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Bis(1,4-di-*tert*-butyl-1,4-diazabutadiene)copper(I) [(3,6-di-*tert*-butyl-*o*-benzosemiquinono)(3,6-di-*tert*-butylcatecholato)cuprate(II)]. The molecular structure and intramolecular electron transfer

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Bis(1,4-di-*tert*-butyl-1,4-diazabutadiene)copper(I) [(3,6-di-*tert*-butyl-*o*-benzosemiquinono)(3,6-di-*tert*-butylcatecholato)cuprate(II)] (**1**) was synthesized. Complex **1** contains the 1,4-di-*tert*-butyl-1,4-diazabutadiene and 3,6-di-*tert*-butyl-*o*-benzoquinone ligands in the reduced form. The structure of **1** was established by X-ray diffraction analysis. The ESR spectra indicate that dissolution of complex **1** in organic solvents (toluene, THF, CH_2Cl_2, *etc.*) leads to its symmetrization to give neutral complex **2**, which occurs in solutions as an equilibrium mixture of two redox isomers, *viz.*, catecholate (Cat) complex **2c** and semiquinone (SQ) complex **2s**. In the coordination sphere of the copper atom, the reversible intramolecular metal—ligand electron transfer can proceed as successive steps as exemplified by the reactions of **2** with CO and 2,6-dimethylphenylisonitrile. Copper(I) *o*-semiquinone complex **2s** can be reversibly transformed into copper(II) catecholate complex **2c** through electron transfer from the copper(I) atom to the SQ ligand. The subsequent addition of the neutral ligand (CO or CNAr) to **2c** induces, in turn, electron transfer from the Cat ligand to the copper(II) atom accompanied by the transformation of the catecholate complex into the *o*-semiquinone complex. In the case of CO, this transformation is also reversible and is efficiently controlled by the temperature.

Key words: copper complexes, *o*-benzosemiquinone, intramolecular electron transfer, X-ray diffraction analysis, ESR spectra.

Being one of the most important bioelements,[1] copper is incorporated into various enzymes involved in redox processes. One of new topical lines of investigation in the chemistry of copper-containing enzymes is concerned with intramolecular redox processes involving the copper center along with a free-radical ligand coordinated to the metal atom. As an example, we refer to a series of studies devoted to the examination and modeling of the mechanism of action of the enzyme galactose oxidase.[2—4] These studies have established that one of the key stages of the process involves the intramolecular metal—ligand electron transfer giving rise to an intermediate copper(II) complex with the aroxyl fragment.

The possibility of the reversible intramolecular electron transfer from the copper atom to a free-radical ligand in solution has been demonstrated for the first time for copper complexes with *o*-quinone derivatives. It has been found[5] that the reversible intramolecular metal—ligand electron transfer can be induced by the replacement of neutral ligands:

$$\mathrm{CatCu^{II}(bpy) + 2\,PPh_3 \rightleftharpoons SQCu^{I}\,(PPh_3)_2 + bpy},$$

where Cat is catecholate and SQ is semiquinone.

Later on, it has been established that the reversible intramolecular metal—ligand electron transfer can proceed also without changes in the composition of the coordination sphere. For example, the transformation of the coordination sphere in copper complexes with the diazabutadiene (DAD) ligands from planar-square (in the catecholate complex of $\mathrm{Cu^{II}}$) into tetrahedral (in the semiquinone complex of $\mathrm{Cu^{I}}$) was accompanied by the reversible electron transfer:[6]

$$\mathrm{CatCu^{II}(\eta^2\text{-}DAD) \rightleftharpoons SQCu^{I}(\eta^2\text{-}DAD)}.$$

Recently, redox-isomeric transformations of such complexes were revealed in the ESR studies of a series of copper *o*-semiquinone complexes with the bidentante

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2-alkylthiomethyl-1-methyl-1*H*-benzimidazole ligand.[7] It was demonstrated that these complexes can serve as models for investigating the action of the enzyme amine oxidase.

Hence, metal *o*-semiquinone complexes are efficient model compounds for studying both substitutions of the ligands and intramolecular redox reactions of metal complexes in solutions and can be used for modeling various elementary stages of complicated bioinorganic processes.

