ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 11, pp. 1846–1854. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © A.S. Burlov, A.S. Antsyshkina, G.G. Sadikov, V.S. Sergienko, A.I. Uraev, E.V. Korshunova, D.A. Garnovskii, T.V. Lifintseva, G.S. Borodkin, A.G. Ponomarenko, G.G. Chigarenko, I.L. Eremenko, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 11, pp. 1856–1864.

Syntheses, Structure, and Tribological Study of 1-Phenyl-3-methyl-4-dodecyliminomethylenepyrazol-5-one and Its Complexes with Copper(II)

A. S. Burlov[a], A. S. Antsyshkina[b], G. G. Sadikov[b], V. S. Sergienko[b], A. I. Uraev[a], E. V. Korshunova[a], D. A. Garnovskii[c], T. V. Lifintseva[d], G. S. Borodkin[a], A. G. Ponomarenko[e], G. G. Chigarenko[e], and I. L. Eremenko[b]

[a] *Research Institute of Physical and Organic Chemistry, Southern Federal University,*
pr. Stachki 194/2, Rostov-on-Don, 344090 Russia
e-mail: garn@ipoc.rsu.ru

[b] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*

[c] *Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don, Russia*

[d] *Pedagogical Institute of Southern Federal University, Rostov-on-Don, Russia*

[e] *Scientific Industrial and Commercial Company “Don-Invek,” Rostov-on-Don, Russia*

Received August 18, 2011

DOI: 10.1134/S1070363212110217

The metal complexes of azomethine compounds occupy an important place in modern coordination chemistry [1–5] and are used as fluorescent [6–9], magnetic [10–14], catalytic [15] and optical materials [16–18]. They are used also as effective additives to lubricants [19–30]. The development of the latter is an important and urgent task.

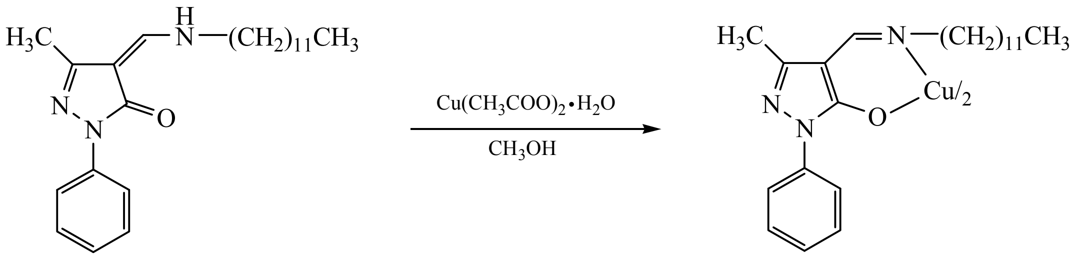
At the metal friction in an environment with complex-forming additives both chemical and tribochemical interactions occur, giving rise to the appearance on the surface of complex compounds formed from the contacting metal and ligand-additives [19–28]. Further a tribochemical processes of the complex exchange proceed: on both the rubbing surfaces a thin polymer film is formed of copper or other complex-forming transition metal. Therewith a process occurs of selective transfer, which leads to a significant improvement of tribochemical characteristics [31]. The effectiveness of the additives is determined by their solubility in oils, structure of the metal complexes formed, and the stability of the latter [19, 20]. To fix the metal complex on the rubbing surface, the complex coordination sphere should have a structure that minimizes the steric strains at the location of the complex in the active points of frictional contact. The steric hindrances at the location of the complex on the friction surface reach minimum when the complex has a square structure. Thus, at the selection of effective additives for lubricants the knowledge of the structure and properties of metal complexes is an important issue.

In extension of the work on the synthesis of new effective additives for lubricants we have prepared 1-phenyl-3-methyl-4-dodecyliminomethylenepyrazol-5-one (HL) and its copper complex CuL_2 (**I**).

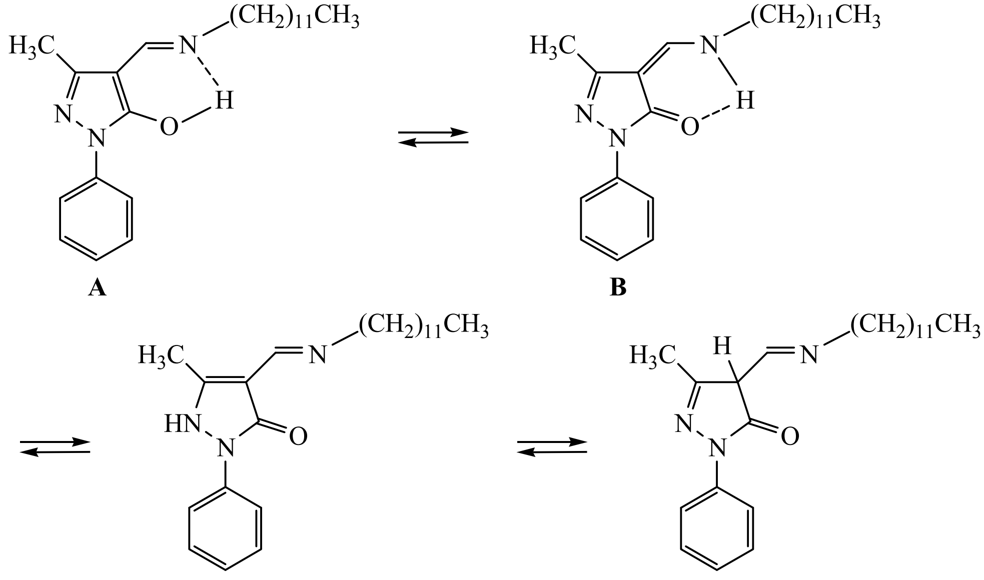
In the compound HL the equilibrium of the **A**–**D** tautomers can be realized [32–34]. The IR spectrum of the HL solution in hexachlorobutadiene includes the following absorption bands: a broad band at 3420 cm^{-1} (ν_{NH}) and a strong band at 1668 cm^{-1} ($\nu_{C=O}$).

