Long-range Coupling in a Mixed-valence Diruthenium Complexes Containing Bis-terpyridine Ligands of Various Lengths as Bridges

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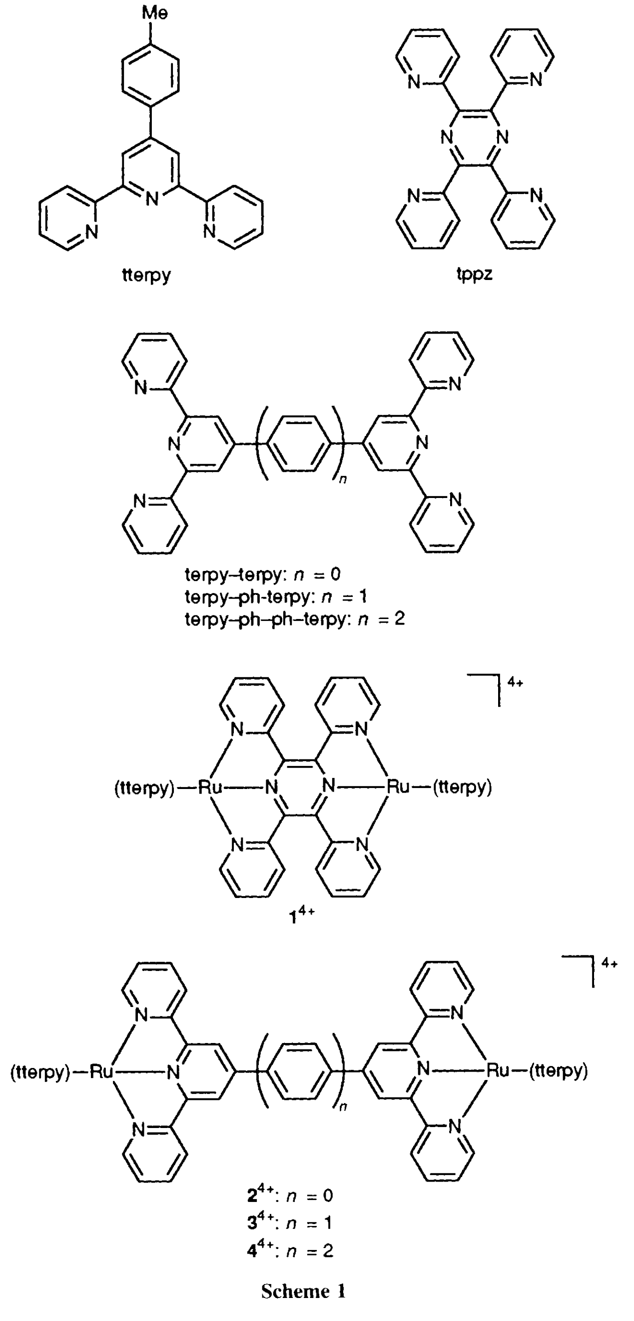
Dinuclear ruthenium(II) complexes have been prepared which contain back-to-back bis-terpyridine ligands of various lengths (Ru···Ru distances between 7 and 20 Å) as bridges; significant electronic coupling is observed in mixed-valence states, even for the system with the longest separation.

Mixed-valence complexes have fostered great theoretical and experimental interests.[1–4] In relation with biological electron transfer processes and molecular electronics, long distance electron transfer has received a revival of attention.[5–12] We now report preparations and spectroscopic studies of four dinuclear ruthenium complexes using back-to-back bis-terpyridine (terpy = 2,2′,6′,2″-terpyridine) as bridging ligand, the distance between both metal centres being adjusted by using various spacers. The ligands and complexes synthesized are shown in Scheme 1.



Scheme 1

From Corey–Pauling–Koltun (CPK) models the metal-to-metal separation ($R_{\text{M-M}}$) can be estimated: 7, 11, 15.5 and 20 Å for $\mathbf{1}^{4+}$, $\mathbf{2}^{4+}$, $\mathbf{3}^{4+}$ and $\mathbf{4}^{4+}$, respectively. The comproportionation equilibrium constant [K_c = (II,III)^2/(II,II) (III,III)] and the characteristics of the intervalence transfer transitions give information about electronic coupling between the two redox sites as a function of distance.

tppz,[13] terpy–terpy[14] and terpy–ph–terpy[15] have been synthesized following the literature methods. The new ligand terpy–ph–ph–terpy has been obtained by homo-coupling of 4′-*p*-bromophenyl-2,2′,6′,2″-terpyridine in the presence of Ni^0 phosphine complex and Zn dust in dimethylformamide (DMF).[16] Complexes $\mathbf{1}^{4+}$ to $\mathbf{4}^{4+}$ have been prepared by heating [Ru(tterpy)L$_3$]$^{2+}$ (2 equiv.) (L = acetone and tterpy = 4′-tolyl-2,2′,6′,2″-terpyridine) and a bridging ligand in DMF at 120 °C for 3 h.[10] ^{1}H NMR and FAB-mass spectra are in accordance with their postulated structures.† Preparation of complexes related to $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ has already been reported.[17,14]

