

New supramolecular synthons based on 3d transition metal complexes with bidentate bispidines: synthesis and structural, spectroscopic, and electrochemical studies*

S. Z. Vatsadze,^{a*} V. S. Semashko,^a M. A. Manaenkova,^a D. P. Krut'ko,^a V. N. Nuriev,^a R. D. Rakhimov,^a D. I. Davlyatshin,^a A. V. Churakov,^b J. A. K. Howard,^c A. L. Maksimov,^a W. Li,^d and H. Yu^d

^aM. V. Lomonosov Moscow State University, Department of Chemistry, Build. 3, 1 Leninskie Gory, 119991 Moscow, Russian Federation.

E-mail: szv@org.chem.msu.ru

^bN. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation.

E-mail: churakov@igic.ras.ru

^cDepartment of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK.

E-mail: judith@olexsys.org

^dState Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China.

E-mail: opl_wl@dial.zju.edu.cn

A new supramolecular synthon, a 2L : 1M complex of bidentate bispidine with transition metal, was suggested. A number of complex compounds of 1,5-dimethylbispidin-9-one with Cu^{II}, Ni^{II}, and Co^{II} salts (perchlorates, chlorides, bromides, nitrates, trifluoroacetates) were synthesized. The structure and composition of complexes obtained were estimated based on the combination of physicochemical methods of analysis (elemental analysis, X-ray diffraction analysis, NMR, IR, and Raman spectroscopy, electron absorption spectroscopy, ESI mass spectrometry, CVA). The composition of most complexes in the solid state corresponds to the formula ML₂X₂, and in a number of cases the fragment [ML₂]²⁺ is retained in solution, which was shown by NMR spectroscopy for nickel complexes and by mass spectrometry for copper complexes. In the case of copper chloride, the composition of the acetonitrile solutions in the presence of the ligand depends on the ratio of starting compounds and their concentration: an increase in proportion of CuCl₂ and concentration shifts the equilibrium to the side of complexes with higher nuclearity. A 2L : 1M complex of bispidine with metal was for the first time structurally characterized using copper(II) nitrate derivative as an example. The CVA method showed existence of reversible electrochemical reduction of the metal for a number of complexes (the products of the reaction of 1,5-dimethylbispidin-9-one with nickel(II) and cobalt(II) chlorides, as well as with nickel(II) bromide). According to the IR and Raman spectra, chelation of metals with 1,5-dimethylbispidin-9-one leads to the shift of the absorption band of the ligand carbonyl group from 1700 to 1721–1744 cm⁻¹. Nickel(II) and copper(II) perchlorates and nitrates were concluded to be the most promising complexation agents for the binding of two NH,NH-bispidine ligands in a coordination polymer.

Key words: supramolecular polymers, coordination polymers, supramolecular synthons, 3,7-diazabicyclo[3.3.1]nonanes, bispidines, transition metal complexes, cyclic voltammetry, X-ray diffraction analysis, mass spectrometry, NMR spectroscopy, IR and Raman spectroscopy.

Supramolecular chemistry is a multidisciplinary field of science combining organic, inorganic, physical chemistry and biochemistry. Knowing supramolecular chemis-

try is necessary for the construction of functional nano-systems by an "bottom-up" method.^{1,2} One of the main problems which supramolecular chemistry solves is synthesis of complex multi-component assemblies with desired structure and properties.

Supramolecular polymers are ordered polymeric assemblies of monomeric units, which are held together by

* According to the materials of the International Symposium "Modern Trends in Organometallic Chemistry and Catalysis" (June 3–7, 2013, Moscow).

reversible secondary interactions such as ion-ion and ion-dipole interactions, coordination bonds, hydrogen bonds, cation- π -system interactions, π - π -stacking, dipole-dipole, metallophilic, van der Waals interactions, solvophobic effects.³⁻⁵ When a certain degree of polymerization is reached, occurs a spontaneous association of supramolecular polymers into a separate phase (a film, a layer, a membrane, a vesicle, a micelle, a gel, a mesomorphous phase, a crystal).

Supramolecular interactions allowing assemblage of molecular building blocks (tectones) by a programmed and reproducible way are generally accepted to be called supramolecular synthons.⁶

The coordination bond is a type of intermolecular interactions widely used in supramolecular synthesis for the construction of coordination polymers, *i.e.*, supramolecular polymers composed of repeating organic molecules (di- or polytopic ligands) and metal ions.⁷⁻¹¹ While crystalline coordination polymers are well studied and found practically useful,^{3,12} similarly organized noncrystalline systems (including metallogels) are studied much less.^{13,14} It should be noted that the search for the systems capable of reversibly changing structure and properties upon influence of external factors (stimulotropic materials) is an important problem of modern materials science and has a wide field of potential application.^{15,16} One of the ways for the preparation of materials with the indicated properties can be the use of monomeric tectones self-organizing to a supramolecular polymer. The supramolecular assemble formed can change its structure and even disintegrate upon a certain external treatment, but after removal of the treatment is capable of restoration with complete return of the starting properties.¹⁷ Such a behavior is based on the reversibility of the supramolecular bond formation.

Supramolecular gels (SMG), which belong to the supramolecular polymer class of systems, are a type of stimulotropic materials. Supramolecular gels are capable of changing their structure (and, therefore, properties) upon treatment with various in nature external factors. Thus, there are known anion-sensitive, thermosensitive, metal-sensitive, receptor-sensitive, redox-sensitive, mechano-sensitive, sound-sensitive SMG.¹⁴

Rapid development of chemistry and technology of supramolecular metallogels (SMMG) began after the work of J.-M. Guenet with coworkers.¹⁸ By now, SMMG are known to be used in such fields as catalysis, luminescence, spin-crossover; gels are used for the preparation of films and synthesis of nanowires, removal of organic materials, as porous templates for the growth of inorganic materials, templates for organopolymerization. A large number of reviews and monographs published in the last 16 years indicate a steady growing interest of researches to these directions.^{13,14,19-24}

Most of known SMMG are built of either discotic metallocenes or symmetrically bound di- and tritopic ligands, whose chelating group serves as a key site for binding with the metal ion (Scheme 1).

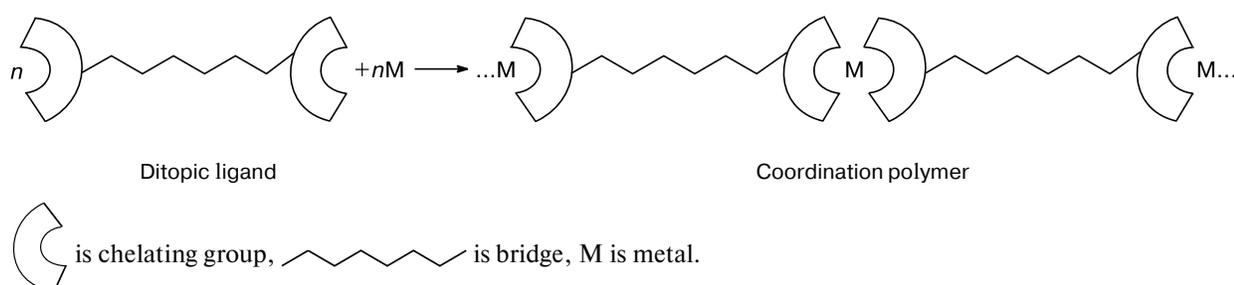
One of the objectives of our new research on the synthesis and study of properties of SMMG is a connection of two 3,7-diazabicyclo[3.3.1]nonane (bispidine) fragments with a bridge for the preparation of ditopic ligands capable of forming coordination polymers (Scheme 2).²⁵

In this case, coordination polymers can be formed with different polymerization degree depending on the linker type and alternative possibilities of connection of chelating groups between each other. Homoconjugation of two bispidine fragments through the nitrogen atoms was used earlier for the development of discrete polynuclear catalysts.²⁶ An approach to the combination of two bispidine fragments through position 9 suggested by us was not yet materialized, however, an idea²⁷ to functionalize position 9 in bis-bispidines to fix the latter on a polymeric matrix has been already suggested.

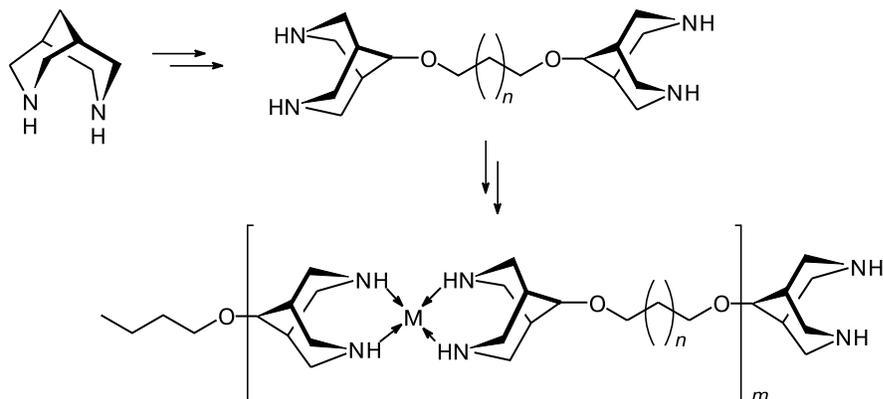
3,7-Diazabicyclo[3.3.1]nonanes (bispidines) are an object of the in depth studies starting from the second half of 20th century. This is due to the fact that they possess pronounced biological activity, as well as are convenient objects for studies of stereochemistry and conformational behavior of bicyclic systems. The results of these studies are summarized in several reviews.²⁸⁻³¹

Bispidines form stable chelate complexes with different metals.³²⁻³⁴ In the fixed conformation of double chair, the bispidine molecule has a rigid adamantane-like skeleton with the placement of donor lone pairs of electrons on

Scheme 1



Scheme 2



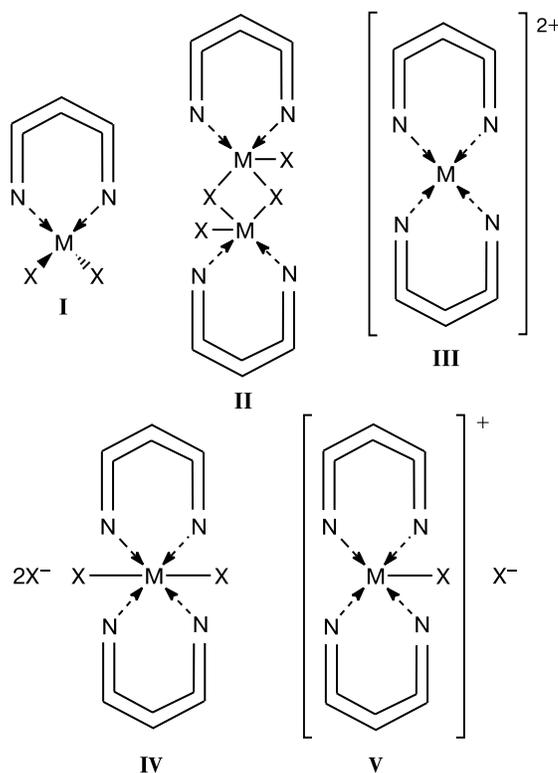
nitrogen atoms optimal for chelation.^{32,35} Depending on the nature of metal and ligand, as well as the nature of possible counterions, one metal atom can coordinate one or two molecules of bispidine ligand, giving 1 : 1 and 1 : 2 complexes, respectively^{36–46} (the types I–V). Bispidine ligands with denticity higher than two are not the objects of the present work. It is obvious that the types III–V and, with some stipulations, the type II satisfy our purpose.

