

## Supporting Information

# Spectroscopic and electrochemical study of the adsorption of $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ on $\gamma$ -alumina: influence of alumina ligand on $\text{Co}^{(\text{III})/(\text{II})}$ redox potential

Vincent Vivier,<sup>1,2,\*</sup> François Aguey,<sup>1</sup> Jeanine Fournier,<sup>1</sup> Jean-François Lambert,<sup>1</sup> Fethi

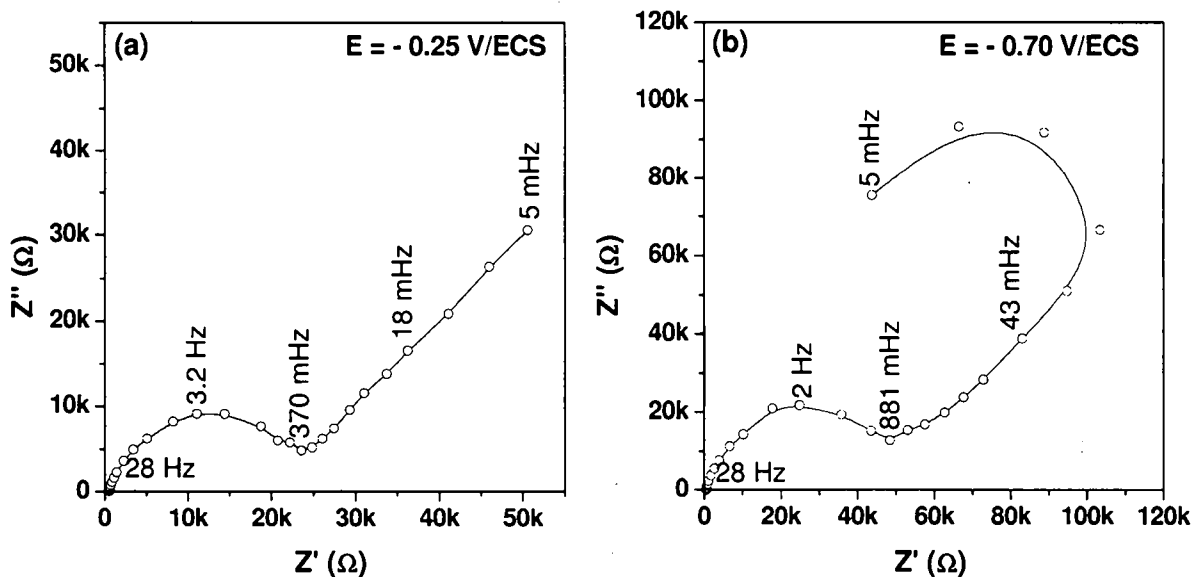
Bedioui,<sup>3</sup> and Michel Che,<sup>1,†</sup>

## Electrochemical Impedance Spectroscopy characterization of the $\text{trans}-[\text{Co}^{(\text{III})}(\text{en})_2\text{Cl}_2]^+$ complex

The Electrochemical Impedance Spectroscopy (EIS) diagram of the  $\text{trans}-[\text{Co}^{(\text{III})}(\text{en})_2\text{Cl}_2]^+$  complex in DMSO obtained at  $-0.25$  V/SCE (Fig. 1a) shows a half positive circle corresponding to the charge transfer and a  $45^\circ$  line which is attributed to a Warburg impedance.<sup>1</sup> There is no evidence of relaxation of any adsorbed species at the metal electrode during the reduction of the complex. The frequency corresponding to the top of the half-circle allows the determination of a double layer capacitance of *ca*  $15 \mu\text{F}$ , which is consistent with a  $2$  mm in diameter gold electrode. The amplitude of the loop gives a charge transfer resistance of  $20 \text{ k}\Omega$ . The apparent heterogeneous rate constant for the  $\text{Co}^{(\text{III})}/\text{Co}^{(\text{II})}$  redox process on Au is determined to be *ca*  $1.3 \cdot 10^{-3} \text{ cm s}^{-1}$ .

The EIS diagram obtained at  $-0.70$  V/SCE (Fig. 1b) also evidences a capacitive behavior for the high frequency domain followed by a Warburg impedance. However, for the lower frequencies, a second capacitive loop indicates that the polarization curve has a negative slope. This can be interpreted in terms of an inhibition reaction.<sup>2</sup> Similar EIS results were

obtained with the *cis* isomer for which the apparent heterogeneous rate constant is  $ca\ 10^{-3}\text{ cm s}^{-1}$ .



**Figure 1:** EIS spectra of  $trans-[Co(en)_2Cl_2]Cl$  in DMSO recorded on a 2 mm in diameter Au-disc electrode. (a)  $E = -0.25\text{ V/SCE}$ , (b)  $E = -0.70\text{ V/SCE}$ .  $C = 5\text{ mmol.L}^{-1}$ .

## References

1. Vetter, K. J. *Electrochemical Kinetics*, Academic Press: New York, USA, 1967.
2. Cachet, C.; Wiart, R. J. *Electrochem. Soc.* 1994, 141, 131.