Metal-Metal Interactions in Binuclear Complexes Exhibiting Mixed Valency; Molecular Wires and Switches

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1 Introduction. Background and Scope

Since the preparation of the Creutz–Taube ion (Figure 1),[1] inorganic chemists have been interested in the study of molecules in which two (or more) metal centres, linked by a bridging ligand of some sort, show a pronounced electronic interaction. The most obvious manifestation of this interaction is a separation of the two metal-centred redox potentials for metals which are apparently in chemically identical environments. Such an interaction may occur through space if the metal ions are close together – a direct link in this case is not necessary, and the interaction occurs because each ion is in the electric field of the other. In complexes such as the Creutz–Taube ion the interaction occurs because the *d*-electrons of the metal ions are in $d(\pi)$ orbitals which can effectively overlap with the π-acceptor ligand and are therefore delocalized to a certain extent between both metals across the conjugated bridge (Figure 2). Oxidation of one metal centre results in a change of electron density which is communicated to the other across the bridging ligand; the second metal ion 'feels' the additional positive charge and is therefore more difficult to oxidize than the first.

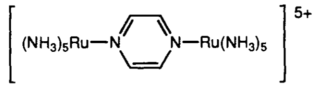


Figure 1 The Creutz–Taube ion

In the Creutz–Taube ion the two successive $\mathrm{Ru^{II}/Ru^{III}}$ couples occur at + 0.37 and + 0.76 V *versus* the standard hydrogen electrode, a separation of 0.39 V. Within the potential domain between these two potentials the complex is therefore in a mixed-valence state (denoted [2,3]), containing one $\mathrm{Ru^{II}}$ and one $\mathrm{Ru^{III}}$ ion. The mixed-valence state is stable with respect to disproportionation to the [2,2] and [3,3] states, primarily for simple electrostatic reasons: for a given metal–metal separation the electrostatic interaction is proportional to the product of the charges on the two ions, and $3^2 + 2^2 > 2[3 \times 2]$. The comproportionation reaction

$$[2,2] + [3,3] \rightleftharpoons 2[2,3] \qquad (1)$$

therefore lies largely to the right, and the stability of a mixed-valence complex relative to the isovalent states is expressed by the compoportionation constant K_c, which is just the equilibrium constant for the above reaction:

$$K_c = [2,3]^2/[2,2][3,3] \qquad (2)$$

Provided the interaction is moderately strong, the value of K_c is simply determined from electrochemical data, since for the comproportionation reaction $\Delta G^{\ominus} = -\mathrm{RT}(\ln K_c) = -nF(\Delta E)$, where ΔE is the separation between the two redox potentials. It should be noted that the lower limit of K_c – *i.e.* when there is no electrochemical interaction between the metals – is 4. For the Creutz–Taube ion, $\Delta E = 0.39$ V and K_c is about 3×10^6. The mixed-valence complex may therefore be prepared and studied effectively free from contamination from the [2,2] and [3,3] complexes. Even if the two redox processes are inseparable, the mixed-valence state may be generated either electrochemically (electrolysis exactly at the coincident redox potential of the two metals) or, more often, chemically (by addition of exactly one equivalent of an appropriate oxidizing agent to a solution of a binuclear complex). In these limiting cases ($K_c = 4$) the mixture will contain the [2,2] species (25%), the [3,3] species (25%) and the mixed-valence [2,3] species (50%), and provided the characteristic spectral features of the [2,2] and [3,3] species are known, information regarding the [2,3] species may be extracted.

In very strongly interacting complexes (class III according to the Robin and Day classification[2]) the odd electron of the mixed-valence state is evenly delocalized between both metals, and a description $[2\frac{1}{2},2\frac{1}{2}]$ is more appropriate than [2,3] for the oxidation states. In such cases the odd electron may be promoted from one orbital delocalized over the whole metal–bridge–metal system to a higher-energy orbital which is likewise delocalized: this process is effectively a π–π^* transition. However, in complexes where the interaction between the metals is weaker (Robin and Day class II), the valences are localized in the mixed-valence state and a description such as [2,3] applies, and there is then the possibility of transferring an electron from the metal in the lower oxidation state to the one in the higher

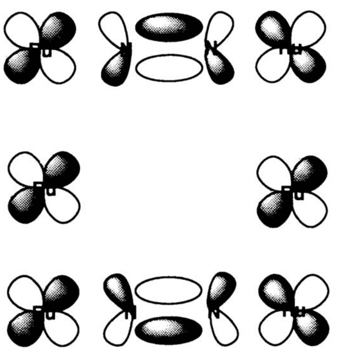
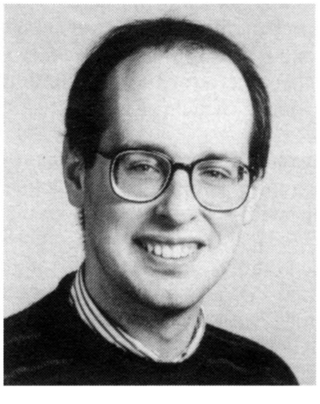


Figure 2 π-Molecular orbitals in the Creutz–Taube ion (from ref. 1)

Mike Ward was born in Kettering in 1964. His first degree was a B.A. in Natural Sciences at Cambridge University (Robinson College) from 1983—86, and he remained in Cambridge for a Ph.D. with Dr. Ed Constable on the coordination chemistry of helicating polypyridine ligands. After a Royal Society post-doctoral fellowship with Dr. Jean-Pierre Sauvage in Strasbourg he moved to a lectureship at Bristol University in 1990. His research interests cover many aspects of coordination chemistry, including the synthesis and coordinating properties of new mixed-donor polydentate ligands and the study of all types of metal-metal interactions (electronic, magnetic and photochemical) in polynuclear transition-metal complexes.



oxidation state. Such a process is called an inter-valence charge transfer (IVCT); after it, the oxidation states have changed ends: *i.e.* [2,3]→[3,2]. The electron transfer is therefore directional, from one end of the complex to the other *via* the bridging ligand.

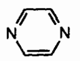
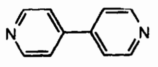
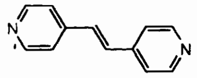
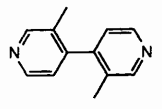
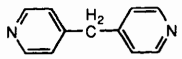
This brings us to the main reason for the intense interest in such binuclear complexes. Long-range electron-transfer reactions are of considerable importance in many areas of chemistry ranging from bioinorganic chemistry to artificial molecular electronic devices. In most cases electron transfer between molecules is dependent on a variety of factors which cannot be accurately known, such as separation between redox centres at the point of transfer, molecular conformation, and so on. However in mixed-valence binuclear complexes the electron transfer occurs *within* the molecule, so it is possible to examine long-range electron-transfer reactions between redox centres whose separation is known, across a bridging ligand whose structure and conformation are (more or less) known. *An IVCT process in a mixed-valence molecule is therefore a model for an intermolecular electron-transfer reaction*, and information regarding IVCT processes is directly relevant to other electron-transfer processes. In addition, measurement of IVCT processes allows easy assessment of the ability of particular bridging ligands to act as 'molecular wires' for potential use in molecule-sized electronic devices.

In the decade following the publication describing the Creutz–Taube ion this area of coordination chemistry mushroomed, with a large number of complexes being prepared comprising two metal fragments (often $\{Ru(NH_3)_5\}^{2+}$) attached to either end of a bridging ligand; a few selected examples are given in Table 1. It is apparent that, for this series of related ligands, the extent of the metal–metal interaction decreases steadily as the π-overlap between the two halves of the bridging ligand decrease, which occurs when the ligand is lengthened, twisted, or contains a saturated fragment. There is an obvious correlation between the various properties of the mixed-valence complexes which relate to the metal–metal interaction: when the interaction is strong, K_c is large, the IVCT band occurs at low energy and is of high intensity; when it is weak, K_c decreases, the energy of the IVCT band increases and its intensity decreases. The magnitude of the interaction is often expressed in terms of a coupling parameter J, in units of cm^{-1}, which may be expressed as

$$J = \frac{2.05 \times 10^{-2}[\epsilon.\nu_{1/2}.E]^{1/2}}{r} \qquad (3)$$

where ϵ is the extinction coefficient for the IVCT band in dm^3 mol^{-1} cm^{-1}, $\nu_{1/2}$ is the width at half-height of the IVCT band in cm^{-1}, E is the energy of the IVCT band maximum in cm^{-1} and r is the metal–metal separation in Å.[3a] The parameter J therefore takes into account all of the significant characteristics of the IVCT band and the metal–metal separation. (In some cases J is also referred to as V_{ab}).

Table 1 Some early examples of mixed-valent $[(NH_3)_5Ru(\mu\text{-}L)Ru(NH_3)_5]^{5+}$ complexes

Bridging ligand (L)	K_c	λ_{max}(IVCT), nm; ϵ, M^{-1} cm^{-1}.	J (cm^{-1})
	3×10^6	1570 (5000)	3300
	20	1030 (920)	390
	14	960 (760)	305
	10	890 (165)	
	6.7	810 (30)	100

The examples given in Table 1 are typical of a great deal of research that was done in the 1970s and 1980s, and such work – together with the theoretical considerations that underpin it – has been comprehensively reviewed.[3] In the past few years the area has developed in two directions, and it is a survey of these more recent developments that is the main purpose of this review. First, the principles outlined above have been extended to a wider variety of metal fragments connected by ever more esoteric bridging ligands. The phenomena of metal–metal interactions and mixed valency have therefore become much more widespread, which has allowed a deeper understanding of exactly what features of the metal fragments and bridging ligands are responsible for strong interactions. Secondly, attempts are being made to *control* these long-range interactions by some form of external manipulation such as changing the conformation of the bridging ligand. These constitute prototypical examples of *molecular switches*, and are the first steps towards the construction of molecule-sized electronic devices: an integrated circuit is, in essence, just a very large number of switches! This review is not intended to be comprehensive, but aims rather to provide a survey of recent developments in this popular area of coordination chemistry which will be accessible to those (like the author) whose main interest is in synthesis and characterization rather than theoretical chemistry. For a recent, comprehensive summary of the properties of bridged polynuclear complexes of Ru^{II} the reader is referred to reference 3(*d*). Photo-induced electron-transfer processes are not covered in this review as there are many other recent articles on the subject.