Bispidine complexes are used as catalysts in cyclopropanation,⁴⁷ alkene aziridination,⁴⁸ asymmetric aldol reaction,⁴⁹ conjugate addition to α,β -unsaturated ketones,^{50,51} enantioselective nucleophilic addition to ketones,^{52,53} oxidation,^{36,54} C–C cross-coupling,⁵⁵ C–N cross-coupling,⁵⁶ oxidative resolution of enantiomeric alcohols.^{57,58} For the proper use of bispidine complexes in catalysis, it is important to know their redox characteristics. Application of chiral bispidines in enantioselective synthesis and catalysis is considered in the recent review.⁵⁹

At the same time, the complexes containing two bispidine ligands coordinated to one metal ion are studied comparatively little. There is no literature X-ray diffraction data on the structure of 2 : 1 bispidine complexes, though this is the building block which is the most favorable for the design of supramolecular coordination polymers.

To obtain polymers, the metals used should have tendency to the formation of the 2 : 1 complexes with bidentate bispidines, in which the metal can bind two bispidine ligands with the formation of the type III–V structures. In the present work, we studied a possibility of the preparation of 2 : 1 complexes with copper(II), cobalt(II), and nickel(II) salts (preferable coordination polyhedra of these metals are well known⁶⁰), the structures of these complexes, their behavior in solution, we also tried to select complexes capable of serving as supramolecular synthons in coordination polymer.

The salt anions can significantly influence the complex structures. Perchlorate is a nonnucleophilic anion, which seldom forms bonds with metals in complexes,⁶¹



M = Cu, Ni, Co; X = Cl, Br, ClO₄

therefore, it can be expected that complexes with the type III structure would be preferable for perchlorates. Chloride and bromide anions form bridged bonds, that sometimes leads to unusual polynuclear structures (for example, the type II structures). Nitrate and trifluoroacetate anions can behave as mono- and bidentate ligands, also they can serve as bridges between metal ions.

One of the widely used approaches to the alternation of structure and, therefore, properties of coordination polymers is electrochemical treatment. Redox-switched supramolecular systems belong to the most actively studied

objects. Taking into account the fact that there is only fragmentary literature information on electrochemistry of bispidine and sparteine complexes^{34,62–67} (though such data can be very useful in the study of redox-catalytic transformations), we included in our work the studies of electrochemical behavior of new bispidine complexes by the RDE method and CVA.

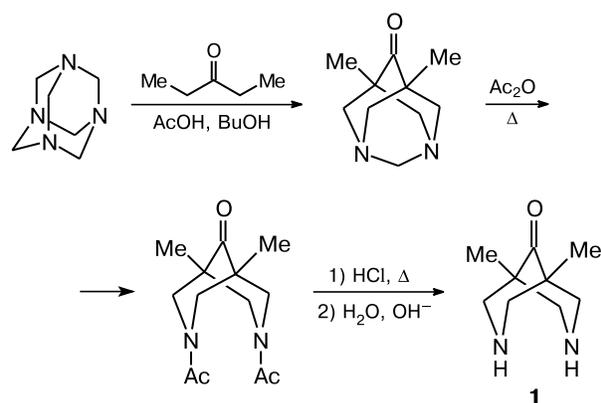
Results and Discussion

Synthesis of ligand and complexes. 3,7-Diazabicyclo[3.3.1]nonan-9-one (**1**) was chosen as a model bispidine bidentate ligand, that is explained by its synthetic availability, the presence of two functionalizable symmetrically placed N—H groups and a potential site for binding two bispidines, *viz.*, the carbonyl group at position 9. Ligand **1** was obtained from available reagents according to Scheme 3 (see Refs 68 and 69).

1,3-Diazaadamantan-6-one was synthesized according to the procedure described in the work,⁶⁸ only using an alternative method of purification instead of passing a hot solution through an alumina layer. Some activated carbon was added to the dark red oil formed after partial concentration of the reaction mixture and repeatedly washed it with hot *n*-heptane; a rapidly crystallizing compound was recrystallized from *n*-heptane several times. A key step of the synthesis is the 1,3-diazaadamantan-6-one ring opening with acetic anhydride. The mechanism of this reaction is similar to that described in the literature.^{25,70,71}

During different steps of purification of ligand **1**, we isolated different crystalline fractions, two of which were suit-

Scheme 3



able for X-ray diffraction studies: hydroacetate (**1**·HOAc) and monohydrate (**1**·H₂O) of bispidine **1** (Figs 1 and 2, respectively). It is obvious that the monoacetate is the product of an incomplete neutralization of the intermediate acetate (a direct product of the ring opening) with alkali. The formation of the monohydrate crystals took several months upon storage of one of the fractions of partially purified product in air, apparently, due to the atmospheric moisture.

Bond distances and bond angles in the structures **1**·HOAc and **1**·H₂O have the values common for organic compounds (Tables 1 and 2). In both products, bispidine has the double chair conformation with the *endo*-directed N—H bonds; in this case the N...N intramolecular distances (2.997(2) and 3.026(2) Å) and a mutual arrangement of these bonds should facilitate chelation of donor

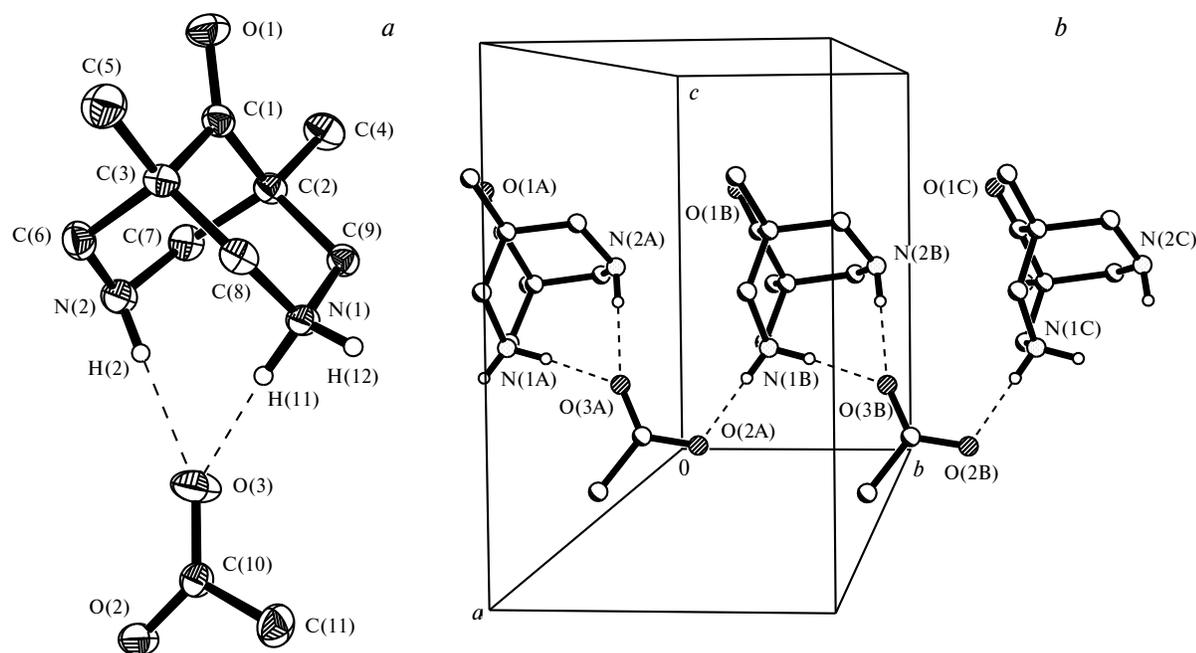


Fig. 1. The structure of the associate **1**·HOAc (*a*) and a fragment of the crystal packing of the hydroacetate (*b*) showing one-dimensional hydrogen-bonded chains in **1**·HOAc. Hydrogen atoms of all groups, except N—H, are not shown.

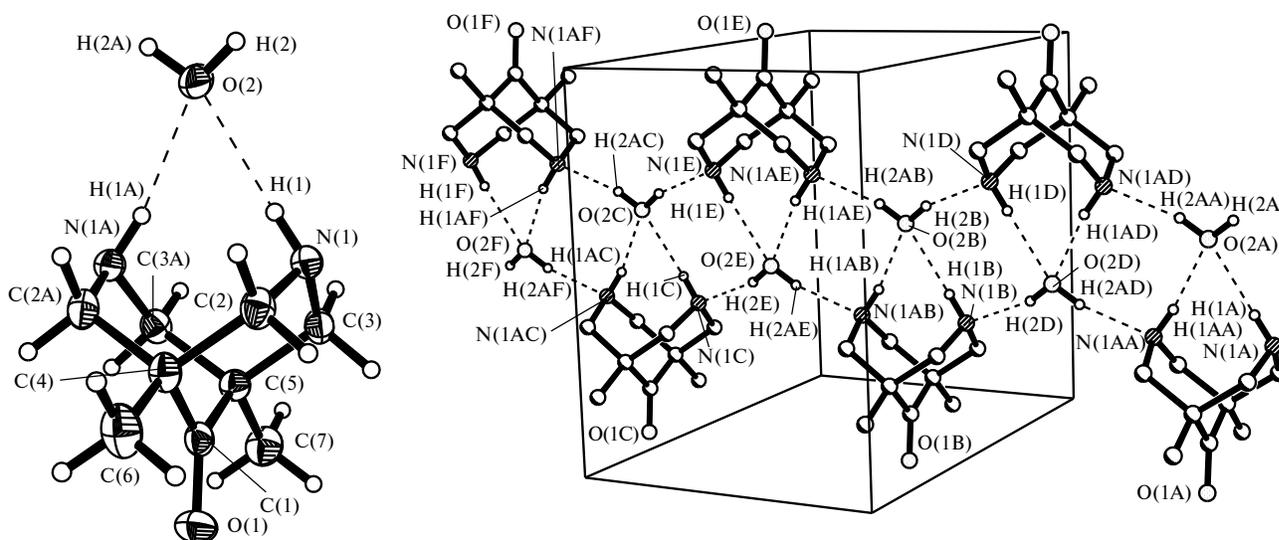


Fig. 2. The structure of the associate $1 \cdot \text{H}_2\text{O}$ (a) and a fragment of the crystal structure of the hydrate (b) demonstrating one-dimensional hydrogen-bonded chains in the associate. Hydrogen atoms of all groups, except N—H and H_2O , are not shown.

atoms. In fact, this pair of bonds in the structures $1 \cdot \text{HOAc}$ and $1 \cdot \text{H}_2\text{O}$ forms hydrogen bonds with one of the oxygen atoms of the acetate anion and the oxygen atom of the water molecule, respectively. In addition to two *endo*-oriented N—H bonds of the bispidine itself, the molecule of its acetate has an *exo*-oriented N—H bond, which is involved in intermolecular binding with another acetate anion. This results in the formation of an infinite chain of molecules $\{[1 \cdot \text{H}]^+ \text{OAc}^-\}_n$. Thus, the acetate anion behaves here as an acceptor of three hydrogen bonds, whereas the bispidine protonated at one of the nitrogen atoms behaves as a donor of three hydrogen bonds. The second nitrogen atom is not involved in hydrogen bonding.

The crystal of monohydrate consists of infinite hydrogen-bonded double chains (bands) made of repeating $1 \cdot \text{H}_2\text{O}$ fragments, which are formed by a hydrogen bond between the oxygen atom of the water molecule and two *endo*-oriented N—H bonds of bispidine. Both O—H bonds of water molecule uninvolved in such "intramolecular" binding and two lone pairs of electrons of both nitrogen atoms participate in the construction of the polymeric band. It is interesting that the chains similar to those observed in compounds $1 \cdot \text{HOAc}$ and $1 \cdot \text{H}_2\text{O}$ were found earlier in the structures of the halide salts of the parent bispidine $\text{C}_7\text{N}_2\text{H}_{14}$ (see Ref. 72).

Table 1. Parameters of hydrogen bonds in the structure $1 \cdot \text{HOAc}$

Bond D—H...A	$d/\text{Å}$			$\omega(\text{DHA})$ /deg
	(D—H)	(H...A)	(D...A)	
N(1)—H(11)...O(3)	0.94(2)	1.83(2)	2.764(2)	176(2)
N(2)—H(2)...O(3)	0.86(3)	2.00(3)	2.864(2)	178(2)
N(1)—H(12)...O(2)*	0.84(2)	1.82(2)	2.663(2)	180(3)

* Symmetric transformation: $x, y-1, z$.

