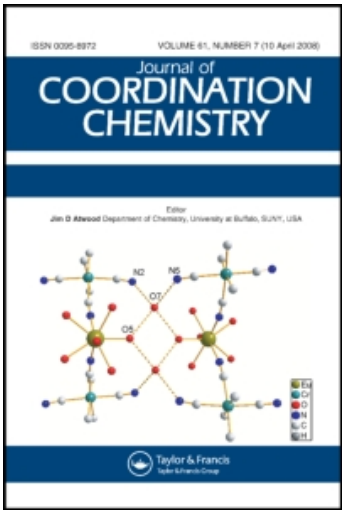

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Direct chemical and electrochemical syntheses of coordination compounds of benzazolyl azo ligands

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Direct chemical and electrochemical syntheses of coordination compounds of benzazolyl azo ligands**

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The chelates of 2-hydroxy(aminophenylnaphthyl)-azo-1-alkylbenzimidazoles were obtained from electrochemical (anodic dissolution of zero-valent d-metals) and chemical (from acetates of the same metals) syntheses in methanol. The EXAFS and X-ray single crystal diffraction data revealed the existence of octahedral nickel, zinc, and cadmium complexes containing four five-membered metallocycles with the N_4O_2 or N_6 ligand environments. The formation of five-membered coordination units, non-typical for azo ligands, is explained on the basis of inner-chelate competitive metal binding of ambidentate ligand systems.

Keywords: Benzazolyl azo ligands; Direct electrochemical synthesis; EXAFS; X-ray diffraction; Octahedral complexes

1. Introduction

Electrosynthesis, an important tool in coordination chemistry [1–15], is mostly carried out by anodic dissolution of zero-valent metals (direct synthesis [7, 8, 10]), although some metal salts could also be used [12, 13]. This method is part of the so-called "direct synthesis" [7], i.e. preparation of metal complexes *via* cryosynthesis, electrosynthesis, tribosynthesis, and metal dissolution in non-aqueous media. Progress in direct synthesis

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**Dedicated to Professor, Dr Sci. (Academician) Vladimir I. Minkin (Research Institute of Physical and Organic Chemistry, South Federal University, Rostov-on-Don, Russia) on occasion of his 75th birthday.

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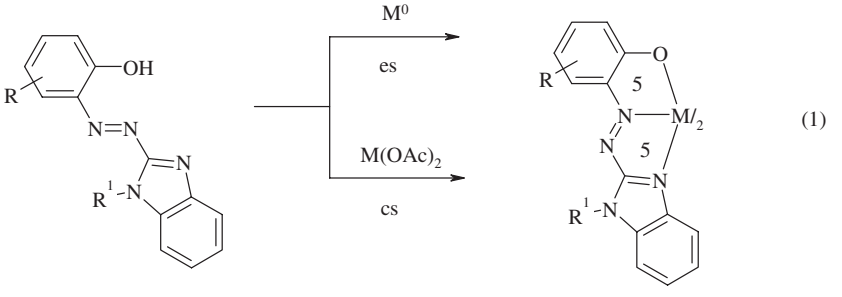
has been reached due to activation of metals (in particular, use of pyrophoric *Rieke* metals [9, 16, 17]), ultrasonic, or ultraviolet irradiation [9, 10].

The advantages of the direct electrochemical method in comparison with standard techniques (those using metal salts of carbonyls [8]) are as follows: the possibility to carry out the synthesis at a relatively low temperature (down to 0°C), variation of non-aqueous solvents, high yields, and isolation of coordination compounds mostly without salt anions [7–10].

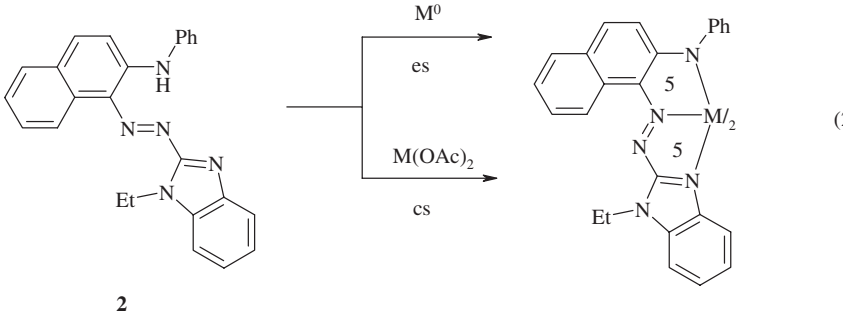
The present work is devoted to a comparison of direct electrochemical (**es**) and standard chemical (**cs**) synthesis (reactions (1) and (2)) of metal chelates **3** and **4** on the basis of 2-(2-aminophenylnaphthyl(hydroxy))azo-1-alkylbenzimidazoles **1** and **2** and elucidation of the product structures by the EXAFS and X-ray single crystal diffraction techniques.



(1)

1: R = 5-Me, R^1 = Me (a);
R = 5-OMe, R^1 = Me (b);
R = 4-OMe, R^1 = Me (c);
R = 5-Me, R^1 = Et (d)

3: M = Co, Ni, Zn, Cd



(2)

2

4: M = Co, Ni, Zn, Cd

2. Experimental

2.1. *Materials*

All solvents, metal acetates, platinum wire, and metal sheets were purchased from Aesar or Lancaster.