2 Novel Systems Displaying Metal-Metal Interactions

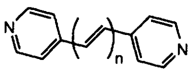
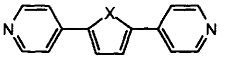
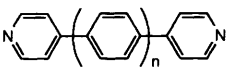
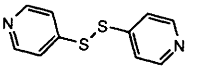
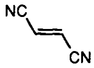
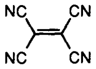
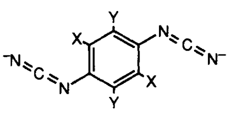
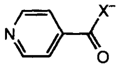
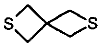
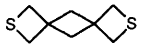
2.1 Complexes Based on $\{Ru(NH_3)_5\}^{2+/3+}$ Fragments

Binuclear complexes containing $\{Ru(NH_3)_5\}^{2+/3+}$ fragments are still popular targets of study owing to their very favourable properties. The complexes are easy to prepare, have a fully reversible $+2/+3$ redox conversion at an accessible potential, and are kinetically stable in both oxidation states. In addition, in the $+2$ state the $\{Ru(NH_3)_5\}^{2+}$ fragment is a strong π-donor which interacts efficiently with π-acceptor bridging ligands. The examples discussed below are summarized in Table 2.

The complexes $[\{Ru(NH_3)_5\}_2(\mu\text{-}L)]^{n+}$ [L = (1), (2), (3); n = 4, 5, 6] were examined in order to test current theories of how the metal–metal interaction should vary with increasing metal–metal separation. In these complexes the metal–metal separation increases from 15.8 Å (two double bonds) to 20.6 Å (four double bonds). The two metal centres undergo their Ru^{II}/Ru^{III} couples at very similar potentials, and $K_c \approx 10$ for all three complexes. However, in the mixed-valence states (generated with a chemical oxidant) strong IVCT bands could be seen despite the large metal–metal distance and the weak electrochemical interaction; moreover the metal–metal interaction decreased rather slowly with increasing metal–metal separation, indicating that these dipyridyl-polyene bridging ligands could make effective long-range molecular wires.[4a,4b] The decrease is approximately linear, although the uncertainty in the data does not preclude an exponential decay which is theoretically predicted.[4c]

The rigidity of the bridging ligands has a significant effect on the metal–metal interaction. Ligands (4) and (5) are analogues of (1) (two double bonds) but with a more rigid, coplanar backbone; $[\{Ru(NH_3)_5\}_2(\mu\text{-}L)]^{n+}$ [L = (4), (5)] have significantly higher K_c values than the complex with (1) as a bridge, and also have more clearly defined IVCT bands.[4b] In contrast, bridging ligands such as (6) and (7) allow only a very weak interaction between $\{Ru(NH_3)_5\}^{2+/3+}$ centres. In the mixed-valence species the IVCT bands have very low intensities and are barely resolved, and the values of K_c are close to 4. This is

Table 2 Metal–metal interactions in binuclear complexes with $\{Ru(NH_3)_5\}^{2+/3+}$ end groups

Bridging ligand		K_c	λ_{max}(IVCT), nm, ϵ, $M^{-1}\,cm^{-1}$	J (cm^{-1})	Ref
	(1) (n = 2)	10 ± 2^a	987 ± 5 $(660 \pm 55)^a$	240 ± 17	4*a*, 4*b*
	(2) (n = 3)	10 ± 2^a	935 ± 5 $(620 \pm 55)^a$	220 ± 17	
	(3) (n = 4)	9 ± 2^a	926 ± 5 $(550 \pm 55)^a$	180 ± 16	
	(4) (X = O)	50 ± 2^a	992 ± 1 $(520 \pm 12)^a$	254 ± 7	4*b*
	(5) (X = S)	14 ± 2^a	985 ± 1 $(410 \pm 20)^a$	240 ± 11	
	(6) (n = 1)	—	≈850(≈160)		5
	(7) (n = 2)	—	?(≈16)		
	(8)	8×10^4	1500 (4260)	855	6
	(9)	55	975 (150)		7
	(10)	[3/3/3/2] 300 [3/3/2/2] 10^5 [3/2/2/2] 950	Not resolved		7
	(11) (X = Y = H)	10^a	$1220\ (2590)^a$		8*a*, 8*b*
		68400^b	$1450\ (19400)^b$		8*b*
	(12) (X = H, Y = Me)	28^a	—		8*a*
		—	$1210\ (18000)^b$		8*c*
	(13) (X = H, Y = Cl)	21^a	—		8*a*
	(14) (X = Y = Cl)	13^a	$1220\ (600)^a$		8*a*
	(15) (X = O)	—	$720\ (260)^a$		9
	(16) (X = NH)	—	$761\ (900)^a$		9
	(17)	≈4	$910\ (43 \pm 2)^a$	113	10, 3*a*
	(18)	≈4	$808\ (9 \pm 1)^a$	45	10, 3*a*
	(19)	≈4	$690\ (2\ 3 \pm 0\ 7)^a$	22	10, 3*a*

[a] Measured in water [b] Measured in MeCN

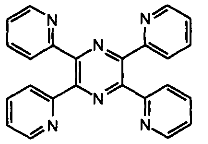
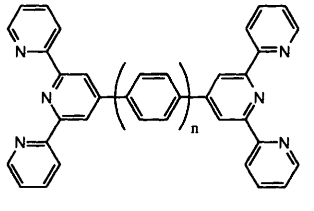
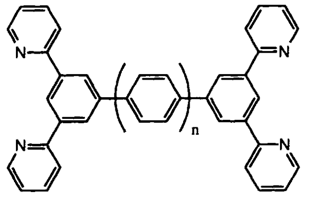
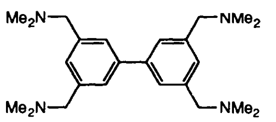
ascribed to the conformational flexibility of the aromatic spacers in the bridging ligand Even though the ruthenium end-groups interact strongly with the π-acceptor pyridine ligands, there will be a dihedral angle of about 40° between adjacent aromatic rings which will decouple the π-overlap necessary for a strong interaction [5]

The disulfide bridge of 4,4'-dithiobipyridine (8) is surprisingly effective at mediating metal–metal interactions, due to a strong *p*(π)–*d*(π) interaction between the pyridyl rings and their sulfur substitutents and strong *d*(π)–*d*(π) overlap between the sulfur atoms The disulfide bridge is also known to mediate redox reactions in biological systems The importance of the *di*-sulfide (as opposed to thioether) bridge is demonstrated by the fact that in $[\{Ru(NH_3)_5\}_2(\mu\text{-dps})]^{5+}$ [dps = di(4-pyridyl)sulfide, pyr-S-pyr] K_c is only 158 instead of 8×10^4 and the IVCT band is likewise much weaker However di(4-pyridyl)sulfide still permits a stronger interaction than does 4,4'-bipyridine ($K_c = 20$) $\{Fe(CN)_5\}^{2+/3+}$ and $\{Ru(CN)_5\}^{2+/3+}$ were also used as end-groups in binuclear complexes of (8), they show generally similar behaviour although the metal–metal interactions are weaker than in the corresponding $\{Ru(NH_3)_5\}^{2+/3+}$ complexes [6] The interaction across the conjugated bridging ligand fumaronitrile (9) is rather weak, however in the tetranucleating analogue tetra(cyano)ethene (10) all of the possible mixed-valence complexes [3,3,3,2], [3,3,2,2], and [3,2,2,2] of the tetranuclear $\{Ru(NH_3)_5\}^{2+/3+}$ complex could be prepared, and their K_c values show that (10) is a more effective bridging ligand than (9) The IVCT bands for these mixed-valence species, although predicted to be strong, were obscured by other metal-to-ligand and ligand-to-metal (MLCT and LMCT) charge-transfer bands in the electronic spectrum [7]

Bis-$\{Ru(NH_3)_5\}^{2+/3+}$ complexes of the dicyanamidobenzene ligands (11)—(14) are very weakly coupled in aqueous solution, with K_c values for the [2,3] systems close to the statistical minimum of 4 The rather weak coupling was ascribed to the fact that, although the Ru^{III}-bridging ligand π-interaction was effective, the orbitals of the Ru^{II} centre could not overlap effectively with the ligand-based π* orbital owing to the energy difference between them [8a] However, the interaction in the [2,3] state is extremely solvent dependent On changing from water to acetonitrile, for $[\{Ru(NH_3)_5\}_2\{\mu\text{-}(11)\}]^{3+}$ K_c increases from 10 to 68400, and the IVCT band likewise becomes an order of magnitude more intense [8b] This was ascribed to donor–acceptor interactions between the solvent and the ammine protons of the Ru^{III} centre, which would be more prevalent in water than MeCN, weakening the Ru^{III}—cyanamide π-bond and thereby decoupling the two metals Such sensitivity of the metal–metal interaction to modest second-sphere coordination effects is encouraging from the point of view of developing workable molecular switches (see later)

Since the Ru^{III}–L interaction is apparently stronger than the Ru^{II}–L interaction for these ligands, any metal–metal interaction should therefore be maximised in the [3,3] state, and although an IVCT is not possible, the magnetic exchange interaction between the two Ru^{III} centres was indeed shown to be unusually strong [8a] These magnetic interactions are also very

Table 3 Metal–metal interactions in binuclear complexes with {polypyridyl-Ru}$^{2+/3+}$ end groups

Bridging ligand		End group	K_c	λ_{max}(IVCT), nm; ϵ, M^{-1} cm^{-1}.	J (cm^{-1})	Ref.
	(20)	{Ru(tterpy)}$^{2+}$	10^5	1520	3200	11
	(21) (n = 0)	{Ru(tterpy)}$^{2+}$	15	1580 (1618)	379	11
	(22) (n = 1)		7	1295 (729)	242	11
	(23) (n = 2)		5	1150 (709)	177	11
	(24) (n = 0)	{Ru(tterpy)}$^{2+}$	690	1936 (2.2×10^4)	1020	12c
	(25) (n = 1)		16	1650 (6600)	600	12c
	(26) (n = 2)		6	1214 (2200)	330	12c
	(24) (n = 0)	{Os(tterpy)}$^{2+}$	100	1410 (1.18×10^4) 1800 (8000)	970	12a
	(27)	{Ru(tterpy)}$^{3+}$	1250	1875 (3.3×10^4)		13

susceptible to solvent effects for the reason mentioned above, to the extent that [{Ru(NH$_3$)$_5$}$_2${μ-(11)}]$^{4+}$ is strongly paramagnetic in water but diamagnetic in MeNO$_2$.[8c]

Isonicotinate (15) and isonicotinamide (16) are examples of asymmetric bridging ligands, with a {Ru(NH$_3$)$_5$}$^{2+}$ fragment at the pyridyl terminus and a {Ru(NH$_3$)$_5$}$^{3+}$ fragment at the carboxylato or imido(N) terminus. The asymmetry means that the redox potentials of the two sites differ by 0.44 V and 0.54 V respectively. Despite this, moderately strong IVCT bands were observed, and it was found that both bridges provide significant coupling between the Ru^{II} and Ru^{III} centres in the mixed-valence complexes.[9]

