

Synthesis, Molecular Structure, and Spectral Properties of New Metal Chelates Based on Organic Autocomplexes and Charge Transfer Therein

V. V. Mel'nikov^a, I. G. Il'ina^a, I. V. Fedyanin^b, and B. N. Tarasevich^a

^a Faculty of Chemistry, Moscow State University, Vorob'evy gory 1, Moscow, 119992 Russia
e-mail: igi@org.chem.msu.ru

^b Nesmeyanov Institute of Organometallic Compounds, Russian Academy of Sciences,
ul. Vavilova 28, Moscow, 119991 Russia

Received May 18, 2007

Abstract—A number of new chelate compounds based on 3*d*-transition metals and autocomplexes of the dinitroquinoline series were synthesized. The crystalline structure of the new complexes was determined by X-ray analysis, and their spectral properties were studied. The complexes have a conformation which gives rise to two modes of contact intramolecular charge transfer: intraligand, which is intrinsic to the initial ligand molecules, and interligand (as in binary charge-transfer complexes). The latter involves the corresponding pairs of donor and acceptor fragments of the initial ligand molecules, which appear spatially close as a result of complex formation.

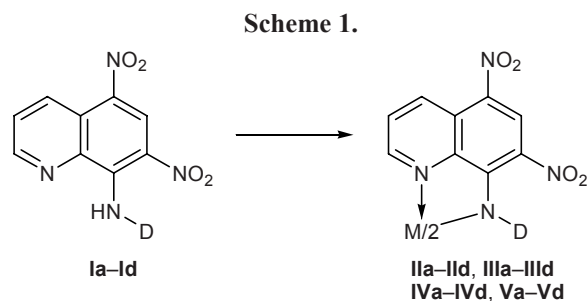
DOI: 10.1134/S1070428008030202

Intramolecular charge-transfer (ICT) processes exert a considerable effect not only on chemical and physical properties of organic compounds. The formation of charge-transfer complexes is assumed in many biological transformations and especially in processes related to energy conversion in living cells. Numerous biologically important functions, such as metabolism, tissue respiration, muscle contraction, and carcinogenesis, are often interpreted from the viewpoint of charge transfer [1, 2]. Under certain conditions, donor–acceptor couples can be formed in complex proteins, where charge transfer occurs between an aromatic amino acid residue and an electron-deficient prosthetic group [3].

The role of trace elements (some metal ions) in some vital processes is also well known. As stated in [4], the importance of trace amounts of some metals for normal vital functions of protein molecules is generally recognized. This becomes especially obvious if we take into account that several hundreds of enzymes (even more than one third of all known enzymes) are metalloenzymes and that their action is impossible in the absence of metals. Here, metal not only stabilizes the structure and gives rise to active conformation of enzyme but also participates directly in catalytic proc-

esses [4]. On the other hand, many enzyme macromolecules acting as catalysts in biological processes are complex multicenter donor–acceptor systems containing a coordinated metal. Metal chelates derived from autocomplexes, i.e., organic compounds with intramolecular charge transfer, can be regarded as most closely related structures simulating active sites in such enzymes.

While performing systematic studies on autocomplex-like compounds we synthesized a number of dinitroquinoline derivatives having donor fragments of different strengths and examined in detail intramolecular charge transfer in their molecules [5]. Among these,

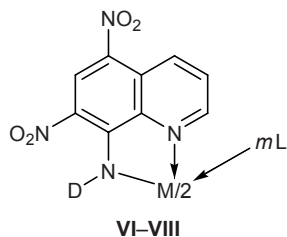


D = Ph (**a**), 4-MeC₆H₄ (**b**), 3,4-Me₂C₆H₃ (**c**), 4-Me₂NC₆H₄ (**d**);
II, M = Ni; III, M = Co; IV, M = Cu; V, M = Zn.

autocomplexes **Ia–Id** (Scheme 1) were obtained; they contained aromatic fragments D whose donor power is determined by their ionization energy (E_i , eV). Using structures **Ia–Id** as examples, in the present work we made an attempt to obtain nickel(II), cobalt(II), copper(II), and zinc(II) chelates ML_2 where L is a bidentate ligand (LH = **Ia–Id**).

