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Copper Oxo Complexes

Molecular Cu^{II}-O-Cu^{II} Complexes: Still Waters Run Deep

*Peter Haack and Christian Limberg**

biomimetic reactions · copper · dinuclear complexes · oxidation · oxo compounds

Research on O_2 activation at ligated Cu^I is fueled by its biological relevance and the quest for efficient oxidation catalysts. A rarely observed reaction is the formation of a Cu^{II}-O-Cu^{II} species, which is more special than it appears at first sight: a single oxo ligand between two Cu^{II} centers experiences considerable electron density, and this makes the corresponding complexes reactive and difficult to access. Hence, only a small number of these compounds have been synthesized and characterized unequivocally to date, and as biological relevance was not apparent, they remained unappreciated. However, recently they moved into the spotlight, when Cu^{II}-O-Cu^{II} cores were proposed as the active species in the challenging oxidation of methane to methanol at the surface of a Cu-grafted zeolite and in the active center of the copper enzyme particulate methane monooxygenase. This Minireview provides an overview of these systems with a special focus on their reactivity and spectroscopic features.

1. Introduction

The selective oxo functionalization of un-activated C–H bonds is still one of the major targets in the fields of homogeneous and heterogeneous catalysis. It provides challenges in basically all fields of chemistry, from catalyst design to the technical realization of the processes found. However, nature has found impressive solutions for many important problems in this area: It has developed enzymes which oxidize the most inert C–H bonds with high efficiency and selectivity even at room temperature. However, the way by which the enzymes perform their interesting chemistry is often unclear and poses many questions to biologists. Hence, the selective oxygenation of hydrocarbons is at the interface of various different research fields and progress made in one of them may have a direct impact on the other ones.[1] For example, a more comprehensive knowledge regarding enzymatic processes may allow for the optimization of currently applied catalytic processes or the development of new industrial catalysts. Alternatively, investigations of surface reactions or of coordination compounds that model the active sites of heterogeneous catalysts and enzymes may contribute to a better understanding of the functionality of metalloproteins. Examples of synergetic effects of this kind come for instance from copper/dioxygen chemistry.[2,3] With the help of the extensive studies on synthetic copper model compounds a Cu^{II}(μ-η^2:η^2-O_2)Cu^{II} motif (**A**, Figure 1) was predicted correctly for the active site in *oxy*-hemocyanine as well as *oxy*-tyrosinase.[4] The first model complexes mimicking the functionality of monooxygenases, such as tyrosinase, were reported more than three decades ago.[5] Aiming at an improved knowledge, especially with regard to metalloenzymes containing two copper ions in their active sites, the investigation of ligand–Cu^I/O_2 chemistry has led to the characterization of a wide range of Cu_2O_2 complexes con-

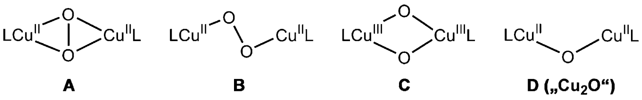

Figure 1. Structural motifs occurring upon O_2 activation at two Cu^I centers.

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[*] Prof. Dr. C. Limberg
Humboldt-Universität zu Berlin, Institut für Chemie
Brook-Taylor-Strasse 2, 12489 Berlin (Germany)
E-mail: christian.limberg@chemie.hu-berlin.de
Homepage: http://www.chemie.hu-berlin.de/aglimberg
Dr. P. Haack
Humboldt-Universität zu Berlin, Institut für Chemie
Brook-Taylor-Strasse 2, 12489 Berlin (Germany)

taining in addition to the abovementioned core **A** also Cu^{II}(*trans*-(μ-η^{1}:η^{1}-O$_2$))Cu^{II} (**B**) or Cu^{III}(μ-O)$_2$Cu^{III} (**C**) moieties (Figure 1).[6–11]

Recently, another copper containing metalloenzyme, particulate methane monooxygenase (pMMO), moved into the focus of the researchers' interest. Crystallographic analyses combined with activity studies on the enzyme and engineered protein variants have indicated that the catalytic function of pMMO—the selective oxygenation of methane to methanol—is based on a dicopper site (Figure 2), but the mechanism is still unclear.[12,13]

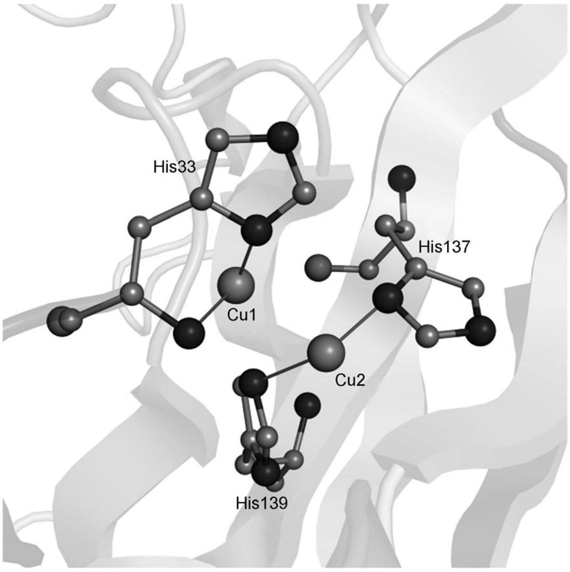


Figure 2. Structure of the active site in pMMO from *Methylococcus capsulatus* (Bath), PDB code: 1YEW.[13]

With regard to industrial research, the selective methane oxidation has been formulated as one of the "ten challenges for catalysis".[14] In contemporary studies, this objective was approached from grafted zeolites: It has been demonstrated that Cu-ZSM-5, after activation with dioxygen, is able to mediate the selective oxidation of methane giving methanol under comparatively mild conditions.[15–18] Furthermore, it has been shown by extensive resonance Raman studies combined with theoretical considerations that this impressive reactivity proceeds at a bent mono-μ-oxo dicopper(II) core, [Cu^{II}-O-Cu^{II}]$^{2+}$, as the active site (Figure 3a). The result of an additional computational investigation using a simplified model of the active species may rationalize the reactivity towards methane—the most inert of all hydrocarbons (C–H bond dissociation energy: 104 kcal mol^{-1}): 1) As the methane molecule approaches the active site, a polarization of one Cu–O bond takes place leading to a Cu^{I}···oxyl-Cu^{II} moiety (Figure 3b), which is capable of abstracting a H atom from the substrate, 2) The H atom abstraction itself is favored considerably through the formation of a very stable O–H bond (90 kcal mol^{-1}) in the resulting Cu-(OH)-Cu complex.[16]

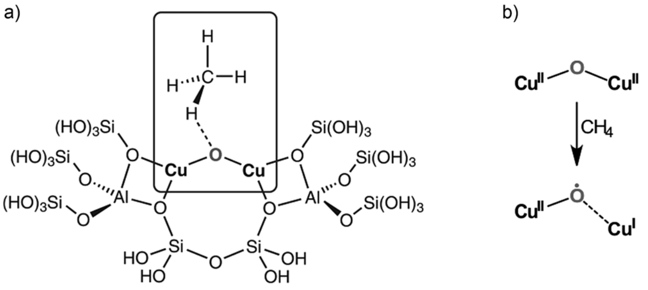


Figure 3. a) Simplified model of the methane-oxidizing active site in oxygen-activated Cu-ZSM-5. b) Formation of the Cu^{I}···oxyl-Cu^{II} intermediate caused by the approach of one methane molecule to the mono(μ-oxo) dicopper(II) core.[16]

In this context it has been communicated that according to theoretical studies the reactivity of the reactive mono-μ-oxo dicopper(II) core with CH$_4$ is retained when the silicate ligand matrix is replaced by the protein environment within the active site of the pMMO enzyme. This result provides grounds to speculate that a μ-oxo dicopper(II) site is also the active species during the hydroxylation of methane by pMMO.[2] As a result of the information gathered on the pMMO active site and Cu-ZSM-5, μ-oxo dicopper(II) complexes (**D**, "Cu$_2$O") moved into the spotlight as potential model compounds.[19] Quotes like "*Future research should focus on how the Cu^{II}-O-Cu^{II} species possibly translates to the context of protein environments; the structure will likely become a focus of a bioinorganic field invigorated by the proposal.*"[20] and "*The mixed-valent oxo dicopper(II/III) or simple oxo dicopper(II) centers are both candidates for the enzyme active site methane oxidizer. The former has not yet been identified or isolated*

