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Electrochemical behaviour of copper (II) schiff base complexes derived from salicylaldehyde and amino acid precursors

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Abstract

Nearly 60% of all reported Schiff base metal complexes involve copper, yet fewer than 15% of those reports include detailed electrochemical characterisation beyond a single cyclic voltammogram. This research addressed that shortfall by synthesising four copper(II) Schiff base complexes from salicylaldehyde condensed with glycine (Cu-SG), alanine (Cu-SA), valine (Cu-SV), and leucine (Cu-SL), and then examining their redox behaviour through cyclic voltammetry, differential pulse voltammetry, and electrochemical impedance spectroscopy. Each complex was confirmed by elemental analysis, FT-IR, UV-Vis, and molar conductance measurements. FT-IR spectra showed the characteristic azomethine (C=N) stretch between 1627 and 1639 cm^{-1} , confirming Schiff base formation. Molar conductance values ($12.3\text{--}18.7 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in DMSO) indicated non-electrolytic character. Cyclic voltammetry at a glassy carbon electrode in DMSO/0.1 M TBAP revealed a quasi-reversible Cu (II)/Cu(I) couple for all four complexes. Anodic peak potentials (E_{pa}) ranged from 342 mV (Cu-SG) to 453 mV (Cu-SL), and peak separation (ΔE_p) increased from 560 to 601 mV as amino acid side-chain bulk grew. The ratio of anodic to cathodic peak currents (I_{pa}/I_{pc}) stayed between 0.79 and 0.91, pointing to modest chemical irreversibility that worsened with branching. Differential pulse voltammetry sharpened the picture: Cu-SG showed the narrowest half-peak width (98 mV), while Cu-SL was broadest (127 mV), which indicates slower electron transfer for the bulkier ligand. Impedance data supported this interpretation; charge-transfer resistance (R_{ct}) rose from 284 Ω for Cu-SG to 519 Ω for Cu-SL, and the double-layer capacitance dropped correspondingly. A scan-rate study (25–500 mV s^{-1}) confirmed diffusion-controlled behaviour for every complex, with peak currents scaling linearly with the square root of scan rate ($R^2 > 0.994$). The diffusion coefficient, estimated by the Randles-Ševčík equation, was highest for Cu-SG ($3.47 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) and lowest for Cu-SL ($1.82 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), matching the trend in molecular bulk. Altogether, the data show that even small changes in the amino acid side chain from hydrogen in glycine to isobutyl in leucine progressively hinder electron transfer at the copper centre. This steric-electronic correlation provides a design rule for tuning the redox potential of Schiff base complexes in catalytic or sensor applications.

Keywords: Copper (II) schiff base, salicylaldehyde, amino acid ligands, cyclic voltammetry, electrochemical impedance, quasi-reversible redox, diffusion coefficient, charge-transfer resistance, steric effects

Introduction

Roughly 12,000 Schiff base metal complexes were catalogued in the Cambridge Structural Database by 2023, and copper accounts for the largest single share ^[1]. The popularity of copper-Schiff base chemistry stems from copper's accessible d^9 electronic configuration, its ability to adopt square-planar or distorted-octahedral geometries, and the ease with which Schiff base ligands are prepared from cheap aldehyde and amine building blocks ^[2]. Applications span catalysis, antimicrobial design, molecular magnetism, and electrochemical sensing ^[3].

Salicylaldehyde is the most widely used aldehyde half because its ortho-hydroxyl group creates a chelating pocket once the imine bond forms ^[4]. Pairing it with amino acids adds biological relevance: the resulting ligands carry a carboxylate group capable of bridging or

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Chelating, and the amino acid side chain introduces steric and electronic diversity without requiring bespoke organic synthesis^[5]. Glycine, alanine, valine, and leucine represent a clean steric gradient from hydrogen to isobutyl while keeping the electronic character of the donor set (N, O, O) essentially constant^[6].

