

Ligand-dependent oxidation of copper bound α -amino-isobutyric acid as 1-aminocyclopropane-1-carboxylic acid oxidase mimics



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ABSTRACT

As a continuity of the $[\text{Cu}^{\text{II}}(\text{AIB})(\text{bpy})(\text{H}_2\text{O})](\text{ClO}_4)_2$ -containing (**1**) ACCO (1-aminocyclopropane-1-carboxylate oxidase) model, two new copper(II)-amino acid complexes $[\text{Cu}^{\text{II}}_2(\text{AIB})_2(\text{PBI})_2](\text{CH}_3\text{OH})(\text{ClO}_4)_2$ (**2**) and $[\text{Cu}^{\text{II}}_2(\text{AIB})_2(\text{PBT})_2](\text{H}_2\text{O})(\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ (**3**) with a modified hetero-bidentate ligands (PBT = 2-pyridin-2-yl-benzothiazole and PBI = 2-pyridin-2-yl-1*H*-benzimidazole) have been synthesized, characterized by various techniques including IR, UV-Vis, electrochemical and X-ray measurements, and investigated their reactivity toward H_2O_2 with respect to the redox behavior compare to **1**.

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1. Introduction

Metal coordinated amino acids (AA) are important due to their involvement in a number of biochemical and catalytic systems, such as oxygen conveyer, electron transfer and oxidation. For example, 1-aminocyclopropane-1-carboxylate (ACC) oxidase (ACCO) is a key enzyme that catalyzes the final step in the biosynthesis of the plant hormone ethylene [1–10]. ACCO has been classified as a member of a family of non-heme iron proteins, and suggested that the substrate oxidation proceeds through two successive mono-electronic oxidation steps including the formation of peroxoiron(III) and oxoiron(IV) intermediates [11–17]. However, there are only few reported functional models of ACCO. These are mainly using iron and copper ions. As heme and nonheme iron-containing functional model of the ACCO we have found, that complexes $[\text{Fe}^{\text{III}}(\text{Salen})\text{Cl}]$ (Salen = *N,N'*-bis(salicylidene)-ethylenediaminato) [18,19], $[\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}]$ (TPP = *meso*-tetraphenylporphyrin) and $[\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})(\text{N}_4\text{Py})](\text{ClO}_4)_2$ (N_4Py = *N,N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine) [20] highly selectively and efficiently catalyze the oxidation of ACCH to ethylene, and the alternate α -aminoisobutyric acid (AIBH) substrate to acetone. In the catalytic cycles of these systems above high-valent oxoiron(IV) species, namely $[\text{Fe}^{\text{IV}}\text{O}(\text{Salen})]^{2+}$ [18,19], $[\text{Fe}^{\text{IV}}\text{O}(\text{TPP})]$ and $[\text{Fe}^{\text{IV}}\text{O}(\text{N}_4\text{Py})]^{2+}$ [20], have been identified as key intermediates, but no evidence has been found for the presence of the proposed peroxo species.

Besides the Fe-based models [18–21], some Cu(II) complexes of ACC and AIB with the NN supporting ligands 2,2'-bipyridine (bpy), 1,10-phenanthroline and 2-picolylamine have also been investigated in their reaction with hydrogen peroxide, where Cu(I)-AA (brown species) and Cu(II)-OOH as possible active species were proposed [22–25]. These complexes serve as Cu-based models for the ACCO analogously to the Cu(I)- α -ketoglutarate complex reported by Tolman – “to emphasize the parallel that might be established between copper and iron systems” [26]. In addition, in Cu-containing enzymes such as the peptidylglycine α -hydroxylating monooxygenases (PHMs, responsible for the production of amidated peptide hormones), the initial α -C–H activation of the C-terminal glycine substrate is promoted by the so-called Cu_M cofactor [27–30]. An analogy to the ACCO is the use of ascorbate cosubstrate. Therefore mechanistic studies on Cu-based models that oxidize AAs can be useful in relevance to PHMs, too.

