

Macrocyclic binuclear copper(II) and nickel(II) complexes: the key role of central ions in hydrogen peroxide electrocatalysis

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The electrochemistry of the macrocyclic dicopper(II) and dinickel(II) complexes $[M_2L]Cl_2$, where L is the [2+2] condensation product of 1,3-diaminopropane and 2,6-diformyl-4-*tert*-butylphenol, is reported in relation to hydrogen peroxide electrocatalysis on mercury. The opposite effects observed with $[Cu_2L]Cl_2$ (inhibition) and $[Ni_2L]Cl_2$ (enhancement) are explained by different reduction mechanisms.

Copper(II) and nickel(II) complexes (insert in Figure 1) are interesting water-soluble binuclear macrocyclic complexes. These compounds can activate small molecules such as CO and O_2 by adduct formation^{1,2} and catalyse important chemical reactions.^{3–5} The catalytic disproportionation of H_2O_2 in aqueous dimethylformamide was reported for a binuclear manganese analogue of $[M_2L]Cl_2$ complexes. H_2O_2 is reduced at a high overvoltage.⁶ The electrocatalytic reduction of H_2O_2 at a mercury electrode was reported for heme-containing solutions.^{7,8} Taking into account the similarity of porphyrins and $[M_2L]Cl_2$ complexes (planar macrocyclic ligands with a system of conjugated bonds), an electrocatalytic effect of $[M_2L]Cl_2$ is expected. We attempted to find a catalytic effect of $[Cu_2L]Cl_2$ and $[Ni_2L]Cl_2$ on H_2O_2 electroreduction in aqueous solutions. Previously,⁹ we studied the general electrochemical features of $[Cu_2L]Cl_2$. Here we report on the electroreduction of $Ni^{II}Ni^{II}L$ † in comparison with that of $Cu^{II}Cu^{II}L$ at a mercury electrode in aqueous solutions (0.1 M acetate buffer solutions with pH 6 were used).⁴

Typical polarographic curves measured in solutions of $Cu^{II}Cu^{II}L$ and $Ni^{II}Ni^{II}L$ are shown in Figure 1.‡ The first electroreduction

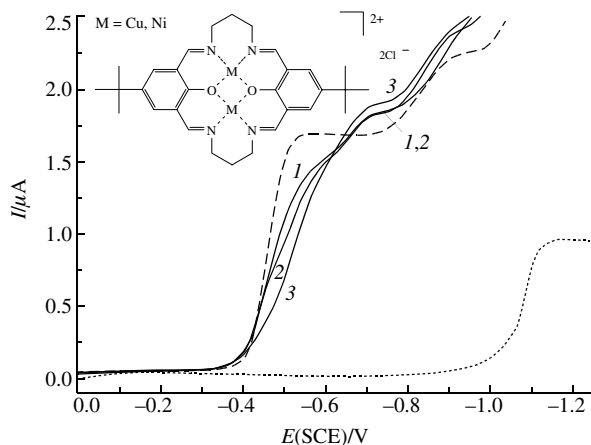


Figure 1 Polarograms of reduction measured on a DME in a 0.1 M acetate buffer solution (pH 6.0) with the addition of: (dashed line) 0.3 mmol dm^{−3} $[Cu_2L]Cl_2$; (dotted line) 1.2 mmol dm^{−3} $[Ni_2L]Cl_2$; (solid lines) 0.3 mmol dm^{−3} $[Cu_2L]Cl_2$ + *x* mmol dm^{−3} $[Ni_2L]Cl_2$, *x* = (1) 0.15, (2) 0.3 and (3) 1.2. Insert: the reactants $[M_2L]Cl_2$.

† This complex $[Ni_2L]Cl_2$ was synthesised using the metal template condensation procedure.¹⁰ In accordance with conductivity data reported for dinickel(II) and dicopper(II) complexes, which differ from $[M_2L]Cl_2$ only by a 4-methyl substituent of the macrocyclic ligand,¹⁰ $[Ni_2L]Cl_2$ and $[Cu_2L]Cl_2$ dissociate in dilute aqueous solutions to form doubly charged cations. Here, we briefly denote $[M_2L]Cl_2$ dissolved in a 0.1 M acetate buffer as $M^{II}M^{II}L$, which corresponds to this cation or its ion pairs.

