Russian Chemical Bulletin, International Edition, Vol. 56, No. 1, pp. 108—114, January, 2007

Structural and physicochemical characteristics of chelate nickel(II) compounds based on 1,2,3-triketone (hydrazone)imines

O. G. Khudina,[a] E. V. Shchegol´kov,[a] Ya. V. Burgart,[a] V. I. Saloutin,[a]★ D. V. Bukhvalov,[b] D. V. Starichenko,[b] Yu. N. Shvachko,[b] A. V. Korolev,[b] V. V. Ustinov,[b] G. G. Aleksandrov,[c] I. L. Eremenko,[c] O. N. Kazheva,[d] G. V. Shilov,[d] O. A. D´yachenko,[d] and O. N. Chupakhin[a]

[b]*I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences,*
22 ul. S. Kovalevskoi, 620219 Ekaterinburg, Russian Federation.
Fax: +7 (343) 374 5954. E-mail: saloutin@ios.uran.ru
[b]*Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences,*
18 ul. S. Kovalevskoi, 620219 Ekaterinburg, Russian Federation.
Fax: +7 (343) 374 5244. E-mail: ustinov@imp.uran.ru
[c]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 955 4835. E-mail: ilerem@igic.ras.ru
[d]*Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (496) 515 5420. E-mail: doa@rfbr.ru

The crystal structures of the chelates $Ni^{II}L$ (L^{2-} are the *N,N´*-(*o*-phenylene)-bis[4-(4-methylphenyl)hydrazono-3-oxo-1,1,2,2-tetrafluorononane-5-iminate], *N,N´*-ethylene-bis[3-(4-methylphenyl)hydrazono-4-oxo-5,5,6,6,7,7,8,8-octafluorooctane-2-iminate], or *N,N´*-ethylene-bis(4-hydroxy-5,5,6,6,7,7,8,8-octafluoro-3-octene-2-iminate) anions) were studied by X-ray diffraction. Magnetic measurements and ESR spectroscopic studies revealed the appearance of paramagnetism due to a tetrahedral distortion of the coordination unit and also the unusual behavior of the effective magnetic moment at low temperatures.

Key words: chelate Ni^{II} compounds, 1,2,3-triketone (hydrazone)imines, crystal structure, magnetic measurements, ESR.

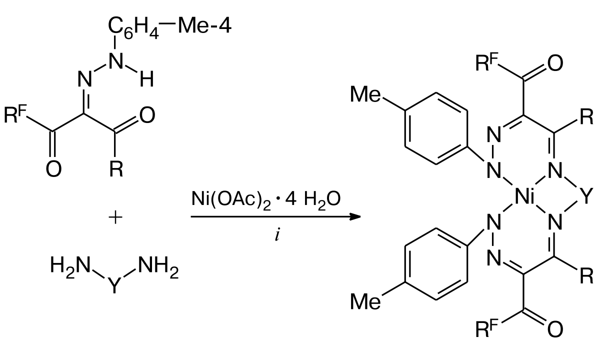
In recent years, chelate transition metal complexes have attracted considerable interest because they hold promise for the construction of polyfunctional magnetoactive materials.[1] The magnetic properties of molecular crystals based on nickel complexes are of particular interest. Bis-chelate Ni^{II} complexes containing the central NiN_4 fragment, in which the metal atom is in a square-planar ligand environment (coordination number is 4), are known to be diamagnetic.[2—10] In these complexes, the ligand environment can be formed, in particular, by different 1,2-diamines used as the starting organic compounds, which, depending on the synthesis conditions, are either involved in the complex in the initial form or oxidized to give semidiimines or diimines.[2,3] The geometry of the resulting metal chelate NiN_4 unit can be controlled by varying the electronic and steric characteristics of chelate ligands is such systems, thus resulting in considerable deviations from the planar geometry, which can give rise to paramagnetism. However, if four nitrogen atoms of the central unit are involved in a complex heterocyclic system, the probability of changing the planar conformation of the central metal fragment becomes much lower, and considerable perturbing factors are required for a tetrahedral distortion. Bulky organic substituents at the nitrogen atoms or a sufficiently labile alkylidene bridge between the chelate rings can serve as such perturbing elements. With the aim of validating this hypothesis, in the present study we synthesized and investigated a series of such molecules containing Ni^{II} atoms bound to organic poly-*N*-donors, which were prepared based on 1,2,3-triketone (hydrazone)imines.

Results and Discussion

Complexes with the chelate NiN_4 unit (compounds **1** or **2**) were synthesized by template condensation of 1-polyfluoro-1,2,3-triketone 2-arylhydrazone with *o*-phenylene- or ethylenediamine in the presence of nickel(II) acetate tetrahydrate (Scheme 1).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 103—109, January, 2007.