Finally, although most examples of metal–metal coupling between {Ru(NH$_3$)$_5$}$^{n+}$ fragments rely on a conjugated π-system involving both metal ions and the bridging ligand, it has been shown that such a bridging pathway is not always necessary. In the mixed-valence complexes [{Ru(NH$_3$)$_5$}$_2${μ-(L)}]$^{5+}$ [L = (17)—(19)] the bridging ligands are completely saturated and, because of the spiro-fused rings, rigid. The rigidity of these ligands is important because it means the metals are a fixed distance apart and cannot come into close contact *via* folding up of the bridge – the metal–metal through-bond bridging path lengths vary between 11.3 Å and 17.5 Å. Although the two redox potentials are inseparable (K_c close to 4), weak IVCT processes were clearly visible, whose intensity decreased with metal–metal separation. These transitions are very weak compared to those across conjugated briding ligands, but the fact that they occur at all is remarkable, and was ascribed to long-range electron tunnelling across the σ-framework of the bridging ligands.[10a] Subsequent work showed that overlap of p_z orbitals on the S and C atoms of the bridging ligands provides a hyperconjugated orbital through which the interaction can occur.[10b]

2.2 Complexes Based on Ru-polypyridyl Fragments

The series of complexes [{Ru(tterpy)}$_2${μ-(L)}]$^{5+}$ [tterpy = 4′-tolyl-2,2′:6′,2″-terpyridine; L = (20)—(23)] constitutes another example of a set of binuclear complexes with a steadily increasing metal–metal separation between the end-groups (7—20 Å) (Table 3). As expected, both K_c and J decrease with distance; however, there are two significant points to notice. First, moving from (20) to (21) as bridging ligand has a very large effect since (20) is necessarily planar whereas (21) (and the longer members of the group) can be twisted. This is similar to the difference between pyrazine and 4,4′-bipyridine as bridging ligands, and indeed the values of K_c and J for [{Ru(tterpy)}$_2${μ-(20)}]$^{5+}$ and {[{Ru(tterpy)}$_2${μ-(21)}]$^{5+}$ are comparable to those of [{Ru(NH$_3$)$_5$}$_2${μ-(L)}]$^{5+}$ (L = pyrazine and 4,4′-bipyridine respectively). Secondly, from (21)—(23) the rate of decrease in the metal–metal interaction with increasing ligand length is rather slow [*cf.* the dipyridyl-polyenes (1)—(3)], indicating that polyphenylene spacers may be effective wires for long-distance interactions. This is in interesting contrast to the behaviour of the analogous ligands (6) and (7), where the polyphenylene spacers were found to make rather poor wires between {Ru(NH$_3$)$_5$}$^{n+}$ units.[11]

The ligand series (24)—(26) are cyclometallating analogues of (21)—(23) in which the central pyridyl rings have been replaced by phenyl rings. In [{Ru(tterpy)}$_2${μ-(L)}]$^{4+}$ [L = (24)—(26)] the metals are therefore linked by polyphenyl-diyl bridges instead of di(4-pyridyl)-type bridges. This has the effect of substantially increasing the metal–metal interactions – comparison of (21) with (24), (22) with (25), and (23) with (26) shows that the values of J are 2 to 3 times higher with the cyclometallating ligands as bridges. This effect is ascribed partly to the strong electron-donating character of the anionic phenyl bridging ligands, and partly to the fact that Ru–C(phenyl) bonds are shorter than Ru–N(pyridyl) bonds, resulting in better overlap between metal and ligand π-orbitals.[12a–c] Replacing the pyridyl donors of (24) with –CH$_2$NMe$_2$ arms in (27) strengthens the interaction still further, with K_c and ϵ(IVCT) for [{Ru(terpy)}$_2${μ-(27)}]$^{3+}$ being considerably larger than for [{Ru(tterpy)}$_2${μ-(24)}]$^{3+}$ despite a similar metal–metal distance (10.83 Å as opposed to 11.01 Å). It appears from these results that the amount of electronic communication between the metal centres may be modified by varying the electron-donating ability of the bridging ligand Interestingly, in the [3,3] state the biphenyldiyl bridge is completely planar and the molecule is diamagnetic, both of which may be due to the presence of a formally $Ru^{II}–Ru^{IV}$ structure (Figure 3) [13]

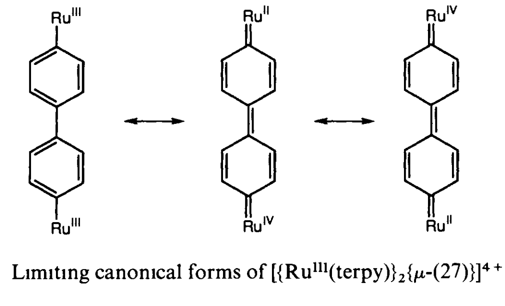


Figure 3 Limiting canonical forms of $[\{Ru^{III}(terpy)\}_2\{\mu\text{-}(27)\}]^{4+}$

The metal–metal interaction in the mixed-valence complex $[\{Ru(bipy)_2Cl\}_2(\mu\text{-}NCSe)]^{2+}$ is thought to occur *via* the π-system Ru(dπ)–3π*(NCSe)–Ru(dπ) [14a] The alkoxide bridges of $[(bipy)_2Ru(\mu\text{-}OR)_2Ru(bipy)_2]^{2+}$ (R = Me, Et) appear to be effective mediators of the metal–metal interaction K_c for the Ru^{II}/Ru^{III} state is 6×10^9 and there is a very strong IVCT band at $\lambda_{max} = 1800$ nm ($\epsilon = 5000$ dm^3 mol^{-1} cm^{-1}), both of which suggest class III behaviour [14b]

2.3 Other Coordination Complexes Displaying Strong Metal–Metal Interactions

Recently it has been shown that complexes of the type $[\{MO(tp^*)(NO)Cl\}_2(\mu\text{-}L)]$ [where tp* is the face-capping terdenate ligand tris(3,5-dimethylpyrazolyl)hydroborate, and L is a bis(4-pyridyl)-polyene type bridging ligand, Figure 4] display remarkably strong electrochemical interactions between the two metal centres The molybdenum centres in these complexes have 17 valence electrons (ve), and undergo both 17ve/18ve and 17ve/16ve redox processes In the bridged binuclear complexes the two 17ve/18ve couples interact very strongly Thus for L = 4,4'-bipyridyl, $\Delta E = 765$ mV and $K_c = 1\ 4 \times 10^{13}$, and even with ligand (3) as a bridge (four double bonds) there is still an appreciable separation of about 110 mV between the redox potentials ($K_c \approx 75$) Only with five double bonds in the bridge do the two reductive processes become unresolvable electrochemically and does K_c approach the minimum value of 4 The values of *ΔE versus* chain length are displayed graphically in Figure 4, for the first four members of the series there is a near-linear decrease of *ΔE versus* chain length [15b] These electrochemical interactions are approximately an order of magnitude stronger than those between $\{Ru(NH_3)_5\}^{2+}$ fragments across the same ligands [15a b] The strength of these interactions may be due to the fact that on reduction from 17ve to 18ve the additional electron is substantially delocalized onto the bridging ligand In contrast the two 17ve/16ve couples, which are apparently more metal-localized, are virtually coincident [15c]

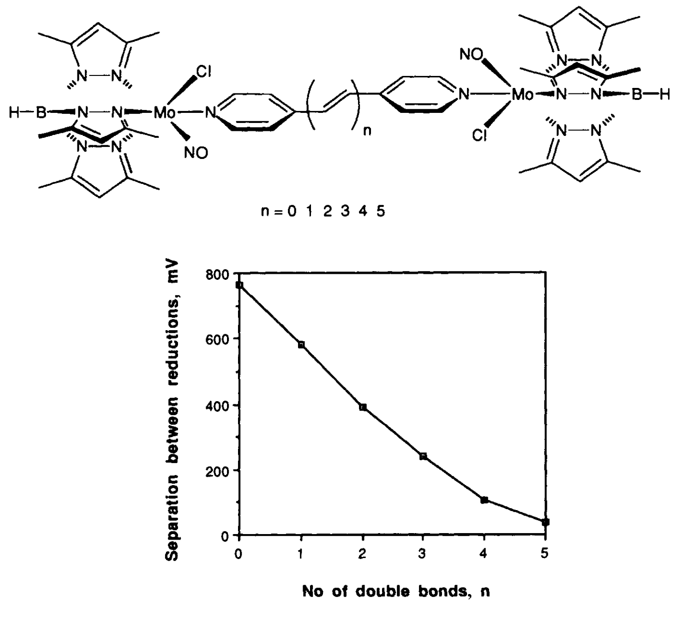
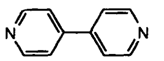
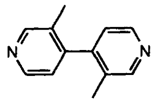
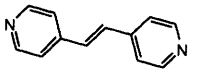
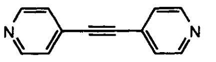
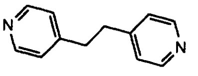
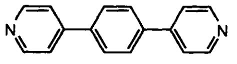
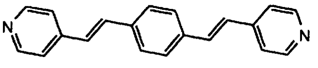
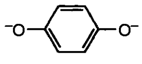
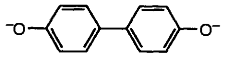
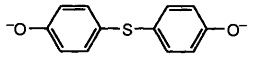
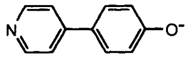
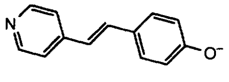
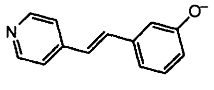
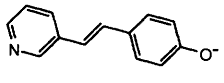


Figure 4 Electrochemical interactions in binuclear molybdenum complexes

The very large separation between the 17ve/18ve couples in binuclear complexes containing the {Mo(tp*)(NO)Cl} fragment has led to it being used to test the communicative abilities of a variety of other bridging ligands (Table 4) For example, changing from 4,4'-bipyridine as the bridge to the twisted analogue 3,3'-dimethyl-4,4'-bipyridine almost exactly halves ΔE_p from 765 mV to 380 mV (*i e* K_c decreases from $1\ 4 \times 10^{13}$ to 3×10^6), [15c] and there is a significant interaction even across the saturated bridge of 1,2-bis(4-pyridyl)ethane [15a] Di-phenol bridging ligands between {Mo(tp*)(NO)Cl} fragments also permit significant electrochemical interactions, despite the lack of a fully conjugated pathway between the metals (the phenolate oxygens are formally sp^3 hybridized) [15d e] It is interesting that a sulfur linkage between the rings increases the electrochemical interaction, this is similar to the behaviour observed for the