2.2. *Synthesis of heterocyclic azo compounds 1 and 2*

1-methyl- and 1-ethyl-2-aminobenzimidazole were prepared according to the literature procedure [18]. A solution of 2.14 g (0.031 mol) of sodium nitrite in 2 mL of water was

added dropwise to a solution of 0.03 mol of 1-methyl-2-aminobenzimidazole or 1-ethyl-2-aminobenzimidazole in 90% H_3PO_4. The latter was prepared by dissolution of 22.5 g of P_4O_{10} in 75 mL of phosphoric acid under intense stirring at 0–5°C. After adding all sodium nitrite, the mixture was kept cold for 30 min, and then the obtained diazonium salt solution was slowly added to a solution of 0.03 mol of *p*-cresol, 3- or 4-methoxyphenol or 2-phenylaminonaphthalene. In 30 min, ice was added and the resulting mixture was treated with saturated solution of Na_2CO_3 adjusted to pH 7–8. The solids formed were filtered off, washed with water, and dried in air at room temperature.

The obtained orange heterocyclic compounds were dissolved in toluene and purified in a chromatographic column (Al_2O_3, eluent toluene). The first portions were thrown away and the main substance was extracted with chloroform, which was then removed in a rotary evaporator. Solids of azo compounds were recrystallized from ethanol.

2.3. *Synthesis of 3 and 4*

The synthesis was carried out by two techniques:

2.3.1. Direct es of the complexes. A solution of 0.001 mol of the corresponding azo compound (**1a**–**d**, **2**) and 0.01 g $[Et_4N]ClO_4$ (electrolyte) in 20 mL of methanol was added in an electrochemical cell with a platinum cathode and the respective Co, Ni, Cu, Zn, or Cd anode. The electrosynthesis was carried out at constant current (40 mA) and initial voltage of 15 V for 1 h. The complexes were filtered, washed with methanol, and recrystallized from a mixture chloroform : methanol (1 : 2).

2.3.2. Chemical synthesis. A solution of 0.0005 mol of the corresponding metal acetate in 10 mL of methanol was added to a solution of 0.266 g (0.001 mol) of **1a**, 0.28 g (0.001 mol) of **1b**, **1c**, **1d** or 0.39 g (0.001 mol) of **2**, respectively, in 20 mL of the same solvent, and boiled for 1 h. After cooling, solids were filtered, washed with methanol, and recrystallized from a mixture chloroform : methanol (1 : 2).

The reactions (**1** and **2**) afforded complexes **3** and **4** with the ML_2 compositions (LH = **1a**–**d**, **2**) in yields 70%–93% (**es**) and 65%–85% (**cs**).

2.4. *Studies of composition and structure of ligands and complexes*

Yields, melting points, and elemental analyses of **1a**–**d**, **2**, **3**, and **4** are shown in table 1. IR, ^{1}H-NMR, and magnetic susceptibility data are summarized in Supplementary material.

2.4.1. IR spectra. The IR spectra of powder samples were recorded with a Varian Excalibur-3100 FT-IR spectrophotometer.

2.4.2. ^{1}H-NMR spectra. The ^{1}H-NMR spectra were measured with Varian Unity-300 equipment (300 MHz) with the signal of residual ^{1}H in $CDCl_3$ as the internal standard.

Table 1. Elemental analysis data for azo compounds **1**, **2** and their complexes **3**, **4**.

Compound	Yield (%)	m.p. (°C)	Brutto formula	Element content (found/calculated) (%)			
				C	H	N	M
1a	20	239–240	$C_{15}H_{14}N_4O$	67.74/67.75	5.28/5.30	21.15/21.04	
3a-Zn	cs 83	>250	$C_{30}H_{26}N_8O_2Zn$	cs 60.57/60.46	4.45/4.40	18.79/18.80	10.87/10.47
	es 89			es 60.58/60.46	4.48/4.40	18.85/18.80	10.60/10.47
1b	60	293–294	$C_{15}H_{14}N_4O_2$	63.94/63.82	5.12/5.00	19.87/19.85	
3b-Ni	cs 75	>250	$C_{30}H_{26}N_8O_4Ni$	cs 58.11/58.00	4.32/4.22	18.17/18.04	9.56/9.45
	es 85			es 58.17/58.00	4.25/4.22	18.14/18.04	9.38/9.45
3b-Cu	cs 65	>250	$C_{30}H_{26}N_8O_4Cu$	cs 57.47/57.55	4.21/4.19	17.86/17.90	10.38/10.15
	es 70			es 57.60/57.55	4.25/4.19	17.92/17.90	10.28/10.15
3b-Zn	cs 81	>250	$C_{30}H_{26}N_8O_4Zn$	cs 57.48/57.38	4.07/4.17	17.78/17.85	10.62/10.41
	es 90			es 57.42/57.38	4.19/4.17	17.89/17.85	10.52/10.41
3b-Cd	cs 80	>250	$C_{30}H_{26}N_8O_4Cd$	cs 53.47/53.38	3.90/3.88	6.65/6.60	16.51/16.45
	es 85			es 53.45/53.38	3.92/3.88	6.70/6.60	16.54/16.45
1c	30	228–229	$C_{15}H_{14}N_4O_2$	63.98/63.82	5.09/5.00	19.77/19.85	
3c-Ni	cs 76	199–200	$C_{30}H_{26}N_8O_4Ni$	cs 58.11/58.00	4.32/4.22	18.15/18.04	9.52/9.45
	es 85			es 58.15/58.00	4.28/4.22	18.10/18.04	9.58/9.45
1d	88	105–106	$C_{16}H_{16}N_4O$	68.64/68.55	5.79/5.75	20.05/19.99	
3d-Ni	cs 75	>250	$C_{32}H_{30}N_8O_2Ni$	cs 62.37/62.26	4.88/4.90	18.26/18.15	9.64/9.51
	es 85			es 62.28/62.26	4.95/4.90	18.17/18.15	9.68/9.51
3d-Cu	cs 70	>250	$C_{32}H_{30}N_8O_2Cu$	cs 61.87/61.77	4.79/4.86	18.15/18.01	10.32/10.21
	es 87			es 61.79/61.77	4.91/4.86	18.20/18.01	10.11/10.21
3d-Zn	cs 85	>250	$C_{32}H_{30}N_8O_2Zn$	cs 61.62/61.59	4.75/4.85	17.78/17.96	10.64/10.48
	es 90			es 61.65/61.59	4.90/4.85	17.87/17.96	10.54/10.48
3d-Cd	cs 65	>250	$C_{32}H_{30}N_8O_2Cd$	cs 57.38/57.28	4.62/4.51	16.84/16.70	16.68/16.75
	es 85			es 57.18/57.28	4.68/4.51	16.65/16.70	16.82/16.75
2	68	218–219	$C_{25}H_{21}N_5$	76.71/76.70	5.51/5.41	17.72/17.89	
4-Co	cs 65	222–223	$C_{50}H_{40}N_{10}Co$	cs 71.62/71.51	4.91/4.804.77/4.80	16.57/16.67	7.17/7.02
	es 70			es 71.54/71.51		16.45/16.67	7.19/7.02
4-Ni	cs 70	236–237	$C_{50}H_{40}N_{10}Ni$	cs 71.64/71.53	4.75/4.80	16.58/16.68	7.15/6.99
	es 80			es 71.60/71.53	4.64/4.80	16.70/16.68	7.00/6.99
4-Cu	cs 75	>250	$C_{50}H_{40}N_{10}Cu$	cs 71.21/71.11	4.68/4.77	16.61/16.59	7.74/7.53
	es 85			es 71.22/71.11	4.71/4.77	16.62/16.59	6.75/7.53
4-Zn	cs 80	>250	$C_{50}H_{40}N_{10}Zn$	cs 70.92/70.96	4.68/4.76	16.47/16.55	7.78/7.72
	es 93			es 70.95/70.96	4.82/4.76	16.50/16.55	7.79/7.72

