

# Unusual Stability of an *End-on* Superoxido Copper(II) Complex under Ambient Conditions

Chiara Eleonora Campi,<sup>[a]</sup> Kostas Parkatzidis,<sup>[b]</sup> Athina Anastasaki,<sup>[b]</sup> and Siegfried Schindler<sup>\*[a]</sup>

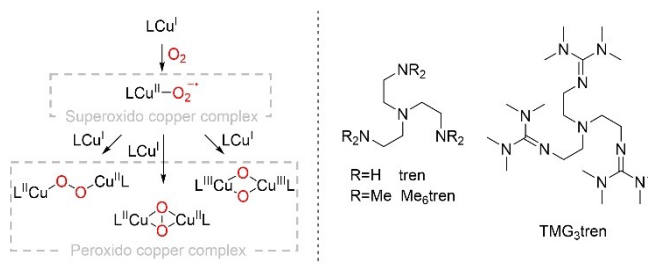
Superoxido copper complexes play an important role as usually short-lived intermediates in biology and chemistry. The unusual stability of an *end-on* superoxido copper complex observed in an oxygen-enhanced atom transfer radical polymerization (ATRP) led to a detailed mechanistic investigation of the formation of  $[\text{Cu}^{\text{II}}(\text{Me}_6\text{tren})(\text{O}_2^{\bullet-})]^+$  ( $\text{Me}_6\text{tren}$  = tris(2-dimethyl-

aminoethyl)amine) under ambient conditions. The persistence of the superoxido copper complex could be explained by a reaction cycle including the peroxido complex  $[(\text{Me}_6\text{tren})_2\text{Cu}^{\text{II}}_2(\text{O}_2)]^{2+}$  together with  $[\text{Cu}^{\text{I}}(\text{Me}_6\text{tren})(\text{DMSO})]^+$  and  $[\text{Cu}^{\text{II}}(\text{Me}_6\text{tren})(\text{OH})]^+$  in the overall reaction.

## Introduction

The superoxide radical anion plays a significant role across various fields of chemistry, including biochemistry/medicine (superoxide belongs to the group of reactive oxygen species – ROS), the development of lithium-dioxygen batteries, and catalysis.<sup>[1,2]</sup> Superoxido transition metal complexes, e.g., well-known oxyhemoglobin (which can be formally described as  $\text{Fe}^{\text{III}}-\text{O}_2$ ), can be obtained in the first step of the reactions with dioxygen.<sup>[3–5]</sup> Furthermore, these species are recognized as crucial reactive intermediates in selective hydroxylation reactions catalyzed by mononuclear copper monooxygenase enzymes, including peptidylglycine  $\alpha$ -hydroxylating monooxygenase (PHM) and dopamine  $\beta$ -monooxygenase (D $\beta$ M).<sup>[6,7]</sup> However, *end-on* superoxido metal complexes are often formed as short-lived intermediates preceding fast consecutive reactions into dinuclear “oxygen adduct” complexes, according to Scheme 1.<sup>[3,8,9]</sup>

The use of ligand Tris[2-(N-tetramethylguanidyl)ethyl]amine ( $\text{TMG}_3\text{tren}$ , Scheme 1), derived from tris(2-aminoethyl)amine (tren), facilitated the stabilization of an *end-on* superoxido copper(II) complex to such an extent that enabled its structural characterization at low temperatures.<sup>[10,11]</sup> In contrast, the use of the fully methylated tren ligand  $\text{Me}_6\text{tren}$  (Scheme 1) only allowed brief spectroscopic observation of the corresponding

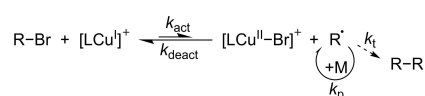


**Scheme 1.** Possible pathways of dioxygen binding to copper complexes (left, charges omitted for clarity); tren-derived ligands (right).

superoxido copper(II) complex at low temperatures before its fast parallel reaction to the dinuclear peroxido copper(II) complex (Scheme 1).<sup>[12]</sup> In this context, detecting a persistent *end-on* superoxido copper(II) complex using the ligand  $\text{Me}_6\text{tren}$  under ambient conditions in an atom transfer radical polymerization (ATRP) was notably unexpected.<sup>[13,14]</sup>

