

■ Macrocyclic Ligands

Activation of Molecular Oxygen by a Cobalt(II) Tetra-NHC Complex**

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Abstract: The first dicobalt(III) μ_2 -peroxo *N*-heterocyclic carbene (NHC) complex is reported. It can be quantitatively generated from a cobalt(II) compound bearing a 16-membered macrocyclic tetra-NHC ligand via facile activation of dioxygen from air at ambient conditions. The reaction proceeds via an end-on superoxo intermediate as demonstrated by EPR studies and DFT. The peroxo moiety can be cleaved upon addition of acetic acid, yielding the corresponding Co^{III} acetate complex going along with H₂O₂ formation. In contrast, both Co^{II} and Co^{III} complexes are also studied as catalysts to utilize air for olefin and alkane oxidation reactions; however, not resulting in product formation. The observations are rationalized by DFT-calculations, suggesting a nucleophilic nature of the dicobalt(III) μ_2 -peroxo complex. All isolated compounds are characterized by NMR, ESI-MS, elemental analysis, EPR and SC-XRD.

The activation of molecular oxygen by iron- and copper-containing metalloproteins plays a vital role in biological processes, comprising oxygen transport and enzymatic oxidation reactions, amongst others.^[1] Active intermediates primarily include superoxo, (hydro)peroxo and oxo species.^[1–2] The remarkable efficiency of these compounds led to the development of several bio-inspired complexes, which have been applied in oxidation catalysis and studied regarding their ability to activate dioxygen, preferably from air at ambient conditions.^[1a, b, 2a–c, 3]

Although of lower biological relevance in comparison to copper and iron, the study of bio-inspired cobalt complexes

towards O₂ activation is of interest due to the higher thermodynamic and kinetic stability of Co^{III} dioxygen adducts formed upon reaction of their corresponding Co^{II} compounds with O₂.^[4] Starting in the 1970s with coboglobin, a cobalt analogue of hemoglobin,^[5] major progress has been made in this research field.^[4, 6] Recently, A. Company et al. reported a Co^{II} complex bearing the bio-inspired pyridine triazacyclononane (PyTACN) ligand, which forms a Co^{III} superoxo species upon reaction with O₂ at –80 °C.^[7] Subsequently, it converts to a dicobalt(III) μ_2 -peroxo compound when increasing the temperature to –35 °C. Further heating to room temperature results in the re-release of O₂ to form the initial Co^{II} complex (Scheme 1, bottom right).^[7] Although those results suggest a catalytic application to make use of air, the low stability of the peroxo species at room temperature requires cooling.^[7] Ideally, O₂ activation should proceed at room temperature to provide more applicable and sustainable conditions. For this purpose, a suitable ligand capable of stabilizing high valent species occurring during this process is vital.

Recently, we reported a heme-analogous iron(II) complex bearing a methylene-bridged 16-membered macrocyclic tetra-NHC ligand (cCCCC; Figure 1, center) and its iron(III) derivative.^[8] This unique ligand induces unprecedented activity in olefin epoxidation catalysis of the respective Fe^{III} complex (TOF up to 180 000 h^{–1} without additives; TOF up to 415 000 h^{–1} in presence of strong Lewis acids),^[8b, 9] considerably exceeding that of the optimized homogeneous benchmark system methyltrioxorhenium (MTO, TOF up to 40 000 h^{–1}).^[10] Both iron and rhenium containing catalysts utilize H₂O₂ as oxidant.^[8b, 10] While it is generally considered environmentally friendly, as water is formed as the only by-product,^[11] risks are associated when

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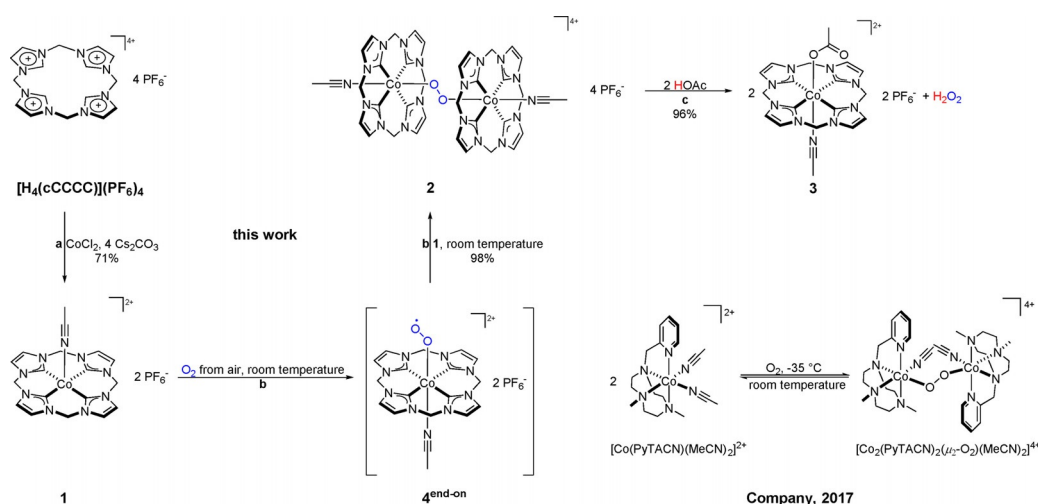
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[**] NHC: *N*-heterocyclic carbene.

