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PAPER

A novel dinuclear Schiff-base copper(II) complex modified electrode for ascorbic acid catalytic oxidation and determination†

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A new dinuclear copper salicylaldehyde-glycine Schiff-base complex $[Cu_2(Sal\text{-}Gly)_2(H_2O)_2]$ was synthesized and structurally characterized. $[Cu_2(Sal\text{-}Gly)_2(H_2O)_2]$ crystallized in the monoclinic system in the $P2_1/c$ space group. The molecule is a dinuclear complex, formed by two $[Cu(Sal\text{-}Gly)(H_2O)]$ units. The electropolymerization properties of the copper complex on a glass carbon electrode were studied at different potential ranges. The electropolymerization occurred when the high scan potential reached 1.4 V. The modified electrode exhibited good electrocatalytic oxidation properties to ascorbic acid and showed a sensitivity of 22.9 nA μM^{-1} ($r^2 = 0.9998$) and detection limit of 0.39 μM (S/N = 3) in the amperometric determination of ascorbic acid. The designed determination method can be used to analyze vitamin C tablets.

Introduction

Ascorbic acid (vitamin C, H_2A) is one of the most important water-soluble small-molecular-weight antioxidants and free-radical scavengers that is used in a large scale in food, beverages, cosmetic and pharmaceutical formulations applications.[1] Moreover, H_2A has been recognized as a neuromodulator for dopamine (DA) and glutamate involved in physiological processes.[2] Due to the important applications and biofunctions, fast and accurate determination of H_2A is required. Various methods have been employed for the analysis of ascorbic acid, including titration,[3] HPLC,[4] UV,[5] fluorimetry,[6] *etc.* Because of the good analytical properties, electroanalytical techniques have also been frequently used for H_2A determination.[7] However, a high overpotential emerged, as well as a low detection current, for direct electrooxidation of ascorbic acid at bare electrodes. This is because the oxidative product adsorbs on the electrode surface and results in electrode fouling.[8] Therefore modified electrodes, especially transition-metal complex modified electrodes, have largely been used as electron mediators for ascorbic acid catalytic oxidation and determination.[9] The modification can lower the overpotential and give a higher response current to improve the detection sensitivity. The electrocatalytic oxidation of ascorbic acid by the modified metal complexes in aqueous solution is considered to be *via* an electron-transfer mechanism. In most cases, the predominant reactive species is the ascorbate ion HA^- which is oxidized by electron transfer followed by deprotonation to give the ascorbyl radical ($A^{\bullet -}$). Then $A^{\bullet -}$ is rapidly converted to dehydroascorbic acid (dA).[10]

Transition-metal salicylaldehyde Schiff-base complexes have been broadly studied and showed a wide variety of properties, such as DNA binding and cleavage activities,[11] antimicrobial and antitumor activities,[12] antiradical activity,[13] organic catalysts,[14] and also a catalyst for H_2A oxidation.[15] Moreover, transition-metal salicylaldehyde Schiff-base complexes were reported to show good electropolymerization properties on electrode surfaces to form a conductive film.[16] Thus they are potential complexes that can be used to modify electrodes for electrocatalytic oxidation and detection of H_2A.

In the present work, we synthesized a new dinuclear copper salicylaldehyde-glycine Schiff-base complex. Its electropolymerization on a glass carbon electrode (GC) and the electrocatalytic activity of the modified GC to the oxidation of H_2A were studied. Then the determination of H_2A with the modified GC by an amperometric method was performed. Finally the proposed method was applied to analysis of vitamin C tablets.

Results and discussion

X-Ray crystal structure determination

Details of the crystal parameters, data collection and refinements are listed in Table 1. $[Cu_2(Sal\text{-}Gly)_2(H_2O)_2]$ was found to crystallize

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Table 1 Crystal data and structure refinement for $[Cu_2(Sal\text{-}Gly)_2(H_2O)_2]$

Empirical formula	$C_{24}H_{26}Cu_2N_2O_{12}$
M_r	661.55
T/K	298(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	13.3741(19)
b/Å	16.9121(10)
c/Å	14.204(2)
β/°	104.985(2)
V/Å^3	1268.4(3)
Z	2
D_c/g cm^{-3}	1.732
μ/mm^{-1}	1.747
$F(000)$	676
θ range for data collection/°	2.97–28.22
Limiting indices, hkl	−17 to 15, − 9 to 7, −17 to 18
Reflections collected/unique	3110/2324
R_{int}	0.0708
Data/restraints/parameters	2324/3/188
Goodness-of-fit on F^2	0.956
Final R indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0651$, $wR_2 = 0.0924$
R indices (all data)^a	$R_1 = 0.0461$, $wR_2 = 0.0854$
$\Delta\rho_{max,\,min}$/e Å^{-3}	0.560, −0.339

^{a} $R_1 = \sum\|F_o\| - |F_c\|/\sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ where $w = q/\sigma^2(F_o^2) + (aP)^2 + bP$.

Table 2 Selected bond distances (Å) and angles (°) for $[Cu_2(Sal\text{-}Gly)_2(H_2O)_2]$

Cu1–N1	1.925(2)	Cu1–O1	1.9556(19)
Cu1–O2	1.9459(19)	Cu1–O1′	1.9911(18)
Cu1–O6	2.544(3)	Cu1 ··· Cu1′	3.0141(7)
N1–Cu1–O2	84.03(9)	O1–Cu1–O1′	80.42(8)
N1–Cu1–O1	93.64(9)	N1–Cu1–O6	87.93(9)
O2–Cu1–O1	173.86(9)	O2–Cu1–O6	90.26(9)
N1–Cu1–O1′	173.69(9)	O1–Cu1–O6	83.97(8)
O2–Cu1–O1′	102.09(8)	N1–Cu1–Cu1′	134.25(7)
O2–Cu1–Cu1′	141.58(6)	O1′–Cu1–Cu1′	39.77(5)
O1–Cu1–Cu1′	40.65(5)	O6–Cu1–Cu1′	88.43(6)

