Unusual magnetic behavior of the new supramolecular ensemble $[Ni_2L_4]_2 \cdot [NiCl_2(LH)_2(MeCN)_2] \cdot 4MeCN$ (LH is 2-mercaptobenzimidazole)

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The diamagnetic dinuclear complex Ni_2L_4 was synthesized by the reaction of $NiCl_2 \cdot 6H_2O$ with 2-mercaptobenzimidazole (LH) in ethanol in the presence of Et_3N. The solid-state reaction (reagent ratio Ni : LH = 1 : 2) followed by recrystallization of the reaction product from a MeCN—THF mixture afforded crystals of the associate $[Ni_2L_4]_2 \cdot [NiCl_2(LH)_2(MeCN)_2]$ containing four acetonitrile solvate molecules. Crystals of **2**·4MeCN exhibit ferromagnetic properties at helium temperatures.

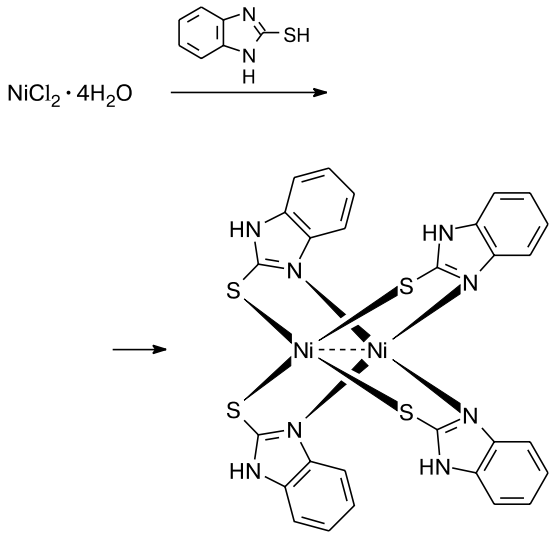
Key words: mono- and dinuclear 2-mercaptobenzimidazole nickel(II) complexes; X-ray diffraction study, magnetic properties.

Molecular magnetic systems containing high-spin transition metal atoms have attracted considerable attention due to their possible use in molecular electronics and spintronics.[1] In the last decade, the number of new compounds exhibiting ferromagnetic properties or at least ferromagnetic spin-spin exchange interactions has increased considerably.[2—5] Among these compounds are polynuclear nickel pivalate complexes containing two,[6—10] four,[11] or five[12] metal atoms characterized by ferromagnetic spin-spin exchange interactions. In these molecules, the Ni^{II} atoms are linked by bridging carboxylate groups, as well as by aqua, hydroxo, or oxo bridges. In the present study, we synthesized new polynuclear nickel(II) complexes with 2-mercaptobenzimidazole (**LH**) containing S—C—N bridges.[13]

Results and Discussion

The reaction of $NiCl_2 \cdot 6H_2O$ with LH in EtOH in the presence of Et_3N produces the dinuclear nickel complex $Ni_2(\mu\text{-}(L))_4$ (**1**) (Scheme 1).

Scheme 1



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Reagents and conditions: 90 °C, EtOH (1 : 1), Et_3N.

† Deceased.

