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Research paper

A structural and functional model of copper(II)-flavonolate ES complex of flavonol 2,4-dioxygenase

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ABSTRACT

A novel mononuclear copper(II)-flavonolate complex [Cu^{II}L(fla)] (LH: 2-{[bis(pyridine-2-ylmethyl)-amino]methyl}-4-methoxy benzoic acid, flaH: flavonol) was prepared as a structural and functional model of the ES (enzyme-substrate) complex of Cu^{II}-containing flavonol 2,4-dioxygenase. Its structure, properties and reactivity towards molecular dioxygen have been investigated in details. The complex shows the best reactivity in the copper(II)-flavonolate ES model system, may it could be contributed to the approximately monodentate coordination of the substrate flavonolate.

1. Introduction

As a member of the cupin superfamily, flavonol 2,4-dioxygenase (FDO, quercetin 2,3-dioxygenase) is responsible for degradation of flavonol [1,2], which can catalyze the oxygenative cleavage of two C—C bonds of the *O*-heterocycle of flavonol to yield the corresponding depsides (phenolic carboxylic acid esters) with concomitant evolution of carbon monoxide [3,4] (Scheme 1). The fungal Cu^{II}-containing flavonol 2,4-dioxygenase have been isolated from *Aspergillus japonicus* [5], *Aspergillus flavus* [6], and *Aspergillus niger* DSM 821 [7]. The crystal structure of the Cu^{II}-containing FDO from *Aspergillus japonicas* [5] reveals that it is homodimer containing one type II copper(II) ion per monomer unit, and the active site has two distinct structures, one is coordinated by three histidine imidazoles (His66, His68, and His112) and a water molecule in a distorted tetrahedral geometry, the other is additionally coordinated by the carboxylate group of Glu73 in a distorted trigonal-bipyramidal geometry. Under anaerobic conditions, the deprotonated 3-hydroxy group of flavonol was coordinated to copper(II) with displacement of the water molecule to form an ES (enzyme-substrate) adduct with a distorted square pyramidal geometry [8]. The carboxylate group of Glu73 could not only act as an active site base for the substrate deprotonation but also stabilize the bound substrate via a hydrogen bonding interaction [5,9].

So far, numerous Cu(II)/Cu(I)-complexes have been reported as biomimetic studies of Cu^{II}-containing FDO [10–18], and almost all of the model ligands used in the reported model complexes are *N*-chelating polyamine ligands, only two reports pay attention to effects of the carboxylate and indicate that adding excess free carboxylate could accelerate the dioxygenation of the bound substrate flavonolate by changing the coordination mode of flavonolate from bidentate to monodentate [19,20] as found in the native enzyme [5]. Only one ligand bearing a carboxylate group was used in the ES (enzyme-substrate) model complex [Cu^{II}L(fla)]·3CH_3OH (LH: 2-{[bis(pyridin-2-ylmethyl) amino]methyl}benzoic acid, fla: flavonolate) have been reported, however, the complex is not characterized structurally [21].

In this communication, to have insight into the effect of carboxylate group in Glu on the structure, properties and reactivity towards molecular O_2, we have prepared and characterized a novel copper(II)-flavonolate complex [Cu^{II}L(fla)] [22] having a carboxylate group in the ligand molecule (LH: 2-{[bis(pyridine-2-ylmethyl)amino]methyl}-4-methoxy benzoic acid, flaH: flavonol) as a structural and functional ES model of FDO. The structure, spectroscopic features, as well as the reactivity toward molecular dioxygen have been investigated in details in order to gain insights into the effect of the carboxylate group in the model ligand on the structure, redox property and oxygenation reactivity of the complex.

Model ligand LH (Fig. 1) was prepared according to the reported procedure [23]. The ES model complex [Cu^{II}L(fla)] was synthesized according to the following procedure. A dry CH_3OH solution (3 mL)

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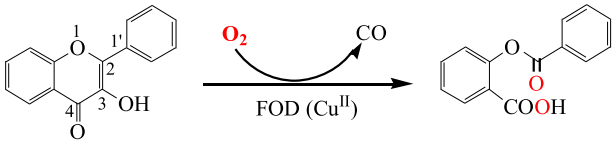


Scheme 1. Oxygenative cleavage of flavonol by natural CuII-containing FDO.