Scheme 1



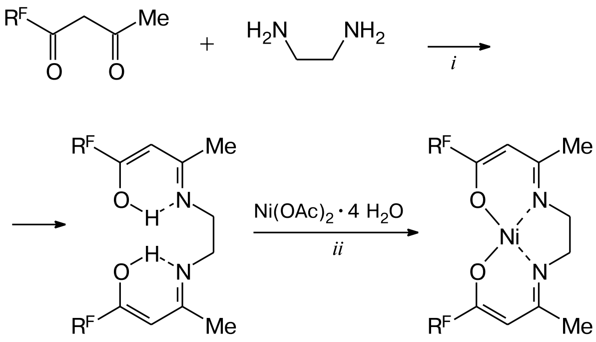
1, 2

i. Ethanol, 78 °C

1: Y = C_6H_4, $R^F = HCF_2—CF_2$, R = Bu
2: Y = $CH_2—CH_2$, $R^F = HCF_2—(CF_2)_3$, R = Me

Another type of compounds containing the NiO_2N_2 unit, *viz*., *N,N′*-ethylene-bis(4-hydroxy-5,5,6,6,7,7,8,8-octafluoro-3-octene-2-iminato)nickel(II) (**3**), was synthesized from the ligand generated by the reaction of ethylenediamine with diketone[11] upon treatment with an aqueous ethanolic solution of nickel acetate (Scheme 2).

Scheme 2



3

$R^F = (CF_2)_3—CF_2H$

i. Ethanol, 78 °C. *ii*. Ethanol, 20 °C

X-ray diffraction study demonstrated that molecule **1** has crystallographic symmetry C_2 (twofold axis passes through the Ni atom and the midpoints of the C(3)—C(3a) and C(5)—C(5a) bonds of the phenylene ring C(3)C(4)C(5)C(5a)C(4a)C(3a)) (Fig. 1). The nickel atom has a strongly tetrahedrally distorted square coordination environment formed by four nitrogen atoms. As a result of the formally tetradentate coordination of the ligand, the molecule contains three fused metallocycles, *viz*., the central five-membered virtually planar ring and two six-membered rings bent along the N(1)...N(3) line by 156.7°. The dihedral angle between the plane of the phenylene ring C(3)C(4)C(5)C(5a)C(4a)C(3a) and the plane of the five-membered metallocycle is 166.7°, the planar phenyl substituents at the N(1) and N(1a) atoms being twisted about the N(1)—C(6) bond by 35.9°. In addition, the nitrogen atoms deviate in the opposite directions from the plane of the five-membered metallocycle by 0.414 Å, resulting in the formation of a rather large dihedral angle between the NiN(3)N(3a) and NiN(1)N(1a) planes (19.4°). In the crystal structure, the molecules of complex **1** are linked to each other only by van der Waals interactions.

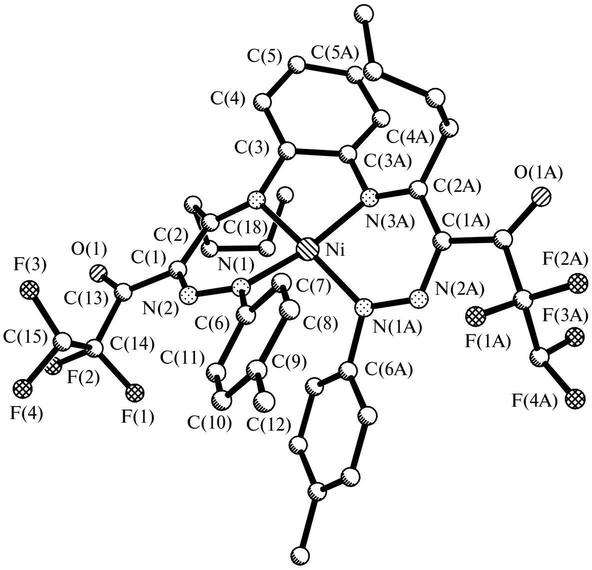


Fig. 1. Molecular structure of complex **1**.

The overall molecular structure of **2** is similar to that of compound **1** (Fig. 2). The coordination polyhedron of the metal atom is a tetrahedrally distorted square (NiN(2)N(6)—NiN(9)N(13) dihedral angle is 22.5°). The deviation of the nitrogen atom from the mean plane of the coordination unit is ±0.26 Å. The vertices of the square are occupied by the N(2), N(6), N(9), and N(13) atoms, and the center of the square is occupied by the Ni atom (Ni—N, 1.870(2), 1.858(2), 1.852(2), and 1.876(2) Å; N(2)—Ni—N(6), N(6)—Ni—N(9), N(9)—Ni—N(13), and N(13)—Ni—N(2), 90.63(8), 87.14(8), 90.73(8), and 95.92(8)°, respectively). The deviation of the Ni atom from the mean plane of the N(2)N(6)N(9)N(13) coordination unit is 0.002 Å. The metallocycles are arranged stepwise. The dihedral angles between the planes of the coordination metal units NiN(2)N(6) and NiN(9)N(13) and the planes of the N(2)N(3)C(4)C(5)N(6) and N(9)C(10)C(11)N(12)N(13) chelates are 153.4° and 153.2°, respectively. In the crystal structure, molecules **2** are arranged so that the fluorinated substituents are oriented toward each other, resulting in the formation of slightly shortened intermolecular F...H interactions