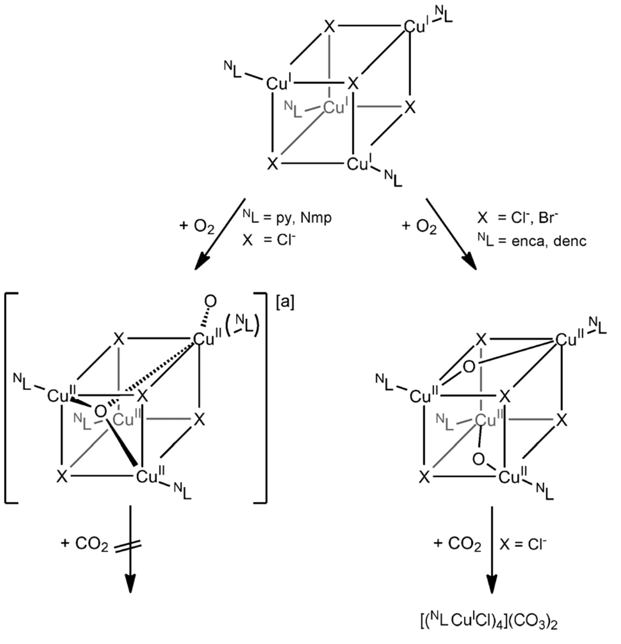
Christian Limberg received his Ph.D. with A. Haas in 1992 in Bochum and subsequently performed postdoctoral work together with A. J. Downs at Oxford University. After completion of his Habilitation in Heidelberg, he became Deputy Chair of Inorganic Chemistry at the TU Munich in 2001 before he was appointed full professor at the Humboldt-Universität zu Berlin in 2002. For his scientific work he was awarded a Karl-Winnacker-Stipendium of the Aventis Foundation, the academy prize of the Academy of Science in Göttingen, as well as the Carl-Duisberg-Gedächtnispreis of the GDCh. In 2009 he received the Horst-Dietrich-Hardt prize of the Universität des Saarlandes.

Peter Haack, born in 1980, started his chemistry studies in 2001 at the Humboldt-Universität zu Berlin. In 2006 he received his Diploma under the supervision of Prof. Dr. Christian Limberg. After time as a visiting researcher in the group of Dr. Philip J. Bailey at the University of Edinburgh he returned to the Limberg Lab in 2007 where he obtained his Ph.D. in 2012. In the same group he continued his research on copper-based coordination and oxidation chemistry until 2013.

among the known crop of Cu_2O_2 synthetic model compounds; the latter has some precedent, but does not have a developed chemistry."[21] illustrate that the synthesis and characterization of Cu_2O complexes has advanced to one of the major goals in current Cu/O_2 chemistry.[18] However, compared to the well-characterized Cu_2O_2 compounds, **A**, **B**,and **C**, molecular Cu_2O complexes have rarely been mentioned in the literature, and therefore in the present contribution we provide an overview of the limited findings regarding these systems in a chronological manner. Herein we summarize the work starting in the 1970s up to recent developments with a special focus on the reactivity and spectroscopic features of these Cu_2O compounds. Afterwards, the derived central features of this class of compounds are summarized in one more general section.

2. Molecular Cu_2O complexes

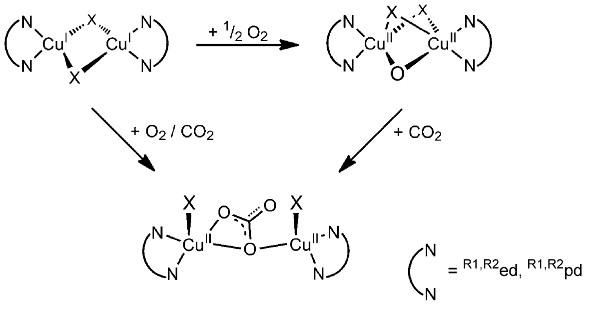
First indications regarding the formation of Cu_2O species were obtained in connection with the reaction between copper(I) halides and dioxygen in the presence of monodentate N-heterocyclic donor molecules. The studies performed by Churchill, Davies, and co-workers showed that depending on the nature of the ligands employed two different cube-like clusters were formed (Scheme 1). Within these compounds the copper ions are either bridged by oxo ligands in a μ- or a μ_4-mode.[22–27] The corresponding oxygenation reactions were investigated with the aid of cryoscopic and dioxygen uptake measurements, UV/Vis, EPR, and IR spectroscopy. The complexes featuring μ-oxo ligands clearly differed from the μ_4-oxo compounds in their stability as well as their reactivity. The μ_4-oxo compounds was reported to be very unstable. Upon standing or concentration N-donor (py, Nmp) coordinated copper(II) oxide-based polymers precipitated and this was accelerated by heat.[22,25] Moreover, only complexes with μ-oxo ligands were EPR silent and capable of forming the corresponding carbonato complexes in the presence of CO_2.



Scheme 1. Products after reactions of the copper(I) halide complexes $[(^{N}LCu^{I}X)_4]$ with O_2 and their reactivity towards CO_2.[25,26] py = pyridine, Nmp = *N*-methylpyrrolidin-2-one, enca = ethyl nicotinate, denc = *N*,*N*-diethylnicotinamide. The proposed structures of the compounds have been reproduced without any change from original paper.[26] While in the case of ^{N}L = py both compositions, $[^{N}L_4Cu^{II}{}_4X_4O_2]$ and $[^{N}L_3Cu^{II}{}_4X_4O_2]$, were discussed, employment of ^{N}L = Nmp exclusively led to $[^{N}L_3Cu^{II}{}_4X_4O_2]$ species. The latter was shown to be unstable during crystallization attempts giving rise to the isolation of $[Nmp_3Cu^{II}{}_4X_4(OH_2{\cdots}Nmp)]$ ($X = Cl^-$).[24]

The IR spectra of the Cu_2O species showed a characteristic vibrational band, which was assigned to the Cu–O stretching vibration. Dependent on the nature of the N-donor ligand employed, the signal was detected at 555 cm^{-1} (enca) or 580 cm^{-1} (denc). Monitoring the oxygenations of the precursors $[(^{N}LCu^{I}X)_4]$ (^{N}L = enca, denc, $X = Cl^-, Br^-$) with the aid of UV/Vis spectroscopy revealed broad absorption bands in the range 700–800 nm ($\varepsilon = 800\,\text{M}^{-1}\,cm^{-1}$) originating from the Cu_2O complexes.[25,26,28]

In the further course of these studies tetra-alkylated diamine-based ligands, ^{R1,R2}ed (ed: 1,2-ethylenediamine) and ^{R1,R2}pd (pd: 1,3-propylenediamine), were used instead of monodentate[27–30] N-bases (several years later such bidentate diamines also allowed for the synthesis of temperature labile **A** and **C** compounds in combination with copper(I) salts containing weakly coordinating anions).[31] The corresponding copper(I) halide compounds, $[(^{R1,R2}ed/^{R1,R2}pdCu^{I})_2(\mu\text{-}X)_2]$ ($R^1 = R^2$ = Me, Et, *n*Pr; $X^- = Cl^-$, Br^- I^-), were shown to react with dioxygen to form copper(II) complexes, which contain an additional O atom. Also in these cases the oxygenation products tended to polymerize,[32,33] but in the presence of CO_2 again stable carbonato complexes were formed, which could be fully characterized (Scheme 2).[28,29,34]

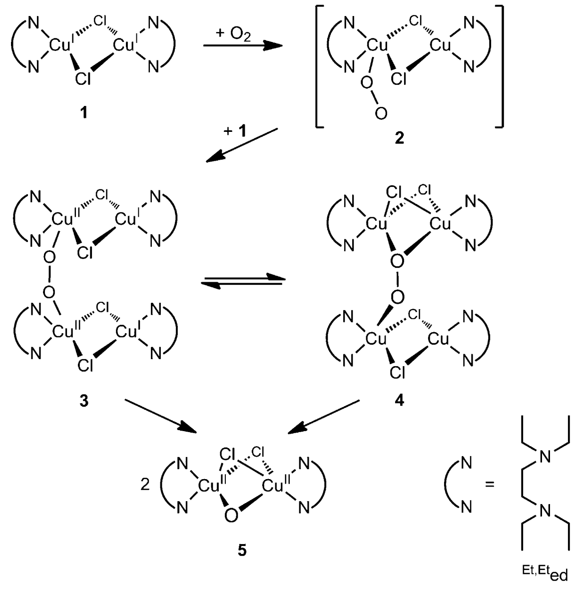


Scheme 2. Reactivity of copper(I) halide complexes of either ^{R1,R2}ed or ^{R1,R2}pd ligands towards O_2 and their conversion with CO_2. ed = 1,2-ethylenediamine, pd = 1,3-propylenediamine; $R^1 = R^2$ = Me, $R^1 = R^2$ = Et, $R^1 = R^2$ = *n*Pr, $R^1 = R^2$ = *n*Pent; $X^- = Cl^-$, Br^-, I^-.