Table 4 Metal–metal interactions in binuclear complexes with {Mo(tp*)(NO)Cl} fragments

Bridging Ligand	ΔE (mV)	K_c	Ref
	765	$1\ 4 \times 10^{13}$	15*a*
	380	$3\ 4 \times 10^6$	15*c*
	582	$1\ 1 \times 10^{10}$	15*a*, 15*b*
	560	$4\ 3 \times 10^9$	15*c*
	105	64	15*a*
	260	$3\ 0 \times 10^4$	15*c*
	160	570	15*c*
	460	$8\ 2 \times 10^7$	15*d*
	110	78	15*e*
	138	240	15*e*
	180	—	15*f*
	160	—	15*f*
	10	—	15*f*
	120	—	15*f*

related pair of ligands 4,4'-bipyridine and di(4-pyridyl)sulfide with $\{Ru(NH_3)_5\}^{2+}$ end-groups (above). Complexes with the hybrid pyridine–phenol ligands shown in Table 4, which are easy to prepare with the donor atoms in a variety of different relative orientations, illustrate the role of the conjugated bridge in mediating electrochemical interactions. In these asymmetric complexes the electrochemical interaction is defined as the increased separation between the two metal-centred reduction potentials compared to the mononuclear analogues. The electrochemical interaction across these ligands is facilitated by the possibility of a quinonoidal contribution to the ligand structure in which an electron is formally transferred from one end to the other (Figure 5) – *cf.* reference 13 and Figure 3. When donor atoms are in the *meta* position to the bridge, such that formation of a quinonoidal structure by delocalization of electron density out of the aromatic rings is not possible, the interaction is substantially reduced.[15f]

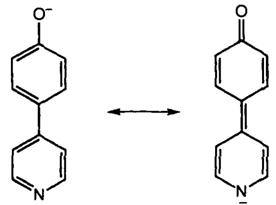
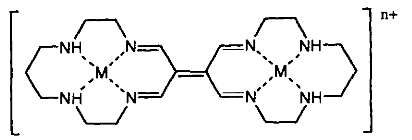


Figure 5 Limiting canonical forms of a pyridine–phenol bridging ligand.

$[\{(PPr^i_3)_2(CO)_2Mo\}_2(\mu\text{-pyrazine})]^+$, in which both molybdenum atoms have the *trans, mer* configuration, has a d^5/d^6 electron configuration and is therefore an electronic and structural analogue of the Creutz–Taube ion. The two Mo^0/Mo^I redox potentials are separated by 0.38 V ($K_c = 3 \times 10^6$), and there is an intense ($\epsilon = 7000\ dm^3\ mol^{-1}\ cm^{-1}$) band at 2150 nm in the electronic spectrum of the mixed-valence state. IR and EPR spectra confirm that in the mixed-valence state both metals are in identical environments with the odd electron fully delocalized, so the complex is in Robin and Day class III and a description [0.5,0.5] is appropriate for the oxidation states; the 2150 nm spectra band is therefore best described as a π–π^* transition between molecular orbitals delocalized over the whole complex rather than a directional IVCT process.[16]

An unusual series of binuclear complexes (28)—(30) has been prepared by oxidative coupling of mononuclear metal cyclam complexes (cyclam is the N_4 macrocycle 1,4,8,11-tetraaza-cyclotetradecane).[17] In these complexes there is a planar, delocalized π-system linking the two metals which permits a strong interaction between them, and all three complexes in the [2,2] state show a strong MLCT band in the electronic spectrum. In the bis-ruthenium complex (28) the Ru^{II}/Ru^{III} couples are separated by 0.92 V ($K_c = 3.5 \times 10^{15}$), and in fact in air the complex exists in the mixed-valence form. Since it is a class III, fully delocalized [2.5,2.5] complex the very intense, sharp band in the electronic spectrum [λ_{max} 805 nm; $\epsilon = 68\,000\ dm^3\ mol^{-1}\ cm^{-1}$] is therefore a π–π^* transition delocalized over the whole conjugated system.[17a] The bis-Ni^{II} complex (29) undergoes two one-electron oxidations, to give a bis-Ni^{III} species, but these are metal-localized and so do not interact strongly and are virtually coincident. The two reductions by contrast are more centred on the conjugated bridging ligand fragment and therefore interact strongly, with $\Delta E_p = 0.19$ V in water and 0.23 V in MeCN ($K_c \approx 1800$ and 9000 respectively).[17b] The bis-Fe^{II} complex (30) was also prepared, but its properties have not yet been reported.[17c]



(28) M = *trans*-$Ru^{II}Cl_2$; n = 0
(29) M = Ni(II); n = 4
(30) M = Fe(II); n = 4

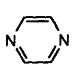
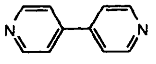
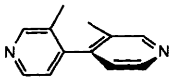
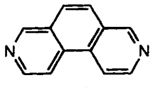
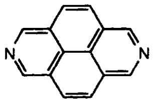
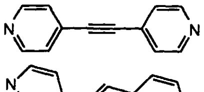
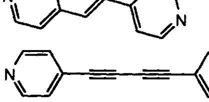
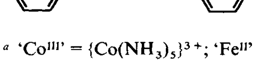
Electron transfer has also been studied across a variety of 4,4'-bipyridyl-type bridging ligands in M^{II}/Co^{III} (M = Fe, Ru) complexes. In these cases the electron transfer is not light-induced, but is instead a more conventional thermodynamically favourable redox reaction. The complexes $[(NH_3)_5Co^{III}(\mu\text{-}L)Fe^{II}(CN)_5]$ were prepared by reaction of $[Co(NH_3)_5L]^{3+}$, where the bridging ligand L is bound *via* one terminus and therefore has a pendant binding site, with $[Fe(CN)_5(H_2O)]^{3-}$; the resulting Co^{III}–Fe^{II} complexes underwent immediate electron transfer.[18a] The related complexes $[(NH_3)_5Co^{III}(\mu\text{-}L)Ru^{III}(EDTA)]^+$ were similarly prepared from $[Ru^{III}(EDTA)(H_2O)]^-$ and $[Co(NH_3)_5L]^{3+}$, but in these cases reduction of Ru^{III} to Ru^{II} with ascorbic acid or dithionite is required to initiate the intramolecular electron transfer.[18b] The electron-transfer rates across the bridging ligands are summarized in Table 5. It is noteworthy that for both series of complexes (with one exception) the decrease in electron-transfer rate constant with increased metal–metal separation is solely due to the increase in solvent reorganization energy, and the electron transfer is therefore adiabatic. In other words, once the effect of solvent reorganization is removed the rate constants for intramolecular electron-transfer are independent of metal–metal separation, the sole exception being for the Co^{III}–Ru^{II} complex with 3,3'-dimethyl-4,4'-bipyridine as bridge. The marked difference in rate constants between the two series Co^{III}–Ru^{II} and [Co^{III}–Fe^{II}] is due to the differing values of the Fe^{II}/Fe^{III} and Ru^{II}/Ru^{III} redox couples.

The recent advent of polynucleating bridging ligands such as (31),[19a] (32),[19b] and (33)[19c] suggests that the principles of long-range metal–metal interactions and electron-transfer will soon be extended to systems of higher nuclearity.

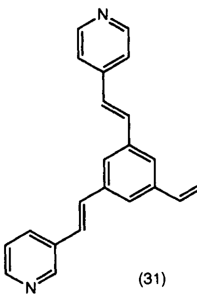
2.4 Bimetallocenes and Related Species

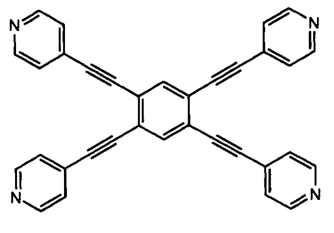
It has been known for a while that biferrocenes [see (34)—(41) for examples] display strong interactions between the metal

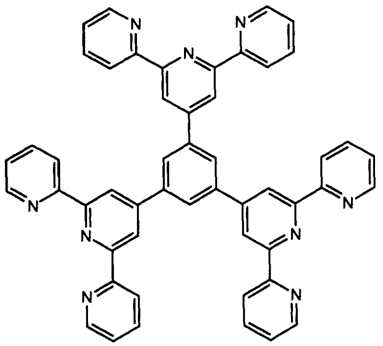
Table 5 Electron-transfer rate constants across various bridging ligands in heterobinuclear complexes

Bridging Ligand	End groups	Electron-transfer rate constant (s^{-1})
	Co^{III}/Ru^{II}[a] Co^{III}/Fe^{II}[a]	22.7 (±0.4)[b] 55×10^{-3}[b]
	Co^{III}/Ru^{II} Co^{III}/Fe^{II}	0.64 (±0.02) 2.7×10^{-3}
	Co^{III}/Ru^{II} Co^{III}/Fe^{II}	0.067 (±0.02) 2.3×10^{-3}
	Co^{III}/Fe^{II}	4.2×10^{-3}
	Co^{III}/Fe^{II}	9.3×10^{-3}
	Co^{III}/Fe^{II}	1.7×10^{-3}
	Co^{III}/Ru^{II} Co^{III}/Fe^{II}	0.21 (±0.01) 1.4×10^{-3}
	Co^{III}/Ru^{II} Co^{III}/Fe^{II}	0.039 (±0.01) 0.50×10^{-3}

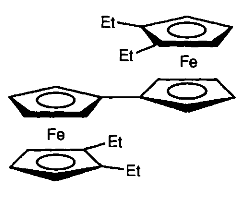
[a] 'Co^{III}' = $\{Co(NH_3)_5\}^{3+}$; 'Fe^{II}' = $\{Fe(CN)_5\}^{3-}$; 'Ru^{II}' = $\{Ru(EDTA)\}^{2-}$. [b] Measurements made in water at 298 K.