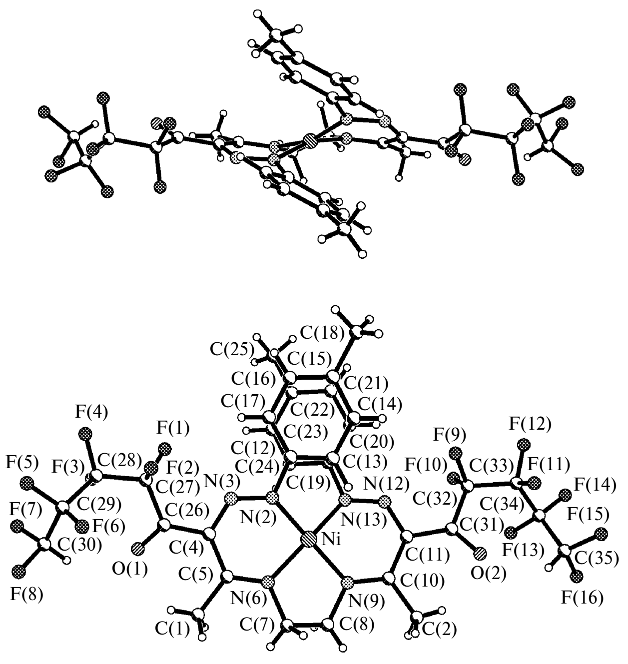


Fig. 2. Molecular structure of complex **2**.

(2.48(8)—2.51(2) Å) (Table 1). The corresponding sums of the van der Walls radii, F...H, are 2.54 Å.[12] The interplanar distances between the chelate rings in molecule **2** are 1.21 Å.

In terms of the ligand field theory (LFT), the square-planar environment of Ni^{II} observed in compound **3** is characterized by d-orbital splitting with the occupied low-lying degenerate d_{yz} and d_{xz} states, the intermediate d_{z^2} and d_{xy} states, and the free high-lying $d_{x^2-y^2}$ orbital.[13] Hence, the $3d^8$ shell of Ni^{II} in the square-planar environment has the spin magnetic moment $S = 0$. A tetrahedral distortion of the square environment of Ni^{II} in molecules **1** and **2** tends to invert the mutual arrangement of the t_{2g} and e_g states, so that the d_{yz}, d_{xz}, and $d_{x^2-y^2}$ orbitals move toward each other as the symmetry is lowered.[14] Even a slight tetrahedral distortion would lead to a substantial decrease in the distance between the $d_{x^2-y^2}$ orbital and the high occupied d orbital, which are in the high-spin state with $S = 1$ according to Hund's rule. Therefore, the observed structural distortions of the coordination unit in compounds **1** and **2** are indicative of the possibility that paramagnetism might exist. However, the experimental results suggest a more complex mechanism of the formation of the magnetic state.

Table 1. Characteristics of the bonds (d) and angles (ω) in the C—H...F fragment of complex **2***

Contact type	d(H...F)	d(C...F)	ω(C—H...F) /deg
	Å		
C(7)—H(7b)...F(2)[#1]	2.48(8)	3.408(5)	139(5)
C(13)—H(13)...F(6)[#1]	2.42(3)	3.322(4)	153(2)
C(24)—H(24)...F(13)[#2]	2.51(2)	3.329(3)	152(2)

* Symmetry codes: [#1] $1 - x, -y, 1 - z$; [#2] $-x, -y, -z$.

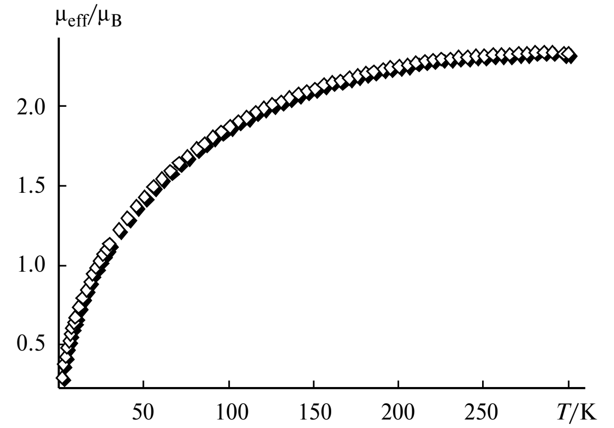


Fig. 3. Temperature dependence of the effective magnetic moment μ_{eff} for complex **1**.