In the present study, we report the results of modeling of the sequence of such reversible transformations proceeding successively at the same metal center. For this purpose, we synthesized copper complex **1** containing the 1,4-di-*tert*-butyl-1,4-diazabutadiene and 3,6-di-*tert*-butyl-*o*-benzoquinone ligands in the reduced form, established its structure in the crystal and solution, and studied its reactions with CO and 2,6-dimethylphenylisonitrile by ESR spectroscopy.

Results and Discussion

Complex **1** was prepared by metathesis of (1,4-di-*tert*-butyl-1,4-diazabutadiene)copper(I) chloride with thallium(I) 3,6-di-*tert*-butyl-*o*-benzosemiquinolate.[6]

According to the data of X-ray diffraction study of dark-claret crystals, complex **1** is the cuprate $[\mathrm{SQCatCu^{II}}]^- \cdot [(\mathrm{Bu^t{-}DAD})_2\mathrm{Cu^I}]^+$ (**1**) (Fig. 1; Tables 1 and 2). The Cu^{II} atom in the anion of complex **1** has a planar-square coordination environment formed by four O atoms of the benzosemiquinone and catecholate ligands (Cu—O$_{Cat}$, 1.850(5) and 1.897(5) Å; Cu—O$_{SQ}$, 1.949(5) and 1.955(4) Å; the OCuO/OCuO angle is 12.9°). The Cu—O distances in the semiquinone and catecholate ligands of complex **1** differ, on the average, by 0.78 Å, which corresponds to the difference in the bond lengths (0.77 Å) found previously in the structure of its 3,5-di-*tert*-buty-4-chloroquinone analog.[8] The geometric characteristics of each coordinated ligand have values typical of the benzoquinone ligands in the SQ and Cat forms (see Table 2).[9] The ligands are virtually planar (the average deviations of the atoms from the planes of the Cat and SQ ligands are 0.013 and 0.03 Å, respectively). The tertiary carbon atoms of the *tert*-butyl substituents are located in the same planes. Unlike the Cu atom in the anion, the copper(I) ion in the cation has the pseudotetrahedral environment formed by four N atoms of two 1,4-di-*tert*-1,4-diazabutadiene ligands (Cu—N, 2.008(6)—2.054(6) Å; the CuN$_2$/CuN$_2$ angle is 88.9°).

