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Observations of an $[Ru_2]^{n+}$ Unit ($n = 3, 4, 5, 6$): Electrochemical Studies into the Molecule $Ru_2(MeC_5NH_3NH)_3(O_2CCH_3)Cl$ in Dimethyl Sulphoxide

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The redox chemistry of dinuclear molecules containing metal–metal bonds is an area of rapidly growing interest. The metals rhenium, rhodium and ruthenium particularly lend themselves to this type of study as many of their compounds undergo uncomplicated electron-transfer reactions to generate new molecules in which the formal metal–metal bond order has been altered. Our particular concern is with the redox properties of the dinuclear ruthenium(II/III) complexes in which the metals are connected by a bond of the order 2.5. Complexes containing this $[Ru_2]^{5+}$ unit have been the subject of numerous electrochemical reports [1–11]. Several compounds, for example the carboxylates $Ru_2(O_2CR)_4Cl$ [1] and $Ru_2(HNCOCF_3)_4Cl$ [2], have been observed to undergo one-electron reductions to give diruthenium(II/II) compounds, while others, e.g. $Ru_2(Me_3CCONH)_4Cl$ [11], undergo oxidation to the related diruthenium(III/III) compounds. In a limited number of cases a single compound can be both oxidised and reduced in reversible one-electron steps. For example, the series of complexes $Ru_2(RNpyr)_4Cl$ can be oxidised to the cations $[Ru_2(RNpyr)_4Cl]^+$ and reduced to the anions $[Ru_2(RNpyr)_4Cl]^-$ [6, 10]; the former contain a ruthenium-to-ruthenium triple bond while the latter contain a double bond between the metal ions. Thus it is the dinuclear cores $[Ru_2]^{4+}$, $[Ru_2]^{5+}$ and $[Ru_2]^{6+}$ which have been recorded for this class of molecule. We now wish to report the electrochemical behaviour of a new diruthenium molecule $Ru_2(MeC_5NH_3NH)_3(O_2CCH_3)Cl$. This molecule is unusual in that it cannot only be oxidised to the diruthenium(III/III) cation but can also be sequentially reduced in two one-electron steps to yield what is formally a diruthenium(II/I) complex ion, containing an $[Ru_2]^{3+}$ core and a bond of the order 1.5 between the metal ions.

Results and Discussion

The new compound $Ru_2(MeC_5NH_3NH)_3(O_2CCH_3)Cl$ was prepared using a general method described previously [10]. The dinuclear structure was confirmed by an X-ray diffraction study [12].

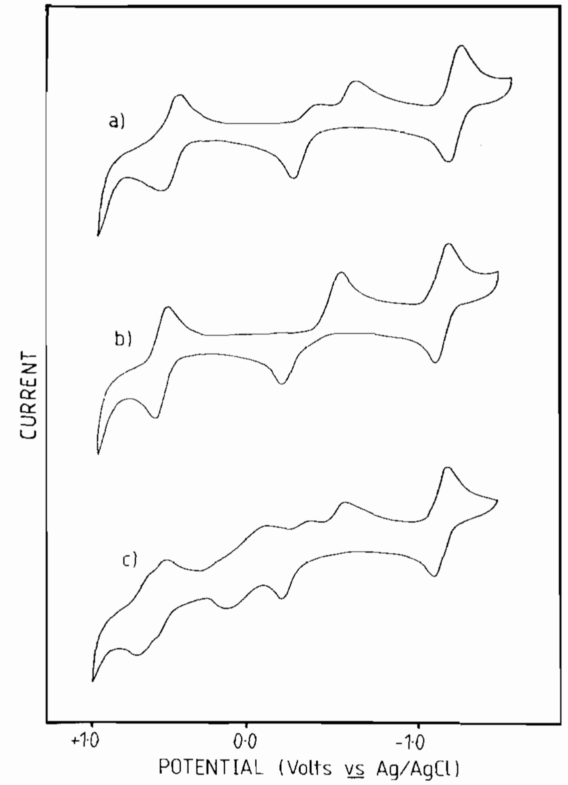

Fig. 1. Cyclic voltammagrams of $Ru_2(MeC_5NH_3NH)_3(O_2CCH_3)Cl$ in DMSO: (a) no added ions; (b) excess of Cl^- ions added; (c) less than one equivalent of Ag^+ ions added.