Preparation of a number of complexes of ligand **1** with copper(II) (**2**), cobalt(II) (**3**), and nickel(II) (**4**) salts (namely, perchlorates, chlorides, bromides, nitrates, and trifluoroacetates of these metals) was the major synthetic problem of our work (Scheme 4).

All the complexes **2–4** (except specified cases) were obtained using the same procedure: reflux in ethanol solution of the ligand and the metal salt (crystal hydrate) taken in the molar ratio 2 : 1. A precipitate of the complex formed after cooling the reaction mixture was filtered and analyzed. The convenience of this simple approach consists in the fact that both the ligand and the metal salts are soluble in ethanol, which makes it possible to avoid heterogeneity of the reaction mixture at the beginning of the reaction.

The data on the complex compositions are given in Table 3.

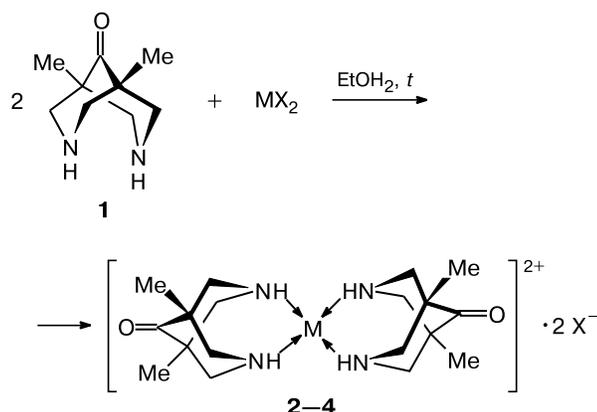
Note the absence of crystal solvents (ethanol, water) in the reaction products isolated and dried prior to elemental analysis. The given material shows that the most of compounds obtained have a desired ratio 2L : 1M. The products generally have the color expected for Cu(II), Co(II), and Ni(II) tetramine complexes. Exceptions are compounds **2b** (see discussion below), **2e**, and **3a**, for which the elemental analysis data do not correspond to the for-

Table 2. Parameters of hydrogen bonds in the structure $1 \cdot \text{H}_2\text{O}$

Bond D—H...A	$d/\text{Å}$			$\omega(\text{DHA})$ /deg
	(D—H)	(H...A)	(D...A)	
N(1)—H(1)...O(2)	0.863(15)	2.142(16)	2.9853(16)	165.5(12)
O(2)—H(2)...N(1)*	0.844(17)	2.013(17)	2.8329(12)	163.5(15)

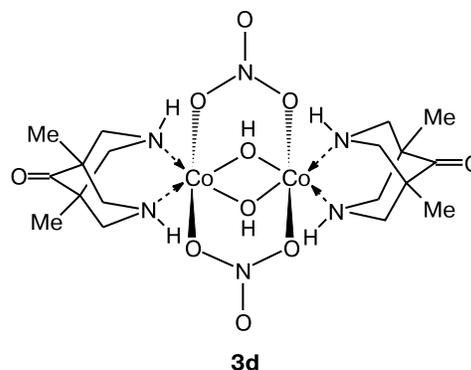
* Symmetric transformation: $-x+1, -y, -z+1$.

Scheme 4



M = Cu (**2**), Co (**3**), Ni (**4**); X = ClO₄ (**a**), Cl (**b**), Br (**c**), NO₃ (**d**), CF₃COO (**e**)

mula L₂MX₂. It should be especially noted that elemental analysis gives the formula [LCo(NO₃)(OH)] for the complex of ligand **1** with Co(NO₃)₂ (**3d**), that, probably, corresponds to a binuclear structure with bridging hydroxide and nitrate anions.

Table 3. Physicochemical properties and elemental composition of ligand **1** complexes

Com- pound	Metal	Anion	Found _____ (%) Calculated			Composition given by elemental analysis	M.p./°C	Color
			C	H	N			
2a^a	Cu	ClO ₄	<u>35.54</u> 36.10	<u>5.47</u> 5.39	<u>9.47</u> 9.35	L ₂ Cu(ClO ₄) ₂	— ^b	Pink
2b	Cu	Cl	<u>41.73</u> 45.91	<u>6.00</u> 6.80	<u>10.62</u> 11.90	— ^c	257 (decomp.)	Bright blue
2c^a	Cu	Br	<u>38.50</u> 38.61	<u>5.50</u> 5.72	<u>9.83</u> 10.01	L ₂ CuBr ₂	238 (decomp.)	Bluish violet
2d^a	Cu	NO ₃	<u>41.40</u> 41.26	<u>5.65</u> 6.11	<u>15.96</u> 16.05	L ₂ Cu(NO ₃) ₂	255 (decomp.)	Violet
2e	Cu	CF ₃ COO	<u>39.99</u> 42.21	<u>4.97</u> 5.12	<u>8.27</u> 8.95	— ^c	155 (decomp.)	Bluish violet
3a	Co	ClO ₄	<u>20.65</u> 36.38	<u>3.90</u> 5.43	<u>5.21</u> 9.43	— ^c	243 (decomp.)	Sand-yellow
3b^a	Co	Cl	<u>46.15</u> 46.35	<u>6.73</u> 6.87	<u>11.86</u> 12.02	L ₂ CuBr ₂	232 (turns blue), 320 (decomp.)	Dark pink
3c^a	Co	Br	<u>38.80</u> 38.92	<u>5.73</u> 5.77	<u>9.98</u> 10.09	2CoBr ₂	235 (turns blue), 294 (decomp.)	Shining dark pink
3d	Co	NO ₃	<u>35.47</u> 35.31	<u>5.93</u> 5.60	<u>13.55</u> 13.72	LCo(NO ₃)(OH)	227 (decomp.)	Brown
3e	Co	CF ₃ COO	— ^b	— ^b	— ^b	— ^c	— ^b	A mixture of brown and violet
4a^a	Ni	ClO ₄	<u>36.45</u> 36.39	<u>5.48</u> 5.43	<u>9.12</u> 9.43	L ₂ Ni(ClO ₄) ₂	— ^b	Light yellow
4b^a	Ni	Cl	<u>46.50</u> 46.35	<u>6.31</u> 6.87	<u>11.83</u> 12.02	L ₂ NiCl ₂	308 (decomp.)	Bright yellow
4c^a	Ni	Br	<u>38.74</u> 38.92	<u>5.78</u> 5.77	<u>9.89</u> 10.09	L ₂ NiBr ₂	>345 (after 300 brown)	Bright yellow
4d^a	Ni	NO ₃	<u>41.46</u> 41.64	<u>6.09</u> 6.21	<u>15.97</u> 16.19	L ₂ Ni(NO ₃) ₂	237 (decomp.)	Bright yellow
4e^a	Ni	CF ₃ COO	<u>42.76</u> 42.51	<u>5.34</u> 5.15	<u>9.11</u> 9.02	L ₂ Ni(CF ₃ COO) ₂	253 (decomp.)	Bright yellow

^a Complexes with the ratio ligand : metal 2 : 1 (elemental analysis data).

^b Was not determined.

^c The product is not uniform.

The color of all nickel complexes **4a–e** corresponds to the square-planar environment of the metal and the low-spin state. This is confirmed by NMR experiments with complexes **4a** and **4d** (see below).

X-ray diffraction and mass spectrometric studies of complexes. Single crystal of complex **1** with $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ suitable for X-ray diffraction studies was grown by recrystallization from water (Fig. 3, Table 4).

In the cation of complex **2d**, the metal can be considered as having a distorted square-planar coordination with the displacement of the copper atom from the plane of four nitrogens by 0.181(3) Å. The nitrate anion completes the coordination environment to the square pyramid. In the crystal **2d**, a complex three-dimensional net is observed, which is formed due to the hydrogen bonds of the type $\text{N}—\text{H}\dots\text{ONO}_2^-$, $\text{N}—\text{H}\dots\text{O}=\text{C}$, and $\text{HOH}\dots\text{ONO}_2^-$.

In the case of the complex with copper chloride(II), the X-ray diffraction analysis of the obtained crystals shows that this is a binuclear complex containing bridging chlorine atoms (**2b**·MeCN, Fig. 4, Table 5). The structure **2b** contains two centrosymmetric crystallographically independent molecules with close geometric parameters. The coordination polyhedron of the copper atom is a square pyramid, with two nitrogen atoms, one terminal, and one bridging chlorine atoms forming its base; the apical position is occupied by the second bridging Cl atom. In the ligand, the bond distances and bond angles correspond to the common values for organic compounds. Generally, the geometry of this compound is close to that found earlier for the binuclear complex of copper chloride with 1,5-dibromo-substituted bispidine.⁴²

Both complexes are characterized by the shorter average distances between the donor nitrogen atoms (2.715 Å for nitrate and 2.712 Å for chloride) as compared to the acetate **1**·HOAc and hydrate **1**·H₂O (2.997 and 3.026 Å, respectively).

It is interesting that during preparation of the complex of ligand **1** with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ by slow diffusion,

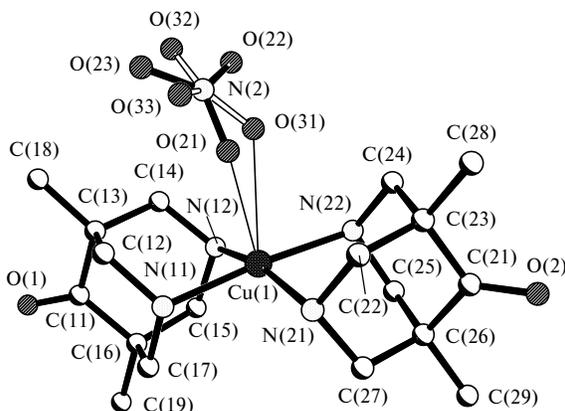


Fig. 3. The structure of complex **1** with $\text{Cu}(\text{NO}_3)_2$ (**2d**). The nitrate anion is rotationally disordered over two positions with the occupancy ratio 0.80 : 0.20.

Table 4. Selected bond distances (*d*) and bond angles (ω) in the structure **2d**·H₂O

Bond	<i>d</i> /Å	Angle	ω /deg
Cu(1)—N(11)	2.002(7)	N(11)—Cu(1)—N(22)	174.9(3)
Cu(1)—N(22)	2.017(6)	N(11)—Cu(1)—N(21)	93.9(2)
Cu(1)—N(21)	2.011(6)	N(22)—Cu(1)—N(21)	85.0(2)
Cu(1)—N(12)	2.021(6)	N(11)—Cu(1)—N(12)	84.6(2)
Cu(1)—O(21)	2.503(9)	N(22)—Cu(1)—N(12)	95.1(2)
Cu(1)—O(31)	2.57(3)	N(21)—Cu(1)—N(12)	164.5(3)

a small amount of the same green crystals of the binuclear chloride complex **2b**·MeCN was formed in the interface between the chloroform phase containing the ligand and the acetonitrile phase containing the metal (confirmed by X-ray diffraction studies). Besides, a few colorless crystals of the complex $\text{CuClO}_4 \cdot 4\text{MeCN}$ were also isolated. The formation of chloride complex can be explained by the presence of chloride ions as the products of the light-induced decomposition of chloroform. Copper(II) is apparently reduced through the oxidation of organic components (*cf.* data in Ref. 73).