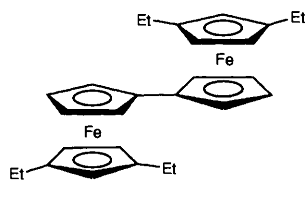

(31)

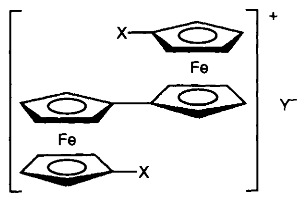

(32)


(33)

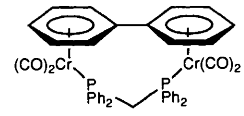
centres because of extensive electronic delocalization across the fulvalene bridge There is a large splitting between the two Fe^{II}/Fe^{III} couples [0 315 V for unsubstituted biferrocene in CH_3CN] and a stable mixed-valent state with an IVCT band in the near-IR spectrum[20a] Work with various substituted biferrocenes has shown that an asymmetric substitution pattern in mixed-valence species (*i e* the two metal centres inequivalent) results in a shift of the IVCT band to higher energy Also, a twist between the two halves of the fulvalene bridge – induced by steric hindrance between substitutents – reduces the metal–metal interaction [$\Delta E_p = 0\ 26$ V in CH_3CN for 2,2′-dimethyl-biferrocene][20a] Much of the early work on biferrocenes has been reviewed[20b] Recent work has shown that minor variations in the twist angle of the fulvalene bridge can have a pronounced effect on the electronic structure and rate of electron transfer in mixed-valence biferrocene derivatives Thus the mixed-valence forms of (34) and (35) (as their I_3^- salts) were shown by Mossbauer spectroscopy to change from valence-trapped (two inequivalent Fe centres) to delocalized (both Fe centres equivalent) solid-state structures above 195 and 125 K respectively The difference in the rates of intramolecular electron-transfer that this implies was ascribed to slight differences in the twist angles between the two halves of the complexes, and extended Huckel MO calculations support this The sensitivity appears to be so great that 'identical' samples with different histories – and therefore possibly slightly different crystalline packing arrangements – gave different transition temperatures[20c] Similar results were obtained for (36)—(41) For (36) and (41) the presence of two polymorphs was established which one forms depends on whether the sample is slowly recrystallized or rapidly precipitated from solution The two forms may have very different electronic properties Thus for (41) the rapidly precipitated polymorph converts from valence-trapped to detrapped on the Mossbauer timescale at 140 K whereas the crystallized isomorph becomes detrapped at 270 K In the former case the detrapping was shown to coincide with the onset of dynamic behaviour of the $[SbF_6]^-$ anion, and the detrapping is *not* due to electronic delocalization but to the change in the crystal environment (dynamic $[SbF_6]^-$ ions and more volume) allowing more rapid vibronic interconversion between the [2,3] and [3,2] states[20d] This is in contrast to the example of reference 20*c* where detrapping occurred by intramolecular electron transfer


(34)


(35)


(36) X = Cl Y = PF_6
(37) X = Br Y = PF_6
(38) X = I Y = PF_6
(39) X = Cl Y = SbF_6
(40) X = Br Y = SbF_6
(41) X = I Y = SbF_6

The rôle of the bridging ligand in determining the electronic nature of the mixed-valence state was examined in binuclear Cr^{I}/Cr^{0} complexes such as (42), which has been shown crystallographically to be delocalized since both metal centres are structurally identical[21a] The bridging biphenyl group is also nearly planar, which raises the question of whether the electron delocalization occurs through the biphenyl π-system (as in the biferrocenes), or whether the interaction can occur through space since the metal centres are constrained to be *syn* to one another by the dppm ligand The binuclear Cr^{0}/Cr^{0} compounds (43)—(45) were prepared in which the biphenyl torsion angles vary between 0° and 100° For steric reasons the twist angles are not expected to be able to change as one metal is oxidized The mixed-valent Cr^{0}/Cr^{I} compounds prepared from these all have a strong electrochemical interaction ($\Delta E \approx 0\ 26$ V), but were shown by a combination of IR and EPR spectroscopy to be valence-trapped – even when the biphenyl bridge is nearly planar This implies that electronic delocalization observed for (42) probably involves direct interaction of the two metals through space despite a separation of over 4Å[21b]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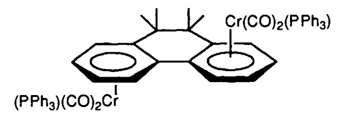
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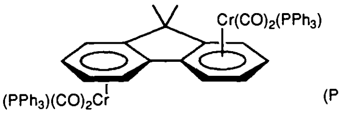
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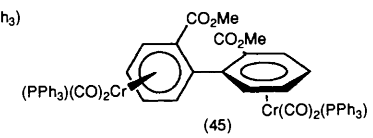
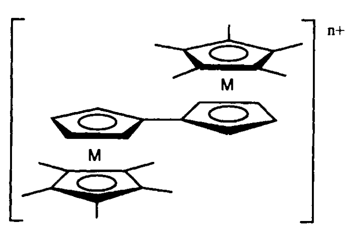
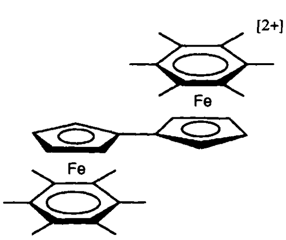

(45)

A series of decamethyl-bimetallocenes (46)—(50) has been prepared and studied electrochemically All show several reversible redox steps, with a similar substantial separation between the redox couples of each metal centre [*e g* 0 385, 0 375, and 0 430 V between the pairs of Ni^{II}/Ni^{III}, Fe^{II}/Fe^{III}, and Co^{II}/Co^{III} couples respectively] In contrast the magnetic exchange in the paramagnetic complexes varies widely across the series[22a] Both the Fe^{II}/Fe^{III} and Fe^{II}/Fe^{I} mixed-valence states of the fulvalene-bridged diiron compounds (47) and (51) were examined by IR spectroscopy In both cases the Fe^{II}/Fe^{I} states are delocalized on the IR timescale [the Fe^{II}/Fe^{I} state of (51) was already known to be delocalized on the slower Mossbauer timescale], but the Fe^{II}/Fe^{III} states are valence-trapped on the IR timescale Interestingly, the presence of the methyl substitutents increases the electrochemical splitting for (47) compared to unsubstituted biferrocene, but has the reverse effect on (51) compared to its unsubstituted analogue[22b]

Finally in this section, the trinuclear complexes (52) and (53) with three mutually interacting metal centres have recently been prepared using the trindenyl ligand as a bridge For (53), three separate one-electron Rh^{0}/Rh^{I} oxidations were seen by cyclic

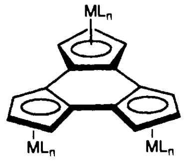


(46) M = V, n = 0
(47) M = Fe, n = 0
(48) M = Co, n = 0
(49) M = Ni, n = 0
(50) M = Co, n = 2



(51)

voltammetry. The first two are separated by 0.17 V, which is typical of electrochemical splittings in trapped-valence (Class II) binuclear complexes; however the second and third oxidations are separated by 0.55 V, which is more typical of fully delocalized (Class III) mixed-valence states.[22c]



(52) $ML_n = Mn(CO)_3$
(53) ML_n = Rh(cod)

2.5 Binuclear Organometallic Species with Conjugated Carbon-chain Bridging Ligands

Compounds in which linear, conjugated, all-carbon chains span two transition metals, $L_nM–C_x–M'L'_n$, have been of particular interest recently, since such bridges constitute appealing molecular wires.[23a,b] Recent work has involved the syntheses and structural characterization of species with bridges of increasing length and the examination of the pronounced metal–metal interactions across these novel bridges. Thus, compound (54) has a three-carbon bridge, and the problem arises as to whether the bridging group is best considered as having alternating triple and single bonds, or having a cumulenic structure with double bonds in each position (Figure 6). Crystal structure analysis suggested that the latter description is more appropriate.[23c]

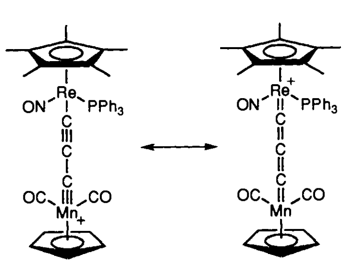
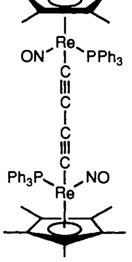


Figure 6 Limiting canonical forms of (54).

Compound (55) has a four-carbon bridge whose structural parameters are very similar to those of butadiyne, *i.e.* alternating triple and single bonds.[23d] The efficacy of this conjugated carbon bridge in permitting communication between the metal centres is shown by the observation that the two reversible oxidations [formally Re^I/Re^{II} couples] are separated by 0.44 V ($K_c = 2.8 \times 10^7$) despite a metal–metal separation of nearly 8Å. The mixed-valence species $[55]^+$ was accordingly prepared by one-electron oxidation, and both IR and EPR spectra showed that the odd electron was fully delocalized between both metals (*i.e.* Robin and Day class III behaviour). Multiple bands were also observed in the near-IR region of the electronic spectrum.[23e] On oxidation of both metal centres to give $[55]^{2+}$ the structure of the bridge becomes cumulenic, $Re^+{=}C{=}C{=}C{=}C{=}Re^+$, according to *X*-ray crystallography.[23d] The related di-iron complex (56) has the remarkably large separation of 0.71 V between the two reversible Fe^{II}/Fe^{III} couples ($K_c = 10^{12}$), confirming that there is extensive delocalization across the C_4 bridge in the mixed-valence state. The mixed-valence species $[56]^+$, like $[55]^+$, appears to be fully delocalized on the IR timescale, and there is an intense transition at 1326 nm (ϵ = 11 700 dm^3 mol^{-1} cm^{-1}) in the electronic spectrum which is a π–π^* transition of the odd electron delocalized over the FeC_4Fe system. The doubly-oxidized bis-Fe^{III} complex $[56]^{2+}$ is EPR silent, presumably due to formation of a $Fe^+{=}C{=}C{=}C{=}C{=}Fe^+$ structure which will couple the unpaired electrons.[23f] The cumulenic five-carbon bridge in (57) confers some unusual properties on the complex: (57) is light-sensitive and the principal band at 480 nm in its electronic spectrum is probably due to rhenium-to-manganese charge transfer. The C_5 bridge therefore mediates electron transfer over a relatively long distance.[23g] The longest bridges of this type reported to date are the C_6 and C_8 bridges of (58) and (59). Like (55) – with a C_4 bridge – both (58) and (59) undergo two reversible one-electron oxidations, the separation between which decreases with metal–metal separation (in CH_2Cl_2 the values of K_c for the three complexes are 1.3×10^9; 3.4×10^6; 6.6×10^4, respectively). At the time of writing the mixed-valence forms of (58) and (59) have not been prepared.[23h]



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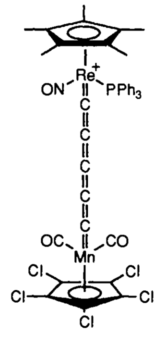

