ELSEVIER

Journal of Molecular Catalysis A: Chemical 129 (1998) 19–26

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Cu(I) and Cu(II) dinuclear complexes of a New Hexaaza Schiff base dinucleating macrocyclic ligand and their oxygenation chemistry

Antoni Llobet [a], Arthur E. Martell [b,*], María A. Martínez [a]

[a] *Departament de Química, Universitat de Girona, Campus Montilivi, 17071 Girona, Spain*
[b] *Department of Chemistry, Texas A and M University, College Station, TX 77845-3255, USA*

Received 12 June 1996; accepted 2 July 1997

Abstract

A new macrocyclic hexaaza binucleating Schiff base ligand 3,7,11,19,23,27-hexaazatricyclo[27.3.1.1^{13,17}]tetratriaconta-1(32),2,11,13(14),15,17(34),18,27,29(33),30-decaene (MX_2DIPN_2 or **1**) has been prepared in good yield by direct condensation of *m*-phthalaldehyde and 3,3′-iminobis(propylamine). MX_2DIPN_2 forms a dinuclear Cu(I) complex that reacts with molecular oxygen to form $[(MX_2DIPN_2)Cu_2(O_2)]^{2+}$. This oxygen complex does not undergo intramolecular oxygen insertion into the phenyl ring in sharp contrast with its macrocyclic analog $[(MX_2DIEN_2)Cu_2(O_2)]^{2+}$ (MX_2DIEN_2 is the macrocyclic ligand formed by the condensation of *m*-phthalaldehyde and diethylenetriamine), the result of the enlargement of the macrocyclic cavity. It has been shown that $[(MX_2DIPN_2)Cu_2(O_2)]^{2+}$ is an efficient and selective catalyst for the oxidation of 3,5-di-*t*-butylcatechol to 3,5-di-*t*-butyl-1,2-benzoquinone in the presence of 1 atm O_2. Furthermore, the measured initial rate constants reveal that it reacts much faster than any of the related macrocyclic systems reported to date.

Keywords: Macrocyclic dinuclear Cu(I) complex; Macrocyclic dinuclear Cu(II) complex; Isophthalaldehyde; Ditrimethylenetriamine; Catalytic oxidation; 3,5-ditertiarybutylcatechol; 3,5-ditertiarybutyl-1,2-benzoquinone

1. Introduction

Dinuclear copper complexes containing two metal centers in close proximity are the subject of recent extensive investigation since this structural unit is involved in a variety of important biochemical processes, such as oxygen transport and oxygen activation by oxidase and monooxygenase enzymes [1–13]. The active sites of hemocyanin and tyrosinase posses this type of molecular arrangement and are thought to be relatively similar based on spectroscopic evidence [11], in sharp contrast with their different biological functions.

Several dinuclear copper complexes with different type of ligands [14–27] have been prepared and characterized in order to understand the relationship between the geometry around the copper metal atoms, the mode of coordination of the oxygen ligand and its reactivity and spectroscopic properties [1,14–28].

* Corresponding author. Tel.: (1-409) 845-2011; Fax: (1-409) 845-4719.

1381-1169/98/$19.00
PII S1381-1169(97)00136-2

The work in this laboratory has focused on the development of hemocyanin and tyrosinase models based on dinucleating macrocyclic type of ligands [29–36]. Such ligands had been chosen because of their inherent stability [37] and because the rigidity imposed on the metal centers permits examination of the role of the metal–metal separation in combining with molecular oxygen. This paper reports the synthesis and spectroscopic characterization of new dinuclear Cu(I) and Cu(II) complexes containing the macrocyclic ligand MX_2DIPN_2 together with their reactivity with oxygen in the presence and absence of 3,5-di-*t*-butylcatechol (3,5-DTBC).

2. Experimental

2.1. Instrumentation

Electronic spectra were recorded on a Perkin Elmer Model 553 fast-scan spectrophotometer using matched 1.000 ± 0.001 cm path length cells. ^{1}H- and ^{13}C-NMR were recorded in a Varian XL 200 FT spectrometer operating at 200 MHz. Thermogravimetric analyses were carried out with a General V4.OD DuPont 2000 operating under nitrogen at a speed of 5° per minute from 25 to 1000°C.

