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Synthesis, Properties and Reactivity Studies of a Heterodicopper Complex Consisting of a Porphyrin and a Bispyridylamine Moiety Connected by a Xanthene Backbone

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Synthesis, characterization and reactivity studies of a heterodicopper complex, particularly towards oxygen reduction are presented. A bischlorido copper(II) trishistidine-type coordination unit is positioned directly above a copper porphyrin unit. The close distance between the two coordination fragments is secured by a rigid xanthene backbone. Surprisingly, the

Introduction

As world energy consumption is increasing so is the awareness that the stocks of fossil fuels are limited. There is a need to focus on alternative sources of (renewable) energy like wind or solar energy. Because of the fluctuating nature of these types of energy sources, the energy storage in chemical bonds is highly attractive, which could be accomplished by, for example water splitting.^[1–3] However, the development of large-scale electrolyzers is currently one of the major bottlenecks for a world-wide distribution of this type of green energy.^[4]

The produced hydrogen and oxygen are combined again in fuel cells leading to green energy on demand with only water as side product.^[5] While at the anode the hydrogen oxidation reaction can be achieved with rather good efficiency nowadays, many problems^[6] are still connected to finding a suitable catalyst for the oxygen reduction reaction (ORR). Since O–O

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202200743 dinuclear complex is not active towards oxygen reduction unlike the earlier published mononuclear analogues with a bispyridylamine copper center. However, the compound architecture of this multinuclear metal complex is interesting and can play an important role in the development of new catalysts for ORR.

bond cleavage is a four-electron transfer process, it requires a high over-potential. Another challenge is to design a catalyst having high selectivity in combination with long-term stability.

Inspiration for designing efficient catalysts that catalyze the ORR at a low overpotential and are based on abundant materials can be found in nature, especially in redox metalloenzymes. For example, cytochrome c oxidase (CcO) is able to sustain the four-electron reduction of dioxygen specifically to two molecules of water with associative energy delivery to drive the movement of protons across the cell membrane.^[7-10] In the enzymatic reaction center, an iron porphyrin unit and a copper trishistidine unit work cooperatively together to guarantee that no reactive oxygen species, for example hydrogen peroxide, is released during this process.^[11-13] The cautious change of the distance between the two metal centers that activates the substrate is very important for the selectivity of the reaction. This fact has been shown by investigations on several mimics of CcO, of which one is presented in Scheme 1a.^[14] As a result of these previous studies, it was concluded that the alignment of two metals should be in a way that they can work cooperatively together, as shown by Karlin and others in Fe-Cu models for CcO mimics.[15,16]

Another well-known example of enzymes able to catalyze oxygen reduction is the multicopper enzyme laccase, which can be found in many natural sources.^[17,18] This enzyme is known to couple the oxidation of a natural substrate near a mononuclear Cu site to ORR catalysis at a trinuclear Cu cluster.^[19,20] Electrochemical examinations on immobilized laccase have shown that the enzyme catalyzes the ORR near the equilibrium potential.^[21-23] However, laccase has generally a low proficiency for the ORR in fuel cells because of the fact that the enzyme is unstable under these conditions.^[24] Nevertheless, the active site of laccase poses a fascinating starting point for the improvement of new Cu-based catalyst for the ORR that work with a low overpotential and a high activity.

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Scheme 1. (a) Structure of a Fe–Cu model complex mimicking the CcO active site by Karlin and coworkers^[14], (b) trinuclear copper complex mimicking the laccase active site,^[24] (c) structure of model complex ^{Cu}L_{zn} from our previous work^[26] and (d) structure of ^{CuCl2}L_{ru} (this work).

