Magnetic properties of binuclear high-spin trimethylacetate nickel(II) complexes

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The static magnetic susceptibility of mononuclear trimethylacetate nickel complex $Ni(NH_2Ph)_4(OOCCMe_3)_2$ (3) and binuclear complexes $Ni_2(\mu\text{-}OH_2)(\mu\text{-}OOCCMe_3)_2(OOCCMe_3)_2(dipy)_2$ (**4**) and $Ni_2(\mu\text{-}OOCCMe_3)_4py_2$ (**5**) was measured in the temperature range of 2—300 K. The magnetic behavior of **3** is typical of mononuclear complexes with the Ni^{II} atom in the octahedral environment. Numerical calculations of the temperature dependence of magnetic susceptibility with inclusion of isotropic exchange interactions (*J*) and single-ion initial splitting parameters showed that the magnetic behavior of complexes **4** and **5** can be interpreted in terms of ferromagnetic (for **4**) and antiferromagnetic (for **5**) interactions.

Key words: magnetic properties, ferromagnetism, antiferromagnetism, nickel(II) trimethylacetates.

The problem of correlation between the magnetic properties and structure of molecular complexes (especially those containing two or several magnetic centers, *e.g.*, transition-metal atoms) is topical. Solving this problem makes it possible not only to simplify many analytical problems at the stage of detecting molecular systems and materials but also to approach targeted variation of magnetic properties of substances. "Magnetic properties—structure" correlations can be used in studies of, *e.g.*, magnetic properties of metal-containing enzymes.[1] However, these studies are hampered by the lack of the detailed structures of at least the metal-containing fragments of natural enzymes. For this reason, it may be convenient to follow an approach which includes modeling using synthetic complexes — analogs of the metal-containing fragment of the enzymes. Probably, such an approach will help to answer the question of why Ni-containing enzyme urease (urea amidohydrolase, EC 3.5.1.5) exhibits both antiferromagnetic and ferromagnetic properties under different conditions.[2] Recently,[3] we synthesized and structurally characterized a series of binuclear trimethylacetate Ni^{II} complexes, which simulate formally the dinickel fragment of urease. It was also shown that the magnetic behavior of such complexes can drastically change despite a similar ligand environment of the metal center.[3,4]

Up to now, studies of magnetic properties of carboxylate Ni^{II} complexes are fragmentary. Their theoretical description is based on the Heisenberg—Dirac—Van Vleck (HDVV) model.[6—9] Magnetic properties of polynuclear transition-metal complexes are strongly dependent on fine details of the electronic and molecular structure of mononuclear fragments linked by bridging ligands. This requires rigorous substantiation of the approximations used in the theoretical models invoked for interpreting the magnetic properties.[10,11]

It was found that the magnetic properties of binuclear Ni^{II} trimethylacetates $py_4Ni_2(\mu\text{-}OH_2)(\mu\text{-}OOCCMe_3)_2(OOCCMe_3)_2$ (**1**) and $py_2Ni_2(HOOC\text{—}CMe_3)_2(\mu\text{-}OH_2)(\mu\text{-}OOCCMe_3)_2(OOCMe_3)_2$ (**2**) with similar geometric characteristics of the central metal framework $Ni_2(\mu\text{-}OH_2)(\mu\text{-}OOCCMe_3)_2$ (Ni...Ni 3.513(1) and 3.461(1) Å, respectively) and differing only in composition of terminal ligands are strongly different.

Complex **1** appeared to be ferromagnetic, whereas complex **2** exhibits antiferromagnetic properties.[3,4] We also observed an antiferromagnetic exchange for the series of "lantern"-type carboxylates $L_2Ni_2(\mu\text{-}OOCCMe_3)_4$ (L = Py, 2,5-dimethylpyridine, Et_3N).[4]

We failed to interpret the magnetic properties of the complexes using the classical HDVV model.[3,4] In this case it was important to perform a detailed analysis of the results obtained and take into account the maximum number of the factors affecting the spin-spin exchange mechanism.

