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Investigations on Water-Soluble Copper Complexes with the Sterically Demanding Triazacyclononane Derivative $(^tBu)_2(^nPrSO_3)Htacn$

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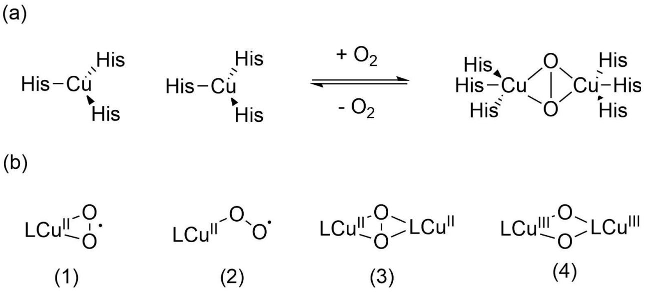
Related to environmentally friendly productions in the industry, the synthesis of catalysts with designed ligands for solubility in protic solvents and reactivity under mild conditions becomes important. Thus, copper complexes were synthesized with a ligand system that was designed for better solubility in protic solvents. The reactivity of copper complexes with hydrogen peroxide under ambient conditions was investigated in water and in methanol. The formation of a μ-η^2:η^2-peroxide copper complex with a stability of a few minutes was observed in contrast to most related complexes reported in the literature. A kinetic analysis was performed, leading to activation parameters of $\Delta H^{\ddagger}$: 66 ± 4 $kJ \cdot mol^{-1}$ and $\Delta S^{\ddagger}$: -5 ± 12 $J \cdot K^{-1} \cdot mol^{-1}$ (in water), a strong indication of an interchange mechanism.

Introduction

Selective oxygenation and oxidation reactions of organic substrates play a key role in industry and nature.[1,2] In industry, for example, the oxygenation of toluene or the production of adipic acid (oxygenation of cyclohexane), a precursor for the synthesis of nylon, are important.[3] In nature, oxidations can occur in active sites of enzymes such as e.g. peptidyl glycine α-hydroxylating monooxygenase (PHM).[4] The copper-mediated enzyme activates dioxygen, followed by hydroxylation of glycine. Another copper-based protein is hemocyanin which is responsible for the oxygen transport in arthropods and mollusks. Here and in the related monooxygenase tyrosinase, copper forms a μ-η^2:η^2-peroxido complex with dioxygen (Scheme 1, (a)).[2] Depending on the system/enzyme, dioxygen can bind differently to the copper center; examples are shown in Scheme 1 (b).[5,6]

These intermediates are generally short-lived and crucial for activating and transferring dioxygen. Model complexes have been developed to investigate these intermediates.[2,5,6] In the past, macrocyclic ligands have proved to be suitable systems for stabilizing copper dioxygen intermediates such as tet b (*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), or derivatives of 1,4,7-triazacyclononane (tacn, Figure 1).[7–9]



Scheme 1. (a) Binding of dioxygen by hemocyanin and tyrosinase; (b) examples of known copper complexes obtained by a reaction with dioxygen (charges are omitted; His = histidine, (1) copper side-on superoxido, (2) copper end-on superoxido, (3) dicopper side-on peroxido, (4) dicopper bis-μ-oxido).

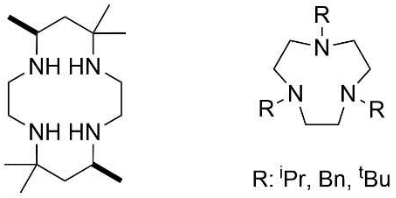


Figure 1. The macrocyclic ligand tet b and derivatives of 1,4,7- triazacyclononane (tacn).

For example, copper complexes with 1,4,7-triazacyclononane derivatives can form different intermediates when reacted with dioxygen, such as μ-η^2:η^2-peroxido or bis-μ-oxido compounds. Even the variation of substituents on the 1,4,7-triazacyclononane is decisive for the reactivity of the respective copper complex.[8–11] Halfen *et al.* were able to detect both a μ-η^2:η^2-peroxido and a bis-μ-oxido complex by investigating $[Cu(^iPr_3tacn)]OTf$ with dioxygen at −78 °C. The formation was dependent on the solvent. In dichloromethane the formation of a side-on-peroxido and in THF a bis-μ-oxido complex was favored.[8] In contrast, a $[Cu(^tBu_3tacn)]OTf$ complex forms preferably a μ-η^2:η^2-peroxido copper complex with a particular