In a recently published article, some of us presented a trinuclear Cu complex with three copper sites facing in the same direction (Scheme 1(b)). In comparison to a structural analogue as well as a mononuclear parent compound, this complex showed improved selectivity for the four electron reduction of O_{2} .^[25]

In another recent article,^[25] one of our groups presented the synthesis of a bimetallic Cu–Zn complex as a potential candidate for CcO mimics: A functionalized xanthene backbone was introduced holding, on the one hand, a zinc ion inside a porphyrin pocket and, on the other hand, a Cu(I) ion in a bispyridylamine moiety (Scheme 1(c), ^{Cu}L_{zn}). The two metal fragments were arranged in such a manner that both the metals are facing towards each other and are separated by a distance of 4.8 Å. Surprisingly, the complex ^{Cu}L_{zn} showed only a very slow reaction towards oxygen activation. These results were explained by a steric crowding around the Cu(I) center due to the unexpected alkene-copper(I) interaction.

Here, following our previous work, we synthesized and characterized a dicopper complex $^{\rm CuCl2} L_{\rm Cu}$ (Scheme 1(d)), and explored its activity towards the ORR. A second redox active metal center should provide more insight into the influence of the compound architecture/composition on the reactivity. Furthermore, multinuclear copper compounds have demonstrated ORR activity as described above.

Results and Discussion

The ligand 2,7-di-tert-butyl-5-(10,20-dimesitylporphyrin-5-yl)-9,9-dimethyl-4-(N,N-bis(pyridin-2-ylmethyl)amino)-9H-xanthen (L_{H2}) was synthesized using literature procedures.^[25] The synthesis of mononuclear L_{cu} and dinuclear copper complex ^{CuCl2} L_{cu}

(Scheme 1) is briefly discussed here; further information can be found in the Experimental Section. Synthesis of copper(II) bischlorido-10-[4-(N,N-bis(pyridin-2-yl-methyl)-amino)-2,7-di-

dimethylxanthen-5-yl]-5,15-dimesityltert-butvl-9.9 porphyrinatocopper(II) (^{CuCl2}L_{Cu}) was straight forward by refluxing a mixture of 2.5 equiv. of $CuCl_2\!\cdot\!2H_2O$ with L_{H2} in $CHCl_3/$ CH₃OH (3:1). Aqueous workup and purification using column chromatography resulted in 90% yield of ^{CuCl2}L_{cu}. Using 1 equiv. of CuCl₂·2H₂O and following the same procedure did not provide L_{cu} in a pure form, but rather a mixture of products was obtained. Purification using column chromatography resulted in 32% of L_{cur} besides some ${}^{CuCl2}L_{cu}$ as well as starting metal-free ligand. The purity of all compounds was confirmed by elemental analysis and mass spectrometry (details in Supporting Information). In the mass spectra of the metalated compounds no peaks related to ligand L_{H2} were observed and isotopic patterns were matching to the simulated ones (SI Figure S1, S2). Furthermore, because of the paramagnetic nature of the copper complexes, EPR spectroscopy has been performed, which will be discussed in more detail below (Figure 2). Crystals suitable for single crystal X-ray crystallographic analysis were obtained for L_{cu} by slow evaporation of a $CHCl_3/C_2H_5OH$ solution and for $^{CuCl2}L_{cu}$ by slow evaporation of a benzonitrile/DCM solution (Table S1). The molecular structures in solid state are shown in Figure 1 and selected bond lengths and angles are listed in Table 1.

In both structures of L_{cu} (Figure 1, left) and ${}^{cucl2}L_{cu}$ (Figure 1, right) the copper ion inside the porphyrin pocket is in a square planar geometry with mean Cu-N_{por} distances of 1.998 and 2.005 Å, respectively. In L_{cu} the distance between N7 and Cu1 is 4.152 Å which is interestingly much larger than the metal-N distance found in the reported structural analogue L_{zn} with 2.244 Å.^[26] A Zn-N_{pyridyl} interaction was determined in our earlier work which is obviously missing in case of the copper analogue here.

