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Dioxygen Activation

Kinetic Investigation of the Reaction of Dioxygen with the Copper(I) Complex $[Cu(Pim^{iPr2})(CH_3CN)]CF_3SO_3$ {Pim^{iPr2} = Tris[2-(1,4-diisopropylimidazolyl)]phosphine}

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Abstract: Model complexes for copper proteins such as hemocyanin or tyrosinase have been investigated in detail during the last four decades due to their potential to become valuable catalysts for selective oxidations of organic substrates. However, so far most of these compounds can only be investigated in aprotic solvents at lower temperatures. Therefore, industrial applications on a larger scale are still missing. In contrast the copper(I) complex with the ligand tris[2-(1,4-diisopropylimidazolyl)]phosphine can form a quite stable dinuclear copper peroxido complex in the protic solvent methanol at room temperature. The kinetic analysis of the reaction of $[Cu(Pim^{iPr2})(CH_3CN)]CF_3SO_3$ with dioxygen in methanol is reported. The results allowed to obtain rate constants and activation parameters ($\Delta H^{\#}$ = 25 ± 2 kJ mol^{-1} and $\Delta S^{\#}$ = −121 ± 8 J mol^{-1} K^{-1}) for the formation of the reactive intermediate, a mononuclear copper superoxido complex, prior to the consecutive reaction to a dinuclear peroxido complex.

Introduction

The interaction of dioxygen with copper(I) complexes has been studied in the past for a better understanding of the reactivity of redox active copper enzymes as well as for oxidation reactions in the lab and industry.[1] Catalytic oxidation reactions are very important, however, this is difficult to accomplish with dioxygen/air as the sole oxidant. Despite recent excellent achievements, selectivity limits still play a crucial role in aerobic oxidations of C–H bonds in more complex molecules.[2] This is in contrast to nature where enzymes such as methane monooxygenase (MMO) are capable to even oxidize unreactive substrates such as methane under ambient conditions.[3] However, during the last four decades it was possible to fully characterize a large number of intermediates of such oxidations, reactive copper "dioxygen adduct" complexes, that are responsible for the oxygen transfer.[1a,1c,4] These intermediates are usually analyzed in aprotic solvents at low temperatures (as low as −140 °C) due to the fact that most of the copper "dioxygen adduct" complexes investigated so far are not very stable, especially in the presence of protons.[1f,1h,5a–5f] Protons can lead to the formation of hydrogen peroxide and finally to the corresponding copper(II) complex and water. Usually reactions in protic solvents do not allow observation of any transient intermediate complex and suppress the potential of these complexes for oxidation reactions of organic substrates.[6]

Up to now we are only aware of two early examples (reported in 1994 and 1997) where reactions of this type were investigated in the protic solvent methanol: While Bol et al. used a macrocyclic ligand to stabilize a (most likely) dinuclear *end-on* peroxido complex,[7] Lynch et al. had based their complex on a trisimidazolate ligand system to obtain a dinuclear *side-on* peroxido unit.[8] Further studies using this ligand system have been performed by Sorrell and co-workers.[9] No crystal structures for the obtained "dioxygen adduct" complexes were reported for either system. Furthermore, quite stable dinuclear copper peroxido complexes were reported by Comba and co-workers as well as by Kodera and co-workers.[10] However, no studies in protic solvents were performed with these complexes. Most recently a *side-on* peroxido complex with a derivative of triazacyclononane (TACN) as a ligand was reported (us-

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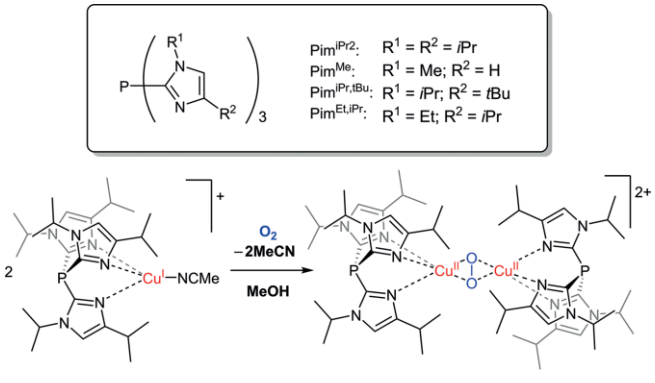
ing sterically demanding *tert*-butyl groups) which turned out to be quite stable in aqueous solutions.[11] Still it was not possible to investigate its formation in protic solvents.

In industrial applications for catalytic oxidations with dioxygen it is necessary to understand the formation of the "dioxygen adduct" complexes within large bubble columns.[12] Kinetic data are necessary for the determination of the hydrodynamics and mass transport mechanisms to allow the calculation/optimization of the overall bubbly flow processes. Most organic solvents present an elevated risk under industrial conditions due to the danger of creating explosive gas mixtures. It is still a challenging task to find metal complexes that can be used as oxidation catalysts in aqueous solutions under ambient conditions.