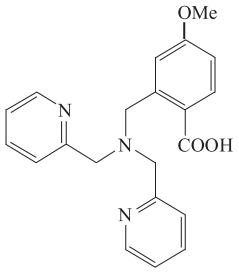


Fig. 1. Structure of ligand **LH**.

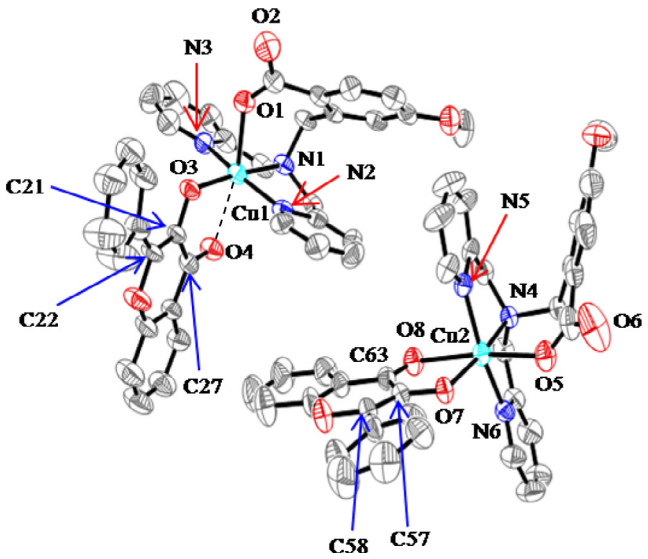


Fig. 2. ORTEP drawing of structure [$Cu^{II}L(fla)$] showing the local coordination environment of the Cu^{2+} ion with 30% thermal ellipsoids. The atoms in asymetry unit are labelled. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°): Cu(1)-O(1)/Cu(2)-O(5) 2.226(3)/2.202(4), Cu(1)-O(3)/Cu(2)-O(7) 1.920(2)/1.956(3), Cu(1)-O(4)/Cu(2)-O(8) 2.479(35)/2.371(3), Cu(1)-N(1)/ Cu(2)-N(4) 2.033(3)/2.051(3), Cu(1)-N(2)/Cu(2)-N(5) 2.009(4)/2.016(3), Cu(1)-N(3)/Cu(2)-N(6) 2.012(4)/2.011(3), O(3)-C(21)/O(7)-C(57) 1.318(4)/1.318(5), O(4)-C(27)/O(8)-C(63) 1.231(4)/1.246(5), C(21)-C(22)/C(57)-C(58) 1.348(5)/1.359(5), O(1)-Cu(1)-O(3)/O(5)-Cu(2)-O(7) 92.74(11)/95.49(12), O(1)-Cu(1)-O(4)/O(5)-Cu(2)-O(8) 165.92(108)/172.28(12), O(1)-M-N(1)/O(5)-Cu(2)-N(4) 93.78(12)/93.88(12), O(1)-Cu(1)-N(2)/O(5)-Cu(2)-N(5) 100.73(13)/95.62(13), O(1)-Cu(1)-N(3)/O(5)-Cu(2)-N(6) 86.01(13)/87.50(14), O(3)-Cu(1)-N(1)/O(7)-Cu(2)-N(4) 173.38(12)/170.62(13), O(3)-Cu(1)-N(2)/O(7)-Cu(2)-N(5) 96.53(13)/96.59(13), O(3)-Cu(1)-N(3)/O(7)-Cu(2)-N(6) 97.46(15)/98.76(13), O(3)- Cu(1)-O(4)/O(7)-Cu(2)-O(8) 75.00(107)/77.76(11), O(4)-Cu(1)-N(1)/O(8)-Cu(2)-N(4) 98.37(119)/92.92(12), O(4)-Cu(1)-N(2)/O(8)-Cu(2)-N(5) 87.72(121)/88.94(12), O(4)-Cu(1)-N(3)/O(8)-Cu(2)-N(6) 88.73(136)/89.82(12), N(1)-Cu(1)-N(2)/N(4)-Cu(2)-N(5) 83.39(15)/82.10(13), N(1)-Cu(1)-N(3)/N(4)-Cu(2)-N(6) 81.86(16)/82.00(14), N(2)-Cu(1)-N(3)/N(5)-Cu(2)-N(6) 164.15(16)/163.97(15).

