ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2012, Vol. 38, No. 2, pp. 126–133. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © A.A. Medzhidov, P.A. Fatullaeva, S.M. Peng, R.G. Ismaiylov, G.H. Lee, S.R. Garaeva, 2012, published in Koordinatsionnaya Khimiya, 2012, Vol. 38, No. 2, pp. 132–140.

Oxidative Dehydrogenation of N-(2-Hydroxy-3,5-R^1,R^2-Benzyl)-4-Aminoantipyrines in the Complexation Reaction

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Received December 20, 2010

Abstract—Reactions of N-(2-hydroxy-3,5-R^1,R^2-benzyl)-4-aminoantipyrines with copper acetate in ethanol gave complexes with Schiff bases (SBs) rather than the expected complexes with reduced SBs; i.e., the starting ligands undergo oxidative dehydrogenation during the complexation reaction. The corresponding complexes with reduced SBs were obtained from sodium salts of the ligands and cupric sulfate in aqueous solutions. Kinetic measurements showed that oxidative dehydrogenation occurs in the heteroleptic complexes $Cu(L^i)(CH_3COO)(X)$ (L^iH are derivatives of N-(2-hydroxy-3,5-R^1,R^2-benzyl)-4-aminoantipyrines; $i = 6–10$; $X = H_2O$, CH_3OH, CH_3CH_2OH) but does not occur in the complexes CH_3OH, CH_3CH_2OH. The absence of oxidative dehydrogenation of the ligands in $Cu(L^i)_2 \cdot H_2O$ can be explained by the octahedral environment of the Cu^{2+} ion and, accordingly, the absence of the coordination site for molecular oxygen. The molecular structures of two Cu(II) complexes with SBs were determined by X-ray diffraction.

DOI: 10.1134/S1070328412010071

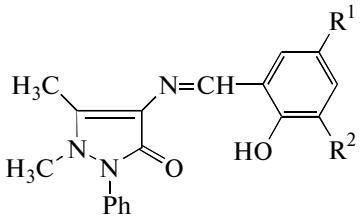
4-Aminoantipyrine derivatives (in particular, Schiff bases (SBs)) and their metal complexes exhibit antimicrobial [1], fungicidal [2], analgesic, and anti-inflammatory properties [3] and catalytic activity [4].

Complexes with various SBs (derived from 4-aminoantipyrine, 2-hydroxyarenecarbaldehydes, furan-2-carbaldehyde, thiophene-2-carbaldehyde, pyrrole-2-carbaldehyde, etc.) have been obtained and examined to date. The results obtained in the synthesis of metal complexes with 4-aminoantipyrine derivatives and the study of their structures and properties have been reviewed in [5]. However, the preparation of metal complexes with N-(2-hydroxybenzyl)-4-aminoantipyrines, which can be regarded as reduced analogs to the corresponding SBs, has not been documented.

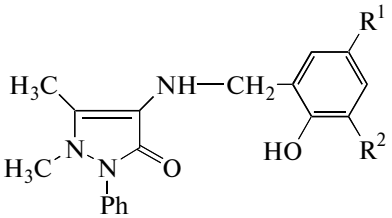
In this study, we found that the synthesis of Cu(II) complexes with N-(2-hydroxy-3,5-R^1,R^2-benzyl)-4-aminoantipyrines ($L^6H–L^{10}H$) in ethanol is accompanied by their oxidative dehydrogenation leading to Cu(II) complexes with the ligands $L^1H–L^5H$. Two of these complexes were examined by X-ray diffraction.

Copper(II) complexes with N-(2-hydroxybenzyl)-4-aminoantipyrine (L^6H) and N-(2-hydroxy-5-bromobenzyl)-4-aminoantipyrine (L^7H) were obtained by reactions of copper salts with sodium salts of these ligands in aqueous solutions.

We also performed kinetic measurements of the oxidative dehydrogenation of L^6H in ethanol in the presence of Cu(II) acetate.



L^1H: $R^1 = R^2 = H$;
L^2H: $R^1 = Br$, $R^2 = H$;
L^3H: $R^1 = OCH_3$, $R^2 = H$;
L^4H: $R^1 = tetr\text{-}C_4H_9$, $R^2 = H$;
L^5H: $R^1 = R^2 = tetr\text{-}C_4H_9$;



L^6H: $R^1 = R^2 = H$;
L^7H: $R^1 = Br$, $R^2 = H$;
L^8H: $R^1 = OCH_3$, $R^2 = H$;
L^9H: $R^1 = tetr\text{-}C_4H_9$, $R^2 = H$;
$L^{10}H$: $R^1 = R^2 = tert\text{-}C_4H_9$.

