## Synthesis and study of N-(1-phenylethylidene)-N-(4H-1,2,4-triazol-4-yl)amine, N'-(4H-1,2,4-triazol-4-yl)benzamidine, and cobalt(II), nickel(II), and copper(II) complexes based on these ligands

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Methods were developed for the synthesis of complexes of Co<sup>II</sup>, Ni<sup>II</sup>, and Cu<sup>II</sup> nitrates and chlorides with *N*-(1-phenylethylidene)-*N*-(4*H*-1,2,4-triazol-4-yl)amine (L<sup>1</sup>) and *N'*-(4*H*-1,2,4-triazol-4-yl)benzamidine (L<sup>2</sup>). The Co<sup>II</sup> and Ni<sup>II</sup> complexes have a linear trinuclear structure. The Cu<sup>II</sup> complexes are polynuclear. Both ligands are coordinated to the metal ions in a bidentate-bridging mode through the N(1) and N(2) atoms of the heterocycle. In all compounds, the coordination polyhedron can be described as a distorted octahedron. The molecular and crystal structure of the [Ni<sub>3</sub>(L<sup>1</sup>)<sub>6</sub>(EtOH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](NO<sub>3</sub>)<sub>6</sub>•2EtOH•4H<sub>2</sub>O complex was established.

**Key words:** synthesis, coordination compounds, 1,2,4-triazoles, structure, UV–Vis and IR spectroscopy, magnetochemistry, X-ray diffraction study.

1,2,4-Triazoles have attracted considerable interest as ligands.<sup>1</sup> Unsubstituted 1,2,4-triazole (HTrz) and its derivatives (RTrz) with free positions 1 and 2 are coordinated to metals predominantly in a bidentate-bridging mode through the N(1) and N(2) atoms of the heterocycle. The first compounds with this coordination mode were synthe-

sized and structurally characterized in the 1960s. These were the polynuclear complex  $Cu(HTrz)Cl_2^2$  and the trinuclear complex  $[Ni_3(HTrz)_6(H_2O)_6](NO_3)_6 \cdot 2H_2O.^{3,4}$ Since that time a large number of polynuclear metal complexes with 1,2,4-triazoles were synthesized<sup>1</sup> (see, for example, M<sub>5</sub>(RTrz)<sub>12</sub>).



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Several types of linear trinuclear complexes, in which pairs of adjacent metal ions are linked by triple bridges through coordination by the N(1) and N(2) atoms of 1,2,4-triazoles, were documented. In all these compounds, the coordination polyhedron of the central metal ion can be described as a distorted octahedron (the  $MN_6$  coordination unit). The terminal ions are also in an octahedral environment due to the involvement of the N atoms of monodentate triazole ligands and (or) the O atoms of water molecules. Depending on the nature of the ligands, the coordination units have the composition  $MN_3O_3$  (type 1),<sup>5–7</sup>  $MN_4O_2$  (type 2),<sup>8,9</sup> or  $MN_5O$  (type 3).<sup>5,10</sup> In addition, triangular trinuclear M<sup>II</sup> complexes with RTrz were described.<sup>11,12</sup>

The poly- or trinuclear structures of metal complexes with 1,2,4-triazoles are responsible for their unusual magnetic properties. Studies of magnetic properties of these complexes revealed both ferro- and antiferromagnetic exchange interactions between paramagnetic ions.<sup>7-9,13,14</sup> Of special interest are compounds of different iron(11) salts with HTrz and its 4-substituted derivatives with the composition Fe(RTrz)<sub>n</sub>A<sub>m</sub>•*p*H<sub>2</sub>O, where A is a singly or doubly charged anion, which is not involved in coordination; n = 2, 3; m = 1, 2; p = 0-5. The thermally induced spin transition  ${}^{1}A_{1} \longrightarrow {}^{5}T_{2}$  accompanied by thermochromism (the pink white color change) was observed in these complexes.<sup>15,16</sup> In most of these compounds, the spin transition is sharp, and the plots  $\mu_{eff}(T)$  show hysteresis. It was of interest to extend the range of coordination compounds with 4-RTrz and to investigate their magnetic properties. In the present study, we synthesized two new 1,2,4-triazole derivatives containing bulky substituents at position 4, *viz.*, *N*-(1-phenylethylidene)-*N*-(4*H*-1,2,4-triazol-4-yl)amine (L<sup>1</sup>) and *N'*-(4*H*-1,2,4-triazol-4-yl)benzamidine (L<sup>2</sup>). Methods were developed for the synthesis of Co<sup>II</sup>, Ni<sup>II</sup>, and Cu<sup>II</sup> complexes with these ligands. The compositions and structures of the coordination units were determined, and the temperature dependences of the effective magnetic moment for these compounds were studied.

## **Results and Discussion**

N-(1-Phenylethylidene)-N-(4H-1,2,4-triazol-4-yl)amine (L<sup>1</sup>) was synthesized by condensation of 4-amino-4H-1,2,4-triazole with acetophenone in the presence of BaO as the dehydrating agent in ethanol (Scheme 1).

N'-(4H-1,2,4-Triazol-4-yl)benzamidine (L<sup>2</sup>) was synthesized by the reaction of 4-amino-4H-1,2,4-triazole with benzonitrile in liquid ammonia (Scheme 2).

The cross-peaks indicative of dipole-dipole interactions between protons of the phenyl and triazole rings are absent in the homonuclear 2D NOESY spectra of  $L^1$  and  $L^2$ . The spectrum of  $L^1$  shows a weak cross-peak corresponding to interactions between protons of the methyl



Type 3







group and the triazole ring. This indicates that both compounds are E isomers.

The Co<sup>II</sup>, Ni<sup>II</sup>, and Cu<sup>II</sup> complexes with the ligands L<sup>1</sup> and L<sup>2</sup> were synthesized by the reactions of hot ethanolic solutions of the corresponding metal salts and the ligands according to Eqs (1)-(4) (Scheme 3, Table 1). Complexes **1–9** precipitated from hot ethanolic solutions.