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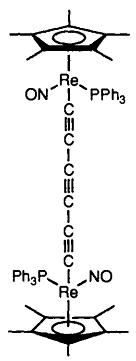

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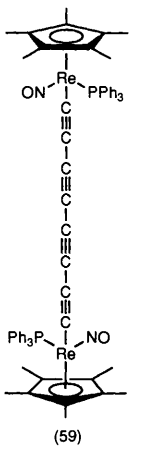

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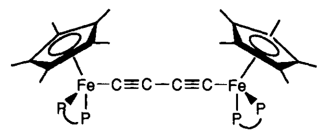
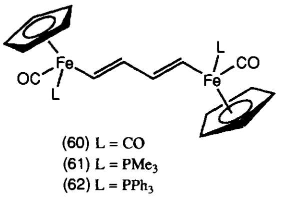


(56)

Since polyene segments have been widely used in bridging ligands, the bis-Fe^{II} complexes (60)—(62) were prepared and examined. Electrochemical experiments indicated a substantial separation of *ca.* 0.4 V between the two Fe^{II}/Fe^{III} couples in each case, and treatment with one equivalent of the one-electron oxidant $[Cp_2Fe][PF_6]$ afforded the (rather unstable) mixed-valence Fe^{II}/Fe^{III} complexes, for which EPR and IR data are both consistent with symmetric, valence-delocalized structures.[23i]



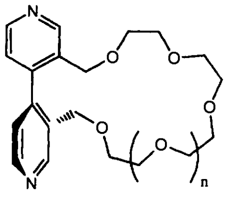
(60) L = CO
(61) L = PMe_3
(62) L = PPh_3

3 Control of Metal–Metal Interactions: The Basis of Molecular Switches

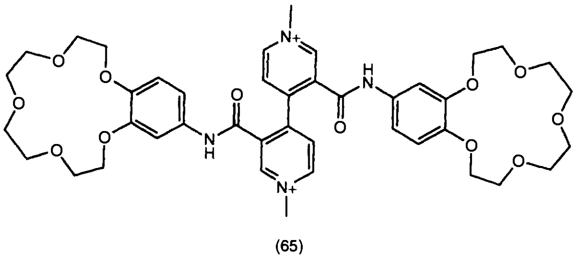
3.1 Control of Bridging Ligand Conformation

In those binuclear complexes where the interaction is transmitted through the delocalized π-system of the bridging ligand – which is the majority – the magnitude of the interaction may be modified by controlling in some way the conformation of the bridging ligand This is particularly appropriate when the bridging ligand contains a biphenyl-type linkage since there is a low potential barrier to rotation about the central C–C bond, and such rotation affects the extent of π-delocalization between the two ends of the ligand [24a] Several examples have already been given in which torsion of the bridging ligand is effected by the presence of sterically bulky substitutents,[15c 18b 20c 20d 21b] and theoretical studies have also shown that the coupling across bridging ligands such as the α,ω-di(4-pyridyl)polyenes[4] is sensitive to the conformation of the polyene bridge [24b] However none of these examples constitute true switches since they do not permit reversible interconversion between two or more distinct states

Two ingenious methods have been recently described by which the dihedral twist angle θ between the two halves of a 4,4′-bipyridyl fragment may be modified in a reversible, controllable manner, by using coordination of alkali metal cations to crown-ether substitutents as the basis of the switching effect In (63) and (64) a poly-oxoethylene chain links the two halves of the 4,4′-bipyridyl fragment The presence of this tethering chain prevents free rotation about the central bond, and θ will be a compromise between π–π effects (conjugation between the two aromatic rings) and steric effects primarily involving the limited flexibility of the chain Coordination of an alkali metal cation into the crown-ether-type cavity will necessitate folding of the poly-oxoethylene chain around the cation to give a stereochemically quite rigid structure The side-effect of this is to constrain θ to a value (or, possibly, a narrow range) which depends on the size of the alkali metal used and hence the degree of folding of the chain The crystal structure of [(63) Na][BPh_4] [Figure 7(a)] shows that θ is 69 7° in the solid state [25a] The second example is provided by compound (65) in which each half of the (*N*-methylated) 4,4′-bipyridyl bears a 15-crown-5 substituent In the absence of alkali metals the ligand is free to rotate about its central bond to the extent permitted by steric hindrance and electronic factors In the presence of K^+ or Ba^{2+}, however, the two crown ether rings come together to form a ten-coordinate sandwich complex, the crystal structure of [(65) Ba](ClO_4)$_2$ [Figure 7(b)] shows that, as a result, the dihedral angle θ in the 4,4′-bipyridyl fragment is 60 3° [25b] Although (63)—(65) have not yet been used as bridging ligands in binuclear complexes, one can easily imagine such complexes in which the interaction between the two terminal metal groups may be modified simply by adding an alkali metal cation to the solution to alter the bridging ligand conformation



(63) n = 1
(64) n = 2



(65)

It is also possible to alter the conformation of a bridging ligand by electrochemical means if the bridging ligand is redox-active The catecholate dianion (cat) is well known to undergo two successive one-electron oxidations to the semiquinone (sq) and then quinone (q) oxidation states in many of its complexes, and this was exploited in the bis-catechol bridging ligand (66) for which five oxidation states may be envisaged (Figure 8), cat–cat, cat–sq, sq–sq, sq–q, and q–q In the sq–sq state the ligand is necessarily planar due to the double bond between the two rings, whereas the single bond of the cat–cat and q–q states permits the two halves to rotate freely The geometry of the mixed-valence cat–sq and sq–q state is not immediately obvious they may be planar, with the odd electron delocalized over the entire bridging

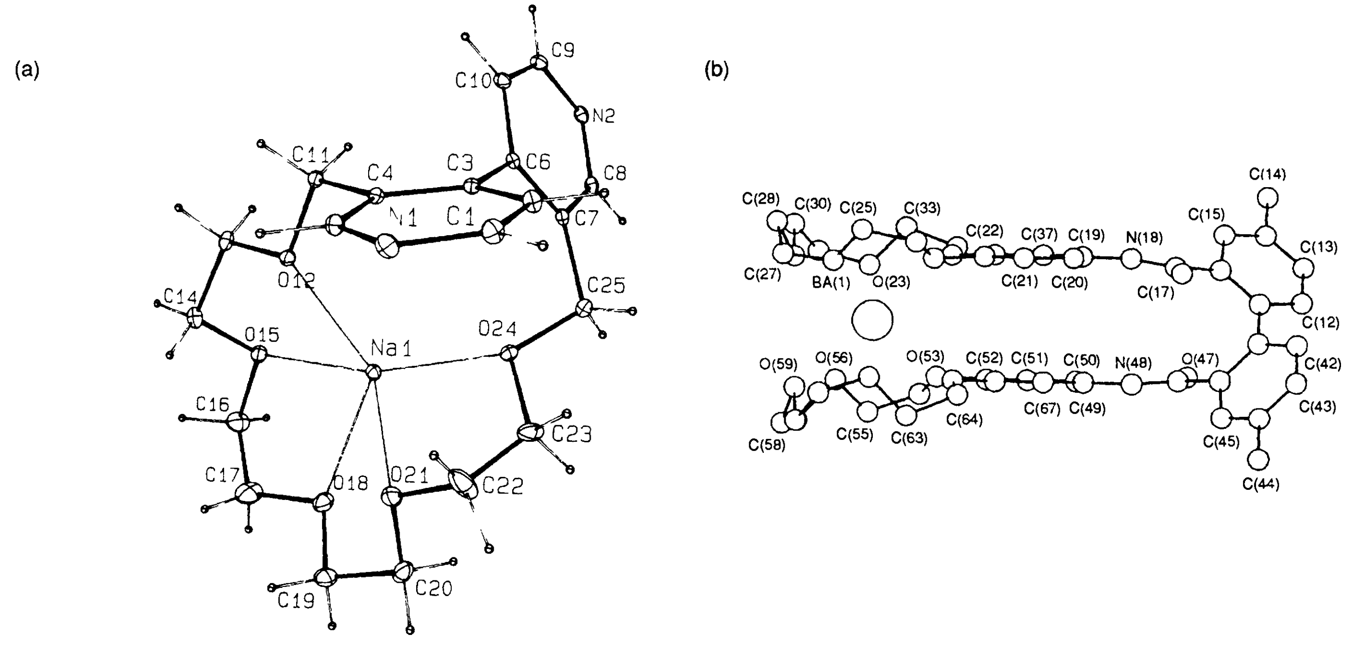


Figure 7 Crystal structures of the cations of (a) [(63) Na]($BPh)_4$ and (b) [(65) Ba](ClO_4)$_2$

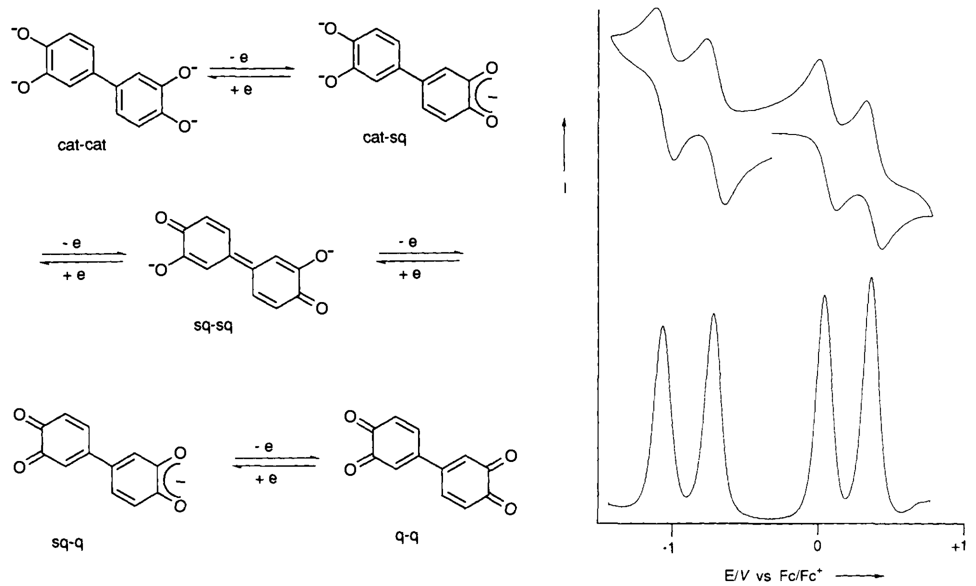


Figure 8 The oxidation states of ligand (66), and the electrochemistry of $[(bipy)_2Ru^{II}\{\mu\text{-}(66)\}Ru^{II}(bipy)_2]^{2+}$.