Table 1. Crystallographic parameters and the data collection statistics for structures **I** and **II**

Parameter	Value	
	I	**II**
M	852.51	982.73
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	9.9663(4)	11.7055(7)
b, Å	15.11376)	14.9925(10)
c, Å	15.5579(7)	31.564(2)
α, deg	82.180(1)	90
β, deg	73.066(1)	90.347(1)
γ, deg	76.303(1)	90
V, Å^3; Z	2172.40(16); 2	5539.3(6); 4
ρ_{calcd}, g/cm^3	1.303	1.178
Molar absorption coefficient	0.000558	0.000447
F(000)	902	2110
Crystal dimensions, mm	0.38 × 0.33 × 0.27	0.50 × 0.25 × 0.25
θ scan range, deg	1.37–27.50	1.29–25.00
Scan mode	ω	ω
Number of measured reflections	28879	28953
Number of independent reflections	9960 (R_{int} = 0.0269)	9747 (R_{int} = 0.0496)
R factor ($I > 2\sigma(I)$)	R_1 = 0.0482, Rw_2 = 0.1363	R_1 = 0.0997, Rw_2 = 0.2597
R factor (for all reflections)	R_1 = 0.0598, Rw_2 = 0.1469	R_1 = 0.1203, Rw_2 = 0.2729
GOOF	1.052	1.171
Residual electron density $\Delta\rho_{max}/\Delta\rho_{min}$, e Å^3	0.456/–0.889	0.750/–0.693

EXPERIMENTAL

IR spectra were recorded on an M-80 spectrometer in the 400–4000 cm^{-1} range (KBr pellets or Nujol). Electronic absorption spectra were recorded on Specord M-40 and UV-VIS 240 spectrophotometer. ^{1}H NMR spectra were recorded on Bruker radio spectrometer (400 MHz) in DMSO-d_6. Mass spectra were measured on a JMS 700 HF mass spectrometer.

The oxidative dehydrogenation rate was determined by measuring the optical densities of solutions at 415 nm. The concentration of the reaction product $Cu(L^1)(CH_3COO)$ was found from a calibrating curve of the optical density plotted versus the concentration of the heteroleptic complex. Calibrating solutions of the heteroleptic complex were prepared by mixing solutions of $Cu(L^1)_2$ and $Cu(CH_3COO)_2 \cdot H_2O$.

An X-ray diffraction study of the complexes $Cu(L^4)_2 \cdot EtOH \cdot H_2O$ (**I**) and $Cu(L^5)_2 \cdot EtOH \cdot H_2O$ (**II**) was performed on a Bruker Smart Apex CCD diffractometer (MoK_α radiation, λ = 0.71073 Å) at 295 K. Structures **I** and **II** were solved by the direct methods with the SHELXS-97 program [6] and refined by the full-matrix least-squares method on F^2 [7]. Crystallographic parameters and the data collection statistics for structures **I** and **II** are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

Atomic coordinates and other structural parameters for complexes **I** and **II** have been deposited with the Cambridge Crystallographic Data Collection (nos. 776110 and 776111, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

The Schiff bases L^1H and L^2H were prepared as described in [8]. The ligands L^3H–L^5H were prepared according to the same procedure: by mixing solutions containing equimolar amounts of an aromatic aldehyde and 4-aminoantipyrine.

L^3H. The yield was 82%, T_m = 200°C.

^{1}H NMR (δ, ppm): 2.40 (s, 3H, C–CH_3), 3.20 (s, 3H, OCH_3), 6.86–6.82 (t, 1H, Ar phenyl, J = 8.0 Hz), 7.05–7.02 (m, 2H, Ar phenyl), 7.40–7.36 (m, 3H, Ar phenyl), 7.55–7.51 (t, 2H, Ar phenyl, J = 7.8 Hz), 9.67 (s, 1H, CH=N), 13.01 (s, 1H, OH).

IR (KBr, ν, cm^{-1}): 3450–2600 br.w (OH), 1656 (C=O), 1592 (C=N).

MS (m/e (I, %)): 338 (100) $[M]^+$.

For $C_{19}H_{19}N_3O_3$			
anal. calcd, %:	C, 67.64;	H, 5.68;	N, 12.64.
Found, %:	C, 67.60;	H, 5.57;	N, 12.43.

L^4H. The yield was 78%, T_m = 180°C.

Table 2. Selected bond lengths and bond angles in structures **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
I		**II**	
Cu–O(3)	1.8819(15)	Cu–O(1)	1.888(4)
Cu–O(1)	1.8834(15)	Cu–O(3)	1.889(3)
Cu–N(4)	1.9525(17)	Cu–N(4)	1.952(4)
Cu–N(1)	1.9560(18)	Cu–N(1)	1.955(4)
Angle	ω, deg	Angle	ω, deg
I		**II**	
O(3)CuO(1)	90.28(7)	O(1)CuO(3)	90.00(17)
O(3)CuN(4)	93.54(7)	O(1)CuN(4)	147.2(2)
O(1)CuN(4)	150.72(8)	O(3)CuN(4)	93.81(16)
O(3)CuN(1)	148.43(8)	O(1)CuN(1)	94.09(17)
O(1)CuN(1)	93.85(7)	O(3)CuN(1)	146.6(2)
N(4)CuN(1)	97.85(7)	N(4)CuN(1)	100.26(17)
C(1)O(1)Cu	128.91(14)	C(1)O(1)Cu	128.9(4)
C(23)O(3)Cu	126.45(14)	C(27)O(3)Cu	129.1(3)

^{1}H NMR (δ, ppm): 1.41 (s, 9H, *tert*-Bu), 2.42 (s, 3H, C–CH_3), 3.21 (s, 3H, N–CH_3), 6.86–6.82 (t, 1H, Ar phenyl, J = 7.6 Hz), 7.28–7.24 (t, 2H, Ar phenyl, J = 7.4 Hz), 7.40–7.36 (t, 3H, Ar phenyl, J = 8.6 Hz), 7.55–7.51 (t, 2H, Ar phenyl, J = 7.6 Hz), 9.67 (s, 1H, CH=N), 13.92 (s, 1H, OH).

IR (KBr, ν, cm^{-1}): 3480–2600 br.w (OH), 1664 (C=O), 1600 (C=N).