2.2. Materials

All reagents were ACS grade and were used without further purification. Argon (99.98% AIRCO) was prescrubbed with a 3% solution of pyrogallol in 0.8 M NaOH and dried by passage through H_2SO_4 and Drierite ($CaSO_4$). Solvents were deoxygenated by purging with argon for approximately 30 min. The preparation of Cu(I) and Cu(II) complexes and all reactions were carried out under argon. MX_2DIPN_2, **1** was prepared as previously described [38].

2.3. Oxygenation of the dinuclear Cu(I) Schiff base complex 3 and its degradation

A 900 mg (2.417 mmol) sample of $[Cu^I(CH_3CN)_4](PF_6)$ was added into a flask containing 600 mg (1.208 mmol) of MX_2DIPN_2 dissolved in 190 ml of CH_2Cl_2 under magnetic stirring. The resulting orange solution was then stirred for one hour under argon. A stream of air was bubbled through it overnight, upon which the orange solution turned green. The volume was then reduced to dryness with a rotary evaporator and the solid obtained was completely redissolved in 10 ml of 6 M HCl. Afterwards, the acidic solution was extracted with $CHCl_3$ (3×50 ml). The volume of the organic phase was then reduced to dryness and 310 mg (96% recovery) of *m*-phthalaldehyde was obtained as a white solid. ^{1}H-NMR ($CDCl_3$): δ (ppm from TMS) 7.75 (t, 1H), 8.18 (d, 2H), 8.40 (s,1H), 10.12 (s, 2H).

2.4. Catalytic oxidation of 3,5-di-t-butylcatechol (3,5-DTBC) with 3(O_2) as catalyst

A 14.9 mg (40 μmol) sample of $[Cu^I(CH_3CN)_4](PF_6)$ was added to a flask containing 9.93 mg (20 μmol) of MX_2DIPN_2 dissolved in 50 ml of CH_3CN:CH_3OH (1:4; v:v) and stirred under argon for 15 min. Then 88.8 mg (0.40 mmol) of 3,5-DTBC were added and the solution was stirred for an additional 5 min. Oxygen was then bubbled through the solution for 5 min and then kept at 1 atm O_2 pressure over the solution. The reaction was allowed to take place until the oxygen consumption had ceased. The 3,5-di-*t*-butyl-1,2-benzoquinone (75.6 mg, 87% yield) oxidation product was then isolated by evaporation of the solvent under reduced pressure followed by column chromatography on silica gel (grade 62 special) using $CHCl_3$ as eluant. ^{1}H-NMR ($CDCl_3$): δ (ppm from TMS) 1.21 (s, 9H), 1.26 (s, 9H), 6.20 (d, 1H), 692 (d, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm from TMS) 27.87 (CH_3), 29.20 (CH_3), 35.47 ($C(CH_3)_3$), 36.02 ($C(CH_3)_3$), 122.08 (CH), 133.46 (CH), 149.93 ($CC(CH_3)_3$), 163.32($CC(CH_3)_3$), 180.03 (CO), 181.12 (CO).

2.5. Cu^{II} catalytic oxidation of 3,5-DTBC

This reaction was carried out in the same manner as previously described for **3**, except

that $CuCl_2.2H_2O$ was used instead of the Cu(I) complex.

