

Full Articles

Exchange coupling in polynuclear nickel(II) complexes with pivalate and hexafluoroacetylacetonate ligands: a quantum chemical analysis

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The electronic structures of polynuclear different-ligand nickel(II) complexes [K₂Ni₆Piv₇(hfac)₃(OH)₄(HPiv)₂(Me₂CO)₂], [Ni₆Piv₄(hfac)₄(OH)₄(Me₂CO)₄], and [Ni₈Piv₁₀(hfac)₂(OH)₂(MeO)₂(MeOH)₂(HPiv)₂] were studied within the framework of the DFT approach. For each complex, the isotropic exchange parameters for all pairs of paramagnetic centers were calculated. Based on the results obtained, models for Heisenberg–Dirac–van Vleck exchange interaction (with minimal number of parameters) were proposed, which can be used to describe the magnetic properties of the compounds under study.

Key words: nickel(II) complexes, quantum chemical calculations, density functional theory, B3LYP functional, exchange coupling, broken symmetry method.

In the last decade, nanoscale transition-metal complexes containing a large number of paramagnetic centers have attracted increased attention of researchers. Unique properties of these systems offer great prospects for their practical applications in the design of nanostructured materials for molecular electronics and spintronics devices and for information carriers with ultrahigh recording density.^{1–5}

The magnetic properties of complexes with exchange-coupled paramagnetic centers (exchange clusters) are described using some model spin Hamiltonians whose eigenvalues specify the relative order of the spin levels in the energy spectrum. Unfortunately, the number of parameters of the spin Hamiltonian considerably increases with an increase in the number of paramagnetic centers. In this case, the problem of determination of the parameters of a particular model from experimental data has numerous solutions. Reliable information on the energy levels of exchange clusters can be obtained using quantum chemistry methods.⁶

* Dedicated to Academician of the Russian Academy of Sciences R. Z. Sagdeev on the occasion of his 70th birthday.

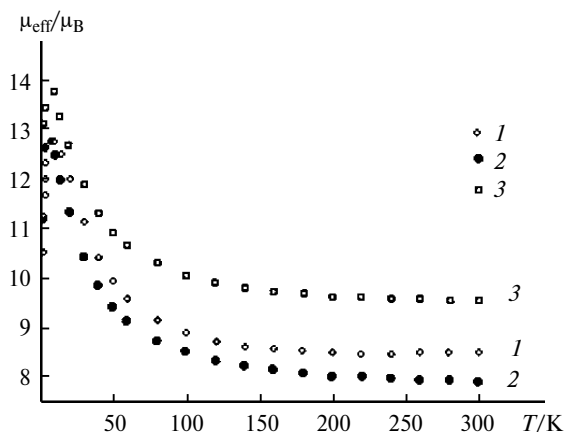


Fig. 1. Experimental temperature dependences of the effective magnetic moments (μ_{eff}) for complexes **1**·1.5C₇H₁₆ (**1**), **2** (**2**), and **3**·C₆H₁₄ (**3**).

In this work, we present the results of quantum chemical analysis of exchange coupling in polynuclear nickel(II) complexes [K₂Ni₆Piv₇(hfac)₃(OH)₄(HPiv)₂(Me₂CO)₂]·1.5C₇H₁₆ (**1**·1.5C₇H₁₆), [Ni₆Piv₄(hfac)₄(OH)₄(Me₂CO)₄] (**2**), and [Ni₈Piv₁₀(hfac)₂(OH)₂(MeO)₂(MeOH)₂(HPiv)₂]·C₆H₁₄ (**3**·C₆H₁₄). These complexes are the first representatives of polynuclear complexes simultaneously containing pivalate (Piv) and hexafluoroacetylacetonate (hfac) ligands.⁷ The magnetic properties of these compounds deserve particular attention because all these systems are prone to ferromagnetic ordering on lowering the temperature (Fig. 1); also, a magnetic phase transition of the complex **3**·C₆H₁₄ to an ordered state is detected below 2.5 K.⁷ For each complex, we calculated parameters of isotropic bilinear exchange (J_{ij}) for all pairs of paramagnetic centers and proposed the simplest model for isotropic exchange (with minimum number of parameters), which is suitable for the description of magnetic properties and for the determination of the optimum values of parameters from the results of magnetochemical measurements.

