The Spectroelectrochemical Study of [Ru$_2$Cl$_8$py]$^{n-}$ (n = 1,2,3; py = pyridine): a Series of Complexes with Two Accessible Mixed-valence States

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The binuclear complex [Ru$_2$Cl$_8$py]$^{2-}$ (py = pyridine), I^{2-}, has two stable mixed-valence states I^{3-} and I^{1-} which are formulated as Class III and Class II systems respectively.

Mixed-valence complexes containing two metal centres in different oxidation states are of considerable interest particularly in the context of new materials, and in the study of electron-transfer rates and metal–metal interactions. The degree of electronic communication between the two metal centres can range from weak interactions where the odd electron is localised only on one metal centre (Class II) to strong interactions where the odd electron is delocalised over both centres (Class III). We have studied the triple chloro-bridged Ru binuclear species [Ru$_2$Cl$_8$py]$^{n-}$ (py = pyridine), I^{n-}, which in common with all other triple-bridged Ru complexes, is assumed to have a confacial bioctahedral structure.[1] We have found that the asymmetric complex I^{2-} can be studied spectroelectrochemically in two separate mixed-valence states, namely I^{3-} [Ru^{III}–Ru^{II}] and I^{1-} [Ru^{IV}–Ru^{III}]. This system provides the opportunity to study two stable mixed-valence ions I^{3-} and I^{1-} with the same chemical formulae and overall structure but different electronic populations (d^5–d^6 and d^4–d^5 configurations respectively). Most Ru binuclear mixed-valence systems that have been investigated previously involve the d^5–d^6 configuration with the only example of a stable d^4–d^5 configuration being the complex anion [Ru$_2$X$_9$]$^{2-}$ (X = Cl$^-$, II^{2-}; Br$^-$).[2]

$$[\text{Ru}_2\text{Cl}_8\text{py}]^{n-} \qquad [\text{Ru}_2\text{Cl}_9]^{n-}$$
$$\text{I}^{n-} \qquad\qquad \text{II}^{n-}$$

Reaction of [Bu$_4$N]$_3$[Ru$_2$Cl$_9$] with one molar equivalent of Ag[ClO$_4$] in the presence of py in refluxing CH$_2$Cl$_2$ under N$_2$ affords the dark brown complex [Bu$_4$N]$_2$[Ru$_2$Cl$_8$py], I^{2-}, in almost quantitative yield.† The complex I^{2-} exhibits two oxidative and two reductive processes in CH$_2$Cl$_2$–0.5 mol dm^{-3} [Bu$_4$N][BF$_4$]. Coulometric studies confirm that each of the four redox steps involves transfer of one electron. It is interesting to note that the first one-electron reduction process at $E_{1/2}$ = −0.23 V vs. Ag–AgCl to yield I^{3-}, which presumably takes place at the Ru centre with the coordinated py, is fully reversible at 240 K, whereas in the parent complex [Ru$_2$Cl$_9$]$^{3-}$ the equivalent reduction is 0.34 V more cathodic and is only quasi-reversible at 240 K.[2] The second reduction process for I^{2-} occurs at E_{pc} = −1.26 V vs. Ag–AgCl and shows only a forward wave at all temperatures and scan rates studied, and is thus a chemically irreversible step. The equivalent redox step in the related parent complex II^{2-} has never been observed. The electron-transfer process to generate I^{4-} is associated with the loss of Cl$^-$ ligands; the nature of the product formed is currently under investigation.

The oxidative processes for I^{2-} are observed at $E_{1/2}$ = + 1.21 V and +1.99 V vs. Ag–AgCl and are 0.29 and 0.41 V

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† The complex has been fully characterised by IR, UV-VIS and FAB mass spectroscopy and CHN analysis.
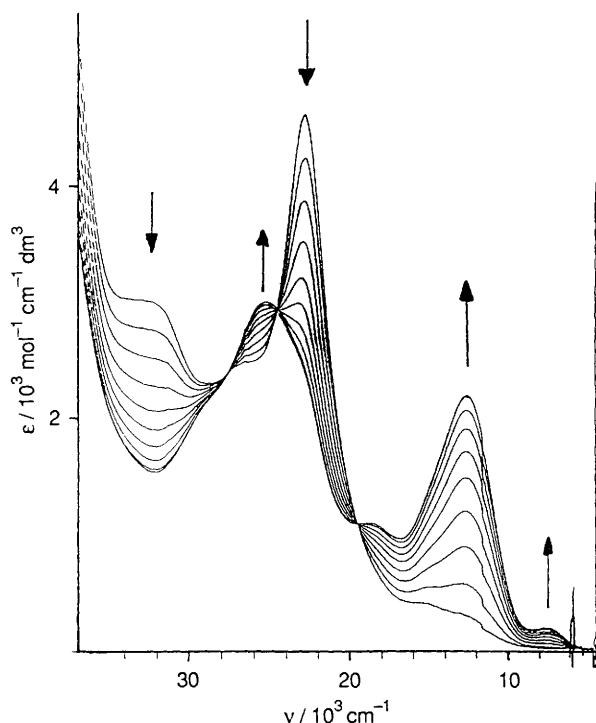
Fig. 1 Spectroelectrochemical study of the generation of $[Ru_2Cl_8py]^{3-}$ from $[Ru_2Cl_8py]^{2-}$ in CH_2Cl_2–0.5 mol dm^{-3} $[Bu_4N][BF_4]$ at 240 K. Applied potential -0.4 V vs. Ag–AgCl on which the ferrocene/ferricinium couple is at $+0.56$ V.