In this work, we studied the magnetic behavior of several related high-spin nickel(II) complexes with pyvalic acid and donor bases. The results of numerical calcula-

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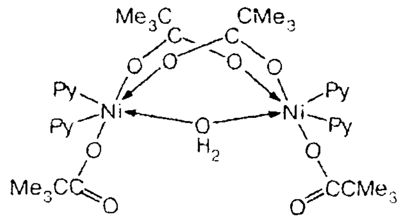
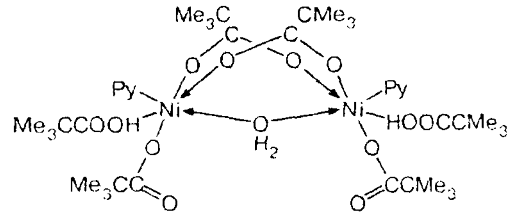


1

ferromagnetic
($-2J = -17$ cm^{-1})



2

antiferromagnetic
($-2J = 265$ cm^{-1})

tions of the magnetic properties of polynuclear complexes in which the spins S_i of paramagnetic ions equal 1 are also presented.

Results and Discussion

Theoretical model. The spin Hamiltonian of polynuclear molecules has a rather complex form[10,12] even in the case of orbital-nondegenerate ions constituting the molecules:

$$\hat{H} = \sum_{i,j}\Big(\beta \boldsymbol{H} g_i \hat{s}_i - 2J_{ij}\hat{s}_i\hat{s}_j - 2j_{ij}(\hat{s}_i\hat{s}_j)^2 + \\ + \hat{s}_i d_{ij}\hat{s}_j + G_{ij}[\hat{s}_i \times \hat{s}_j] + \hat{s}_i D_i \hat{s}_i\Big), \qquad (1)$$

where β is the Bohr magneton,[10,11] $\boldsymbol{H}$ is the vector of the external magnetic field, g_i are the g-tensors of the magnetic ions, $\hat{s}_i$ are the spin operators of the magnetic ions, and the summation is performed over all ions (i) and pairs of ions ($i \neq j$).

As can be seen, the spin Hamiltonian (1) includes a large number of unknown scalar and tensor parameters that can hardly be determined from the smooth curve of the temperature dependence of magnetic susceptibility $\chi(T)$. Therefore, the spin Hamiltonian (1) can be used for reliable interpretation of experimental data only after simplification.

The first term of expression (1) describes the interaction with the external magnetic field. It is this interaction that makes it possible to detect magnetic properties. Therefore, this term cannot be ignored even in the case of weak fields.

The second term is the isotropic exchange operator (negative and positive values of the $-2J$ constant correspond to ferro- and antiferromagnetic exchange, respectively). As a rule, this interaction is to the greatest extent responsible for temperature dependence of the effective magnetic moment[10,11]:

$$\mu_{ef} = \sqrt{7.997\chi T}\,. \qquad (2)$$

The number of independent exchange parameters $-2J_{ij}$ can usually be reduced owing to symmetry considerations since most polynuclear molecules can at least be considered as approximately symmetrical.

The next three terms are the operators of biquadratic, anisotropic, and antisymmetric interactions.[10—12] In the general case, they include a large number of independent parameters since d_{ij} are tensors and G_{ij} are vectors. As a rule, the values of these parameters are much less than $|-2J|$[10—12] and can be neglected in routine experiments.

The last term includes the single-ion initial splitting tensors, which should be taken into account only if $s_i > 1/2$. They are independent of the exchange parameters and cannot be arbitrarily neglected because the $|D_i|$ values can amount to several tens (in cm^{-1} units).[13,14] Precise measurements of the six components of D_i tensors can likely be carried out only by single-crystal ESR.[13,14] However, the direction of the highest anisotropy can usually be distinguished in the mononuclear fragment. Then, assuming that the Z axis in the system of local axes is directed along the direction of highest anisotropy, we can write the approximate expression for the initial splitting operator[13,14]

$$D_i[\hat{s}_{zi}^2 - \hat{s}_i(\hat{s}_i + 1)], \qquad (3)$$

where $D_i \equiv D_{zi}$ is the z-component of the D_i tensor reduced to the local axes.

In the local axial symmetry approximation, it is also reasonable to take into consideration only three components of the g-tensor written in the system of local axes, namely, g_z, g_x, and g_y ($g_x = g_y$). As a result, the spin Hamiltonian of a polynuclear complex containing high-spin ions is simplified and takes the form

$$\hat{H} = \sum_{i,j}\Big\{\beta[g_{zi}\hat{s}_{zi}H_z + g_{xi}(\hat{s}_{xi}H_x + \hat{s}_{yi}H_y)] - \\ - 2J_{ij}\hat{s}_i\hat{s}_j + D_i[\hat{s}_{zi}^2 - \hat{s}_i(\hat{s}_i + 1)]\Big\}, \qquad (4)$$

where i and j are the summation indices and g and D are defined in the system of local axes.

