Russian Chemical Bulletin, International Edition, Vol. 53, No. 7, pp. 1477—1487, July, 2004

Influence of intermolecular hydrogen bonding on magnetic properties of mononuclear cobalt and nickel pivalates with amidine ligands

**I. G. Fomina,[a] A. A. Sidorov,[a] G. G. Aleksandrov,[a] T. B. Mikhailova,[a] E. V. Pakhmutova,[a]
V. M. Novotortsev,[a] V. N. Ikorskii,[b] and I. L. Eremenko[a]★**

*[a]N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 955 4835. E-mail: ilerem@igic.ras.ru
[b]International Tomography Center, Siberian Branch of the Russian Academy of Sciences,
3a ul. Institutskaya, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 4489*

The magnetic properties of the mononuclear cobalt(II) amidine complex $Co(Me_3CCOO)_2\{H_2N(C_5H_3N)NH(MeC=NH\}$ (**1**) having a tetrahedral structure and its solvate $\mathbf{1} \cdot HOOCCMe_3 \cdot 0.5C_6H_6$ (**1a**) are substantially different. Complex **1** possesses ferromagnetic properties and exhibits residual magnetization at liquid-helium temperatures, whereas solvate **1a** and the octahedral amidine complex $Ni(Me_3CCOO)_2\{H_2N(C_5H_3N)NH(MeC=NH\} \cdot MeCN$ ($\mathbf{3} \cdot MeCN$) show antiferromagnetic properties. Apparently, this is associated with the difference in the type of intermolecular nonbonded interactions in the crystals of **1**, **1a**, and $\mathbf{3} \cdot MeCN$, which form channels for spin-spin exchange. The tetrahedral isostructural mononuclear complexes ML_2 (M = Co (**5**), Ni (**6**), L is *N*-tosyl-2,5-dimethyl-8-aminoquinoline) were synthesized. These complexes exhibit antiferromagnetic properties.

Key words: cobalt(II), nickel(II), trimethylacetate complexes, *N*-(6-amino-2-pyridyl)acetamidine, *N*-tosyl-2,5-dimethyl-8-aminoquinoline, synthesis, X-ray diffraction analysis, crystal structure, hydrogen bonds, magnetic properties.

Earlier,[1] we have found that the mononuclear complex $Co(Me_3CCOO)_2\{H_2N(C_5H_3N)NH(MeC=NH)\}$ (**1**) containing the tetrahedral cobalt atom and the amidine ligand exhibits ferromagnetic properties at helium temperatures. At 2 K, the hysteresis loop is observed with a coercive force of 1 kOe (Fig. 1).

It was hypothesized that this effect is caused by intermolecular spin-spin couplings, which are particularly pronounced at low temperatures due to the unit-cell contraction and, as a result, a decrease in the distance between the magnetic centers. Analysis of the molecular packing in the crystal of complex **1** at 110 K revealed the presence of the (OOCR)O...H—N(amidine) hydrogen bonds between the adjacent molecules, which could potentially serve as channels for intermolecular exchange. One would expect that if the magnetic properties were determined predominantly by intermolecular spin-spin couplings between the paramagnetic Co^{II} atoms, the

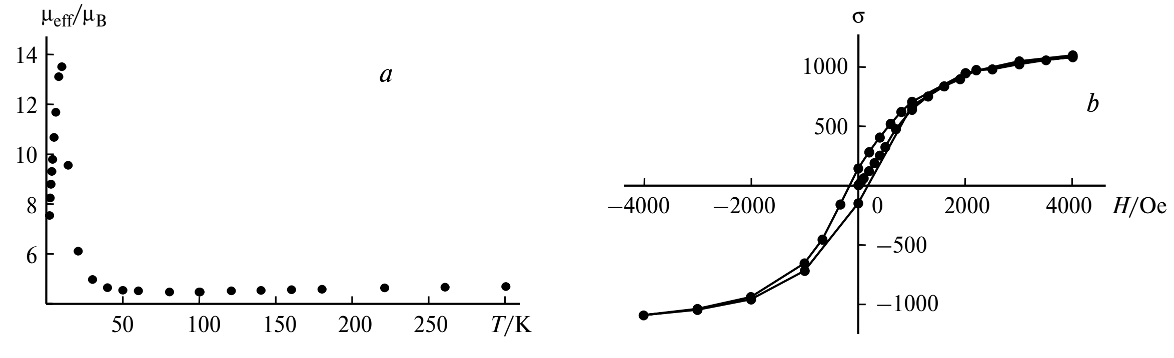


Fig. 1. Magnetic properties of $Co\{H_2N(C_5H_3N)NH(MeC=NH)\}(Me_3CCOO)_2$ (**1**): the temperature dependence of the effective magnetic moment (*a*) and the plot of the magnetization *vs.* the magnetic field strength (*b*).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1422—1431, July, 2004.

change in the hydrogen bond network in the crystal structure of **1** would change the exchange channels and, correspondingly, the magnetic properties of the compound. This assumption can be verified by modifying the network of hydrogen bonds between paramagnetic molecules **1** through blocking some protons of the N—H groups of the amidine ligands with diamagnetic solvate molecules. Another way is to change the spin state of the magnetic center, which could lead to a different type of exchange interactions.

It should be noted that the change in the type of exchange interactions from antiferromagnetic to ferromagnetic has been observed earlier upon the replacement of the cobalt atoms with the nickel atoms in dinuclear trimethylacetates $M_2(\mu\text{-}OH_2)(\mu\text{-}OOCCMe_3)_2(OOCCMe_3)_2L_4$ (M = Co [2,3] or Ni;[4,5] L is a pyridine base). However, the exchange in these system is intramolecular in character. In the present study, we used both ways of varying the magnetic properties, *viz.*, the introduction of diamagnetic solvate molecules of trimethylacetic acid and benzene, which can alter the hydrogen bond network in the crystal, and the replacement of the cobalt(II) atoms with nickel(II) atoms, which are in another spin state (S = 1).

Results and Discussion

Earlier, we have prepared the solvate of complex **1** with benzene and trimethylacetic acid as a by-product of the reaction of 2,6-diaminopyridine with the dinuclear complex $Co_2(\mu\text{-}OH_2)(OOCCMe_3)_4(HOOCCMe_3)_4$ in benzene followed by recrystallization of the amino complex that formed from a benzene-acetonitrile solution.[1] It appeared that, unlike the unsolvated complex, the solvate $Co(Me_3CCOO)_2\{H_2N(C_5H_3N)NH(MeC{=}NH)\} \cdot Me_3CCOOH \cdot 0.5C_6H_6$ (**1a**) exhibits antiferromagnetic properties. Its effective magnetic moment decreases from 4.52 to 2.61 μ_B in the temperature range of 300—2 K due to spin-orbital interactions and antiferromagnetic spin-spin exchange[6,7] (Fig. 2).

