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Dinuclear and polymeric (µ-formato)nickel(II) complexes: Synthesis, structure, spectral and magnetic properties

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ABSTRACT

Two (μ -formato)nickel(II) complexes [Ni₂(HCOO)(bz)₈(H₂O)₂)(HCOO)₃·4H₂O (**1**) and [Ni(tren)(HCOO)] ClO₄·H₂O (**2**) were synthesized and characterized by spectroscopic methods. The structure of complexes has been determined by X-ray crystallography. The formato ligand bridges the Ni(II) central atoms forming a dinuclear cation in **1** and a polymeric cationic chain in **2**, respectively. The coordination environment of Ni(II) atom is nearly octahedral. Based upon the magnetic data, these two compounds display an exchange interaction of the antiferromagnetic nature along with the zero-field splitting. The results from magnetic analysis of **1** and **2**, namely the isotropic exchange constants and the zero-field splitting parameters were further confirmed and studied by DFT method using at B3LYP/def2-TZVP and by CASSCF/NEVPT2, respectively.

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1. Introduction

Different possible coordination of the carboxyl group leads to the various crystal structures of coordination compounds mononuclear, binuclear or polynuclear. Review papers of carboxylato complexes deal mostly with acetato and trifluoroacetato complexes [1]. Only little attention is paid to the formate ion as a bridging ligand although as the smallest carboxylate it has been reported to display not only monodentate but multiple bridging modes. To our knowledge only a few formato-nickel(II) complexes have been structurally characterized [2–6]. In a simple formate Ni(HCOO)₂(H₂O)₂ the formate ions are coordinated as bridging bidentate ligands [7]. In a double formato complex $Ba_2Ni(HCOO)_6(H_2O)_2$ three coordination modes of the formato ligands were found: a monodentate, a bridging-bidentate, and a monoatomic-bridging one [8]. A report about synthesis and spectral characterization of seven new nickel(II)-formato-complexes with imidazole ligands appeared recently [9].

Molecule-based magnetic polymers have attracted intense interest in recent years, due to not only the fundamental research of magnetic interaction and magnetostructural correlations, but also the development of new functional molecule based materials. The rational design of these polymers remains to be one of the major challenges. Depending on the geometrical properties of formate and the transition metal atom, formato ligand can adopt different bridging modes and they mediate ferro- or antiferromagnetic exchange coupling between metal ions. Although a variety of Mn(II), Mn(III), Co(II) and Cu(II) compounds containing formate as the bridging ligand has been structurally characterized [10–17], a few reports involved the magnetic studies of them. The most extensively magnetic investigations have been focused to the simply metal formate complexes M(HCOO)₂·2H₂O and their anhydrous counterparts [18–20]. Previously we have reported studies on nickel(II) carboxylate

complexes including formate group [21]. In these papers we reported structures, magnetic behavior and structural-magnetic correlations of the mononuclear compounds. Some of these investigated complexes reveal formate group as uncoordinated anion and also unidentate terminal ligand. To take this concept further we decided to prepare polynuclear compounds with bulky and a blocking ligands.

In the present communication the synthesis, structural and spectroscopic characterization of a dinuclear complex [Ni₂(HCOO) (bz)₈(H₂O)₂](HCOO)₃·4H₂O (**1**) and a polynuclear compound [Ni(tren)(HCOO)]ClO₄·H₂O (**2**) is reported along with the magnetic and theoretical studies.







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2. Experimental

2.1. Synthesis

Ethanol and methanol were purified before use by standard methods. Nickel(II) formate, as a hydrate was synthesized by slowly adding the stoichiometric amount of the nickel(II)-carbonate to the aqueous-ethanol solution of the formic acid in excess. All other chemicals were purchased commercially and used without further purification.