Thus, calculations of the energy spectrum for the spin Hamiltonian (4) begins with reducing the operators to the same axes using the Wigner D-functions.[15] Generally, the complex form of the reduced spin Hamiltonian makes it impossible to divide the spin Hamiltonian matrix into blocks. Therefore, the energy levels were determined by diagonalization of the spin Hamiltonian matrix written in a complete basis of all possible functions (products of the spin projections). Then the temperature dependences of the magnetic susceptibility ($\mathrm{cm}^3\,\mathrm{g\text{-}atom}^{-1}$) and/or effective magnetic moment (2) were calculated as functions of the parameters of the spin Hamiltonian using the Gerloch—McMeeking formula.[10,16]

The theoretical dependences of the effective magnetic moment (μ_{ef}) on kT/J for a model dimer with $s_1 = s_2 = 1$, $g_z = g_x = g_y = 2$, and parallel local axes are shown in Fig. 1. As can be seen, at low temperatures ($|D| < kT$) the initial splitting effect can much exceed the experimental error (~1%). At $D > 0$, this effect is much stronger since positive D values correspond to stabilization of the one-center states $\mathrm{M_s} = |0\rangle$ relative to doublets $\mathrm{M_s} = |\pm1\rangle$ (see expression (3)). In the case of dimers with ferromagnetic exchange ($-2J < 0$), the initial splitting always results in suppression of the magnetic moment owing to a decrease in the effective spin value. In the systems with $-2J > 0$, the magnetic moment increases due to partial disruption of the antiferromagnetic ordering.

Figure 2 illustrates the effect of nonparallel local axes. This effect can be rather strong for ferromagnetic systems at low temperatures.

Experimental data were processed by fitting the theoretical (χ^t) values of the static magnetic susceptibility (per g-atom of paramagnetic centers) to the measured (χ^e) values. The error functional was given as an expression dependent on the geometry of the Ni—O—Ni fragment. The root-mean-square error was calculated using the formula

$$\sigma_w = \left[\frac{1}{N-p}\sum_i(\chi_i^e - \chi_i^t)^2 w_i^2\right]^{1/2}, \qquad (5)$$

where N is the number of temperature points, p is the number of independent parameters, w_i are the weighting factors, and summation is performed over all N points.

The w_i values were given as $w_i = 1/\chi_i^e$ for equally significant χ_i^e values or as $w_i = T_i$ in the case of large low-temperature errors (as a rule, this is due to low susceptibility in antiferromagnetic systems). In order to reproduce the properties of real systems more correctly, terms describing an admixture of mononuclear complex (without initial splitting) and intermolecular isotropic exchange were introduced in the theoretical expression for magnetic susceptibility. In the molecular field approximation, the isotropic exchange parameter has the form[10,15]

$$-2\langle z\rangle J', \qquad (6)$$

where $\langle z\rangle$ is the number of nearest neighbors. Minimization of expression (5) was performed using the Newton—Raphson method,[17] whose efficiency for this class of problems has been established experimentally. The hypotheses were tested using the Fisher test.[18,19] Since $N \approx 20$ and $p << N$ in our studies, then, according to the Fisher test, the replacement or addition of varied parameters is significant if σ_w decreases by a factor of 1.5 to 2.

Mononuclear complex $\mathrm{Ni(NH_2C_6H_5)_4(OOCCMe_3)_2}$ (**3**) and binuclear complexes with different structure of the metal framework, *viz.*, the three-bridged cluster $\mathrm{Ni_2(\mu\text{-}OH_2)(\mu\text{-}OOCCMe_3)_2(OOCCMe_3)_2(dipy)_2}$ (**4**) and four-bridged cluster $\mathrm{Ni_2(\mu\text{-}OOCCMe_3)_4py_2}$ (**5**), were chosen as examples.