We will present here the synthesis, crystal structure and properties of two copper(II)-AIB complexes $[\text{Cu}^{\text{II}}_2(\text{AIB})_2(\text{PBI})_2](\text{CH}_3\text{OH})(\text{ClO}_4)_2$ (**2**) and $[\text{Cu}^{\text{II}}_2(\text{AIB})_2(\text{PBT})_2](\text{H}_2\text{O})(\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ (**3**) with a various hetero-bidentate ligands (PBT = 2-pyridin-2-yl-benzothiazole and PBI = 2-pyridin-2-yl-1*H*-benzimidazole) that exhibit efficient ACCO activity under ambient conditions using H_2O_2 as an oxidant. To get insight into the structure–activity relationships, reactivity of these complexes toward H_2O_2 was systematically studied and will be discussed with respect to the stereochemistry and redox behavior compare to the recently published $[\text{Cu}^{\text{II}}(\text{AIB})(\text{bpy})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (**1**) system (Schemes 1 and 2).

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2. Experimental

2.1. Materials

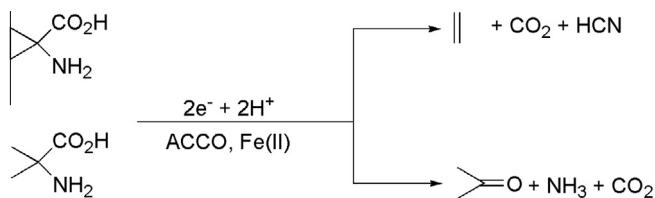
Solvents used for the reactions were purified by literature methods and stored under argon. The 2,2'-bipyridine (bpy), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and the AIBH were purchased from commercial sources. $[\text{Cu}^{\text{II}}(\text{AIB})(\text{bpy})]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**1**) [22], PBT [31] and PBI [31] were synthesized following a previously described procedures. **CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and handled with caution.**

2.2. Analytical and physical measurements

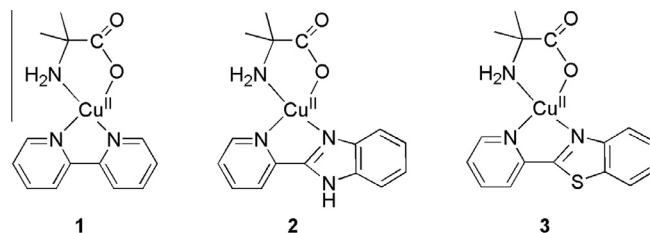
Infrared spectra were recorded on an Avatar 330 FT-IR Thermo Nicolet instrument using samples milled in KBr pellets. UV–Vis spectra were recorded on a Cary 60 spectrophotometer equipped with a fiber-optic probe with 1 cm pathlength. Microanalyses were done by the Microanalytical Service of the University of Pannonia. Cyclic voltammograms (CV) were taken on a VoltaLab 10 potentiostat with VoltaMaster 4 software for data process. The electrodes were as follows: glassy carbon (working), Pt (auxiliary), and Ag/AgCl in 3 M KCl (reference). The potentials were referenced versus the ferrocenium ferrocene redox couple (+416 mV in methanol in our setup). The crystal evaluations and intensity data collections were performed on a Bruker–Nonius Kappa CCD single-crystal diffractometer (**2**, **3**) using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. Data collection was performed with COLLECT [32], cell refinement and data reduction with DENZO/SCALEPACK [33]. The structure were solved with SIR92 [34] and SHELXL-2013 [35] was used for full matrix least squares refinement. Crystallographic data and details of the structure determination are given in Table 1, whereas selected bond lengths and angles are listed in Tables 2 and 3. CIF files are available in the CCDC database: CCDC 1036340–1036341 (**2**, **3**). GC measurements were performed on a HP 5890 gas chromatograph equipped with a 30 m Supelcowax column.

2.3. Synthesis of $[\text{Cu}^{\text{II}}(\text{AIB})_2(\text{PBI})_2(\text{CH}_3\text{OH})(\text{ClO}_4)]\text{ClO}_4$ (**2**)