ATRP is one of the most prevalent techniques in reversible deactivation radical polymerization (RDRP).<sup>[15–18]</sup> It relies on the dynamic equilibrium between active and dormant states of polymers. The metal complex in a low oxidation state, typically a copper(I) complex ( $\text{LCu}^{\text{I}}$ ,  $\text{L} = \text{Me}_6\text{tren}$ ) had turned out to be beneficial for ATRP,<sup>[19]</sup> abstracts the halogen from the initiator, usually an alkyl halide ( $\text{R-X}$ ), to give a carbon-centered radical and a metal complex in a higher oxidative state. While the radical species induce the propagation of the polymeric chain, the copper(II) complex ( $\text{LCu}^{\text{II}}-\text{Br}$ ) promotes its fast deactivation, minimizing termination reactions and shifting the equilibrium towards the dormant state (Scheme 2).<sup>[18]</sup>

The observation of the formation of an unusual persistent *end-on* superoxido copper complex under these conditions led



**Scheme 2.** General ATRP mechanism.

[a] C. E. Campi, Prof. Dr. S. Schindler  
Institute of Inorganic and Analytical Chemistry  
Justus Liebig University Giessen  
Giessen, Hessen 35392, Germany  
E-mail: siegfried.schindler@chemie.uni-giessen.de

[b] Dr. K. Parkatzidis, Prof. Dr. A. Anastasaki  
Laboratory of Polymeric Materials, Department of Materials  
ETH Zurich  
Zurich 8093, Switzerland

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/chem.202401634>

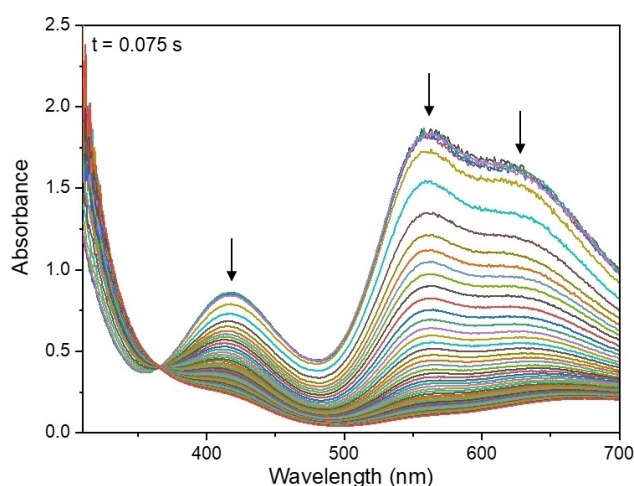
© 2024 The Authors. Chemistry - A European Journal published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

us to investigate in detail the mechanism behind the stabilization of this otherwise extremely reactive intermediate.

## Results and Discussion

To gain a better understanding of the persistence of the *end-on* superoxido copper(II) complex, we first examined the early stages of the oxidation of [Cu(Me<sub>6</sub>tren)(Br)] (1) under aerobic conditions. Stopped-flow UV-vis measurements (Figure 1) were performed by mixing a deoxygenated solution of 1 in DMSO with a saturated O<sub>2</sub> solution of pure solvent at 25.0 °C. The rapid formation of the *end-on* superoxido copper complex [Cu<sup>II</sup>(Me<sub>6</sub>tren)(O<sub>2</sub><sup>•-</sup>)]<sup>+</sup> (3) was detected by the characteristic absorption band at λ = 418 nm.<sup>[12,20]</sup> Concurrently, the absorbance maxima at λ = 560 and 633 nm indicated the formation of the dinuclear *end-on* peroxido copper complex [(Me<sub>6</sub>tren)Cu<sup>II</sup>-O-O-Cu<sup>II</sup>(Me<sub>6</sub>tren)]<sup>2+</sup> (4), in accordance with previous results.<sup>[12,20]</sup> Notably, the measurements showed a fast decrease in spectral absorption over the first 0.075 seconds, indicating the decomposition of species 3 and 4. This finding confirmed the high reactivity of the oxygenated complexes at room temperature, as reported in other solvents.<sup>[12,20–22]</sup> However, it contradicted our previous findings, as the Raman measurements (λ<sub>Laser</sub> = 402 nm) had provided evidence that the superoxido complex persisted over hours after the oxygenation.<sup>[13]</sup>

To clarify this point, the measurement time was extended to 350 seconds. Notably, a gradual band increase at λ = 418 nm was detected, reaching its maximum after 80 seconds (Figure S1). This behavior suggested the involvement of the oxygenated species in a cycle that leads to the regeneration and slight accumulation of 3 in solution over time. Moreover, this finding explained the remarkable and unusual persistence of the oxygenated intermediate at room temperature, which can still be detected over minutes.