ligand and chemically equivalent ends, or twisted (decoupled) with chemically distinct ends. In $[(bipy)_2Ru^{II}\{\mu\text{-}(66)\}Ru^{II}(bipy)_2]^{2+}$ the ligand is in the planar sq–sq state, and cyclic voltammetry showed the expected four reversible one-electron ligand-based couples at well-separated potentials. UV/VIS spectroelectrochemistry of all five oxidation states suggested that in the mixed-valence cat–sq and sq–q states both ligand termini were equivalent, so the ligand is therefore planar with the odd electron delocalized. In this complex the conformation of the bridging ligand is therefore predicted to be twisted (cat–cat state), planar (cat–sq, sq–sq, and sq–q states), twisted (q–q state).[26a]

In complex (67) the ligand, a nitrogen analogue of (66), has two extreme resonance forms: in one of them the sq–sq ligand is 'polarized' into diamine and diimine ends, with a single bond between the aromatic rings, and in the other both halves of the ligand are in the same oxidation state with a double bond between them (Figure 9), like the sq–sq state of (66). In the first extreme there is a substantial twist between the aromatic rings ($\approx 46°$ computed), whereas in the second the rings are necessarily coplanar. Electronic spectroscopy showed that in the presence of strong hydrogen-bond donors or electron-acceptors (*e.g.* BF_3, H^+, H_2O) the first form predominates due to the favourable interactions with the free di-amine binding site. Strong electron-donors or hydrogen-bond acceptors, in contrast (NH_3, Cl^-) interact more effectively with the other limiting form of the complex in which there is a positive charge at the vacant binding site. The torsion angle of the biphenyl fragment may therefore be varied over a wide range according to the nature of the solvent or other species dissolved in it, in contrast to the electrochemical method used to achieve the same effect in the previous example. Although this is a mononuclear complex the potential for using this type of behaviour in a switch of some kind is clear.[26b]

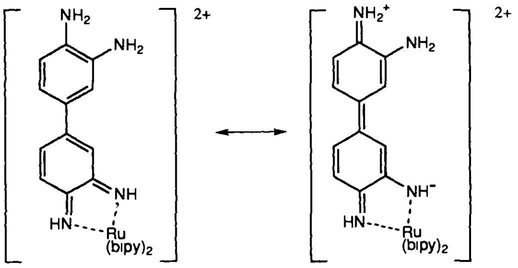


Figure 9 Limiting canonical forms of (67).

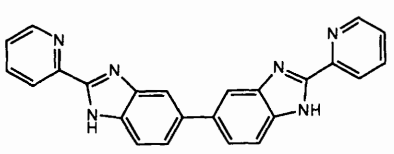
Photochemical isomerization is another possible switching mechanism: some organic molecules such as butadienes and azobenzene are bi-stable and undergo a conformational change on irradiation with light of the appropriate wavelength. Although this method has been successfully used to change the affinity of various macrocyclic complexes for different metal ions[27] there appear to be no examples of control of long-range metal–metal interactions in a bridged binuclear complex by this type of mechanism.

3.2 pH-Induced Switching

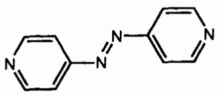
There are two distinct types of pH-induced control of metal–metal interaction. In one case, a basic site on the bridging ligand is protonated: in the other, a pH-sensitive terminal ligand on one of the metal fragments is the site of reaction.

The first case is exemplified by ligand (68), which contains two bidentate chelating sites and two additional nitrogen atoms in the imidazole rings which may be protonated or deprotonated. The binuclear complexes $[L_2M^{II}\{\mu\text{-}(68)\}M^{II}L_2]^{4+}$ (M = Ru, Os; L = bipy or 1,10-phenanthroline) act as dibasic acids since the imidazoles remain protonated on the N atoms which are not coordinated. The M^{II}/M^{III} oxidation potentials and the electronic spectra are highly pH dependent. When the bridging ligand is protonated, the valence-localized M^{II}/M^{III} complexes (generated electrochemically) display weak IVCT bands at 1370 nm ($\epsilon < 100$ dm^3 mol^{-1} cm^{-1}) and 1100 nm ($\epsilon < 20$ dm^3 mol^{-1} cm^{-1}) for M = Ru and Os respectively. However, deprotonation of the bridging ligand results in a shift of these to lower energy coupled to a substantial increase in intensity [for M = Ru; $\lambda_{max} = 1700$ nm, $\epsilon = 2000$: for M = Os, $\lambda_{max} = 1300$ nm, $\epsilon = 420$ dm^3 mol^{-1} cm^{-1}]. Using equation 3 it was shown that the degree of electronic coupling between the metals was increased by a factor of 4—6 on deprotonation of the bridging ligand. This was ascribed to (i) the shorter metal–ligand bond distances as a result of the improved electron-donor ability of the bridge, and (ii) a significant change in the energy of the HOMO of the bridging ligand which brings it nearer in energy to the metal $d\pi$ orbitals. A change in pH therefore acts as an effective switch for the metal–metal interaction.[28a]

A slightly different switching mechanism operates with 4,4′-azopyridine (69). In $[(NH_3)_5Ru^{II}\{\mu\text{-}(69)\}Ru^{II}(NH_3)_5]^{4+}$ the metal fragments coordinate to the pyridyl nitrogen atoms of the bridging ligand. The interaction between the metals is modest with $K_c \approx 40$ and an IVCT band ($\lambda_{max} \approx 1200$ nm, $\epsilon \approx 500$ dm^3 mol^{-1} cm^{-1}) not clearly resolved due to the presence of a nearby



(68)



(69)

strong MLCT band Addition of acid to the complex in aqueous solution is followed immediately by the reaction

$$\mathrm{Ru^{II}py{-}N{=}N{-}pyRu^{II} + 2H^{+} \rightarrow Ru^{III}py{-}NH{-}NH{-}pyRu^{III}}$$

in which protonation of the azo-nitrogen atoms of the bridging ligand is followed immediately by intramolecular electron transfer, resulting in reduction of the bridging ligand to 1,2-bis(4-pyridyl)-hydrazine and oxidation of both $\mathrm{Ru^{II}}$ centres to $\mathrm{Ru^{III}}$ In this reduced form the conjugated pathway across the bridging ligand is removed, and subsequent reduction of the metals to give the $\mathrm{Ru^{II}/Ru^{III}}$ and then $\mathrm{Ru^{II}/Ru^{II}}$ complex of 1,2-bis(4-pyridyl)hydrazine showed that the interaction across the reduced form of the bridging ligand was greatly decreased ($K_c \approx 4$, $\epsilon_{\mathrm{IVCT}} \approx 40\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$) The pH-induced reduction of the bridging ligand is reversible, in basic media the bis-$\mathrm{Ru^{II}}$ complex of 4,4′-azopyridine is regenerated, so the bridging ligand is genuinely switchable between conjugated and non-conjugated states according to pH [28b] The same ligand-based switching system was used to modify interactions in oligomers of ruthenium(II) porphyrins [28c]

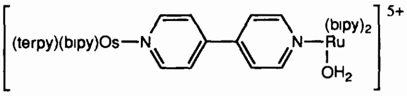
The second type of pH-induced switching involves protonation or deprotonation of a terminal ligand on one of the metals Complex (70) contains an ionisable $\mathrm{H_2O}$ ligand bound to the $\mathrm{Ru^{II}}$ centre, and consequently displays pH-dependent $\mathrm{Ru^{II}(H_2O)/Ru^{III}(OH)}$ and $\mathrm{Ru^{III}(OH)/Ru^{IV}(O)}$ couples in addition to the pH-independent $\mathrm{Os^{II}/Os^{III}}$ couple It is possible to induce intramolecular electron-transfer between the ligand-bridged metal sites by varying the pH In the $\mathrm{Os^{III}/Ru^{II}}$ oxidation state combination of the starting complex, a pH jump from 1 1 to 8 9 induces net intramolecular electron transfer

$$\mathrm{Os^{III}(\mu\text{-}4,4'bipy)\{Ru^{II}(H_2O)\} \rightarrow Os^{II}(\mu\text{-}4,4'\text{-}bipy)\{Ru^{III}(OH)\} + H^{+}}$$

which is reversible on re-acidification (the ancillary ligands on the metals have been omitted for clarity) Similarly, starting in the $\mathrm{Os^{III}/Ru^{III}}$ state, a change in pH to above 7 results in the intramolecular electron-transfer process

$$\mathrm{OH \quad + Os^{III}(\mu\text{-}4,4'\text{-}bipy)\{Ru^{III}(OH)\} \rightarrow Os^{II}(\mu\text{-}4,4'\text{-}bipy)\{Ru^{IV}(O)\} + H_2O}$$

in which both oxidative equivalents are concentrated at the ruthenium site and stabilized by the oxo ligand Long-range electron-transfer between redox sites can therefore be switched on or off according to the ambient pH [28d] Photo-induced electron-transfer to the ^{3}MLCT excited-state of the $\mathrm{Os^{II}}$ chromophore from the ruthenium terminus may also be controlled by a pH switch, since the $\mathrm{Ru^{II}(OH)}$ fragment is a better electron donor than the $\mathrm{Ru^{II}(H_2O)}$ fragment [28c]

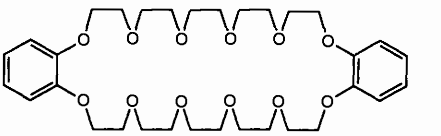


(70)

3.3 Environmental Effects on Metal–Metal Interactions

Genuine IVCT bands (*i e* those involving vectorial electron-transfer in valence-localized mixed-valence complexes) are solvatochromic, since the extent of reorganization of the coordination sphere (which includes solvation) required at the two ends of the complex following charge transfer is solvent-dependent In a $\mathrm{Ru^{II}/Ru^{III}}$ complex for example, the coordination environment of the $\mathrm{Ru^{II}}$ terminus – which encompasses metal–ligand bonds in the primary coordination sphere and solvent interactions in the secondary coordination sphere – will be different from that of the $\mathrm{Ru^{III}}$ terminus, where the metal–ligand bonds are likely to be shorter and, for example, dipolar interactions with the solvent more pronounced The IVCT process proceeds much faster than nuclear motion (Franck–Condon principle), so the $\mathrm{Ru^{III}/Ru^{II}}$ species initially generated contains a $\mathrm{Ru^{III}}$ ion in a coordination environment appropriate for $\mathrm{Ru^{II}}$, and a $\mathrm{Ru^{II}}$ ion in a coordination environment appropriate for $\mathrm{Ru^{III}}$ This is therefore a high-energy state, which accounts for the energy required to initiate the process Since the secondary solvation contributes to the overall coordination environment the energy required to effect the IVCT and generate the high-energy $\mathrm{Ru^{III}/Ru^{II}}$ species depends to some extent on the solvent After the electron transfer, metal–ligand bonds in the primary coordination sphere and solvent interactions in the second coordination sphere must then readjust to their new equilibrium values In a simple sense therefore the extent of metal–metal interaction in a binuclear complex may be controlled by the nature of the solvent,[3c 29] although in practice the effect is not large enough to constitute what most people would consider by a switch It does illustrate however how a change in the second-sphere coordination of a complex may be the basis for control of metal–metal interactions, and one dramatic example has already been mentioned in which K_c for a binuclear ruthenium complex increased from 10 to 68400 on changing the solvent from $\mathrm{H_2O}$ to MeCN [8b]

