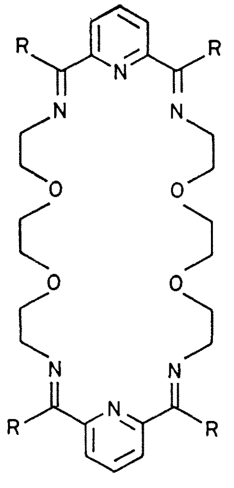
A Bi-copper(I)/Bi-copper(II) Redox Cycle in the Co-ordination and Activation of Dioxygen by a Bi-copper(I) Complex of a Macrocyclic Ligand

By Michael G. Burnett, Vickie McKee, and S. Martin Nelson
(*Department of Chemistry, Queen's University, Belfast* BT9 5AG, *N. Ireland*)

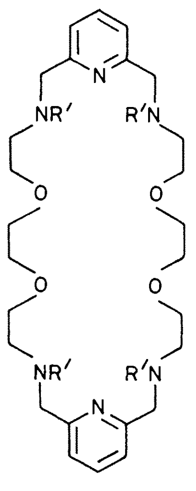
and Michael G. B. Drew
(*Department of Chemistry, The University, Reading* RG6 2AD)

Summary The rapid absorption of one mol of dioxygen by one mol of a bi-Cu^I macrocyclic complex in MeCN is followed by a slower anaerobic oxidative dehydrogenation of the ligand by the bound dioxygen to regenerate the Cu^I centres so that the cycle may be repeated, at least once again although more slowly.

The biological function of many metalloproteins is believed to be associated with the occurrence of pairs of adjacent metal ions capable of mutual interaction *via* small bridging ligands.[1] Among these are the O_2-carrying haemocyanins for which a μ-peroxo-di-Cu^{II} structure has been suggested for the active site in the oxygenated form.[2,3] Some bi-Cu^{II} complexes of the tetra-imine (Schiff's base) macrocycle L^1 containing both single-atom (OH^-) and three-atom (imidazolate, N_3^-) bridges, which may model some of the properties of the natural systems, have recently been described.[4] We here report the reaction of dioxygen with the bi-Cu^I complexes of the closely related macrocycles L^3 {obtained by BH_4^- reduction of $[Pb_2L^2(SCN)_4]$} and L^4 (obtained by methylation of L^3).



L^1, R = Me
L^2, R = H



L^3, R′ = H
L^4, R′ = Me

$[Cu_2L^3][ClO_4]_2$
(1)

$[Cu_2L^4][ClO_4]_2$
(2)

$[Cu_2L^3][ClO_4]_2$, (**1**), and $[Cu_2L^4][ClO_4]_2$, (**2**), are bright yellow diamagnetic solids that turn green on exposure to O_2 in solution and, less rapidly, in the solid state. The full curves in the Figure are experimental records of the amount of O_2 consumed by (**1**) (pressure change at constant volume) as a function of time in dry MeCN at 50 °C, the total uptake being in excess of 3 mol of O_2 per mol of complex. The O_2 uptake shown in the Figure has been fitted by points calculated using an integrated rate-equation deduced for a set of three consecutive rate-determining first-order reactions, each consuming one mol of O_2, and each slower than the previous step by a factor of *ca.* 10 or more. The uptake of the first mol of O_2 is accompanied by the development of an absorption band at 15,300 cm^{-1} (ϵ_M *ca.* 250 $dm^3\ mol^{-1}\ cm^{-1}$), characteristic of Cu^{II}, which did not intensify on further oxygenation. Oxygenated solutions were analysed both for H_2O_2 (spectrophotometric iodide method[5]) and for H_2O (g.l.c.[6]). No H_2O_2 was detected

