Reactivity of Copper(I) Complexes Towards Dioxygen

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Efforts to model the reactions of copper enzymes with dioxygen with low molecular weight complexes have been quite successful during recent years. Guided by Nature, intriguing model systems for the active sites of such proteins have been developed. In the course of these investigations, it has been discovered that a whole variety of copper–dioxygen adducts form when simple copper(I) complexes are oxidized with dioxygen. The course of these reactions depends on the temperature, the ligands present, and the solvent. The effects of these parameters (especially the effect of ligand modification) on the reactivity of copper(I) complexes towards dioxygen are discussed in detail in this review.

Introduction

Oxidations play important roles in biochemistry, industrial processes, and organic syntheses.[1] For example, controlled partial oxidation of hydrocarbons is necessary to convert petrochemical feedstock into industrial organic chemicals. For economic reasons, there is much interest in the chemical industry in the use of dioxygen as the primary oxidant. However, these processes depend greatly on metal catalysts to promote the rates and enhance the selectivities of the reactions.

Copper ions are found in the active sites of many redox-active metalloproteins that transport (hemocyanin) or transfer molecular oxygen [e.g. tyrosinase (an oxygenase), dopamine β-hydroxylase, or ascorbate oxidase].[2–9] A key step in these redox reactions is the activation of dioxygen upon binding at the active site prior to the reaction with a substrate (Equation (1)).

$$\begin{array}{l}\text{Metalloenzyme}\\ \text{or Metal Complex}\end{array} \overset{O_2}{\rightleftharpoons} \text{Oxy-Form} \xrightarrow{\text{Substrate}} \text{Product} \tag{1}$$

The interest in preparing low molecular weight model complexes for such copper enzymes is twofold. First, the models provide a better understanding of the biological molecules.[3,8] Second, they assist in the development of new catalysts for selective oxidations under mild conditions.[1,10] Therefore, it is of great interest to elucidate the factors that govern the (reversible) binding and activation of dioxygen in various natural oxygen transport systems, i.e. mono- and dioxygenases. Guided by Nature, intriguing model systems for the active sites of copper-containing dioxygen-binding enzymes have been synthesized. These systems are discussed here in detail.

Considerable effort has been directed towards the development of useful catalytic systems for mild and selective oxidations with dioxygen. The feasibility of this has recently been demonstrated with different model compounds for galactose oxidase. In the presence of these complexes, alcohols were catalytically oxidized to aldehydes.[11,12]

This review article gives an overview of the structurally characterized compounds that have been obtained by re-

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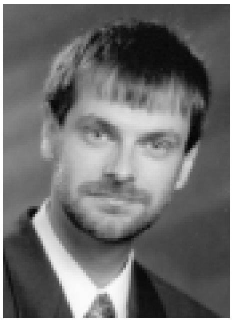

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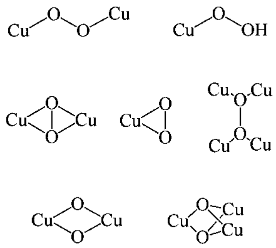
acting copper(I) complexes with dioxygen [or in some cases copper(II) complexes with hydrogen peroxide]. Coordination modes of "dioxygen" adopted in copper complexes that have been structurally characterized are shown in Scheme 1. More detailed information on these compounds can be found in the original references as well as in a series of review articles on various aspects of copper(I)/dioxygen chemistry.[3,8,10,13–15] Furthermore, this article deals with binding and activation of dioxygen in copper(I) complexes according to the first part of Equation (1). It details how this reaction can be optimized, mainly through ligand modification ("ligand tuning"), but also by varying reaction conditions such as concentration, solvent, and temperature.

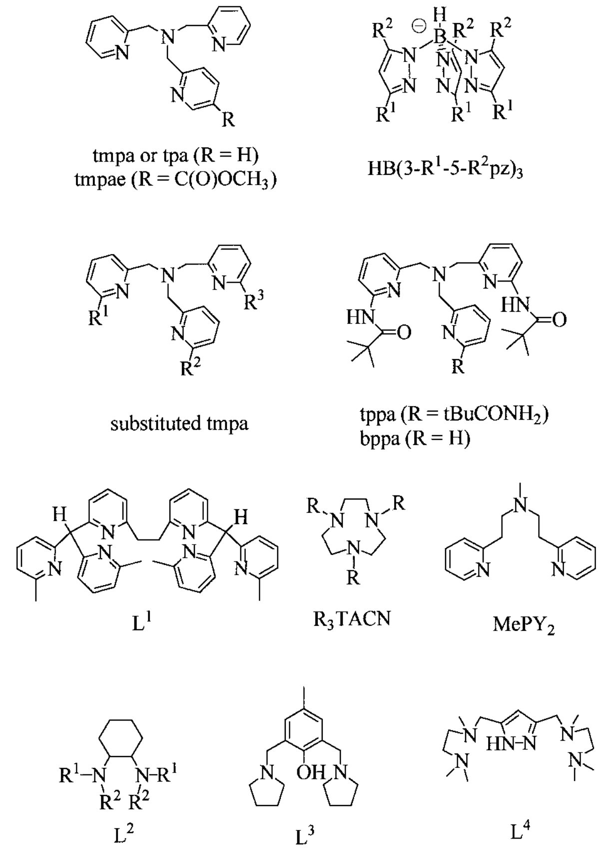


Scheme 1. Dioxygen binding modes in structurally characterized copper complexes

Structurally Characterized Copper Peroxo, Superoxo, and Oxo Complexes

For a long time, copper−peroxo complexes were postulated as intermediates in the reaction of copper(I) complexes with dioxygen.[16,17] However, a structural characterization of such a complex was not available until 1988.[18] At that time, Karlin and co-workers synthesized and characterized a complex incorporating a *trans*-μ-1,2-peroxo-bridged dicopper(II) moiety.[18,19] It was obtained from the reaction of $[(\text{tmpa})\text{Cu}(\text{CH}_3\text{CN})]^+$ {tmpa = tris[(2-pyridyl)-methyl]amine, sometimes abbreviated as tpa; Scheme 2} with dioxygen. Shortly thereafter, a copper complex with a μ-η^2:η^2-peroxo bridge, prepared by the reaction of [Cu{HB(3,5-$i\text{Pr}_2$pz)$_3$}] [HB(3,5-$i\text{Pr}_2$pz)$_3$ = hydrido-tris(3,5-isopropyl)pyrazolylborate anion, Scheme 2; HB(3-R^1-5-R^2pz)$_3$, $\text{R}^1 = \text{R}^2 = i\text{Pr}$] with O_2 (or by careful addition of aqueous hydrogen peroxide to the μ-dihydroxo dimer complex [Cu_2{HB(3,5-$i\text{Pr}_2$pz)$_3$}$_2$(OH)$_2$]) was described by Kitajima and co-workers.[3,20] Its spectroscopic features closely resembled those observed for oxy-hemocyanin, the oxygen-transport protein of arthropods and molluscs, which has a dinuclear copper center in its active site. The similarity of the model complex and the protein was confirmed soon afterwards when the crystal structure of the *oxy*-hemocyanin of *Limulus polyphemus* subunit II was solved.[2]

When HB(3-*t*Bu-5-*i*Pr$_2$pz)$_3$ [Scheme 2; HB(3-R^1-5-R^2pz)$_3$, $\text{R}^1 = t\text{Bu}$, $\text{R}^2 = i\text{Pr}$] was used instead of HB(3,5-$i\text{Pr}_2$pz)$_3$ it was possible to isolate and structurally characterize a side-on bound superoxo copper complex.[21] To date, only one other X-ray crystal structure of a copper−superoxo complex has been reported by Jitsukawa, Masuda, and co-workers with a η^1 "end-on" superoxide stabilized by hydrogen-bonding interactions with the surrounding tppa ligand (tppa = tris{[6-(pivaloylamido)-2-pyridyl]methyl}amine; Scheme 2).[22] This finding was questioned by Tolman and co-workers, who showed that the published X-ray data had probably been misinterpreted.[13] It now seems more likely that a monocopper hydroxide was obtained rather than a superoxo complex.



Scheme 2. Ligands used in structurally characterized copper−dioxygen adducts

When Jitsukawa, Masuda, and co-workers reacted [Cu$^{\text{II}}$(bppa$^-$)]ClO$_4$ or [Cu$^{\text{II}}$(bppa)(CH$_3$COO)]ClO$_4$ (bppa = bis[(6-pivaloylamido)-2-pyridylmethyl](2-pyridylmethyl)amine; Scheme 2) with hydrogen peroxide in acetonitrile, they obtained a mononuclear copper hydroperoxo complex, which was characterized by X-ray crystallography and resonance Raman spectroscopy.[23]

Recently, Kodera et al. succeeded in synthesizing and structurally characterizing a new dinuclear copper complex with a μ-η^2:η^2-peroxo bridge that proved to be unusually stable at room temperature (the half-life at 25 °C was reported to be 25.5 h).[24] This compound was obtained when the dinuclear complex [Cu$_2$L^1](PF$_6$)$_2$ (L^1 = 1,2-bis{2-[bis(6-methyl-2-pyridyl)methyl]-6-pyridyl}ethane; Scheme 2) was reacted with O_2 in dichloromethane.

An important finding with regard to understanding the reactions of copper(I) with dioxygen was reported by Tolman and co-workers.[13,14,25–29] Using substituted triazacyclononane (Scheme 2; R$_3$TACN), these authors showed for the first time that copper μ-η^2:η^2-peroxo-bridged complexes can undergo interconversion with bis(μ-oxo)dicopper(III) complexes. These new species were characterized spectroscopically, and the crystal structures were solved for $[(BN_3TACN)_2Cu_2(\mu\text{-}O)_2]^{2+}$ (BN_3TACN = 1,4,7-tribenzyl-1,4,7-triazacyclononane) and $[(i\text{Pr}_4\text{-dtne})Cu_2(\mu\text{-}O)_2]^{2+}$ [$i\text{Pr}_4$-dtne = 1,2-bis(4,7-diisopropyl-1,4,7-triaza-1-cyclononyl)ethane, Scheme 4; L^7: X = *m*-xylyl].[13,14]

When copper(I)−MePY2 {MePY2 = *N*,*N*-bis[2-(2-pyridyl)ethyl]methylamine; Scheme 2} was reacted with dioxygen at low temperatures, $[(MePY2)Cu{-}(O_2){-}Cu(MePY2)]^{2+}$ was obtained.[30] Its crystal structure reveals a geometry halfway between that of a side-on peroxide and that of a bis(μ-oxo) core. However, X-ray absorption and resonance Raman spectroscopy provided clear evidence that this does not describe the true structure. Thus, the crystalline material was in fact found to be a solid solution composed of approximately 20% of the bis(μ-oxo) core and 80% of the side-on peroxide isomer. A mixture of these two species was also observed in solution.[31]

Very recently, it has been shown that introduction of two 6-methylpyridyl groups into the tmpa ligand (substituted tmpa, R^1 = H, R^2, R^3 = Me; Scheme 2) prevents the formation of *trans*-μ-1,2-peroxo-bridged dicopper(II) species in a trigonal-bipyramidal structure, probably due to the steric requirements of the two 6-methylpyridyl groups. Instead, formation of a brown bis(μ-oxo)dicopper(III) complex, $[Cu_2(O)_2(Me_2\text{-tmpa})_2](PF_6)_2{\cdot}(CH_3)_2CO$, is observed, the crystal structure of which has been reported.[32]

Two further examples of oxo-bridged copper complexes with peralkylated 1,2-cyclohexanediamine ligands (L^2, Scheme 2; R^1 and R^2 = Me and/or Et) have been structurally characterized by Stack and co-workers.[33,34] With R^1 = Me and R^2 = Et, a $Cu_2(\mu\text{-}O)_2$ core almost isostructural with that of $[(BN_3TACN)_2Cu_2(\mu\text{-}O)_2]^{2+}$ was obtained, although the Cu···Cu distance was shorter by 0.05 Å.[34] Interestingly, with $R^1 = R^2$ = Me, a unique trinuclear cluster compound with two μ_3-oxide ligands and three copper ions was obtained.[33] The structure was formally described as a mixed-valence cluster of two copper(II) ions and a single copper(III) ion bridged by two μ_3-oxo ligands.