The temperature dependence of the effective magnetic moment ($\mu_{eff}(T)$) measured at $B = 3$ T is shown in Fig. 3. At 300 K, μ_{eff} is 2.33 μ_B, which is lower than the theoretical value (2.83 μ_B) for $S = 1$. The dependence $\mu_{eff}(T) \to 0$ when $T \to 0$ resembles the behavior of molecules characterized by a short-range antiferromagnetic order,[15,16] which suggests that there are several interacting spin subsystems in the vicinity of the coordination unit. However, based on the structural data, it is difficult to propose a realistic model of such magnetically coupled clusters. An ESR signal from a polycrystalline sample is characteristic of Ni^{II} with $\Delta B = 400$ G and the anisotropic g factor with $g_1 = 2.203$ and $g_2 = 3.378$. The normalized spectra for three different polycrystalline samples are presented in Fig. 4. All spectra show an additional component with $g_3 = 5.456$, which is apparently associated with a distortion of the coordination unit. The dependence of the magnetization (M) on the magnetic field strength at $T = 2$ K is shown in Fig. 5. The abscissa axis is chosen in the relative B/T units. The experimental curve is not described by the Brillouin formula, and $M = 0.04$ μ_B at $B = 5$ T, which is consistent with μ_{eff} at 2 K. The temperature changes in μ_{eff} are unlikely to be explained by the influence of spin-orbital splitting, which is rather small for Ni^{II} and is estimated at $\lambda \approx 800$ cm^{-1}.[14] A more probable mechanism involves an intramolecular interaction between the d shell of Ni^{II} and the p orbitals of the chelate unit. In this case, the dependence $\mu_{eff}(T)$ reflects the evolution of the total magnetic moment of the molecule. The ligand field theory does not allow a more detailed analysis of the electronic structure and magnetic properties.

Taking into account the similar structures of compounds **1** and **2** and the composition of the coordination

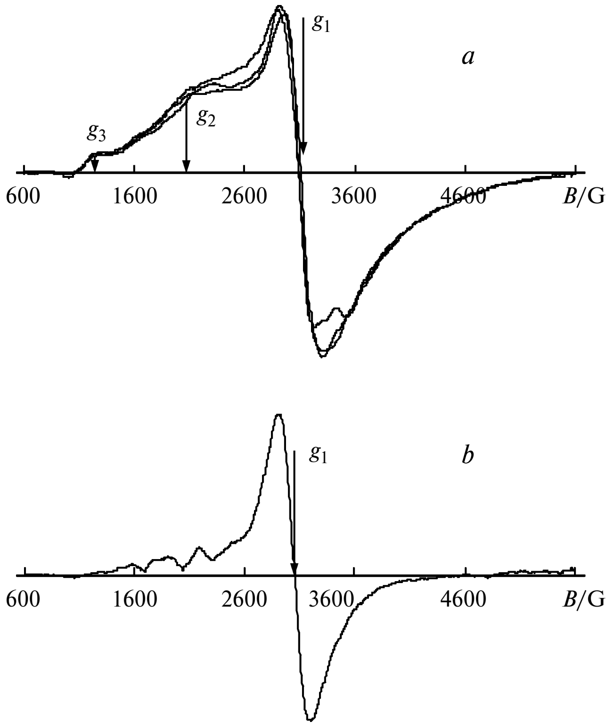


Fig. 4. ESR spectra of complexes **1** (*a*) and **3** (*b*) at 293 K (ΔB = 400 G (*a*) and 290 G (*b*)).

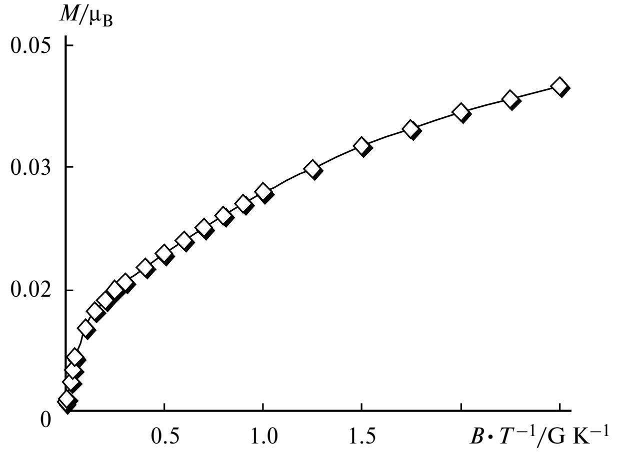


Fig. 5. Magnetic moment of complex **1** *vs*. the B/T ratio.

unit in these compounds, the diamagnetism of complex **2** seems to be unusual. The diamagnetism is confirmed experimentally by the absence of a paramagnetic contribution in the $\chi(T)$ plots obtained in SQUID measurements and the absence of an ESR signal. A comparison of the structures shows that the character of tetrahedral distortion in **2** differs from that in **1** only quantitatively. The NiN(2)N(6)—NiN(9)N(13) dihedral angle in **2** (22.5°) is larger than that in **1** (19.4°), and the deviation of the nitrogen atoms from the mean plane in **2** decreases to 0.26 Å compared to 0.414 Å in **1**. In terms of the ligand field theory, the energy level diagrams of these chelate compounds cannot be distinguished.

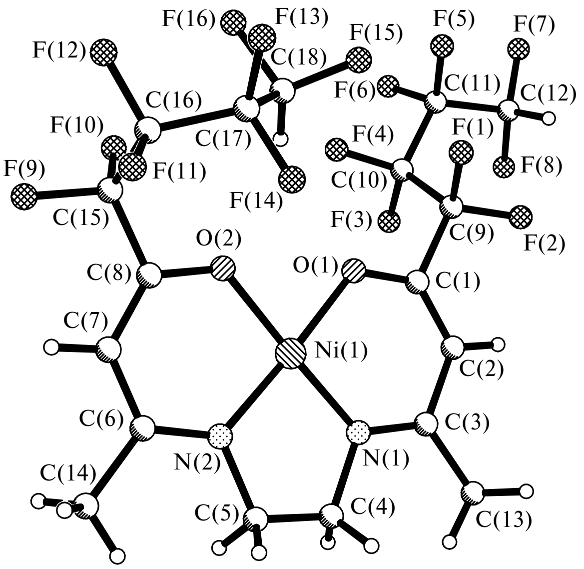


Fig. 6. Molecular structure of complex **3**.

