Crystal Structure, Spectroscopic and Redox Properties of Copper(II) Bis{2-[(2,6-dimethylphenyl)iminomethyl-3-methoxyphenolate]}

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The coordination chemistry of *N*-(2,6-di-methylphenyl)-2-hydroxy-3-methoxybenzaldimine (**1**) with Cu(II) has been investigated by X-ray crystallography, electronic and EPR spectroscopies, as well as by electro- and magnetochemistry. The title complex **2** crystallizes in the orthorhombic space group $P2_12_12_1$ (a = 8.1538, b = 17.7466, c =19.8507 Å). The mononuclear square-planar molecules **2** featuring *trans*-N_2O_2 coordination are connected *via* weak intermolecular C–H$\cdots\pi$ interactions into infinite chains parallel to the *a* axis. Although the intermolecular Cu$\cdots$Cu separations within individual chains and between chains are very long (8.154 and 9.726 Å), the exchange interaction parameter $G = 2.03 < 4$, estimated from solid state EPR spectra, suggests the existence of long-distance superexchange pathways between adjacent Cu(II) centers. The electronic and electrochemical features of the compound are also discussed.

Key words: Crystal Structure, C–H$\cdots\pi$(Ph) Bonding, Superexchange

Introduction

Schiff bases such as bidentate or tetradentate salicylaldimines (SA), quite familiar ligands in metal complexes, are of interest for their versatile chemistry, stereochemistry and photophysical properties [1 – 4]. The salen and bis-chelate SA complexes show interesting structural and magnetic properties [3 – 5], and exhibit a marked tendency to oligomerize, leading to novel structure types due to π-π stacking interactions and to geometrical changes due to the aggregation [6]. Furthermore, metal Schiff base complexes have been used recently as building blocks in the construction of multicomponent supramolecular assemblies [7]. Although simple systems such as bis(SA)metal complexes have been extensively studied, there are still some stereochemical and conformational questions. For instance, it has been reported that tetrahedral distortion is enhanced in bis(*N*-alkyl-SA)copper(II) complexes as the bulkiness of the alkyl group increases, and in parallel to this the reduction potential shifts to more positive values as the distortion from planarity of these complexes is enhanced [8]. However, in analogous bis(*N*-cycloalkyl-naphthaldiminato)copper(II) complexes, the above trend is inversed [9]. Recently, we have structurally characterized bis(*N*-3,5-^{t}Bu$_2$-phenyl-SA)copper(II) [10], which unlike the *trans* square-planar bis(*N*-4-OCH$_3$-3,5-^{t}Bu$_2$-phenyl-SA)copper(II) [11] and all other bis(*N*-R-Ph-SA)copper(II)-type analogs [4] shows a distorted *cis* square-planar N_2O_4Cu geometry. A *cis* arrangement is rarely encountered for Cu(II) bound to *N,O*-bidentate SA ligands [4, 12]. In addition, the adoption of the *cis* geometry is surprising since the 3,5-^{t}Bu$_2$-phenyl groups are sterically demanding.

Following our earlier studies [11, 13 – 15] on the structure, chemistry and reactivity of the metal complexes with sterically hindered redox active SA, we report here the crystal structure, spectroscopic characteristics and electrochemical behavior of the bis{2-[(2,6-dimethyl-phenyl)iminomethyl-3-methoxy-phenolate]}copper(II) complex (**2**). Supplementary data for the ligand (**1**) are also presented.

Experimental Section

Physical measurements

The experimental procedures and instruments used for the physical property measurements (IR, UV/vis, ^{1}H NMR, ESR, magnetic measurements) were as previously described [11]. Electrochemical measurements were recorded on a PC-controlled Eco Chemie-Autolab-12 potentiostat/galvanostat in nitrogen-degassed solutions of *ca.* 10^{-3}–10^{-4} M solutions of **1** and **2** in acetonitrile containing

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0.05 M Et_4NBF_4 as the supporting electrolyte. The potentiostat/galvanostat has an iR compensation option. Cyclic voltammetry measurements were carried out in a conventional three-electrode cell consisting of a Pt auxiliary electrode, an Ag/AgCl reference electrode and a 2 mm sized Pt disc working electrode. Prior to running voltammograms the solutions were purged with dry nitrogen for 3 – 4 min in order to remove dissolved oxygen. The potentials are referenced to Ag/AgCl in the range from +1.85 to −1.85 V.

