

STRUCTURE-POTENTIAL RELATIONSHIPS FOR THE DINITRILE COMPLEXES $trans\text{-}[\text{Fe}(\text{NCR})_2(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)_2][\text{BF}_4]_2$

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SUMMARY

The electrochemical behaviour, in aprotic medium, of the 18-electron octahedral-type dinitrile complexes $trans\text{-}[\text{Fe}(\text{NCR})_2(\text{depe})_2][\text{BF}_4]_2$ (R = alkyl, aryl, NH_2 , NMe_2 or NEt_2 ; $\text{depe} = \text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$) was studied by cyclic voltammetry and controlled potential electrolysis. They undergo one single-electron reversible oxidation, and electrochemical ligand and metal site parameters [which measure the electronic properties of the nitrile ligands and their binding iron(II) centre] were estimated from the measured half-wave oxidation potential values.

RESULTS AND DISCUSSION

The electrochemical behaviour of the complexes $trans\text{-}[\text{Fe}(\text{NCR})_2(\text{depe})_2][\text{BF}_4]_2$ (R = Me, Et, $\text{CH}_2\text{C}_6\text{H}_4\text{OMe-4}$, $\text{C}_6\text{H}_4\text{OMe-4}$, $\text{C}_6\text{H}_4\text{Me-4}$, C_6H_5 , $\text{C}_6\text{H}_4\text{F-4}$, $\text{C}_6\text{H}_4\text{NO}_2\text{-4}$, NH_2 , NMe_2 or NEt_2 ; $\text{depe} = \text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$) was studied by cyclic voltammetry (CV) and controlled potential electrolysis (CPE), in 0.2 M $[\text{NBu}_4][\text{BF}_4]/\text{CH}_2\text{Cl}_2$, at a Pt-wire or -gauze electrode, respectively, at room temperature.

These complexes exhibit, by CV, one single-electron reversible anodic wave at $E_{1/2}^{\text{ox}}$ ca. 1.27 to 1.43 V vs. SCE (wave I, Fig. 1), assigned to the Fe(II) to Fe(III) oxidation and a single-electron irreversible cathodic wave at E_p^{red} in the range -1.17 to -1.73 V vs. SCE (wave II). Cyanamides appear as the strongest net electron donors (with the lowest $E_{1/2}^{\text{ox}}$ values) whereas the aromatic organonitriles with electron-accepting substituents behave as the weakest ones.

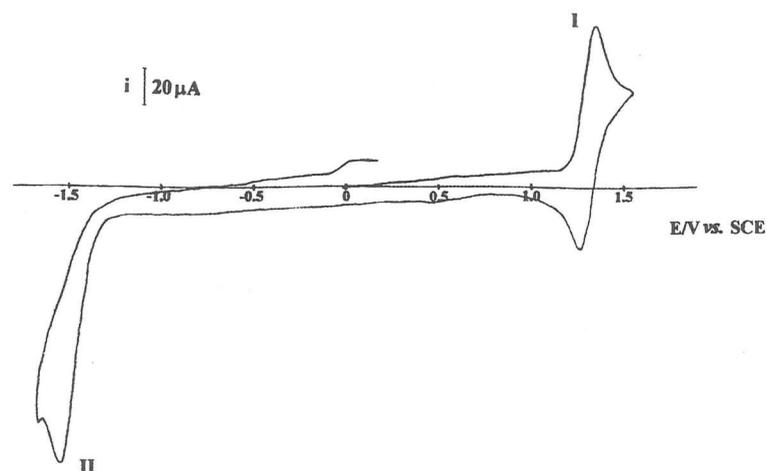


Fig. 1 - Cyclic voltammogram of *trans*-[Fe(NCCH₂C₆H₄OMe-4)₂(depe)₂][BF₄]₂ in 0.2 M [NBu₄][BF₄] / CH₂Cl₂, at a Pt disc electrode (scan rate = 200 mV s⁻¹). Potential in Volt vs. SCE.

The $E_{1/2}^{ox}$ values measured for these complexes and the knowledge of the E_s (electron-richness) and β (polarisability) parameters [1] for the related *trans*-{FeBr(depe)₂}⁺ metal centre ($E_s = 1.26$ V and $\beta = 1.1$, as estimated in a previous work [2]), as well as of the P_L parameter for the bromide [1] and the nitrile ligands [2], allowed us, by using expression (1) [3a)], to predict the $E_{1/2}^{ox}$ value (2.3 V vs. SCE) for the dicarbonyl complex *trans*-[Fe(CO)₂(depe)₂]²⁺.

$$E_{1/2}^{ox} [Fe(CO)_2(depe)_2]^{2+} = \frac{E_{1/2}^{ox} [Fe(NCR)_2(depe)_2]^{2+} \left[\frac{2P_L(NCR)}{P_L(Br^-)} - \frac{P_L^2(NCR)}{P_L^2(Br^-)} \right] E_s [FeBr(depe)_2]^+}{\left[1 - \frac{P_L(NCR)}{P_L(Br^-)} \right]^2} - \frac{\frac{P_L(NCR)}{P_L(Br^-)} \beta [FeBr(depe)_2]^+}{\left[1 - \frac{P_L(NCR)}{P_L(Br^-)} \right]^2} \quad (1)$$