In systems which are closely balanced between two states the relatively small effects of second-sphere coordination may tip the balance one way or the other In the binuclear complex $\mathrm{[(bipy)_2ClOs(\mu\text{-}pyrazine)Ru(NH_3)_5]^{4+}}$ the choice of ancillary ligands is such that the $\mathrm{Os^{II}/Os^{III}}$ and $\mathrm{Ru^{II}/Ru^{III}}$ couples are very close, and the $\mathrm{Ru^{II}/Ru^{III}}$ couple is markedly solvent dependent The oxidation state distribution in the mixed-valence form was found to be $\mathrm{Os^{III}{-}L{-}Ru^{II}}$ in weakly basic solvents but $\mathrm{Os^{II}{-}L{-}Ru^{III}}$ in more strongly basic solvents, so that intramolecular electron-transfer could be induced in either direction by changing the composition of the solvent In addition analysis of the IVCT band showed that the extent of valence delocalization in the mixed-valence state was also solvent dependent The source of this solvent dependence may be similar to that discussed in reference 8(*b*), *viz* hydrogen-bonding between the ammine protons of the $\mathrm{\{Ru(NH_3)_5\}^{n+}}$ fragment and the solvent perturbing the Ru-ammine interactions [30a] Similar behaviour was observed in the mixed-valence complex *trans*-$\mathrm{[(py)(NH_3)_4Ru(\mu\text{-}NCpy)Ru(bipy)_2Cl]^{4+}}$ (py = pyridine, NCpy = 4-cyanopyridine), which exists as $\mathrm{Ru^{II}{-}NCpy{-}Ru^{III}}$ in weakly basic solvents but $\mathrm{Ru^{III}{-}NCpy{-}Ru^{II}}$ in more strongly basic solvents The same effect was obtained by addition of ≤ 1 equivalent of poly(ethyleneglycol) or the polyether macrocycle dibenzo-36-crown-12 (71) to the solvent Polyethers of this kind form outer-sphere complexes with ammine ligands *via* hydrogen-bonding interactions, and therefore take the place of the solvent interactions The efficacy of these polyethers at inducing the redox isomerization – only one equivalent is required for a limiting effect, in contrast to the several-fold excess of a basic solvent – is presumably ascribable to a 'chelate effect' [30b]



(71)

The symmetrical Creutz–Taube ion $\mathrm{[(NH_3)_5Ru(pyrazine)Ru(NH_3)_5]^{5+}}$ and the pyridyl-substituted analogue *trans*-$\mathrm{[(NH_3)_4(py)Ru(pyrazine)Ru(py)(NH_3)_4]^{5+}}$ could be rendered asymmetric by addition of one equivalent of a polyether macrocycle such as (71), which results in encapsulation of only one end of each binuclear molecule *via* hydrogen-bonding interactions with the ammine ligands. This resulted in a shift of the IVCT band in each case to higher energy, a loss of intensity, and an increase in width, all of which indicate the onset of valence localization induced by the asymmetry in the second coordination sphere (*i.e.* a move from Class III towards Class II behaviour).[30c] Addition of a second equivalent of the crown ether results in encapsulation of both ends of each binuclear complex, thereby restoring the symmetry and nearly (but not quite[30d]) restoring the original appearance of the IVCT band.[30c] The variation of the IVCT band can be used to measure the extent of encapsulation of a $\{Ru(NH_3)_5\}^{3+}$ terminus of binuclear complexes by a polyether macrocycle.[30e]

Some other interesting environmental factors have been observed to modify the properties of the IVCT process in $[(NH_3)_5Ru\{\mu\text{-}(17)\}Ru(NH_3)_5]^{5+}$. The saturated bridge in this complex ensures that the intramolecular electron-transfer is non-adiabatic (*i.e.* relatively slow) and the coupling between the metals is weak.[10] The energy of the IVCT process in the presence of different concentrations of tetra-n-butylammonium hexafluorophosphate was found to be markedly dependent on the ionic strength of the medium. This is due to ion-pairing of the complex cations with some of the PF_6^- ions: such ion-pairing stabilizes the ground-state Ru^{II}–Ru^{III} complex, but does not stabilize the excited state [the Ru^{III}–Ru^{II} state after electron transfer but before reorganization of the coordination sphere] because its lifetime is short compared to the time that would be required to reorganize the ion pair into a configuration compatible with the new electronic state. The IVCT energy therefore increases with ionic strength.[31a] The IVCT energy of $[(NH_3)_5Ru\{\mu\text{-}(17)\}Ru(NH_3)_5]^{5+}$ was also found to be dependent on the nature of the chemical oxidant used to generate it, which is likewise ascribed to aggregation of the mixed-valence binuclear complex and the reduced oxidant.[31b] Similar phenomena have been seen in other systems: a strong concentration dependence of the IVCT band energy of mixed-valence biferrocenium triiodide was ascribed to ion-pairing.[31c]

4 Conclusion

To put this review into some of context it is worth mentioning very briefly some other types of molecular wires and switches which are currently attracting much attention, since the systems described above only constitute one small corner of the rapidly expanding area of molecular electronics. The two main additional areas are photochemical electron/energy transfer, and one-dimensional oligomers. It is only possible to gloss over these areas in the very briefest detail, but together with the main part of this review they show the directions in which research is moving.

Photochemically-induced electron-transfer is distinct from optical electron-transfer in that it is a two-step process: initial absorption of a photon by a chromophore, which then enters a relatively long-lived electronically excited state, can be followed by long distance electron-transfer either to or from another group which thereby quenches the initial excited state.[32a–c] Since the chromophore and quencher are often directly linked by a bridging ligand, the electron transfer between them is dependent on the properties of the bridge in exactly the same way as for the examples of optical electron-transfer described above. Alternatively, energy transfer can occur in which absorption of light by one chromophore is followed by emission of light from another, so 'photonic molecular wires' are possible in addition to electronic ones.[32c–f] Two notable recent examples are shown in Figure 10; these photonic wires rely on energy transfer between ruthenium(II) and osmium(II) polypyridyl fragments in one case,[32d] and between porphyrin fragments in the other.[32f] This type of long-distance communication between chromophore and quencher is also amenable to switching, and many complexes have been prepared whose luminescence properties can be modified reversibly by some external perturbation.[32g,h]

One-dimensional oligomers allow the possibility of very long distance delocalization of electron density and metal–metal interactions between large numbers of metal centres. Molecular wires based on 'side-to-side' oligomerization of porphyrins [*e.g.* (72)][33a] have been particularly popular,[33] as have 'shish-kebab' oligomers prepared by bis-axial coordination of bridging ligands such as pyrazine or 4,4′-bipyridine to planar macrocyclic complexes.[34] Polyacetylide complexes such as (73) are of interest for their electrical conductivities and non-linear optical properties,[35] whilst poly(metallocene) oligomers such as (74)—(77) contain large numbers of redox-active [Fe^{II}/Fe^{III} in this case] units in close association which offers interesting possibilities for the study of mixed-valence behaviour in high nuclearity species.[36]

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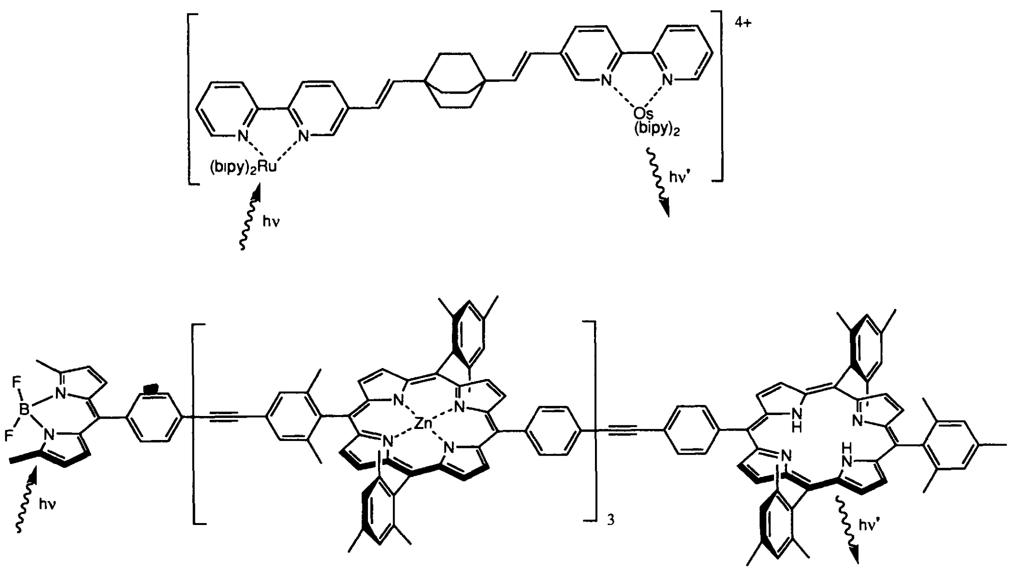
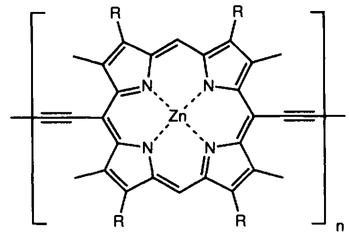
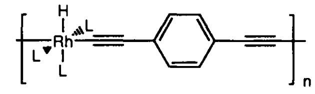


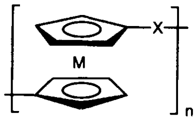
Figure 10 Two examples of 'photonic molecular wires' which function by energy transfer.



(72)



(73)



(74) $X = SiR_2$
(75) $X = GeR_2$
(76) $X = PR$
(77) $X = CH_2CH_2$

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