In this context tris(imidazolyl)phosphine and its derivatives are quite interesting ligands because as discussed above they can support formation of copper peroxido complexes in the protic solvent methanol. The copper(I) complex $[Cu(Pim^{iPr2})CH_3CN]^+$ {**1**, Pim = tris[2-(1,4-diisopropylimidazolyl)]-phosphine with $R^1 = R^2 = iPr$} reacts reversibly with dioxygen to the dinuclear *side-on* peroxido complex $[\{Cu(Pim^{iPr2})\}_2O_2]^{2+}$ (**2**) according to Scheme 1.[9]



Scheme 1. Overview of the tris-(imidazolyl)phosphine ligands (top). Reaction of **1** with O_2 to form the copper peroxido complex **2** (with $R^1 = R^2 = iPr$).

During these studies the large influence of the R^1/R^2 groups was observed e.g. the copper(I) complex $[Cu(Pim^{iPr,tBu})(CH_3CN)]BF_4$ was unreactive towards dioxygen.[8,9] Furthermore, intramolecular ligand hydroxylation occurred in good yields (35–45 %; 50 % would be quantitative for this reaction) when $[Cu(Pim^{iPr2})CH_3CN]^+$ was treated with dioxygen.[13] The oxidation of a colorless solution of **1** at low temperatures led to the intensively purple colored peroxido complex **2** easily observed in a benchtop experiment with **1** CF_3SO_3 (Figure S1, Supporting Information). Warming the solution to room temperature caused a color change to green and it was found that an oxygen atom had been inserted into the tertiary C–H bond of one of the isopropyl groups of the ligand.

Due to the fact that **1** allowed formation of a quite stable copper peroxido complex in a protic solvent it seemed worthwhile to investigate the kinetics of this reaction in more detail and to test it for its possible application in bubble columns.

Results and Discussion

Syntheses and Characterization

The ligand Pim^{iPr2} was prepared and characterized as described previously (NMR and MS data are reported in the Experimental Section and Supporting Information, Figure S2.1 and Figure S2.2).[9,13] The aqueous work-up of the reaction mixture had to be performed under inert conditions to avoid formation of a sticky solid (caused by oxidation) that makes the isolation of the ligand rather difficult. However, under inert conditions pure product could be obtained and crystals were obtained by recrystallization from methanol that could be structurally characterized (the molecular structure, Figure S2.3, and crystallographic data of Pim^{iPr2} are reported in the Supporting Information).

Furthermore, temperature control of the reaction is important due to the possible formation of an isomer of the ligand. The reason for this is the deprotonation/lithiation of the "wrong" methine-position on 1,4-diisopropylimidazole followed by further reaction with PCl_3. The poor solubility of Iso-Pim^{iPr2} (Pim^{iPr2} where one "imidazole-arm" is flipped) allowed to crystallize it (NMR data are reported in the Experimental Section and furthermore, together with crystallographic data in the Supporting Information). The corresponding copper(I) complex with Iso-Pim^{iPr2} did not form a "dioxygen" adduct complex when reacted with dioxygen and therefore was not investigated further.

Additionally we prepared the sterically less demanding known ligand tris(1-methylimidazol-2-yl)phosphane (Pim^{Me}; R^1 = Me and R^2 = H) according to the literature.[14] Efforts to obtain crystals of a copper(I) complex with Pim^{Me} as a ligand were not successful. A solution of a 1:1 mixture of $[Cu(CH_3CN)_4]CF_3SO_3$ and Pim^{Me} did not react with dioxygen under all conditions applied. We believe that here the complex $[Cu(Pim^{Me})_2]^+$ formed which is quite stable towards oxidation. This is a typical finding for copper(I) complexes that react in a ratio of 2:1 (ligand to copper ratio) and has been already discussed in the past.[9] Most of the time this can lead to a dramatic stabilization of copper(I) complexes towards dioxygen and has been observed by some of us previously when using bidentate ligands.[15] Efforts to observe/obtain a peroxido complex with this ligand by treating a solution of the copper(I) complex with hydrogen peroxide at ambient conditions were not successful either. Only the corresponding copper(II) complex, $[Cu(Pim^{Me})_2](CF_3SO_3)_2$, with a ligand to copper ratio of 2:1 was formed [supporting the proposed same stoichiometry for the corresponding copper(I) complex]. The molecular structure of $[Cu(Pim^{Me})_2](CF_3SO_3)_2$ (see Supporting Information, Figure S4) is in accordance with crystallographic data reported previously for the perchlorate analogue.[14]

In contrast the copper(I) complex $[Cu(Pim^{iPr2})CH_3CN]CF_3SO_3$ (**1** CF_3SO_3) was synthesized in good yields and characterized according to the literature.[9,13] Furthermore, it was possible to obtain crystals of **1** CF_3SO_3 and its molecular structure is presented in Figure 1 (crystallographic as well as NMR and MS data are reported in the Supporting Information). The molecular structure of this complex is quite similar to the related complex