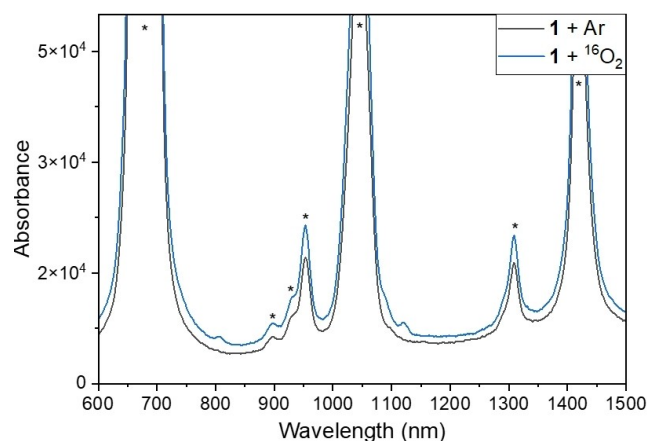
**Figure 1.** Time-dependent UV-vis spectra, recorded by stopped-flow measurements in the first 0.075 seconds of the reaction between 1 and oxygenated DMSO. [CuBr] = 0.002 mol/L, [Me<sub>6</sub>tren] = 0.014 mol/L (before mixing), T = 25.0 °C.

Raman measurements were performed anew to support further the assignments postulated by UV-vis spectroscopy. As shown in Figure 2, the peaks at 1128 cm<sup>-1</sup> and 809 cm<sup>-1</sup> appeared upon oxygenation of 1 in DMSO. These peaks are characteristic of the vibrational frequency of the <sup>16</sup>O–<sup>16</sup>O unit and can be attributed to complexes 3 and 4, respectively.<sup>[11,12,22,23]</sup> Once again, the peaks were visible both immediately after the oxygenation and over several minutes after mixing, supporting the involvement of species 3 and 4 in a catalytic cycle.

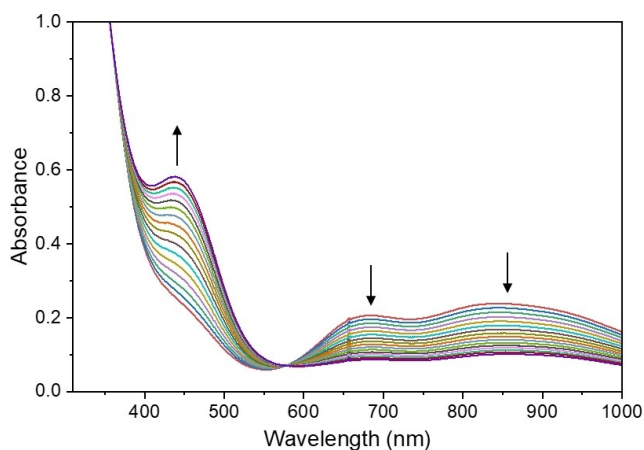
To elucidate the pathway that leads to the reformation of the superoxido copper(II) complex 3 and the nature of the species involved, the spectral changes were monitored over 10 minutes in a range of λ = 300–1000 nm. The analysis was conducted at 25.0 °C immediately after exposing the deoxygenated solution of 1 to air. The solution of 1, which appeared slightly yellow under inert conditions (see below), rapidly turned its color to dark green upon oxygenation and ultimately became dark yellow (Figure S2). The UV-vis measurements revealed the prompt rise of two bands at λ = 673 and 847 nm, which undergo a fast decrease over 5 minutes, concurrently with an increase of the absorption band at λ = 443 nm (Figure 3).

The presence of bands at λ = 673 and 847 nm is associated with the formation of the species [Cu<sup>II</sup>(Me<sub>6</sub>tren)(OH)]Br 5. The nature of the copper(II) intermediate was confirmed through comparison with the UV-vis spectrum of the isolated [Cu<sup>II</sup>(Me<sub>6</sub>tren)(OH)](ClO<sub>4</sub>) complex (Figure S3).<sup>[24]</sup> The formation of 5 was additionally proved by detecting an ion peak at m/z of 310.1782 in the electrospray ionization spectrum (ESI-MS) of the solution of 1 upon oxygenation. The observed mass and isotope distribution pattern corresponded to [Cu<sup>II</sup>(Me<sub>6</sub>tren)(OH)]<sup>+</sup> (calculated m/z of 310.1783).