Scheme 3

$$3 M^{2+} + 6 L + 6 NO_{3}^{-} + (6 + n) H_{2}O \longrightarrow (1)$$

$$\longrightarrow [M_{3}(L)_{6}(H_{2}O)_{6}](NO_{3})_{6} \cdot nH_{2}O$$

$$1, 2, 4, 5$$

$$L = L^{1}, M = Ni, n = 0 (1); M = Co, n = 2 (2);$$

$$L = L^{2}, n = 2, M = Co (4), Ni (5)$$

$$3 M^{2+} + 6 L + 6 CI^{-} + 6 H_{2}O \longrightarrow (2)$$

$$\longrightarrow [M_{3}(L)_{6}(H_{2}O)_{6}]CI_{6}$$

$$3, 6$$

$$L = L^{1}, M = Ni (3); L = L^{2}, M = Co (6)$$

$$3 Ni^{2+} + 8 L^{2} + 6 CI^{-} + 4 H_{2}O \longrightarrow (3)$$

$$\longrightarrow [Ni_{3}(L^{2})_{8}(H_{2}O)_{4}]CI_{6}$$

$$7$$

$$Cu^{2+} + 2 L^{2} + 2 A^{-} + 2 H_{2}O \longrightarrow (4)$$

$$\longrightarrow [Cu(L^{2})_{2}(H_{2}O)_{2}]A_{2}$$

$$8, 9$$

 $A = NO_3^{-}(8), Cl^{-}(9)$ 

Solutions of the copper salts were acidified with the corresponding acids to prevent reduction of  $Cu^{2+}$ . The  $[Ni_3(L^1)_6(H_2O)_4(EtOH)_2](NO_3)_6 \cdot 2EtOH \cdot 4H_2O$  com-

Table 1. Elemental analysis data for the  $M^{\rm II}$  complexes with  $L^1$  and  $L^2$ 

Compound	Found (%) Calculated						Empirical formula
	С	Н	Со	Cu	Ν	Ni	
$[Ni_{3}(L^{1})_{6}(H_{2}O)_{6}](NO_{3})_{6}$ (1)	$\frac{41.1}{40.6}$	$\frac{4.0}{4.1}$	_	—	$\frac{24.1}{23.7}$	<u>9.5</u> 9.9	$C_{60}H_{72}N_{30}Ni_{3}O_{24}$
$[Co_3(L^1)_6(H_2O)_6](NO_3)_6 \cdot 2H_2O$ (2)	<u>38.1</u> 39.8	$\frac{4.0}{4.2}$	<u>9.7</u> 9.8	_	<u>23.3</u> 23.2	_	$C_{60}H_{76}Co_{3}N_{30}O_{26}$
$[Ni_{3}(L^{1})_{6}(H_{2}O)_{6}]Cl_{6}(\textbf{3})$	<u>45.1</u> 44.6	<u>4.4</u> 4.5	—	—	$\frac{21.2}{20.8}$	$\frac{10.7}{10.9}$	$C_{60}H_{72}Cl_6N_{24}Ni_3O_6$
$[\mathrm{Co}_{3}(\mathrm{L}^{2})_{6}(\mathrm{H}_{2}\mathrm{O})_{6}](\mathrm{NO}_{3})_{6} \cdot 2\mathrm{H}_{2}\mathrm{O} (4)$	<u>35.3</u> 35.7	<u>3.8</u> 3.9	<u>9.4</u> 9.7	—	<u>26.5</u> 27.7	—	$C_{54}H_{70}Co_{3}N_{36}O_{26}$
$[Ni_{3}(L^{2})_{6}(H_{2}O)_{6}](NO_{3})_{6} \cdot 2H_{2}O $ (5)	<u>35.1</u> 35.7	$\frac{4.0}{3.9}$	_	_	<u>26.6</u> 27.8	<u>9.4</u> 9.7	$C_{54}H_{70}N_{36}Ni_{3}O_{26}$
$[Co_3(L^2)_6(H_2O)_6]Cl_6(6)$	$\frac{40.6}{40.0}$	<u>3.9</u> 4.1	<u>10.5</u> 10.9	_	<u>26.2</u> 25.9	_	$C_{54}H_{66}Cl_6Co_3N_{30}O_6$
$[Ni_3(L^2)_8(H_2O)_4]Cl_6(7)$	<u>44.5</u> 44.1	<u>4.3</u> 4.1	_	_	<u>28.6</u> 28.6	<u>9.2</u> 9.0	$C_{72}H_{80}Cl_6N_{40}Ni_3O_4$
$[Cu(L^2)_2(H_2O)_2](NO_3)_2$ (8)	<u>36.9</u> 36.2	<u>3.3</u> 3.7	—	<u>10.6</u> 10.6	<u>28.7</u> 28.1	—	$C_{18}H_{22}CuN_{12}O_8$
$[Cu(L^2)_2(H_2O)_2]Cl_2(9)$	<u>39.9</u> 39.7	<u>3.9</u> 4.1	_	<u>11.6</u> 11.7	<u>26.1</u> 25.7	_	$C_{18}H_{22}Cl_2CuN_{10}O_2$

plex was obtained (10) after prolonged storage of a dilute ethanolic solution of nickel nitrate and the ligand  $L^1$ .

The metal-to-ligand molar ratio used for the synthesis of coordination compounds 1-3, 9, and 10 was 1:2; for the synthesis of compounds 4, 5, and 8, 1:1; for the synthesis of compounds 6 and 7, 1:3. The elemental analysis of the phases prepared with the use of other M : L ratios showed that these phases partially contain coordination compounds with other compositions.

The resulting coordination compounds are moderately soluble in ethanol and water and are poorly soluble in propan-2-ol, acetone, and CHCl<sub>3</sub>.

The main characteristic frequencies in the IR spectra of the ligands and the complexes are given in Table 2. The spectra of the ligands  $L^1$  and  $L^2$  show two bands in the 1520–1500 cm<sup>-1</sup> region. These bands are assigned to stretching-bending vibrations of the triazole ring, which are sensitive to coordination. In the IR spectra of the coordination compounds, one band shifts to higher frequencies compared to that in the spectra of the ligands. This is

evidence that the nitrogen atoms of the heterocycle are coordinated to the metal atoms. The IR spectra of all coordination compounds show one band in the region of torsional vibrations of the heterocycle at  $625-640 \text{ cm}^{-1}$  (see Table 2). This spectral pattern is characteristic of the bidentate-bridging coordination of 1,2,4-triazoles to metal ions.<sup>170</sup>

The IR spectra of nitrate coordination compounds **1** and **2** show two bands at 1390–1300 cm<sup>-1</sup> belonging to vibrations of  $NO_3^-$  ions (see Table 2). The IR spectra of coordination compounds **4**, **5**, and **8** have one intense band at 1380–1370 cm<sup>-1</sup>. These data are indicative of the outer-sphere coordination of the nitrate ion in these complexes.<sup>18</sup> The splitting of  $v_3(NO_3)$  into two components is evidently attributed to hydrogen bonding with water molecules.