To a stirred solution of $\text{Cu}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.372 g, 1 mmol) of in methanol (20 mL) PBI (0.195 g, 1 mmol) and AIBH (0.11 g, 1 mmol) were added. Dropwise addition of triethylamine (140 μL , 1 mmol, freshly distilled and stored under argon) resulted in a dark blue solution. After stirring for 1 h at room temperature the solution was filtered and left to evaporate slowly to $\sim 3 \text{ mL}$. A dark blue crystalline product was formed that was filtered, briefly washed with a minimal amount of cold methanol and dried. Yield: 0.64 g (66%). *Anal. Calc.* for $\text{C}_{34}\text{H}_{42}\text{Cl}_2\text{Cu}_2\text{N}_8\text{O}_{13}$: C, 42.15; H, 4.37; N, 11.57. *Found*: C, 41.98; H, 4.37; N, 11.39%. FT-IR bands (KBr pellet, cm^{-1}) 3441, 3288, 3157, 2971, 2926, 1637, 1609, 1593, 1483, 1458, 1430, 1390, 1370, 1317, 1236, 1199, 1118, 1073, 1009, 923, 733, 616, 567. UV–Vis (CH_3OH)



Scheme 1. Reactions catalyzed by ACCO.



Scheme 2. Structures of the complexes (ligands) used in this study.

Table 1
Crystal structure details for **2** and **3**.

Compound reference	2	3
Chemical formula	$\text{C}_{33}\text{H}_{38}\text{Cl}_2\text{Cu}_2\text{N}_8\text{O}_{13}$	$\text{C}_{32.5}\text{H}_{36}\text{Cl}_2\text{Cu}_2\text{N}_6\text{O}_{13.5}\text{S}_2$
Formula mass	952.69	494.39
Crystal system	monoclinic	monoclinic
<i>a</i> (Å)	10.6516(3)	9.9792(3)
<i>b</i> (Å)	15.6635(5)	17.9434(7)
<i>c</i> (Å)	24.1701(8)	22.5983(8)
β (°)	90.341(1)	99.095(1)
Unit cell volume (Å ³)	4021.0(2)	3995.6(2)
<i>T</i> (K)	293(2)	293(2)
Space group	$P2_1/c$	$P2_1/c$
Number of formula units per unit cell (<i>Z</i>)	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
Absorption coefficient ($\mu \text{ mm}^{-1}$)	1.263	1.375
No. of reflections measured	9140	10302
No. of independent reflections	6167	4894
R_{int}	0.0515	0.065
Final <i>R</i> 1 values ($I > 2\sigma(I)$)	0.0658	0.0685
Final <i>wR</i> values ($I > 2\sigma(I)$)	0.1830	0.1662
Final <i>R</i> 1 values (all data)	0.0984	0.1679
Goodness of fit	1.025	1.041
CCDC number	1036340	1036341

Table 2
Selected bond lengths (Å) for **2** and **3**.

2			
O1–Cu1	1.917(3)	O2–Cu2	2.252(3)
N1–Cu1	2.015(3)	O3–Cu2	1.948(3)
N2–Cu1	1.989(3)	N5–Cu2	2.085(4)
N4–Cu1	1.982(3)	N6–Cu2	1.962(4)
O16–Cu1	2.788(4)	N8–Cu2	1.974(4)
O7–Cu1	2.744(6)	C13–O1	1.272(5)
C5–N1	1.354(5)	C13–C14	1.523(6)
C5–C6	1.463(6)	C14–N4	1.499(5)
3			
O1–Cu1	1.926(4)	O2–Cu2	2.252(4)
O5–Cu1	2.314(4)	O3–Cu2	1.931(4)
N1–Cu1	2.035(5)	N4–Cu2	2.016(4)
N2–Cu1	2.024(4)	N5–Cu2	2.036(4)
N3–Cu1	1.998(4)	N6–Cu2	1.992(4)
C14–N3	1.498(6)	C6–N1	1.313(7)
C13–O1	1.276(6)	C5–C6	1.439(8)
C13–C14	1.518(7)	C5–N2	1.339(7)

Table 3
Selected bond angles (°) for **2** and **3**.

2			
N1–Cu1–N4	174.84(14)	O3–Cu2–N5	168.65(15)
O1–Cu1–N2	172.54(15)	N6–Cu2–N8	178.83(16)
–	–	$\tau(\text{Cu2})$	0.166
3			
N1–Cu1–O1	173.33(17)	N4–Cu2–N6	170.56(18)
N3–Cu1–N2	162.72(18)	O3–Cu2–N5	166.49(17)
$\tau(\text{Cu1})$	0.176	$\tau(\text{Cu2})$	0.067

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