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Copper-(I) and -(II) complexes of a macrocycle derived from 2:2 condensation of pyridine-2,6-dicarbaldehyde and 4-azaheptane-1,7-diamine; oxygenation of the copper(I) complex

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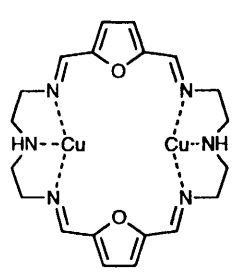
A Schiff-base macrocycle was prepared by the 2:2 condensation of pyridine-2,6-dicarbaldehyde and 4-azaheptane-1,7-diamine. It crystallized in the orthorhombic space group *Fdd*2 with $a = 16.984(8)$, $b = 31.322(12)$, $c = 11.026(6)$ Å and $Z = 16$. This 20-membered ring-contracted form, with two Schiff-base double bonds, forms a deep red dinuclear copper-(I) complex having two charge-transfer absorptions at 415 and 550 nm in methanol–acetonitrile (4:1). The complex forms a deep purple dicopper–dioxygen complex having absorption bands at 390 and 530 nm, with a rate constant at 25.0 °C of 5.6×10^{-5} s^{-1}. This is spontaneously converted into a copper(II) complex with a half-life of 240 min. The dinuclear copper(I)–dioxygen complex oxidizes 3,5-di-*tert*-butylcatechol catalytically to 3,5-di-*tert*-butyl-1,2-benzoquinone. The dinuclear copper(II) complex of the macrocycle was also found to oxidize this substrate to the same product at a much faster rate.

Dinuclear copper(I) complexes are of interest to researchers since they have been shown to contribute to the understanding of the functioning of specific types of copper-containing proteins (such as haemocyanin and tyrosinase)[1–5] and also because of their potential use in organic synthesis.[6] Interest has been mainly in the suitability of such complexes as functional models for copper-containing enzymes. A number of dinuclear complexes based on acyclic and linear ligand systems have been prepared and investigated for oxygen uptake.[7–42] Of particular note are the modelling studies of the dinuclear active site of haemocyanin accomplished by Solomon and co-workers[43–46] through the use of complexes prepared by Kitajima and Karlin. An important development was the publishing of a crystal structure of a side-on μ-η^2:η^2 dimer prepared by Kitajima *et al.*,[36] which led to the reinterpretation of the spectral data for the active site of oxyhaemocyanin. Several of these complexes react with dioxygen to produce dioxygen complexes which are usually well characterized spectroscopically. There are mainly three possibilities for oxygen binding which are considered in theoretical studies, *cis*-μ-1,2, *trans*-μ-1,2 and side-on bridging μ-η^2:η^2.[43–48] In some instances the oxygen uptake is reversible, and in a few cases the dioxygen complex is stable enough to be isolated.

Our previous work in this regard was concerned specifically with the assessment of macrocyclic complexes as functional models[49,50] and examination of their catalytic properties for oxidation of phenols, catechols and hydroquinones.[51,52] Whereas acyclic and linear ligand systems allow a convenient approach for copper(I) ions in the oxygenated forms of the dicopper(I) complexes, for macrocyclic systems the copper ions are, to a large extent, constrained at a limited internuclear separation. This arrangement allows the study of the oxidative effectiveness of the oxygenated complex as a function of internuclear distance. Two systems previously examined[49,51] are shown as **1** and **2**. These complexes, when oxygenated at room temperature were eventually converted into dicopper(II) complexes *via* a proposed dioxygen intermediate, involving a four-electron transfer process. Kinetic studies[53] have corroborated the argument proposing the existence of an oxygenated intermediate. It has been found that, on substituting the furan system with a pyridine unit, the oxygenated form of the dicopper(I) complex persists longer at room temperature and results in an enhancement in the catalytic properties of the



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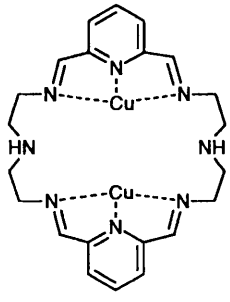

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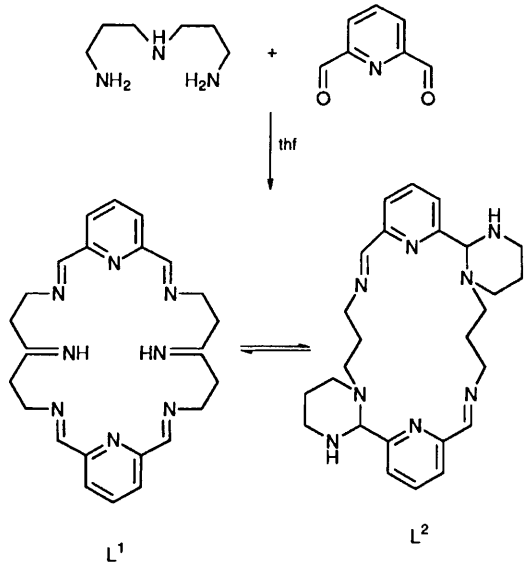
dinuclear complex. This improvement in the oxidation efficiency is partly attributed to the greater internuclear separation of the copper ions in **2** and flexibility of the ligand structure. In the current investigation a copper(I) complex with a ligand prepared from the 2:2 condensation of pyridine-2,6-dicarbaldehyde and 4-azaheptane-1,7-diamine is characterized and examined for its reactivity. The use of a larger ring in the macrocycle is expected to impart greater flexibility to the complex and in so doing make possible stronger binding of dioxygen to form a more stable peroxo-complex. This report presents the results of reactivity studies on the dicopper(I) complex in its oxygenated form and also the dicopper(II) complex of the same ligand.

Results and Discussion

Synthesis of the macrocycle

This compound was prepared by a direct condensation method and found to precipitate with a small amount of the 1:1 product, which was effectively removed on a silica gel column treated with triethylamine. When the product was prepared in acetonitrile, slow evaporation of the solvent gave large rounded crystals. It was also prepared by the procedure of Alcock *et al.*,[54] in which case tetrahydrofuran (thf) was used as solvent. No details were given in the literature report; however, a synthetic scheme suggests that they obtained the ring-expanded form (L^1, Scheme 1) as the product. The present investigation has shown that the product is obtained as an oil when prepared in thf and gives identical ^{1}H and ^{13}C NMR spectra to those obtained in

the acetonitrile preparation. The results of X-ray crystal analysis (discussed below) demonstrate that the ring-contracted form (L^2, Scheme 1) crystallizes out. Analysis of the ^1H NMR spectrum suggests that this form persists in solution. Such an isomeric form may be obtained when the imine group of the open Schiff-base macrocycle (L^1, Scheme 1) is attacked by an amine function, resulting in a decrease in ring size (from 28- to 20-membered). In previous preparations[55] of the compound a template synthesis with silver(I) resulted in a dinuclear complex of the fully expanded form, whereas preparations with smaller ions such as Ca^{2+} and Sr^{2+} as templates gave the ring-contracted isomer. This is the first reported preparation of the ring-contracted form by a direct condensation method. Other related examples have been reported.[56,57]