An example of an exceptionally stable copper−peroxo complex has been reported by Krebs and co-workers.[15,35,36] By reacting a mixture of 2,6-bis(pyrrolidinomethyl)-4-methylphenol (L^3, Scheme 2), copper(II) perchlorate, and triethylamine with hydrogen peroxide (or 3,5-di-*tert*-butylcatechol), these authors obtained a tetranuclear copper complex with the peroxo ligand bound end-on in a μ_4-$(\eta^1)_4$ mode. When the same reaction was performed in the absence of hydrogen peroxide (or 3,5-di-*tert*-butylcatechol), a tetranuclear copper−oxo complex with a μ_4-O^{2-} unit was formed. The crystal structures of the two complexes are closely related; there is also evidence to suggest that the two species are interconvertible.

A further new example of a tetranuclear copper complex with a slightly different μ_4-peroxo coordination has recently

Table 1. Crystallographic and spectroscopic properties of copper−dioxygen adducts

Complex	Binding Mode	X-ray O---O/Cu---Cu (Å)	Resonance Raman cm^{-1}	UV-vis λ (nm) (ε ($cm^{-1}M^{-1}$))	Reference
$[(HB(3\text{-tBu-5-iPr}_2pz)_3)Cu(O_2)]$	side-on bound superoxo	1.22(3)/–	1111 ($^{16}O_2$) 1062 ($^{18}O_2$)	352 (2330) 510 (230) 660 (shoulder)	21
$[(tmpa)_2Cu_2(O_2)]^{2+}$	*trans*-μ-1,2-peroxo	1.432(6)/4.359(1)	832 ($^{16}O_2$)	440 (2000) 525 (11500) 590 (shoulder)	18, 19
$[\{HB(3,5\text{-iPr}_2pz)_3\}_2Cu_2(O)_2]$	μ-η^2:η^2-peroxo	1.412/3.560	741 ($^{16}O_2$) 698 ($^{18}O_2$)	349 (21000) 551 (800)	3, 20
$[Cu(bppa)(OOH)]^+$	end-on bound hydroperoxo	1.460(6)/–	856 ($^{16}O_2$) 810 ($^{18}O_2$)	380 (890) 660 (150) 830 (250)	23
$[L^1Cu_2(O_2)]^{2+}$	μ-η^2:η^2-peroxo	1.485(8)/3.477(7)	760 ($^{16}O_2$) 719 ($^{18}O_2$)	360 (24700) 532 (1530)	24
$[(BN_3TACN)_2Cu_2(\mu\text{-}O)_2]^{2+}$	bis(μ-oxo)	2.287(5)/2.794(2)	602, 612 ($^{16}O_2$) 583 ($^{18}O_2$)	318 (12000) 430 (14000)	14, 27
$[(iPr_4\text{-dtne})Cu_2(\mu\text{-}O)_2]^{2+}$	bis(μ-oxo)	2.35/2.783(1)	585 ($^{16}O_2$) 564 ($^{18}O_2$)	316 (13000) 414 (14000)	14, 29
$[(MePY2)_2Cu_2(O_2)]^{2+}$	μ-η^2:η^2-peroxo and bis(μ-oxo)	1.67/3.45	577 ($^{16}O_2$) 551 ($^{18}O_2$)	355 (14700) 410 (2500) 530 (400)	30
$[Cu_2(O)_2(Me_2\text{-tmpa})_2](PF_6)_2$	bis(μ-oxo)	2.32(1)/2.758(4)	590 ($^{16}O_2$) 564 ($^{18}O_2$)	378 (~22000) 494 (330)	32
$[(L^2)_2Cu_2(\mu\text{-}O)_2]^{2+}$ R^1 = Me and R^2 = Et	bis(μ-oxo)	2.344(1)/2.743(1)	610 ($^{16}O_2$) 587 ($^{18}O_2$)	306 (21000) 401 (28000)	34
$[(L^2)_3Cu_3O_2]^{3+}$ R^1 and R^2 = Me	μ_3-oxide	2.37/2.641(3) and 2.704(3)	607 ($^{16}O_2$) 583 ($^{18}O_2$)	355 (15000) 480 (1400) 620 (800)	33
$[Cu_4(L^3)_2(O_2)(OMe)_2(ClO_4)]^+$	μ_4-peroxo	1.453(4)/2.994(2) and 3.030(2)	878 ($^{16}O_2$) 841 ($^{18}O_2$)	384 (9700) 587 (610)	35, 36
$[Cu_4(L^4)_2(O_2)(OH)_2]^{2+}$	μ_4-peroxo	1.497(5)/2.986 and 3.902	not reported	360 (3100) 631 (260)	37

been reported by Meyer and Pritzkow using a multidentate pyrazolate ligand (L^4, Scheme 2).[37]

Crystallographic and spectroscopic properties of the aforementioned copper−dioxygen adducts are summarized in Table 1.

Kinetics and Thermodynamics of Copper(I)/Dioxygen Interaction

As described above, copper superoxo, peroxo, and bis(μ-oxo) complexes are rather unstable and are therefore difficult to crystallize. Consequently, other methods have to be used to identify and characterize these species, especially when they are only short-lived oxidation intermediates. Oxidations with dioxygen can be followed by UV/Vis spectrophotometry (see below). However, this technique should not be used exclusively to characterize the complexes that are formed in these reactions. Instead, resonance Raman spectra should also be recorded. This method allows detailed insight into the binding mode of the dioxygen.[30,33,34,38]

Among the most powerful tools for detailed investigations of bioinorganic transformations are kinetic studies.[10,39] Among the first researchers to investigate the oxidation of copper(I) complexes with dioxygen in water were Zuberbühler and co-workers.[16] Although dioxygen complexes could not be detected spectroscopically at first, unstable copper−dioxygen intermediates were postulated.[16,17] In a number of cases, kinetic evidence clearly implied the intermediacy of CuO_2^+ and $Cu_2O_2^{2+}$ species.[16] However, no information concerning their stabilities, spectroscopic properties, or structures was available. This situation improved dramatically when it was discovered that $[(tmpa)Cu(CH_3CN)]^+$ reacts with dioxygen to form a copper−peroxo complex that is stable at low temperatures (see above). After detailed kinetic investigations, a mechanism for the reaction of $[(tmpa)Cu(CH_3CN)]^+$ with dioxygen was postulated (Equations (2)−(4); L = tmpa).[40] Most importantly, for the first time it was possible to spectroscopically detect the formation of a superoxo complex (Equation (2)) prior to the formation of a peroxo compound.

$$[(L)Cu(RCN)]^+ + O_2 \rightleftharpoons [(L)Cu(O_2)]^+ + RCN \tag{2}$$

$$[(L)Cu(RCN)]^+ + [(L)Cu(O_2)]^+ \rightleftharpoons [(L)Cu(O_2)Cu(L)]^{2+} + RCN \tag{3}$$

$$[(L)Cu(O_2)Cu(L)]^{2+} \longrightarrow \text{irreversible decay} \tag{4}$$

Since most of these reactions are very fast, their kinetic investigation requires special low-temperature stopped-flow instruments operating with diode-array techniques. Furthermore, data fitting of the obtained time-resolved UV/Vis spectra is only possible with modern global fitting routines (including all data sets and spectra of intermediates).[17] These methods allow the determination of multi-step kinetic mechanisms, including kinetic and equilibrium constants, and the elucidation of complete UV/Vis spectra of intermediates.

A recent review article describes the kinetics and thermodynamics of the copper(I)/dioxygen interaction.[17] Therefore, only selected aspects concerning this particular interaction are mentioned in the present article, together with some new findings.

As mentioned above, copper μ-η^2:η^2-peroxo-bridged complexes are capable of interconversion with bis(μ-oxo)dicopper(III) compounds. A kinetic study has shown that there is a rapid equilibrium between these two species (ligand R_3TACN, R = *i*Pr; Scheme 2).[28,41] Furthermore, it has been proposed that the oxygenation involves rate-determining formation of a mononuclear superoxo complex followed by a faster reaction with a second molecule of the monomeric copper(I) complex.

Dinuclear copper(I) complexes have been synthesized by linking mononuclear units as described below, in the hope that these "pre-organized" systems would stabilize the copper−peroxo unit. Kinetic measurements showed that this could indeed be achieved, but that this approach only works when the linked mononuclear units are not under any strain.[13,14,17,29,42−45] A linker that introduces steric strain leads to intermolecular rather than intramolecular formation of copper−peroxo complexes. Consequently, the dinuclear peroxo complexes should not be more stable than those obtained from the mononuclear compounds. This was confirmed in principle, but it was also observed that intermolecular oxidation can lead to quite stable polynuclear copper−peroxo complexes.[43]

Recently, the author's group succeeded in carrying out kinetic investigations on the reaction of a dinuclear copper(I) complex, $[Cu_2{-}H{-}XYL{-}H]^{2+}$ (ligand H−XYL−H is shown in Scheme 8), with dioxygen under high-pressure conditions.[46] This study turned out to be quite a challenge because the reaction of the oxygen-sensitive compound could only be investigated in organic solvents at low temperatures by means of stopped-flow techniques *and* under high pressure (this was accomplished using a high-pressure stopped-flow unit assembled in-house). For the first time, activation volumes for the formation $\Delta V^{\#} = -15.0 \pm 2.5$ cm^3/mol (as well as for the back reaction, $\Delta V^{\#} = +4.4 \pm 0.5$ cm^3/mol) and the decomposition ($\Delta V^{\#} = -4.1 \pm 0.7$ cm^3/mol) of a dinuclear copper−peroxo complex were obtained. Furthermore, solvent effects on this reaction were investigated. The reaction mechanism in acetone was shown to be more complicated than that in dichloromethane owing to an additional equilibrium between the dinuclear copper(I) complex and a less reactive isomer.

It should be pointed out that while there are clearly many similarities between dinuclear copper(I) complexes and hemocyanin, there are also many differences. For example, the reaction of the dinuclear copper(I) complex $[Cu_2{-}H{-}XYL{-}H]^{2+}$ (Scheme 8) with dioxygen is pressure dependent while that of deoxy-Hc is not.[46,47] More importantly, the oxidation of the protein proceeds very rapidly in water, while the model complexes investigated to date could only be studied in organic solvents.[48] Moreover, when the protein is reacted with carbon monoxide it only binds one molecule, clearly indicating that the two copper(I) sites are differently shielded towards the reaction with substrates. The model complexes studied thus far bind one carbon monoxide molecule per copper(I) ion.[49]

General Approach

To optimize the reactions of copper(I) complexes with dioxygen in order to obtain stable copper−dioxygen adducts, most research groups follow a similar general strategy.

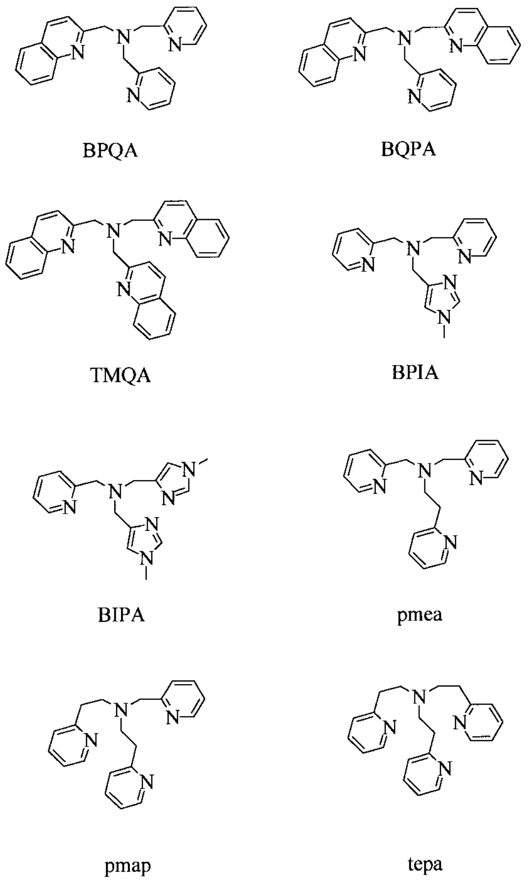
Temperature variation offers an important means of stabilizing copper superoxo, peroxo, or bis(μ-oxo) complexes. Thus, while many of these compounds are unstable at room temperature, they can be stored at low temperatures for months and can be isolated under these conditions. For example, by working at −80 °C, Karlin and co-workers were able to isolate and structurally characterize the first copper−peroxo complex.[18] For this reason, many studies on the behavior of copper(I) complexes towards dioxygen are performed using low-temperature techniques.[14,17,28,46,50] In principle, it should also be possible to bring about some of the temperature effects through pressure changes. However, for the relevant systems it is quite difficult and often impossible to accomplish pressure changes with the given experimental set-ups.

