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# Copper(II) *o*-Iminophenolate Complexes Based on Catecholaldimines

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**Abstract**—The exchange reactions of 4,6-di-*tert*-butylpyrocatechols containing in position 3 different *N*-aryliminomethyl groups (aryl is *p*-halophenyl; halogen is fluorine (**I**), chlorine (**II**), bromine (**III**), and iodine (**IV**); *p*-tolyl (**V**)) with copper(II) acetate in a molar ratio of 2 : 1 afford planar square copper(II) *o*-iminophenolate complexes of the general formula $[(\text{R-CatH})_2\text{Cu}]$, where R is the aryl substituent in the Ar–N=CH group. The molecular structures of complexes **I**, **III**, and **V** in the crystalline state are determined by X-ray diffraction (XRD) (CIF files CCDC nos. 2227448 (**I**), 2226727 (**III**), and 2227449 (**V**)). The electrochemical properties of compounds **I**–**V** are studied by cyclic voltammetry.

**Keywords:** pyrocatechol, Schiff base, copper(II), cyclic voltammetry, XRD

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## INTRODUCTION

Pyrocatechols (hydroquinones) occupy a special place in the chemistry of complexes of phenolate ligands. This class of compounds is abundant in many natural systems and plays a substantial role in living organisms [1–3] and in food industry [4–6]. These ligands are formally redox-active, since they can reversibly donate one or several electrons, being in the coordination sphere of the metal, to form various redox forms with the retention of the coordination compound, which finds use in the preparation of functional materials [7–10], synthesis of antitumor agents [11], fabrication of organic batteries, and studying biologically significant redox processes [12, 13].

Schiff bases are universe ligands characterized by the azomethine (>C=N–) group, which demonstrates strong coordination with diverse metals [14–16]. A combination of the Schiff bases with phenol, pyrocatechol, and ferrocenyl fragments in coordination compounds makes it possible to vary widely both redox properties and steric hindrances around the metallocenter, which is accompanied by a change in the chemical behavior of the complexes and, in particular, affects their catalytic and redox activity. These systems exhibit biological activity [17–21] and are widely used in coordination chemistry [22–25], catalysis, and photochemistry [26–29]. New functional complexes with extended redox properties and additional coordination possibilities due to the redox-active ligands of the pyrocatechol series are promising from the viewpoint of the applied character of investigation and are interesting in the respect of studying fundamental aspects of the electronic and molecular structures.

In this work, we synthesized a series of bis(ligand) O,N-chelate copper(II) complexes with substituted Schiff bases of the pyrocatechol series, determined their molecular structures, and studied the electrochemical properties of the synthesized compounds.

## EXPERIMENTAL

All procedures on the synthesis of the copper complexes with substituted catecholaldimines were carried out without air oxygen and moisture access. The solvents used in the syntheses were purified and dehydrated using standard procedures [30, 31]. The ligands were synthesized using a standard procedure [32]. Commercially available reagents (copper(II) acetate monohydrate, triethylamine) were used as received. IR spectra in a range of 400–4000 cm$^{-1}$ were recorded on an FSM-1201 FT-IR spectrometer in Nujol. EPR spectra were detected on a Bruker Magnettech ESR5000 spectrometer. Elemental analysis was carried out on an Elementar Vario EL cube elemental analyzer. Electrochemical measurements were conducted on an Elins P-45X potentiostat of a standard three-electrode configuration. Glassy carbon served as the working electrode ($d$ = 1.6 mm). A platinum wire and a 3.5 M Ag/AgCl/KCl (sat.) electrode were used as the counter electrode and reference electrode, respectively. All measurements were carried out under argon. The scan rate was 100 mV/s. The electrolyte was $n$-$Bu_4NClO_4$ (0.1 M).

**General procedure for the synthesis of copper(II) complexes I–V from substituted Schiff bases.** Substituted catecholaldimine (2 equiv) was dissolved in methanol (20 mL). The resulting solution was added at room temperature to copper(II) acetate hydrate (1 equiv). The reaction mixture was permanently stirred at the boiling point for several hours until all $Cu(OC(O)CH_3)_2 \cdot H_2O$ entered into the reaction with the initial ligand. The precipitate formed in the reaction was separated by filtration, washed with cold methanol, and dried in vacuo. Crystals of complexes **I** and **V** suitable for XRD were grown from a THF solution.

