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Two air oxidation copper(II) complexes of salicylaldehyde derivatives obtained by *in situ* copper(II) ion catalysis and complexation

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ABSTRACT

A new salicylaldehyde derivative **1**, i.e. 5-chloro-3-(ethoxymethyl)-2-hydroxybenzaldehyde, has been prepared and structurally characterized. A novel dinuclear copper(II) complex of its air-oxidized product **2** has been successfully yielded from the *in situ* copper(II) ion catalysis and complexation. Additionally, another control experiment has been carried out by using 3,5-dibromo-2-hydroxybenzaldehyde as the starting material, and a similar mononuclear air oxidation copper(II) complex **3** is obtained, where 3,5-dibromo-2-hydroxybenzaldehyde has also been *in situ* transformed to the divalent anion of 3,5-dibromo-2-hydroxybenzoic acid.

The oxidation of aldehydes to their corresponding carboxylic acids has been a longstanding issue in synthetic organic chemistry [1]. To date, the most popular method is using the Jones reagent [2], however, the Cr-based side products can be regarded as environmental hazards. Other efficient reagents can also achieve such transformation; for example, oxone [3], calcium hypochlorite [4] and 2-hydroperoxyhexafluoro-2-propanol [5], urea-hydrogen peroxide complex [6], etc. Furthermore, some convenient approaches, such as Baeyer–Villiger oxidation [7], Cannizzaro reaction [8], and catalyzed oxidation [9] have also been widely investigated. In catalyzed oxidation, different metal sources including $[Ni(acac)_2]$, $NiCl_2$, $Hg(OAc)_2$, $Cs_6H_2P_2W_{17}O_{61}Co\cdot H_2O$, $AgNO_3$, Au/C, Pt/C, [Fe(TPP)Cl], and CuX [10], have been utilized to promote the reactions in the presence of some oxidants such as molecular oxygen, hydrogen peroxide, dioxygen, *tert*-butyl hudroperoxide, and so on. We have also reported a series of cyano-bridged mixed-valent copper complexes (mono-, di-, tri-, and tetranuclear) obtained from *in situ* cleavage of C—C bond in acetonitrile and their effective catalysis on the oxidation of benzaldehyde by peroxide [11].

Although many reagents can oxidize aldehydes to their carboxylic acids, it is much more difficult to achieve the transformation under very mild procedures and isolate the *in situ* formed metal carboxylate complexes. To our knowledge, direct air oxidation of aldehydes to their carboxylic acids under the catalysis of $[Cu(bpy)]^{2+}$ species has not been reported before. By using a $[Cu(bpy)]^{2+}$ catalyst instead of a free copper ion, it is possible for us to isolate the copper(II) complexes of air-oxidized products because two coordination sites of copper(II) center have been previously occupied by bpy molecule which will greatly simplify the structures of final copper(II) complexes. In this work, we focus on the air oxidation of salicylaldehyde derivatives to corresponding acids under a mild experimental condition and *in situ* catalyzed by a $[Cu(bpy)(NO_3)_2]$ (bpy = 2,2′-bipyridine) complex as well as the formation of resultant mononuclear and dinuclear copper(II) complexes of air-oxidized divalent anionic carboxylates.

New organic compound **1** is prepared according to a previously reported method [12] and full characterizations have been carried out. Copper(II) complexes **2** and **3** are synthesized by the treatment of equal molar ratio of $[Cu(bpy)(NO_3)_2]$ and 5-chloro-3-(ethoxymethyl)-2-hydroxybenzaldehyde in **2** and 3,5-dibromo-2-hydroxybenzaldehyde in **3** [13], as shown in Scheme 1, where the air-oxidized products of aldehydes are formed and they are *in situ* coordinated with the copper(II) ions as bidentate dianionic ligands. It should be mentioned that no additional oxidant is introduced during the reaction and only the oxygen in air can serve as an oxidant. It is also certain to us from the reference experiment that the aldehyde cannot be oxidized so easily without the presence of a Cu^{II} ion catalyst. Routine analyses including ^1H NMR spectrum have been for characterizing related compounds **1**–**3** and their UV–vis spectra in methanol (Fig. 1) show typical intraring π–π^* absorptions and charge transfer between the C=O chromophores and their conjugated phenol rings. In addition, X-ray single-crystal diffraction method has been used for characterizing the structures of complexes **1**, **2** and **3** [14].