The most important method for modulating the reaction behavior of copper(I) complexes is modification of their ligands, either by introducing different donor atoms, changing chelate ring sizes, or using substituents that can influence the ligand sterically or electronically. Moreover, mononuclear units can be linked to form larger pre-organized ligand systems. This review is mainly focussed on how these chemical modifications affect the reactivity of copper complexes towards dioxygen. Quite recently, theoretical calculations have been used to predict the structures and/or reactivities of promising copper complexes (see below). Furthermore, the solvent can play an important role in the reaction of copper(I) complexes with dioxygen.

In general, a detailed study starts with a copper(I) complex that shows an interesting reaction behavior towards dioxygen. A detailed kinetic investigation is then undertaken and, in some cases, theoretical calculations are performed. The results are used to chemically modify the ligand in order to optimize the desired transformation.

Copper(I) Complexes with Tripodal Ligands Derived from tmpa

As discussed above, the tripodal complex [Cu(tmpa)-(CH_3CN)]$^+$ has proved to be very useful for studying the reactions of copper(I) complexes with dioxygen. In order to gain further insight into these transformations, tmpa has been chemically modified and the resulting effects have been investigated.



Scheme 3. tmpa and derivatives

Karlin and co-workers replaced the pyridine moieties with sterically more demanding quinolyl groups in a stepwise manner. This yielded the ligands BPQA [bis(2-pyridylmethyl)(2-quinolylmethyl)amine], BQPA [bis(2-quinolylmethyl)(2-pyridylmethyl)amine], and TMQA [tris(2-quinolylmethyl)amine] shown in Scheme 3.[40,51] On going from tmpa to TMQA, dramatic differences in the reactivities of the corresponding copper(I) complexes towards dioxygen were observed. A detailed kinetic study showed that when [Cu(BPQA)]$^+$ was reacted with dioxygen at low temperatures, only the peroxo complex [(BPQA)Cu(O_2)-Cu(BPQA)]$^{2+}$ could be detected; the formation of a superoxo complex was not observed under these conditions. In contrast, although reaction of [Cu(BQPA)]$^+$ with dioxygen led initially to the peroxo complex, this then immediately formed the 1:1 adduct, i.e. the superoxo complex [(BQPA)Cu(O_2)]$^+$. In the case of [Cu(TMQA)]$^+$, no interaction with dioxygen was observed.[40] According to the authors, steric effects are the most important factors in rationalizing these variations in reactivity.

Similar effects have been observed upon the successive introduction of three methyl groups at the 6-positions of the three pyridine moieties of tmpa (Scheme 2; substituted tmpa: R^1, R^2, R^3 = CH_3 or H).[52,53] As discussed above, with Me_2tmpa as ligand a bis(μ-oxo)dicopper(III) complex was obtained.[32] However, no detailed kinetic study has yet been performed.

Furthermore, the introduction of three phenyl groups at the 6-positions of the three pyridine moieties of tmpa renders the resulting copper(I) complex (Scheme 2; substituted tmpa: R^1, R^2, R^3 = phenyl) inert towards dioxygen.[54]

The introduction of steric hindrance in the tris(pyrazolyl)borate ligand [HB(3-R^1-5-R^2pz)$_3$, Scheme 2] allowed the synthesis and structural characterization of a copper−superoxo complex (see above).[21] Using the same approach, Jitsukawa, Masuda, and co-workers introduced three pivalolylamino groups at the 6-positions of the pyridine moieties of tmpa (Scheme 2; tppa). They hoped that the increased steric hindrance would lead to the formation of a copper−superoxo (1:1 adduct) instead of a peroxo complex.[22,55,56] Although these authors claimed to have structurally characterized a superoxo complex $[(tppa)Cu(O_2)]^+$, there is strong evidence that the described compound was actually $[(tppa)Cu(OH)]^+$ (see above).[57] Using bppa (Scheme 2), the same researchers were able to isolate and structurally characterize a copper−hydroperoxo complex (see above). Here, the hydroperoxo ligand is stabilized by hydrogen bonding.[23]

Karlin and co-workers also synthesized copper(I) complexes with tripodal ligands incorporating imidazolyl donor groups rather than pyridine (BPIA = {bis[(2-pyridyl)methyl(1-methylimidazol-2-yl)methyl]amine}; BIPA = {bis[(1-methylimidazol-2-yl)methyl]-(2-pyridyl)methylamine}, Scheme 3).[58] Interestingly, these complexes are dinuclear as solids, but dissociate into mononuclear species in solution. When $[Cu(BPIA)]^+$ was reacted with dioxygen at low temperatures, it exhibited very similar UV/Vis spectroscopic features to those of the parent $[(TMPA)Cu(RCN)]^+$, as well as of the quinolyl-containing $[Cu(BPQA)]^+$. For this reason, the formation of the peroxo complex $[(BPIA)CuO_2(BPIA)]^{2+}$ with a *trans*-(μ-1,2 peroxo) dicopper(II) moiety was postulated. This indicates that when one of the three pyridyl rings is substituted by some other donor group, the steric and electronic environment around the copper(I) center remains the same. However, when two pyridine groups are substituted by two imidazole donors, the copper−dioxygen chemistry becomes greatly altered. When $[Cu(BIPA)]^+$ was exposed to dioxygen at low temperatures in propionitrile, a red species was formed. It could not be fully characterized as it proved to be unstable under these conditions. Its UV/Vis spectrum was similar to that of the μ-η^2:η^2-peroxo compound $[\{HB(3,5\text{-}i\mathrm{Pr}_2pz)_3\}Cu(O_2)Cu\{HB(3,5\text{-}i\mathrm{Pr}_2pz)_3\}]$ described above. However, the molar extinction coefficients were much lower, probably owing to rapid decomposition of the red compound. In view of the lack of further evidence, these results that are based on UV/Vis measurements alone must be treated with caution.

Clearly, all these studies on Cu^I and Cu^{II} species with similar ligands show that small changes in ligand architecture can have a strong influence on the reactivity. In the active sites of enzymes, the nature of the ligand donors plays an important role in forcing the metal ions to participate in the desired biochemical transformations. Thus, further studies of ligand variations should provide valuable insights into fundamental aspects of biologically relevant coordination chemistry. With this in mind, it was decided to compare the reactivity of copper(I), copper(I)/O_2, and copper(II) complexes of other tripodal ligands derived from tmpa.[59]

On coordination of tmpa to copper ions, five-membered chelate rings are formed. If the carbon chain lengths in tmpa are increased by the introduction of pyridineethyl instead of pyridinemethyl groups, the ligands pmea {*N*,*N*-bis[(2-pyridyl)methyl]-2-(2-pyridyl)ethylamine}, pmap {*N*,*N*-bis[2-(2-pyridyl)ethyl]-(2-pyridyl)methylamine}, and tepa {tris[2-(2-pyridyl)ethyl]amine} are obtained (Scheme 3). Recently, the copper(I) and copper(II) complexes of pmea and pmap have been structurally characterized in this laboratory;[59] the copper(I) and copper(II) complexes of tmpa and tepa have been described previously.[19,60−62] In the case of tmpa and tmpae (Scheme 2), the copper(I) complex normally crystallizes in a trigonal-bipyramidal geometry with an additional acetonitrile molecule in the axial position.[19,60] This is not the case when the sterically demanding triphenylphosphane is used as an additional ligand.[19] The trigonal-bipyramidal geometry of $[(tmpa)Cu(CH_3CN)]^+$ is retained when this compound is oxidized with dioxygen to give a copper(II)−peroxo complex.[19] Furthermore, the copper(II) complex $[(tmpa)CuCl]^+$ is structurally very similar to the peroxo complex.[19,61] That the trigonal-bipyramidal geometries of the copper(II) complexes are retained in solution was confirmed by UV/Vis and EPR measurements.[19] In contrast, neither Cu^I nor Cu^{II} complexes of pmea, pmap, or tepa are trigonal bipyramidal.[59,61,62] The copper(I) complexes are best described as distorted tetrahedra without any additional ligands. The copper(II) complexes show distorted square-pyramidal geometries.

These differences are reflected in the reaction behavior towards dioxygen. While $[(tmpa)Cu(CH_3CN)]^+$ is oxidized at low temperatures to give a stable peroxo complex, this is not the case for any other compound of this series.[59] When $[(pmea)Cu]^+$ is reacted with dioxygen at low temperatures, only a very unstable peroxo complex is produced. With $[(pmap)Cu]^+$, no such intermediate is detected during oxidation; $[(tepa)Cu]^+$ does not react with dioxygen.[59] From these findings, it is clear that in this series of complexes an increase in chelate ring size leads to a dramatic destabilization of the copper−dioxygen adducts.

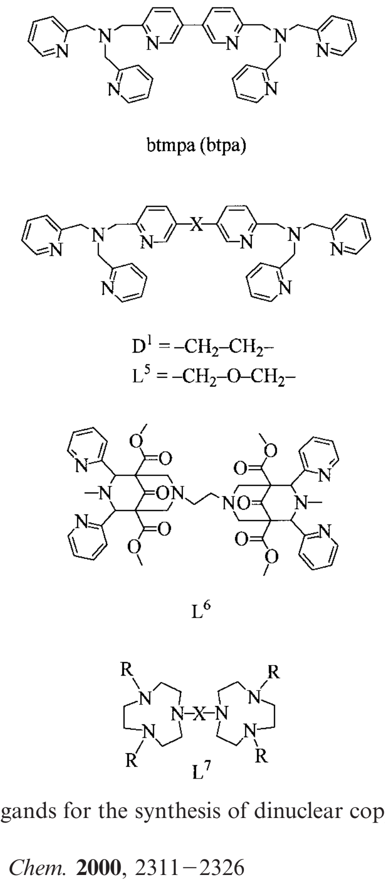
A similar effect has been observed on increasing the carbon chain lengths in tren [tren = tris(2-aminoethyl)amine; Scheme 5]. As discussed below, it proved impossible to isolate crystals of a copper(I) complex with tren, because at higher concentrations this compound undergoes disproportionation to copper(II) and copper metal.[50] However, using $N[(CH_2CH_2CH_2NH_2)_2CH_2CH_2NH_2]$ or $N(CH_2CH_2CH_2NH_2)_3$, the copper(I) complexes could be isolated and structurally characterized.[63] Again, it was found that in contrast to the other complexes of this series, the copper(I) complex with $N(CH_2CH_2CH_2NH_2)_3$ as ligand is stable towards dioxygen, similar to $[(tepa)Cu]^+$ described above. Crystal structures of the copper(II) complexes of these ligands have been reported.[64]

Linking Mononuclear Units and Theoretical Calculations

The studies on the oxidation of copper(I) complexes with tmpa-like ligands clearly demonstrate that the copper−peroxo complex with tmpa is most stable. Therefore, it should be possible to optimize this reaction by chemically connecting two tmpa units to a pre-organized dinuclear copper(I) site.

An interesting approach in this regard was the use of bipyridine as the "bridging" unit. The resulting ligand btmpa (6,6′-bis{[bis(2-pyridylmethyl)amino]methyl}-2,2′-bipyridine, also abbreviated as btpa) is shown in Scheme 4. Crystal structures of its dinuclear copper(II) complexes have been published.[65,66] When the dinuclear copper(I) complex was reacted with dioxygen, only a very slow oxidation was observed; dioxygen intermediates could not be detected.[66,67] Karlin and co-workers rationalized this finding in terms of a steric hindrance created by the chelate sites, which influences the molecular geometry around the copper ions.[66] This causes the dinuclear copper complexes to exhibit spectroscopic and electrochemical properties dissimilar to those of their parent tmpa analogues.