**Complex $(FC_6H_4CatH)_2Cu$ (I)** as a yellow-orange finely crystalline powder was synthesized from 4,6-di-*tert*-butyl-3-(4-fluorophenyliminomethyl)pyrocatechol (0.065 g, 0.190 mmol) and $Cu(OC(O)CH_3)_2 \cdot H_2O$ (0.019 g, 0.095 mmol). The yield was 0.059 g (83%).

For $C_{42}H_{50}N_2O_4F_2Cu$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 67.56 | H, 6.84 | N, 3.59 |
| Found, % | C, 67.40 | H, 6.73 | N, 3.74 |

IR (Nujol; ν, cm$^{-1}$): 3341 s, 1889 w, 1601 s, 1588 s, 1524 s, 1506 s, 1460 s, 1422 w, 1396 s, 1378 s, 1309 s, 1265 w, 1230 s, 1184 w, 1165 m, 1154 m, 1091 m, 1027 w, 998 m, 983 w, 859 m, 844 s, 805 s, 783 w, 720 s, 677 w, 642 s, 619 m, 587 s, 556 w, 538 w, 504 m, 409 m, 467 m.

**Complex $(ClC_6H_4CatH)_2Cu$ (II)** as a yellow finely crystalline powder was synthesized from 4,6-di-*tert*-butyl-3-(4-chlorophenyliminomethyl)pyrocatechol (0.069 g, 0.192 mmol) and $Cu(OC(O)CH_3)_2 \cdot H_2O$ (0.019 g, 0.096 mmol). The yield was 0.065 g (87%).

For $C_{42}H_{50}N_2O_4Cl_2Cu$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 64.67 | H, 6.57 | N, 3.50 |
| Found, % | C, 64.56 | H, 6.45 | N, 3.59 |

IR (Nujol; ν, cm$^{-1}$): 3345 m, 1894 w, 1598 s, 1522 s, 1455 s, 1396 s, 1308 s, 1230 s, 1182 w, 1164 m, 1087 s, 1015 m, 996 m, 961 w, 914 w, 914 m, 860 m, 835 m, 776 m, 740 w, 718 m, 688 w, 675 w, 640 s, 609 s, 584 s, 555 s, 488 s.

**Complex $(BrC_6H_4CatH)_2Cu$ (III)** as a yellow finely crystalline powder was synthesized from 4,6-di-*tert*-butyl-3-(4-bromophenyliminomethyl)pyrocatechol (0.142 g, 0.351 mmol) and $Cu(OC(O)CH_3)_2 \cdot H_2O$ (0.035 g, 0.175 mmol). The yield was 0.134 g (88%).

For $C_{42}H_{50}N_2O_4Br_2Cu$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 57.84 | H, 5.69 | N, 3.31 |
| Found, % | C, 57.97 | H, 5.79 | N, 3.22 |

IR (Nujol; ν, cm$^{-1}$): 3350 s, 1902 w, 1593 s, 1523 s, 1484 s, 1461 s, 1422 m, 1396 s, 1385 s, 1309 s, 1264 m, 1243 s, 1230 s, 1183 m, 1164 s, 1090 m, 1069 s, 1030 w, 1013 s, 997 s, 940 w, 914 w, 859 s, 836 s, 818 s, 774 m, 740 w, 719 m, 675 m, 641 s, 610 s, 584 s, 548 s, 491 m, 471 w.

**Complex $(IC_6H_4CatH)_2Cu$ (IV)** as a yellow finely crystalline powder was synthesized from 4,6-di-*tert*-butyl-3-(4-iodophenyliminomethyl)pyrocatechol (0.198 g, 0.438 mmol) and $Cu(OC(O)CH_3)_2 \cdot H_2O$ (0.044 g, 0.219 mmol). The yield was 0.178 g (84%).

For $C_{42}H_{50}N_2O_4I_2Cu$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 52.21 | H, 5.13 | N, 3.04 |
| Found, % | C, 52.32 | H, 5.23 | N, 2.91 |

IR (Nujol; ν, cm$^{-1}$): 3352 s, 1900 w, 1593 s, 1523 s, 1463 s, 1421 m, 1396 s, 1384 s, 1308 s, 1264 m, 1241 s, 1228 s, 1183 m, 1164 s, 1090 m, 1057 m, 1030 m, 1009 s, 996 s, 940 w, 915 w, 858 s, 835 s, 818 s, 773 m, 740 m, 719 m, 685 w, 675 m, 658 w, 641 s, 609 s, 580 s, 544 s, 490 m, 469 w.