MS (*m/e* (*I*, %)): 364 (100) $[M]^+$.

For $C_{22}H_{25}N_3O_3$

anal. calcd, %:	C, 72.70;	H, 6.93;	N, 11.56.
Found, %:	C, 72.62;	H, 6.90;	N, 11.44.

L^5H. The yield was 85%, T_m = 205°C.

^{1}H NMR (δ, ppm): 1.27 (s, 9H, *tert*-Bu), 1.41 (s, 9H, *tert*-Bu), 2.41 (s, 3H, C–CH_3), 3.21 (s, 3H, N–CH_3), 7.40–7.21 (m, 5H, Ar phenyl), 7.55–7.51 (t, 2H, Ar phenyl, J = 8.0 Hz), 9.68 (s, 1H, CH=N), 13.70 (s, 1H, OH).

IR (KBr, ν, cm^{-1}): 3450–2700 br.w (OH), 1660 (C=O), 1595 (C=N).

MS (*m/e* (*I*, %)): 420 (100) $[M]^+$.

For $C_{26}H_{33}N_3O_2$

anal. calcd, %:	C, 74.43;	H, 7.93;	N, 10.02.
Found, %:	C, 74.33;	H, 7.76;	N, 10.27.

Synthesis of L^6H–L^{10}H. The ligand L^1H–L^5H (0.01 mol) was dissolved in ethanol (20 mL). Then $NaBH_4$ (~0.015 mol) was added in portions with vigorous stirring until the yellow color of the solution disappeared completely. The reaction mixture was diluted with water (100 mL) and acidified with 1 N HCl to pH 7. The white crystals that formed were isolated, dried, and recrystallized from an appropriate solvent.

L^6H. The yield was 84%, T_m = 123°C.

IR (ν, cm^{-1}): 3340 (OH), 3360 (NH), 1630 (C=O).

MS (*m/e* (*I*, %)): 309 (100) $[M]^+$.

For $C_{18}H_{19}N_3O_2$

anal. calcd, %:	C, 69.68;	H, 6.19;	N, 10.58.
Found, %:	C, 69.92;	H, 6.30;	N, 13.62.

L^7H. The yield was 80%, T_m = 163°C.

IR (ν, cm^{-1}): 3480 (OH), 3184 (NH), 1640 (C=O).

MS (*m/e* (*I*, %)): 389 (100) $[M]^+$.

For $C_{18}H_{18}N_3O_2Br$

anal. calcd, %:	C, 55.61;	H, 4.68;	N, 10.82.
Found, %:	C, 55.75;	H, 4.57;	N, 10.46.

L^8H. The yield was 66%, T_m = 155°C.

IR (KBr, cm^{-1}): 3450 (OH), 3240 (NH), 1640 (C=O).

MS (*m/e* (*I*, %)): 339 (100) $[M]^+$.

For $C_{19}H_{21}N_3O_3$

anal. calcd, %:	C, 67.24;	H, 6.24;	N, 12.38.
Found, %:	C, 67.32;	H, 6.12;	N, 12.45.

L^9H. The yield was 82%, T_m = 156°C.

IR (ν, cm^{-1}): 3480 (OH), 3210 (NH), 1630 (C=O).

MS (*m/e* (*I*, %)): 365 (100) $[M]^+$.

For $C_{22}H_{27}N_3O_2$

anal. calcd, %:	C, 72.05;	H, 7.45;	N, 11.58.
Found, %:	C, 72.22;	H, 4.52;	N, 11.42.

L^{10}H. The yield was 83%, T_m = 170°C.

IR (ν, cm^{-1}): 3500–2900 (OH), 3320 (NH), 1648 (C=O).

MS (*m/e* (*I*, %)): 421 (100) $[M]^+$.

For $C_{26}H_{35}N_3O_2$

anal. calcd, %:	C, 74.04;	H, 8.37;	N, 9.97.
Found, %:	C, 74.35;	H, 8.51;	N, 9.83.

Synthesis of complex I. A solution of the ligand L^4H (0.01 mol) and $Cu(CH_3COO)_2 \cdot H_2O$ (0.01 mol) in

ethanol was stirred with a magnetic stirring bar at 50–60°C for 20 min, concentrated to 1/3 of its initial volume, and left for 24 h. The resulting dark green crystals of complex **I** were suitable for X-ray diffraction. The yield was 57%, $T_m = 310$°C.

IR (ν, cm^{-1}): 1645 (C=O), 1580 (C=N).

UV-VIS (λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$)): 374 (6700), 425 (4800), 520 sh, 730 (45).

For $C_{46}H_{56}N_6O_6$

anal. calcd, %:	C, 64.81;	H, 6.62;	N, 9.86.
Found, %:	C, 64.65;	H, 6.73;	N, 9.46.

Complex II was obtained from L^5H as described above for the synthesis of complex **I**. The yield was 81%, $T_m = 335$°C.

IR (ν, cm^{-1}): 1640 (C=O), 1600 (C=N).

UV-VIS (λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$)): 378 (7200), 440 (5300), 550 sh, 750 (60).

For $C_{52}H_{74}Cu\,N_6O_7$

anal. calcd, %:	C, 69.09;	H, 7.57;	N, 9.85.
Found, %:	C, 69.15;	H, 7.42;	N, 9.80.