There are almost no published data on metal chelates derived from autocomplexes as ligands; exceptions are analogous derivatives based on compound **Ia** [6]; however, the latter was not considered to be an autocomplex. The results of our first study in this line were reported in [7] where the synthesis, spectral properties, and crystalline structure of gold chelate derived from an autocomplex of the trinitrobenzene series were described.

Metal chelates **II–V** were synthesized following a standard procedure by direct reaction of equimolar amounts of ligands **Ia–Id** in acetonitrile and the corresponding metal acetates in methanol (Scheme 1). Depending on the reaction conditions, specifically on the reactant ratio, the products were either bis-chelates of the composition $L_2M \cdot nH_2O$ (**II–V**) or adducts $L_2M \cdot mLH$ (**VI–VIII**) where LH is the initial ligand or solvent molecule. The other known methods, such as template synthesis and homogeneous precipitation [8], did not ensure complete conversion of the reactants.



VI, D = 3,4-Me₂C₆H₃, L = **Ic**, $m = 2$, M = Ni; **VII**, D = 3,4-Me₂C₆H₃, L = Me₂CO, $m = 2$, M = Cu; **VIII**; D = 4-Me₂NC₆H₄, L = **Id**, $m = 2$, M = Zn.

All compounds were isolated as crystalline substances, as a rule dark green with metal luster. The structure of chelates **II–V** was determined on the basis of their elemental analyses and IR and UV spectra. The steric structure and conformation of autocomplex **Ib** and its nickel chelate **Iib** were determined by X-ray analysis* (Figs. 1, 2).

The IR spectra of compounds **II–V** (KBr) contained absorption bands belonging to asymmetric and sym-

metric stretching vibrations of the nitro groups in the aromatic ring (1570–1530 and 1340–1290 cm⁻¹, respectively) and stretching vibrations of C–H bonds in the quinoline fragment (3100–2900 cm⁻¹), while no NH absorption typical of initial autocomplexes **Ia–Id** (3280–3110 cm⁻¹) was present.

Important results were obtained by studying the electronic absorption spectra of metal chelates in comparison with the spectra of the initial autocomplexes. The electronic absorption spectra were measured from solutions in acetonitrile with a concentration of 10⁻³ to 10⁻⁵ M. The observed maxima were assigned by an empirical method [9] which was developed for polysubstituted donor–acceptor benzene derivatives. This method allowed us to determine the number of bands in the electronic absorption spectra and their

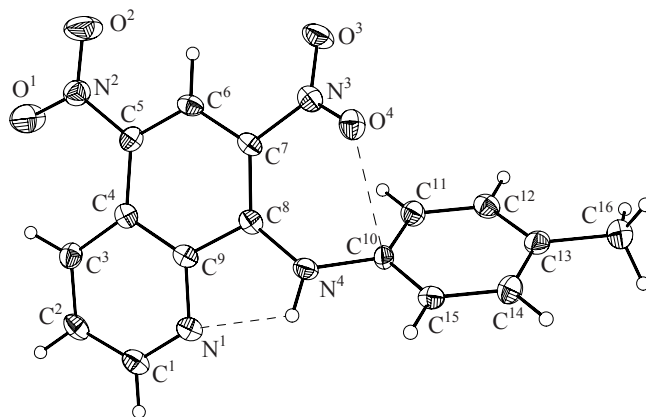


Fig. 1. Structure of the molecule of *N*-(4-methylphenyl)-5,7-dinitroquinolin-8-amine (**Ib**) according to the X-ray diffraction data.