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stability.[9] As a result, this complex could be crystallized and was structurally characterized. Furthermore, Karahalis *et al.* performed stability tests in different solvents, showing that the copper-dioxygen intermediate was also stable in the protic solvent methanol as well as in water for a certain time. Catalytic oxidation reactions were performed with electron-rich compounds such as 3,5-di-tert butyl catechol.[9]

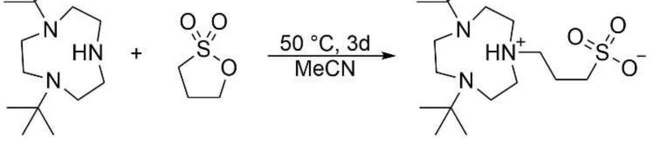
Concerning green/sustainable chemistry, our focus was on modifying the 1,4,7-triazacyclononane system for high solubility and high reactivity in water (or methanol) to develop an environmentally friendly catalyst that could work under mild conditions. The modification of ligands to increase water solubility is not unknown and usually, phosphonic acid, sulphonic acid or carboxylic acid substituents have been used.[12,13] Pasachenik *et al.*, as well as Clegg *et al.*, already investigated the pH dependence of 1,4,7-triazacyclononane derivatives with phosphonic acid substituents. Pasachenik *et al.* measured the pH dependence as a part of the characterization of the copper(II) complexes, while Clegg *et al.* performed NMR studies on small macrocycles with methylenephosphonates.[13,14] Furthermore, soluble 1,4,7-triazacyclononane derivatives are applied in bleaching or in medicine where these ligands function as chelators for copper radioisotopes (radiotracers) for positron emission tomography (PET), as a contrast agent in pH-responsive magnetic resonance imaging or emission computed tomography (SPECT).[15]

Results and Discussion

Synthesis of the Ligand and Characterization of the Complexes

To achieve solubility in protic solvents, one of the *tert*-butyl groups was substituted with a sulphonic group attached through a propyl spacer. For the synthesis of the target ligand, a precursor ligand with two *tert*-butyl groups (^{t}Bu$_2$tacn) was prepared according to Pickel *et al.*[11] This compound was reacted with 1,3-propane sultone to obtain the final ligand (Scheme 2). The synthesis of (^{t}Bu)$_2$(^{n}PrSO$_3$)Htacn **1** required a reaction time of about 3 days and the conditions for this reaction were selected according to a similar reaction in the literature.[16] **1** was obtained as a white powder with a yield of 54%. ^{1}H-NMR and ^{13}C-NMR spectroscopy confirmed the purity of the ligand.

In Figure 2 the molecular structure of **1** is presented. Interestingly, the sulphonic group is fully deprotonated, and one nitrogen is protonated (see SI for further details). The O–S distances and the O–S–O angles confirmed the assumption of a full deprotonation of the sulphonic group. This ligand represented the starting point for the synthesis of several complexes.



Scheme 2. Synthesis of **1**.

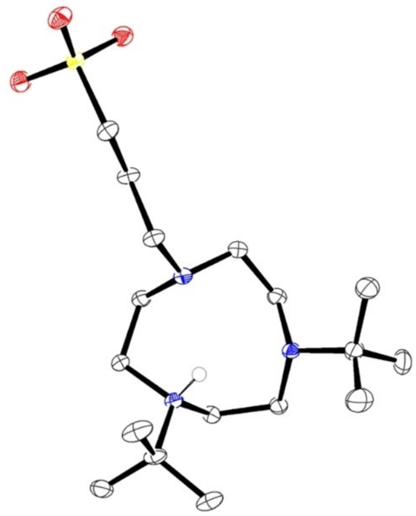


Figure 2. ORTEP Plot of the molecular structure of **1**. Ellipsoids are drawn at 50% probability. Selected bond length (°): S(1)–O(1): 1.4568; S(1)–O(2): 1.4558; S(1)–O(3): 1.4545. Selected bond angles (Å): O(1)–S(1)–O(2): 112.69; O(1)–S(1)–O(3): 112.61; O(2)–S(1)–O(3): 113.31. The N–H hydrogen interacts with the other nitrogen compounds in the ring, these are also shown in Table S4.