A slight bending of the xanthene backbone was also observed in both cases which can be seen when the molecules are looked at from a different angle (Figure S3). In case of L_{cu} the bending was ca. 6 degrees while in case of $^{cucl2}L_{cu}$ bending amounted to ca. 9 degrees because of accommodation of the CuCl₂ fragment in the bispyridylamine moiety. The copper ion



Figure 1. Molecular structures of L_{cu} (left, only one independent molecule within the unit cell is shown) and ^{Cucl2} L_{cu} (right); hydrogen atoms and solvent molecules have been omitted for clarity (ellipsoids at 50% probability level). Further structural information is given in the Supporting Information.

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Table 1. Selected bond lengths and bond angles for both mononuclear complex L_{cu} and dinuclear complex $^{cucl2}L_{cu.}$						
Compound	LCu	CuCl2LCu				
Distances (Å)						
Cu1-N1	1.999(2)	2.008(5)				
Cu1-N2	1.996(2)	2.008(5)				
Cu1-N3	2.001(2)	1.994(5)				
Cu1-N4	1.996(2)	2.012(6)				
Cu2-Cl1		2.271(3)				
Cu2-Cl2		2.451(2)				
Bond Angles (°)						
N1-Cu1-N3	176.32(8)	178.85(2)				
N2-Cu1-N4	178.71(8)	179.15(2)				
N6-Cu2-N7		159.93(2)				
N5-Cu2-Cl1		150.16(2)				
Cl1-Cu2-Cl2		115.09(1)				
N5-Cu2-N6		80.16(2)				
N5-Cu2-N7		80.45(2)				

in the bispyridylamine moiety in complex ^{CuCl2}L_{Cu} resides in a square pyramidal geometry, which is corroborated by a τ value^[27] of 0.17. The base is formed by two nitrogen donor atoms from the two pyridyl substituents (N6 and N7), Cl1 and N_{amine} (N5); while Cl2 represents the tip of the pyramid (Figure 1, right). The axial Cu1-Cl2 bond (2.451 Å) is longer than the equatorial Cu1-Cl1 bond (2.271 Å). The Cu–Cu distance with ca. 6.5 Å is greater than the earlier reported Cu–Zn distance in complex ^{Cu}L_{Zn} (ca. 4.8 Å),^[24] because in the latter case an attractive interaction between the Cu(l) ion and the porphyrin macrocycle brought the two metal centers closer to each other (see also Scheme 1). Overall, the found bond distances and angles (Table 1) are very similar to molecular structures already presented in the literature for copper porphyrins and copper bispyridylamine compounds.^[28,29]

Since all copper ions in the two complexes L_{cu} and $^{Cucl2}L_{cu}$ are paramagnetic d⁹ species, interpretable NMR data could not be obtained. Thus, EPR spectra were recorded for both complexes as well as for a mononuclear copper complex (4-bromo-5-(N,N-bis(pyridin-2-yl-methyl)-amino)-2,7-di-tert-

butyl-9,9-dimethylxanthene) copper(II) dichloride ($^{CuCl2}L_{Br}$) for comparison (Figure 2, Table 2). The latter compound was synthesized by us in an earlier publication, where x-ray crystallographic data supported the same square pyramidal coordination environment for the copper ion in the bispyridyl-amine coordination pocket.^[26]

 L_{cu} (red line in Figure 2) shows a signal centered around g = 2.05, 2.20 that is typical for a square planar copper(II) complex^[30] with hyperfine couplings to the nitrogen donor atoms. In contrast, ^{CuCl2}L_{Br} (blue line in Figure 2) shows EPR spectral characteristics that are typical for a penta-coordinated copper(II) ion with diminshed hyperfine coupling to the nitrogen donor atoms. ^{CuCl2}L_{cu} (black line in Figure 2) represents an overlay of the spectra for the two mononuclear copper complexes. The determination of g-values and hyperfine coupling constants is difficult because of the strong overlay of the individual contributions. This result can be interpreted as two weekly interacting copper(II) centers in ^{CuCl2}L_{cu}, which is also confirmed by SQUID magnetometery (inset in Figure 2 and



Figure 2. EPR spectra of ^{CuCl2}L_{cu} (black), L_{cu} (red) and ^{CuCl2}L_{Br} (blue) in CHCl₃ at 77 K. Simulation of the EPR spectra of L_{cu} and ^{CuCl2}L_{Br} was carried out by the use of EasySpin software (version 6.0) supported by MATLAB giving the values provided in Table 2. (inset) SQUID measurement at 7 T with a plot of $\mu_{\rm eff}$ vs Temperature (K).