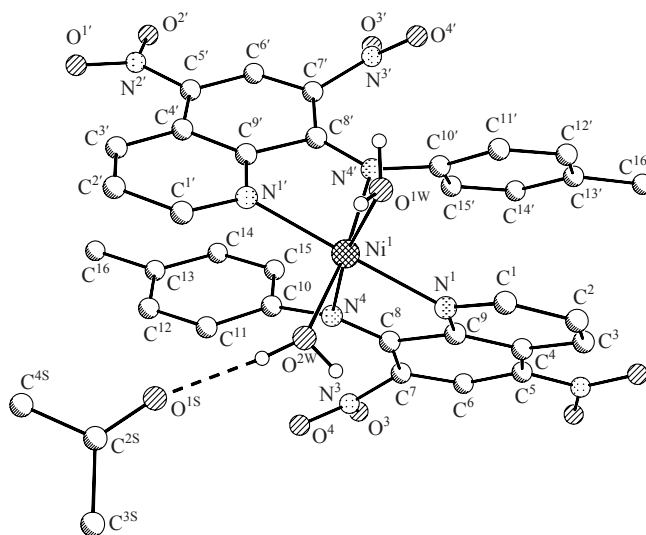


Fig. 2. Structure of the molecule of bis[*N*-(4-methylphenyl)-5,7-dinitroquinolin-8-amido]nickel(II)·2H₂O (**Iib**) according to the X-ray diffraction data.

* Crystals suitable for X-ray analysis were obtained with participation of senior research worker O.V. Mikhalev.

Table 1. Electronic absorption spectra of autocomplexes **Ia–Id** and chelates **II–V** derived therefrom in acetonitrile ($c = 10^{-3} - 10^{-5}$ M) and ionization energies E_i of the donor fragments

Compound no.	E_i , eV	λ_{\max} , nm ($\epsilon \times 10^{-3}$)			
		CT(<i>p</i> -NO ₂ /NHD)	CT(<i>o</i> -NO ₂ /NH-D)	ICT-I (autocomplex)	ICT-II (chelate)
Ia	9.25	291 (14215)	384 (9.7)	426 (11.6)	
IIa		302 (inflection)	367 (18.8)	440 (25.3)	483 (38.0)
IIIa		309 (inflection)	362 (24.6)	455 (31.5)	492 (16.0)
IVa		305 (inflection)	362 (25.4)	419 (29.1)	465 (24.8)
Va		293 (inflection)	361 (2.8)	382 (4.0)	424 (8.8)
Ib	8.82	290 (14390)	392 (11.0)	436 (16.3)	
IIb		— ^a	368 (16.8)	441 (15.9)	488 (44.5)
IIIb		— ^a	362 (33.8)	434 (16.6)	486 (55.2)
IVb^b		— ^a	336 (23.2)	478 (36.0)	484 (34.5)
Ic	8.27	290 (14393)	400 (13.9)	439 (10.6)	
IIc		323 (inflection)	362 (24.6)	407 (18.6)	485 (26.8)
IIIc		311 (inflection)	365 (18.8)	433 (11.7)	492 (12.2)
IVc		323 (inflection)	360 (24.4)	441 (14.9)	477 (36.3)
Id	7.14	322 (6131)	370 (5.6)	463 (9.3)	
IIId		— ^a	371 (25.8)	430 (20.8)	489 (25.3)
IIIId		— ^a	385 (22.8)	441 (17.3)	494 (34.6)
IVId		— ^a	372 (34.7)	396 (27.2)	515 (31.0)
VId^b		— ^a	341 (21.6)	475 (25.5)	525 (22.7)

^a Disappears.^b The spectrum was measured in DMF.

origin without resorting to quantum-chemical calculations. Its suitability for interpretation of electronic absorption spectra of autocomplexes was demonstrated by us previously using NH-bridged trinitrobenzene derivatives [10] and was also confirmed by studying the spectra of initial autocomplexes **Ia–Id** [5].

Table 1 contains the experimental absorption maxima λ_{\max} (nm) and molar absorption coefficients ϵ ($\text{l mol}^{-1} \text{cm}^{-1}$) of charge-transfer bands in the electronic spectra of compounds **I–V**, their assignments according to the procedure described in [9], and known [11, 12] ionization energies E_i (eV) of model donor fragments.