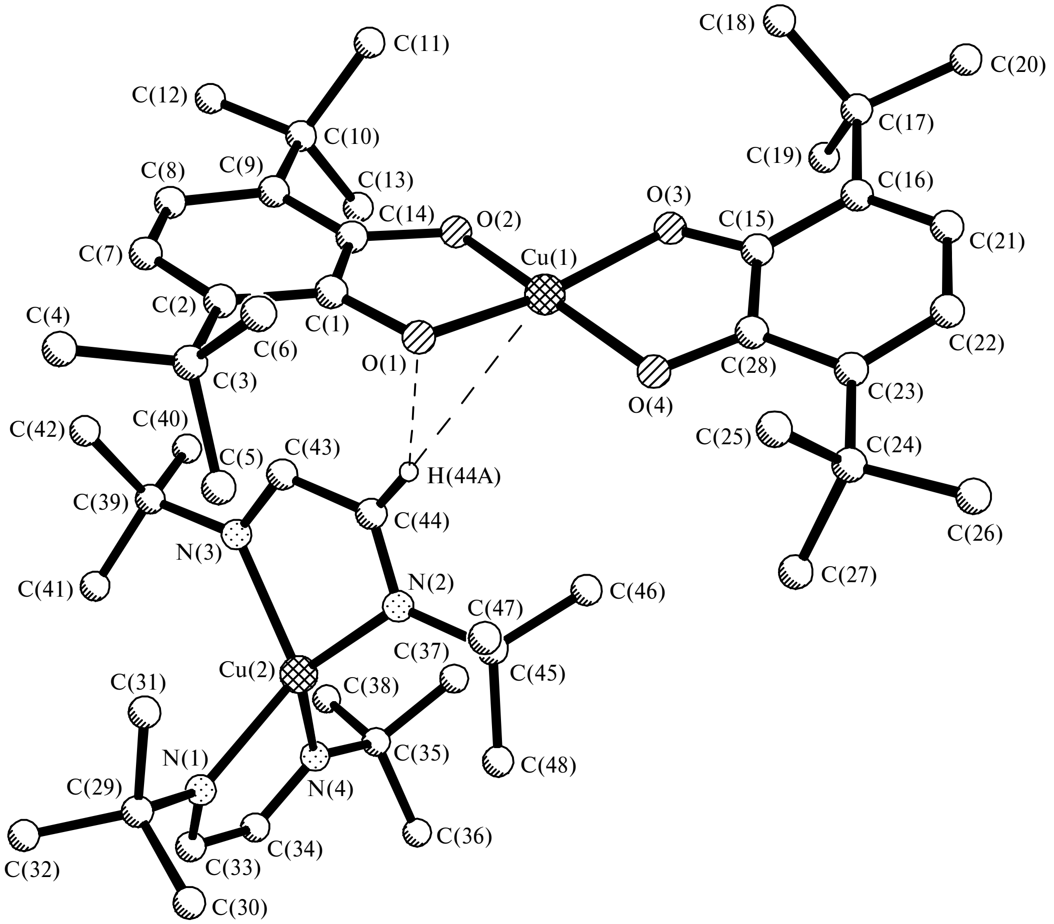


Fig. 1. Structure of the cation-anionic complex **1** (the H atoms, except for the H(44A) atom involved in hydrogen bonding, are omitted).

Table 1. Crystallographic parameters of complex **1**

Parameter	Characteristic
Molecular formula	$C_{48}H_{80}Cu_2N_4O_4$
Molecular weight	904.24
Space group	$P2_1/n$
a/Å	11.269(5)
b/Å	23.145(11)
c/Å	21.527(5)
α/deg	90
β/deg	95.74(3)
γ/deg	90
V/Å^3	5586(4)
Z	4
ρ_{calc}/g cm^{-3}	1.075
μ/cm^{-1}	0.800
$\theta/2\theta$ Scan range	1.30—22.04
Number of measured reflections	6401
Number of reflections with $I > 2\sigma$	5986 (R_{int} = 0.0503)
Number of parameters in the refinement	523
R_1 ($I > 2\sigma(I)$)	0.0532
$_wR_2$	0.1297

Unlike the anion in complex **1** which adopts a planar-square conformation, the five-coordinate anion in its 3,5-di-*tert*-butyl-4-chloroquinone analog[8] has a tetragonal-pyramidal structure with the THF molecule in the apical position. However, in the crystal there is a short contact between the H(44A) atom of the butylene fragment of the diazabutadiene metallocycle of the cation and the O(1) and Cu(1) atoms of the anion (2.607 and 2.997 Å, respectively; see Fig. 1).

Complex **1** is paramagnetic. When dissolved in organic solvents, complex **1** underwent reversible symmetrization to neutral complex **2**, which, in turn, existed in solutions as an equilibrium mixture of two redox isomers, *viz.*, catecholate **2c** and semiquinone **2s**:

$$1/2\ \mathbf{1} \rightleftharpoons 1/(1+K)\ \underset{\mathbf{2c}}{\mathrm{CatCu^{II}}(\eta^2\text{-}\mathrm{Bu^t}\text{—}\mathrm{DAD})} +$$
$$+\ K/(1+K)\ \underset{\mathbf{2s}}{\mathrm{SQCu^{I}}(\eta^2\text{-}\mathrm{Bu^t}\text{—}\mathrm{DAD})}.$$

The redox isomerism inherent in sterically shielded copper diazabutadiene complexes with *o*-quinones has