The band assignment at 443 nm proved more challenging. Initially, we had attributed it to the formation of the *end-on* superoxido copper(II) complex 3, in accordance with the absorption of the corresponding complex [Cu<sup>II</sup>(TMG<sub>6</sub>tren)(O<sub>2</sub><sup>•-</sup>)]<sup>+</sup> at 442 nm, and the resonance Raman



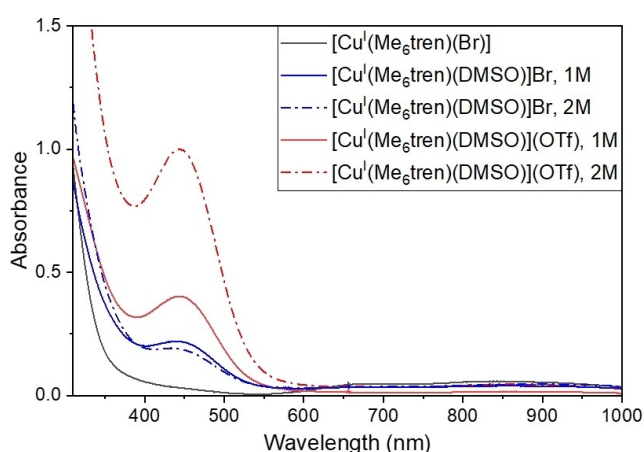
**Figure 2.** Resonance Raman spectra of compound 1 in DMSO before its reaction with dioxygen (black line) and after its reaction with <sup>16</sup>O<sub>2</sub> (blue line). All the peaks denoted with stars belonged to the solvent. [CuBr] = 0.001 mol/L, [Me<sub>6</sub>tren] = 0.007 mol/L, T = 25.0 °C.



**Figure 3.** Time-dependent UV-vis spectra were recorded in the first 350 s of the reaction between **1** and air in DMSO.  $[\text{CuBr}] = 0.001 \text{ mol/L}$ ,  $[\text{Me}_6\text{tren}] = 0.007 \text{ mol/L}$ ,  $T = 25.0^\circ\text{C}$ .

measurements.<sup>[11,13]</sup> We first attributed the shift from 418 nm, previously observed for complex **3** in different solvents, to 443 nm using DMSO as solvent.<sup>[12]</sup> However, as demonstrated above with the results of the stopped-flow measurements, the absorbance at 443 nm cannot be associated with the formation of **3**. To identify the nature of the species responsible for this absorption, the reactivity of **1** in DMSO was investigated under inert conditions. The colorless solution turned to a pale yellow color when argon was bubbled through it over a period of 40 minutes (Figure S2). An increase in the band at  $\lambda = 443 \text{ nm}$  was detected over time (Figure 4, blue solid line) and was attributed to the slow formation of the DMSO adduct  $[\text{Cu}^{\text{I}}(\text{Me}_6\text{tren})(\text{DMSO})]\text{Br}$  (**2**).

DMSO is widely recognized as a strong coordinating solvent that competes with other ligands to bind to copper ions.<sup>[25–28]</sup> Thus, it is likely that an equilibrium between species **1** and **2** exists in solution. To validate this idea,  $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4](\text{OTf})$  was



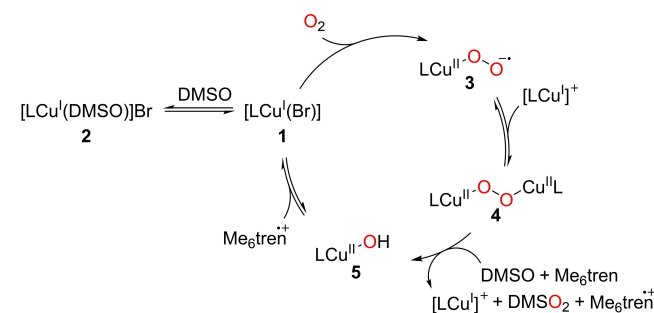
**Figure 4.** UV-vis spectra of compounds **1** and **2** in DMSO under inert conditions at room temperature: **1**, immediately after mixing (black line);  $[\text{Cu}^{\text{I}}(\text{Me}_6\text{tren})(\text{DMSO})]\text{Br}$  **2**, after 40 minutes under an argon stream (blue line: 1 mol/L solid line, 2 mol/L dotted line);  $[\text{Cu}^{\text{I}}(\text{Me}_6\text{tren})(\text{DMSO})](\text{OTf})$  after 40 minutes under argon stream (red line: 1 mol/L solid line, 2 mol/L dotted line).