2.4.3. Magnetic susceptibility. The magnetic susceptibility of a solid phase was determined by the Faraday method at room temperature [19].

2.4.4. EXAFS measurements. The Ni*K*-, Zn*K*-, Cd*K*- and Cu*K*-edge EXAFS spectra for the complexes were obtained at the Station K1.3b "Structural Materials Science" of the Kurchatov Center for Synchrotron Radiation and Nanotechnology (KCSRNT, Moscow, Russia) [20]. The storage ring with electron beam energy of 2.5 GeV and a current of 70–90 mA was used as the source of radiation. All the spectra were recorded in the transmission mode using a channel-cut Si(1 1 1) (Ni*K*-, Zn*K*-, and Cu*K*-edges) or Si(2 2 0) (Cd*K*-edge) monochromators and two N_2- or Ar-filled ionization chambers as detectors. The EXAFS data were analyzed using the IFEFFIT data analysis package [21]. The EXAFS data reduction followed standard procedures for pre-edge subtraction and spline background removal.

The radial pair distribution functions around Ni, Zn, Cd, and Cu were obtained by Fourier transformation of the k^3-weighted EXAFS functions over the range of

photoelectron wavenumbers 2.2–12.0 $Å^{-1}$. The structural parameters, including interatomic distances (R), coordination numbers (CNs) and the distance mean-square deviation Debye–Waller factors (σ^2), were found by non-linear fit of theoretical spectra to experimental. Experimental data were simulated using the theoretical EXAFS amplitude and phase functions, which were calculated using the FEFF7 program [22]. The amplitude reduction factor, S_0^2, and threshold energy, E_0, were calibrated by fitting the EXAFS data for crystallographically characterized models. The amplitude reduction factor, S_0^2, was found equal to 0.9 in all cases.

The quality of fits was estimated from discrepancy factors between the experimental and simulated functions (Q-factor).

2.4.5. X-ray crystallography. Dark blue crystals of bis-[2-(hydroxy-5-methylphenylazo)-1-ethylbenzimidazolato]zinc(II) $C_{32}H_{30}N_8O_2Zn$ (**3d-Zn**) are triclinic: $a = 10.471(2)$ Å, $b = 11.026(2)$ Å, $c = 13.956(4)$ Å, $\alpha = 69.22(3)^\circ$, $\beta = 80.64(2)^\circ$, $\gamma = 80.48(2)^\circ$, $V = 1476.1(2)$ $Å^3$, $M = 624.01$, $F(0\,0\,0) = 648$, $\rho_{calcd} = 1.404$ g cm^{-1}, $\mu = 0.876$ g cm^{-1}, $Z = 2$, space group P-1.

Dark blue crystals of bis-[2-(phenylaminonaphthylazo)-1-ethylbenzimidazolato]-nickel(II) $C_{50}H_{40}N_{10}Ni$ (**4-Ni**) are triclinic: $a = 11.305(2)$ Å, $b = 12.337(2)$ Å, $c = 17.293(3)$ Å, $\alpha = 96.08(1)^\circ$, $\beta = 105.82(2)^\circ$, $\gamma = 110.70(1)^\circ$, $V = 2115.1(3)$ $Å^3$, $M = 419.82$, $F(0\,0\,0) = 876$, $\rho_{calcd} = 1.318$ g cm^{-1}, $\mu = 0.507$ g cm^{-1}, $Z = 2$, space group P-1.

Experimental data for **3d-Zn** and **4-Ni** were obtained with an Enraf-Nonius CAD-4 difractometer (λ Mo-Kα, graphite monochromator, $\theta/2\theta$-scanning, $\theta_{max} = 25^\circ$). For **3d-Zn**, intensities of 5126 reflections were measured; 7274 reflections were obtained for **4-Ni**.