In the  $3360-3200 \text{ cm}^{-1}$  region, the IR spectra of the coordination compounds show stretching bands of coordinated water molecules. In the same region, the spectra of the coordination compounds with L<sup>2</sup> have bands assigned

Table 2. Main vibrational frequencies  $(cm^{-1})$  in the IR spectra of the ligands and complexes 1-9

Compound	v(NH <sub>2</sub> ), v(OH)	v(CH)	$\delta(\mathrm{NH}_2)$	R <sub>Ph</sub>	R <sub>Trz</sub>	v(NO <sub>3</sub> )	$\boldsymbol{\tau}_{Trz}$	v(M-O)	v(M-N)
L <sup>1</sup>	_	3124	_	1612, 1592, 1573	1519, 1500	_	625		_
1	3316	3085	—	1610, 1597, 1573	1529	1390, 1309	631	490, 429, 399	282
2	3331	3084	—	1610, 1599, 1570	1528	1377, 1326	630	487, 472, 375	287, 263
3	3338	3143, 3050	—	1610, 1596, 1571	1529	_	631	486, 438, 398	276
L <sup>2</sup>	3359, 3321	3122, 3059	1653	1599, 1566	1523, 1500	_	631	_	_
4	3400, 3334, 3206	3142, 3097	1652	1600, 1561	1527	1380	632	467, 396, 367	283, 260
5	3400, 3335, 3207	3143, 3101	1651	1600, 1562	1527	1380	632	469, 398, 372	278
6	3340, 3304	3140, 3096	1656	1601, 1549	1530	_	633	459, 410, 381	271, 256
7	3300	3134, 3056	1641	1597, 1559	1530	—	635	463	—
8	3352, 3320	3096	1655	1601, 1558	1530	1370	637	455, 412, 380	278
9	3345, 3278	3190, 3104	1641	1597, 1557	1531	_	633	450, 408, 369	274

to stretching vibrations of the  $NH_2$  group overlapping with the stretching bands of water molecules. The spectra of coordination compounds **4** and **5** show bands at 3400 cm<sup>-1</sup> assigned to vibrations of outer-sphere water molecules.<sup>18</sup>

The spectra of all compounds have bands in the  $3200-3050 \text{ cm}^{-1}$  region characteristic of CH stretching vibrations. In the spectra of the ligand L<sup>2</sup> and coordination compounds **4**–**9**, the band in the 1640–1655 cm<sup>-1</sup> region belongs to bending vibrations of the NH<sub>2</sub> group. This band in the spectra of the complexes remains unchanged compared to that in the spectrum of the ligand, which indicates that this group is not coordinated to the metal atom.

The low-frequency region has bands at  $490-360 \text{ cm}^{-1}$  assigned to v(M–O). The bands in the 280–260 cm<sup>-1</sup> region are attributed to v(M–N) vibrations. Their positions are characteristic of coordination compounds with 1,2,4-triazoles.<sup>19</sup>

A comparison of the number and positions of the bands in the diffuse reflectance spectra of the Co<sup>II</sup> and Ni<sup>II</sup> coordination compounds with the data published in the literature<sup>20</sup> shows that the coordination polyhedra in these compounds can be described as distorted octahedra (Table 3). For example, the spectrum of coordination compound **2** has two bands with maxima at 20747 cm<sup>-1</sup> (v<sub>2</sub>) and 9671 cm<sup>-1</sup> (v<sub>1</sub>), which can be assigned to d-d transitions in the octahedral ligand field, the spectrum of compound **4** shows bands at 20833 cm<sup>-1</sup> (v<sub>2</sub>) and 10000 cm<sup>-1</sup> (v<sub>1</sub>), and the spectrum of compound **6** contains three bands at 19230 cm<sup>-1</sup> (v<sub>3</sub>), 15650 cm<sup>-1</sup> (v<sub>2</sub>), and 9346 cm<sup>-1</sup> (v<sub>1</sub>).

Table 3. Characteristics of the diffuse reflectance spectra of the  $M^{\rm II}$  complexes with the ligands  $L^1$  and  $L^2$ 

Com- pound	Color	λ <sub>max</sub> /nm	Assignment	$\Delta \cdot 10^{-3}$ /cm <sup>-1</sup>
1	Lilac	361	${}^{3}A_{2} \rightarrow {}^{3}T_{1}(P)$	10.8
		584	${}^{3}A_{2} \rightarrow {}^{3}T_{1}(F)$	
		924	${}^{3}A_{2} \rightarrow {}^{3}T_{2}$	
2	Orange	482	${}^{4}T_{1}(F) \rightarrow {}^{4}T_{1}$	11.0
		1034	${}^{4}T_{1} \rightarrow {}^{4}T_{2}$	
3	Lilac	365	${}^{3}A_{2} \rightarrow {}^{3}T_{1}(P)$	10.7
		592	${}^{3}A_{2} \rightarrow {}^{3}T_{1}(F)$	
		934	${}^{3}A_{2} \rightarrow {}^{3}T_{2}$	
4	Orange	480	${}^{4}T_{1}(F) \rightarrow {}^{4}T_{1}$	11.4
		1000	${}^{4}T_{1} \rightarrow {}^{4}T_{2}$	
5	Lilac	365	${}^{3}A_{2} \rightarrow {}^{3}T_{1}(P)$	10.7
		577	${}^{3}A_{2} \rightarrow {}^{3}T_{1}(F)$	
		932	${}^{3}A_{2} \rightarrow {}^{3}T_{2}$	
6	Pink	520	${}^{4}T_{1}(F) \rightarrow {}^{4}T_{1}$	10.6
		639	${}^{4}T_{1} \rightarrow {}^{4}A_{2}$	
		1070	${}^{4}T_{1} \rightarrow {}^{4}T_{2}$	
7	Lilac	562	${}^{3}A_{2} \rightarrow {}^{3}T_{1}(F)$	11.2
		893	${}^3A_2 \rightarrow {}^3T_2$	
8	Blue	622	$^{2}E \rightarrow ^{2}T_{2}$	_
9	Blue	635	$^{2}E \rightarrow ^{2}T_{2}^{2}$	—

The spectra of the Ni<sup>II</sup> complexes show the following d—d transition bands: at 27700 cm<sup>-1</sup> (v<sub>3</sub>), 17123 cm<sup>-1</sup> (v<sub>2</sub>), and 10823 cm<sup>-1</sup> (v<sub>1</sub>) for compound **1**, at 27397 cm<sup>-1</sup> (v<sub>3</sub>), 16892 cm<sup>-1</sup> (v<sub>2</sub>), and 10707 cm<sup>-1</sup> (v<sub>1</sub>) for compound **3**, at 27397 cm<sup>-1</sup> (v<sub>3</sub>), 17331 cm<sup>-1</sup> (v<sub>2</sub>), and 10730 cm<sup>-1</sup> (v<sub>1</sub>) for compound **5**, and at 17794 cm<sup>-1</sup> (v<sub>2</sub>) and 11198 cm<sup>-1</sup> (v<sub>1</sub>) for compound **7**.

The assignment of the bands and the splitting parameters  $\Delta$  for the Co<sup>II</sup> and Ni<sup>II</sup> complexes are given in Table 3 (for the Co<sup>II</sup> coordination compounds, the parameter  $\Delta$ was calculated from the condition v<sub>1</sub> = 8.8 Dq).

