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Direct Electrochemical and Chemical Syntheses, Structures, and Properties of Metal Complexes of Azo Compounds with an Additional Azo Group in the Amine Fragment

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Abstract—New complexes of Cu(II), Co(II), and Ni(II) with 1-phenyl-3-methyl-4-[(4-phenylazophenyl)hydrazono]-5H-pyrazol-5-one and 1-phenyl-3-methyl-4-[4-methyl-2-(4-methylphenylazophenyl)hydrazono]-5H-pyrazol-5-one are synthesized by the chemical and electrochemical methods and characterized by IR, ^{1}H NMR, and EXAFS spectroscopy and X-ray diffraction analysis. Depending on the complexing metal and position of the additional azo group, the latter is involved or not in coordination with the metal to form heterounit five- and six-membered metallocycles.

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INTRODUCTION

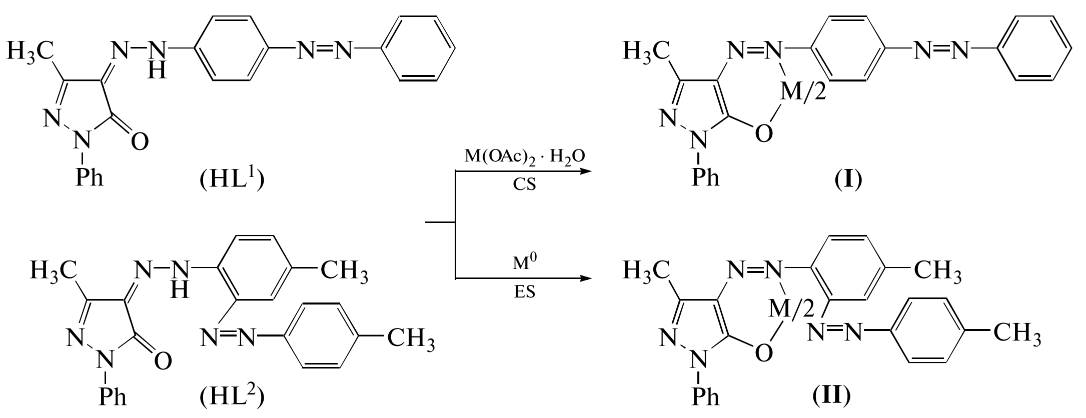
Azo compounds of the aromatic and heterocyclic series and their metal complexes find wide use in diverse areas. For instance, the azo compounds of arylazobenzimidazoles and their complexes are photostable cationic dyes for polyacrylonitrile fiber [1, 2] and are used as indicators for the photometric determination of thallium and stibium in analytical chemistry [3–5].

The azo compounds and their complexes manifested themselves as efficient oil additives to lubricating oils that improve their characteristics (load, antiwear, and antifriction) [6–8] and as extracting agents for metals [9].

Concepts about intrachelate isomerism (a possibility of the existence of metallocycles with different numbers of units inside one chelate molecule) were formulated and developed on the basis of the complexes of azo ligands of the aromatic and heterocyclic series [10–13]. The binuclear complexes with the exchange magnetic interaction were synthesized from polydentate azo ligands [14, 15] and applied for the production of magnetically active materials.

An addition azo group in an azo complex molecule, either being or not in the composition of the coordination mode, makes it possible to use its capability of photoinduced E/Z isomerization for the synthesis of coordination compounds with the properties of molecular switchers and photoactive materials [15–18].

In this work, we present the results of the chemical (CS) and electrochemical (ES) syntheses and EXAFS and X-ray diffraction studies of metal chelates **Ia–Ic** and **IIa–IIc** based on 1-phenyl-3-methyl-4-[(4-phenylazophenyl)hydrazono]-5H-pyrazol-5-one (HL^1) and 1-phenyl-3-methyl-4-[4-methyl-2-(4-methylphenylazophenyl)hydrazono]-5H-pyrazol-5-one (HL^2) containing the additional azo group in the *para*- (HL^1) and *ortho*-positions (HL^2) of the amine fragment.



M = Cu (a), Co (b), Ni (c)

EXPERIMENTAL

Commercially available 4-aminoazobenzene, 6-amino-4,4'-dimethylazobenzene, and 3-methyl-1-phenylpyrazol-5-one were used.