In the light of these findings, it became clear that the two mononuclear units had to be separated by a real spacer. This was accomplished by linking two tmpae units (Scheme 2), giving rise to the ligand D^1 shown in Scheme 4 (X = $-CH_2CH_2-$).[42,43] The crystal structure of the dinuclear copper(I) complex shows that the bond lengths and angles at each copper(I) ion are very similar to those in the mononuclear units of the copper(I) complexes of tmpa and tmpae. A detailed kinetic study on the reaction of dioxygen with these complexes showed that there was a big difference between the behavior of the copper(I) complexes of tmpa and tmpae and that of the dinuclear complex, so that different reaction pathways must exist.[42,43]



Scheme 4. Ligands for the synthesis of dinuclear copper complexes

While the formation of a copper−superoxo (dinuclear complex:O$_2$ = 1:1) and a copper−peroxo complex (1:1) could still be observed, the formation of a 1:2 superoxo complex and intermolecular copper−peroxo complexes was also detected. The intramolecular formation of $[(D^1)Cu_2(O_2)]^{2+}$ was found to be significantly faster than the generation of the corresponding 2:1 complexes $[(tmpa)Cu(O_2)(tmpa)]^{2+}$ and $[(tmpae)Cu(O_2)(tmpae)]^{2+}$, the latter being formed in an intermolecular fashion from mononuclear precursors. However, its structure seems to be strained. Therefore, the intermolecular arrangement of oligomeric peroxo complexes is preferred; in particular, a stable cyclic trimer is observed. As the authors point out, the Cu_2-O_2 μ-peroxo complex (or complexes) containing D^1 is (or are) in fact more stable than those of the mononucleating ligands tmpa or tmpea. However, it was not the naively expected intramolecular species $[(D^1)Cu_2(O_2)]^{2+}$, but rather highly associated Cu_2-O_2 compounds that formed in an intermolecular fashion (species that cannot possibly form with ligands such as tmpa and tmpae).

A combination of synthetic work and molecular mechanics modelling on these intramolecular copper−peroxo complexes with different spacer groups X (Scheme 4) led to the preparation of the ligand L^5 (X = CH_2-O-CH_2).[44][68] When the corresponding dinuclear copper complex was reacted with dioxygen, a relatively stable peroxo complex was formed, indicating that the longer linker arm in L^5 relieves the strain observed for $[(D^1)Cu_2(O_2)]^{2+}$ and significantly enhances adduct formation at room temperature.

The same approach of combining theoretical calculations with synthetic work for linking mononuclear units has been used by Comba and co-workers.[69] This group investigated the reaction of dioxygen with a mononuclear copper(I) complex {with the ligand methyl 2,4-bis(2-pyridinyl)-3,7-diazabicyclo[3.3.1]nonane-9-diol-1,5-dicarboxylate} and detected a quite stable peroxo compound. In order to further increase the stability of the oxygenation product, a linker for two of the mononuclear units had to be designed. Molecular mechanics modelling studies showed that an ethyl spacer would be most appropriate. The calculations were confirmed when a much more stable copper−peroxo complex was obtained after the dinuclear copper(I) complex of this ligand (L^6, Scheme 4) was reacted with dioxygen. In collaboration with this group, investigations of the oxidation of these complexes using low-temperature stopped-flow instrumentation have been started in this laboratory. A complex kinetic behavior has been observed, with several dioxygen adducts being detected spectrophotometrically. As yet, these have not been unequivocally identified.[70]

Furthermore, theoretical calculations have been used to design a macrocyclic ligand (MEPY22PZ, Scheme 6) for a dinuclear copper(I) complex, which has again been shown to form a quite stable peroxo complex on reaction with dioxygen (see below).[71]

As discussed above, Kodera et al. successfully increased the stability of copper−peroxo complexes by linking mononuclear structures.[24] Indeed, they synthesized and structurally characterized the most stable dinuclear copper μ-η^2:η^2-peroxo complex (ligand L^1, Scheme 2) yet published.

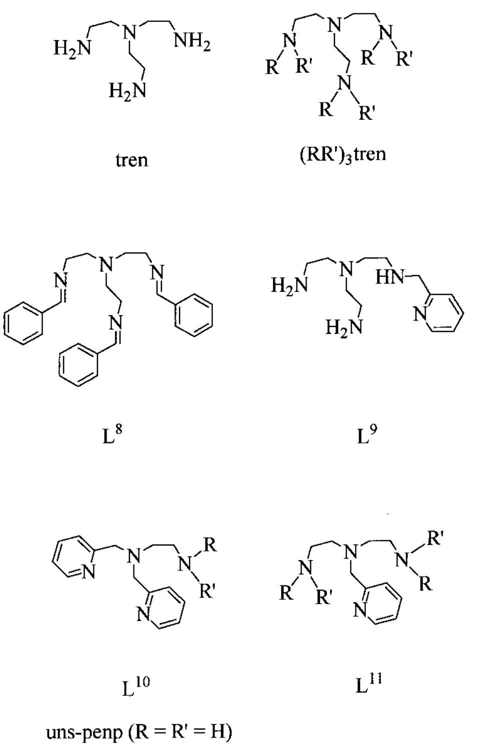
The choice of the linker X in L^7 (Scheme 4) also influences the reaction pathways of the corresponding copper(I) complexes.[14] With $X = -CH_2-CH_2-$, only the bis(μ-oxo) core is obtained and there are no spectroscopic indications of the presence of a peroxo isomer. With the more expanded *m*-xylyl linker, complications occur because here again both intra- and intermolecular complex formation is observed.

Ligands Derived from tren

Because small changes in the ligand environment can have a dramatic effect on the reactivity of copper(I) complexes towards dioxygen, it is important to chemically vary the ligands in a systematic manner and to study the effects. One of the disadvantages of using tmpa and derivatives, as well as many other ligands described above, is the fact that chemical modification of these compounds can be difficult and time consuming. Therefore, a series of tripodal ligands that could be easily modified and then studied kinetically was sought.

As a starting material, tren (Scheme 5), an amine produced in industrial quantities, was chosen. It is a versatile tetradentate ligand, known to form trigonal-bipyramidal complexes with copper(II) ions in the solid state as well as in solution [similar to the copper(II) tmpa complexes discussed above]. One of the axial positions is occupied by the tertiary amine nitrogen, the other by water or some other monodentate ligand.[72−77] This geometry is important with regard to ligand substitution reactions because copper(II) complexes with tetragonal distorted geometry react very rapidly (approaching the diffusion limit), whereas copper(II) complexes with trigonal-bipyramidal geometry react much more slowly [this may be one of the reasons for the different reaction behavior of the copper(I) complexes with tmpa, pmea, and pmap discussed above].[76,78−82] Furthermore, tren can easily be modified to yield a whole family of tripodal ligands.

As yet, it has proved impossible to isolate crystals of a copper(I) complex with tren, because at higher concentrations this compound undergoes disproportionation to copper(II) and copper metal.[50] Nevertheless, dilute solutions of $[Cu(tren)]PF_6$ {or more likely $[Cu(tren)(RCN)]PF_6$} could be obtained by mixing stoichiometric amounts of $[Cu(CH_3CN)_4]PF_6$ and tren in propionitrile or acetone under inert conditions. Using low-temperature stopped-flow equipment, it was possible to detect spectrophotometrically the fast formation (faster than the mixing time of the instrument) of an unstable dioxygen adduct at −90 °C in propionitrile.[77] Its UV/Vis spectrum is very similar to that of the superoxo complex $[(tmpa)CuO_2]^+$ (characteristic absorbance at $\lambda_{max} = 410$ nm). Therefore, it is proposed that the complex $[(tren)CuO_2]^+$ had been formed. Owing to its instability, resonance Raman data that might have provided further evidence for the formation of a superoxo complex could not be obtained. The decomposition of this compound became faster on increasing the temperature; time-resolved spectra of this reaction at −70 °C are shown in Figure 1.



Scheme 5. tren and derivatives

In contrast to $[(tmpa)Cu(O_2)]^+$, which reacts with $[(tmpa)Cu(CH_3CN)]^+$ to yield $[(tmpa)Cu(O_2)Cu(tmpa)]^{2+}$ (Equation (3)), no copper tren peroxo complex could be detected under these conditions. Most probably, the superoxo complex reacts with protons provided by tren and a copper(II) complex and hydrogen peroxide are formed as final products. In tmpa copper(I) complexes, protons are not provided by the ligand and this reaction is not observed in propionitrile. In contrast, the formation of $[(tmpa)Cu(O_2)Cu(tmpa)]^{2+}$ is also dramatically disfavored when the reaction of $[(tmpa)Cu(CH_3CN)]^+$ with dioxygen is performed in methanol, a protic solvent. Furthermore, it was found that when acid was added to $[(tmpa)Cu(O_2)Cu(tmpa)]^{2+}$, a copper(II) complex and hydrogen peroxide were produced as the final products.[83] The structural characterization of a hydroperoxo complex discussed above lends further support to this alternative reaction pathway.

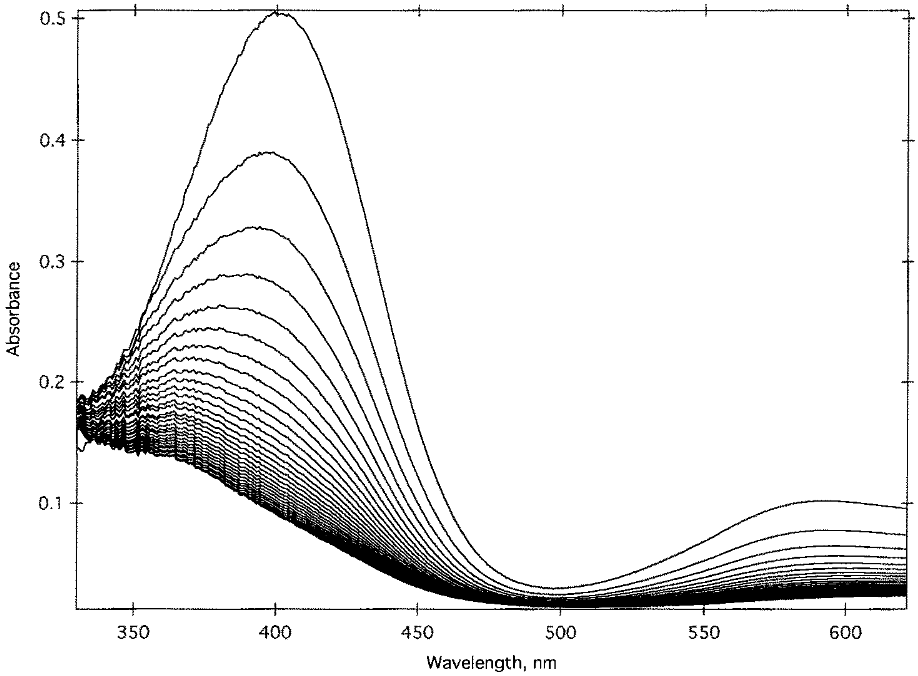


Figure 1. Reaction of $[(tren)Cu(RCN)]PF_6$ with dioxygen at −70 °C in dry propionitrile ([complex] = 0.26 mM, $[O_2]$ = 0.8 mM, Δt = 1.1 s)

To gain further insight into the reaction mechanism, Me_3tren [2,2′,2′′-tris(2-monomethylamino)triethylamine, Scheme 5; R = H, R′= Me] was synthesized. Once again, however, it proved impossible to isolate a solid copper(I) complex.[77] However, copper(II) complexes with Me_3tren could easily be synthesized and characterized.[76,77] First, the dinuclear species $[(Me_3tren)Cu{-}CN{-}Cu(Me_3tren)](ClO_4)_3$ was obtained, which is a further example of the few known $Cu^{II}{-}CN$ complexes.[76] Additionally, the trigonal-bipyramidal complex $[(Me_3tren)CuCl]ClO_4$ could be crystallized, which is structurally very similar to $[(tren)CuCl]ClO_4$.[77]

The reaction of a stoichiometric mixture of $[Cu(CH_3CN)_4]PF_6$ and Me_3tren in propionitrile with dioxygen at −90 °C also provided spectroscopic evidence for the superoxo complex $[(Me_3tren)Cu(O_2)]^+$. As in the oxidation of the copper(I) tren complex described above, a copper−peroxo complex was not observed under these conditions. However, there is one clear difference between the two systems. For reasons not yet understood, $[(Me_3tren)CuO_2]^+$ is much more stable than $[(tren)CuO_2]^+$. Work is currently in progress aimed at clarifying this.

As shown above, an increase in steric hindrance can facilitate the synthesis of a copper−superoxo complex. To test this approach further, the ligand Bz_3tren [tris(2-benzylaminoethyl)amine, Scheme 5; (RR′)$_3$tren: R = H, R′ = benzyl] was used instead of Me_3tren.[77] As expected, it proved impossible to isolate a solid copper(I) complex because of disproportionation. Crystal structures of the copper(II) complexes $[(Bz_3tren)Cu(H_2O)](ClO_4)_2$ and $[(Bz_3tren)CuCl]ClO_4$ have been determined.[77] Both show trigonal-bipyramidal geometry, with the latter being very similar to $[(Me_3tren)CuCl]ClO_4$ and $[(tren)CuCl]ClO_4$. An ORTEP plot of $[(Bz_3tren)Cu(H_2O)]^{2+}$ is shown in Figure 2. Evidently, there is no significant steric hindrance when only three hydrogen atoms in tren are replaced by bulky groups; the three benzyl groups are turned away sideways.