Molecular structure of compound **1** with the atom-numbering scheme is shown in Fig. 2a. It crystallizes in the monoclinic $P2_1/c$ space group and each asymmetric unit contains one 5-chloro-3-(ethoxymethyl)-2-hydroxybenzaldehyde molecule. The C–O bond

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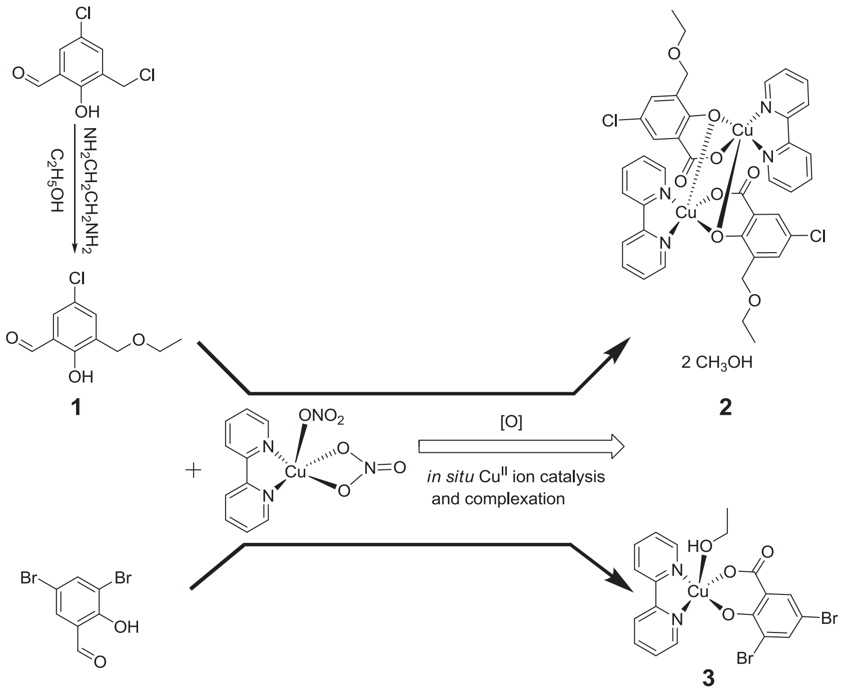

Scheme 1. Air oxidation of salicylaldehyde derivatives by *in situ* Cu^{II} ion catalytic and complexation.

lengths of phenolic and aldehyde units are 1.343(3) Å (C6–O1) and 1.212(3) Å (C7–O2), respectively, indicative of the right assignment of corresponding functional groups. However, no π–π stacking interactions can be observed between contiguous aromatic rings in the crystal packing of **1** mainly because of the steric hindrance of ethoxymethyl group.

Molecular structure of dinuclear complex **2** with the atom-numbering scheme is shown in Fig. 2b. It crystallizes in the monoclinic $P2_1/c$ space group and the coordination geometry of each copper(II) center is square pyramidal, where two nitrogen atoms from the chelating 2,2′-bipyridine ligand and two oxygen atoms from the dianion of 5-chloro-3-(ethoxymethyl)-2-hydroxybenonic acid are located at the basal coordination plane. The apical position is occupied by another phenolic oxygen atom of adjacent dianion of air-oxidized product of aldehyde **1**, and the Cu–O and Cu–N bond lengths are very analogous in the range of 1.869(4) –1.985(5) Å. The phenolic oxygen atom O3 serves as a μ_2-oxo bridging unit and the carboxylic group adopts a monodentate coordination mode with the O1–C11 and O2–C11 bond lengths of 1.293(7) and 1.224(7) Å and the O2–C11–O1 angle of 123.0(6)°, indicative of the formation of a typical carboxylate unit in **2**. The dihedral angle between the bpy and the phenol planes within the molecule is 20.4(2)° and the centroid-to-centroid separations between the phenol ring and two adjacent pyridyl rings of the same bpy molecule are 4.145(4) and 4.312(4) Å, respectively.