Synthesis and Characterization of the Copper (I)/(II) Complexes with 1

The copper(I) complex [Cu(**1**)(MeCN)]OTf (**2**) was synthesized by stirring [Cu(MeCN)$_4$]OTf and **1** for 3 h in dichloromethane at room temperature. The formation of the copper(I) complex could be confirmed by elemental analysis, while, attempts to obtain crystals for structural characterization failed. However, the molecular structure of the closely related complex [Cu(^{t}Bu$_3$tacn)(MeCN)]PF$_6$ was reported previously and supports our formulation.[17a] Furthermore, ^{1}H-NMR spectroscopy confirmed the formation of **2**, but some disproportionation was observed (Figure S14).

The synthesis of the copper(II) complex took 3 d stirring the reactants (**1** and Cu(OTf)$_2$) in dichloromethane. A small unknown precipitate was observed during the synthesis, which was removed by filtration. The main product, obtained as a green solid, was characterized by elemental analysis. The results revealed a formation of a copper complex in a metal cation-to-ligand ratio of 1:2 that we assigned as [Cu(**1**)$_2$(H$_2$O)](OTf)$_2$ (**3**). This has been observed for several copper complexes in the past, but here, it was assumed that the sterically demanding ligand would suppress it. However, one of the sterically demanding *tert*-butyl groups had been replaced by a somewhat less demanding sulfonate group. Furthermore, and most likely the main reason, the ligand was protonated at one nitrogen of the macrocycle, thus making coordination of all nitrogen atoms unlikely. With this the ligand is only coordinated through two nitrogen atoms of each ligand and most likely a water molecule (or a triflate anion) as a fifth ligand.

In contrast, it was possible to obtain the molecular structure of a copper(II) complex with **1**, when $Cu(OAc)_2$ was used instead of $Cu(OTf)_2$ under different conditions. The molecular structure of compound [Cu(**1**)]OAc (**4**) is presented in Figure 3. The deprotonated ligand and one acetate are the anions. The copper ion is coordinated in a distorted square pyramidal geometry by the ligands (τ: 0.3) and such a five-coordinated copper(II) complex is in accordance with the literature.[8,17]

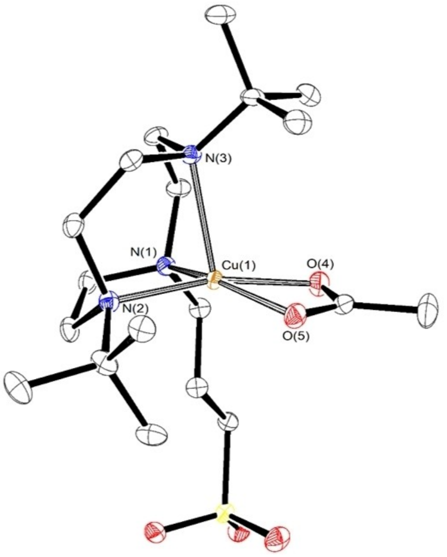


Figure 3. ORTEP Plot of the molecular structure of [Cu(**1**)]OAc, **4**. Ellipsoids are drawn at 50% probability. Selected bond length (Å): Cu(1)–N(1): 2.002; Cu(1)–N(2): 2.044; Cu(1)–N(3): 2.273; Cu(1)–O(4): 2.038; Cu(1)–O(5): 2.020. Selected bond angles (°): N(1)–Cu(1)–N(2): 87.74; N(1)–Cu(1)–N(3): 87.03; N(2)–Cu(1)–N(3): 87.18; N(1)–Cu(1)–O(4): 96.62; N(1)–Cu(1)–O(5): 158.26; N(2)–Cu(1)–O(4): 166.82; N(2)–Cu(1)–O(5): 108.21; N(3)–Cu(1)–O(4): 105.41; N(3)–Cu(1)–O(5): 107.90 ; O(4)–Cu(1)–O(5): 64.67.

