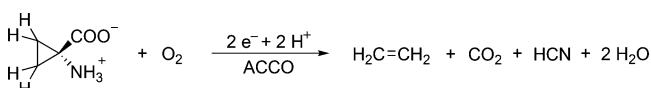


A Structural and Functional Model for the 1-Aminocyclopropane-1-carboxylic Acid Oxidase**

Madleen Sallmann, Fabio Oldenburg, Beatrice Braun, Marius Réglier, A. Jalila Simaan,* and Christian Limberg*

Abstract: The hitherto most realistic low-molecular-weight analogue for the 1-aminocyclopropane-1-carboxylic acid oxidase (ACCO) is reported. The ACCOs 2-His-1-carboxylate iron(II) active site was mimicked by a $TpFe$ moiety, to which the natural substrate ACC could be bound. The resulting complex $[Tp^{Me,Ph}FeACC]$ (**1**), according to X-ray diffraction analysis performed for the nickel analogue, represents an excellent structural model, featuring ACC coordinated in a bidentate fashion—as proposed for the enzymatic substrate complex—as well as a vacant coordination site that forms the basis for the first successful replication also of the ACCO function: **1** is the first known ACC complex that reacts with O_2 to produce ethylene. As a $FeOOH$ species had been suggested as intermediate in the catalytic cycle, H_2O_2 was tested as the oxidant, too, and indeed evolution of ethylene proceeded even more rapidly to give 65 % yield.

Ethylene is a gaseous hormone for plants that induces fruit ripening.^[1] It is produced from the amino acid 1-aminocyclopropane-1-carboxylic acid, through oxidation with O_2 as the oxidant and ascorbate as the coreductant, mediated by the enzyme 1-aminocyclopropane-1-carboxylic acid oxidase (ACCO).^[2] CO_2 and HCN are generated concomitantly (Scheme 1). For not well-understood reasons, the enzyme



Scheme 1. The last step of the biosynthesis of ethylene.

also requires CO_2 (or bicarbonate ions) to develop its reactivity.

The crystal structure of the ACCO from *Petunia hybrida* has been determined in 2004 by Schofield and co-workers.^[3] It belongs to the family of non-heme iron enzymes featuring a structural motif termed the 2-His-1-carboxylate facial triad: The active center contains an iron(II) ion coordinated by two histidine moieties and one aspartate residue in a facial arrangement, leaving the other three sites of the iron ion vacant for the binding of ACC and potentially O_2 . The mechanism, by which the complex conversion shown in Scheme 1 is realized, is still discussed controversially, but it is generally assumed that the oxidation of ACC into ethylene follows a radical mechanism including two successive single-electron oxidation steps.^[4] Spectroscopic studies have shown that in the first step of the reaction the substrate ACC binds to the Fe^{II} ion in a bidentate mode most likely followed by O_2 activation to generate an Fe^{III} -superoxide intermediate.^[5] For the events after O_2 binding several suggestions have been made that all involve an $Fe^{IV}=O$ intermediate but differ in the sequence of the electron transfer steps with ascorbate and in the nature of the intermediates responsible for the successive oxidations of ACC. Rocklin et al. have proposed that binding of ACC and O_2 is followed by one electron reduction to provide an iron(III)-hydroperoxide intermediate that performs the first ACC oxidation step leading to an $Fe^{IV}=O$ species responsible for the second oxidation step.^[6] One electron from ascorbate would then complete the catalytic cycle. Alternatively, Mirica et al. have proposed an ascorbate-dependent formation of the $Fe^{IV}=O$ intermediate that would act as the first oxidizing species.^[7]

Many questions thus remain unanswered regarding the interaction mode with the substrate, the role of the different cofactors/co-substrates (ascorbic acid, dioxygen, and carbon dioxide) and the catalytic mechanism.

Bioinorganic model studies can provide valuable information, both with regard to structural issues and requirements for reactivity. However, there are hardly any compounds known which may be regarded as models of ACCO, applying the minimum requirement that they contain ACC and that they display substantial ACCO-like activities.^[8,9] One iron complex has been reported, which is dinuclear, though, contains iron(III) ions and two bridging ACC ligands.^[8] Whereas iron(II) complexes have long remained unknown, mononuclear 1:1 metal-ACC complexes have been accessed for copper(II).^[9] An Fe^{II} -ACC complex has very recently been described, but it can hardly be considered as a functional replicate of the ACCO: the iron center is coordinated octahedrally by six donor atoms, and hence