HL^1 and HL^2 were synthesized by the diazotization of 4-aminoazobenzene (0.02 mol) or 6-amino-4,4'-dimethylazobenzene (0.02 mol) followed by cross-coupling with 3-methyl-1-phenylpyrazol-5-one (0.02 mol) in alcohol [19]. The obtained azo compounds were recrystallized from a chloroform–ethanol (1 : 2) mixture.

For HL^1, IR (ν, cm^{-1}): 3058 (NH), 1662 (C=O). ^1H NMR ($CDCl_3$), δ, ppm: 2.38 (s, 3H, CH_3), 7.20–8.01 (m, 14H, C_{Ar}–H), 13.67 (s, 1H, NH).

For HL^2, IR (ν, cm^{-1}): 3034(NH), 1660 (C=O). ^1H NMR ($CDCl_3$), δ, ppm: 2.37–2.44 (m, 9H, CH_3), 7.19–8.10 (m, 12H, C_{Ar}–H), 14.68 (s, 1H, NH).

Chemical synthesis of complexes I and II. A solution of the corresponding metal acetate (0.5 mmol) in methanol (10 mL) was poured to a solution of HL^1 or HL^2 (1 mmol) in a chloroform–methanol (1 : 2) mixture (20 mL). The mixture was refluxed for 1 h. Brown precipitates of the complexes formed upon cooling were filtered off, washed with methanol, and recrystallized from a chloroform–methanol (1 : 2) mixture.

Electrochemical synthesis of complexes I and II. The working solution of the corresponding azo compound HL^1, or HL^2 (0.001 mol) in methanol (20 mL) and $[Et_4N]ClO_4$ (0.01 g) as the electrolyte were placed in an electrochemical cell with the platinum cathode and an anode of the complexing metal (Co, Ni, Cu). Electrochemical synthesis was conducted at a constant current strength of 40 mA and a voltage of 15 V for 1 h. Dark red precipitates of the complexes were filtered off, washed with methanol, and recrystallized from a chloroform–methanol (1 : 2) mixture.

IR (ν(C–O), cm^{-1}): 1310, 1304, 1305 (**Ia**, **Ib**, and **Ic**) and 1317, 1302, 1304 (**IIa, IIb**, and **IIc**). μ_{eff} (294 K) = 2.15, 3.94, 3.12 (**Ia**, **Ib**, and **Ic**) and 1.84, 3.89, 3.05 μ_B (**IIa**, **IIb**, and **IIc**). Single crystals of complexes **Ia** and **IIb** suitable for X-ray diffraction analysis were grown from a chloroform–methanol (1 : 2) mixture.

The elemental analysis results for the ligands and complexes **I** and **II** are presented in Table 1.

IR spectra were recorded on a Varian Excalibur-3100 FT-IR instrument in powders using the attenuated total internal reflection method.

All ^1H NMR experiments were carried out using the equipment of the Center of Cooperative Use "Molecular Spectroscopy." ^1H NMR spectra were measured on a Varian Unity-300 instrument (300 MHz) in the internal stabilization mode of the ^2H polar resonance line in $CDCl_3$.

The X-ray absorption Cu, Co, and Ni*K* edges for compounds **I** and **II** were obtained on the station "Structural Materials Science" at the Kurchatov Center of Synchronous Radiation and Nanotechnologies (Moscow) [20]. The energy of the electron beam, which was used as an X-ray synchronous radiation source, was 2.5 GeV at a current of 60–80 mA. A two-crystal monochromator with a slit of the Si(111) single crystal was used to monochromatize the X-ray radiation. The X-ray beam intensities before and after irradiation were measured using two ionization chambers filled with nitrogen–argon mixtures, which gave 20 and 80% absorption for I_0 and I_t, respectively.

The obtained X-ray absorption spectra were processed using standard procedures of the extraction of the background, normalization to the value of the *K* edge jump, and isolation of the atomic absorption μ_0 [21] followed by the Fourier transform of the obtained EXAFS (χ) spectra in the range of wave vectors of photoelectrons *k* from 2.6 to 12–13 $Å^{-1}$ with the weight function k^3. The obtained Fourier transform moduli (FTM) of the χ spectra correspond to the radial function of the distribution of atoms around the absorbing metal atom with the accuracy to the phase shift. The threshold ionization energy E_0 was chosen

Table 1. Elemental analysis results for the ligands and complexes **I** and **II**