Table 3 Overview of hydrogen bond lengths (Å) and angles (°)

D–H ··· A	d(D–H)	d(H ··· A)	d(D ··· A)	∠D–H ··· A
O6–H6A ··· O3 (i)	0.82(3)	2.30(4)	3.005(3)	146(4)
O6–H6B ··· O3′(ii)	0.82(2)	1.99(3)	2.784(3)	162(3)

Symmetry code: i = 1 − x, −1/2 + y, 3/2 − z; ii = x, 3/2 − y, −1/2 + z.

in the monoclinic system in the $P2_1/c$ space group. The molecule is a dinuclear complex, formed by two [Cu(Sal-Gly)(H_2O)] units. The perspective view along the b axis of the structure is shown in Fig. 1(A) and selected bond lengths and angles are summarized in Table 2. The Cu^{II} ion is five-coordinated in a square-pyramidal configuration, with one imine N atom (N1), one phenolate O atom (O1), one carboxylate O atom (O2) of the Schiff-base and one phenolate O atom (O1′) of the other Schiff-base moiety defining the basal plane, and the O atom (O6) of a coordinated water molecule occupying the apical position. The bond length of Cu1–O6 is much longer than other Cu–O bond lengths indicating the occurrence of a strong Jahn–Teller effect. The Cu^{II} atoms are bridged by two phenolic O atoms (O1, O1′), with a Cu ··· Cu distance of 3.0141 (7) Å, falling in the relatively small range of 2.93–3.10 Å indicative of weak metal–metal interactions.[17] The two units are nearly coplanar, with the least-square plane Cu1, O1, O2, N1, Cu1′, O1′, O2′, N1′ deviations ranging from −0.085(2) to 0.085(2) Å. The Cu distance from the equatorial coordination least-squares plane is only 0.0298(4) Å for Cu1 and −0.0300(4) Å for Cu1′. The structure is somewhat different from most of other reported dinuclear copper salicylaldehyde-amino acid Schiff-base complexes, in which the two coordination units of the molecules are not in a plane.[18] Only two similar structures were found for this kind of dinuclear copper complex.[19]

For $[Cu_2(Sal\text{-}Gly)_2(H_2O)_2]$, the packing structure view towards the (1 0 0) plane is shown in Fig. 1B. In the crystal structure, there are two kinds of hydrogen-bond interactions among the molecules: O6–H6A ··· O3i (i = 1 − x, −1/2 + y, 3/2 − z) and O6–H6B ··· O3′ii (ii = x, 3/2 − y, −1/2 + z) (see Table 3). The hydrogen bonds are formed between the coordinated water and carboxyl oxygen. Through the hydrogen bonds, the four oxygen atom (O6, O3′ii, O6′, O3ii), from the four adjacent molecules, are connected to form a four-membered ring (see Fig. 1B), that was also found in other reported dinuclear copper Sal-Gly Schiff-base complexes.[18c] The molecules are linked by these hydrogen bonds,

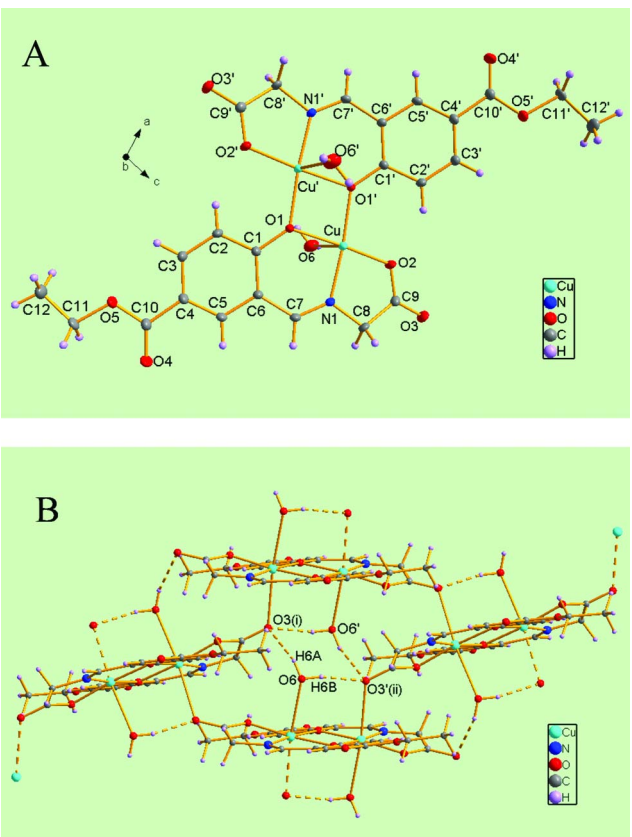


Fig. 1 (A) View of $[Cu_2(Sal\text{-}Gly)_2(H_2O)_2]$ along the b axis with the atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at 30% probability level. (B) View of crystal packing towards the (1 0 0) plane with hydrogen bonds. Symmetry code: i = 1 − x, −1/2 + y, 3/2 − z; ii = x, 3/2 − y, −1/2 + z.

Cu1–O3 and Cu1′–O3′ bonds (2.5572(21) Å) forming an infinite two-dimensional network in the (1 0 0) plane.