Mononuclear complex $\mathrm{Ni(NH_2C_6H_5)_4(OOCCMe_3)_2}$ (3) has four N atoms from four coordinated aniline molecules in the equatorial plane of the nickel atom, whereas the axial positions are occupied by two terminal $\mathrm{OOCCMe_3}$ fragments. Thus, the local environment of the $\mathrm{Ni^{II}}$ atom is a distorted octahedron.[3,4] The magnetic behavior of complex **3** is typical of mononuclear $\mathrm{Ni^{II}}$ complexes in which the $\mathrm{Ni^{II}}$ atom is in the octahedral environment. The effective magnetic moment of complex **3** (3.09 μ_B) is temperature-independent down to

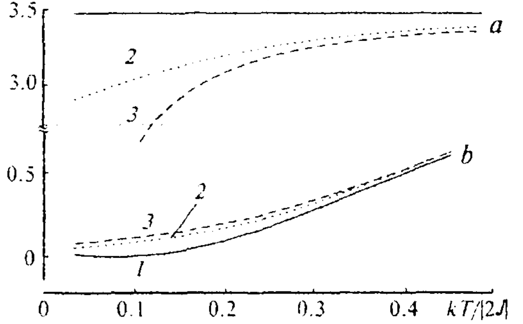


Fig. 1. Theoretical dependences of the effective magnetic moment (μ_{ef}) on $kT/|2J|$ for the model binuclear cluster with $s_1 = s_2 = 1$, $g_z = g_x = g_y = 2$ and parallel local axes: *a*) $-2J < 0$; *b*) $-2J > 0$: $D = 0$ (*1*), $D = -0.5|-2J|$ (*2*), and $D = 0.5|-2J|$ (*3*).

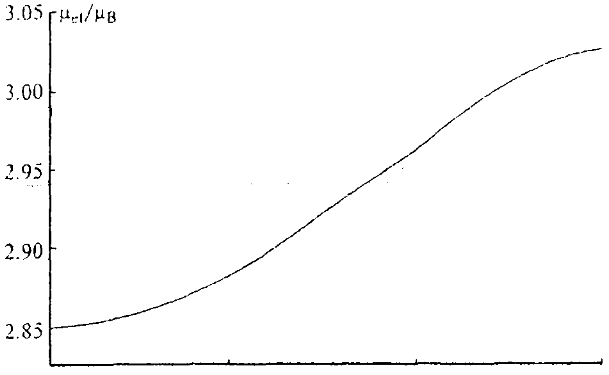
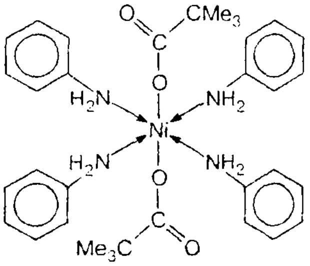


Fig. 2. Theoretical dependence of the effective magnetic moment (μ_{ef}) on the angle θ between local Z axes for the model binuclear cluster with $s_1 = s_2 = 1$, $g_z = g_x = g_y = 2$ at $kT/|2J| = 0.15$ and $D = 0.5|-2J|$.

5 K, which corresponds to S = 1 and g = 2.18 for the Ni atom.



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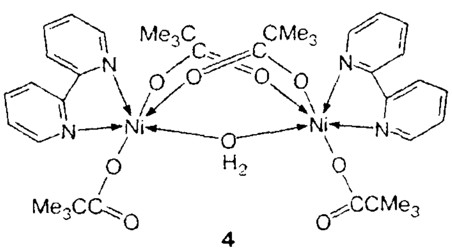

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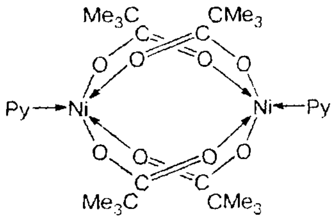

5

The magnetic moment monotonically decreases as temperature decreases down to 2 K, which can likely be explained by weak antiferromagnetic intermolecular interaction (Fig. 3).

Binuclear nickel complex $Ni_2(\mu\text{-}OH_2)(\mu\text{-}OOCCMe_3)_2(OOCCMe_3)_2(dipy)_2$ (4) has a three-bridged metal framework. The metal atoms in the molecules are located at nonbonding distances (Ni...Ni 3.513 Å). As in complex **3**, the ligand environment of the metal centers is close to an octahedron.[3,4] The magnetic moment of complex **4** (per paramagnetic center) slowly increases from 3.077 to 3.134 μ_B in the temperature range from 20 to 2 K (Fig. 4).