Scheme 1

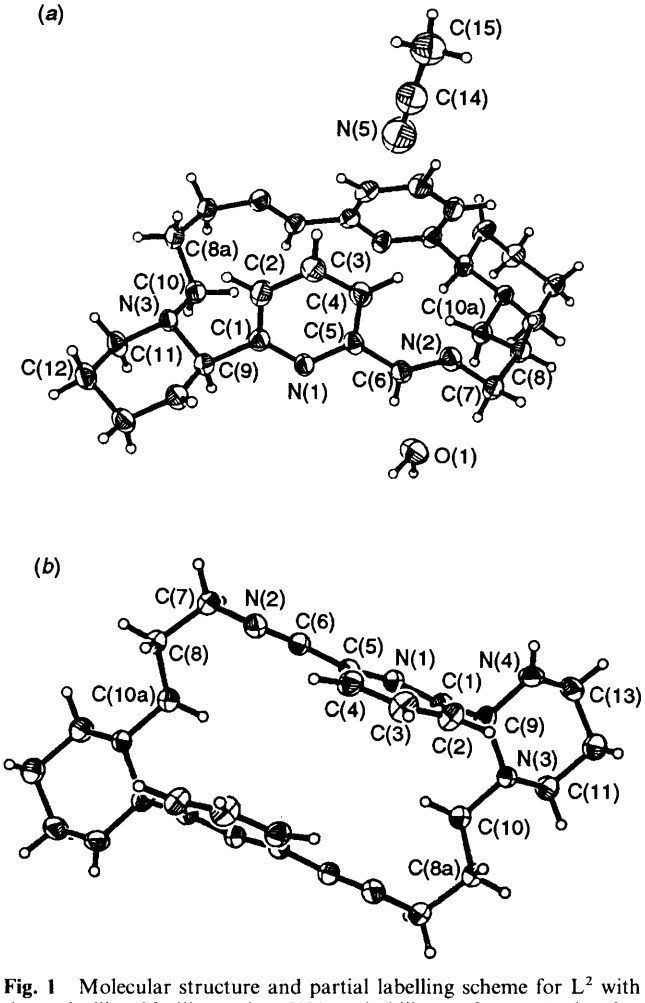


Fig. 1 Molecular structure and partial labelling scheme for L^2 with thermal ellipsoids illustrating 50% probability surfaces: (*a*) showing MeCN and H_2O of crystallization; (*b*) view along the crystallographic two-fold axis

X-Ray structural analysis of the macrocycle

X-Ray diffraction determinations show that the compound crystallizes in the space group *Fdd*2. There are 16 molecular units in the unit cell together with one molecule each of water and acetonitrile. A thermal ellipsoid plot (50% probability) with a partial labelling scheme is shown in Fig. 1. The molecule contains a crystallographic C_2 axis which passes through the midpoint of the structure. The aromatic rings are slightly twisted relative to each other and are approximately perpendicular to the aliphatic rings. In other words, the plane containing N(1) and N(2) is oriented approximately perpendicular to that containing N(3) and N(4). The adoption of this geometric configuration is most likely associated with the minimization of electron repulsion between the aromatic and aliphatic rings. The C(6)–N(2) bond length (1.267 Å) and the C(6)–N(2)–C(7) bond angle (118.7°) demonstrate that there is an imine function and consequently the pyridine imine section of the molecule is planar.

Spectra of the macrocycle

The infrared spectrum shows the expected features of an ν(N–H) stretch at 3257 cm $^{-1}$, a ν(C=N) stretch at 1647 cm^{-1} and a ν(C–N) (aromatic) split absorption at 1589 and 1573 cm^{-1}. The ^1H NMR spectrum (Fig. 2) shows a singlet at δ 8.04 and multiplets at δ 7.53 and 7.65. The multiplet at δ 7.53 is complex in nature but that at δ 7.65 is observed as a doublet of triplets. The crystal structure shows that the protons on C(3) and C(3a) are equivalent and consequently ought to give one signal in the ^1H NMR spectrum. This equivalence is observed (a, Fig. 2), however the signals pertaining to the pyridine *para* protons appear as a doublet of triplets with J = 3.4 Hz for the doublet. On close examination of this multiplet it is concluded that the doublet of triplets does not arise from coupling of protons as such but rather is a manifestation of the chair and boat conformations of the heterocyclic ring. This argument is corroborated by the observed presence of two singlets, corresponding to the proton attached to C(9) (Fig. 1), at a separation of 0.1 ppm. If the aromatic protons are used as a reference then the signals between δ 1.5 and 4.5 integrate as 14 protons, which is consistent with their association with methylene signals. The two signals at d account for the protons which are between the two aliphatic nitrogens and adjacent to the aromatic ring. The multiplets e–i have not been completely assigned, however a few conclusions are possible. Assignment was attempted through the use of the results of decoupling

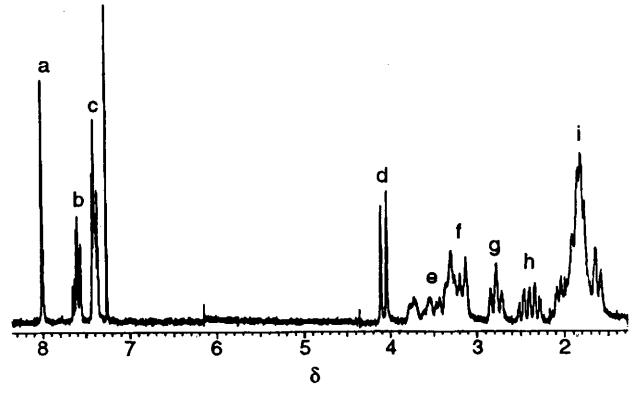


Fig. 2 Proton NMR (200 MHz) spectrum of L^2 in $CDCl_3$

experiments. The multiplets at i are probably signals due to the aliphatic ring protons while those at e and f are a complex mixture of overlapping signals from the ring and extended trimethylene groups.

The dicopper(I) complex $[Cu_2L^2][ClO_4]_2$ 3

This complex was prepared by the addition of either $[Cu(MeCN)_4]ClO_4$ or $[Cu(MeCN)_4]PF_6$ dissolved in acetonitrile to a methanolic solution of L^2. A deep red solution developed immediately, signalling formation of the dicopper(I) complex. The solid obtained from this solution is red. The positions of the maxima in the electronic absorption spectrum vary somewhat with the solvent in which the spectrum is recorded. Table 1 gives the wavelengths corresponding to the maxima for various solvents. When the electronic spectrum is recorded in methanol–acetonitrile (4:1) the compound shows absorptions at 415 and 550 nm with respective molar absorption coefficients of 3350 and 4140 $dm^3\ mol^{-1}\ cm^{-1}$. These absorptions may be assigned to copper(I)–ligand charge-transfer transitions by comparison with other similar systems.[50,54] In particular, the transitions are considered to be associated with the pyridine ring, thus implicating the involvement of pyridine nitrogen in bonding to the copper ions. The infrared spectrum (Table 2) shows ν(C=N) (imine) and ν(C=N) (pyridine) absorptions at 1630 (shifted from 1647 cm^{-1} for free L^2) and 1598 cm^{-1} respectively while a sharp ν(N–H) stretch is observed at 3231 cm^{-1}. The doublet at 1589 and 1573 cm^{-1} pertaining to the ν(C=N) stretch of the pyridine ring in free L^2 appears as a single broad absorption at 1598 cm^{-1} for the complex, presumably because of the lowering in symmetry when the pyridine nitrogen becomes bonded to copper.

The ^1H NMR spectrum of the complex at room temperature in $CDCl_3$–CD_3CN (3:1) displays regions of very ill defined signals over the entire spectral range. When the temperature is lowered to −20 °C (Fig. 3) the signals acquire greater definition and the sharper multiplets associated with the aromatic rings display a splitting pattern similar to that observed for L^2. In fact, the triplet of the pyridine *p*-proton (δ 7.85) and the doublets of the two non-equivalent protons (δ 7.00, 7.55) are clearly observed. Also the doublet at δ 7.45 reduces in intensity as the temperature is lowered from 0 to −20 °C (Fig. 3). This is attributed to through-space coupling of either the NH proton or the lone pair of electrons on nitrogen in the aliphatic ring, with the *m*-proton on the aromatic ring (discussed below). Overall, a shift in most resonances is observed indicating that the electron-density distribution has changed, relative to free L^2, due to the bonding of copper.