Calculation Procedure

The exchange parameters of the Heisenberg—Dirac—van Vleck (HDvV) spin Hamiltonian

$$\mathbf{H}(n) = -2 \sum_{i < j} J_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j),$$

n is the number of J_{ij} parameters; $\mathbf{S}_i \cdot \mathbf{S}_j$ is the scalar product of the vector operators of the electron spins of the centers i and j ,

were calculated by the broken symmetry method^{8–11} using the B3LYP hybrid exchange–correlation functional,^{12,13} the spin-unrestricted SCF procedure, and the GAUSSIAN-98 program.¹⁴ For each complex, we calculated single-determinant wave functions (HS- and BS-determinants) representing nonequivalent spin con-

figurations with $S_i = 1$, $M_i = \pm S_i$. The J_{ij} values were determined by solving the system of linear equations relating the energy differences $E_{\text{BS}} - E_{\text{HS}}$ to the J_{ij} parameters by the least squares method. Based on the standard errors of the exchange parameters, one can assess the consistency of the equations derived for the orthonormalized set of determinants with the calculated energies of the HS- and BS-states.^{6,15–17}

A correct estimation of the J_{ij} parameters requires calculations of all possible single-determinant wave functions;⁶ however, their number for polynuclear complexes can be very large (e.g., 128 for complex **3**), which may lead to an appreciable increase in the computing time. In this connection, calculations for complex **3** were performed using not only the computational procedure described above, but also the fragmental approach successfully employed earlier.¹⁸ It involves calculations of the J_{ij} parameters using some model systems in which all paramagnetic centers, except the centers i and j , are replaced by diamagnetic zinc(II) ions. As a result, the total number of the single-determinant solutions necessary for evaluation of a complete set of the J_{ij} parameters is reduced to, e.g., 56 for complex **3**.

The single-determinant wave functions were calculated using a tight convergence criterion (parameter scf = "tight"), which provided the necessary accuracy of the estimates of the energies of the HS- and BS-states. For all states, stability analysis of the solutions obtained was performed (parameter stable = "opt"). Calculations were carried out using the X-ray data obtained at 293 K (for **1**·1.5C₇H₁₆ and **3**·C₆H₁₄) and 298 K (for **2**). In all cases, the discrepancy between the calculated and expected $\langle \mathbf{S}^2 \rangle_{\text{HS}}$ and $\langle \mathbf{S}^2 \rangle_{\text{BS}}$ values was at most 0.02. All calculations were performed with two basis sets, TZVP (for Ni and O) and SVP (for Zn, K, F, C, and H),^{19,20} which proved themselves in the evaluation of the J_{ij} constants using the UB3LYP-BS computational procedure.^{15–17,21–33}

Having evaluated the complete set of the J_{ij} parameters, the spin Hamiltonian was successively simplified. The correctness of the simplification was assessed from the changes in the standard errors of the exchange parameters. Also, the lack of significant changes in the eigenvalue spectrum of the simplified spin Hamiltonian was treated as an additional necessary condition. Since in all cases, the spin Hamiltonian has no analytical solution, its eigenvalues (energies of the spin levels) were determined by numerical diagonalization of the corresponding matrix. The spin-level energies thus obtained were used to construct the temperature dependences of the effective magnetic moment.

Results and Discussion

The spatial configurations of complexes **1**, **2**, and **3** are shown in Figs 2, 3, and 4, respectively. Note that in com-