Compound (empirical formula)	Content (found/calculated), %				Color	T_m, °C	Yield, %
	C	H	N	M			
HL^1 ($C_{22}H_{18}N_6O$)	69.35/69.20	4.68/4.74	21.77/21.98		Orange powder	206–207	47
HL^2 ($C_{24}H_{22}N_6O$)	70.07/70.23	5.53/5.40	20.68/20.47		Red crystals	215–216	40
Ia ($C_{44}H_{34}N_{12}O_2Cu$)	CS 62.39/63.95	4.02/4.1	20.12/20.33	20.12/7.69	Brown powder	>250	93
	ES 62.41/63.95	4.09/4.1	20.15/20.33	7.91/7.69			97
Ib ($C_{44}H_{34}N_{12}O_2Co$)	CS 65.29/64.31	4.83/4.17	20.37/20.45	7.24/7.17	Dark brown crystals	>250	98
	ES 65.26/64.41	4.81/4.17	20.41/20.45	7.21/7.17			99
Ic ($C_{44}H_{34}N_{12}O_2Ni$)	CS 64.42/64.33	4.27/4.17	20.34/20.46	7.20/7.14	Brown crystals	225–226	85
	ES 64.45/64.33	4.31/4.17	20.38/20.46	7.18/7.14			91
IIa ($C_{48}H_{42}N_{12}O_2Cu$)	CS 65.23/65.33	4.67/4.80	19.12/19.05	7.09/7.20	Dark brown crystals	238–239	97
	ES 65.27/65.33	4.71/4.80	19.17/19.05	7.13/7.20			99
IIb ($C_{48}H_{42}N_{12}O_2Co$)	CS 65.48/65.67	4.90/4.82	19.11/19.15	6.65/6.71	Dark brown crystals	151–152	95
	ES 65.44/65.67	4.87/4.82	19.07/19.15	6.59/6.71			97
IIc ($C_{48}H_{42}N_{12}O_2Ni$)	CS 65.51/65.69	4.91/4.82	19.22/19.15	6.61/6.69	Brown powder	>250	89
	ES 65.48/65.69	4.95/4.82	19.27/19.15	6.65/6.69			95

from the maximum value of the first derivative of the K edge and was further varied by fitting.

The exact values of the structure parameters of the nearest environment of the metal atoms in the metal complexes were determined by the nonlinear fitting of the parameters of the corresponding coordination spheres by comparing the calculated EXAFS signal and that isolated from the full EXAFS spectrum by the Fourier filtration method. This nonlinear fitting was conducted using the IFFEFIT program package [22]. The scattering phases and amplitudes of the photoelectron wave necessary for the construction of the model spectrum were calculated using the FEFF7 program [23]. The X-ray structural data for single crystals of the metal complexes with the similar atomic environment of metal atoms were taken as the starting coordinates necessary for the calculation of the scattering phases and amplitudes and further fitting. These structures were found in the Cambridge Structural Database.

The goodness-of-fit function (Q), which was minimized when finding the parameters of the nearest environment structure, was calculated by the formula

$$Q(\%) = \frac{\sum [k\chi_{\exp}(k) - k\chi_{th}(k)]^2}{\sum [k\chi_{\exp}(k)]^2} \times 100.$$

X-ray diffraction analysis of IIb was carried out on a Bruker SMART APEX II diffractometer equipped with a CCD detector and a monochromatic radiation source (MoK_α, $\lambda = 0.71073$ Å) using a standard procedure [24]. A semiempirical absorption correction was applied [25]. The structures were solved by a direct method and refined in the full-matrix anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were geometrically generated and refined in the riding model. The calculations were performed using the SHELXS-97 and SHELXL-97 programs [26].

The crystallographic information for the low-temperature variant of complex **IIb** was deposited with the Cambridge Crystallographic Data Centre (no. 942526; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

The magnetic susceptibility in the solid phase was determined by the Faraday method at ambient temperature on a setup mounted at the Southern Federal University [27].

RESULTS AND DISCUSSION

The metal complexes of azo compounds containing the benzimidazole [28–32] or imidazole [33] fragments have previously been synthesized and studied. Unlike the aromatic azo complexes [34–38] mainly forming structures with six-membered metallocycles, these complexes provide compounds with four five-membered or two six-membered rings, or even the polymer structure is formed as in the case of the zinc complex of 4,5-dichloro-2-phenylazoimidazole [33].

The question about the influence of the number of units and donor atoms in the coordination mode on the stereochemistry of metal complexes is still urgent. In the course of our investigations, we obtained azo compounds HL^1 and HL^2, and their metallochelates **I** and **II** were synthesized by the chemical and electrochemical methods.