Molecular structure of complex **3** with the atom-numbering scheme is shown in Fig. 3. Different from the dinuclear complex **2**, it crystallizes in the triclinic $P\overline{1}$ space group and each asymmetric unit contains one mononuclear copper(II) structure. The coordination geometry of copper(II) center is elongated pyramidal, in which two nitrogen atoms from 2,2-bipyridine and two oxygen atoms from 3,5-dichloro-2-hydroxybenzaldehyde constitute the basal coordination plane while another coordination ethanol molecule occupies the apical position. The axial Cu1-O4 bond length [2.516(4) Å] is much longer than those Cu–O [1.995(4) and 2.002(4) Å] and Cu–N [1.884(3) and 1.897(3) Å] bond lengths in the coordination plane, indicative of typical Jahn–Teller distortions for the central copper(II) ion. It is also noted that the bond lengths of C7–O3 and C7–O2 are 1.235(5) and 1.279(5) Å and the bond angle of O3–C7–O2 is 122.4 (5)°, showing the presence of a typical carboxylic structure. The bpy and the phenol planes in **3** are almost parallel with the dihedral angle of 1.1(2)°. In this case, typical π–π stacking interactions are found between neighboring phenol ring and one of the pyridyl rings of bpy molecule with the centroid-to-centroid separation of 3.689 (5) Å, forming a dimeric packing fashion with two coordination ethanol molecules pointing outside of the unit.

In summary, we have firstly used the $[Cu(bpy)]^{2+}$ catalytic system in the study of *in situ* oxidation from aldehydes to their corresponding carboxylic acids in air under mild reaction. It is proved to be an efficient approach and two $[Cu(bpy)]^{2+}$ based complexes **2** and **3** have been successfully obtained by *in situ* catalysis and complexation. Two salicylaldehyde derivatives, namely 5-chloro-3-(ethoxymethyl)-2-hydroxybenzaldehyde and 3,5-dibromo-2-hydroxybenzaldehyde, undergo the aforementioned air oxidation to their corresponding salicylic acid derivatives, where steric hindrance effects of different substituent groups are believed to be responsible for the formation of a mononuclear complex in **2** and a dinuclear complex in **3** with double μ_2-oxo

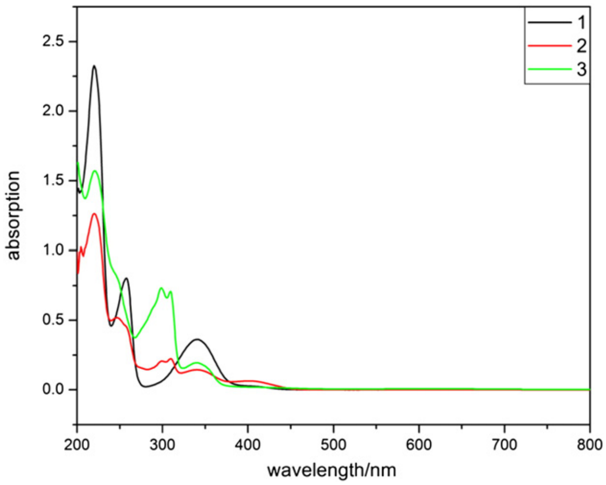

Fig. 1. UV–vis spectra of complexes **1**, **2** and **3** in methanol.