The elemental analysis data for the major product of the reaction of **1** with CuCl_2 do not agree with the com-

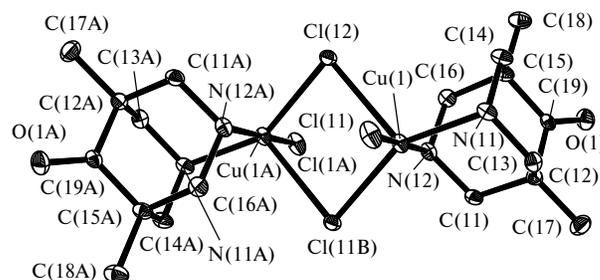
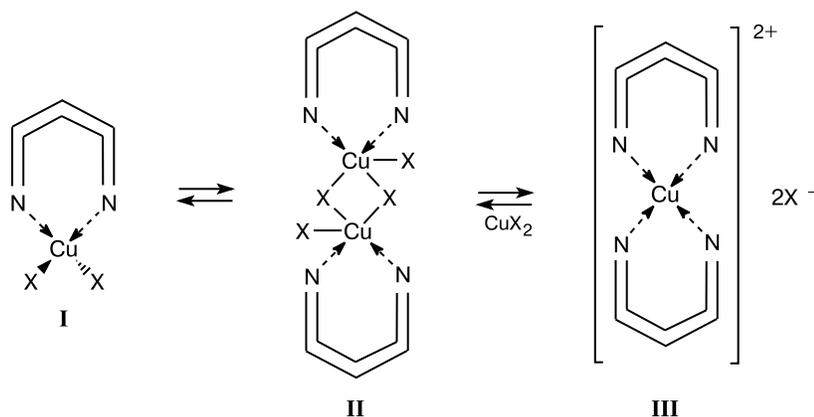


Fig. 4. The molecular structure of complex **1** with CuCl_2 (**2b**). Only one independent molecule is shown. Acetonitrile solvent molecules are not shown.

Table 5. Selected bond distances (*d*) and bond angles (ω) in the structure **2b**·MeCN

Parameter	Value	Parameter	Value
Bond	<i>d</i> /Å	Bond	<i>d</i> /Å
Cu(1)—N(11)	2.011(2)	Cu(2)...Cu(2)	3.3468(5)
Cu(1)—N(12)	2.028(2)	Angle	ω /deg
Cu(1)—Cl(11)	2.2790(6)	Cl(12)—Cu(1)—Cl(12)	95.63(2)
Cu(1)—Cl(12)	2.3585(6)	Cl(12)—Cu(1)—Cl(11)	93.33(2)
Cu(1)—Cl(12)	2.6105(6)	Cl(12)—Cu(1)—N(12)	89.97(6)
Cu(1)...Cu(1)	3.3421(5)	Cl(12)—Cu(1)—N(11)	89.97(6)
Cu(2)—N(22)	2.013(2)	Cl(12)—Cu(1)—N(11)	111.78(6)
Cu(2)—N(21)	2.031(2)	Cl(22)—Cu(2)—Cl(22)	96.23(2)
Cu(2)—Cl(21)	2.2505(6)	Cl(22)—Cu(2)—Cl(21)	95.71(2)
Cu(2)—Cl(22)	2.3408(6)	Cl(22)—Cu(2)—N(22)	94.03(6)
Cu(2)—Cl(22)	2.6595(6)	Cl(22)—Cu(2)—N(21)	101.57(6)

Scheme 5

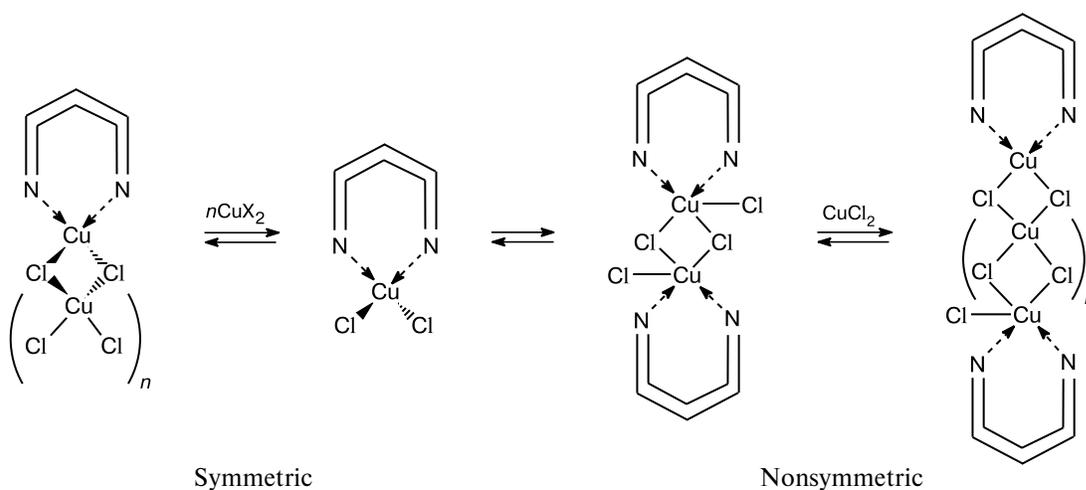
X = Cl, NO₃

position obtained for the single crystal by X-ray diffraction analysis, therefore, the major component of complex **2b** contains another compounds (see Table 3). In order to find out the nature of these products, we used ESI mass spectrometry to analyze solutions of complex **2b**, as well as solutions of ligand **1** with CuCl₂ in acetonitrile with an insufficient and excessive amount of the salt. It turned out that when the amount of the metal salt is insufficient, the peaks corresponding to the [LH]⁺ and [L₂CuCl]⁺ species have the maximum intensities; when the salt is in excess, the only peak is observed corresponding to the [L₂Cu₂Cl₃]⁺ species. Similar picture is also observed for solutions of the ligand with Cu(NO₃)₂. Moreover, the mass spectra of the acetonitrile solutions of 1,5-diphenyl analog of ligand **1** containing methyl groups at the nitrogen atoms in the presence of copper(II) chloride also exhibited the peaks of the complex [L₂Cu₂Cl₃]⁺, while the peaks of the complex [L₂Cu₃Cl₄]⁺ were detected when the concentration of the chloride was increased.

Based on the results of mass spectrometric studies, we suggest existence of the following equilibrium between species in solutions of bispidine ligands with CuCl₂ and Cu(NO₃)₂ (Scheme 5).

To confirm the hypothesis on the existence of several polynuclear species in the system **1**/CuCl₂, we attempted to synthesize a polynuclear copper complex. The reaction of ligand **1** with CuCl₂ in the ratio 1 : 4 in EtOH led to the yellowish orange complex **2b**^{*}, whose elemental analysis corresponded to the formula L·2CuCl₂. The ESI mass spectrum of this complex does not exhibit peaks with *m/z* 168 and 434 attributable to the species [LH]⁺ and [L₂CuCl]⁺, respectively, while the peak with *m/z* 787 is observed, which corresponds to the species [L₂Cu₃Cl₅(CH₃CN)₂]⁺. This means that several more polynuclear species of "symmetric" (with two ligands) and "nonsymmetric" (with one ligand) structure can exist in the equilibrium with the structures of the type **I** and **II** shown in Scheme 5. As a result, the equilibrium scheme becomes significantly more complicated (Scheme 6).

Scheme 6



Symmetric

Nonsymmetric

We believe that the synthesized polynuclear copper complex **2b*** is either symmetric with $n = 2$ or nonsymmetric with $n = 1$. It is difficult to distinguish these two forms in the solid state, whereas in solution they are interconvertible. According to the literature data,^{60,74} copper can form bi- or tetranuclear complexes, therefore, in our case a symmetric tetranuclear structure is more probable in the solid state. Similar changes in the nuclearity of complexes is observed for the products of the reaction of sparteine and copper(I) chloride taken in different ratios.⁷⁵

The ESI mass spectra of the acetonitrile solutions of all perchlorate complexes (**2a**, **3a**, **4a**) exhibit peaks corresponding to the species $[L_2M(ClO_4)]^+$ ($M = Cu, Co, Ni$) and $[LH]^+$.

Studies of the complexes by NMR spectroscopy. Elemental analysis data show that nickel complexes **4a–e** have the composition L_2MX_2 . All of them have yellow color. NMR spectra were recorded for complexes **4a** and **4d**. The 1H NMR spectra of solutions of complexes in DMSO- d_6 exhibit a doublet around δ 4.0 attributable to the equatorial protons of the ligand framework. The axial and equatorial protons in the 1H NMR spectra of nickel complexes, the starting ligand, and its precursors were assigned based on the literature data for similar com-

pounds. The signals for the axial protons overlap with the residual signal of the deuterated solvent ($\delta \sim 2.5$). The protons of the amino groups give a singlet at $\delta \sim 4.6$ with the intensities corresponding to two protons. The signals for the methyl groups at the bridgehead are also found as singlets at $\delta \sim 1.0$. In the 1H NMR spectrum of the solution of complex **4a** in DMF- d_7 , the signal for the axial protons also overlaps with the residual high-field signal of the deuterated solvent ($\delta \sim 2.8$). Its position was confirmed by the experiment with the selective homonuclear decoupling. In the ^{13}C spectrum in the same solvent, four signals are observed, which correspond to four types of carbon nuclei in the ligand framework (CH_3 , $\underline{C}CH_3$, CH_2 , and CO). The simple pattern of the spectra agrees with the fact that in the complexes both ligands occupy equivalent positions. The absence of broadening and the strong shift of the lines in the spectra indicate that complexes **4a** and **4d** in solution are diamagnetic and, therefore, have a square-planar geometry (the type **III**). No spectra were recorded for other nickel complexes because of their low solubility.

Studies of the complexes by Raman and IR spectroscopy. Absorption spectra of synthesized complexes **2–4** were studied using IR and Raman spectroscopy (Tables 6 and 7).

Table 6. The IR spectroscopic data of the synthesized complexes

Compound	Metal	Anion	IR, ν/cm^{-1}			
			NH	C=O	Anion	Other vibrations
1		Ligand	3350.3, 3315.2, 3170.4 (v.br)	1700.7	—	1447.6, 1382.9, 1210.6, 1122.7, 968.6, 909.0 (br), 823.8, 677.3 (v.br), 548.5
2a	Cu	ClO_4	3280.0 (s); 3183.3, 3112.7 (br, s)	1729.6	1147.5, 1110.0, 1090.5	1484.8, 1463.9, 1383.1, 1359.4, 911.8, 627.7
2b	Cu	Cl	3197.2, 3094.5	1727.2	—	1466.3, 1450.4, 1359.6, 913.3, 857.7
2c	Cu	Br	3182.8, 3109.8	1727.7	—	1464.8, 1358.1, 911.8
2d	Cu	NO_3	3182.8, 3110.3	1727.6	1385.0	1464.0, 1359.0, 1109.4, 1069.1, 944.1, 910.7, 855.1
2e	Cu	CF_3COO	3220.6, 3110.07	1730.9	1674.8 (br), 1203.2; 1171.4, 1126.8	1465.4, 1361.7, 910.3, 837.3, 830.2, 798.8, 721.3
3a	Co	ClO_4	3274.7 (s), 3110 (sh)	1730.2	1150.2, 1120.5, 1108.0, 1093.9	1483.9, 1467.6, 1359.9, 912.0, 626.9
3b	Co	Cl	3184.9, 3120.3	1727.5	—	1467.9, 1450.6, 1359.6, 912.2
3c	Co	Br	3168.6, 3108.4	1727.5	—	1464.2, 1358.1, 911.8
3d	Co	NO_3	3224.7	1727.2	1384.5	1465.6, 1359.8 (sh); 913.9
4a	Ni	ClO_4	3272.3 (s), 3124.3 (br, s)	1730.8	1155.3, 1097.7	1462.6, 914.1, 627.7, 604.0, 582.4
4b	Ni	Cl	3123.5, 3046.5	1730.0	—	1462.4, 1357.5, 1338.7, 1289.4, 946.1, 918.2 (o.s), 539.0
4c	Ni	Br	3146.4	1731.4	—	1463.3, 1355.5, 1335.9, 1288.7, 918.3
4d	Ni	NO_3	3227.2, 3190.6, 3128.5	1729.4	1386.3, 1358.6	1462.7, 917.7
4e	Ni	CF_3COO	3131.9	1740.1	1689.0 (br); 1676.2 (br), 1202.5, 1175.1, 1127.4	1460.7, 1288.0, 916.5, 830.6, 798.8, 720.0