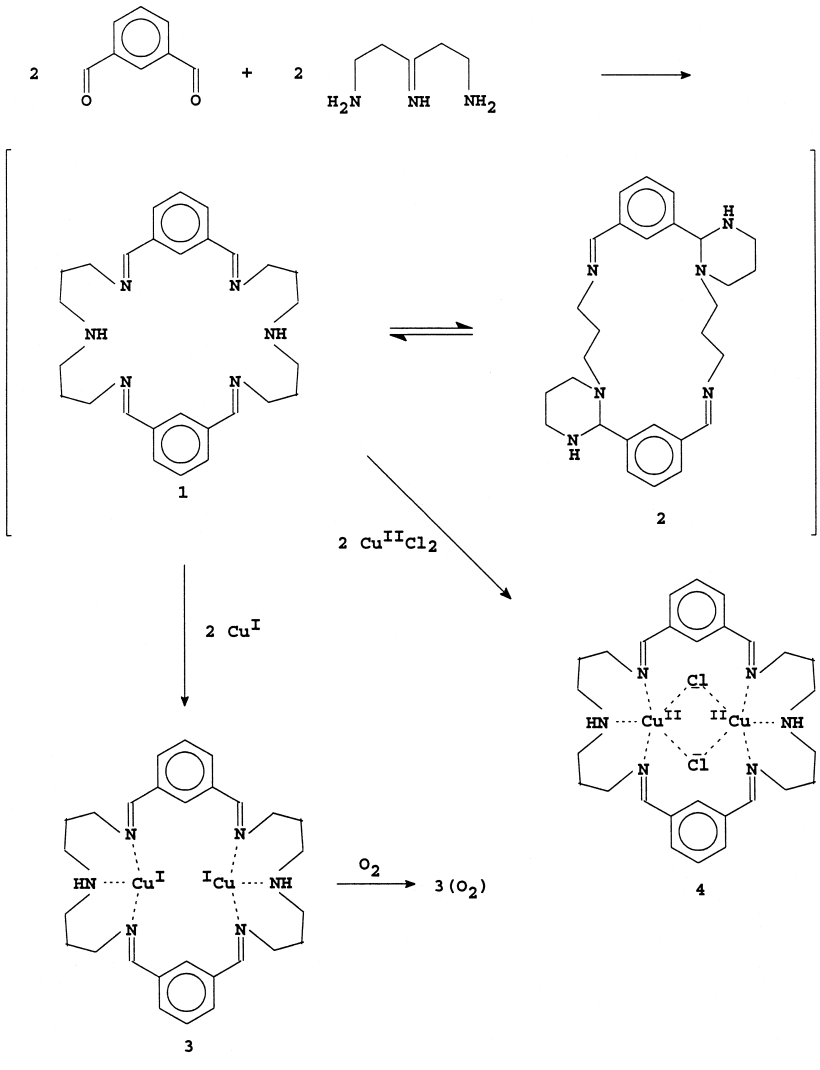
2.6. Kinetic studies

Kinetic studies were performed in a 100 ml water-jacketed reaction vessel containing inlet and outlet tubes for gases. The vessel was thermostated at 25.0 ± 0.1°C and connected to a quartz flow cell of 1.000 cm path length. The flow cell was placed in the cell holder compartment of the UV-vis spectrophotometer, and the reaction solution was circulated through the flow cell by means of a peristaltic pump. The spectral changes of the solution were monitored over the wavelength range 300–800 nm.

3. Results and discussion

3.1. Synthesis and characterization of the Schiff base, *1*, and its copper complexes

The non-template procedure for preparing the macrocyclic Sciff base ligand **1**, shown in Scheme 1, is straightforward and gives a good



Scheme 1.

yield. This Schiff base is obtained as a microcrystalline solid that contains both water and acetonitrile of solvation, a fact that is not unusual for this type of compound [39,40] as demonstrated by X-ray diffraction analysis. The extent of solvation was inferred from the elemental analysis and corroborated by thermogravimetric analysis. An initial 7.5% weight loss occurs in the temperature range 200–270°C preceding the decomposition of the Schiff base ligand, suggesting that the solvated molecules are trapped within the crystalline network of the macrocyclic ligand. The ^{1}H and ^{13}C NMR spectra of **1** are both complex, indicating the existence of isomers in equilibrium, a phenomenon that has also been observed for related systems [29–34,39,40] (Scheme 1).

Reaction of the Schiff base **1** with two equivalents of Cu(I) leads to the formation of the light-orange binuclear copper(I) complex $[(MX_2DIPN_2)Cu^{I}_2]^{2+}$, **3**, as indicated in Scheme 1. This reaction proceeds in a manner very analogous to similar dinucleating macrocyclic ligands [29–35] with Cu(I). The spectroscopic properties displayed by the dinuclear complex **3** ($\lambda_{max} = 420$ nm, $\varepsilon = 937\ M^{-1}\ cm^{-1}$, Fig. 1) are also very much like those of dinuclear Cu(I) complexes reported previously with similar macrocyclic ligands.