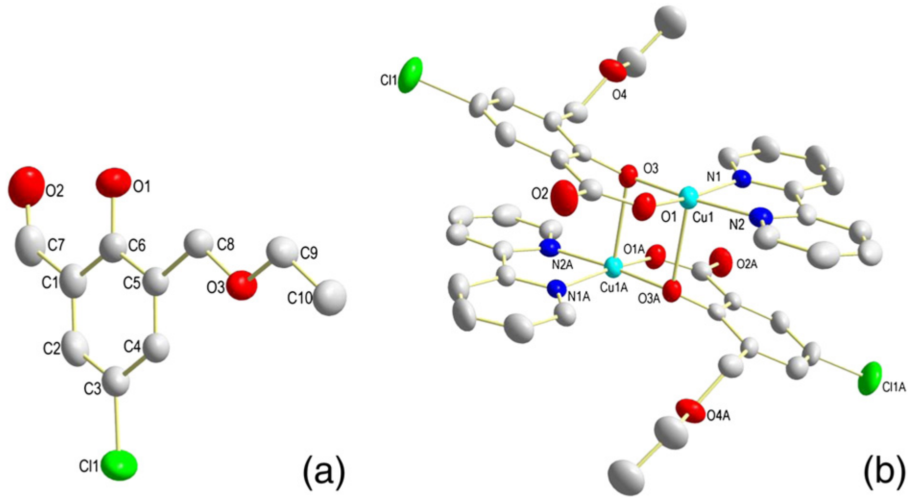

Fig. 2. ORTEP diagrams of (a) molecular structure of complex **1** and (b) molecular structure of complex **2** (A: –*x*, 2-*y*, 1-*z*) with the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): **1**: C6–O1, 1.343(3); C7–O2, 1.212(3); O2–C7–C1, 124.5(3); O2–C7–H7, 117.8; O1–C6–C1, 122.3(2); O1–C6–C5, 117.5(2). **2**: Cu1–O1, 1.869(4); Cu1–O3, 1.893(4); Cu1–N1, 1.976(5); Cu1–N2, 1.985(5); O1–C11, 1.293(7); O2–C11, 1.224(7); O3–C17, 1.331(6); O1–Cu1–O3, 93.87(16); O1–Cu1–N1, 167.97(19); O3–Cu1–N1, 93.13(19); O1–Cu1–N2, 92.1(2); O3–Cu1–N2, 173.6(2); N1–Cu1–N2, 80.6(2); O2–C11–O1, 123.0(6); O2–C11–C12, 118.7(6); O1–C11–C12, 118.3(6); O3–C17–C12, 123.9(5); O3–C17–C16, 117.0(6).

bridges. The main limitation of this study is the use of a stoichiometric catalyst. Further work is being undertaken on the effective oxidation reactions of similar aldehyde derivatives having certain chiral units in the presence of small amount of catalysts as well as similar oxidation reactions catalyzed by other complex catalysts, for example, $[Cu(bpy)_2]^{2+}$ or $[Ru(bpy)_2]^{2+}$ species.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.09.025.

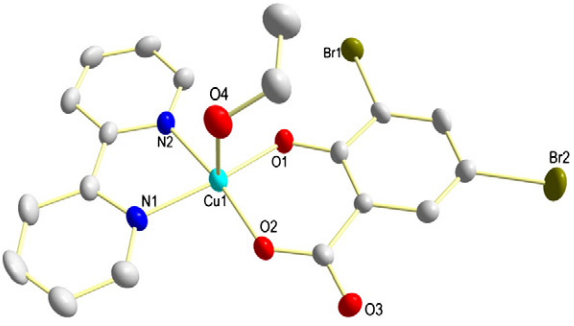

Fig. 3. ORTEP diagram of molecular structure of complex **3** with the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): **3**: Cu1–O1, 1.884(3); Cu1–O2, 1.897(3); Cu1–N2, 1.995(4); Cu1–N1, 2.002(4); Cu1–O4, 2.516(4); C7–O3, 1.235(5); C7–O2, 1.279(5); C1–O1, 1.309(5); O1–Cu1–O2, 94.9(1); O1–Cu1–N2, 91.1(2); O2–Cu1–N2, 170.9(2); O1–Cu1–N1, 170.3(2); O2–Cu1–N1, 92.8(2); N2–Cu1–N1, 80.6(2); O1–Cu1–O4, 96.0(2); O2–Cu1–O4, 91.6(2); N2–Cu1–O4, 94.7(2); N1–Cu1–O4, 89.8(2); O1–C1–C6, 126.2(4); O1–C1–C2, 117.3(4); O3–C7–O2, 122.4(5); O3–C7–C6, 118.3(4); O2–C7–C6, 119.3(4).

Appendix A. Supplementary data

CCDC 833072-833074 contain the supplementary crystallographic data for **1**, **2** and **3**. These 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.

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.09.003.

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[13] Preparation of $C_{10}H_{11}ClO_3$ (**1**), $[Cu(bpy)(C_{10}H_{11}ClO_4)]\cdot CH_3OH$ (**2**) and $[Cu(bpy)(C_7H_2Br_2O_3)(C_2H_5OH)]$ (**3**). **1**: To a solution of 5-chloro-3-(chloromethyl)-2-hydroxybenzaldehyde (1.000 g, 4.88 mmol) in ethanol (50 cm^3) was added a few drops of ethane-1,2-diamine. The mixture was heated to reflux for 2 h and then cooled down to the room temperature. After the solvent was removed, the residue was subjected to column chromatography (SiO_2; eluent, ethyl acetate:petroleum ether = 1:20) to afford compound **1** in a yield of 0.832 g (79.5% based on phenol).