The presence of a broad signal of the protons of NH group in the ^{1}H NMR spectrum of HL in $CDCl_3$ at 09.07 ppm and a doublet signal at 7.43 ppm of the (C$\underline{H}$–NH) protons in combination with the IR spectral studies and published data [32–34] indicate the existence of HL in aminomethylene tautomeric form **B** with the intramolecular hydrogen bond with the oxygen atom of the pyrazole fragment.

In the IR spectrum of the Cu(I) complex the absorption bands of HL at 3420 and 1668 cm^{-1} dis-



HL I



A **B**

C **D**

appear, but a stretching vibration band appears at 1622 cm^{-1} ($\nu_{C=N}$). The value of μ_{eff} = 1.98 MB at 295 K of the complex **I** does not change with temperature, indicating its mononuclear structure. According to elemental analysis, complex **I** has the composition of CuL_2, which together with spectral studies indicates the formation of the chelate structure.

The final conclusion on the structure of **I** was made on the basis of XRD data at low temperature (173 K). Crystals of **I** are dark-brown needles. Figure 1 shows a molecular structure of the complex. The Cu atom is coordinated by two ligands L, which contain aromatic and aliphatic fragments. Both ligands are of the same composition and have close parameters.

In molecule **I** the Cu atom is coordinated by two N atoms and two O atoms of two bidentate chelate ligands L with the formation of highly distorted *trans*-planar configuration. The dihedral angle between the planes $O^1Cu^1N^3$ and $O^2Cu^1N^6$ is 33.5°. The molecule contains a C_2 pseudo-axis. The metallocycles formed at the coordination of the metal with the ligands have a 9.0° distortion along the $N^3\cdots O^1$ line in the $Cu^1\cdots N^3$ ring and an 11° distortion along the $N^6\cdots O^2$ line in the $Cu^1\cdots N^6$ metallocycle. The five-membered rings $C^1N^1N^2C^2C^3$ and $C^{24}N^4N^5C^{25}C^{26}$ are almost planar, the first is fused with the phenyl ring $C^4\cdots C^9$, the second with the ring $C^{27}\cdots C^{32}$, the corresponding dihedral angles are 11.4° and 6.3°. The bonds involving the N^1 and N^6 atoms are in the *gauche* conformation, the C–C bonds of both hydrocarbon chains are in the *anti* conformation. In both chains the amplitude of thermal vibrations increases insignificantly with increasing distance from the corresponding nitrogen atom. The average planes of the hydrocarbon chains are almost perpendicular to each other, the dihedral angle between them is 85°. The chains are directed to one side, their planes form the following dihedral angles with the corresponding aromatic fragments: $C^{12}C^{23}/O^1C^1C^3C^{11}N^3$, 76°; $C^{35}C^{46}/O^2C^{24}C^{26}C^{34}N^6$, 85°. The average bond lengths in the coordination square of the central atom are as follows: Cu^1–O 1.927(2), Cu^1–N 1.973(2) Å.

The specific hydrogen bond $C^{28}–H^{28b}\cdots O^2$ involves a hydrogen atom of the phenyl ring, and the distances are as follows: $C^{28}\cdots O^2$ 2.911, $C^{28}–H^{28b}$ 0.93, $H^{28b}\cdots O^2$

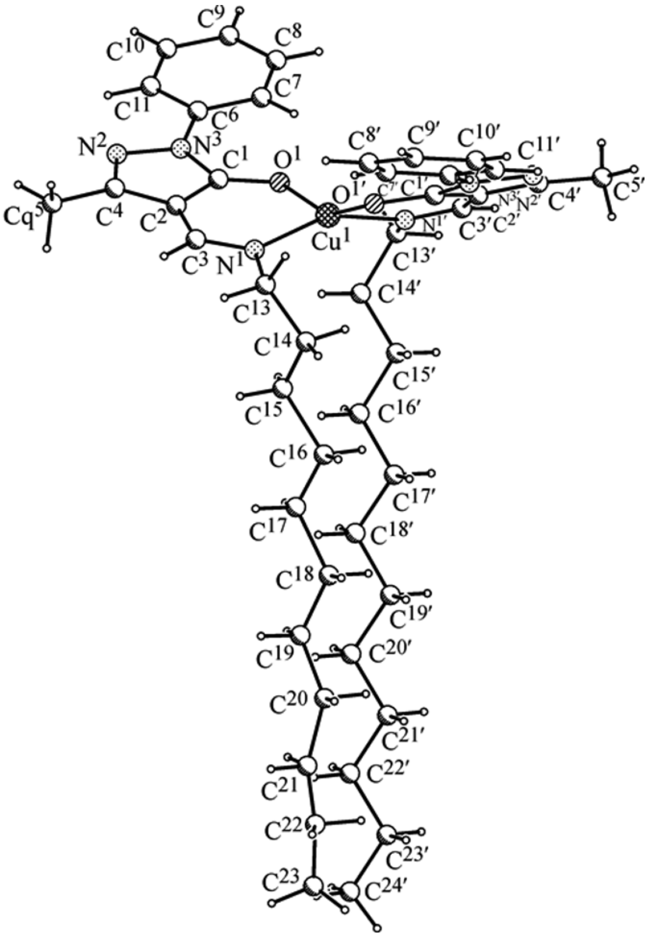


Fig. 1. Molecular structure of complex **I**.

2.27 Å, the $C^{28}H^{28b}O^{2}$ angle is 124°. The hydrogen bond closes a six-membered H-ring $O^{2}C^{24}N^{4}C^{27}C^{28}H^{28b}$, which together with the phenyl and coordination rings also is involved in the π–π stacking interaction.

The influence of π–π stacking interactions between the individual planar fragments (associated through the inversion center) leads to formation of dimers (Fig. 2). The distance between parallel planes in the dimer is 3.24 Å, which is consistent with the usually observed range (3.3–3.8 Å) and indicates indirectly the strength of π–π stacking interactions. Within the dimer an intermolecular interaction occurs in the direction of the central atom of the complex, $Cu^{1}\cdots C^{31A}$ 3.35 Å, which can be considered as a supplement converting the coordination square into the elongated tetragonal pyramid (4+1).

