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Structurally Characterized μ -1,2-Peroxo/Superoxo Dicopper(II) Pair

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d(0-0) = 1.44 Å d(0-0) = 1.33 Å $\tilde{v}(0-0) = 793 \text{ cm}^{-1}$ $\tilde{v}(0-0) = 1073 \text{ cm}^{-1}$

complex). Interconversion of 2 and 3 occurs at low potential (-0.58 V vs Fc/Fc⁺) and is reversible both chemically and electrochemically. Comparison of metric parameters (d(O-O) = 1.441(2) Å for 2 vs 1.329(7) Å for 3) and of spectroscopic signatures ($\tilde{\nu}(^{16}O^{-16}O) = 793$ cm⁻¹ for 2 vs 1073 cm⁻¹ for 3) reflects that the redox process occurs at the bridging O₂-derived unit. The Cu^{II} $-O_2^{\bullet}$ -Cu^{II} complex has an S = 1/2 spin ground state according to magnetic and EPR data, in agreement with density functional theory calculations. Computations further show that the potential associated with changes of the Cu-O-O-Cu dihedral angle is shallow for both 2 and 3. These findings provide a structural basis for the low reorganization energy of the kinetically facile 1e⁻ interconversion of μ -1,2-superoxo/peroxo dicopper(II) couples, and they open the door for comprehensive studies of these key intermediates in Cu_x/O₂ chemistry.

INTRODUCTION

Superoxo complexes are the first intermediates formed upon binding of O_2 to redox active metal ions accompanied by 1e⁻ transfer. They represent key reactive species in a variety of biological oxidases and oxygenases, in particular in iron and copper containing metalloenzymes, and they are also considered as crucial intermediates in important catalytic processes such as water oxidation or O_2 reduction.¹⁻³ The study of metal-superoxo complexes has thus received much interest, but because of their mostly high reactivity the isolation and crystallization have remained challenging.^{4,5}

dicopper(II) superoxo complexes, but structural characterization of these important intermediates was so far lacking. Here we report

the first crystallographic structure determination of a superoxo

dicopper(II) species (3) together with the structure of its $1e^{-}$ reduced peroxo congener (2; a rare *cis-µ*-1,2-peroxo dicopper(II)

Although a number of mononuclear $Cu^{II}-O_2^{\bullet-}$ complexes have meanwhile been identified and their electronic structures have been analyzed in great detail,⁶⁻⁹ crystallographic information is scarce. So far, only for a single example of an end-on (η^1) (superoxo)copper(II) complex could the molecular structure be determined by X-ray diffraction (**A**, Figure 1).¹⁰

In Cu₂/O₂ chemistry, $(\mu \cdot \eta^2 : \eta^2 \cdot \text{peroxo})$ dicopper(II) complexes and their valence tautomeric bis(μ -oxo) forms as well as dicopper(II) complexes with a *trans*- μ -1,2-peroxo bridge (^TP; Figure 1) have been quite well studied.^{8,11} Employing a compartmental pyrazolate/tacn hybrid ligand [L¹]⁻ (tacn = 1,4,7-triazacyclononane),^{12,13} a few years ago we contributed



Figure 1. Structurally characterized end-on (η^1) (superoxo)copper-(II) complex A^{10} (left) and μ -1,2-peroxo dicopper(II) motifs (right).

the first structural characterization of a *cis-µ*-1,2-peroxo dicopper(II) complex (^CP type) that was shown to strongly interact with Na⁺ ions both in solution and in solid state (**B**, Scheme 1).¹⁴ Further elaboration via elongation of the ligand side arms in $[L^2]^-$ induced a shortening of the Cu···Cu distance and a Cu-O-O-Cu torsion angle close to 90° in the (peroxo)dicopper(II) complex C; such near-orthogonal

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Scheme 1. Dinucleating Pyrazolate/Tacn Hybrid Ligands $[L^1]^-$ and $[L^2]^-$ and Their Previously Studied Dicopper(II) Peroxo and Superoxo Complexes



arrangement in between the ^C**P** and ^T**P** forms was shown to lead to ferromagnetic coupling and an unprecedented S = 1 ground state.¹⁵