Reactions of N-(2-hydroxy-3,5-R^1,R^2-benzyl)-4-aminoantipyrines (L^6H–$L^{10}H$) with copper acetate in ethanol gave complexes with SBs L^1H–L^5H rather than the expected complexes with reduced SBs. This transformation is described below with L^9H as an example.

A solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.199 g, 0.001 mol) in methanol was added at 50°C to a stirred solution of L^9H (0.706 g, 0.002 mol) in ethanol (20 mL).The resulting solution was concentrated to 1/3 of its initial volume to produce dark crystals, $T_m =$ 310°C.

The IR and UV-VIS spectra of the crystals formed are fully identical with those of the complex $Cu(L^4)_2$ obtained from L^4H.

Synthesis of the complex $Cu(L^6)_2 \cdot H_2O$. The ligand L^6H (0.307 g, 0.001 mol) and NaOH (0.040 g, 0.001 mol) were dissolved in water (100 mL). Then a solution of $CuSO_4 \cdot 5H_2O$ (0.125 mg, 0.5 mmol) in water (50 mL) was added. The light green crystals that formed were isolated and dried in vacuo. The yield was 91%, $T_m = 201$°C.

UV-VIS (λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$)): 420 (1300), 560, 720 (20).

For $C_{36}H_{38}Cu\,N_6O_5$

anal. calcd, %:	C, 61.93;	H, 5.48;	N, 12.04.
Found, %:	C, 61.70;	H, 5.25;	N, 12.15.

Complex $Cu(L^7)_2 \cdot H_2O$ was obtained from L^7H as described above for the synthesis of the complex $Cu(L^6)_2 \cdot H_2O$. The yield was 93%, $T_m = 175$°C.

UV-VIS (λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$)): 440 (930), 670, 750 (20).

For $C_{36}H_{36}Cu\,N_6O_6Br_2$

anal. calcd, %:	C, 50.51;	H, 4.24;	N, 9.80.
Found, %:	C, 50.80;	H, 4.32;	N, 9.65.

RESULTS AND DISCUSSION

Reactions of L^6H–$L^{10}H$ with Cu(II) acetate in methanol–ethanol (1 : 1) were accompanied by oxidative dehydrogenation of the ligands, giving the complexes $Cu(L^6)_2$–$Cu(L^{10})_2$ rather than the expected complexes $Cu(L^1)_2$–$Cu(L^5)_2$. The overall oxidation of the ligand L^6H can be represented by the following scheme:

$$2L^6H + Cu(CH_3COO)_2 + O_2 \rightarrow Cu(L^6)_2 + 2CH_3COOH + H_2O_2.$$

The complexes $Cu(L^1)_2$–$Cu(L^5)_2$ can also be obtained immediately from copper acetate and L^1H–L^5H in methanol–ethanol mixtures.

The electronic absorption spectra of the complexes $Cu(L^1)_2$–$Cu(L^5)_2$ show bands at 26800–27300 and 23400–24400 cm^{-1} (ligand–metal charge transfer bands) and a low-intensity wide band at 19000–20000 cm^{-1} (*d–d* transition).

The IR spectra of these complexes contain intense bands at 1640–1650 (ν(C=O)) and ~1580–1600 cm^{-1} (ν(C=N)).

The sodium salts of the ligands L^6H and L^7H react with copper(II) sulfate or copper(II) chloride to give the complexes $Cu(L^i)_2 \cdot H_2O$ ($i = 6$ and 7). Copper(II) complexes with L^8H–$L^{10}H$ were not obtained because of the poor solubilities of these ligands and the high rate of their oxidative dehydrogenation.

The IR spectra of the complexes $Cu(L^6)_2 \cdot H_2O$ and $Cu(L^7)_2 \cdot H_2O$ show absorption bands at 3250 and 3240 cm^{-1}, respectively (NH). In the IR spectra of the free ligands, these bands appear at 3336 and 3200 cm^{-1}, respectively. This indicates the coordination of the amino group to the metal ion. The band at ~1640 cm^{-1} due to the carbonyl group at the antipyrine ring is shifted to the lower frequencies (1630 cm^{-1}) upon the complexation.

The visible range of the UV-VIS spectrum of $Cu(L^6)_2 \cdot 2H_2O$ exhibit a wide absorption band at 420 nm, which can be attributed to the ligand–metal charge transfer, and two low-intensity bands at 575 and 680 nm due to the *d–d* transitions.

For $Cu(L^7)_2 \cdot H_2O$, similar absorption bands appear at 425, 560, and 675 nm.

An X-ray diffraction study of similar nickel complexes $Ni(L^6)_2 \cdot H_2O$ (**III**) and $Ni(L^7)_2 \cdot H_2O$ (**IV**) showed[1] that each Ni atom has a distorted octahedral environment made up of two N atoms of secondary

[1] The crystallographic studies performed by Samatov and supervised by Ibragimov will be published elsewhere.