applied as an initial copper source. A more significant increase in the absorption band at  $\lambda = 443 \text{ nm}$  was observed over 40 minutes (Figure 4, red solid line). This finding can be attributed to the less coordinating nature of the triflate counterion compared to bromide, thereby favoring the coordination of DMSO to the copper center.

Additionally, different amounts of copper(I) complex **1**, as well as  $[\text{Cu}^{\text{I}}(\text{Me}_6\text{tren})(\text{OTf})]$ , were used to investigate the effect of the concentration on the equilibrium. When the concentration of copper(I) was increased from 1 mol/L to 2 mol/L, the solutions of **1** and  $[\text{Cu}^{\text{I}}(\text{Me}_6\text{tren})(\text{OTf})]$  exhibited marked differences in the absorption features (Figure 4). Specifically, the absorption at  $\lambda = 443 \text{ nm}$  increased proportionally to the concentration of  $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4](\text{OTf})$ , while no discernible variation in the absorption bands was detected at different concentrations of CuBr. These results confirmed that the formation of complex  $[\text{Cu}^{\text{I}}(\text{Me}_6\text{tren})(\text{DMSO})](\text{OTf})$  increases with the amount of copper(I) salt in solution. On the contrary, the formation of complex **2** is enhanced by the use of a higher concentration of DMSO and hampered by the increase in the concentration of bromide ion, thus resulting in similar absorption at  $\lambda = 443 \text{ nm}$  in both the 1 mol/L and 2 mol/L solutions. Additionally, our hypothesis was further confirmed as no absorption at  $\lambda = 443 \text{ nm}$  was observed when DMSO was replaced with different solvents such as methanol, acetonitrile, and toluene. However, similar behavior was observed in DMF, thus indicating that the absorbance could be attributed to an MLCT from copper to oxygen. Under the conditions previously applied, the absorbance of **2** at 443 nm overlaid the absorbance of **3** at 418 nm, which caused our wrong assignment of this band.<sup>[13]</sup>

Based on the overall results presented above, a mechanism that explains the persistence of the superoxido complex can be postulated according to Scheme 3.

The copper(I) complex **1** first reacts with dioxygen to form the superoxido and peroxide complexes **3** and **4**. We further propose that the formation of complex **5** occurs by the homolytic cleavage of the peroxide O–O bond of the intermediate **4**. The cleavage is facilitated by the presence of DMSO, which is oxidized to the corresponding sulfone,  $\text{DMSO}_2$ , and results in the reformation of **1**. The copper(I) complex that is thus generated *in-situ* can further react fast with the dioxygen dissolved in solution and start the cycle again, which leads to



**Scheme 3.** Proposed mechanism for the cyclic formation of the superoxido copper(II) complex **3** ( $L = \text{Me}_6\text{tren}$ ).

the formation and accumulation of the **3** and **4**. This hypothesis is supported by detecting the sulfone DMSO<sub>2</sub> exclusively upon oxygenation, as confirmed by GC-MS analysis (Figure S8).

Concurrently, the excess of ligand Me<sub>6</sub>tren promotes the formation of the hydroxido complex **5** through hydrogen atom abstraction (HAA). The formation of complex **5** is found to be promoted by the presence of trace amounts of water and atmospheric moisture, which can act as an additional hydrogen source. A significant enhancement of the absorption bands at  $\lambda = 673$  and  $847$  nm can indeed be observed upon adding water to the solution of complex **1** in dry DMSO (Figure S4). Nevertheless, it's important to note that the water content should not exceed a threshold of 5% (v/v) in dry-DMSO to prevent the promotion of competitive reaction pathways, which can hinder the overall cycle. Although water can contribute to the formation of complex **5**, it is important to notice that it is insufficient to sustain the cycle of reformation of **3** on its own.