In subsequent work, it was demonstrated that C can be reversibly oxidized at low potential (-0.59 V vs Fc/Fc⁺), giving the spectroscopically characterized μ -1,2-superoxo dicopper(II) complex D (Scheme 1) whose H atom abstraction (HAA) thermochemistry could be established.¹ Using a ligand scaffold with a central phenolate bridge, Karlin et al. studied a related $Cu_2^{II}(O_2^{\bullet-})$ complex, which was obtained by reacting the mixed-valent Cu^ICu^{II} precursor with O_2 and was shown to consist of a mixture of μ -1,2 and μ -1,1 superoxo isomers in rapid equilibrium.^{17,18} A kinetically facile superoxo/peroxo interconversion with low reorganization energy (at E = -0.24 V vs Fc/Fc⁺) was revealed, reflecting that the redox process occurs at the O₂-derived unit.^{18,19} Most recent work focused on correlations between properties of the supporting ligands and superoxo HAA capabilities,²⁰ in view of the very different OO-H bond dissociation free energies (BDFEs) of the hydroperoxo products derived from D^{21} and one of Karlin's phenolate-based Cu^{II}₂(O₂^{•-}) complexes (69.4 kcal/mol²² vs 81.8 kcal/mol).^{16,20} However, crucial structural characterization of any dicopper superoxo species is lacking so far.

Here we report the first X-ray crystallographic structure determination of a *cis-µ*-1,2-superoxo dicopper(II) complex, based on the dinucleating ligand scaffold $[L^1]^-$. In addition, we report the molecular structure of the parent type **B** peroxo complex without associated Na⁺, viz with a "naked" *cis*-peroxo bridge, which allows for the direct comparison of unperturbed μ -1,2-peroxo and μ -1,2-superoxo dicopper(II) units in identical ligand settings.

RESULTS AND DISCUSSION

Dicopper(I) and μ -Peroxo Dicopper(II) Complexes. Initial experiments showed that high-purity material of the dicopper(I) starting complex $[L^1Cu_2]^+$ (1) is essential for Article

successful isolation and crystallization of any reactive oxygenated intermediates formed from 1. We thus devised an improved synthesis of complex 1 by changing the solvent from propionitrile (EtCN) to methanol (MeOH) and precipitating the target compound with NaBPh₄, followed by recrystallization from acetone/diethyl ether (see the Supporting Information for synthesis and spectroscopic details). 1(BPh₄) could now be isolated as single-crystalline material and its molecular structure was determined via X-ray diffraction (Figure 2). The two copper ions are coordinated in strongly



Figure 2. Molecular structures of 1 (top) and 2 (bottom) in solid state with thermal displacement ellipsoids given at 30% probability. Counterion BPh_4^- not shown and all hydrogen atoms omitted for clarity.

distorted tetrahedral geometry, and the wide open cleft between them appears predestined for accommodating O_2 in a μ - η^1 : η^1 bridging mode. As expected, the Cu-Cu distance in 1 (4.15 Å) is significantly larger than in the related complex $[L^2Cu_2]^+$ that has longer chelate arms (3.97 Å),¹⁵ reflecting that the metal---metal separation can be tuned by the ligand scaffold; further crystallographic details and metric parameters are provided in the Supporting Information. When dry O_2 is added to a colorless solution of $1(BPh_4)$ in MeCN at -40 °C, the solution turns deep purple immediately. After workup and Et₂O diffusion into a solution of the oxygenated complex in acetone at -26 °C, single-crystalline material was obtained and the structure of the μ - η^1 : η^1 *cis*-peroxo complex **2**(BPh₄) could be determined crystallographically (see the Supporting Information for further details). The molecular structure of the cation 2 shows two copper ions in a distorted trigonal bipyramidal coordination environment ($\tau_5(Cu1) = 0.63$, $\tau_{\rm s}({\rm Cu}2) = 0.60)^{23}$ with a Cu-Cu separation of 3.741 Å, significantly shorter than in the precursor complex 1. The O-O bond length in "naked" 2 (1.441(2) Å) is in the range typical for end-on bound peroxides but clearly shorter than in the sodium ion adduct B (1.498(7)).¹⁴ The Cu_2/O_2 core in 2 features a ^CP geometry with a Cu-O-O-Cu torsion angle of 55.3°, which is 10.1° smaller compared to the previously reported B (vide infra). Density functional theory calculations find isoenergetic triplet and open-shell singlet configurations

for **2** with geometries that match the experiment (^{OSS}2: $d_{CuCu,calc} = 3.750$ Å, $d_{OO,calc} = 1.391$ Å; ^T2: $d_{CuCu,calc} = 3.784$ Å, $d_{OO,calc} = 1.382$ Å; $\Delta E(^{OSS}2, ^{T}2) < 1$ kcal/mol, see the Supporting Information for details).