Table 2. Selected bond length and bond angles in complex **1**

Bond	d(Å)	Angle	ω/deg	Angle	ω/deg
Cu(1)—O(1)	1.897(5)	O(1)—Cu(1)—O(4)	96.5(2)	C(8)—C(9)—C(14)	114.3(7)
Cu(1)—O(2)	1.850(5)	O(1)—Cu(1)—O(3)	168.6(2)	C(14)—C(9)—C(10)	121.3(7)
Cu(1)—O(3)	1.955(4)	O(2)—Cu(1)—O(1)	88.1(2)	O(2)—C(14)—C(1)	115.0(6)
Cu(1)—O(4)	1.949(5)	O(2)—Cu(1)—O(3)	92.9(2)	C(1)—C(14)—C(9)	123.3(7)
Cu(2)—N(1)	2.054(6)	O(2)—Cu(1)—O(4)	173.5(2)	O(2)—C(14)—C(9)	121.7(7)
Cu(2)—N(2)	2.018(5)	O(4)—Cu(1)—O(3)	83.4(2)	O(3)—C(15)—C(28)	117.2(6)
Cu(2)—N(3)	2.047(6)	N(2)—Cu(2)—N(3)	81.9(2)	O(3)—C(15)—C(16)	121.2(7)
Cu(2)—N(4)	2.008(6)	N(2)—Cu(2)—N(1)	123.4(3)	C(21)—C(16)—C(15)	114.3(7)
O(1)—C(1)	1.357(8)	N(3)—Cu(2)—N(1)	114.6(2)	C(15)—C(16)—C(17)	120.6(7)
O(2)—C(14)	1.374(8)	N(4)—Cu(2)—N(1)	82.5(3)	C(16)—C(15)—C(28)	121.5(7
O(3)—C(15)	1.285(8)	N(4)—Cu(2)—N(2)	133.9(3)	C(16)—C(17)—C(18)	109.8(6)
O(4)—C(28)	1.294(8)	N(4)—Cu(2)—N(3)	124.6(3)	C(16)—C(21)—C(22)	124.0(7)
N(1)—C(29)	1.492(9)	C(1)—O(1)—Cu(1)	108.6(4)	C(21)—C(16)—C(17)	125.1(7)
N(1)—C(33)	1.273(8)	C(14)—O(2)—Cu(1)	110.7(4)	C(22)—C(23)—C(24)	124.2(7)
N(2)—C(44)	1.271(8)	C(15)—O(3)—Cu(1)	110.8(4)	C(22)—C(23)—C(28)	114.3(6)
N(2)—C(45)	1.502(9)	C(33)—N(1)—C(29)	119.9(6)	C(23)—C(22)—C(21)	124.7(7)
N(3)—C(39)	1.494(9)	C(29)—N(1)—Cu(2)	130.6(4)	C(23)—C(28)—C(15)	121.0(7)
N(3)—C(43)	1.280(8)	C(44)—N(2)—Cu(2)	111.4(5)	C(28)—C(23)—C(24)	121.4(7)
N(4)—C(34)	1.277(9)	C(43)—N(3)—Cu(2)	110.2(5)	O(4)—C(28)—C(23)	123.4(7)
N(4)—C(35)	1.451(10)	C(34)—N(4)—Cu(2)	111.2(5)	O(4)—C(28)—C(15)	115.6(7)
C(1)—C(2)	1.437(10)	O(1)—C(1)—C(14)	117.3(7)	N(1)—C(29)—C(30)	108.3(7)
C(1)—C(14)	1.404(9)	C(14)—C(1)—C(2)	121.3(7)	N(1)—C(29)—C(31)	106.6(6)
C(2)—C(3)	1.525(10)	C(28)—O(4)—Cu(1)	111.8(4)	N(1)—C(29)—C(32)	111.3(7)
C(2)—C(7)	1.406(10)	C(33)—N(1)—Cu(2)	109.4(5)	N(1)—C(33)—C(34)	118.3(7)
C(7)—C(8)	1.331(10)	C(44)—N(2)—C(45)	117.6(6)	N(2)—C(44)—C(43)	118.1(7)
C(8)—C(9)	1.406(10)	C(45)—N(2)—Cu(2)	130.7(5)	N(2)—C(45)—C(46)	108.8(7)
C(9)—C(10)	1.522(10)	C(39)—N(3)—Cu(2)	129.4(4)	N(2)—C(45)—C(47)	111.0(7)
C(9)—C(14)	1.403(9)	C(35)—N(4)—Cu(2)	130.2(5)	N(2)—C(45)—C(48)	105.5(7)
C(15)—C(16)	1.451(9)	C(7)—C(2)—C(1)	112.1(7)	N(3)—C(39)—C(41)	107.7(6)
C(15)—C(28)	1.450(9)	O(1)—C(1)—C(2)	121.4(7)	N(3)—C(39)—C(42)	110.9(7)
C(16)—C(17)	1.516(10)	C(1)—C(2)—C(3)	122.4(7)	N(3)—C(43)—C(44)	118.1(7)
C(16)—C(21)	1.360(9)	C(7)—C(2)—C(3)	125.5(7)	N(4)—C(34)—C(33)	117.6(7)
C(21)—C(22)	1.400(9)	C(2)—C(3)—C(5)	109.1(6)	N(4)—C(35)—C(36)	112.6(8)
C(22)—C(23)	1.381(9)	C(7)—C(8)—C(9)	122.2(8)	N(4)—C(35)—C(37)	108.1(8)
C(23)—C(24)	1.517(9)	C(8)—C(7)—C(2)	126.6(8)	N(4)—C(35)—C(38)	112.1(8)
C(23)—C(28)	1.428(9)	C(8)—C(9)—C(10)	124.3(7)	C(40)—C(39)—N(3)	109.6(8)
C(33)—C(34)	1.483(10)				
C(43)—C(44)	1.462(10)				