On the basis of the molecular structures of known copper(I) halide precursors with diamine-based ligands as elucidated by single-crystal X-ray diffraction[27,35,36] in combination with the analytical data gathered for the Cu_2O products formed after oxygenation, structures were postulated for the complexes. In addition to the two halide anions, the copper(II) ions are bridged by an oxo ligand originating from dioxygen (Scheme 2, right).[33,37] While the Raman spectrum recorded for a solution of $[(^{Et,Et}edCu^{II})_2(\mu\text{-}Cl)_2(\mu\text{-}O)]$,[33] (**5**) in CH_2Cl_2 did contain two weak, ambiguous signals at 627 cm^{-1} and 701 cm^{-1}, the IR spectrum recorded for $[(^{Et,Et}edCu^{II})_2(\mu\text{-}Br)_2(\mu\text{-}O)]$ showed a new intense band at 600 cm^{-1}, which was proposed to arise from the Cu–O stretching vibration.[35]

In contrast to the UV/Vis spectra recorded for the denc and enca compounds mentioned above, all the diamine-based Cu_2O halide complexes show their characteristic absorption features between 600–700 nm ($\varepsilon = 800\,M^{-1}cm^{-1}$).[32,37] These differences may be ascribed to the varying degrees of aggregation and therefore to different electronic situations: While use of monodentate ligands resulted in tetranuclear products (denc, enca) containing two oxo ligands, the use of bidentate ligands (^{R1,R2}ed, ^{R1,R2}pd) led to dinuclear copper complexes featuring just one oxo bridge.[35] The formation mechanism of **5**, was investigated in detail. Under ambient conditions a direct four-electron reduction of the dioxygen molecule was observed. However, while studying the oxygenation of $[(^{Et,Et}edCu^{I})_2(\mu\text{-}Cl)_2]$ (**1**) at low temperatures the formation of mixed-valent tetranuclear peroxocopper intermediates was indicated by the combined results from stopped-flow experiments as well as UV/Vis, Raman, and EPR spectroscopic measurements. These temperature-labile species were shown to decompose at room temperature to give the Cu_2O complex **5** (Scheme 3). Complex **5** was found to effectively oxidize 2,6-dimethylphenol yielding 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone and phenol-based polymers, respectively.[33]

In 1981 Roselli et al. reported a Cu_2O complex with 1,10-phenanthroline (phen) instead of diamine-based molecules as the supporting ligand. The complex was accessible through the reaction of four equivalents of the corresponding copper(I) chloride precursor $[phenCu^{I}Cl]$ (**6**), with one molecule of dioxygen.[38] A dinuclear structure of the thermally unstable product $[(phenCu^{II}Cl)_2(\mu\text{-}O)]$ (**7**) exhibiting two exchange-coupled copper(II) centers with a triplet ground state was suggested based on the results of EPR spectroscopy. Although labeling studies employing $^{18}O_2$ did not lead to the detection of isotope sensitive Cu–O vibration bands in the IR spectrum, the presence of one bridging oxo ligand bound to the copper ions was indicated by the reaction with phosphanes: In the presence of an excess of PPh_3, $[phenCu^{I}Cl(PPh_3)]$ (**8**), as well as $(O)PPh_3$ were isolated as the products. Roselli et al. classified this reaction as "*the first example of a direct oxygen transfer to an organic substrate from an oxygenated copper complex*." Seven years later Zink and Henary presented an alternative access to **7** by the photoexpulsion of CO_2 from the corresponding carbonato complex $[(phenCu^{II}Cl)_2(\mu\text{-}CO_3)]$ (**9**).[39] Moreover, it was shown that the photodissociation and thermal binding of CO_2 proceeded reversibly.



Scheme 3. Reaction steps of the low-temperature oxygenation of **1**, finally yielding in the Cu_2O complex **5**.[27,33] Intermediate **2** has never been observed. In the cases of **3** and **4** the oxidation states of the copper ions involved were not specified.

Shortly afterwards Nelson, Drew, and co-workers found that a dicopper(II) complex **10** with a macrocyclic ligand featuring imine-based N- as well as furan-based O-donor functions (L_{MC}, Figure 4) undergoes auto-reduction upon warming its solutions in acetonitrile. The resulting dicopper(I) complex reacted with dioxygen in a ratio $Cu/O_2 = 4{:}1$. Hence, the formation of a Cu_2O species was suspected.[40]

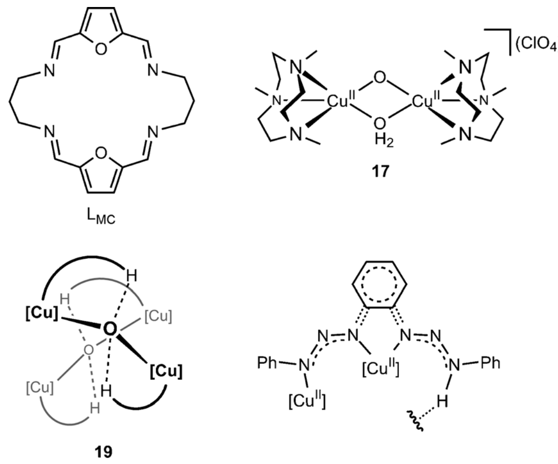
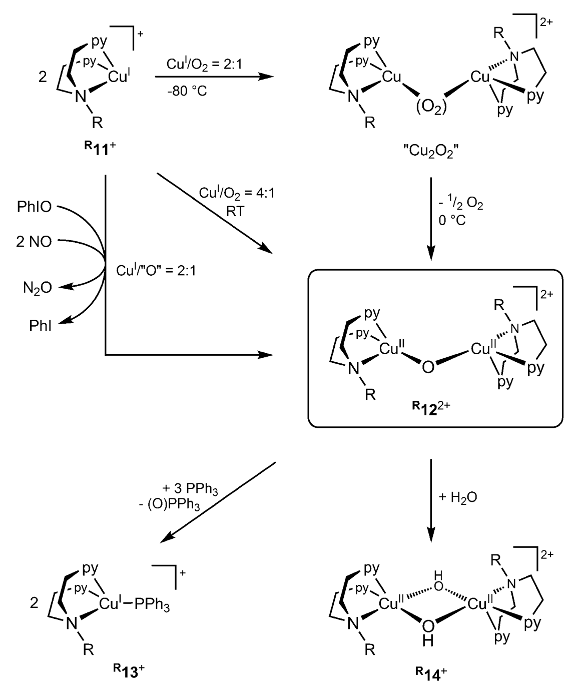


Figure 4. The potential ligand L_{MC}, a putative Me_3tacn-based Cu_2O complex, $[(Me_3tacnCu^{II})_2(\mu\text{-}O)(\mu\text{-}OH_2)](ClO_4)_2$ (**17**) and (below) the bonding situation within $[(PhN_3C_6H_4N_3(H)Ph)_4Cu^{II}_4(\mu\text{-}O)_2]$ (**19**): At the bottom right hand side the coordination mode of the ligand within **19** is shown, while on the left hand side the tetrahedral coordination spheres of the oxo ligands is illustrated.

Karlin and co-workers observed the formation of Cu_2O complexes upon use of the tridentate ligand system, ^{R}Py2 (*N*-R-*N*,*N*-bis(2-(2-pyridyl)ethyl)amine, with varying N-bound substituents (R = Me, Ph, Bn)).[41–43] Detailed low-temperature investigations showed that upon treatment of $[^{R}Py2Cu^{I}]PF_6$ ($^{\mathbf{R}}\mathbf{11}PF_6$) with dioxygen Cu_2O_2 complexes are formed initially, which decompose after annealing to 0 °C. The corresponding Cu_2O complexes were assumed to form by peroxide disproportionation (Scheme 4) in the course of further reaction of the Cu_2O_2 intermediate with the corre-



Scheme 4. Formation of Cu$_2$O complexes based on ^{R}Py2 ligands (R = Me, Ph, Bn) and their reactivity towards H$_2$O and PPh$_3$. The weakly coordinating anions (PF$_6^-$, BArF$^-$) were omitted for clarity.