The structures of both compounds were determined by direct methods (SHELXS-86) [23], refined by full-matrix least-squares on F^2 (SHELXL-97) [24] in the anisotropic approximation for all non-hydrogen atoms. Hydrogens were placed in the calculated positions and refined according to the riding model with fixed Debye factors of $U_H = 0.08$ $Å^2$.

The final fitting parameters for **3d-Zn** are: $R_1 = 0.0478$, $wR_2 = 0.1373$ on 2858 reflections with $F_o \geq 2\sigma(F_o)$, $R_1 = 0.1252$, $wR_2 = 0.1821$ on all reflections, 388 variable parameters, index range: $-11 \leq h \leq 11$, $0 \leq k \leq 12$, $-15 \leq l \leq 16$, goodness-of-fit = 0.983, residual electronic density $\Delta\rho_{min} = -0.453$, $\Delta\rho_{max} = 0.525$ e $Å^{-3}$.

The fitting parameters for **4-Ni** are: $R_1 = 0.0386$, $wR_2 = 0.1162$ on 3976 reflections with $F_o \geq 2\sigma(F_o)$, $R_1 = 0.1200$, $wR_2 = 0.1776$ on all reflections, 549 variable parameters, index range: $-12 \leq h \leq 12$, $0 \leq k \leq 13$, $-19 \leq l \leq 19$, goodness-of-fit = 0.843, residual electronic density $\Delta\rho_{min} = -0.266$, $\Delta\rho_{max} = 0.254$ e $Å^{-3}$.

3. Results and discussion

3.1. *Ligands structure*

According to the IR and ^{1}H-NMR data (Supplementary material), **1** and **2** exist mostly in the hydroxy (amino) azo form. The IR spectra of **1a–d** have a broad stretching vibration at 2800–3400 cm^{-1} typical of an OH involved in an intramolecular hydrogen

bond (IMHB). The IMHB considerably decreases the absorption intensity for HNPh, which becomes non-characteristic for **2**. In the IR spectrum of the benzazolylazo **2**, vibrations of the secondary amino group occur from 2800 to 3400 cm^{-1} as a broad low-intensity band, observed for the majority of *o*-aminoarylazo compounds [25].

For the **3** and **4** IR bands from 1600 to 1618 cm^{-1} attributable to the benzimidazole fragment does not change compared to **1** and **2**. Frequencies of vibrations for the azo of heterocyclic azo compounds at 1330–1350 cm^{-1} slightly increase upon complexation. At 1227–1280 cm^{-1}, $\nu_{(Ph-O)}$ absorption bands occur for **1a**–**1d**, which shift upon complexation to shorter wavenumbers by 10–29 cm^{-1} due to the metal chelate formation [26].

Distinct signals related to OH-protons (3.53–4.9 ppm) **1** and HNPh (13.16 ppm) **2** are observed in ^{1}H-NMR spectra (Supplementary material).

3.2. *Structure of the coordination compounds*

IR and ^{1}H-NMR spectra of **3** and **4** (Supplementary material) do not reveal absorptions of proton-donor fragments. Proton signals of the methyl (methoxyl) groups from aromatic fragments and ethyl substituents of benzimidazole of azo compounds in ^{1}H-NMR spectra of zinc and cadmium complexes slightly shift to stronger field by 0.10–0.18 ppm on average. Aromatic proton signals upon complexation also shift to stronger field by 0.27–0.82 ppm on average.

Magnetic properties of copper, nickel, and cobalt complexes were studied at room temperature (Supplementary material). The values of $\mu_{eff} = 3.12$–3.35 BM for nickel and 4.32 BM for cobalt complexes are characteristic for chelates with tetrahedral or octahedral structure. Probably, copper complexes ($\mu_{eff} = 1.72$–2.09 BM) also possess an analogous structure.

Fourier transforms (MFT) of the Ni*K*-, Zn*K*-, and Cu*K*-edge EXAFS data for **3** and **4** are shown in figures 1–3. The best-fit local structural parameters of the respective metal ions in **3** and **4** are compiled in tables 2–4.

There is an intense metal-nearest neighbor feature at $R = 1.5$ Å, together with two resolvable features at longer distances. For MFT of all **3** and **4**, the first peak at 1.5 Å is associated with the M···O/N (M···N for **4**) first-shell contribution, while the second and following peaks within a range 2.45–3.5 Å are essentially due to the M···C/N, M–C second- and third-shell contributions as well as M–C···N, M–N···N multiple scattering signals. Multiple scattering refers to the event when the X-ray excited photoelectron is scattered by two (or more) atoms of the heterocyclic ligands prior to returning to the central atom. All the EXAFS spectra of the Ni, Zn, and Cu complexes were fitted with the inclusion of a second low-*Z* shell at a longer distance.

Similarity of the coordination geometry around nickel in **3b**, **3c**, **3d**, and **4** and around zinc in **3a**, **3b**, and **4** has been verified by the quantitative EXAFS spectra analysis. All four Ni spectra can be fitted with a single low-*Z* (oxygen/nitrogen) nearest neighbor shell at an average distance of 2.05 ± 0.01 Å with a CN of six. The resultant single-shell fits are characterized by relatively large Debye–Waller factors, indicating disorder in the metal–ligand bond lengths. For **3a**, **3b**, and **4**, the nearest neighbor shell consists of 6 N/O atoms at average distances Zn···O of $R = 2.07$–2.10 Å and Zn···N of $R = 2.11$ Å (**3a**, **3b**, and **4**), assuming octahedral coordination. The best fits for the cadmium complexes **3b** and **3d** were also obtained within the model with