Materials

All chemicals and solvents were reagent grade and used without further purification. Copper(II) acetate monohydrate, 2-hydroxy-3-methoxybenzaldehyde and 2,6-dimethylaniline were purchased from Aldrich Chemical Co.

*Synthesis and characterization of **1** and **2***

N-(2,6-di-methylphenyl)-2-hydroxy-3-methoxybenzaldimine (**1**) was prepared by refluxing a 1 : 1 molar ratio mixture of 2-hydroxy-3-methoxybenzaldehyde and 2,6-dimethylaniline in methanol. Yield: 92 %; m. p. 141 °C. – UV/vis (C_2H_5OH): λ_{max} (lg ε) = 210 (4.81), 220 (2.86), 267 (4.70), 330 (4.45), 428 (2.12) nm. – IR (KBr pellet): ν = 1625 (CH=N), 2650 (OH···N) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 2.30 (s, 3 H), 4.05 (s. 3 H), 6.97 – 7.21 (m, 6 H), 8.44 (s, 1 H), 13.65 ppm (s, 1 H OH/NH). – Analysis for $C_{16}H_{17}NO_2$ (255.31): calcd. C 75.27, H 6.71, N 5.48; found C 74.16, H 6.79, N 5.18.

Bis{2-[(2,6-dimethylphenyl)iminomethyl-3-methoxyphenolate]}copper(II) (**2**) was prepared by adding 10 mL of a methanolic solution of copper(II) acetate (1 mmol) to 80 mL of a stirred solution of **1** (2 mmol). The resulting solution was refluxed for 1.5 h and then the mixture was allowed to evaporate slowly at r. t. After standing for 5 – 6 h, dark green crystals precipitated which were suitable for X-ray structural analysis. Yield 72 %; m. p. 199 – 201 °C. – UV/vis (C_2H_5OH): λ_{max} (lg ε) = 206 (4.92), 229 (4.98), 277 (4.82), 316 (4.55), 401 (sh) (4.65), 745 (sh) (2.03) nm. – IR (KBr pellet): ν = 1606 (CH=N), 1542 cm^{-1}. – Magnetic moment μ_{eff}/μ_{BM} = 1.98. – Analysis for $C_{32}H_{32}N_2O_4Cu$ (572.16): calcd. C 67.17, H 5.64, N 4.89; found C 67.01, H 5.66, N 4.49.

*X-Ray crystallography of complex **2***

Suitable single crystals were mounted on a glass fiber and data collections were performed on a Stoe IPDSII image plate detector using MoK_α radiation (λ = 0.71019 Å). Crystal and refinement data are given in Table 1. Data collection and cell refinement: Stoe X-AREA [16], data reduction: Stoe X-RED [16]. The structure was solved by Direct Methods using SIR-97 [17]. Anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [18]. All hydrogen atoms were positioned geometrically and refined by a riding model with U_{iso} 1.2 times that of the attached atom. Molecular drawings: ORTEP-III [19].

Table 1. Crystal data and structure refinement for complex **2**.

Formula	$C_{32}H_{32}CuN_2O_4$
Formula weight	572.15
Temperature, K	297(2)
Radiation; wavelength, Å	MoK_α; 0.71073
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, Å	8.1538(4)
b, Å	17.7466(13)
c, Å	19.8507(11)
Volume, Å^3	2872.4(3)
Z	4
Calculated density, g cm^{-3}	1.323
μ(MoK_α), mm^{-1}	0.799
F(000), e	1196.0
Crystal size, mm	0.17 × 0.25 × 0.32
θ range, deg.	2.05 – 27.17
hkl ranges	$-10 \le h \le 10$, $-22 \le k \le 22$, $-25 \le l \le 25$
Reflections collected/independent	23051/6338
R_{int}	0.086
Reflections observed [$I \ge 2\sigma(I)$]	3308
Absorption correction	Integration
Data/restraints/parameters	6338/0/358
Goodness-of-fit on F^2	0.91
*R*1/*wR*2 [$I \ge 2\sigma(I)$]	0.0497/0.0836
*R*1/*wR*2 (all data)	0.1165/0.1011
Absolute structure Flack Param.	−0.016(15)
Largest diff. peak and hole, e Å^{-3}	0.185/−0.306