Table 7. The Raman spectroscopic data of the synthesized complexes

Com- pound	Metal	Anion	Raman, ν/cm^{-1}			
			NH	C=O	Anion	Other vibrations
1	Ligand	—	—	1699.9	—	1459 (sh), 1450.8, 1177.6, 583.6, 329.4
2a	Cu	ClO_4	3283.0	1729.5	1161.3, 1087.2	1483.9, 1468.1, 939.8 (v.s), 627.2, 608.5, 342.4
2b	Cu	Cl	3199.3, 3089.6	1725.5	—	1474.1, 1458.7, 1446.4 (sh), 1227.2, 1213.4, 1151.4, 610.3, 445.1, 351.3
2c	Cu	Br	3181.8, 3108.4	1724.8	—	1471.5, 1459.3, 1145.9 (sh), 1212.1, 1148.7, 608.0, 444.9, 347.5
2e	Cu	CF_3COO	3210.9	1735.7	—	1484.5, 1471.2, 1462.7, 607.3, 445.6, 347.9
3a	Co	ClO_4	3274.5	1730.2	—	1463.2, 940.4 (v.s), 627.1, 609.7, 521.7, 348.1
3b	Co	Cl	3195.8, 3118.6	1727.5	—	1475.3, 1459.7, 1209.0, 605.3, 344.1
3c	Co	Br	3169.6, 3102.6	1724.9	—	1473.0, 1458.8, 608.4
3d	Co	NO_3	3221.9	1725.8	—	1487.4, 1470.0, 1045.7, 613.3, 453.8, 358.0
4a	Ni	ClO_4	3272.4	1721.0	—	1481.3, 1462.5, 937.9 (v.s), 627.2, 613.3, 348.1
4b	Ni	Cl	3045.9	1733.4	—	1479.1, 1468.4, 1445.1, 1370.5, 1308.9, 1250.6, 1173.8, 618.6 (v.s), 536.2, 491.5, 457.6, 350.3
4c	Ni	Br	3154.1	1728.4	—	1474.4, 1457.9, 1208.2, 618.1, 353.1
4d	Ni	NO_3	3226.7, 3197.1	1731.8	—	1487.4, 1470.0, 1045.7, 620.8, 536.3, 459.8; 358.0
4e	Ni	CF_3COO	3135.9	1743.5	—	1478.2, 1460.6, 1447.6, 1415.0 (v.s), 618.4, 534.7, 454.1, 351.1

As it is seen from Tables 6 and 7, the absorption band of the carbonyl group in the complexes is shifted toward higher wave numbers as compared to those in the ligand (from 1701 to 1727–1740 cm^{-1}). This is a general specific feature characteristic of the formation of the chelate complexes of bispidin-9-ones.⁴⁰

The IR spectra of all perchlorate complexes (**2a**, **3a**, **4a**) exhibit two and more bands in the region 1000 cm^{-1} . The ClO_4^- ion has only one band in this region,⁷⁶ therefore, the perchlorate anion in all the complexes is bound either with the metal or with the hydrogen atom of the NH group. The latter is more probable, since the IR spectra of the perchlorate complexes exhibit a sharp strong band at 3280–3272 cm^{-1} . All the perchlorates have absorption bands in the region 939 and 348 cm^{-1} . The spectra of the nickel and cobalt perchlorate complexes are virtually the same, though, the elemental analysis data gives for the cobalt derivative the formula other than $\text{ML}_2(\text{ClO}_4)_2$.

Also note almost ideal similarity of the IR spectra of the nickel and cobalt nitrate complexes, though, the elemental analysis data for the cobalt derivative do not correspond to the formula $\text{ML}_2(\text{NO}_3)_2$. All three nitrate complexes have three bands at 1045, 619, and 538 cm^{-1} in the Raman spectra.

The IR spectra of copper and cobalt chloride complexes are similar enough, whereas the nickel derivative has several additional bands. The same is true for the bromide complexes. All the halide complexes possess similar absorption in the IR spectra in the regions 600–620 and 350 cm^{-1} . The latter band is also present in the spectra of

two trifluoroacetates (for the Co complex, no spectra were recorded because of the clearly seen nonuniformity of the product).

Electron absorption spectroscopy of the synthesized complexes. Recording electron absorption spectra for most complexes was a complicated matter because of their low solubility even in DMF, therefore, further we report only the most reliable data. Absorption bands of the ligand lie beyond the range of the wavelengths studied (250–900 nm), therefore, all the bands observed are attributable to the complexes. The spectra of the copper complexes exhibit the charge transfer bands (below 350 nm) and the weak wide bands of the d-d-transitions around 550 nm, that indicates the absence of the center of symmetry in the molecule.⁷⁷ The spectra of the nickel complexes exhibit two charge transfer bands, one of which (~450 nm) is responsible for the yellow color of these complexes. There are no absorption bands at larger wavelengths, that indicates the centrosymmetric geometry of the molecules. In the electron absorption spectrum of polynuclear complex **2b***, the band of the d-d-transitions is shifted toward larger wavelengths as compared to the spectra of other copper complexes (**2a–e**).

Electrochemical studies. It is known that the data on oxidation and reduction potentials in a number of cases allow one to obtain additional information on the structure of complexes in solution. As it was already indicated, the information on the electrochemical behavior of copper complexes with bispidine ligands is scarce.^{34,64–67}

ical anions decreases in the following order of anions: Br^- , NO_3^- , ClO_4^- . The ratio of the cathode and anode peak heights (i_p^a/i_p^c), which characterizes stability of the radical anion, decreases to 0.45 for the complex with $\text{Cu}(\text{NO}_3)_2$ and a complete irreversibility in the case of complex with $\text{Cu}(\text{ClO}_4)_2$. As it is seen from Fig. 5 (curve 1), only a desorption peak of oxidation of Cu^0 ($E^{\text{Ox}} = -0.15$ V) is observed in the reverse anode branch of the reduction curve of the complex with $\text{Cu}(\text{ClO}_4)_2$. If behavior of all three complexes during reduction is similar, the anodic properties of the complex with CuBr_2 differ from those of complexes with $\text{Cu}(\text{NO}_3)_2$ and $\text{Cu}(\text{ClO}_4)_2$. For the last two complexes, the CVA data indicate that the first step of oxidation proceeds through the formation of the radical anion (oxidation in both cases is quasireversible), rather than through the step of the electron transfer from the copper–anion bond. It is seen from the data in Table 4 that in the order ligand **1**—complex with $\text{Cu}(\text{NO}_3)_2$ —complex with $\text{Cu}(\text{ClO}_4)_2$, reduction of the complexes is facilitated, whereas oxidation becomes more difficult, *i.e.*, the electron changes are localized on one site during reduction and oxidation processes. It is possible that these differences in electrochemical properties, especially in the anodic behavior, of complexes with the copper salts are due to the fact that, according to the data given above, the complex with CuBr_2 exists in solution in form **V**, whereas the complexes with nitrate and perchlorate, demonstrating similarities with each other, exist in form **III**. The fact that complex with $\text{Cu}(\text{NO}_3)_2$ in crystal belongs to the type **III** was confirmed based on the X-ray diffraction studies (see above).

Complexes **1** with CoCl_2 , NiBr_2 , and NiCl_2 (Fig. 6) demonstrate electrochemical uniformity (see Table 8). The complexes are irreversibly oxidized at a significant anodic potentials and are reduced in a single one-electron quasireversible wave, whose potential lies in the region of $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ ($\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$) transition (and approximately by 300 mV more cathodic than the peak of the free ligand

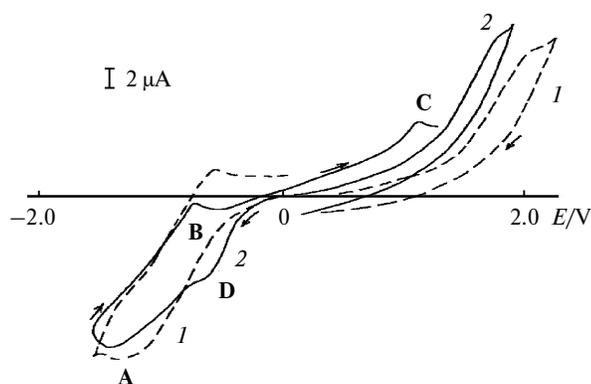


Fig. 6. The CVA curves of oxidation and reduction of complex **1** with CoCl_2 (**3b**) (1) and complex **1** with NiCl_2 (**4b**) (2) (concentration 10^{-3} M, Bu_4NBF_4 , $\text{Ag}/\text{AgCl}/\text{KCl}$ (sat.), 20°C , DMF).

reduction). As it is seen from Fig. 6, the oxidation peak of the free chloride ion (peak C ($E^{\text{Ox}} = 1.06$ V)) is registered in the reverse anodic scan of the CVA curve after reduction of NiCl_2 complex (peak A) together with the oxidation peak of the radical anion (peak B). It is possible that, in contrast to the radical anion of the copper complex, in the radical anions of the nickel and cobalt complexes electron density is mainly concentrated on the orbitals of the metal, rather than on the ligand orbitals.

In the case of NiCl_2 and CoCl_2 complexes, the absence of the oxidation peak for free chloride anion in the CVA curve indicates that chloride anion is bound with the metal atom and can emerge in the free form only from the reduced complex (see Fig. 6, peak C). In this case, the behavior of these complexes differs from that of the complex with CuBr_2 belonging to the type **V**. Therefore, these complexes correspond to the octahedral type **IV**, also having a metal–anion bond in the structure. In the case of complexes with NiCl_2 and NiBr_2 , the presence of the reduction peaks of -0.60 and -0.70 V, respectively, (see Fig. 6, peak D) close to the reduction peak of free ligand indicates that in their solutions the octahedral form **IV** can be transformed to the square-planar form **I** with the liberation of free ligand. Form **IV**, probably, is much more stable in the case of complex with CoCl_2 . This can be indicated, in particular, by the absence in the cathodic region of the reduction peak of the free ligand (peak D).

The electrochemical behavior of complex with CuCl_2 differs from the behavior of all the complexes considered above, however, we used mass spectrometry to confirm that it is composed by species of different composition. It cannot be excluded that the bridged structure found in the crystal by X-ray diffraction studies can be also retained in solution.

Out of other complexes, for which elemental analysis did not give an unambiguous formula, let us mention the complex with $\text{Co}(\text{ClO}_4)_2$ (**3a**). The peak of electrochemical reduction at -0.49 V observed in this case, probably, indicates the presence of the species formed by Co^{III} .

In conclusion, we synthesized a series of complex compounds of 1,5-dimethyl-3,7-diazabicyclo[3.3.1]nonan-9-one (**1**) with copper(II), nickel(II), and cobalt(II) chlorides, bromides, nitrates, trifluoroacetates, and perchlorates. The structure and composition of these complexes were established based on the combination of physicochemical analytical methods (elemental analysis, X-ray diffraction studies, NMR and IR spectroscopy, electron absorption spectroscopy, ESI mass spectrometry, CVA). The results obtained allowed us to determine which type belong to most of the synthesized complexes of ligand **1**. Binuclear complex with CuCl_2 belongs to the type **II**, complexes with $\text{Cu}(\text{NO}_3)_2$, $\text{Cu}(\text{ClO}_4)_2$, $\text{Ni}(\text{ClO}_4)_2$, and $\text{Ni}(\text{NO}_3)_2$ belong to the type **III**, NiCl_2 and NiBr_2 complexes and complex with CoCl_2 belong to the type **IV**, complexes with CuBr_2 belong to the type **V**. Complex with

CoBr₂ (**3c**) belongs to the type IV (tetragonal-bipyramidal environment, a typical color of the complexes is pink); complex with Ni(CF₃COO)₂ belongs to the type III (a typical color of the complexes is yellow). Other complexes, the products of the reactions with Cu(CF₃COO)₂ (**3e**), Co(ClO₄)₂ (**3a**), Co(CF₃COO)₂ (**3e**) cannot be specified by the indicated types based on the available data.