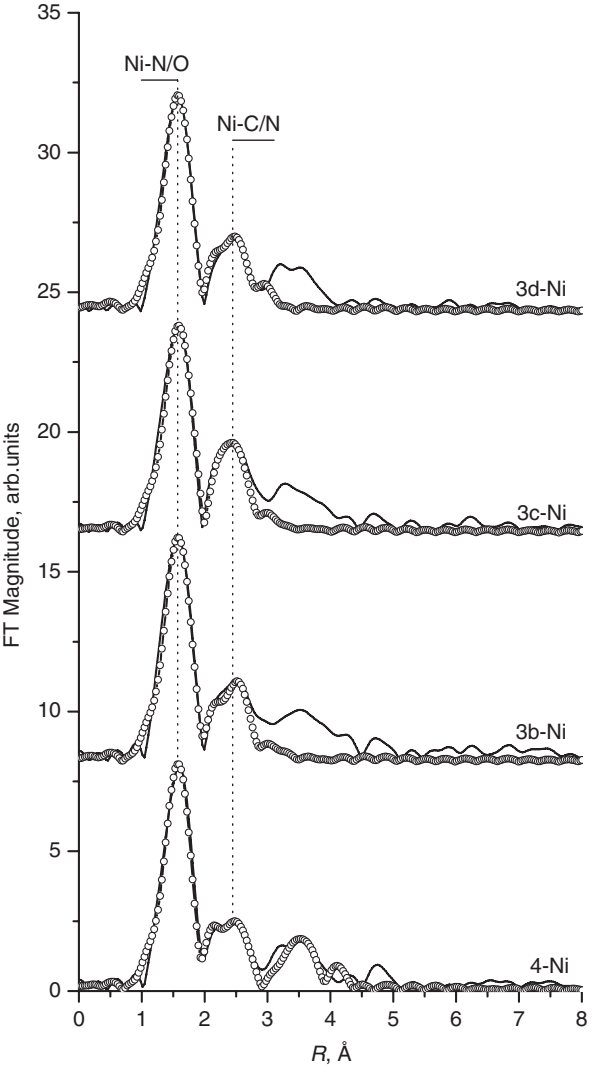


Figure 1. MFT of the Ni*K*-edge EXAFS spectra for the Ni complexes studied: experiment (solid lines) and best-fits (open circles).

octahedral environment. The Cd · · · O and Cd · · · N distances obtained are considerably longer than those in other studied complexes, according to the larger ionic radii of the cadmium ion. However, for two copper complexes **3a** and **4**, best-fit simulations afford the CN of the nearest neighbor shell less than 6, which demonstrates the possible tetrahedral coordination.

In both cases of crystallographically characterized complexes **3d-Zn** and **4-Ni** (see below), the agreement between the best-fit simulations and the crystallographic data is very good, pointing to the correctness and reliability of the EXAFS data analysis.

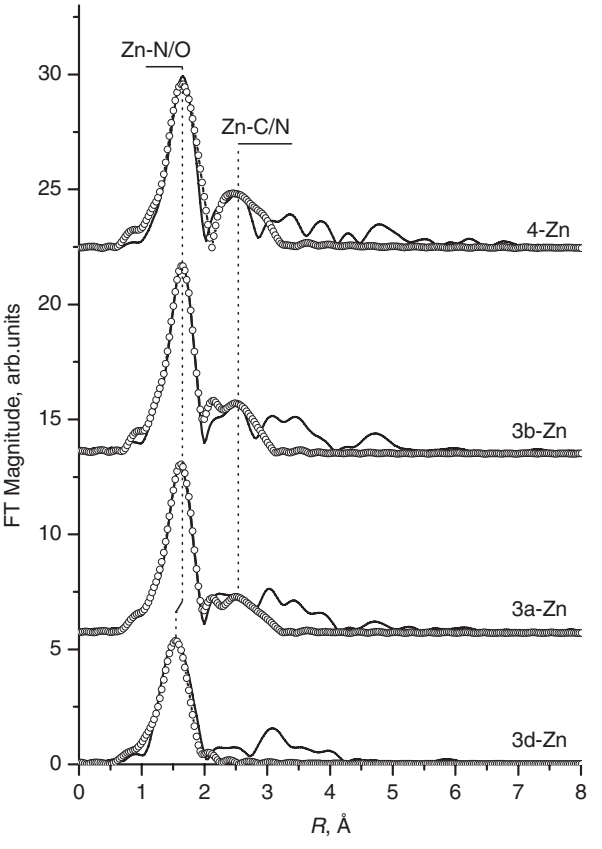


Figure 2. MFT of the Zn*K*-edge EXAFS spectra for the Zn complexes studied: experiment (solid lines) and best-fits (open circles).

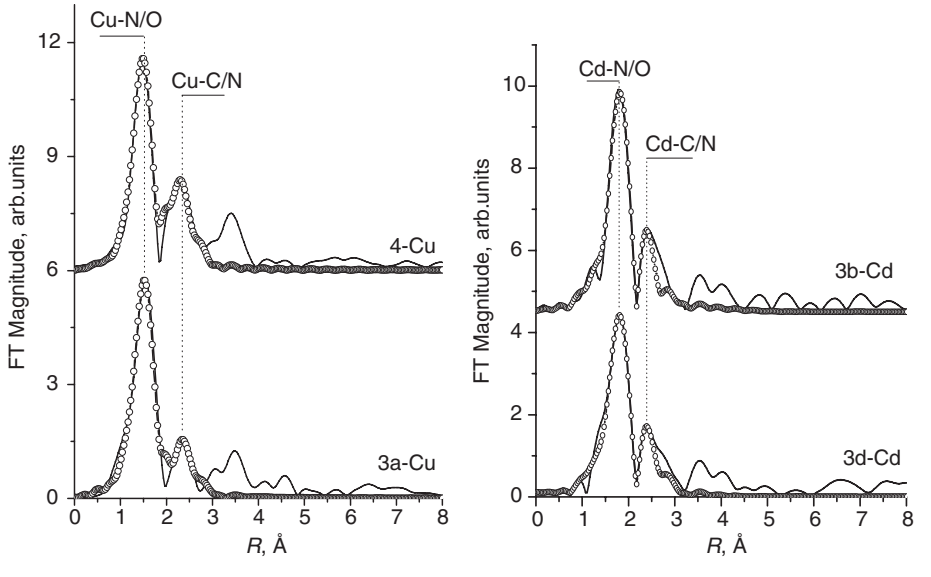


Figure 3. MFT of the Cu*K*-edge (left panel) and Cd*K*-edge (right panel) EXAFS spectra for the Cu and Cd complexes studied: experiment (solid lines) and best-fits (open circles).