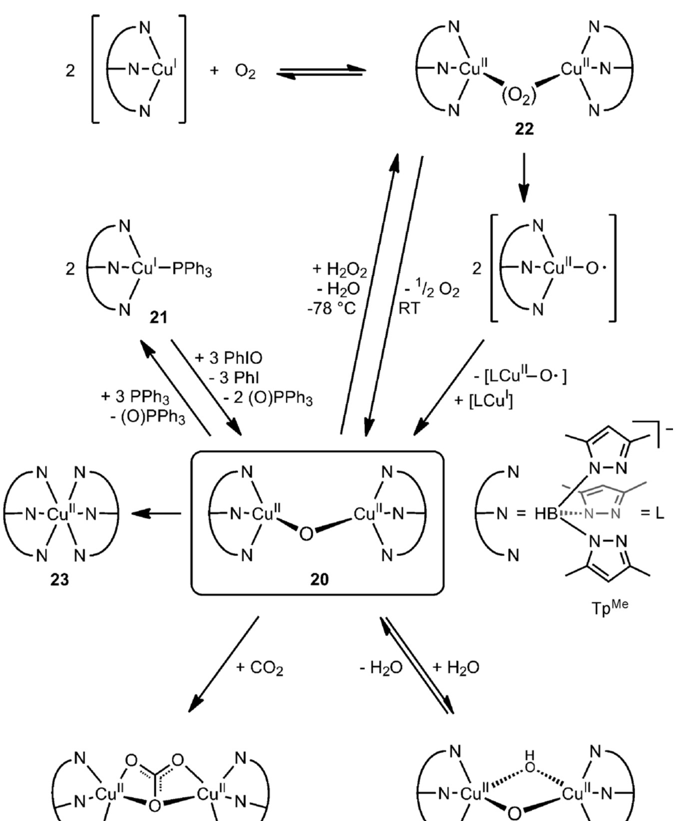
sponding copper(I) precursor leading to a Cu/O$_2$ ratio of 4:1 for the overall reaction.[42] These kinds of peroxide decays were also postulated for other cases.[44] However, in the presence of excess dioxygen, the Cu$_2$O$_2$ intermediates were found to decompose by N-dealkylation reactions at low temperatures. The Cu$_2$O complexes were isolated then analyzed by elemental analysis, IR, UV/Vis, and EPR spectroscopy. While IR spectroscopic studies did not provide any further insights, the results from EPR measurements suggested the formation of a product containing two bridged copper(II) centers: **^{Me}12**PF$_6$ and **^{Ph}12**PF$_6$ dissolved in CH$_2$Cl$_2$ were found to be EPR silent while for the case of **^{Bn}12**PF$_6$ observations comparable to those described in the case of [(phenCu^{II}Cl)$_2$(μ-O)] (**7**) were made.[38] Upon dissolving **^{R}12**PF$_6$ in protic solvents, such as methanol, the dinuclear structure was reported to break up resulting in the typical tetragonal EPR spectra known for mononuclear copper(II) complexes. The UV/Vis spectra of all the ^{R}Py2-based Cu$_2$O complexes exhibited an absorption band in the range 620–710 nm ($\varepsilon < 900\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$) originating from copper(II) d–d transitions. The μ-oxo dicopper(II) complexes were found to effectively transfer the oxygen atom onto PPh$_3$, yielding (O)PPh$_3$ and [^{R}Py2Cu^I(PPh$_3$)]PF$_6$ (**^{R}13**PF$_6$) in the presence of excessive amounts of the phosphane.[41,43] Additionally, they are prone to hydrolysis forming the corresponding bis(μ-hydroxo) dicopper(II) compounds [(^{R}Py2Cu^{II})$_2$(μ-OH)$_2$]-(PF$_6$)$_2$, (**^{R}14**PF$_6$; Scheme 4). Alternatively, Cu$_2$O complexes of this kind were accessible by the reaction of two equivalents of the copper(I) precursor with the oxygen-atom transfer reagent iodosobenzene (PhIO) or even with NO—as the compounds [(N4Cu)$_2$O](PF$_6$)$_2$ (**15**; N4 = *N*,*N*′-[*N*,*N*,*N*′,*N*′-tetra(2-(2-pyridyl)ethyl)]*n*butane-1,4-diamine),[45] and [(tmpaCu)$_2$O](PF$_6$)$_2$ (**16**; tmpa = tris(2-pyridylmethyl)amine),[45] also the Cu$_2$O complex [(^{Me}Py2Cu^{II})$_2$(μ-O)](BArF)$_2$ (**^{Me}12**BArF; BArF$^-$ = [B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$]$^-$), could be generated by the reaction of the copper(I) precursor [^{Me}Py2Cu^I]BArF (**^{Me}11**BArF) with NO in THF, and the side product N$_2$O was detected quantitatively by gas chromatography (GC).[43]

The ^{1}H NMR spectrum of **^{Me}12**BArF proved to be nearly identical to that of the corresponding copper(I) precursor **^{Me}11**BArF. The diamagnetic behavior of **^{Me}12**BArF was rationalized by a strong antiferromagnetic coupling between the copper(II) ions. Structural information was obtained with the aid of EXAFS spectroscopy. Accordingly, each copper(II) ion within **^{Me}12**BArF interacts with three N atoms (from ^{Me}Py2; Cu–N 2.023 Å) and additionally with a single ligand at a distance of 1.906 Å. This single ligand was identified as an oxo ligand by comparing the interatomic distance with bond lengths determined within Cu^{II}(μ-OH)$_2$Cu^{II}, Cu^{III}(μ-O)$_2$Cu^{III}, and Cu^{II}(μ-peroxo)Cu^{II} entities.

Chaudhuri et al. published in 1985 the synthesis of [(Me$_3$tacnCu^{II})$_2$(μ-O)(μ-OH$_2$)](ClO$_4$)$_2$ (**17**; Figure 4, Me$_3$tacn = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane) starting however, with copper(II) precursors.[46] The green μ-aqua-μ-oxo complex **17** was shown to transform into its blue tautomer [(Me$_3$tacnCu^{II})$_2$(μ-OH)$_2$](ClO$_4$)$_2$ (**18**) in the presence of traces of water underlining the high sensitivity of Cu$_2$O complexes to water. Also the determination of the molecular structures of the two different-colored compounds with the aid of single-crystal X-ray diffraction was reported. However, the structural parameters must be regarded with caution since the data collections for crystals of both **17** and **18** were carried out at room temperature. While in case of the blue single crystals (**18**) a commonly known Cu^{II}(μ-OH)$_2$Cu^{II} motif[7,47] was determined, the unambiguous structural characterization of the green Cu$_2$O compound **17** was hampered by a disorder of the chemically inequivalent O atoms. For that reason the H atoms belonging to the aqua ligand could not be localized. A further investigation showed that the tautomers differed in their magnetic behavior, and the IR spectra recorded for the two compounds gave rise to different signal patterns.

In 1994 Hörner and co-workers reported the synthesis and crystal structure of the tetranuclear copper(II) complex [{PhN$_3$C$_6$H$_4$N$_3$(H)Ph}$_4$Cu$^{II}_4$(μ-O)$_2$] (**19**).[48] Within the solid state structure each μ-oxo ligand interacts not only with the two copper ions but also with two N bound H atoms of the bis(phenyltriazeno)benzene-based ligands giving rise to a tetrahedral coordination geometry. Consequently, **19** cannot be regarded as a true Cu$_2$O complex—the situation in **19** rather has to be regarded as halfway between a Cu^{II}(μ-OH)Cu^{II} and a Cu$_2$O compound. However, the Cu–O bond lengths and Cu-O-Cu angles in the molecular structure were found to amount to 1.900(3) Å and 114.5(6)° (second molecule: 1.925(4) Å and 110.9(5)°), respectively, the two copper(II) ions within one Cu-O(⋯H)$_2$-Cu motif being separated by 2.983(1) Å (3.168(1) Å).

Kitajima et al. generated a Cu$_2$O complex, [(Tp^{Me}Cu^{II})$_2$(μ-O)] (**20**; Tp^{Me-} = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) through two different routes: In one route **20** was accessed by treating [Tp^{Me}Cu^{I}(PPh$_3$)] (**21**), with an excess of PhIO.[49] After the transformation of the PPh$_3$ ligand into (O)PPh$_3$ by the first equivalent of PhIO the reaction of the second one caused the formation of **20**. In the second route **20** was detected after the spontaneous thermal decomposition of the corresponding dicopper(II) peroxo complex [(Tp^{Me}Cu^{II})$_2$(μ-O$_2$)] (**22**) accompanied by the liberation of O$_2$.[50] In contrast to the peroxide disproportionation reaction of the ^{R}Py2-based Cu$_2$O$_2$ species assumed by Karlin and co-workers (Scheme 4)[42] the cleavage of the O–O bond in **22** was proposed to proceed by the formation of an intermediate mononuclear copper(II) oxyl species ([Tp^{Me}Cu^{II}-O·]), which, however, has not been detected.[11,50] The oxyl species is believed to combine with a copper(I) fragment—originating from the equilibrium between Tp^{Me}Cu^{I}/O$_2$ and **22**—giving **20** (Scheme 5). Complex **20** in turn reacts at low-temperature with H$_2$O$_2$ to yield **22**.[51]



Scheme 5. Different routes to the Cu$_2$O complex [(Tp^{Me}Cu^{II})$_2$(μ-O)] (**20**) and its reactivity towards PPh$_3$, H$_2$O, and CO$_2$. Tp^{Me-} = hydrotris(3,5-dimethyl-1-pyrazolyl)borate.