The structures of the initial azo compounds HL^1 and HL^2 were determined by IR and ^{1}H NMR spectroscopy.

It is known that molecules of 1-phenyl-3-methyl-4-(arylazo)pyrazolone exist in the hydrazone tauto-

Table 2. Structural data for the local atomic environment of Cu, Co, and Ni in metal complexes **I** and **II** obtained from the EXAFS data*

Compound	N	R, Å	σ^2, Å^2	Atoms of coordination sphere	Q, %
Ia	2	1.94	0.0035	O/N	0.2
	2	1.95	0.0035	O/N	
IIa	2	1.95	0.0032	O/N	0.4
	2	1.98	0.0032	O/N	
Ib	2	1.95	0.0035	O/N	0.1
	2	1.98	0.0035	O/N	
IIb	2	1.96	0.0040	O/N	0.8
	4	2.07	0.0040	O/N	
Ic	2	2.00	0.0040	O/N	0.6
	2	1.98	0.0040	O/N	
IIc	2	2.03	0.0035	O/N	0.6
	2	1.98	0.0035	O/N	
	2	2.16	0.0035	N	

* R are interatomic distances, N is the coordination number, σ^2 is the Debye–Waller factor, and Q is the goodness of fit function.

meric form [13, 19, 39, 40]. Compounds HL^1 and HL^2 are similar in structure, which is indicated by the data of IR and ^{1}H NMR spectral studies.

The IR spectra exhibit stretching vibration bands of the C=O groups (1662 cm^{-1} in HL^1 and 1660 cm^{-1} in HL^2). In the ^{1}H NMR spectra, the downfield signals from the NH protons of the =N–NH– group appear at 13.67 (HL^1) and 14.68 ppm (HL^2), which is consistent with literature data and indicates that these compounds include the hydrazone tautomeric form.

The metal complexes based on ligands HL^1 and HL^2 have the composition ML_2 regardless of the synthesis method.

In the IR spectra of the complexes, the absorption bands of the NH groups of the ligands disappear and absorption bands of the coordinated C–O groups appear in a region of 1305–1317 cm^{-1}. This spectral behavior indicates the formation of chelate structures.

Complexes **I** and **II** are paramagnetic. The values of μ_{eff} are 2.15 (**Ia**) and 1.84 μ_B (**IIa**) for the copper chelates, 3.94 (**Ib**) and 3.89 μ_B (**IIb**) for the cobalt chelates, and 3.12 (**Ic**) and 3.05 μ_B (**IIc**) for the nickel chelates at 294 K and remain unchanged as the temperature decreases, also indicating their monomeric structure.

The local atomic environment of the complexing metals in the chelates was studied by the EXAFS method.

The XANES and FTM EXAFS spectra of the *K* absorption edge of the copper, nickel, and cobalt complexes (**I** and **II**) are shown in Fig. 1. The parameters of the nearest environment of the metal ions in these compounds obtained by the approximation of the theoretically calculated $\chi(k)$ of the chosen models to the experimental EXAFS spectra are given in Table 2.

As can be seen from Fig. 1 (left panel), the XANES spectra of metal complexes **I** somewhat differ from those of **II**, which is especially pronounced in the structure of the first edge derivatives. The first derivative of the Co*K* edge of **IIb** (Fig. 1b, left panel) has a narrow intense maximum, unlike the first derivative for **Ib**, where it is split into several maxima. The same tendency is also observed for the first derivatives of the Ni*K* edges of **Ic** and **IIc**, although they are less pronounced (Fig. 1c, left panel). Thus, it can be assumed that, on going from **I** to **II**, in the nickel complexes, the coordination number of the first coordination sphere increases due to the interaction with the nitrogen atoms of the additional azo groups in the *ortho*-position in the ligands and the symmetry of the environment of the metal ions increases.

In the case of copper compounds **Ia** and **IIa**, the first derivatives of the Cu*K* edges have nearly the same splitting (Fig. 1a, left panel). This structure of the absorption edge is characteristic of the copper complexes in which the metal atom has the environment from planar to tetrahedral, where the degree of distortion is manifested in the value of splitting of the first derivative. Thus, it follows from the qualitative consideration of the structure of the absorption *K* edges that no additional interaction of the copper ions with the atoms of the azo groups of the ligands occurs on going from **Ia** and **IIa**.