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$[Cu(T1Et_4iPrIP)CH_3CN]PF_6$ ($T1Et_4iPrIP$ = $Pim^{Et,iPr}$) described by Kurtz and co-workers.[8] Both structures demonstrate that due to sterically demanding R groups the formation of complexes with a ligand to copper ratio of 2:1 is suppressed. Copper(II) complexes with Pim^{iPr2} have been reported previously by Sorrell et al.[9]

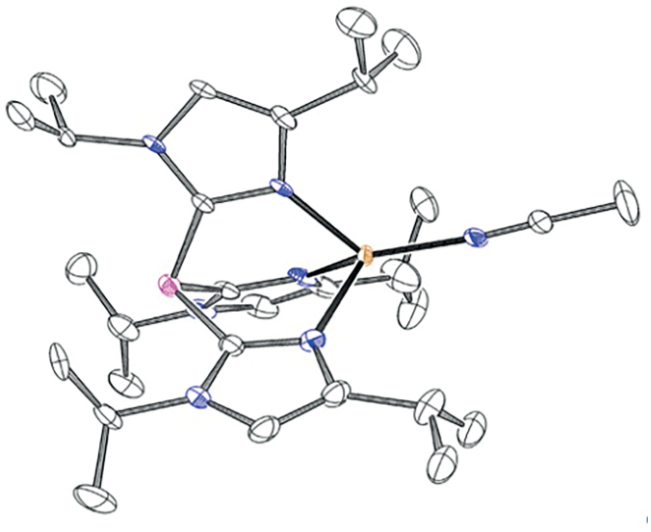

Figure 1. ORTEP plot of **1**. Hydrogen atoms are omitted for clarity, thermal ellipsoids were set to 50 % probability.

As described above copper(I) salts with the ligand Pim^{iPr2} react with dioxygen (in CH_3OH or CH_2Cl_2 as solvents) to form the corresponding dinuclear *side-on* peroxido copper complexes (Scheme 1). However, despite the fact that **2** has been thoroughly characterized by spectroscopy[9] it has not been possible so far to structurally characterize it or its derivatives.[8] All our efforts failed as well, most likely a consequence of the equilibrium between the starting material **1** and the product **2**.[9]

DFT Calculations

To further confirm the molecular structure of **2**, DFT calculations were performed. They reveal that the peroxide species is energetically stabilized against the *bis(μ-oxido)* species by 12 kcal/mol (broken-symmetry approach for peroxide species). Figure 2 depicts the optimized structure of **2**. The Cu–N(eq) bond lengths are in the range of 1.987 Å to 2.074 Å and the Cu–N(ax) bond lengths are 2.172 Å or 2.300 Å whereas the Cu···Cu distance is predicted to 3.394 Å and the O–O distance to 1.440 Å (see Supporting Information Table S22).

Stopped-Flow Measurements

To gain better understanding of the reaction of **1** CF_3SO_3 with dioxygen (Scheme 1) a low temperature stopped-flow investigation was performed. The oxidation of **1** CF_3SO_3 in methanol can be observed spectrophotometrically, and a representative plot of time-resolved UV/Vis spectra for the formation of **2** $(CF_3SO_3)_2$ at 0.0 °C is shown in Figure 3.

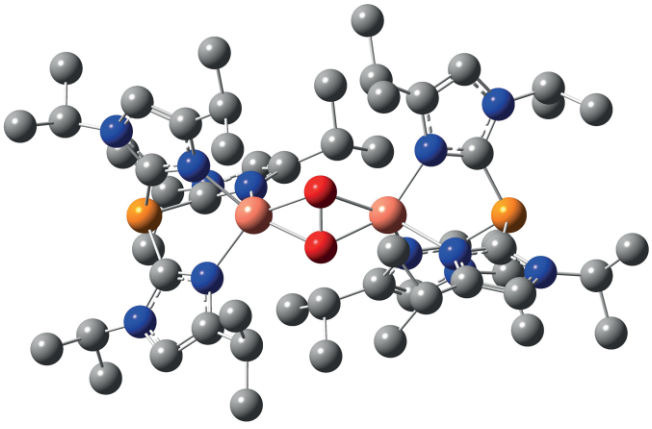

Figure 2. Optimized geometry of **2** (TPSSh/def2-TZVP, MeOH, GD3BJ, broken-symmetry; hydrogen atoms are omitted for clarity).