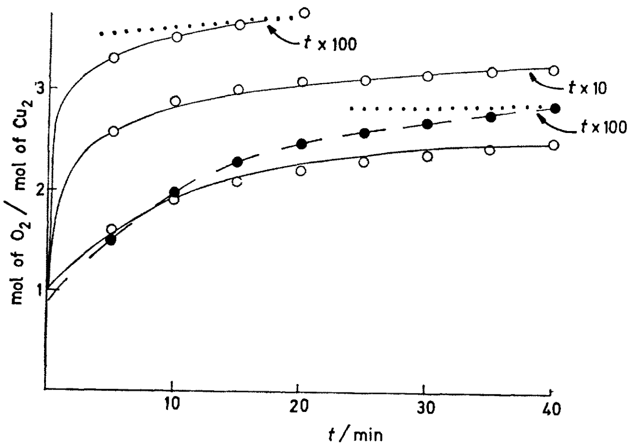


FIGURE. O_2 uptake at 50 °C in MeCN at 1 atm. The full curves refer to complex (**1**) ($1{\cdot}66 \times 10^{-3}$ M), the dashed curve to complex (**2**) ($6{\cdot}89 \times 10^{-3}$ M), and the dotted curves to the oxidation of MeCN in the absence of complex. The points represented by open circles are calculated for consecutive first-order reactions ($0{\cdot}005\ k_2 = 0{\cdot}04\ k_3 = k_4 = 8 \times 10^{-4}\ \text{min}^{-1}$); the points represented by closed circles are calculated for a single step ($k = 7 \times 10^{-4}\ \text{min}^{-1}$); the experimental curves are transcribed from continuous plots of pressure made by a recording manometer.

at any stage and no H_2O was detected immediately after absorption of the first mol of O_2 although it was found later in the reaction.

When the O_2 uptake was interrupted at various stages by replacement of the O_2 atmosphere by one of argon the green colour (ν_{max} 15,300 cm^{-1}) of the solutions changed to amber (ν_{max} 21,700 cm^{-1}) without gas evolution. The change was fairly rapid in the early stages, but became progressively slower later in the oxidation. Re-admission of O_2 reversed the spectral changes with an isosbestic point at 15,900 cm^{-1}, while further O_2 was absorbed at an accelerated rate. We account for the anaerobic 'green' $\rightarrow$ 'amber' reaction in terms of a bi-Cu^{II} $\rightarrow$ bi-Cu^{I} reduction, and the strong band at 21,700 cm^{-1} by a Cu^{I} $\rightarrow$ imine charge transfer transition.[7]

Attempts to isolate pure samples of the oxidised complexes have not been successful. However, i.r. spectra of the crude (green) products differed from that of (**1**) in the development of a medium intensity band at 1635 cm^{-1} and in the virtual disappearance of the N–H stretching vibrations at 3325 and 3240 cm^{-1}. These observations are strong evidence for an oxidative dehydrogenation of the secondary amine ($-CH_2-NH-$) to imine ($-CH{=}N-$) functions.

The results suggest that the reaction of (**1**) with O_2 proceeds by the following series of consecutive reactions (Scheme 1) in which (L^3 $-4H$) and (L^3 $-8H$) represent dehydrogenated forms of the macrocyle containing, respectively, two and four imine groups and $k_1 \gg k_2 > k_3 > k_4$ and $k' > k'' > k'''$, *etc.* The final incomplete step may be associated with the dehydrogenation of $-CH_2-CH_2-$ groups (see below).

A possible mechanism for the aerobic/anaerobic cycle is that suggested in Scheme 2 (first cycle). The formation of a μ-peroxo-di-Cu^{II} intermediate (**3**) is consistent with the observed stoicheiometry while the nitrogen-to-co-ordinated-peroxide proton transfer to give (**4**) is consistent with the

$$[Cu^{I}_2L^3]^{2+} + O_2 \xrightarrow{k_1} [Cu^{II}_2L^3(O_2)]^{2+}$$

$$[Cu^{II}_2L^3(O_2)]^{2+} \xrightarrow[\text{(anaerobic)}]{k_2} [Cu^{I}_2(L^3 -4H)]^{2+} + 2H_2O$$

$$[Cu^{I}_2(L^3 -4H)]^{2+} + O_2 \xrightarrow{k'} [Cu^{II}_2(L^3 -4H)(O_2)]^{2+}$$

$$[Cu^{II}_2(L^3 -4H)(O_2)]^{2+} \xrightarrow[\text{(anaerobic)}]{k_3} [Cu^{I}_2(L^3 -8H)]^{2+} + 2H_2O$$