The similarities in spectral features between the ^1H NMR spectra of L^2 and the dicopper(I) complex leads to the proposal that it is the ring-contracted form of the macrocycle which forms the metal complex. In order to examine the feasibility of this interpretation, simulations of the complex were constructed by use of the molecular modelling program ALCHEMY,[58] starting with the coordinates for L^2 as obtained from its crystal structure. Fig. 4 shows the molecular structure which was generated. Basically four possibilities were taken into account: (1) N(1) and N(2) bonded to copper but not N(3) or N(4); (2) N(1), N(2) and N(4) bonded to copper but not N(3); (3) N(1), N(2) and N(3) bonded to copper but not N(4) and (4) N(1) and N(3) bonded but not N(2) and N(4). Only reasonable bonding modes were taken into consideration. For (2) the copper(I) ions were considered to be co-ordinated outside of the cavity of the ligand. Reasonable torsional strain energies were obtained only with (1), and only in this case the distance between the proton on C(1) and that on N(4) is close enough (≈2.00 Å) so that proposing a through-space interaction would be justifiable. The proximity of NH to an aromatic proton leading to the proposed through-space coupling exhibited in the ^1H NMR spectrum is evident in the general structure. It is acknowledged that the through-space interaction may involve the lone pair of electrons on the nitrogen atom and not necessarily the *m*-proton on the pyridine function.

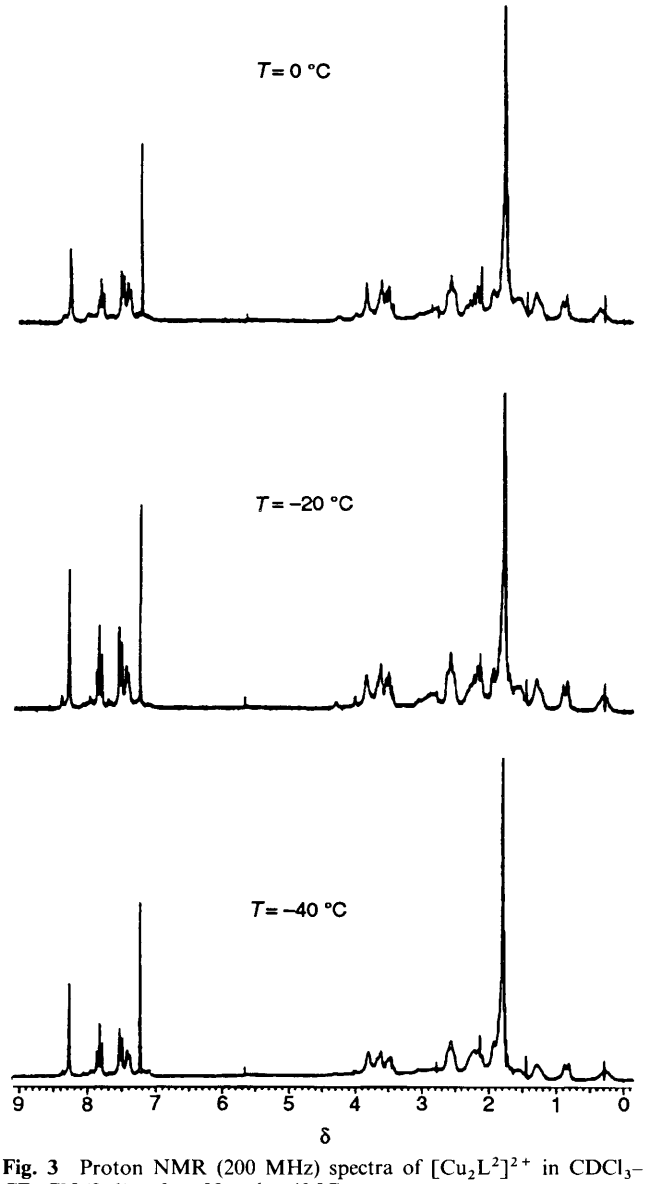


Fig. 3 Proton NMR (200 MHz) spectra of $[Cu_2L^2]^{2+}$ in $CDCl_3$–CD_3CN (3:1) at 0, −20 and −40 °C

Table 1 Wavelengths (nm) of absorption maxima of solutions of $[Cu_2L^2][ClO_4]_2$

Solvent	λ_1	λ_2
Methanol	380	505
Dichloromethane	390	510
Dimethylformamide	385	505

Reactivity of $[Cu_2L^2]^{2+}$

The dicopper(I) complex **3** absorbs oxygen in methanol–acetonitrile (3:1) at 25 °C to the extent of a 1:1 ratio (Fig. 5), with k_{obs} for the process calculated as $5.6 \times 10^{-5}\ s^{-1}$. The rate of absorption is a function of the solvent, being very slow in acetonitrile. On oxygenation, a red solution of the copper(I) complex changes to purple. The spectral changes during the oxygenation process, shown in Fig. 6, are such that the characteristic absorption bands of the complex give way to an intermediate spectrum with a band centred at 530 nm and a shoulder at 410 nm. These bands are considered to be

Table 2 Electron peramagnetic resonance, IR and mass spectrometry data for the macrocyclic complexes

Complex	$g_\perp$	IR/cm^{-1} ν(N–H)	ν(C=N)	ν(C–N)	*m/z*
$[Cu_2L^2][ClO_4]_2$	—	3231	1630	1598	586 (Cu_2L^2)
$[CuL^1][ClO_4]_2$	2.099	3296	1636	1598	523 (CuL^2)
$[Cu_2L^2]Cl_4$	2.097	3205	1636	1598	586 (Cu_2L^1)

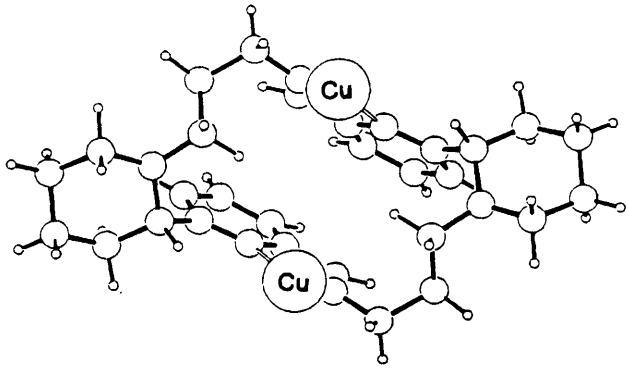


Fig. 4 Structure of $[Cu_2L^2]^{2+}$ as deduced with the molecular modelling program ALCHEMY

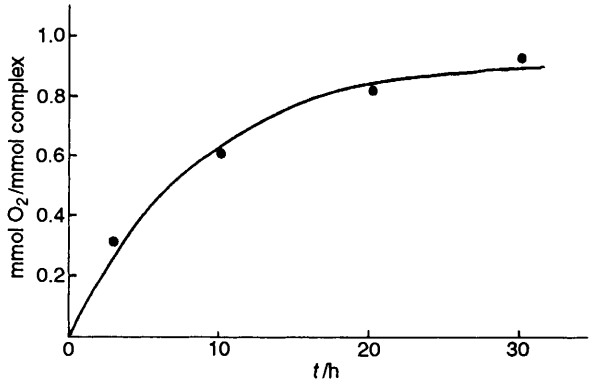


Fig. 5 Oxygen uptake by the complex $[Cu_2L^2]^{2+}$ (5.40×10^{-3} mol dm^{-3}) at 25.0 ± 0.1 °C and p_{O_2} = 1.00 atm (*ca.* 10^5 Pa) in methanol–acetonitrile (3:1)

