1572 Russian Chemical Bulletin, International Edition, Vol. 59, No. 8, pp. 1572—1581, August, 2010

Azamacrocyclic nickel(II) and copper(II) complexes bearing aryl substituents: synthesis, properties, and crystal structures

L. V. Tsymbal,[a] I. L. Andriichuk,[a] Ya. D. Lampeka,[a]* and H. Pritzkow[b]

[a]L. V. Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of the Ukraine,
31 prosp. Nauki, 03028 Kiev, Ukraine.
Fax: +38 (044) 525 2570. E-mail: lampeka@adamant.net
[b]Universität Heidelberg, Anorganisch-Chemisches Institut,
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany.
Fax: +49 (6221) 54 6617

A synthetic procedure for preparation of new amphiphilic copper(II) and nickel(II) azamacrocyclic complexes bearing aromatic substituents is developed. The nature of substituents is shown to exert a negligible influence on spectral and electrochemical characteristics of the prepared compounds. The X-ray diffraction analysis of three copper complexes revealed the formation of the dimers of macrocyclic cations associated by noncovalent interactions, nature of which is determined by the structure of the substituent in the macrocyclic ligand.

Key words: nickel(II), copper(II), azamacrocyclic complexes, absorption spectra, redox properties, X-ray diffraction analysis.

Noncovalent interactions (NI) including van der Waals interactions, π—π-stacking, CH—π, hydrophobic, ion-dipole, dipole-dipole, and some other types of weak interactions[1—3] play very essential role in chemistry and biochemistry. These attractive forces are invoked to explain different aspects of physicochemical behavior of various systems, particularly, functioning of proteins,[4] interactions of metals with amino acids[5] and DNA,[6] mechanisms of molecular recognition,[7,8] to develop chemical sensors,[9] and find many other applications.[10,11]

Crystal engineering is yet another rapidly growing field where NI play an essential role.[12,13] In many cases, the ability of compounds to aggregate with involvement of just these forces leads to materials with anisotropic crystal structures (for example, with porous or layered structure) and possessed valuable applied properties.[14] However, the purposeful construction of such materials is impossible without disclosing the forces that govern crystal formation. Hence, it is necessary to accumulate empirical data of the influence of structural modifications of molecules on features of their packing in crystals.

Azamacrocyclic complexes of transition metals, particularly, nickel(II) and copper(II), are currently widely used as building blocks for construction of new materials.[15,16] One of the obvious advantages of such compounds along with their high thermodynamic stability and kinetic inertness[17] is the possibility of synthetically convenient chemical modification of macrocyclic framework using the template synthetic methods.[18]

The present work deals with the synthesis and study of spectral and electrochemical characteristics of novel copper(II) and nickel(II) complexes with related penta-azamacrocyclic ligands L^1—L^5 bearing aryl substituents and analysis of crystal structures of some copper(II) complexes with these ligands aiming at finding the features of noncovalent interactions in their crystals.

Experimental

The starting hexahydrates of nickel(II) and copper(II) perchlorates $M(ClO_4)_2 \cdot 6H_2O$ (a. p.), *N,N′*-bis(2-aminoethyl)-propane-1,3-diamine (2,3,2-tet) (Acros), benzylamine, 4-methylbenzylamine, 2-(4-methylphenyl)ethylamine, tyramine hydrochloride (all Aldrich), and 4-methoxybenzylamine (Fluka) were used without additional purification. The complexes $[I(2,3,2\text{-tet})](ClO_4)_2$ (I = Cu^{II} or Ni^{II}) were prepared according to the published methods.[19,20]

Synthesis of macrocyclic complexes $[ML](ClO_4)_2$ (general procedure). A mixture of $[M(2,3,2\text{-tet})](ClO_4)_2$ (M = Cu^{II}, Ni^{II}) (2.4 mmol), amine (2.4 mmol), 30% aqueous formaldehyde (1.0 mL, 13.3 mmol), and triethylamine (0.2 mL) in methanol (30 mL) was refluxed for 24 h. After cooling and filtration, the solution was kept in a refrigerator. The red-purple (copper complexes) or yellow (nickel complexes) precipitates were filtered off, recrystallized from 1 : 1 acetonitrile—water ($[ML^1](ClO_4)_2$) and 1 : 1 acetonitrile—ethanol ($[ML^2](ClO_4)_2$) mixtures, acetone ($[ML^3](ClO_4)_2$), or acetonitrile ($[ML^4](ClO_4)_2$), and dried in a vacuum desiccator. The complex $[CuL^5](ClO_4)_2$ was isolated form the reaction mixture by chromatography on a column loaded with a cation exchanger SP-Sephadex C-25

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1535—1543, August, 2010.

1066-5285/10/5908-1572 © 2010 Springer Science+Business Media, Inc.

(Na^+-form) (eluent, 0.2 *M* $NaClO_4$). The analytical data and yields of the prepared compounds are given below.

(3-Benzyl-1,3,5,8,12-pentaazacyclotetradecane)copper(II) diperchlorate, $[CuL^1](ClO_4)_2$. Yield 0.57 g (46%). Found (%): C, 34.6; H, 12.4; N, 5.1. $C_{16}H_{29}Cl_2CuN_5O_8$. Calculated (%): C, 34.70; H, 12.64; N, 5.28.

[3-(4-Methylbenzyl)-1,3,5,8,12-pentaazacyclotetradecane]-copper(II) diperchlorate, $[CuL^2](ClO_4)_2$. Yield 0.37 g (30%). Found (%): N, 36.0; H, 12.3; N, 5.5. $C_{17}H_{31}Cl_2CuN_5O_8$. Calculated (%): C, 35.95; H, 12.33; N, 5.50.

[3-(4-Methoxybenzyl)-1,3,5,8,12-pentaazacyclotetradecane]-copper(II) diperchlorate, $[CuL^3](ClO_4)_2$. Yield 0.30 g (26%). Found (%): N, 34.8; H, 12.0; N, 5.4. $C_{17}H_{31}Cl_2CuN_5O_9$. Calculated (%): C, 34.97; H, 11.99; N, 5.35.

{3-[2-(4-Methylphenyl)ethyl]-1,3,5,8,12-pentaazacyclotetradecane}copper(II) diperchlorate, $[CuL^4](ClO_4)_2$. Yield 0.27 g (17%). Found (%): N, 37.0; H, 12.1; N, 5.6. $C_{18}H_{33}Cl_2CuN_5O_8$. Calculated (%): C, 37.15; H, 12.03; N, 5.72.

{3-[2-(4-Hydroxyphenyl)ethyl]-1,3,5,8,12-pentaazacyclotetradecane}copper(II) diperchlorate, $[CuL^5](ClO_4)_2$. Yield 0.21 g (15%). Found (%): N, 33.8; H, 12.3; N, 5.3. $C_{16}H_{30}Cl_2CuN_5O_9$. Calculated (%): C, 33.66; H, 12.27; N, 5.30.

[3-Benzyl-1,3,5,8,12-pentaazacyclotetradecane]nickel(II) diperchlorate, $[NiL^1](ClO_4)_2$. Yield 0.32 g (42%). Found (%): N, 35.1; H, 12.8; N, 5.4. $C_{16}H_{29}Cl_2N_5NiO_8$. Calculated (%): C, 35.00; H, 12.76; N, 5.32.