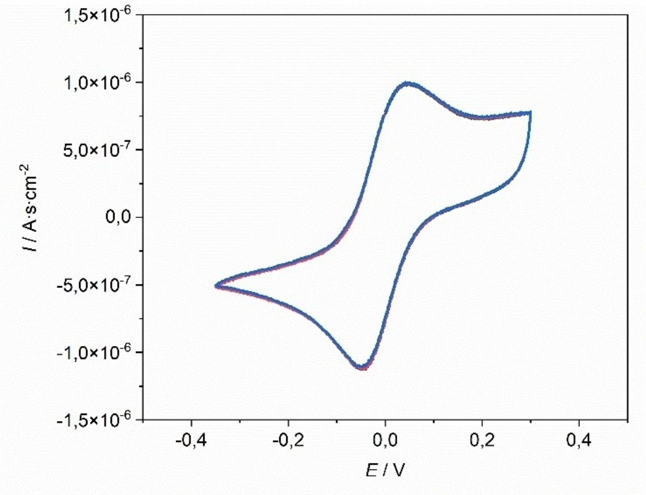


Figure 4. Cyclic voltammogram of the **2** in acetone at 25.0 °C ([complex] = 0.9 mmol/L, $[nBu_4NBF_4] = 0.1$ mol/L, scan rate: 100 mV/s, cycle number: 3). Ag/AgCl was used as a reference electrode.

Electrochemistry

The redox potentials of the complexes [Cu(**1**)(MeCN)]OTf (**2**) and $[Cu(\mathbf{1})_2(H_2O)](OTf)_2$ (**3**) were investigated by cyclic voltammetry. In protic solvents, we could not observe a redox reaction at all for complex **2** (SI, Figure S1). In contrast, **2** in acetone showed a quasi-reversible redox behavior with an $E_{1/2}$ potential of −0.001 V (Figure 4 and Table 1).

Complex **3** was investigated in H_2O, MeOH, and MeCN and showed quasi-reversible behavior in all three solvents. The cyclic voltammogram of **3** in water is presented in Figure 5, and data are reported in Table 1. The redox potential of complex **3** in methanol is shifted to a much higher positive value compared to the measurement in acetonitrile. The results of the measurements in water were compared with one of the few other examples in which the electrochemistry of a related copper complex (a derivative of tacn as a ligand) was investigated in an aqueous solution.[18] Experiments with the conducting salt $LiClO_4$ were performed with **3** and **4**, but the CVs turned out to be featureless (Figures S4 and S5). In contrast, when KCl was applied as an electrolyte, the excess of chloride anions obviously stabilized the electrochemical system. While

Table 1. Potentials of the copper(I) complex **2** in acetone and the copper(II) complex **3** in water (a), methanol (b, Figure S2) and acetonitrile (c, Figure S3) in comparison with their reference substances $K_3[Fe(CN)_6]$ in H_2O (d) and ($[Fe(Cp)_2]$ in acetone (e) and in MeCN (f) (In V vs. Ag/AgCl).

	E_p^{red} [V]	E_p^{ox} [V]	$E_{1/2}$ [V]	ΔE [V]
2	−0.049	0.047	−0.001	0.096
(a) **3**	−0.193	−0.041	−0.117	0.152
(b) **3**	0.322	0.416	0,369	0.094
(c) **3**	−0.060	0.172	0.056	0.230
(d) $K_3[Fe(CN)_6]$	−0.154	−0.028	−0.091	0.126
(e) $[Fe(Cp)_2]$	0.352	0.422	0.387	0.070
(f) $[Fe(Cp)_2]$	0.382	0.467	0.425	0.085

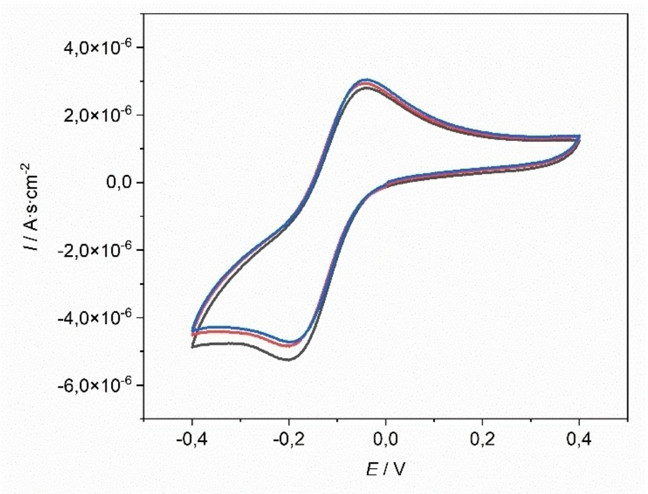


Figure 5. Cyclic voltammogram of **3** in H_2O at 25.0 °C ([complex] = 0.7 mmol/L, ([KCl] = 0.1 mol/L, scan rate: 100 mV/s, cycle number: 3). Ag/AgCl was used as a reference electrode.

the $E_{1/2}$ values of the two complexes cannot be compared to the reported systems due to different reaction conditions, the overall behavior is quite similar. Thus, in principle, it might also be possible to prepare the copper(I) complex by electrolysis.