The spectra of the copper(II) complexes have one d-d transition band (at 16077  $\text{cm}^{-1}$  for **8** and at 15748  $\text{cm}^{-1}$  for **9**).

The splitting parameters  $\Delta$  for the Co^{II} and Ni^{II} complexes corresponding to the average energy of the d—d transitions  ${}^{4}T_{1} \rightarrow {}^{4}T_{2}$  and  ${}^{3}A_{2} \rightarrow {}^{3}T_{2}$ , respectively, in chromophores of the trinuclear cations of these coordination compounds are indicative of the presence of weaker-field ligands (water molecules) in the coordination polyhedra of the terminal Co^{2+} and Ni^{2+} ions.

Complex 10 is a ionic compound. In the trinuclear complex cation  $[Ni_3(L^1)_6(H_2O)_4(EtOH)_2]^{6+}$  (Fig. 1, *a*), three nickel atoms are linked together by the bridging ligands L<sup>1</sup> to form a linear chain. The cation occupies an inversion center in the space group  $P2_1/n$ . The coordination polyhedra of all nickel(II) ions are octahedra, the central and terminal nickel atoms being in a different coordination environment (Fig. 1, b). Each pair of nickel(II) ions is linked by three bidentate-bridging ligands L<sup>1</sup> coordinated through the N(1) and N(2) atoms of the triazole ring. The coordination environment of the central nickel atom consists of six nitrogen atoms of the ligands due to which it is virtually undistorted. The three other coordination sites at each terminal nickel atom are occupied by one ethanol molecule and two water molecules. The nitrate ions are not involved in coordination and are located in the outer sphere.

The Cambridge Structural Database<sup>21</sup> contains six compounds structurally similar to the trinuclear nickel(II) complexes with unsubstituted 1,2,4-triazole<sup>4</sup> and with substituted 3,5-diamino-<sup>22</sup> (Table 4; NADNOV, NADHAB, and NADPAJ) and 4-(2-pyridyl)-1,2,4-triazoles.<sup>7</sup> The Ni—N bonds with the central nickel atom in the trinuclear coordination compounds (2.082–2.130 Å) are always longer than the corresponding bonds with the terminal nickel atoms (2.047–2.093 Å, see Table 4). The Ni...Ni distances are in the range of 3.680–3.831 Å. The interatomic distances in the structure of compound **10** vary within the same range.

In the crystal structure of compound **10**, each complex cation  $[Ni_3(L^1)_6(EtOH)_2(H_2O)_4]^{6+}$  is surrounded by a thick shell formed by solvate water and ethanol molecules and nitrate ions. In the crystal structure, the complex cation is surrounded by 50 molecules and ions, only 14 of



**Fig. 1.** Structure of the trinuclear complex cation  $[Ni_3(L^1)_6(H_2O)_4(EtOH)_2]^{6+}(a)$ ; the atoms are represented by displacement ellipsoids drawn at the 50% probability level; the hydrogen atoms are omitted. The numbering scheme for the nearest environment of the nickel atoms (*b*).

these moieties being other cations. The complex cations are linked to each other by an extensive hydrogen bond network involving the solvate ethanol and water molecules to form layers parallel to  $(101^{-})$ . The O(H)...O bond lengths are in the range of 2.635(2) - 3.138(2) Å, and the O...H-O angles vary from 125(2)° to 179(3)° (Fig. 2). Virtually all solvate water molecules and part of nitrate ions lie in the plane of the layer. The other nitrate ions are located between the layers. In the crystal structure, the layers are linked to each other by nonbonded interactions between the phenyl substituents of the ligand L<sup>1</sup> belonging to the complex cations from two adjacent layers and the solvate ethanol molecules occupying the cavities between the phenyl rings. In spite of the fact that interactions between the aromatic systems of the ligands of the adjacent complex cations can exist (intramolecular interactions cannot occur due to the geometric features of the cation),  $\pi$ -stacking interactions were not found in the crystal structure of 10. Apparently, the hydrogen bonding in the crystal structure is energetically more favorable than stacking interactions.

In the earlier studies of the crystal structures of related compounds,<sup>4,7,23</sup> it has been noted that the crystal packing is determined primarily by hydrogen bonding between the donor and acceptor atoms of the cationic complex, the anions, and the solvate molecules. However, the packing of the molecules and ions in the crystal structures of complex **10**, as well as of six known related nickel compounds, has another distinguishing feature that persists irrespective of the difference in the crystallographic symmetry and the

nature of the ligands. In the crystal structure of **10**, the arrangement of the sextuply charged complex cations can be described as a distorted face-centered cubic (FCC) packing (Fig. 3), whereas the cations in the six structurally similar compounds form a body-centered cubic (BCC) lattice (see Table 4). Other structural units (solvate water and ethanol molecules and the  $ClO_4^-$  and  $NO_3^-$  anions) are of minor importance and fill the cavities in this crystal packing. This conclusion is supported by variations in the hydration number and the diverse numbers of the nearest neighbors of the complex cations (see Table 4).

It is noteworthy that complex 10 does not have a BCC structure characteristic of trinuclear complex cations. It should be noted that complex 10 is the only compound structurally studied at low temperature because crystals of this complex undergo rapid aging in air. This suggests that the packing of the cations depends both on the temperature and the bulky substituent  $L^1$ . This phenomenon will be investigated in the future.

The X-ray powder diffraction study showed that complexes 1 and 2 with the composition  $[M_3(L^1)_6(H_2O)_6](NO_3)_6 \cdot nH_2O$  (M = Ni or Co) give different diffraction patterns. The compound  $[Ni_3(L^1)_6(H_2O)_6]Cl_6$  (3) is X-ray amorphous. In the series of the complexes with L<sup>2</sup>, coordination compounds **4**–**6** are crystalline. It should be noted that the X-ray powder diffraction data for the first two compounds indicate that they are isostructural. The other complexes with L<sup>2</sup> are X-ray amorphous.