[3-(4-Methylbenzyl)-1,3,5,8,12-pentaazacyclotetradecane]-nickel(II) diperchlorate, $[NiL^2](ClO_4)_2$. Yield 0.59 g (44%). Found (%): N, 36.2; H, 12.4; N, 5.6. $C_{17}H_{31}Cl_2N_5NiO_8$. Calculated (%): C, 36.26; H, 12.44; N, 5.55.

[3-(4-Methoxybenzyl)-1,3,5,8,12-pentaazacyclotetradecane]-nickel(II) diperchlorate, $[NiL^3](ClO_4)_2$. Yield 0.62 g (45%). Found (%): N, 35.2; H, 12.0; N, 5.5. $C_{17}H_{31}Cl_2N_5NiO_9$. Calculated (%): C, 35.26; H, 12.09; N, 5.40.

{3-[2-(4-Methylphenyl)ethyl]-1,3,5,8,12-pentaazacyclotetradecane}nickel(II) diperchlorate, $[NiL^4](ClO_4)_2$. Yield 0.21 g (15%). Found (%): N, 37.2; H, 12.1; N, 5.6. $C_{18}H_{33}Cl_2N_5NiO_8$. Calculated (%): C, 37.46; H, 12.14; N, 5.76.

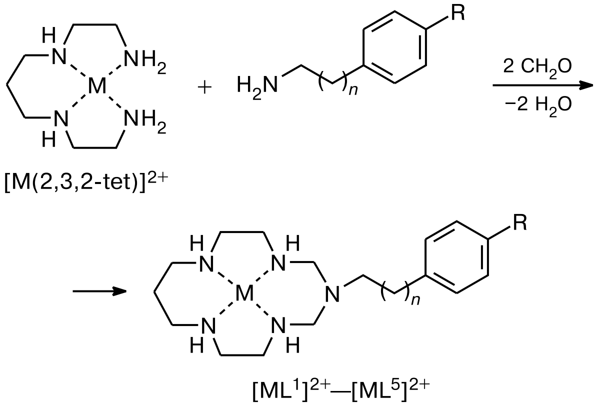
Physicochemical measurements. The electronic absorption spectra were obtained on a Specord M-40 spectrophotometer. The IR spectra in the range of 400—4000 cm^{-1} were recorded on a Perkin—Elmer spectrometer (in KBr pellets). The electrochemical properties of the compounds were studied by cyclic voltammetry (CV) in aqueous solutions containing 0.1 *M* $NaClO_4$ or 0.5 *M* Na_2SO_4 (nickel complexes) and in acetonitrile solutions containing 0.1 *M* $[NEt_4]ClO_4$ as an electrolyte (nickel and copper complexes). A three-electrode circuit equipped with platinum auxiliary and working electrodes and silver-chloride reference electrode (Ag/AgCl) was used for the measurements. The potential was maintained using a PI-50.1.1 potentiostat controled with a PR-8 programmer. The voltammograms were recorded with an H-307 XY recorder. The potential sweep rate in the range of 0.5—1.0 V in the aqueous solutions and 0.5—2.0 V in the acetonitrile solutions was 50 mV s^{-1}, the accuracy of measurements of $E_{1/2}$ values was ±5 mV. The elemental analysis was performed at the Institute of Physical Chemistry, National Academy of Sciences of the Ukraine using a Carlo Erba instrument.

X-ray diffraction study. Single crystals of the complexes $[CuL^2](ClO_4)_2$ and $[CuL^4](ClO_4)_2$ were obtained by slow crystallization from a acetonitrile—ethanol (1 : 1, v/v) mixture, the crystals of $[CuL^3](ClO_4)_2$ were obtained by diffusion of hexane vapor into an acetone solution of the compound. The diffraction experiments were performed using a Bruker AXS SMART 1000 diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, ω-scanning technique). The structures were solved by the direct method and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms using the program package SHELXL97.[21] The crystallographic data and the main refinement parameters are given in Table 1. In the crystal structure of $[CuL^2](ClO_4)_2$, the substituent in the macrocyclic ligand is disordered over two positions, the perchlorate anions in the structure of $[CuL^4](ClO_4)_2$ are also disordered.

Results and Discussion

Synthesis of macrocyclic nickel(II) and copper(II) complexes was carried out using the formerly developed method,[19,20,22] *viz.*, the template condensation of complexes of acyclic tetramine $[M(2,3,2\text{-tet})]^{2+}$ (M = Cu^{II} or Ni^{II}) with formaldehyde and primary aliphatic amines bearing aryl substituents (Scheme 1). Such one-pot reactions are synthetically convenient and allow obtaining the desired products in moderate yields even without optimization of the reaction conditions.

Scheme 1



Compound	*n*	R	Compound	*n*	R
$[ML^1]^{2+}$	0	H	$[ML^4]^{2+}$	1	Me
$[ML^2]^{2+}$	0	Me	$[ML^5]^{2+}$	1	OH
$[ML^3]^{2+}$	0	OMe			

In addition to elemental analysis, the formation of the macrocyclic compounds is confirmed by IR spectroscopy. There are well-defined differences in the IR spectra of the starting complexes $[M(2,3,2\text{-tet})](ClO_4)_2$ and the condensation products. Particularly, the bands of moderate intensity assigned to vibrations of the secondary amino groups of the macrocyclic ligands (ν(NH) = 3220—3200 and 3180—3160 cm^{-1}, δ(NH) = 1660—1610 cm^{-1}) are present in the spectra of the condensation products instead of the intensive bands of stretching and deformation

Table 1. The X-ray diffraction data and refinement parameters for the macrocyclic copper complexes

Parameter	$CuL^2(ClO_4)_2$	$CuL^3(ClO_4)_2$	$CuL^4(ClO_4)_2$
Molecular formula	$C_{17}H_{31}Cl_2CuN_5O_8$	$C_{17}H_{31}Cl_2CuN_5O_9$	$C_{18}H_{33}Cl_2CuN_5O_8$
Molecular weight	567.91	583.91	581.93
T/K	103(2)	298(2)	103(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P(-)1$	$P(-)1$	$P(-)1$
a/Å	8.160(3)	8.2813(4)	8.1665(9)
b/Å	8.3789(15)	8.3130(4)	12.3777(14)
c/Å	18.488(3)	19.0046(8)	12.5582(14)
α/deg	96.465(13)	86.300(1)	77.547(2)
β/deg	93.409(16)	86.396(1)	84.196(2)
γ/deg	112.27(3)	67.243(1)	76.662(2)
V/Å^3	1155.1(6)	1202.94(10)	1204.3(2)
Z	2	2	2
d_{calc}/g cm^{-3}	1.627	1.612	1.605
μ/mm^{-1}	1.231	1.187	1.183
F(000)	586	606	606
Crystal dimensions/mm	0.35×0.16×0.15	0.29×0.27×0.05	0.18×0.15×0.02
Total number of reflections	22962	21215	5500
Number of independent reflections (R_{int})	7829 (0.0266)	8217 (0.0300)	5500 (0.0000)
Number of refinement parameters	438	431	470
GOOF (on F^2)	1.030	1.003	1.030
R_1 (on F for reflections with $I > 2\sigma(I)$)	0.0305	0.0381	0.0493
wR_2 (on F^2 for reflections with $I > 2\sigma(I)$)	0.0826	0.0941	0.1204
R_1 (for all reflections)	0.0368	0.0632	0.0736
wR_2 (on F^2 wR_2 for all reflections)	0.0873	0.1102	0.1327
Residual electron density/e • Å^{-3}, $\Delta\rho_{max}/\Delta\rho_{min}$	0.640/–0.360	0.895/–0.722	1.196/–0.742

vibrations of the primary amino groups of the coordinated tetramine 2,3,2-tet ($\nu(NH_2)$ = 3495—3345 cm^{-1}, $\delta(NH_2)$ ~1640 cm^{-1}). In addition, in the IR spectra of all macrocyclic complexes, a set of strong absorption bands appears in the range of 1450—1560 cm^{-1}, which is assigned to stretching vibrations ν(C=C) of the aromatic substituents.