Electrochemical polymerization

Cyclic voltammetry (CV) curves for electropolymerization of $[Cu_2(Sal\text{-}Gly)_2(H_2O)_2]((L)Cu^{II})$ in DMSO at the potential range of –0.3 to 1.4 V are illustrated in Fig. 2A. The cyclic voltammogram exhibits three anodic peaks at 0.22 (I), 0.53 (II) and 0.91 V (III). Peaks I and II are ascribed to oxidation of $(L)Cu^{I}$ to $(L)Cu^{II}$ and $(L)Cu^{II}$ to $(L)Cu^{III}$, respectively. Peak III corresponds to the electron transfer from predominantly ligand-centered orbitals[16b,20] that was also present in previously reported anodic oxidation of metal-salen complexes.[16a,21] The $(L)Cu^{II}/(L)Cu^{I}$ reductive peak was observed at about 0 V (I′). The redox peaks increase with subsequent scans for over 40 cycles, demonstrating that copper-salen films are continuously deposited on the electrode surface.[22] The electropolymerization did not occur at low scan potentials (Fig. 2B) as found in the electropolymerization of tetraruthenated nickel-porphyrin,[23] indicating electropolymerization of $(L)Cu^{II}$ needs a high potential. Plots of the selected peak I′ *vs.* the cycle number are shown in inset b. The growth rate of peak I′ decreased with the number of scanning passes, indicating that the conductivity decreased with deposition.[16a,24]

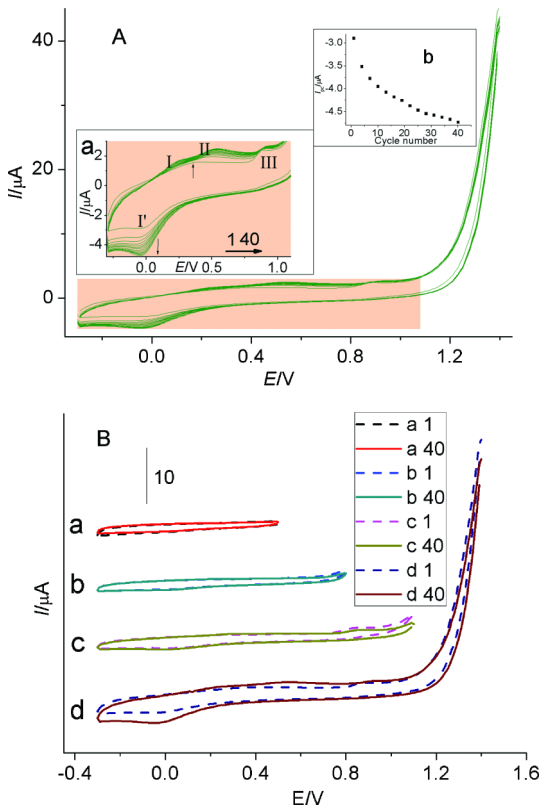


Fig. 2 Cyclic voltammetry for electropolymerization of 1 mM $(L)Cu^{II}$ in DMSO 0.1 M $NaNO_3$ (supporting electrolyte) on GC, 50 mV s^{-1}. (A) Electropolymerization cycles from 1, 5, … , 40 at –0.3 to 1.4 V; inset (a) is an amplified figure, insert (b) is the plot of reduction peak current *vs.* scans. (B) Electropolymerization at different potential ranges: (a) –0.3 to 0.5 V, (b) –0.3 to 0.8 V, (c) –0.3 to 1.1 V, (d) –0.3 to 1.4 V; dashed line is the first cycle, solid line is the 40th cycle.

The apparent surface coverage (Γ) of modified electrode is 2.95×10^{-9} mol cm^{-2} estimated by integrating the charge under the reduction peak of Cu(II)/Cu(I), using eqn (1).

$$\Gamma = Q/nFA \quad (1)$$

where Q/C is the charge under the metal oxidation peak, n (= 1) is the number of electrons, A is the effective area of the electrode (calculated from eqn (1)) and F is the Faraday constant (95 485 C mol^{-1}).[25]

A scan rate dependent study was conducted on poly$(L)Cu^{II}$ ($P(L)Cu^{II}$) in a monomer-free DMSO solution containing 0.1 M $NaNO_3$ and is shown in Fig. 3. As shown in the inset of Fig. 3, the peak currents increased linearly with sweep rate up to 200 mV s^{-1}, which is consistent with the voltammetric response for a surface confined film.[25] This result indicates a strongly adsorbed electroactive material that is not limited by the ionic flux of counter ions and also implies conductivity of the polymer film.[26]

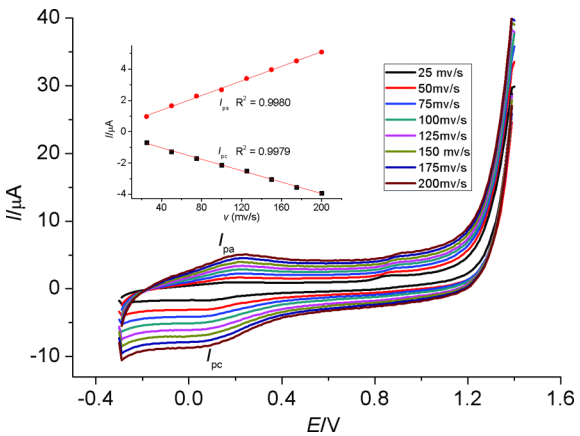


Fig. 3 $P(L)Cu^{II}$ scan-rate dependence. Inset: plot of linear current increase *vs.* scan rate.

Electrochemistry impedance spectrum (EIS) is a useful tool for studying the interface properties of surface modified electrodes.[27] It can give information on the impedance changes in the modification process. The complex impedance can be presented as a combination of the real impedance (Z') and imaginary impedance (Z''), Nyquist plot. The Nyquist plots of EIS investigations of bare GC and $P(L)Cu^{II}$ modified GC registered in 0.1 M KCl containing 5 mM mol equiv. of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ are shown in Fig. 4. The inset figures show the Randle's equivalent circuit corresponding to the Nyquist plots, top for bare GC, bottom for modified GC. In these circuits, R_s is the solution resistance, CPE_f the constant phase element referred as film capacitance, R_f the film resistance, CPE_{dl} the constant phase element that represents all the frequency dependent electrochemical phenomena, namely double-layer capacitance, R_{ct} the charge transfer resistance, and W the Warburg impedance resulting from the diffusion of charged species from the bulk of the electrolyte solution to the interface and through the interface layer.[28] The values of the equivalent circuit elements are shown in Table 4. R_{ct} increased significantly when GC was modified as well as the CPE_{dl}. And also the new elements R_f and CPE_f were presented because of the $P(L)Cu^{II}$ formation.