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Scheme 1. Synthesis of cobalt tetra-NHC **1**; activation of O_2 from air resulting in formation of **2** via superoxo intermediate **4** e^{nd-on} ; reaction of μ_2 -peroxo complex **2** with HOAc resulting in formation of **3** and H_2O_2 . Reaction conditions: a: $75^\circ C$, 18 h, (MeCN); b: r.t., 2 h, (MeCN); c: r.t., 30 min, (MeCN) (Supporting Information for experimental details). Bottom right: formation of $[Co_2(PyTACN)_2(\mu_2-O_2)(MeCN)_2]^{4+}$ by activation of O_2 at $-35^\circ C$ and re-release of O_2 at r.t. reported by A. Company et al.^[7].



Figure 1. Structurally related macrocyclic tetra-NHC ligands by F. Meyer et al., D. M. Jenkins et al. and our group.^[8a,15a,17]

working with higher concentrations.^[12] In contrast, O_2 from air is far less problematic, environmentally benign, readily accessible and exhibits superior atom-efficiency. Hence, it is the ideal oxidant candidate, which motivated us to study the reactivity of Fe^{II} cCCCC complex with O_2 .^[11,13] When exposed to air, a μ_2 -oxo diiron(III) compound is formed. Although such $Fe^{III}-O-Fe^{III}$ compounds are generally regarded inactive,^[14] the respective cCCCC complex catalytically oxidizes 1,4-hydroquinone employing O_2 .^[13c]

Utilizing a different, yet related 18-membered tetra-NHC (Figure 1, left), F. Meyer et al. could isolate and crystallize an iron(IV) oxo complex, usually considered a highly reactive intermediate.^[15] Employing another related dianionic 16-membered tetra-NHC (Figure 1, right), D. M. Jenkins et al. synthesized a Cr^V oxo and Fe^V imide.^[16] Although slight structural differences modify their reactivity, the ligands illustrated in Figure 1 share a common characteristic, that is, they stabilize high valent metal centers exceptionally well.^[1a,3a,14c,18] Lately, we were able to utilize this remarkable trait of cCCCC to isolate the first bench-stable copper(III)-NHC complex.^[19]

The successful stabilization of high valent Fe and Cu centers by macrocyclic tetra-NHC ligands led to the question, whether this also holds true for related cobalt compounds and their application in dioxygen activation. Intrigued by this question, in this work, we report the synthesis of cobalt(II) complex **1** bearing the cCCCC ligand, its reactivity with molecular oxygen

from air and first studies towards hydrogen peroxide formation.

The reaction of external bases and imidazolium salts in the presence of metal salts comprises a well-established method for the preparation of various transition metal-NHC complexes^[20] and has been found to be most efficient for the synthesis of cobalt(II) tetra-NHC **1**. When reacting ligand precursor $[H_4(cCCCC)](PF_6)_4$, anhydrous $CoCl_2$ and an excess of CS_2CO_3 , **1** is obtained as a yellow solid in 71 % yield (Scheme 1 a). Due to the paramagnetic nature of 17-valence-electron Co^{II} complex **1**, two broad NMR peaks are observed in the 1H -NMR spectrum at 27.18 ppm and 4.58 ppm with relative integrals of 8 corresponding to the backbone and methylene protons, respectively. An equimolar amount of non-coordinating MeCN conforming to a sharp singlet at 1.96 ppm is observed, indicating the lability of the axial ligand and a fast exchange process with the deuterated solvent.

