

# THE NATURE OF THE OXIDATION PRODUCTS OF DICYANORUTHENIUM PHTHALOCYANINE IN AQUEOUS AND NON-AQUEOUS SOLVENTS

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**Abstract**—The cyclic voltammetry of  $[(\text{CN})_2\text{Ru}^{\text{II}}\text{Pc}]^{2-}$  in acetonitrile or dichloromethane shows two oxidation couples at  $E_{1/2} = 0.31$  and  $0.85$  V (vs S.C.E.) in  $\text{CH}_2\text{Cl}_2$  and  $E_{1/2} = 0.45$  and  $1.15$  V (vs S.C.E.) in acetonitrile. The spectroelectrochemistry of  $[(\text{CN})_2\text{Ru}^{\text{II}}\text{Pc}]^{2-}$  in these solvents showed that oxidations occur at the phthalocyanine ligand.  $\text{K}_2[(\text{CN})_2\text{Ru}^{\text{II}}\text{Pc}]$  dissolves in water at pHs greater than 5. The cyclic voltammetry of this complex showed oxidation couples at  $0.32$  and  $0.29$  V (vs S.C.E.) for aqueous solutions containing sodium sulphate ( $0.1$  M) and for buffered solutions ( $\text{pH} = 9$ ), respectively. Both cyclic voltammetry and controlled potential coulometry gave evidence of electrocrystallization of the oxidation product. Chemical oxidations of  $[(\text{CN})_2\text{Ru}^{\text{II}}\text{Pc}]^{2-}$  in water also showed phthalocyanine ligand oxidation.

Phthalocyanine complexes have established themselves industrially as green or blue dyes. Potential applications of metal phthalocyanine (MPc; Pc = phthalocyanine dianion) complexes include uses in catalysis, pollution control, electronic devices, photovoltaic devices and many others. Most of these applications involve the exchange of one or two electrons per reaction and hence, an understanding of the redox properties of the phthalocyanine complexes is very important. There is also an interest in metal-based drugs that can act against the rapid toxic effects of cyanide, and for this metalloporphyrin complexes have been suggested.<sup>1–5</sup> Phthalocyanines are structurally similar to the porphyrins and hence, studies of the cyano complexes of MPc complexes are of interest; a number of  $(\text{CN})_2\text{MPc}$  complexes have been reported.<sup>6–8</sup>

Cyclic voltammetry (CV) studies of a series of dicyanometallo phthalocyanines have been reported.<sup>6</sup> In these studies the first oxidation potential in  $[(\text{CN})_2\text{Ru}^{\text{II}}\text{Pc}]$  was assigned to the oxidation of the ruthenium metal to ruthenium(III), based on the comparison with the CV results of ruthenium porphyrin complexes. In this work, we take a closer look at the electrochemical properties of the  $[(\text{CN})_2\text{Ru}^{\text{II}}\text{Pc}]$  complex. The CV studies will be coupled with controlled potential coulometry and the site of the first and second oxidations will be determined.

Phthalocyanine complexes are normally insoluble in water. Attaching sulphonic acid groups to the outer periphery of the phthalocyanine ring renders these complexes soluble in water.<sup>9–12</sup> Sulphonated phthalocyanine complexes, however, aggregate in aqueous solution and are photoinactive.  $[(\text{CN})_2\text{Ru}^{\text{II}}\text{Pc}]$  shows solubility in water; the redox properties of this complex in water are reported in this work.

## EXPERIMENTAL

### Materials

Crude RuPc was synthesized from  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and *o*-cyanobenzamide and extracted with glacial acetic acid following the method of Dolphin *et al.*<sup>13</sup>

$\text{K}_2[(\text{CN})_2\text{RuPc}]$  was prepared according to synthetic procedures for other  $[(\text{CN})_2\text{MPc}]^{2-}$  complexes.<sup>7,8</sup> Crude RuPc ( $0.05$  g,  $0.08$  mmol) and KCN ( $0.05$  g,  $0.77$  mmol) were suspended in absolute ethanol or DMF ( $10\text{ cm}^3$ ) and refluxed for  $3$  h, giving a blue solution. The solution of  $\text{K}_2[(\text{CN})_2\text{RuPc}]$  was filtered to remove the insoluble RuPc and the filtrate evaporated to dryness, giving a purple solid which was washed in hexanes and recrystallized from acetone, giving  $40$  mg ( $66\%$ ) of  $\text{K}_2[(\text{CN})_2\text{RuPc}] \cdot 3\text{H}_2\text{O}$ .