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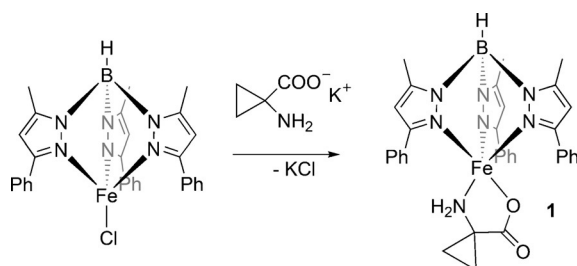
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oxidants have no access to the iron center. This explains that no reactivity with O_2 was observed and that the yield of ethylene produced in reactions with H_2O_2 was only 7 % higher as compared to the blank experiments.^[10]

To mimic mononuclear non-heme iron dioxygenases based on a 3-His structural motif, we have in recent years successfully employed the tris(pyrazolyl)borato (Tp) ligand system,^[11] which in the past has also been employed to simulate representatives based on the 2-His-1-carboxylate structural motif.^[12] It thus appeared a promising choice also for the development of replicates of the ACCO. One problem that has emerged in the past with regard to the modeling of this enzyme is the tendency of ACC to bridge two metal centers, as both polynuclearity and ACC in bridging coordination modes rather limit the model character of the resulting complexes (see above). Hence, we chose phenyl residues at the 3-position of the pyrazole donors within Tp to create a shielding reaction pocket approaching the situation in the enzyme. A suitable starting material was therefore the complex $[Tp^{Me,Ph}FeCl]$ ^[13] ($Tp^{Me,Ph} = 3$ -Phenyl-5-methylhydrido-trispyrazol-1-ylborato), which after dissolution in dichloromethane was reacted with the potassium salt of the amino acid 1-amino-cyclopropane-1-carboxylic acid (Scheme 2).



Scheme 2. Synthesis of $[Tp^{Me,Ph}FeACC]$ (**1**).

After work-up a light yellow solid was isolated, which was characterized by elemental analysis, IR, and 1H NMR spectroscopy (see the Supporting Information, SI). The IR spectrum showed characteristic bands for the NH_2 stretching vibrations as well as for the carboxylate absorptions, and the $\nu(BH)$ band, which is typical for Tp complexes and sensitive to the environment, appeared at 2549 cm^{-1} . While all analytical and spectroscopic data pointed to the envisaged complex $[Tp^{Me,Ph}FeACC]$ (**1**), all attempts to crystallize this compound led to crystals of $[Tp^{Me,Ph}_2Fe]$.^[20] To clarify whether the latter complex represents an impurity that has favorable crystallization properties, or whether it forms through ligand exchange during attempts to crystallize **1**, it was prepared independently (see SI) and characterized by 1H NMR spectroscopy. Comparison showed that $[Tp^{Me,Ph}_2Fe]$ was not present in freshly prepared samples of **1** nor in 7 h old ones; however, after storing the solutions for 5 days, $[Tp^{Me,Ph}_2Fe]$ could be detected in significant amounts. This clearly showed that **1** is stable enough in solution for reactivity studies but does not readily crystallize, and crystallization can neither be achieved by allotting additional time as this leads to ligand exchange. Mössbauer spectroscopy was used to further

characterize the complex. The spectrum of **1** shows a doublet typical of high-spin iron(II) species with an isomeric shift $\delta = 1.0906\text{ mm s}^{-1}$ and an electronic quadrupole splitting of $\Delta E_q = 2.7\text{ mm s}^{-1}$.

To obtain structural information we have prepared a corresponding nickel complex $[Tp^{Me,Ph}NiACC]$ (**2**) in the same way setting out from $[Tp^{Me,Ph}NiBr]$ (see SI). After work-up of the blue-green reaction solution a light green solid could be isolated, which showed an almost identical IR spectrum as compared to the one displayed by **1**, with respect to band shape, pattern, and intensities (Figure 1). Since this indicated that the structure of **2** is rather similar to the one of **1**, too, a structural investigation of **2** was of high interest.

Compound **2** thf could be crystallized through overlaying a THF solution with hexane, and Figure 2 shows the

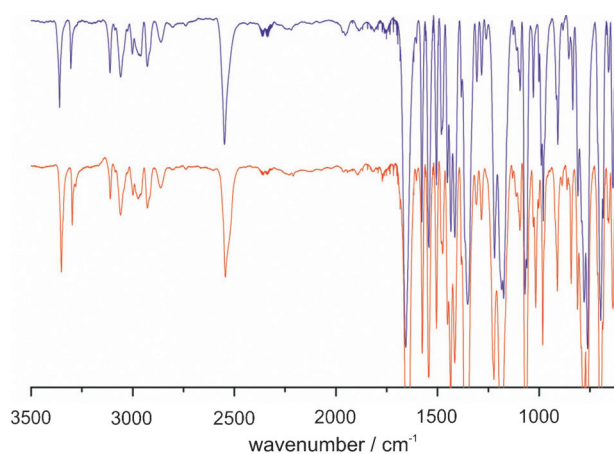


Figure 1. Comparison of the IR spectra of **1** (blue) and **2** (red) as recorded from KBr discs.