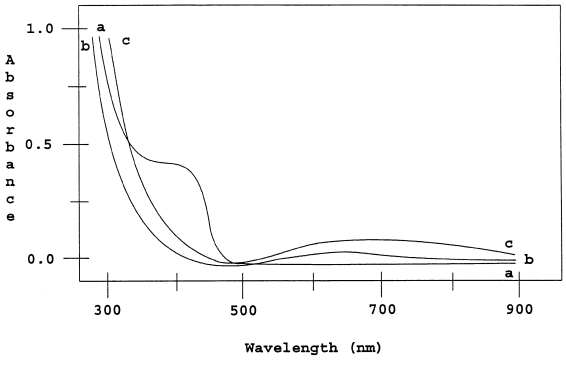
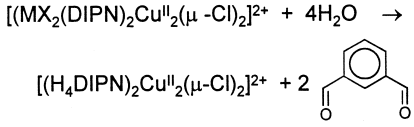


Fig. 1. UV-visible spectra of (a) $[(MX_2DIPN_2)Cu^{I}_2]^{2+}$ **3**, (b) $[(MX_2DIPN_2)Cu^{II}_2(\mu\text{-}OMe)_2]^{2+}$ **5**, (c) $[(MX_2DIPN_2)Cu^{II}_2(m\text{-}Cl)_2]^{2+}$ **4**. The spectra were recorded in MeCN:MeOH(1:4; v:v) and the concentration of the complexes was 0.40 mM.

Addition of a methanolic solution of $CuCl_2 \cdot 2H_2O$ to a methanolic solution that contains half the equimolecular amount of the Schiff base MX_2DIPN_2, results in the immediate formation a blue dinuclear copper complex, presumably $[(MX_2DIPN_2)Cu^{II}_2(\mu\text{-}Cl)_2]^{2+}$, **4**, (broad band 620–790, $\varepsilon_{705} = 204\ M^{-1}\ cm^{-1}$, Scheme 1 and Fig. 1) in agreement with the spectroscopic properties reported for amine complexes like $[(H_4DIEN)_2Cu^{II}_2(\mu\text{-}Cl)_2]^{2+}$ [41] and $[(H_4DIPN)_2Cu^{II}_2(\mu\text{-}Cl)_2]^{2+}$ [42] which also contain the $Cu(\mu\text{-}Cl)_2Cu$ core. It is also in agreement with the reactivity of **4**, since its hydrolysis yields quantitatively $[(H_4DIPN)_2Cu^{II}_2(\mu\text{-}Cl)_2]^{2+}$,

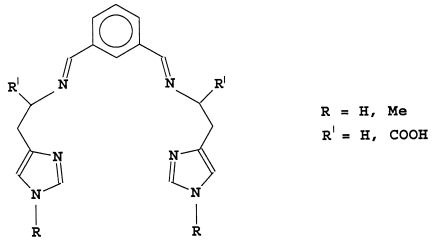


3.2. Oxygenation of the Cu(I) dinuclear complex

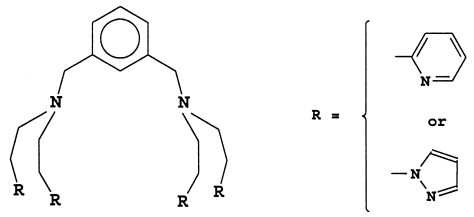
Exposing **3** to molecular oxygen at 25°C causes the dinuclear copper orange solution to slowly turn green. The green complex has the spectral features associated with the totally degraded oxygen complex and thus is considered to be $[(MX_2DIPN_2)Cu^{II}_2(\mu\text{-}OMe)_2]^{2+}$, **5**, found in other related macrocyclic systems studied previously by this group [32,33]. The spectrum consists of a very intense band at the UV region and a very weak and broad band at 620 nm ($\varepsilon_{620} = 123\ M^{-1}\ cm^{-1}$; curve (b), Fig. 1). No long-lived intermediate species could be spectroscopically detected in the present case even when the oxygenation reaction was carried out at 5°C, in contrast to related systems studied previously [32–34]. However, by the use of a stopped flow UV-vis spectrophotometer an intermediate (presumably the dinuclear Cu(I)-dioxygen adduct) was detected [36].