of 0.1 mmol $Cu^{II}(OAc)_2{\cdot}H_2O$ was added dropwise to a CH_2Cl_2 (5 mL) solution containing flaH (23.8 mg, 0.10 mmol) and LH (36.3 mg, 0.1 mmol) at room temperature under N_2. In this case, both the LH and flaH could be deprotonated by the acetate (OAc^-) of $Cu^{II}(OAc)_2$. After stirring for 30 min, the [$Cu^{II}L(fla)$] was isolated as dark green powder by treating with ether. Olive green micro crystal was obtained by diffusion ether into the CH_2Cl_2 solution of the complex at room temperature.

The structure of [$Cu^{II}L(fla)$] comprises two crystallographically inequivalent molecules, which are different from each other slightly only in the bond lengths and angles (Fig. 2). Each Cu(II) center exhibits a distorted octahedral geometry with the N3O3 donor set consisting of two oxygen atoms from flavonolate (O(3)/O(7), 3-hydroxylate; O(4)/O(8), 4-carbonyl), one carboxylate oxygen O(1) (primary structural mimic of the carboxyl group of Glu73), and three nitrogen atoms from LH, where the three nitrogen atoms and the hydroxylate oxygen atom O(3)/O(7) from flavonolate occupy the equatorial position, and the carbonyl oxygen atom O(4)/O(8) and the carboxylate oxygen atom O(1)/O(5) of the ligand L^- occupy the axial positions. The bond lengths of Cu(1)-O(1) and Cu(2)-O(5) are 2.226(3) Å and 2.202(4) Å, respectively, which are similar to the Cu-O_{Glu73} distance (2.28 Å) of the natural ES adduct of FDO [8]. The Cu-$O_{3\text{-hydroxylate}}$ distances Cu(1)-O(3) and Cu(2)-O(7) are 1.920(2) Å and 1.956(3) Å, respectively, but the Cu-$O_{4\text{-carbonyl}}$ distances Cu(1)···O(4) and Cu(2)-O(8) are 2.479(35) Å and 2.371(3) Å, respectively, which are longer than all of the reported Cu^{II}-containing ES model complexes for FDO (Table 1), obviously, the coordinated carboxylate group renders a weaker interaction between carbonyl oxygen atom O(4)/O(8) and the Cu^{II} center. It's remarkable that the differences of the Cu-$O_{3\text{-hydroxylate}}$ and Cu-$O_{4\text{-carbonyl}}$ distances Δd(Cu–O) are 0.559 Å and 0.415 Å, respectively, which are also longer than all of the reported Cu^{II}-containing ES model complexes (Table 1). All the results indicate that the substrate flavonolate is somewhat inclined to monodentate, which may be attributed to the introduced carboxylate group. The torsion angles of C(21)–C(22)–C(30)–C(31) and C(57)–C(58)–C(66)–C(67) are 10.223(732)° and 16.625(44)°, respectively, indicating that the C(22)/C(58) atom (corresponding to C(2) of substrate flavonol, Scheme 1) in the complex has some sp3 character by pyramidalization, which is also observed in the ES adduct of the Cu^{II}-containing FDO from *Aspergillus japonicus* [5]. Such a structural feature should stabilize substrate radical fla· produced from the single electron transfer between Cu^{II} and the coordinated fla^- [21]. [$Cu^{II}L(fla)$] is the first structurally characterized Cu^{II}-containing FDO ES model complex introducing carboxylate group in the model ligand L^-, and its coordination geometry is more close to the natural ES adduct with compared to other ES model [24–30] with *N*-chelating ligands. Maybe the approximated monodentate coordination mode of flavonolate should be attributed to the carboxylate group of the ligand L^- and it may be the primary reason for the higher reactivity discussed below.