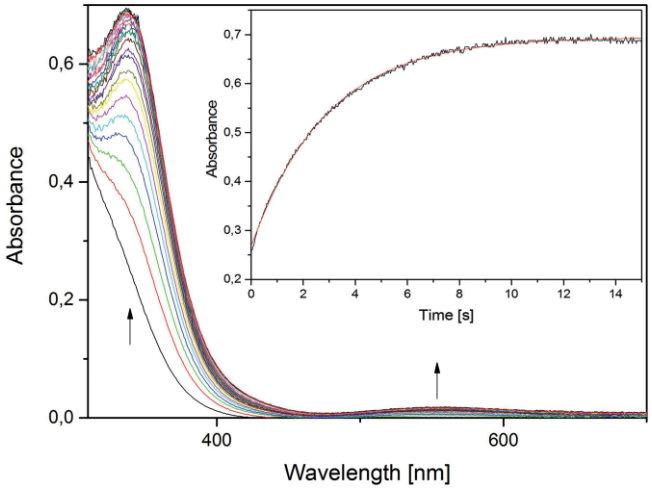

Figure 3. Time-resolved UV/Vis spectra of the reaction of **1**CF_3SO_3 with dioxygen in methanol (T = 0.0 °C, [**1**CF_3SO_3] = 0.4 mmol/L, $[O_2]$ = 5.2 mmol/L). Inset: absorbance vs. time trace at 370 nm together with one exponential fit.

The obtained UV/Vis spectra show maxima at 343 nm and 549 nm typical for a *side-on* peroxido copper complex. Again TD-DFT calculations reproduced the measured UV/Vis spectra very well with 360 nm for the in-plane feature and 493 nm for the out-of-plane peroxide feature (Supporting Information, Figure S6).

The reaction was carried out under pseudo first order conditions ($[O_2]$ > [**1** CF_3SO_3]). Absorbance vs. time data in the wavelength range between 340 nm and 700 nm could be fitted perfectly well to a single exponential function leading to a first order dependence of [**1**] in the rate law. At longer time scales or higher temperatures, the decomposition of the peroxido complex is detectable (Supporting Information Figure S7).

The variation of $[O_2]$ from 0.65 to 5.2 mmol/L at different temperatures (–25.0 to +20.0 °C) leads to straight lines with an intercept in a plot of the observed rate constants k_{obs} vs. $[O_2]$ (Figure 4). Therefore, $[O_2]$ also will be first order in the rate law. The intercept is a consequence of the reversibility of the reaction. Turning around the pseudo first order conditions

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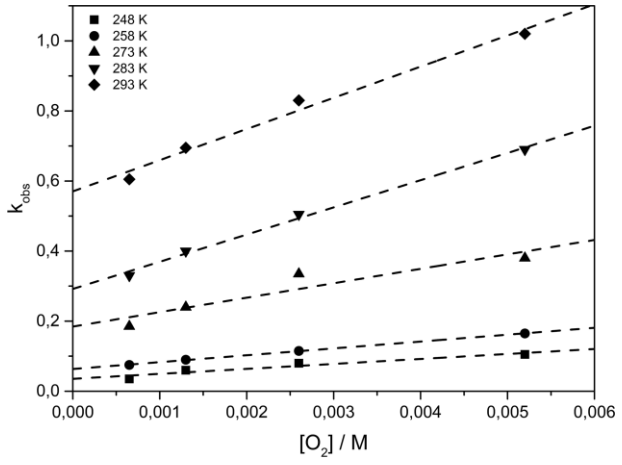

Figure 4. Plot of k_{obs} vs. $[O_2]$.

([**1** CF_3SO_3] > $[O_2]$) did lead to the same results (Supporting Information, Figure S 8).

Regarding the mechanism of this reaction it should proceed at least in two steps. In the first step a superoxido complex must form according to Equation 1. In a consecutive reaction with a second copper(I) complex (Equation 2) the dinuclear *side-on* peroxido complex is formed.

$$\mathbf{1}^+ + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cu(Pim^{iPr2})(O_2)]^+ + CH_3CN \qquad (1)$$

$$[Cu(Pim^{iPr2})(O_2)]^+ + \mathbf{1}^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathbf{2}^{2+} + CH_3CN \qquad (2)$$

Such a reaction sequence has been observed and kinetically analyzed in detail previously for the formation of dinuclear copper *end-on* peroxido complexes.[5b,5c,5d,16] In contrast to these studies the formation of a copper superoxido complex according to Equation 1 when reacting **1** with dioxygen was not observed (even when the temperature was lowered to −90.0 °C). This is not unusual and similar findings were reported for the formation of analogous dinuclear *side-on* peroxido as well as *bis(μ-oxido)* copper complexes.[15a,15c,17] For the irreversible formation of a related *bis(μ-oxido)* copper complex it could be shown by DFT calculations that it would not be possible to observe this intermediate spectrocscopically.[15b] Here the formation of the mononuclear superoxido complex is rate-determining and the following steps are "extremely downhill without any larger transition states confirming experimental results".[15b]

This holds true for our studies as well: the reversible reaction to form the mononuclear superoxido complex is rate-determining while the formation of the dinuclear peroxido complex is much faster thus leading to a treatment of the superoxido complex as a steady state species. A detailed description of this approach has been reported in the literature for the irreversible reaction of dioxygen with the complex $[Cu(iPr_3TACN)(CH_3CN)]^+$.[4h,4k,17b]