In addition, **1** was characterized by SC-XRD, displaying a slightly distorted quadratic pyramidal structure, as the $C_{NHC}-Co1-N9$ angles between 93° and 98° differ from the ideal 90° (Figure 2). The $Co-C$ distances between 1.889(2) Å and 1.901(2) Å are within the typical range of other Co^{II} NHCs reported in literature.^[21] As expected, the $Co-C$ distances are in between those of the octahedral Fe^{II} (1.904(3) to 1.912(3) Å) and Fe^{III} (1.937(3) to 1.944(2) Å) complexes on the one hand and square planar Cu^{III} complex (1.879(5) to 1.833(5) Å) on the other hand, also bearing cCCCC ligand.^[8,19]

When a solution of **1** in MeCN is exposed to air at room temperature, an immediate color change from yellow to green is observed. After addition of Et_2O , a green precipitate is formed. Interestingly, the 1H -NMR spectrum of the latter depicts one multiplet in the range of 7.8 ppm to 7.4 ppm attributable to the backbone protons and a second between 6.5 ppm and 5.9 ppm belonging to the methylene bridges with an integral ratio of approximately 1:1, thus conforming to one diamagnetic compound. These findings point to a reaction

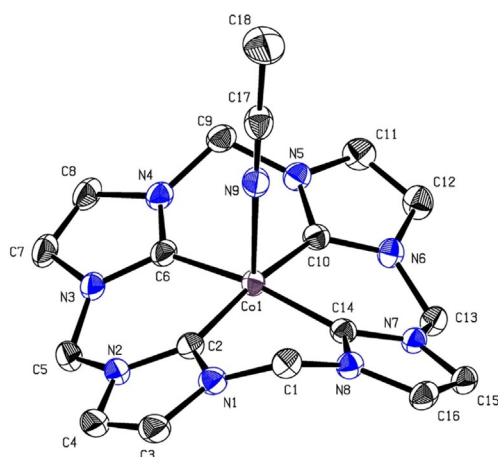


Figure 2. ORTEP-style representation of the cationic fragment of compound **1**.^[30] Hydrogen atoms, co-crystallized solvent molecules and hexafluorophosphate anions are omitted for clarity. Thermal ellipsoids are shown at a 50% probability.

of complex **1** with dioxygen, which is often only observed at lower temperatures for other related Co^{II} complexes.^[7,22] After growing crystals, *trans* μ_2 -peroxo dicobalt(III) complex **2** is unequivocally identified as the newly obtained species (Scheme 1 b; Figure 3). It is formed in a redox-reaction oxidizing two Co^{II} centers to Co^{III} and reducing O_2 to a μ_2 -peroxo ligand bridging two Co-centers in *trans* configuration.

The driving force of the reaction is the formation of a thermodynamically favored 18-valence-electron complex, which ex-

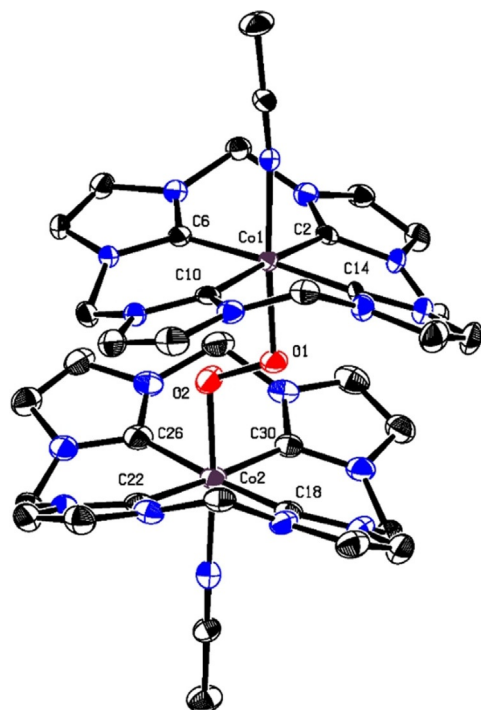


Figure 3. ORTEP-style representation of the cationic fragment of compound **2**.^[30] Hydrogen atoms, co-crystallized solvent molecules and hexafluorophosphate anions are omitted for clarity. Thermal ellipsoids are shown at a 50% probability.

plains the quantitative reaction (98% isolated yield of **2**).^[4,7] Each Co atom is coordinated in a distorted octahedral fashion (Figure 3). Both Co centers are bridged by a *trans* μ_2 peroxo ligand, which is a commonly observed coordination mode of Cu complexes and enzymes capable of O_2 activation.^[23] The Co–C distances between 1.888(5) Å and 1.905(5) Å are in range of other Co^{III} NHCs reported in literature.^[21a,b,24] The Co–O bond lengths of 1.902(4) Å and 1.890(4) Å as well as the O–O distance of 1.442(5) Å are also in good accord with other Co^{III} μ_2 peroxo complexes.^[21b,25]