The prepared nickel(II) complexes are well soluble in polar organic solvents (nitromethane, acetonitrile, DMSO), moderately soluble in water, and poorly soluble in ethanol. The similar and even more pronounced behavior is also characteristic of the copper(II) complexes. These features give evidence of considerable hydrophobicity of these compounds, which is explained by the presence of aromatic substituents in the ligands. This is confirmed by the fact that complexes $[CuL^1](ClO_4)_2$, $[CuL^2](ClO_4)_2$, and $[CuL^4](ClO_4)_2$ are virtually insoluble in water and ethanol, whereas introduction of the oxygen-containing substituents in the aryl fragments increases hydrophility of the compounds resulting in their better solubility in these solvents.

The electronic absorption spectra of the macrocyclic compounds. The spectral characteristics of the examined compounds in different solvents are given in Table 2; they are typical of the complexes of these ions with tetradentate azamacrocyclic ligands.[17]

The band of electronic d—d-transitions in the nickel(II) complexes at ~22000 cm^{-1} is characteristic of the low-spin compounds of this ion with a square-planar chromophore.[17] Its energy does not depend on the structure of the

Table 2. The spectral characteristics of the perchlorate salts of the macrocyclic nickel(II) and copper(II) complexes in different solvents.

Cation	$\nu_{max} \cdot 10^{-3}$/cm^{-1} (ε/L mol^{-1} cm^{-1})				
	$MeNO_2$	EtOH	H_2O	DMSO	MeCN
$[NiL^1]^{2+}$	22.4 (81)	22.3 (63)	22.4 (59)	22.0 (37)	21.7 (20)
$[NiL^2]^{2+}$	22.4 (72)	22.1 (62)	22.4 (49)	21.9 (39)	21.6 (20)
$[NiL^3]^{2+}$	22.5 (81)	22.1 (56)	22.4 (52)	22.1 (39)	21.6 (16)
$[NiL^4]^{2+}$	22.4 (91)	—[a]	22.4 (54)	22.1 (37)	21.9 (27)
$[NiL^6]^{2+}$ [b]	22.1 (60)	—	22.3 (50)	—	21.7 (21)
$[CuL^1]^{2+}$	20.6 (81)	—[a]	—[a]	19.4 (77)	19.5 (85)
$[CuL^2]^{2+}$	20.5 (85)	—[a]	—[a]	19.5 (85)	19.9 (91)
$[CuL^3]^{2+}$	20.4 (84)	19.8 (95)	19.8 (114)	19.4 (77)	20.0 (90)
$[CuL^4]^{2+}$	20.5 (85)	—[a]	—[a]	19.5 (85)	19.9 (91)
$[CuL^5]^{2+}$	20.4 (76)	19.4 (80)	19.4 (82)	19.5 (75)	19.7 (87)
$[CuL^6]^{2+}$ [b]	20.4 (78)	—	19.8 (75)	—	19.8 (72)

[a] The compound is poor soluble in this solvent.

[b] According to Refs 20 and 23; hereinafter L^6 is 3-methyl-1,3,5,8,12-pentaazacyclotetradecane.

aromatic substituent in the macrocycle and is close to the energy of the complex with the methyl-substituted ligand $[\mathrm{NiL}^6]^{2+}$ (see Table 2).[20,23] This fact gives evidence of the absence of electronic interaction between the substituent and chromophore and suggests the similar conformation of the macrocyclic ligands in the examined complexes. The latter agrees with the X-ray diffraction data of the copper complexes (see below).

Noteworthy is the fact that the molar extinction coefficient (ε) of the absorption band of the nickel complexes is considerably dependent on the nature of the solvent (see Table 2), whereas the value of energy is practically constant. This feature gives evidence of the presence of an equilibrium between the four-coordinate low-spin (ls) and six-coordinate high-spin (hs) forms of the complex in solutions:[17]

$$\underset{S = 0}{[\mathrm{NiL}]^{2+} + 2\,\mathrm{Solv}} \overset{K_{\mathrm{eq}}}{\rightleftharpoons} \underset{S = 3/2}{[\mathrm{NiL(Solv)}_2]^{2+}}, \qquad (1)$$

where Solv is a solvent; the complex with $S = 0$ is square-planar, the complex with $S = 3/2$ is tetragonal-bipyramidal.

The spectrum of the high-spin form of the complex is characterized[22—24] by the presence of the absorption bands at ~30000, 15000, and <11000 cm^{-1}. Due to the low intensity of these bands ($\varepsilon_{\mathrm{hs}} \leq 10$ L mol^{-1} cm^{-1})[17] as well as low equilibrium concentration of the high-spin form, the main visible effect of the equilibrium (1) is a decrease in the molar extinction coefficient of the absorption band of the low-spin form at ~22000 cm^{-1}, which becomes an effective parameter ($\varepsilon_{\mathrm{eff}}$). The highest ε values are observed in a noncoordinating solvent, nitromethane (in this case $\varepsilon_{\mathrm{eff}} = \varepsilon_{\mathrm{ls}}$), and the presence of several additional low-intensity absorption bands in acetonitrile solutions comprising maximal amount of high-spin form among the examined solvents agree with this interpretation.

The equilibrium constants (1) can be estimated from the formula $K_{\mathrm{eq}} = (\varepsilon_{\mathrm{ls}} - \varepsilon_{\mathrm{eff}})/\varepsilon_{\mathrm{eff}}$.* The obtained values K_{eq} are 2.4—4.1, 0.9—1.5, 0.5—0.7, and 0.2—0.4 for the solutions in acetonitrile, DMSO, water, and ethanol, respectively. This allows us to arrange them in a series that reflects the increase in the ability of the solvent molecules to coordinate at the axial positions of the nickel(II) ion: nitromethane (2.7) < ethanol (20) < water (≥18) < DMSO (29.8) < acetonitrile (14.1) (Gutman's donor numbers of solvents are given in the parantheses). The specific position of acetonitrile in this series is typical of nickel(II) amine complexes.[26] A comparison of the obtained constants with the constants for $[\mathrm{NiL}^6]^{2+}$ (2.0 and 0.2 in acetonitrile and aqueous solutions, respectively) allows us to infer that the substitution of the aryl substituent in the macrocyclic ligand for the alkyl fragment results in a slight increase in the values of K_{eq}. Probably, the observed effect is not caused by the differences in the inductive properties of the substituents and reflects the changes in the structures of the solvate spheres of the complexes.