The complex $[Ni_2(HCOO)(bz)_8(H_2O)_2](HCOO)_3 \cdot 4H_2O$ (1) was prepared by reaction of benzimidazole (2.5 g) with Ni(HCOO)₂. 2H₂O (1 g) in molar ratio 4:1 in warm dried ethanol under reflux conditions for 4 h. After a few days of slow evaporation the solid substances were filtered off. Within several days small turquoise crystals suitable for X-ray crystallographic studies had formed. Found: N, 16.7; C, 53.2; H, 4.97; Ni, 9.0. [Ni₂(HCOO)(bz)₈(H₂O)₂] (HCOO)₃·4H₂O requires N, 16.6; C, 53.4; H, 4.78; Ni, 8.7%.

From water-methanol solution the compound of composition [Ni(tren)(HCOO)]ClO₄·H₂O (2) has been prepared. To dissolved $Ni(ClO_4)_2 \cdot 6H_2O$ (0.50 g) in 10 cm³ of methanol in the first beaker tris(2-aminoethyl)amine (tren, 0.40 g) has been added producing a purple solution. The solution consisting of Ni(HCOO)₂·2H₂O (0.25 g) and distilled water (20 cm^3) was prepared in the second beaker and combined with the first one. After a few minutes of stirring 10 cm³ of methanol was added and then 30 cm³ of distilled water. The mixture was stirred ca one and half h. and fine precipitate was filtered off. The clear solution was allowed to stand for two months while violet crystals crystallized. Found: N, 15.25; C, 22.88; H, 5.76; Ni, 15.97. [Ni(tren)(HCOO)]ClO₄·H₂O requires N, 15.26; C, 23.01; H, 5.68; Ni, 16.00%.

2.2. Physical measurements

Nickel content was determined by chelatometry after mineralization of the complexes. Elemental analysis (C, H, N) was carried out on Flash EA 1112 (ThermoFinnigan).

IR spectra were measured on Magna-FTIR-750 spectrometer (Nicolet) in KBr pellets in the 4000–400 cm^{-1} region. Electronic spectra in the region 50000–10000 cm⁻¹ were recorded in the Nujol mull on Specord 200 (Analytical Jena) spectrometer.

The single-crystal X-ray diffraction experiments were performed using Xcalibur, sapphire CCD diffractometer (Oxford Diffraction). The diffraction intensities were corrected for Lorentz and polarization factors. The empirical absorption corrections were performed by multi-scan method using SCALE3 ABSPACK in CRYSALISPRO [22]. The structures were solved by the direct methods with SHELXS-97 [23] or SIR-2011 [24], and refined by the full-matrix least squares procedure with SHELXL-2014 [23]. Geometrical analyses were performed using SHELXL-2014 and the structures were drawn using the OLEX2 [25] and PLATON [26]. Final crystal data and structure refinement parameters are given in Table 1. Selected bond distances are listed in Table 2.

The compound **1** forms poorly single crystals. More time was tried to separate crystals for collecting data and only the best crystal was used for structural analysis using. The refinement of crystals structure of 1 had to be made using more constrains and restrains. The complex cation $[Ni_2(HCOO)(bz)_8(H_2O)_2]^{3+}$ of **1** has been modeled using rigid-body constrains (FRAG/FEND) [27] and rigid-bond restrains (RIGU) [28] for benzimidazole rings and bridging formato ligand. The bridging formato ligand is disordered occupying two statistical positions, represented by atoms [01,C1,O2]/[01i,C1i,O2i] with site occupancy factors 0.54/0.46. The uncoordinated formate anions and uncoordinated water molecules in 1 are strongly disordered in the cavities between