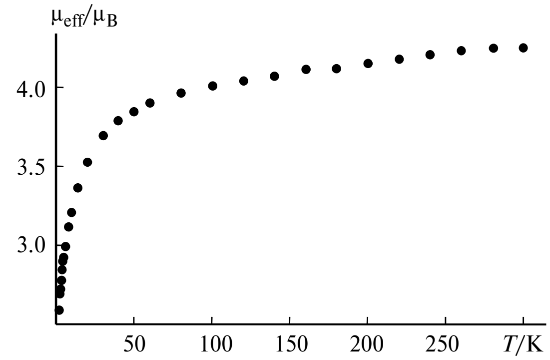


Fig. 2. Magnetic properties of the solvate $Co(Me_3CCOO)_2\{H_2N(C_5H_3N)NH(MeC{=}NH)\} \cdot Me_3CCOOH \cdot C_6H_6$ (**1a**).

Analysis of the crystal structures of complex **1** and solvate **1a** demonstrates that the molecular packing of the paramagnetic amidine complex in the unsolvated state differs noticeably from that of the solvated complex (Fig. 3).

It should be noted that the crystal packing of solvate **1a** is more loose. In the crystals of unsolvated compound **1** (see Figs 3, *a* and 4), molecules **1** are linked to each other by two O(C=O)...H—N hydrogen bonds (amino group of the amidine fragment; the length is 1.88(5) Å) to form centrosymmetrical dinuclear fragments. The latter, in turn, are linked to each other by the H(C=C)O...H—N hydrogen bonds (imino group of the amidine fragment; the length is 2.14 Å). The fused six-membered metallocycles and pyridine rings in the dimeric fragments are packed in stacks (distance between the metal—amidine—pyridine planes of the adjacent molecules is 3.26 Å, the intermolecular N(2)...N(2), N(2)...C(11), and N(2)...C(16) distances in the dinuclear fragment are 3.31, 3.66, and 3.40 Å, respectively; C(11)...C(16), 3.39 Å) (see Fig. 4), which does not exclude the formation of π-exchange channels similar to those in the known ionic analogs.[9] This gives rise to close-packed double layers, in which spin-spin exchange channels of different electronic nature are present between the paramagnetic cobalt atoms.

X-ray diffraction study performed at 113 K°[1] demonstrated that in the crystal of solvate **1a**, the proton of the imino group of the amidine fragment is also involved in hydrogen bonding. However, this proton interacts with the carbonyl oxygen atom of the solvate molecule of trimethylacetic acid (C=O...H—N, 2.08(4) Å; see Figs 3, *b* and 5), and the proton of the hydroxy group of the latter is, in turn, linked to the carbonyl oxygen atom of the carboxylate ligand (C—OH...O=C, 1.84(5) Å) present in the same molecule of complex **1**. This oxygen atom interacts with the proton of the amino group bound to the pyridine ring of the amidine ligand of the adjacent molecule (C=O...H_2N(Py), 2.34(5) Å) (see Fig. 5).

Therefore, the network of hydrogen bonds between the paramagnetic molecules of complex **1** in the crystal of **1a** is radically different from that observed in the crystal of unsolvated complex **1**. In addition, the benzene molecules are located between the molecules of complex **1** in the crystal of **1a**. Apparently, these benzene molecules prevent the metal centers from approaching each other closer upon cooling of the solvate to helium temperatures.

In the structures of **1** and **1a**, the carboxylate groups bound to the cobalt atom are in different orientations with the respect to the metalloamidine chelate ring and each other (Fig. 6 *a*, *b*). In particular, the OCO planes form different angles with the Co—N(H)$_{amid}$ bond in molecules **1** (125.9° and 41.8°) and **1a** (149.4° and 55.7°). The angle between the O—C—O planes of the carboxylate

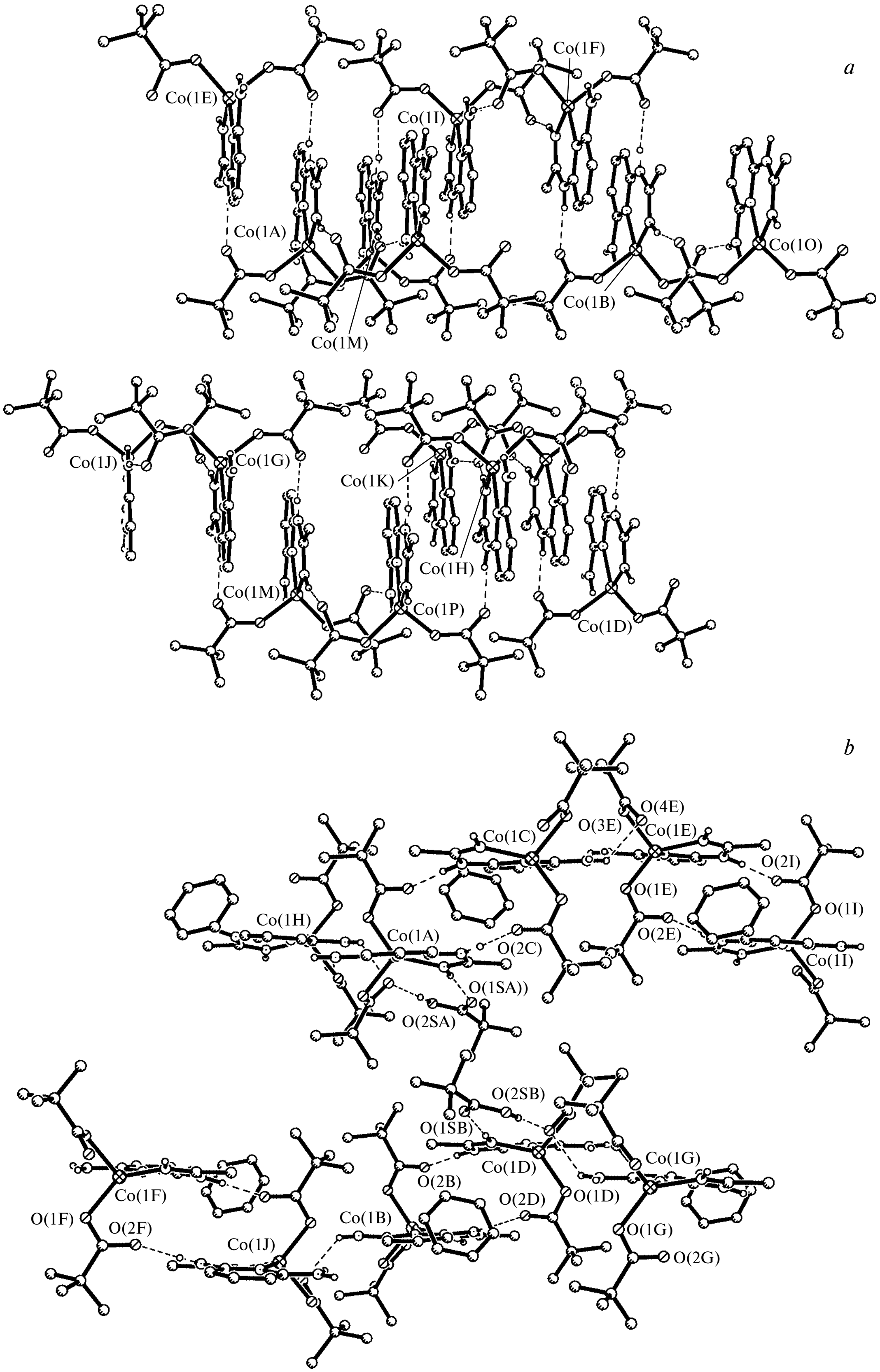


Fig. 3. Fragment of the molecular packing of compounds **1** (*a*, without solvate molecules) and **1a** (*b*, solvate with benzene and trimethylacetic acid).