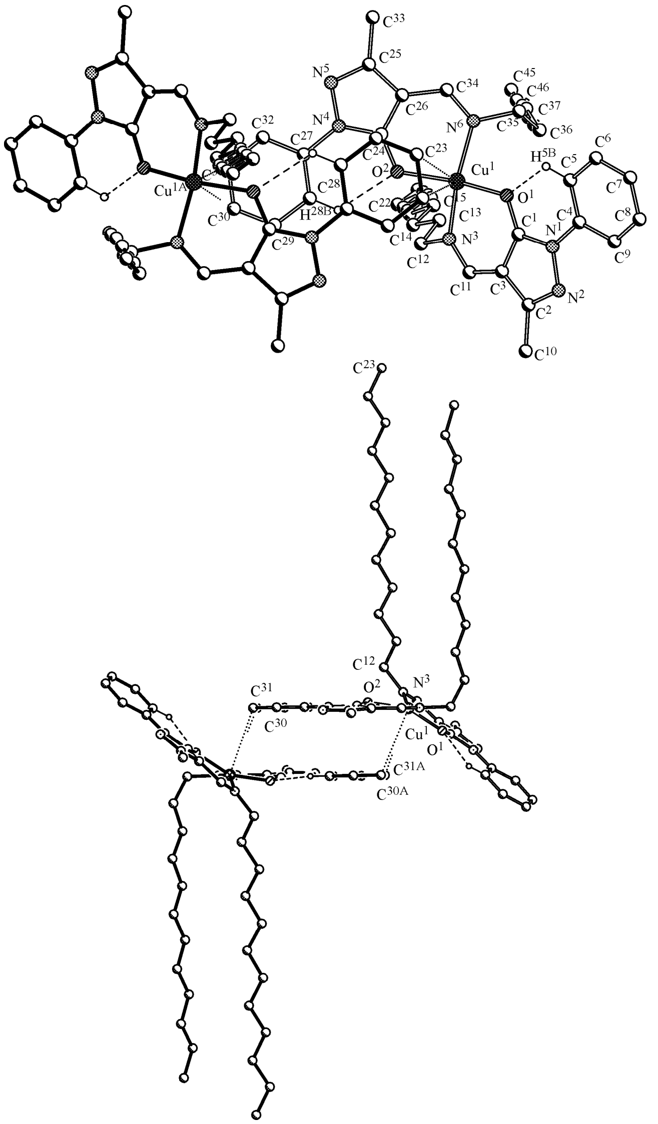


Fig. 2. π–π-Stacking interaction between the molecules (two mutually orthogonal projection).

Specific interest attracts in the structure **I** the packing of the rather symmetrical molecular dimers in the unit cell. A feature of the packing is the formation of alternating layers containing only aromatic (associated with the complexing metal atom), or only aliphatic fragments that run through the entire structure (Fig. 3a). The layers differ by the packing density: in the aromatic region there are numerous intermolecular contacts and the π–π stacking interaction is realized, while in the aliphatic region the contacts between the atoms of the hydrocarbon chains are absent and the packing is loose.

The packing of the molecules in structure **I** is similar the packing characteristic of extended organic molecules containing alternating aromatic and aliphatic region. Compare the projection of the unit cells of the crystals of **I** and 4-(3-acryloyloxy) octyloxy-4'-cyanobisphenol (**II**) (Figs. 3a and 3b) [35].

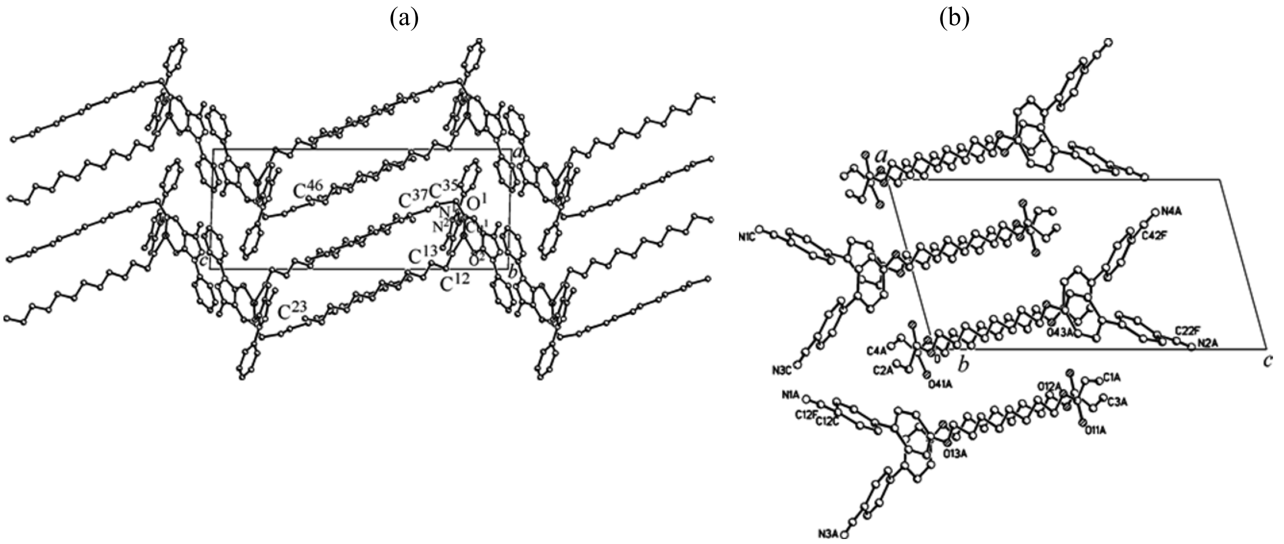


Fig. 3. Packing of molecules in supramolecular assemblies within the structures of (a) **I** and (b) **II**.

Such a structure containing the regions contrasting by the strength of intermolecular interactions is characteristic of compounds capable to exhibit mesogenic (liquid crystalline) properties. It can be assumed that the structure **I** or its analogs also may be able to exhibit specific physical properties.

