Electrochemical One-electron Oxidation of $[Ru(NO)Cl_5]^{2-}$: Spectroscopic and Magnetic Evidence for the $(t_{2g}{}^5)$ Ruthenium(III) Pentachloronitrosyl Complex Monoanion $[Ru(NO)Cl_5]^-$

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Voltammetric measurements establish a reversible one-electron oxidation for $[Ru(NO)Cl_5]^{2-}$ in CH_2Cl_2; the i.r. and e.s.r. spectra and magnetic properties of the electrogenerated deep green product are consistent with low-spin $[Ru(NO)Cl_5]^-$, and quite different from the properties recently attributed to this anion.

Recently, Pandey *et al.*[1] have reported that NOCl reacts with hydrated ruthenium trichloride in the presence of an eightfold excess of triphenylphosphine to give, amongst other products, the pink ruthenium(III) complex $NH_4[Ru(NO)Cl_5]$ which is claimed to be the first example both of high-spin Ru^{III} and of a Ru^{III} nitrosyl complex. Since this would entail reappraisal of well established and soundly based expectations of low-spin behaviour in complexes of 4d tervalent metal ions {*cf.* the isoelectronic $[Ru(CO)Cl_5]^{2-}$ anion[2]}, we are prompted to report some relevant observations.

We have investigated a direct method of generating this species by controlled electrogeneration from the well known,[3] redox-related, 18-electron complex anion, $[Ru(NO)Cl_5]^{2-}$. Cyclic (C.V.) and linear a.c. voltammetry (a.c.V.) at a Pt electrode in CH_2Cl_2 (Figure 1) establish that $[Ph_3(PhCH_2)P]_2$-$[Ru(NO)Cl_5]$ is resistant to oxidation except at extreme potentials where a well defined oxidation is observed. This oxidation is *chemically* reversible although apparently characterised by sluggish heterogeneous charge-transfer kinetics [*i.e.* at 293 K, i_p(anodic)/i_p(cathodic) ratio = 1 at all scan rates (ν) from 50 to 500 mV s^{-1}, but E_p = 100 mV at ν = 50 mV s^{-1} and 120 mV at ν = 200 mV s^{-1}]. The one-electron nature of the process is indicated by the a.c.V. peak width at half height (100 mV, independent of ω in the range 20—600

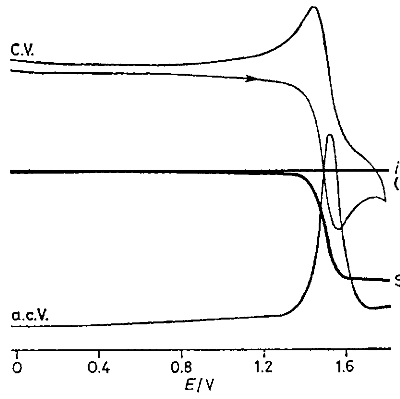

Figure 1. Voltammetry of $[Ru(NO)Cl_5]^{2-}$ in CH_2Cl_2. Scan rates: 100 mV s^{-1} (C.V.), 10 mV s^{-1} (S.V. and a.c.V.). Potentials *vs.* Ag/AgCl reference (against which ferrocene is oxidised at +0.55 V).

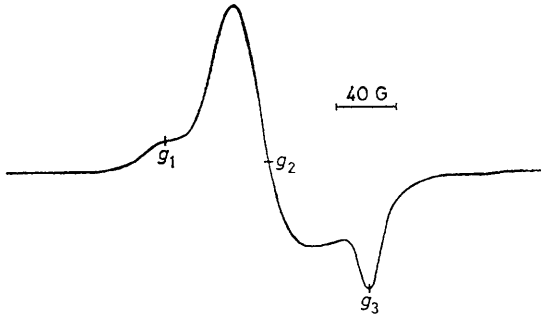

Figure 2. E.s.r. spectrum of $[Ru(NO)Cl_5]^-$ (see text) at 153 K, g_1, 2.16; g_2, 2.11; g_3, 2.06.