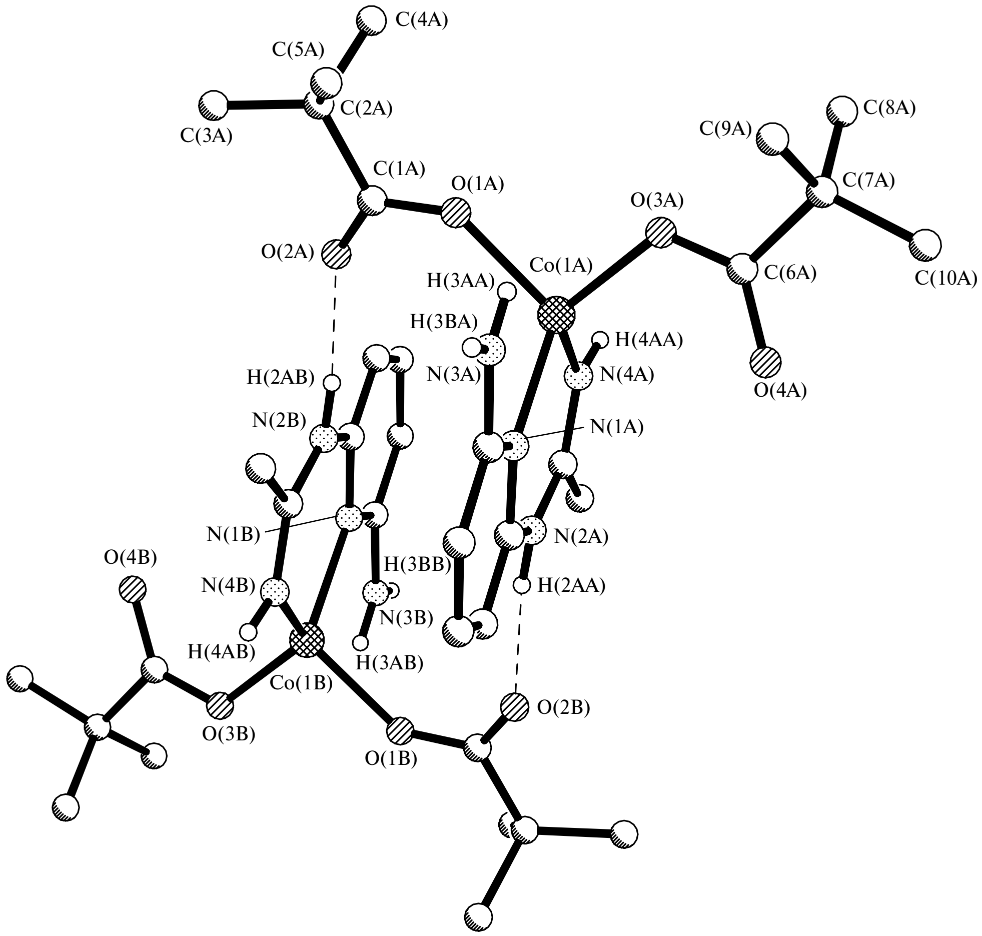


Fig. 4. Dimeric fragment of the molecular packing of unsolvated complex **1**.

anions in molecule **1** (19.3°) also differs from that in molecule **1a** (82.3°). The nonbonded Co—O distances in the structures of **1** and **1a** are also noticeably different (Co(1)...O(2) and Co(1)...O(4) in **1** are 3.311(3)3 and 3.076(3) Å, respectively; Co...O(2) and Co...O(4) in **1a** are 2.667(3) and 2.529(3) Å, respectively). Presumably, the hydrogen bonds stabilize the tetrahedral ligand environment about the cobalt(II) atom in spite of the fact that the metal center in complex **1** formally has the electron-deficient 15-electron configuration. In this case, the protons of the amino or amido groups of the amidine fragment (in compound **1**) or the amino groups bound to the pyridine ring and the acid solvate molecule (in compound **1a**) compete substantially with the cobalt atom for binding with the carbonyl group of the carboxylate ligand, thus hindering chelation. All these differences are also noticeably reflected in the geometric parameters of molecule **1** in the crystals of both the unsolvated complex and solvate (see Fig. 6, Table 1).

Unlike cobalt atoms, nickel atoms are prone to form octahedral metal centers in the mononuclear trimethylacetate complexes[4,5] in spite of formation of an electron-excessive 20-electron configuration. This environment about the nickel(II) atom (S = 1) was observed[1] in the $Ni(OOCCMe_3)_2\{H_2N(C_5H_3N)NH(MeC{=}NH)\}$ complex (**3**), which was synthesized by the reaction of 2,6-diaminopyridine with the dinuclear complex $Ni_2(\mu\text{-}OH_2)(OOCCMe_3)_4(HOOCCMe_3)_4$ (**2**) in an acetonitrile solution.

Compound **3** possessing antiferromagnetic properties (Fig. 7) was isolated in low yield (7%) as the solvate with the acetonitrile molecule. In compound **3**, the *N*-(6-amino-2-pyridyl)acetamidine molecule, like the ligand in complex **1**, is coordinated bidentately to the metal atom (Ni—N, 1.967(4) and 2.097(3) Å) (Fig. 8, Table 2). However, two trimethylacetate anions in complex **3** are coordinated to the metal center in a chelate fashion ($Ni—O(\eta^2\text{-}OOCCMe_3)$, 2.060(3)—2.154(3) Å), and the nickel atom is in an octahedral environment formed by two nitrogen atoms and four oxygen atoms.

In the crystal of solvate **3**·MeCN, the proton of the imino group of the amidine ligand weakly interacts with the nitrogen atom of the acetonitrile solvate molecule ((MeCN)N...H—N(amidine), 2.57(4) Å), which is not involved in binding with other molecules of complex **3** and serves as a pendand. In spite of the difference in the