The electron absorption spectra (EAS) of solution of compound HL in methylene chloride include a system of overlapping diffuse bands (Table 1). A shoulder located in the vicinity of 329 nm in the long-wavelength wing of the intense asymmetric broad band at 298 nm can be attributed, by analogy with the spectra of the previously investigated pyrazolone aminomethylene derivatives [36, 37], to the $n \to \pi$ transitions. The absorption in the range of 264–298 nm is probably associated with the transitions in the pyrazolone, 1-phenylpyrazolone, and aminomethylene-pyrazol-5-one fragments [36, 37].

As a result of the complex formation of the aminomethylene derivative of pyrazol-5-one with copper acetate monohydrate, in the EAS a slight blue shift (~6.7 nm) of the maxima of the envelopes of the intraligand bands is observed with a decrease and redistribution of their intensity (Fig. 5). The shoulder at 329 nm clearly expressed in the spectra of the ligand is not seen in the spectrum of the complex, apparently due to the merging with a strong band in the region of 291 nm. Along with the intraligand transitions, in the EAS of the complex a low-intensity band occurs at 473 nm, which can be associated with the transitions either at the ligand–metal O→Cu charge transfer [38–41], or at the metal–ligand Cu→O charge transfer [42–45]. In the range of 600–900 nm a poorly expressed shoulder is observed with the poorly resolved structure, which is attributed to the *d*–*d* transitions. Judging from the position of these bands it can be assumed that the complex has, like other similar compounds with bidentate ligands, a distorted pseudo-tetrahedral configuration of the chelate site [37, 45].

As noted above, the structure of coordination compounds formed at the friction is an important factor in determining their effectiveness as additives to oils. In this regard, the square structure of **I** and its high solubility in oil was expected to give the desired effect. We tested compounds HL and **I** as additives to lubricating oils. At adding HL and **I** in the M-10DM oil in amount 4% by weight the friction coefficient in a steel–steel pair decreases from 0.043 for pure M-10DM oil to 0.0037, that is, approximately by an order of magnitude. The maximum load $P_{\max}$ increases by

Table 1. Parametes of EAS of compounds HL and **I**

Compound	$\lambda_{\max}$ CH_2Cl_2, nm	ε, g mol^{-1} cm^{-1}
HL	264	29839
	298	41887
	329 sh	9518
I	258	28364
	291	25702
	473	1163
	675	145

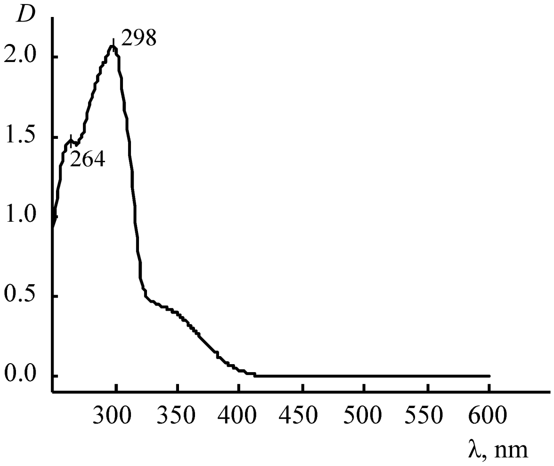


Fig. 4. Electron absorption spectra of solution of compound HL in methylene chloride at a concentration $c = 5\times10^{-5}$ M.

11.3 and 34.2 MPa for the HL and **I**, respectively, and the wear rate decreases from 7.8 μm km^{-1} for the M-10DM to 0.88 and 1.1 μm km^{-1} at the adding HL and **I**, respectively.

Thus, the introduction of compounds HL and **I** in the motor oil M-10DM leads to a significant increase in the oil characteristics: the load capacity increases 3 times and the wear resistance, 7 times. The compounds HL and **I** may be promising additives for the development of new motor and other industrial oils.

EXPERIMENTAL

IR spectra were obtained on a Varian 1000-FT-IR spectrometer from mulls in hexachlorobutadiene and mineral oil. ^{1}H NMR spectra were taken on a Varian Unity-300 instrument, the internal stabilization mode using the $CDCl_3$ polar-resonance ^{2}H line. The electron absorption spectra (EAS) of the methylene chloride solutions of studied substances were measured on a Helios Unicam instrument in the range 195–1100 nm.

The tribochemical measurements were performed on the machine for the mechanical friction (AE-5). The samples and rider were made of steel-45. The load was varied in the range of 10-150 MPa with increments 0.5–10 MPa. Sliding speed was 0.8 m s^{-1}. The seizure load P_{max} and the friction coefficient were controlled. Wear was determined gravimetrically, from these data the rate of wear of the samples were calculated. The test duration was 5 h.

The XRD experiment: The structure was solved by the direct method (SHELXS-86) [46] and refined by the full matrix least-squares method (SHELXS-97)