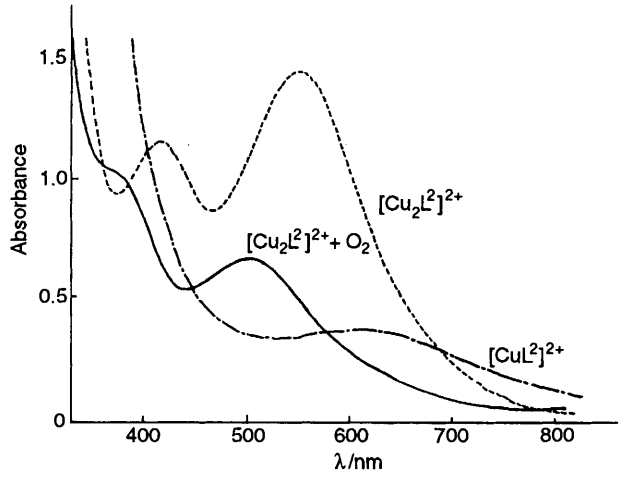


Fig. 6 Electronic absorption spectrum in methanol–acetonitrile (3:1) of $[Cu_2L^2]^{2+}$ (3.51×10^{-4} mol dm^{-3}) (– – –) and in the presence of dioxygen after 10 h (——) and 24 h (— — — —)

characteristic of the copper(I)–dioxygen complex [probably a μ-peroxo dinuclear copper(II) structure]. The ^{1}H NMR spectrum as a function of temperature shows that the complex is not oxygenated at lower temperatures. Also, no electronic absorption spectral changes were observed when **3** was treated with oxygen at low temperatures. The reason for this lack of reactivity (between 0 and −60 °C) may be related to an extensive conformational change, required for accommodation of dioxygen, which is kinetically unfavourable at lower temperatures. In this paper the dinuclear copper(I)–dioxygen complex is considered to be the same as the dinuclear μ-peroxo-dicopper(II) complex, with no implication of the structure and bonding of the μ-peroxo group to the copper atoms.

In order to investigate the reactivity of the oxygenated form of the complex, its reaction with a suitable substrate was examined. The substrate chosen was 3,5-di-*tert*-butylcatechol since this compound showed good reaction kinetics with other oxygenated copper(I) complexes.[51,52] Reactions with the substrate were performed both under catalytic and stoichiometric conditions. Under catalytic conditions the reactants were present in an atmosphere of oxygen since it was found that, similar to related systems,[51,52] catalysis is effective only when both the oxygenated copper(I) and the copper(II) forms of the complex are active. A turnover number of 25 was obtained when catalysis was initiated with **3** in an excess of dioxygen.[59] Reactions with stoichiometric conditions were performed under an atmosphere of argon with an excess of substrate. When making comparisons the initial rates of reaction were used so as to avoid the complication of oxidation by copper(II) when the copper(I)–dioxygen complex is the initiator. It has been previously shown[60] that copper(II) dinuclear complexes are active in the oxidation of substituted catechols. The initial rates for oxidations with the copper(I)–dioxygen [or peroxocopper(II)] and copper(II) complexes are determined as 1.3×10^{-4} and 4.6×10^{-3} s^{-1} mol dm^{-3}, respectively. The rate of oxidation of 3,5-di-*tert*-butylcatechol by the copper(I)–dioxygen complex is slow in contrast to the more rapid reaction when oxidation is initiated by copper(II). This is opposite to the order previously observed for dicopper complexes of related macrocycles.[51,52]

An explanation for the kinetics observed was sought by examining the reactivity of a copper(II) complex **6** prepared by a direct reaction between L^2 and copper(II) chloride. A mass spectral analysis of the resulting solid green complex (Table 2) showed that there are two copper ions per molecule and an infrared analysis (Table 2) revealed absorption bands similar to those of the dicopper(I) complex **3**. It was therefore concluded that a dinuclear copper(II) complex of the ring-contracted form L^2 was obtained. When recorded in dry methanol, the visible absorption spectrum of this complex shows one band centred around 700 nm. No changes are observed over a period of 48 h. However, when a small amount of water is added, the band maximum shifts, ultimately to 620 nm, and isosbestic points appear at 490 and 710 nm. There is also an increase in intensity of the band maximum with time (Fig 7). A blue complex displaying the same visible spectral features is obtained from L^2 with $Cu(ClO_4)_2 \cdot 6H_2O$ as the source of copper(II). The copper(II) complex reported by Drew *et al.*[61] has a chemical composition $[Cu_2L^2(H_2O)_4][ClO_4]_4$ and gives a visible spectrum with an absorption band centred on 628 nm and it is noted that this contains the ring-expanded form L^1. The similarities in the spectral features of **6** with those of the complex prepared by Drew *et al.*[61] suggest that the spectral changes of Fig. 7 represent conversion of **6** from the ring-

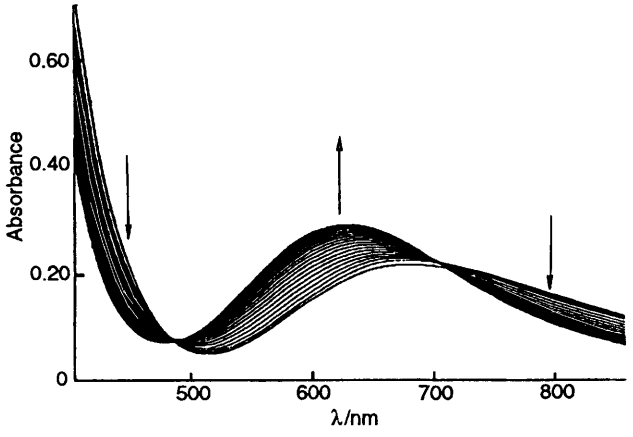


Fig. 7 Spectral changes accompanying the addition of water to $[Cu_2L^2]^{4+}$ (7.78×10^{-4} mol dm^{-3}) in methanol. Spectra recorded at 15 min intervals

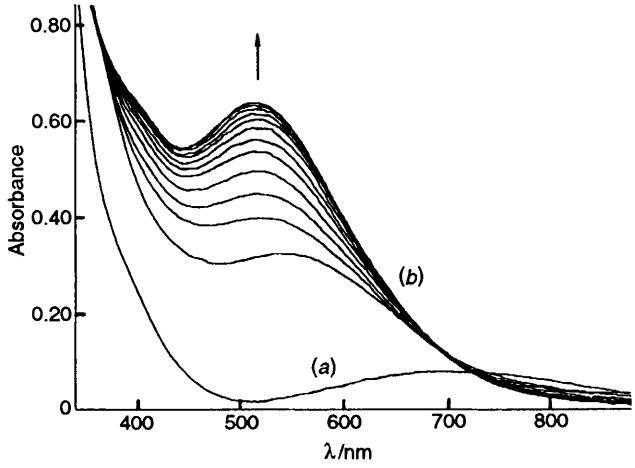


Fig. 8 Electronic absorption spectrum of $[Cu_2L^2]^{4+}$ (4.0×10^{-4} mol dm^{-3}) (ring-contracted form) (*a*) in methanol and formation of the dioxygen complex (*b*) on addition of H_2O_2 and triethylamine

contracted to the ring-expanded form, **4**. The shift of the band maximum to shorter wavelength is explained in terms of the increase in crystal-field parameter due to the bonding of the secondary amine nitrogen atoms which were not previously co-ordinated to the metal ion. It is noted that there is an increase in intensity of the band which is accounted for in terms of a lowering of symmetry due to a possible distorted-trigonal-bipyramidal disposition of co-ordinated atoms about copper(II). The change in intensity is a strong indication of a change in co-ordination about copper since the absorption band is a result of a Laporte-forbidden d–d transition. The conformational conversion is initiated in the presence of water because water is probably co-ordinated and is a more strongly held ligand than either methanol or chloride.