Oxygenation of the $[(MX_2DIEN_2)Cu^I_2]^{2+}$ complex (MX_2DIEN_2 is the corresponding macrocyclic Schiff base ligand obtained by the condensation of *m*-phthalaldehyde and diethylenetriamine) under the same conditions as reported here leads to hydroxylation of the macrocyclic aromatic ring. In sharp contrast, oxygenation of $[(MX_2DIPN_2)Cu^I_2]^{2+}$ does not hydroxylate the macrocyclic aromatic ring at all in any of the solvents in which the reaction was performed (CH_2Cl_2, CH_3OH or CH_3CN). The lack of hydroxylation was evidenced by the nearly quantitative recovery of the initial dialdehyde, *m*-phthaldehyde, upon treating the final complex with 6 M HCl. Space-filling models show that for MX_2DIEN_2, the macrocyclic cavity is relatively small and once it has accommodated the two copper metal atoms, two phenyl hydrogen atoms point towards the center of its cavity. Thus when the dioxygen complex is formed, those hydrogen atoms easily interact with the bridging dioxygen. In MX_2DIPN_2, there are four more $-CH_2-$ units in the bridging arms bonded to the imine nitrogen atoms, significantly increasing the size of the macrocyclic cavity with respect to MX_2DIEN_2. In this case the phenyl hydrogen atoms are too far from the bonded dioxygen and therefore intramolecular hydroxylation does not occur.

Casella and coworkers [43] studied a family of dinucleating imine type ligands (type A ligands)



derived from the condensation of benzene-1,3-dicarboxaldehyde and two molecules of substituted histamine or histidine. Those ligands are capable of forming dinuclear Cu(I) complexes which bind dioxygen. They showed that the intramolecular hydroxylation of the phenyl ring could be controlled by choosing the appropriate solvent. Sorrell and coworkers [44] studied xylyl type dinucleating ligands substituted with either pyrazolyl or pyridyl groups (type B ligands).



Those ligands form dinuclear Cu(I) complexes and some are also capable of binding dioxygen. They demonstrated that the intramolecular hydroxylation of the phenyl ring depends on the substituent. With pyrazolyl type of substituents the hydroxylation reaction does not proceed whereas when using pyridyl as the substituent the intramolecular hydroxylation reactions do take place. Karlin and coworkers [45] have investigated the effects caused by electron donor and electron withdrawing groups attached to the xylyl group of the B type of ligands, containing pyridyl as substituents, with regard to the intramolecular hydroxylation reactions. They have shown that the former reaction does occur in all these type of complexes and is clearly favored by electron donors and disfavored by electron withdrawing groups. Recently Mukherjee and coworkers [46], have reported a new system containing a variation of the type B ligands with pyridyl substituents that is also capable of producing an intramolecular hydroxylation of the phenyl ring. In this case, one of the diethylenepyridine arms bonded to the amino group is substituted by a simple methyl group.

The macrocyclic dinuclear copper(I) complexes studied by our group constitute an example of how the intramolecular hydroxylation reaction can be controlled by carefully choosing the appropriate geometry, nature and cavity size of the macrocyclic ligand. Thus, with a 24

member ring macrocyclic ligand MX_2DIEN_2 the intramolecular hydroxylation reaction occurs whereas the opposite happens with a 28 member ring macrocyclic ligand MX_2DIPN_2; a similar ligand but with a larger cavity size.

3.3. Oxidation of 3,5-di-t-butylcatechol (3,5-DTBC)

3,5-Di-*t*-butyl-1,2-benzoquinone (3,5-DTBQ) was the only product obtained from the reaction of either the dinuclear Cu(I) complex **3**, or the dinuclear Cu(II) complex **4**, with 3,5-DTBC under 1 atm O_2; no oxidatively coupled products were detected.

The system containing the Cu(I) complex **3**, (**3** 0.4 mM/O_2 1 atm/3,5-DTBC 8 mM in 50 ml of CH_3CN:CH_3OH 1:4) yielded 6.96 mM 3,5-DTBQ. This represents an efficiency of 87.0% with respect to the initial substrate and 17.4 redox cycles. Fig. 2 shows the time-dependence of the 420 nm band assignable to the quinone with the above mentioned Cu(I) and the Cu(II) complexes as catalysts. The calculated initial rates of formation are reported in Table 1 along with other initial rates for related macrocyclic systems.