Table 2. EPR parameters for complexes calculated in easy-spin software.						
Compound	g(⊥,)	A ^[Cu]	A ^[N]			
L _{Cu} ^{CuCl2} L	2.05, 2.20 1.98, 2.20	—48, —600 55, 495	50, 39, 40 -			



Figure 3. CVs of ^{CuCl2}L_{cu} (0.14 mM), in dry MeCN/0.1 M Bu₄NPF₆ under Ar (left) and in the presence of 20 mM HNEt₃PF₆ (acid) in presence and absence of O₂ (right) at a scan rate of 100 mV/s. Oxygen activity was studied only in the range of 0 to -1.0 V to avoid stripping of copper.

Figure S4). Variable field and variable temperature measurements were done and a μ_{eff} value of 2.59 μ_B at 7 T agrees with two weekly interacting copper(II) ions (see Supporting Information for further information).

Copper compounds with the bispyridylamine-type coordination pocket have previously been used in oxygen activation experiments.^[31,32] We were thus interested in investigating the electrocatalytic oxygen reduction potential of the here synthesized compounds, in particular ^{CuCl2}L_{cu}. Electrochemical experiments were initially performed under argon atmosphere in acetonitrile solution with 0.1 M NBu₄PF₆ as electrolyte using a glassy carbon (GC) working electrode (Figure 3, left). A reversible redox couple at -0.33 V vs. Fc⁺/Fc with a peak-to-peak separation of 206 mV at a scan rate of 100 mV/s can be

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observed and is assigned to the Cu^{II}/Cu^I redox couple of the bispyridylamine moiety. In addition, a second, reversible redox event around -1.71 V vs Fc/Fc⁺ is assigned to the redox couple of the Cu porphyrin moiety. The half-wave potential $(E_{1/2})$ of the redox couple of the bispyridylamine moiety is shifted around 150–200 mV more negative compared to mononuclear copper complexes with bispyridylamine-type ligands in an acetonitrile solution, but is only around 20 mV more positive than the redox couple of the trispyridylamine complex in acetonitrile.^[33] This shift is smaller than the 100 mV shift determined previously in aqueous solutions for the bispyridylamine and trispyridylamine complexes.^[34] The peak-to-peak separation of 206 mV of the redox event is significantly larger than the 56 mV reported previously^[34] for the mononuclear copper complex with a bispyridylamine ligand in aqueous solution. In addition, the peak-to-peak separation of the Cu porphyrin moiety is only 78 mV, and the peak-to-peak separations found for modified bispyridylamine-type ligands with chloride counterions are usually around 100–150 mV.^[33] The relatively large peak-to-peak separation of the bispyridylamine moiety in ^{CuCl2}L_{cu} most probably originates from the introduced copper porphyrin causing steric crowding due to its close proximity, and the rigidity of the xanthene backbone that make reorganization of the bispyridylamine copper site slow upon reduction and reoxidation. A study of the scan rate dependence of the redox couple between 10 mV/s and 500 mV/s shows that the peak current linearly depends on the square root of the scan rate (Figure S6). This indicates that both reduction and oxidation are diffusion-controlled, homogeneous processes as is expected for this system. From a Laviron plot^[35] of the peak potential of the redox couple as a function of the logarithm of the scan rate it is clear that the peak-to-peak separation increases at high scan rates. This increase is indicative of the inability of the slow electron transfer to keep up with the faster scan rate.