In molecule **3** (Figs 6 and 7), the nickel atom is in a square-planar coordination environment formed by two oxygen atoms and two nitrogen atoms of the tetradentate ligand. The oxygen and nitrogen atoms bound to the metal atom and the C(1)—C(8) atoms involved in the formation of two six-membered metallocycles and one five-membered metallocycle lie virtually in a single plane (average deviation of the atoms from the $NiO_2N_2C(1)C(8)$ plane is ±0.034 Å). The planes of the metallocycles are approximately parallel to each other, and the distance

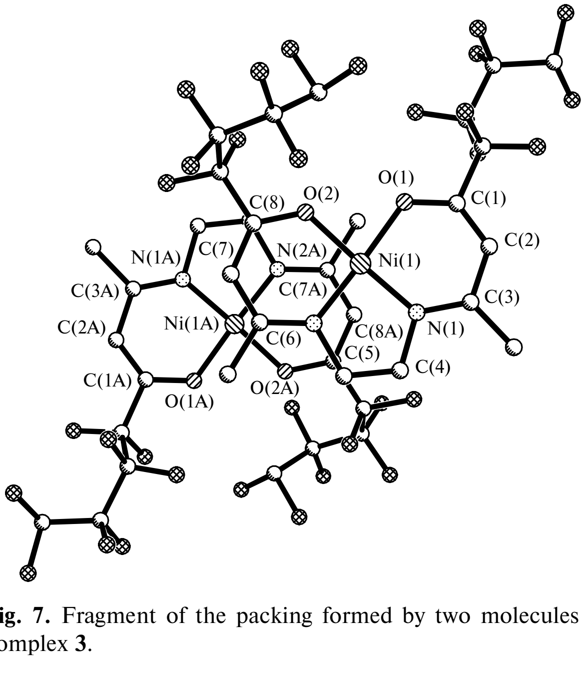


Fig. 7. Fragment of the packing formed by two molecules of complex **3**.

between these planes is ~3.7 Å. In the crystal structure, molecules of complex **3** are linked to each other only by van der Waals interactions. As a result, in spite of the presence of two oxygen atoms in the metal chelate unit NiO_2N_2, which leads to an asymmetry of this fragment, the square-planar geometry is the key factor.

X-ray diffraction data suggest that complex **3** has diamagnetic properties. However, weak paramagnetism was observed experimentally. Along with the possible presence of a small fraction of defect paramagnetic complexes in a polycrystalline sample, the above fact can be attributed to the spin contribution due to a distortion of the coordination unit as a result of a deviation of the Ni atoms (±0.034 Å) from the chelate unit NiO_2N_2. Polycrystals of **3** show a single ESR signal with the isotropic g factor (see Fig. 4). At 293 K, the main value of the g factor is $g_1 = 2.251$. Cooling from 350 to 220 K leads to an increase in the ESR linewidth, ΔB, from 265 to 370 G. However, further cooling to 100 K is accompanied by a narrowing of the ESR signal to 170 G. The temperature evolution of the integrated intensity of the ESR signal in the range of 100—350 K does not obey Curie's law, which is consistent with the results of SQUID measurements. A weak paramagnetism is evidenced by the small magnetic moment ($\sim 10^{-2}\ \mu_B$) at 2 K. It should be noted that the ESR spectra show two weak lines with $g = 3.164$ and 3.681. For the more detailed identification, it is necessary to perform precise investigations using a single crystal.

Since the distances between the nickel atoms in compounds **1—3** are at most 9 Å, the intermolecular exchange is close to zero. In this case, it is reasonable to attribute a decrease in μ_{eff} with decreasing temperature, which is observed for **1**, to intermolecular interactions. Apparently, hybridization of the d states of Ni^{II} and the p states of the chelate environment plays the key role. Taking into account that the hybridization effects are sensitive to both the chemical composition and the total molecular symmetry, the magnetic state of complexes **1—3** would be determined not only by the spin state of Ni^{II} but also by the local spin density distribution in the ligand. To validate this assumption, it is necessary to perform *ab initio* calculations taking into account the electronic correlations and carry out additional magnetic experiments.

Experimental

The NMR spectra were measured on a Bruker DRX-400 spectrometer (400 MHz for ^1H and 100.6 MHz for ^{13}C relative to $SiMe_4$; 376 MHz for ^{19}F relative to C_6F_6). The UV spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer. Elemental analysis (C, H, N) was carried out on a Perkin Elmer PE 2400 (series II) analyzer.

