Electrocatalysis of Oxygen Reduction by a Copper(II) Hexaazamacrocyclic Complex

Krzysztof Słowiński,[a] Zenon Kublik,[a] Renata Bilewicz*[a] and Marek Pietraszkiewicz[b]

[a] Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
[b] Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

The soluble binuclear Cu[II] complex with hexaazamacrocyclic ligand leads to a 440 mV decrease in the overpotential of oxygen reduction on glassy carbon electrode.

Electrocatalytic reduction of oxygen using transition metal complexes is an area of active research in electrochemistry.[1,2] Several macrocyclic complexes have been examined as potential catalysts, however, there is a lack of reports on the application of the copper complexes with macrocyclic ligands. The problems in using them as electrocatalytic systems are due to the fact that most of the macrocyclic Cu[II] complexes exhibit irreversible electrochemistry and/or unstable Cu[I] complexes or directly Cu[0] complexes are produced upon reduction.[3,4] These features of the electroreduction process are connected with the difference in the coordination geometry preferred by the Cu[II] and Cu[I] ions, so that large inner-coordination sphere rearrangements are required during the redox process in order to produce a stable Cu[I] form of the complex. More success is reported for simpler Cu[II] complexes, especially for those adsorbed on the electrode surface, where the interaction between the electrode and the complex stabilizes the Cu[I] catalytically active isomer.[5-8] In recent publications we have described the high-yield synthesis of the hexaazamacrocycle ligand L, and elsewhere we gave the crystal structure and spectroscopic data of its Cu[II] binuclear complex.[9,10] Here two sets of nitrogen donors are able to coordinate two copper centres and two additional small coligands are necessary to complete the coordination environment of the metallic centres. The structural data show that one of the chlorides is only weakly bound to the copper centre [Cu···Cl, 3.41 Å] as compared to the other one [2.22 Å], hence the complex can easily loose the less firmly bound chlorides in the solution and become a cation.

L
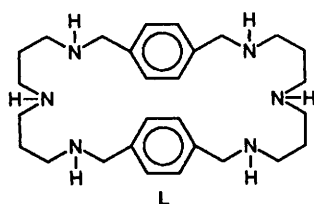
Here we describe the unique electrochemical behaviour of the complex, i.e. its high electrocatalytic properties towards oxygen reduction.

Electroreduction of oxygen at the glassy carbon electrode in the borate buffer solution containing 10^{-3} mol dm^{-3} chlorides, pH 7.3, takes place at -0.62 V vs. SCE (Fig. 1 curves 1 and 1'). In the presence of the Cu[II] complex with the hexaazamacrocyclic ligand L the overpotential for O$_2$ reduction is decreased by more than 400 mV (Fig. 1 curves 3 and 3'). The electrode potential has to be close to the redox potential of the Cu[II]$_2$LCl$_4$ complex (Fig. 1 curve 2) before oxygen reduction can take place. The oxidation counterpart of the voltammetric reduction peak of the Cu[II] complex disappears when the ratio of oxygen : complex concentration is higher than 0.5. This indicates that the electrochemically generated reduced form of the binuclear complex is required for the catalytic reduction of oxygen.

The electrochemical properties of the Cu[II] complex with the hexaazamacrocyclic ligand were studied voltammetrically under an argon atmosphere. The binuclear Cu[II] complex undergoes reversible 2e reduction on glassy carbon, gold and platinum electrodes (Fig. 2) with the peak-to-peak separation

of 60 mV and the half-width of the reduction peak equal to 58 mV at 20 mV s^{-1} scan rate. This, together with the height of the peak corresponding to a 2e process show that both Cu[II] centres of the complex are independently reduced at a similar potential to Cu[I]. The two-electron reduction of the complex is confirmed by exhaustive electrolysis at -0.3 V using large glassy carbon electrode as the cathode. The value of heterogeneous electron transfer rate constant, k^0, was estimated by the method of Nicholson[11] from the dependence of the anodic–cathodic peak separation on scan rate and was found to be 6.5 × 10^{-3} cm s^{-1}. In solutions of pH 7–13 containing chlorides the Cu[II] macrocyclic complex is stable and the reaction proceeds according to eqn. (1).