From the above values it was possible, by using expressions (2) and (3) [3b), 3c)], to estimate the E_s and β parameters, respectively, for the dicationic metal centres *trans*-{Fe(NCR)(depe)₂}²⁺: $E_s = 1.65 - 1.96$ V, $\beta = 0.75 - 1.10$.

$$E_s [Fe(NCR)(depe)_2]^{2+} = \left[1 - \frac{P_L(NCR)}{P_L(Br^-)} \right] E_{1/2}^{ox} [Fe(CO)_2(depe)_2]^{2+} + \frac{P_L(NCR)}{P_L(Br^-)} E_s [FeBr(depe)_2]^+ \quad (2)$$

$$\beta [Fe(NCR)(depe)_2]^{2+} = \frac{\left[1 - \frac{P_L(NCR)}{P_L(Br^-)} \right] E_s [FeBr(depe)_2]^+ - \left[1 - \frac{P_L(NCR)}{P_L(Br^-)} \right] E_{1/2}^{ox} [Fe(CO)_2(depe)_2]^{2+}}{P_L(Br^-)} + \frac{\beta [FeBr(depe)_2]^+ P_L(NCR)}{P_L(Br^-)} \quad (3)$$

The polarisability is comparable with that known [1] for the related *trans*-{FeH(Ph₂PCH₂CH₂PPh₂)₂}⁺ site ($\beta = 1.0$), but the former dicationic centres present an electron-rich character which is lower than that exhibited by the monocationic sites *trans*-{FeBr(depe)₂}⁺ and *trans*-{FeH(Ph₂PCH₂CH₂PPh₂)₂}⁺ ($E_s = 1.04$ V [1]), indicating a weaker net electron donor ability of the nitrile compared with the bromide or hydride ligands, respectively, as measured by the P_L ligand parameter.

The P_L value of the cyanamide ligands was shown to be dependent on the nature of the metal binding site. Therefore, it had to be estimated from the more general expression (4) [3d)], where this dependence is taken into account by using different P_L values, each one being associated to the concerned metal centre. The P_L values estimated in this way (Table 1) show that the cyanamide ligands behave as stronger net electron donors at the dicationic centres *trans*-{Fe(NCR)(depe)₂}²⁺ than at the *trans*-{FeBr(depe)₂}⁺ site, and also as stronger net electron donors (with the lowest P_L values) than the organonitriles.

$$E_{1/2}^{\text{ox}} [\text{Fe}(\text{NCNR}_2)_2(\text{depe})_2]^{2+} = \left[1 - \frac{2 P_L(\text{NCNR}_2)\{\text{Fe}(\text{NCNR}_2)(\text{depe})_2\}^{2+}}{P_L(\text{Br}^-)} + \frac{P_L^2(\text{NCNR}_2)\{\text{Fe}(\text{NCNR}_2)(\text{depe})_2\}^{2+}}{P_L^2(\text{Br}^-)} \right] \cdot E_{1/2}^{\text{ox}} [\text{Fe}(\text{CO})_2(\text{depe})_2]^{2+} + \left[\frac{2 P_L(\text{NCNR}_2)\{\text{Fe}(\text{NCNR}_2)(\text{depe})_2\}^{2+}}{P_L(\text{Br}^-)} - \frac{P_L^2(\text{NCNR}_2)\{\text{Fe}(\text{NCNR}_2)(\text{depe})_2\}^{2+}}{P_L^2(\text{Br}^-)} \right] \left[E_S\{\text{FeBr}(\text{depe})_2\}^+ + \beta\{\text{FeBr}(\text{depe})_2\}^+ \right] \cdot P_L(\text{NCNR}_2)\{\text{Fe}(\text{NCNR}_2)(\text{depe})_2\}^{2+} \cdot P_L(\text{NCNR}_2)\{\text{FeBr}(\text{depe})_2\}^+ \cdot \frac{1}{P_L(\text{Br}^-)} \quad (4)$$

Table 1 - P_L values for the cyanamide ligands at the *trans*- $\{\text{Fe}(\text{NCR})(\text{depe})_2\}^{2+}$ centres.

L	$P_L(\text{L}) / \text{V}$
NCNH_2	-0.82
NCNMe_2	-0.79
NCNEt_2	-0.78

A linear relationship was also observed between $E_{1/2}^{\text{ox}}$ for the Fe(II/III) redox couple, in the complexes of this study, and the sum of the values of the Lever E_L ligand parameter [4] for all the ligands of the complexes, being expressed by eq. (5) (in which $E_{1/2}^{\text{ox}}$ is in V vs. NHE).

$$E_{1/2}^{\text{ox}} = (1.07 \pm 0.08) \sum E_L(\text{L}) - (0.3 \pm 0.1) \quad (5)$$

This expression was analysed in terms of a more general relationship proposed by Lever [4], $E_{1/2}^{\text{ox}} = S_M(\sum E_L) + I_M$, allowing to estimate the S_M and I_M parameters for our Fe(II/III) redox couple: $S_M = 1.07$ and $I_M = 0.3$ V vs. NHE. Although these values are somewhat different from those previously proposed by Lever [4] ($S_M = 1.10$, $I_M = 0.43$ V vs. NHE) by taking into consideration a variety of iron(III/II) centres, they characterize more accurately the metal centres of this study.

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