1,2,3-Triketone 2-arylhydrazones were synthesized by azo-coupling of fluorine-containing 1,3-diketones with aryldiazonium chlorides.[17]

Synthesis of *N,N´*-(*o*-phenylene)-bis[4-(4-methylphenyl)-hydrazono-3-oxo-1,1,2,2-tetrafluorononane-5-iminato]nickel(II) (1) and *N,N´*-ethylene-bis[3-(4-methylphenyl)-hydrazono-4-oxo-5,5,6,6,7,7,8,8-octafluorooctane-2-iminato]nickel(II) (2). A solution of nickel(II) acetate tetrahydrate (0.25 g, 1 mmol) in ethanol (10 mL) was added to a solution of a mixture of 1-polyfluoro-1,2,3-triketone 2-arylhydrazone (2 mmol) and *o*-phenylene- or ethylenediamine (2 mmol) in ethanol (10 mL). The reaction mixture was refluxed for 16 h (3 h for the synthesis of complex **2**). The precipitate that formed was filtered off.

After column chromatography (chloroform—hexane, 1 : 1, as the eluent), the yield of complex **1** was 0.66 g (80%), m.p. 188—189 °C. ^1H NMR (DMSO-d_6/CCl_4), δ: 0.93 (s, 6 H, 2 Pr-C$\underline{H}_3$, J = 7 Hz); 1.48, 1.65, and 3.64 (all m, 4 H each, 2 $\underline{Pr}$—CH_3, J = 7 Hz); 2.27 (s, 6 H, 2 Me); 6.22 (tt, 2 H, 2 $H(CF_2)_2$, $^2J_{H,F}$ = 54 Hz, $^3J_{H,F}$ = 6 Hz); 6.82—7.19 (m, 8 H, 2 C_6H_4); 7.27—7.53 (m, 4 H, C_6H_4). UV ($CHCl_3$), λ_{max}/nm (ε): 246 (26400), 321 (34420), 355 sh (30440), 429 sh (10480), 485 sh (5140), 544 (3380). Found (%): C, 55.7; H, 4.9; F, 18.2; N, 10.4. $C_{38}H_{38}F_8N_6O_2Ni$. Calculated (%): C, 55.6; H, 4.7; F, 18.5; N, 10.2.

After column chromatography (chloroform as the eluent), the yield of chelate **2** was 0.62 g (70%), m.p. 190—191 °C. ^1H NMR ($CDCl_3$), δ: 2.24 (s, 6 H, 2 $\underline{Me}$—C_6H_4); 2.57 (s, 6 H, 2 Me); 3.47 (br.s, 4 H, 2 CH_2); 6.22 (tt, 2 H, 2 $H(CF_2)_4$, $^2J_{H,F}$ = 52 Hz, $^3J_{H,F}$ = 6 Hz); 6.98 (m, 8 H, 2 C_6H_4). Found (%): C, 43.50; H, 2.89; F, 33.84; N, 9.42. $C_{32}H_{26}F_{16}N_6O_2Ni$. Calculated (%): C, 43.22; H, 2.95; F, 34.18; N, 9.45.

Synthesis of *N,N´*-ethylene-bis(4-hydroxy-5,5,6,6,7,7,8,8-octafluoro-3-octene-2-iminato)nickel(II) (3). A solution of ethylenediamine (0.06 g, 1 mmol) in ethanol (8 mL) was added to a solution of 5,5,6,6,7,7,8,8-octafluorooctane-2,4-dione (0.57 g, 2 mmol) in ethanol (10 mL). The reaction mixture was refluxed for 2 h. The precipitate that formed was filtered off and washed with carbon tetrachloride. Then the resulting ligand was dissolved in ethanol (10 mL), and a solution of nickel(II) acetate tetrahydrate (0.25 g, 1 mmol) in water (8 mL) was added at room temperature. The precipitate that formed was filtered off. The yield of complex **3** was 0.38 g (58%), m.p. 188—189 °C. ^1H NMR ($CDCl_3$), δ: 2.03 (s, 6 H, 2 Me); 3.14 (s, 4 H, 2 CH_2); 5.49 (s, 2 H, 2 CH=); 6.22 (tt, 2 H, 2 $H(CF_2)_4$, $^2J_{H,F}$ = 52 Hz, $^3J_{H,F}$ = 6 Hz). UV ($CHCl_3$), λ_{max}/nm (ε): 203 (36440), 242 (30620), 290 (28460), 360 (42200), 477 sh (7700). Found (%): C, 29.9; H, 2.0; F, 46.2; N, 4.4. $C_{18}H_{14}F_{16}N_2O_2Ni$. Calculated (%): C, 33.1; H, 2.2; F, 46.6; N, 4.3.

X-ray diffraction study. Single crystals of complexes **1—3** were grown by crystallization from chloroform. Experimental X-ray data sets for complexes **1** and **3** were collected on an automated Enraf-Nonius CAD-4 diffractometer (λ(Mo-Kα) = 0.71073 Å, 293 K, graphite monochromator, ω/2θ scanning technique). The structures of complexes **1** and **3** were solved by direct methods and refined by the least-squares method using the SHELXS-97[18] and SHELXL-97[19] program packages with anisotropic displacement parameters (isotropic displacement parameters for H atoms).