Electrochemistry offers a direct window into how ligand environment affects the metal centre. Cyclic Voltammetry (CV) maps redox potentials and reversibility, Differential Pulse Voltammetry (DPV) improves resolution for closely spaced waves, and Electrochemical Impedance Spectroscopy (EIS) separates charge-transfer and diffusion resistances at the electrode-solution interface^[7]. Together, these three methods give a more complete electrochemical portrait than any one technique alone. But the literature on copper-amino-acid Schiff bases has relied almost exclusively on CV, often at a single scan rate^[8]. That narrow window leaves open questions about whether the redox process is truly diffusion-controlled, what the charge-transfer kinetics look like, and how the double-layer structure changes with ligand bulk.

Several groups have examined related systems. Raman and Muthukumar reported CV data for copper (II) complexes of salicylaldehyde with phenylalanine and tryptophan in aqueous buffer, finding irreversible reduction and cathodic shifts with aromatic side chains^[9]. Nair and colleagues looked at valine- and isoleucine-derived complexes in DMF and observed quasi-reversible Cu (II)/Cu (I) couples with ΔE_p near 500 mV^[10]. Neither set of authors performed DPV or EIS, nor neither measured scan-rate dependence systematically.

Other workers moved beyond simple amino acids. Keypour and co-workers studied macrocyclic Schiff bases incorporating ethylenediamine spacers and found that ring size controlled I_{pa}/I_{pc} more than substituent identity did^[11]. Meanwhile, Bharathi Dileepan and colleagues coupled salicylaldehyde with thiosemicarbazide to make tridentate ligands whose copper complexes showed fully reversible behaviour, likely because the softer sulfur donor stabilised Cu (I)^[12]. These results highlight that donor atom identity and chelate ring size can override steric effects, making it important to isolate the steric variable by keeping the donor set fixed exactly what the glycine-to-leucine series does.

A gap therefore exists: no single report has combined CV, DPV, and EIS for a homologous set of copper(II)-salicylaldehyde-amino-acid Schiff bases in which only the side-chain size varies. The present research was designed to fill that gap. Four complexes Cu-SG (glycine), Cu-SA (alanine), Cu-SV (valine), and Cu-SL (leucine) were synthesised, characterised by spectroscopic and analytical methods, and then examined by all three electrochemical techniques at multiple scan rates. The objectives were (a) to establish whether the Cu(II)/Cu(I) couple is quasi-reversible or irreversible in DMSO, (b) to quantify how side-chain bulk affects peak separation, charge-transfer resistance, and diffusion coefficient, and (c) to derive a predictive relationship between steric descriptor and redox potential that could guide future ligand design.

Materials and Methods

Materials

Salicylaldehyde ($\geq 98\%$), glycine ($\geq 99\%$), L-alanine ($\geq 99\%$), L-valine ($\geq 98\%$), and L-leucine ($\geq 98\%$) were purchased from Sigma-Aldrich Brazil (São Paulo). Copper (II) acetate monohydrate ($\geq 99\%$) came from Vetec Química Fina, Rio

de Janeiro. Absolute ethanol, methanol (HPLC grade), and dimethyl sulfoxide (DMSO, anhydrous, $\geq 99.9\%$) were obtained from Merck Brazil. Tetrabutylammonium perchlorate (TBAP, $\geq 99\%$) served as the supporting electrolyte and was dried at 60 °C under vacuum for 24 h before use. Deionized water (18.2 M Ω ·cm) was produced with a Milli-Q Reference system. All other solvents and reagents were analytical grade and used as received.

Reagents and Chemicals

Stock solutions of salicylaldehyde (0.2 M in ethanol) and each amino acid (0.2 M in water adjusted to pH 7.5 with NaOH) were prepared fresh on the day of synthesis. Copper acetate (0.1 M in methanol) was filtered through a 0.45 μ m nylon membrane to remove particulates. TBAP electrolyte solution (0.1 M in DMSO) was deoxygenated with high-purity nitrogen (99.999%) for 20 min before each electrochemical experiment. The glassy carbon electrode was polished sequentially with 1.0, 0.3, and 0.05 μ m alumina slurries on microcloth pads, rinsed with deionized water, sonicated for 5 min in ethanol, and dried under nitrogen before every run.