By systematically scanning the CV experiment to more negative potentials (Figure 3, left), several irreversible redox features appear in the reverse scan that are reminiscent of copper stripping.^[34,36] Apparently, metallic copper has formed at the electrode surface as a result from demetallation of ^{cuct2}L_{cu} under reductive conditions. Given that these features already emerge when the reduction potential is not scanned over the redox couple assigned to the copper porphyrin moiety at -1.71 V, we tentatively assign these events to the demetallation of the Cu bispyridylamine moiety, as was observed before for Cu-bispyridylamine in aqueous solution.^[34] The demetallation process starts at potentials below -1.0 V, as from this point on irreversible oxidation peaks are observed in the reverse scan (Figure 3, left).

To check the effect of solvent on the electrochemical behavior of $^{CuCl_2}L_{Cu}$, scans were performed in a different solvent (DCM) (Figure S8). Furthermore, Karlin and coworkers showed that O₂ binding is stronger in non-coordinating solvents than in MeCN (or DMF).^[37] Although the complex was a bit more stable in DCM, stripping of copper was still visible, so this behavior is not solvent specific. There is a broad redox feature of low intensity at around -0.36 V which corresponds to the Cu^{II}/Cu^{II} redox couple of the bispyridyl moiety.

We also investigated the electrochemical properties of the complex under oxygen atmosphere and in the presence of a proton source (Figure 3, right and Figure S5). The addition of 20 mM HNEt₃PF₆, to the above mentioned solution under argon atmosphere gave a Cu^{II}/Cu^I redox couple of the bispyridylamine copper with a larger peak-to-peak separation that shifted to a less negative potential of -0.22 V vs. Fc/Fc⁺ (Figure S5). Scan rate dependence studies show that the redox behavior still is a homogeneous process, but the peak-to-peak separation increases even more at higher scan rates (Figure S7). The origin of this change is unclear, but indicates an interaction between the acid and the copper center that hampers electron transfer. A possible detachment of one of the pyridyl arms cannot be neglected. Changing to a dioxygen atmosphere has, surprisingly, no impact on the shape of the CV (Figure 3, right). In fact, oxygen reduction occurs at the same potential as is observed when omitting the copper complex, i.e. with a bare GC electrode.

As mentioned above, oxygen activation at Cu⁺ centers is well known, so an electrocatalytic response in the presence of oxygen was expected. In case of ^{cuc12}L_{cu} it is hypothesized that the absence of any oxygen reduction activity is caused by the inability of the bispyridylamine copper site to bind oxygen in close proximity to the porphyrin copper ion or due to the presence of the chloride ligands that bind strongly to the copper site and block the binding of substrate.

To see whether the absence of catalytic activity is specific for the ORR, the activity of the ^{CuCl2}L_{Cu} complex towards the hydrogen evolution reaction (HER) was also investigated. Although in presence of acid a catalytic wave is observed with an earlier onset than the bare GC electrode (figure S9), it is uncertain that this activity belongs to the intact complex, as a large copper stripping peak is observed around -0.8 V vs. Fc⁺/ Fc. This is often an indication that free copper metal is produced during electrochemistry, again indicating the instability of this complex at more negative potentials. Moreover, the possible catalytic activity for the HER is observed at a potential close to the reduction of the Cu^{II} moiety in the porphyrin unit. This indicates that the copper center in the bispyridylamine site is not catalytically active, neither for the ORR, nor for the HER.

Conclusion

We can thus conclude that the compound architecture of multinuclear metal complexes plays an important role in not only the ORR but also the HER activity. As realized in an earlier study,^[30] the catalytic unit needs to support a certain amount of flexibility to accommodate the right redox reaction. The catalytic performance and the reorganization energies accompanying the Cu^{II/I} couple are very likely related to each other.^[34] The presence of the chloride substituents on the copper ion in the bispyridylamine moiety in ^{CuCI2}L_{cu} as well as the proximity to the porphyrin unit hamper dioxygen binding (to the reduced metal center) and thus the catalytic activity. Furthermore, binding of O_2 is most probably further slowed down by

system.[38]