The IR spectrum of the solid sample shows a C=O stretching vibration ν(CO) of coordinated carbonyl group of flavonolate at 1543 cm^{-1}, which is red shifted compared with the free flavonol (1649 cm^{-1}) [31]. The asymmetric $\nu_{as}(CO_2)$ and symmetric $\nu_s(CO_2)$ stretching frequencies of the carboxylate group of L^- appear at 1611 and 1420 cm^{-1}, respectively. The difference between them ($\Delta\nu = \nu_{as}(CO_2) - \nu_s(CO_2)$) is about 191 cm^{-1}, rendering a monodentate carboxylate binding mode [32], it is in good accordance with the X-ray structure shown in Fig. 2.

The redox property of [$Cu^{II}L(fla)$] was performed by cyclic voltammetry under N_2 in DMF with a complex concentration of 2 mM and $KClO_4$ (0.5 M) as the supporting electrolyte. The scan rate was 50 mV s^{-1}. The experimental setup consisted of a glassy carbon working electrode, an SCE reference electrode, and a platinum wire auxiliary electrode. All potentials are reported *versus* SCE. There is a quasi-reversible redox couple appeared at $E_{1/2}$ = −0.459 V (ΔE_p = 142 mV, i_{pc}/i_{pa} = 1.06), which is comparable to the analogue [$Cu^{II}L^H(fla)$] [21] and can be assigned to the single electron transfer between Cu^{II} and Cu^{I} (Fig. 3). Interestingly, another quasi-reversible redox couple appeared at $E_{1/2}$ = +0.399 V (ΔE_p = 156 mV, i_{pc}/i_{pa} = 0.84), which can be assigned to the single

Table 1
Structural data and reactivity for synthetic Cu^{II}-containing ES model complexes.

	Cu-$O_{hydroxyl\ oxygen}$	Cu-$O_{carbonyl\ oxygen}$	△Cu-O	k ($M^{-1}\ s^{-1}$)	T (°C)
[Cu^{II}L(fla)]	1.920	2.479	0.559	1.46 ± 0.05	70
	1.956	2.371	0.415		
Enzyme-substrate adduct of Cu^{II} containing FDO	2.29	3.50	1.21		
[Cu^{I}(fla)(ind)] [27]	1.942	2.206	0.264		
[Cu^{II}(fla)(Bz-TAC)]ClO_4 [26]	1.917	2.012	0.095	$(3.31 \pm 0.01) \times 10^{-3}$	120
[Cu^{II}(bpy)(fla)]ClO_4 [28]	1.897	1.970	0.073		
[Cu^{II}(fla)$_2$] [24]	1.901	1.944	0.043	$(1.57 \pm 0.08) \times 10^{-2}$	100
[Cu^{II}(fla)(idpa)]ClO_4 [25]	1.918	2.210	0.292	$(6.13 \pm 0.16) \times 10^{-3}$	100
[Cu^{II}(6-Ph_2TPA)(fla)]ClO_4 [29]	1.921	2.010	0.089		
[Cu^{I}(PPh_3)$_2$(fla)] [23]	2.056	2.164	0.108	4.16 ± 0.48	90

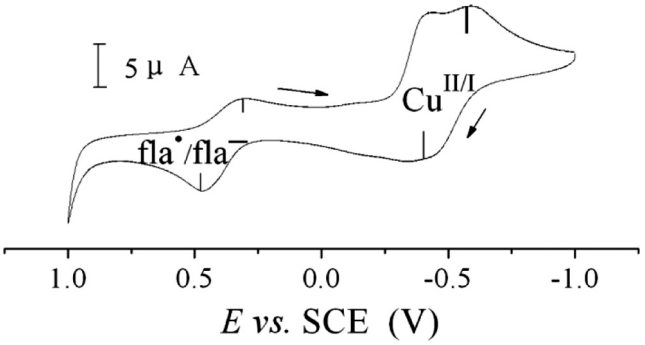


Fig. 3. Cyclic voltammogram of [Cu^{II}L(fla)] under N_2 in DMF.