**Complex $(CH_3C_6H_4CatH)_2Cu$ (V)** as a yellow finely crystalline powder was synthesized from 4,6-di-*tert*-butyl-3-(4-tolyliminomethyl)pyrocatechol (0.100 g, 0.293 mmol) and $Cu(OC(O)CH_3)_2 \cdot H_2O$ (0.029 g, 0.146 mmol). The yield was 0.091 g (85%).

For $C_{44}H_{56}CuN_2O_4$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 71.28 | H, 7.51 | N, 3.86 |
| Found, % | C, 71.37 | H, 7.62 | N, 3.78 |

IR (Nujol; ν, cm$^{-1}$): 3347 s, 1900 w, 1674 m, 1590 s, 1524 m, 1508 m, 1454 m, 1395 s, 1385 s, 1312 s, 1263 w, 1242 s, 1181 m, 1166 m, 1112 w, 1091 m, 1027 m, 998 m, 963 w, 942 w, 916 m, 862 m, 856 m, 827 m, 817 m, 792 w, 783 w, 718 m, 676 w, 642 s, 620 s, 591 s, 556 w, 506 w, 463 w.

**XRD** of compounds **I** and **V** was carried out on a Bruker D8 Quest automated diffractometer using the APEX3 software [33]. Experimental sets of intensities were integrated and an absorption correction was applied using the SAINT and SADABS programs [35] for complex **I** and CrysAlis$^{Pro}$ [34] for complex **V**. Both structures were solved using the dual-space algorithm in the SHELXT program [36] and refined by full-matrix least squares for $F^2_{hkl}$ in the anisotropic approximation for all non-hydrogen atoms using the SHELXTL software [37]. Hydrogen atoms in complexes **I** and **V**, except for the hydrogen atom of the hydroxy group in complex **V**, were placed in geometrically calculated positions and refined isotropically by the riding model ($U(H)_{iso} = 1.5U(C)_{equiv}$ for the hydroxy group and methyl groups and $U(H)_{iso} = 1.2U(C)_{equiv}$ for other groups). The H(1) hydrogen atom in complex **V** was objectively localized from the

**Table 1.** Crystallographic data and experimental and structure refinement parameters for complexes **I**, **III**, and **V**

| Parameter | Value | | |
|---|---|---|---|
| | **I** | **III** | **V** |
| Empirical formula | $C_{42}H_{50}N_2O_4F_2Cu$ | $C_{42}H_{50}N_2O_4Br_2Cu$ | $C_{44}H_{56}N_2O_4Cu$ |
| *FW* | 748.38 | 870.20 | 740.44 |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | | |
| *T*, K | 100(2) | | |
| λ, Å | 0.71073 (Mo) | | |
| *a*, Å | 5.8833(11) | 5.8970(12) | 5.8999(4) |
| *b*, Å | 12.275(4) | 12.598(2) | 12.6459(8) |
| *c*, Å | 13.140(4) | 13.762(3) | 13.6915(9) |
| α, deg | 79.882(8) | 69.471(9) | 70.328(6) |
| β, deg | 82.706(8) | 82.460(19) | 81.384(5) |
| γ, deg | 84.210(8) | 84.936(17) | 84.843(5) |
| $V$, Å$^3$ | 923.6(5) | 948.2(3) | 950.19(11) |
| *Z* | 1 | 1 | 1 |
| $\rho_{calc}$, g/cm$^3$ | 1.346 | 1.524 | 1.294 |
| μ, mm$^{-1}$ | 0.646 | 3.154 | 0.620 |
| *F*(000) | 395 | 447 | 395 |
| Crystal sizes, mm | 0.13 × 0.11 × 0.07 | 0.19 × 0.02 × 0.02 | 0.38 × 0.08 × 0.04 |
| Scan range over θ, deg | 2.118–25.079 | 1.683–26.684 | 1.592–25.404 |
| Number of measured/ independent reflections | 10676/3226 | 3289/3289 | 6241/6241 |
| Number of reflections with $I > 2\sigma(I)$ | 2661 | 3289 | 4741 |
| Number of refined parameters/restraints | 239/211 | 243/0 | 244/0 |
| $R_1$, $wR_2$ ($F^2 > 2\sigma(F^2)$) | 0.0937, 0.2424 | 0.0600, 0.1526 | 0.0558, 0.1512 |
| $R_1$, $wR_2$ (for all data) | 0.1176, 0.2603 | 0.0695, 0.1571 | 0.0729, 0.1559 |
| $S(F^2)$ | 1.085 | 1.185 | 1.023 |
| Residual electron density (max/min), e/Å$^3$ | 0.599/–0.511 | 0.839/–0.739 | 0.989/–0.625 |