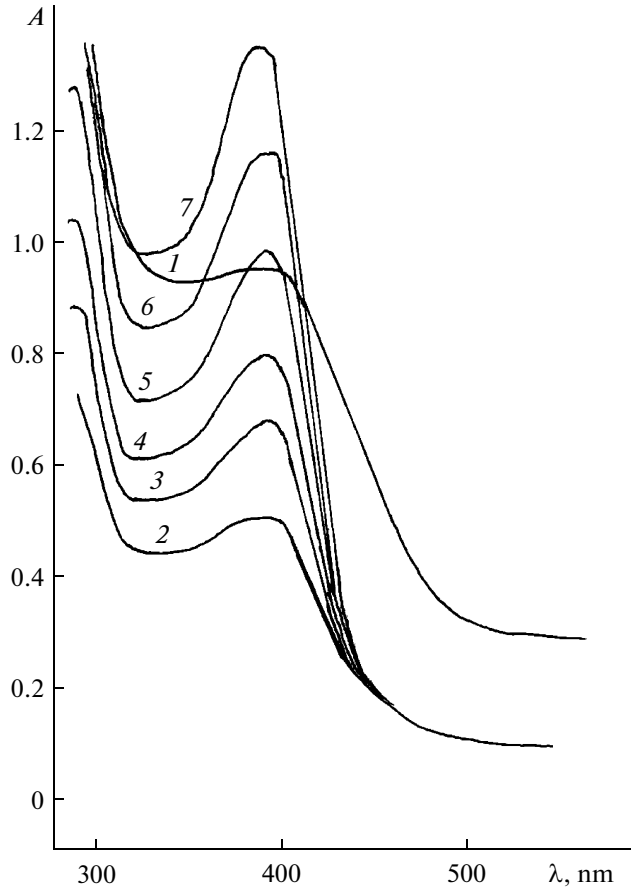
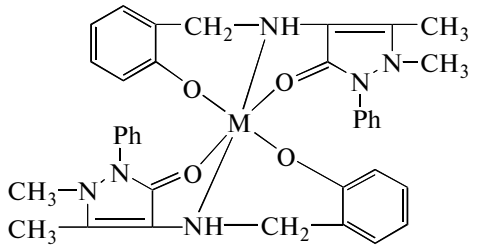


Fig. 1. Electronic absorption spectra of the reaction mixture of L^6H and $Cu(CH_3COO)_2 \cdot H_2O$; $c_{L^6H} = 7.5 \times 10^{-5}$, $c_{Cu(CH_3COO)_2 \cdot H_2O} = 5 \times 10^{-3}$ mol/L. Spectra *1*–*8* are recorded at time intervals of 3 min.

amino groups, two phenolate O_{phen} atoms, and two O_{ant} atoms of the antipyrine fragment. The Ni–O_{ant} bonds (2.167 Å) are substantially longer than the Ni–O_{phen} and Ni–NH bonds (2.036 and 2.120 Å, respectively). Since the diffraction patterns of complexes **III** and **IV** and $Co(L^7)_2 \cdot H_2O$ are fully identical with those of $Cu(L^6)_2 \cdot H_2O$ and $Cu(L^7)_2 \cdot H_2O$, these complexes are isostructural. Thus, Cu(II) complexes with reduced SBs are six-coordinate entities



as distinct from four-coordinate complexes with unreduced analogs.

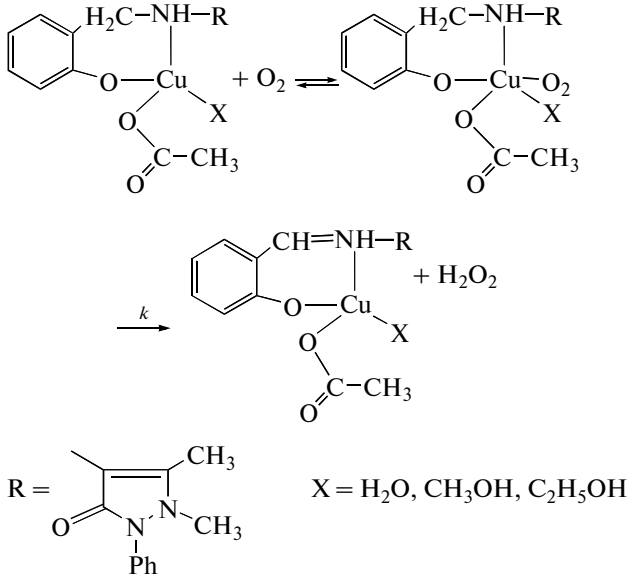
As mentioned above, the reduced SBs L^6H–$L^{10}H$ in reactions with copper acetate in ethanol undergo oxidative dehydrogenation leading to the complexes $Cu(L^1)$–$Cu(L^5)$. Neither Co(II) acetate nor Ni(II) acetate reacts with the ligands L^6H–$L^{10}H$ under these conditions.

The complexes $M(L^i)_2$ (where L^iH – L^6H and L^7H) can be obtained from sodium salts of these ligands and transition metal sulfates or chlorides. These complexes are resistant to oxidative dehydrogenation. For instance, a solution of $Cu(L^6)_2$ in methanol–ethanol remains unchanged at ambient temperature for several hours (i.e., the reduced SBs undergo no oxidative dehydrogenation).

At the same time, when mixing solutions of the ligand and copper acetate in alcohols, we observed rapid oxidative dehydrogenation because the electronic absorption spectrum exhibits a band characteristic of the coordinated azomethine group (Fig. 1). Note that no oxidative dehydrogenation occurs in the absence of oxygen.

The decomposition of the complex $Cu(L^6)_2$ is also accompanied by oxidative dehydrogenation. For instance, when a small amount of acetic acid is added to a solution of $Cu(L^6)_2$ in ethanol, the wide absorption band at 420 nm disappears because of the decomposition of the starting complex. Instead, the spectrum contains a relatively narrow peak at 415 nm due to the heteroleptic complex with the dehydrogenated ligand, $Cu(L^1)(CH_3COO)$. This peak becomes more intense with time (Fig. 2).