Peroxo complex 2 in MeCN solution is thermally unstable above -20 °C. It shows a characteristic UV-vis absorption spectrum with two maxima at 648 nm (ε = 3900 M⁻¹ cm⁻¹; TDDFT: excitation from Cu ions into the π -manifold) and 527 nm (ε = 5000 M⁻¹ cm⁻¹; TDDFT: excitation within the π manifold on the Cu-O₂-Cu unit) and a shoulder at 456 nm (ε = 2600 M⁻¹ cm⁻¹; TDDFT: excitation within the π manifold on the Cu-O₂-Cu unit) (see also Figure 5 below; for TDDFT assignments, see Table S5). Although the spectrum looks similar to those of related ^TP systems whose electronic structures have been analyzed in detail,²⁴ these LMCT bands for 2 are less intense, as was previously observed for ^CP species C and the Na⁺ adduct B.¹⁴ Raman spectroscopy of solid 2 (λ_{ex} = 633 nm; Figure 3) shows a pronounced



Figure 3. Raman spectra of crystalline material of $2(BPh_4)$ ($\lambda_{ex} = 633$ nm).

feature around 793 cm⁻¹ that is split into two bands, which is attributed to Fermi resonance. When using ¹⁸O₂ this absorption shifts to 752 cm⁻¹ (Δ (¹⁸O₂-¹⁶O₂) = -41 cm⁻¹, $\tilde{\nu}$ (¹⁶O-¹⁶O)/ $\tilde{\nu}$ (¹⁸O-¹⁸O) = 1.055, calculated 1.060 for an isolated harmonic O–O oscillator), and hence these bands are assigned to the peroxide O–O stretch. DFT calculations support this assignment with a predicted O–O stretch at 884 cm⁻¹ for ^{OSS}2 that shifts by -48 cm⁻¹ with ¹⁸O isotopes (see Table S5).

μ-Superoxo Dicopper(II) Complex. Cyclic voltammetry of peroxo complex 2 (MeCN, 0.1 M ["Bu₄N]PF₆, T = 0 °C; for details see Supporting Information) revealed a reversible redox event at -0.58 V vs Fc/Fc⁺, followed by an irreversible oxidation at ca. 0.7 V (Figure 4). Monitoring the first anodic process by UV–vis spectroelectrochemistry at a controlled potential of -0.2 V vs Fc/Fc⁺ shows the formation of a new species featuring an intense absorption at 444 nm ($\varepsilon = 10$ mM⁻¹ cm⁻¹). In view of the findings for [L²]⁻-based complexes C and D (440 nm, $\varepsilon = 11.5$ mM⁻¹ cm⁻¹),¹⁶ the event at -0.58 V is assigned to oxidation of peroxo complex 2 to the new superoxo complex 3.

Titration of a solution of $2(BPh_4)$ in MeCN with AgSbF₆ at -40 °C ($E^0(AgSbF_6) = 0.04$ V vs Fc/Fc⁺) confirmed the formation of a 1e⁻ oxidized product with a characteristic absorption at $\lambda_{max} = 444$ nm ($\varepsilon = 10 \text{ mM}^{-1} \text{ cm}^{-1}$) and a weak shoulder at ca. 570 nm ($\varepsilon = 1.5 \text{ mM}^{-1} \text{ cm}^{-1}$; Figure 5). These features are reminiscent of the electronic absorption spectra of



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Figure 4. Cyclic voltammogram of a 2.8 mM solution of $2(BPh_4)$ in MeCN at 100 mV/s (0.1 M ["Bu₄N]PF₆, T = 0 °C). The inset shows the process at $E^\circ = -0.58$ V vs Fc/Fc⁺ at different scan rates; the anodic peak current I_p shows a linear dependence on the square root of the scan rate ($v^{1/2}$; see Figure S5).