Table	1		
-			

Chemical formula	$C_{57}H_{53}N_{16}Ni_2O_4 (HCO_2)_3$	$C_7H_{19}N_4NiO_2 \cdot (ClO_4) \cdot (H_2O)$
	4H ₂ 0	
M _r	1374.10 ^b	367.44
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	$P2_1/n$
T (K)	300(1)	95(1)
a (Å)	16.680(2)	12.7790(10)
b (Å)	24.021(2)	7.5944(4)
c (Å)	17.071(2)	15.6210(10)
α(°)	90	90
β (°)	98.67	109.724(9)
γ(°)	90	90
$V(Å^3)$	6775.76	1427.06
Ζ	4	4
λ (Mo Kα)/Å	0.71037	0.71037
μ (mm ⁻¹)	1.13	1.583
Crystal size (mm)	$0.44 \times 0.28 \times 0.20$	$0.20\times0.14\times0.06$
$ ho_{\rm calc}~({\rm g~cm^{-3}})$	1.121	1.710
S	0.984	1.184
$R_1 \left[I > 2\sigma(I) \right]$	0.1138	0.0584
wR ₂ [all data]	0.3426	0.1484
$\Delta \rangle_{\rm max}, \Delta \rangle_{\rm min} \ (e \ {\rm \AA}^{-3})$	0.74, -0.49	0.83, -0.50
CCDC	1005076	1005077

^a The solvent water molecule content was estimated from the electron density attributed to the disordered solvent contribution by SQUEEZE.

^b The molecular weight was calculated using disordered solvent and anion molecules

able 2				
Selected	hond	lengths	(Å) of 1	and 2

Selected	bond	lengths	(Å)) of	1	and	2	•
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1			
Ni1-N11	2.087(2)	Ni2-N51	2.105(2)
Ni1-N21	2.062(2)	Ni2-N61	2.114(2)
Ni1-N31	2.109(2)	Ni2-N71	2.049(2)
Ni1-N41	2.069(2)	Ni2-N81	2.051(2)
Ni1-01	2.010(10)	Ni2-02	2.023(10)
Ni1-01I	2.061(12)	Ni2-02I	1.966(13)
Ni1-01W	2.134(5)	Ni2-02W	2.204(6)
2			
Ni1-N1	2.110(5)	Ni1-N4	2.104(5)
Ni1-N2	2.076(5)	Ni1-01	2.045(4)
Ni1-N3	2.086(5)	Ni1-02	2.116(4)

Symmetry codes: (i) -x + 1, -y + 1, -z + 1; (ii) -x + 1, -y, -z + 1.

 $[Ni_2(HCOO)(bz)_8(H_2O)_2]^{3+}$ cations. Attempts in resolving the disorder adequately failed, and therefore, the utility SQUEEZE [29] in the program PLATON [26] was used to remove diffuse electronic density. The crystal structure of 1 contains in the unit cell one void of 1924 Å per cell containing 436 electrons, which represents three formate anions and 4 molecules of water.

Temperature dependence of the magnetic susceptibility was taken using SQUID magnetometer (MPMS, Quantum Design) at the applied field of $B_{\rm DC}$ = 0.1 T. Raw data were corrected for the signal of the nylon-made sample holder as well as for underlying diamagnetism using the set of Pascal constants [30]. The effective magnetic moment has been calculated as usual: μ_{eff}/μ_B = 798 $(\chi'T)^{1/2}$ when SI units are employed. The magnetization data was taken at *T* = 2.0. 4.6 and 20.0 K.

2.3. Ab initio calculations

ORCA 3.0 computational package [31] was employed in all the calculations using def2-TZVP(-f) basis set [32] for Ni, O and N atoms and def2-SVP basis set for C and H atoms. Also, the RI approximation with the decontracted auxiliary def2-TZV/I and def2-SVP/I Coulomb fitting basis set or def2-TZV/C and def2-SVP/ C auxiliary basis sets for correlation calculations together with and the chain-of-spheres (RIJCOSX) approximation to exact exchange was utilized [33]. Increased integration grids (Grid4 in ORCA convention) and tight SCF convergence criteria were used in all calculations. The isotropic exchange parameters were calculated using DFT method and well-known B3LYP functional [34] by Ruiz's approach [35]. The zero-field splitting parameters determination was based on the state average complete active space self-consistent field (SA-CASSCF) [36] wave functions complemented by N-electron valence second order perturbation theory (NEVPT2) [37]. The active space of the CASSCF calculation on metal-based *d*-orbitals was CAS(8,5). The ZFS parameters, based on dominant spin-orbit coupling contributions from excited states, were calculated through quasi-degenerate perturbation theory (QDPT), [38] in which an approximations to the Breit-Pauli form of the spin-orbit coupling operator (SOMF approximation) [39] and the effective Hamiltonian theory [40] were utilized. The spin densities were plotted with program Gabedit [41].