An electronic absorption spectrum of the copper(II) complex in the presence of H_2O_2 and triethylamine displays copper(I)–dioxygen [μ-peroxo-dicopper(II)] features, including a band at 510 nm (Fig. 8). Solvent effects and the fact that the spectrum was recorded in ethanol may account for small differences between this and the spectrum obtained when **3** is exposed to oxygen. It is unfortunate that the positions of the absorption maxima for the copper(I) complex coincide with the regions where the dioxygen complex is expected to absorb. The fact that a copper(I)–dioxygen type spectrum is obtained when H_2O_2 is added to a solution of **6** supports the idea of the presence of a peroxocopper(II) complex since it means that, for the absorbing species, there is, to some extent, charge transfer to the copper(II) ion when peroxide is added to a solution of **6**. The results in Fig. 8 also support the idea that a peroxocopper(II) complex is formed. It should be pointed out that this spectrum was not obtained for a solution of the copper(II) complex in the presence of triethylamine and in the absence of H_2O_2, therefore discounting formation of a simple copper(II)–amine complex. In addition, it is noted that almost identical spectra are obtained (Fig. 9) for the ultimate reaction product of **3** with dioxygen as well as the species finally obtained on adding hydrogen peroxide to **6**.

Slow oxygenation reflected in the changes in the absorption spectrum and the slow oxidation of 3,5-di-*tert*-butylcatachol leads to the interpretation that there are conformational changes prior to formation of the dioxygen adduct (Scheme 2). Attempts at removing the oxygen by an argon purge show that the oxygenation of complex **3** is essentially irreversible or that the dioxygen complex **4** is thermodynamically very stable. This species is converted initially into a dinuclear copper(II) complex **5**, then to a mononuclear complex. It is suggested that dioxygen undergoes a four-electron reduction to water.

The reactivities of complex **3** with PPh_3 and CO were also examined and the results are shown in the spectra in Fig. 10. As

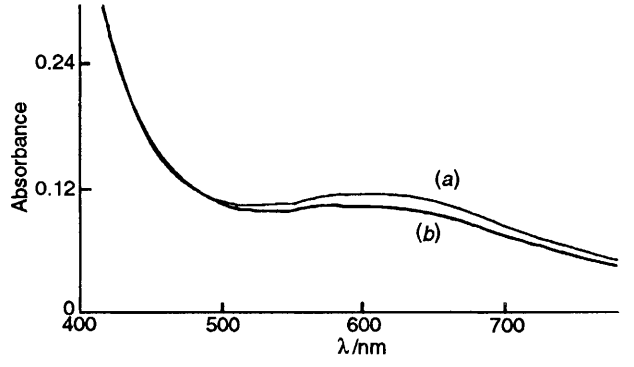


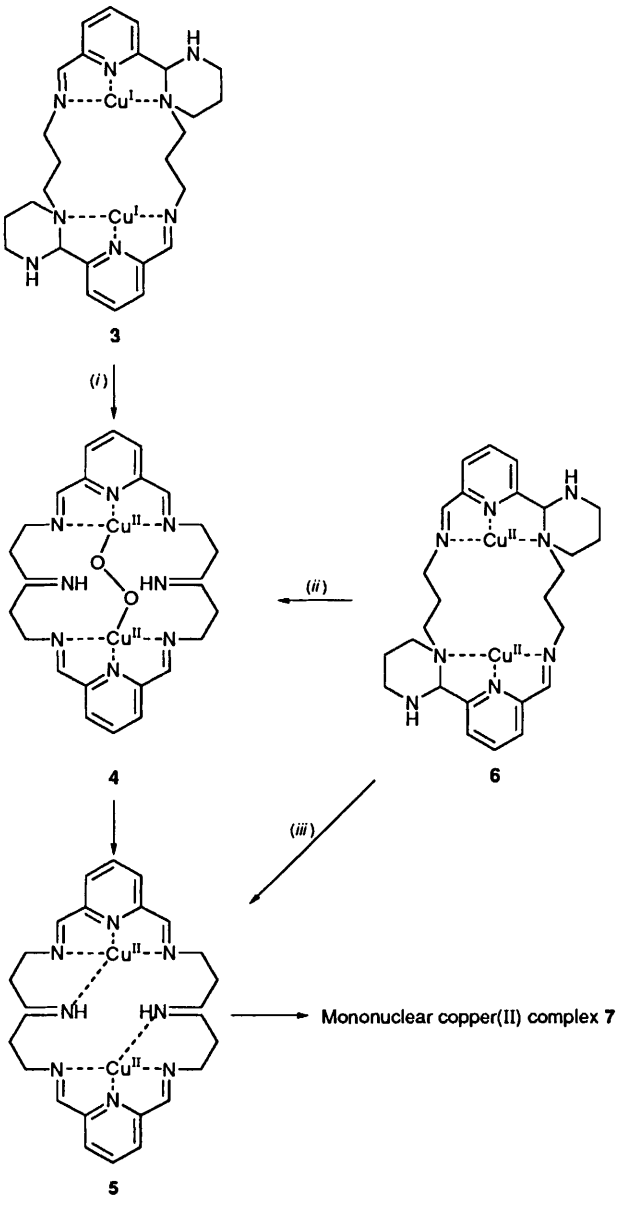
Fig. 9 Electronic absorption spectra (*a*) of the degradation product (in methanol) of $[Cu_2L^2(O_2)]^{2+}$ generated by adding H_2O_2 to $[Cu_2L^2]^{4+}$ (4.0×10^{-4} mol dm^{-3}) and (*b*) of the reaction product of $[Cu_2L^2(O_2)]^{2+}$ generated by oxygenation of $[Cu_2L^2]^{2+}$ (3.5×10^{-4} mol dm^{-3}) in methanol–acetonitrile (3:1)

is the case with dioxygen, these reactions occur at room temperature and above. Reaction of both PPh_3 and CO with **3** is indicated by the spectra and by the fact that the resulting solutions are relatively inert to oxygen uptake. The observed shifts in band maxima in relation to the original complex which is assumed to have axially co-ordinated acetonitrile (Fig. 6) is a clear indication that acetonitrile, triphenylphosphine and carbonyl all bind to copper(I). The addition of CO to a dichloromethane solution of complex **3** results in a rather dramatic change in the spectrum, producing a profile which is similar to that obtained when a solution of **3** is oxygenated (Fig. 6).

The $[Cu^{II}L^1]^{2+}$ monuclear complex 7

When a solution of complex **3** was treated with dioxygen it became purple and then, over a period of about 24 h, green. The green solid which precipitated was analysed as a mononuclear copper(II) complex of L^2. The infrared spectrum shows a broad imine stretch at 1636 cm^{-1} and the pyridine ν(C–N) absorption at 1598 cm^{-1}. The visible electronic absorption spectrum in methanol displays a broad band with a maximum at 600 nm, which indicates a square-pyramidal environment for the copper(II) ion. The results of elemental analysis are supported by mass spectral data which show an $m/z = 523$ signal assigned to the complex ion $[CuL^1]^{2+}$

In the electronic absorption spectrum of complex **6** the maximum for the dinuclear copper(II) complex is located around 720 nm. The observed shift (Fig. 7) from around 720 to 620 nm on adding water to a solution of it is interpreted as a



Scheme 2 (*i*) O_2; (*ii*) H_2O_2, NEt_3; (*iii*) water

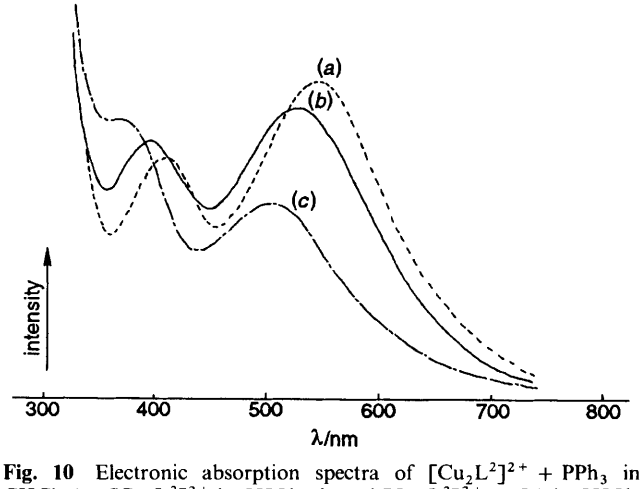


Fig. 10 Electronic absorption spectra of $[Cu_2L^2]^{2+}$ + PPh_3 in $CHCl_3$ (*a*), $[Cu_2L^2]^{2+}$ in $CHCl_3$ (*b*) and $[Cu_2L^2]^{2+}$ + CO in $CHCl_3$ (*c*)

change in conformation from the ring-contracted to the ring-expanded form. It is therefore reasonable to suggest that the ultimate product **7** of the oxygenation of **3** is of the ring-expanded form L^1. The EPR spectrum of **7** in the $g = 2$ region (Table 2) is characterized by an axial signal with hyperfine coupling, which results from the coupling of electronic and nuclear spins on copper(II). Since lines in the high-field region of the $g_\perp$ signal are absent, the $g_\parallel$ signal is interpreted as part of a four-line pattern; $g_\parallel > g_\perp$ which indicates that there is a $d_{x^2-y^2}$ ground state for the copper ion.