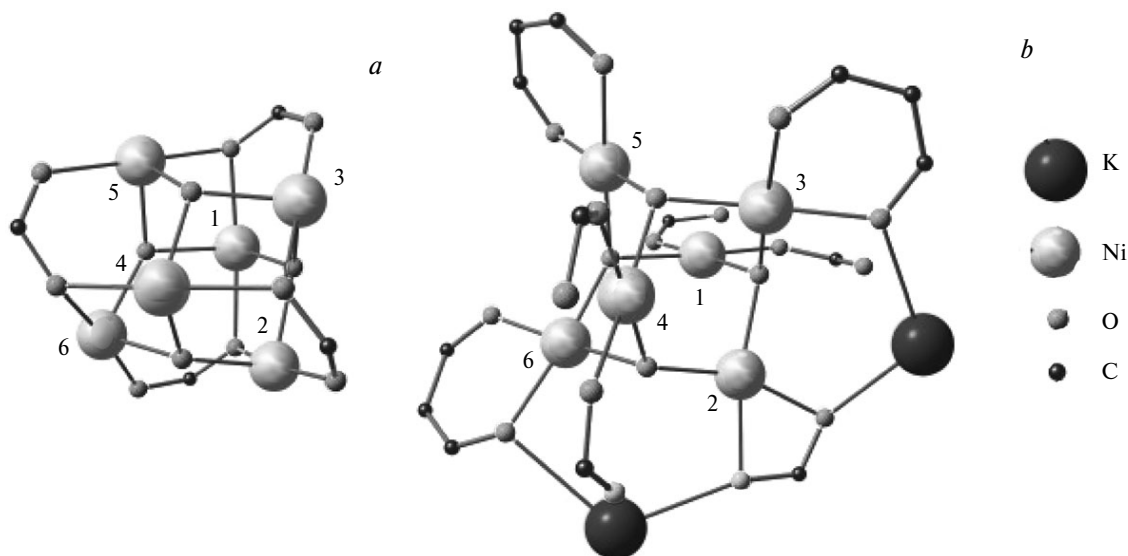


Fig. 2. Spatial configuration of complex **1**: the structure of the metal core with bridging ligands $\{\text{Ni}_6(\text{OH})_4\text{Piv}_4\}$ (a) and coordination of terminal ligands (bridging Piv anions are not shown) (b). The H atoms, the Bu^t , CH_3 , and CF_3 groups, as well as Me_2CO molecules are not shown.

plex **1**, the potassium(I) ions and Me_2CO molecules bonded to them are in the second coordination sphere (see Fig. 2).

Complexes **1** and **2** contain six nickel(II) ions ($S_i = 1$). Since the metal core is asymmetric, the number of non-equivalent spin configurations with $S_i = 1$, $M_i = \pm S_i$ in both cases is 32, while the HDvV exchange Hamiltonian includes fifteen parameters. The calculated J_{ij} values and their standard errors are listed in Table 1. The indices of the exchange parameters correspond to the numbering schemes of the metallic centers shown in Figs 2 and 3. In both cases, the system of equations for calculation of the J_{ij} constants (a total of 31 equations, 15 unknowns) is consistent (standard errors are small). Similar calculations were also carried out for the crystal structure of com-

plex **1** without atoms of the second coordination sphere (**1***). The sets of the J_{ij} values, the energy spectra, and the temperature dependences of the effective magnetic moment obtained for **1** and **1*** almost coincide with each other, but in the latter case, the computational procedure is less time-consuming.

For complex **1**, the set of exchange parameters can be divided into three subsets, namely, $\{J_{12}, J_{15}, J_{34}, J_{46}\}$, $\{J_{13}, J_{16}, J_{23}, J_{24}, J_{26}, J_{35}, J_{45}, J_{56}\}$, and $\{J_{14}, J_{25}, J_{36}\}$. The first subset characterizes coupling in the dimeric fragments linked through oxygen atoms of the OH group and Piv anion (Ni—Ni distances in these fragments vary from 3.06 to 3.09 Å). The next subset describes coupling in the dimeric fragments linked through the hydroxyl oxygen atom and

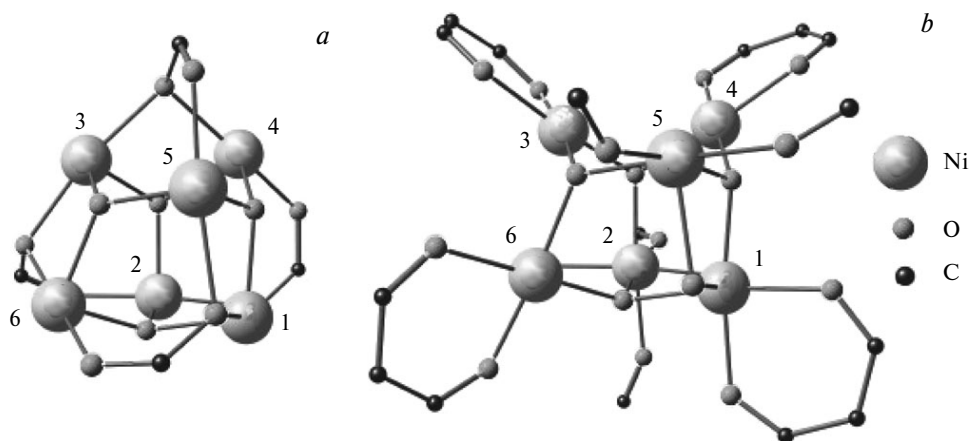


Fig. 3. Spatial configuration of complex **2**: the structure of the metal core with bridging ligands $\{\text{Ni}_6(\text{OH})_4\text{Piv}_4\}$ (a) and coordination of terminal ligands (bridging Piv anions are not shown) (b). The H atoms as well as the Bu^t , CH_3 , and CF_3 groups are not shown.