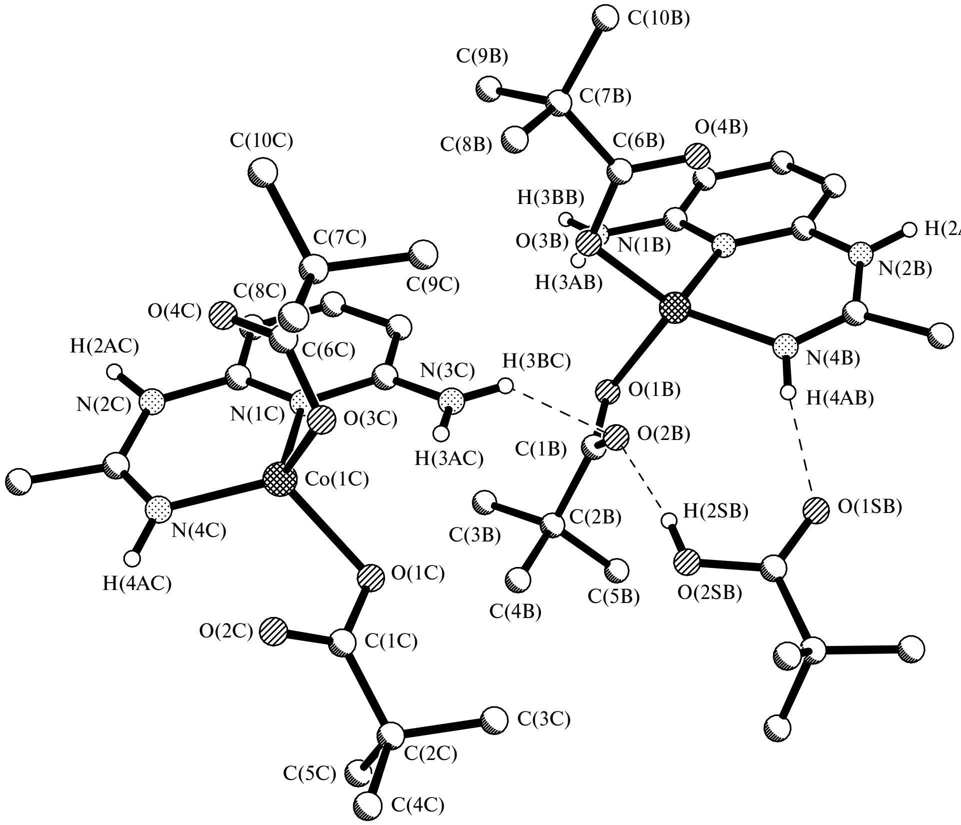


Fig. 5. Hydrogen bonding between the molecules of complex **1a** in the crystal.

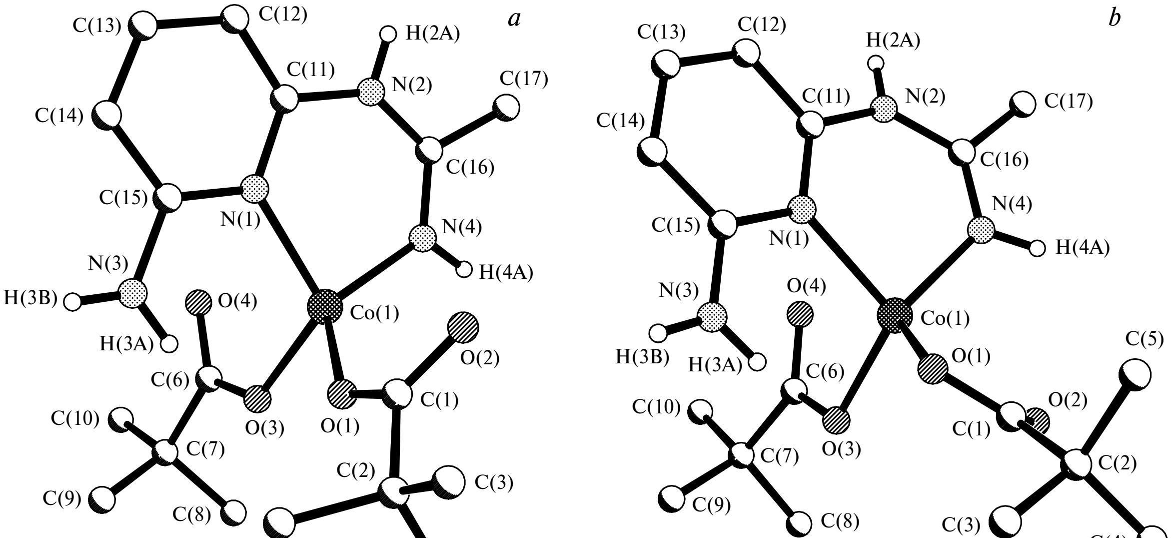


Fig. 6. Structure of complex **1** in the unsolvated (*a*) and solvated (*b*) states.

coordination mode of the carboxylate groups in complexes **1** and **3**, the character of intermolecular interactions in the crystal of the nickel solvate with acetonitrile is analogous to that observed in the crystal of the unsolvated cobalt analog. In the crystals of the nickel derivative (Fig. 9), there are also dimeric fragments formed through the O(C=O)...H—N(amidine) hydrogen bonds between the oxygen atoms of the carboxylate group and the proton

Table 1. Selected geometric characteristics of the coordination spheres of the cobalt atoms in the unsolvated (**1**) and solvated (**1a**) complexes

Parameter	**1**	**1**·HOOCCMe$_3$·0.5C$_6$H$_6$ (**1a**)
Bond	*d*/Å	
Co(1)—O(1)	1.937(4)	1.959(3)
Co(1)—O(3)	1.952(4)	2.001(3)
Co(1)—N(1)	2.022(5)	2.054(3)
Co(1)—N(3)	1.942(4)	1.950(3)
Angle	ω/deg	
O(1)—Co(1)—O(3)	91.72(19)	101.88(12)
O(1)—Co(1)—N(1)	109.78(19)	113.07(13)
O(1)—Co(1)—N(3)	123.86(18)	129.68(13)
O(3)—Co(1)—N(1)	117.60(17)	102.39(12)
O(3)—Co(1)—N(3)	122.13(17)	114.65(12)
N(1)—Co(1)—N(3)	93.33(18)	92.23(13)

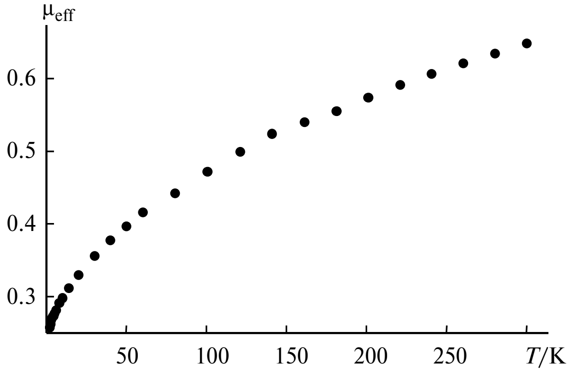


Fig. 7. Magnetic properties of complex **3**.

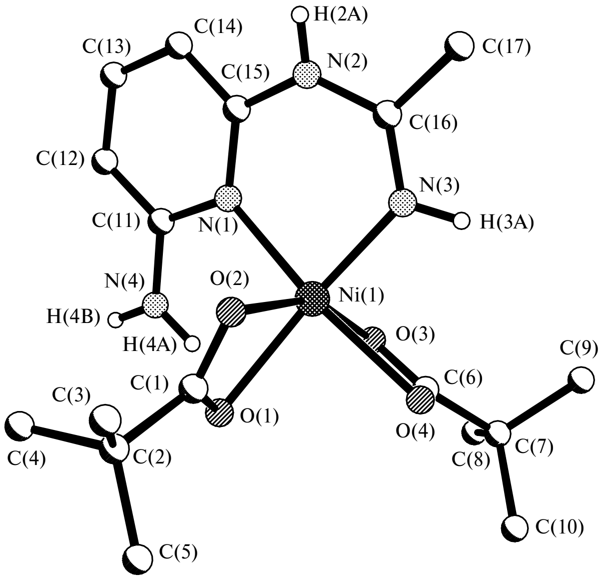


Fig. 8. Molecular structure of the Ni(OOCCMe$_3$)$_2${H$_2$N(C$_5$H$_3$N)NH(MeC=NH)} complex (**3**).