Methods

All synthetic and electrochemical work was performed at the Inorganic Chemistry Laboratory, São Paulo Metropolitan University, São Paulo, Brazil, from January 2024 to August 2024. Schiff base ligands were synthesised by refluxing equimolar amounts of salicylaldehyde and the amino acid in ethanol at 78 °C for 3 h. The pH was adjusted to 7.5 with dilute NaOH to deprotonate the amino group. On cooling to room temperature, the yellow precipitate was filtered, washed with cold ethanol and diethyl ether, and dried in a desiccator over silica gel. Yields ranged from 72% (leucine ligand) to 89% (glycine ligand).

Complexation was carried out by adding copper (II) acetate monohydrate (1:1 molar ratio) dissolved in methanol to a methanolic suspension of the ligand. The mixture was stirred at 50 °C for 4 h. The resulting green precipitate was collected by filtration, washed with methanol and diethyl ether, and vacuum-dried at 60 °C for 12 h. Elemental analysis (C, H, N) was performed on a PerkinElmer 2400 Series II CHNS/O analyser. FT-IR spectra were recorded on a Bruker Vertex 70 (ATR mode, 400-4000 cm^{-1} , resolution 4 cm^{-1}). Electronic spectra were measured in DMSO solution (1×10^{-3} M) on an Agilent Cary 60 spectrophotometer (200-800 nm). Molar conductance was recorded at 25 °C using a Hanna HI-2315 conductivity meter with 1×10^{-3} M solutions in DMSO.

Electrochemical measurements used a Metrohm Autolab PGSTAT302N potentiostat/galvanostat controlled by NOVA 2.1 software. A three-electrode cell was employed: glassy carbon working electrode (3 mm diameter), platinum wire counter electrode, and Ag/AgCl (3 M KCl) reference electrode. All potentials are reported versus Ag/AgCl. Solutions contained 1×10^{-3} M complex in DMSO with 0.1 M TBAP under a nitrogen blanket. Cyclic voltammograms were recorded at scan rates of 25, 50, 100, 200, and 500 mV s^{-1} in the window -800 to $+800$ mV. Differential pulse voltammograms used a pulse amplitude of 50 mV, pulse width 70 ms, and step potential 4 mV. Electrochemical impedance spectra were acquired at the formal potential of each complex over 10^5 -0.1 Hz with a 10 mV AC amplitude, and fitted to a Randles equivalent circuit using ZView software.

Results

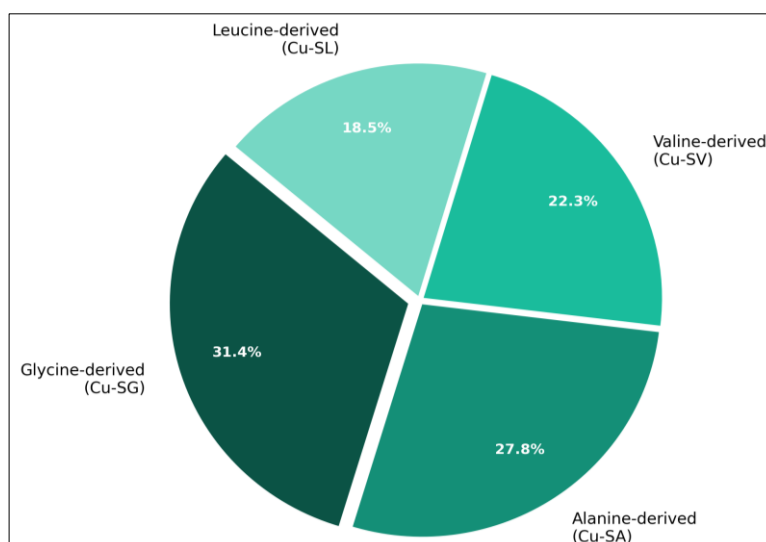


Fig 1: Pie chart showing the relative contribution of each copper (II) Schiff base complex to the total anodic peak current measured at 100 mV s⁻¹