Reactivity of the Copper complex 2 Towards Dioxygen

Our original hope to spectroscopically observe the formation of a “dioxygen adduct” complex as an intermediate when **2** would be reacted with dioxygen in a protic solvent unfortunately was not fulfilled. Reacting **2** with dioxygen in the protic solvent methanol led to a slow unspecified oxidation of the complex (Supporting Information, Figure S6) to the corresponding copper(II) complex. However, this was not completely surprising because up to now only very few copper(I) complexes are known that react with dioxygen in protic solvents leading to “dioxygen adduct” complexes that can be spectroscopically observed.[19] To the best of our knowledge no copper complex is known so far that reacts in such a way in water in contrast to the copper proteins e.g. hemocyanin.[20] Mainly, this is a problem caused by the kinetics of the reaction. While most likely such a “dioxygen adduct” copper complex is formed, this reaction is rate determining while the consecutive reactions of its decomposition are much faster and thus do not allow the detection of this species. This is often also the case for studies in protic solvents.[21] Furthermore, even the μ-η^2:η^2-peroxido copper complex obtained from [Cu(^{t}Bu$_3$tacn)]OTf complex, while stable for some time in aqueous solutions, cannot be formed directly by reacting the copper(I) complex with dioxygen in water.[9]

To test if a “dioxygen adduct” complex as an intermediate would form in organic solvents, we switched to the non-protic solvent acetone. Here, it was possible to observe the slow formation of a μ-η^2:η^2-peroxido copper complex with characteristic absorbance maxima at 390 and 520 nm that is stable for several hours (Figure 6).

Reactivity of the Copper(II) Complexes with Hydrogen Peroxide in Protic Solvents

Since the reaction of the copper(I) complex **2** with dioxygen in a protic solvent only showed the slow formation of a species that so far could not be characterized, we switched to the reaction of the corresponding copper(II) complex with hydrogen peroxide (an oxidant that can be regarded as an environmentally friendly compound). Therefore, reactions of **3** with hydrogen peroxide in the protic solvents water and methanol were performed. While, in principle, being more interested in the reactions in water, methanol allows us – if necessary – to study these reactions at temperatures as low as −80 °C, thus having a chance to observe short-lived reactive intermediates spectroscopically.

When **3** was reacted with H_2O_2 in water at 25 °C, two absorbance maxima at 380 and 520 nm were observed (Figure 7), clearly indicating the formation of a μ-η^2:η^2-peroxido copper complex. The complex is quite stable at room temperature and a buffer system was not needed. With regard to DNA cleavage the reaction of hydrogen peroxide with copper complexes with pyridyl ligands were investigated in phosphate buffered aqueous solutions by Zhu *et al.*[22] Herein, again not all complexes showed the formation of an intermediate that could be spectroscopically observed. However, especially the reaction behavior of the reported mononuclear complex is quite similar to our system.

In Figure 8 the reaction of **3** with H_2O_2 in methanol is presented. No low-temperature measurements were necessary. Two bands could be observed at 378 nm and 520 nm indicating again the formation of a μ-η^2:η^2-peroxido copper complex at room temperature.

Furthermore, the reactivity of **4** with hydrogen peroxide at 25 °C was investigated in water, and likewise, the formation of a μ-η^2:η^2-peroxido copper complex could be observed (Supporting Information, Figure S8). This clearly shows that complexes **3**

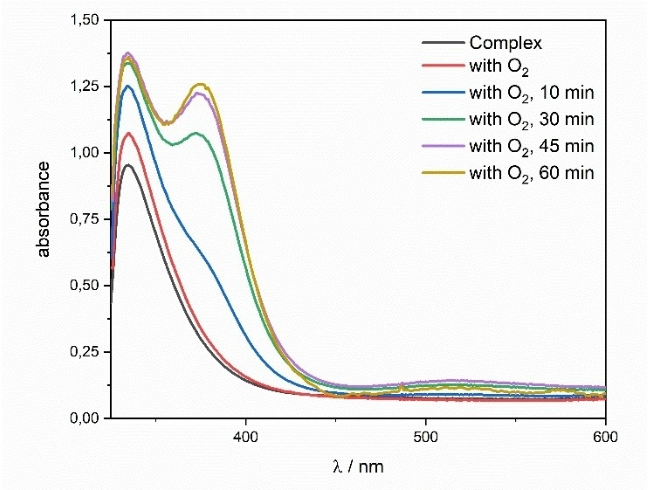


Figure 6. UV-Vis spectra of **2** ([complex] = 0.9 mmol/L) with and without dioxygen in acetone at −30 °C.

