

## Kinetics of electron transfer between thiols and a nickel(III) complex of oxime-imine ligand

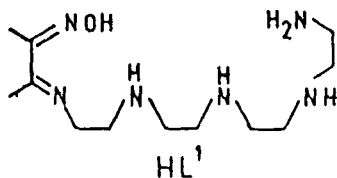
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The kinetics of electron transfer between  $[\text{Ni}^{\text{III}}(\text{L}^+)]^{2+}$  ( $\text{HL}^1 = 15\text{-amino-3-methyl-4,7,10,13-tetraazapentadec-3-en-2-one oxime}$ ) and two thiols, RSH (thioglycolic acid and glutathione) have been investigated by stopped flow spectrophotometry at  $30^\circ\text{C}$  over a range of pH 2.5–8.2 at constant ionic strength,  $I = 0.2 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ). A 1:1 stoichiometric ratio is encountered at pH 5.0 and represented by  $2[\text{Ni}^{\text{III}}(\text{L}^1)]^{2+} + 2\text{RSH} \rightarrow 2[\text{Ni}^{\text{II}}(\text{HL}^1)]^{2+} + \text{RSSR}$ . The reactions conform to the general rate-law

$$-d/dt[\text{Ni}^{\text{III}}(\text{L}^1)^{2+}] = k[\text{Ni}^{\text{III}}(\text{L}^1)^{2+}][\text{RSH}] = k_{\text{obs}}[\text{Ni}^{\text{III}}(\text{L}^1)^{2+}]$$

The reactivity of the various thiolate species is evaluated by fitting the experimental pH-rate profiles through computer generated programs.



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