Inorganica Chimica Acta, 118 (1986) L49–L51

The Electro-oxidation of the Binuclear Ruthenium(II/III) Tetra-amidate Complex, $Ru_2(Me_3CCONH)_4Cl$

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(Received June 10, 1986)

In the past few years the redox behaviour of the dinuclear metal–metal bonded ruthenium(II/III) complexes has received considerable attention in the literature [1–9]. The single most extensively studied compound has undoubtedly been the tetra-amidate $Ru_2(CF_3CONH)_4Cl$. The redox behaviour of this compound was examined in 11 non-aqueous solvents [2]. Irrespective of the identity of the solvent the molecule only underwent reduction processes. The number of such reactions and the potentials at which they occurred were observed to be a function of the complexing power of the solvent.

Recently the reactivity of several of the tetra-amidato diruthenium(II/III) complexes, $Ru_2(RCONH)_4Cl$, towards triarylphosphines, PAr_3, has been examined. When the substituent on the amidate ion is a phenyl or substituted phenyl group the phosphine undergoes metal assisted P–C bond cleavage leading to the tansfer of an aryl group from PAr_3 to Ru, thus giving the new edge-sharing bioctahedral diruthenium(III/III) compounds $Ru_2(Ar)_2(RCONH)_2[Ar_2POC(R)N]_2$ [4, 10]. Clearly the oxidation of the tetra-amidato bridged unit, $[Ru_2(RCONH)_4]^+$, is a key step in this process and thus we have set out to investigate the electro-oxidation of $Ru_2(RCONH)_4Cl$ complexes. Since the complex containing the strongly electron-withdrawing trifluoracetamide ligands only underwent reduction reactions the logical place to begin this study was with the diruthenium(II/III) compound $Ru_2(Me_3CCONH)_4Cl$, containing four electron-donating amidate ligands. We will now report the results of our investigations into the solvent-dependent electro-oxidation or $Ru_2(Me_3CCONH)_4Cl$.

Experimental

$Ru_2(Me_3CCONH)_4Cl$ was prepared in high yield using an analogous procedure to that described by Bear *et al.* for the preparation of $Ru_2(CF_3CONH)_4Cl$ [2].

Electrochemical measurements were performed in DMSO, EtOH, MeOH, CH_3NO_2, THF, PhCN, CH_3CN, $ClCH_2CH_2Cl$ and propylene carbonate, using 0.1 M tetra-n-butyl-ammonium tetrafluoroborate ($TBABF_4$) as supporting electrolyte, and in CH_2Cl_2, using 0.25 M $TBABF_4$ as supporting electrolyte.

Cyclic voltammetric and a.c.V. measurements were made using a conventional three electrode cell and instrumentation described previously [11]. A non-aqueous $Ag/AgCl/Cl^-$, CH_2Cl_2 electrode (against which ferrocene was oxidised at a potential of +0.60 V) was used as a reference electrode.

Results

The compound $Ru_2(Me_3CCONH)_4Cl$ was examined in 11 solvents by cyclic and a.c. voltammetry. Depending upon the solvent and the concentration of chloride ions present a number of different current-voltage curves are observed for the oxidation of $Ru_2(Me_3CCONH)_4Cl$. At least one, and up to four, oxidation processes are observed in the potential range 0–1.5 V (see Table I). In the strongly bonding solvent DMSO only a single process is observed, at +0.85 V. In solvents such as alcohols and CH_3NO_2 two processes are observed. In the other seven solvents examined a total of four oxidation processes are observed, the first occurring within the range *ca.* 0.55–0.75 V, the second within *ca.* 0.75–0.90 V, the third within 0.90–1.10 V, and the final oxidation at a potential >1.10 V, depending on the solvent. In CH_2Cl_2 three well-defined quasi-reversible waves (at potentials of 0.68, 0.93 and 1.09 V, and with potential separations, $E_{p,a}-E_{p,c}$, of 90–

TABLE I. Peak Potentials[a] for the Oxidation of $Ru_2(Me_3CCONH)_4Cl$ in Non-aqueous Solvents