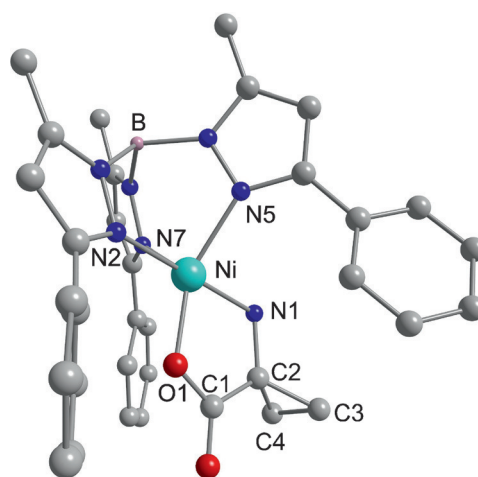


Figure 2. Molecular structure of **2** thf (all hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Ni–O1 1.9585(11), Ni–N1 2.0859(14), Ni–N2 2.0993(13), Ni–N5 2.0698(13), Ni–N7 2.0510(13); O1–Ni–N1 82.19(5), N2–Ni–N5 87.29(5), N2–Ni–N7 90.03(5), N5–Ni–N7 95.17(5), O1–Ni–N2 95.59(5), O1–Ni–N5 146.53(5), O1–Ni–N7 118.12(5), N1–Ni–N2 175.66(5), N1–Ni–N5 92.51(5), N1–Ni–N7 94.31(5).

molecular structure determined by single-crystal X-ray analysis.

As expected the ACC ligand binds as a chelating ligand. The nickel(II) center is thus coordinated by the three N atoms of the $\text{Tp}^{\text{Me,Ph}}$ ligand as well as by the amine and carboxylate functions of the O-deprotonated ACC creating a ligand sphere that is in-between trigonal bipyramidal and square pyramidal ($\tau = 0.48$). Although in previous models the C–C bond of the cyclopropyl unit appeared shortened,^[9] such an effect was not noticeable in case of **2**: The C3–C4 bond length in **2** (1.496(3) Å) was almost identical with the one found for free ACC^[14] (1.490–1.497 Å).

Based on the striking resemblance of the IR spectra of **1** and **2** a corresponding structure is suggested also for **1**, which thus features one free coordination site for the potential binding and activation of O_2 or alternative oxidants.^[18] Accordingly, reactivity studies were carried out. It has been suggested that a prerequisite for O_2 reactivity of iron(II) complexes is $E_{1/2}(\text{Fe}^{\text{III/II}}) < -0.1$ V versus Fc^+/Fc .^[16] A cyclic voltammetry (CV) investigation of **1** dissolved in dichloromethane indicated a reversible redox event, but the oxidation and reduction peaks were separated by 410 mV indicating reversible structural changes upon oxidation/reduction (see SI). The oxidation peak occurred at 0.03 V, which appeared not negative enough for O_2 reactivity. On the other hand reactivity trends observed in previous work for TpFe -based Dke1 models could not be rationalized on the basis of redox potentials,^[17] and indeed **1** was found to react with O_2 .

Complex **1** was dissolved in DMF and added to O_2 -saturated DMF placed in hermetically sealed vials. Analysis of the headspace gas by GC revealed the presence of ethylene, and the conversion yield reached a maximum of ca. 17 % after a few minutes at 70 °C. Importantly, no ethylene was detected when ACC alone (in form of its NBu_4^+ salt) was placed in aerated DMF for one hour indicating that the observed activity is not due to free ACC (potentially released from the complex) in solution. Furthermore, ethylene production was found to be three times lower (conversion yields of ca. 6 %) when $\text{Fe}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ in combination with $(\text{NBu}_4)\text{ACC}$ was employed instead of complex **1** under the same conditions. Notably, the nickel complex **2** does not react with O_2 , which suggests an initiation of the reaction by binding of O_2 at the iron center in the first step.

Under single turn-over conditions and in the absence of ascorbate, Rocklin et al. found that only 0.35 mol of ethylene per mol of ACCO are formed, and hence they proposed that the electrons needed for catalysis are provided by a fraction of the initial ACCO enzyme.^[6] Also in case of our experiments it is conceivable that the required electrons are provided by a fraction of complex **1**, therefore limiting the reaction yield as observed for the enzymatic system. Attempts to provide electrons by adding different reductants (ascorbate or benzoine) remained unsuccessful, though.