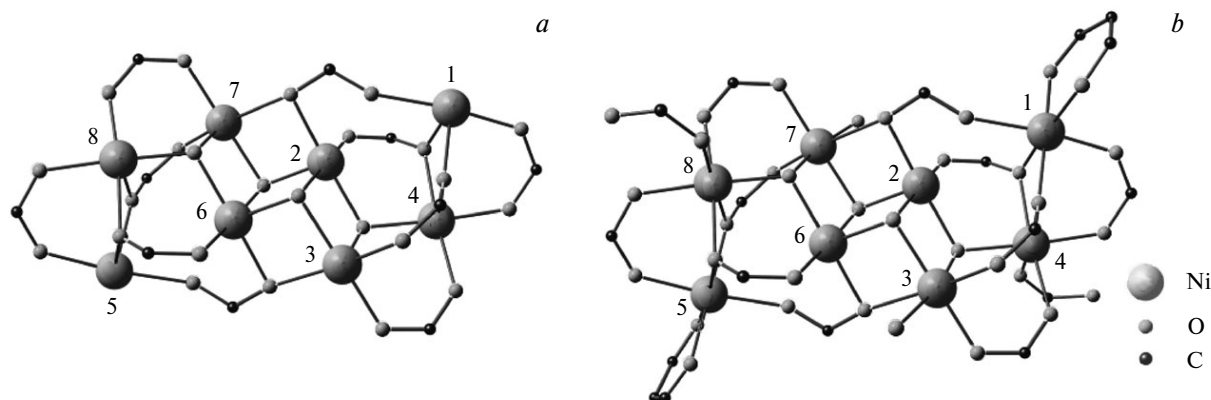


Fig. 4. Spatial configuration of complex **3**: the structure of the metal core with bridging ligands $\{\text{Ni}_8(\text{OH})_2(\text{MeO})_2\text{Piv}_{10}\}$ (a) and a general view of the complex (b). The H atoms as well as the Bu^t , CH_3 , and CF_3 groups are not shown.

Table 1. Distances (d) between the centers i and j and the J_{ij} exchange parameters of complexes **1** and **2**

Centers		$d/\text{\AA}$	J_{ij}/cm^{-1}
i	j		
Complex 1			
1	2	3.06	15.444(5)
1	5	3.07	13.945(5)
3	4	3.09	14.166(5)
4	6	3.07	14.634(5)
1	3	3.49	4.753(5)
1	6	3.58	−0.212(5)
2	3	3.47	4.971(5)
2	4	3.51	5.407(5)
2	6	3.47	3.900(5)
3	5	3.49	3.489(5)
4	5	3.52	4.810(5)
5	6	3.51	1.699(5)
1	4	4.46	−0.072(5)
2	5	4.81	−0.047(5)
3	6	4.86	−0.078(5)
Complex 2			
1	2	3.08	15.502(6)
1	5	3.08	15.521(6)
3	4	3.08	12.776(6)
3	6	3.08	12.785(6)
1	4	3.50	1.200(6)
1	6	3.50	1.256(6)
2	3	3.50	4.576(6)
3	5	3.50	4.582(6)
2	4	3.50	−1.852(6)
5	6	3.50	−1.853(6)
2	6	3.53	−1.134(6)
4	5	3.53	−1.132(6)
1	3	4.39	0.013(6)
2	5	4.89	−0.135(6)
4	6	4.89	−0.118(6)

Note. Here and in Table 2, the standard errors expressed in units of the last decimal place are given in parentheses.

the carboxylate fragment of the Piv anion (Ni–Ni distances vary from 3.47 to 3.58 Å). The third subset characterizes coupling between distant centers (see Table 1 and Fig. 2). Clearly, the spin Hamiltonian can be simplified by setting the parameters of the last-mentioned subset equal to zero. In addition, one can neglect some interactions in the dimeric fragments, namely, $J_{16} = J_{56} = 0$ (see Table 1). Other parameters of the second subset, as well as the parameters of the first subset, can be set to be equal to J_1 and J_2 , respectively. As a result, the spin Hamiltonian takes the form:

$$\begin{aligned} \text{H}(2) = & -2J_1(\text{S}_1 \cdot \text{S}_3 + \text{S}_2 \cdot \text{S}_3 + \text{S}_2 \cdot \text{S}_4 + \text{S}_2 \cdot \text{S}_6 + \\ & + \text{S}_3 \cdot \text{S}_5 + \text{S}_4 \cdot \text{S}_5) - 2J_2(\text{S}_1 \cdot \text{S}_2 + \text{S}_1 \cdot \text{S}_5 + \\ & + \text{S}_3 \cdot \text{S}_4 + \text{S}_4 \cdot \text{S}_6). \end{aligned} \quad (1)$$

The exchange parameters calculated using this model are $J_1 = 4.5(3)$ and $J_2 = 15.1(4) \text{ cm}^{-1}$. The standard errors somewhat increase when the simplified spin Hamiltonian is used; however, they still remain small compared to the values of the parameters, thus indicating the correctness of our simplifications.