The FTM EXAFS spectra of the Cu, Co, and Ni absorption *K* edges of the studied metallochelates are presented in Fig. 1 (right panels). A basic feature of all obtained FTM is the main peak at r = 1.51–1.60 Å corresponding to the first nearest coordination sphere consisting of the nitrogen and oxygen atoms of the coordinating ligands and a series of peaks with a low amplitude at long r distances that characterize the sub-

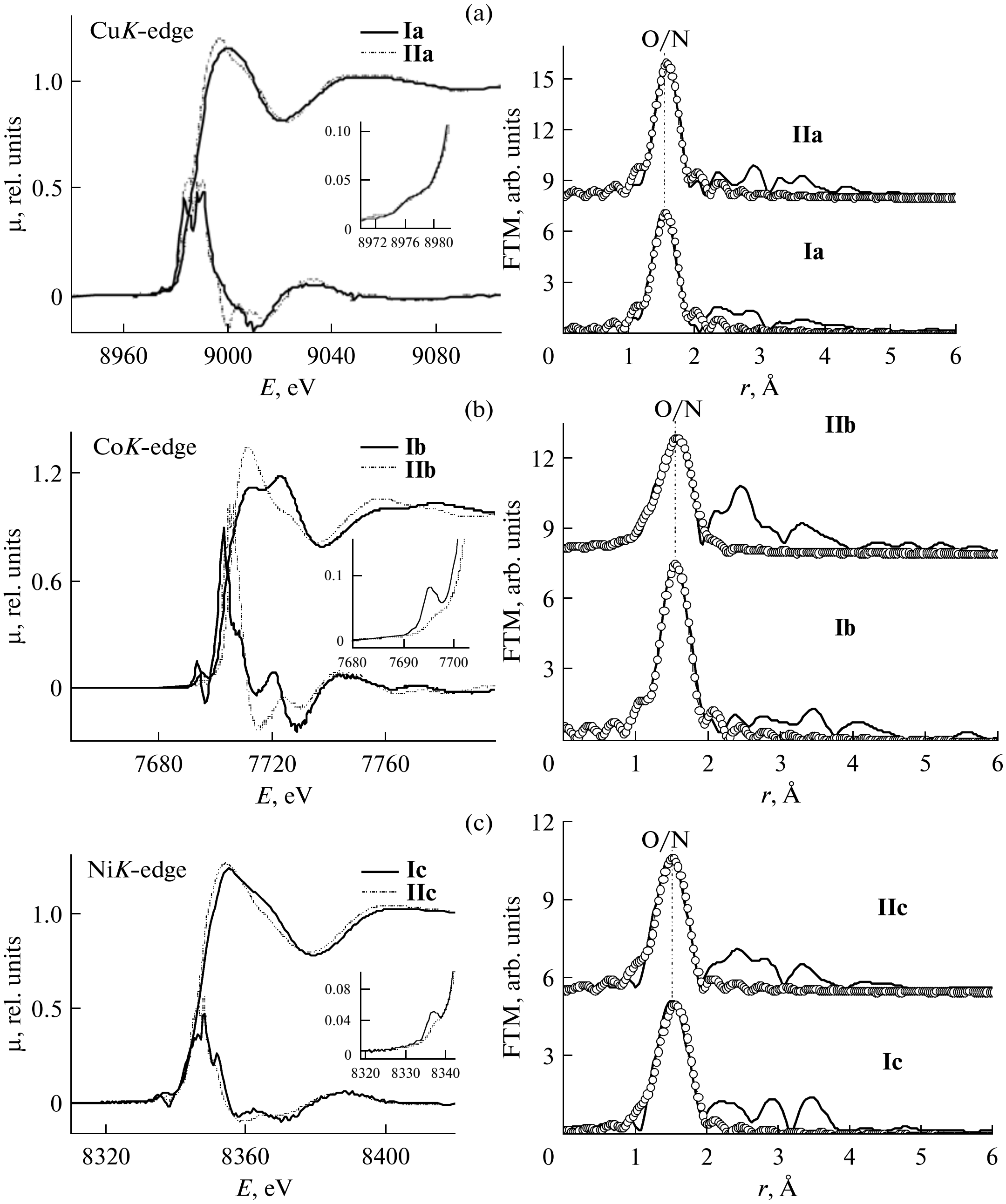


Fig. 1. XANES of the (a) Cu*K*, (b) Co*K*, and (c) Ni*K* edges for the X-ray absorption spectra and their first derivatives. Inset: the pre-edge structure (left panel) and the FTM EXAFS for copper metal complexes (a) **Ia** and **IIa**, (b) **Ib** and **IIb**, and (c) **Ic** and **IIc**: solid line is experiment, and empty circles are theoretical data (right panel).

sequent coordination spheres. The quantitative characteristics for the first coordination sphere obtained by the multisphere nonlinear fitting are listed in Table 2.