difference Fourier synthesis and refined isotropically without restraints on thermal or geometric parameters. When refining the structure of compound **I**, the RIGU instruction was used to obtain appropriate thermal parameters of the atoms. The structure of complex **V** was refined as a merohedral twin (for HKLF 5) with a domain ratio of 0.58 : 0.42.

The XRD data for complex **III** were obtained at the Belok beamline of the Kurchatov synchrotron radiation source at the National Research Center Kurchatov Institute at 100 K (λ = 0.75268 Å) using a Rayonix SX165 CCD detector [38]. Unit cell parameters were determined and refined, reflections were integrated, and an absorption correction of reflection intensities was applied using the XDS software [39]. The structure was solved by direct methods and refined by full-matrix least squares [36, 37] in the anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were placed in the calculated positions and refined by the riding model, except for the hydrogen atom forming the intramolecular hydrogen bond, which was revealed from electron density maps and refined without restrains on thermal or geometric parameters. The crystallographic data and experimental and structure refinement parameters for compounds **I**, **III**, and **V** are given in Table 1. Selected bond lengths and angles are listed in Table 2.

The structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2227448 (**I**), 2226727 (**III**), and 2227449 (**V**); ccdc.cam.ac.uk/structures).

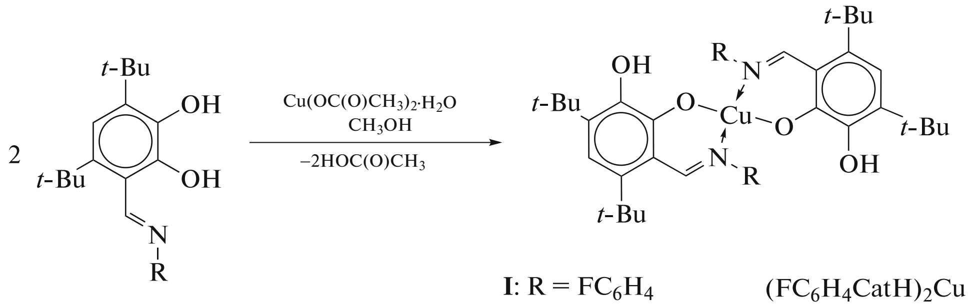
## RESULTS AND DISCUSSION

Copper(II) complexes **I**–**V** with the O,N-chelate ligands based on 4,6-di-*tert*-butylpyrocatechols con-

**Table 2.** Selected bond lengths (Å) and bond angles (deg) in $(FC_6H_4CatH)_2Cu$ (**I**), $(BrC_6H_4CatH)_2Cu$ (**III**), and $(CH_3C_6H_4CatH)_2Cu$ (**V**) according to the XRD data

| Bond | I | III | V |
|---|---|---|---|
| | *d*, Å | | |
| Cu(1)–O(1) | 1.886(5) | 1.884(5) | 1.885(2) |
| Cu(1)–N(1) | 1.976(5) | 1.985(5) | 1.978(3) |
| O(1)–C(1) | 1.314(8) | 1.318(8) | 1.324(4) |
| O(2)–C(2) | 1.386(8) | 1.373(8) | 1.366(4) |
| N(1)–C(15) | 1.301(9) | 1.292(9) | 1.304(4) |
| N(1)–C(16) | 1.439(9) | 1.443(8) | 1.444(4) |
| C(1)–C(6) | 1.413(9) | 1.415(9) | 1.411(5) |
| C(1)–C(2) | 1.410(10) | 1.413(9) | 1.429(5) |
| C(2)–C(3) | 1.367(9) | 1.379(10) | 1.376(5) |
| C(3)–C(4) | 1.394(2) | 1.412(10) | 1.405(5) |
| C(4)–C(5) | 1.422(9) | 1.388(9) | 1.380(4) |
| C(5)–C(6) | 1.435(9) | 1.440(9) | 1.443(5) |
| Angle | ω, deg | | |
| O(1)Cu(1)O(1A) | 180.0 | 180.0 | 180.0 |
| O(1)Cu(1)N(1) | 88.2(2) | 88.4(2) | 88.78(11) |
| O(1)Cu(1)N(1A) | 91.8(2) | 91.6(2) | 91.22(11) |