From Fig. 3 and data of Table 1 it follows that in complex **2**, there are six pairs of isostructural dimeric fragments, namely, {12, 15}, {34, 36}, {14, 16}, {23, 35}, {24, 56}, and {26, 45}, each pair being characterized by almost equal J_{ij} values. In the first two pairs, the role of bridges is played by oxygen atoms of the OH group and Piv anion, whereas other pairs are linked through the hydroxyl oxygen atom and the carboxylate fragment of the Piv anion. An obvious way to simplify the spin Hamiltonian is to introduce one parameter for isostructural dimeric fragments ($J_{12} = J_{15}$, $J_{34} = J_{36}$, $J_{14} = J_{16}$, $J_{23} = J_{35}$, $J_{24} = J_{56}$, $J_{26} = J_{45}$). Then, one can neglect interactions between distant metallic centers ($J_{13} = J_{25} = J_{46} = 0$) as well as interactions in the pairs {14, 16}, {24, 56}, and {26, 45} (see Table 1). In addition, interactions in the pairs {12, 15}

and {34, 36} with identical bridges can be described by a single parameter ($J_{12} = J_{15} = J_{34} = J_{36}$). As a result, one gets the following simplified spin Hamiltonian:

$$H(2) = -2J_1(S_2 \cdot S_3 + S_3 \cdot S_5) - \\ - 2J_2(S_1 \cdot S_2 + S_1 \cdot S_5 + S_3 \cdot S_4 + S_3 \cdot S_6). \quad (2)$$

In this case, the calculated values of the exchange parameters are $J_1 = 4.0(5)$ and $J_2 = 13.6(3)$ cm⁻¹. The standard errors remain small.

It should be emphasized that in both cases, successive simplification of the HDvV exchange Hamiltonian does not lead to any significant changes in the eigenvalue spectrum. Figure 5, *a* presents the theoretical temperature dependences of the effective magnetic moment ($g = 2$). According to calculations, all significant interactions in the complexes **1** and **2** are ferromagnetic in character ($J_{ij} > 0$); therefore, in both cases, the ground level corresponds to the state with the maximum total spin value ($S = 6$). From Fig. 5, *a* it follows that at very low temperatures, the effective

magnetic moment reaches its maximum value (12.96 μ_B) corresponding to the ground level. Also, interactions in complex **2** are somewhat weaker, so the energy spectrum of **2** should be narrower. Therefore, at any nonzero temperature, the populations of the excited levels ($S < 6$) should be higher. As a result, at a nonzero temperature, the μ_{eff} value for complex **2** is smaller than for compound **1** (see Fig. 5, *a*). At 300 K, the μ_{eff} values equal to 7.6 (for **1**) and 7.4 μ_B (for **2**) approach the spin-only value for six noninteracting nickel(II) ions (6.93 μ_B).

The theoretical curves $\mu_{\text{eff}}(T)$ plotted using the isotropic exchange Hamiltonians and the calculated values of parameters reproduce the shape of the experimental curves (except the low-temperature region) and their relative position (the curve for complex **2** passes below the curve for compound **1**); however, there is no reasonable quantitative agreement between the theoretical and experimental data. The experimental curves pass above the theoretical ones (see Figs 1 and 5, *a*).

It should be noted that the ground state of the nickel(II) ion in octahedral ligand field ($^3A_{2g}$) is mixed with the excited triplet states ($^3T_{2g}$ and $^3T_{1g}$) through spin-orbital interaction, which leads to $g > 2$ and even to anisotropy of the g -tensor ($g_x, g_y, g_z > 2$) and zero-field splitting (ZFS) of the ground-state levels upon symmetry reduction.^{34,35} These effects should be taken into account in the description of the magnetic properties of polynuclear nickel(II) complexes. If the effect of the ZFS for the ground state of the metallic centers can be neglected, the results of magnetochemical measurements can be described using the isotropic exchange model assuming that the g -tensors of the metallic centers are isotropic with $g = (g_x + g_y + g_z)/3 > 2$ (if measurements were carried out for a powdered sample)* and varying g along with J_{ij} . Otherwise, the HDvV exchange Hamiltonian should be augmented with a term describing the influence of this effect on the structure of the spin levels of the exchange cluster. In addition, non-Heisenberg exchange, *viz.*, asymmetric and/or antisymmetric exchange, should be taken into account for some systems.^{34–36}