Conclusion

A ring-contracted form L^2 of a Schiff-base macrocycle was prepared by a non-template method. When treated with copper(I) in a 2:1 metal to ligand ratio, a dicopper(I) complex was formed. This complex reacts with dioxygen, at room temperature and above but not at low temperatures, to produce an oxygenated intermediate which is gradually converted into a mononuclear complex. The oxygenated intermediate catalyses the oxidation of 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butyl-1,2-benzoquinone. The dicopper(II) complex of L^2 was also found to be an active catalyst for the oxidation of 3,5-di-*tert*-butylcatechol. When the oxidation reactions were performed in a stoichiometric manner the initial rates of reaction with the dinuclear copper(I)–dioxygen complex and the dinuclear copper(II) complex were found to be widely different, with the latter a faster rate. Kinetic experiments and comparisons with analogous systems also suggest that a conformational rearrangement may be responsible for the slower oxidation of substrate with the copper(I) complex in the presence of dioxygen.

Experimental

Instrumentation

Proton and carbon-13 NMR spectra were recorded in CD_2Cl_2, $CDCl_3$, CD_3CN and mixed $CDCl_3$–CD_3CN solvents, compatible with the solubility of the compound under investigation, on a Varian XL 200 FT spectrometer. Chemical shifts are reported relative to tetramethylsilane as an external standard. X-Band electron paramagnetic resonance spectra were recorded on a Bruker ESP 300 spectrometer which was field calibrated with an NMR O3SM gaussmeter. Samples were prepared in acetonitrile and run at 77 K. Infrared spectra were recorded on samples prepared as KBr discs, on a Mattson Galaxy Series FTIR 300 spectrophotometer, ultraviolet–visible spectra on a Perkin–Elmer model 553 fast scan spectrophotometer. Melting points were determined on a Fisher–Johns apparatus. Mass spectral data were obtained on a VG Analytical VG-705 spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Oxygen-uptake measurements were made as previously described.[62]

Materials

Schlenk-line techniques were used to prepare copper(I) complexes in an argon atmosphere. Argon (99.98%) was dried by passage through anhydrous calcium sulfate. Solvents were deoxygenated by evacuation prior to purging with argon for at least 20 min. Deoxygenated solvents were used in experiments on oxygen uptake and all preparations and reactions involving the dicopper(I) complex. Methanol, acetonitrile, dichloromethane, dimethylformamide and nitromethane were used as anhydrous solvents and dispensed from Sure Seal™ bottles for the storage of moisture-sensitive reagents. All other reagents were of the highest grade commercially available, supplied by the Aldrich Chemical Company or Janssen Chimica and were used without further purification.

Pyridine-2,6-dicarbaldehyde. This compound was prepared by the method of Alcock *et al.*[54] The crude product was dissolved in chloroform, filtered through a bed of silica gel

Table 3 Crystal data and structure refinement for L^2

Empirical formula	$C_{10}H_{20}N_4O$
Formula weight	212.30
T/K	193(2)
Crystal system	Orthorhombic
Space group	*Fdd*2
a/Å	16.984(8)
b/Å	31.322(12)
c/Å	11.026(6)
U/Å^3	5866(5)
Z	16
D_c/Mg m^{-3}	0.962
μ/mm^{-1}	0.065
F(000)	1856
Crystal size/mm	0.35 × 0.35 × 0.35
θ range for data collection/°	2.60–25.00
Reflections collected	1440
Independent reflections	1360 (R_{int} = 0.0000)[a]
Absorption correction	ψ Scan
Maximum, minimum transmission	0.982, 0.971
Data/restraints/parameters	1360/1/178
Goodness of fit on F^2	1.034
Final R indices [$I > 2\sigma(I)$]	$R1$[b] = 0.048, $wR2$[c] = 0.129
(all data)	$R1$ = 0.054, $wR2$ = 0.134
Absolute structure parameter	8(3)
Largest difference peak and hole/e Å^{-3}	0.38, −0.18

[a] $R_{int} = [\Sigma F^2 - (F_{mean})^2]/\Sigma F^2$. [b] $R1 = \Sigma|F_o - F_c|/\Sigma F_o$. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\max(F_o^2 \text{ or } 0) + 2F_c^2]/3$.

approximately 1.5 cm in thickness, and then recrystallized from a chloroform–light petroleum (b.p. 35–60 °C) mixture. ^{1}H NMR ($CDCl_3$): δ 8.15 (m, 3 H) and 10.18 (s, 2 H).

The macrocycle L^2. This Schiff-base macrocycle was prepared in reagent-grade acetonitrile by a direct condensation method which is a minor modification of that reported by Alcock *et al.*[54] 4-Azaheptane-1,7-diamine (exactly 1.181 g, 9.00 mmol) was dissolved in acetonitrile (300 cm^3) in a round-bottomed flask (1000 cm^3). An equivalent amount (1.216 g, 9.00 mmol) of pyridine-2,6-dicarbaldehyde was dissolved separately in acetonitrile and added dropwise to the amine solution over approximately 4 h. A white finely divided crystalline product appeared approximately 3 h subsequent to complete addition of the aldehyde. Stirring was continued for 12 h and the product was then filtered off, dried and weighed (1.14 g, 26% yield). It was recrystallized by dissolving in the minimum of chloroform, adding acetonitrile and stirring until crystallization occurred, m/z = 461, $[M + H]^+$; m.p. 175–180 °C (decomp.) (Found: C, 65.50; H, 7.95; N, 24.05. Calc. for $C_{26}H_{36}N_8 \cdot 0.5CH_3CN \cdot 0.75H_2O$: C, 65.25; H, 7.95; N, 23.95%).

The dicopper(I) complex $[Cu_2L^2][ClO_4]_2$ 3. The complex was prepared on a Schlenk line which facilitates switching between vacuum and inert atmosphere. The Schiff base (0.197 g, 0.4 mmol) was dissolved in methanol (30 cm^3), under argon, in a Schlenk flask (100 cm^3). Two molar equivalents of $[Cu(MeCN)_4]ClO_4$ were dissolved in acetonitrile (10 cm^3) and added by syringe to the Schiff base, immediately forming a deep red solution. This was stirred for 1 h and then diethyl ether was added to precipitate the crude purple-red product. The product was dissolved in acetonitrile (10 cm^3) and then precipitated upon the addition of ether, m/z = 586, $[Cu_2L^2]^{2+}$ (Found: C, 37.90; H, 4.90; N, 13.45. Calc. for $C_{26}H_{36}Cl_2Cu_2N_8O_8 \cdot 2H_2O$: C, 37.95; H, 4.90; N, 13.6%).