Although a variety of dicobalt(III) peroxo compounds with porphyrins and other *N*-donor ligands are known, in general such organometallic NHC complexes are extremely rare.^[7,22] In fact, the only other Co^{III} -NHC peroxo complex besides octahedral **2** was reported by K. Meyer et al. and is a mononuclear compound with a trigonal bipyramidal structure featuring a side-on coordinating η^2 -peroxo ligand. The side-on coordination is facilitated by a more flexible tripodal $[\text{C}_3\text{N}]$ ligand bearing bulky mesityl wingtips, preventing the formation of a μ_2 -peroxo complex.^[21b] Thus, **2** is the first reported NHC complex with a Co^{III} -O-O- Co^{III} structural motif, making it particularly interesting for studies towards an application of the observed selective dioxygen activation, especially when considering its remarkable stability at room temperature in comparison to other bio-inspired μ_2 -peroxo dicobalt(III) complexes like $[\text{Co}_2(\text{PyTACN})_2(\mu_2\text{O}_2)(\text{MeCN})_2]^{4+}$, which is only stable at -35°C and re-releases O_2 at room temperature (Scheme 1).^[7] The formation of such compounds usually occurs stepwise via superoxo intermediates.^[7,26] In order to investigate the existence of an elusive Co superoxo species in the present case, in situ EPR spectroscopy studies were conducted, monitoring the reaction of **1** with O_2 from air. The X-band EPR spectrum of **1** was recorded at 173 K in a frozen solution of MeCN (Figure 4, left top). As characteristic for ^{59}Co ($I=7/2$) EPR, eight splitting lines are observed, six of which are resolved and two overlap with the low-field components, in accordance with comparable ^{59}Co compounds.^[27] Simulation of the recorded spectrum was achieved with $g=(2.230, 2.225, 2.015)$ and $A(^{59}\text{Co})=(70, 70, 405)$ MHz. The values of $g_x \approx g_y > g_z \approx g_e$ correspond to the highly symmetrical spin density of **1** in the plane of the tetra-NHC ligand, in line with calculated values using DFT (Supporting Information, Figure S4, Table S1). Repeated short exposure of the EPR sample to air leads to reduction of the signal of compound **1** and the concurrent appearance of a second, high-field shifted signal assignable to a new paramagnetic species (Figure 4, left bottom), also measured after full disappearance of **1** (Figure 4, center top). It exhibits a strong interference pattern with significantly smaller values for the hyperfine coupling tensor and g -values, marginally shifted from g_e pointing to a non-cobalt centered radical. Simulation of the spectrum is achieved with $g=(2.005, 2.005, 2.079)$ and $A(^{59}\text{Co})=(25.4, 36.5, 42.7)$ MHz. This signal is attributable to a superoxo species, as observed for other Co compounds upon reaction with O_2 .^[7,21b,28] As assigned by DFT calculations, the species depicts an end-on superoxo and an additional *trans* axial MeCN ligand (**4**^{end-on}), thereby ruling out a side-on coordination, amongst other conceivable structures of the intermediate in

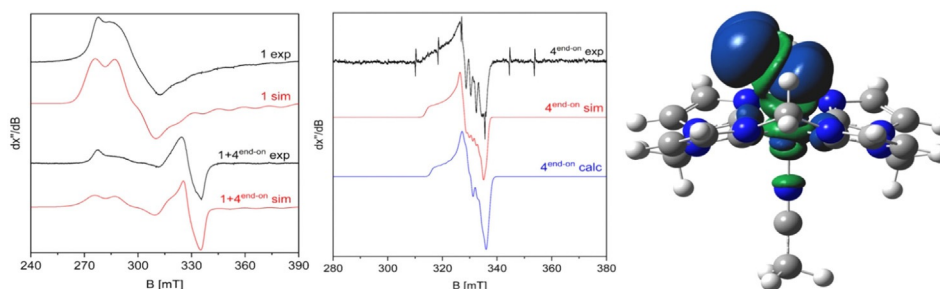


Figure 4. Left: EPR spectra of **1** (top) and after exposure to air (bottom); experimental spectra in black and simulated in red. Center: EPR spectra of **4** ^{end-on}; experimental spectrum in black, simulated in red and calculated for end-on **4** ^{end-on} in blue. Right: Spin density of **4** ^{end-on}. (Isovalues: MO=0.02, Density=0.0004).

the formation of diamagnetic **2** (see the Supporting Information for discussion).

As **2** shows a remarkable stability at room temperature, when compared to other μ_2 -peroxy dicobalt(III) complexes,^[7] the compound is studied to make use of its ability to activate molecular oxygen from air at ambient conditions.