In the case of complexes **1** and **2**, better agreement with experimental data can be attained by jointly optimizing J_1 , J_2 , and the g -factor. The appearance of maxima instead of plateau regions in the low-temperature regions of the experimental curves can be explained by intermolecular exchange interactions (IMEI) with $J' < 0$; their influence can be described by augmentation of the spin Hamiltonians (1) and (2) with the corresponding term.^{34,35} To confine the region of solutions, the J_1 and J_2 values obtained from UB3LYP-BS calculations should be specified as the initial approximation. However, the observed low-temperature behavior of the complexes under study can be due to the effect of ZFS for the ground state of

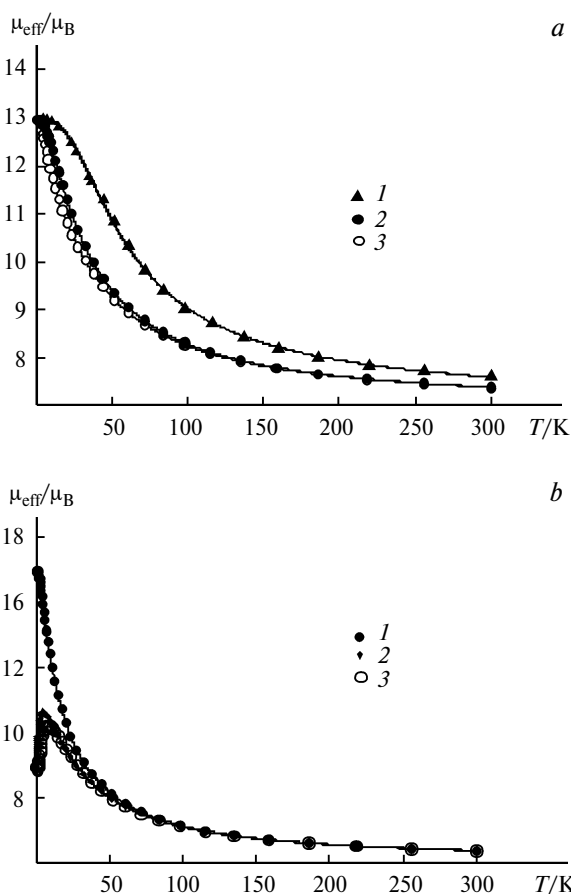


Fig. 5. Theoretical temperature dependences of the effective magnetic moment plotted for complexes **1**, **2** (*a*), and **3** (*b*) using the isotropic exchange Hamiltonians $H(2)$ (**1**, **2**) and $H(15)$ (**1**, **3**) for complexes **1** (**1**) and **2** (**2**, **3**) (*a*) and $H(2)$ (**1**), $H(3)$ (**2**), and $H(28)$ (**3**) for complex **3** (*b*).

* Usually, one has $g_{Ni} \approx 2.2$.

metallic centers.³⁷ In this case, the spin Hamiltonians (1) and (2) should be augmented with the term

$$\sum_i \mathbf{S}_i \cdot \mathbf{D} \cdot \mathbf{S}_i.$$

As a result, the number of the parameters to be varied increases to 5 $\{J_1, J_2, D, E, \text{ and } g\}$ assuming $D_1(E_1) = D_2(E_2) = \dots = D_6(E_6) = D(E)$ (D and E are the axial and rhombic ZFS parameters, respectively). It is more appropriate to carry out the two-step search for optimum values of the parameters of this model, starting with optimization of the J_1 and J_2 parameters and the g -factor using no low-temperature experimental data and specifying the J_1 and J_2 values calculated by the UB3LYP-BS method as the initial approximation. The next step includes optimization of all parameters using the whole array of experimental data and the J_1, J_2 , and g values determined in the first step as the starting ones.

Unlike compounds **1** and **2**, complex **3** contains eight nickel(II) ions ($S_i = 1$). In this case, the number of non-equivalent spin configurations with $S_i = 1, M_i = \pm S_i$ is 128 and the HDvV exchange Hamiltonian includes 28 parameters (C_1 symmetry). As mentioned above, correct evaluation of the J_{ij} parameters requires calculations of all possible single-determinant wave functions; however, their number for polynuclear complexes can be very large. Here, one can reduce himself to one or a few subsets of the BS-determinants with the same values of the total spin projection M . For complex **3**, we calculated all possible BS-determinants with $M = 0$ (35), $M = 4$ (28), and $M = 6$ (8). The calculated J_{ij} values and their standard errors are listed in Table 2. The indices of the exchange parameters correspond to the numbering scheme of the metallic centers shown in Fig. 4. The system of equations for calculation of the J_{ij} constants (a total of 71 equations, 28 unknowns) is consistent (standard errors are small) and the J_{ij} values thus obtained are almost equal to the values calculated using the fragmental approach (see the rightmost column in Table 2).