Electrocatalytic oxidation of ascorbic acid

The remarkable electrocatalytic properties of the modified electrode towards the oxidation of ascorbic acid in pH 6.8 PBS (0.1 M KCl) are demonstrated in Fig. 5. At a bare GC, an irreversible oxidation peak was observed at 0.28 V with a current of 20 μA

Table 4 Fitting values of the equivalent circuit elements for bare and modified GC

	R_s/Ω	$10^5 CPE_{dl}/F$	R_{ct}/Ω	W/Ω	R_f/Ω	$10^6 CPE_f/F$)
B-GC	82.1	3.059	189.6	0.00168		
M-GC	100.1	40.25	2399	0.0032	1505	8.568

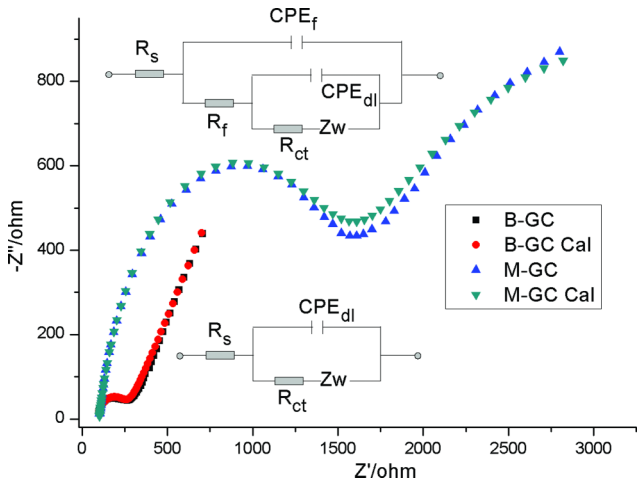


Fig. 4 Nyquist plots of bare and modified GC in 5 mM $Fe(CN)_6^{3-/4-}$ solution containing 0.1 M KCl, in the frequency range 0.1 to 20 kHz. B-GC and M-GC are the experimental data for bare GC and modified GC, respectively, Cal is calculated data. Insets show Randle's equivalent circuits, top for bare GC, bottom for modified GC

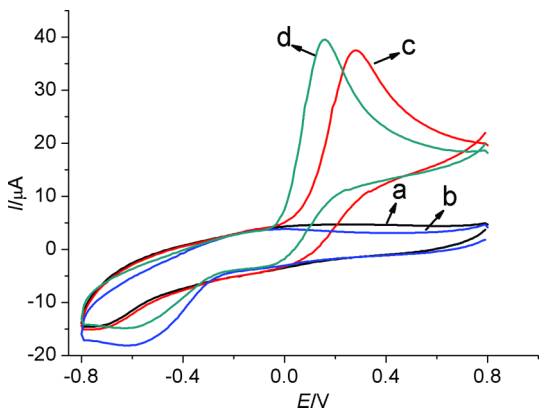
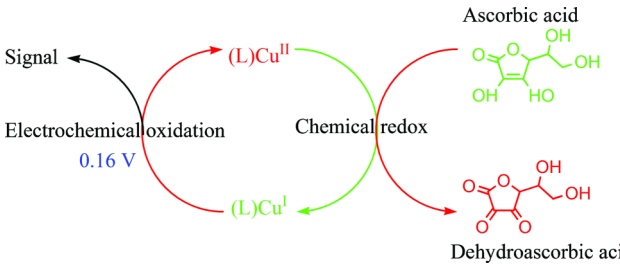


Fig. 5 CVs of bare (a, c) and modified GC (b, d) electrodes in pH6.8 PBS (0.1 M KCl) solution: H_2A = 0 mM (a, b), 3 mM (c, d); scan rate 100 mV s^{-1}

(Fig. 5c). At the modified GC, the oxidation peak shifted to 0.16 V and the current increased to 35 μA (Fig. 5d). The remarkable enhancement in the peak current and the lowering of overpotential provided clear evidence of the catalytic effect of $P(L)Cu^{II}$ toward H_2A.[7a,9a,29]

The electrochemical oxidation of H_2A is considered to undergo two consecutive one-electron transfer processes involving the participation of a radical anion intermediate to form dehydroascorbic acid (dA).[30] This species subsequently undergoes a hydration reaction characteristic of carbonyl groups to form an electroinactive product. The electrocatalytic oxidation of ascorbic acid at the modified electrode can be described by the following equations and Scheme 1:



Scheme 1 Reaction mechanism of ascorbic acid at the modified electrode.

$$H_2A \rightleftarrows HA^- + H^+ \quad (2)$$

$$HA^- + (L)Cu^{II} \rightleftarrows A^{\bullet -} + H^+ + (L)Cu^{I} \quad (3)$$

$$A^{\bullet -} + (L)Cu^{II} \rightleftarrows dA + (L)Cu^{I} \quad (4)$$

$$(L)Cu^{I} - e^- \rightleftarrows (L)Cu^{II} \quad (5)$$

Here, pK_{a1} for ascorbic acid is about 4.5,[30b] so the predominant reactive species is the ascorbate ion HA^-. HA^- is initially oxidized by $(L)Cu^{II}$ to produce the ascorbate radical anion ($A^{\bullet -}$) and $(L)Cu^{I}$, $A^{\bullet -}$ is subsequently oxidized by $(L)Cu^{II}$ to produce dehydroascorbic acid (dA) and $(L)Cu^{I}$. $(L)Cu^{I}$ is finally electrochemically oxidized to give an anodic peak shown in Fig. 5d, which indicated both the Cu(I) centers in $[Cu^{I}_2L_2(H_2O)_2]$ undergo simultaneous oxidation at 0.16 V.[31]