On the basis of the results obtained in this and previous work with similar macrocyclic

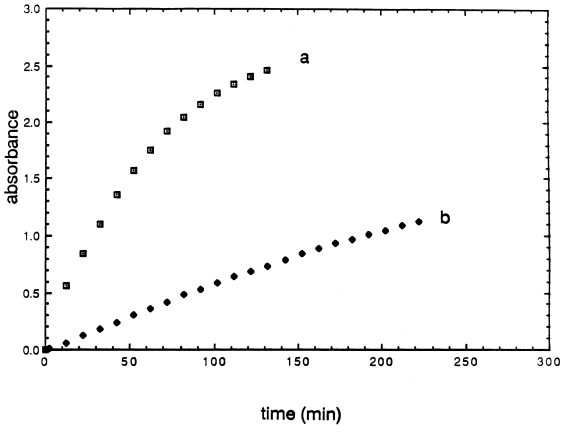


Fig. 2. Time dependence of the catalytic formation of 3,5-DTBQ in the presence of (a) $[(MX_2DIPN_2)Cu^I_2]^{2+}$–$O_2$(3($O_2$)) and (b) $[(MX_2DIPN_2)Cu^{II}_2(\mu\text{-Cl})_2]^{2+}$ **4**, both under 1 atm oxygen and monitored at 420 nm. (t = 25°C; solvent = MeCN:MeOH(1:4; v:v)).

Table 1
Initial rates in the oxidation of 3,5-DTBC to 3,5-DTBQ by LCu^I_2-dioxygen and LCu^{II}_2

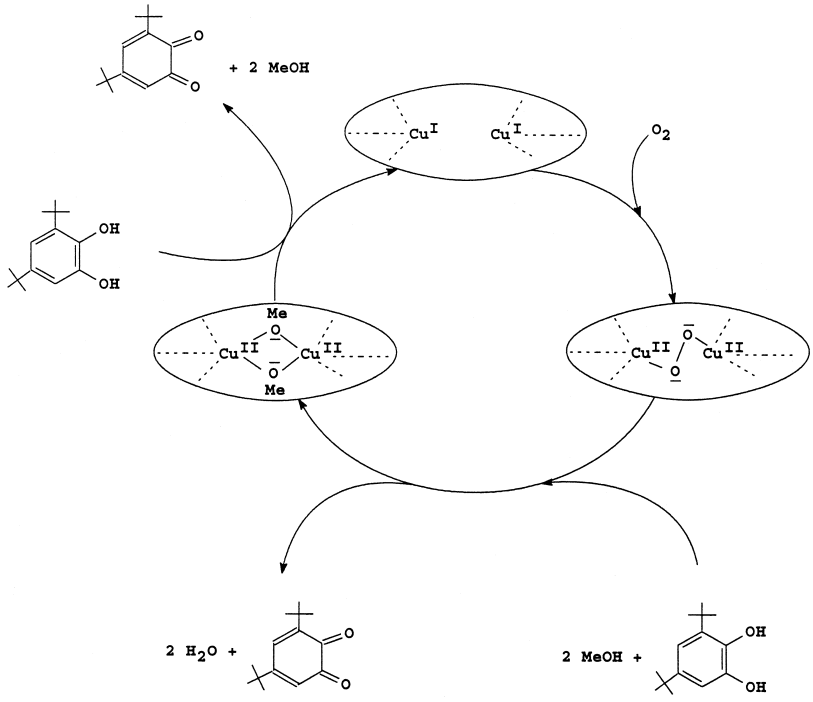
Macrocyclic ligand L[a]	Initial, pseudo-first order rate, Ms^{-1}		Refs.
	$LCu^I_2 + O_2$	LCu^{II}_2	
FD_2DIEN_2	1.4×10^{-8}	0.0	[33]
PD_2DIEN_2	3.8×10^{-4}	3.8×10^{-5}	[34]
PD_2DIPN_2	1.3×10^{-4}	4.6×10^{-3}	[39,40]
MX_2DIPN_2	7.8×10^{-3}	1.1×10^{-4}	this work

[a] 2:2 dialdehyde (FD = 2,5-furan; PD = 2,6-pyridine; MX = 1,3-benzene) condensation products with triamines (H_4DIEN = 1,4,7-triazaheptane; H_4DIPN = 1,5,9-triazanonane).

dinuclear Cu(I) complexes [33,35,40], a plausible catalytic cycle is depicted in Scheme 2 for the oxidation of 3,5-DTBC by **3** in excess dioxygen. The steps involve (i) oxygenation of the dinuclear copper(I) complex to produce possibly a μ-peroxo species **3(O_2)**, (ii) oxidation of 3,5-DTBC by the dioxygen complex to form 3,5-DTBQ and a dinuclear copper(II) complex with two methoxy groups bridging the metal centers and (iii) oxidation of another molecule of substrate by the Cu(II) species yielding the original dinuclear Cu(I) complex and 3,5-DTBQ.