Table 2. Selected geometric parameters of the coordination spheres of the cobalt atoms in four crystallographically independent molecules I—IV of complex **5**

Parameter	I	II	III	IV
Bond		*d*/Å		
Co—N(1)	1.996(18)	2.026(15)	2.009(16)	1.987(14)
Co—N(2)	1.960(14)	1.991(15)	1.940(16)	1.951(16)
Co—N(3)	2.008(14)	2.055(14)	1.963(16)	2.001(15)
Co—N(4)	1.927(14)	1.947(15)	1.928(14)	1.908(17)
Angle		ω/deg		
N(1)—Co—N(2)	82.9(7)	83.6(6)	81.3(6)	81.4(6)
N(1)—Co—N(3)	115.1(6)	110.5(6)	111.1(6)	109.1(6)
N(1)—Co—N(4)	118.9(6)	123.8(6)	121.7(6)	125.5(6)
N(2)—Co—N(3)	125.4(6)	128.8(6)	123.7(6)	119.8(6)
N(2)—Co—N(4)	134.9(6)	131.4(6)	137.3(6)	137.5(6)
N(3)—Co—N(4)	83.0(6)	82.2(6)	84.0(6)	84.8(6)

of the amino group of the amidine fragment (1.97(5) Å). The planar fragments of the adjacent molecules formed by the chelate and pyridine rings are also located one above another (distance between the planes is 3.20 Å). Hence, π interactions between these fragments are not inconceivable.

However, the mode of hydrogen bonding between the dimeric fragments in the nickel compound differs from that in the cobalt complex, in which the protons of the amino group of the amidine fragment are involved in hydrogen bonds. In the nickel complex, such dimers are linked to each other through hydrogen bonds between the proton of the amino group bound to the pyridine ring and the oxygen atom of the carboxylate group (NH$_2$...O(OOCR), 2.11(5) Å) of the complex involved in the adjacent dinuclear fragment (see Fig. 9). Apparently, the difference in the magnetic behavior of these compounds is associated not only with the difference in the spin state and ligand environment about the metal center but also with the difference in the mode of intermolecular bonding.

The results of the present study provide evidence that the magnetic properties of compounds depend substantially on the type of hydrogen bonding between complexes with the same composition in the crystals. Apparently, the difference in nonbonded interactions of magnetic molecules containing metal centers in the same or different spin states results in the difference in the orientation of the magnetic orbitals and the degree of splitting between these orbitals, which is the main reason for the difference in the magnetic behavior of these compounds.

Although the composition of amidine complex **1** is identical to that of complex **3**, their structures are substantially different. To synthesize structurally identical complexes containing a tetrahedral metal center, we used *N*-tosyl-2,4-dimethyl-8-aminoquinoline (**HL**, **4**). It should be noted that the introduction of the bulky tosyl

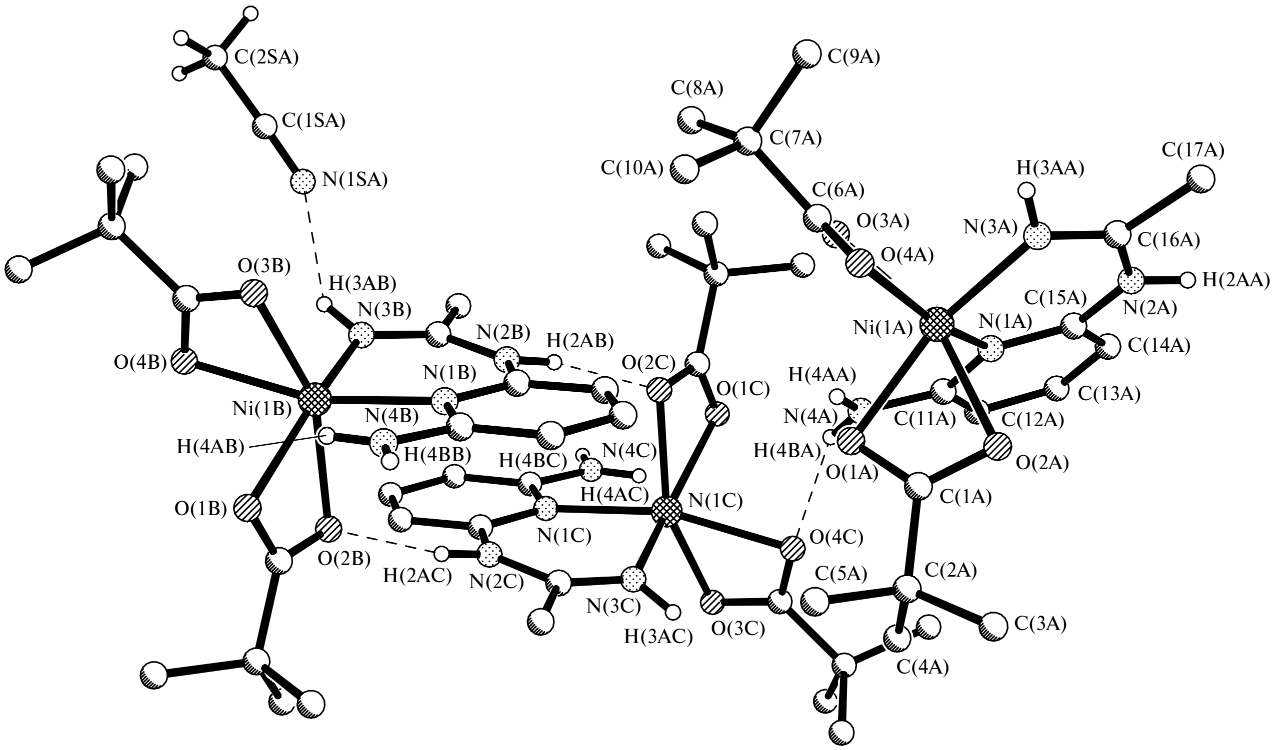


Fig. 9. Fragment of the molecular packing of complex **3** and the acetonitrile molecules in the crystal.

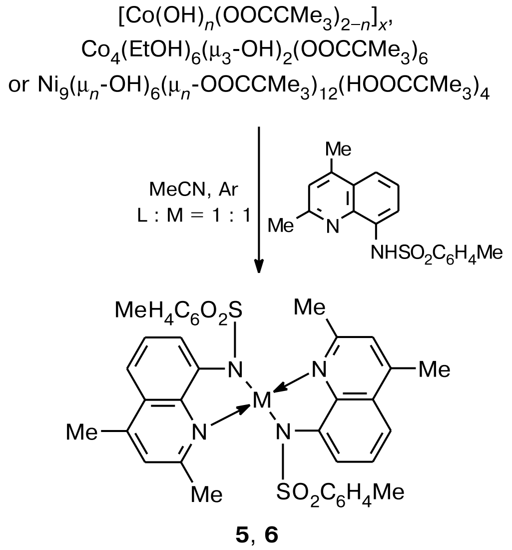
substituent into the amino group hinders the formation of amide bridges, and the acidic properties of the proton that remained intact are substantially enhanced because the sulfo group is highly electrophilic and causes an inductive shift of electrons, thus facilitatating hydrogen abstraction.[9]

It appeared that the reactions of the polynuclear cobalt(II) trimethylacetate complexes $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ (n = 0.05—0.1),[10] $Co_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$,[11] or the nickel(II) trimethylacetate complex $Ni_9(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_n\text{-}OOCCMe_3)_{12}(HOOCCMe_3)_4$ [12] with compound **4** (20 °C, MeCN, M : **HL** = 1 : 1, Scheme 1) resulted in elimination of all trimethylacetate and hydroxy ligands in the starting compounds giving rise to the isostructural mononuclear complexes with composition ML_2 ($M\{Me_2C_9H_4N[N—O_2S(C_6H_4)Me]\}_2$, L is *N*-tosyl-2,4-dimethyl-8-aminoquinoline, M = Co (**5**) or Ni (**6**); the yields were 38 and 43%, respectively).