Amperometric determination of H_2A

Amperometric experiments of H_2A were carried out using $P(L)Cu^{II}$ modified GC in a well-stirred PBS (pH 6.8) solution with 0.1 M KCl as supporting electrolyte. The oxidation peak currents were measured at 0.2 V and plotted against the bulk concentration of H_2A after background subtraction (Fig. 6A and B). The modified GC electrode has high sensitivity and specificity to ascorbic acid. It has almost no response in a 10 μM citric acid (CA), glucose and H_2O_2 solution but an obvious current increase when 2 μM H_2A was injected to the system (Fig. 6A). The electrode also showed a relatively rapid response time with the current increasing and reaching a steady-state within only 20 s. The amperometric response was found to be linear to the H_2A concentration over the range 2–500 μM with a sensitivity of 22.9 nA μM^{-1}, $r^2 = 0.9998$. The detection limit is 0.39 μM (S/N = 3). The reconstructed $P(L)Cu^{II}$ modified GC used for H_2A titration showed a sensitivity of 21.7 nA μM^{-1}, $r^2 = 0.9999$, indicating that the $P(L)Cu^{II}$ modified electrode had a good reproducibility. The different aspects of proposed method compared with those from recent references are listed in Table S1 (ESI†). From the data shown in Table S1, our proposed set-up has a wide linear

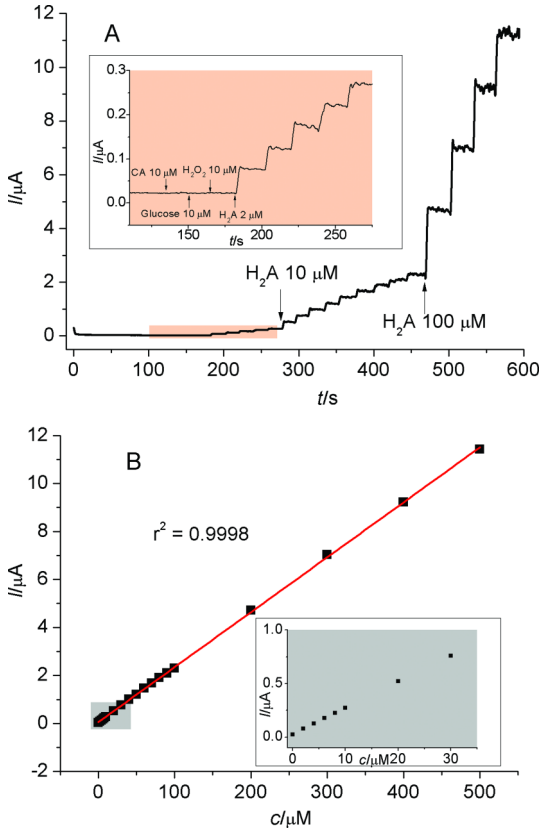


Fig. 6 Typical amperometric curve obtained with a modified GC in pH 6.8 PBS (0.1 M KCl) at an applied potential of 0.2 V *vs.* SCE: (A) successive injection of H_2A in the range 2–500 μM, (B) the corresponding standard addition plots.

range similar to that reported in the literature, with an oxidation potential and detection limit lower than most of the reported values.

The proposed method was further applied to analyze vitamin C tablets. The recovery was studied by the corresponding tablets added with certain value of standard solution of H_2A. The determination results are shown in Table 5. The RSD and recovery were in the range of 0.01–1.09% and 94.76–103.9%, respectively, which were acceptable,[7a] showing that the proposed method can be used for sample determination and presented a good stability.

Conclusion

The new dinuclear copper salicylaldehyde-amino acid Schiff-base complex $[Cu_2(Sal\text{-}Gly)_2(H_2O)_2]$, crystallizing in the $P2_1/c$ space group, contains two symmetric units connected through Cu–O bonds. Unlike the reported dinuclear copper salicylaldehyde-amino acid Schiff-base complexes, the two units of the molecule here are nearly coplanar. This copper complex can be electropolymerized on a glass carbon electrode when the high scan potential reached 1.4 V, but at low scan potential no polymerization occurred. The complex modified electrode showed good electrocatalytic oxidation properties to ascorbic acid that leads to a lower oxidation potential and higher oxidation peak than for bare GC in CV scans. This modified electrode can show amperometric determination of H_2A with a sensitivity of 22.9 nA μM^{-1} ($r^2 = 0.9998$) and detection limit of 0.39 μM (S/N = 3). It showed acceptable RSD and recovery in the analysis of vitamin C tablets showing that the present system could be used for sample determination.

Experimental

Materials and instrumentation

All common reagents were of analytical grade and used as received. The vitamin C tablets were purchased from Hubei Huazhong Pharmaceutical Co., Ltd. (20101142) and Guangxi Zhengtang Pharmaceutical Co., Ltd. (20100901) with the specified amount of 100 and 49.5 mg per tablet, respectively.

The crystal structure was determined using a Bruker SMART APEX CCD-based diffractometer. Infrared spectra were recorded on a Nicolet AVATAR360 spectrometer as KBr pellets (4000–400 cm^{-1}), elemental analysis was performed on a Vario EL-III CHNSO Elementar, ^1H NMR spectra were obtained on a Mercury Plus 400 NMR spectrometer in $CDCl_3$ solvent, the electronic spectrum of DMSO solution of $[Cu_2(Sal\text{-}Gly)_2(H_2O)_2]$ ($c = 1 \times 10^{-4}$ M) was measured in the 200–800 nm region on a Lambda35 spectrometer.

Synthesis of ligand

3-Formyl-4-hydroxybenzoic acid ($C_8H_6O_4$). 3-Formyl-4-hydroxybenzoic acid was prepared according to the literature[32] with slight modification. 20.0 g of NaOH was dissolved in 40 mL of water and 10 mL of methanol and 10 g of 4-hydroxybenzoic acid were added. 20 mL of chloroform was added dropwise later at 60 °C. After refluxing at 60 °C for 10 h, the solution was sufficiently cooled with ice and filtered to obtain a slightly yellow solid. The crude product was dissolved by concentrated ammonia and precipitated by 15% $CuSO_4$ to obtain a green precipitate. Then, the green precipitate was dissolved in hot sulfuric acid solution and cooled to obtain the white product, yield 30%. Anal.