Oxygenation of the dicopper(I) complex

The Schiff base (0.2053 g, 0.4 mmol) was dissolved in degassed chloroform (50 cm^3), under argon, and solid $[Cu(MeCN)_4]ClO_4$ (0.272 g, 0.8 mmol) was added directly to the reaction vessel. The red solution was stirred for 30 min before the argon atmosphere was removed by vacuum and the system purged with oxygen. During exposure to oxygen the solution changed from red to purple, indicating the formation of a peroxodicopper(II) complex **4**. The oxygen uptake was monitored quantitatively by recording the volume change in a gas burette as described previously.[62] After 48 h the solution became green and a pale green precipitate formed. The crude product was recrystallized from an acetonitrile–chloroform mixture, m/z = 523, $[CuL^1]^{2+}$ (Found: C, 40.80; H, 4.90; N, 14.25. Calc. for $C_{26}H_{36}Cl_2CuN_8O_8 \cdot 2.5H_2O$: C, 40.65; H, 4.85; N, 14.60%).

The oxygen uptake was also monitored spectrophotometrically. A solution 4.3 × 10^{-3} mol dm^{-3} in the complex was prepared by the addition of $[Cu(MeCN)_4]PF_6$ (0.159 g, 0.43 mmol) to a solution of the macrocycle (0.1053 g, 0.21 mmol) in methanol–acetonitrile (3:1, 50 cm^3). The solution of the complex was made up under argon in a reaction vessel which was connected to a 1 cm flow cell placed in a spectrophotometer. The reaction solution was oxygenated and then circulated through the flow cell by means of a peristaltic pump. The electronic absorption spectrum was recorded every 30 min.

Analysis of the copper(II) reaction product

The product (0.1863 g) was decomposed with *ca.* 10 mol dm^{-3} hydrochloric acid (20 cm^3) to give a pale yellow-green solution. The pH was adjusted to 7.3 and the solution then extracted with 2 × 60 cm^3 portions of chloroform. The organic phases were combined and dried over magnesium sulfate prior to removal of the solvent on a rotary evaporator. The solid residue was analysed by ^{1}H NMR spectroscopy and found to be pyridine-2,6-dicarbaldehyde.

The acidic aqueous layer was made up to 100 cm^3 and an excess of sodium sulfide then added with stirring, resulting in the formation of a black precipitate. Stirring was continued for 1 h and then the precipitate was allowed to settle over a period of 18 h. The solution was filtered and purified by use of charcoal and then filtered again. The purified solution was adjusted to pH 10 and then extracted with 2 × 50 cm^3 of chloroform. The organic phase was dried over magnesium sulfate and the solvent removed on a rotary evaporator. The residue was identified by ^{1}H NMR spectroscopy as 4-azaheptane-1,7-diamine.

Preparation of complex 6

The complex was formed by the addition of either $CuCl_2$ or $Cu(ClO_4)_2 \cdot 6H_2O$ to a methanolic solution of the macrocycle. When $CuCl_2$ was the source of copper(II) a green solution was obtained. However, with $Cu(ClO_4)_2 \cdot 6H_2O$ the precipitate is initially pale green and then subsequently becomes blue.

X-Ray crystallography for L^2

Crystals suitable for X-ray analysis were obtained by slow evaporation of an acetonitrile solution of L^2. A colourless sphere (diameter 0.35 mm) was mounted on a glass fibre with epoxy cement at room temperature and cooled to 193 K in a cold dinitrogen stream (Siemens LT-2). Preliminary examination and data collection were performed on a Siemens R3m/V X-ray diffractometer [oriented graphite monochromator; λ(Mo-Kα) = 0.710 73 Å]. A summary of crystallographic data is given in Table 3. Data were collected for 2.6 ≤ 2θ ≤ 25° [ω (Wyckoff) scans, −20 ≤ h ≤ 0, −37 ≤ k ≤ 0, −13 ≤ l ≤ 0] at 193 K. The scan width, on ω, for the data collection was 2.05°, with a variable scan rate of 3.97–13.79° min^{-1}. Three control reflections, collected every 97, showed no significant trends. Background measurement was carried out by the stationary crystal and stationary counter technique at the beginning and end of each scan. Lorentz and polarization

Table 4 Atomic coordinates ($\times 10^4$) for L^2

Atom	x	y	z
O	1579(2)	4413(1)	−477(3)
N(1)	−522(2)	4217(1)	2415(3)
N(2)	1505(2)	4314(1)	3195(3)
N(3)	−2538(2)	4491(1)	2206(3)
N(4)	−2236(2)	3729(1)	2175(3)
N(5)	0	5000	7558(7)
C(1)	−1244(2)	4228(1)	2907(4)
C(2)	−1379(2)	4310(1)	4119(4)
C(3)	−746(2)	4407(1)	4856(4)
C(4)	0(2)	4411(1)	4373(3)
C(5)	93(2)	4301(1)	3159(3)
C(6)	879(2)	4279(1)	2588(4)
C(7)	2254(2)	4302(1)	2561(4)
C(8)	2670(2)	4732(1)	2667(4)
C(9)	−1923(2)	4158(1)	2020(3)
C(10)	−2209(2)	4922(1)	2017(3)
C(11)	−3196(2)	4421(1)	1344(4)
C(12)	−3540(2)	3977(1)	1495(4)
C(13)	−2897(2)	3648(1)	1360(4)
C(14)	0	5000	8582(7)
C(15)	0	5000	9906(7)

corrections were applied to 1440 reflections. An absorption correction was applied. A total of 1197 unique reflections, with $|I| \geqslant 2.0\ \sigma(I)$, were used in further calculations.

Crystal structure solution and refinement. The structure was solved by direct methods (SHELXTL PLUS program packages).[63] Full-matrix least-squares anisotropic refinement on F^2 for all non-hydrogen atoms [least-squares parameters = 178; quantity minimized $\Sigma w(F_o - F_c)^2$; $w = 1.0$] yielded $R1 = 0.048$ and $S = 1.03$ at convergence (largest $\Delta/\sigma = 0.087$; mean $\Delta/\sigma = 0.0015$; largest positive and negative peaks in the final Fourier-difference map = 0.38 and −0.18 e Å^{-3}). The Hamilton significance test[64] indicated that the correct absolute configuration was chosen. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å^2. Neutral atom scattering factors and anomalous scattering correction terms were taken from ref. 65 and ref. 66 respectively. Positional parameters for the non-hydrogen atoms are given in Table 4.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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References