The UV/Vis spectrum recorded for a solution of **20** in CHCl$_3$ showed an absorption band at 660 nm (ε = 105 $\text{M}^{-1}\,\text{cm}^{-1}$) characteristic for a copper(II) d–d transition. A further absorption with a maximum at 335 nm (ε = 2560 $\text{M}^{-1}\,\text{cm}^{-1}$) was tentatively ascribed to the O→Cu charge transfer. Mass spectrometric experiments including isotope labeling studies also confirmed the existence of the Cu$_2$O complex **20**. As in the case of [(^{Me}Py2Cu^{II})$_2$(μ-O)](BArF)$_2$ (**^{Me}12** BArF) EPR as well as NMR spectroscopic investigations pointed to an antiferromagnetic coupling of the two copper(II) ions mediated by the monoatomic bridging (oxo) ligand in **20**. In the absence of appropriate reaction partners [(Tp^{Me}Cu^{II})$_2$(μ-O)] (**20**) was described to be stable only for a limited time decomposing partly to [(Tp$^{Me}{}_2$Cu^{II}] (**23**)[52] and it showed the expected reactivity towards H$_2$O, CO$_2$, and PPh$_3$ yielding in the bis(μ-hydroxo) dicopper(II) complex [(Tp^{Me}Cu^{II})$_2$(μ-OH)$_2$] (**24**), the μ-carbonato dicopper(II) complex [(Tp^{Me}Cu^{II})$_2$(μ-CO$_3$)] (**25**), and (O)PPh$_3$/[Tp^{Me}Cu^{I}(PPh$_3$)] (**21**), respectively.[50,51]

The first Cu$_2$O complex featuring a ligand that had been developed especially to pre-orientate two copper ions was described by Réglier and co-workers.[53] Starting from the dinuclear copper(I) complex [BPImPy{Cu^{I}(NCCH$_3$)$_2$}$_2$](PF$_6$)$_2$ (**26**; BPImPy = 1,1′-biphenyl-2,2′-dimethylidene-*N*,*N*′-(2-(2-pyridyl)-ethylamine, see Figure 5)) the reaction with dioxygen yielded room-temperature stable [BPImPy{Cu$^{II}_2$(μ-O)}]-(PF$_6$)$_2$ (**27**) which was isolated and characterized. The corresponding UV/Vis spectrum was reported to exhibit an absorption band at 650 nm (ε = 180 $\text{M}^{-1}\,\text{cm}^{-1}$) and the determination of the dioxygen uptake of **26** as well as the ability of the reaction product to transfer an O atom onto PPh$_3$ also supported the identity of **27**.

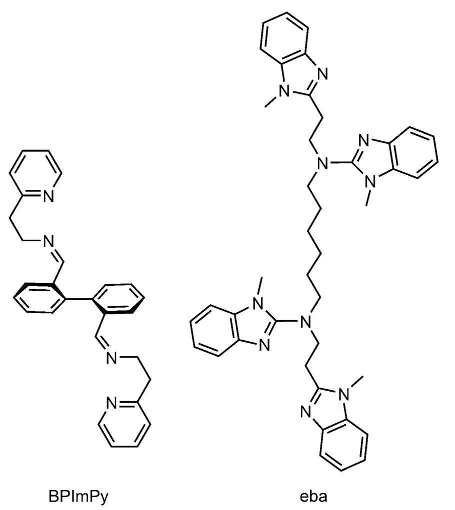
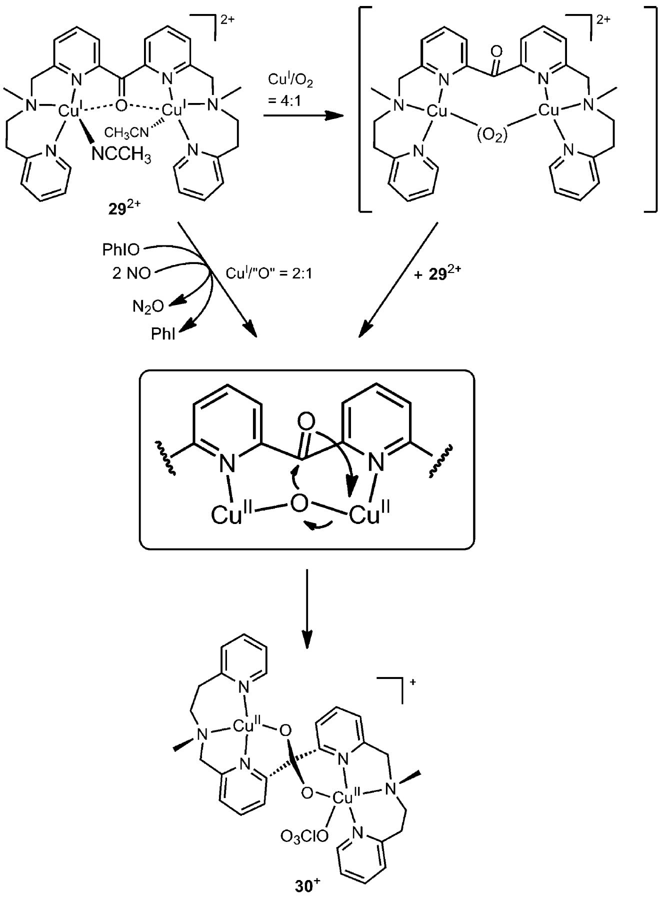


Figure 5. The potentially dinucleating ligands BPImPy and eba.

In the course of studies on the catecholase activity of dinuclear copper complexes, Casella et al. found out that the low-temperature oxygenation of [eba{Cu^{I}(NCCH$_3$)}$_2$](PF$_6$)$_2$ (**28**; eba = 1,6-bis[[bis(1-methyl-2-benzimidazolyl)methyl]-amino]*n*-hexane Figure 5) does not produce the expected dioxygen adduct (Cu$_2$O$_2$), but a Cu$_2$O species.[54] This was deduced from the observation of a moderately intense ligand-to-metal charge transfer (LMCT) band at 350 nm (ε = 6500 $\text{M}^{-1}\,\text{cm}^{-1}$) and its immediate disappearance upon the addition of a small excess of acid at low temperatures. In contrast to the acidic quenching of related dicopper(II) peroxo compounds no hydrogen peroxide was detected. However, an explanation for the unusual hypsochome shift of the band originating from the copper(II) d–d transition was not provided (550 nm ($\varepsilon = 300\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$)).

In a further contribution again Karlin and co-workers suggested the formation of an intermediate Cu_2O species being able to nucleophilically attack the keto group of the bis(2-pyridyl)methanone-based dinucleating ligand L=O employed:[55] Starting from the corresponding dicopper(I) complex $[L{=}O\{Cu^I(NCCH_3)\}_2](ClO_4)_2$ (**29**) the reaction with dioxygen at room temperature surprisingly produced the μ-1,3-bridged *gem*-diolate dicopper(II) complex $[\{L(O)_2\}Cu^{II}\{Cu^{II}(ClO_4)\}]ClO_4$ (**30**) as the product (Scheme 6). A detailed investigation on the formation steps of **30** showed that both O atoms of O_2 are consumed, and the reaction stoichiometry was $Cu/O_2 = 4{:}1$ as shown by manometry. Furthermore, $^{18}O_2$ labelling experiments indicated an incorporation of one O atom, originating from dioxygen, per diolate unit, while the second one was derived from the original ketone moiety of L=O. The initial product of the reaction between **29** and dioxygen was proposed to be an unstable Cu_2O_2 species or a O_2 adduct ($[L{=}OCu^I_2O_2](ClO_4)_2$), although they have never been detected. A Cu^{II}-O-Cu^{II} species formed in the next step featuring a nucleophilic oxo ligand was held to be responsible for the attack at the carbonyl group. Support for this hypothesis came from experiments employing oxygen-atom transfer reagents as the O atom source: The reactions between **29** and PhIO and NO, respectively, also led to the isolation of complex **30**; additionally the expected by-products PhI and N_2O were detected.



Scheme 6. Generation of an intermediate Cu_2O species from the reaction of **29** and 0.5 O_2, PhIO or NO, and subsequent nucleophilic attack, by the oxo bridge, on the ligand's carbonyl group leading to the μ-1,3-bridged *gem*-diolate dicopper(II) complex **30**. The non-coordinating ClO_4^- ions were omitted for clarity.