Following the procedure proposed in [9] and taking into account our previous results [5], charge-transfer bands in the spectra of metal chelates **II–V**, as well as of initial ligands **Ia–Id**, were assigned mainly to intraligand transitions (Table 1). The short-wave band corresponds to charge transfer from the NH–D donor fragment to the acceptor *p*-NO₂ group (*para* band); next follows (in the series of decreasing excitation energy) electron transition from the NH–D fragment to the

o-NO₂ group (*ortho* band) and intramolecular contact (through space) charge transfer (ICT-I) between the NH–D fragment and *o*-NO₂ group which is forced out from the quinoline ring plane. In keeping with the X-ray diffraction data for ligand **Ib** (Fig. 1), the *o*-NO₂ group appears as if it hangs over the donor fragment.

The spectra of metal chelates contain an additional long-wave absorption maximum in the region λ 480–526 nm, which should be assigned to contact charge transfer (ICT-II) of different nature: it reflects donor–acceptor interligand interaction (as in binary CTCs) between donor fragment of one ligand molecule and acceptor fragment of the other ligand molecule, which appear spatially close as a result of chelation (Fig. 2).

It is known that steric interactions forcing a substituent to turn about the bond connecting it to a ring reduce the intensity of CT bands involving the corresponding groups [13]. Comparison of the electronic absorption spectra of the ligands (autocomplexes) and chelates derived therefrom (Table 1) shows the following variations in the spectra as a result of coordination: the *para* band decreases in intensity so strongly that it

either appears as a plateau at about $\lambda \sim 300$ nm or almost disappears; the *ortho* band in the spectra of chelates **II–IV** based on autocomplexes with weak donor fragments suffers a blue shift. Reduction in the intensity of the CT(*p*-NO₂-NHD) band is induced by deviation of orbitals of the benzene rings in the acceptor nitroquinoline and donor fragments from parallel orientation due to chelation. The blue shift results from decrease in the donor power of the ND fragment [7].

The formation of chelate structure also follows from the appearance in the electronic absorption spectra of a long-wave band in the region λ 480–526 nm (ICT-II; no such band is present in the spectra of the initial autocomplexes) and 1.5–2-fold increase in the intensity of all absorption bands due to doubling of interacting fragments in the chelate molecule.

According to the X-ray diffraction data (Fig. 2), the MN₄ coordination entity in chelate **IIb** includes two water molecules as extra ligands and adopts a distorted octahedral configuration. However, deviation from octahedral symmetry is small: the maximal deviation from the ideal value is observed for the bond angle N¹NiN⁴ equal to 83.6°. The ligands are oriented in such a way that they hang over each other and the planes of the donor and acceptor fragments of different ligands are almost parallel, the distance between them being 3.12 Å; such conformation implies the possibility for donor–acceptor interaction like that typical of binary charge-transfer complexes. Through-space charge transfer between donor and acceptor fragments of different ligands may be interpreted as intramolecular intraligand charge transfer; it contributes most to ICT-II in the electronic absorption spectra of metal chelates. Analysis of the spectra of nickel(II) chelates **IIa–IId** (Table 2) suggests that analogous structure of coordination entity is typical of the other nickel complexes, for their spectral parameters are similar.

The molecular structure of chelate **IIb** is characterized by considerable redistribution of bond lengths in both acceptor dinitroquinoline and donor phenyl fragments, as compared to the corresponding parameters of the initial autocomplex. The bond lengths and bond angles in the two ligands of a chelate molecule are very similar (Table 3).

The *ortho*-nitro group in chelate molecule **IIb** is turned relative to the quinoline ring plane through almost the same angle as in autocomplex **Ib**: the torsion angle C⁸C⁷N³O⁴ is 28.0 and 28.4°, respectively. On the other hand, the *para*-nitro group (torsion angle C⁶C⁵N²O²) deviates from the quinoline ring plane in