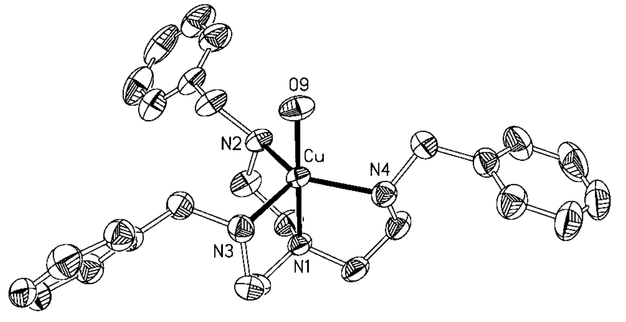


Figure 2. ORTEP view of $[(Bz_3tren)Cu(H_2O)]^{2+}$; thermal ellipsoids are drawn at a 50% probability level; hydrogen atoms are omitted for the sake of clarity

Most surprisingly, a stoichiometric mixture of $[Cu(CH_3CN)_4]PF_6$ and Bz_3tren in propionitrile showed a reaction behavior towards dioxygen different from that of Me_3tren.[77] Time-resolved spectra recorded at −70 °C are shown in Figure 3. Even though a detailed kinetic study has not yet been performed, the spectra provide evidence for the formation of $[(Bz_3tren)CuO_2]^+$ and $[(Bz_3tren)CuO_2Cu(Bz_3tren)]^{2+}$ as the spectral features are similar to the known UV/Vis spectra of copper−superoxo and −peroxo complexes.[40,51] The absorbance maxima of the superoxo $[(Bz_3tren)CuO_2]^+$ (λ_{max} = 406 nm) and peroxo $[(Bz_3tren)CuO_2Cu(Bz_3tren)]^{2+}$ (λ_{max} = 506 nm) complexes were assigned accordingly. However, resonance Raman spectra are still needed to confirm this assignment. According to these results, the reaction pathway is similar to that described for $[(tmpa)Cu(CH_3CN)]^+$ by Equations (2)−(4). The considerable differences in the behavior of the three

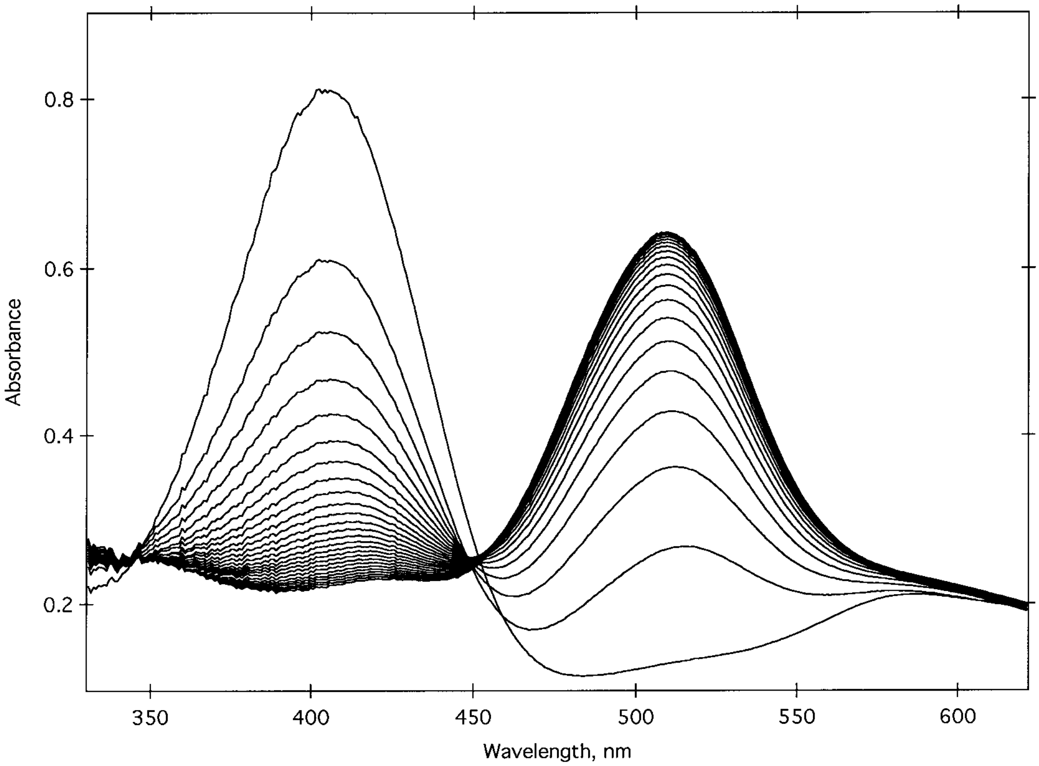


Figure 3. Reaction of $[(Bz_3tren)Cu(RCN)]PF_6$ with dioxygen at −80 °C in dry propionitrile ([complex] = 0.25 mM, $[O_2]$ = 4.4 mM, Δt = 35.2 s)

complexes $[Cu(tren)]^+$, $[Cu(Me_3tren)]^+$, and $[Cu(Bz_3tren)]^+$ towards dioxygen have yet to be explained; further investigations are necessary.

At the beginning of these investigations, the now commercially available amine Bz_3tren was synthesized by reacting benzaldehyde with tren followed by a reduction with sodium borohydride.[84] This prompted investigations of the reaction behavior of the copper(I) complex with the initially formed imine ligand (L^8, Scheme 5).[77,85,86] In contrast to tren and its derivatives, the soft imine donor groups in L^8 have a large stabilizing effect on the soft copper(I) ion. Therefore, the corresponding copper(I) complex can easily be synthesized and structurally characterized.[85,86] However, when this complex was reacted with dioxygen in a variety of solvents at different temperatures, dioxygen intermediates were not detected.[77,85] This finding is well in line with earlier results on the reaction of dioxygen with various copper imine complexes.[87−89] All kinetic investigations suggest the formation of a copper peroxo (or superoxo) complex, but it has proved impossible to detect these compounds spectroscopically. Most probably, the dioxygen intermediate immediately reacts further to yield a decomposition product (steady-state concentration of dioxygen intermediates). As yet, no explanation has been offered as to why this especially seems to be the case for copper(I) imine complexes.

To avoid effects caused by ligand protons, Me_6tren [tris(2-dimethylaminoethyl)amine, Scheme 5; R = R′ = Me], i.e. fully methylated tren, was used.[50,90] The solutions of Me_6tren and Cu^I salts proved to be extremely sensitive towards traces of dioxygen or moisture; oxidation or disproportionation of the complex was frequently observed before the pure, crystalline copper(I) complex $[Cu(Me_6tren)]ClO_4$ could be isolated.[50]

The geometry of $[Cu(Me_6tren)]ClO_4$ is best described as trigonal pyramidal, but a weak interaction with the perchlorate anion cannot be neglected. This anion occupies the axial position of a trigonal-bipyramidal arrangement constituted by three of the four oxygen atoms and the copper(I) ion. This structure is unusual because of the weak interaction between the perchlorate anion and the copper(I) cation. After crystallizing $[Cu(Me_6tren)]ClO_4$ from acetonitrile, one would expect to find an additional acetonitrile molecule coordinated to the copper ion in the axial position (instead of perchlorate); this was found for the copper(I) complex with tmpa as discussed above. A comparison of this complex with $[Cu(Me_6tren)]ClO_4$ reveals that the bond lengths and bond angles are quite different.[50]

When $[Cu(Me_6tren)]ClO_4$ was reacted with dioxygen at low temperatures in a stopped-flow instrument, spectral changes indicative of the formation of the superoxo $[Cu(Me_6tren)O_2]^+$ and peroxo $[(Me_6tren)Cu(O_2)Cu(Me_6tren)]^{2+}$ complexes were observed; the latter was further characterized by resonance Raman measurements, ν(O−O) = 880 cm^{-1}.[50] A detailed kinetic study of this reaction is currently in progress. From the data obtained to date, it is clear that the reaction pathway is similar to that described for $[(tmpa)Cu(CH_3CN)]^+$ by Equations (2)−(4). However, there is one major difference: $[Cu(tmpa)O_2]^+$ immediately undergoes further reaction to give the peroxo complex (Equation (3)), whereas $[Cu(Me_6tren)O_2]^+$ reacts much more slowly.[50]

The aforementioned findings show that copper(I) complexes with tren or its derivatives form dioxygen adducts during oxidation. Consequently, this represents an excellent approach for systematically synthesizing a series of tripodal ligands that can be used to test the differences in behavior of the corresponding copper(I) complexes towards dioxygen. In principle, combinatorial chemistry could now be used to synthesize and investigate copper(I) complexes with a large variety of tripodal ligands.

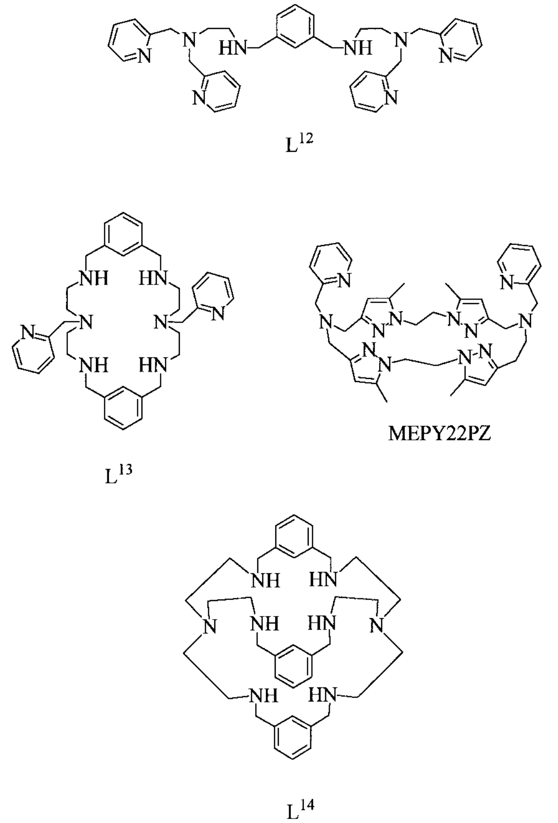
By reacting tren with aldehydes followed by reduction, a series of R_3tren ligands (Scheme 5; R′ = H) can be synthesized. Further reaction with organic chlorides or the use of aldehydes and sodium cyanoborohydride allows the preparation of a wide variety of $R_3R'_3$tren ligands (Scheme 5). When these R groups provide additional donor atoms, several copper ions can be bound by the ligand; for example, reaction of tren with picolyl chloride or 2-vinylpyridine allowed the isolation of trinuclear copper complexes.[91,92] It is also possible to chemically alter tren without modifying all three arms. An example where only one amine arm was altered has been described by Spiccia and co-workers (L^9, Scheme 5).[93]

In order to avoid ligand mixtures when only one or two additional groups were introduced into tren, the amines L^{10} and L^{11} were used (Scheme 5; R = R′ = H; ligand L^{10} is abbreviated as uns-penp[94]). Both of these amines have been known for a long time[94,95] (uns-penp was actually "rediscovered" after 10 years as a "new" ligand![96]) but surprisingly they have been little used in the synthesis of novel transition metal complexes.[94−98] The reaction of uns-penp with an aldehyde (pyridinealdehyde or salicylaldehyde, for example), followed by a reduction, allows the selective introduction of one additional donor group. Recent work has shown the modified uns-penp ligand to be extremely useful in the synthesis of iron and manganese complexes.[99−102] Ligand L^{11} permits the selective introduction of two further donor groups. Further work in this area using these new ligands for the synthesis and investigation of copper(I)/(II) complexes is ongoing in the author's laboratory.[103]

There is a further advantage in using these ligands. As discussed above, pyridine donors stabilize copper(I) complexes and facilitate their investigation. Preliminary experiments have indicated that the copper(I) uns-penp complex does not form a peroxo compound when it is reacted with dioxygen,[104] although this needs to be confirmed. In contrast, when the protons in L^{10} and L^{11} (Scheme 5; R = R′ = Me) were replaced by methyl groups, quite stable peroxo complexes could be detected as intermediates during oxidation.[103] These new ligands can be regarded as the two "missing links" between Me_6tren and tmpa.