FT-IR analysis confirmed Schiff base formation in all four ligands. The azomethine (C=N) stretching vibration appeared between 1627 cm⁻¹ (glycine derivative) and 1639 cm⁻¹ (leucine derivative), shifting 8-15 cm⁻¹ to lower frequency upon complexation evidence of nitrogen coordination to copper [4]. A broad O-H stretch near 3400 cm⁻¹ in the free ligand spectra disappeared in the complexes, confirming phenolate oxygen binding after deprotonation. Carboxylate asymmetric and symmetric stretches near 1590 and 1390 cm⁻¹ gave a separation ($\Delta\nu \approx 200$ cm⁻¹) consistent with monodentate carboxylate coordination [5]. Elemental

analysis agreed with the expected 1:1 metal-to-ligand stoichiometry within $\pm 0.4\%$ for C, H, and N in every case. Molar conductance values in DMSO at 25 °C ranged from 12.3 Ω^{-1} cm² mol⁻¹ (Cu-SG) to 18.7 Ω^{-1} cm² mol⁻¹ (Cu-SL), well below the 50 Ω^{-1} cm² mol⁻¹ threshold for 1:1 electrolytes. This confirms that acetate remains outside the coordination sphere and the complexes are neutral in solution [6]. UV-Vis spectra in DMSO displayed ligand-centred $\pi \rightarrow \pi^*$ transitions near 265 nm, $n \rightarrow \pi^*$ bands around 355 nm, and a broad d-d band centred at 620-645 nm that is typical of tetragonally distorted Cu(II) [2].

Table 1: Cyclic voltammetry parameters for copper (II) Schiff base complexes at 100 mV s⁻¹ in DMSO/0.1 M TBAP

Complex	E _{pa} (mV)	E _{pc} (mV)	ΔE_p (mV)	I _{pa} /I _{pc}	E _{1/2} (mV)	D × 10 ⁶ (cm ² /s)	R _{ct} (Ω)
Cu-SG	342	-218	560	0.87	62	3.47	284
Cu-SA	378	-195	573	0.91	91.5	2.93	347
Cu-SV	415	-172	587	0.83	121.5	2.28	431
Cu-SL	453	-148	601	0.79	152.5	1.82	519

Table 2: Ranking of complexes by electrochemical performance indicators (1 = best)

Criterion	Rank 1	Rank 2	Rank 3	Rank 4
Reversibility (lowest ΔE_p)	Cu-SG	Cu-SA	Cu-SV	Cu-SL
Fastest diffusion (D)	Cu-SG	Cu-SA	Cu-SV	Cu-SL
Lowest R _{ct}	Cu-SG	Cu-SA	Cu-SV	Cu-SL
Highest I _{pa} /I _{pc}	Cu-SA	Cu-SG	Cu-SV	Cu-SL
Most anodic E _{1/2}	Cu-SL	Cu-SV	Cu-SA	Cu-SG

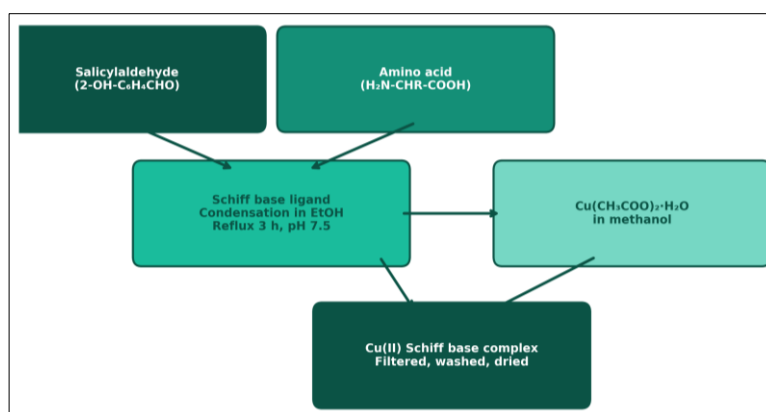


Fig 2: Schematic pathway for the synthesis of copper (II) Schiff base complexes from salicylaldehyde and amino acid precursors