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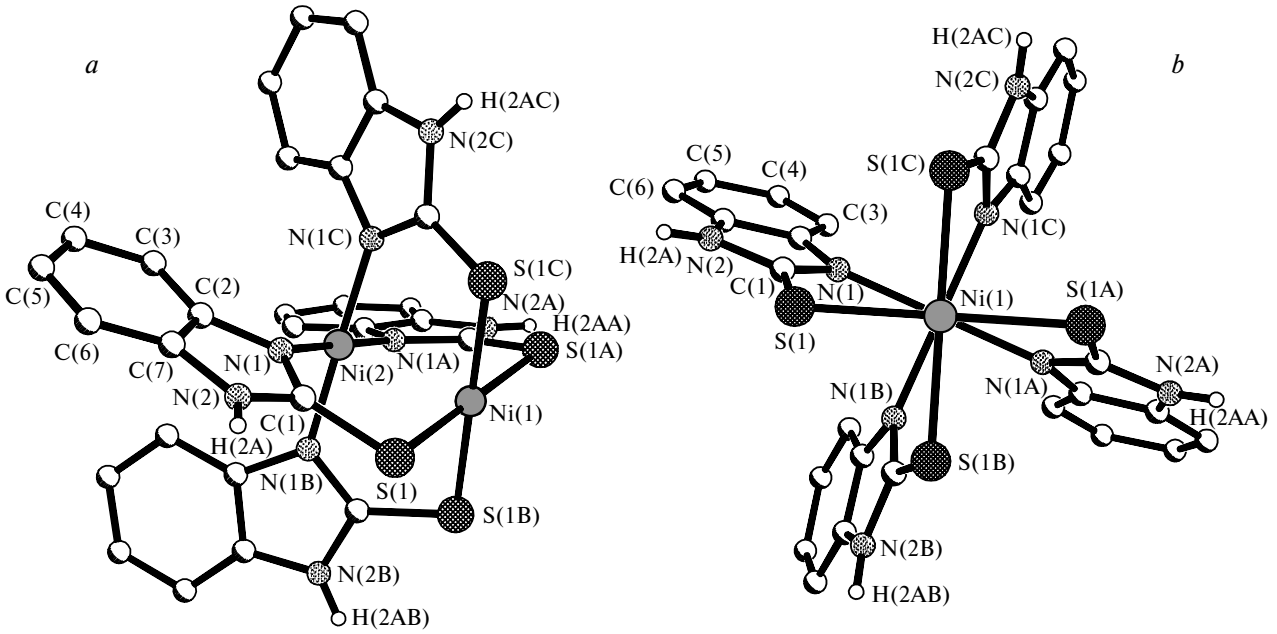


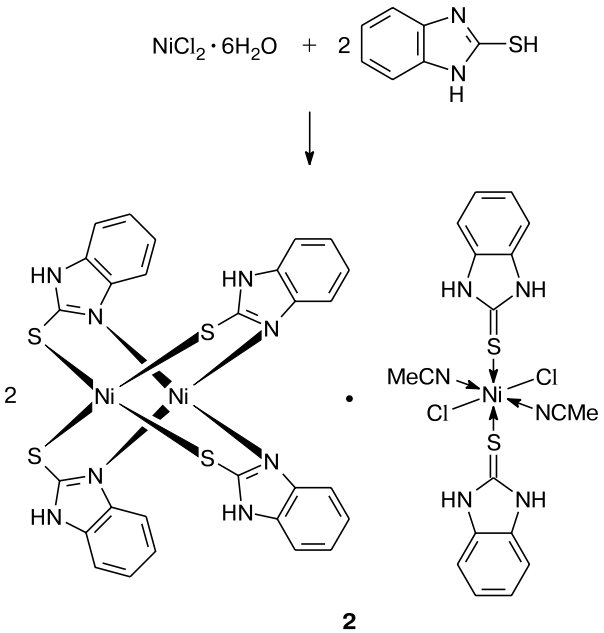
Fig. 1. Molecular structure of dinuclear nickel complex **1** (*a*) and the projection of molecule **1** along the Ni...Ni axis (*b*).

Complex **1** was isolated as a solvate with four water molecules (**1**·4H_2O). X-ray diffraction study of the solvate revealed that the nickel atoms in diamagnetic molecule **1** are located at a short distance (2.616(2) Å), which is apparently nonbonded because the metal atoms are in a low-spin square-planar ligand environment. The molecule contains two different types of Ni^{II} atoms. One nickel atom is coordinated by four sulfur atoms (Ni—S, 2.235(2) Å) of four bridging S—C—N fragments, whereas another nickel atom is coordinated by four nitrogen atoms (Ni—N, 1.884(6) Å) of these bridging groups. In this structure, the metal atom in the NiN_4 fragment is sterically shielded because the phenylene rings of the bridging ligands point in the same direction, whereas the nickel atom in the NiS_4 fragment is formally accessible for further coordination by donor atoms (Fig. 1, *a*). The protons of the NH groups form hydrogen bonds with water solvate molecules (N—H...O(H_2O), 2.04(2) Å).

The NiSCNNi fragments in molecule **1** are nonplanar. The nickel atoms deviate from the SCN plane by 0.736 Å (Fig. 1, *b*). Apparently, the nonplanar conformation of this fragment is associated with a decrease in the electron density delocalization in this fragment, although the steric factors also cannot be ruled out.