An analysis of the obtained results (Table 2) shows that the first coordination sphere for the cobalt and nickel ions in metal complexes **I** consists of two nitrogen atoms and two oxygen atoms, whereas in **II** the total coordination number of the first coordination sphere is 6 and its average radius increases. The data agree with the qualitative conclusions obtained by an analysis of the XANES spectra of these compounds. In copper complexes **I** and **IIa**, all parameters of the local atomic environment are similar and correspond (to different extents) to the distorted pseudo-tetrahedral environment of the copper atoms in these compounds.

Thus, an analysis of the XANES and EXAFS spectra of the absorption *K* edges shows the octahedral coordination due to additional bonds of nitrogen of

Table 3. Selected bond lengths (Å) and angles (deg) in compound **IIa**

Bond	*d*, Å	Bond	*d*, Å
N(1)–N(2)	1.263(3)	N(3)–N(4)	1.305(3)
N(5)–N(6)	1.412(4)	N(7)–N(8)	1.261(3)
N(9)–N(10)	1.295(3)	N(11)–N(12)	1.407(3)
C(16)–O(1)	1.259(3)	C(40)–O(2)	1.266(3)
Cu–O(1)	1.939(2)	Cu–O(2)	1.928(2)
Cu–N(3)	1.974(3)	Cu–N(9)	1.994(2)
Angle	ω, deg	Angle	Angle
O(1)CuN(3)	93.40(9)	O(2)CuN(3)	157.37(10)
O(1)CuO(2)	84.09(9)	O(2)CuN(9)	92.42(10)
O(1)CuN(9)	157.45(10)	N(3)CuN(9)	98.03(10)
N(3)N(4)C(15)	117.8(3)	N(9)N(10)C(39)	117.6(3)
N(8)N(7)C(25)	114.03	N(2)N(1)C(1)	114.10(3)
CuO(1)C(16)	118.8(2)	CuO(2)C(40)	119.2(2)

the azo group with the metal ion in cobalt and nickel complexes **IIb** and **IIc** having an additional azo group in the *ortho*-position of the amine fragment. This interaction is sterically hindered for the compounds of Co and Ni (**Ib** and **Ic**) with the azo group in the *para*-position, and the coordination is close to the tetrahedral one. The tetrahedral environment of the metal ion, regardless of the ligand type, is observed in copper compounds **Ia** and **IIa**.

The results of an X-ray diffraction analysis for chelates **IIa** and **IIb** (Fig. 2) confirm the EXAFS data.

Compound **IIa** is a mononuclear complex in which two HL^2 molecules are coordinated to the central metal atom through chelating mode and act as bidentate O,N-ligands. The central copper(II) atom is in the distorted square-planar environment of two nitrogen atoms and two oxygen atoms. The structure includes two six-membered nonplanar metallocycles with identical compositions. The bend angles of the metallocycles along the O(1)–N(4) and O(2)–N(10) lines are 14.23(3)° and 17.31(4)°, respectively.

The bond lengths and angles in each ligand forming the bis-chelate discussed somewhat differ for **IIa** and **IIb**. The main structural characteristics of **IIa** are given in Table 3.

The angles between the planes are the following: 28.1° for the pyrazole cycles N(5)–C(17) and N(11)–C(40), 15.04(9)° for the phenyl rings C(8)–C(13) and C(32)–C(37), 34.31(9)° for the pyrazole N(5)–C(17) and phenyl C(8)–C(13) rings, and 27.59(10)° for the N(11)–C(40) and C(32)–C(37) cycles.

The structural units at the azo groups N(1)–N(2) and N(3)–N(4) are in the *trans* configuration. The C(13)–N(3)–N(4)–C(15) and C(1)–N(1)–N(2)–C(8) torsion angles are characterized by values of 175.77(6)° and 173.48(3)°, respectively. The C(25)–N(7)–N(8)–C(32) and C(37)–N(9)–N(10)–C(39*A*) torsion angles are 173.93(5)° and 176.55(3)°, respectively.

The shortened contacts between the coordination center and the nearest nitrogen atoms of the azo group that are not involved in coordination suggest the possibility of intrachelate isomerism for the coordination compound discussed (Cu···N(2) 2.757(3), Cu···N(8) 2.717(2) Å).