CCDC 640054 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Infrared, NMR and electronic spectra

The IR spectrum of **1** exhibits a characteristic medium broad band centered around 2650 cm^{-1} and a strong sharp absorption at 1625 cm^{-1}, attributable to the intramolecularly H-bonded phenolic-OH and to the ν(CH=N) stretching mode, respectively. Upon complexation, the former band disappears and the latter is shifted to lower frequency (1606 cm^{-1}) in the spectrum of **2**, suggesting the coordination of the imino nitrogen and the deprotonated phenolic oxygen to the central copper atom [20]. The assignment and the chemical shift data of the ^1H NMR spectrum of **1** are presented in the Experimental Section.

The absorptions < 330 nm detected in the electronic spectrum of **1** in absolute ethanol are assigned to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions within the aromatic and azomethine groups of the enoliminic tautomer form [21]. The low intensity band at 428 nm is assigned to an $n \rightarrow \pi^*$ transition in the dipolar zwitterionic or ketoamine tautomeric structures of **1** [22]. The electronic spectra of **2** recorded in absolute ethanol [(λ_{max}(lg ε) = 206 (4.92), 229 (4.98), 277 (4.82), 316 (4.55), 401 (4.65) (sh), 745 (2.03) (sh) nm] and chloroform [(λ_{max} (lg ε) = 278 (4.60), 381(3.96), 715(2.03) nm (sh)] solutions along with intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands also exhibit solvent dependent *d-d* bands (715 and 740 nm) which are attributed to $d_{xz/yx} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions in a distorted tetragonal ligand field [23]. The observed red shift in the *d-d* bands suggests axial interactions of **2** with solvent molecules, which lead to a tetrahedral distortion of the planar geometry. In general, as the basicity (coordinating ability) of the ligands increases, the band is shifted to lower energy. According to our X-ray crystallographic results, complex **2** has a *trans* square-planar CuN_2O_2 chromophore in the solid state. However, the wavelengths of the observed visible *d-d* absorption bands are significantly longer than that usually observed in a square-planar geometry (a single band around 500 – 600 nm in ideal D_{4h} symmetry actually is the envelope of three *d-d* transitions) [23, 24]. The intense peaks at 381 and 401 nm are due to LMCT transitions.

ESR Spectra

The solid-state spectrum of **2** at 300 K exhibits only one exchange-averaged broad isotropic signal with $g_{\|}$ = 2.083, $g_{\perp}$ = 2.042, g_{av} = 2.063 and line widths $H_{\|}$ = 60 G and $H_{\perp}$ = 44 G. Similar exchange-averaged broad isotropic Cu(II) signals have been interpreted by the existence of dipolar interaction between crystallographically non-equivalent Cu(II) centers in the solid state [25, 26], but as can be seen from the extended packing structure in Fig. 2, the Cu(II) centers of **2** are crystallographically identical and the nearest Cu···Cu distances are 8.154 and 9.726 Å within chains and between neighboring chains, respectively. The exchange parameter, $G = (g_{\|} - g_e)/(g_{\perp} - g_e)$, reflects the exchange interaction between the copper(II) centers in polycrystalline solids [27]. According to Hathaway [27], if $G > 4$ the exchange interaction is negligible. A value of $G < 4$ indicates considerable exchange interaction in the solid complex, and $G = 2.03$ for **2** falls into the latter range. Therefore, according to Hathaway's criteria, the existence of a considerable exchange interaction between adjacent Cu(II) centers and the misalignment of the local tetragonal axes is predicted to be appreciable in the solid state of **2** [26, 27]. According to our X-ray determination the nearest Cu···Cu distance (8.154 Å) between the parallel oriented complex molecules in the unit cell of **2** are too large for effective coupling [28]. However, adjacent molecules in the parallel chains are linked by weak C–H···π(Ph) noncovalent (H···π) interactions in the solid state providing a long distance superexchange pathway between Cu(II) centers, which appears to be rather unique considering the large distance that is involved.

