Proton-coupled Electron-transfer Reactions. Observation of a Reversible Os^{IV}(amide)–Os^{III}(amine) Redox Couple with 2,3-Diamino-2,3-dimethylbutane

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The complex *trans*-$[Os^{III}(L)_2Cl_2]^+$ (L = 2,3-diamino-2,3-dimethylbutane) is the first to display a reversible pH-dependent Os^{IV}(amide)–Os^{III}(amine) couple in aqueous solution.

The study of proton-coupled electron-transfer reactions is an important and new development in inorganic chemistry. Despite the fact that numerous examples of reversible pH-dependent $M^{n-1}(OH)$–$M^{n-2}(OH_2)$ and $M^n(=O)$–$M^{n-1}(OH)$ couples have been observed in many oxo complexes of osmium,[1,2] ruthenium[1,2] and rhenium,[3] studies on the corresponding pH-dependent redox couples of $M^n(NHR)$–$M^{n-1}(NH_2R)$ are sparse.[4,5] Moreover the observation of the latter is important to the basic understanding of the mechanism of the oxidation of an amine to an imine and of ammonia to nitrite. Herein we describe the electrochemistry of a *trans*-dichloro osmium(III) complex with the primary amine ligand 2,3-diamino-2,3-dimethylbutane (L), which exhibits a reversible pH-dependent Os^{IV}(amide)–Os^{III}(amine) couple over a wide pH range in aqueous medium. The redox interconversion between the two species involves a rapid proton exchange that is fast compared with the time-scale of the cyclic voltammetric scans. In the related complex *trans*-$[Os^{III}(NH_3)_4Cl_2]Cl$ studied by Taube and co-workers,[6] the *trans*-$[Os^{IV}(NH_3)_4Cl_2]^{2+}$–*trans*-$[Os^{III}(NH_3)_4Cl_2]^+$ couple was found to be reversible but its $E°$ value pH independent. Recently Ludi and co-workers[7] showed that the reduction of $[Os^{IV}(L')_2L]^{2+}$ (L = $NH_2CMe_2CMe_2NH_2$ and L′ = $NH_2CMe_2CMe_2NH$) to $[Os^{II}L_3]^{2+}$ was accompanied by a gain of two protons but the redox couple was completely irreversible.

The complex *trans*-$[Os^{III}(L)_2Cl_2]Cl$ was prepared by the dropwise addition of $Na_2[OsCl_6]$ (0.5 g) to an ethanolic solution of L (0.4 g in 100 cm^3) in the presence of finely divided tin foil under reflux and with stirring.[8,9] The addition process took 4 h to complete and the reaction mixture was refluxed for 1 d. It was then filtered and a few drops of HCl added. The filtrate was rotary evaporated to dryness and the solid dissolved in hot 0.1 mol dm^{-3} HCl. Slow evaporation of the solvent gave yellow crystals of *trans*-$[Os^{III}(L)_2Cl_2]Cl$ (yield > 70%). Its UV/VIS absorption spectrum [λ/nm (ε/dm^3 mol^{-1} cm^{-1}) in 0.1 mol dm^{-3} CF_3CO_2H: 289 (1.46×10^3) and 304 (1.01×10^3)] is similar to *trans*-tetraaminedichloroosmium(III) complexes reported in the literature.[8]

The cyclic voltammogram of *trans*-$[Os^{III}(L)_2Cl_2]Cl$ shows a reversible couple I and an irreversible couple II, at 0.46 and 0.98 V *vs.* saturated calomel electrode (SCE) respectively, with an edge-plane pyrolytic graphite electrode in aqueous medium at pH 1 (Fig. 1). Couple I is at least quasi-reversible with scan rates in the range 50–200 mV s^{-1}. Importantly, $E°$ shifts −60 mV per pH unit from pH 1 to 5 (Fig. 2). Therefore we assign couple I tentatively to a one-proton one-electron oxidation. The corresponding electrode reaction is shown by equation (1)

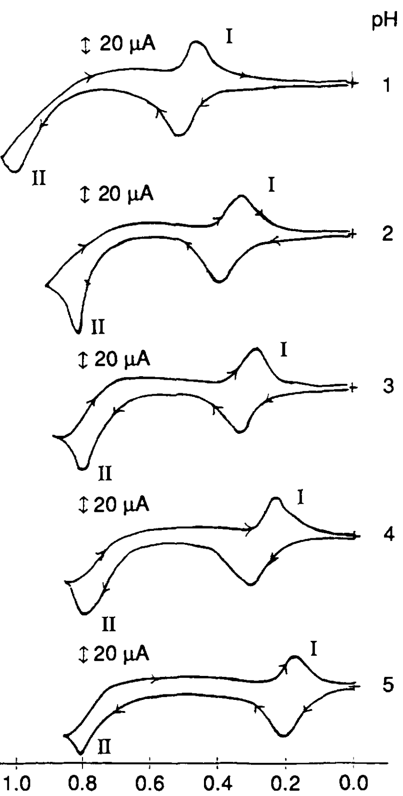

Fig. 1 Cyclic voltammograms of *trans*-$[O_s(L)_2Cl_2]^+$ in aqueous solution at various pH; scan rate = 100 mV s^{-1}

$$trans\text{-}[Os^{IV}L'(L)Cl_2]^+ + H^+ + e^- \longrightarrow trans\text{-}[Os^{III}(L)_2Cl_2]^+ \quad (1)$$