3. Results and discussion

3.1. Crystal structure

The structure of **1** is built up of dinuclear $[Ni_2(HCOO)(bz)_8]$ (H₂O)₂]³⁺ cations, uncoordinated formate anions and water molecules (Fig. 1a). The nickel atoms are linked by a single bridging formato ligand, which is disordered into two positions (Fig. 1b). Each Ni(II) atom is hexacoordinate: in the equatorial plane four nitrogen atoms from benzimidazole ligands coordinate [Ni-N distances are in the range 2.049(2)-2.114(2) Å (Table 2)], and the axial positions are occupied by the oxygen atoms from aqua ligands [bond distances Ni1-O1W and Ni2-O2W are 2.134(5) and 2.204(6) Å, respectively (Table 2)] and one oxygen atom of the bridging formato ligand [Ni-O distances are in the range 1.966(13)-2.061(12) Å]. The formato bridging ligand is disordered in two positions. Bond lengths of four nickel atoms in the two dinuclear units are different (see Table 2). Cavities of space in the unit cell including unsolved disordered uncoordinated formate anions and water molecules are shown in Fig. 1c.

The complex **2** crystallizes in the monoclinic system, space group $P2_1/n$ (Fig. 2). The complex consists of a cation zig-zag chains {[Ni(tren)(HCOO)]⁺}_n, perchlorate anions and uncoordinated water molecules. Each nickel atom is octahedrally bonded (Fig. 2a) by four amine nitrogen atoms from *tren* molecule coordinated in a tetradentate fashion [Ni–N distances are in the range 2.076(4)–2.110(5) Å (Table 2)]. Two remaining coordination sites are occupied by oxygen atoms from bidentate bridging formato ligands [bond distances Ni1–O1 and Ni1–O2 are 2.045(4) and 2.116(4) Å, respectively], ones from another unit forming a polymeric chain. The bridging formato ligands are situated in *cis* positions of the *anti-anti* mode. The formato ligands link metal ions to form zig-zag chains running along *a* direction Fig. 2b. The framework displays open channels, which are filled with perchlorate anions.

The zig-zag coordination chain of cation $\{[Ni(tren)(HCOO)]^+\}_n$, perchlorate anions and water molecules are connected into 2D supramolecular networks through N–H…O hydrogen bonds (see Supplementary Information, Table S1) between amine groups of the *tren* ligands and oxygen atoms of perchlorate anions or water molecules (Fig. 2a). The water molecules are also connected trough O–H…O hydrogen bonds between water molecules and oxygen atoms of perchlorate anions or neighbouring water molecules.

3.2. Spectroscopic data

All typical features of the IR spectra are clearly compatible with the structural characteristics of the complexes under study. The



Fig. 1. Crystal structure of cation $[Ni_2(HCOO)(bz)_8(H_2O)_2]^{3+}$ in $[Ni_2(HCOO)(bz)_8(H_2O)_2](HCOO)_{3-}4H_2O$: (a) molecular structure of cation $[Ni_2(HCOO)(bz)_8(H_2O)_2]^{3+}$, (b) detail of disordered bridging formato ligands, (c) cavities plot of unsolved disordered formate anions and uncoordinated water molecules.

infrared spectra show absorption band about 3600 cm^{-1} referring to the OH stretching vibration of the crystal water. The band of stretching vibration at about 3300 cm^{-1} and the band of bending vibration at 1630 cm^{-1} can be attributed to coordinated molecules of water in the compound **1**.