Table 2. Selected bond lengths (Å) and angles (deg) for compound **2**.

N1–Cu1	1.995(3)	C9–N1	1.285(6)
N2–Cu1	1.987(3)	C25–N2	1.304(6)
O1–Cu1	1.877(3)	C25–C26	1.403(7)
O2–Cu1	1.876(3)	C31–O2	1.296(5)
C1–N1	1.441(6)	C14–O3	1.363(6)
O2–Cu1–O1	179.06(17)	O2–Cu1–N1	87.79(15)
O2–Cu1–N2	91.61(15)	O1–Cu1–N1	91.87(15)
O1–Cu1–N2	88.73(15)	N2–Cu1–N1	179.25(17)

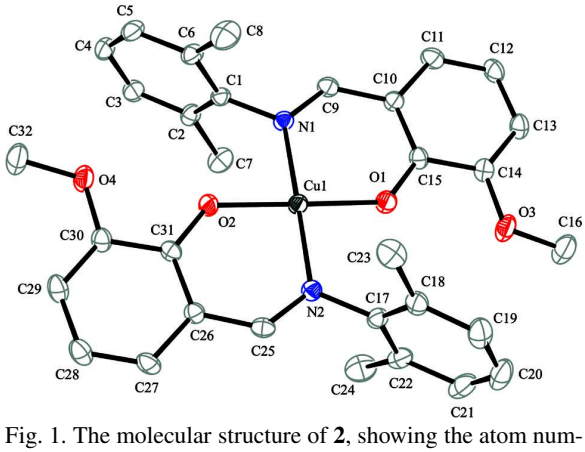

Fig. 1. The molecular structure of **2**, showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are omitted for clarity.

The solution ESR spectra at 300 and 133 K show four copper hyperfine splittings without ^{14}N ($I = 1$) superhyperfine resolution on the highest $m_I = -3/2$ components and in the $g_{\perp}$ region. The spin Hamiltonian parameters extracted from the solution spectra were as follows: g_{iso} = 2.113, A_{iso} = 76 G, $g_{\|}$ = 2.232, $A_{\|}$ = 168 G, $g_{\perp}$ = 2.054, $A_{\perp}$ = 34 G, $g_{\|}/A_{\|}$ = 150 cm and G = 4.43. The $g_{\|} > g_{\perp} > g_e$ trend, observed in both

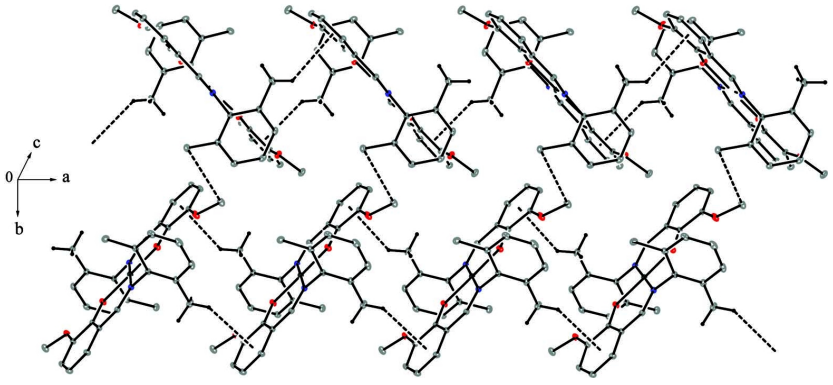

Fig. 2. Packing diagram of compound **2**, showing intermolecular interactions as dashed lines.

solid-state and frozen-glass spectra suggests that the unpaired electron is in the d_{xy} or $d_{x^2} - d_{y^2}$ ground state characteristic of axial symmetry [29]. The degree of distortion $g_{\|}/A_{\|}$ is regarded as an index of the deviation from idealized planar geometry [30, 31]. Values of 105 – 135 cm^{-1} are typical for planar Cu(II) complexes, while the range of 135 – 150 cm^{-1} is characteristic of slight to moderate distortion, and values of 180 – 250 cm^{-1} indicate considerable distortion [30]. The value 150 cm^{-1} for the present complex suggests a little to moderately distorted geometry in $CHCl_3$ solution for complex **2**. Thus ESR examination and UV/vis spectral data indicate that upon dissolving the complex its planar geometry is moderately distorted.