Figure 5. Titration of a 70 μ M solution of 2 with a solution of AgSbF₆ in MeCN at -40 °C in steps of 0.11 equiv. with overall 1.1 equiv. being added, isosbestic point at 485 nm.

other reported dinuclear superoxo complexes.^{16,17,21} Oxidation of **2** to **3** is also possible with various Cu^{II} salts (e.g., $Cu(OTf)_2$) and is chemically reversible, as demonstrated by the following experiment: after **3** was generated from complex **2** and $Cu(OTf)_2$ in MeCN (giving **3** and $[Cu(MeCN)_4]^+$), a solution of the disodium salt of bis(salicyliden)ethylendiamin, $Na_2(salen)$, was added. As deprotonated salen is known to stabilize its Cu^{II} complex ($E^{\circ}(Cu^{I}/Cu^{II}) = -1.66$ V versus Fc/ Fc⁺ in MeCN),²⁵ superoxide complex **3** is reduced back to peroxo complex **2** (now as the Na⁺ adduct **B**), concomitant with formation of the Cu^{II} -salen complex; this sequence can be nicely monitored via the characteristic UV—vis signatures of **2**, **3**, and **B** (cf. Scheme S1 and Figure S8).

The superoxo species **3** is remarkably stable, with a half-life of ca. 8 h at 20 °C in MeCN. However, extensive screening of crystallization conditions was required to finally yield single-crystalline material. This was obtained when using $[(Pr_3TACN)Cu^{II}(CH_3CN)_2](SbF_6)_2^{26}$ as a 1e⁻ oxidant in

Article

acetone solution and diffusion of Et_2O into the reaction mixture at -36 °C within a few days. The molecular structure of the cation of $3(BPh_4)(SbF_6)$ determined by X-ray diffraction is shown in Figure 6. The O–O bond length in 3

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Figure 6. Molecular structure of **3** with thermal displacement ellipsoids given at 30% probability. Only one of the two crystallographically independent molecules is shown. Counteranions BPh_4^- and SbF_6^- are omitted for clarity; for structural parameters, see the Supporting Information.

(1.33 Å) is significantly shorter than in 2 (1.44 Å), reflecting that oxidation occurs at the O₂-derived ligand. The availability of structural information for both 2 and 3 now allows for unprecedented comparison of this pair of peroxo and superoxo complexes. Upon oxidation, the Cu–O bonds elongate from 1.8900(13)/1.8971(14) Å in 2 to 1.924(5)/1.940(5) Å in 3, suggesting a weakening of the Cu–O interaction. Furthermore, the Cu–O–O–Cu dihedral angle increases (from 55.3 to 75.4°). In contrast to 2, the coordination geometries of the two Cu^{II} ions in 3 are distinctly different, with Cu2 in nearly square pyramidal and Cu1 in strongly distorted trigonal bipyramidal coordination environment ($\tau_5 = 0.08$ vs 0.63). Selected structural parameters are collected in Table 1. DFT

Table 1. Summary of Selected Structural Parameters ofDicopper(II) Peroxo and Superoxo Complexes 2 and 3

	d(О–О) (Å)	d(Cu-O) (Å)	$\phi(ext{Cu-O}_2- ext{Cu})\ (ext{deg})$	$ au_5(\mathrm{Cu})$
2	1.441(2)	1.890(2)/1.897(2)	55.3	0.60, 0.63
3 ^{<i>a</i>}	1.329(7)	1.924(5)/1.940(5)	75.4	0.08, 0.63

^aValues taken from the crystallographically independent molecule that shows no disorder in the O–O part (see the Supporting Information for details).

geometry optimizations show that a doublet ground state is preferred over a quartet state for 3; both structures are in good agreement with experiment (^D3: $d(\text{Cu}\cdots\text{Cu})_{\text{calc}} = 3.777$ Å, $d(O-O)_{\text{calc}} = 1.337$ Å; ^Q3: $d(\text{Cu}\cdots\text{Cu})_{\text{calc}} = 3.845$ Å, $d(O-O)_{\text{calc}} = 1.334$ Å; $\Delta E(^{D}3, ^{Q}3) = 8.1$ kcal/mol; see the Supporting Information for details). Importantly, the potential associated with changes of the Cu-O-O-Cu dihedral angle appears shallow in both the μ -1,2-superoxo and μ -1,2-peroxo complexes: constraining this parameter close to the experimental value is associated with a negligible energy penalty of less than 1 kcal/mol. This is confirmed with a relaxed surface scan of the dihedral angle for the peroxo and superoxo complexes, see Figure 7. A second, slightly destabilized minimum is found for a flipped coordination of the {O₂} bridge in both systems, which is in line with the disorder