$$Cu^{II}{}_2LCl_4 + 2e^- \longleftrightarrow Cu^I{}_2LCl_2 + 2Cl^- \tag{1}$$

The shift of the formal potential upon increasing chloride concentration in the solution proved the release of two chloride ions in the process. The binuclear Cu[I] complex can be prepared in the thoroughly deoxygenated solution either by reduction of the Cu[II] complex or by mixing Cu[I](MeCN)$_4$BF$_4$ with the ligand and chloride ions. It is stable under argon atmosphere but exhibits high reactivity towards both oxygen and hydrogen peroxide. On the other hand the Cu[II] complex itself does not react with oxygen. These observations lead to the suggestion that oxygen is reduced in the presence of the Cu[II] complex according to an EC catalytic regeneration mechanism with the Cu[I] bimetallic complex acting as the catalyst. The rate constant of the chemical reaction between the Cu[I] complex and oxygen was determined under pseudo–first-order conditions maintained by appropriate excess of oxygen. Using the working curve for catalytic current in linear sweep voltammetry[12] the value of the rate constant was found to be 1.5 × 10^5 dm^3 mol^{-1} s^{-1}.

The Cu[I] reoxidation signal is absent at ratios [O$_2$]/[Cu[II]$_2$LCl$_4$] higher than 0.5. The products of oxygen reduction were found to depend on the oxygen : catalyst concentration ratio. At higher ratios, H$_2$O$_2$ can be detected by the