Description of the X-ray structure of ***2***

The molecular structure of complex **2** with the atom labeling scheme is shown in Fig. 1. The copper(II) ion is bonded to oxygen and nitrogen donor atoms of the two bidentate ligand molecules in the usual *trans*-N_2O_2 arrangement. Except for the dimethylphenyl fragments, the complex molecule is nearly planar. In particular, the copper(II) ion lies in an almost perfectly square-planar coordination environment with the largest deviation from the mean plane of 0.0112 Å observed for the O2 atom. Concerning the Cu1–O and Cu1–N bond lengths we can note that, although the covalent radii of oxygen and nitrogen differ only by 0.02 Å (N = 0.75, O = 0.73 Å), in the structure the Cu1–N bond lengths (1.987(3)–1.995(3) Å) are significantly longer than the Cu1–O distances (1.876(3) and 1.877(3) Å). A similar difference was noted in the structures of bis[*N,N′*-polymethylene-bis(salicylaldiminato)] copper(II) [32] and bis[*N*-(1-adamantyl) salicylaldiminato]copper(II) [33]. The O1–C15 and O2–C31 phenolic bonds (1.300(5) and 1.296(5) Å, respectively) are similar to those in other salicylaldimine complexes. The N=C imine bonds (1.285(6) and 1.304(6) Å) and also the C9–C10 and C25–C26 bond lengths (1.435(7) and 1.403(7) Å) suggest an electron delocalization of the salicylidine benzene ring extending to the oxygen donor atoms. Each benzene ring of the salicylidine groups shows three consecutive longer (than expected for benzene) and three shorter bonds (see Table 2 for details). This is a general observation for the SA series [32 – 35].

The salicylidine benzene rings are approximately co-planar with respect to the copper(II) basal mean plane with dihedral angles of 4.8(10) (C10/C15) and 7.8(3)° (C26/C31), whereas the dimethylphenyl moieties are approximately perpendicular with respect to this mean plane with dihedral angles of 87.0(1) (C1/C6) and 89.1(1)° (C17/C22). The dihedral angles between two dimethylphenyl rings and between two salicylidine benzene rings are 2.5(3) and 4.1(10)°, respectively.

There is no conventional hydrogen bonding in the extended structure. It can be seen from Fig. 2 that two symmetry related copper(II) complexes are only joined by C8–H8A$\cdots\pi$ and C24–H24A$\cdots\pi$ interactions, which leads to the formation of a chain along the crystallographic *a* axis. For the C8–H8A$\cdots$A^{i} contact, the distance between atom H8A and the center of the salicylidine benzene ring (ring A^{i}: C10–C15; symmetry code (i): $1 + x$, y, z) is 2.874 Å, the distance between atom H8A and the plane of ring A is 2.815 Å, and the angle C8–H8A$\cdots$A^{i} is 131.53°. For the other C24–H24A$\cdots$ B^{ii} interaction, the distance between atom H24A and the center of the benzene ring (ring B^{ii}: C29–C31; symmetry code (ii): $x - 1$, y, z) is 2.865 Å, the distance between atom H24A and the plane of ring A is 2.821 Å,