been described previously.[6] In solutions, isomers **2c** and **2s** undergo rapid (within the NMR time scale) interconversion so that the ESR spectrum has an averaged signal with the parameters determined by the equilibrium constant (K) and the isotropic parameters of the following limiting forms:

$$\mathrm{CatCu^{II}(\eta^2\text{-}Bu^t{-}DAD)} \xrightleftharpoons{K} \mathrm{SQCu^{I}(\eta^2\text{-}Bu^t{-}DAD)}.$$

The observed ESR spectrum shows hyperfine interactions of the unpaired electron with the magnetic isotopes ^{63}Cu (69.09%; $I = 3/2$; $\mu_N = 2.2206$) and ^{65}Cu (30.91%; $I = 3/2$; $\mu_N = 2.3790$).[10] Lowering of the temperature and an increase in polarity of the solvent led to the shift of the equilibrium to the catecholate isomer and, correspondingly, to the increase in the g_i and $A_i(^{63,65}Cu)$ values. The presence of cuprate **1** in solutions is still an open question. In the cited study, possible pathways of the reversible isomerization were not considered. Apparently, the ligand exchange in dimer **2c** · **2s** is one of these pathways. The formation of such dimers is typical of *o*-semiquinone and catecholate complexes of copper.[11,12]

$$\begin{gathered}\mathrm{CatCu^{II}(\eta^2\text{-}Bu^t{-}DAD) + SQCu^{I}(\eta^2\text{-}Bu^t{-}DAD)} \rightleftharpoons \\ \rightleftharpoons \mathrm{(Cat)Cu^{II}(\mu\text{-}\eta^3\text{-}Bu^t{-}DAD)_2Cu^{I}(SQ)} \\ \mathrm{(Cat)Cu^{II}(\mu\text{-}\eta^3\text{-}Bu^t{-}DAD)_2Cu^{I}(SQ)} \rightleftharpoons \\ \rightleftharpoons \mathrm{[SQCatCu^{II}]^- \cdot [(Bu^t{-}DAD)_2Cu^{I}]^+}\end{gathered}$$

The reactions of complex **2** with CO and 2,6-dimethylphenylisonitrile, which can form stable complexes with copper(I),[13] were studied by ESR spectroscopy.

It was found that the reaction of the diazadiene complex with CO gave rise to the mixed-ligand four-coordinate *o*-semiquinone complex of copper(I) $SQCu(\eta^1\text{-}DAD)CO$ (**3**) in which the diazadiene ligand, unlike that in complex **2**, is coordinated to the Cu atom only through one N atom. The structure of complex **3** followed from analysis of the hyperfine structure of its isotropic ESR spectrum (Fig. 2), which revealed interactions of the unpaired electron with the ^{63}Cu and ^{65}Cu isotopes, the ^{14}N nucleus of one nitrogen atom, and two protons of the *o*-semiquinone ligand ($g_i = 2.0046$; $A_i(^{63}Cu) = 9.48$ Oe; $A_i(^{65}Cu) = 10.25$ Oe; $A_i(^{14}N) = 1.20$ Oe; $A_i(H_{SQ}) = 3.25$ Oe). Hence, the addition of CO was accompanied by the change in the mode of coordination of the diazadiene ligand from η^2 to η^1.

$$\mathbf{2} + \mathrm{CO} \rightleftharpoons \mathrm{SQCu(\eta^1\text{-}DAD)CO}$$

This transformation is reversible and depends substantially on the temperature. The ESR spectra measured at two different temperatures are shown in Fig. 3. At 300 K, the character and the parameters of the ESR spectrum are typical of a redox-isomeric mixture of **2c** and **2s**.[6] Components of the low-intensity ESR spectrum of complex **3** are in evidence in the high-field region of the spectrum. At 200 K, the equilibrium is virtually completely shifted to complex **3** and, correspondingly, the ESR spectrum has only its components. The initial shape of the ESR spectrum was regained as the temperature was raised. The removal of CO from the reaction mixture also led to the shift of the equilibrium to initial complex **2**.