Figure 7. Relative electronic energies (kcal/mol) for a relaxed surface scan of the Cu–O–O–Cu dihedral angle in ^T2 (blue) and ^D3 (red); the lines are drawn strictly as a guide to the eye. The energies of models in which the dihedral angle is fixed to the crystal structure value are shown as squares (peroxo, light blue; superoxo, orange).

observed for one of the crystallographically independent molecules in solid $3(BPh_4)(SbF_6)$ (see Figure S13).

The superoxo character of 3 was confirmed by resonance Raman spectroscopy of a solution of 3 in MeCN ($\lambda_{ex} = 457$ nm, Figure 8), which shows one oxygen isotope sensitive



Figure 8. Raman spectrum of a 1.4 mM solution of 3 in MeCN recorded at 22 °C, $\lambda_{ex} = 457$ nm. The inset shows the difference spectrum.

feature at 1073 cm⁻¹ (Δ (¹⁸O-¹⁶O) = -60 cm⁻¹; $\tilde{\nu}$ (¹⁶O-¹⁶O)/ $\tilde{\nu}$ (¹⁸O-¹⁸O) = 1.059, calculated 1.060 for an isolated harmonic O-O oscillator). This is significantly higher than for peroxo complex **2** and in the typical region for a superoxide vibration, yet the O-O bond appears to be slightly weakened compared to the mononuclear end-on Cu^{II}-O₂^{•-} complex **A** ($\tilde{\nu}$ = 1122 cm⁻¹).¹⁰ DFT calculations are in good agreement with this assignment; the O-O stretch is found at 1011 cm⁻¹ and shifts by ca. -60 cm⁻¹ for the ¹⁸O isotope.

SQUID magnetometry of a frozen solution of **3** in MeCN confirms an S = 1/2 spin ground state in accordance with the DFT predictions (Figure S9), indicating overall antiferromagnetic coupling between the two Cu^{II} (d⁹) ions and the O₂^{•-} bridge. The computed electronic structure of **3** is consistent with such an electronic configuration (Mulliken spin populations with PBE0: Cu1 0.57, Cu2 0.58, μ -O₂^{•-} -0.65). The X-band EPR spectrum of **3** also reflects the S = 1/2 cupric superoxide signature (Figure 9). Excellent simulations of the EPR spectrum were obtained when hyperfine coupling to both Cu^{II} ions was assumed, which is best reflected by the second



Figure 9. X-band EPR spectrum of a 0.01 M frozen solution of 3 in MeCN, recorded at 161 K (left) and second derivative spectrum (right); the red line is the simulation with parameters given in the text.

derivative spectrum, yielding $g_x = 2.03$, $g_y = 2.08$, $g_z = 2.15$ (with $a_1 = 5.2$ G, $a_2 = 5.0$ G, $a_3 = 73$ G).

SUMMARY AND CONCLUSION

In summary, we were able to crystallographically characterize a μ -1,2-superoxo dicopper(II) complex as well as its 1e⁻ reduced peroxo congener, the latter representing the first structurally authenticated example of a "naked" cis-µ-1,2-peroxo dicopper-(II) complex of the ${}^{C}P$ type. Comparison of metric parameters for this unique pair of complexes, together with their spectroscopic signatures, supports that the redox process occurs at the O2-derived unit within the bimetallic cleft. Experimental and computational evidence reveal an S = 1/2spin ground state for the $Cu^{II}-O_2^{\bullet-}-Cu^{II}$ core and a negligible energy penalty associated with moderate changes of the Cu-O-O-Cu dihedral angle in both the peroxo and superoxo species. This work provides a structural basis for the previously observed^{18,19} low reorganization energy of the kinetically facile 1e⁻ interconversion of such superoxo/peroxo dicopper(II) couples.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c04316.

Experimental details and synthetic procedures, further spectroscopic and analytical data, crystallographic information, details of DFT calculations (PDF)

Accession Codes

CCDC 2079339–2079341 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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