Compound	Space	R			$d^{b}/\text{\AA}$			n <sup>c</sup>	Packing	Reference <sup>e</sup>
	group $(R_{\rm f})$		NiNi	Ni <sub>centr</sub> -N	Ni <sub>term</sub> –N	Ni <sub>term</sub> —O(H <sub>2</sub> O)	Ni <sub>term</sub> -X		mode <sup>d</sup>	
$[Ni_3(L^1)_6(EtOH)_2(H_2O)_4](NO_3)_6 \cdot 2EtOH \cdot 4H_2O^J$	$P2_{1/n}$ (0.0346)	NC(Me)Ph	3.7869(2)	2.0962(14)- -2.1420(14); 2.11[3]	2.0468(14)- -2.0644(14); 2.056[9]	2.0533(13)- -2.0685(13); 2.06[1]	2.0659(13) O(EtOH)	50	FCC	This study
$[Ni_3(L)_6(H_2O)_6](NO_3)_6$	C2/c (0.0793)	Py	3.759	2.082– —2.130; 2.10[3]	2.050– —2.066; 2.056[9]	2.066— —2.085; 2.08[1]	I	38	BCC	Ч
$[Ni_3(L)_6(H_2O)_6](NO_3)_6 \cdot H_2O$	$P2_{1/n}$ (0.0730)	2(NH <sub>2</sub> )	3.725	2.086– –2.112; 2.10[1]	2.054— —2.073; 2.06[1]	2.081— —2.120; 2.10[2]	I	36	BCC	NADNOV
$ \begin{split} & [\mathrm{Ni}_3(\mathrm{L})_6(\mathrm{H}_2\mathrm{O})_4(\mathrm{NO}_3)_2]  \bullet \\ & \bullet [\mathrm{Ni}_3(\mathrm{L})_6(\mathrm{H}_2\mathrm{O})_6](\mathrm{NO}_3)_4  \bullet \\ & \bullet 6\mathrm{H}_2\mathrm{O} \end{split} $	$P\bar{1}$ (0.0742)	2(NH <sub>2</sub> )	3.680, 3.710	2.096- -2.130; 2.11[2]	2.039— —2.059; 2.049[7]	2.097— —2.138, 2.12[2]	2.134 O(NO <sub>3</sub> )	36, 38	BCC	NADHAB
[Ni <sub>3</sub> (L) <sub>6</sub> (H <sub>2</sub> O) <sub>6</sub> ](CIO <sub>4</sub> ) <sub>6</sub> • 6H <sub>2</sub> O	$P2_{1/n}$ (0.0744)	2(NH <sub>2</sub> )	3.697	2.104- -2.130; 2.12[1]	2.041– –2.056; 2.047[8]	2.099— —2.123; 2.11[1]	I	42	BCC	NADPAJ
$[Ni_3(L)_6(NCS)_6] \cdot 6H_2O$	$R\bar{3}$ (0.0350)	2(NH <sub>2</sub> )	3.831	2.127	2.093	I	2.097 N(NCS)	38	BCC	23
$[Ni_3(L)_6(H_2O)_6](NO_3)_6 \cdot 2H_2O$	$P2_{1/c}$ (0.0450)	Н	3.737	2.095– –2.112; 2.105[9]	2.052- -2.059; 2.057[4]	2.048— —2.087; 2.07[2]	I	30	BCC	4
<sup>a</sup> At room temperature. <sup>b</sup> The bond length ranges, the average <sup>c</sup> The number of neighbors of the com	e bond length nplex cations,	s, and the rms o <i>i.e.</i> , the numbe	leviations (ir r of molecule	n brackets) are g es or ions of any	iven. type that form	substantial nonbon	ided contacts w	vith this ca	tion in the cr	stal structure.

Metal(II) complexes with 1,2,4-triazoles

<sup>*d*</sup> The packing mode of the complex cations was calculated according to the known procedure.<sup>28</sup> <sup>*e*</sup> The CSD refcodes for the compounds designated as unpublished data<sup>21</sup> are given. <sup>*f*</sup> The data for T = 90 K are given.



**Fig. 2.** View of the (101<sup>-</sup>) layer formed *via* (NO<sub>3</sub>)O...H $-O(H_2O)$  hydrogen bonds involving both the solvate water molecules and the water molecules coordinated to the nickel atoms projected along the *x* axis. The trinuclear complex cations are represented by coordination polyhedra of nickel atoms. The ligand environment, except for the water and ethanol molecules involved in hydrogen bonding (dashed lines), are omitted.

The temperature dependences of the effective magnetic moment ( $\mu_{eff}$ ) of the Ni<sup>II</sup> complexes with the ligands L<sup>1</sup> and  $L^2$  are presented in Fig. 4. At room temperature, the magnetic moments  $\mu_{eff}$  are 4.95, 5.05, and 5.07  $\mu_B$  for complexes 1, 3, and 5, respectively. These moments are similar to the theoretical value  $(4.90 \,\mu_B)$  for three virtually noninteracting spins (s = 1, g factor = 2). The magnetic moments  $\mu_{eff}$  for the Ni<sup>II</sup> complexes monotonically decrease as the temperature decreases. At temperatures below 20 K, the moments approach the constant value  $(\sim 3 \mu_{\rm B})$ , which is similar to the pure spin magnetic moment  $(2.87 \mu_{\rm B})$  for s = 1. The observed magnetic behavior of the coordination compounds is indicative of the presence of antiferromagnetic exchange interactions between the Ni<sup>II</sup> ions, resulting in the complete spin-spin coupling in the three-center molecules at low temperatures. A further decrease in  $\mu_{eff}$  with decreasing temperature is attributed to intermolecular antiferromagnetic exchange interactions.

The theoretical analysis of the experimental dependences for the Ni<sup>II</sup> complexes was carried out in the clus-

ter approximation with the use of the isotropic spin-Hamiltonian  $\hat{H} = -2\sum_{i,j} \hat{S}_i \hat{S}_j$  in terms of the approach developed earlier.<sup>24</sup> The approximation was performed with the use of the three-center exchange clus-



ter where  $M = Ni^{II}$ . The optimal spin-Hamiltonian parameters are given in Table 5. The corresponding calculated curves are shown in Figs 4, a-c (solid lines).

The Cu<sup>II</sup> compounds show different magnetic behavior. The plots  $\mu_{\text{eff}}(T)$  for compounds **8** and **9** are presented in Figs 5, *a*, *b*. The magnetic moments  $\mu_{\text{eff}}$  of compounds **8** and **9** are 1.49 and 1.59  $\mu_{\text{B}}$ , respectively, already at room temperature. These moments are smaller than the theoretical value (1.73  $\mu_{\text{B}}$ ) for s = 1/2 with g = 2, which is associated with the effective antiferromagnetic exchange inter-



Fig. 3. Fragment of the sublattice of the complex cations viewed as a FCC lattice. The nickel atoms are represented as coordination polyhedra.

actions between CuII ions. These interactions lead to a strong monotonic decrease in  $\mu_{\text{eff}}$  as the temperature decreases throughout the range under study. In the 50-100 Ktemperature range, the plots  $\chi(T)$  show a flat maximum (the insets in Fig. 5). This magnetic behavior of compounds 8 and 9 characterizes their structures as exchangecoupled linear chains. It can be seen that the magnetic moments  $\mu_{eff}$  of the Cu<sup>II</sup> compounds do not turn to zero when  $T \rightarrow 0$ , which is attributed to the fact that we studied powdered samples (the so-called effect of an "impurity monomer"). We performed the theoretical analysis of the temperature dependences for the Cu<sup>II</sup> complexes with the use of the chain exchange cluster taking into account the effect of an "impurity monomer."<sup>25</sup> The optimal exchange parameters are given in Table 5. The theoretical curves corresponding to these parameters are in good agreement with the experimental curves (solid lines in Figs 5, a, b).