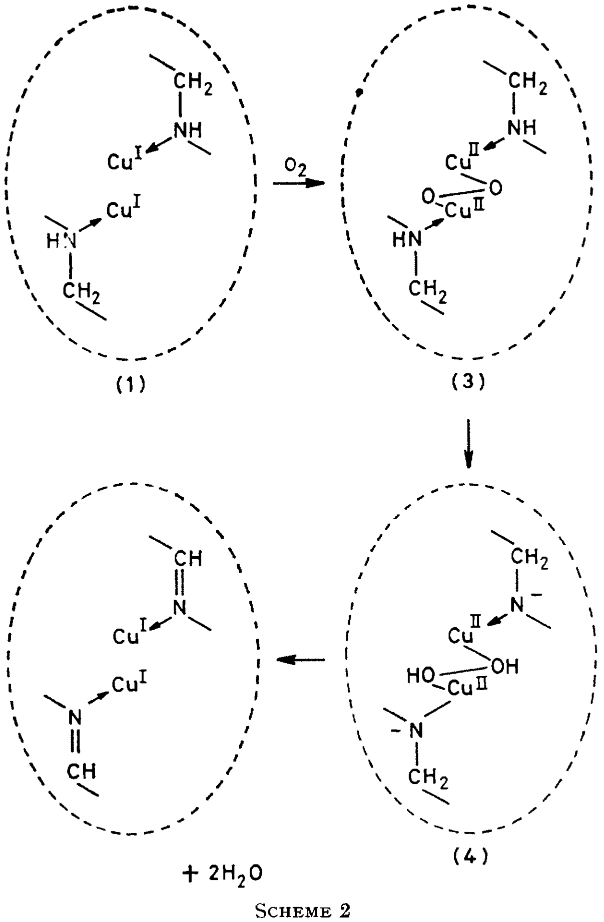
$$[Cu^{I}_2(L^3 -8H)]^{2+} + O_2 \xrightarrow{k''} [Cu^{II}_2\,(L^3 -8H)(O_2)]^{2+}$$

$$[Cu^{II}_2(L^3 -8H)(O_2)]^{2+} \xrightarrow[\text{(anaerobic)}]{k_4} [Cu^{I}_2(L^3 -12H)]^{2+} + 2H_2O$$

$$[Cu^{I}_2(L^3 -12H)]^{2+} + O_2 \xrightarrow{k'''} [Cu^{II}_2(L^3 -12H)(O_2)]^{2+}$$

SCHEME 1

high basicity ($pK_a > 14$)[8] of $[O_2]^{2-}$ and the acidity of co-ordinated (secondary) amines.[9] In support of the participation of the amino hydrogens of L^3 in the ligand oxidation are the results of experiments performed on (**2**), which lacks



SCHEME 2

such hydrogens. As with (**1**), this complex also absorbs *ca.* one mol of O_2 per mol of complex very rapidly, but the subsequent consumption of O_2 (2 mol in a single first-order step) is very much slower. This is attributed to a higher activation energy for the dehydrogenation of $-CH_2-CH_2-$ compared to $-CH_2-NH-$ groups. The crude oxidised product from this reaction showed a new medium intensity band at $1642\ cm^{-1}$ assignable to the $-CH{=}CH-$ group. The O_2 uptake for complex (**2**) shown in the Figure has been fitted by points calculated using a simple integrated first-order rate law corresponding to this slow step.

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