In contrast to the nickel(II) complexes, the axial coordination of the solvent molecules to the copper(II) ion practically does not influence the intensity of the observed absorption band at 20000 cm^{-1} and appears in the bathochromic shift of its maximum.[17] Taking into account the value of this shift, the examined solvents could be arranged in the series according to their coordination ability with respect to the copper ion(II) in a macrocyclic environment: $\mathrm{MeNO_2} < \mathrm{MeCN} < \mathrm{H_2O} < \mathrm{EtOH} < \mathrm{DMSO}$. This series agrees with the increase in Gutman's donor numbers of solvents.

Redox characteristics of the complexes. The voltammograms in the anodic region in aqueous and acetonitrile solutions give evidence of the existence of only one redox process for each compound. On the basis of an approximate equality of the currents of the cathodic and anodic peaks and the distance between them, $\Delta E \leq 100$ mV (Table 3), this process can be treated as quasireversible.

Table 3. Redox potentials ($E_{1/2}$) of the pairs $\mathrm{M^{III/II}L}$ of nickel and copper complexes in different solvents[a]

Complex	$E_{1/2}$/mV		
	$\mathrm{H_2O}$		MeCN,
	0.1 M $\mathrm{NaClO_4}$	0.5 M $\mathrm{Na_2SO_4}$	0.1 M $[\mathrm{NEt_4}]\mathrm{ClO_4}$
$[\mathrm{NiL}^1]$	820 (75)	525 (70)	1045 (70)
$[\mathrm{NiL}^2]$	830 (85)	530 (80)	1035 (100)
$[\mathrm{NiL}^3]$	820 (85)	530 (80)	1040 (100)
$[\mathrm{NiL}^4]$	850 (90)	535 (70)	1030 (90)
$[\mathrm{NiL}^6]$[b]	775 (80)	500 (70)	960 (60)
$[\mathrm{CuL}^1]$	—	—	1440 (110)
$[\mathrm{CuL}^2]$	—	—	1425 (90)
$[\mathrm{CuL}^4]$	—	—	1460 (160)
$[\mathrm{CuL}^3]$	—	—	1430 (120)
$[\mathrm{CuL}^5]$	—	—	1230 (75)
$[\mathrm{CuL}^6]$[b]	—	—	1455 (90)

[a] $E_{1/2}$ (mV) *vs.* Ag/AgCl electrode, the distances between cathodic and anodic peaks ΔE (mV) are given in parentheses.

[b] According to Ref. 22.

---

* More strict formula for the calculation of equilibrium constant (1) is $K_{\mathrm{eq}} = (\varepsilon_{\mathrm{ls}} - \varepsilon_{\mathrm{eff}})/(\varepsilon_{\mathrm{eff}} - \varepsilon_{\mathrm{hs}})$, where $\varepsilon_{\mathrm{hs}}$ is the molar absorption coefficient of the high-spin form at the maximum of the absorption band of the low-spin complex. Since the 100% content of a high-spin form is not observed in any of the solvents, the estimated value of this parameter can be obtained by decomposition of the observed spectrum on the Gauss components. Earlier,[24] we have shown that $\varepsilon_{\mathrm{hs}}$ is ~6 L mol^{-1} cm^{-1} for such-type complexes. However, slight changes in $\varepsilon_{\mathrm{hs}}$ values in this approach considerably influence the value of the denominator and, thereby, K_{eq}. Thus, this calculation method was not used in the present work.

By analogy with earlier published data,[19,20,22,23] this process is a single-electron redox transformation of the metal center, *i.e.*, transition in the redox-pair $I^{III/II}L$. On the whole, the observed values of the redox potentials $E_{1/2}$ calculated as average values between potentials of the cathodic and anodic peaks appear in the renges that are typical of the nickel and copper complexes with tetradentate azamacrocyclic ligands.

The redox potentials of the pair $Ni^{III/II}L$ appear to considerably depend on the nature of the solvent and the electrolyte. Since the azamacrocyclic nickel(III) complexes exist in solution in the six-coordinate form,[27] this feature could be explained by the different nature of the axial ligands. Particularly, the coordination of the sulfate anions results in considerably higher thermodynamic stabilization of nickel(III) than the coordination of neutral water molecules (in perchlorate-containing aqueous media) or acetonitrile.[28] On the whole, the changes in the values $E_{1/2}$ of the pair $Ni^{III/II}L$ depending on the nature of the aryl substituent in the ligand have a nonsystematic character, however, they are slightly higher than that for the complex of their methyl-substituted analog L^6.

As is known, the azamacrocycles less efficiently stabilize copper(III) as compared with nickel(III)[29] and this fact is confirmed by the results obtained in the present work. Particularly, on the voltammograms of the copper complexes in aqueous solutions, only anodic peak at potentials > 1 V was observed. The values $E_{1/2}$ of the pair $Cu^{III/II}L$ measured in acetonitrile solutions (see Table 3) similar to nickel complexes give evidence about insignificant effect of the nature of the aryl substituent on their values. The only exception is the complex of the ligand L^5 bearing the phenolic substituent. On the basis of literature data,[30] it is most probable that the redox process observed in this case is the transition phenol/phenoxyl radical.

Molecular structure of the macrocyclic copper complexes. The complexes $[CuL^2(ClO_4)_2]$, $[CuL^3(ClO_4)_2]$, and $[CuL^4(ClO_4)_2]$ studied by X-ray diffraction are characterized by similar molecular structures (see Fig. 1). The coordination polyhedron of the copper(II) ions in all compounds is represented by the elongated tetragonal bipyramid (*trans*-N_4O_2) where four nitrogen atoms of the macrocyclic ligand form the nearly ideal equatorial plane (the deviations from the mean plane of N_4 do not exceed 0.01 Å for the nitrogen atoms and 0.03 Å for the copper ions in all three complexes), and two oxygen atoms of the perchlorate anions occupy the axial positions. The distances Cu—N and angles N—Cu—N in the equatorial plane (Table 4) have values in the range typical of such types of macrocyclic complexes,[17,31] while the relatively larger axial distances Cu—O (2.46—2.60 Å) give evidence of weak coordinative interaction of the metal ion with the perchlorate anions.