Table 2. Electronic absorption spectra of nickel complexes **IIa–IId**

Compound no.	λ_{\max} , nm ($\epsilon \times 10^{-3}$)		
	CT(<i>o</i> -NO ₂ /NHD)	ICT-I	ICT-II
IIa	367 (18.8)	440 (25.3)	483 (38.0)
IIb	368 (16.8)	441 (15.9)	488 (44.5)
IIc	362 (24.6)	407 (18.6)	485 (26.8)
IId	371 (25.8)	430 (20.7)	489 (25.3)

the complex by an angle of $\sim 10^\circ$, whereas in the corresponding ligand molecule it is almost coplanar to the quinoline fragment. Conjugation between the *para*-nitro group and the aromatic ring in such chelate structure is weaker, and the intensity of the corresponding *para*-band decreases so strongly that it almost disappears from the electronic spectrum. The formally single N⁴–C⁸ bond in chelate **IIb** is shorter than the corresponding bond in autocomplex **Ib**, and rotation about this bond is hindered even more strongly: the torsion angle for rotation of the quinoline ring about the N⁴–C⁸ bond in molecule **IIb** is 11.7° against 25.8° in autocomplex **Ib**. On the other hand, the angle of rotation of the donor fragment about the N⁴–C¹⁰ bond in **IIb** is larger than the corresponding angle in structure **Ib** (55.7° and 36.6°, respectively), which indicates that the lone electron pair on N⁴ is almost forced out from conjugation with the donor phenyl ring.

Thus the X-ray diffraction data are fully consistent with the chelate structure assumed on the basis of their electronic absorption spectra. This provides further support to the ability of the above empirical method to appropriately describe donor–acceptor interactions not only in autocomplexes but also in metal chelates based thereon.

Table 3. Some bond lengths (*d*, Å) and torsion angles (φ , deg) in the molecules of autocomplex **Ib** and chelate **IIb**^a

Parameter (bond length or torsion angle)	Ib	IIb
N ⁴ –C ⁸	1.3403	1.3170
N ⁴ –C ¹⁰	1.423	1.415
N ¹ –C ⁹	1.357	1.363
C ⁸ –C ⁹	1.460	1.484
C ⁶ C ⁵ N ² O ²	4.20	9.70
C ⁸ C ⁷ N ³ O ⁴	28.40	28.00
C ¹¹ C ¹⁰ N ⁴ C ⁸	36.60	55.70
C ⁷ C ⁸ N ⁴ C ¹⁰	25.8	11.7

^a Short intramolecular contact C¹⁰...N¹ 3.12 Å.

Table 4. Crystallographic data and parameters of X-ray diffraction experiments for compounds **Ib** and **IIb**

Parameter	Ib	IIb
Formula	C ₁₆ H ₁₂ N ₄ O ₄	C ₃₅ H ₃₂ N ₈ NiO ₁₁
Molecular weight	324.30	799.40
Temperature, K	98	120
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>Z</i>	4	2
<i>a</i> , Å	4.6669(9)	11.101(3)
<i>b</i> , Å	22.465(4)	13.898(3)
<i>c</i> , Å	13.784(3)	13.940(3)
α , deg	90	100.008(5)
β , deg	97.601(5)	112.905(5)
γ , deg	90	112.073(5)
<i>V</i> , Å ³	1432.4(5)	1701.9(7)
<i>d</i> _{calc} , g cm ⁻³	1.504	1.560
μ , cm ⁻¹	1.12	6.47
<i>F</i> (000)	672	828
2 θ _{max} , deg	54	54
Total number of reflections	10115	12538
Number of independent reflections	3107	7381
Number of reflections with <i>I</i> > 2 σ (<i>I</i>)	1736	4844
Number of refined parameters	218	500
<i>R</i> ₁	0.0524	0.0496
<i>wR</i> ₂	0.1118	0.1042
Goodness of fit	1.014	1.045
Residual electron density, e Å ⁻³ (<i>d</i> _{min} / <i>d</i> _{max})	1.262/−0.510	0.555/−0.416