‡ All polarographic measurements were carried out at a dropping mercury electrode (flow rate of 0.84 mg s^{−1}; open circuit drop life time of 7.8 s) in a three-electrode cell. The reference electrode was a saturated calomel electrode (SCE). All solutions were deaerated with hydrogen before each measurement. Currents are presented with background subtraction.

wave of $Cu^{II}Cu^{II}L$ species (dashed curve) corresponds to four-electron transfer,^{9,11} and its limiting current is diffusion-controlled. The half-wave potential is −0.46 V at pH 6.0 and shifts towards less negative potentials for 60 mV/pH with a decrease of pH from 6 to 4.

Being an analogue of $Cu^{II}Cu^{II}L$, $Ni^{II}Ni^{II}L$ manifests different redox features. The onset of the reduction wave is −1 V (dotted curve in Figure 1). In contrast to the first wave of $Cu^{II}Cu^{II}L$ reduction (dashed curve in Figure 1), no distinct pH-dependent shift was observed in this wave. Instead of a linear dependence of the limiting current (I_{lim}) on the square root of mercury column height (*h*), which would confirm the diffusion control of the reduction process,¹² the following correlation was found: $I_{lim} = \text{const} \cdot h^{4/5}$. The dependence of current at −1.2 V on the concentration of $[Ni_2L]Cl_2$ deviates from linearity starting from ~0.3 mmol dm^{−3}. These observations are indicative of adsorption-induced complications.

An attempt to determine the total number of electrons transferred in the course of the reduction of $Ni^{II}Ni^{II}L$ species by controlled potential electrolysis§ was unsuccessful. Neither pronounced absorption spectrum changes (in the range 400–650 nm) nor changes in polarographic curves as compared to an initial solution were observed. Assuming that the diffusion coefficient of $Ni^{II}Ni^{II}L$ species is the same, the number of electrons associated with the wave of $Ni^{II}Ni^{II}L$ reduction does not exceed two.

An interesting phenomenon is observed at the simultaneous presence of both $Cu^{II}Cu^{II}L$ and $Ni^{II}Ni^{II}L$. The slope of the first wave for $Cu^{II}Cu^{II}L$ reduction being 22 mV (dotted curve in Figure 1) increases when $[Ni_2L]Cl_2$ is added (solid curves); i.e., the reduction of $Cu^{II}Cu^{II}L$ slows down in the presence of $Ni^{II}Ni^{II}L$. The wave slope is independent of the concentration of $[Ni_2L]Cl_2$ higher than 0.6 mmol dm^{−3} and changes from 43 to 50 mV (solid curves 1–3) when the addition of $[Ni_2L]Cl_2$ is in the range from 0.15 to 0.6 mmol dm^{−3}. Another effect is a slightly elevated plateau current (first wave) under conditions of the coadsorption of complexes as compared to the algebraic sum of currents measured in $[Cu_2L]Cl_2$ and $[Ni_2L]Cl_2$ solutions. This feature of the polarographic curves is assumed to result from the presence of an indistinct but reproducible additional wave (at −0.65 V) besides the first wave of $Cu^{II}Cu^{II}L$ reduction. Presumably, these differences in the electroreduction of the complexes at a DME are caused by a stronger adsorption effect of $Ni^{II}Ni^{II}L$ compared to that of $Cu^{II}Cu^{II}L$. Since strongly adsorbing $Ni^{II}Ni^{II}L$ slows down the $Cu^{II}Cu^{II}L$ reduction, the mixed adlayer formation in the course of reduction is assumed, and one should conclude that the adsorbed $Cu^{II}Cu^{II}L$ species are involved in reduction at the DME in an aqueous medium.

A quantitative study of an adsorption equilibrium was limited by slow diffusion in dilute solutions and by a large molecular size, which prevents the use of an electrocapillary technique.

§ The controlled potential electrolysis was carried out at −1.2 V in a cell with separated cathodic and anodic compartments, as described in ref. 9 for $[Cu_2L]Cl_2$. The working electrode was a stirring mercury pool (~7 cm²).