However, in contrast to this system formation of **2** is not complete and the reversibility (Equation 1 and 2) has to be included. Applying the steady state approach, we obtained (see Supporting Information for the derivation) the following equation for k_{obs}:

$$k_{obs} = k_1 [O_2] + \frac{k_{-1}\, k_{-2}}{k_2\, [\mathbf{1}]} \qquad (3)$$

Thus, it is possible from the slopes of the plot of k_{obs} vs. $[O_2]$ (Figure 3, $k_{obs} = k_1[O_2]$) to determine the second order rate constants for the forward reaction at different temperatures (Table 1) while the intercept is caused by the reversibility of the reaction. With an Eyring plot for k_1 (Supporting Information, Figure S9) activation parameters were calculated to $\Delta H^{\#}$ = 25 ± 2 kJ mol^{-1} and $\Delta S^{\#}$ = −121 ± 8 J mol^{-1} K^{-1}.

Table 1. Kinetic and thermodynamic parameter for the O_2-interaction with $[Cu(P(Im^{iPr2})_3)(CH_3CN)]^+$ (**1**) and $[Cu(iPr_3TACN)(CH_3CN)]^+$.

Parameter	Temperature	**1**	$[Cu(iPr_3TACN)(CH_3CN)]^+$
k_1	248 K	13.0	–
(mol^{-1} Ls^{-1})	258 K	19.5	
	273 K	41.1	243.2
	283 K	78.1	–
	293 K	87.8	–
$\Delta H^{\#}$		25 ± 2	37.2 ± 0.5
(kJ mol^{-1})			
$\Delta S^{\#}$		−121 ± 8	−62 ± 2
(J K^{-1} mol^{-1})			

While the reaction of **1** with dioxygen (similar to the reaction of $\{[Cu(HB(3,5\text{-}^{iPr2}pz)_3)]_2(O_2)\}$, Scheme 1) described previously[4f] quite nicely models the chemical reaction of the oxygen carrier protein hemocyanin there are still – as expected – huge differences in their reactivity. The preorganized active site in hemocyanin reacts much faster with dioxygen than the model compound and its oxygen uptake had to be measured using temperature jump methods.[18] Furthermore, an activation volume of close to zero had been obtained for hemocyanin (therefore indicating an activation entropy of close to zero as well) leading to an interchange mechanism (facile substitution of a water molecule by dioxygen in contrast to replacing strongly coordinated acetonitrile in the model complex).[18] While activation entropies in principle cannot be obtained with high accuracy (due to its calculation from the intercept in the Eyring plot at $T = \infty$) a quite large negative activation entropy for the reaction of **1** with dioxygen accounts for an associative mechanism.[16,19] Together with the relatively small activation enthalpy this is quite typical for the formation of a dinuclear copper peroxido complex.[4h,16–17,20] The "O_2 adduct" formation leads to a tighter metal-dioxygen bond and a species with fewer degrees of freedom.

Kinetic data compare quite well for the analogous irreversible reaction of dioxygen with the complex $[Cu(iPr_3TACN)(CH_3CN)]^+$ (Table 1)[4h,4k] and furthermore with observed copper superoxido complex formation with tripodal ligands.[5c,16,21] In contrast kinetic data for the formation of some other copper peroxido complexes are different.[17a,17c,20,22]

However, these findings should not be overinterpreted due to the fact that these reactions are extremely sensitive towards ligand modification and/or solvent. Thus the complex $[Cu(Pim^{iPr,tBu})(CH_3CN)]PF_6$ (Scheme 1: R^1 = *i*Pr, R^2 = *t*Bu) showed no reactivity towards dioxygen, obviously due to the increase of the steric hindrance in this system.[9] Furthermore, when the reaction of dioxygen with $[Cu(Pim^{iPr2})(CH_3CN)]PF_6$ was per-

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formed in dichloromethane a relatively stable copper peroxido complex was observed at low temperatures as well. However, the reaction became so slow that subsequent decay started to play an important role and affected the formation of the peroxido complex. The rate-determining step in the formation of the copper superoxido complex is the breaking of the copper–nitrile bond and the consecutive reaction with dioxygen. In this case the acetonitrile molecule has a strong coordination tendency to copper(I) ions and slows down the reaction with dioxygen and acts as a competitive ligand. This effect is more recognizable when the reaction is carried out in nitrile solvents. Under these conditions no reaction of **1** with dioxygen was observed. Therefore, no kinetic analysis was carried out in dichloromethane or nitrile solvents.

To avoid the presence of acetonitrile and thus pushing the equilibrium further to the formation of **2**, Pim^{iPr2} was treated with the copper(I) triflate toluene complex in methanol. Under these conditions a dinuclear complex, $[Cu_2(Pim^{iPr2})_2](CF_3SO_3)_2$, was formed that could be structurally characterized (crystallographic data are reported in the Supporting Information). A solution of this compound in either methanol or acetone still reacted with dioxygen to form the deep purple colored complex **2**. However, without the stabilization of acetonitrile disproportionation was also observed and therefore no further experiments with this compound were performed.