X-ray diffraction data for chelate **2** were collected on a KM-4 KUMA DIFFRACTION diffractometer (ω/2θ scanning technique, Mo-Kα radiation, 293 K, graphite monochromator). The crystal structure was solved by direct methods followed by analysis of Fourier maps with the use of the SHELXS-97 program package.[18] The structure was refined by the least-squares method with anisotropic displacement parameters for all nonhydrogen atoms using the SHELXL-97 program package.[19] The intensities of reflections were corrected for absorption by the semiempirical method.[20] The coordinates of hydrogen atoms were revealed in electron density maps and refined isotropically.

Principal crystallographic data for compounds **1—3** are given in Table 2. The bond lengths and bond angles for the coordination units in complexes **1—3** are listed in Table 3.

Magnetic studies. Magnetic measurements were carried out on a SQUID MPMS-5-XL (QUANTUM DESIGN) magnetometer. The static magnetic susceptibility, $\chi(T)$, of polycrystalline samples was measured at a magnetic field strength B_0 = 30 kG in the temperature range of 2—293 K. The magnetization curves $M(B)$ were measured at 2 K in the field range of 0—50 kG. The paramagnetic susceptibility was determined by subtracting the diamagnetic contribution of the organic core and the capsule, which were measured throughout the temperature range, from the total magnetic response.

The ESR spectra were recorded in the temperature range of 93—350 K on a standard homodyne ERS-231 spectrometer equipped with a TE_{102} rectangular resonator. The frequency range was ~9.3 GHz (X range); the power was 2 mW. The sample was strictly fixed at an antinode of the microwave magnetic field of the resonator. The temperature was set and stabilized at a rate of 1—2 K min^{-1} and an accuracy of 0.1 K using a continuous-flow nitrogen cryostat.

The temperature dependence of the spin contribution to the magnetic susceptibility was estimated by the double integration of the ESR signal (Schumacher—Slichter method) provided that the sweep width $\delta B_{sw} > 5\Delta B$ (ΔB is the ESR peak-to-peak linewidth). In this case, the error of the method for the ESR Lorentz line is ~10%. A coal pyrolyzate with g = 2.00283 was used as the standard.

Table 2. Principal crystallographic data and the X-ray data collection and refinement statistics for chelates **1—3**

Parameter	1	2	3
Molecular formula	$C_{38}H_{38}F_8N_6NiO_2$	$C_{32}H_{26}F_{16}N_6NiO_2$	$C_{18}H_{14}F_{16}N_2NiO_2$
Molecular weight	821.45	889.30	653.02
T/K	293(2)	293(2)	293(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a/Å	15.251(3)	14.742(3)	10.361(4)
b/Å	13.442(3)	11.402(3)	11.078(4)
c/Å	19.580(4)	13.185(2)	11.180(4)
α/deg	90	89.87(3)	92.07(3)
β/deg	107.22(2)	60.24(3)	99.65(3)
γ/deg	90	67.12(3)	113.69(3)
V/Å^3	3834.1(14)	1721.4(6)	1150.8(7)
Z	4	2	2
d_{calc}/g cm^{-3}	1.423	1.716	1.884
μ/mm^{-1}	0.587	0.693	0.993
F(000)	1696	896	648
Crystal dimensions/mm	0.43×0.22×0.13	0.58×0.32×0.20	0.55×0.50×0.25
2θ-Scan range/deg	2.06—26.98	1.99—30.06	1.86—28.00
$(2\theta)_{max}$/deg	54	60.12	56
Ranges of indices	$0 \le h \le 14$, $0 \le k \le 17$, $-24 \le l \le 23$	$-10 \le h \le 11$, $-12 \le k \le 11$, $-14 \le l \le 11$	$-6 \le h \le 13$, $-14 \le k \le 13$, $-14 \le l \le 14$
Total number of reflections	3738	9042	5610
Number of independent reflections	3592	8932	5570
R_{int}	0.1602	0.1370	0.1000
Number of reflections with $I > 2\sigma(I)$	2671	5716	—
Number of parameters in refinement	249	618	352
Absorption correction	Psi-scan	Psi-scan [8]	—
Transmission, maximum/minimum	0.9276/0.7864	0.7171/0.2644	0.7894/0.6112
GOOF on F^2	1.001	0.968	1.000
R factors			
R_1	0.0742	0.0450	0.0641
wR_2 (based on reflections with $I > 2\sigma(I)$)	0.2010	0.1117	0.1731
R factors (based on all reflections)			
R_1	0.1008	0.0991	0.0929
wR_2	0.2314	0.1215	0.2000
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.002/–0.902	0.507/–0.588	1.005/–0.704

Table 3. Bond lengths (d) and bond angles (ω) in the coordination units of complexes **1—3***