The coordinated macrocyclic ligands exist in the most energetically favorable form *trans-III* (*R*,*R*,*S*,*S*)[31] with

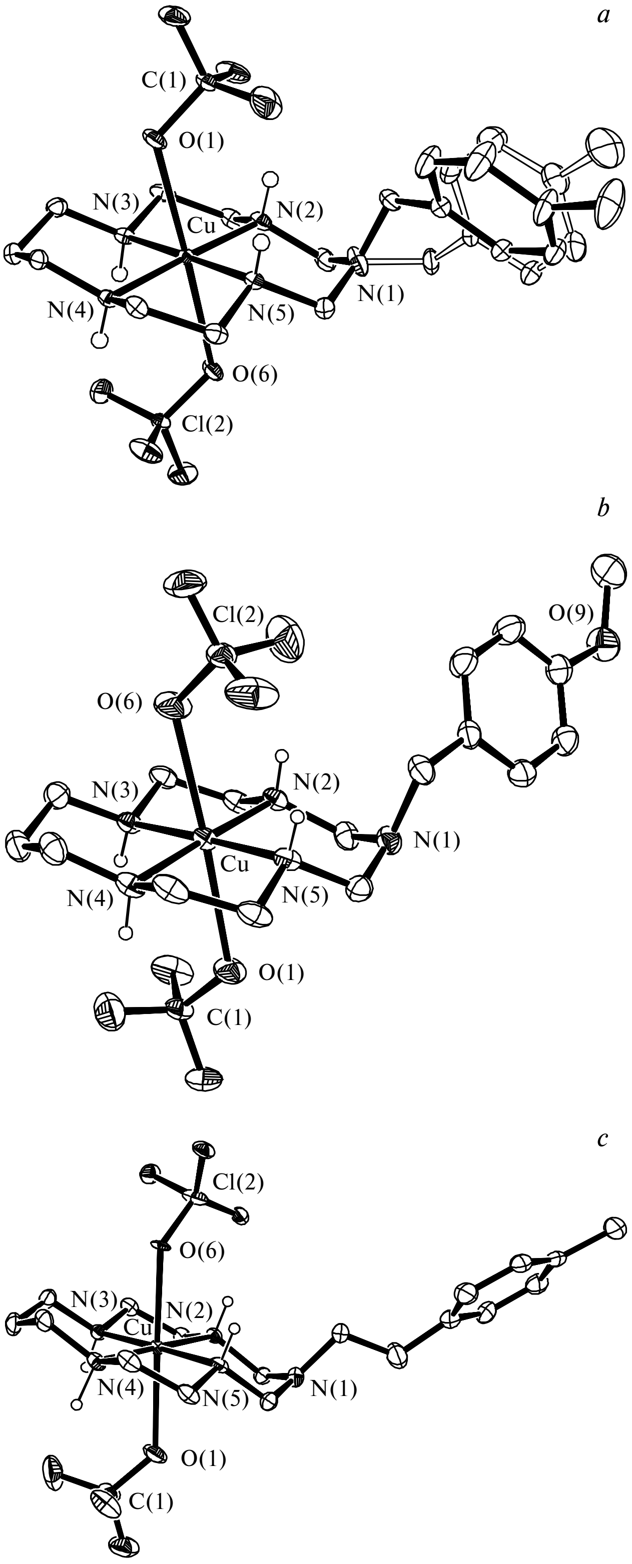


Fig. 1. Molecular structures of macrocyclic copper(II) complexes $[CuL^2(ClO_4)_2]$ (*a*), $[CuL^3(ClO_4)_2]$ (*b*), and $[CuL^4(ClO_4)_2]$ (*c*). The thermal ellipsoids are given at 30%-probability level, hydrogens at the nitrogen atoms are outlined as the spheres with arbitrary radii, hydrogens at the carbon atoms are not shown.

Table 4. Some characteristics of the coordination polyhedrons of the macrocyclic copper(II) complexes

Parameter	$[CuL^2(ClO_4)_2]$	$[CuL^3(ClO_4)_2]$	$[CuL^4(ClO_4)_2]$
Bond length		d/Å	
Cu—N(2)	2.018(1)	2.019(2)	2.011(3)
Cu—N(3)	2.021(1)	2.017(2)	2.028(3)
Cu—N(4)	2.019(1)	2.024(2)	2.018(3)
Cu—N(5)	2.025(1)	2.017(2)	2.011(3)
Cu—O(1)	2.517(1)	2.580(2)	2.576(3)
Cu—O(6)	2.591(1)	2.548(2)	2.459(2)
Cu—N/Cu—C[a]	3.306/3.350	3.342/3.348	3.296/3.343
Angle		ω/deg	
N—Cu—N[b]	86.1(1), 86.6(1)	86.3(1), 86.2(1)	85.8(1), 86.3(1)
N—Cu—N[c]	93.1(1), 94.1(1)	93.3(1), 94.2(1)	93.6(1), 94.3(1)
Torsion angles[b]	−56.1, 56.2	−56.7, 55.4	−55.1, 55.1
Sum of the angles C—N—C at the N(1) atom	351.2	346.0	353.7

[a] The distance from the copper ion to the distal atom N/C in six-membered chelate rings.

[b] In five-membered chelate rings.

[c] In six-membered chelate rings. The first digit relates to the chelate ring with noncoordinated nitrogen atom.

the six-membered chelate rings in the chair conformation and five-membered chelate rings in the *gauche* conformation. In each ligand, the six-membered metallacycles differ in chemical structures, since they contain different distal atoms (a noncoordinated nitrogen atom or a carbon atom of the methylene group) and are structurally nonequivalent, which is manifested in slight differences in both angles N—Cu—N and distances between the copper ions and the respective distal atoms (see Table 4).

As follows form Table 4, the sums of the angles between the bonds N—C formed by the noncoordinated nitrogen atom N(1) are considerably larger than the expected values for the tetrahedral configuration (~330°). This feature is well-known for such types of the macrocyclic ligands and is explained by the fact that the mentioned nitrogen atoms have intermediate hybridization between sp^2 and sp^3. Due to certain "flatness" of the fragment under consideration, the assignment of orientation of the substituents in the respective six-membered chelate rings (equatorial or axial) is rather tentative. Nevertheless, the orientation of substituents in the complexes $[CuL^3(ClO_4)_2]$ and $[CuL^4(ClO_4)_2]$ can be considered to be axial. At the same time, the substituent in the complex $[CuL^2(ClO_4)_2]$ is disordered, and this compound is the example of the simultaneous presence in the crystal of the molecules with axial and equatorial orientations (see Fig. 1, *a*).

Crystal structures of the compounds. All studied complexes have virtually identical structural and chemical parameters (metal ion, anion, hydrophobic nature of the substituent) essential for the formation of crystals. Therefore, the examined compounds are convenient subjects to study the effect of small differences in their molecular structure on the packing in the crystal state.

The common feature of the crystal state of the copper(II) complexes is the presence of one-dimensional (1D) chains formed by the hydrogen bonds (HB) between the oxygen atoms of the coordinated perchlorate anions and the secondary amino groups of the adjacent cations (the distances O...N are 3.26, 3.16, and 2.99 Å for $[CuL^2(ClO_4)_2]$, $[CuL^3(ClO_4)_2]$, and $[CuL^4(ClO_4)_2]$, respectively). The spatial arrangement of the chain constituents is similar, which is confirmed by the closeness of the distances between the adjacent copper ions (8.379, 8.313, and 8.166 Å for $[CuL^2(ClO_4)_2]$, $[CuL^3(ClO_4)_2]$, and $[CuL^4(ClO_4)_2]$, respectively). Two additional HB for $[CuL^2(ClO_4)_2]$ and $[CuL^3(ClO_4)_2]$ are observed (the distances O...N were 3.077, 3.081 and 3.173, 3.152 Å, respectively), which connect 1D chains in 2D layers.