The slower initial oxidation rate for the system with the Cu(II) macrocyclic complex **4** as catalyst, containing the $Cu(\mu\text{-Cl})_2Cu$ core, compared to the system with complex **3** (Fig. 2, Table 1) reveals the existence of different catalytic cycles. As a consequence, the latter system yields 3.4 times more 3,5-DTBQ than the former after 120 min reaction time. Therefore in this particular system, there is no or slow conversion of the $Cu(\mu\text{-Cl})_2Cu$ complex into the $Cu(\mu\text{-OMe})_2Cu$ as had been found for previous macrocyclic systems described by our group [34,39,40].

Table 1 clearly shows that the Cu(I) complex described in the present work reacts faster than any of the macrocyclic systems described previously under similar reaction conditions. In particular $[(MX_2DIPN_2)Cu^I_2]^{2+}$ produces 3,5-DTBQ twenty times faster than the most reactive macrocyclic system $[(PD_2DIEN_2)Cu^I_2]^{2+}$ [34,35] (PD_2DIEN_2 is the macrocyclic ligand



Scheme 2.

obtained by the condensation of pyridine-2,6-dicarboxaldehyde and 1,4,7-triazaheptane) reported so far. It is also interesting to note that for the PD_2DIEN_2 system the oxidation rates are negligible unless a small amount of base is added whereas for the present system no base at all is needed, thus unquestionably demonstrating that the dioxygen complex **3(O_2)** is a much more powerful catalyst than any of the analogous macrocyclic complexes tested to date.

The ranges of initial rates displayed in Table 1 clearly manifest a strong sensitivity of the $Cu^I_2(O_2)$ core with regard to small steric and electronic variations. This feature is also typical of bioinorganic systems containing binucleating active sites, such as for instance hemocyanin and tyrosinase [2,28].

Acknowledgements

This research is supported by The Robert A. Welch Foundation under grant No. A259. A.L. is grateful to DGICYT (PB96-0467) of Spain for partial financial support.

References

[1] E.I. Solomon, in: T.G. Spiro (Ed.), Copper Proteins, Wiley, New York, NY, 1981, ch. 2.
[2] E.I. Solomon, M.J. Baldwin, M.D. Lowery, Chem. Rev. 92 (1992) 521–542.
[3] A.E. Martell, Adv. Supramolecular Chem. 1 (1990) 145.
[4] T.N. Sorrell, Tetrahedron 45 (1989) 3.
[5] K.D. Karlin, Y. Gultneh, Prog. Inorg. Chem. 35 (1987) 219.
[6] Z. Tyeklar, K.D. Karlin, Acc. Chem. Res. 22 (1989) 241.
[7] K.D. Karlin, Z. Tyeklar, in: G.L. Eichhorn, L.G. Marzilli (Eds.), vol. 9, Models in Inorganic Biochemistry, Prentice Hall, Englewood Cliffs, NJ, 1993, pp 123–172.
[8] K.D. Karlin, Z. Tyeklar (Eds.), Bioinorganic Chemistry of Copper, Chapman and Hall, New York, NY, 1993.
[9] B. Reinhammar, Adv. Inorg. Biochem. 1 (1979) 91.
[10] H. Beinert, Coord. Chem. Rev. 33 (1980) 55.
[11] K. Lerch, Life Chem. Rep. 5 (1987) 221.
[12] H. Beinert, J. Inorg. Biochem. 44 (1991) 173–218.
[13] E.T. Adman, Adv. Protein Chem. 42 (1991) 145–197.
[14] M.S. Nasir, K.D. Karlin, Q. Chen, J. Zubieta, J. Am. Chem. Soc. 114 (1992) 2264.