Bond	d/Å	Compound	Angle	ω/deg	Compound	Angle	ω/deg	Compound
Ni—N(1)	1.860(3)	**1**	N(1)—Ni—N(1A)	94.79(17)	**1**	N(3)—Ni—N(3A)	87.56(17)	**1**
	1.855(3)	**3**	N(1)—Ni—N(2)	87.60(14)	**3**	N(6)—Ni—N(9)	87.14(8)	**2**
Ni—N(1A)	1.860(3)	**1**	N(1)—Ni—N(3)	90.48(12)	**1**	N(6)—Ni—N(13)	163.41(9)	**2**
Ni—N(2)	1.870(2)	**2**	N(1A)—Ni—N(3)	165.75(13)	**1**	N(9)—Ni—N(13)	90.73(8)	**2**
	1.852(3)	**3**	N(1)—Ni—N(3A)	165.75(13)	**1**	O(1)—Ni—O(2)	82.87(10)	**3**
Ni—N(3)	1.871(3)	**1**	N(1A)—Ni—N(3A)	90.48(12)	**1**	O(1)—Ni—N(1)	94.94(13)	**3**
Ni—N(3A)	1.871(3)	**1**	N(2)—Ni—N(6)	90.63(8)	**2**	O(1)—Ni—N(2)	177.19(12)	**3**
Ni—N(6)	1.858(2)	**2**	N(2)—Ni—N(9)	163.51(9)	**2**	O(2)—Ni—N(1)	177.79(11)	**3**
Ni—N(9)	1.852(2)	**2**	N(2)—Ni—N(13)	95.92(8)	**2**	O(2)—Ni—N(2)	94.59(12)	**3**
Ni—N(13)	1.876(2)	**2**						
Ni—O(2)	1.843(2)	**3**						
Ni—O(1)	1.847(2)	**3**						

* The atoms labeled with the suffix A are related to the unlabeled atoms by the symmetry operation $-x$, y, $-z + 0.5$.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 05-03-32384a, 05-02-17704, and 06-03-08141), the Russian Science Support Foundation, the Council on Grants of the President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grants NSh-9178.2006.3 and NSh-5869.2006.2, and Program for State Support of Young Scientists, Grant MK-1707.2005.3), the Siberian Branch of the Russian Academy of Sciences (Program No. 29), and the Ural Branch of the Russian Academy of Sciences (Program No. 24).

References

1. V. I. Ovcharenko and R. Z. Sagdeev, *Usp. Khim.*, 1999, **68**, 381 [*Russ. Chem. Revs.*, 1999, **68** (Engl. Transl.)].
2. T. Ishizuki, S. M. Peng, Y. Wang, and Ch. K. Chiang, *Acta Chystallogr., Sect. C*, 1984, **40**, 1541.
3. 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.)].
4. N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Am. Chem. Soc.*, 1966, 1015.
5. N. F. Curtis, *J. Am. Chem. Soc.*, 1971, 2834.
6. E. K. Barefield and D. H. Busch, *Inorg. Chem.*, 1971, **10**, 108.
7. V. L. Goedken and D. H. Busch, *Inorg. Chem.*, 1971, **10**, 2679.
8. C. J. Hipp, L. F. Lindoy, and D. H. Busch, *Inorg. Chem.*, 1972, **11**, 1988.
9. S. M. Peng, J. A. Ibers, M. Millar, and R. H. Holm, *J. Am. Chem. Soc.*, 1976, **98**, 8037.
10. S. M. Peng and V. L. Goedken, *J. Am. Chem. Soc.*, 1976, **98**, 8500.
11. R. Belcher, K. Blessel, T. Cardwell, M. Pravica, W. I. Stephen, and P. S. Uden, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1127.
12. Yu. V. Zefirov, *Kristallografiya*, 1999, **44**, 1091 [*Crystallography Reports*, 1999, **44** (Engl. Trans.)].
13. S. A. Al´tshuler and B. M. Kozyrev, *Elektronnyi paramagnitnyi rezonans soedinenii elementov promezhutochnykh grupp* [*Electron Paramagentic Resonance in Compounds of Transition Elements*], Nauka, Moscow, 1972 (in Russian).
14. A. F. Orchar, *Magnetochemistry*, Oxford University Press, Oxford, 2003.
15. R. L. Carlin*, Magnetochemistry*, Springer, Berlin, 1986.
16. Yu. N. Shvachko, D. V. Bukhvalov, D. V. Starichenko, A. V. Korolev, V. V. Ustinov, O. G. Khudina, E. V. Shchegol´kov, Ya. V. Burgart, V. I. Saloutin, and O. N. Chupakhin, *Tez. dokl. Mezhdunar. nauchn. konf. "Vysokospinovye molekuly i molekulyarnye magnetiki"* [*Abstrs. of Papers, International Scientific Conf. "High-Spin Molecules and Molecular Magnets" (June 13—16, 2006, Ivanovo)*, Ivanovo, 2006, 86 (in Russian).
17. O. G. Kuzueva, Ya. V. Burgart, and V. I. Saloutin, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 695 [*Russ. Chem. Bull.*, 1998, **47**, 673 (Engl. Transl.)].
18. G. M. Sheldrick, *SHELXS-97*, *Program for the Solution of Crystal Structures*, Göttingen University, Göttingen (Germany), 1997.
19. G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, Göttingen University, Göttingen (Germany), 1997.
20. A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

Received September 11, 2006;
in revised form November 29, 2006