Bridging Ligands Derived from tren and Derivatives

The use of uns-penp is also advantageous in that this ligand can be easily linked together, much more easily than tmpa itself. By reacting uns-penp with dialdehydes and reducing the imines to amines (organic chlorides can also be used), it was found that different bridging groups (or spacer molecules) could be introduced between the two units. This allowed a "tuning" of the distances between the two uns-penp units. It has been found that different xylyl linkers dramatically affect the stabilities of the corresponding copper−peroxo complexes. A peroxo complex with a *m*-xylyl spacer bridging the two uns-penp units (L^{12}, Scheme 6) proved to be the most stable.



Scheme 6. Ligands for the synthesis of dinuclear copper complexes

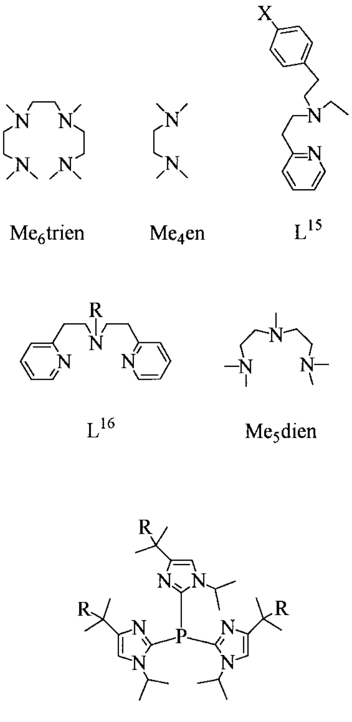
The above results suggest that the mononuclear units should be connected through more than one linker molecule. Connecting the tripodal amines with two linkers leads to macrocyclic ligands; an example currently being synthesized in the author's laboratory is shown in Scheme 6 (L^{13}). The potential of this approach has been highlighted by Bol et al., who synthesized the macrocyclic ligand MEPY22PZ (Scheme 6).[71,105] In this example, the tripodal units are connected through pyrazolyl/ethyl linkers. When the dinuclear copper(I) complex of this ligand was reacted with dioxygen, an extremely stable peroxo complex was formed. Theoretical calculations were also employed in the design of this ligand.[71]

When three linkers are used to connect two tren units, cryptands are obtained. A typical example is L^{14}, shown in

Scheme 6. However, when dinuclear copper(I) complexes of this and other cryptands with different linker molecules were reacted with dioxygen, only slow oxidation was observed and dioxygen intermediates could not be detected spectroscopically [this is similar to the reaction described above with btmpa (btpa); Scheme 4].[106]

Other Amines Related to tren

Once it had been established that aliphatic amines derived from tren are useful tools for studying copper(I)/dioxygen reactions, it was decided to investigate an additional series of amines.[48] The copper(I) complex of Me_6trien {*N*,*N*′-bis[2′-(dimethylamino)ethyl]-*N*,*N*′-dimethylethane-1,2-diamine; Scheme 7}, an isomer of Me_6tren, can be synthesized by a comproportionation reaction in water.[107] With this in mind, attempts were made to characterize a copper−dioxygen adduct in aqueous solution. However, although the copper(I) and copper(II) complexes of Me_6trien could be synthesized and characterized, no copper−dioxygen adduct could be detected when the copper(I) complex was treated with dioxygen (neither in aqueous nor organic media).[48]



Scheme 7. Various amine ligands

Me_4en (tetramethylethylenediamine; Scheme 7) can be viewed as being a part of Me_6trien or Me_6tren. The behavior of its copper(I) complex with a ratio of ligand to copper of 2:1 resembles that of the copper(I) complex of Me_6trien.[48] Crystal structures show the two compounds to be isostructural. The situation changes when Me_4en and copper(I) are used in a stoichiometric ratio of 1:1. Under these circumstances, complexes with Me_4en or other alkylated ethylenediamines become quite reactive towards dioxygen; on the basis of kinetic data, a variety of peroxo and oxo complexes have been postulated to form during oxidation.[108−112] This was proven by the fact that ligand L^2 (Scheme 2), which is very similar to the alkylated ethylenediamines, could be used to obtain the structurally characterized bis(μ-oxo) copper complexes described above.[33,34]

Furthermore, it has been shown that such bidentate ligands can be used for intramolecular aromatic and aliphatic hydroxylations.[113][114] In a recent study, copper(I) complexes of *N*-ethyl-*N*-[2-(2-pyridyl)ethyl]-2-phenylethylamine (L^{15}, Scheme 7; X = OMe, Me, H, Cl, NO_2) were investigated.[114] Time-resolved UV/Vis spectra as well as resonance Raman spectra provided strong evidence that bis(μ-oxo) complexes were formed during the oxidations.

Copper complexes with bidentate and tridentate ligands have been successfully employed in investigating the oxidation of intramolecular ligands or substrates.[25,31,115−121] Copper complexes incorporating L^{16} (Scheme 7; R = Me, phenyl) provide important insight into these reactions.[31,118,119]

The above results are corroborated by investigations on tridentate ligands carried out in this laboratory. Copper(I) and copper(II) complexes of Me_5dien (1,1,4,7,7-pentamethyldiethylethylenetriamine; Scheme 7) have previously been structurally characterized.[122,123] Me_5dien can be regarded as Me_6trien or Me_6tren with one arm missing.[48,50] Time-resolved spectra of the reaction of copper(I) Me_5dien with dioxygen at −90 °C are shown in Figure 4.[104] These spectra strongly suggest that a bis(μ-oxo) complex is formed. However, as yet it has not been possible to obtain resonance Raman data to prove this. Since Me_5dien can also be regarded as an open-chain analogue of a substituted triazacyclononane (Scheme 2), it will be interesting to investigate whether increased steric hindrance in this amine will allow the observation of similar peroxo/bis(μ-oxo) equilibria as seen for the copper complexes of R_3TACN.

These results suggest that in future researchers should turn from complicated ligand systems to simple amines that can be easily modified. Combinatorial chemistry might also be considered as being potentially helpful. It should be mentioned at this point that Karlin and co-workers have already succeeded in producing peroxo complexes by reacting copper(I) complexes of the simple ligand imidazole with dioxygen.[124,125]

Many of the hitherto characterized dinuclear copper complexes have not been mentioned in this article. Most of these have been described in detail in several monographs or review articles; some more recent work is described in refs.[8,10,49,126−132] It should be pointed out that these dinuclear complexes can be described as linked mononuclear units (Scheme 8).

Ligand type (a) represents a general example of the linked tripodal units discussed above (e.g. L^{12}, Scheme 6). Reducing the number of donor atoms leads to ligands of types (b) and (c). Here, bidentate or tridentate ligands (sim-

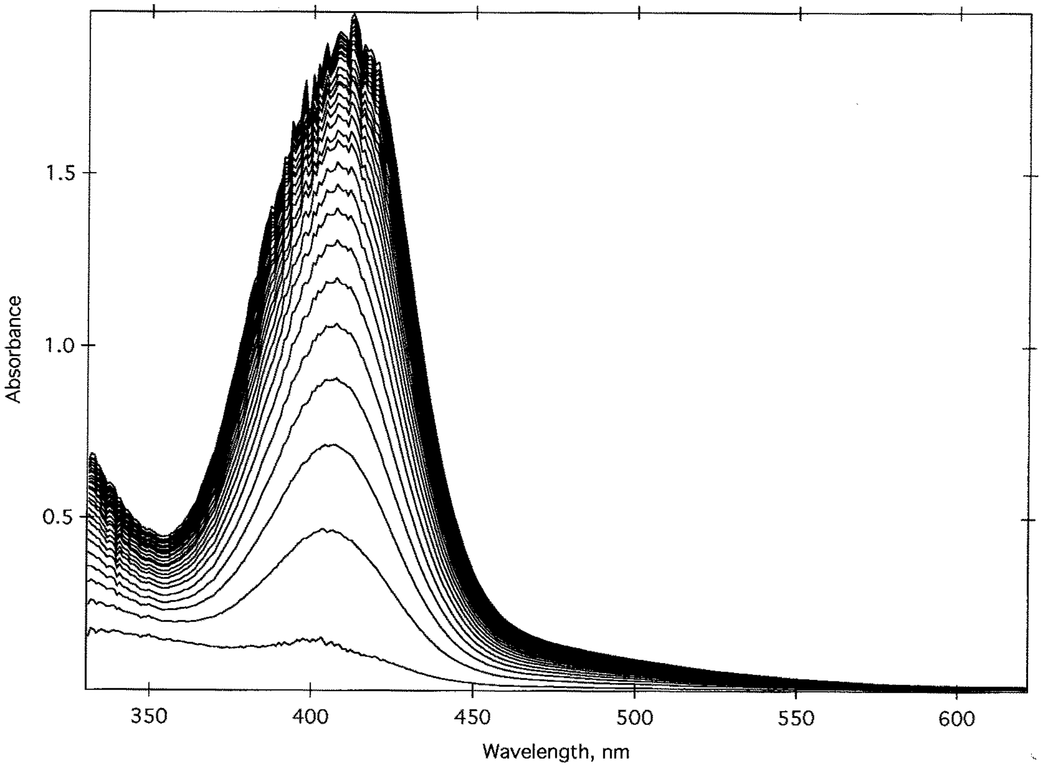
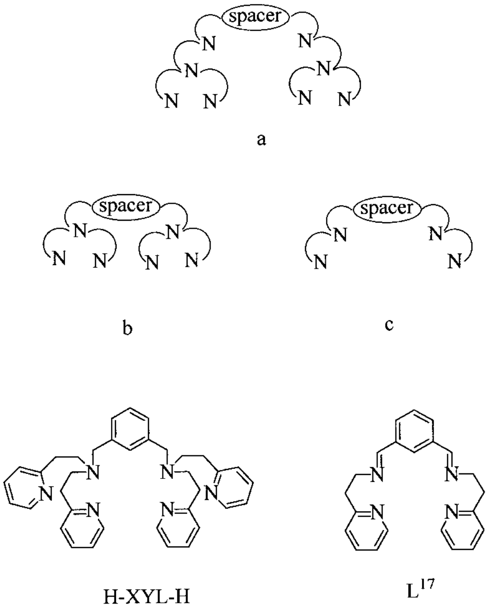


Figure 4. Reaction of $[(Me_5dien)Cu(RCN)]PF_6$ with dioxygen at −90 °C in dry propionitrile ([complex] = 0.36 mM, $[O_2]$ = 4.4 mM, Δt = 0.15 s)



Scheme 8. Ligands for the synthesis of dinuclear copper complexes

ilar to en, dien, or derivatives thereof) are connected through spacer molecules. An example of ligand type (b) is provided by H−XYL−H shown in Scheme 8 (another example would be ligand L^7 in Scheme 4, where the N donor units constitute a tridentate macrocycle).[46] The dinuclear copper complex of this ligand was discussed above. The ligand itself can be described as two L^{16} units (Scheme 7) bridged by a *m*-xylyl spacer. An example of ligand type (c) is the imine ligand L^{17} shown in Scheme 8.[8] Recently, amine ligands similar to L^{17} have been used in investigations of dinuclear copper complexes.[130,131,133]

The dinuclear copper(I) complexes of ligands of types (b) and (c) have been used to study the intramolecular benzene hydroxylation that occurs when some of these are reacted with dioxygen.[8,10,46,49,87,126−131,133] As yet, the mechanisms of such intramolecular aromatic or aliphatic hydroxylations are not well understood.[113]

Effect of Solvent

In the course of the investigations described above, it was found that the solvent played an important role in many reactions of copper(I) complexes with dioxygen. Propionitrile proved to be useful for studying the oxidations of copper(I) complexes with tripodal ligands such as tmpa or Me_6tren.[17,50] However, according to Equations (2) and (3), propionitrile is not only a solvent but a competing ligand as well, shifting the equilibria to the left. Acetone only shows weak ligating properties towards copper(I), so a dramatic effect was observed when this solvent was used instead of propionitrile.[44,50] In acetone, it proved possible to observe the copper−peroxo complexes of tmpa and Me_6tren even at room temperature. It was not possible to use dichloromethane as the copper(I) complexes of the tripodal ligands reacted with this solvent.[134] Methanol was not suitable either as it was found to have a dramatic destabilizing effect on the peroxo complexes.[50] This can probably be attributed to the protons of this solvent, similar to the effect observed when tren was used as a ligand (see above).

Such solvent effects are not observed with other copper(I) complexes. For example, the copper(I) complex of Pim*i*Pr$_2$ (Scheme 7) produced a dioxygen adduct (evidence was found for the formation of a copper−peroxo complex) in both methanol and acetone.[135,136] Here, the protons of the solvent do not seem to have a destabilizing effect.