An alternative strategy for the generation of a Cu_2O entity was presented by Chan et al. The reaction of the **C** complex $[^{Et,Et}edCu^{III}(\mu\text{-}O)_2](ClO_4)_2$ with one equivalent of PPh_3 led to the corresponding μ-oxo dicopper(II) complex and the conversion was monitored by EPR and Cu K-edge X-ray absorption spectroscopy. Furthermore, during attempts to crystallize the Cu_2O compound the corresponding bis(μ-hydroxo) dicopper(II) compound was isolated.[56]

In 2007 the same group published several trinuclear copper(I) complexes $[^RL3\{Cu^I_2Cu^I\}]X$ ($^RL3$ = 3,3′-(1,4-diazepane-1,4-diyl)bis(1-((2-(dimethylamino)ethyl)(R)amino)propan-2-ol; R = Me, Et; X = BF_4^-, ClO_4^-), capable of mediating an oxygen-atom insertion into C−C and C−H bonds of several substrates in presence of dioxygen, and very recently even the oxidation of methane giving methanol under ambient conditions has been reported.[57,58] Corroborated by theoretical studies, the reactivity was assumed to be based on a $[Cu^{II}Cu^{II}(\mu\text{-}O)_2Cu^{III}]$ complex as the active species. At low temperatures and in the absence of suitable substrates this complex was suggested to react further through a cascade of inter-cluster electron-transfer steps between copper species in different oxidation states first to a putative **A** species, $[Cu^{II}Cu^{II}(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)Cu^{II}]$, and finally to yield a Cu_2O complex $[^RL3\{Cu^{II}_2(\mu\text{-}O)Cu^{II}\}]X_2$ (^{R}**31**X).[59] Cu_2O complex ^{R}**31**X was investigated in more detail, and its identity was supported with the help of mass spectrometry, including ^{18}O labeling studies. In all cases the UV/Vis spectra recorded for solutions of ^{R}**31**X in acetonitrile showed an absorption band at 650 nm ($\varepsilon = 200\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$) originating from copper(II) d–d transitions. A band with a maximum at 272 nm ($\varepsilon = 5000\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$) was assigned to a O→Cu charge transfer. The substrates benzoin as well as acetoin were reported to cause the reduction of ^{R}**31**X leading back to the tricopper(I) precursor as well as benzil and 2,3-butanedione, respectively. Chan and co-workers stated that they succeeded in characterizing ^{Et}**31**BF_4 structurally with the help of single-crystal X-ray diffraction; the crystallization process occurred in the presence of five equivalents $NaPF_6$ under air. Surprisingly, in addition to four molecules of $[^{Et}L3\{Cu^{II}_2(\mu\text{-}O)Cu^{II}\}](BF_4)_2$ (^{Et}**31**BF_4), the unit cell also contained two PF_6^- ions. Since the presence of copper(III) ions in the sample was explicitly excluded, the charge balance was accounted for by the assumption of a protonation of the basic μ-oxo ligand at 50% within the single crystal. Thus, the molecular structure published in the original article represents an average of a 1:1 mixture between ^{Et}**31**BF_4 and its protonated pendant $[H^{Et}$**31**$BF_4]PF_6$ (as depicted in Figure 6), and for this reason a discussion of the binding parameters is not adequate. However, this issue demonstrates the affinity of μ-oxo dicopper(II) sites for protons once more.

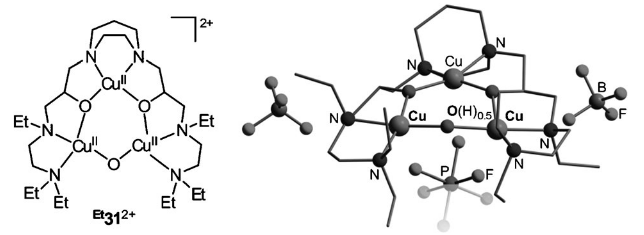
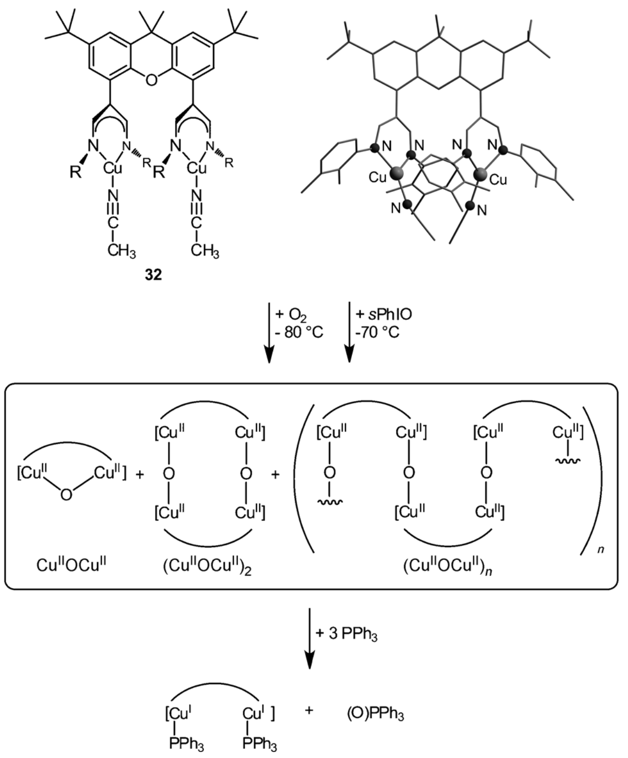


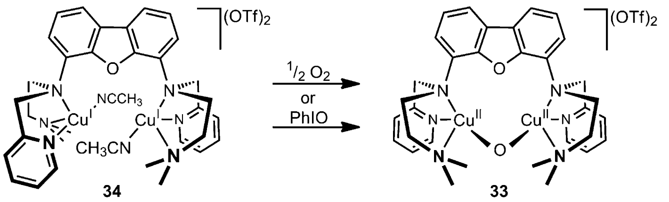
Figure 6. A stable tricopper(II) dication, $^{Et}\mathbf{31}^{2+}$, featuring a μ-oxo dicopper(II) entity (left) and the result of a single-crystal X-ray diffraction of a 1:1 mixture $^{Et}\mathbf{31}\,BF_4$ and $[H^{Et}\mathbf{31}\,BF_4]PF_6$ (right).[57] The charge balance requires a 50 percent protonation of the basic μ-oxo ligand. All hydrogen atoms have been omitted for clarity.



Scheme 7. Formation of different Cu_2O aggregates ($(Cu^{II}OCu^{II})_{1,2,n}$) from the reaction of $[Xanthdim\{Cu^{I}(NCCH_3)\}_2]$ (**32**) and O_2 or sPhIO, at low temperatures and the capability of $(Cu^{II}OCu^{II})_{1,2,n}$ to transfer O atoms onto PPh_3.

In 2011 Limberg and co-workers reported the characterization of an unstable Cu_2O complex based on a ligand system containing two β-diiminato binding sites linked by a xanthene-based backbone (Scheme 7).[60] Whereas, under ambient conditions, the corresponding dicopper(I) complex $[Xanthdim\{Cu^{I}(NCCH_3)\}_2]$ (**32**) reacted with dioxygen within seconds to give intractable compounds, the oxygenation at −80 °C led to the formation of a green intermediate which was identified as a paramagnetic Cu_2O species. Monitoring of the reaction with the aid of UV/Vis spectroscopy showed a new absorption band at 640 nm ($\varepsilon = 1000\,M^{-1}cm^{-1}$), which disappeared upon annealing to room temperature. Finally, the fact that identical results were obtained after the reaction between **32** and oxygen-atom transfer reagents, such as 2-*tert*-butylsulfonyl)iodosobenzene (*s*PhIO), a soluble derivative of iodosobenzene, suggested the formation of a Cu_2O compound. Detailed low-temperature Raman studies, including ^{18}O isotope labeling experiments, allowed the (μ-oxo)dicopper(II) product to be distinguished from a Cu_2O_2 species which could conceivably have been formed in the course of a dioxygenation process starting from **32**. Furthermore, different numbers of Raman signals were detected for different concentrations of the reaction solution indicating the formation of different Cu_2O-based aggregates ($(Cu^{II}OCu^{II})_{1,2,n}$, Scheme 7)—an observation which has also been made in connection with a couple of Cu_2O_2 systems.[10,61] The successful O atom transfer from the intermediate to PPh_3 as well as the ability of **32** to catalytically couple phenols giving the corresponding biphenols in the presence of excess O_2 was also reported.