All these data suggest that the oxidative dehydrogenation of the coordinated ligand occurs in the heteroleptic complex Cu(L^6)(CH3COO), in which the metal : ligand ratio is 1 : 1. This process can be represented by the scheme:



Our kinetic studies of the reaction of L^6H with copper acetate in methanol–ethanol (1 : 1) showed that the reaction rate at $[Cu(CH_3COO)_2 \cdot H_2O] \gg [L^6H]$

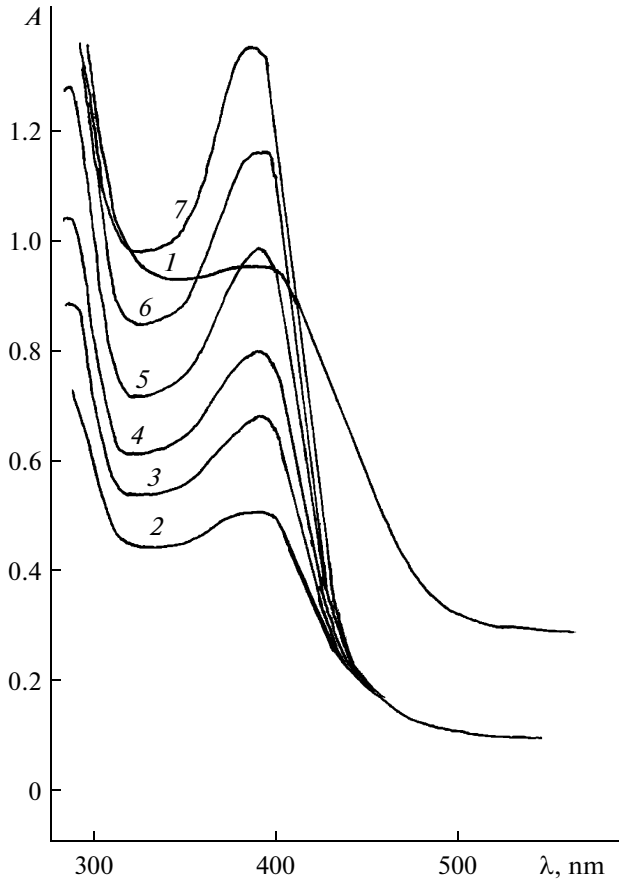


Fig. 2. Electronic absorption spectra of (*1*) $Cu(L^6) \cdot H_2O$ and (*2–6*) its mixture with acetic acid in ethanol; $c_{Cu(L^6)_2 \cdot H_2O} = 10^{-4}$ mol/L; $c_{CH_3COOH} = 0.1$ mol/L. Spectrum 2 is recorded immediately upon the addition of acetic acid. Spectra *3–6* are recorded at time intervals of ~6 min.

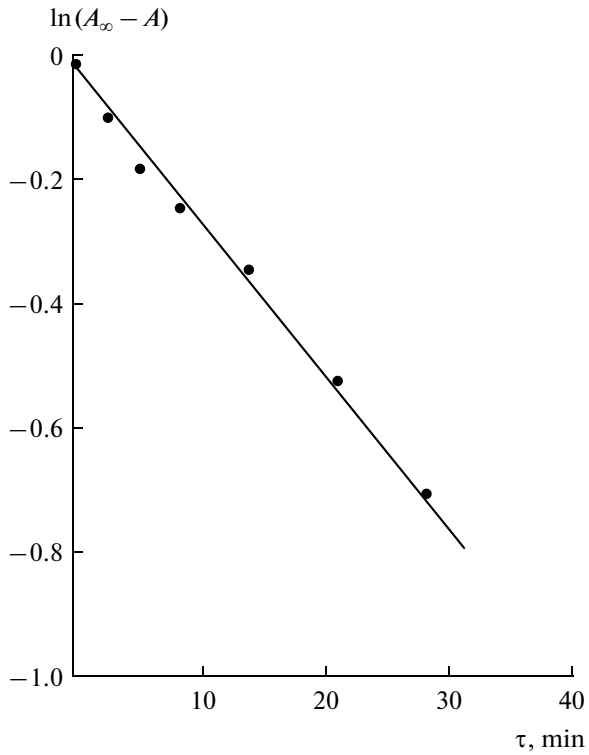


Fig. 3. Time dependence of $\ln(A_\infty - A)$ for a mixture of L^6H and $Cu(CH_3COO)_2 \cdot H_2O$; $c_{L^6H} = 7.5 \times 10^{-5}$, $c_{Cu(CH_3COO)_2 \cdot H_2O} = 5 \times 10^{-3}$ mol/L.

obeys the first-order equation in the concentration of L^6H (Fig. 3). At equal concentrations of the reaction components or for $[Cu(CH_3COO)_2 \cdot H_2O] < [L^6H]$, the oxidative dehydrogenation is strongly inhibited and stopped by the formation of the inactive complex $Cu(L^6)_2$.

The overall kinetic scheme of the reaction including complexation equilibria (1), (2), and (4) and oxidative dehydrogenation (3) can be written as follows:

$$Cu(CH_3COO)_2 \cdot H_2O + L^6H \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cu(L^6)CH_3COO + CH_3COOH, \quad (1)$$

$$CuL^6CH_3COO + L^6H \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Cu(L^6)_2 + CH_3COOH, \quad (2)$$

$$CuL^6CH_3COO + O_2 \xrightarrow{k} CuL^1CH_3COO + H_2O_2, \quad (3)$$

$$2CuL^1CH_3COO \rightleftarrows Cu(L^1)_2 + Cu(CH_3COO)_2. \quad (4)$$

When the ligand concentration is low and the concentration of copper acetate is high, equilibrium (2) can be ignored. Experimental data suggest that the ligand L^6H is found in the heteroleptic complex only (i.e., $k_1 \gg k_{-1}$).