EXPERIMENTAL

The electronic absorption spectra were measured on a Helios α spectrophotometer (UNICAM, Great Britain) from solutions in acetonitrile with concentrations of 10⁻³ to 10⁻⁵ M; resolution 2 nm, spectral range 200–800 nm, cell path length 0.1 cm. The spectra were recorded in a digital form and were processed using Origin program. The IR spectra were obtained from samples prepared as KBr pellets or dispersed in mineral oil on a IR 200 spectrometer with Fourier transform (Thermo-Nicolet, USA); resolution 2 cm⁻¹; scan number 64. In some cases, internal reflection spectroscopy was applied to avoid undesirable absorption in the

region of 3400 cm⁻¹ (OH stretching vibrations) due to high hygroscopicity of KBr. The progress of reactions and the purity of products were monitored by thin-layer chromatography on Silufol UV-254 plates using eluent systems based on benzene, acetone, and chloroform. The X-ray diffraction data for single crystals of ligand **Ib** and complex **IIb** were acquired on a Smart 1000 CCD diffractometer (MoK α irradiation, graphite monochromator, ω -scanning). The structures were solved by the direct method and were refined by the least-squares procedure in full-matrix anisotropic approximation with respect to F^2_{hkl} . Hydrogen atoms in water molecules in complex **IIb** were localized by the Fourier difference syntheses, and positions of the other hydrogen atoms were calculated from the geometry consideration; the positions of all hydrogen atoms were refined using the riding model. The principal crystallographic data and refinement parameters for structures **Ib** and **IIb** are collected in Table 4. All calculations were performed using SHELXTL PLUS 5.1 software package [14].

Initial autocomplexes **Ia–Id** were synthesized according to the procedures described by us previously [5]. Aniline, *p*-toluidine, 3,4-dimethylaniline, *p*-dimethylaminoaniline, 8-hydroxyquinoline, Ni(OAc)₂, Co(OAc)₂·4H₂O, Cu(OAc)₂·H₂O, and Zn(OAc)₂·2H₂O were commercial products. 5,7-Dinitroquinolin-8-ol [15] and 8-chloro-5,7-dinitroquinoline [16] were synthesized by known methods.

Chelates II–V (general procedure). A solution of autocomplex **Ia–Id** in acetonitrile was added to a hot methanolic solution of the corresponding metal acetate (2 equiv plus small excess). The mixture was heated to the boiling point, cooled, and left to stand on exposure to air to allow it to slowly evaporate. The precipitate was filtered off, washed in succession with cold ethanol or methanol and water, and dried under reduced pressure.

Adducts VI–VIII (general procedure). A solution of nickel(II), copper(II), or zinc(II) acetate in methanol was added to a solution of an equimolar amount of autocomplex **Ic** or **Id** in the corresponding solvent, and the subsequent procedure was the same as in the synthesis of chelates **II–V**.

Bis(5,7-dinitro-*N*-phenylquinolin-8-amido)-nickel(II)·2H₂O (IIa). Yield 39%, black–green crystals with metallic luster, mp 232–235°C (decomp.) Found, %: C 49.84; H 3.02; N 15.20. C₃₀H₂₂N₈NiO₁₀. Calculated, %: C 50.32; H 3.11; N 15.71.

Bis(5,7-dinitro-*N*-phenylquinolin-8-amido)cobalt(II)·2C₂H₅OH (IIIa). Yield 81%, black–green crystals with metallic luster, mp 239–241°C (decomp.). Found, %: C 52.99; H 3.50; N 14.23. C₃₄H₃₀CoN₈O₁₀. Calculated, %: C 53.06; H 3.93; N 14.56.

Bis(5,7-dinitro-*N*-phenylquinolin-8-amido)copper(II) (IVa). Yield 73%, black–green crystals with metallic luster, mp 231–233°C. Found, %: C 53.33; H 2.59; N 16.23. C₃₀H₁₈CuN₈O₈. Calculated, %: C 52.83; H 2.66; N 16.43.

Bis(5,7-dinitro-*N*-phenylquinolin-8-amido)zinc(II)·H₂O (Va). Yield 71%, black–green crystals with metallic luster, mp 233–235°C. Found, %: C 51.87; H 2.98; N 15.89. C₃₀H₁₈N₈O₈Zn. Calculated, %: C 51.33; H 2.87; N 15.96.