(L = $NH_2CMe_2CMe_2NH_2$ and L′ = $NH_2CMe_2CMe_2NH$). This assignment was confirmed by constant-potential coulometry at +0.6 V *vs.* SCE in 0.1 mol dm^{-3} CF_3CO_2H which established n = 1.0. After controlled-potential electrolysis, the UV/VIS absorption spectrum of the solution showed an intense absorption peak at λ_{max} 279 nm, due to $[Os^{IV}L'(L)Cl_2]^+$. Upon leaving the same solution to stand in the air for 2 d *trans*-$[Os^{VI}(L)_2O_2]^{2+}$ was identified by UV/VIS and IR spectro-

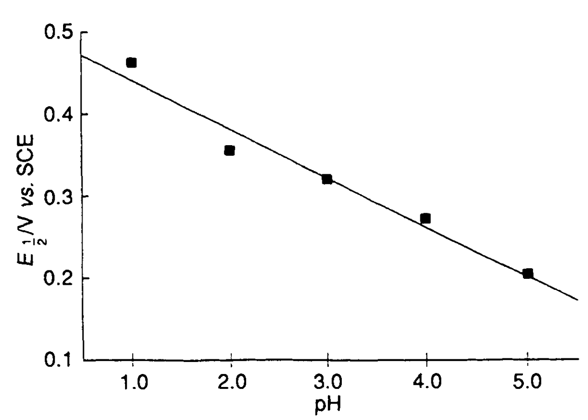

Fig. 2 Plot of $E_{\frac{1}{2}}$ *vs.* pH for the *trans*-$[Os^{IV}L'(L)Cl_2]^+$–*trans*-$[Os^{III}(L)_2Cl_2]^+$ couple

scopy.[9] Rotating-disc voltammetry verified that the limiting current of couple II is twice as large as couple I. Thus, couple II corresponds to the oxidation of Os^{IV} to Os^{VI}, but it is irreversible. The overall reaction proposed is shown in Scheme 1.

The observation of a reversible pH-dependent Os^{IV}–Os^{III} couple for *trans*-$[Os^{III}(L)_2Cl_2]^+$ rather than for *trans*-$[Os^{III}(NH_3)_4Cl_2]^+$ [6] is intriguing and suggests that an organic amido group such as L′ is useful in the generation and stabilization of high-valent metal complexes. That L′ is a good π donor is also illustrated by the recent work on an osmium(IV) complex of L′ which has an average osmium(IV)–amido distance of 1.88 Å.[7] To our knowledge, there is no precedent in the literature for a reversible pH-dependent Os^{IV}(amide)–Os^{III}(amine) couple. Once the amido complex is formed, it will undergo aquation to form a *trans*-diaqua osmium(IV) complex. Because of the strong π-bonding interaction between the amido N of L′ and Os^{IV}, the two Os–Cl bonds will be weakened thereby leading to the aquation. On standing, the aqua complex will be oxidized by air to form a *trans*-dioxo osmium(VI) complex. A similar mechanism has previously been reported by Taube and co-workers[6] to account for the disproportionation reactions of $[Os^{IV}(NH_3)_4Cl_2]^{2+}$.

Acknowledgements

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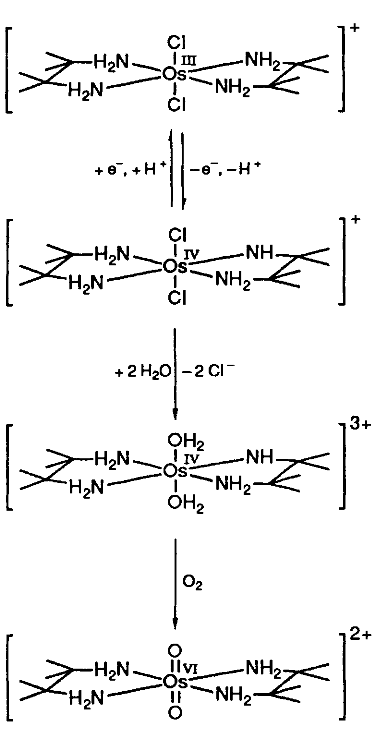

Scheme 1

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