According to the results of X-ray diffraction study of the solvates with acetonitrile **5**·0.75MeCN and **6**·3MeCN, the metal atom in both complexes is in a tetrahedral environment formed by two chelate-coordinated tosylated aminoquinoline fragments (Co—N_{py}, 1.963(15)—2.055(14) Å; Co—N_{Ts}, 1.908(17)—1.991(15) Å; Ni—N_{py}, 2.003(5)—2.014(6) Å; Ni—N_{Ts}, 1.937(6)—1.949(6) Å) (Fig. 10, Tables 2 and 3).

The acetonitrile solvate molecules are not coordinated to the molecules of the complexes. The latter are also not linked to each other by hydrogen bonds because of the absence of protons at the nitrogen atoms of the amido groups. However, the crystals can be described as consisting of pairs of complexes **5** or **6**, which are located rather close to each other (Fig. 11, *a*, *b*) due, apparently, to

Scheme 1



5, **6**

M = Co (**5**), Ni (**6**)

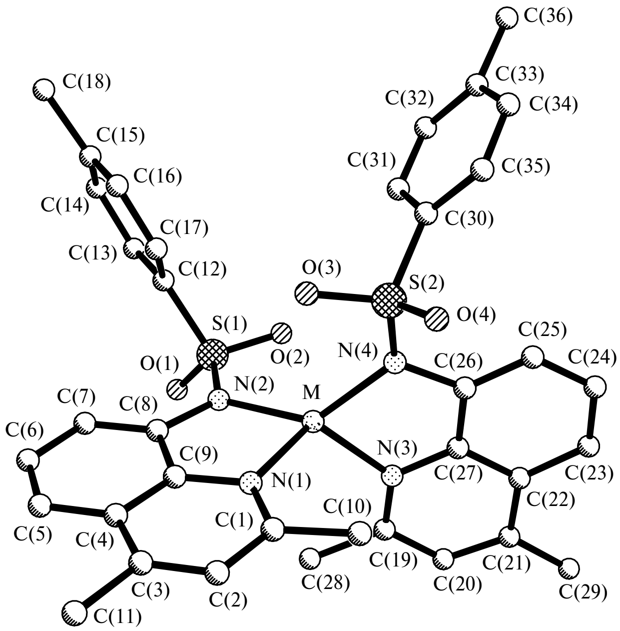


Fig. 10. Molecular structures of the $M\{Me_2C_9H_4N(NO_2S(C_6H_4)Me)\}_2$ complexes (M = Co (**5**), Ni (**6**)).

Table 3. Selected geometric parameters of the coordination sphere of the nickel atom in complex **6**

Bond	*d*/Å	Angle	ω/deg
Ni(1)—N(2)	1.937(6)	N(2)—Ni(1)—N(4)	144.4(2)
Ni(1)—N(1)	2.003(5)	N(4)—Ni(1)—N(1)	120.4(2)
Ni(1)—N(4)	1.949(6)	N(4)—Ni(1)—N(3)	81.8(2)
Ni(1)—N(3)	2.014(6)	N(2)—Ni(1)—N(1)	81.7(2)
		N(2)—Ni(1)—N(3)	120.9(2)
		N(1)—Ni(1)—N(3)	106.6(2)

weak π—π interactions between the delocalized metalloquinoline fragments.

The distances between the planes of the parallel metallocycles in compounds **5** and **6** are 3.35(2) and 3.46(2) Å, respectively. The minimum distances between the atoms of the aminoquinoline rings in the dinuclear fragments in the structures of **5** and **6** (see Fig. 11, the projection of the structure of **5** is shown) are in the range of 3.45—3.68 Å.

In spite of the different nature of the metal centers, mononuclear compounds **5** and **6**, unlike complex **1**, exhibit antiferromagnetic properties (Fig. 12 *a*, *b*).

Apparently, in the absence of hydrogen bonds between the magnetic molecules, spin-spin exchange can occur through π channels or due to the occurrence of the weak C—H...O(O_2S-*p*-Ts) interaction between the aromatic rings of the quinoline fragment and the tosylate substituents of the amido groups of the adjacent molecules. However, these nonbonded interactions lead only to antiferromagnetic exchange.

Therefore, one would expect the manifestation of ferromagnetic properties in the presence of strong hydrogen bonding between the magnetic molecules (or ions) to form polynuclear supramolecular architectures (chains or networks), as was observed in the crystal of complex **1** or in the molecular ferromagnetic complex $\{Co_3[(\eta^2\text{-}1,2\text{-}NH_2)_2C_6H_2Me_2]_2(\mu\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)_2(OOCCMe_3)_2(HOOCCMe_3)_2\}\cdot\{Co[(\eta^2\text{-}1,2\text{-}NH_2)_2C_6H_2Me_2]_2(OOCCMe_3)_2\}$ composed of the mononuclear and trinuclear fragments, which we have prepared recently.[13] It should be noted that hydrogen bonding between magnetic molecules alone is, apparently, not necessarily sufficient for the manifestation of ferromagnetism. In this case, a polymeric magnetic matrix should, presumably, be formed due to the presence of different types of intermolecular nonbonded interactions. Hence, the difference in the character of nonbonded interactions between magnetic molecules containing metal centers in the same or different spin states is likely to be responsible for the difference in orientation of the magnetic orbitals and the degree of splitting between these orbitals, which is the main reason for the difference in the magnetic behavior of these compounds.

Experimental

The complexes were synthesized in air using anhydrous solvents. The starting polynuclear cobalt and nickel trimethylacetate complexes[10—12] and the complexes and solvates **1**, **1a**, and **3**·MeCN were prepared according to procedures described earlier. New compounds were synthesized with the use of *N*-tosyl-2,4-dimethyl-8-aminoquinoline purchased from Fluka. The IR spectra were recorded on a Specord M-80 spectrophotometer in KBr pellets. The static magnetic susceptibility was measured on a SQUID MPMS-59 Quantum Design magnetometer in the temperature range of 2—300 K. The effective magnetic moments were calculated by the equation $\mu_{eff} = (8\chi_M T)^{1/2}$.[6]