Table 5 Detection of H_2A in vitamin C tablets

Sample	Specified (mg)	Detected (mg) ($n = 5$)	RSD (%)	Added (μM)	Detected (μM)	Recovery (%)
HZ-1[a]	100	89	1.09	10	9.825	98.25
HZ-2	100	92	0.28	20	20.79	103.9
HZ-3	100	88	0.47	10	9.782	97.82
ZT-1[b]	49.5	44.7	0.01	10	10.16	101.6
ZT-2	49.5	47.2	0.70	10	9.782	97.82
ZT-3	49.5	46.3	0.42	10	9.476	94.76

[a] Tablets from Hubei Huazhong Pharmaceutical Co., Ltd. [b] Tablets from Guangxi Zhengtang Pharmaceutical Co., Ltd.

Calc. for $C_8H_6O_4$: C 57.83, H 3.61. Found: C 57.85, H 3.62%. Mp 240–242 °C. Significant IR bands (KBr, ν cm^{-1}): 3550–3200 ν(O–H), 1669 ν(C═O), 1319 ν(C–H, aldehyde), 1288 ν(C–O). ^{1}H NMR ($CDCl_3$) δ/ppm: 7.08 (d, 1H, ph-H), 8.26 (d, 1H, ph-H), 8.398 (s, 1H, ph-H), 9.98 (s, 2H, CHO), 11.49 (s, 1H, OH).

3-Formyl-4-hydroxybenzoic acid ethyl ester ($C_{10}H_{10}O_4$). 3-Formyl-4-hydroxybenzoic acid (0.02 mol, 3.32 g) was dissolved in 20 mL ethanol and then 1 mL sulfuric acid was added with stirring. After refluxing for 10 h the solution was added into 200 mL cold water to obtain the crude product. The crude product was extracted by 0.01 M sodium carbonate aqueous solution and then dried in vacuum to obtain a pure white solid (81%). Anal. Calc. for $C_{10}H_{10}O_4$: C 61.86, H 5.15. Found C 61.79, H 5.30%. Mp 60.2–60.8 °C. Significant IR bands (KBr, ν cm^{-1}): 3401 ν(O–H), 1709 ν(C═O, aldehyde), 1661 ν(C═O, ester), 1281 ν(C_{ph}–O), 1214, 1179 ν(C–O–C). ^{1}H NMR ($CDCl_3$) δ/ppm: 1.41 (t, 3H, CH_3), 4.39 (m, 2H, CH_2), 7.04 (d, 1H, ph-H), 8.20 (d, 1H, ph-H), 8.33 (s, 1H, ph-H), 9.96 (s, 1H, CHO), 11.39 (s, 1H, OH).

Synthesis of complex $[Cu_2(Sal\text{-}GLy)_2(H_2O)_2]$

3-Formyl-4-hydroxybenzoic acid ethyl ester (1 mmol, 0.194 g) and glycine (1.2 mmol, 0.090 g) were dissolved in aqueous methanol (80%, 20 mL). The mixture was stirred at room temperature for 30 min to give a clear yellow solution. Then an aqueous solution (10 mL) of copper acetate (1 mmol, 0.200 g) was added with stirring. The mixture was stirred and refluxed at 323 K for 6 h, then cooled to room temperature. After filtration, the filtrate was left to stand at room temperature. Green crystals were obtained after two weeks, yield 0.204 g (61.5%). Anal. Calc. for $C_{24}H_{26}Cu_2N_2O_{12}$: C 43.53, N 4.23, H 3.93; found C 43.77, N 4.26, H 3.89%. Significant IR bands (KBr, ν cm^{-1}): 3420 ν(O–H, coord. water), 1690 ν(C═O, ester), 1605 ν_{as}(COO^-), 1646 ν(C═N), 1375 ν_s(COO^-), 1276 ν(C_{ph}–O), 1240, 11193 ν(C–O–C). UV-Vis (DMSO, $c = 1 \times 10^{-4}$ M) λ_{max} = 361 (3.77), 297 (4.36), 264 (log ε = 4.31) nm.

X-Ray crystallography

Details of the crystal parameters, data collection and refinements are listed in Table 1. Diffraction data were collected on a Bruker SMART APEX CCD diffractometer with a graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation source using the ω–2θ scan technique at 298(2) K. Raw data collection and cell refinement were achieved using SMART; data reduction was performed using SAINT$^+$ and corrected for Lorentz and polarization effects. Absorption corrections were applied using the SADABS routine.[33] The structure was solved by direct methods using SHELXTL and was refined by full-matrix least-squares on F^2 using SHELX-97.[34] Visualization of the structures was performed using DIAMOND.[35] All non-hydrogen atoms were refined anisotropically. All non-solvent H-atoms were located in their calculated positions and treated as riding on the atoms to which they were attached with isotropic displacement parameters U_{iso} values were set to 1.2U_{eq} for aryl H and 1.5U_{eq} for methyl H and amino H. Hydrogen atoms riding on H_2O were placed in optimised positions and refined isotropically to be constrained to ride on their parent atom.

Electrochemical measurements

Electrochemical measurements were controlled on a CH Instruments model 660B Electrochemical Workstation (Shanghai Chenhua Instruments, Shanghai) using a three electrode set-up comprising of a glassy carbon disc (surface area of 0.071 cm^2) working, platinum wire auxiliary and a saturated calomel reference (SCE) electrode (All potentials relative to this electrode).