Main FT-IR absorptions (KBr pellets, cm^{-1}): 3419 (m), 2862 (w), 1617 (s), 1536 (s), 1416 (s), 1122 (s), 732 (m). Elemental Anal. Calcd. for $C_{10}H_{11}ClO_3$: C 55.96; H 5.17%. Found: C 55.84; H 5.44%. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 11.18$ (1H, s), 9.88 (1H, s), 7.68 (1H, s), 7.50 (1H, s), 4.60 (2H, s) 3.64–3.68 (2H, m), 1.31–1.34 (3H, t). UV–vis in methanol: $\lambda_{max} = 342$, 258 and 220 nm. EI-TOF-MS: m/z = 140.1 [$PhCH_2ClOH$] (100%) and 170.1 [$PhCH_2ClOHCHO$] (29.9%). **2:** A solution of [$Cu(bpy)(NO_3)_2$] (80.2 mg, 0.233 mmol) in ethanol (20 cm^3) was added into a solution of **1** (50.0 mg, 0.233 mmol) in ethanol (20 cm^3). After refluxed for 2 h, the mixture was cooled to the room temperature and then left for slow evaporation in air. Finally, dark green crystals suitable for X-ray diffraction determination were obtained after several days. Yield: 47.5 mg (41.3% based on metal). Main FT-IR absorptions (KBr pellets, $cm–^1$): 3419 (w), 1617 (s), 1417 (m), 1122 (m), 732 (m). Elemental Anal. Calcd. for $C_{42}H_{42}Cl_2Cu_2N_4O_{10}$: C 52.50; N 5.83; H 4.41%. Found: C 52.22; N 5.99; H 4.74%. UV–vis in methanol: $\lambda_{max} = 405$, 299, 245 and 221 nm. Positive ESI-MS in methanol: m/z = 401.15 [$Cu(bpy)C_6H_2COOClCO$]$^+$. **3**: Complex **3** was prepared in the same method as complex **2**. The only difference is using 3,5-dibromo-2-hydroxybenzaldehyde (50.0 mg, 0.179 mmol) instead of 5-chloro-3-(ethoxymethyl)-2-hydroxybenzaldehyde and the mass of [$Cu(bpy)(NO_3)_2$] was reduced to 61.6 mg (0.179 mmol). Yield: 42.7 mg (42.7% based on metal). Main FT-IR absorptions (KBr pellets, cm^{-1}): 3415 (s), 1599 (m), 1445 (m), 1244 (w), 1099 (w). Elemental Anal. Calcd. for $C_{19}H_{16}Br_2CuN_2O_4$: C 40.77; N 5.01; H 2.88%. Found: C 40.43; N 4.76; H 3.07%. UV–vis in methanol: $\lambda_{max} = 299$, 268 and 222 nm. Positive ESI-MS in methanol: m/z = 513.75 [$M-C_2H_5OH$]$^+$ (100%).

[14] Single crystal samples of **1**, **2** and **3** were glue-covered and mounted on the top of the glass fibers and used for data collection on a Bruker SMART 1K CCD diffractometer at 291(2) K using graphite mono-chromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystallographic data for $C_{10}H_{11}ClO_3$ (**1**): $M = 214.64$ g/mol, light green, needle, $0.10 \times 0.12 \times 0.14$ mm, monoclinic, space group $P2_1/c$ (No. 14), $a = 13.804(13)$, $b = 9.238(9)$, $c = 8.435(6)$ Å, $\alpha = 90°$, $\beta = 103.31(3)°$, $\gamma = 90°$, $V = 1046.8(16)$ Å^3, $Z = 4$, $Dc = 1.362$ g/cm^3, $\mu = 0.343$ mm^{-1}, $F(000) = 448$, $S = 0.98$. $R1 = 0.0439$, $wR2 = 0.1127$. For $C_{42}H_{42}Cl_2Cu_2N_4O_{10}$ (**2**): $M = 960.78$ g/mol, dark green, needle, $0.10 \times 0.11 \times 0.11$ mm, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.057(3)$, $b = 23.761(9)$, $c = 13.076(4)$ Å, $\alpha = 90°$, $\beta = 117.390(18)°$, $\gamma = 90°$, $V = 2222.7$ (14) Å^3, $Z = 2$, $Dc = 1.436$ g/cm^3, $\mu = 1.136$ mm^{-1}, $F(000) = 988$, $S = 0.79$. $R1 = 0.0581$, $wR2 = 0.1529$. For $C_{19}H_{16}Br_2CuN_2\ O_4$ (**3**): $M = 559.70$ g/mol, dark green, block, $0.10 \times 0.11 \times 0.12$ mm, triclinic, space group $P\ 1$ (No. 2), $a = 9.614(7)$, $b = 10.725(8)$, $c = 11.723(8)$ Å, $\alpha = 63.870(9)°$, $\beta = 81.907(10)°$, $\gamma = 71.562(10)°$, $V = 1029.6(13)$ Å^3, $Z = 2$, $Dc = 1.805$ g/cm^3, $\mu = 4.969$ mm^{-1}, $F(000) = 550$, $S = 0.63$. $R1 = 0.0382$, $wR2 = 0.0580$.