Bis(*N*-tosyl-2,4-dimethyl-8-amidoquinolino)cobalt(II), solvate with acetonitrile, $Co[\eta^2\text{-}Me_2C_9H_4N(NSO_2C_6H_4Me)]_2\cdot0.75MeCN$, (5·0.75MeCN). Acetonitrile (30 mL) was added to the $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ polymer (0.13 g, 0.5 mmol based on the formula unit $Co(OOCCMe_3)_2$) or the $Co_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\eta^2\text{-}OOCCMe_3)_2(EtOH)_6$ complex (0.14 g, 1.2 mmol) and compound **4** (0.16 g, 0.5 mmol). The reaction mixture was stirred at 80 °C for 15 min until the reagents were completely dissolved. The solution was concentrated to 5 mL at 0.1 Torr (60 °C) and kept at ~20 °C for 24 h. The crimson crystals of solvate **5**·0.75MeCN that precipitated were separated from the solution by decantation, washed with cold hexane, and dried under a stream of argon. The yield of **5**·0.75MeCN was 0.14 g (38% with respect to the starting amount of cobalt). Found (%): C, 60.4; H, 4.7; N, 8.9. $C_{37.5}H_{36.25}N_{4.75}CoO_4S$. Calculated (%): C, 60.82; H, 4.98; N, 8.99. IR (KBr), ν/cm^{-1}: 3420 w, 3080 w, 2920 w, 1664 m, 1568 m, 1556 m, 1508 m, 1456 s, 1436 m, 1404 w, 1376 w,

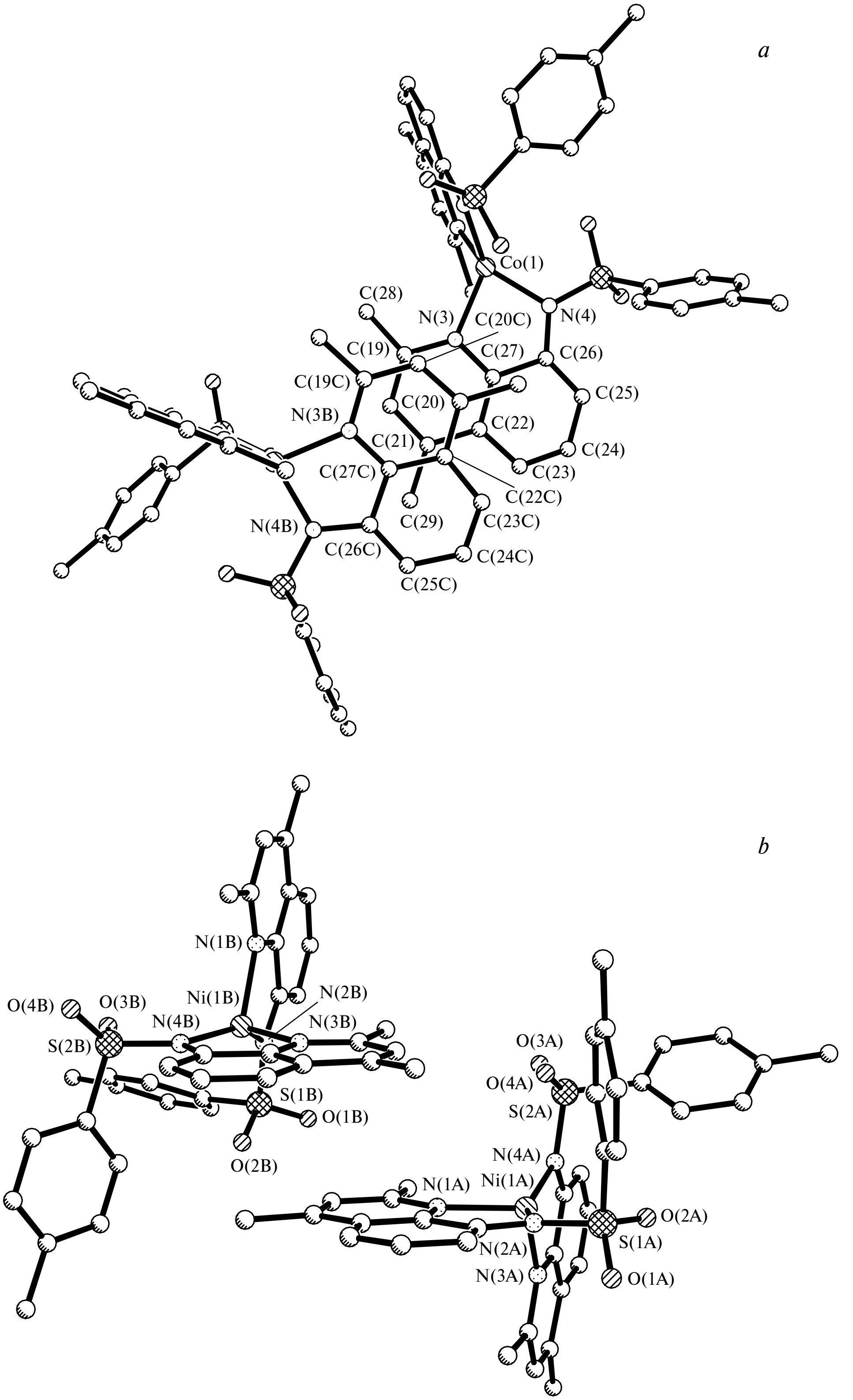


Fig. 11. Fragment of the arrangement of the molecules of complexes **5** (*a*, the dimeric fragment of the packing of **5** projected onto the plane of the amidoquinoline fragment) and **6** (*b*) in the crystals.

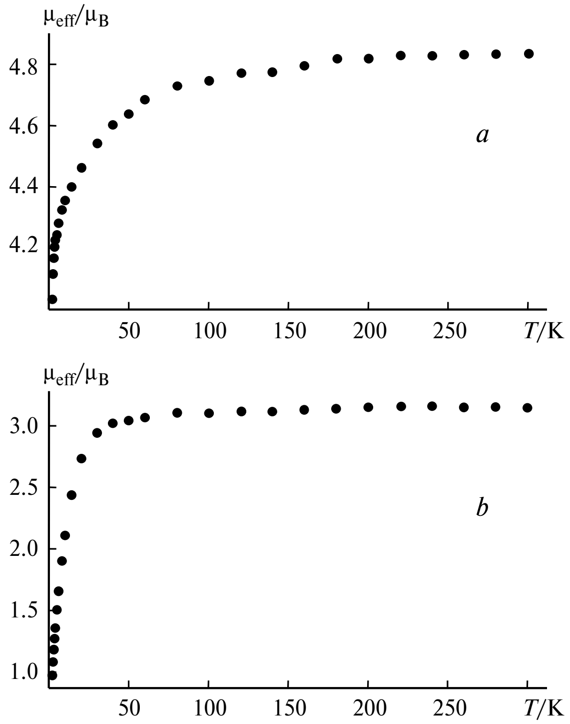


Fig. 12. Magnetic properties of complexes **5** (*a*) and **6** (*b*).

1348 w, 1328 s, 1280 s, 1236 w, 1160 m, 1140 v.s, 1088 s, 1028 s, 992 w, 976 w, 884 m, 860 m, 776 m, 748 m, 660 s, 620 w, 576 s, 552 s.

The crystals were suitable for X-ray diffraction study.