Solvent	No added chloride ion				10 equivalents of Cl^- added
	Ox(1)	Ox(2)	Ox(3)	Ox(4)	
DMSO		0.85			0.78
CH_3OH	1.01	1.07			0.96
C_2H_5OH	0.97	1.06			0.89
CH_3NO_2	0.78	1.00			0.74
DMF	0.67	0.78	0.91	1.14	0.62
THF	0.55	0.90	1.03	1.32	0.54
PhCN	0.63	0.85	1.03	1.12	0.61
CH_3CN	0.78	0.92	1.10	1.34	0.73
$ClCH_2CH_2Cl$	0.61	0.84	1.00	1.23	0.60
PC	0.77	0.90	1.04	1.27	0.73
CH_2Cl_2	0.68	0.93	1.09	1.33	0.66

[a] The values for the peak potentials quoted are taken from the a.c. voltammetric measurements due to the poorer resolution in some of the cyclic voltammograms.

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0020-1693/86/\$3.50

120 mV, increasing with scan rate) and one irreversible wave ($E_{p,a}$ = 1.33 V) are observed. The addition of chloride ions (in the form of benzyltriethylammonium chloride) to the electrochemical cell produces a decrease in the height of second and third wave with a concomitant increase in the height of the first wave. When one equivalent of chloride ions is added the peak currents for the second and third wave drop to zero. Further additions of chloride ions result in a narrowing of the peak shape for the first wave, suggesting an increased reversibility for the electrochemical process, and a shifting of the wave to slightly more cathodic potentials (see Table I). The fourth wave apparently remains unaffected by the addition of Cl^-.

In CH_3NO_2 two quasi-reversible oxidation waves are observed. The half-wave potentials for these oxidations are 0.78 and 1.00 V respectively. These values are very similar to the potentials of the first two waves observed in CH_2Cl_2. The addition of chloride ions to the electrochemical cell results in a collapse of the wave at 1.00 V and the growth of the peak at more cathodic potentials. Finally in DMSO only a single quasi-reversible, single-electron-transfer redox couple is observed at $E_{1/2}$ = +0.85 V. The addition of one equivalent of chloride ions to this electrochemical solution does not significantly influence the peak current; however, the reversibility of the process is enhanced and the potential shifts to $E_{1/2}$ = 0.78 V. A cyclic voltammogram identical with that obtained initially can be regenerated by the addition of one equivalent of $AgBF_4$ to the electrochemical solution.