taining in position 3 of the nitrogen atom various aryl substituents (*p*-halophenyl, where halogen is fluorine (**I**), chlorine (**II**), bromine (**III**), and iodine (**IV**); *p*-tolyl (**V**)) of the general formula $(RCatH)_2Cu$ (R = Hal-$C_6H_4$ group at the imine substituent) were synthesized by the exchange reaction of the corresponding pyrocatechol with copper(II) acetate in a molar ratio of 2 : 1 in a methanol solution. The synthesis of copper(II) bis-*o*-iminophenolate complexes **I**–**V** is shown in Scheme 1.



**I**: R = $FC_6H_4$ $(FC_6H_4CatH)_2Cu$
**II**: R = $ClC_6H_4$ $(ClC_6H_4CatH)_2Cu$
**III**: R = $BrC_6H_4$ $(BrC_6H_4CatH)_2Cu$
**IV**: R = $IC_6H_4$ $(IC_6H_4CatH)_2Cu$
**V**: R = $CH_3C_6H_4$ $(CH_3C_6H_4CatH)_2Cu$

**Scheme 1.**

Bis-O,N-chelate complexes **I**–**V** are powders with the color from light yellow (**I**–**IV**) to orange (**V**), resistant to air oxygen and moisture, and highly soluble in the most part of usually used organic solvents (THF, acetonitrile, dichloromethane, and others). The solubility of the complexes in polar aprotic solvents (THF, dichloromethane) decreases on going from fluorine to iodine in the Hal-$C_6H_4$-N=CH substituent.

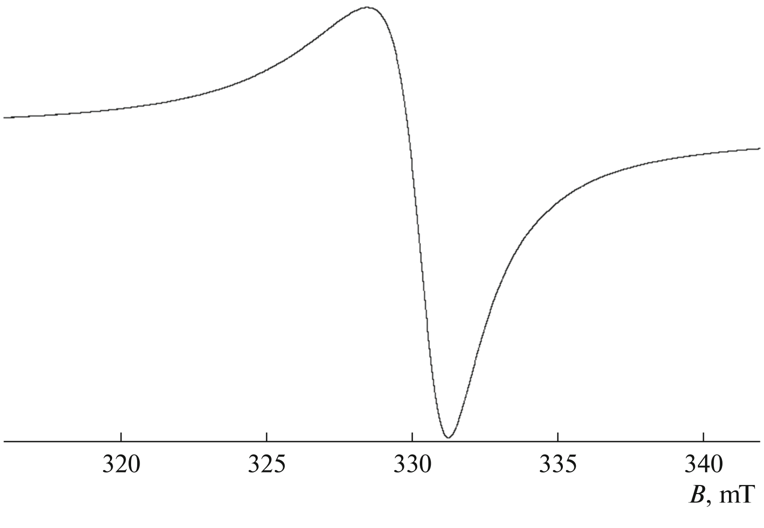


**Fig. 1.** Experimental EPR spectrum of complex **V** in the solid state at room temperature.

Compounds **I**–**V** were characterized by IR spectroscopy and elemental analysis. The molecular structures of complexes **I**, **III**, and **V** in the crystalline state were determined by XRD.

The formation of copper(II) *o*-iminophenolate complexes **I**–**V** is unambiguously indicated by the presence in the IR spectra of intense characteristic bands corresponding to stretching vibrations of the C–O ordinary bonds of the iminophenolate ligands in a range of 1220–1280 $cm^{-1}$ and the band at 3350–3100 $cm^{-1}$ attributed to stretching vibrations of the free hydroxy group of the Schiff bases. The stretching vibrations of the CH=N double bond in the spectra of the complexes are shifted to a weak range by 10–15 $cm^{-1}$ compared to the corresponding vibrations in the free ligands.