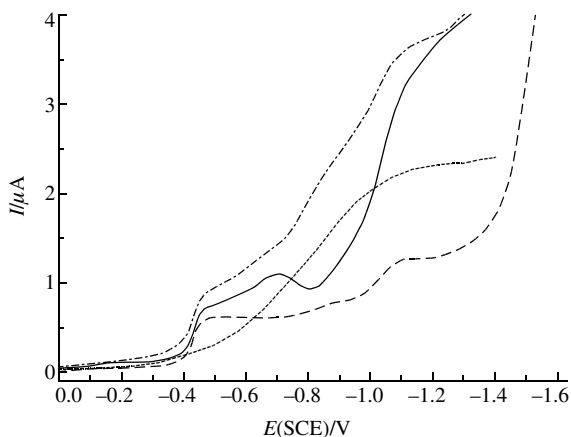


Figure 2 Polarograms of reduction measured on a DME in a 0.1 M acetate buffer solution (pH 6.0) with the addition of: (dashed line) 0.1 mmol dm⁻³ [Cu₂L]Cl₂; (dotted line) 0.4 mmol dm⁻³ H₂O₂; (solid line) 0.4 mmol dm⁻³ H₂O₂ + 0.1 mmol dm⁻³ [Cu₂L]Cl₂, (dash dotted line) algebraic sum of dashed and dotted lines.

A pronounced decrease in the drop life time at potentials preceding Ni^{II}Ni^{III}L reduction manifested strong adsorption of the reactant on mercury already at 0.05 mmol dm⁻³. The treatment[†] of the drop life time vs. potential and concentration data demonstrated the shift of a zero-charge potential towards more positive potentials. Consequently, the decrease of the drop life time results from the presence of strongly adsorbing cations.

Our approximate estimate of the surface coverages based on various adsorption isotherms confirms that, for [Ni₂L]Cl₂ concentrations higher than 0.5 mmol dm⁻³ at a negatively charged electrode surface, a close-packed monolayer is formed. Taking into account a structural similarity of the complexes under study, a pronounced adsorption of Cu^{II}Cu^{III}L at the DME should also be assumed. Since the Cu^{II}Cu^{III}L reduction commences at less negative potentials than that of Ni^{II}Ni^{III}L (dashed curve in Figure 1), that is, at less negative charges of the electrode, the contribution of adsorption (possible effect of self-inhibition) is more pronounced for Ni^{II}Ni^{III}L reduction (dotted curve in Figure 1). On this basis, an analogy in adsorption effects between Ni^{II}Ni^{III}L and some other reactants^{13,14} can be drawn, namely, a sort of self-inhibition (electrochemically active reactants in a diffuse layer are screened from the surface by inactive strongly adsorbed reactants). We cannot also exclude that stronger adsorption of Ni^{II}Ni^{III}L results from some difference in geometry.

In mixed [Cu₂L]Cl₂–H₂O₂ solutions, an effect was observed, which can be considered as the inhibition of Cu^{II}Cu^{III}L and/or H₂O₂ reduction (Figure 2). When comparing this data with the curves for Cu^{II}Cu^{III}L (dashed line) and H₂O₂ (dotted line) reduction in the absence of the second reactant, the following points are to be mentioned. The half-wave potential and slope of the first wave (solid curve) undergo no changes after the addition of H₂O₂ to the [Cu₂L]Cl₂ solution. A pronounced minimum is detected in the potential range of –0.7 to –0.9 V, which corresponds to the second Cu^{II}Cu^{III}L reduction wave. In this potential range, the H₂O₂ reduction takes place and, probably, interferes with the reduction of Cu^{II}Cu^{III}L by a chemical reaction with intermediates formed in the course of electroreduction. The depth of the minimum varies with the concentration ratio of the reactants. For H₂O₂/[Cu₂L]Cl₂ ratios from 0.33 to 8, the measured polarographic currents are lower than the algebraic sum of currents for separate reactants (dash dotted curve in Figure 2) in the entire potential range from 0 to –1.4 V. This fact manifests an interaction or mutual distortion of reaction layers. This point may also result from the change of the electrode coverage by adsorbed Cu^{II}Cu^{III}L.

When electroreduction of H₂O₂ takes place in the presence of Ni^{II}Ni^{III}L, a pronounced electrocatalytic effect is found. The