electron transfer between fla^- and $fla^{\cdot}$ [21,23], this phenomenon is not observed in other Cu^{II}-containing ES model complex for FDO. The two redox couples Cu^{II}/Cu^{I} and $fla^-/fla^{\cdot}$ appear simultaneously indicates that there exists quick single electron transfer between the coordinated substrate fla^- and the Cu^{II} center as proposed in other ES model complex for Cu^{II}-FDO [10,11,21], and the $fla^{\cdot}$ is more stable in our complex, maybe the negative charge of the introduced carboxylate group should stabilize the radical $fla^{\cdot}$ through the Cu^{II} center.

The dioxygenation of [Cu^{II}L(fla)] in DMF at 70 °C give 25.4% *O*-benzoylsalicylic acid (HObs) as the primary product and then it was hydrolyzed with small amount of water in the solvent and amidated by the solvent DMF to give 60.2% benzoic acid, 73.4% salicylic acid and 12.4% *N*,*N*-dimethylbenzamide (characterized by LC-MS). The dioxygenation reaction products are similar to that of the natural ES adduct of FDO, indicating that our model complex [Cu^{II}L(fla)] has enzymatic reactivity.

Since [Cu^{II}L(fla)] exhibits an intense absorption band at 416 nm ($\varepsilon = 1.08 \times 10^4\ M^{-1}\cdot cm^{-1}$), which can be assigned to the $\pi \rightarrow \pi^*$ transition of the coordinated flavonolate [33], the dioxygenation of the complex could be followed by monitoring the disappearance of the band at 416 nm (Fig. 4a). The plots of the initial reaction rate *versus* the initial concentrations of [Cu^{II}L(fla)] (Fig. 4b) and O_2 (Fig. 4c) are both linear, so the rate law can be described as $-d[Cu^{II}L(fla)]/dt = k[Cu^{II}L(fla)][O_2]$. Thus, the reaction rate constant k was determined as $(1.46 \pm 0.05)\ M^{-1}\cdot S^{-1}$ at 70 °C ($\Delta H^{\#} = 62 \pm 2\ kJ\cdot mol^{-1}$, $\Delta S^{\#} = -63 \pm 3\ J\cdot mol^{-1}\cdot K^{-1}$) (Table S1, Fig. S1). Reactivity of the previously reported Cu^{II}-containing FDO model complexes was much lower and required high temperatures (Table 1), but our complex can react at lower temperature (50 ~ 70 °C, Table S1). Thus, [Cu^{II}L(fla)] shows the highest reactivity (Table 1) among the models reported so far. The high reactivity could be attributed to the carboxylate group of the ligand, which may make the flavonolate coordinate to the Cu^{II} center with a approximated monodentate coordination mode and enhance the reactivity of [Cu^{II}L(fla)] toward O_2 by donating electron.

On the basis of the above results, we suggest the dioxygenation mechanism of [Cu^{II}L(fla)] as shown in Scheme 2: Firstly, there is a fast equilibrium between [Cu^{II}L(fla)]/[Cu^{I}L($fla^{\cdot}$)] (A), which is more favorable than dioxygen activation. Then [Cu^{I}L($fla^{\cdot}$)] reacts with one O_2 molecular to form [Cu^{II}L($fla^{\cdot}$)] (B) and superoxide radical $O_2^{\cdot-}$ slowly by direct one electron transfer from Cu^{I} to O_2. Then B react with $O_2^{\cdot-}$ quickly and release CO.