The absorption spectra of $\mathbf{2}^{4+}$, $\mathbf{3}^{4+}$ and $\mathbf{4}^{4+}$ exhibit similar metal-to-ligand charge transfer (MLCT) transition (Table 1). The Π^* levels of the ligands are less and less perturbed from $\mathbf{2}^{4+}$ to $\mathbf{4}^{4+}$, the position of the MLCT band for this latter complex being almost the same as that for [Ru(tterpy)$_2$]$^{2+}$ (λ_{max} = 490 nm).[18] By contrast, the MLCT transition in $\mathbf{1}^{4+}$ clearly occurs at much lower energy. As expected, the mixed-valence species Ru$^{\text{II}}$, Ru$^{\text{III}}$ also displays MLCT transition in the visible region. This band disappears by oxidation to the Ru$^{\text{III}}$, Ru$^{\text{III}}$ state.

From the results of Table 1, $\mathbf{1}^{4+}$ is the only complex to show strongly communicating metal centres. By contrast $\mathbf{2}^{4+}$, $\mathbf{3}^{4+}$ and $\mathbf{4}^{4+}$ seem to contain electrochemically isolated subunits.

For $\mathbf{1}^{4+}$, the constant K_c is 10^5 (ΔE = 300 mV), in agreement with the value determined for the Creutz–Taube pyrazine bridged system.[3] The corresponding K_c values for $\mathbf{2}^{4+}$, $\mathbf{3}^{4+}$ and $\mathbf{4}^{4+}$ are respectively 15, 7 and 5.[19] Interestingly, $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ also lead to two one-electron waves in the cathodic region.

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† *Spectroscopic data* for $\mathbf{1}^{4+}$: ^{1}H NMR (200 MHz, CD$_3$CN) δ 9.14 (4H, s), 8.97 (4H, d, 8.0), 8.77 (4H, d, 7.1), 8.20 (4H, d, 8.2), 8.08 (4H, m), 7.93 (4H, m), 7.83 (4H, d, 4.8), 7.76 (4H, d, 4.8),7.64 (4H, d, 8.0), 7.43 (4H, m), 7.30 (4H, m), 2.58 (6H, s). ESMS *m*/*z* = 763.8, [Ru$_2$(tppz)(tterpy)$_2$(PF$_6$)$_2$]$^{2+}$/2 requires 763.6.

For $\mathbf{2}^{4+}$ NMR [200 MHz, (CD$_3$)$_2$SO] δ 9.96 (4H, s), 9.52 (4H, s), 9.2 (8H, d, 8.1), 8.40 (4H, d, 8.3), 8.17 (8H, m), 7.71 (4H, d, 5.4), 7.61 (4H, d, 8.3), 7.54 (4H, d, 5.4), 7.38 (8H, ddd, 12.8, 6.6), 2.55 (6H, s). FAB-MS: 1748.6, [Ru$_2$(terpy–terpy)(tterpy)$_2$(PF$_6$)$_3$]$^+$ requires 1748.4.

For $\mathbf{3}^{4+}$: ^{1}H NMR (200 MHz, CD$_3$CN) δ 9.23 (4H, s), 9.70 (4H, s), 8.81 (4H, d, 8.3), 8.72 (4H, d, 8.0), 8.64 (4H, s), 8.17 (4H, d, 8.5), 8.03 (4H, m), 7.64 (4H, d, 8.2), 7.53 (8H, d, 5.5), 7.27 (8H, m), 2.59 (6H, s). FAB-MS *m*/*z* = 1825.1, [Ru$_2$(terpy–ph–terpy)(tterpy)$_2$(PF$_6$)$_3$]$^+$ requires 1824.5.

For $\mathbf{4}^{4+}$: ^{1}H NMR [200 MHz, (CD$_3$)SO] δ 9.60 (4H, s), 9.50 (4H, s), 9.16 (8H, dd, 7.04), 8.68 (4H, d, 8,85), 8.37 (8H, m), 8.10 (8H, m), 7.59 (12H, m), 7.31 (8H, m), 2.52 (6H, s). FAB-MS *m*/*z* = 1902.4, [Ru$_2$(terpy–ph–ph–terpy)(tterpy)$_2$(PF$_6$)$_3$]$^+$ requires 1901.