Under the assumption that the reaction of CuL^6CH_3COO with oxygen is the rate-limiting step of the overall process, the reaction rate for $[Cu(CH_3COO)_2 \cdot H_2O] \gg [L^6H]$ and $k_1 \gg k_{-1}$ can be written as

$$w = k[CuL^6\,CH_3COO \cdot H_2O][O_2] = k[L^6H][O_2]$$

or $w = k'[L^6H]$, where $k' = k[O_2]$.

Thus, we obtain the pseudofirst-order equation of the reaction rate in the concentration of the starting ligand, which is confirmed experimentally.

The pseudofirst-order reaction rate constant determined from a plot of log*w* vs. log*c* (Fig. 4) is $k' = 1.1 \approx 10^{-1}$ s^{-1}. Note that the pseudofirst order in the ligand concentration under the aforementioned stipulations ($[Cu(CH_3COO)_2 \cdot H_2O] \gg [L^6H]$ and $k_1 \gg k_{-1}$) holds with Eq. (1) as the rate-limiting step. However, the substantial increase in the oxidative dehydrogenation rate of L^8H–$L^{10}H$, which are stronger electron donors

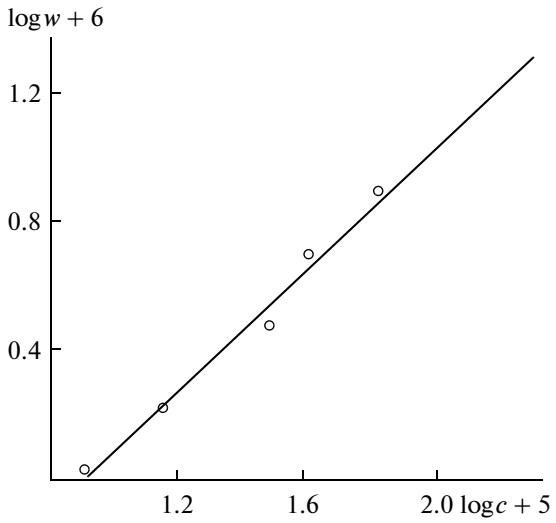


Fig. 4. Plot of log*w* vs. log*c* of the ligand L^6H for its oxidative dehydrogenation.

than L^6H, suggests that the rate-limiting step has a redox character, thus corresponding to Eq. (2).

According to X-ray diffraction data, the ligands L^4 in the crystal structure **I** are *cis* to each other, much the same as in copper(II) N-(4-aminoantipyrine)-3,6-dihydroxysalicylaldiminate. Note that a similar complex with a dichlorinated ligand has a *trans* structure [9].

The central Cu^{2+} ion has a square planar environment with a tetrahedral distortion. The environment consists of two O atoms and two N atoms of two ligands L^4 (Fig. 5). The average distances Cu–N and Cu–O (1.954(2) and 1.882(2) Å, respectively) are close to the values found for similar complexes [9].

The crystal structure of $Cu(L^5)_2$ in complex **II** is shown in Fig. 6. The coordination environment of the copper atom is also a *cis*-square with a tetrahedral distortion, which is made up of two azomethine N atoms and two nonprotonated phenolate O atoms of two ligands L^5. The average distances Cu–O and Cu–N (1.888(4) and 1.955(4) Å, respectively) are close to those in $Cu(L^4)_2$.

Thus, oxidative dehydrogenation in $Cu(L^6)_2$ is precluded by the absence of a coordination site for atmospheric oxygen since the Cu^{2+} ion in $Cu(L^6)_2 \cdot H_2O$ is hexacoordinated. However, this reaction readily occurs in heteroleptic complexes in which the C.N. of the metal ion is lower.

It should also be noted that the oxidative dehydrogenation rates of coordinated reduced Schiff bases derived from 4-aminoantipyrine are higher than those of similar coordinated N-substituted 2-hydroxybenzylamines [10, 11]. This is probably due to the pres-