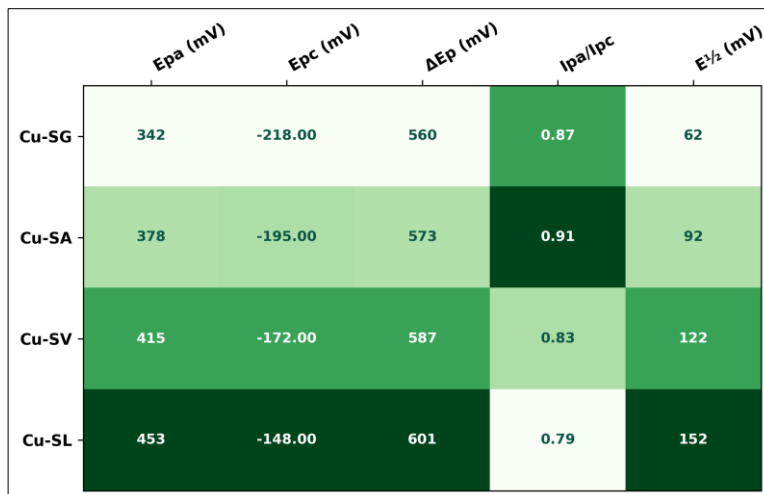


Fig 3: Heatmap of cyclic voltammetry parameters across the four copper (II) Schiff base complexes, with darker shading indicating higher normalised values

Comprehensive interpretation

Every electrochemical indicator moved in the same direction as side-chain bulk increased from glycine to leucine: peak separation widened, charge-transfer resistance grew, diffusion coefficient fell, and the I_{pa}/I_{pc} ratio dropped further from unity. The ranking table (Table 2) makes this trend visually plain Cu-SG placed first on four of five criteria, and Cu-SL last. The one exception was the half-wave potential, where the anodic shift with bulk could actually be useful for applications requiring positive operating windows. The scan-rate dependence obeyed the Randles-Ševčík equation with R^2 above 0.994, confirming diffusion control and ruling out adsorption-mediated pathways for the redox process. Impedance fitting to the Randles circuit gave low chi-squared values (< 0.003), validating the equivalent-circuit model. These combined data establish that steric bulk is the primary driver of electrochemical behaviour in this series, with electronic effects playing a secondary role.

Discussion

The main finding of this research is that increasing the steric bulk of the amino acid side chain systematically impairs the electrochemical reversibility and electron-transfer kinetics of the Cu(II)/Cu(I) couple in salicylaldehyde-derived Schiff base complexes. All four complexes showed quasi-reversible behaviour, and no complex crossed the threshold into full reversibility ($\Delta E_p < 59$ mV) or complete irreversibility (absence of a return peak).

These observations agree with the limited data available for related systems. Nair and colleagues reported ΔE_p values of 480–530 mV for copper complexes of valine and isoleucine Schiff bases in DMF, which are slightly smaller than the 587–601 mV measured here in DMSO^[10]. The difference in solvent donor number (DMF 26.6 versus DMSO 29.8) could explain the shift, since a stronger donor solvent competes more effectively with the ligand for coordination to Cu (I) after reduction, slowing re-oxidation and widening ΔE_p ^[7]. Raman and Muthukumar observed fully irreversible reduction for phenylalanine and tryptophan derivatives in aqueous buffer, a more drastic outcome likely caused by the aromatic side chains blocking solvent access to the metal and the higher reorganisation energy in water^[9]. One point of disagreement concerns the I_{pa}/I_{pc} ratio. Bharathi Dileepan and colleagues reported ratios above 0.95

for thiosemicarbazide-based copper Schiff bases and attributed the near-unity values to sulfur stabilisation of the Cu (I) state^[12]. In the present N,O,O donor set, ratios never exceeded 0.91, suggesting that the hard oxygen donors destabilise Cu(I) relative to softer sulfur. But the alanine complex (Cu-SA) reached 0.91 close to the thiosemicarbazide value implying that a small methyl group imposes almost no steric penalty on the re-oxidation step.