Table 1 Spectrochemical and electrochemical data[a]

	MLCT λ_{max}/nm ($\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1})	$E_{1/2}$/V *vs.* SCE[b] Anodic		Cathodic		
1^{4+}	553 (6.5)	1.40[c]	1.70[c]	−0.35[c]	−0.85[c]	−1.40
2^{4+}	520 (5.8)	1.31		−0.93[c]	−1.24[c]	−1.36
3^{4+}	499 (6.3)	1.27		−1.18		−1.45
4^{4+}	495 (7.4)	1.26		−1.21		−1.44

[a] In acetonitrile. [b] Cyclic voltammetry in 0.1 mol dm^{-3} Bu_4NBF_4 on Pt electrode (ν = 200 mV s^{-1}); all the redox processes are two electron transfers except when specified; SCE = saturated calomel electrode. [c] One-electron process.

Table 2 Intervalence band parameters and derived electronic coupling V_{ab} for the Ru^{II}, Ru^{III} complexes

Complex	λ_{max}/nm	ε_{max}/ dm^3 mol^{-1} cm^{-1}	$\Delta\bar{\nu}_{1/2}$/ cm^{-1}	R_{M-M}/Å	V_{ab}/eV
2^{5+}	1580	1618	4008	11	0.047
3^{5+}	1295	729	6036	15.5	0.030
4^{5+}	1150	709	4934	20	0.022

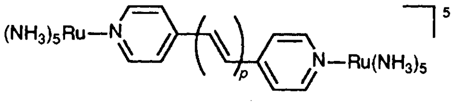
Near infrared (NIR) spectroscopy allows observation of intervalence bands of various positions and intensities from which important information regarding delocalisation of the Ru^{II}, Ru^{III} system is obtained.

The complexes **2^{4+}** to **4^{4+}** (5×10^{-5} to 10^{-4} mol dm^{-3}) were titrated by Ce^{IV} in acetonitrile acidified by 0.5 mol dm^{-3} CF_3CO_2H. During the oxidation, the usual behaviour was observed, *i.e.* (*i*) decay of the MLCT band; (*ii*) rise of a ligand-to-metal charge transfer; (*iii*) rise and decay of the intervalence band which appeared in NIR. From the latter variation, comproportionation constants were found near the statistical limit. This allowed the calculation of the corrected spectra of the mixed-valence species. Intervalence transitions were observed as clearly resolved bands for **2^{5+}** and **3^{5+}** and a shoulder for **4^{5+}**. Finally, the intervalence band parameters were obtained by a spectral deconvolution with least-square fitting.

For **1^{4+}**, which is more difficult to oxidize, the mixed-valence species was generated by electrolysis in acetonitrile with NBu_4BF_4 as supporting electrolyte. Owing to the high comproportionation constant, no correction for disproportionation was necessary.‡

The data are collected in Table 2. The matrix-element V_{ab} has been calculated using the classical method.[20] **1^{5+}** (λ_{max} = 1520 nm and V_{ab} = 0.4 eV) shows very strong coupling and seems to belong to Class III.[3] Significant coupling is still observed in the longest system **4^{5+}**. Moreover, the extent of coupling decreases only slightly along the series **2^{5+}** to **4^{5+}**. The bis-trpy containing family of molecules presently reported can be compared to another group of compounds with polyene bridges[6,20,21] (Scheme 2 and Table 3).

The analogy between the V_{ab} values of both series of mixed-valence complexes is striking which tends to indicate that a phenyl ring behaves as two double bonds. Consequently, poly-phenylated bridges are promising analogues of the synthetically less accessible and chemically more fragile polyene systems. They should also find applications in photoinduced electron transfer systems.



5_p^{5+} $p = 0,1,2,3,4$

Scheme 2

Table 3 Calculated matrix-element V_{ab} (eV) as a function of number of atoms bridging the two metals

Number of atoms	8	10	12	14	16
5_p^{5+}	0.047[20] ($p = 0$)	0.039[20] ($p = 1$)	0.031[21] ($p = 2$)	0.028[21] ($p = 3$)	0.023[21] ($p = 4$)
The present series	0.047 (**2^{5+}**)	—	0.030 (**3^{5+}**)	—	0.022 (**4^{5+}**)

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‡ For **1^{5+}**, the V_{ab} coupling is taken as half the band energy. For the other compounds, the following relation is used; $V_{ab} = 2.05 \times 10^{-2} (\varepsilon_{max}\,\bar{\nu}_{max}\,\Delta\bar{\nu}_{1/2})^{1/2}/R_{MM}$ where V_{ab} is the coupling (in cm^{-1}), ε_{max} is the maximum extinction coefficient, $\bar{\nu}_{max}$ is the band position in cm^{-1}, $\Delta\bar{\nu}_{1/2}$ is the full width at half maximum (cm^{-1}) and R_{MM} is the metal–metal distance in Å. See N. S. Hush, *Coord. Chem. Rev.*, 1985, **64**, 135.