Infrared spectra of both complexes (Table 3) show intense and sharp absorption bands of antisymmetric and symmetric stretching vibrations of COO⁻ group in the region 1587, 1592 and 1364–1394 cm⁻¹. The bands assigned to symmetric stretching vibration are split into two subbands. The separation between the antisymmetric stretch $v_{as}(COO^-)$ and symmetric stretch $v_{s}(COO^-)$, $\Delta(COO^-)$, brings information about the bonding mode of the carboxylato group [1]. The higher observed values of $\Delta(COO^-)$ 224 and 228 cm⁻¹ are higher relative to 201 cm⁻¹ observed in the IR spectrum of the solid sodium formate [42] or



Fig. 2. Crystal structure of 2 showing the atom labelling scheme (a) and zig-zag coordination chain of 2 (b).

Table 3

IR and ligand-field data (cm⁻¹).^a

	1	2
v _s (COO ⁻)	1363, 1393	1364, 1394
$v_{\rm as}({\rm COO^-})$	1587	1592
$\Delta v(\text{COO}^-)$	224, 194	228, 198
$E_1({}^3T_{2g} \leftarrow {}^3A_{2g})/hc = 10Dq$	11000	8900
		(8200)
$E_2({}^3T_{1g}(F) \leftarrow {}^3A_{2g})/hc^a$	17800	16 400
		(13500)
$E_3({}^3T_{1g}(P) \leftarrow {}^3A_{2g})/hc$	27 500	28 300
		(26 900)

^a Band-arms in parentheses.

 209 cm^{-1} of nickel formate dihydrate [43]. The positions of carboxylate stretching vibrations and the separation between them in **1** and **2** are in the range expected for bridging carboxylato ligands [1].

The principal modes of vibration of NH₂ group in the *tren* ligand are symmetric and antisymmetric stretching (str), bending (bend), scissoring (sci), wagging (wag), twisting (twi) and rocking (rock). The very strong bands at 3344 and 3300 cm⁻¹ can be attributed to NH₂ *str.*, strong band at 2885 to CH₂ *str.* vibrations. Assignment of other bands is as follows [44]: 1650 and 1606 cm⁻¹ to NH₂ *sci*; 1465 cm⁻¹ to CH₂ *sci*, *wag*; 1082 cm⁻¹ to CH₂ *twi*; 997 and 979 cm⁻¹ to NH₂ *twi*; 805 cm⁻¹ to CH₂ *rock*; 748 cm⁻¹ belong to NH₂ *rock* modes. The stretching vibrations of the NH₂ groups are shifted towards lower frequencies if compared with the vibrations of free amine [44] hence *tren* is coordinated. The bands at 1106 and 624 cm⁻¹ in **2** are assigned to the perchlorate anion.

The electronic spectra (Table 3) of the complexes under study show three d-d bands at 8900–11 000, 16 400–17 800, and 27 500–28 300 cm⁻¹, respectively. The number of bands, their widths and the positions of the absorption maxima of these bands indicate tetragonally distorted octahedral configuration of the ligands around Ni(II) [45]. The bands may be assigned to the spin allowed transition ${}^{3}T_{2g} \leftarrow {}^{3}A_{2g}$, ${}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}$, ${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}$ in octahedral approximation.

3.3. Ab initio calculations

Contemporary theoretical methods were applied to compounds **1** and **2** in order to calculate both the isotropic exchange constants *J* and zero-field splitting parameters *D* and *E* for Ni(II) ions using the ORCA computational package. First, the DFT method with B3LYP functional was used to calculate energy difference Δ between high spin (HS) and broken-symmetry (BS) spin states.

$$\Delta = E_{\rm BS} - E_{\rm HS} \tag{1}$$

for both dinuclear molecular fragments $[Ni_2(HCOO)(bz)_8(H_2O)_2]^{3+}$ of **1** based on a disorder in bridging ligand found in experimental X-ray structure, where following spin Hamiltonian for dimer was used

$$\hat{H} = -J(\vec{S}_1 \cdot \vec{S}_2) \tag{2}$$

The isotropic exchange *J*-values were calculated by Ruiz's approach.