The complex was sufficiently soluble in dimethyl sulphoxide for its redox behaviour to be studied by cyclic voltammetry. In a solution containing 0.1 M $[N(C_4H_9)_4][BF_4]$ as supporting electrolyte there are three well-defined responses in the potential range +1.0 to −1.6 V†, as shown in Fig. 1a. The electron-transfer reactions at *ca.* −0.5 and −1.5 V can be assigned as reductions of the dinuclear molecule, while that at *ca.* +0.55 V is due to oxidation. The one-electron nature of the reduction processes was confirmed by comparison of the diffusion-limited currents in the stirred voltammagrams with those obtained from known quantities of ferrocene.

The first reduction process contains two components, at −0.41 and −0.64 V. This observation is not altogether surprising and can be rationalised by invoking the establishment of equilibria between different axially solvated dinuclear units in solution.

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†All potentials were measured with respect to an Ag/AgCl reference electrode against which ferrocene was oxidised at a potential of +0.60 V.

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Such equilibria have been described previously [2, 3, 10, 11]. Although there are three components in equilibrium, only two waves are observed and therefore two of the components must be in rapid equilibrium. Surprisingly, only a single reoxidation wave is observed at −0.27 V (Fig. 1a), implying that the three reduced species $[ClRu^{II}(MeC_5NH_3NH)_3(O_2CCH_3)Ru^{II}Cl]^{2-}$, $[(DMSO)Ru^{II}(MeC_5NH_3NH)_3(O_2CCH_3)Ru^{II}Cl]^{1-}$ and $[(DMSO)Ru^{II}(MeC_5NH_3NH)_3(O_2CCH_3)Ru^{II}(DMSO)]^0$ are in rapid equilibrium. On scanning to more negative potentials, a second reduction wave is observed at *ca.* −1.3 V. The current carried by this reversible wave is equal to that of its precursor. The observation of only a single wave confirms that the various mono-reduced species are in rapid equilibrium. Although the observation of a second reduction wave is not entirely unprecedented, previously such waves have either been highly irreversible or alternatively assigned to the reduction of coordinated ligands [4]. Addition of the free ligand to the electrochemical solution does not affect the reversibility of the process and argues for the reduction of the dinuclear unit to one which formally contains a diruthenium(II/I) centre. Although both reduction products are stable on the cyclic voltammetric timescale, spectroelectrochemical measurements in dimethyl sulphoxide show that the reduced complexes undergo slow chemical decomposition.

The oxidation wave at +0.56 V is uncomplicated although a slight broadness in the peaks may be consistent with the equilibrium between differently axially substituted molecules occurring on a timescale comparable to that of the electrochemical experiment.

Addition of an excess of chloride ions to the electrochemical cell results in a sharpening of the voltammetric peaks and the loss of the reduction wave at −0.41 V (Fig. 1b). The three waves observed each carry an identical current (within 2%) and are assigned to reductions or the oxidation of the bischloride adduct $[ClRu(MeC_5NH_3NH)_3(O_2CCH_3)RuCl]^-$, as appropriate.

Addition of less than one equivalent of Ag^+ ions to the electrochemical cell displaces the equilibrium between the different axially ligated species in the direction of the bisdimethyl sulphoxide adducts. In the cyclic voltammagram (Fig. 1c), new reduction and oxidation waves are observed at −0.15 and +0.75 V, respectively, which must be assigned to the bis solvent adduct $[(DMSO)Ru(MeC_5NH_3NH)_3(O_2CCH_3)Ru(DMSO)]^+$. Surprisingly, neither the addition of Cl^- ions nor Ag^+ ions has any significant observable effect on the character of the second reduction process, under the experimental conditions which were employed.

Further studies into the kinetics of axial ligand exchange are in progress.

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