The EPR spectra of complexes **I**–**V** in the solid state (powder) have an axial symmetry of the *g* tensor and indicate in favor of an unpaired electron on the molecular orbital of the metallocenter, which is characteristic of the planar square copper(II) compounds: $g_{\|} = 2.052$ for **I**, 2.053 for **II**, 2.054 for **III**, 2.055 for **IV**, and 2.054 for **V** (Fig. 1). It seems impossible to calculate the $g_{\perp}$ component because of the unresolved structure of the EPR spectra on the parallel component of the *g* tensor caused by hyperfine splitting on the magnetic nuclei of copper ($^{63}$Cu, $I = 3/2$, 69.1%; $^{65}$Cu, $I = 3/2$, 30.9% [40]).

The crystal structures of complexes **I**, **III**, and **V** containing 4-fluoro-, 4-bromo-, and 4-methylphenyl substituents, respectively, in position 3 at the nitrogen atom were determined by XRD. Complexes **I**, **III**, and **V** have similar molecular and crystal structures (Figs. 2, 3). The XRD data show that the complexes crystallize in the triclinic space group $P\overline{1}$. In all three complexes, the copper atom is localized at the inversion center. As a result, only half a molecule exists in the independent part of the unit cell.

The copper atom in complexes **I**, **III**, and **V** is coordinated by the O(1) oxygen atoms of the hydroxyphenolate moiety and N(1) atom of the imino group of two ligands: monodeprotonated Schiff bases. The sum of the OCuN angles is 360° and indicates a planar square geometry around the central copper atom. The O–C and N=C distances in the *o*-iminophenolate ligands (1.314(8) and 1.301(9) Å for **I**, 1.318(8) and 1.292(9) Å for **III**, and 1.324(4) and 1.304(4) Å for **V**, respectively) are characteristic of ordinary and double bonds of C–O and C=N groups, respectively, in diverse metal complexes (C–O 1.32–1.36 Å, C–N 1.29–1.31 Å) [14, 41, 42]. On the one hand, the Cu(1)–O(1) bond length (1.886(5) Å for **I**, 1.884(5) Å for **III**, and 1.885(2) Å for **V**) is somewhat less than the sum of covalent radii of the corresponding atoms ($r_{cov}$(Cu) = 1.17 Å, $r_{cov}$(O) = 0.73 Å [43]) and corresponds to these bonds in similar *o*-iminophenolate copper complexes [44, 45]. On the other hand, the Cu(1)–N(1) interatomic distances in the complexes (1.976(5) Å in **I**, 1.985(5) Å in **III**, and 1.978(3) Å in **V**) slightly exceed the sum of covalent radii of the corresponding atoms ($r_{cov}$(Cu) 1.17 Å, $r_{cov}$(N) 0.74 Å) [44]) but are significantly less than the sum of van der Waals radii ($r_W$(Cu) 2.0 Å, $r_W$(N) 1.6 Å [47], indicating the donor-acceptor character of the bond.

The C–C distances of the C(1–6) aromatic ring in the *o*-iminophenolate ligand (1.367(9)–1.413(9) Å for **I**, 1.379(10)–1.440(9) Å for **III**, and 1.376(5)–1.443(5) Å for **V** with average values of 1.407, 1.408, and 1.407 Å, respectively) are close to those in the *o*-iminophenolate complexes of different metals [44, 47, 48].