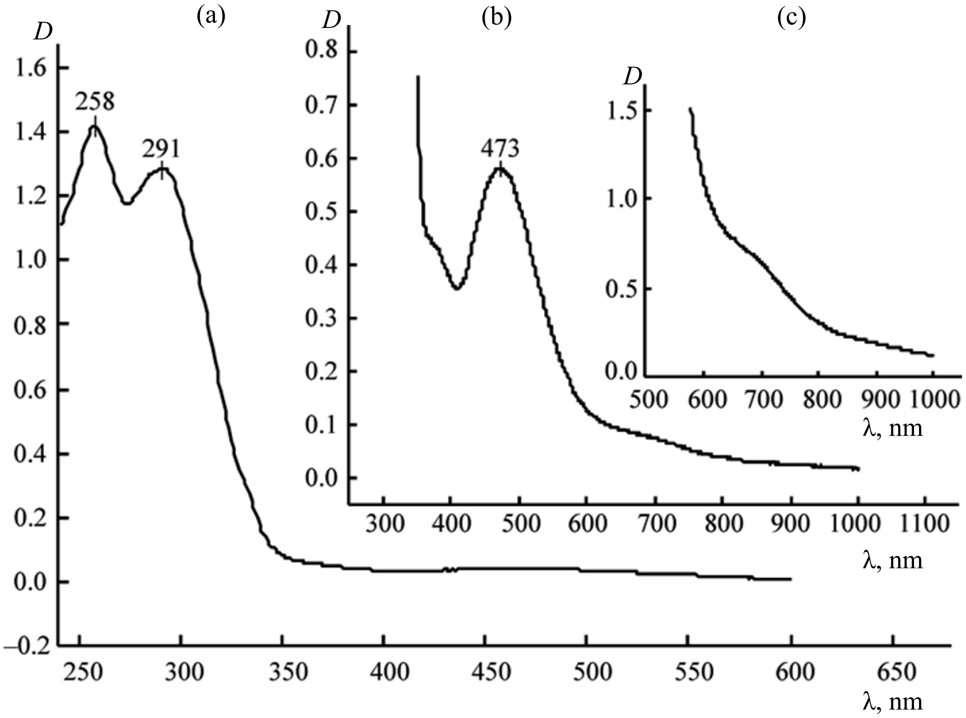


Fig. 5. Electron absorption spectra of **I** in methylene chloride solutions at the following concentrations: (a) 5×10^{-5}, (b) 5×10^{-4}, and (c) 5×10^{-3} M.

[37] with respect to F^2. The hydrogen atoms were placed in calculated positions and refined isotropically within the *rider* model. The crystallographic data and characteristics of the experiment are given in Table 2, the main bond lengths and bond angles in the coordination polyhedron are given in Tables 3 and 4. The experimental data are deposited in the Cambridge Structural Database (CCDC 831652).

Synthesis of 1-phenyl-3-methyl-4-dodecylimino-methylenepyrazol-5-one (HL). To a solution of 2.2 g (0.01 mol) of 1-phenyl-3-methyl-4-formylpyrazole-5-one in 10 ml of benzene was added a solution of 1.85 g (0.01 mol) of dodecylimine in 10 ml of benzene. The mixture was boiled with a Dean–Stark trap for 1 h to complete separation of water, then 2/3 of the benzene volume was distilled off on a rotary evaporator. The precipitate was filtered off and HL was recrystallized from hexane. Yellow powder, yield 96%, mp 49–50°C. IR spectrum, hexachlorobutadiene (ν, cm^{-1}): 3240 br (NH), 2926, 2854 ($C_{12}H_{25}$), 1668 (C=O). ^{1}H NMR spectrum (δ, ppm): 0.86 t [3H, J = 6.6 Hz, $(CH_2)_{11}C\underline{H}_3$], 1.17–1.35 m (18H, CH_2), 1.66 m [2H, $(C\underline{H}_2)_{11}CH_3$], 2.22 s (3H, CH_3), 3.40 q [2H, ^3J = 6.5 Hz, NH (CH_2)], 7.01–7.14 m (1H, $C_{Ar}H$), 7.33–7.38 m (2H, $C_{Ar}H$), 7.43 (2H, d, ^3J = 13.4 Hz, C$\underline{H}$NH, $C_{Ar}H$), 9.71 br.s (1H, NH). Found, %: C 74.80, H 9.61; N 11.40. $C_{23}H_{35}N_3O$. Calculated, %: C 74.75, H 9.55; N 11.37.

Synthesis of copper bis[1-phenyl-3-methyl-4-dodecyliminomethylenepyrazol-5-onate] (I). To a solution of 0.74 g (0.002 mol) of HL in 10 ml of methanol was added 0.2 g (0.001 mol) of copper acetate monohydrate in 10 ml of ethanol. The mixture was refluxed for 2 h. The complex precipitated at cooling was filtered off, washed with 5 ml of methanol, and recrystallized from ethanol:hexane (2:1). Brown crystals, yield 75%, mp 119–120°C.

Electrochemical synthesis of **I** was performed by the usual method through the interaction of HL with the copper cations formed at dissolving the copper anode during the electrolysis. Methanol solution (10 ml) contained 0.002 mol of HL and 0.01 g of $[Et_4N]ClO_4$ as a conductive additive. Electrosynthesis was performed at a 40 mA current at 15 V voltage for 1 h. The precipitated complex was filtered off, recrystallized from ethanol–hexane (2:1) mixture, and dried in a vacuum drying cabinet. Yield 91%. The melting point and spectral characteristics of complex **I** obtained by chemical and electrochemical method are identical. IR spectrum (hexachlorobutaniene, ν, cm^{-1}):

Table 2. Crystallographic parameters and experimental data for compound **I**

Parameter	Value
Empirical formula	$C_{45}H_{66}CuN_6O_2$
M	786.58
Color, habitus	Black, a prism
Sample size, mm	0.20×0.35×0.55
Temperature, K	293
Crystal system	Triclinic
Space group	P-1
Unit cell parameters:	
a, Å	9.344(3)
b, Å	10.092(3)
c, Å	24.298(5)
α, deg	91.83(2)
β, deg	91.43(2)
γ, deg	93.63(3)
V, Å^3	2284.6(4)
Z	2
d_{calc}, g cm^{-3}	1.143
μ, cm^{-1}	0.518
F(000)	846
Scan interval θ, deg	1.68–44.11
Indices interval	$-11 \leq h \leq 11, -11 \leq k \leq 11, -2 \leq l \leq 27$
Total number of measured reflections	13373
Number of independent reflections	12980 (R_{int} 0.0226)
Number of reflections with $I > 2\sigma(I)$	2978
Correction for extinction	487
$GOOF$ with respect to F^2	1.143
R [$I > 2\sigma(I)$]	R_1 0.0512, wR_2 0.1294
R (all reflections)	R_1 0.2400, wR_2 0.3473
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e Å^{-3}	0.330–0.441