Table 2. Structural parameters of the nearest environment of the nickel ions in the complexes from the EXAFS data analysis.

Compound	Atom	CN	R (Å)	σ^2 (Å^2)	Q (%)
4-Ni	N	6	2.05	0.0040	
	C/N	6	2.92	0.0065	3.5
	C/N	2	3.32	0.0065	
	C	14	4.22	0.0065	
3b-Ni	N/O	6	2.04	0.0040	4.6
	C/N	6	2.93	0.0066	
	C/N	2	3.30	0.0065	
3c-Ni	N/O	6	2.05	0.0047	
	C/N	6	2.88	0.0050	4.8
	C/N	2	3.28	0.0050	
3d-Ni	N/O	6	2.04	0.0045	
	C/N	6	2.92	0.0063	4.9
	C/N	2	3.24	0.0060	

R: the average distances; CN: coordination number; σ^2: Debye–Waller factors.

Table 3. Structural parameters of the nearest environment of the zinc ions in the complexes from the EXAFS data analysis.

Compound	Atom	CN	R (Å)	σ^2 (Å^2)	Q (%)
3a-Zn	O	2	2.07	0.0045	
	N	4	2.11	0.0060	4.7
	C/N	8	3.21	0.0046	
3b-Zn	O	2	2.10	0.0030	
	N	4	2.11	0.0045	5.7
	C/N	12	3.15	0.0050	
3d-Zn	O	2	1.98	0.0045	3.9
	N	2	2.05	0.0050	
4-Zn	N	6	2.11	0.0030	6.1
	C/N	12	3.15	0.0050	

R: the average distances; CN: coordination number; σ^2: Debye–Waller factors.

Table 4. Structural parameters of the nearest environment of the copper and cadmium ions in the complexes from the EXAFS data analysis.

Compound	Atom	CN	R (Å)	σ^2 (Å^2)	Q (%)
4-Cu	N	2	1.95	0.0037	
	N	2	2.05	0.0035	5.5
	C/N	4	2.90	0.0050	
3a-Cu	O	2	1.93	0.0030	6.0
	N	2	2.04	0.0035	
	C/N	6	2.85	0.0050	
3b-Cd	O	2	2.31	0.0030	
	N	4	2.38	0.0030	3.5
	C/N	4	3.05	0.0040	
3d-Cd	O	2	2.29	0.0030	3.3
	N	4	2.39	0.0030	
	C/N	6	3.08	0.0040	

R: the average distances; CN: coordination number; σ^2: Debye–Waller factors.

Table 5. Selected bond lengths (Å) and angles (°) for **3d-Zn** from crystallographic data.

Zn(1)–O(1)	2.107(4)	Zn(1)–O(2)	2.094(4)
Zn(1)–N(1)	2.138(4)	Zn(1)–N(4)	2.162(4)
Zn(1)–N(5)	2.124(4)	Zn(1)–N(8)	2.188(4)
O(1)Zn(1)O(2)	95.1(2)	O(1)Zn(1)N(1)	76.3(2)
O(1)Zn(1)N(4)	149.6(2)	O(1)Zn(1)N(5)	110.9(2)
O(1)Zn(1)N(8)	93.2(2)	O(2)Zn(1)N(1)	114.3(2)
O(2)Zn(1)N(4)	95.0(2)	O(2)Zn(1)N(5)	76.7(2)
O(2)Zn(1)N(8)	150.0(2)	N(1)Zn(1)N(4)	73.4(2)
N(1)Zn(1)N(5)	166.8(2)	N(1)Zn(1)N(8)	95.7(2)
N(4)Zn(1)N(5)	99.2(2)	N(4)Zn(1)N(8)	92.1(2)
N(5)Zn(1)N(8)	73.4(2)	Zn(1)O(1)C(1)	113.2(4)

Table 6. Selected bond lengths (Å) and angles (°) for **4-Ni** from crystallographic data.

Ni(1)–N(1)	2.073(4)	Ni(1)–N(2)	2.046(3)
Ni(1)–N(3)	2.073(4)	Ni(1)–N(6)	2.093(4)
Ni(1)–N(7)	2.040(4)	Ni(1)–N(8)	2.075(4)
N(1)Ni(1)N(2)	77.6(2)	N(1)Ni(1)N(3)	153.7(2)
N(1)Ni(1)N(6)	98.5(1)	N(1)Ni(1)N(7)	96.0(2)
N(1)Ni(1)N(8)	89.9(2)	N(2)Ni(1)N(3)	76.9(1)
N(2)Ni(1)N(6)	97.8(1)	N(2)Ni(1)N(7)	171.3(2)
N(2)Ni(1)N(8)	108.7(2)	N(3)Ni(1)N(6)	91.0(1)
N(3)Ni(1)N(7)	110.1(2)	N(3)Ni(1)N(8)	92.6(2)
N(6)Ni(1)N(7)	77.3(2)	N(6)Ni(1)N(8)	153.4(2)
N(7)Ni(1)N(8)	76.7(2)	Ni(1)N(1)C(1)	114.3(3)

The most precise information on the structure was obtained on the basis of X-ray single crystal diffraction data for **3d-Zn** and **4-Ni** as examples. The crystal structures are built of octahedral complex molecules ML_2 with coordination units ZnN_4O_2 and NiN_6 (figure 4a and b). Bond lengths and angles in the corresponding coordination polyhedra are summarized in tables 5 and 6.