Electropolymerization was performed in nitrogen-saturated DMSO solution containing 5×10^{-4} M copper complex and 0.1 M $NaNO_3$ as supporting electrolyte. The modified electrode was used to perform the scan-rate dependent study in nitrogen saturated DMSO solution. The EIS was performed in 5 mM equiv. molar ratio of $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ solution containing 0.1 M KCl, at 0.188 V and frequency ranges from 0.1 to 20 kHz.

Electrocatalytic oxidation of ascorbic acid and amperometric determination of H_2A were all performed in pH 6.8 PBS solutions containing 0.1 M KCl with a volume of 8 mL. Amperometric determination was performed at an applied potential of 0.2 V *vs.* SCE and 8 µL of different concentrations of H_2A were injected to the electrolytic cell successively with constant magnetic stirring. For the vitamin C tablets analysis, the ground vitamin tablets were dissolved in double distilled water. 8 µL of tablet solution was injected to the determination system five times and then 8 µL of H_2A solution of known concentration was added.

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References

1 (*a*) M. N. Zhang, K. Liu, L. Xiang, Y. Q. Lin, L. Su and L. Q. Mao, *Anal. Chem.*, 2007, **79**, 6559; (*b*) H. A. Kontos, *Stroke*, 2001, **32**, 2712.
2 G. Glgelashvili and A. Schousboe, *Brain Res. Bull.*, 1998, **45**, 233.
3 R. Kirk and R. Sawyer, *Pearson's Composition and Analysis of Food*, 9th edn, Longman, Harlow, UK, 1991.
4 (*a*) E. S. Wagner, B. Lindley and R. D. Coffin, *J. Chromatogr.*, 1979, **153**, 225; (*b*) A. Khan, M. I. Khan, Z. Iqbal, Y. Shah, L. Ahmad, S. Nazir, D. G. Watson, J. A. Khan, F. Nasir, A. Khan and Ismail, *Talanta*, 2011, **84**, 789.
5 W. M. Zeng, F. Martinuzzi and A. MacGregor, *J. Pharm. Biomed. Anal.*, 2005, **36**, 1107.
6 (*a*) T. Egberg, *J. Assoc. Off. Anal. Chem.*, 1977, **60**, 126; (*b*) K. Ishii, K. Kubo, T. Sakurada, K. Komori and Y. Sakai, *Chem. Commun.*, 2011, **47**, 4932.
7 (*a*) S. A. Kumar, P. H. Lo and S. M. Chen, *Biosens. Bioelectron.*, 2008, **24**, 518; (*b*) A. P. dos Reis, C. R. T. Tarley, N. Maniasso and L. T. Kubota, *Talanta*, 2005, **67**, 829.
8 (*a*) R. N. Adams, *Anal. Chem.*, 1976, **48**, 1126A; (*b*) C. R. Raj, K. Tokuda and T. Ohsaka, *Bioelectrochemistry*, 2001, **53**, 183.
9 (*a*) R. S. Freire and L. T. Kubota, *Analyst*, 2002, **127**, 1502; (*b*) S. Shahrokhian and M. Karimi, *Electrochim. Acta*, 2004, **50**, 77; (*c*) S. Sadeghi, A. Gafarzadeh, M. A. Naseri and H. Sharghi, *Sens. Actuators, B*, 2004, **98**, 174; (*d*) E. A. Huttona, R. Pauliukaitė, S. B. Hocevara, B. Ogorevca and M. R. Smythb, *Anal. Chim. Acta*, 2010, **678**, 176.
10 Y. N. Wang, K. C. Lau, W. W. Y. Lam, W. L. Man, C. F. Leung and T. C. Lau, *Inorg. Chem.*, 2009, **48**, 400.
11 (*a*) X. Y. Zhang, Y. Wang, Q. R. Zhang and Z. S. Yang, *Spectrochim. Acta, Part A*, 2010, **77**, 1; (*b*) Y. Y. Kou, J. L. Tian, D. D. Li, W. Gu, X. Liu, S. P. Yan, D. Z. Liao and P. Cheng, *Dalton Trans.*, 2009, 2374; (*c*) P. A. N. Reddy, M. Nethaji and A. R. Chakravarty, *Eur. J. Inorg. Chem.*, 2004, 1440.
12 (*a*) N. Poulter, M. Donaldson, G. Mulley, L. Duque, N. Waterfield, A. G. Shard, S. Spencer, A. T. A. Jenkins and A. L. Johnson, *New J. Chem.*, 2011, **35**, 1477; (*b*) M. T. Kaczmarek, R. Jastrząb, E. Hołderna-Kędzia