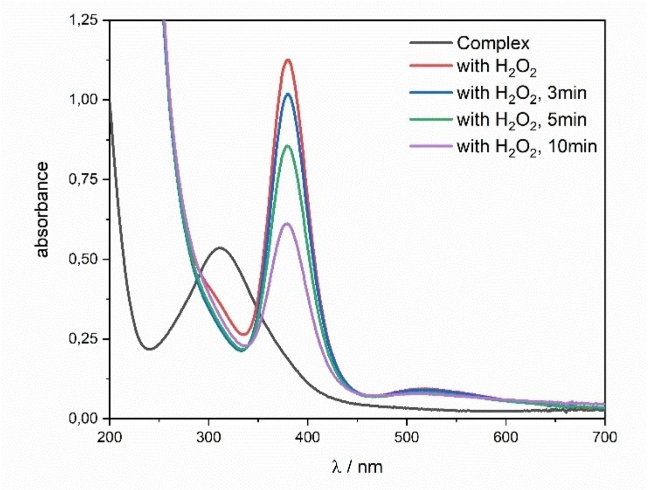


Figure 7. UV-Vis spectra of **3** before and after the reaction with H_2O_2 in water at 25 °C ([complex] = 0.3 mmol/L).

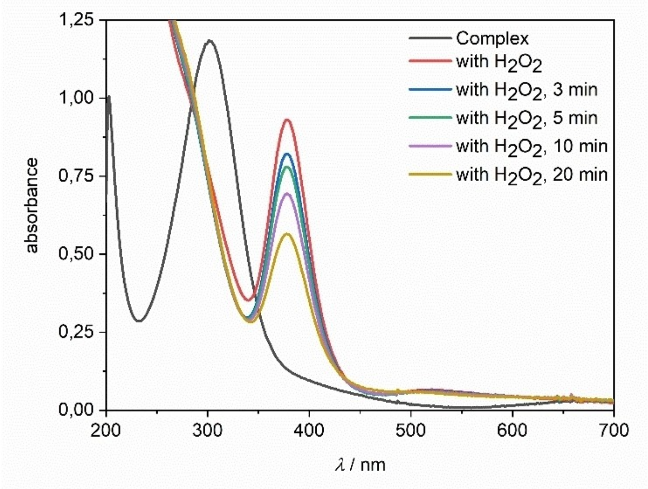


Figure 8. UV-Vis spectra of **3** before and after the reaction with H_2O_2 in methanol at room temperature ([complex] = 0.3 mmol/L).

and **4** will form copper complexes L–Cu–OH_2 in aqueous solutions, which accounts for the identical behavior.

To determine the activation parameters and, thus the mechanism of the copper dioxygen adduct formation, the reaction of **3** with hydrogen peroxide in water was analyzed in more detail. The plot absorbance vs. time (Figure S9) under pseudo-first-order conditions ($[H_2O_2] \gg [\mathbf{3}]$) could be fitted to a single exponential function. Accordingly, it is a first-order reaction in terms of the copper complex concentration. In the next step, the concentration dependence of H_2O_2 was investigated with a plot of k_{obs} vs. the concentration of hydrogen peroxide (Figure 9). The obtained linear correlation without an intercept leads to a first-order reaction related to the H_2O_2 concentration and overall to a rate law of (v = rate of formation of the peroxido complex):

$$v = k\,[\mathbf{3}] \times [H_2O_2]$$

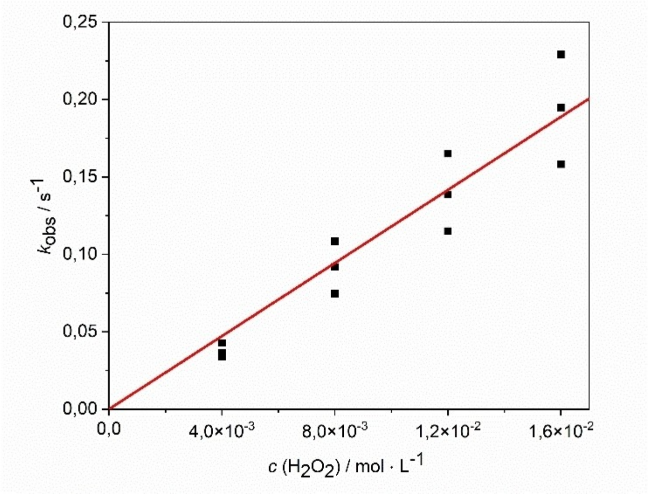


Figure 9. k_{obs} vs. $c(H_2O_2)$ at 15 °C for the reaction of **3** with hydrogen peroxide in water.