Further, the copper porphyrin moiety in ^{cucl2} L_{cu} has a too negative redox couple to actively take part in the oxygen reduction reaction. Hence, our future work will be aiming at the removal of the chloride ions and at the substitution of the copper ion in the porphyrin macrocycle towards iron in order to obtain a more accurate and more kinetically competent mimic of the CcO reaction center. The results of this work will be presented in an upcoming publication. **Experimental Section** All chemicals were purchased from commercial suppliers (e.g. Sigma-Aldrich, VWR, Acros Organics or ABCR) and, unless otherwise noted, used as received. L_{H2} was synthesized according to the published procedure (details in Supporting Information).^[18] Solvents were purified and dried according to standard procedures or directly taken from a MBraun solvent purification system (e.g. THF, acetonitrile or toluene). Dry DMF (99.8%) and dioxane (>99.8%)

were purified and dried according to standard procedures or directly taken from a MBraun solvent purification system (e.g. THF, acetonitrile or toluene). Dry DMF (99.8%) and dioxane (>99.8%) were purchased from Sigma-Aldrich and stored over molecular sieves (3 Å) prior to use. Unless otherwise stated, all reactions which are sensitive towards air or moisture were carried out under dry argon by using Schlenk techniques. For thin layer chromatography (TLC) TLC Silicagel 60 F254 plates from Merck were used. Column chromatography was performed with silica gel purchased from

competition with acetonitrile molecules and chloride ions for a

coordination place at copper. It is thus important for the design

of functional laccase and CcO mimics, that not only the structural elements are considered but also the flexibility of the

Acros Organics (Silica Gel 60, 0.035-0.070 mm). Synthesis of $^{CuCl2}L_{Cu}$: 53 mg (50 µmol) of L_{H2} and 20 mg of $CuCl_2 \cdot 2H_2O$ (120 µmol) were taken up in 60 mL CHCl_3:CH_3OH mixture (2:1) and was heated to reflux for 4 h. Solvents were removed from the dark red solution by rotary evaporation and the solid residue was dissolved again in ca. 40 mL of CHCl_3 and was washed with water 3 times (each 30 mL). The organic phase was dried over Na₂SO₄ and evaporated again to get red solid which was purified by column chromatography (silica, ethyl acetate/hexane 1:1). After some impurities in front the product was collected and after removal of solvents isolated with a high yield: 57 mg (45 µmol), 90%.

ESI-TOF-MS ([M–Cl⁻]⁺): m/z: found: 1224.3999; calc. for $C_{73}H_{71}ClCu_2N_7O^+$: 1224.4200 (Figure S1).

Synthesis of L_{cu} : 53 mg (50 µmol) of L_{H2} and 9 mg of CuCl₂·2H₂O (approx. 50 µmol) were taken up in 60 mL CHCl₃:CH₃OH mixture (2:1) and was heated to reflux for 4 h. Solvents were removed from the dark red solution by rotary evaporation and the solid residue was dissolved again in ca. 40 mL of CHCl₃ and was washed with water 3 times. The organic phase was dried over Na₂SO₄ and evaporated again. On TLC (ethyl acetate/hexane, 1:1) 3 major spots were observed so column chromatography (silica, ethyl acetate/hexane 1:1, changed to neat ethyl acetate later) was done for purification, first band from column was analyzed as free base porphyrin (L_{H2} starting material) after collection of second band (^{CuCl2} L_{cu}) last band was the desired product (L_{cu}), yield: 18 mg (16 µmol), 32%.

ESI-TOF-MS ([M + H^+]^+): m/z: found: 1125.5226; calc. for $C_{73}H_{72}CuN_7O^+{:}$ 1125.5188 (Figure S2).

Deposition Numbers 2212053 (for $^{cucl2}L_{cu})$ and 2212054 (for $L_{cu})$ contain the supplementary crystallographic data for this paper.

These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

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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