The rapid decrease in the absorption bands at  $\lambda = 673$  and  $847$  nm (Figure 3) indicates the fast consumption of species **5** over 5 minutes. Since a consistent reduction of the bands was observed only upon oxygenation of the solution of complex **1** containing an excess of ligand, we assumed that the excess of Me<sub>6</sub>tren plays a central role in the reductive step. To test this hypothesis, 6 fold excess of ligand was added to a DMSO solution of complex **5** and the spectral changes were monitored over 30 min. Notably, no reduction of the copper(II) intermediate was detected (Figure S5). Therefore, we assumed that the reduction of complex **5** is promoted by the radical cation Me<sub>6</sub>tren<sup>•+</sup>, previously generated *in-situ* from Me<sub>6</sub>tren via HAA (Scheme 3). Whether the exact mechanism of the reductive step is yet to be clarified, the detection of by-products such as N<sup>1</sup>-(2-aminoethyl)ethane-1,2-diamine and N<sup>2</sup>-[2-(dimethylamino)ethylidene]-N<sup>1</sup>,N<sup>1</sup>-dimethyl-1,2-ethanediamine that are consistent with ligand modifications upon oxygenation (Figure S9), strongly suggest the formation of the radical-cation on the Me<sub>6</sub>tren and its involvement in the reduction of the hydroxido intermediate. Furthermore, it is important to point out that other ligands, such as e.g., tris(2-methylpyridyl)amine (tmpa), were tested and did not show the same reactivity. No superoxido copper complexes could be detected with these ligands and demonstrated the particular properties of Me<sub>6</sub>tren to form a radical cation.

To prove the ability of complex **5** to follow a radical-based reductive pathway under our working conditions, TEMPO-H was added to a solution of [Cu<sup>II</sup>(Me<sub>6</sub>tren)(OH)]Br in DMSO and the reaction was monitored via UV-Vis spectroscopy.<sup>[29]</sup> The measurements revealed a consistent decrease of the absorption bands at  $\lambda = 673$  and  $887$  nm within 20 minutes (Figure S6), thus confirming the reduction of the copper(II) hydroxido species. To further prove the process's radical nature and confirm the system's catalytic application, we tested the phenol derivative 2,6-di-tert-butylphenol (DTBP). A solution of 5 mol% of complex **1**, 20 mol% of Me<sub>6</sub>tren, and DTBP in DMSO was prepared under inert conditions and oxygenated for 2 minutes. After 12 hours of stirring, DTBP was converted into a mixture of 2,6-di-tert-butyl-1,4-benzoquinone (DTBQ, 1%) and 3,5,3',5'-tetra-tert-butyl-4,4'-diphenoquinone (TTDBQ, 45%). The forma-

tion of the main product TTDBQ is coherent with a radical coupling reaction promoted by HAA.<sup>[30–33]</sup>

Finally, being aware that the reduction of certain Cu(II) complexes can be enhanced by UV irradiation in the presence of excess ligand, we examined the effect of UV light on our DMSO solution of complex **1** and Me<sub>6</sub>tren ([Cu<sup>I</sup>(Me<sub>6</sub>tren)]:[Me<sub>6</sub>tren]=1:6).<sup>[34,35]</sup> The UV-Vis measurements performed after oxygenation revealed a significant acceleration in the reduction rate of complex **5** to complex **1**, as evidenced by the faster decrease in the absorption bands at  $\lambda = 673$  and  $847$  nm upon UV irradiation (Figure S7). These data support the hypothesis of a radical-based mechanism, and they also are in line with the findings of Anastasaki and co-workers, who observed a strong increase in polymerization rates under similar irradiation conditions.<sup>[14]</sup> Although the overall results confirmed the formation of persistent reactive oxygenated species, namely complex **3**, **4**, and **5**, under conditions analogous to ATRP, further work should be carried out to completely elucidate the role of this catalytic system in the polymerization process.

## Conclusions

*End-on* superoxido copper complexes form in the first step when copper(I) complexes are reacted with dioxygen. These reactive species are often difficult to catch, and sometimes temperatures as low as  $-140$  °C are needed to observe their formation at least spectroscopically.<sup>[35]</sup> In so far, the very unusual persistence of an *end-on* superoxido copper complex under ambient conditions applied in oxygen-enhanced atom transfer radical polymerization (ATRP) has been quite puzzling. However, it was possible to explain this finding by identifying additional copper complexes as intermediates in a reaction cycle. Furthermore, the importance of the solvent and the special properties of the tripodal ligand Me<sub>6</sub>tren (that need to be applied in excess) could be clarified. A dinuclear peroxido copper complex, in equilibrium with the superoxido copper complex is responsible for hydrogen abstraction of the Me<sub>6</sub>tren ligand. Hydrogen abstraction, applying a related dinuclear peroxido complex (with the ligand tmpa), had been demonstrated previously for the selective oxygenation of toluene to benzaldehyde.<sup>[36]</sup>