The exchange parameters J of the Ni<sup>II</sup> and Cu<sup>II</sup> complexes (see Table 5) are similar to those of the complexes with triazole derivatives studied earlier.<sup>9</sup>

Hence, we synthesized trinuclear and polynuclear M<sup>II</sup> complexes with new 1,2,4-triazole derivatives containing a bulky substituent at position 4. It was shown that the introduction of these substituents has no effect on the coordination mode of 1,2,4-triazoles but influences the composition and magnetic properties of the compounds. The nitrogen atoms of the substituents are not involved in coordination. Only the nitrogen atoms of the triazole rings are bound to the metal atoms. The coordination environment of the central ions in the trinuclear Co<sup>II</sup> and Ni<sup>II</sup> complexes is formed by six N atoms of six ligands L. The coordination units of the terminal metal ions are also octahedral due to coordination by three oxygen atoms of the water molecules in complexes **1–6** (the coordination unit

Compound	Exchange	g Factor	-J	-nJ'	σ
	cluster		cm <sup>-1</sup>		
$[Ni_3(L^1)_6(H_2O)_6](NO_3)_6$ (1)	Trimer	2.12±0.01	12.09±0.05	$0.06 \pm 0.03$	0.00001
$[Ni_3(L^1)_6(H_2O)_6]Cl_6(3)$	Trimer	$2.11 \pm 0.01$	$4.46 {\pm} 0.03$	$0.02 {\pm} 0.01$	0.01956
$[Ni_3(L^2)_6(H_2O)_6](NO_3)_6 \cdot 2H_2O$ (5)	Trimer	$2.15 \pm 0.01$	$11.47 {\pm} 0.05$	$0.12 {\pm} 0.01$	0.00063
$[Cu(L^2)_2(H_2O)_2](NO_3)_2$ (8)	Chain	2.06	67.6	—	0.0029
$[Cu(L^2)_2(H_2O)_2]Cl_2(9)$	Chain	2.01	61.9	—	0.0013

Table 5. Calculated magnetochemical parameters\* for the complexes with L<sup>1</sup> and L<sup>2</sup>

\* g is the effective g factor, J is the exchange parameter, and nJ' is the intermolecular interaction parameter.





 $MN_3O_3$ ) or one N atom of the monodentate ligand L<sup>2</sup> and two oxygen atoms of water molecules in complex 7 (the coordination unit  $MN_4O_2$ ). The Cu<sup>II</sup> complexes have the CuN<sub>4</sub>O<sub>2</sub> coordination unit formed by four nitrogen atoms of two bidentate-bridging ligands and two oxygen



**Fig. 5.** Plots  $\mu_{eff}(T)$  and  $\chi(T)$  (inset) for the complexes  $[Cu(L^2)_2(H_2O)_2](NO_3)_2$  (8) (a) and  $[Cu(L^2)_2(H_2O)_2]Cl_2$  (9) (b).

atoms of water molecules. The influence of the central atom is manifested in that cobalt(II) and nickel(II) form trinuclear complexes, whereas copper(II) forms polynuclear complexes. These conclusions were drawn from the compositions of the compounds and were confirmed by physicochemical studies.

## **Experimental**

The elemental analyses for C, H, and N were carried out on a Carlo—Erba 1106 instrument in the Laboratory of Microanalysis of the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The metal content in the complexes was analyzed by titrating with Trilon after decomposition of the samples by heating in a mixture of concentrated  $H_2SO_4$  and  $HClO_4$  (1 : 2). The number of the outer-sphere water molecules was determined by thermogravimetric analysis. The TGA curves were recorded in air on a Paulik—Paulik—Erdey derivatograph in quartz crucibles at a heating rate of 2.5 °C min<sup>-1</sup> with the use of  $Al_2O_3$  as the standard; the weight of the samples was 50 mg.

The single-crystal X-ray diffraction study of complex **10** was performed according to a standard procedure on an automated

 Table 6. Crystallographic characteristics and the X-ray diffraction data collection and refinement statistics for complex 10

Parameter	Characteristic
Molecular formula	C <sub>68</sub> H <sub>100</sub> N <sub>30</sub> Ni <sub>3</sub> O <sub>30</sub>
М	1993.91
Temperature/K	90.0(2)
Radiation $(\lambda/\text{Å})$	Μο-Κα (0.71073)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	15.0985(4)
b/Å	12.3684(3)
c/Å	23.5680(6)
α/deg	90
β/deg	95.1980(10)
γ/deg	90
$V/Å^3$	4383.09(19)
Ζ	2
$\rho_{calc}/g \text{ cm}^{-3}$	1.511
$\mu/mm^{-1}$	0.735
<i>F</i> (000)	2084
Crystal dimensions/mm	$0.291 \times 0.273 \times 0.062$
θ/deg	1.54-28.34
hkl range	$-18 \le h \le 20,$
	$-16 \le k \le 11$ ,
	$-24 \le l \le 31$
Number of measured reflections	24871
Number of independent reflections	10866 ( $R_{\rm int} = 0.0187$ )
Number of reflections with $I \ge 2\sigma(I)$	9079
Method of refinement	Full-matrix
	least-squares based on $F^2$
Number of refinement	627
parameters	027
GOOF	1.039
$R_1(I \ge 2\sigma(I))$	0.0346
$wR_2$ (based on all reflections)	0.0915
Residual electron density $/e Å^{-3}$ , min/max	-0.522/0.829

four-circle Bruker-Nonius X8Apex diffractometer equipped with an area CCD detector at 90 K using a molybdenum anode  $(\lambda = 0.71073 \text{ Å})$  and a graphite monochromator. The intensities of reflections were measured by  $\varphi$  scanning of narrow (0.5°) frames to  $2\theta = 56.7^{\circ}$ . The empirical absorption correction was applied using the SADABS program.<sup>26</sup> The structure of complex 10 was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms using the SHELX-97 program package.<sup>27</sup> The hydrogen atoms in the organic moiety were refined using a riding model. The hydrogen atoms of the solvate water molecules and the hydroxy groups of the ethanol molecules were located in difference electron density maps and refined without restrictions. The X-ray diffraction data collection and refinement statistics are given in Table 6. Selected bond lengths and bond angles are listed in Table 7. The molecular coordination numbers and the topological characteristics of the cation sublattices were calculated using the TOPOS program package<sup>28</sup> according to a procedure described earlier.<sup>22</sup>