To get more detailed information about the reaction mechanism, time-resolved UV-Vis measurements were performed in a temperature range of 10.0 to 35.0 °C under first-order conditions. The activation parameters of the second order rate constant were calculated to $\Delta H^{\neq}$: $66 \pm 4\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta S^{\neq}$: $-5 \pm 12\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ from an Eyring plot (Figure 10).

Despite the large error of the activation entropy, its value close to zero clearly indicates an interchange mechanism of substituting a water molecule with hydrogen peroxide followed by deprotonation and formation of the dinuclear peroxido copper complex according to Scheme 3.

The overall reaction is quite similar to the formation of a peroxido iron complex investigated previously. Here as well the activation entropy is close to 0 and most likely both reactions follow the same mechanism.[23]

Subsequently, first investigations of catalytic oxidation reactions with **3** and hydrogen peroxide with different substrates and in different solvents were made. Herein electron-rich substrates such as 2,4-di-*tert*-butylphenol similar to Karahalis *et al.* were used because of their successful oxidation with the catalyst $[Cu(^tBu_3tacn)]OTf$ and dioxygen.[9] Unfortunately, an oxidation of a substrate under our conditions could not be observed.

Conclusions

The results obtained showed that it is possible to develop copper complexes that can form peroxido complexes in aqueous solutions similar to copper enzymes, e.g., tyrosinase. While so far, we have not achieved this formation by the

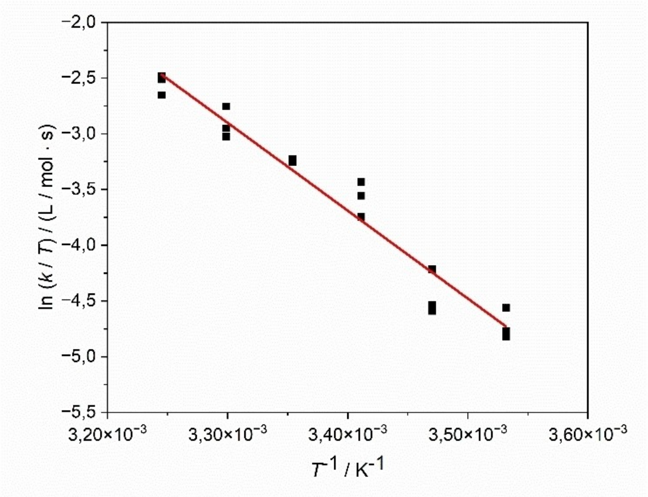
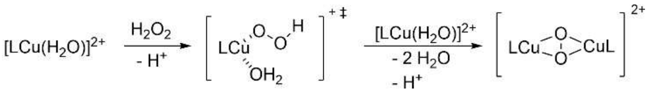


Figure 10. Eyring plot for the reaction of **3** with H_2O_2 between 10 to 35 °C.



Scheme 3. Proposed mechanism for the formation of the μ-η^2:η^2-peroxido copper complex (L: $(^tBu)_2(^nPrSO_3)$Htacn (anions were omitted for clarity).

reaction of a copper(I) complex with dioxygen, ligand design should lead to this in the near future. Furthermore, despite the fact that we could not observe catalytic activity for our system, again, this will be only a question of time and appropriate ligand design. The complexes reported here might be too stable for performing oxygenation, similar to a copper superoxido complex we reported in the past.[24] However, the quite high stability of these complexes allowed us to study the kinetics of the reaction of the copper(II) complexes with hydrogen peroxide and to postulate a reasonable interchange mechanism. In general, the results imply a step forward in the development of a more environmentally friendly catalyst in the future.