It was found that nickel(II) and copper(II) perchlorates and nitrates are the most promising complexation agents for the binding of two NH₂NH bispidine ligands in the coordination polymer. We also found specificities in the behavior of copper chloride complexes in solution at various salt—ligand ratios: an increase in the concentration of the salt leads to the shift of the equilibrium to the aide of species with larger nuclearity.

Experimental

Reagents and solvents were purified according to the standard procedures.^{78,79}

¹H and ¹³C NMR spectra were recorded on a Varian VXR-400 spectrometer at 27 °C (400 and 100 MHz, respectively), using TMS as an internal standard. IR spectra were recorded on Bruker-EQUINOX-55 and Bruker TENSOR-27 IR Fourier-transform spectrometers in the range of 4000–400 cm⁻¹ in KBr pellets (*d* = 3 mm). Raman spectra were recorded on a Bruker-EQUINOX-55 IR Fourier-transform spectrometer equipped with a FRA 160/S Raman appliance in the range of 3500–100 cm⁻¹ (in the Stokes region) and 2000–100 cm⁻¹ in the anti-Stokes region. It should be noted that the band intensities in the anti-Stokes region were considerably weaker. The power of the excitation laser (λ = 1064 nm) was 20–500 mW, the time of scanning was found experimentally. The resolution of the IR and Raman spectra was 4 cm⁻¹.

Electron absorption spectra were recorded on a Helios Alpha spectrometer (Thermo Electron, USA). Melting points were determined in unsealed capillary tubes on a heating block and were not corrected. Elemental analysis of compounds synthesized was performed on a Carlo-Erba CHN-analyzer. Electrochemical studies were performed on a PI-50-1.1 potentiostat with a programmer. Mass spectra were recorded on an Agilent 1100 Series LC/MSD Trapp SL mass spectrometer.

X-ray diffraction studies of crystals **1**·HOAc, **1**·H₂O, **2b**·MeCN, and **2d**·H₂O were performed using a MoK α -radiation (λ = 0.71073 Å, graphite monochromator). The structures were solved by direct method and refined by full-matrix least squares on *F*² with anisotropic thermal parameters for all the nonhydrogen atoms.⁸⁰ In the structure **1**·HOAc, all the hydrogens on carbon atoms were placed in the calculated positions and refined using a riding model, the hydrogen atoms of both amino groups were localized from the difference Fourier synthesis and refined isotropically. In compound **1**·H₂O, all the hydrogen atoms were found objectively from the difference Fourier synthesis and refined isotropically. In complex **2b**·MeCN, all the hydrogen atoms (except the methyl) were localized from the difference Fourier synthesis and refined isotropically, whereas positions of hydrogens on the Me groups were calculated geometrically and refined using a riding model. For compound **2d**·H₂O, all the hydrogen atoms were placed in the calculated

positions and refined using a riding model. In the structure **2d**·H₂O, one of the nitrate anions is rotationally disordered over two positions with the occupancy ratio 0.80 to 0.20. The results of structural studies are given in Table 9.

Crystallographic data for compounds **1**·HOAc, **1**·H₂O, **2b**·MeCN, and **2d**·H₂O were deposited with the Cambridge Structural Database (CCDC 930637–930640, respectively).

5,7-Dimethyl-1,3-diazaadamantan-6-one. A mixture of methanamine (25.00 g, 0.178 mol), diethyl ketone (18.87 mL, 15.36 g, 0.178 mol), glacial acetic acid (20.42 mL, 21.43 g, 0.357 mol), and *n*-butanol (100 mL) was refluxed for 2 h using a reflux condenser. Then, the dark red solution was concentrated on a rotary evaporator to 1/4 of its volume. After addition of some charcoal powder, the residue was extracted with hot *n*-heptane several times. A solidified compound was repeatedly recrystallized from *n*-heptane until snow-white needles of the product were obtained. The yield was 20.21 g, 63%, m.p. 124 °C (Ref. 68: 130–131 °C). ¹H NMR (CDCl₃), δ : 0.90 (s, 6 H, 2 Me); 3.06 (d, 4 H, H(4a), H(8a), H(9a), H(10a), ²*J*_{H,H} = 12.4 Hz); 3.30 (d, 4 H, H(4e), H(8e), H(9e), H(10e), ²*J*_{H,H} = 12.4 Hz); 4.14 (s, 2 H, NCH₂N).

3,7-Diacetyl-1,5-dimethyl-3,7-diazabicyclo[3.3.1]nonan-9-one. 5,7-Dimethyl-1,3-diazaadamantan-6-one (5.0 g, 28 mmol) was dissolved in acetic anhydride (50 mL, 54.09 g, 530 mmol) and refluxed for 10 h using a reflux condenser. After cooling, the solution was allowed to stand for 12 h in refrigerator. The crystals formed were filtered off, washed with water and diethyl ether. The mother liquor was concentrated to dryness, a yellow oil obtained was recrystallized from ethyl acetate. The crystals were filtered off, washed with ethyl acetate, and dried in air. The yield was 5.46 g (77%), m.p. 264–265 °C (Ref. 81: 264–265 °C). ¹H NMR (CDCl₃), δ : 1.05 (s, 6 H, 2 Me); 2.15 (s, 6 H, 2 MeC(O)); 2.76 (dd, 2 H, H(4a), H(6a)/H(8a), ²*J*_{H,H} = 13.8 Hz, ⁴*J*_{H,H} = 2.4 Hz); 3.28 (dd, 2 H, H(2a), H(8a)/H(6a), ²*J*_{H,H} = 13.3 Hz, *J* = 2.4 Hz); 4.08 (dd, 2 H, H(2e), H(8e)/H(6e), ²*J*_{H,H} = 13.3 Hz, ⁴*J*_{H,H} = 2.8 Hz); 5.05 (dd, 2 H, H(4e), H(6e)/H(8e), ²*J*_{H,H} = 13.8 Hz, ⁴*J*_{H,H} = 2.8 Hz).

1,5-Dimethyl-3,7-diazabicyclo[3.3.1]nonan-9-one (1). 3,7-Diacetyl-1,5-dimethyl-3,7-diazabicyclo[3.3.1]nonan-9-one (5.00 g, 20 mmol) was dissolved in 5*M* aqueous HCl and refluxed for 24 h using a reflux condenser. A precipitate of hydrochloride was filtered off, dissolved in some aqueous NaOH (pH 10), and extracted with chloroform. The mother liquor left after filtration was also treated with aqueous NaOH to pH 10 and extracted with chloroform. The combined organic phases were dried with Na₂SO₄ and concentrated to dryness. An oil obtained was recrystallized from ethyl acetate. The yield of compound **1** was 2.30 g (68%), m.p. 68–69 °C (Ref. 69: 66–68 °C). ¹H NMR (CDCl₃), δ : 0.83 (s, 6 H, 2 Me); 2.61 (s, 2 H, 2 NH); 2.90 (d, 4 H, H(2a), H(4a), H(6a), H(8a), ²*J*_{H,H} = 12.0 Hz); 3.31 (d, 4 H, H(2e), H(4e), H(6e), H(8e), ²*J*_{H,H} = 12.0 Hz). ¹³C NMR (CDCl₃), δ : 17.20 (s, 2 Me); 49.36 (s, 2 CMe); 61.80 (s, 4 CH₂); 215.39 (s, C=O). IR (KBr), ν /cm⁻¹: 3350.27, 3315.17 (NH); 1700.74 (C=O).

Complexes of 1,5-dimethyl-3,7-diazabicyclo[3.3.1]nonan-9-one (1) (general procedure). An ethanolic solution of the metal salt hydrate in the molar ratio ligand : metal = 2 : 1 (0.2 mmol) was added to a solution of the ligand (67 mg, 0.4 mmol) in EtOH. The mixture was refluxed for 2 h using a reflux condenser. After cooling, the solution was allowed to stand at 4 °C. A precipitate formed was filtered off, washed with ethanol, and dried.

Table 9. The data of X-ray diffraction studies of crystals **1**·HOAc, **1**·H₂O, **2b**·MeCN, and **2d**·H₂O

Compound	1 ·HOAc	1 ·H ₂ O	2b ·MeCN	2d ·H ₂ O
Molecular formula	C ₁₁ H ₂₀ N ₂ O ₃	C ₉ H ₁₈ N ₂ O ₂	C ₂₀ H ₃₅ C ₁₄ Cu ₂ N ₅ O ₂	C ₁₈ H ₃₄ CuN ₆ O ₉
Molecular weight	228.29	186.25	646.41	542.05
Crystal size/mm	0.40×0.20×0.04	0.30×0.20×0.15	0.40×0.20×0.10	0.20×0.10×0.10
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	<i>Pna</i> 2 ₁	<i>Pnma</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	21.670(5)	10.256(2)	7.6879(2)	7.413(4)
<i>b</i> /Å	5.7871(13)	8.0948(17)	12.5863(4)	14.945(7)
<i>c</i> /Å	9.414(2)	12.141(3)	14.0491(4)	20.499(7)
α /deg	90	90	79.795(1)	90
β /deg	90	90	87.895(1)	95.11(4)
γ /deg	90	90	73.737(1)	90
<i>V</i> /Å ³	1180.5(5)	1008.0(4)	1284.26(6)	2262.0(18)
<i>Z</i>	4	4	2	4
<i>d</i> _{calc} /g cm ⁻³	1.284	1.227	1.672	1.592
μ /mm ⁻¹	0.093	0.087	2.100	1.029
<i>F</i> (000)	496	408	664	1140
Diffractionmeter	Bruker SMART APEX II	Bruker SMART APEX II	Bruker SMART 1K	Enraf-Nonius CAD4
Temperature/K	150(2)	150(2)	110(2)	295(2)
θ range/deg	1.88–28.33	2.60–27.99	2.05–27.00	2.42–24.97
Number of measured reflections	11423	8082	9711	7249
Number of independent reflections (<i>R</i> _{int})	1562 (0.0386)	1297 (0.0331)	5529 (0.0235)	3962 (0.1379)
Number of reflections with <i>I</i> ≥ 2σ(<i>I</i>)	1389	1072	4791	1544
Number of variables	160	108	383	339
<i>R</i> ₁ (for reflections with <i>I</i> ≥ 2σ(<i>I</i>))	0.0315	0.0385	0.0302	0.0657
<i>wR</i> ₂ (on all the reflections)	0.0817	0.1113	0.0804	0.1666
GOOF on <i>F</i> ²	1.037	1.078	1.054	0.934
Residual electron density (max/min)/e Å ⁻³	0.243/−0.138	0.345/−0.159	0.561/−0.571	0.562/−0.654

Complex of compound 1 with Cu(ClO₄)₂ (2a) was obtained using the hydrate Cu(ClO₄)₂·6H₂O as a pink powder (m.p. was not measured). The yield was 120 mg (95%). Found (%): C, 35.54; H, 5.47; N, 9.47. C₁₈H₃₂Cl₂CuN₄O₁₀. Calculated (%): C, 36.10; H, 5.39; N, 9.35. IR (KBr), ν /cm⁻¹: 3279.95, 3183.29, 3112.65 (NH); 1729.62 (C=O); 1147.54, 1110.04, 1090.47 (ClO₄). ESR (DMF), λ_{\max} /nm: 284, 450–730 (br, w).

Complex of compound 1 with CuCl₂ (2b) was obtained using the hydrate CuCl₂·2H₂O as a bright blue powder, m.p. 257 °C (decomp.), the yield was 80 mg. Found (%): C, 41.73; H, 6.00; N, 10.62. C₁₈H₃₂Cl₂CuN₄O₂. Calculated (%), for the formula [Cu(1)₂Cl₂]: C, 45.91; H, 6.80; N, 11.90. IR (KBr), ν /cm⁻¹: 3197.16, 3094.47 (NH); 1727.23 (C=O). ESR (DMF), λ_{\max} /nm: 273, 284 (sh).