The chelate molecules contain two ligands with similar structures whose planes are perpendicular to each other. Each ligand is coordinated in a tridentate-chelate manner forming an essentially planar system of five- (**3d**) and six-conjugated (**4**) rings, forming the *trans*-meridional octahedral environment for the central metal atom. The ethyl groups (present in both of the above ligands) and phenyl substituents in **4-Ni** are also nearly perpendicular to the corresponding main planes (the dihedral angle at the phenyl ring C(45)–C(50) 76.8° is slightly smaller).

Distances to the metal (Zn or Ni) demonstrate that both complexes possess approximate C_2 symmetry, which is preserved up to most remote C atoms (tables 5 and 6). The experimental dispersion in formally equivalent distances (Δ) is comparable to the nominal accuracy in the determination of atomic coordinates. Specific mutual dispositions of the complex molecules in the crystal structures are worth noting. In particular, in **3d-Zn** centrosymmetric dimers exist with a distance between the Zn atoms and contacting planes of 6.47 and 3.21 Å, respectively (figure 5). Dimers, in their turn, are joined by π–π stacking interactions into supramolecular assemblies along the *c*-axis of the crystal (figure 6). The distance between contacting planes is 3.43 Å (the distance

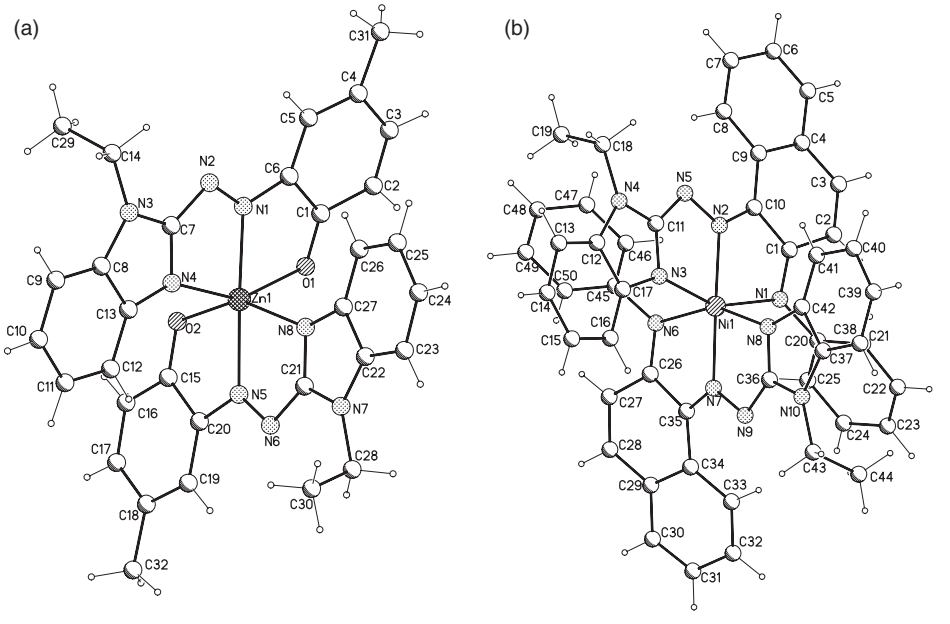


Figure 4. (a) Complex **3d-Zn**. (b) Complex **4-Ni**. Pseudo-axes C_2 are perpendicular to the plane of the figure.

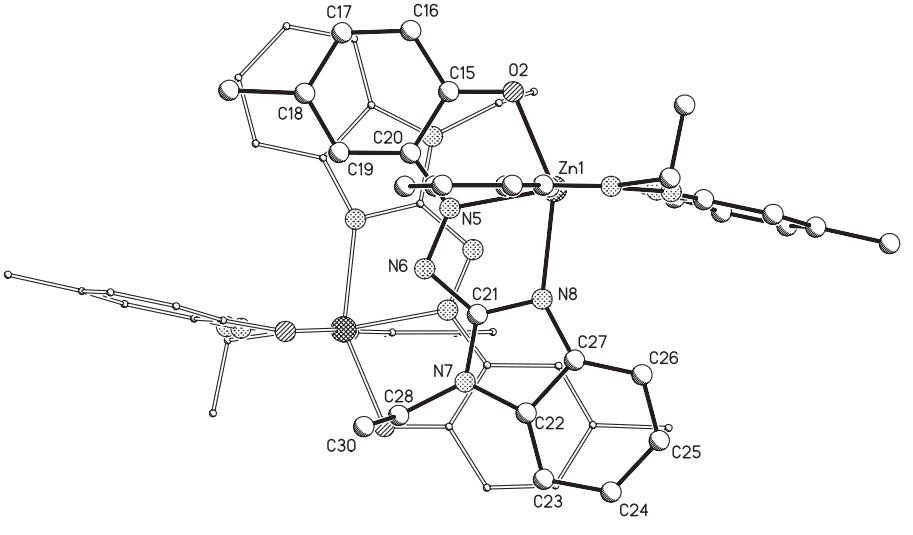


Figure 5. Molecular dimer in **3d-Zn**.

between the Zn atoms in the supramolecular chain is 8.82 Å). In **4-Ni**, specific non-bonding intermolecular interactions are less pronounced. Nevertheless, pairs of molecules related to each other by an inversion center forming a T-type intermolecular contact can be recognized [27] (figure 7). The shortest distance between Ni atoms is 8.58 Å.