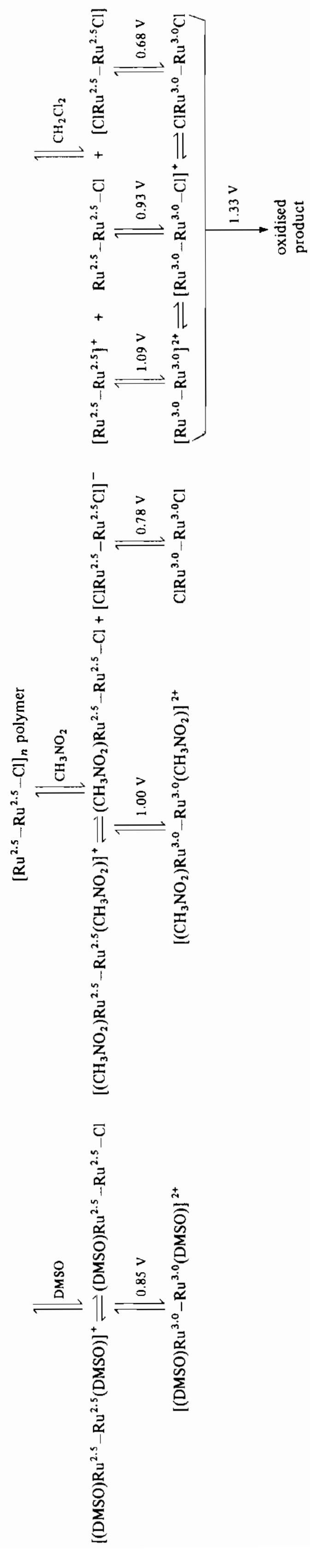
Discussion

Two X-ray structural determinations have shown that in the solid state $Ru_2(RCONH)_4Cl$ molecules exist in a polymeric form with chloride ions bridging adjacent dinuclear ruthenium cations to form infinite zigzag chains of $(Ru-CuCl)_n$ [12, 13]. Upon dissolution this polymeric structure is split to yield complexes of the form (S)Ru–RuCl, and/or $[(S)Ru-Ru(S)]^+$ and $[ClRu-RuCl]^-$, where S is the solvent molecule. In the latter case, ion pair formation can occur between negatively and positively charged dimeric units.

In the non-bonding solvent CH_2Cl_2 the breaking up of the polymer is slow and we have detected all three constituents in the equilibrium mixture. The addition of chloride ion increases the solubility of $Ru_2(Me_3CCONH)_4Cl$ and drives the equilibrium

$$[Ru-RuCl]_n + nCl^- \rightleftharpoons n[ClRu-RuCl]^-$$

to the right-hand side. This observation allows the redox process at +0.68 V to be assigned to the couple



Scheme 1. Reaction path for the electrochemical behaviour of $Ru_2(Me_3CCONH)_4Cl$ in DMSO, CH_3NO_2 and CH_2Cl_2 solutions.

$[ClRu(Me_3CCONH)_4RuCl]^{-/0}$. The processes which occur at 0.93 and 1.09 V may then be assigned to the redox reactions (1) and (2), respectively.

$$Ru_2(Me_3CCONH)_4Cl \rightleftharpoons [Ru_2(Me_3CCONH)_4Cl]^+ + e^- \qquad (1)$$

$$[Ru_2(Me_3CCONH)_4]^+ \rightleftharpoons [Ru_2(Me_3CCONH)_4]^{2+} + e^- \qquad (2)$$

The origin of the fourth oxidation wave is less certain. However, the extreme potential, and irreversible characteristics, are not inconsistent with a second oxidation of the dinuclear core followed by rapid irreversible fragmentation of that unit.

In the strongly bonding solvent DMSO the single complex $[(DMSO)Ru(Me_3CCONH)_4Ru(DMSO)]^+$ is present and only one oxidation wave is observed. However, the addition of excess Cl^- shifts the equilibrium from that of a bis solvated species to one containing either one or two axial Cl^- ligands. The molecule containing the chloride ion(s) is then oxidised at a more cathodic potential (+0.78 V *versus* +0.85 V for the bis solvated molecule). The removal of Cl^-, by addition of Ag^+, displaces the equilibrium back towards the bis solvate molecule.

When the solvent is of intermediate bonding strength, e.g. CH_3NO_2, two oxidation waves are observed. The observation that it is the more cathodic peak which grows on addition of Cl^- allows the assignment of that wave to the couple $[ClRu(Me_3CCONH)_4RuCl]^{-/0}$. The second wave is then assigned to the oxidation of $[(CH_3NO_2)Ru(Me_3CCONH)_4Ru(CH_3NO_2)]^+$ and $(CH_3NO_2)Ru(Me_3CCONH)_4RuCl$, which must be in rapid equilibrium. The various mechanisms for the oxidation of $Ru_2(Me_3CCONH)_4Cl$ have been summarised in Scheme 1.

Clearly the substitution of the electron-donating Me_3C-group for the electron-withdrawing CF_3-group in the diruthenium tetra-amidate complexes increases the tendency of the $[Ru_2]^{5+}$ unit to undergo oxidation ractions. The precise species present in solution are a function of the solvent employed, and may be detected electrochemically. Further studies into the influence of the substituent group on the position and rate of these equilibria are in progress.

Acknowledgements

We wish to thank Dr. J. H. Tocher for useful discussion and Johnson Matthey plc for generous loans of ruthenium trichloride.

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