Complex of compound 1 with CuBr₂ (2c) was obtained using the hydrate CuBr₂·2H₂O as a bluish violet powder, m.p. 238 °C (decomp.), the yield was 76 mg (68%). Found (%): C, 38.50; H, 5.50; N, 9.83. C₁₈H₃₂Br₂CuN₄O₂. Calculated (%): C, 38.61; H, 5.72; N, 10.01. IR (KBr), ν /cm⁻¹: 3182.79, 3109.84 (NH); 1727.66 (C=O). ESR (DMF), λ_{\max} /nm: 272, 482–750 (br, w).

Complex of compound 1 with Cu(NO₃)₂ (2d) was obtained using the hydrate Cu(NO₃)₂·3H₂O as a violet powder, m.p. 255 °C (decomp.). The yield was 53 mg (51%). Found (%): C, 41.40;

H, 5.65; N, 15.96. C₁₈H₃₂CuN₆O₈. Calculated (%): C, 41.26; H, 6.11; N, 16.05. IR (KBr), ν /cm⁻¹: 3182.76, 3110.34 (NH); 1727.59 (C=O); 1388.05, 1360.49 (NO₃). ESR (DMF), λ_{\max} /nm: 288, 450–750 (br, w).

Complex compounds 1 with Cu(CF₃COO)₂ (2e) was obtained using the hydrate Cu(CF₃COO)₂·4H₂O as a bluish violet powder, m.p. 155 °C (decomp.), the yield was 62 mg. Found (%): C, 39.99; H, 4.97; N, 8.27. C₂₂H₃₂CuF₆N₄O₆. Calculated (%), for the formula [Cu(1)₂(CF₃COO)₂]: C, 42.21; H, 5.12; N, 8.95. IR (KBr), ν /cm⁻¹: 3220.60, 3110.07 (NH); 1730.91 (C=O); 1674.75 (C=O in CF₃COO); 1436.37; 1403.17; 1385.16; 1362; 1202.44; 1171.55; 1125.23 (C–F). ESR (DMF), λ_{\max} /nm: 284, 485–770 (br, w).

Complex of compound 1 with Co(ClO₄)₂ (3a) was obtained using the hydrate Co(ClO₄)₂·6H₂O as a sand-yellow powder, m.p. 243 °C (decomp.), the yield was 33 mg. Found (%): C, 20.65; H, 3.90; N, 5.21. C₁₈H₃₂Cl₂CoN₄O₁₀. Calculated (%), for the formula [Co(1)₂(ClO₄)₂]: C, 36.38; H, 5.43; N, 9.43. IR (KBr), ν /cm⁻¹: 3274.67 (NH); 1730.24 (C=O); 1150.21, 1120.51, 1108.00, 1093.93 (ClO₄).

Complex of compound 1 with CoCl₂ (3b) was obtained using the hydrate CoCl₂·6H₂O as a dirty pink powder, m.p. 320 °C (decomp.), the yield was 67 mg (72%). Found (%): C, 46.15;

H, 6.73; N, 11.86. $C_{18}H_{32}Cl_2CoN_4O_2$. Calculated (%): C, 46.35; H, 6.87; N, 12.02. IR (KBr), ν/cm^{-1} : 3184.91, 3120.26 (NH); 1727.46 (C=O).

Complex of compound 1 with $CoBr_2$ (3c) was obtained using the hydrate $CoBr_2 \cdot 6H_2O$ as a shining dark pink powder, m.p. 294 °C (decomp.). The yield was 78 mg (70%). Found (%): C, 38.80; H, 5.73; N, 9.98. $C_{18}H_{32}Br_2CoN_4O_2$. Calculated (%): C, 38.92; H, 5.77; N, 10.09. IR (KBr), ν/cm^{-1} : 3168.58, 3108.43 (NH); 1727.51 (C=O).

Complex of compound 1 with $Co(NO_3)_2$ (3d) was obtained using the hydrate $Co(NO_3)_2 \cdot 6H_2O$ as a brown powder, m.p. 227 °C (decomp.), the yield was 34 mg (56%) calculated on the formula $[Co(1)(NO_3)(OH)]$. Found (%): C, 35.47; H, 5.93; N, 13.55. $C_9H_{17}CoN_3O_5$. Calculated (%), calculated for the formula $[Co(1)(NO_3)(OH)]$: C, 35.29; H, 5.56; N, 13.73. IR (KBr), ν/cm^{-1} : 3224.69 (NH); 1727.21 (C=O); 1384.52 (NO_3).

Complex of compound 1 with $Co(CF_3COO)_2$ (3e) was obtained using the hydrate $Co(CF_3COO)_2 \cdot 4H_2O$ as a mixture of brown and violet precipitates.

Complex of compound 1 with $Ni(ClO_4)_2$ (4a) was obtained by the slow diffusion method, the amount and the ratio of reagents was the same as in the preceding experiments. A layer of acetonitrile was added carefully by a thin stream using a pipette to a solution of the ligand in chloroform. A solution of $Ni(ClO_4)_2 \cdot 6H_2O$ in acetonitrile was added similarly to the two-phase system obtained. The complex was obtained as a light yellow powder (m.p. was not determined). The yield was 110 mg (93%). 1H NMR (DMSO- d_6), δ : 0.95 (s, 6 H, 2 Me); 2.50–2.60 (H(2a), H(4a), H(6a), H(8a), overlaps with the signal of the solvent); 3.98 (d, 4 H, H(2e), H(4e), H(6e), H(8e), $J = 10.8$ Hz); 4.55 (br.s, 2 H, 2 NH). 1H NMR (DMF- d_7), δ : 1.00 (s, 6 H, 2 Me); 2.76 (H(2a), H(4a), H(6a), H(8a), overlaps with the high-field signal of the solvent); 4.37 (d, 4 H, H(2e), H(4e), H(6e), H(8e), $^2J_{H,H} = 12.8$ Hz); 4.81 (br.s, 2 H, 2 NH). ^{13}C (DMF- d_7), δ : 16.33 (Me); 45.47 (CMe); 58.11 (CH_2); 209.35 (C=O). Found (%): C, 36.45; H, 5.48; N, 9.12. $C_{18}H_{32}Cl_2N_4NiO_{10}$. Calculated (%): C, 36.39; H, 5.43; N, 9.43. IR (KBr), ν/cm^{-1} : 3272.33, 3124.34 (NH); 1730.79 (C=O); 1155.28, 1097.73 (ClO_4). ESR (DMF), λ_{max}/nm : 268, 407 (sh), 439 (br).

Complex of compound 1 with $NiCl_2$ (4b) was obtained using the hydrate $NiCl_2 \cdot 6H_2O$ as a bright yellow powder, m.p. 308 °C (decomp.), the yield was 64 mg (69%). Found (%): C, 46.50; H, 6.31; N, 11.83. $C_{18}H_{32}Cl_2N_4NiO_2$. Calculated (%): C, 46.35; H, 6.87; N, 12.02. IR (KBr), ν/cm^{-1} : 3123.53, 3046.47 (NH); 1729.97 (C=O). ESR (DMF), λ_{max}/nm : 403 (w), 440 (w).

Complex of compound 1 with $NiBr_2$ (4c) was obtained using the hydrate $NiBr_2 \cdot 2H_2O$ as a light yellow powder, m.p. >345 °C (decomp.), the yield was 87 mg (78%). Found (%): C, 38.74; H, 5.78; N, 9.89. $C_{18}H_{32}Br_2N_4NiO_2$. Calculated (%): C, 38.92; H, 5.77; N, 10.09. IR (KBr), ν/cm^{-1} : 3146.43 (NH); 1731.42 (C=O). ESR (DMF), λ_{max}/nm : 283, 440 (br).

Complex of compound 1 with $Ni(NO_3)_2$ (4d) was obtained using the hydrate $Ni(NO_3)_2 \cdot 6H_2O$ as a light yellow powder, m.p. 237 °C (decomp.), the yield was 78 mg (75%). 1H NMR (DMSO- d_6), δ : 0.94 (s, 6 H, 2 Me); 2.50–2.60 (H(2a), H(4a), H(6a), H(8a), overlaps with the signal of the solvent); 4.01 (d, 4 H, H(2e), H(4e), H(6e), H(8e), $^2J_{H,H} = 12.8$ Hz); 4.56 (br.s, 2 H, 2 NH). Found (%): C, 41.46; H, 6.09; N, 15.97. $C_{18}H_{32}N_6NiO_8$. Calculated (%): C, 41.64; H, 6.21; N, 16.19. IR (KBr), ν/cm^{-1} : 3227.19, 3190.64, 3128.51 (NH); 1729.40 (C=O);

1386.25, 1358.6, 1293.55 (NO_3). ESR (DMF), λ_{max}/nm : 270, 337, 398 (w, bend).

Complex of compound 1 with $Ni(CF_3COO)_2$ (4e) was obtained using the hydrate $Ni(CF_3COO)_2 \cdot 4H_2O$ as a bright yellow powder, m.p. 253 °C (decomp.), the yield was 80 mg (64%). Found (%): C, 42.76; H, 5.34; N, 9.11. $C_{22}H_{32}F_6N_4NiO_6$. Calculated (%): C, 42.51; H, 5.15; N, 9.02. IR (KBr), ν/cm^{-1} : 3131.85 (NH); 1740.12 (C=O); 1689.02, 1676.24 (C=O in CF_3COO); 1415.49; 1383.75; 1371.66; 1361.08; 1201.95; 1174.8; 1126.89 (C—F). ESR (DMF), λ_{max}/nm : 271, 440 (br).

Complex of compound 1 with excess $CuCl_2$ (1b*). An alcoholic solution of $CuCl_2 \cdot 2H_2O$ was added to a solution of the ligand in EtOH in the molar ratio ligand : metal = 1 : 4 and the mixture was refluxed for 2 h with a reflux condenser. After cooling, the solution was allowed to stand at 4°C. A dark orange precipitate formed was filtered off, washed with ethanol and some diethyl ether, and dried. M.p. 245–250 °C (decomp.), the yield was 104 mg (57%). Found (%): C, 24.96; H, 3.79; N, 6.06. $C_9H_{16}N_2OCu_2Cl_4$. Calculated (%): C, 24.73; H, 3.69; N, 6.41. ESR (DMF), λ_{max}/nm : 278, 319 (w, sh), 370 (sh), 433 (sh); 660, 800, 860 (all br. with shoulder).

References

1. J.-M. Lehn, *Supramolecular Chemistry. Concepts and Perspectives*, Wiley, 1995, 271.
2. J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, Wiley, 2005, 1002.
3. S. Z. Vatsadze, *Aktual'nye problemy khimii koordinatsionnykh polimerov. Uspekhi sinteza ekzo-dentatnykh tektonov [Comprehensive Problems of Chemistry of Coordination Polymers. Success in the Synthesis of exo-Dentate Tectones]*, Academic Publishing, 2011. 276 pp. (in Russian).
4. *Supramolecular polymers*, Ed. Ciferri, CRC Press Taylor & Francis Group, 2005.
5. T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* 2009, **109**, 5687.
6. G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
7. S. R. Batten, S. M. Neville, D. R. Turner, *Coordination Polymers — Design, Analysis and Application*, RSC, 2008.
8. *Design and Construction of Coordination Polymers*, Ed. M.-C. Hong, L. Chen, John Wiley & Sons, Inc., Hoboken, New Jersey, 2009.
9. *Functional Metal-Organic Frameworks Gas Storage, Separation and Catalysis*, Ed. M. Schröder, Springer-Verlag, Berlin—Heidelberg, 2010.
10. *Metal-organic frameworks. Design and Application*, Ed. L. R. Macgillivray, John Wiley & Sons, Inc., Hoboken, New Jersey, 2010.
11. *Metal-Organic Frameworks. Applications from Catalysis to Gas Storage*, Wiley-VCH Verlag & Co. KGaA, Weinheim, 2011.
12. C. Janiak, *Dalton Trans.*, 2003, 2781.
13. F. Fages, *Angew. Chem., Int. Ed. Engl.*, 2006, **45**, 1680.
14. M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke, J. W. Steed, *Chem. Rev.*, 2010, **110**, 1960.
15. *Handbook of Stimuli-Responsive Materials*, Ed. M. W. Urban, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2011.
16. R. Yerushalmi, A. Scherz, M. E. van der Boom, H.-B. Kraatz, *J. Mater. Chem.*, 2005, **15**, 4480.