These findings should interest not only ATRP scientists but also researchers working on superoxide interaction in other research areas. Keeping a superoxido/peroxido copper complex persistent under ambient conditions for some time makes the overall system quite interesting for more testing in stoichiometric or catalytic oxygenation reactions. Furthermore, as pointed out in the introduction, alkali/air batteries can have problems with the formation of superoxide, and our results might help with finding a solution to overcome these. Additionally, superoxide as ROS (reactive oxygen species) plays an important role in biology and medicine. DMSO is a common solvent used in some of these studies and could influence the fate of the superoxide, as observed in our work.

## Supporting Information

The data supporting this study's findings are available in the article's Supporting Information, which includes additional references cited by the Authors.<sup>[20,24,37,38]</sup>

## Acknowledgements

We acknowledge the German Academic Scholarship Foundation (Studienstiftung des deutschen Volkes) for financial support. We thank Prof. Dr. Peter J. Klar and Dr. Limei Chen for their assistance with Raman measurements. We also acknowledge Friedemann Dreßler and Alexander Petrillo for their scientific discussions and valuable suggestions. Open Access funding enabled and organized by Projekt DEAL.

## 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.

**Keywords:** Copper · Superoxido complex · Polymerisation · Mechanism · Dioxygen Activation

- [1] M. Hayyan, M. A. Hashim, I. M. Al Nashef, *Chem. Rev.* **2016**, *116*, 3029–3085.
- [2] C. Wang, Z. Zhang, W. Liu, Q. Zhang, X. Wang, Z. Xie, Z. Zhou, *Angew. Chem. Int. Ed.* **2020**, *59*, 17856–17863.
- [3] S. Schindler, *Eur. J. Inorg. Chem.* **2000**, *11*, 2311–2326.
- [4] S. Itoh, *Acc. Chem. Res.* **2015**, *48*, 2066–2074.
- [5] H. Kim, P. J. Rogler, S. K. Sharma, A. W. Schaefer, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2020**, *142*, 3104–3116.
- [6] J. M. Bollinger, C. Krebs, *Curr. Opin. Chem. Biol.* **2007**, *11*, 151–158.
- [7] J. P. Klinman, *J. Biol. Chem.* **2006**, *281*, 3013–3016.
- [8] A. Brinkmeier, R. A. Schulz, M. Buchhorn, C.-J. Spyra, S. Dechert, S. Demeshko, V. Krewald, F. Meyer, *J. Am. Chem. Soc.* **2021**, *143*, 10361–10366.
- [9] T. Hoppe, S. Schaub, J. Becker, C. Würtele, S. Schindler, *Angew. Chem. Int. Ed.* **2013**, *52*, 870–873.
- [10] C. Würtele, E. Gaoutchenova, K. Harms, M. C. Holthausen, J. Sundermeyer, S. Schindler, *Angew. Chem. Int. Ed.* **2006**, *45*, 3867–3869.
- [11] M. Schatz, V. Raab, S. P. Foxon, G. Brehm, S. Schneider, M. Reiher, M. C. Holthausen, J. Sundermeyer, S. Schindler, *Angew. Chem. Int. Ed.* **2004**, *43*, 4360–4363.
- [12] M. Becker, F. W. Heinemann, S. Schindler, *Chem. Eur. J.* **1999**, *5*, 3124–3129.
- [13] K. Parkatzidis, N. P. Truong, R. Whitfield, C. E. Campi, B. Grimm-Lebsanft, S. Buchenau, M. A. Rübhausen, S. Harrison, D. Konkolewicz, S. Schindler, A. Anastasaki, *J. Am. Chem. Soc.* **2023**, *145*, 1906–1915.