From Fig. 4 and data in Table 2 one can see that the symmetry of complex **3** is close to C_i ; therefore, interactions in the pairs $\{12, 56\}, \{13, 57\}, \{14, 58\}, \{23, 67\}, \{24, 68\}, \{27, 36\}, \{34, 78\}, \{16, 25\}, \{17, 35\}, \{18, 45\}, \{28, 46\}$, and $\{38, 47\}$ are characterized by almost equal J_{ij} values. According to calculations, ferromagnetic exchange dominates in complex **3**; however, metallic centers in the $\{17, 35\}$ pair are coupled through antiferromagnetic interactions whose energy is higher than 2 cm^{-1} (despite the fact that the metal–metal distance is longer than 6 \AA). Exchange between the centers 1 and 7 (3 and 5) occurs by the superexchange mechanism through the carboxylate bridge (see Fig. 4). A clearly seen way to simplify the spin Hamiltonian is to describe coupling in the pairs mentioned above by a single parameter ($J_{12} = J_{56}, J_{13} = J_{57}, J_{14} = J_{58}, J_{23} = J_{67}, J_{24} = J_{68}, J_{27} = J_{36}, J_{34} = J_{78}, J_{16} = J_{25}$,

Table 2. Distances (d) between centers i and j and the exchange parameters (J_{ij}) calculated for complex **3** using the **H**(28) spin Hamiltonian and within the framework of the fragmental approach

Centers		$d/\text{\AA}$	J_{ij}/cm^{-1}	
i	j		Ni ₈	Ni ₂ Zn ₆
1	2	3.59	−0.838(2)	−0.620
5	6	3.59	−0.841(2)	
1	3	4.98	−0.007(2)	−0.049
5	7	4.98	0.011(2)	
1	4	3.07	5.248(2)	5.549
5	8	3.07	5.247(2)	
2	3	3.06	4.271(2)	4.671
6	7	3.06	4.223(2)	
2	4	3.36	1.361(2)	1.597
6	8	3.36	1.362(2)	
2	7	3.10	3.921(2)	4.062
3	6	3.10	3.971(2)	
3	4	3.29	7.715(2)	7.596
7	8	3.29	7.759(2)	
2	6	2.97	18.960(2)	19.534
1	6	6.36	0.014(2)	0.027
2	5	6.36	0.014(2)	
1	7	6.21	−2.101(2)	−2.152
3	5	6.21	−2.100(2)	
1	8	8.75	0.011(2)	0.016
4	5	8.75	0.011(2)	
2	8	5.49	0.100(2)	0.088
4	6	5.49	0.099(2)	
3	8	6.38	−0.255(2)	−0.373
4	7	6.38	−0.253(2)	
1	5	9.89	0.001(2)	0.000
3	7	5.39	0.057(2)	0.126
4	8	8.61	−0.013(2)	−0.027

$J_{17} = J_{35}, J_{18} = J_{45}, J_{28} = J_{46}, J_{38} = J_{47}$). Then, one can neglect coupling in the pairs $\{12, 56\}, \{13, 57\}, \{24, 68\}, \{16, 25\}, \{18, 45\}, \{28, 46\}$, and $\{38, 47\}$, as well as coupling between the centers 1 and 5, 3 and 7, 4 and 8 (see Table 2). In addition, one can assume the same values of the exchange parameters for the pairs $\{14, 58\}, \{23, 67\}, \{27, 36\}$, and $\{34, 78\}$. Thus, the **H**(28) spin Hamiltonian takes the form:

$$\begin{aligned} \mathbf{H}(3) = & -2J_1(\mathbf{S}_1 \cdot \mathbf{S}_4 + \mathbf{S}_5 \cdot \mathbf{S}_8 + \mathbf{S}_2 \cdot \mathbf{S}_3 + \mathbf{S}_6 \cdot \mathbf{S}_7 + \\ & + \mathbf{S}_2 \cdot \mathbf{S}_7 + \mathbf{S}_3 \cdot \mathbf{S}_6 + \mathbf{S}_3 \cdot \mathbf{S}_4 + \mathbf{S}_7 \cdot \mathbf{S}_8) - \\ & - 2J_2(\mathbf{S}_2 \cdot \mathbf{S}_6) - 2J_3(\mathbf{S}_1 \cdot \mathbf{S}_7 + \mathbf{S}_3 \cdot \mathbf{S}_5). \end{aligned} \quad (3)$$

The values of the parameters calculated using this model are $J_1 = 5.4(1), J_2 = 18.8(6)$, and $J_3 = -2.1(4) \text{ cm}^{-1}$. The standard errors are still small.