The solid-state reaction of $NiCl_2 \cdot 6H_2O$ with LH in the presence of KOH (2—3 drops of EtOH, 20 °C, 20 min) (Scheme 2) produces a mononuclear complex, which is apparently an intermediate in this process. The resulting cocrystals consist of complex **1** and the mononuclear nickel(II) complex containing the coordinated neutral ligands LH in the thione form.

Scheme 2



Reagents and conditions: 80 °C, KOH, THF/MeCN.

The crystals of the associate $[Ni_2L_4]_2 \cdot [NiCl_2(LH)_2(MeCN)_2]$ (**2**) with four MeCN solvate molecules (**2**·4MeCN) were obtained in 76% yield after crystallization of the solid-state reaction product from a MeCN—THF mixture. According to the X-ray diffraction data for the crystals of **2**·4MeCN, two molecules of complex **1** and one molecule of the $NiCl_2(LH)_2(MeCN)_2$

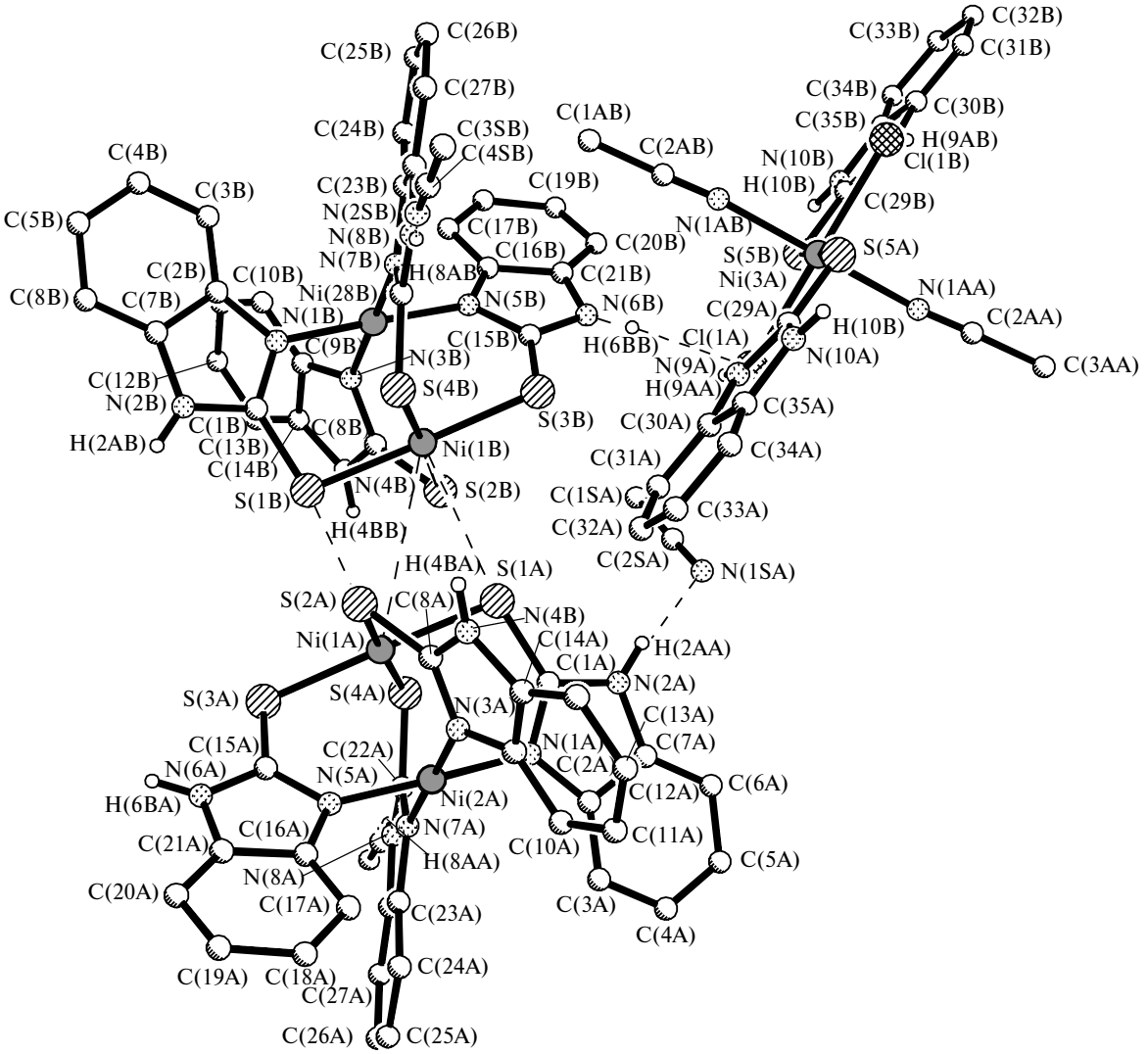


Fig. 2. Structure of associate **2**·4MeCN.