Table 3. Bond lengths (*d*) and bond angles (ω) of compound **I**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Cu^{1}–O1	1.923(3)	C^{9}–C^{10}	1.370(8)	N^{3}–C^{6}	1.422(6)	C$^{2'}$–C$^{3'}$	1.402(7)
Cu^{1}–O$^{1'}$	1.931(3)	C^{10}–C^{11}	1.377(7)	C^{1}–C^{2}	1.407(6)	C$^{2'}$–C$^{4'}$	1.420(7)
Cu^{1}–N^{1}	1.974(4)	O$^{1'}$–C$^{1'}$	1.274(5)	C^{2}–C^{3}	1.383(7)	C$^{4'}$–C$^{5'}$	1.494(7)
Cu^{1}–N$^{1'}$	1.983(4)	N$^{1'}$–C$^{3'}$	1.287(6)	C^{2}–C^{4}	1.405(7)	C$^{6'}$–C$^{11'}$	1.366(8)
O^{1}–C^{1}	1.283(5)	N$^{1'}$–C$^{13'}$	1.465(6)	C^{4}–C^{5}	1.491(7)	C$^{6'}$–C$^{7'}$	1.368(7)
N^{1}–C^{3}	1.297(6)	N$^{2'}$–C$^{4'}$	1.308(7)	C^{6}–C^{11}	1.381(7)	C$^{7'}$–C$^{8'}$	1.381(8)
N^{1}–C^{13}	1.441(6)	N$^{2'}$–N$^{3'}$	1.385(6)	C^{6}–C^{7}	1.393(7)	C$^{8'}$–C$^{9'}$	1.344(9)
N^{2}–C^{4}	1.316(6)	N$^{3'}$–C$^{1'}$	1.368(6)	C^{7}–C^{8}	1.370(7)	C$^{9'}$–C$^{10'}$	1.344(9)
N^{2}–N^{3}	1.402(5)	N$^{3'}$–C$^{6'}$	1.413(7)	C^{8}–C^{9}	1.364(7)	C$^{10'}$–C$^{11'}$	1.387(9)
N^{3}–C^{1}	1.377(6)	C$^{1'}$–C$^{2'}$	1.402(7)				
Angle	**ω, deg**	**Angle**	**ω, deg**	**Angle**	**ω, deg**	**Angle**	**ω, deg**
O^{1}Cu^{1}O$^{1'}$	151.65(14)	O^{1}C^{1}C^{2}	130.3(5)	C^{8}C^{9}C^{10}	119.3(6)	C$^{3'}$C$^{2'}$C$^{4'}$	130.9(5)
O^{1}Cu^{1}N^{1}	96.5(2)	N^{3}C^{1}C^{2}	106.0(4)	C^{9}C^{10}C^{11}	120.9(5)	C$^{1'}$C$^{2'}$C$^{4'}$	104.8(5)
O$^{1'}$Cu^{1}N^{1}	90.1(2)	C^{3}C^{2}C^{4}	130.7(5)	C^{10}C^{11}C^{6}	119.9(5)	N$^{1'}$C$^{3'}$C$^{2'}$	125.0(5)
O^{1}Cu^{1}N$^{1'}$	89.9(2)	C^{3}C^{2}C^{1}	123.8(5)	C$^{1'}$O$^{1'}$Cu^{1}	121.6(3)	N$^{2'}$C$^{4'}$C$^{2'}$	112.4(5)
O$^{1'}$Cu^{1}N$^{1'}$	95.5(2)	C^{4}C^{2}C^{1}	105.5(5)	C$^{3'}$N$^{1'}$C$^{13'}$	117.9(4)	N$^{2'}$C$^{4'}$C$^{5'}$	119.6(5)
N^{1}Cu^{1}N$^{1'}$	155.5(2)	N^{1}C^{3}C^{2}	125.8(5)	C$^{3'}$N$^{1'}$Cu^{1}	123.5(3)	C$^{2'}$C$^{4'}$C$^{5'}$	128.0(6)
C^{1}O^{1}Cu^{1}	119.9(3)	N^{2}C^{4}C^{2}	112.4(4)	C$^{13'}$N$^{1'}$Cu^{1}	118.5(3)	C$^{11'}$C$^{6'}$C$^{7'}$	119.4(5)
C^{3}N^{1}C^{13}	117.7(4)	N^{2}C^{4}C^{5}	119.6(5)	C$^{4'}$N$^{2'}$N$^{3'}$	105.1(4)	C$^{11'}$C$^{6'}$N$^{3'}$	118.2(5)
C^{3}N^{1}Cu^{1}	122.6(4)	C^{2}C^{4}C^{5}	128.0(5)	C$^{1'}$N$^{3'}$N$^{2'}$	111.8(4)	C$^{7'}$C$^{6'}$N$^{3'}$	122.4(5)
C^{13}N^{1}Cu^{1}	119.6(3)	C^{11}C^{6}C^{7}	118.8(5)	C$^{1'}$N$^{3'}$C$^{6'}$	129.5(5)	C$^{6'}$C$^{7'}$C$^{8'}$	119.8(6)
C^{4}N^{2}N^{3}	105.4(4)	C^{11}C^{6}N^{3}	119.4(5)	N$^{2'}$N$^{3'}$C$^{6'}$	118.6(4)	C$^{9'}$C$^{8'}$C$^{7'}$	121.0(7)
C^{1}N^{3}N^{2}	110.7(4)	C^{7}C^{6}N^{3}	121.8(5)	O$^{1'}$C$^{1'}$N$^{3'}$	124.7(5)	C$^{10'}$C$^{9'}$C$^{8'}$	119.2(6)
C^{1}N^{3}C^{6}	130.4(4)	C^{8}C^{7}C^{6}	120.2(5)	O$^{1'}$C$^{1'}$C$^{2'}$	129.4(5)	C$^{9'}$C$^{10'}$C$^{11'}$	121.5(7)
N^{2}N^{3}C^{6}	118.7(4)	C^{9}C^{8}C^{7}	120.9(6)	N$^{3'}$C$^{1'}$C$^{2'}$	105.9(4)	C$^{6'}$C$^{11'}$C$^{10'}$	119.1(6)
O^{1}C^{1}N^{3}	123.7(4)			C$^{3'}$C$^{2'}$C$^{1'}$	124.3(5)		

Table 4. The shortest intermolecular contacts in structure **I**

A···B	*d*, Å	Matrix for atom B
N^{2}···C$^{8'}$	3.44	$1 - x, 1 - y, 1 - z$
N^{3}···C^{8}	3.45	$2 - x, 1 - y, 1 - z$
C^{1}···C^{8}	3.31	$2 - x, 1 - y, 1 - z$
C^{3}···N$^{2'}$	3.39	$x, 1 + y, z$
C^{6}···C^{7}	3.46	$2 - x, 1 - y, 1 - z$
C^{9}···C^{1}	3.48	$2 - x, 1 - y, 1 - z$

2951, 2918, 2851 ($C_{12}H_{25}$), 1622 (C=N). Found, %: C 69.15, H 8.52, N 10.61, Cu 8.02 (chemical synthesis), C 69.10, H 8.59, N 10.45, Cu 8.12. (electrochemical synthesis). $C_{46}H_{68}N_6O_2Cu$. Calculated, %: C 69.09, H 8.56, N 10.50, Cu 7.94.