Further association of the structural fragments (1D chains in $[CuL^4(ClO_4)_2]$ or 2D layers in two other complexes) in the three-dimensional crystal structure is effected by NI. The energy of such interactions (for example, 7—11 kJ mol^{-1} (see Ref. 32) for the CH—π-contacts) is close to the lower limit of the energy of a classical NI being 12—30 kJ mol^{-1} (see Ref. 32). In the case of the studied systems, where the intermolecular NI are relatively weak (the distances O...N > 3 Å), it could be supposed that both HB and NI are essential for the crystal formation.

Indeed, the crystal structures of all three complexes are characterized by the existence of NI, especially, it clearly appears in the formation of dimeric aggregates (Fig. 2).

In the dimer of the complex $[CuL^2(ClO_4)_2]$ (see Fig. 2, *a*), the distance between the planes of the parallel aromatic rings (2.67 Å) is rather short, while they are shifted with respect to each other (the distance between the centers of

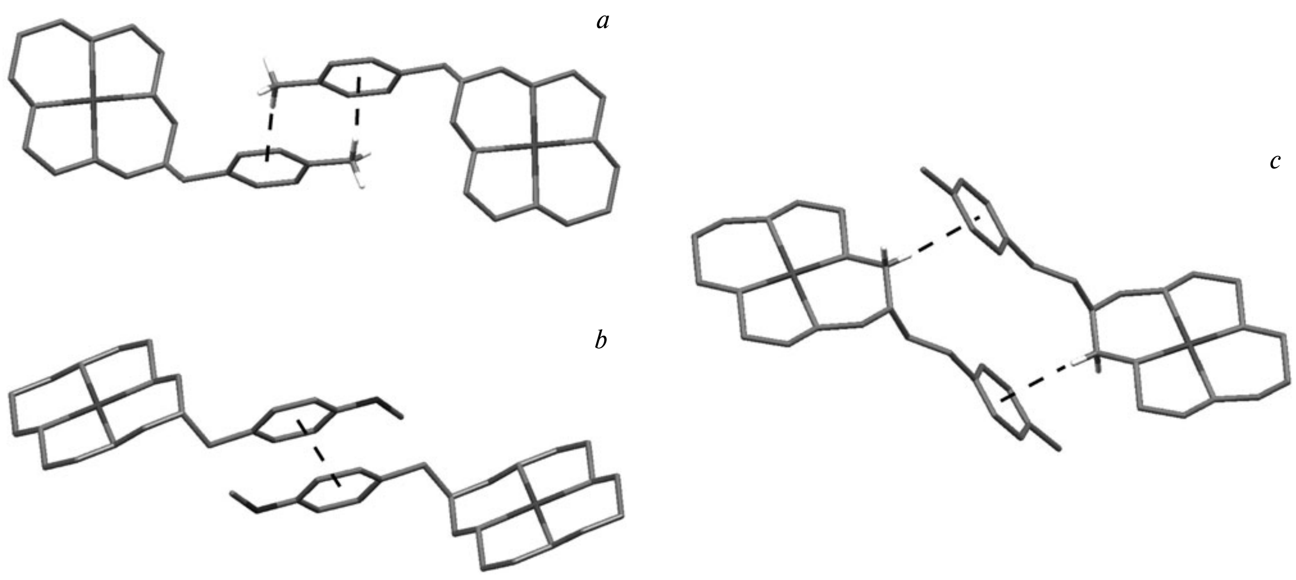


Fig. 2. The structures of dimers in crystals $[CuL^2(ClO_4)_2]$ (*a*), $[CuL^3(ClO_4)_2]$ (*b*), and $[CuL^4(ClO_4)_2]$ (*c*) (only hydrogens involved in noncovalent interactions are shown).

Table 5. The structural characteristics of noncovalent interactions in crystal lattices of the aryl-substituted macrocyclic nickel(II) and copper(II) complexes

Compound[a] (packing type)[b]	*d*/Å			Reference
	CH (aliphatic)...π[c]	CH (aromatic)...π[c]	π...π[d]	
$[NiL^7](ClO_4)_2$ (*A*)	3.94/3.15	—	—	33
$[NiL^7(N_3)_2]$ (*A*)	3.96/3.12	3.68/2.82	(3.71/4.70)[e]	34
$[NiL^7(in)_2]$ (*A*)	—	—[f]	—[g]	35
$[NiL^7(tp)]_n$ (*B*)	3.60/2.84; 3.91/3.24	—[f]	—	36
$[NiL^8](ClO_4)_2$ (*A*)	3.70/3.15	4.12/3.19	(3.70/4.72)[e]	37
$[NiL^8](BF_4)_2$ (*A*)	3.66/3.11	4.01/3.12	(3.69/4.64)[e]	38
$[NiL^8(tp)]_n$ (*B*)	—	—	(2.69/5.35)[e,h]	36
$\{[NiL^8(bdc)]\cdot 2DMF\}_n$ (*A*)	3.75/2.86	—	—	36
$\{[(NiL^8)_3(btc)_2]\cdot 6H_2O\}_n$ (*A*)	3.85/2.91	3.73/2.94[e]	3.75/4.03	39
$[Ni(R)\text{-}L^9)](ClO_4)_2$ (*A*)	—	3.48/2.86	—	40
$[Ni(S)\text{-}L^9)](ClO_4)_2$ (*A*)	—	3.48/2.87	—	40
$[Ni((R)\text{-}L^9)(NCS)_2]$ (*A*)	3.92/2.95	3.54/2.69	—	41
$[CuL^8(ClO_4)_2]$ (*A*)	3.84/—	—	3.65/4.16	42
$[CuL^2(ClO_4)_2]$ (*A*)	2.85/2.43	—	(2.67/4.35)[e]	This work
$[CuL^3(ClO_4)_2]$ (*A*)	—	—	3.44/3.79	This work
$[CuL^4(ClO_4)_2]$ (*B*)	3.45/2.79	—	—	This work

[a] Ligand designation: L^7 is 3,10-dibenzyl-1,3,5,8,10,12-hexaazacyclotetradecane, L^8 is 3,10-diphenethyl-1,3,5,8,10,12-hexaazacyclotetradecane, L^9 is 3,10-di((R/S)-α-methylbenzyl)-1,3,5,8,10,12-hexaazacyclotetradecane, in is isonicotinate, tp is terephthalate, bdc is *trans*-butenedicarboxylate, btc is 1,3,5-benzenetricarboxylate.

[b] The presence (*A*) and absence (*B*) of layered packing with alternation of hydrophobic and hydrophilic layers.

[c] The distances C...Ct/H...Ct, where Ct is the center of the aromatic ring.

[d] The distance between the parallel planes of the aromatic rings/distance Ct...Ct.

[e] The absence of overlapping of π-systems of the aromatic rings.

[f] The presence of additional CH...π-interactions ("edge-to-face") between the hydrogen atoms of the aromatic substituents and the aromatic ring of the carboxylate.

[g] The presence of the π—π-interaction between the carboxylate anions.

[h] The presence of the additional π—π-interaction between the substituent in the macrocycle and bridging carboxylate.

the benzene rings is 4.35 Å) and their aromatic systems do not overlap. It allows us to rule out π—π-stacking as a driving force of the aggregation of the macrocyclic cations. The most probable reason of the formation of the dimer in this compound is the CH—π-interaction between the methyl substituent in the aromatic ring of one cation and the aromatic fragment of the other cation. One hydrogen of the CH_3 group is situated practically above the center (the deviation from the vertical is 5.3°) of the benzene ring of the adjacent molecule at a distance of 2.43 Å (the distance C...centroid C_6 is 2.85 Å).