Previously, it has been demonstrated[14] that mixed-ligand copper *o*-semiquinone complexes of such a composition can be prepared by the reactions of CO with copper(II) bis-semiquinone complexes in organic solvents in the presence of amines. It has also been established that copper(I) *o*-semiquinone complexes containing amines (Et_2NPh or Bu_2NPh) exist in solutions as two geometric isomers. These isomers occur in equilibrium and undergo the interconversion as the temperature changes. No isomerization was observed for complex **3** as evidenced by the fact that the hyperfine interaction constants $A_i(^{63,65}Cu)$ in the ESR spectrum remained unchanged (even in the presence of a large excess of diazadiene) in the temperature range under study.

In the reaction of complex **2** with 2,6-dimethylphenylisonitrile, the primary mixed-ligand complex $SQCu(\eta^1\text{-}DAD)CNAr$ was not detected in the solution. Even the first stage of the reaction with CNAr resulted in elimination of diazadiene to form the monoisonitrile complex, which was transformed into the bis-isonitrile complex in the presence of an excess of the isonitrile ligand.

$$\begin{gathered}\mathbf{2} + \mathrm{CNAr} \rightleftharpoons \mathrm{DAD + SQCuCNAr} \\ \mathrm{SQCuCNAr + CNAr} \rightleftharpoons \mathrm{SQCu(CNAr)_2}\end{gathered}$$

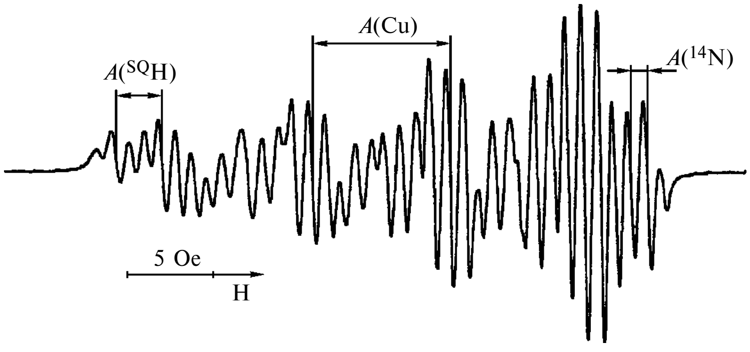


Fig. 2. Isotropic ESR spectrum of complex **3** (toluene—CH_2Cl_2; 220 K).

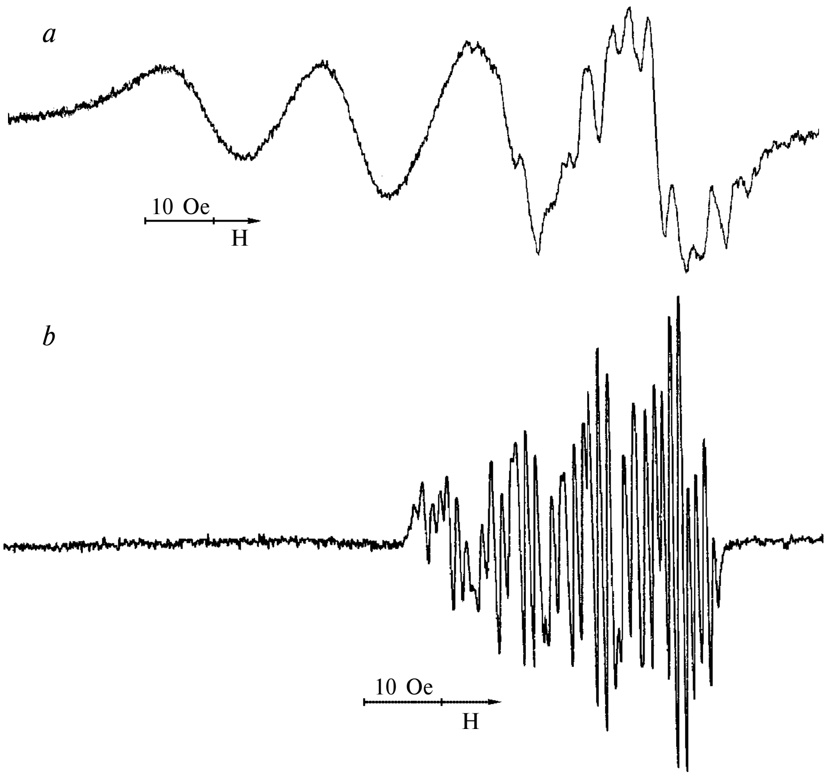


Fig. 3. Isotropic ESR spectra observed in the reaction of complex **2** with CO (toluene—CH_2Cl_2) at 300 K (*a*) and 200 K (*b*).