complex form a hydrogen bond system resulting in the formation of channels and layers in the crystal structure (Figs 2 and 3). The NH groups in the benzimidazole-2-thiolate anions L of the dinuclear complex are involved in hydrogen bonding with the MeCN solvate molecules (N—H...NCMe, 2.02(2)—2.09(2) Å) and the S and Cl atoms of the mononuclear complex (N—H...S, 2.62(2) Å; N—H...Cl, 2.36(2) Å). In addition, the NH groups of the mononuclear complex form hydrogen bonds with the S atoms of the ligand of the adjacent complex (N—H...S, 2.62(2) Å).

The main geometric characteristics of the dinuclear molecule in the associate (Ni...Ni, 2.622(1) Å; Ni—S, 2.222(2)—2.254(2) Å; Ni—N, 1.878(5)—1.912(5) Å) are analogous to those found for complex **1**. However, there is a weak interaction between the NiS_4 fragments of two adjacent dinuclear molecules (Ni...S, 3.242(2) Å; Ni...Ni, 3.840(1) Å) in the crystals of **2**·4MeCN. The Ni^{II} atom in the mononuclear complex $NiCl_2(LH)_2(MeCN)_2$ in **2**·4MeCN is in an octahedral coordination environment formed by two *trans*-Cl atoms (Ni—Cl, 2.406(2) Å), two *trans*-LH ligands (in the thione form) (Ni—S, 2.477(2) Å), and two *trans*-MeCN molecules (Ni—N, 2.084(5) Å).

In the supramolecular system, only the mononuclear complex $NiCl_2(LH)_2(MeCN)_2$ containing the metal atom in an octahedral environment is magnetoactive (Ni^{II}, $S = 1$), whereas the dinuclear complexes Ni_2L_4 are diamagnetic. However, associate **2**·4MeCN exhibits unusual magnetic behavior. The magnetic moment of this associate gradually decreases from 1.586 μ_B (300 K) to 1.388 μ_B (100 K), passes through a minimum, then increases with decreasing temperature, and reaches a maximum (2.019 μ_B) at 14 K. In the temperature range of 14—2 K, the magnetic moment again sharply decreases to 0.981 μ_B (2 K) due, apparently, to antiferromagnetic intermolecular exchange (Fig. 4). This unexpected mag-