Bis(*N*-tosyl-2,4-dimethyl-8-amidoquinolino)nickel(II), trisolvate with acetonitrile, Ni[η^2-$Me_2C_9H_4N(NSO_2C_6H_4Me)]_2\cdot$ $\cdot$3MeCN (6·3MeCN). Acetonitrile (20 mL) was added to the $Ni_9(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_n\text{-}OOCCMe_3)_{12}(HOOCCMe_3)_4$ cluster (0.09 g, 0.28 mmol) and compound **4** (0.07 g, 0.03 mmol). The reaction mixture was stirred under argon at 80 °C for 15 min until the reagents were completely dissolved. The solution was concentrated to 5 mL at 0.1 Torr (20 °C) and kept at ~20 °C for 24 h. The red crystals of solvate **6**·3MeCN that precipitated were separated from the solution by decantation, washed with cold hexane, and dried under a stream of argon. The yield of **6**·3MeCN was 0.09 g (43% with respect to the starting amount of nickel). Found (%): C, 60.7; H, 5.5; N, 10.7. $C_{40}H_{40}N_6NiO_4S_2$. Calculated (%): C, 60.67; H, 5.1; N, 10.62. IR (KBr), ν/cm^{-1}: 3420 w, 3080 w, 2920 w, 1664 m, 1600 m, 1568 m, 1556 w, 1508 m, 1460 s, 1436 s, 1404 m, 1380 w, 1348 w, 1328 s, 1280 s, 1236 w, 1180 w, 1140 v.s, 1088 s, 1024 s, 988 w, 976 w, 880 m, 860 m, 776 m, 748 m, 708 w, 680 w, 660 s, 620 w, 576 s, 558 s.

The crystals were suitable for X-ray diffraction study.

X-ray diffraction study. The experimental data sets for the solvates **5**·0.75MeCN and **6**·3MeCN were collected on an automated Bruker AXS SMART 1000 diffractometer equipped with a CCD detector using a standard procedure.[14] The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The hydrogen atoms of the tosylate group, the quinoline fragment, the methyl substituents, and the acetonitrile solvate molecules were generated geometrically and refined using the riding model. All calculations were carried out with the use of the SHELX97 program package.[15,16] The selected geometric parameters of molecules **5** and **6** are listed in Tables 2 and 3, respectively. The crystallographic parameters and details of structure refinement are given in Table 4.

Table 4. Crystallographic parameters of the compounds studied

Parameter	**5**·0.75MeCN	**6**·3MeCN
Molecular formula	$C_{38}H_{42}CoN_4O_4S_2\cdot$ 0.75MeCN	$C_{38}H_{42}N_4NiO_4S_2\cdot$ 3MeCN
Space group	$P\bar{1}$	$C2/c$
a/Å	16.625(12)	30.327(11)
b/Å	21.855(13)	14.580(4)
c/Å	22.192(13)	23.607(6)
α/deg	67.74(9)	90
β/deg	83.52(4)	124.315(14)
γ/deg	75.55(3)	90
V/Å^3	7225(8)	8622(5)
Z	8*	8
ρ_{calc}/g cm^{-3}	1.373	1.220
μ/mm^{-1}	0.637	0.591
Number of measured reflections	18885	10213
Number of reflections with $I > 2.0\sigma$	13791	6343
R_1	0.0758	0.0812
wR_2	0.1468	0.2134

* There are four independent molecules of complex **5** and three acetonitrile molecules per asymmetric unit cell.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos. 04-03-32883, 04-03-32880, and 02-03-33075), the Chemistry and Materials Science Division of the Russian Academy of Sciences (Target Program of Basic Research "Chemistry and Physical Chemistry of Supramolecular Systems and Atomic Clusters"), and INTAS (Grant 03-51-4532).

References

1. T. B. Mikhailova, E. V. Pakhmutova, A. E. Malkov, I. F. Golovaneva, A. A. Sidorov, I. G. Fomina, G. G. Aleksandrov, V. N. Ikorskii, V. M. Novotortsev, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1994 [*Russ. Chem Bull.*, *Int. Ed.*, 2003, **52**, 2105].
2. M. A. Golubnichaya, A. A. Sidorov, I. G. Fomina, L. T. Eremenko, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Zh. Neorg. Khim.,* 1999, **44**, 1479 [*Russ. J. Inorg. Chem.*, 1999, **44** (Engl. Transl.)].
3. T. B. Mikhailova, A. E. Malkov, A. A. Sidorov, G. G. Aleksandrov, I. F. Golovaneva, V. M. Dem´yanovich, V. M. Novotortsev, V. N. Ikorskii, S. E. Nefedov, and I. L. Eremenko, *Zh. Neorg. Khim.,* 2002, **47**, 1829 [*Russ. J. Inorg. Chem.*, 2002, **47** (Engl. Transl.)].

4. I. L. Eremenko, S. E. Nefedov, A. A. Sidorov, M. A. Golubnichaya, P. V. Danilov, V. N. Ikorskii, Yu. G. Shvedenkov, V. M. Novotortsev, and I. I. Moiseev, *Inorg. Chem.*, 1999, **38**, 3764.
5. I. L. Eremenko, S. E. Nefedov, A. A. Sidorov, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 409 [*Russ. Chem. Bull.*, 1999, **48**, 405 (Engl. Transl.)].
6. Yu. V. Rakitin and V. T. Kalinnikov, *Sovremennaya magnetokhimiya* [*Modern Magnetochemistry*], Nauka, St.-Petersburg, 1994, 272 pp. (in Russian).
7. M. V. Eremin, V. N. Kalinenkov, and Yu. V. Rakitin, *Phys. Stat. Sol. (b)*, 1978, **89**, 503.
8. J.-M. Lehn, *Supramolecular Chemistry. Concepts and Perspectives*, VCH, New York, 1998, 140.
9. L. F. Fieser and M. Fieser, *Organic Chemistry*, D. C. Healh, Boston, 1944.
10. M. A. Golubnichaya, A. A. Sidorov, I. G. Fomina, M. O. Ponina, S. M. Deomidov, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1773 [*Russ. Chem. Bull.*, 1999, **48**, 1751 (Engl. Transl.)].
11. A. A. Sidorov, I. G. Fomina, G. G. Aleksandrov, M. O. Ponina, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 960 [*Russ. Chem. Bull.*, *Int. Ed.*, 2000, **49**, 958].
12. A. A. Sidorov, P. V. Danilov, S. E. Nefedov, M. A. Golubnichaya, I. G. Fomina, O. G. Ellert, V. M. Novotortsev, and I. L. Eremenko, *Zh. Neorg. Khim.,* 1998, **43**, 930 [*Russ. J. Inorg. Chem.*, 1998, **43** (Engl. Transl.)].
13. A. E. Malkov, I. G. Fomina, A. A. Sidorov, G. G. Aleksandrov, V. M. Novotortsev, V. N. Ikorskii, and I. L. Eremenko, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 489 [*Russ. Chem. Bull.*, *Int. Ed.*, 2003, **52**, 513].
14. SMART (Control) and SAINT (Integration) Software, Version 5.0, Bruker AXS Inc., Madison, WI, 1997.
15. G. M. Sheldrick, *SADABS*, *Program for Scanning and Correction of Area Detector Data*, Göttingen University, Göttinngen, Germany, 1997.
16. G. M. Sheldrick, *SHELX-97*, *Program for the Solution of Crystal Structures*, Göttingen University, Göttingen, Germany, 1997.

Received March 4, 2004;
in revised form June 23, 2004