Very recently the same group has described the access and detailed investigation of a Cu_2O complex, $[FurNeu\{Cu^{II}_2(\mu\text{-}O)\}](OTf)_2$ (**33**), with the aid of the novel dinucleating neutral ligand FurNeu.[62] Starting from $[FurNeu\{Cu^{I}(NCCH_3)\}_2](OTf)_2$ (**34**) the reactions with O_2 and PhIO, respectively, were shown to result in the room-temperature stable product **33** (Scheme 8).

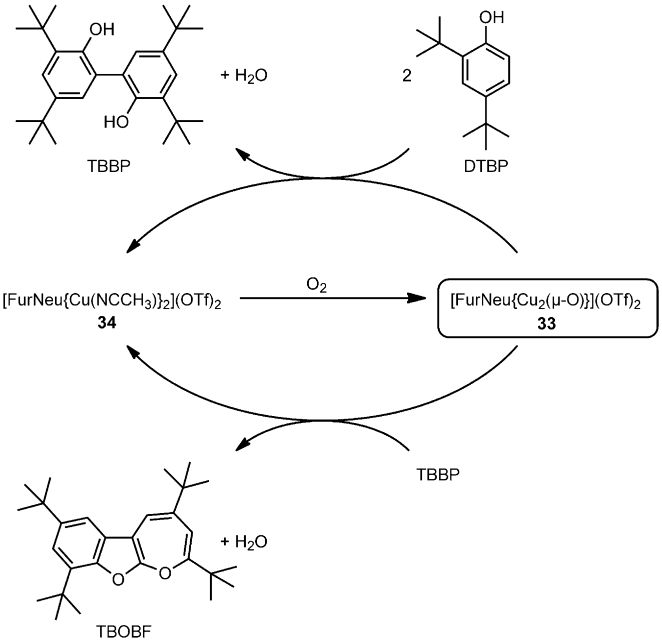


Scheme 8. Synthesis of $[FurNeu\{Cu^{II}_2(\mu\text{-}O)\}](OTf)_2$ (**33**) starting from $[FurNeu\{Cu^{I}(NCCH_3)\}_2](OTf)_2$ (**34**) through the reaction with O_2 and PhIO, respectively.

In addition to a characteristic absorption band originating from a copper(II) d–d transition at 644 nm (PhIO: $\varepsilon = 140\,M^{-1}cm^{-1}$) the UV/Vis spectrum of solutions of **33** showed enhanced absorption features in the regions 400–500 nm and 800–1100 nm. The diamagnetism of the product suggested a strong antiferromagnetic coupling of the copper(II) ions within **33** and, hence, it was possible to investigate it with the help of NMR spectroscopy, including DOSY NMR experiments which confirmed its discrete, molecular, monomeric character (and thus the absence of aggregation and intermolecular reactions). Furthermore, detailed mass spectrometric results combined with ^{18}O labeling studies indicated the formation of **33**.

Structural investigations on solutions of **33** by EXAFS analysis supported by DFT calculations revealed a structure featuring a Cu-O-Cu angle that amounts to 105.17°. Theoretical studies (TD-DFT) regarding its spectroscopic features allowed for the rationalization of the UV/Vis absorption features of **33** mentioned above. For example, the absorption around 450 nm mainly derives from a ligand-to-metal (LM) charge transfer with prominent involvement of the oxo ligand. Moreover, vibrational frequency calculations gave rise to three bands that involve the $[Cu^{II}\text{-}O\text{-}Cu^{II}]^{2+}$ motif: the Cu-O-

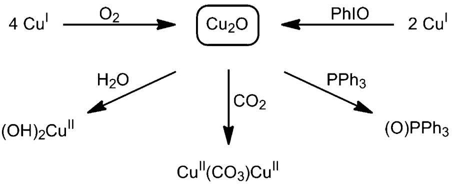
Cu bending mode is predicted at $236\,\text{cm}^{-1}$, while the symmetric and antisymmetric metal–oxo stretches are calculated to occur at 565 (ν_s) and $619\,\text{cm}^{-1}$ (ν_{as}), respectively. Over longer periods, **33** was found to decompose to give [Cu(picoloyl)$_2$], formed through an oxidative N-dealkylation reaction followed by further oxidation of the ligand. Studies regarding the reactivity towards 2,4-di-*tert*-butylphenol (DTBP) showed that **33** mediates the oxidative coupling giving 3,3′,5,5′-tetra-*tert*-butyl-2,2′-biphenol (TBBP). While this type of reactivity has been observed in numerous investigations on dinuclear copper compounds, **33** turned out to be a strong-enough oxidizer to convert TBBP even further yielding 2,4,7,9-tetra-*tert*-butyloxepino[2,3-*b*]benzofuran (TBOBF) in the presence of excessive O_2 (Scheme 9). Moreover, the results of mechanistic studies rationalized that, both **33** and **34** can also be employed as catalysts for the transformations mentioned.



Scheme 9. Catalytic cycle for the oxidative coupling of DTBP giving TBBP and to the rarely observed oxidation of TBBP giving TBOBF mediated by **33**. DTBP = 2,4-di*tert*butylphenol, TBBP = 3,3′,5,5′-tetra-*tert*-butyl-2,2′-biphenol, TBOBF = 2,4,7,9-tetra-*tert*-butylo-xepino[2,3-b]benzofuran.

3. General Reactivity and Spectroscopic Features

The majority of the Cu_2O complexes described above were accessible by the reaction of a corresponding copper(I) precursor with dioxygen. Transformations of this kind were found to proceed in a $Cu^I/O_2 = 4{:}1$ stoichiometry, and as a central intermediate a Cu_2O_2 adduct was assumed, which reacts further in the presence of residual copper(I) species. Alternatively Cu_2O compounds were accessible by employing oxygen-atom transfer reagents such as PhIO and NO as the O atom source (Scheme 10). However, regarding the reactions with oxygen-atom transfer reagents it is necessary to take into account that also complexes of type **C** may form by this route.[63]



Scheme 10. Formation and general reactivity of μ-oxo dicopper(II) complexes, Cu_2O.

The bridging oxo ligand in the Cu_2O compound was described to be strongly nucleophilic—often to an extent that allowed for the fixation of CO_2 giving the corresponding dicopper(II) carbonato complexes. Surprisingly, some of the μ-oxo dicopper(II) compounds were also found to efficiently transfer the copper-bound O atom onto phosphanes—a reactivity that is known for electrophilic metal oxygen units.[8,9,64] Also in the course of other substrate monooxygenations and oxidations Cu_2O species were suspected to play a central role.[65] In some cases the formation of the corresponding bis(μ-hydroxo) dicopper(II) complexes in the presence of water indicates a high basicity of the oxo ligand. Especially because of this sensitivity to hydrolysis accompanied by a lack of stability, an unambiguous structural characterization of a Cu_2O complex by single-crystal X-ray diffraction has to our knowledge not been achieved to date. Also three structures published recently[66] may not be considered as exceptions. Based on the quality of the structural data collected in some cases and on the experimental conditions applied, the formation of Cu_2O entities is questionable.

Whereas copper-based μ_3-,[67] μ_4-,[68] and μ_5-oxo[69] as well as mono(μ-hydroxo) compounds,[70] which can be regarded as protonated Cu_2O complexes (= "[$Cu_2O(H)$]X"), have been described and fully characterized, almost every group dealing with target-oriented Cu_2O chemistry has reported the failure of several attempts to grow single crystals.

In contrast to the families of **A**, **B**, and **C** complexes, to date it has not been possible to derive a spectroscopic fingerprint, which allows the unambiguous identification of **D** ("Cu_2O") complexes. However, the absorption band originating from the copper(II) d–d transition can be expected in the range 620–690 nm ($\varepsilon = 100\text{–}1000\,\text{M}^{-1}\,\text{cm}^{-1}$) based on the findings made for the majority of μ-oxo dicopper(II) entities. Only compounds exhibiting a cage-like structure, such as $[(^{N}LCu^{II}X)_4O_2]$ (^{N}L = enca, denc, X = Cl^-, Br^-) and oxygen activated Cu-ZSM-5 represent exceptions, whichmay be attributed to an aberrant binding geometry within these structures causing a variation of the energetic transitions. However, the positions of the O→Cu charge transfer bands, if observed, clearly differed among all representatives. The same applies to the few sets of vibrational data that have been reported so far: The positions of the respective bands appear to strongly depend on the predominant geometry of the Cu_2O motif. To provide a broader view on these issues a summary of the UV/Vis as well as vibrational spectroscopic data of all the compounds discussed herein is given in Table 1.

Table 1: Summary of the UV/Vis and Raman spectroscopic data of Cu$_2$O complexes.