The X-ray powder diffraction study was carried out on a Philips-PW1700 diffractometer (Cu-Ka radiation, Ni filter, scintillation detector, the step was 0.015°, the 20-angle range from 5 to 30°). The measurements were carried out at room temperature using a silicon powder (a = 5.4309 Å) as the internal standard. The magnetochemical measurements were performed on a Quantum Design SQUID magnetometer in the 5-300 K temperature range at an external magnetic field strength of 5 kOe. The molar magnetic susceptibility  $(\chi)$  was calculated taking into account the atomic diamagnetism according to the Pascal additive scheme. The effective magnetic moment was calculated by the equation  $\mu_{\text{eff}} = \{[3k/(N_A\beta^2)]\chi T\}^{1/2} \approx (8\chi T)^{1/2}$ , where k is the Boltzmann constant,  $N_A$  is Avogadro's number, and  $\beta$  is the Bohr magneton. The diffuse reflectance spectra were recorded on a Shimadzu UV-3101 PC scanning spectrophotometer at room temperature. The IR absorption spectra of the complexes were measured on a Scimitar FTS 2000 spectrometer in the 375–4000 cm<sup>-1</sup> region and on a BOMEM MB-102 spectrometer in the 200-400 cm<sup>-1</sup> region. The IR spectra of the ligands  $L^1$  and  $L^2$ were recorded on a Specord 75 IR spectrometer in KBr pellets. The <sup>1</sup>H NMR spectra were measured on a Bruker DPX-400 instrument (400 MHz); the <sup>13</sup>C NMR spectra, on a Bruker DPX-250 instrument (62.5 MHz, in DMSO-d<sub>6</sub>, HMDS as the

Table 7. Selected bond lengths (d) and bond angles ( $\omega$ ) in compound 10

Parameter*	Value	Parameter*	Value	Parameter*	Value
Bond	d/Å	Bond	d/Å	Angle	ω/deg
Ni(1)Ni(2)	3.7869(2)	Ni(1)-N(21)#1	2.0983(14)	O(1) - Ni(2) - N(32)	91.97(6)
Ni(1)-N(11)	2.1420(14)	Ni(1)—N(31)#1	2.0963(14)	O(1) - Ni(2) - O(3)	88.94(6)
Ni(1)-N(21)	2.0983(14)	Angle	ω/deg	O(3)-Ni(2)-O(2)	93.25(5)
Ni(1)-N(31)	2.0962(14)	N(21)-Ni(1)-N(11)	88.98(5)	N(12)-Ni(2)-O(3)	92.74(5)
Ni(2) - O(1)	2.0533(13)	N(31)-Ni(1)-N(11)	89.66(5)	N(22)-Ni(2)-O(1)	88.37(6)
Ni(2) - O(2)	2.0685(13)	N(31)-Ni(1)-N(21)	89.35(5)	N(22)-Ni(2)-O(2)	87.59(6)
Ni(2)—N(12)	2.0644(14)	N(31)#1-Ni(1)-N(21)	90.65(5)	N(22)-Ni(2)-N(12)	89.99(6)
Ni(2)—N(22)	2.0468(14)	N(31)#1-Ni(1)-N(11)	90.34(5)	N(22)-Ni(2)-N(32)	91.94(6)
Ni(2)—N(32)	2.0558(14)	N(21)#1-Ni(1)-N(11)#1	88.98(5)	N(32)-Ni(2)-N(12)	90.00(6)
Ni(2)—O(3)	2.0659(13)	N(21)-Ni(1)-N(11)#1	91.02(5)	N(32)-Ni(2)-O(3)	87.10(5)
Ni(1)-N(11)#1	2.1420(14)	O(1) - Ni(2) - O(2)	85.62(6)	N(12)-Ni(2)-O(2)	92.40(6)

\* The symmetry code (1) -x + 1, -y - 1, -z + 1.

internal standard); the <sup>15</sup>N NMR spectrum, on a Bruker DPX-400 spectrometer (46 MHz); the chemical shifts are given with respect to nitromethane.

Commercial reagents were used as the starting compounds for the synthesis of the ligands  $L^1$  and  $L^2$ . Acetophenone and benzonitrile were purified by distillation (b.p. 200 and 190 °C for acetophenone and benzonitrile, respectively). 4-Amino-1,2,4triazole was recrystallized from EtOH (m.p. 84–86 °C). The reactants Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, and CuCl<sub>2</sub>·2H<sub>2</sub>O (high-purity grade) were used without additional purification.

N-(1-Phenylethylidene)-N-(4H-1,2,4-triazol-4-yl)amine (L<sup>1</sup>). Acetophenone (100 g, 0.83 mol), EtOH (50 mL), BaO (10 g), and 4-amino-1,2,4-triazole (70 g, 0.83 mol) were mixed in a round-bottom flask. The reaction mixture was stirred at ~20 °C for 2 days. The precipitate was filtered off and washed with chloroform. Then the solution was collected, and the solvent was evaporated to dryness. Ethanol was distilled off from the mother liquor also to dryness. The dry residues were combined and washed with water. The undissolved precipitate was filtered off and dried. The yield was 83.5 g (54%), m.p. 155-156 °C. Found (%): C, 64.1; H, 5.2; N, 29.7. C<sub>10</sub>H<sub>10</sub>N<sub>4</sub>. Calculated (%): C, 64.5; H, 5.4; N, 30.1. IR, v/cm<sup>-1</sup>: 3124, 1612, 1572, 1500, 1491, 1442, 1370, 1285, 1168, 1060, 856, 769, 692, 624, 567, 449. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 8.23 (s, 2 H, HC=N, ring); 7.92 (d, 2 H, o-Ph, J = 7.2 Hz); 7.55 (t, 1 H, p-Ph, J = 7.0 Hz); 7.48 (t, 2 H, *m*-Ph, J = 7.3 Hz); 2.39 (s, Me). <sup>13</sup>C NMR,  $\delta$ : 174 (C=N); 140.25 (HC=N, ring); 136.3 (C(1)-Ph); 132.4 (C(4)-Ph); 129 (C(2)-Ph, C(6)-Ph); 128 (C(3)-Ph, C(5)-Ph); 17 (Me).

N'-(4H-1,2,4-Triazol-4-yl)benzamidine (L<sup>2</sup>). Sodium hydroxide (0.3 g, 7.5 mmol) was added to a solution containing benzonitrile (3 g, 0.025 mol) and 4-amino-1,2,4-triazole (2.79 g, 0.033 mol) in liquid ammonia (200 mL). The reaction mixture was stirred at -33 °C for 6 h. Ammonia was removed, and the residue was washed with water and diethyl ether. The yield was 5.2 g (96%), m.p. 245-247 °C. Found (%): C, 57.9; H, 4.7; N, 37.4. C<sub>9</sub>H<sub>9</sub>N<sub>5</sub>. Calculated (%): C, 57.7; H, 4.9; N, 37.4. IR, v/cm<sup>-1</sup>: 3350, 3180, 3110, 3050, 1640, 1590, 1550, 1490, 1440, 1310, 1305, 1300, 1170, 1090, 1030, 970, 930, 920, 840, 830, 770, 700, 610, 570. <sup>1</sup>H NMR, (CDCl<sub>3</sub>), δ: 8.46 (s, 2 H, HC=N, ring); 7.91 (d, 2 H, o-Ph, J = 8.3 Hz); 7.53 (t, 1 H, p-Ph, J = 8.0 Hz); 7.46 (t, 2 H, *m*-Ph, J = 8.1 Hz); 7.3 (s, 2 H, NH<sub>2</sub>). <sup>13</sup>C NMR,  $\delta$ : 163.22 (C=N); 141.25 (HC=N, ring); 132.93 (C(1)-Ph); 131.65 (C(4)-Ph); 128.78 (C(2)-Ph, C(6)-Ph); 127.71 (C(3)-Ph, C(5)-Ph). <sup>15</sup>N NMR, δ: 64.92 (N-N); 163.75 (N(4), ring); 177.62 (N(1), N(2), ring); 294.99 (NH<sub>2</sub>).