In conclusion, we have succeeded to develop a good structural and functional ES model of flavonol 2,4-dioxygenase. The structure, properties as well as the reactivity towards O_2 have been investigated in details. The complex [Cu^{II}L(fla)] shows a higher enzymatic reactivity, which is greatly enhanced by the carboxylate group introduced in the model ligand. [Cu^{II}L(fla)] is the first structurally characterized copper(II)-flavonolate ES model complex bearing a

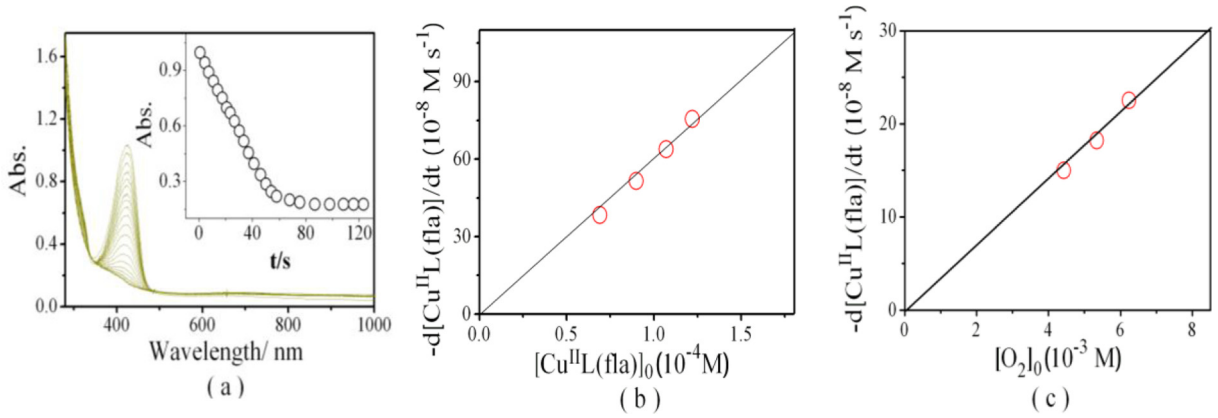
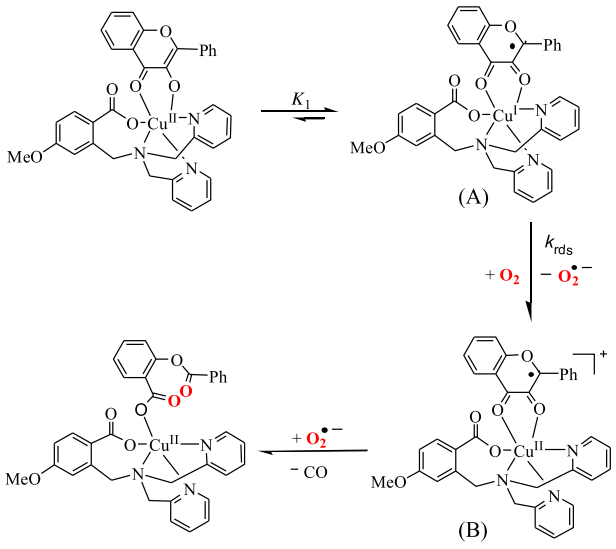


Fig. 4. Dioxygenation of the [Cu^{II}L(fla)] at 70 °C under O_2. (a) Spectral change observed upon addition of O_2 gas into a DMF solution of [Cu^{II}L(fla)] (0.901×10^{-4} M) at 70 °C. Inset: time course of the absorption changes of [Cu^{II}L(fla)] at 416 nm. Plot of $-d[Cu^{II}L(fla)]/dt$ *vs* $[Cu^{II}L(fla)]_0$. (c) Plot of $-d[Cu^{II}L(fla)]/dt$ *vs* $[O_2]_0$.



Scheme 2. Proposed dioxygenation reaction mechanism of the model complex [Cu^{II}L(fla)].

carboxylate group in the ligand for flavonol 2,4-dioxygenase. As expected, the carboxylate group coordinates to the metal ion Cu^{II}, resulting an approximated monodentate coordination mode of the substrate fla^-. The complex is the best structural ES model complex of Cu^{II}-containing flavonol 2,4-dioxygenase, and good structure makes better reactivity.

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Appendix A. Supplementary data

CCDC 1541455 contains the supplementary crystallographic data for [Cu^{II}L(fla)]. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax:(+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Additional kinetic data and eyring plot are available as electronic supplementary information in the online version, at http://dx.doi.org/10.1016/j.ica.2017.07.037.

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