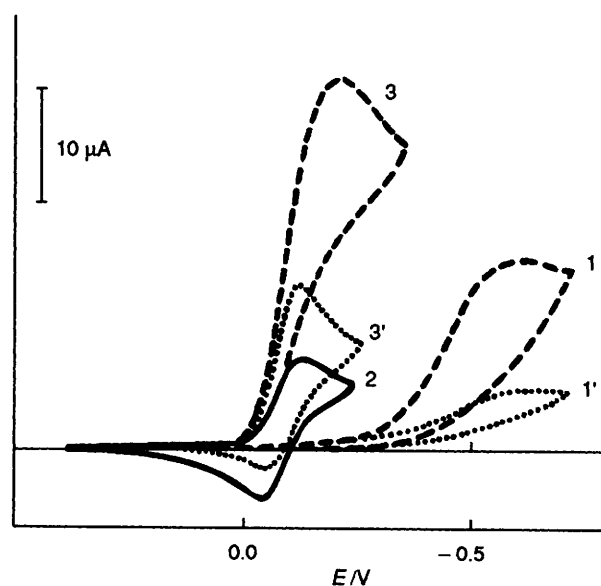0.0 -0.5

E /V

Fig. 1

appearance of an anodic signal close to 0.7 V at pH 9, corresponding to peroxide oxidation. Under excess of the complex no similar peak is detected, which indicates that H_2O_2 is transformed into a different species. For various $[O_2]/[Cu^{II}_2LCl_4]$ ratios we determined the normalized current,[13] $I_N = (i_{cat} - i_{complex})/i_{pn} = 1$, where i_{cat} is the catalytic peak current and $i_{complex}$ is the peak current of the complex reduction in deoxygenated solution, and $i_{pn} = 1$ is the current expected for one-electron reduction of oxygen to superoxide. The I_N value is 2 at $[O_2]/[Cu^{II}_2LCl_4]$ ratios higher than 0.5, while it increases to well above 2 ($2 < I_N < 4$) when the complex is in excess. This may point to the participation of a
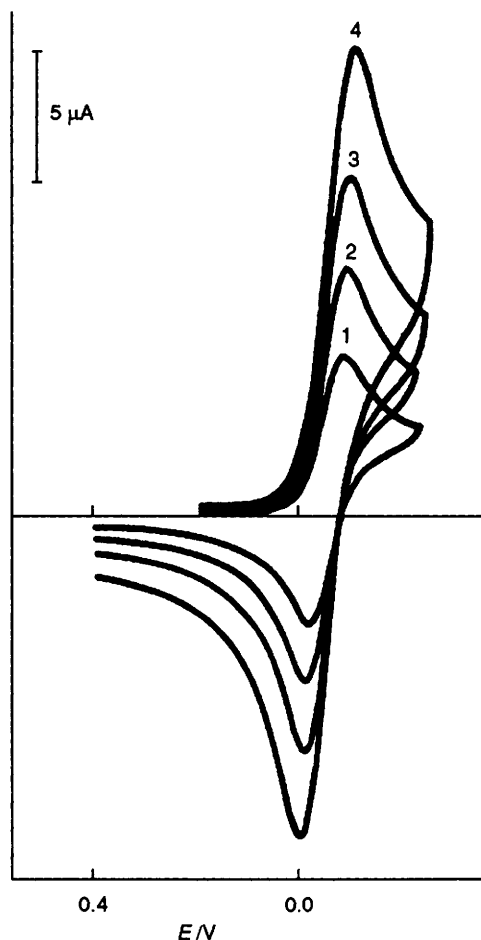

Fig. 2

multistep 2 + 2 reduction mechanism proposed by Forshey and Kuwana[13] for the iron porphyrin catalyst. This mechanism involves oxygen reduction in a two step pathway through hydrogen peroxide to water, the latter being the product at high excess of the catalyst. In our case the reduction of peroxide by Cu^I was found to be slower than that of oxygen which explains why the I_N value of 4 is not reached on the voltammetric time scale used.

to the binuclear Cu^I form, together with the high degree of reversibility of the process is rare for the Cu^{II}/Cu^I electrode processes. More importantly the electrocatalytic activity exhibited by the complex is unique among the solution soluble copper complexes. These features are attributed to the geometric constraints imposed upon the reactive centre by the surrounding rigid macrocyclic framework of the ligand.[10] The electrocatalytic behaviour towards oxygen reduction has not been observed for any other macrocyclic binuclear copper complex. The separation of copper centres in the Cu^{II} complex is 8.40 Å and the characteristics of the cyclic voltammogram fully support the lack of exchange coupling between the copper centres postulated on basis of the ESR spectrum.[10]

References

1 Electrochemistry of Porphyrins, M. R. Tarasevich, K. A. Radyushkina and V. A. Bogdanovskaya, Nauka publ., Moscow 1991, p. 177–197.
2 J. H. Zagal, Coord. Chem. Rev., 1992, 119, 89.
3 P. Zanello, S. Tamburini, P. A. Vigato and G. A. Mazzocchin Coord. Chem. Rev., 1987, 77, 165.
4 M. M. Bernardo, P. V. Robandt, R. R. Schroeder and D. B. Rorabacher, J. Am. Chem. Soc., 1989, 111, 1224.
5 M. R. Tarasevich, M. E. Fol'pin, A. Bogdanovskaya, S. B. Orlov, G. N. Novodarowa and E. M. Kolosova, Elektrokhimiya, 1981, 17, 1327.
6 K. Sugiyama and K. Aoki, J. Electroanal. Chem., 1989, 262, 211.
7 J. Zhang and F. C. Anson, J. Electroanal. Chem., 1992, 341, 323.
8 J. Zhang and F. C. Anson, J. Electroanal. Chem., 1993, 348, 81.
9 M. Pietraszkiewicz and R. Gąsiorowski, Chem. Ber., 1990, 123, 405.
10 C. J. McKenzie, H. Toftlund, M. Pietraszkiewicz, Z. Stojek and K. Słowiński, Inorg. Chim. Acta, 1993, 210, 143.
11 R. S. Nicholson, Anal. Chem., 1965, 37, 1351.
12 R. S. Nicholson and I. Shain, Anal. Chem., 1964, 36, 706.
13 P. A. Forshey and T. Kuwana, Inorg. Chem., 1983, 22, 699.