When acetic acid is added to a solution of **2** in MeCN, an immediate deepening of the green color occurs, resulting from the quantitative formation of octahedral 18-valence-electron complex **3** featuring Co^{III} and an additional axial acetate (Scheme 1c; Figure 5). Thereby, the peroxy ligand is cleaved. Possible reactions of the peroxy moiety include the formation of H₂O and O₂ on the one hand, as well as H₂O₂ on the other, which often occur as competing reactions.^[26b] Following a previously applied procedure to unequivocally detect H₂O₂ in presence of iron complexes, when treated with diluted reaction solution (1:5 ratio in water), test strips sensitive to low H₂O₂ concentrations react positively.^[29] The detection of H₂O₂ in conjunction with the quantitative formation of **3** shows, that the peroxy species is accessible with Brønsted acids.

This reactivity is supported by DFT calculations revealing a nucleophilic oxygen species, as the HOMO of **2** (Figure 6) is of

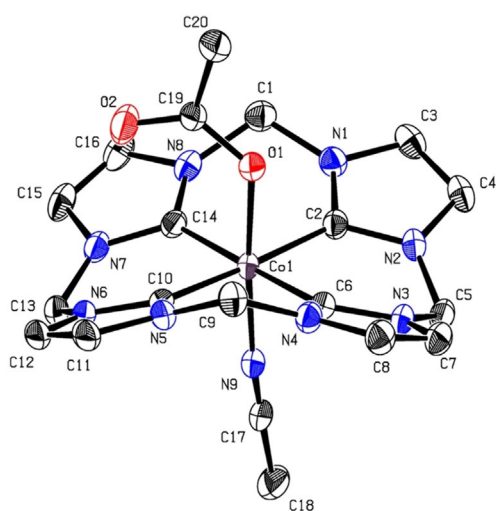


Figure 5. ORTEP-style representation of the cationic fragment of compound **3**.^[30] Hydrogen atoms, co-crystallized solvent molecules and hexafluorophosphate anions are omitted for clarity. Thermal ellipsoids are shown at a 50% probability.

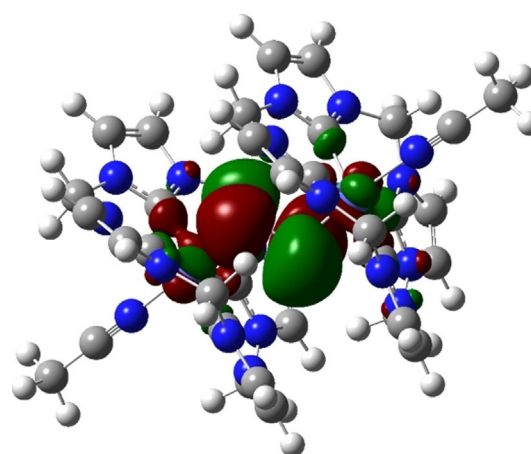


Figure 6. Electronic structure of the HOMO of **2**, with mostly π^* character located on the O–O bond (Isovalues: MO=0.02, Density=0.0004).

π^* character, mainly being localized on the peroxy moiety, and further affirmed by the fact, that no oxygen centered orbitals are observed for the LUMO and energetically higher orbitals (analyzed for LUMO to LUMO₊₂₆). In line with the reactivity assigned by DFT, control experiments for electrophilic oxygen species like olefin epoxidation and C–H oxidation do not result in formation of oxidized products (Supporting Information for details).

In summary, Co^I complex **1** bearing the 16-membered macrocyclic tetra-NHC ligand cCCCC is synthesized and characterized by NMR spectroscopy, elemental analysis, ESI-MS, EPR spectroscopy and SC-XRD. The yellow 17-valence-electron complex selectively activates dioxygen from air at ambient conditions, resulting in the formation of green 18-valence-electron dicobalt(III) μ_2 -peroxy complex **2**, the first reported NHC-complex with a Co–O–O–Co structural motif. The reaction proceeds via an elusive end-on coordinated superoxo intermediate (**4** ^{end-on}), as demonstrated by EPR spectroscopy, simulations and supported by DFT calculations. Conversion of **2** with acetic acid, providing the simplest electrophile, that is, protons, results in the cleavage of the peroxy moiety. Thereby, dark green octahedral Co^{III} complex **3** bearing a monodentate axial acetate ligand is quantitatively formed, going along with hydrogen peroxide formation. DFT calculations suggest a nucleophilic nature of the peroxy moiety, explaining the observed reactivity. These results pave the way to utilize dioxygen from air as a

sustainable in situ hydrogen peroxide source for co-catalytic reactions. Optimization of a potentially competing formation of water and dioxygen is in the focus of future research.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cobalt · dioxygen activation · dioxygen ligands · macrocyclic ligands · *N*-heterocyclic carbenes

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