The crystals of **IIb** were studied: at ambient and low temperatures (Table 4). The complex contains the same ligand as **IIa**, but the central atom is Co(II) instead of Cu(II). Unlike the bidentate-coordinated complex **IIa**, in **IIb** the ligand is attached through the tridentate chelate mode to form the meridional isomer (Fig. 2b).

A similar coordination of the planar tridentate ligand results in the formation of a substantially distorted coordination polyhedron. The octahedron with the axial vertices N(1) and N(1a) and the equatorial plane O(1)O(1a)N(5)N(5a) was chosen as a coordination polyhedron in **IIb**. The bond lengths in the octahedron are listed in Table 5 for both variants of the structure. At ambient temperature, the linear angles are 160.7°, 160.7°, and 169.6°, and the rectangular angles are 75.9°–112.5°. The corresponding values at low temperature are 160.2°, 160.2°, 170.3°, and 70.2°–117.9°. The coordination of the tridentate ligand to the Co(II) atom is accompanied by the closure of two six-membered Co(1)O(1)C(1)C(2)N(2)N(1) and two five-membered Co(1)N(1)C(4)C(9)N(5) metallocycles of the nonplanar conformation.

At ambient temperature, the dihedral angle between the metallocycles is 15.6°. The six-membered metallocycle includes an inflection along the N(2)–O(1) line with a dihedral angle between the O(1)Co(1)N(1)N(2) and N(2)C(2)C(1)O(1) fragments of 22.1°. The five-membered metallocycle with the conjugated C(4)–C(9) cycle forms a dihedral angle of 2.7°. The C(11)–C(16) phenyl cycle is unfolded relatively to the Co(1)N(1)C(4)C(9)N(5) metallocycle at an angle of 54.0°. The dihedral angle between the C(19)–C(24) cycle and C(1)C(2)C(3)N(3)N(4) pyrazole cycle is 36.2°.

Thus, according to the X-ray diffraction data, in the considered chelates **IIa** and **IIb**, the azo group in the *ortho*-position of the amine fragment can either be involved or not in coordination with the metal, depending on the metal nature. As a result, various structures can be formed in the intracomplex com-