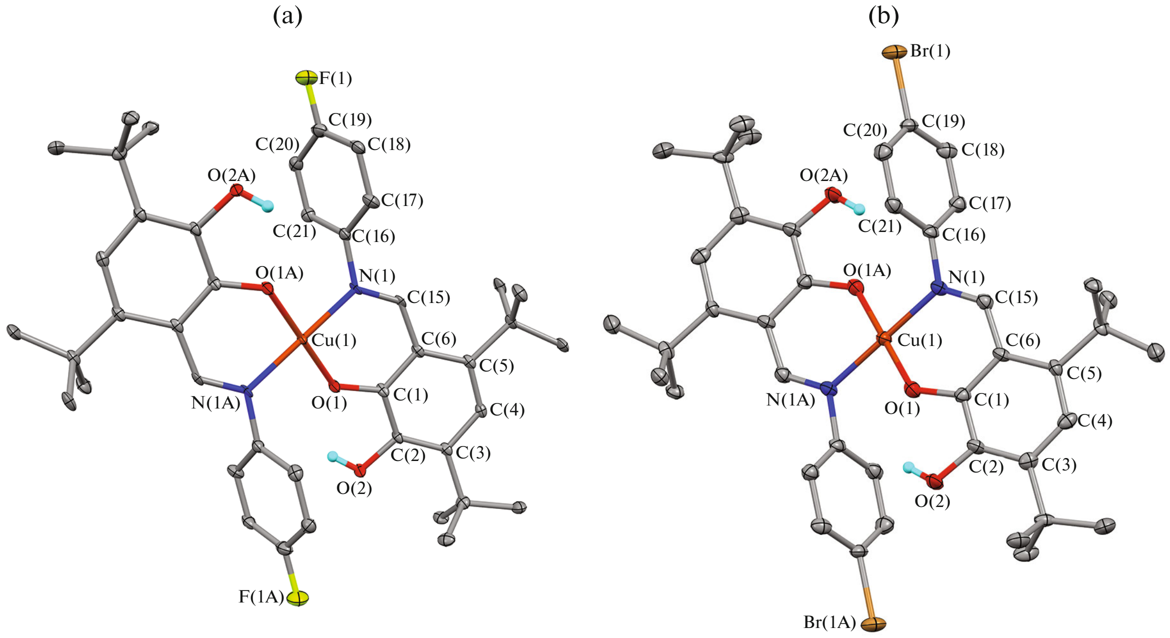


**Fig. 2.** Molecular structures of complexes (a) **I** and (b) **III**. Thermal ellipsoids are given with 50% probability. Hydrogen atoms are omitted.

The six-membered CuOCCCN metallocycles in complexes **I**, **III**, and **V** are nonplanar. The dihedral angles between the CuON and OCCCN planes are 26.9°, 25.9°, and 24.5°. The phenyl ring with the halogen or methyl substituent is turned relative to the ligand plane by 50.8°, 56.4°, and 57.5° in complexes **I**, **III**, and **V**, respectively.

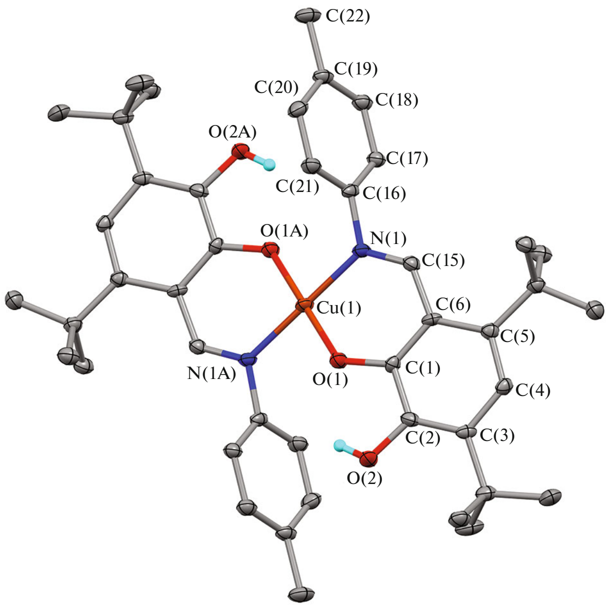


**Fig. 3.** Molecular structure of complex **V**. Thermal ellipsoids are given with 50% probability. Hydrogen atoms are omitted.

The redox properties of O,N-chelate copper(II) complexes **I**–**V** were studied by cyclic voltammetry (CV) in a dichloromethane solution (Table 3).

The CV curves of copper(II) complexes **I**–**V** at the potential scan from –500 to 1200 mV demonstrate one step of electrochemical oxidation in the range from 995 to 1125 mV, which is an irreversible two-electron wave and corresponds to the oxidation of the O,N-chelate cycle to the phenoxy cation. For complexes **I**–**V** in the cathodic CV range in the potential scan range from –1300 to +500 mV, irreversible peaks are observed in the range from –931 to –1149 mV and can correspond to the reduction of the R–CH=N–R' fragment [48, 49]. Complexes **II**, **IV**, and **V** also exhibit irreversible peaks in the cathodic range (from –1515 to –1613 mV) corresponding, as we believe, to the reduction of Cu(II) to Cu(I). This is exemplified by the CV curve of the oxidation of complex **I** based on pyrocatechol containing the 4-fluorophenyl substituent in position 3 (Fig. 4). Note that owing to the considerably remote substituent in the *para*-position of the benzene ring of the imine group, the nature of this substituent (halogen in complexes **I**–**IV** or methyl in complex **V**) makes no substantial contribution to the electron density distribution of the CH=N group and iminophenolate center involved in the redox process and exerts almost no effect on the electrochemical oxidation and reduction potentials (Table 3).