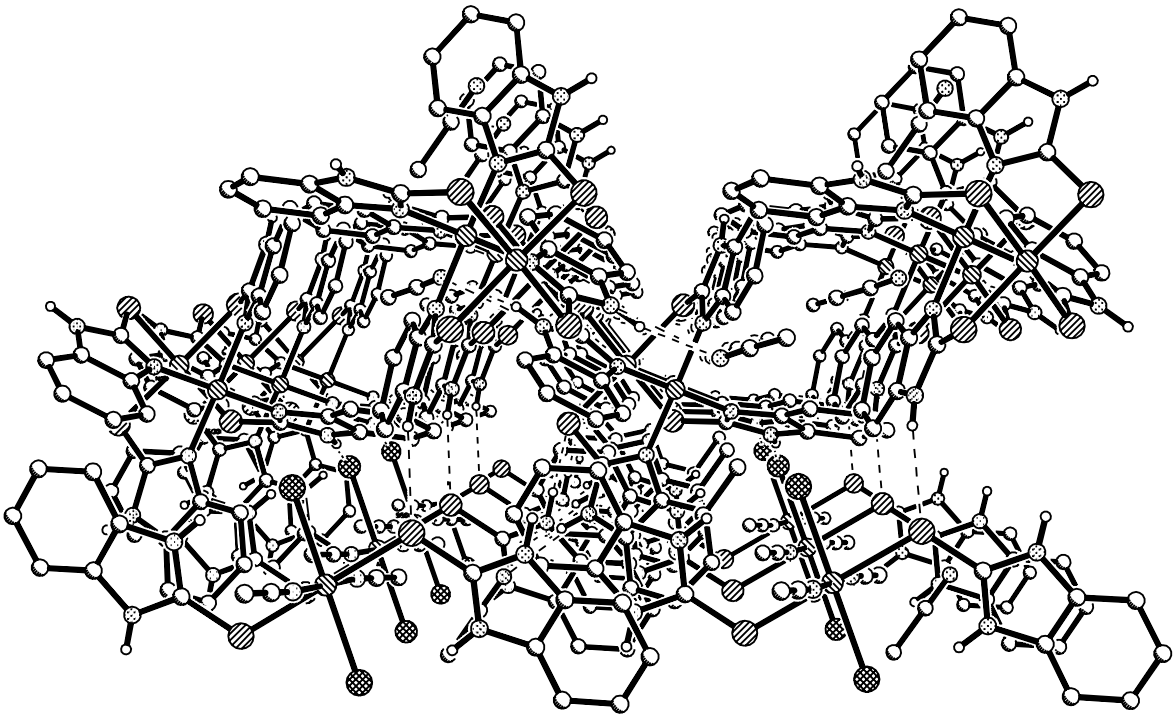


Fig. 3. Fragment of the crystal packing of the associate $[Ni_2L_4]_2 \cdot [NiCl_2(LH)_2(MeCN)_2] \cdot 4MeCN$.

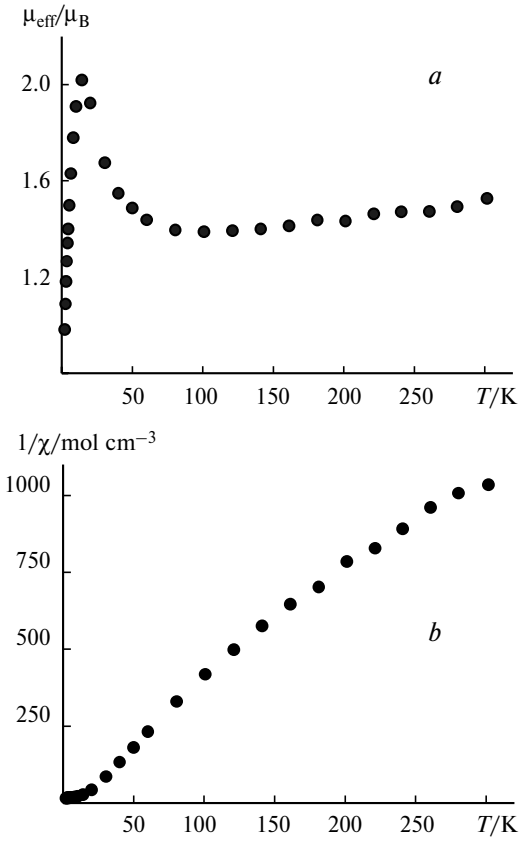


Fig. 4. Plots of the effective magnetic moment (*a*) and the magnetic susceptibility (*b*) *vs.* the temperature for complex **2**·4MeCN.

netic behavior of associate **2**·4MeCN (actually, the strongly diamagnetically diluted mononuclear complex $NiCl_2(LH)_2(MeCN)_2$) remains unclear. Nevertheless, ferromagnetic interactions at helium temperatures give hope that the crystals of molecular ferromagnets may be prepared from rather simple mononuclear molecules capable of forming supramolecular ensembles.

Experimental

All operations associated with the synthesis and isolation of complex **1** and associate **2**·4MeCN were carried out in air. The IR spectra were recorded on a Specord M82 instrument in KBr pellets. The temperature dependence of the magnetic susceptibility (χ'_m) was measured on a SQUID MPMS-5S Quantum Desing magnetometer in the temperature range of 300—2 K. The magnetic moments were calculated by the known equation $\mu_{eff} = (8\chi'_m T)^{0.5}$.[14]