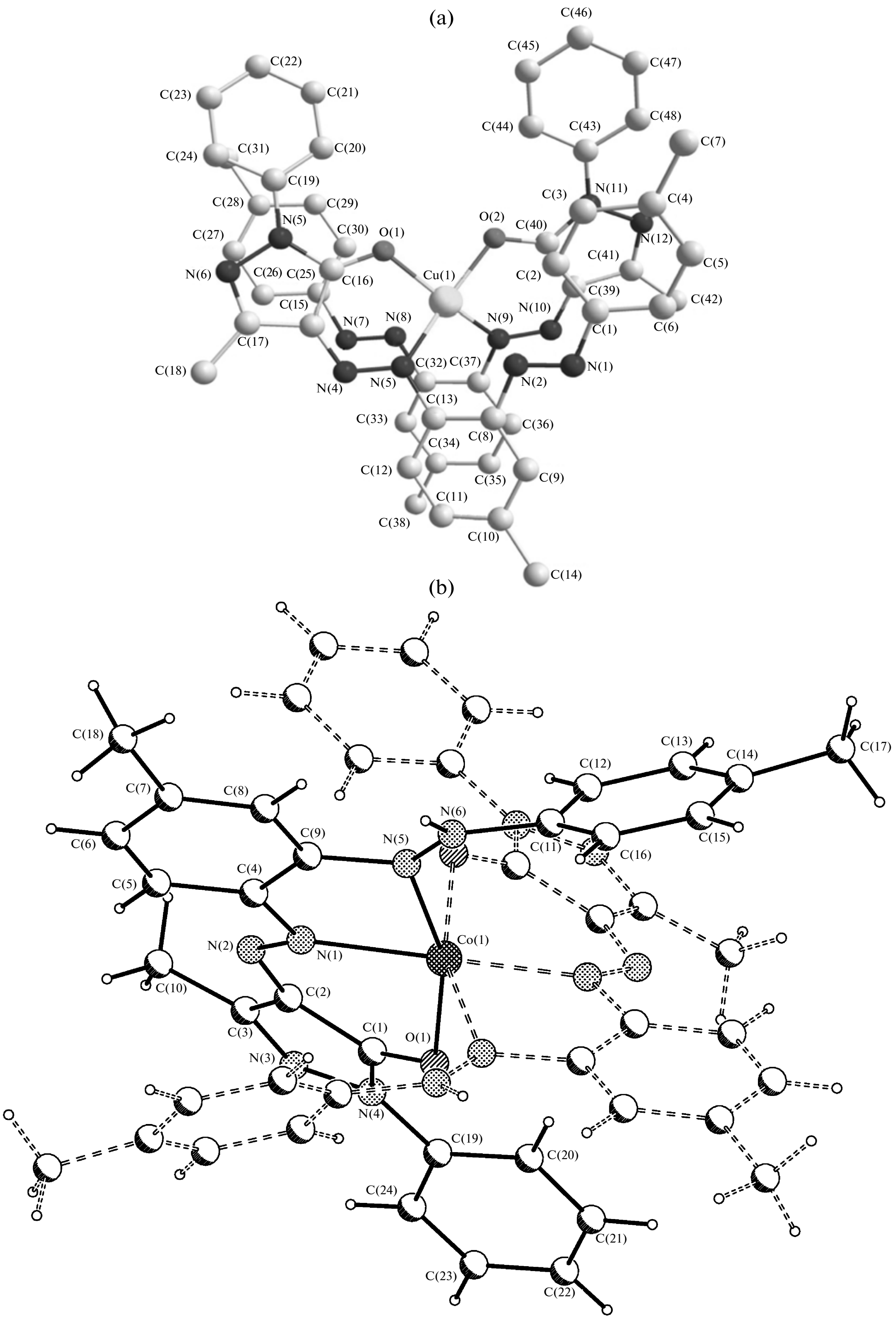


Fig. 2. Molecular structures for compounds (a) **IIa** and (b) **IIb**.

Table 4. Crystallographic parameters and experimental data for crystals of **IIb**

Parameter	Value	
Temperature	293 K	173 K
Chemical formula	$C_{48}H_{42}N_{12}O_2Co$	
FW	439.94	
Color, habitus	Green, prisms	
Sample size, mm	0.12 × 0.08 × 0.03	0.40 × 0.10 × 0.10
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell parameters:		
a, Å	18.362(6)	18. 131(2)
b, Å	11.366(3)	11.3729(13)
c, Å	22.136(5)	22.021(4)
β, deg	108.29(1)	108.232(2)
V, Å^3	4386.7(5)	4312.6(1)
Z	8	
ρ_{calcd}, g/cm^3	1.332	1.352
μ, cm^{-1}	0.446	0.453
F(000)	1828	
Diffractometer	Enraf-Nonius Cad-4	Bruker Apex-II CCD
Radiation	MoK_α (0.71073) Graphite monochromator	
θ scan range, deg	1.94–23.54	2.15/–26.73
Index range	$-22 \le h \le 18$, $-14 \le k \le 14$, $-27 = l \le 27$	
Total number of measured reflections	3159	4504
Number of independent reflections	2693	3915
Number of refined parameters	285	
Goodness-of-fit for F^2	1.223	1.037
R ($I > 2\sigma(I)$)	$R_1 = 0.05854$ $wR_2 = 0.0714$	$R_1 = 0.0436$ $wR_2 = 0.0509$
R (for all reflections)	$R_1 = 0.1860$, $wR_2 = 0.1801$	$R_1 = 0.1205$ $wR_2 = 0.1272$
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.034/–0.006	0.0/–0.0

Table 5. Selected bond lengths (Å) in compound **IIb**

Bond	d, Å (293 K)	d, Å (173 K)
Co(1)–O(1)	2.078(3)	1.995(1)
Co(1)–N(4)	2.074(3)	2.265(2)
Co(1)–N(5)	2.248(3)	2.261(2)
O(1)–C(1)	1.271(5)	1.328(2)1)
N(4)–C(19)	1.421(5)	1.465(3)
N(1)–C(4)	1.413(5)	1.465(3)
N(1)–N(2)	1.287(4)	1.319(2)
N(2)–C(2)	1.339(5)	1.374(3)
N(3)–(N4)	1.406(5)	1.515(2)
N(3)–C(3)	1.297(5)	1.367(3)
N(4)–C(1)	1.353(5)	1.352(2)
N(5)–N(6)	1.245(6)	1.244(2)
N(6)–C(11)	1.431(5)	1.557(3)
N(6)–C(19)	1.46(1)	1.506(3)

pounds: with two six-membered (M = Cu) or two six- and two five-membered (M = Co) metallocycles.

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