Dichloromethane has been used for investigating the reactions of dinuclear copper(I) complexes with dioxygen at low temperatures. For example, the oxidation of $[Cu_2{-}H{-}XYL{-}H]^{2+}$ (H−XYL−H; Scheme 8) has been studied in both dichloromethane and acetone.[46] While differences in the reaction behavior were observed, no dramatic stabilization of the peroxo complex was evident in either of these solvents. In contrast, nitrile solvents suppress the intramolecular hydroxylation observed in the former two solvents. Again, this may be explained in terms of the strong binding of nitrile molecules.

Furthermore, depending on the solvent, the formation of either μ-η^2:η^2-peroxo-bridged or bis(μ-oxo)dicopper(III) compounds can be favored.[28]

Decomposition Reactions

While the binding of dioxygen is not yet perfectly understood, much insight into this reaction has been gained. This is much less true for decomposition reactions. In some instances, hydrogen peroxide is probably formed while the ligand of the complex remains intact. However, oxidation of the ligand is also a possibility. Only in a few cases has selective intramolecular hydroxylation been observed, leading to products that could be characterized (examples are given above). The detailed mechanisms of these reactions are still not understood.

A very interesting reaction ensues following the oxidation of $[(tmpa)Cu(CH_3CN)]PF_6$, which involves a fluoride abstraction. The product, a fluoride-bridged copper(II) complex, has been isolated and structurally characterized.[137]

Conclusions

In this article, an overview of the progress that has been made concerning the activation of dioxygen with copper(I) complexes has been presented. While it is still not possible to predict the reaction pathway for a copper(I) complex and dioxygen, the studies performed in recent years allow a much better understanding of these reactions than in the past. As indicated above, a more systematic investigation on this type of oxidation is still necessary. The contribution of the author's group to this task has been the development of a ligand building block system starting from simple amines. This system (similar to Lego or Tinker Toys) allows the synthesis of a large number of new ligands for copper(I) complexes. In principle, it should also permit a combinatorial approach. Even though selective substrate oxidation with copper(I) complexes and dioxygen has not been discussed in detail here, it seems most likely that in the near future many more oxidation catalysts will be based on these systems.

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Note Added in Proof (June 20, 2000): While this microreview was accepted for publication, a summary on copper−dioxygen species and copper−oxo species was published: A. G. Blackman, W. B. Tolman, "Copper−Dioxygen and Copper−Oxo Species Relevant to Copper Oxygenases and Oxidases", in *Structure & Bonding* (Ed.: B. Meunier), Springer-Verlag, Berlin, Heidelberg, **2000**, vol. 97, p. 179−211.

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[1] R. A. Sheldon, *J. Mol. Cat., A*: Chemical, Special Edition, **1997**, 117.

[2] K. A. Magnus, H. Ton-That, J. E. Carpenter, *Chem. Rev.* **1994**, *94*, 727−735.

[3] N. Kitajima, Y. Moro-oka, *Chem. Rev.* **1994**, *94*, 737−757.

[4] K. Lerch, *A.C.S. Symp. Ser.*, **1995**, *600*, 64−80.

[5] Á. Sánchez-Ferrer, J. N. Rodríguez-López, F. García-Cánovas, F. García-Carmona, *Biochim. Biophys. Acta* **1995**, *1247*, 1−11.

[6] J. P. Klinman, *Chem. Rev.* **1996**, *96*, 2541−2561.

[7] E. I. Solomon, U. M. Sundaram, T. E. Machonkin, *Chem. Rev.* **1996**, *96*, 2563−2605.

[8] K. D. Karlin, Z. Tyeklár (Eds.), *Bioinorganic Chemistry of Copper*, Chapman & Hall, New York, **1993**.

[9] M. Pascaly, I. Jolk, B. Krebs, *Chemie in unserer Zeit* **1999**, *33*, 334−341.

[10] J. Reedijk (Ed.), *Bioinorganic Catalysis*, Second Edition, Marcel Dekker, New York, **1999**.

[11] Y. Wang, J. DuBois, B. Hedman, K. Hodgson, T. Stack, *Science* **1998**, *279*, 537−540.

[12] P. Chaudhuri, M. Hess, T. Weyhermüller, K. Wieghardt, *Angew. Chem. Int. Ed.* **1999**, *38*, 1095−1098.

[13] W. B. Tolman, *Acc. Chem. Res.* **1997**, *30*, 227−237.

[14] P. L. Holland, W. B. Tolman, *Coord. Chem. Rev.* **1999**, *190−192*, 855−869.

[15] R. Than, A. Feldmann, B. Krebs, *Coord. Chem. Rev.* **1999**, *182*, 211−241.

[16] A. D. Zuberbühler in *Metal Ions in Biological Systems* (Ed.: H. Sigel), Marcel Dekker, New York, **1976**, *5*, 325−368.

[17] K. D. Karlin, S. Kaderli, A. D. Zuberbühler, *Acc. Chem. Res.* **1997**, *30*, 139−147.

[18] R. R. Jacobson, Z. Tyeklár, A. Farooq, K. D. Karlin, S. Liu, J. Zubieta, *J. Am. Chem. Soc.* **1988**, *110*, 3690−3692.

[19] Z. Tyeklár, R. R. Jacobson, N. Wei, N. N. Murthy, J. Zubieta, K. D. Karlin, *J. Am. Chem. Soc.* **1993**, *115*, 2677−2689.

[20] N. Kitajima, K. Fujisawa, Y. Mor-oka, K. Toriumi, *J. Am. Chem. Soc.* **1989**, *111*, 8975−8976.

[21] K. Fujisawa, M. Tanaka, Y. Moro-oka, N. Kitajima, *J. Am. Chem. Soc.* **1994**, *116*, 12079−12080.

[22] M. Harata, K. Jitsukawa, H. Masuda, H. Einaga, *J. Am. Chem. Soc.* **1996**, *116*, 10817−10818.

[23] A. Wada, M. Harata, K. Hasegawa, K. Jitsukawa, H. Masuda, M. Mukai, T. Kitagawa, H. Einaga, *Angew. Chem. Int. Ed.* **1998**, *37*, 798−799.

[24] M. Kodera, K. Katayama, Y. Tachi, K. Kano, S. Hirota, S. Fujinami, M. Suzuki, *J. Am. Chem. Soc.* **1999**, *121*, 11006−11007.

[25] S. Mahapatra, J. A. Halfen, E. C. Wilkinson, L. J. Que, W. B. Tolman, *J. Am. Chem. Soc.* **1994**, *116*, 9785−9786.

[26] S. Mahapatra, J. A. Halfen, E. C. Wilkinson, G. F. Pan, C. J. Cramer, L. Que, W. B. Tolman, *J. Am. Chem. Soc.* **1995**, *117*, 8865−8866.

[27] S. Mahapatra, J. A. Halfen, E. C. Wilkinson, G. F. Pan, X. D. Wang, V. G. Young, C. J. Cramer, L. Que, W. B. Tolman, *J. Am. Chem. Soc.* **1996**, *118*, 11555−11574.

[28] J. A. Halfen, S. Mahapatra, E. C. Wilkinson, S. Kaderli, V. G. Young, L. Que, A. D. Zuberbühler, W. B. Tolman, *Science* **1996**, *271*, 1397−1400.

[29] S. Mahapatra, V. Young, S. Kaderli, A. D. Zuberbühler, W. Tolman, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 130−133.

[30] E. Pidcock, S. DeBeer, H. V. Obias, B. Hedman, K. O. Hodgson, K. D. Karlin, E. I. Solomon, *J. Am. Chem. Soc.* **1999**, *121*, 1870−1878.

[31] H. V. Obias, Y. Lin, N. N. Murthy, E. Pidcock, E. I. Solomon, M. Ralle, N. J. Blackburn, Y.-M. Neubold, A. D. Zuberbühler, K. D. Karlin, *J. Am. Chem. Soc.* **1998**, *120*, 12960−12961.

[32] H. Hayashi, S. Fujinami, S. Nagatomo, S. Ogo, M. Suzuki, A. Uehara, Y. Watanabe, T. Kitagawa, *J. Am. Chem. Soc.* **2000**, *122*, 2124−2125.

[33] A. P. Cole, D. E. Root, P. Mukherjee, E. I. Solomon, T. D. P. Stack, *Science* **1996**, *273*, 1848−1850.

[34] V. Mahadevan, Z. Hou, A. P. Cole, D. E. Root, T. K. Lal, E. I. Solomon, T. D. P. Stack, *J. Am. Chem. Soc.* **1997**, *119*, 11996−11997.

[35] J. Reim, B. Krebs, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2040.

[36] J. R. Reim, R. Werner, W. Haase, B. Krebs, *Chem. Eur. J.* **1998**, *4*, 289−298.

[37] F. Meyer, H. Pritzkow, *Angew. Chem*. **2000**, in press.

[38] E. I. Solomon, F. Tuczek, D. E. Root, C. A. Brown, *Chem. Rev.* **1994**, *94*, 827−856.

[39] H. H. Thorp, V. L. Pecoraro (Eds.), *Mechanistic Bioinorganic Chemistry*, A.C.S., Washington DC, **1995**.

[40] K. D. Karlin, N. Wei, B. Jung, S. Kaderli, P. Niklaus, A. Zuberbühler, *J. Am. Chem. Soc.* **1993**, *115*, 9506−9514.

[41] J. Cahoy, P. L. Holland, W. B. Tolman, *Inorg. Chem.* **1999**, *38*, 2161−2168.

[42] N. Wei, D.-H. Lee, N. N. Murthy, Z. Tyeklár, K. D. Karlin, S. Kaderli, B. Jung, A. D. Zuberbühler, *Inorg. Chem.* **1994**, *33*, 4625−4626.

[43] D. H. Lee, N. Wei, N. N. Murthy, Z. Tyeklár, K. D. Karlin, S. Kaderli, B. Jung, A. D. Zuberbühler, *J. Am. Chem. Soc.* **1995**, *117*, 12498−12513.

[44] K. D. Karlin, D.-H. Lee, S. Kaderli, A. D. Zuberbühler, *Chem. Commun.* **1997**, 475−476.

[45] S. Mahapatra, S. Kaderli, A. Llobet, Y. Neuhold, T. Palanché, J. Halfen, V. Young, T. Kaden, L. Que, A. D. Zuberbühler, W. Tolman, *Inorg. Chem*. **1997**, *36*, 6343−6356.

[46] M. Becker, S. Schindler, K. D. Karlin, T. K. Kaden, S. Kaderli, T. Palanché, A. D. Zuberbühler, *Inorg. Chem.* **1999**, 1989−1995.

[47] H. D. Projahn, S. Schindler, R. van Eldik, D. G. Fortier, C. R. Andrew, A. G. Sykes, *Inorg. Chem.* **1995**, *34*, 5935−5941.

[48] M. Becker, F. Heinemann, F. Knoch, W. Donaubauer, G. Liehr, S. Schindler, G. Golub, H. Cohen, D. Meyerstein, *Eur. J. Inorg. Chem.* **2000**, 719−726.

[49] T. N. Sorrell, *Tetrahedron* **1989**, *45*, 3−68.

[50] M. Becker, F. Heinemann, S. Schindler, *Chem. Eur. J.* **1999**, *5*, 3124−3129.

[51] N. Wei, N. N. Murthy, Q. Chen, J. Zubieta, K. D. Karlin, *Inorg. Chem.* **1994**, *33*, 1953−1965.

[52] K. Uozumi, Y. Hyashi, M. Suzuki, A. Uehara, *Chem. Lett.* **1993**, 963−966.

[53] H. Nagao, N. Komeda, M. Mukaida, M. Suzuki, K. Tanaka, *Inorg. Chem.* **1996**, *35*, 6809−6815.

[54] C.-l. Chuang, K. Lim, Q. Chen, J. Zubieta, J. W. Canary, *Inorg. Chem.* **1995**, *34*, 2562−2568.

[55] M. Harata, K. Jitsukawa, H. Masuda, H. Einaga, *Chem. Lett.* **1996**, 813−814.

[56] M. Harata, K. Jitsukawa, H. Masuda, H. Einaga, *Bull. Chem. Soc. Jpn*. **1998**, *71*, 637−645.

[57] L. M. Berreau, S. Mahapatra, J. A. Halfen, V. G. Young, W. B. Tolman, *Inorg. Chem.* **1996**, *35*, 6339−6342.

[58] N. Wei, N. N. Murthy, Z. Tyeklár, K. D. Karlin, *Inorg. Chem.* **1994**, *33*, 1177−1183.