This fact is in agreement with a superposition of the mono- and bis-isonitrile complexes observed in the ESR spectrum (Fig. 4.).

Isonitrile complex:	g_i	$A_i(^{63}Cu)$	$A_i(^{65}Cu)$	$A_i(H_{SQ})$
			Oe	
mono	2.0036	3.98	4.28	3.46
bis	2.0049	9.55	10.22	3.17

It should be noted that the presence both of the catecholate and semiquinone forms in solutions suggests two possible mechanisms of the substitution reactions, *viz.*, dissociative and associative (Scheme 1). The first path is typical of the semiquinone form. Thus, the complex is reversibly transformed into a three-coordinate compound through the cleavage of one Cu—N coordination bond and the latter complex is converted into a mixed-ligand complex by adding one ligand molecule. This reaction is not accompanied by the intramolecular electron transfer. In the case of the catecholate form, the reaction proceeds according to the associative mechanism. Due to the planar-square environment, the copper atom can coordinate a ligand molecule without experiencing steric hindrances, the ligand occupying the apical position and the coordination number of copper being increased to 5. The intermediate is subsequently transformed into the mixed-ligand semiquinone four-coordinate complex of Cu^{I} by changing the mode of coordination of the diazabutadiene ligand from bidentate to monodentate accompanied by the intramolecular ligand—metal electron transfer. In our opinion, the latter mechanism is more probable, and it is also supported by the fact that the three-coordinate intermediate SQCu(η^1-Bu^t—DAD) was not detected in solutions of **2** by ESR spectroscopy up to 350 K.

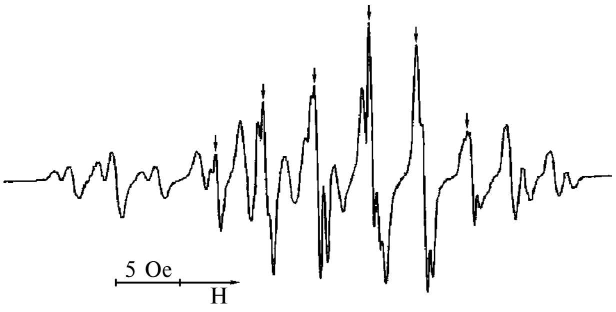
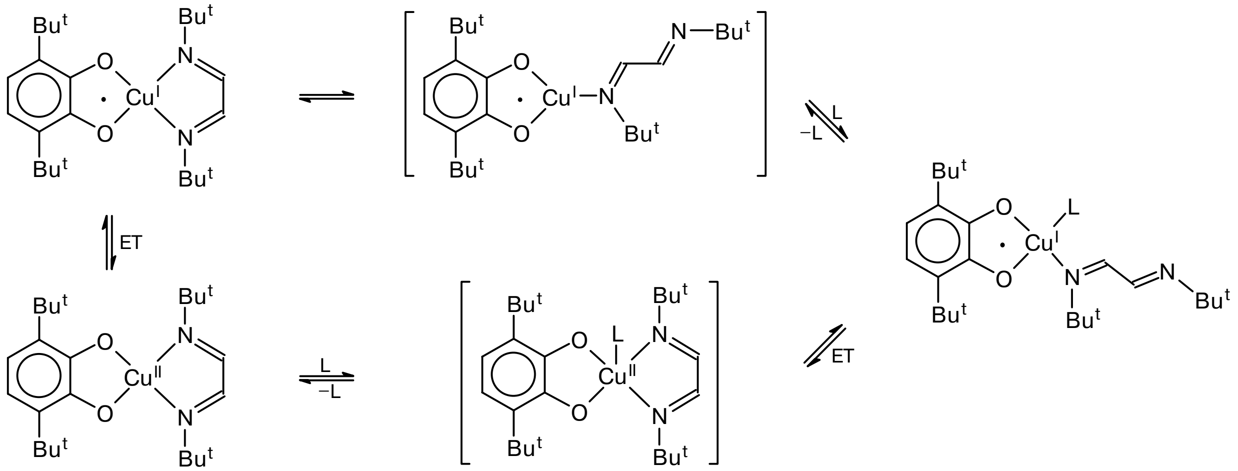


Fig. 4. Superposition of the isotropic ESR spectra of the complexes $(ArNC)_2Cu(3,6\text{-}Bu^t\text{—}SQ)$ and $(ArNC)Cu(3,6\text{-}Bu^t\text{—}SQ)$ (indicated by arrows) (toluene—CH_2Cl_2; 270 K).

