A highly coupled Ru^{III}–Ru^{II} system incorporating sulfur donor ligands

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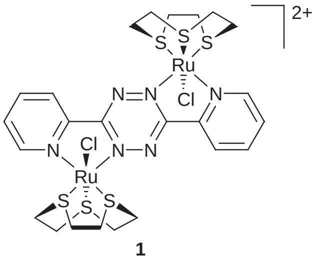
Bimetallic complex 1, which is based on a Ru^{II} metal centre incorporating sulfur donor ligands, shows strong intermetallic coupling in its mixed valence state comparable to those observed in complexes incorporating conventional nitrogen donors.

Mixed valence coordination chemistry has been dominated for some time by ruthenium(III/II) complexes,[1] most of them being modelled on the Creutz–Taube ion.[2] Theoretical models[3] have been used to understand their spectral properties, especially of the characteristic metal-to-metal charge transfer or intervalence transitions.

Previous research has revealed that the electron transfer properties of such systems are highly dependent on the nature of the metal centres and ligand bridge. Such systems have also played an important part in the development of devices for molecular electronics,[4] where they have formed the basic components of molecular wires and molecular switches. The goal of such research is to develop systems displaying electronic communication between metal centres and thus long range electron transfer and photoinduced charge separation.[5] So far, research has involved changing the bridging ligands[6] and the metal ion.[7] However, all of the metal centres in these complexes contain nitrogen based ligands, such as NH_3 and 2,2′-bipyridine (bpy), coordinated to the metal ion. Our attempt has been to broaden the experimental basis of mixed valence chemistry, by introducing new metal organic fragments incorporating sulfur donor ligands such as the crown ether 1,4,7-trithiacyclononane.

An ideal starting material for these complexes is the previously reported $[Ru(Me_2SO)Cl_2([9]aneS_3)]$.[8] When refluxed overnight with the ligand 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine[9] (bptz) in ethanol–water (1 : 1), a crude product is isolated on the addition of ammonium hexafluorophosphate. After alumina column chromatography, the bimetallic complex cation **1**$^{2+}$ was isolated as its PF_6 salt as a blue powder in 48% yield. This compound is air and moisture stable and has been characterised by ^1H NMR, UV–VIS and FAB mass spectroscopy.‡



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The UV–VIS spectrum of **1**$^{2+}$ shows two bands (Table 1). The first at 302 nm has a large absorption coefficient (ε = 3497 dm^3 mol^{-1} cm^{-1}) and has been assigned to a π–π^* transition. The second intense band has ε = 2281 dm^3 mol^{-1} cm^{-1} and occurs at 751 nm. A comparison with structurally similar complexes allows this band to be to assigned metal-to-ligand charge transfer (MLCT).[1b]

Table 1 UV–VIS spectra data for complex **1** in acetonitrile

Complex	λ_{max}/nm	ε/ dm^3 mol^{-1} cm^{-1}	Assignment
1^{2+}	302	3497	π–π^*
	751	2281	MLCT
1^{3+}	310	3158	π–π^*
	678	2312	MLCT
	1852	519	IVCT

In an attempt to quantify the ligand bridge mediated intermetallic interaction, cyclic voltammetry was used. This was carried out in acetonitrile (Table 2). Complex **1**$^{2+}$ displays a first oxidation at $E_{1/2}$ 1.36 V. The first oxidations for the related complexes $[\{Ru(NH_3)_4\}_2(bptz)]^{4+}$ (**2**$^{4+}$) and $[\{Ru(bpy)_2\}_2(bptz)]^{4+}$ (**3**$^{4+}$) occur at 0.72 and 1.52 V respectively. The difference in these values can be explained by considering the nature of the coordination bonding in these complexes. While NH_3 is a purely σ-donor ligand, bpy ligands are also π-acceptors and as such stabilise the Ru^{II} oxidation state producing the observed anodic potential shifts. The electrochemical behaviour of **1**$^{2+}$ indicates that the $[RuCl([9]aneS_3)]^+$ metal centre is also appreciably stabilised by π back-donation interactions. Such an observation is consistent with, and confirms, recent findings on the coordination chemistry of thioether ligands.[10]