and W. Radecka-Paryzek, *Inorg. Chim. Acta*, 2009, **362**, 3127; (*c*) W. Rehman, A. Badshah, S. Khan and L. T. A. Tuyet, *Eur. J. Med. Chem.*, 2009, **44**, 3981.
13 (*a*) Z. Puterová, J. Valentová, Z. Bojková, J. Kožíšek and F. Devínsky, *Dalton Trans.*, 2011, **40**, 1484; (*b*) J. Vančo, J. Marek, Z. Trávníček, E. Račanská, J. Muselík and O. Švajlenová, *J. Inorg. Biochem.*, 2008, **102**, 595.
14 (*a*) P. Mukherjee, P. Kar, S. Ianelli and A. Ghosh, *Inorg. Chim. Acta*, 2011, **365**, 318; (*b*) M. R. Maurya, A. K. Chandrakar and S. Chand, *J. Mol. Catal. A: Chem.*, 2007, **274**, 192; (*c*) X. H. Lu, Q. H. Xia, H. J. Zhan, H. X. Yuan, C. P. Ye, K. X. Su and G. Xu, *J. Mol. Catal. A: Chem.*, 2006, **250**, 62.
15 G. D. Liu, Z. Q. Li, S. S. Huan, G. L. Shen and R. Q. Yu, *Anal. Lett.*, 2000, **33**, 175.
16 (*a*) P. H. Aubert, P. Audebert, M. Roche, P. Capdevielle, M. Maumy and G. Ricart, *Chem. Mater.*, 2001, **13**, 2223; (*b*) S. V. Vasil'eva, N. A. German, P. V. Gaman'kov and A. M. Timonov, *Russ. J. Electrochem.*, 2001, **37**, 317; (*c*) I. Tchepournaya, S. Vasilieva, S. Logvinov, A. Timonov, R. Amadelli and D. Bartak, *Langmuir*, 2003, **19**, 9005.
17 (*a*) K. Itoh, H. Hayashi, H. Furutachi, T. Matsumoto, S. Nagatomo, T. Tosha, S. Ter-ada, S. Fujinami, M. Suzuki and T. Kitagawa, *J. Am. Chem. Soc.*, 2005, **127**, 5212; (*b*) N. N. Murthy, M. Mahroof-Tahir and K. D. Karlin, *Inorg. Chem.*, 2001, **40**, 628; (*c*) K. D. Karlin, P. Ghosh, R. W. Cruse, A. Farooq, Y. Gultneh, R. R. Jacobson, N. J. Blackburn, R. W. Strange and J. Zubieta, *J. Am. Chem. Soc.*, 1988, **110**, 6769; (*d*) M. Mahroof-Tahir, N. N. Murthy, K. D. Karlin, N. J. Blackburn, S. N. Shaikh and J. Zubieta, *Inorg. Chem.*, 1992, **31**, 3001.
18 (*a*) S. Khatua, S. H. Choi, J. Lee, J. O. Huh, Y. Do and D. G. Churchill, *Inorg. Chem.*, 2009, **48**, 1799; (*b*) S. A. Warda, *Z. Kristallogr.*, 1998, **213**, 771; (*c*) J. H. Cai, Y. H. Huang and Y. M. Jiang, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **62**, m2064; (*d*) R. E. Marsh and A. L. Spek, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2001, **57**, 800.
19 (*a*) Y. G. Li, D. H. Shi, H. L. Zhu, H. Yan and S. W. Ng, *Inorg. Chim. Acta*, 2007, **360**, 2881; (*b*) K. Pang, D. Guo, C. Duan, H. Mo and Q. Meng, *Inorg. Chem.*, 2003, **42**, 5453.
20 (*a*) S. V. Vasil'eva, I. A. Chepurnaya, S. A. Logvinov, P. V. Gaman'kov and A. M. Timonov, *Russ. J. Electrochem.*, 2003, **39**, 310; (*b*) T. Yu. Rodyagina, P. V. Gaman'kov, E. A. Dmitrieva, I. A. Chepurnaya, S. V. Vasil'eva and A. M. Timonov, *Russ. J. Electrochem.*, 2005, **41**, 1101.
21 T. R. L. Dadamos and M. F. S. Teixeira, *Electrochim. Acta*, 2009, **54**, 4552.
22 A. B. Powell, C. W. Bielawski and A. H. Cowley, *J. Am. Chem. Soc.*, 2009, **131**, 18232.
23 M. do S. M. Quintino, H. Winnischofer, M. Nakamura, K. Araki, H. E. Toma and L. Angnes, *Anal. Chim. Acta*, 2005, **539**, 215.
24 C. Demetgül, D. Deletıoğlua, F. Karacab, S. Yalçinkayaa, M. Tımura and S. Serın, *J. Coord. Chem.*, 2010, **63**, 2181.
25 A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd edn, Wiley, New York, 2001.
26 X. J. Zhu and B. J. Holliday, *Macromol. Rapid Commun.*, 2010, **31**, 904.
27 (*a*) A. Gomila, N. L. Poul, N. Cosquer, J. M. Kerbaol, J. M. Noël, M. T. Reddy, I. Jabin, O. Reinaud, F. Conan and Y. L. Mest, *Dalton Trans.*, 2010, **39**, 11516; (*b*) R. Khan and M. Dhayal, *Biosens. Bioelectron.*, 2009, **24**, 1700; (*c*) Y. Oztekin, Z. Yazicigil, A. Ramanaviciene and A. Ramanavicius, *Sens. Actuators, B*, 2011, **152**, 37.
28 (*a*) F. Zhou, H. Y. Hu, B. Yu, V. L. Osborne, W. T. S. Huck and W. M. Liu, *Anal. Chem.*, 2007, **79**, 176; (*b*) V. Shinde and P. P. Pati, *Mater. Sci. Eng., B*, 2010, **168**, 142.
29 J. J. Fei, L. M. Luo, S. S. Hu and Z. Q. Gao, *Electroanalysis*, 2004, **16**, 319.
30 (*a*) I. F. Hu and T. Kuwana, *Anal. Chem.*, 1986, **58**, 3235; (*b*) M. Rueda, A. Aldaz and F. Sanchez-Burgos, *Electrochim. Acta*, 1978, **23**, 419.
31 (*a*) J. L. Chou, J. P. Chyn, F. L. Urbach and D. F. Gervasio, *Polyhedron*, 2000, **19**, 2215; (*b*) M. Kato, T. Tanase and M. Mikuriya, *Inorg. Chem.*, 2006, **45**, 2925; (*c*) S. C. N. Hsu, H. H. Z. Chen, I. J. Lin, J. J. Liu and P. Y. Chen, *J. Organomet. Chem.*, 2007, **692**, 3676.
32 (*a*) H. Wynberg, *J. Am. Chem. Soc.*, 1954, **76**, 4998; (*b*) M. Komiyama and H. Hirai, *Makromol. Chem. Rapid Commun.*, 1981, **2**, 759.
33 *Bruker AXS, SAINT Software* Reference Manual, Madison, WI, 1998.
34 G. M. Sheldrick, *SHELX-97: Program System is Used in the Solution and Refinement of Crystal Structure*, University of Gottingen, Germany, 1997.
35 *Brandenburg, DIAMOND. Visual, Information System for Crystal Structures*, Bonn, Germany, 1998.