polarographic curves of the reactant mixture (solid curves in Figure 3) manifest the reduction onset at less negative potentials, and the corresponding wave slope decreased as compared to that of pure H₂O₂ (dotted curve). The wave slope correlates with [Ni₂L]Cl₂ concentrations from 0.001 to 0.05 mmol dm⁻³ and becomes constant when the quantity of Ni^{II}Ni^{III}L exceeds 0.05 mmol dm⁻³. The obtained slope values varied from 122 to 59 mV with the addition of [Ni₂L]Cl₂; *i.e.*, they are much lower than the value for the pure H₂O₂ reduction wave (147 mV). Apparently, the electrocatalytic effect results from the capability of Ni^{II}Ni^{III}L to form an adduct with H₂O₂ being adsorbed at the electrode surface. This assumption is in agreement with the fact that the complete electrode surface coverage by Ni^{II}Ni^{III}L is attained when increasing the Ni^{II}Ni^{III}L concentration. In accordance with polarographic data (solid curve 6), the wave with the onset at –1 V should be assigned to Ni^{II}Ni^{III}L reduction. The wave height is close to that of pure Ni^{II}Ni^{III}L reduction (dashed curve). A slight difference in the limiting currents of H₂O₂ reduction with and without the addition of [Ni₂L]Cl₂ should be mentioned. This difference does not exceed 0.37 μA, and H₂O₂ diffusion coefficient calculated from these values varies from 1.4×10⁻⁵ to 2×10⁻⁵ cm² s⁻¹. We can conclude that in the region from –0.5 to –1 V we observed a catalytic effect of Ni^{II}Ni^{III}L, when both H₂O₂ and the catalyst are reduced simultaneously at more negative potentials.

The electrocatalytic effect of Ni^{II}Ni^{III}L on hydrogen peroxide reduction was also observed in the course of polarographic measurements in a Ni^{II}Ni^{III}L solution (in an acetate buffer at pH 6.0) without deaeration. This data showed that the polarographic maximum known for the oxygen reduction at a DME¹⁵ was suppressed in the presence of Ni^{II}Ni^{III}L. This fact is in agreement with the strong adsorption of Ni^{II}Ni^{III}L. The slope of the second reduction wave became lower, and the half-wave potential shifted towards less negative values as compared to that measured in a [Ni₂L]Cl₂-free solution. Since the second wave of oxygen reduction at a DME⁶ is associated with the reduction of H₂O₂ as an intermediate, the described effect should be interpreted as a decrease of hydrogen peroxide overvoltage in the presence of Ni^{II}Ni^{III}L. This is the first observation of aqueous electrocatalysis by binuclear complexes with a Robson-type ligand. The effect on mercury is of the same order as that for heme-type molecular catalysts.⁸ An important advantage can result from the additional possibilities of catalyst immobilization at solid electrodes.^{11,16}

In conclusion, we found a possibility to enhance H₂O₂ reduction on mercury with Ni^{II}Ni^{III}L, in contrast to inhibition with Cu^{II}Cu^{III}L. This qualitative difference results from the difference in reduction onset potentials and mechanisms for complex species with different central ions. Fast four electron reduction of adsorbed Cu^{II}Cu^{III}L prevents the existence of an adsorbed mediator in the overall potential region of H₂O₂ reduction. The

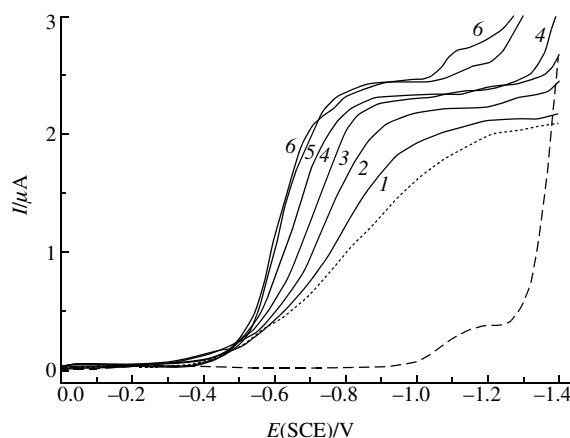


Figure 3 Polarograms of reduction measured on a DME in a 0.1 M acetate buffer solution (pH 6.0) with the addition of: (dotted line) 0.36 mmol dm⁻³ H₂O₂; (dashed line) 0.3 mmol dm⁻³ [Ni₂L]Cl₂; (solid line) 0.36 mmol dm⁻³ H₂O₂ + *x* mmol dm⁻³ [Ni₂L]Cl₂, *x* = (1) 0.001, (2) 0.005, (3) 0.01, (4) 0.02, (5) 0.05 and (6) 0.3.

[†] The measured drop life time (τ) vs. potential (E) data were recalculated into the surface tension (σ)– E relationship by the equation $\sigma = \tau \sigma_0 \tau_0$, where σ_0 and τ_0 are the values for supporting electrolyte solution at pzc (–0.475 V).

molecular-level reasons of the observed difference are to be considered.

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