Tetrakis(μ_2-benzimidazole-2-thiolato)dinickel(II), solvate with water, $Ni_2(\mu\text{-}(L))_4 \cdot 4H_2O$ ($1 \cdot 4H_2O$). A solution of 2-mercaptobenzimidazole (0.24 g, 1.60 mmol) and $NiCl_2 \cdot 6H_2O$ (0.19 g, 0.8 mmol) in EtOH (25 mL) was refluxed for 30 min. The resulting red-brown solution was cooled to room temperature, concentrated to 12 mL (20 °C C, 0.1 Torr), and kept at room temperature for 72 h. The crystalline precipitate that formed was filtered off and dissolved in boiling ethanol (30 mL). The transparent red-brown solution was cooled to room temperature, concentrated to 7 mL (20 °C, 0.1 Torr), and kept for 14 days. The brown prismatic crystals of $1 \cdot 4H_2O$ that formed were separated by decantation, washed with cold ethanol, and dried under argon. The crystals were used for X-ray diffraction.

The yield of **1**·4H_2O was 0.22 g (68% based on the starting $NiCl_2 \cdot 6H_2O$). Found (%): C, 42.78; H, 3.56; N, 14.26. $C_{28}H_{28}N_8Ni_2O_4S_4$. Calculated (%): C, 42.80; H, 3.90; N, 14.40. IR (KBr), ν/cm^{-1}: 3572 (s), 3412 (s), 3244 (s), 1612 (s), 1492 (m), 1432 (v.s), 1420 (s), 1384 (s), 1364 (w), 1348 (w), 1300 (m), 1280 (m), 1228 (m), 1148 (w), 1116 (m), 1028 (w), 1004 (m), 928 (w), 844 (w), 804 (w), 756 (s), 664 (w), 612 (w), 516 (w), 432 (w), 420 (m).

Cocrystals of tetrakis(μ$_2$-benzimidazole-2-thiolato)dinickel(II) and dichloro[bis(benzimidazole-2-thione)]bis(acetonitrile)nickel(II), solvate with acetonitrile, [Ni_2L_4]$_2$·[$NiCl_2(LH)_2(MeCN)_2$]·4MeCN (2·4MeCN). 2-Mercaptobenzimidazole (0.19 g, 1.26 mmol) and potassium hydroxide (0.08 g, 1.39 mmol) were ground in an agate mortar with 2—3 drops of ethanol until a homogeneous mixture was obtained. Then $NiCl_2 \cdot 6H_2O$ (0.15 g, 0.63 mmol) was added, and the resulting mixture was again ground in the mortar with 3—4 drops of EtOH until a homogeneous dark-brown powder was obtained. Acetonitrile (40 mL) was added to the solid product and the mixture was heated to 60 °C. Undissolved KCl was separated from the brown solution by filtration, THF (5 mL) was added to the filtrate, and the mixture was kept at room temperature for 2 days. The dark-brown crystals were separated by decantation, washed with cold acetonitrile, and dried at 20 °C (0.1 Torr). The crystals were used for X-ray diffraction. The yield of **2**·4MeCN was 0.20 g (76% based on the starting $NiCl_2 \cdot 6H_2O$). Found (%): C, 46.70; H, 3.12; N, 17.10. $C_{82}H_{70}Cl_2N_{26}Ni_5S_{10}$. Calculated (%): C, 46.80; H, 3.40; N, 17.30. IR (KBr), ν/cm^{-1}: 3568 (s), 3476 (s), 3416 (s), 3236 (s), 1664 (m), 1636 (m), 1616 (s), 1520 (m), 1492 (m), 1460 (w), 1432 (s), 1420 (s), 1384 (s), 1360 (m), 1348 (m), 1300 (m), 1276 (m), 1228 (m), 1208 (w), 1148 (m), 1112 (m), 1028 (w), 1004 (m), 928 (w), 908 (w), 844 (w), 756 (s), 660 (w), 624 (w), 612 (w), 516 (w), 476 (m), 432 (w), 420 (m).