17. Y. Zhao, J. B. Beck, S. J. Rowan, A. M. Jamieson, *Macromolecules*, 2004, **37**, 3529.
18. C. Dammer, P. Maldivi, P. Terech, J.-M. Guenet, *Langmuir*, 1995, **11**, 1500.
19. P. Terech, R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133.
20. *Low Molecular Weight Gelators*, Eds F. Fages, Springer-Verlag, Berlin—Heidelberg, 2005.
21. N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.*, 2005, **34**, 821.
22. *Molecular Gels. Materials with Self-Assembled Fibrillar Networks*, Eds R. G. Weiss, P. Terech, Springer, 2006.
23. D. K. Smith, *Molecular Gels – Nanostructured Soft Materials*, in *Organic Nanostructures*, Eds J. L. Atwood, J. W. Steed, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008.
24. J. W. Steed, *Chem. Soc. Rev.*, 2010, **39**, 3686.
25. S. Z. Vatsadze, V. S. Semashko, M. A. Manaenkova, N. V. Zyk, *Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 1555 [*Izv. Akad. Nauk, Ser. Khim.*, 2007, 1496].
26. K. Born, P. Comba, A. Daubinet, A. Fuchs, H. Wadepohl, *J. Biol. Inorg. Chem.*, 2007, **12**, 36.
27. J. Islam, M. Miller, E. J. Gordner, J. S. Patel, D. Wang, *Tetrahedron Lett.*, 2013, 2133.
28. N. S. Zefirov, *Usp. Khim.*, 1975, **44**, 413 [*Russ. Chem. Rev. (Engl. Transl.)*, 1975, **44**].
29. R. Jeyaraman, S. Avila, *Chem. Rev.*, 1981, **81**, 149.
30. N. S. Zefirov, V. A. Palyulin, *Topics in Stereochemistry*, 1991, **20**, 171.
31. S. Weidmann, *Ann. Rev. Physiology*, 1993, **55**, 1.
32. P. Comba, M. Kerscher, W. Schiek, *Bispidine Coordination Chemistry*, in *Progress in Inorganic Chemistry*, Wiley, 2007.
33. P. Comba, M. Kerscher, *Tuning of Structures and Properties of Bispidine Complexes*, in *Activating Unreactive Substrates: The Role of Secondary Interactions*, Eds C. Bolm, F. E. Hahn, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2009, 53 pp.
34. S. Z. Vatsadze, V. S. Tyurin, N. V. Zyk, A. V. Churakov, L. G. Kuz'mina, E. V. Avtomonov, R. D. Rakhimov, K. P. Butin, *Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1825 [*Izv. Acad. Nauk, Ser. Khim.*, 2005, 1773].
35. P. Comba, M. Kerscher, *Crystal Eng. Commun.*, 2003, **6**, 197.
36. O. I. Levina, K. A. Potekhin, E. N. Kurkutova, Yu. T. Struchkov, O. N. Zefirova, V. A. Palyulin, N. S. Zefirov, *Dokl. Akad. Nauk SSSR*, 1986, **289**, 876 [*Dokl. Chem. (Engl. Transl.)*, 1986, **289**].
37. S. V. Emets, N. I. Kurto, V. A. Palyulin, N. S. Zefirov, K. A. Potekhin, A. E. Lysov, *Vestn. MGU, Ser. 2, Khimiya [MSU Bull., Ser. 2, Chemistry]*, 2001, **42**, 390.
38. V. A. Palyulin, Ph.D. Thesis (Chem.), M. V. Lomonosov Moscow State University, Moscow, 1985, 139 pp. (in Russian).
39. S. Z. Vatsadze, N. V. Zyk, A. V. Churakov, L. G. Kuz'mina, *Chem. Heterocycl. Compd. (Engl. Transl.)*, 2000, 1266 [*Khim. Geterotsikl. Soedin.*, 2000, 1266].
40. S. Z. Vatsadze, V. K. Bel'skii, S. E. Sosonyuk, N. V. Zyk, N. S. Zefirov, *Chem. Heterocycl. Compd.*, 1997, 300 [*Khim. Geterotsikl. Soedin.*, 1997, 356].
41. V. A. Palyulin, S. V. Emets, K. A. Potekhin, A. E. Lysov, Yu. G. Sumskaia, N. S. Zefirov, *Dokl. Akad. Nauk*, 2001, **381**, 789 [*Dokl. Chem. (Engl. Transl.)*, 2000, **381**].
42. V. A. Palyulin, O. M. Grek, S. V. Emets, K. A. Potekhin, A. E. Lysov, N. S. Zefirov, *Dokl. Akad. Nauk*, 2000, **374**, 634 [*Dokl. Chem. (Engl. Transl.)*, 2000, **374**].
43. H. Stetter, R. Merten, *Chem. Ber.*, 1957, **90**, 868.
44. H. Stetter, J. Schäfer, K. Dieminger, *Chem. Ber.*, 1958, **91**, 598.
45. J. E. Douglass, T. B. Ratliff, *J. Org. Chem.*, 1968, **33**, 355.
46. D. St. C. Black, G. B. Deacon, M. Rose, *Tetrahedron*, 1995, 2055.
47. G. Lesma, C. Cattenati, T. Pilati, A. Sacchetti, *Tetrahedron*, 2007, 659.
48. P. Comba, C. Lang, C. Lopez de Laorden, A. Muruganatham, G. Rajaraman, H. Wadepohl, M. Zajackowski, *Chem. Eur. J.*, 2008, **14**, 5313.
49. J. Liu, Z. Yang, Z. Wang, F. Wang, X. Chen, X. Liu, X. Feng, Z. Su, C. Hu, *Synfacts*, 2008, 0647.
50. H. Maheswaran, K. Leon Prasanth, G. Gopi Krishna, K. Ravikumar, B. Sridhar, M. Lakshmi Kantam, *Chem. Commun.*, 2006, 4066.
51. J. Liu, Z. Yang, X. Liu, Z. Wang, Y. Liu, S. Bai, L. Lin, X. Feng, *Org. Biomol. Chem.*, 2009, **7**, 4120.
52. G. Lesma, B. Danieli, D. Passarella, A. Sacchetti, A. Silvani, *Tetrahedron: Asymmetry*, 2003, **14**, 2453.
53. J. Spieler, O. Huttenloch, H. Waldmann, *Eur. J. Org. Chem.*, 2000, 391.
54. M. Breuning, M. Steiner, C. Mehler, A. Paasche, D. Hein, *J. Org. Chem.*, 2009, **74**, 1407.
55. M. Haberberger, C. I. Someya, A. Company, E. Irran, S. Enthaler, *Catal. Lett.*, 2012, **142**, 557.
56. J. P. Collman, M. Zhong, C. Zhang, S. Costanzo, *J. Org. Chem.*, 2001, **66**, 7892.
57. J. A. Mueller, M. S. Sigman, *J. Am. Chem. Soc.*, 2003, **125**, 7005.
58. J. T. Bagdanoff, B. M. Stoltz, *Angew. Chem., Int. Ed. Engl.*, 2004, **43**, 353.
59. M. Breuning, M. Steiner, *Synthesis*, 2008, **18**, 2841.
60. *Comprehensive Coordination Chemistry*, Ed. G. Wilkinson, Pergamon Books Ltd., 1987.
61. M. R. Rosenthal, *J. Chem. Educ.*, 1973, **50**, 331.
62. S. Z. Vatsadze, N. V. Zyk, R. D. Rakhimov, K. P. Butin, N. S. Zefirov, *Russ. Chem. Bull. (Engl. Transl.)*, 1995, **44**, 440 [*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1995, 456].
63. S.-N. Choi, J.-H. Park, Y.-I. Kim; Y.-B. Shim, *Bull. Korean Chem. Soc.*, 1991, **12**, 276.
64. Y.-M. Lee, Y.-K. Kim, H.-C. Jung, Y.-I. Kim, S.-N. Choi, *Bull. Korean Chem. Soc.*, 2002, **23**, 412.
65. S.-N. Choi, W.-S. Jung, M.-J. Lee, Y.-M. Lee, Y.-I. Kim, *Polyhedron*, 2004, **23**, 2111.
66. H. Börzel, P. Comba, K. S. Hagen, C. Katsichtis, H. Pritzkow, *Chem. Eur. J.*, 2000, **6**, 914.
67. P. Comba, S. Hunoldt, M. Morgen, J. Pietzsch, H. Stephan, H. Wadepohl, *Inorg. Chem.*, 2013, **52**, 8131.
68. A. I. Kuznetsov, E. B. Basargin, A. S. Moskovkin, M. Kh. Ba, I. V. Miroshnichenko, M. Ya. Botnikov, B. V. Unkovskii, *Khim. Geterotsikl. Soedin.*, 1985, 1679 [*Chem. Heterocycl. Compd. (Engl. Transl.)*, 1985].
69. G. G. Minasyan, Ts. E. Agadzhanian, G. G. Adamyan, *Khim. Geterotsikl. Soedin.*, 1994, 106 [*Chem. Heterocycl. Compd. (Engl. Transl.)*, 1994].
70. S. Z. Vatsadze, V. S. Tyurin, A. I. Zatsman, M. A. Manaenkova, V. S. Semashko, D. P. Krut'ko, N. V. Zyk, A. V. Churakov, L. G. Kuz'mina, *Russ. J. Org. Chem. (Engl. Transl.)*, 2006, **42**, 1225 [*Zh. Org. Khim.*, 2006, **42**, 8, 1244—1249].

71. V. S. Semashko, S. Z. Vatsadze, N. V. Zyk, I. A. Godovikov, *Russ. Chem. Bull., Int. Ed.*, 2008, **57**, 2207 [*Izv. Acad. Nauk, Ser. Khim.*, 2008, 2165].
72. H. Cui, R. Goddard, K.-R. Pörschke, *J. Phys. Org. Chem.*, 2012, **25**, 814.
73. X.-M. Liu, S.-B. Miao, B.-M. Ji, *J. Phys. Chem. Solids*, 2007, **68**, 1375.
74. R. E. Caputo, M. J. Vukosavovich, R. D. Willett, *Acta Crystallogr., Sect. B*, 1976, **32**, 2516.
75. A. Johansson, M. Vestergren, M. Hakansson, B. Gustafsson, S. Jagner, *New J. Chem.*, 2004, **28**, 1000.
76. K. Nakamoto, *Infrared and Raman spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, 1986.
77. G. Henrici-Olive, S. Olive, *Coordination and Catalysis*, Verlag Chemie, Weinheim-New York, 1977.
78. L. Tietze, T. Eicher, *Reaktionen und Synthesen im organisch-chemischen Praktikum und Forschungslaboratorium*, Georg Thieme Verlag, Stuttgart-New York, 1991.
79. *Organikum*, V. 2, VEB Deutscher Verlag der Wissenschaften, Berlin, 1990, 487 pp.
80. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.
81. Ts. E. Agadzhanian, A. D. Arutyunyan, G. L. Arutyunyan, *Khim. Geterotsikl. Soedin.*, 1992, **7**, 929 [*Chem. Heterocycl. Compd. (Engl. Transl.)*, 1992, 7].

Received November 15, 2013;
in revised form March 24, 2014