To obtain information about the fate of the residual skeleton of **1** we have performed GC/MS studies with the gas phase after the reaction, which revealed CO_2 as a further product, as one should expect.^[19] Monitoring the UV/Vis spectrum of a DMF solution of **1** with time at RT and at 70 °C

showed that even at RT after O_2 addition the main changes (general increase of absorption in the range of 300–500 nm) occur within 0–5 min (see SI). After this time the spectrum remains nearly constant displaying only discrete changes, while ethylene yield increases within ca. 2 h. Hence, there is probably an initial fast step (perhaps only partially as part of an equilibrium), followed by a much slower reaction producing ethylene. At RT ethylene yield reaches a plateau at ca. 7 %. This suggests that a decomposition reaction competes with the productive path, which, however, can be accelerated to a significant extent by warming to 70 °C (resulting in 17 % yield).

For many O_2 activating non-heme iron enzymes and models thereof the initial O_2 binding step with formation of iron(III) superoxide intermediates has been found to be endergonic in theoretical investigations. The subsequent steps are usually exothermic but in case of low-molecular-weight analogues often characterized by substantial barriers, which—together with the endergonic O_2 binding step—decrease the reaction rates. If enzymes are considered, which—as the ACCO—in parallel to O_2 consume electrons to reach substrate oxidation and feature peroxide or $\text{Fe}^{\text{IV}}=\text{O}$ intermediates, this problem can be circumvented by employing reduced forms of dioxygen, that is, for instance H_2O_2 , or O-atom transfer reagents. Significant ethylene production was observed when complex **1** was placed in the presence of PhIO or *m*CPBA (*meta*-chloroperoxybenzoic acid). However, the latter reagents significantly oxidize ACC already in the absence of the iron complex (ca. 75 % and 35 % yield within 2–3 h respectively), so that their employment does not provide any information (see SI). Hence, different concentrations of hydrogen peroxide were tested, and interestingly, for a 0.5 mM solution of complex **1** the ACC conversion into ethylene reaches 65 % yield employing 10–20 mM of hydrogen peroxide after 20 min. Under the same conditions, ACC alone was hardly oxidized to produce ethylene (less than 2 % conversion yield) confirming that the observed activity is not due to released ACC in solution. Also the reactivity of **2** toward H_2O_2 was found to be rather limited (less than 2 % conversion yield), emphasizing the importance of the nature of the metal center. Finally, ethylene production from a 0.5 mM solution of $\text{Fe}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}/(\text{NBu}_4)\text{ACC}$ in DMF in the presence of 10–20 mM H_2O_2 was found to be six times lower (conversion yields of ca. 10–12 %) than that observed for complex **1**, which demonstrates the importance also of the co-ligand to control the reactivity.

Altogether, these results imply that the observed ethylene production from complex **1** after reaction with O_2 or hydrogen peroxide crucially depends on the suitability of the $\text{Tp}^{\text{Me,Ph}}\text{Fe}$ moiety to mimic the 2-His-1-carboxylate iron core within the ACCO. It has been rather well established that H_2O_2 can react with Fe^{II} or Fe^{III} complexes to provide the corresponding, reactive $\text{Fe}^{\text{III}}\text{--OOH}$ intermediates.^[15] Reaction of H_2O_2 with complex **1** can thus be expected to first result in the oxidation of the Fe^{II} to Fe^{III} and then in the formation of the $\text{Fe}^{\text{III}}\text{--OOH}$ intermediate. In the presence of dioxygen, the formation of the $\text{Fe}^{\text{III}}\text{--OO}^\bullet$ intermediate followed by one-electron reduction by a further equivalent of **1** and protonation (for instance through residual water in

DMF) could lead to a $\text{Fe}^{\text{III}}\text{--OOH}$ intermediate as well. Our results thus suggest that a $\text{Fe}^{\text{III}}\text{--OOH}$ species is indeed involved in the catalytic cycle of the ACCO and that its formation probably precedes the oxidation of the bound substrate, in agreement with the two proposed mechanisms for the enzymatic system.

In conclusion we have described here the first Fe^{II} -based low-molecular-weight analogue which faithfully mimics the structure of the ACCO active site and at the same time also simulates the function. Indeed, this Fe^{II} complex in contact with O_2 shows an oxidase activity (17%), which is remarkable as the enzymatic one is only ca. 35% under single turn-over conditions. Future studies, including various alternative oxygenation reagents, electron and proton donors as well as kinetic and theoretical calculations, will focus on the further elucidation of the mechanism of this biomimetic oxidation.

Keywords: aminocyclopropane-1-carboxylic acid · enzyme models · iron · oxidase · oxygen

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