1 *Bioinorganic Chemistry of Copper*, eds. K. D. Karlin and Z. Tyeklar, Chapman and Hall, New York, 1993.
2 K. D. Karlin, Z. Tyeklar and A. D. Zuberbuhler, in *Bioinorganic Catalysis*, ed. J. Reedijk, Marcel Dekker, New York, 1993, p. 216.
3 E. I. Solomon, F. Tuczek, D. E. Root and C. A. Brown, *Chem. Rev.*, 1994, **94**, 827.
4 K. D. Karlin, *Science*, 1993, **261**, 701.
5 E. I. Solomon, M. J. Baldwin and M. Lowery, *Chem. Rev.*, 1992, **92**, 521.
6 R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
7 N. Kitajima and Y. Moro-oka, *Chem. Rev.*, 1994, **94**, 737.
8 N. Wei, N. N. Murthy and K. D. Karlin, *Inorg. Chem.*, 1994, **33**, 6093.
9 K. D. Karlin, M. S. Nasir, B. I. Cohen, W. Cruse, S. Kaderli and A. D. Zuberbuhler, *J. Am. Chem. Soc.*, 1994, **116**, 1324.
10 N. Wei, N. N. Murthy, Q. Chen, J. Zubieta and K. D. Karlin, *Inorg. Chem.*, 1994, **33**, 1953.
11 N. Wei, N. N, Murthy, Z. Tyeklar and K. D. Karlin, *Inorg. Chem.*, 1994, **33**, 1177.
12 T. N. Sorrell, M. L. Garrity, J. L. Richards and P. S. White, *Inorg. Chim. Acta*, 1994, **218**, 103.
13 Z. Tyeklar, R. R. Jacobson, N. Wei, N. N. Murthy, J. Zubieta and K. D. Karlin, *J. Am. Chem. Soc.*, 1993, **115**, 2677.
14 I. Sanyal, N. N. Murthy and K. D. Karlin, *Inorg. Chem.*, 1993, **32**, 5330.
15 F. Jiang, K. D. Karlin and J. Peisach, *Inorg. Chem.*, 1993, **32**, 2576.
16 N. Kitajima, K. Fugisawa, S. I. Hikichi and Y. Moro-oka, *J. Am. Chem. Soc.*, 1993, **115**, 7874.
17 M. Mahroof-Tahir and K. D. Karlin, *J. Am. Chem. Soc.*, 1992, **114**, 7599.
18 A. Nanthakumar, M. Sarwar Nasir, K. D. Karlin, N. Ravi and H. B. Hanh, *J. Am. Chem. Soc.*, 1992, **114**, 6564.
19 M. Mahroof-Tahir, N. N. Murthy, K. D. Karlin, N. J. Blackburn, S. N. Shaikh and J. Zubieta, *Inorg. Chem.*, 1992, **31**, 3001.
20 J. Ling, A. Farooq, A. K. D. Karlin, T. M. Loehr and J. Sanders-Loehr, *Inorg. Chem.*, 1992, **31**, 2552.
21 I. Sanyal, M. Mahroof-Tahir, M. Sarwar Nasir, P. Ghosh, B. I. Cohen, Y. Gultneh, R. W. Cruse, A. Farooq, K. D. Karlin, S. Liu and J. Zubieta, *Inorg. Chem.*, 1992, **31**, 4322.
22 K. D. Karlin, Z. Tyeklar, A. Farooq, M. S. Haka, P. Ghosh, R. W. Cruse, Y. Gultneh, J. C. Hayes, P. J. Toscano and J. Zubieta, *Inorg. Chem.*, 1992, **31**, 1436.
23 N. Kitajima, K. Fujisawa, C. Futimoto, Y. Moro-oka, S. I. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi and A. Nakamura, *J. Am. Chem. Soc.*, 1992, **114**, 1277.
24 N. Kitajima, *Adv. Inorg. Chem.*, 1992, **39**, 1.
25 R. R. Jacobson, Z. Tyeklar, K. D. Karlin and J. Zubieta, *Inorg. Chem.*, 1991, **30**, 2035.
26 K. D. Karlin, N. Wie, B. Jung, S. Kaderli and A. D. Zuberbuhler, *J. Am. Chem. Soc.*, 1991, **113**, 5868.
27 I. Sanyal, R. W. Strange, N. J. Blackburn and K. D. Karlin, *J. Am. Chem. Soc.*, 1991, **113**, 4692.
28 N. Kitajima, T. Koda, S. Hashimoto, T. Kitagawa and Y. Moro-oka, *J. Am. Chem. Soc.*, 1991, **113**, 5664.
29 T. N. Sorrell and M. L. Garrity, *Inorg. Chem.*, 1991, **30**, 210.
30 T. N. Sorrell, V. A. Vankai and M. L. Garrity, *Inorg. Chem.*, 1991, **30**, 207.
31 T. N. Sorrell and V. A. Vankai, *Inorg. Chem.*, 1990, **29**, 1687.
32 M. A. Elsayed, A. Eltouky, K. Z. Ismael and A. A. Elmaradne, *Inorg. Chim. Acta*, 1990, **177**, 155.
33 K. D. Karlin, A. Sanyal, A. Farooq, R. R. Jacobson, S. N. Shaikh and J. Zubieta, *Inorg. Chim. Acta*, 1990, **174**, 13.
34 E. Asato, S. Hashimoto, N. Matsumoto and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1990, 1741.
35 Z. Tyeklar and K. D. Karlin, *Acc. Chem. Res.*, 1989, **22**, 241.
36 N. Kitajima, F. Fujisama, Y. Moro-oka and K. Toriumi, *J. Am. Chem. Soc.*, 1989, **111**, 8975.
37 R. R. Jacobson, Z. Tyeklar, K. Farooq, K. D. Karlin, S. Liu and J. Zubieta, *J. Chem. Soc.*, 1988, **110**, 3690.
38 N. Kitajima, T. Koda, S. Hashimoto, T. Kitagawa and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1988, 151.
39 K. D. Karlin, R. W. Cruse, Y. Gultneh, A. Farooq, J. C. Hayes and J. Zubieta, *J. Am. Chem. Soc.*, 1987, **109**, 2668.
40 L. Casella and L. Rigoni, *J. Chem. Soc., Chem. Commun.*, 1985, 1668.
41 K. D. Karlin, R. W. Cruse, Y. Gultneh, J. C. Hayes and J. Zubieta, *J. Am. Chem. Soc.*, 1984, **106**, 8372.
42 Y. Nishina, K. Takahashi, H. Kuramoto and S. Kida, *Inorg. Chim. Acta*, 1981, **54**, L103.
43 F. Tuczek and E. I. Solomon, *J. Am. Chem. Soc.*, 1994, **116**, 6916.
44 E. I. Solomon, M. J. Baldwin and M. Lowery, *Chem. Rev.*, 1992, **92**, 521.
45 M. J. Baldwin, D. G. Root, J. E. Pate, K. Fujisawa, N. Kitajima and E. I. Solomon, *J. Am. Chem. Soc.*, 1992, **114**, 10 421.
46 P. K. Ross and E. I. Solomon, *J. Am. Chem. Soc.*, 1991, **113**, 3246.
47 I. Bytheway and M. B. Hall, *Chem. Rev.*, 1994, **94**, 639.
48 M. Lundeen and A. B. Anderson, *Polyhedron*, 1993, **12**, 739.
49 M. P. Ngwenya, D. Chen, A. E. Martell and J. Reibenspies, *Inorg. Chem.*, 1991, **30**, 2732.
50 D. A. Rockcliffe and A. E. Martell, *J. Mol. Catal.*, 1995, **99**, 87, 101.
51 D. A. Rockcliffe and A. E. Martell, *Inorg. Chem.*, 1993, **32**, 3143.
52 D. A. Rockcliffe and A. E. Martell, *J. Mol. Catal.*, in the press.
53 M. Becker, S. Schindler and R. van Eldik, *Inorg. Chem.*, 1994, **33**, 5370.
54 N. W. Alcock, R. G. Kingston, P. More and C. Pierpont, *J. Chem. Soc., Dalton Trans.*, 1984, 1937.
55 M. G. B. Drew, M. McCann and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1868.

56 M. G. B. Drew, J. Nelson and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1678.
57 H. Adams, N. A. Bailey, D. E. Fenton, R. G. Good, R. Moody, O. Cecilin and R. J. De Barbarin, *J. Chem. Soc., Dalton Trans.*, 1988, 207.
58 ALCHEMY II, molecular modelling program TRIPOS Associates, St. Louis, MO, 1988.
59 D. A. Rockcliffe and A. E. Martell, *J. Mol. Cat.*, in the press.
60 N. Oishi, Y. Nishida, K. Ida and S. Kida, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2847.
61 M. G. B. Drew, B. P. Murphy, J. Nelson and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1987, 873.
62 D. Chen and A. E. Martell, *Inorg. Chem.*, 1993, **32**, 3143.
63 G. M. Sheldrick, SHELXTL PLUS, (version 4.11), University of Göttingen, 1990.
64 W. C. Hamilton, *Acta Crystallogr.*, 1965, **17**, 502; HAMM, L. Daniels and L. Falvello, Texas A & M University, College Station, TX, 1987.
65 *International Tables for X-Ray Crystallography*, eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4, p. 99.
66 *International Tables for X-Ray Crystallography*, eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4, p. 149.

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