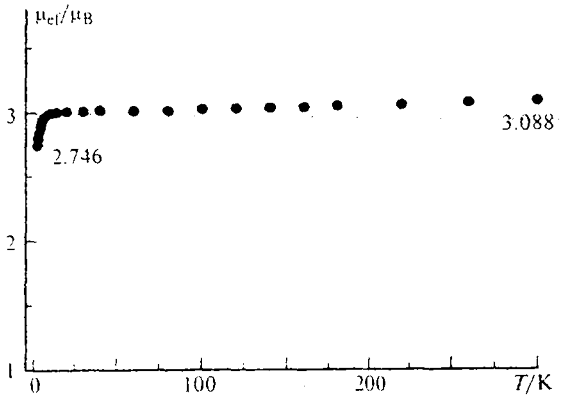

Fig. 3. Magnetic characteristics of complex 3.

Several sets of the parameters obtained are listed below to illustrate the calculation procedure. Based on the symmetry considerations, the one-center parameters for molecule **4** were assumed to be equal and the angle between the local Z axes was assumed to be 115° (see below).

Variant	$\langle g \rangle$	D	$-2J$	$-2\langle z \rangle J'$	σ_χ
		cm^{-1}			
1	1.869	0*	−71.2	0*	0.059
2	2.222	0.006	0*	0*	0.0779
3	2.202	0*	0*	−0.214	0.0674
4	2.118	−10.1	−4.44	0*	0.0116
5	2.131	0*	−3.77	0.526	0.0095
6	2.199	−2.78	0*	−0.410	0.064

Note. Asterisked are the parameters with fixed values: $\langle g \rangle = g_z = g_{x,y}$.

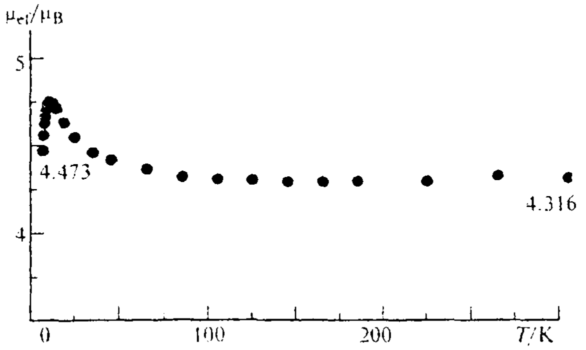

Fig. 4. Magnetic characteristics of binuclear complex **4** (μ_{ef} was calculated per entire molecule).

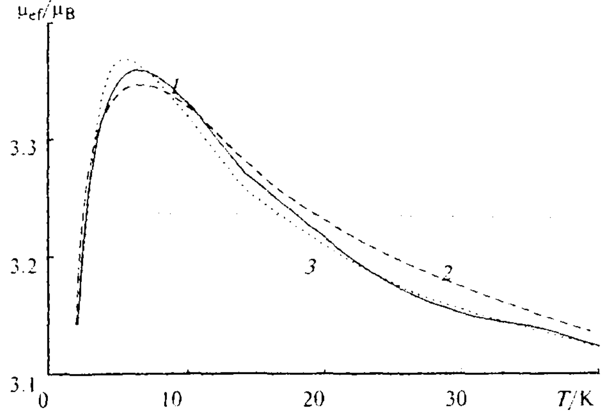

Fig. 5. Low-temperature part of experimental $\mu_{ef}(T)$ curve (*1*) (μ_{ef} was calculated per paramagnetic ion) for complex **4** and theoretical best fit values calculated using versions 4 (*2*) and 5 (*3*).

Since the temperature dependence of the effective magnetic moment of the cluster has a maximum in the low-temperature region (Fig. 5), one of the interactions responsible for the temperature dependence of μ_{ef} was taken into account in the first stage of calculations. As can be seen (versions 1—3), the σ_χ values obtained are much larger than the experimental error (~1%). Additionally, the *g*-factor obtained for version 1 is unsatisfactory (*g* = 2.1—2.2 for Ni^{II} atoms).[14,15] Simultaneous consideration of two interaction parameters (see versions 4 and 5) leads to appreciable decrease in σ_χ. Qualitatively, both curves (see Fig. 5) and the corresponding errors differ only slightly, so it is difficult to decide between the two versions.

Since the σ_χ value obtained in versions 4 and 5 is comparable with the experimental error, it is of no sense to increase the number of independent parameters even in the case of appreciable decrease in σ_χ.

Binuclear nickel complex $Ni_2(\mu\text{-}OOCCMe_3)_4py_2$ (5) has a "lantern"-type four-bridged dinickel fragment. The metal atoms in the molecule are located at nonbonding distances (Ni...Ni 2.603 Å). The ligand environment of the metal centers is close to the octahedral one with consideration of the second metal center to complete the coordination sphere.[4] The magnetic moment of complex 5 monotonically decreases over the whole temperature range (Fig. 6).