Experimental Section

The used reagents and solvents have the degree of purity p.a. and were bought from Acros Organics, Alfa Aesar, Merck and Sigma Aldrich or were synthesized as described below. The solvents were distilled over a drying agent under an argon atmosphere and stored in the glove box. $[Cu(MeCN)_4]OTf$ and $^tBu_2Htacn$ were prepared according to the literature. Oxygen and water-sensitive experiments were performed under inert conditions. ^1H-NMR and ^{13}C-NMR spectra were obtained using an Avance III 400 MHz HD (Bruker BioSpin GmbH, Rheinstetten). The measurements were performed at room temperature and the program MestReNova 14.1.2 was used for data analysis. The UV-Vis measurements were carried out at certain temperatures with an Agilent 8543-spectrometers. For GC-MS measurements a MS 5977B with a 7820A GC-system by Agilent Technologies was used. Electrospray-ionization MS (ESI-MS) were performed with a Bruker Mikro-TOF. For elemental analysis the CHN-Analysator Thermo FlashEA – 1112 Series was used. Electrochemical data were recorded with an e-corder 410 by edaq (eDAQ, Colorado Springs, US) and the program eChem. For cyclic voltammetry, a glassy carbon electrode as a working electrode, a platinum/titanium electrode (counter electrode) and an Ag/AgCl reference electrode were used. As a conducting salt NBu_4BF_4, KCl or $LiClO_4$ (0.1 M) was applied dependent on the solvent. The complex concentrations were adjusted to $1\cdot 10^{-3}$ M and ferrocene or prussian red were used as an internal standard. Details of X-Ray crystal structure determination are reported in the Supporting Information. CCDC- 2299680 (1) and CCDC- 2299681 (4) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ products/csd/request/ (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of $(^tBu)_2(^nPrSO_3)$Htacn: $(tBu)_2$tacn (400 mg, 1.66 mmol) and 1,3-Propane sultone (204 mg, 1.67 mmol) were added to 25 mL acetonitrile and was heated to 70 °C for 2 d. Afterward, the solvent was removed under reduced pressure and the received solid **1** was recrystallized in acetonitrile/water (324 mg, 0.891 mmol, Yield: 54 %). ^1H-NMR(δ/ppm): 3.31–3.15 (m, 4H); 3.00–2.94 (m, 2H), 2.86–2.82 (m, 10H), 1.30 (s, 18H); ^{13}C-NMR (δ/ppm): 64.18, 59.17, 54.81, 53.90, 51.68, 51.12, 30.27, 26.85. Anal. Calc. (%) for $C_{17}H_{37}N_3O_3S$: C 56.16, H 10.16, N 11.56, found: C 55.89, H 10.29, N: 11.53. ESI-MS (m/z) calculated ($C_{17}H_{37}N_3O_3Na^+$) 386.245; found 386.237 $[M+Na]^+$.

Synthesis of [Cu(**1**)(MeCN)]OTf, **2**: $[Cu(MeCN)_4]OTf$ (15.2 mg, 0.0403 mmol) and **1** (15.0 mg, 0.0412 mmol) were stirred in 4 mL dichloromethane for 3 h and afterward the solvent was removed under reduced pressure. It was received a colourless solid (24.5 mg, 0.0396 mmol, Yield: 98 %). Anal. Calc. (%) for $C_{20}H_{40}CuF_3N_4O_6S_2$: C 38.92, H 6.53, N 9.08, found: C 38.77, H 6.41, N: 8.39.

Synthesis of $[Cu(\mathbf{1})_2(H_2O)](OTf)_2$, **3**: $Cu(OTf)_2$ (36.2 mg, 0.105 mmol) and **1** (38.2 mg, 0.105 mmol) were stirred in 8 mL dichloromethane for 3 days. The resulting green suspension was filtered, and the solvent was removed under reduced pressure. It was received a green solid (49.5 mg, 0.0448 mmol, Yield: 43 %). Anal. Calc. (%) for $C_{36}H_{76}CuF_6N_6O_{13}S_4$: C 39.07, H 6.92, N 7.59, found: C 38.78, H 6.45, N: 7.09.

Synthesis of [Cu(**1**)]OAc, **4**: $Cu(OAc)_2$ (7,5 mg, 0.041 mmol) and **1** (15 mg, 0.041 mmol) were stirred in 1 mL methanol. After 2 h, the resulting turquoise solution was filtered and the solvent was removed. It was received a turquoise solid (18,4 mg, 0,034 mmol, Yield: 82 %). The slow diffusion of Et_2O in the complex solution at −35 °C led to the formation of a crystalline solid 4.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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