Complex **1**$^{3+}$ displays a strong intermetallic interaction with $\Delta E_{1/2}$ = 0.48 V resulting in a comproportionation constant (K_c) of 1.48 × 10^8, suggesting that it is a Robin and Day class III system.[12] This value is greater than the previously reported value of $\Delta E_{1/2}$ = 0.39 V for the Creutz–Taube ion,[13] and is similar to complex **3**$^{5+}$ ($\Delta E_{1/2}$ = 0.5 V) but less than the value for complex **2**$^{5+}$ ($\Delta E_{1/2}$ = 0.84 V). On this evidence, it would appear that **1**$^{2+}$ is a less strongly interacting system than **2**$^{4+}$. However, a comparison of the optical properties of the mixed valence complexes is more informative.

The intermetallic interaction in **1**$^{3+}$ was further investigated using spectroelectrochemistry. The formation of several isosbetic points after the oxidation of **1**$^{2+}$ shows a clean conversion taking place, with the MLCT band showing a hypsochromic shift (Table 1). A significant observation is the formation of an new band at 1852 nm (5375 cm^{-1}). This band, which has been assigned to an intervalence charge transfer (IVCT), has an absorption coefficient of ε = 519 dm^3 mol^{-1} cm^{-1}. By

Table 2 Electrochemical data[a] for some ruthenium complexes

Complex	$E_{1/2}(1)$/V	$E_{1/2}(2)$/V	$\Delta E_{1/2}$/V	K_c[b]	Ref.
1^{2+}	1.36	1.84	0.48	1.4 × 10^8	This work
2^{4+}	0.72	1.56	0.84	1 × 10^{15}	1(*a*)
3^{4+}	1.52	2.02	0.5	3 × 10^8	11

[a] Cyclic voltammogram of complex cation **1**$^{2+}$ was carried out at a scan rate of 200 mV s^{-1} in acetonitrile containing tetrabutylammonium hexafluorophosphate as supporting electrolyte (0.1 M). Potentials were measured *vs.* SCE. All couples were reversible with I_{pc} and I_{pa} equal and ΔE_p < 100 mV. [b] K_c values calculated using $\log K_c = \Delta E_{1/2}/0.059$.

comparison, the IVCT band found for **2**$^{5+}$ is observed at 1453 nm with ε = 500 dm^3 mol^{-1} cm^{-1}.[1a]

Application of Hush theory[3b,c] to the IVCT spectral data of **1**$^{3+}$ yields a bandwidth at half-height, $\Delta\nu_{1/2}$, which is much higher than the experimental value: $\Delta\nu_{1/2} = (2310\nu)^{1/2}$ cm^{-1}, $\Delta\nu_{1/2}$ (**1**$^{3+}$, calc.) = 3524 cm^{-1}, $\Delta\nu_{1/2}$ (**1**$^{3+}$, exptl.) $\approx$ 1375 cm^{-1}.

This discrepancy indicates that, like **2**$^{5+}$, **1**$^{3+}$ is a delocalised (class III) system, to which the above treatment is not applicable. Accordingly, the degree of electronic coupling, H_{AB}, can be estimated to approximately $1/2\nu$ = 2687.5 cm^{-1}.[3c]

Concluding, not only is this a new structural motif for such studies, it also seems effective in facilitating bridge mediated intermetallic interactions. With an aim to designing functional molecular devices, future studies will concentrate on variations in the metal ion, co-ordination sphere of the metal centre, and the bridging ligand.

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Notes and References

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‡ *Elemental analysis*. Found C, 23.49; H, 3.06; N, 6.74. Calc. for $Ru_2C_{24}H_{40}S_6N_6Cl_2P_2F_{12}$: C, 23.39; H, 3.25; N, 6.82%. ^{1}H NMR (200 MHz, CD_3COCD_3): δ 8.00 (dt, 2 H), 8.40 (dt, 2 H), 8.89 (dd, 2 H), 9.31 (dd, 2 H). FABMS: peaks at *m*/*z* 1016 [(**1** + PF$_6$)$^+$, 15%], 871 [(**1**)$^{2+}$, 30%].

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