Reactions in Water

Unfortunately, efforts to analyze the reaction of **1** with dioxygen in water were unsuccessful. Only oxidation to copper(II) compounds with some foam formation was observed (caused by shaking of the suspension of the complex), without any indication of the occurrence of an intermediate. However, adding an excess of a H_2O_2/Et_3N solution (1:2 in methanol) to a Pim^{iPr2}/$[Cu(H_2O)_6](ClO_4)_2$ solution (1:1 in methanol) allowed to observe the brief formation (less than one second) of **2** (deep purple solution) at room temperature. At –80 °C the purple color is persistent for a few seconds.

Continuous Flow Measurements

Previously we used a SuperFocus mixer to investigate the kinetics of fast reactions by continuous flow.[12c,23] Due to the short mixing time of this setup it was possible to analyze the formation of $[Cu_2O_2(btmgp)_2]I_2$, a temperature sensitive guanidine-stabilized *bis(μ-oxido)* species at room temperature.[23] In contrast, the reaction of **1** with O_2 at room temperature is slower with a faster decay (for decay k_{obs} = 0.06 s^{-1} at 25 °C, see below). Hence, the detection of **2** with the SuperFocus mixer was difficult. Variation of complex concentration and flow rates revealed that formation and decay of **2** already occur during mixing and thus prevent kinetic data collection (Supporting Information, Figure S10). This is supported by stopped-flow measurements under the same conditions (Supporting Information, Figure S7) indicating that reliable kinetic data for the formation of **2** only can be obtained using this instrumentation.

To gain more information on the decay of **2** it was kinetically analyzed. Decomposition of **2** (decay of the peroxido UV/Vis band at 449 nm) is a first-order reaction and time resolved UV/Vis spectra are reported in the Supporting Information (Figure S11). The Eyring plot for this reaction (Supporting Information, Figure S12) allowed to calculate the activation parameters to $\Delta H^{\#}$ = 43 ± 1 kJ mol^{-1} and $\Delta S^{\#}$ = –124 ± 2 J mol^{-1} K^{-1}. These data compare well with previous reports.[17b] No H_2O_2 formation was observed during/after the decomposition of the peroxide complex.

Conclusions

The copper(I) complex **1** with the ligand Pim^{iPr2} (Scheme 1) reversibly forms a dinuclear μ-η^2:η^2-*side-on* peroxido complex thus modeling the reactivity of the oxygen carrier protein hemocyanin in some aspects (reversible reaction with dioxygen to form a dinuclear peroxide complex in a protic solvent). In contrast to previous kinetic studies on the reaction of copper(I) complexes with dioxygen we were able to investigate this reaction of **1** in detail in the protic solvent methanol. Mechanistic studies in protic solvents so far have not been very successful. E.g. in our own work we could not detect any intermediate complex during the oxidation of a copper(I) complex with the ligand *N*,*N*′-bis[2-(dimethylamino)ethyl]*N*,*N*-dimethylethane-1,2-diamine (Me_6trien) in water in contrast to the reaction of hemocyanin with dioxygen.[6,18] However, the results of our analysis of the reaction of **1** with dioxygen together with a recent report[11] on a quite stable copper peroxido complex in water are promising for finding a copper system that can be used in aqueous solutions for industrial applications of selective oxidations in the future. While it turned out that **1** is not suitable for the investigation of its reactivity with dioxygen in bubbly flows this is different for an iron peroxido complex reported by some of us previously.[12c,24] Besides the problems with protic solvents, rates for formation and decay of reactive intermediates need to be in a time window to allow their study in an industrial setup such as a bubble flow column.

It seems to be important to point out one more time how much reactions of copper(I) complexes with dioxygen are affected by ligand design and solvents (sometimes also anions can show an effect). Especially the formation of a copper(I) complex with a ligand to copper ion ratio of 2:1 is a serious problem that can completely suppress the reactivity of these complexes.[15] At the moment the question still remains what the requirements are to stabilize a "dioxygen adduct" copper complex in a protic solvent.

Experimental Section

All reagents and solvents were purchased from commercial sources. The solvents were purified by distillation and dried by standard procedures or used from the solvent purification system SPS-800 by MBraun (Garching, Germany). Preparations under anaerobic conditions were carried out in Schlenk tubes using dry nitrogen or in a glovebox by MBraun under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II 200 spectrometer

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(^{1}H at 200 MHz; ^{13}C at 50 MHz), Bruker Avance II 400 spectrometer (^{1}H at 400 MHz; ^{13}C at 100 MHz) and Bruker Avance III HD 400 spectrometer (^{1}H at 400 MHz; ^{13}C at 100 MHz; ^{31}P at 162 MHz) in $CDCl_3$ using TMS as internal standard. The ^{31}P NMR spectra were referenced to external 85 % H_3PO_4, the ^{1}H and ^{13}C NMR spectra were calibrated against the proton and carbon signals of tetramethylsilane.