Table 1 Near-IR band characteristics of I^{1-} and I^{3-} in various solvents at 240 K[a]

Solvent	$[Ru_2Cl_8py]^{1-}$	$[Ru_2Cl_8py]^{3-}$
Dichloromethane	10 250 (1220)	7 600 (290)
		12 600 (3440)
Acetone	9 675 (1130)	7 600 (230)
		12 550 (2240)
Acetonitrile	10 100 (1070)	7 550 (220)
		12 650 (2850)

[a] Position of band maximum, v_{max} in cm^{-1} (extinction coefficient ϵ in mol^{-1} cm^{-1} dm^3).

more anodic than the corresponding steps for II^{3-}. These redox potential shifts reflect the substitution of a π-donor Cl$^-$ ligand in II^{3-} by a π-accepting py ligand in I^{2-}.

Importantly, the mixed-valence states I^{1-} and I^{3-} can be electrogenerated quantitatively and fully reversibly from I^{2-}. Electrogeneration of either I^{1-} or I^{3-} in bulk in a conventional H-type cell at 240 K was not accompanied by any chemical reactions. Thus, cyclic voltammograms before and after electrogeneration are superimposable, while stirred voltammograms at a rotating disc electrode show that transfer of one electron had taken place on both occasions. In neither electrogeneration step was there evidence (electrochemical or chemical) for the presence of free Cl$^-$ ions, i.e. I^{1-} and I^{3-} are chemically stable at 240 K under Ar. The one-electron transfer products I^{1-} and I^{3-} are both extremely air and/or moisture sensitive and thus further characterisation of both products were pursued using in situ techniques only.

Fig. 1 shows the spectral changes associated with the electrogeneration of I^{3-} from I^{2-} recorded in an optically transparent electrode cell at 240 K. Both mixed-valence states

show low energy absorption bands in the near-IR (Table 1) which, significantly, are missing in the parent I^{2-} complex. The higher energy bands in the VIS and UV regions of the spectrum of I^{3-}, I^{2-} and I^- are assigned to charge-transfer transitions involving the Ru centres and the Cl$^-$ and py terminal ligands and are not discussed further here.

The position of the single broad low energy absorption band in I^{1-}, v_{max}, exhibits a marked solvent dependence as given in Table 1. This result indicates that in I^{1-} the Ru^{III} and Ru^{IV} centres are only weakly interacting (a Class II complex in the Robin and Day nomenclature of mixed-valence systems[3]). We therefore classify the near-IR band in I^{1-} as an intervalence charge transfer (IVCT) band or a metal–metal charge transfer (MMCT) band which can be formulated as in eqn. (1). The

$$[Cl_3Ru^{IV}Cl_3Ru^{III}Cl_2py]^{1-} \xrightarrow{hv} {}^*[Cl_3Ru^{III}Cl_3^{IV}Cl_2py]^{1-} \quad (1)$$
$$I^{1-}$$
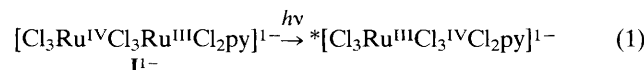
IVCT band is broad and featureless with a measured band half-width of 4400 cm^{-1} which is in acceptable agreement[4] with the calculated value of 4860 cm^{-1}. The delocalisation coefficient is calculated to be 0.2 which is also indicative of a localised system.

In marked contrast to this, there are two near-IR absorption bands for I^{3-} neither of which show a solvent dependence for v_{max} (Table 1). The bands are narrower than in I^{1-} and the band at 12 500 cm^{-1} has a high energy shoulder. Thus, in I^{3-} the Ru^{III} and Ru^{II} centres cannot be considered as discrete but rather delocalised (Class III) containing two Ru(2.5) centres. Several other delocalised systems have multiple bands in the near-IR region which are ascribed to transitions within the molecular orbital manifold resulting from the strong interaction of the Ru-based d-orbitals.[5] We assign the near-IR bands in I^{3-} to such transitions. We note that this is an example of an asymmetric mixed-valence species having a delocalised electron.

We attribute the dramatic change on going from a delocalised system in I^{3-} to a localised system in I^{1-} to the increasing positive charge on the metal centres. As the oxidation states of the Ru centres are made progressively more positive there will be significant metal d-orbital contraction and an increasing electrostatic repulsion between the two Ru centres. The combination of these effects should lead to an elongation in the Ru–Ru vector with a concomitant decrease in metal–metal interaction on going from I^{3-} to I^{1-}. Such an increase in metal–metal bond length has been observed in the species $[W_2Cl_9]^{3-}$ and $[W_2Cl_9]^{2-}$.[6]

Further studies on related asymmetric binuclear complexes are being pursued in order to probe systems with more than one mixed-valence state.

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