Similar type of interactions is typical of a dimer of the complex $[CuL^4(ClO_4)_2]$ as well (see Fig. 2, *b*). However, in this case, the methylene groups of the six-membered metallacycle are responsible for the molecular interaction with the aromatic system (the distances from H and C atoms to the center of the benzene ring are 2.79 and 3.45 Å, respectively, the deviation of the H atom from the perpendicular to the center of the ring is 7.4°).

The formation of dimer aggregates due to the interactions between the hydrophobic parts of the molecules is also observed in the complex $[CuL^3(ClO_4)_2]$ (see Fig. 2, *b*). However, on the base of mutual orientation of the aryl fragments (the distance between their parallel planes is 3.44 Å, the distance between the centers of the benzene rings is 3.79 Å), the appreciable overlapping of the π-electronic systems leading to efficient stacking-interaction could be expected.

The data from X ray diffraction analysis of a number of nickel(II) and copper(II) complexes with related macrocyclic ligands L^7—L^9 are documented, which allows performing the comparative analysis of types of NI observed in the crystals of such compounds (Table 5).

The tabulated data show that the interactions between the aromatic systems of the substituents and hydrogens of the methylene groups of the macrocycles are the most common. Similar "edge-to-face" type interactions of hydrogens of the aromatic rings in the compounds containing inorganic anions are less common, thought the presence of aromatic carboxylates in the structure of the compounds results in additional interactions of this type.

As a rule, in crystals of the majority of the considered complexes, the planes of the aromatic rings of the aryl substituents are located close to each other and are parallel, but in most cases their centers are considerably shifted, which makes impossible the overlapping of the π-systems. Thus, these interactions cannot be characterized as π—π-stacking. The compounds examined in this work are distinguished from the set of compounds in the shortest contacts responsible for NI (CH—π in $[CuL^2(ClO_4)_2]$ and $[CuL^4(ClO_4)_2]$; π—π in $[CuL^3(ClO_4)_2]$, see Table 5).

Yet another type of NI, which plays an essential role in the formation of the crystals of such compounds, is hydrophobic interactions between aromatic fragments. In the case of complexes $[CuL^2(ClO_4)_2]$ and $[CuL^3(ClO_4)_2]$,

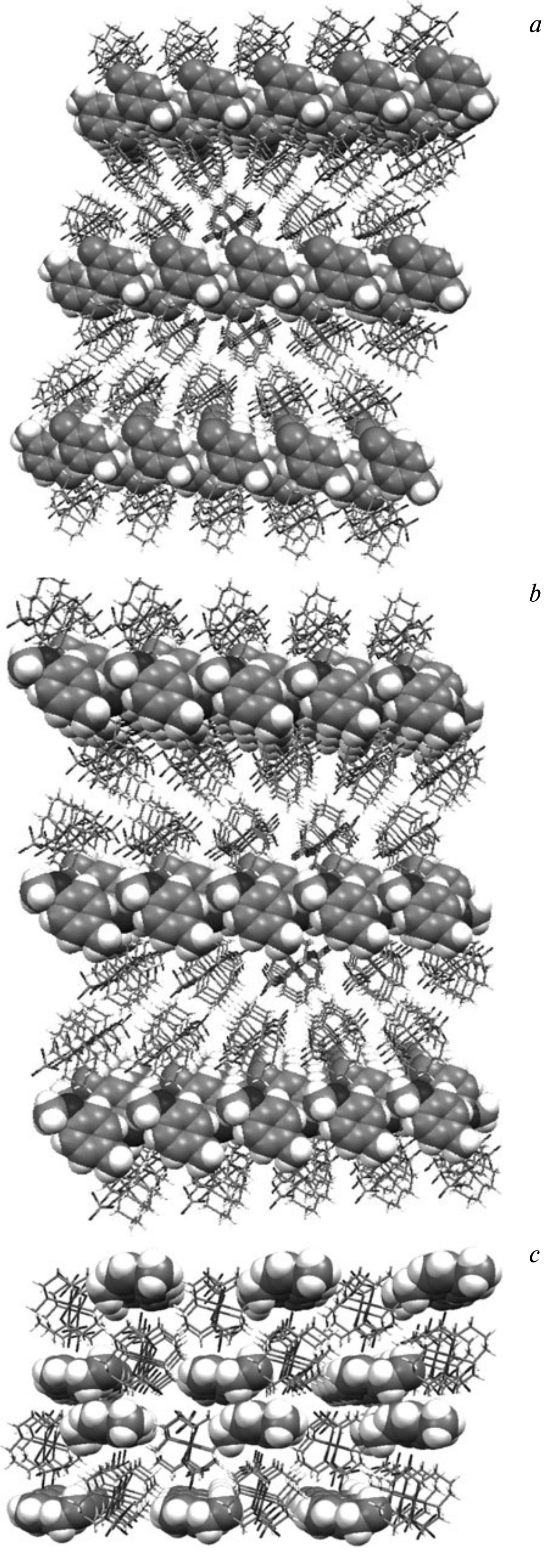


Fig. 3. The crystal packing of the complexes $[CuL^2(ClO_4)_2]$ (*a*), $[CuL^3(ClO_4)_2]$ (*b*), and $[CuL^4(ClO_4)_2]$ (*c*). The hydrophobic substituents are shown as the spheres with the van der Waals radii.

these interactions result in lamellar crystal structures (Fig. 3), which are formed by the alternating hydrophobic and hydrophilic layers as a result of "face-to-face" packing of cations. On the whole, such layered structure is characteristic of a majority of macrocyclic compounds bearing aryl substituents (Table 5). Similar packing is typical of the complex $[CuL^4(ClO_4)_2]$; however, due to other spatial orientation of the aromatic fragment, it does not lead to the layered structure.

In conclusion, in the present work we developed a method for the synthesis of novel amphiphilic azamacrocyclic copper(II) and nickel(II) complexes bearing different aromatic substituents. It is shown that the nature of the substituent does not considerably influence spectral and electrochemical properties of the compounds obtained. On the base of the X-ray diffraction analysis of three copper complexes, we established the presence of similar stack structures in the crystals, where the perchlorate anions serve as the bridges between the macrocyclic cations due to formation of coordination bonds with the metal ion and hydrogen bonds with the amino groups of the adjacent macrocycle. The substitution of the methoxy group for the methyl group in the aromatic fragment has negligible effect on the crystal structure, thought it results in replacement of the CH—π-interaction for π—π-stacking as the attractive noncovalent forces. At the same time, the introduction of additional methylene unit in the bridge between the aryl and macrocyclic fragments considerably changes crystal packing. In this case, CH—π-interactions between the aromatic substituents and methylene groups of the six-membered chelate rings of the macrocyclic ligand are present. The crystal structure of the former two compounds is layered with alternate hydrophobic and hydrophilic regions.

The obtained data show that slight variations in the structure of the related compounds is a promising approach for fine control over their packing in the crystal state and can result in appearance of one or other types of noncovalent intermolecular interactions.