Stopped-Flow Measurements: Solutions of copper(I) complexes for stopped-flow measurements were prepared in glass syringes under argon in a glove box. Saturated solutions of dioxygen were prepared by bubbling dry dioxygen (grade 5.5, Messer Griesheim, Germany) through the solvent in a syringe for about 10 min. Dioxygen concentration in a saturated methanol solution has been reported to be 10.4×10^{-3} mol/L at 25 °C.[25] Different concentrations of dioxygen were obtained by mixing a dioxygen saturated solution with an argon saturated solution using two connected syringes (thus leading to a variation of dioxygen concentration of 0.65 to 5.20×10^{-3} mol/L in the measurements) Temperature dependent stopped-flow analysis was performed in a range from –25.0 °C to +25.0 °C. All measurements were repeated about 5 times at each concentration and temperature and gave consistent results. The kinetic data were obtained using a Hi-Tech SF-61SX2 low-temperature stopped-flow unit equipped with a diode array spectrophotometer (Hi-Tech, Salisbury, UK; now TgK Scientific, Bradford-on-Avon, UK). Kinetic data were analyzed either using the integrated software Kinetic Studio (TgK Scientific) or Igor Pro (Wavemetrics, Lake Oswego, USA). Details on the setup and kinetic measurements have been described previously.[5c,16,26]

The SuperFocus mixer setup was described in detail previously including analyses of the results.[12c,23]

Deposition Numbers 1998658, 1998659, 2001562, 2001563, 2001564 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 www.ccdc.cam.ac.uk/structures.

Density functional theory (DFT) calculations were performed with Gaussian 16, Revision B01.[27] For the calculations we used TPSSh[28] as functional and the Ahlrichs type basis set def2-TZVP[29] as implemented in Gaussian 16, Revision B01.[27] As solvent model, we used the Polarizable Continuum Model (PCM) as implemented in Gaussian 16. As empirical dispersion correction, we used the D3 dispersion with Becke–Johnson damping as implemented in Gaussian16, Revision B.01.[30]

Synthesis of Tris(1-methylimidazol-2-yl)phosphane (Pim^{Me}): The ligand was prepared according to the method reported by Tolmachev et al.[31] However, we used a modified procedure of the synthesis described in a patent by Hätzelt.[32] The product was obtained as a slightly yellow solid (1.39 g, 5.10 mmol, 48 % yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.18 (s, 3H, 3 × Ar-CH), 7.06 (s, 3H, 3 × Ar-CH), 3.62 (s, 9H, 3 × CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 140.2 (d, Ar-C_q), 130.6 (d, Ar-CH), 125.1 (s, Ar-CH), 34.4 (d, CH_3). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) = –60.5 (s). MS (ESI): m/z = 275.12 [M + H]$^+$.

Synthesis of Tris[2-(1,4-diisopropylimidazolyl)]phosphane (Pim^{iPr2}): This Ligand was prepared in a four-step synthesis according to procedure described by Sorrell et al.[9] Because of the slow oxidation of the phosphor backbone under aerobic conditions, the workup of the ligand is quite challenging. It is important to note that the aqueous work-up should be carried out largely in the absence of air (deoxygenated solvents). The product was obtained as a fine colorless powder (4.55 g, 9.39 mmol, 39 % yield). Crystals suitable for X-ray diffraction were grown by cooling a saturated pentane solution to 0 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.80 (s, 3H, 3 × Ar-CH), 4.77–4.65 (m, 3H, 3 × *i*Pr-CH), 2.85 (quin, 3H, 3 × *i*Pr-CH), 1.19 (d, 18H, 6 × *i*Pr-CH_3), 1.12 (d, 18H, 6 × *i*Pr-CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.4 (s, Ar-C_q), 138.4 (d, Ar-C_q),113.2 (s, Ar-CH), 49.1 (d, *i*Pr-CH), 28.3 (s, *i*Pr-CH), 23.8 (s, *i*Pr-CH_3), 22.8 (s, *i*Pr-CH_3). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) = –60.6 (s). MS (ESI): m/z = 485.35 [M + H]$^+$, 407.34 [M + Na]$^+$.