ACKNOWLEDGMENTS

This work was supported by the President of the Russian Federation (grants MK-170.2011.3 and NSh-3233.2010.3), Russian Foundation for Basic Research (grants 11-03-00475a, 10-03-90735-mob_st) and the program of the of the Presidium of Rissiasn Academy of Sciences “Support for Innovation.”

REFERENCES

1. Garnovskii, A.D., Nivorozhkin, A.L., and Minkin, V.I., *Coord. Chem. Rev.*, 1993, vol. 126, no. 1, p. 1.
2. Garnovskii, A.D. and Vasil’chenko, I.S., *Usp. Khim.*, 2002, vol. 71, no. 11, p. 1064.
3. Hernandez-Molina, R. and Menderos, A., *Comprehensive Coordination Chemistry*, Lever, A.B.P., Ed., Amsterdam: Elsevier–Pergamon Press, 2003, vol. 1, p. 411.
4. Garnovskii, A.D., Vasilchenko, I.S., Garnovskii, D.A., and Kharisov, B.I., *J. Coord. Chem.*, 2009, vol. 62, no. 2, p. 151.
5. Garnovskii, A.D., Sadimenko, A.P., Vasilchenko, I.S., Garnovskii, D.A., Sennikova, E.V., and Minkin, V.I., *Adv. Heterocycl. Chem.*, 2009, vol. 93, p. 291.
6. Metelitsa, A.V., Burlov, A.S., Bezuglyi, S.O., Borodkina, I.G., Bren’, V.A., Garnovskii, A.D., and Minkin, V.I., *Koord. Khim.*, 2006, vol. 32, no. 12, p. 894.
7. Metelitsa, A.V., Burlov, A.S., Bezuglyi, S.O., Borodkina, I.G., Vasil’chenko, I.S., Garnovskii, D.A., Mashchenko, S.A., Borodkin, G.S., Garnovskii, A.D., and Minkin, V.I., RF Patent, no. 2395512., 2010, *Byul. Izobr.*, no. 21, 27.07.2010.
8. You, Y. and Park, Y., *J. Chem. Soc. Dalton Trans.*, 2009, no. 8, p. 1267.
9. Zhang, L., Jiang, F., and Zhou, Y., *J. Coord. Chem.*, 2009, vol. 62, no. 9, p. 1476.
10. Burlov, A.S., Uraev, A.I., Ikorskii, V.N., Nikolaevskii, S.A., Koshchienko, Yu.V., Vasil’chenko, I.S., Garnovskii, D.A., Vlasenko, V.G., Zubavichus Ya.V., Divaeva, L.N., Borodkin, G.S., and Garnovskii, A.D., *Zh. Obshch. Khim.*, 2008, vol. 78, no. 6, p. 1002.
11. Garnovskii, A.D., Vasil’chenko, I.S., Garnovskii, D.A., Burlov, A.S., Uraev, A.I., *Ross. Khim. Zh.*, 2009, vol. 53, no. 1, p. 100.
12. Burlov, A.S., Ikorskii, V.N., Nikolaevskii, S.A., Koshchienko, Yu.V., Vlasenko, V.G., Zubavichus, Ya.V., Uraev, A.I., Vasil’chenko, I.S., Garnovskii, D.A., Borodkin, G.S., and Garnovskii, A.D., *Zh. Neorg. Khim.*, 2008, vol. 53, no. 10, p. 1677.
13. Burlov, A.S., Nikolaevskii, S.A., Bogomyakov, A.S., Vasil’chenko, I.S., Koshchienko, Yu.V., Vlasenko, V.G., Uraev, A.I., Garnovskii, D.A., Sennikova, E.V., Ikorskii, V.G., Borodkin, G.S., Garnovskii, A.D., and Minkin, V.I., *Koord. Khim.*, 2009, vol. 35, no. 7, p. 495.
14. Garnovskii, A.D., Burlov, A.S., Starikov, A.G., Metelitsa, A.V., Vasil’chenko, I.S., Bezuglyi, S.O., Nikolaevskii, S.A., Borodkina, I.G., and Minkin, V.I., *Koord. Khim.*, 2010, vol. 36, no. 7, p. 483.
15. Gibson, V.S. and Spitzmesser, S.K., *Chem. Rev.*, 2003, vol. 103, no. 2, p. 283.
16. Bren’, V.A., *Usp. Khim.*, 2001, vol. 70, no. 12, p. 1152.
17. Burgette, S.C., Lippard, S.J., *Coord. Chem. Rev.*, 2001, vol. 216-217, p. 334.
18. Bren’, V.A., Dubonosov, A.D., Tsukanov, A.V., and Minikn, V.I., *Ross. Khim. Zh.*, 2009, vol. 53, no. 1, p. 42.
19. Chigarenko, G.G., Ponomarenko, A.G., Bolotnikov, V.S., Alekseev, V.A., Burlov, A.S., Garnovskii, A.D., and Barchan, G.P., *Trenie i Iznos*, 1989, vol. 10, no. 6, p. 1050.
20. Kuzharov, A.S., *Effect Beziznosnosti i Tribotekhnologii*, 1992, no. 2, p. 3.
21. Kuzharov, A.S., Burlakova, A.E., Zadoshchenko, E.G., Kuzharov, A.A., Uraev, A.I., Burlov, A.S., Kravchik, K., and Garnovskii, A.D., *Trenie i Iznos*, 2005, vol. 26, no. 6, p. 628.
22. Chigarenko, G.G., Ponomarenko, A.G., Burlov, A.S., Vasil’chenko, I.S., Uraev, A.I., and Garnovskii, A.D., *Trenie i Iznos*, 2006, vol. 27, no. 2, p. 225.
23. Chigarenko, G.G., Ponomarenko, A.G., Burlov, A.S., Chigarenko, A.G., Vasil’chenko, I.S., Uraev, A.I., and Garnovskii, A.D., *Trenie i Iznos*, 2007, vol. 28, no. 4, p. 397.
24. Garnovskii, A.D., Burlov, A.S., Lysenko, K.A., Garnovskii, D.A., Borodkina, I.G., Ponomarenko, A.G., Chigarenko, G.G., Nikolaevskii, S.A., and Minkin, V.I., *Koord. Khim.*, 2009, vol. 35, no. 2, p. 122.
25. Ponomarenko, A.G., Chigarenko, G.G., Burlov, A.S., Bicherov, A.V., Shiryaeva, T.A., Konoplev, B.G., Ageev, O.A., Kolomiitsev, A.S., Zaichenko, S.B., Chetverikova, V.A., Garnovskii, A.D., and Minikn, V.I., *Trenie i Iznos*, 2010, vol. 31, no. 5, p. 353.
26. Chigarenko, G.G., Ponomarenko, A.G., Burlov, A.S., Vasil’chenko, I.S., Garnovskii, A.D., and Minkin, V.I., RF Patent no. 2339682, 2007, *Byul. Izobr.*, no. 33, 27.11.2008.
27. Chigarenko, G.G., Ponomarenko, A.G., Burlov, A.S., Vasil’chenko, I.S., Garnovskii, A.D., and Minkin, V.I., RF Patent no. 2339683, 2007, *Byul. Izobr.*, no. 33, 27.11.2008.
28. Chigarenko, G.G., Ponomarenko, A.G., Burlov, A.S., Vasil’chenko, I.S., Uraev, A.I., Shiryaeva, T.A., Ostrovskaya, L.S., Garnovskii, A.D., and Minkin, V.I., RF Patent no. 2374309, 2009, *Byul. Izobr.*, no. 33, 27.11.2009.
29. Ponomarenko, A.G., Chigarenko, G.G., Burlov, A.S., Nikolaevskii, S.A., Shiryaeva, T.A., Pavlyuk, O.V., Garnovskii, A.D., and Minkin, V.I., RF Patent no. 2374310, 2009, *Byul. Izobr.*, no. 33, 27.11.2009.
30. Garnovskii, A.D., Ponomarenko, A.G., Chigarenko, G.G., Burlov, A.S., Vakulenko, E.V., Bicherov, A.V., Chetverikova, V.A., and Minkin, V.I., RF Patent no. 2374311, 2009, *Byul. Izobr.*, no. 33, 27.11.2009.