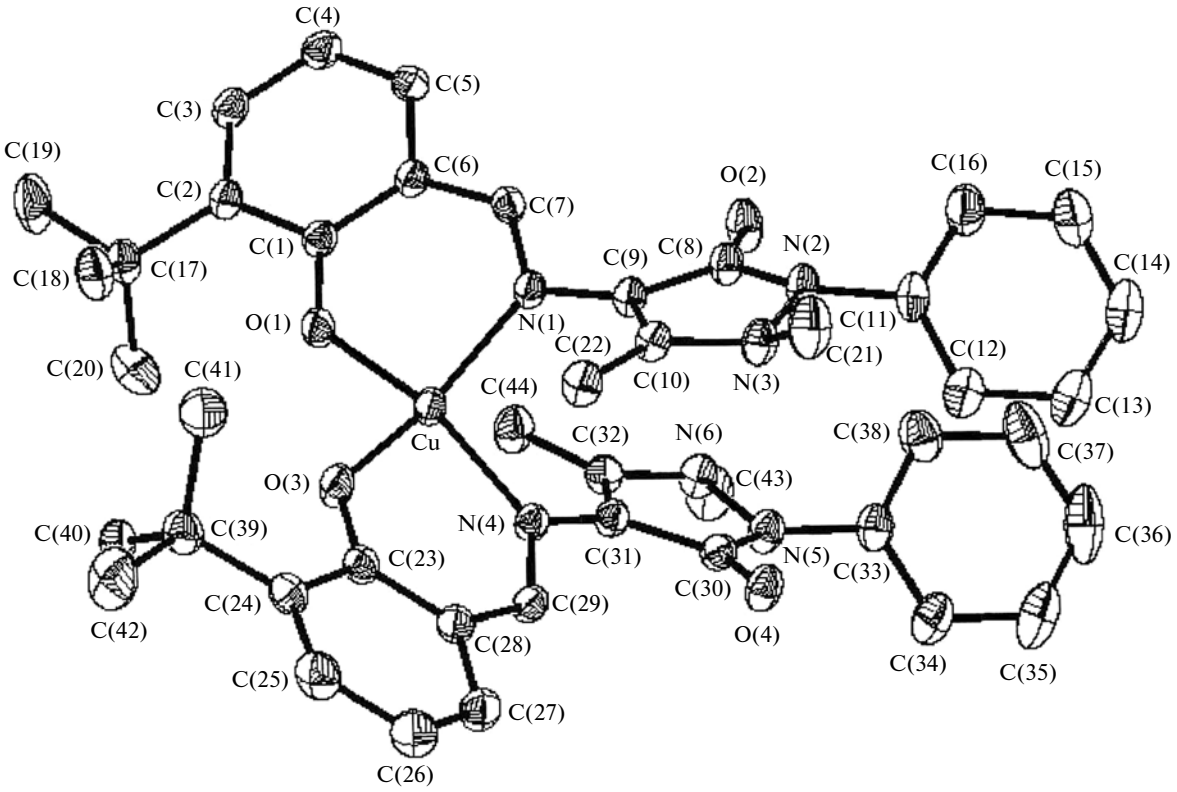


Fig. 5. Molecular structure of $Cu(L^4)_2$.

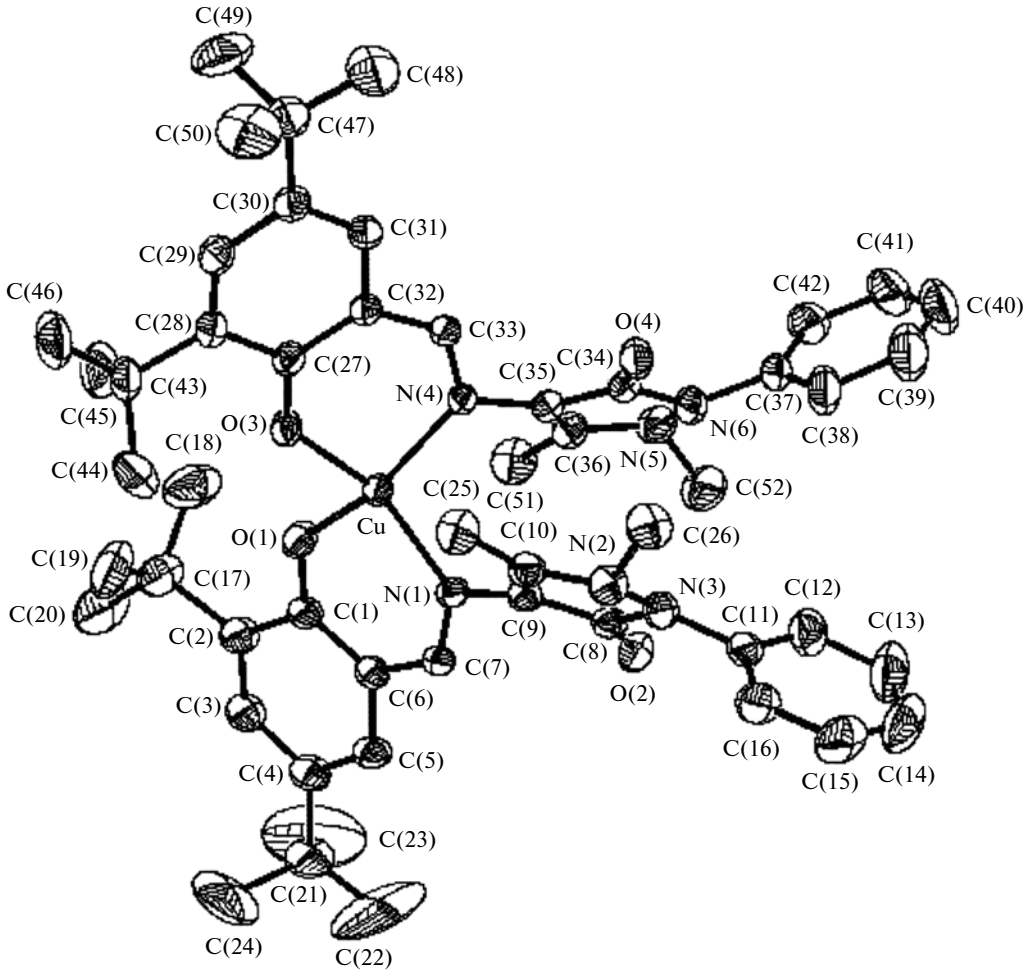


Fig. 6. Molecular structure of $Cu(L^5)_2$.

ence of the double bond at the secondary amino group.

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