Hence, using complex **2** as an example, it was demonstrated that the reversible intramolecular metal—ligand electron transfer can occur successively in the coordination sphere of the copper atom. Copper(I) *o*-semiquinone complex **2s** can be reversibly transformed into copper(II) catecholate complex **2c** through the electron transfer from the Cu^{I} atom to the SQ ligand. The subsequent addition of the neutral ligand (CO or CNAr) to **2c** induces, in turn, the electron transfer from the Cat ligand to the Cu^{II} atom, which is accompanied by the transformation of the catecholate complex into the *o*-semiquinone complex. In the case of CO, this trans-

Scheme 1



formation is also reversible and is efficiently controlled by the temperature.

Experimental

Anhydrous copper(I) chloride, 1,4-di-*tert*-butyl-1,4-diazabutadiene, and thallium 3,6-di-*tert*-butyl-*o*-benzosemiquinolate were prepared according to known procedures.[15—17]

The ESR spectra were recorded on a Bruker ER 200D-SRC spectrometer equipped with an ER 4105DR double-mode resonator (operating at ~9.5 GHz) and an ER 4111 VT temperature-controlled block. The values of the g factor were determined with the use of diphenylpicrylhydrazyl (DPPH) as the standard. The IR spectra were measured on a Specord M-80 spectrometer.

Bis(1,4-di-*tert*-butyl-1,4-diazabutadiene)copper(I) [(3,6-di-*tert*-butyl-*o*-benzosemiquinono)(3,6-di-*tert*-butylcatecholate)cuprate(II)] (1). A mixture of anhydrous copper(I) chloride (0.15 g, 1.5 mmol) and 1,4-di-*tert*-butyl-1,4-diazabutadiene (0.252 g, 1.5 mmol) in degassed THF (50 mL) was placed in an evacuated tube and shaken until copper chloride was completely dissolved. Then a solution of thallium 3,6-di-*tert*-butyl-*o*-benzosemiquinolate, which was prepared from 3,6-di-*tert*-butyl-*o*-benzosemiquione (0.33 g, 1.5 mmol), was added. The dark-claret precipitate that formed was dissolved in dichloromethane after removal of THF. The reaction mixture was filtered off from thallium chloride that precipitated. Then the solution was concentrated to approximately one-half of the initial volume, toluene (~10 mL) was added, and the tube was cooled to −5 °C. Dark-claret needle-like crystals that precipitated were filtered, washed with toluene (20 °C), and dried *in vacuo*. The yield was 0.406 g (60%), m.p. 219—220 °C. Found (%): C, 63.00; H, 8.75; Cu, 14.01. $C_{24}H_{40}O_2N_2Cu$. Calculated (%): C, 63.79; H, 8.86; Cu, 14.06. IR, ν/cm^{-1}: 495 w, 505 w, 600 w, 740 m, 785 w, 825 w, 945 m, 960 m, 975 m, 985 w, 1210 m, 1250 w, 1260 m, 1365 w, 1370 m, 1405 m, 1460 s, 1560 m, 1635 m.

The experiments with carbon monoxide were carried out directly in tubes suitable for ESR spectroscopic studies. Carbon monoxide was supplied to a degassed solution of **2** in the corresponding solvent and the changes were monitored by ESR spectroscopy. To remove CO, the solution was degassed once again.

X-ray diffraction study. X-ray diffraction analysis was performed in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) on a Siemens-P3/R3 diffractometer (λMo-Kα radiation, graphite monochromator, 153 K, $\theta/2\theta$ scanning technique). The crystallographic data and selected details of the refinement of complex **1** are given in Table 1. The structure was solved by the direct method using the SHELXS-86 program package[18] and refined anisotropically by the full-matrix least-squares method using the SHELXL-93 program package.[19] The hydrogen atoms were placed in geometrically calculated positions and refined using the riding model.

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