Bis[*N*-(4-methylphenyl)-5,7-dinitroquinolin-8-amido]nickel(II)·2H₂O (IIb). Yield 79%, black–green crystals with metallic luster, mp 234–235°C (decomp.). Found, %: C 54.40; H 3.02; N 15.65. C₃₂H₂₂N₈NiO₈. Calculated, %: C 54.65; H 3.15; N 15.93.

Bis[*N*-(4-methylphenyl)-5,7-dinitroquinolin-8-amido]cobalt(II)·2H₂O (IIIb). Yield 59%, black–green crystals with metallic luster, mp 230–231°C (decomp.). Found, %: C 54.51; H 3.22; N 15.49. C₃₂H₂₂CoN₈O₈. Calculated, %: C 54.48; H 3.14; N 15.88.

Bis[*N*-(4-methylphenyl)-5,7-dinitroquinolin-8-amido]copper(II)·2H₂O (IVb). Yield 70%, black–green crystals with metallic luster, mp 224–226°C (decomp.). Found, %: C 53.75; H 3.76; N 14.43. C₃₂H₂₂CuN₈O₈. Calculated, %: C 54.13; H 3.12; N 15.78.

Bis[*N*-(3,4-dimethylphenyl)-5,7-dinitroquinolin-8-amido]nickel(II)·2H₂O (IIc). Yield 91%, black crystals, mp 254–256°C (decomp.). Found, %: C 53.63; H 3.26; N 14.19. C₃₄H₃₀N₈NiO₁₀. Calculated, %: C 53.38; H 3.93; N 14.56.

Bis[*N*-(3,4-dimethylphenyl)-5,7-dinitroquinolin-8-amido]cobalt(II)·H₂O (IIIc). Yield 61%, black–green crystals, mp 256–257°C (decomp.). Found, %: C 54.41; H 3.88; N 14.86. C₃₄H₂₈CoN₈O₉. Calculated, %: C 54.33; H 3.76; N 14.91.

Bis[*N*-(3,4-dimethylphenyl)-5,7-dinitroquinolin-8-amido]copper(II)·2H₂O (IVc). Yield 91%, black–brown powder, mp 243–245°C. Found, %: C 53.43; H 3.11; N 14.07. C₃₄H₃₀CuN₈O₁₀. Calculated, %: C 53.25; H 3.71; N 14.47.

Bis[*N*-(4-dimethylaminophenyl)-5,7-dinitroquinolin-8-amido]nickel(II) (IIId). Yield 67%, black–green

lustrous crystals, mp 237–239°C (decomp.). Found, %: C 53.38; H 3.75; N 18.10. C₃₄H₂₈N₁₀NiO₈. Calculated, %: C 53.49; H 3.69; N 18.35.

Bis[*N*-(4-dimethylaminophenyl)-5,7-dinitroquinolin-8-amido]cobalt(II) (IIIId). Yield 68%, black–green lustrous crystals, mp 238–240°C (decomp.). Found, %: C 53.30; H 3.48; N 18.07. C₃₄H₂₈CoN₁₀O₈. Calculated, %: C 53.48; H 3.69; N 18.35.

Bis[*N*-(4-dimethylaminophenyl)-5,7-dinitroquinolin-8-amido]copper(II)·4H₂O (IVd). Yield 73%, black lustrous crystals, mp 244–246°C. Found, %: C 48.35; H 3.41; N 15.99. C₃₄H₃₆CuN₁₀O₁₂. Calculated, %: C 48.60; H 4.12; N 16.37.

Bis[*N*-(4-dimethylaminophenyl)-5,7-dinitroquinolin-8-amido]zinc(II)·H₂O (Vd). Yield 52%, black crystals, mp 241–243°C. Found, %: C 51.32; H 3.88; N 17.61. C₃₄H₃₀N₁₀O₉Zn. Calculated, %: C 51.82; H 3.83; N 17.78.

Bis[*N*-(3,4-dimethylphenyl)-5,7-dinitroquinolin-8-amido]nickel(II)–*N*-(3,4-dimethylphenyl)-5,7-dinitroquinolin-8-amine(1:2) (VI). Yield 33%, black crystals, mp 260–262°C (decomp.). Found, %: C 58.11; H 3.99; N 15.88. C₆₈H₅₄N₁₆NiO₁₆. Calculated, %: C 57.93; H 4.07; N 15.90.