References

1. J.-M. Lehn, *Supramolecular Chemistry. Concepts and Perspectives*, VCH Verlags GmbH, Weinheim—New York—Basel—Cambridge—Tokyo, 1995, 271 pp.
2. J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, John Wiley and Sons, Chichester—New York—Weinheim—Brisbane—Singapore—Toronto, 2000, 772 pp.
3. H.-J. Schneider, A. K. Yatsimirsky, *Principles and Methods in Supramolecular Chemistry*, John Wiley and Sons, Chichester—New York—Weinheim—Brisbane—Singapore—Toronto, 1999, 349 pp.
4. M. Muraki, *Protein Peptide Lett.*, 2002, **9**, 195.
5. K. M. Guckian, B. A. Schweitzer, R. X.-F. Ren, C. J. Sheils, D. C. Tahmassebi, E. T. Kool, *J. Am. Chem. Soc.*, 2000, **122**, 2213.
6. J. Liu, T. Zhang, T. Lu, L. Qu, H. Zhou, Q. Zhang, L. Ji, *J. Inorg. Biochem.*, 2002, **91**, 269.
7. D. B. Amabilino, J. F. Stoddart, *Chem. Rev.*, 1995, **95**, 2725.
8. K. A. Hirsch, S. R. Wilson, J. S. Moore, *Chem. Eur. J.*, 1997, **3**, 765.
9. E. Arunkumar, P. Chithra, A. Ajayaghosh, *J. Am. Chem. Soc.*, 2004, **126**, 6590.
10. D. Horn, J. Rieger, *Angew. Chem.*, *Int. Ed. Engl.*, 2001, **40**, 4331.
11. M. S. Gudiksen, L. J. Lauhon, J. Wang, D. C. Smith, C. M. Lieber, *Nature*, 2002, **415**, 617.
12. G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Material Science Monographs 54, Elsevier, Amsterdam—New York, 1989, 312 pp.
13. G. R. Desiraju, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 2311.
14. P. Sozzani, S. Bracco, A. Comotti, L. Ferretti, R. Simonutti, *Angew. Chem.*, *Int. Ed. Engl.*, 2005, **44**, 1816.
15. M. P. Suh, H. R. Moon, in *Adv. Inorg. Chem.*, Eds R. van Eldik, K. Bowman-James, Academic Press, San Diego, 2006, Vol. **59**, p. 39.
16. Ya. D. Lampeka, L. V. Tsymbal, *Teoret. Eksperim. Khimiya*, 2004, **43**, 331 [*Theor. Experim. Chem.* (*Engl. Transl.*), 2004, **43**, 345].
17. K. B. Yatsimirsky, Ya. D. Lampeka, *Fizikokhimiya kompleksov metallov s macrotsiklicheskimi ligandami* [*Physicochemistry of metal complexes with macrocyclic ligands*], Naukova dumka, Kiev, 1985, 256 pp. (in Russian).
18. M. P. Suh, in *Adv. Inorg. Chem.*, Ed. G. Sykes, Academic Press, San Diego, 1996, Vol. **44**, p. 93.
19. I. M. Maloshtan, Ya. D. Lampeka, *Zh. Neorgan. Khim.*, 1996, **41**, 1845 [*Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1996, **41**, 1749].
20. I. M. Maloshtan, S. V. Rosokha, Ya. D. Lampeka, *Zh. Neorgan. Khim.*, 1994, **39**, 792 [*Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1994, **39**, 759].
21. G. M. Sheldrick, *SHELXTL 5.1*, Bruker AXS, Madison, WI, 1998.
22. S. V. Rosokha, Ya. D. Lampeka, I. M. Maloshtan, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 631.
23. L. V. Tsymbal, S. V. Rosokha, Ya. D. Lampeka, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2633.
24. P. Comba, Ya. D. Lampeka, A. Y. Nazarenko, A. I. Prikhod'ko, H. Pritzkow, J. Taraszewska, *Eur. J. Inorg. Chem.*, 2002, 1871.
25. V. Gutmann, G. Resch, W. Linert, *Coord. Chem. Rev.*, 1982, **43**, 133.
26. M. Boiocchi, L. Fabbrizzi, F. Foti, M. Vazquez, *Dalton Trans.*, 2004, 2616.
27. A. G. Lappin, A. McAuley, in *Adv. Inorg. Chem.*, Ed. G. Sykes, Academic Press, San Diego, 1988, Vol. **32**, p. 241.
28. E. Zeigerson, G. Ginzburg, L. J. Kirschenbaum, D. Meyerstein, *J. Electroanal. Chem. Intefacial Electrochem.*, 1981, **127**, 113.
29. M. Ciampolini, L. Fabbrizzi, M. Licchelli, A. Perotti, F. Pezzini, A. Poggi, *Inorg. Chem.*, 1986, **25**, 4131.
30. P. Chaudhuri, K. Wieghardt, in *Progr. Inorg. Chem.*, Ed. K. D. Karlin, John Wiley and Sons, Chichester—New York, 2001, Vol. **50**, p. 151.
31. J. C. A. Boeyens, S. M. Dobson, in *Stereochemistry of Organometallic and Inorganic Compounds*, Vol. **2**, Ed. I. Bernal, Elsevier, Amsterdam—New York, 1987, p. 1.
32. M. Nishio, Y. Umezawa, K. Honda, S. Tsuboyama, H. Suezawa, *CrystEngComm.*, 2009, **11**, 1757.

33. Y.-W. Li, H. Xiang, T.-B. Lu, S. W. Ng, *Acta Crystallogr.*, *Sect. E: Struct. Rep. Online*, 2004, **60**, m309.
34. J. W. Shin, K. S. Min, *Acta Crystallogr.*, *Sect. E: Struct. Rep. Online*, 2008, **64**, m941.
35. J. H. Han, B. G. Kim, K. S. Min, *Acta Crystallogr.*, *Sect. E: Struct. Rep. Online*, 2008, **64**, m366.
36. T.-B. Lu, H. Xiang, R. L. Luck, Z.-W. Mao, X.-M. Chen, L.-N. Ji, *Inorg. Chim. Acta*, 2003, **355**, 229.
37. T. Lu, H. Xiang, X. Li, Z. Mao, L. Ji, *Inorg. Chem. Commun.*, 2000, **3**, 597.
38. Y.-W. Li, H. Xiang, T.-B. Lu, S. W. Ng, *Acta Crystallogr.*, *Sect. E: Struct. Rep. Online*, 2004, **60**, m314.
39. T.-B. Lu, H. Xiang, R. L. Luck, Z.-W. Mao, D. Wang, C. Chen, L.-N. Ji, *CrystEngComm.*, 2001, **3**, 168.
40. J. H. Han, M. J. Cha, B. G. Kim, S. K. Kim, K. S. Min, *Inorg. Chem. Commun.*, 2008, **11**, 745.
41. J. W. Shin, K. S. Min, *Acta Crystallogr.*, *Sect. E: Struct. Rep. Online*, 2009, **65**, m234.
42. J. Liu, H. Zhang, C. Chen, H. Deng, T. Lu, L. Ji, *Dalton Trans.*, 2003, 114.

Received November 5, 2008;
in revised form March 11, 2010