- [14] S. D. Casa, K. Parkatzidis, N. P. Truong, A. Anastasaki, *J. Polym. Sci.* **2023**, *pol.20230479*.
- [15] J.-S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **1995**, *117*, 5614–5615.
- [16] K. Matyjaszewski, *Macromolecules* **2012**, *45*, 4015–4039.
- [17] K. Matyjaszewski, *Adv. Mater.* **2018**, *30*, 1706441.
- [18] F. Lorandi, M. Fantin, K. Matyjaszewski, *J. Am. Chem. Soc.* **2022**, *144*, 15413–15430.
- [19] W. Tang, K. Matyjaszewski, *Macromolecules* **2006**, *39*, 4953–4959.
- [20] M. Weitzer, S. Schindler, G. Brehm, S. Schneider, E. Hörmann, B. Jung, S. Kaderli, A. D. Zuberbühler, *Inorg. Chem.* **2003**, *42*, 1800–1806.
- [21] S. Y. Quek, S. Debnath, S. Laxmi, M. Van Gastel, T. Krämer, J. England, *J. Am. Chem. Soc.* **2021**, *143*, 19731–19747.
- [22] K. Komiyama, H. Furutachi, S. Nagatomo, A. Hashimoto, H. Hayashi, S. Fujinami, M. Suzuki, T. Kitagawa, *B. Chem. Soc. Jpn.* **2004**, *77*, 59–72.
- [23] M. Bhadra, W. J. Transue, H. Lim, R. E. Cowley, J. Y. C. Lee, M. A. Siegler, P. Josephs, G. Henkel, M. Lerch, S. Schindler, A. Neuba, K. O. Hodgson, B. Hedman, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2021**, *143*, 3707–3713.
- [24] S. C. Lee, R. H. Holm, *J. Am. Chem. Soc.* **1993**, *115*, 11789–11798.
- [25] S. Monge, V. Darcos, D. M. Haddleton, *J. Polym. Sci. Part A* **2004**, *42*, 6299–6308.
- [26] R. D. Willett, G. Pon, C. Nagy, *Inorg. Chem.* **2001**, *40*, 4342–4352.
- [27] S. Racioppi, L. Orian, C. Tubaro, A. Gennaro, A. A. Isse, *Catalysts* **2022**, *12*, 1656.
- [28] T. J. Zerk, M. Martinez, P. V. Bernhardt, *Inorg. Chem.* **2016**, *55*, 9848–9857.
- [29] M. C. Ryan, L. D. Whitmire, S. D. McCann, S. S. Stahl, *Inorg. Chem.* **2019**, *58*, 10194–10200.
- [30] K. V. N. Esguerra, Y. Fall, L. Petitjean, J.-P. Lumb, *J. Am. Chem. Soc.* **2014**, *136*, 7662–7668.
- [31] J. J. Liu, D. E. Diaz, D. A. Quist, K. D. Karlin, *Isr. J. Chem.* **2016**, *56*, 738–755.
- [32] S. E. Allen, R. R. Walvoord, R. Padilla-Salinas, M. C. Kozłowski, *Chem. Rev.* **2014**, *114*, 899–899.
- [33] T. Wu, S. N. MacMillan, K. Rajabimoghadam, M. A. Siegler, K. M. Lancaster, I. Garcia-Bosch, *J. Am. Chem. Soc.* **2020**, *142*, 12265–12276.
- [34] T. G. Ribelli, D. Konkolewicz, S. Bernhard, K. Matyjaszewski, *J. Am. Chem. Soc.* **2014**, *136*, 13303–13312.
- [35] A. Anastasaki, V. Nikolaou, Q. Zhang, J. Burns, S. R. Samanta, C. Waldron, A. J. Haddleton, R. McHale, D. Fox, V. Percec, P. Wilson, D. M. Haddleton, *J. Am. Chem. Soc.* **2014**, *136*, 1141–1149.
- [36] M. Bhadra, W. J. Transue, H. Lim, R. E. Cowley, J. Y. C. Lee, M. A. Siegler, P. Josephs, G. Henkel, M. Lerch, S. Schindler, A. Neuba, K. O. Hodgson, B. Hedman, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2021**, *143* (10), 3707–3713.
- [37] C. Noß, R. Göttlich, S. Schindler, *Chem. Eur. J.* **2023**, *29*, e202301142.
- [38] G. J. P. Britovsek, J. England, A. J. P. White, *Inorg. Chem.* **2005**, *44*, 8125–8134.
- [39] S. Srivastava, A. Ali, A. Tyagi, R. Gupta, *Eur. J. Inorg. Chem.* **2014**, 2113–2123.

Manuscript received: May 8, 2024

Accepted manuscript online: May 8, 2024

Version of record online: June 24, 2024