Synthesis of Bis[2-(1,4-diisopropylimidazolyl)][4-(1,4-diisopropyl-imidazolyl)]phosphane (Iso-Pim^{iPr2}): This compound was synthesized in the same manner like Pim^{iPr2} with the exception of slightly higher temperatures in the deprotonation/lithiation of 1,4-diisopropylimidazole (inefficient cooling) and the crystallization directly out of a acetonitrile solution at room temperature. The product was obtained as a colorless solid with some crystals suitable for X-ray diffraction (1.05 g, 2.17 mmol, 9 % yield). ^{1}H-NMR (400 MHz, [D_6]acetone): δ (ppm) = 7.84 (s, 1H, 1 × Ar-CH), 7.09 (s, 2H, 2 × Ar-CH), 5.06 (quin, 1H, 1 × *i*Pr-CH), 4.50 (sext, 2H, 2 × *i*Pr-CH), 3.52–3.42 (m, 1H, 1 × *i*Pr-CH), 2.77 (quin, 2H, 2 × *i*Pr-CH), 1.42 (d, 6H, 1 × *i*Pr-CH_3), 1.22 (d, 6H, 1 × *i*Pr-CH_3), 1.19–1.13 (m, 18H, 3 × *i*Pr-CH_3), 1.08 (d, 6H, 1 × *i*Pr-CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 159.3 (s, Ar-C_q), 151.7 (s, Ar-CH), 140.5 (d, Ar-C_q), 139.8 (d, Ar-C_q), 113.8 (s, Ar-CH),113.6 (d, Ar-C_q), 49.9 (d, *i*Pr-CH), 49.4 (s, *i*Pr-CH), 29.2 (s, *i*Pr-CH), 28.0 (d, *i*Pr-CH), 24.7 (s, *i*Pr-CH_3), 24.2 (s, *i*Pr-CH_3), 23.9 (s, *i*Pr-CH_3), 23.7 (s, *i*Pr-CH_3), 23.2 (s, *i*Pr-CH_3), 23.1 (s, *i*Pr-CH_3). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) = –77.5 (s). MS (ESI): m/z = 485.35 [M + H]$^+$.

Synthesis of [Cu(Pim^{iPr2})(CH_3CN)]CF_3SO_3 (1CF_3SO_3): This Ligand was prepared according to the literature.[13] The product was obtained in form of colorless crystals suitable for X-ray diffraction (2.03 g, 2.75 mmol, 92 % yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.78 (s, 3H, 3 × Ar-CH), 5.12–4.99 (m, 3H, 3 × *i*Pr-CH), 2.97 (quin, 3H, 3 × *i*Pr-CH), 2.38 (s, 3H, acetonitrile-CH_3), 1.48 (d, 18H, 6 × *i*Pr-CH_3), 1.28 (d, 18H, 6 × *i*Pr-CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.6 (s, triflate-C_q), 137.8 (d, Ar-C_q), 138.4 (d, Ar-C_q), 114.4 (s, acetonitrile-C_q),113.3 (s, Ar-CH), 49.8 (d, *i*Pr-CH), 28.2 (s, *i*Pr-CH), 24.1 (s, *i*Pr-CH_3), 22.1 (s, *i*Pr-CH_3), 2.92 (s, acetonitrile-CH_3). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) = –117.8 (s). MS (ESI): m/z = 547.27 [M – CH_3CN - CF_3SO_3]$^+$.

Synthesis of [Cu_2(Pim^{iPr2})$_2$](CF_3SO_3)$_2$: 242 mg of Pim^{iPr2} (0.50 mmol) were dissolved in 3 mL of methanol. A solution of 129 mg of copper(I) triflate toluene complex (0.25 mmol) in 3 mL of methanol was added dropwise to the ligand solution and the reaction mixture was stirred 30 min at room temperature. Diethyl ether was added to the green solution until the solution became cloudy. After few minutes at –30 °C colorless crystals suitable for X-ray diffraction were grown. The crystals were filtered off and washed with diethyl ether. The slightly green solid was dried in vacuo to obtain a colorless powder (245 mg, 0.18 mmol, 72 % yield). MS (ESI): m/z = 547.27 [(0.5 M) – CF_3SO_3]$^+$.

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Keywords: Copper · Dioxygen · Peroxides · Kinetics · Superoxides

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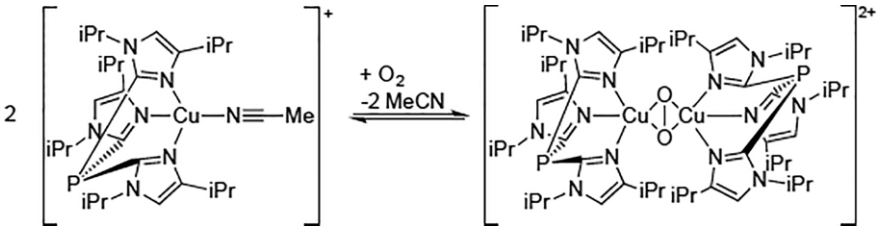
Dioxygen Activation

*M. Lerch, M. Weitzer, T.-D. J. Stumpf, L. Laurini, A. Hoffmann, J. Becker, A. Miska, R. Göttlich, S. Herres-Pawlis, S. Schindler** 1–9

Kinetic Investigation of the Reaction of Dioxygen with the Copper(I) Complex [Cu(Pim^{iPr2})(CH_3CN)]CF_3SO_3 {Pim^{iPr2} = Tris[2-(1,4-diisopropylimidazolyl)]phosphine}



The copper(I) complex with the ligand tris[2-(1,4-diisopropylimidazolyl)]phosphine can be regarded as a model compound for the oxygen carrier protein hemocyanin. It can form a quite stable dinuclear copper peroxido complex in the protic solvent methanol at room temperature. The kinetics of this reaction have been studied in detail.

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