[15] M.S. Nasir, I.C. Brett, K.D. Karlin, J. Am. Chem. Soc. 114 (1992) 2482.
[16] M. Mahroof-Tahir, K.D. Karlin, J. Am. Chem. Soc. 114 (1992) 7599.
[17] K.D. Karlin, Z. Tyeklar, A. Farooq, M.S. Haka, P. Ghosh, R.W. Cruse, Y. Gultneh, J.C. Hayes, P.J. Toscano, J. Zubieta, Inorg. Chem. 31 (1992) 1436.
[18] I. Sanyal, N.N. Murthy, K.D. Karlin, Inorg. Chem. 23 (1993) 5330.
[19] N. Kitajima, T. Koda, Y. Iwata, Y.J. Moro-oka, J. Am. Chem. Soc. 112 (1990) 8833.
[20] N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S.I. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi, A. Nakamura, J. Am. Chem. Soc. 114 (1992) 1277.
[21] N. Kitajima, K. Fujisawa, S. Hikichi, Y. Moro-oka, J. Am. Chem. Soc. 115 (1993) 7874.
[22] T.N. Sorrell, M.L. Garrity, Inorg. Chem. 30 (1991) 210.
[23] T.N. Sorrell, V. Vankai, M.L. Garrity, Inorg. Chem. 31 (1992) 207.
[24] L. Casella, M. Gullotti, R. Radaelli, P. DiGennaro. J. Chem, Soc. Chem. Commun. (1991) 1611.
[25] M.A. Elsayed, A. Eltouky, K.Z. Ismael, A.A. El-Maradne, Inorg. Chim. Acta. 177 (1990) 155.
[26] E. Asato, S. Hashimoto, N. Matsumoto, S. Kida, J. Chem. Soc. Dalton Trans. (1990) 1741.
[27] J.S. Thompson, J. Am. Chem. Soc. 106 (1984) 8308.
[28] P.K. Ross, E.I. Solomon, J. Am. Chem. Soc. 113 (1991) 3246.
[29] R. Menif, A.E. Martell, J. Chem. Soc. Chem. Commun. (1990) 1207.
[30] R. Menif, A.E. Martell, P.J. Squattrito, A. Clearfield, Inorg. Chem. 29 (1990) 4723.
[31] M.P. Ngwenya, A.E. Martell, J. Reibenspies, J. Chem. Soc. Chem. Commun. (1990) 1207.
[32] M.P. Ngwenya, D. Chen, A.E. Martell, J.H. Reibenspies, Inorg. Chem. 30 (1991) 2732.
[33] D.A. Rockcliffe, A.E. Martell, Inorg. Chem. 32 (1993) 3143.
[34] D.A. Rockcliffe, A.E. Martell, J. Mol. Catal. A 99 (1995) 87.
[35] D.A. Rockcliffe, A.E. Martell, J. Mol. Catal. A 99 (1995) 101.
[36] G. Gonzalez, A. Llobet, A.E. Martell, M. Martinez, M.A. Martinez, J. Chem. Soc., Dalton. Trans., submitted.
[37] D.W. Margerum, G.R. Cayley, D.C. Weatherburn, F.K. Pagenkopf, in: A.E. Martell (Ed.), vol. 2, Coordination Chemistry, American Chemical Society, Washington, DC, 1978, ch. 1.
[38] A. Llobet, J. Ribenspies, A.E. Martell, Inorg. Chem. 33 (1994) 5946.
[39] D.A. Rockcliffe, A.E. Martell, J.H. Reibenspies, J. Chem. Soc., Dalton Trans. (1996) 167.
[40] D.A. Rockcliffe, A.E. Martell, J. Mol. Catal. A 106 (1996) 211.
[41] S.K. Hoffman, D.K. Towle, W.E. Hatfield, Mol. Cryst. Liq. Cryst. 107 (1984) 161.
[42] M. Rodriguez, A. Llobet, M. Corbella, J. Reibenspies, A.E. Martell, manuscript in preparation.
[43] L. Casella, M. Gullotti, G. Pallanza, L. Rigoni, J. Am. Chem. Soc. 110 (1988) 4221–4227.
[44] T.N. Sorrell, M.R. Malachowski, D.L. Jameson, Inorg. Chem. 21 (1982) 3250.
[45] K.D. Karlin, M.S. Nasir, B.I. Cohen, R.W. Cruse, S. Kaderli, A.D. Zuberbuhler, J. Am. Chem. Soc. 116 (1994) 1324–1336.
[46] D. Ghosh, T.K. Lal, S. Ghosh, R. Mukherjee, J. Chem. Soc. Chem. Commun. (1996) 13.