Hz), the characteristic diffusion coefficient ($D = 5 \times 10^{-6}$ cm^2 s^{-1} at 293 K),[4] and ultimately confirmed by coulometry (see below). Successive scans give no indication of expulsion of chloride or any other fragmentation/rearrangement to redox-active products other than the $[Ru(NO)Cl_5]^{2-}/[Ru(NO)Cl_5]^-$ couple.

Controlled potential electrolysis in CH_2Cl_2–0.50M$[Bu_4N]BF_4$ at +1.80 V and 223 K proceeds smoothly with the expected exponential decay of current. Percentage conversion was monitored by stirred voltammetry (S.V.) and the electrolysis was interrupted at an arbitrary 80% conversion. Simultaneous coulometric measurements establish that 1.0 electrons are lost per molecule of $[Ru(NO)Cl_5]^{2-}$.

The deep-green electrogenerated product [$\lambda_{max}(\epsilon)$: 690sh, 655 (4 300), 398 (2 100), and 294 nm (10 900)] present in 80% yield in the chilled anolyte solution has been characterised *in situ* as indicated below and its properties are completely consistent with its formulation as the *low-spin* $[Ru(NO)Cl_5]^-$ anion. Thus, magnetic measurements by the Evans' method[5] give $\mu = 2.28\ \mu_B$ at 183 K, and a plot of $1/\chi_M$ *vs.* T in the range 263—183 K shows strict Curie–Weiss behaviour with $\theta = +28$ K {*cf.* $K_2[Ru(CO)Cl_5]H_2O$ where $\mu = 1.87\ \mu_B$ at 296 K[2]}. The e.s.r. spectrum of the green product at 153 K (Figure 2) is typical of that observed for many low-spin ruthenium(III) complexes.[6] I.r. studies on the electrogenerated solution using a chilled flow-through cell reveal a strong NO band at 1920 cm^{-1}, compared to 1850 cm^{-1} for the ruthenium(II) anion (Figure 3). This shift to higher frequency on decrease in formal negative charge on the complex is compatible with the behaviour observed in related metal carbonyl compounds.

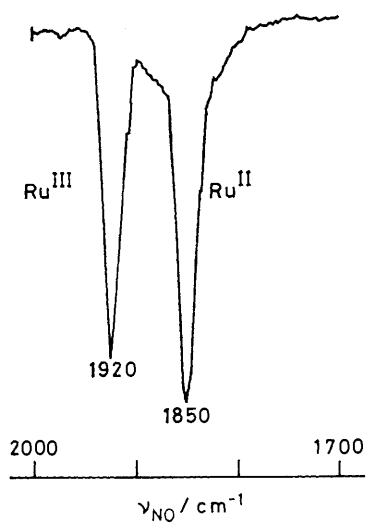

Figure 3. Solution i.r. spectrum of 1 : 1 mixture of $[Ru(NO)Cl_5]^{2-}$ and $[Ru(NO)Cl_5]^-$ (see text).

At temperatures above 260 K, the deep-green product exhibits 1 : 1 reversion to the mauve $[Ru(NO)Cl_5]^{2-}$ ion as demonstrated independently by relaxation of the solution i.r. and electronic spectra, and by successive stirred voltammograms. This offers strong circumstantial evidence for its formulation as the $[Ru(NO)Cl_5]^-$ anion.

The observed oxidation potential (+1.53 V) implies that, in contrast to Pandey's report,[1] the $[Ru(NO)Cl_5]^-$ anion is thermodynamically unstable towards reduction by water (or even free Cl^-), although it may be that under strict vacuum-line conditions the compound would be indefinitely stable at room temperature.

Hence, there are serious discrepancies between the properties we deduce for $[Ru(NO)Cl_5]^-$ and those ascribed to it by Pandey *et al.* Little experimental detail is given in their preliminary communication and, to date, all our attempts to reproduce their results have proved unsuccessful. Thus, although shaking a solution of '$RuCl_3.xH_2O$' and PPh_3 (1 : 8 molar ratio) with NOCl (1 atm) in CH_2Cl_2–EtOH resulted in the precipitation of an orange-brown, water-soluble material containing NH_4^+ ions and no PPh_3, e.s.r. and magnetic studies indicated that only traces of paramagnetic material were present. Under reflux conditions, the only product isolated was the well known $[Ru(NO)Cl_3(PPh_3)_2]$.[7]

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