Successive simplification of the HDvV exchange Hamiltonian to **H**(3) causes no significant changes in the eigenvalue spectrum. The ground level corresponds to the state with $S = 5$. It should be emphasized that the total

spin of the ground state is smaller than the maximum value $S_{\max} = 8$ due to antiferromagnetic exchange in the {17, 35} pair. In the low-energy region, the spin levels are almost degenerate and therefore their relative positions in the energy spectrum can change upon minor changes in the exchange parameters. In particular, changes in the exchange parameters of the {17, 35} pair toward less negative values cause the total spin of the ground state to increase up to the maximum value. Neglecting interactions in the {17, 35} pair, the spin Hamiltonian takes the form:

$$\begin{aligned} \mathbf{H}(2) = & -2J_1(\mathbf{S}_1 \cdot \mathbf{S}_4 + \mathbf{S}_5 \cdot \mathbf{S}_8 + \mathbf{S}_2 \cdot \mathbf{S}_3 + \mathbf{S}_6 \cdot \mathbf{S}_7 + \\ & + \mathbf{S}_2 \cdot \mathbf{S}_7 + \mathbf{S}_3 \cdot \mathbf{S}_6 + \mathbf{S}_3 \cdot \mathbf{S}_4 + \mathbf{S}_7 \cdot \mathbf{S}_8) - 2J_2(\mathbf{S}_2 \cdot \mathbf{S}_6). \end{aligned} \quad (4)$$

In this case, the ground level corresponds to the state with the maximum value of the total spin at any (positive) J_1 and J_2 values. The values calculated using the model with the $\mathbf{H}(2)$ spin Hamiltonian are $J_1 = 4.9(1)$ and $J_2 = 18.5(7) \text{ cm}^{-1}$.

As should be expected, the theoretical temperature dependences of the effective magnetic moment ($g = 2$) plotted using the $\mathbf{H}(28)$, $\mathbf{H}(3)$, and $\mathbf{H}(2)$ spin Hamiltonians with the calculated values of the exchange parameters differ only in the low-temperature region (see Fig. 5, *b*). At $T \rightarrow 0 \text{ K}$, the effective magnetic moment takes the values 10.95 and 16.97 μ_B corresponding to the ground levels with $S = 5$ and $S = 8$, respectively. An increase in the effective magnetic moment on heating is due to the population of the levels with $S > 5$ (see curves 2 and 3 plotted using the $\mathbf{H}(3)$ and $\mathbf{H}(28)$ spin Hamiltonians that include interactions in the {17, 35} pair). Note that the maximum in curve 2 is shifted toward lower temperatures, being somewhat higher. These discrepancies are due to a decrease in the energy intervals between the spin levels in the low-energy spectral region and to the changes in the order of some spin levels. For instance, the first six energy levels obtained using the models with the $\mathbf{H}(28)$ and $\mathbf{H}(3)$ Hamiltonians are respectively arranged as follows: $S = 5, 4, 6, 3, 7, 8$ and $S = 5, 6, 4, 7, 3, 8$. Thus, in the latter case, the level with $S = 6$ is lower than the level with $S = 4$, whereas the level with $S = 7$ is lower than the level with $S = 3$. At 300 K, the μ_{eff} value (8.4 μ_B) approaches the spin-only value for eight noninteracting nickel(II) ions (8.00 μ_B).

From Figs 1 and 5, *b* one can see that theoretical data do not fit the experimental dependence $\mu_{\text{eff}}(T)$. As mentioned above, the low-temperature behavior of the complexes **1**·1.5C₇H₁₆ and **2** is due to the influence of IMEI or ZFS for the ground state of metallic centers. For complex **3**·C₆H₁₄, the influence of one of these two factors can also play the decisive role at low temperatures. Better agreement with experimental data using one or another model can be attained by jointly optimizing the parameters of the model and the g -factor. Note that the values obtained at temperatures below T_c (2.5 K) should be excluded from the experimental data array.

Summing up, based on the results of quantum chemical calculations, we propose the spin Hamiltonians including the minimum number of parameters to describe isotropic exchange in complexes **1**, **2**, and **3**. It is these spin Hamiltonians augmented with the term responsible for the influence of IMEI or ZFS for the ground state of metallic centers that should be used to describe the magnetic properties and to determine the optimum values of parameters from experimental data. The values of the parameters of isotropic exchange obtained from UB3LYP-BS calculations should be specified as the initial approximation. The choice of a particular model (HDvV + IMEI or HDvV + ZFS), including the conclusion about the significance of isotropic exchange in the {17, 35} pair in complex **3**, can be drawn based on the accuracy of reproduction of the results of magnetochemical measurements. Additional studies (by ESR spectroscopy, inelastic neutron scattering, *etc.*) will help to refine the structure of the spin levels and are necessary to verify the correctness of the model.

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