Thus, the series of bis(ligand) copper(II) complexes with the substituted catecholaldimine ligands was synthesized. The molecular structures of three complexes, $(FC_6H_4CatH)_2Cu$ (**I**), $(BrC_6H_4CatH)_2Cu$ (**III**), and $(CH_3C_6H_4CatH)_2Cu$ (**V**), in the crystalline state were determined by XRD. The redox properties of the synthesized compounds were studied by the CV method. The electrochemical oxidation of the complexes proceeds at 0.995–1.125 V as a two-electron process and involves both iminophenolate ligands. The electrochemical reduction proceeds at the imine groups in the potential range from –931 to –1149 mV.

It should be mentioned that the reactions studied in this work of copper(II) acetate with the indicated catecholaldimines afford just the *o*-iminophenolate derivatives with the O,N-chelating ligands, and the hydroxy groups of the ligands remain free. This route of complex formation differs from the earlier studied reactions of similar catecholaldimines with the organometallic tin and antimony derivatives affording the complexes with the O,O-chelating ligands [48].

**Table 3.** Electrochemical potentials (mV) of the oxidation of complexes **I**–**V** (298 K, $c = 1 \times 10^{-3}$ mol/L, 0.1 M $[n\text{-}Bu_4N]ClO_4$, $V = 0.2$ V/s)

| Complex | $E_2^{red}$, mV | $E_1^{red}$, mV | $E^{Ox}p_1$, mV* |
|---|---|---|---|
| **I** | | –1100 | 1099 |
| **II** | –1515 | –968 | 998 |
| **III** | | –931 | 995 |
| **IV** | –1544 | –982 | 1027 |
| **V** | –1613 | –1149 | 1125 |

* *E*p is the peak potential for the irreversible process.

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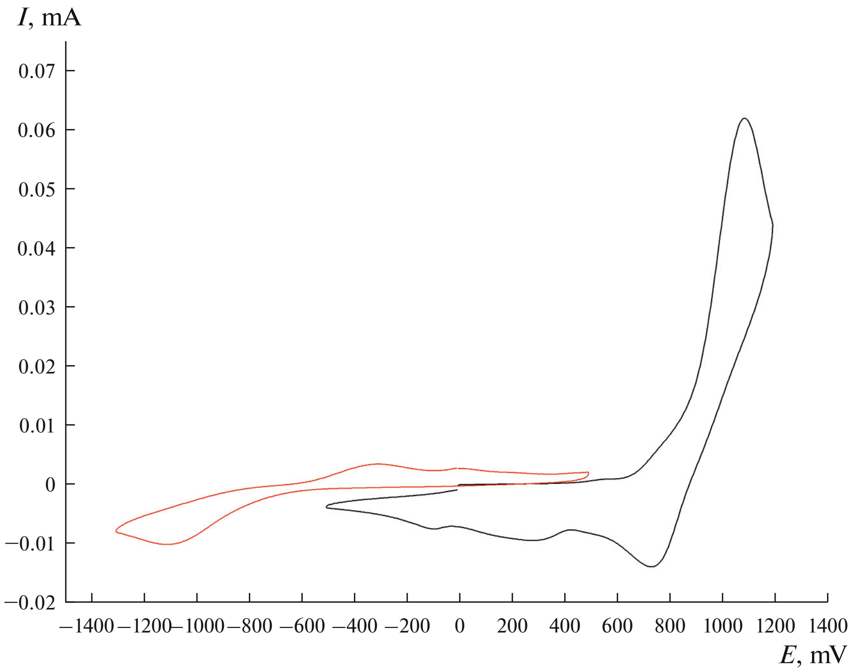

**Fig. 4.** CV curves for the oxidation of complex **I** in the potential ranges from –1300 to +500 mV (red line) and from –500 to +1200 mV (gray line) (298 K, $c = 1 \times 10^{-3}$ mol/L, 0.1 M $[n\text{-}Bu_4N]ClO_4$, $V = 0.2$ V/s).

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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