[59] M. Schatz, M. Becker, F. Thaler, F. Hampel, S. Schindler, M. Schatz, R. R. Jacobson, Z. Tyeklár, N. N. Murthy, Q. Chen, J. Zubieta, K. D. Karlin, submitted to *Inorg. Chem.*

[60] B. S. Lim, R. H. Holm, *Inorg. Chem.* **1998**, *37*, 4898−4908.

[61] K. Karlin, J. Hayes, S. Juen, J. Hutchinson, J. Zubieta, *Inorg. Chem.* **1982**, *21*, 4106−4108.

[62] K. Karlin, J. Hayes, J. Hutchinson, J. Hyde, J. Zubieta, *Inorg. Chim. Acta* **1982**, *64*, L219−L220.

[63] A. M. Dittler-Klingemann, F. E. Hahn, unpublished results

[64] A. M. Dittler-Klingemann, F. E. Hahn, *Inorg. Chem.* **1996**, *35*, 1996−1999.

[65] A. Dossing, A. Hazell, H. Toftlund, *Acta Chem. Scand.* **1996**, *50*, 95−101.

[66] D. Lee, N. N. Murthy, K. D. Karlin, *Inorg. Chem.* **1997**, *36*, 5785−5792.

[67] S. Schindler, H. Toftlund, unpublished results.

[68] P. Comba, P. Hilfenhaus, K. Karlin, *Inorg. Chem.* **1997**, *36*, 2309−2313.

[69] H. Börzel, P. Comba, C. Katsichis, W. Kiefer, A. Lienke, V. Nagel, H. Pritzkow, *Chem. Eur. J.* **1998**, *5*, 1716−1721.

[70] H. Börzel, P. Comba, M. Schatz, S. Schindler, manuscript in preparation

[71] J. E. Bol, W. L. Driessen, A. Y. N. Ho, B. Maase, L. Que, J. Reedijk, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 998−1000.

[72] P. C. Jain, E. C. Lingafelter, *J. Am. Chem. Soc.* **1967**, *89*, 6131−6136.

[73] M. Duggan, N. Ray, B. Hathaway, G. Tomlinson, P. Brint, K. Pelin, *J. Chem. Soc., Dalton Trans.* **1980**, 1342−1348.

[74] A. Marzotto, A. Ciccarese, D. A. Clemente, G. Valle, *J. Chem. Soc., Dalton Trans.* **1995**, 1461−1468.

[75] Z.-L. Lu, C.-y. Duan, Y.-P. Tian, X.-z. You, H.-K. Fun, B.-C. Yip, *Polyhedron* **1996**, *15*, 1769−1774.

[76] F. Thaler, C. D. Hubbard, F. W. Heinemann, R. van Eldik, S. Schindler, I. Fábián, A. M. Dittler-Klingemann, F. E. Hahn, C. Orvig, *Inorg. Chem.* **1998**, *37*, 4022−4029.

[77] M. Schatz, G. Rommualdo Torres, M. Becker, G. Liehr, O. Walter, S. Schindler, manuscript in preparation.

[78] G. Cayley, D. Cross, P. Knowles, *J. Chem. Soc., Chem. Commun.* **1976**, 837−838.

[79] G. R. Cayley, I. D. Kelly, P. F. Knowles, K. D. S. Yadav, *J. Chem. Soc., Dalton Trans.* **1981**, 2370−2372.

[80] D. H. Powell, P. Furrer, P. Pittet, A. E. Merbach, *J. Phys. Chem*. **1995**, *99*, 16622−16629.

[81] D. H. Powell, A. E. Merbach, I. Fábián, S. Schindler, R. van Eldik, *Inorg. Chem.* **1994**, *33*, 4468−4473.

[82] A. M. Dittler-Klingemann, C. Orvig, F. E. Hahn, F. Thaler, C. Hubbard, R. van Eldik, S. Schindler, I. Fábián, *Inorg. Chem.* **1996**, *35*, 7798−7803.

[83] P. P. Paul, Z. Tyeklár, R. R. Jacobson, K. D. Karlin, *J. Am. Chem. Soc.* **1991**, *113*, 5322−5332.

[84] A. A. Naiini, W. M. P. B. Menge, J. G. Verkade, *Inorg. Chem.* **1991**, *30*, 5009−5012.

[85] D. Walther, K. Hamza, H. Görls, W. Imhof, *Z. Anorg. Allg. Chem*. **1997**, *623*, 1135−1143.

[86] E. C. Alyea, G. Ferguson, M. Jennings, Z. Xu, *Polyhedron* **1990**, *9*, 739−741.

[87] M. Becker, S. Schindler, R. van Eldik, *Inorg. Chem.* **1994**, *33*, 5370−5371.

[88] S. Ryan, H. Adams, D. Fenton, M. Becker, S. Schindler, *Inorg. Chem.* **1998**, *37*, 2134−2140.

[89] A. Feldmann, B. Krebs, S. Schindler, unpublished results

[90] S. Schindler, C. D. Hubbard, R. van Eldik, *Chem. Soc. Rev.* **1998**, *27*, 387−393.

[91] K. Karlin, Q. Gan, A. Farooq, S. Liu, J. Zubieta, *Inorg. Chim. Acta* **1989**, *165*, 37−39.

[92] S. T. Frey, H. H. J. Sun, N. N. Murthy, K. D. Karlin, *Inorg. Chim. Acta* **1996**, *242*, 329−338.

[93] G. A. McLachlan, G. D. Fallon, R. L. Martin, L. Spiccia, *Inorg. Chem.* **1995**, *34*, 254−261.

[94] J. Mandel, C. Maricondi, B. Douglas, *Inorg. Chem.* **1988**, *27*, 2990−2996.

[95] H. Adams, N. A. Bailey, W. D. Carlisle, D. E. Fenton, G. Rossi, *J. Chem. Soc., Dalton Trans.* **1990**, 1271−1283.

[96] G. S. Matouzenko, A. Bousseksou, S. Lecocq, P. J. van Koningsbruggen, M. Perrin, O. Kahn, A. Collet, *Inorg. Chem.* **1997**, *36*, 2975−2981.
[97] J. Mandel, B. Douglas, *Inorg. Chim. Acta* **1989**, *155*, 55−69.
[98] O. Horner, M.-F. Charlot, A. Boussac, E. Anxolabéhère-Mallart, L. Tchertanov, J. Guilhem, J.-J. Girerd, *Eur. J. Inorg. Chem.* **1998**, 721−727.
[99] I. Bernal, I. M. Jensen, K. M. Jensen, C. J. McKenzie, H. Toftlund, J. P. Tuchagues, *J. Chem. Soc., Dalton Trans.* **1995**, 3667−3675.
[100] K. B. Jensen, C. J. McKenzie, L. P. Nielsen, J. Z. Pedersen, H. M. Svendson, *Chem. Commun.* **1999**, 1313−1314.
[101] A. J. Simaan, F. Banse, P. Mialane, A. Boussac, S. Un, T. Kargar-Grisel, G. Bouchoux, J.-J. Girerd, *Eur. J. Inorg. Chem.* **1999**, 993−996.
[102] O. Horner, E. Anxolabéhère-Mallart, M.-F. Charlot, L. Tchertanov, J. Guilhem, T. A. Mattioli, A. Boussac, J.-J. Girerd, *Inorg. Chem.* **1999**, *38*, 1222−1232.
[103] M. Schatz, M. Leibold, O. Walther, F. Heinemann, S. Schindler, manuscript in preparation
[104] M. Schatz, S. Schindler, unpublished results
[105] R. H. Bode, J. E. Bol, W. L. Driessen, F. B. Hulsbergen, J. Reedijk, A. L. Spek, *Inorg. Chem.* **1999**, *38*, 1239−1243.
[106] M. Becker, J. Nelson, S. Schindler, unpublished results
[107] G. Golub, H. Cohen, D. Meyerstein, *J. Chem. Soc., Chem. Commun.* **1992**, 397−398.
[108] M. A. El-Sayed, *Inorg. Chim. Acta* **1992**, *197*, 197−201.
[109] M. A. El-Sayed, K. Z. Ismail, T. A. El-Zayat, G. Davies, *Inorg. Chim. Acta* **1994**, *217*, 109−119.
[110] M. A. El-Sayed, G. Davies, T. S. Kasem, *Inorg. Chem.* **1990**, *29*, 4730−4735.
[111] G. Davies, M. A. El-Sayed, M. Henary, *Inorg. Chem.* **1987**, *26*, 3266−3273.
[112] G. Davies, M. A. El-Sayed, *Comments Inorg. Chem.* **1985**, *4*, 151−162.
[113] P. L. Holland, K. R. Rodgers, W. B. Tolman, *Angew. Chem. Int. Ed.* **1999**, *38*, 1139−1142.
[114] S. Itoh, M. Taki, H. Nakao, P. L. Holland, W. B. Tolman, L. J. Que, S. Fukuzumi, *Angew. Chem. Int. Ed.* **2000**, *39*, 398−400.
[115] M. Réglier, C. Jorand, B. Waegell, *J. Chem. Soc., Chem. Commun.* **1990**, 1752−1755.
[116] J. A. Halfen, V. G. Young, W. B. Tolman, *J. Am. Chem. Soc.* **1996**, *118*, 10920−10921.
[117] D. H. Lee, N. N. Murthy, K. D. Karlin, *Inorg. Chem.* **1996**, *35*, 804−805.
[118] S. Itoh, T. Kondo, M. Komatsu, Y. Ohshiro, C. Li, N. Kanehisa, Y. Kai, S. Fukuzumi, *J. Am. Chem. Soc.* **1995**, *117*, 4714−4715.
[119] S. Itoh, H. Nakao, L. M. Berreau, T. Kondo, M. Komatsu, S. Fukuzumi, *J. Am. Chem. Soc.* **1998**, *120*, 2890−2899.
[120] V. Mahadevan, J. L. DuBois, B. Hedman, K. O. Hodgson, T. D. P. Stack, *J. Am. Chem. Soc.* **1999**, *121*, 5583−5584.
[121] I. Blain, M. Giorgi, I. De Riggi, M. Réglier, *Eur. J. Inorg. Chem.* **2000**, 393−398.
[122] M. J. Scott, R. H. Holm, *J. Am. Chem. Soc.* **1994**, *116*, 11357−11367.
[123] M. J. Scott, S. C. Lee, R. H. Holm, *Inorg. Chem.* **1994**, *33*, 4651−4662.
[124] I. Sanyal, K. D. Karlin, R. W. Strange, N. J. Blackburn, *J. Am. Chem. Soc.* **1993**, *115*, 11259−11270.
[125] I. Sanyal, R. W. Strange, N. J. Blackburn, K. D. Karlin, *J. Am. Chem. Soc.* **1991**, *113*, 4692−4693.
[126] E. Spodine, J. Manzur, *Coord. Chem. Rev.* **1992**, *119*, 171−198.
[127] T. N. Sorrell, V. A. Vankai, M. L. Garrity, *Inorg. Chem.* **1991**, *30*, 207−210.
[128] E. Monzani, L. Quinti, A. Perotti, L. Casella, M. Gullotti, L. Randaccio, S. Geremia, G. Nardin, P. Faleschini, G. Tabbi, *Inorg. Chem.* **1998**, *37*, 553−562.
[129] G. Alzuet, L. Casella, M. L. Villa, O. Carugo, M. Gullotti, *J. Chem. Soc., Dalton Trans.* **1997**, 4789−4794.
[130] D. Ghosh, R. Mukherjee, *Inorg. Chem.* **1998**, *37*, 6597−6605.
[131] D. Ghosh, T. K. Lal, S. Ghosh, R. Mukherjee, *Chem. Commun.* **1996**, 13.
[132] L. Santagostini, M. Gullotti, E. Monzani, L. Casella, R. Dillinger, F. Tuczek, *Chem. Eur. J.* **2000**, *6*, 519−522.
[133] F. Thaler, G. Liehr, S. Schindler, manuscript in preparation.
[134] R. R. Jacobson, Z. Tyeklár, K. D. Karlin, *Inorg. Chim. Acta* **1991**, *181*, 111−118.
[135] W. E. Lynch, D. M. J. Kurtz, S. Wang, R. A. Scott, *J. Am. Chem. Soc.* **1994**, *116*, 11030−11038.
[136] T. N. Sorrell, W. E. Allen, P. S. White, *Inorg. Chem.* **1995**, *34*, 952−960.
[137] R. R. Jacobson, Z. Tyeklár, K. D. Karlin, J. Zubieta, *Inorg. Chem.* **1991**, *30*, 2035−2040.

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