Processing the $\chi(T)$ data for this compound using an analogous procedure gives the following best fit values:

$$\langle g\rangle = 2.175;\ D = 0^*;\ -2J = 260;\ -2\langle z\rangle J' = 0^*;\ \sigma_\chi = 0.0062.$$

Since both complexes 4 and 5 have a binuclear structure in which the Ni atoms are linked by bridges rather than bound by a direct metal—metal bond, the results obtained using version 4 of calculations can be accepted as "reliable" for complex 5 (taking into account that the negative sign of *D* is consistent with theoretical estimates[13,14]).

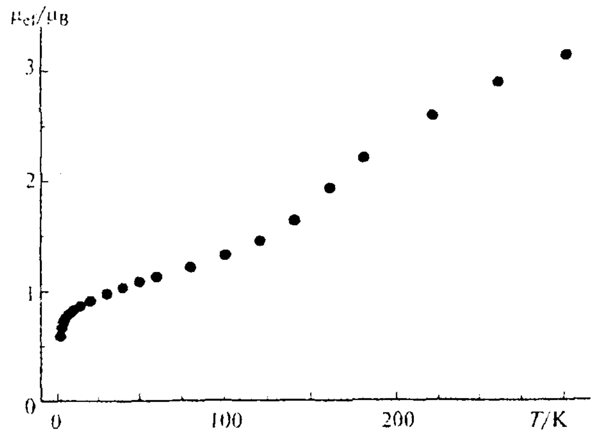

Fig. 6. Magnetic properties of complex 5 (μ_{ef} was calculated per entire molecule).

Irrespective of the accepted versions, the most intriguing is transition from paramagnetism in 3 to weak antiferromagnetism in 5 and ferromagnetism in 4. Actually, the antiferromagnetic behavior of 5 is typical of "lantern"-type dimers,[10] characterized by superexchange involving four carboxylate bridges. In complex 4, the number of these bridges reduces to 2, which should decrease the contribution of this mechanism to antiferromagnetic exchange. In addition, this complex contains the bridging oxygen atom as a constituent, which makes possible transition from antiferromagnetic to ferromagnetic superexchange. By and large, the bridging geometry is very close to that of the dimeric fragment of strongly antiferromagnetic trinuclear transition-metal μ-oxocomplexes.[20] Since the exchange parameters in Fe^{III} trimers with the maximum number of exchange channels, but with different (carboxylate[20] and sulfate[21]) bridges are very close ($-2J \approx 60$ and 53 cm^{-1}, respectively), it is possible to focus our attention on the bridging O atoms as the most effective exchange channel. In the trimers, this is a monatomic ligand with an M—O—M angle of ~120°. The Ni—O—Ni angle in the dimers under study is decreased to ~115° and the bridging O atom belongs to a water molecule, *i.e.*, it forms strong bonds with two H atoms. A small decrease[10,11] in the angle far from the critical value (~105°) corresponding to ferromagnetic-to-antiferromagnetic transition seems to be insignificant. However, strong O—H bonds can substantially affect the magnitude and sign of the interaction.[10,22] Low accuracy of the determination of the coordinates of H atoms in the X-ray diffraction experiment and small magnitude of the experimentally observed effect of "change over" of the interaction sign hampers a detailed consideration of this phenomenon. Mention may be made that consideration of p-orbitals of the monatomic bridge only leads to a critical angle of the ferromagnetic-to-antiferromagnetic transition of 90° and that its increase to ~115° is completely due to "interference" of the interactions through the p- and s-orbitals of the bridge.[10,22] Efficient competition of hydrogen atoms with the metal atoms for p-orbitals results in an increase in the relative contribution of s-orbitals to the exchange, thus increasing the critical angle.

Thus, going from mononuclear carboxylate complex 3 to binuclear three-bridged and four-bridged complexes 4 and 5, respectively, is accompanied by change in the magnetic behavior of the complexes from paramagnetic (for 3) to ferromagnetic (for 4) and antiferromagnetic (for 5).

Experimental

Measurements of static magnetic susceptibility were carried out at the International Tomography Center of the Siberian Branch of the Russian Academy of Sciences on an MPMS-5S SQUID magnetometer (Quantum Design) in the temperature range 2—300 K.

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