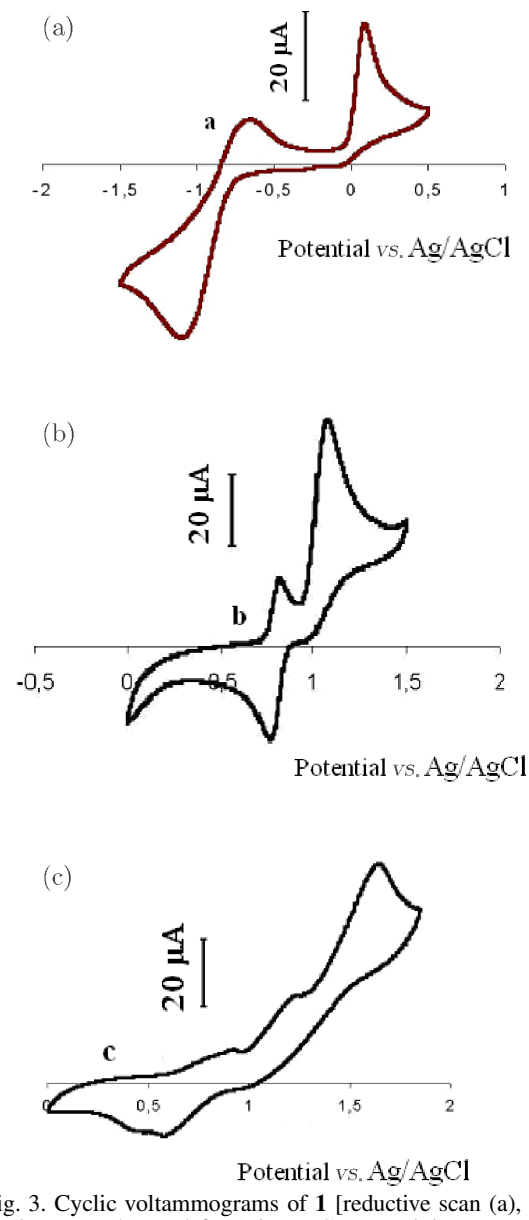

Fig. 3. Cyclic voltammograms of **1** [reductive scan (a), oxidative scan (b)] and **2** (c) in MeCN containing Et_4NBF_4 (0.05 M) as supporting electrolyte at a Pt working electrode. Scan rate 0.3 V s^{-1}.

and the angle C24–H24A···B^{i} is 131.53°. Two polymeric chains are joined by short contacts between the symmetry related C16^{iii} and C7 atoms (C7···C16^{iii}: 3.662(2) Å; symmetry code (iii): $1-x$, $y+1/2$, $1/2-z$), as shown in Fig. 2. The shortest copper-copper separation in the chains is 8.154 Å and the closest distance between copper centers in adjacent chains is 9.726 Å.

Thus, the analysis of the packing structure of complex **2** indicates that in each chain the molecule **2** is linked by weak intermolecular C–H···π(Ph) interactions and the parallel chains are assembled *via* short C···C contacts.

*Redox properties of **1** and **2***

The electrochemical properties of **1** and **2** have been studied by cyclic voltammetry in acetonitrile (MeCN) containing 0.05 M Et_4NBF_4 as supporting electrolyte under anaerobic conditions. Typical cyclic voltammograms (CV) of **1** and **2** are presented in Fig. 3. By scanning in the negative direction from −1.5 to 0.5 V, the CV of **1** exhibits a reduction wave at −1.14 V and reversal anodic oxidation responses at −0.655 and 0.102 V *vs.* Ag/AgCl (Fig. 3a) which are assigned to the two-electron reduction process of the iminic group [36]. The CV of **1** recorded in the anodic potential range from 0.0 to 1.5 V *vs.* Ag/AgCl exhibits well defined quasi-reversible oxidation waves at $E^1_{1/2}$ = 0.79 V (E^1_{pa} = 0.85 V and E^1_{pc} = 0.73 V) and $E^2_{1/2}$ = 1.05 V (E^2_{pa} = 1.12 V and E^2_{pc} = 0.97 V) (Fig. 3b) which are assigned to oxidation processes of the phenolate/phenoxyl couple [37, 12]. No redox processes on the cathodic scan of complex **2** in MeCN solution in the potential range from −1.85 to 0.0 V were detected, suggesting its complete stability towards reduction in this solvent. However, a sweep (scan rate 0.2 V/s) from 0.0 to 1.85 V *vs.* Ag/AgCl for **2** shows well defined oxidation peaks at E_{pa} of 1.08 and 1.72 V, and the back sweep exhibits two curves at *ca.* E_{pc} of 0.95 and 0.44 V (Fig. 3c). Repeated scanning of the voltammogram in the same range causes a decay in the intensities of both the anodic and cathodic peaks, demonstrating the overall chemical irreversibility of this electrochemical process.

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