Hexa-*N*-(1-phenylethylidene)-*N*-(4*H*-1,2,4-triazol-4-yl)aminohexaaquatrinickel(11) hexanitrate and hexa-*N*-(1-phenylethylidene)-*N*-(4*H*-1,2,4-triazol-4-yl)aminohexaaquatricobalt(11) hexanitrate dihydrate  $[M_3(L^1)_6(H_2O)_6](NO_3)_6 \cdot nH_2O$  (M = Ni, n = 0 (1); M = Co, n = 2 (2)). The ligand L<sup>1</sup> (0.19 g, 1 mmol) was dissolved in ethanol (7 mL) by heating in a water bath. The hot solution of the ligand was added with magnetic stirring to a solution of metal nitrate Ni(NO\_3)\_2 \cdot 6H\_2O or Co(NO\_3)\_2 \cdot 6H\_2O (0.5 mmol, 0.15 g) in ethanol (5 mL), and the precipitates formed immediately. The solutions with the precipitates were stirred with gradual cooling to room temperature for 30 min. The precipitates were filtered off, twice washed with hot ethanol, and dried in air. The yields of complexes 1 and 2 were 0.22 g (76%) and 0.29 g (96%), respectively. Hexa-*N*-(1-phenylethylidene)-*N*-(4*H*-1,2,4-triazol-4-yl)aminohexaaquatrinickel(II) hexachloride  $[Ni_3(L^1)_6(H_2O)_6]Cl_6$  (3). A hot solution of L<sup>1</sup> (0.19 g, 1 mmol) in ethanol (7 mL) was added with stirring to a solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.12 g, 0.5 mmol) in ethanol (3 mL). The precipitate was formed after evaporation of the excess solvent to ~1/2 of the initial volume and cooling of the solution. The solution with the precipitate was allowed to age for 15 h. Then the precipitate was filtered off, washed with hot ethanol, and dried in air. The yield of complex **3** was 0.21 g (78%).

Hexa-N'-(4H-1,2,4-triazol-4-yl)benzamidinehexaaquatricobalt(11) hexanitrate dihydrate and hexa-N'-(4H-1,2,4-triazol-4-yl)benzamidinehexaaquatrinickel(11) hexanitrate dihydrate [ $M_3(L^2)_6(H_2O)_6$ ](NO<sub>3</sub>)<sub>6</sub>·2H<sub>2</sub>O (M = Co (4), Ni (5)). A hot solution of L<sup>2</sup> (0.19 g, 1 mmol) in ethanol (7 mL) was added with stirring to a solution of metal nitrate Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1 mmol, 0.29 g) in ethanol (3 mL). The complexes precipitated after evaporation of the excess solvent to ~1/2 of the initial volume. The precipitates were filtered off, washed with hot ethanol, and dried in air. The yields of complexes 4 and 5 were 0.25 g (83%) and 0.19 g (63%), respectively.

Hexa-N'-(4H-1,2,4-triazol-4-yl)benzamidinehexaaquatricobalt(II) hexachloride [Co<sub>3</sub>(L<sup>2</sup>)<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>6</sub> (6) and octa-N'-(4H-1,2,4-triazol-4-yl)benzamidinetetraaquatrinickel(II) hexachloride [Ni<sub>3</sub>(L<sup>2</sup>)<sub>8</sub>(H<sub>2</sub>O)<sub>4</sub>]Cl<sub>6</sub> (7). A solution of metal chloride (0.24 g, 1 mmol) in ethanol (5 mL) was added with stirring to a hot solution of L<sup>2</sup> (0.57 g, 3 mmol) in ethanol (20 mL). Complex 6 precipitated immediately after removal of the excess solvent. Complex 7 precipitated after evaporation of the sovent and storage at ~20 °C for 15 h. The precipitates were filtered off, washed with hot ethanol, and dried in air. The yields of complexes 6 and 7 were 0.26 g (48%) and 0.34 g (52%), respectively.

Di-N'-(4H-1,2,4-triazol-4-yl)benzamidinediaquacopper(II) dinitrate and di-N'-(4H-1,2,4-triazol-4-yl)benzamidinediaquacopper(II) dichloride [Cu(L<sup>2</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]A<sub>2</sub> (A = NO<sub>3</sub> (8), Cl (9)). A hot solution of L<sup>2</sup> (0.19 g, 1 mmol for 8 or 0.38 g, 2 mmol for 9) in ethanol (7 or 15 mL, respectively) was added with stirring to a solution of the copper salt Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.24 g, 1 mmol) or CuCl<sub>2</sub>·2H<sub>2</sub>O (0.17 g, 1 mmol) in ethanol (3 mL). The complexes precipitated immediately after mixing of the starting solutions. The precipitates were filtered off, washed with hot ethanol, and dried in air. The yields of complexes 8 and 9 were 0.25 g (84%) and 0.50 g (92%), respectively.

The elemental analysis data for complexes 1-9 are given in Table 1. The spectroscopic characteristics are listed in Tables 2 and 3.

Hexa-*N*-(1-phenylethylidene)-*N*-(4*H*-1,2,4-triazol-4-yl)aminodiethanoltetraaquatrinickel(n) hexanitrate diethanol tetrahydrate Ni<sub>3</sub>(L<sup>1</sup>)<sub>6</sub>(C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](NO<sub>3</sub>)<sub>6</sub> · 2C<sub>2</sub>H<sub>5</sub>OH · 4H<sub>2</sub>O (10). The ligand L<sup>1</sup> (0.0186 g, 0.1 mmol) was dissolved in ethanol (7 mL), and the solution was added to a solution containing nickel nitrate (0.0158 g, 0.05 mmol) in ethanol (3 mL). The reaction solution was kept at ~20 °C. The slow crystallization during one month afforded single crystals of the lilac-colored complex suitable for X-ray diffraction. According to the elemental analysis and IR spectroscopic data, the polycrystalline phase obtained in the synthesis with the use of large amounts of the starting reagents corresponds to compound 1.

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