Five-membered metallocycles are formed in **3** and **4**; these structures are non-typical for amino and hydroxyphenylazo compounds [28–30]. Low stability of four-membered

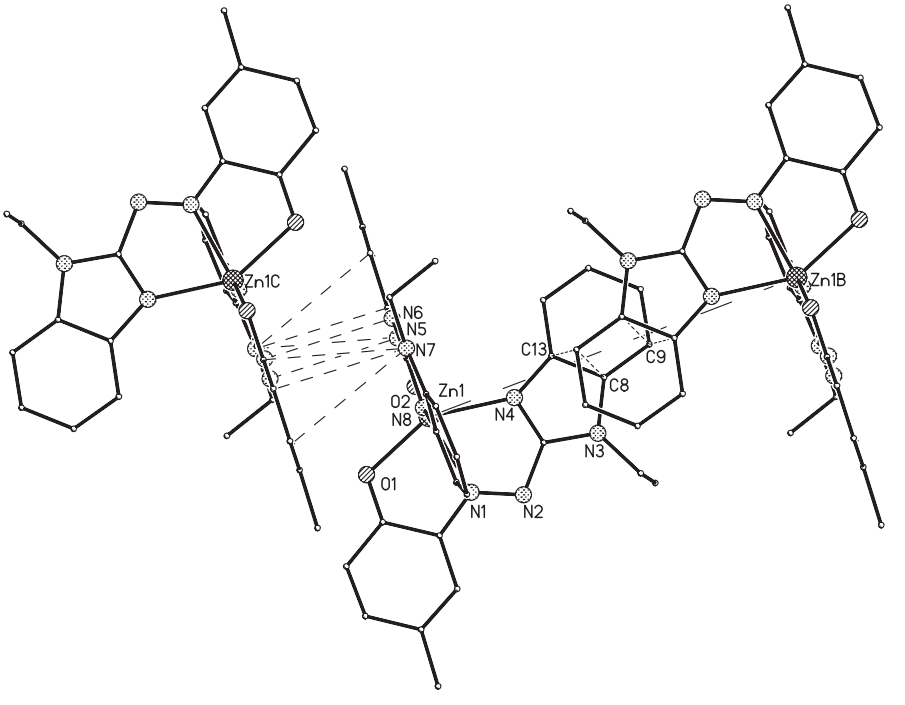


Figure 6. Supramolecular assembly in **3d-Zn**. Planes of contacting phenyl rings are parallel to the plane of figure.

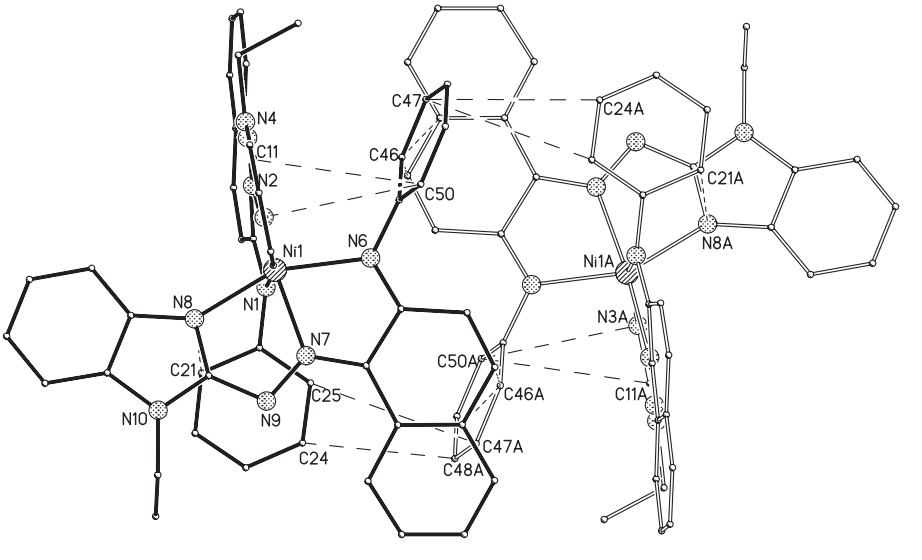


Figure 7. Molecular dimer (T-type) in **4-Ni**. The shortest distances between ligands are marked by dotted lines.

chelate fragments in comparison with five-membered fragments probably prevents other possible combinations of polyhedra, for example two four- and two six-membered units in **3** and **4**.

The existence of the above structures with four five-membered metallocycles is caused by high donor activity of the nitrogen of the benzimidazole fragment, which favors formation of five-membered metallocycles. Similar results were reported earlier for coordination units with the N_2S_2 ligand environment [8, 31].

4. Conclusions

The results obtained in the present work demonstrate the potential of the electrochemical technique in the synthesis of chelates of amino and hydroxyazo compounds [8, 28–30, 32, 33], of interest to address the problem of the inner-chelate isomery of metal complexes [8, 34] on the basis of amino, hydroxy, and mercapthoazo compounds. This problem is characteristic for the chelates, including azo fragments which allow creation of metallocycles of distinct linkage (five; six; five and six). This considerably expands the available toolset within the molecular design of tautomeric ambidentate systems [35, 36], including azomethine [37–40], β-diketone [41] ligands and their azo analogues [28, 41–43]. Competitive coordination of azo fragments is observed not only upon the formation of metallocycles in chelates but also upon the formation of molecular complexes with the protonated hydroxyazo on the basis of 1-(pyridilazo)-2-naphthol [33].

Supplementary material

The crystallographic information on the reported complexes (in the form of CIF files) is deposited with Cambridge Crystallographic Data Centre: CCDC No. 720925 for **4-Ni** and No. 720926 for **3d-Zn**.

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