,75]. The strong coupling observed in the $Ru(bpy)_2$ based binuclear complex has been attributed to the low-energy LUMO of the ligand and the high coefficient of the LUMO on the nitrogen atoms, which facilitates effective overlap of the metal based and ligand based orbitals (i.e., facilitates superexchange processes). In this complex a separation between the 1st and 2nd metal oxidation wave of 450 mV was observed, indicating that the interaction is very strong. A very narrow IT band observed at 1534 nm confirms that the interaction is Type III. The pH chemistry of this complex shows a $pK_a$ of 1.0 (measured in acetonitrile:water 2:1) with a large red shift in the absorption spectrum on protonation, attributable to a stabilization of the bridging ligand's LUMO. In contrast the $Ru(acac)_2$ based binuclear complex [75], show very large separation of the 1st $\{Ru_2(II, II) \rightarrow Ru_2(II, III)\}$ and 2nd $\{Ru_2(II, III) \rightarrow Ru_2(III, III)\}$ oxidation processes ($K_c = 10^{13.9}$), however, with no detectable IT band. The observation of a

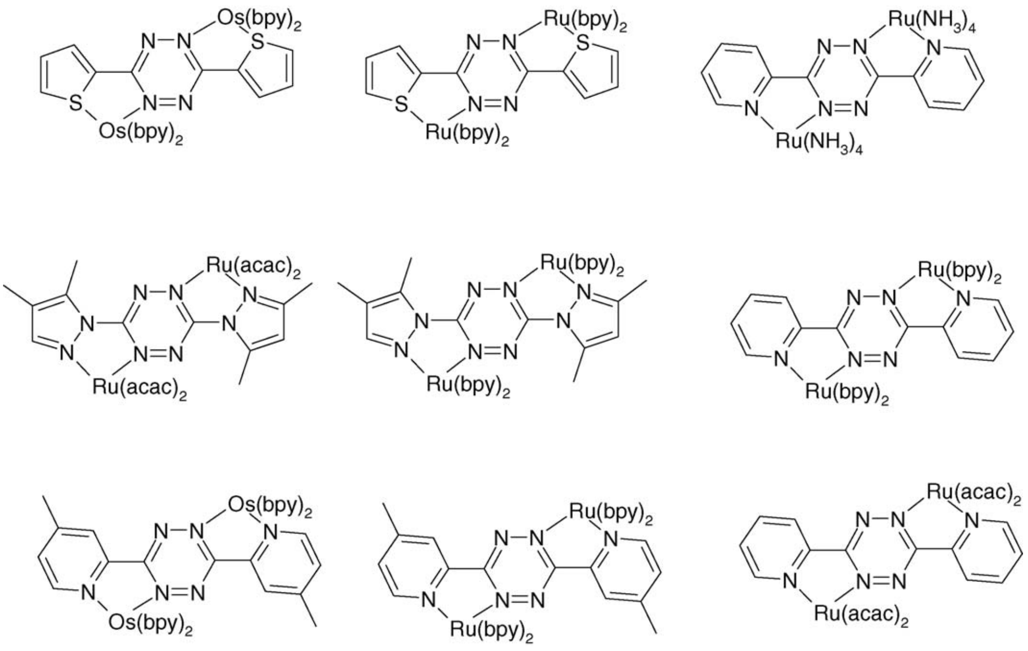


Fig. 16. 1,2,4,5-Tetrazine based dinuclear complexes (charges omitted for clarity).

bridging ligand radical anion by EPR spectroscopy in the formally $Ru_2$II, II state may explain the absence of an IT band as it indicates that although there is a strong interaction between the metal centers; the LUMO orbitals of the bridging ligand are very close in energy to the SOMO of the mixed valence state.

## 5. Conclusions and outlook

Dinuclear compounds are ideally suited for investigating electron and energy transfer processes since parameters such as the distance between reactive centers and the nature of the connecting bridge can be changed systematically. However, it is important to point out that ‘interaction’ as a term is often unclear. Although, in the present review we have focused on ‘ground state’ interaction and specifically intervalence complexes, bridge mediated interaction is equally important in other situations such as excited state, photoinduced, interaction or energy transfer. A further point is that when one considers interaction in the ground state, the oxidation state of the bridge is an important factor also. Interaction, therefore, should be defined carefully, before comparisons of interaction strengths between different systems are made.

The investigation of the dinuclear compounds becomes of value when designing electron or energy transfer pathways. These rely on the presence of well-defined energy gradients and by a systematic change of the components such gradients can be achieved. As the above discussion shows, processes such as delocalization and electron hopping interactions are influenced by the energy differences of HOMO and LUMO orbitals of both the bridging ligands and the metal centers. The mechanism for interaction is controlled by the energy match between the metal orbitals and those of the bridge. It is clear that in the compounds discussed above the interaction for anionic bridging ligands is by interaction of the HOMO of the metal center with the HOMO of the bridge, via a hole-transfer mechanism. However, for the neutral azine type bridges interaction is via interaction of the metal-based HOMO with the LUMO of the azine component of the bridge. In these cases the interaction is controlled by the relative energies of these orbitals and the orbital coefficients at the coordinating atoms. The issue of distance does not arise in this change in interaction mechanism; it is driven by the relative energy levels of the orbitals involved. Equally important is the effect of the peripheral ligands, which contribute significantly to the energy difference of these metal and bridging ligand orbitals. For example, they will affect the energy of the HOMO level of the metal center.

Finally, it is clear that the dominant factor in controlling both the extent and mechanism of interaction is that of the unit which forms the direct bridge between the metals centers. For example the presence of a negatively charged triazolato ring will only lead to a hole transfer based interaction when this group bridges between the two metal centers directly. As shown above when it is present in a peripheral location and only bound to one metal center the group will contribute to the HOMO level of the metal center but the mechanism for interaction is based on the properties of the central bridging unit.

The basic theory of hole (HOMO) and electron (LUMO) bridge mediated superexchange interaction between metal centers was established nearly half a century ago and has undergone, surprisingly, little modification in the intervening time. It is perhaps testament to the work of Hush, Robin, Day, Sutin and Creutz to name but a few, that despite the last two decades of intensive investigation of internuclear interactions in mixed valence systems and the very large number of systems examined, the theoretical basis for understanding intervalence transitions remains a valid and useful model. With the advent of computational chemistry accessible to transition metal based systems, the nature of the interaction, in terms of the involvement of ligands orbitals, will become increasingly apparent and is likely to lead to a more quantitative understanding of the superexchange phenomenon.

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