X-ray diffraction study. X-ray diffraction data sets for compounds **1**·4H_2O and **2**·4MeCN were collected on a Bruker AXS SMART 1000 diffractometer (CCD detector, graphite monochromator, 120(2) K, ω-scanning technique, the scan step was 0.3°, the exposure time per frame was 30 s) using the standard technique.[15] The structures were solved by direct methods and refined with anisotropic displacement parameters for all nonhydrogen atoms (F^2). The hydrogen atoms of the NH groups in the ligands of complex **1**·4H_2O and associate **2**·4MeCN were located in difference Fourier maps and refined isotropically. The other hydrogen atoms were calculated geometrically and refined using a riding model. All calculations were carried out with the use of the SHELX97 program package.[16] Complex $Ni_2(\mu\text{-}L)_4 \cdot 4H_2O$ (**1**·4H_2O): $C_{28}H_{28}N_8Ni_2O_4S_4$; M = 786.24; dark-brown prismatic crystal of dimensions 0.65×0.35×0.13 mm; T = 120(2) K, tetragonal system, $P4/ncc$, a = 13.661(3), c = 16.744(4) Å, V = 3124.8(12) Å^3, Z = 4, D_{calc} = 1.671 g cm^{-3}, μ(Mo-Kα) = 0.71073 Å; R_1 = 0.0612, wR_2 = 0.1279, measured/independent reflections 4353/1239. Complex [Ni_2L_4]$_2$·[$NiCl_2(LH)_2(MeCN)_2$]·4MeCN (**2**·4MeCN): $C_{82}H_{70}Cl_2N_{26}Ni_5S_{10}$; M = 2104.69; dark-brown prismatic crystal of dimensions 0.47×0.24×0.15 mm; T = 120(2) K, triclinic system, $P\bar{1}$, a = 11.9319(8), b = 13.4086(9), c = 14.5891(10) Å, α = 70.961(2), β = 84.877(2), γ = 86.262(2)°, V = 2196.0(3) Å^3, Z = 1, d_{calc} = 1.591 g cm^{-3}, μ(Mo-Kα) = 0.71073 Å; R_1 = 0.0712, wR_2 = 0.1013, measured/independent reflections 13278/7415.

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References

1. V. A. Ivanov, T. G. Aminov, V. M. Novotortsev, and V. T. Kalinnikov, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2255 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2357].
2. R. Z. Sagdeev and V. I. Ovcharenko, *Usp. Khim.*, 1999, **68**, 345 [*Russ. Chem. Rev.*, 1999, **68** (Engl. Transl.)].
3. O. Khan, *Molecular Magnetism*, VCH, New York, 1993.
4. O. Khan, *Acc. Chem. Res.*, 2000, **33**, 647.
5. M. Verdaguer, *Polyhedron*, 2001, **20**, 1115.
6. V. T. Kalinnikov, Yu. V. Rakitin, and V. M. Novotortsev, *Usp. Khim.*, 2003, **72**, 995 [*Russ. Chem. Rev.*, 2003, **72** (Engl. Transl.)].
7. I. L. Eremenko, M. A. Golubnichaya, A. A. Sidorov, S. E. Nefedov, I. F. Golovaneva, V. I. Burkov, O. G. Ellert, V. M. Novotortsev, A. Sousa, and M. R. Bermejo, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 725 [*Russ. Chem. Bull.*, 1998, **47**, 704 (Engl. Transl.)].
8. 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**, 396 (Engl. Transl.)].
9. 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.
10. 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, **53**, 2105].
11. A. A. Sidorov, S. M. Diamidov, S. E. Nefedov, I. G. Fomina, P. V. Danilov, V. M. Novotortsev, V. N. Ikorskii, and I. L. Eremenko, *Zh. Neorg. Khim.,* 1999, **44**, 3 [*Russ. J. Inorg. Chem.*, 1999, **44** (Engl. Transl.)].

12. A. E. Malkov, I. G. Fomina, A. A. Sidorov, G. G. Aleksandrov, I. M. Egorov, N. I. Latosh, O. N. Chupakhin, Yu. V. Rakitin, G. L. Rusinov, V. M. Novotortsev, V. N. Ikorskii, and I. I. Moiseev, *J. Mol. Struct.*, 2003, **656**, 207.
13. J. Jolley, W. I. Cross, R. G. Pritchard, C. A. McAuliffe, and K. B. Nolan, *Inorg. Chim. Acta*, 2001, **319**, 36.
14. Yu. V. Rakitin and V. T. Kalinnikov, *Sovremennaya magnetokhimiya* [*Modern Magnetochemistry*], Nauka, St. Petersburg, 1994 (in Russian).
15. G. M. Sheldrik, SADABS, *Program for Scanning and Correction of Area Detector Data*, Götinngen University, Götinngen, Germany, 1997.
16. G. M. Sheldrik, SHELX97, *Program for Solution of Crystal Structures*, Götinngen University, Götinngen, Germany, 1997.

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