Compound	Solvent	λ_{max}/nm [ε/M^{-1} cm^{-1}]	ν(Cu-^{16}O)/cm^{-1} (ν(Cu-^{18}O)/cm^{-1})	Ref.
[(encaCu^{II}Cl)$_4$O$_2$]	PhNO$_2$	720 (1200), 810 (1200)	555[a]	[26]
[(encaCu^{II}Br)$_4$O$_2$]	PhNO$_2$		555[a]	[26]
[(dencCu^{II}Cl)$_4$O$_2$]	CH$_2$Cl$_2$	235 (30600), 255 (27800), 770 (710), 850 (715)	580[a] (m)	[25]
[(dencCu^{II}Br)$_4$O$_2$]	CH$_2$Cl$_2$	230 (39200) 250 (35200) 750 (910), 825 (910)	580[a]	[25]
[(^{Me,Me}edCu^{II})$_2$(μ-Cl)$_2$(μ-O)]	PhNO$_2$	690 (210)		[32]
[(^{Me,Me}edCu^{II})$_2$(μ-Br)$_2$(μ-O)]	PhNO$_2$	675 (280)		[32]
[(^{Me,Me}edCu^{II})$_2$(μ-I)$_2$(μ-O)]	PhNO$_2$	435 (810), 600 (130)		[37]
[(^{Et,Et}edCu^{II})$_2$(μ-Cl)$_2$(μ-O)] (**5**)	PhNO$_2$	675 (228)	627 701	[32,33]
[(^{Et,Et}edCu^{II})$_2$(μ-Br)$_2$(μ-O)]	PhNO$_2$	700 (265)		[32]
[(^{Et,Et}edCu^{II})$_2$(μ-Br)$_2$(μ-O)]	CH$_2$Cl$_2$	280 (4400), 320 (5300), 500 (sh, 380), 700 (265)	600	[35]
[(^{Et,Et}edCu^{II})$_2$(μ-I)$_2$(μ-O)]	PhNO$_2$	430 (1100), 640 (140)		[37]
[(^{nPr,nPr}edCu^{II})$_2$(μ-Cl)$_2$(μ-O)]	PhNO$_2$	675 (190)		[32]
[(^{nPr,nPr}edCu^{II})$_2$(μ-Br)$_2$(μ-O)]	PhNO$_2$	675 (260)		[32]
[(^{nPr,nPr}edCu^{II})$_2$(μ-I)$_2$(μ-O)]	PhNO$_2$	425 (960), 625 (80)		[37]
[(^{nPent,nPent}edCu^{II})$_2$(μ-Cl)$_2$(μ-O)]	PhNO$_2$	675 (185)		[32]
[(^{nPent,nPent}edCu^{II})$_2$(μ-Cl)$_2$(μ-O)]	PhNO$_2$	685 (220)		[32]
[(^{Me,Me}pdCu^{II})$_2$(μ-Cl)$_2$(μ-O)]	PhNO$_2$	675(195)		[32]
[(^{Me,Me}pdCu^{II})$_2$(μ-Br)$_2$(μ-O)]	PhNO$_2$	675 (115)		[32]
[(^{Me,Me}pdCu^{II})$_2$(μ-I)$_2$(μ-O)]	PhNO$_2$	450 (1140), 650 (240)		[37]
[(^{Me}Py2Cu^{II})$_2$(μ-O)](PF$_6$)$_2$ ($^{\mathbf{Me}}$**12** PF$_6$)	CH$_3$CN	260 (30700), 300 (sh 9070), 708 (190)		[42]
[(^{Me}Py2Cu^{II})$_2$(μ-O)](BArF)$_2$ ($^{\mathbf{Me}}$**12** BArF)	thf	345 (4000), 680 (100)		[43]
[(^{Me}Py2Cu^{II})$_2$(μ-O)](BArF)$_2$ ($^{\mathbf{Me}}$**12** BArF)	thf[c]	345 (4000), 620 (100)		[43]
[(^{Me}Py2Cu^{II})$_2$(μ-O)](ClO$_4$)$_2$ ($^{\mathbf{Me}}$**12** ClO$_4$)	CH$_2$Cl$_2$	345 (4000), 680 (150)		[43]
[(^{Bn}Py2Cu^{II})$_2$(μ-O)](PF$_6$)$_2$ ($^{\mathbf{Bn}}$**12** PF$_6$)	CH$_2$Cl$_2$	257 (24400), 630 (860)		[42]
[(^{Ph}Py2Cu^{II})$_2$(μ-O)](PF$_6$)$_2$ ($^{\mathbf{Ph}}$**12** PF$_6$)	CH$_2$Cl$_2$	660 (760)		[41,42]
[N4Cu$_2$O](PF$_6$)$_2$ (**15**)	CH$_3$CN	370 (2040), 619 (130)		[45]
[(tmpaCu)$_2$O](PF$_6$)$_2$ (**16**)	C$_2$H$_5$CN	403 (530), 736 (220), 900 (320)		[45]
[(Me$_3$tacnCu^{II})$_2$(μ-OH$_2$)(μ-O)](ClO$_4$)$_2$ (**17**)	solid	630		[46]
[(Tp^{Me}Cu^{II})$_2$(μ-O)] (**23**)	CHCl$_3$	335 (2560), 660 (105)		[49]
[BPImPy{Cu$^{II}{}_2$(μ-O)}]PF$_6$ (**27**)	CH$_2$Cl$_2$	650 (180)		[53]
[eba{Cu^{I}(NCCH$_3$)}$_2$](PF$_6$)$_2$ (**28**) + O$_2$ at -78 °C	acetone[b]	350 (6500), 550 (300)		[54]
[^{R}L3{Cu$^{II}{}_2$(μ-O)Cu^{II}}]X$_2$ ($^{\mathbf{R}}$**31** X), X$^-$ = BF$_4{}^-$, ClO$_4{}^-$	CH$_3$CN	272 (5000), 650 (200)		[57]
[^{Me}L3{Cu$^{II}{}_2$(μ-O)Cu^{II}}](ClO$_4$)$_2$ ($^{\mathbf{Me}}$**31** ClO$_4$)	C$_2$H$_5$CN	265 (5000), 660 (190)		[59]
Cu-ZSM-5 after activation with O$_2$	solid	441, 752	δ: 237 (234), ν_s: 456 (448), ν_{as}: 870 (830)	[15,16]
[(Cu^{II}OCu^{II})$_{1,2,n}$]	thf[c]	640 (1000)	593 (568), 612 (598),[d] 640 (622)[d]	[60]
[FurNeu{Cu$_2$(μ-O)}](OTf)$_2$, (**33**; generated with PhIO)	CH$_3$CN	400-500 (sh) 644 (140), 800–1100 (br)	δ: 236,[e] ν_s: 565,[e] ν_{as}: 619[e]	[62]

[a] This signal was determined by means of IR spectroscopy. [b] $T = -78$ °C. [c] $T = -80$ °C. [d] Only observed using an excitation wavelength of 647 nm. [e] Calculated (B3LYP/def2-TZVP level).

4. Summary and Outlook

In the past Cu$_2$O complexes have been seen as undesired products which received little attention in copper–oxygen chemistry. Additionally, many of them were found to be thermally unstable and sensitive to water, that is, they were difficult to access, and as at the same time a biological relevance was not apparent, more detailed investigation on the electronic and geometric structures as well as on their reactivity was not carried out. Cu$_2$O complexes have lived a shadowy existence. However, the recent finding that oxygen-activated Cu-ZSM-5 selectively oxidizes methane to methanol and the respective mechanistic insights obtained suggest that, in search of catalysts for oxyfunctionalization of non-activated C–H bonds, (beyond entities **A**–**C**) [Cu^{II}-O-Cu^{II}] cores may indeed be considered as "the motifs of choice", and corresponding knowledge derived from investigations on molecular compounds may also represent a basis for the understanding of the enzymatic oxygenation of methane by pMMO. Since the synthesis and investigation of model compounds is a common way to unravel reaction mechanisms as well as the functioning of enzymes this Minireview provides an overview of the limited number of synthetic Cu$_2$O complexes which have been published to date and their reactivity. Future research should aim at the collection of further experimental information on their properties including absorption and vibrational data. Determination of pK_B values for the oxo ligands of Cu^{II}-O-Cu^{II} units would also be highly enlightening. Furthermore, the structural characterization of Cu_2O complexes by single-crystal X-ray diffraction remains an important goal to gain access to structural parameters and geometries, and in addition, this knowledge would facilitate accompanying theoretical considerations. Advanced studies should and will address the one-electron oxidation or reduction of well-defined Cu_2O complexes giving the corresponding mixed-valent oxo dicopper(II/III) and oxo dicopper(I/II) species as these can be expected to be even more highly reactive homogeneous oxidizers.

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