Bis[*N*-(3,4-dimethylphenyl)-5,7-dinitroquinolin-8-amido]copper(II)–acetone(1:2) (VII). Yield 84%, black–brown powder, mp 256–257°C (decomp.). Found, %: C 56.02; H 3.86; N 12.90. C₄₀H₃₈CuN₈O₁₀. Calculated, %: C 56.23; H 4.18; N 13.12.

Bis[*N*-(4-dimethylaminophenyl)-5,7-dinitroquinolin-8-amido]zinc(II)–*N*-(4-dimethylaminophenyl)-5,7-dinitroquinolin-8-amine(1:2) (VIII). Yield 77%, orange powder, mp 230–232°C (decomp.). UV spectrum, λ_{\max} , nm ($\epsilon \times 10^{-3}$): 291 inf, 320 (5.06), 392 (8.52), 433 (15.84). Found, %: C 58.55; H 3.72; N 15.07. C₆₈H₅₄N₁₆O₁₆Zn. Calculated, %: C 57.85; H 3.84; N 15.42.

REFERENCES

1. Radda, G. and Calvin, M., *Biochemistry*, 1964, vol. 3, p. 384.
2. Pullman, A. and Pullman, B., *Adv. Cancer Res.*, 1955, vol. 3, p. 117.
3. Freimanis, Ya.F., *Organicheskie soedineniya s vnutrimolekulyarnym perenosom zaryada* (Organic Compounds with Intramolecular Charge Transfer), Riga: Zinatne, 1985, p. 190.
4. Kondrat'ev, K.Ya. and Fedchenko, P.P., *Vestnik Ross. Akad. Nauk*, 2005, vol. 75, p. 522.
5. Il'ina, I.G., Mel'nikov, V.V., Tarasevich, B.N., and Butin, K.P., *Russ. J. Org. Chem.*, 2006, vol. 42, p. 996.

6. Hennig, H., Tauchnitz, J., and Schone, K., *Z. Chem.*, 1971, p. 267.
7. Grandberg, K.I., Kuz'mina, L.G., Aleksandrov, G.G., Il'ina, I.G., Mikhalev, O.V., Rakhimov, R.D., and Butin, K.P., *Khim. Geterotsikl. Soedin.*, 1999, no. 8, p. 1028.
8. Garnovskii, A.D., Vasil'chenko, I.S., and Garnovskii, D.A., *Sovremennye aspekty sinteza metallokompleksov. Osnovnye ligandy i metody* (Modern Aspects of the Synthesis of Metal Complexes. Ligands and Methods), Rostov-on-Don: LaPo, 2000, p. 24.
9. Milliari, E.E., Ruchkin, V.E., Orlova, T.I., and Efremov, V.V., *Dokl. Akad. Nauk SSSR*, 1972, vol. 205, p. 353.
10. Il'ina, I.G., Ivanova, E.V., Ashkinadze, L.D., Zabaznova, S.V., and Butin, K.P., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1996, p. 1188.
11. Vedenev, V.I. and Gurvich, L.V., *Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu* (Dissociation Energies of Chemical Bonds. Ionization Potentials and Electron Affinities), Moscow: Nauka, 1974, p. 229.
12. Traven', V.F., *Elektronnaya struktura i svoistva organicheskikh molekul* (Electronic Structure and Properties of Organic Molecules), Moscow: Khimiya, 1989, p. 384.
13. Braude, E.A. and Sondheimer, F., *J. Chem. Soc.*, 1955, p. 3754.
14. Sheldrick, G.M., *SHELXTL v. 5.10, Structure Determination Software Suite*, Madison, WI, USA: Bruker AXS.
15. Dikshoorn, R.P., *Recl. Trav. Chim. Pays-Bas*, 1929, vol. 48, p. 550.
16. Khilkova, N.L., Knyazev, V.N., Patalakha, N.S., and Drozd, V.N., *Zh. Org. Khim.*, 1992, vol. 28, p. 1048.