31. Garkunov, D.A., *Tribotekhnika (iznos i bezyznosnost')* Tribotecknique (Wear and Wearless), Moscow: MSKhA, 2001.
32. Kurkovskaya, L.N., Shapet'ko, N.N., Kvitko, I.Ya., Koshelev, Yu.N., and Samartseva, E.D., *Zh. Org. Khim*., 1974, vol. 10, no. 10, p. 2210.
33. Minkin, V.I., Garnovskii, A.D., Elguero, J., Katritzky, A.R., and Denisko, O.V., *Adv. Het. Chem*., 2000, vol. 76, p. 157.
34. Antsyshkina, A.S., Sadikov, G.G., Uraev, A.I., Korshunov, O.Yu., Nivorozhkin, A.L., and Garnovskii, A.D., *Kristallograf.*, 2000, vol. 45, no. 5, p. 850.
35. Antsyshkina, A.S., Sadikov, G.G., Syrbu, S.A., Rodnikova, M.N., Kiselev, M.R., Burmistrov, V.A., Kuvshinova, S.A., and Syrbu, A.A., *Zh. Neorg. Khim*., 2011, vol. 56, no. 11, p. 1883.
36. Rtishchev, N.I., El'tsov, A.V., Kvitko, I.Ya., and Allam, L.V., *Zh. Obshch. Khim*., 1980, vol. 50, no. 9, p. 2070.
37. Kvitko, I.Ya., Alam, L.V., Bobrovnikov, M.N., Avetikyan, G.B., and Panasyuk, S.L., *Zh. Obshch. Khim*., 1994, vol. 64, no. 4, p. 657.
38. John, R.P., Sreekanth, A., Rajakannan, V., Ajith, T.A., and Kurup, M.R.P., *Polyhedron*, 2004, vol. 23, no. 16, p. 2549.
39. Li, P., Solanki, N., K., Ehrenberg, H., Feeder, N., Davies, J.E., Rawson, J.M., and Halcrow, M.A., *J. Chem. Soc., Dalton Trans*., 2000, p. 1559.
40. Jazdzewski, B.A., Holland, P.L., Pink, M., Young, V.G., Spencer, Jr., D.J.E., and Tolman, W.B., *Inorg. Chem*., 2001, vol. 40, no. 5, p. 6097.
41. Sreenivasulu, B., Zhao, F., Gao, S., and Vittal, J.J., *Eur. J. Inorg. Chem*., 2006, p. 2656.
42. Losada, J., del Peso, I., and Beyer, L., *Inorg. Chim. Acta*., 2001, vol. 321, nos. 1–2, p. 107.
43. Subramanian, P.S., Suresh, E., and Dastidar, P., *Polyhedron*, 2004, vol. 23, no. 16, p. 2515.
44. Correia, I., Dornyei, A., Jakusch, T., Avecilla, F., Kiss, T., and Pessoa, J.C., *Eur. J. Inorg. Chem*., 2006, no. 14, p. 2819.
45. Liver, E., *Elektronnaya spektroskopiya neorganicheskikh soedinenii* (Electronic Spectroscopy of Inorganic Compounds), Tsivadze, A.Yu., Ed., Moscow: Mir, 1987, vol. 1.
46. Sheldrick, G.M., *SHELXS-86*, Gottingen (Germany): Univ. of Gottingen, 1986.
47. Sheldrick, G.M., *SHELXS-97*, Gottingen (Germany): Univ. of Gottingen, 1986.