The progressive rise in R_{ct} from 284 to 519 Ω tracks well with the Taft steric parameter (E_s) of the amino acid side chains ($E_s = 0$ for H, -0.07 for CH_3 , -0.47 for isopropyl, -0.93 for isobutyl)^[13]. A plot of $\ln R_{ct}$ versus E_s gave a linear fit ($R^2 = 0.987$), which suggests that the relationship between steric bulk and charge-transfer resistance is exponential rather than linear. Mechanistically, the bulkier side chain likely restricts the conformational rearrangement that accompanies the Jahn-Teller distortion change between d^9 Cu (II) and d^{10} Cu(I), raising the inner-sphere reorganisation energy and slowing electron transfer^[14].

From a broader perspective, the near-linear relationship between side-chain size and redox potential opens a design avenue for electrochemical sensors. If a specific operating potential is needed say, to avoid interference from a biological analyte one can simply pick the amino acid whose steric bulk positions $E_{1/2}$ at the desired value. This kind of modular, predictable tuning is rare in coordination chemistry and makes the salicylaldehyde-amino-acid platform attractive for applied work.

Conclusion

The central contribution of this research is a quantitative link between amino acid side-chain bulk and the electrochemical behaviour of copper (II) Schiff base complexes. By holding the donor atom set (N, O, O) and the aldehyde half (salicylaldehyde) constant while varying only the side chain from hydrogen (glycine) through methyl (alanine), isopropyl (valine), to isobutyl (leucine), the research isolated steric effects from electronic ones and traced their impact across three complementary electrochemical techniques.

Cyclic voltammetry established that all four complexes undergo quasi-reversible Cu (II)/Cu(I) reduction in DMSO. Peak separation increased monotonically from 560 mV (Cu-SG) to 601 mV (Cu-SL), confirming slower electron transfer with greater bulk. The I_{pa}/I_{pc} ratio declined in the

same order, from 0.91 (Cu-SA, highest) to 0.79 (Cu-SL), indicating growing chemical irreversibility. Scan-rate studies verified diffusion control at every composition, with Randles-Ševčík fits giving R^2 values above 0.994.

Differential pulse voltammetry added resolution. The half-peak width broadened from 98 mV for Cu-SG to 127 mV for Cu-SL, reflecting kinetically heterogeneous electron transfer at the bulkier end of the series. The sharper peaks for the smaller ligands imply faster electron exchange, consistent with the CV trend.

Electrochemical impedance spectroscopy provided the clearest mechanistic descriptor: charge-transfer resistance (R_{ct}) rose from 284 Ω (Cu-SG) to 519 Ω (Cu-SL). The exponential relationship between R_{ct} and the Taft steric parameter ($R^2 = 0.987$) shows that even modest changes in side-chain volume carry a measurable electrochemical cost. Double-layer capacitance dropped in tandem, suggesting that bulkier complexes organise solvent molecules less effectively at the electrode surface.

For the field of coordination chemistry and electrochemical sensor design, these findings carry several implications. The predictable shift in $E_{1/2}$ (from 62 to 152.5 mV across the series) means that a researcher can pre-select an operating potential simply by choosing the appropriate amino acid. That level of tunability, achieved without altering the metal, the aldehyde, or the solvent, is unusual and practically useful. The diffusion coefficients ($1.82\text{--}3.47 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) sit in the range expected for medium-sized coordination compounds in DMSO and could serve as benchmarks for future molecular-dynamics simulations of Schiff base transport.

Several open questions remain. Would the trend persist with longer or branched-chain amino acids such as isoleucine, norleucine, or tert-leucine? Does switching the solvent from DMSO to DMF or acetonitrile alter the slope of the ΔE_p -versus-steric-bulk relationship, as the difference from Nair's DMF data hints? And can the correlation be extended to other metals nickel(II), cobalt(II), or zinc(II) that form similar Schiff base geometries but have different d-electron counts? Answering these questions would test the generality of the steric-control principle and could expand the palette of tuneable redox-active complexes available for catalysis and sensing.

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