$$J = 2\Delta / [(S_1 + S_2)(S_1 + S_2 + 1)]$$
(3)

The BS state was found lower in energy in both fragments of **1**, thus confirming antiferromagnetic exchange mediated by formate ions with following quantities: $J = -16.4 \text{ cm}^{-1}$ for molecular fragment comprising [O1, C1, O2] atoms of formato bridge (site occupancy factors 0.54) and $J = -14.2 \text{ cm}^{-1}$ for molecular fragment comprising [O1i, C1i, O2i] atoms of formato bridge (site occupancy factors 0.46). These results show sensitivity of *J*-value to small geometry change of bridging ligand. The spin density for BS spin state of **1** is visualized in Fig. 3, where partial spin delocalization on all N/O donor atoms of the chromophore is visible.

In case of polymeric compound **2**, dinuclear $[Ni_2(tren)_2 (HCOO)_3]^+$, trinuclear $[Ni_3(tren)_3(HCOO)_4]^{2+}$ and pentanuclear $[Ni_5(tren)_5(HCOO)_6]^{4+}$ molecular fragments were used in calculation of *J*-parameter to test whether the computed *J* differs depending on the size of model system. The calculation for dinuclear unit using Eqs. (1)–(3) resulted in J = -12.3 cm⁻¹. For trinuclear unit following spin Hamiltonian was used

$$\hat{H} = -J(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3)$$
(4)

for which *J*-parameter was calculated as

$$I = \Delta_2/6 \tag{5}$$



Fig. 3. The calculated the isodensity surfaces of the broken symmetry spin states using B3LYP for $[Ni_2(HCOO)(bz)_8(H_2O)_2]^{3+}$ of **1** (left) and $[Ni_2(tren)_2(HCOO)_3]^+$ of **2** (right). Positive and negative spin densities are represented by violet and yellow surfaces with the cutoff values of 0.01 e boh⁻³, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

where $\Delta_2 = E_{BS2} - E_{HS}$. The *J*-values was found to be equaled to -11.7 cm^{-1} . Finally, the spin Hamiltonian for pentanuclear unit (with labeling of Ni atoms: 1-2-3-4-5) was postulated as

$$\hat{H} = -J_a(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_4 \cdot \vec{S}_5) - J_b(\vec{S}_2 \cdot \vec{S}_3 + \vec{S}_3 \cdot \vec{S}_4)$$
(6)

where J_a is the isotropic exchange affected by the ends of the chain, while J_b is the parameter describing the exchange inside the chain. Then, *J*-parameters can be evaluated by these expressions

$$\Delta_3 = E_{\rm BS3} - E_{\rm HS} = 6J_h \tag{7}$$

$$\Delta_{24} = E_{\rm BS24} - E_{\rm HS} = 6J_a + 6J_b \tag{8}$$

which ended at $J_a = -12.7 \text{ cm}^{-1}$ and $J_b = -11.6 \text{ cm}^{-1}$. To conclude, the calculated antiferromagnetic exchange slightly decreases with size of the model as follows: $J_{\text{dimer}} = -12.3 \text{ cm}^{-1} \rightarrow J_{\text{trimer}} = -11.7 \text{ cm}^{-1} \rightarrow J_{\text{pentamer}} = -11.6 \text{ cm}^{-1}$. Generally, DFT calculations of *J*-values led to moderate antiferromagnetic exchange in both compounds **1** and **2**.

The calculations of ZFS parameters were performed on mononuclear molecular fragments $[Ni(HCOO)(bz)_4(H_2O)]^+$ of **1** and $[Ni(tren)(HCOO)_2]$ of **2** using CASSCF/NEVPT2 methodology with active space defined by metal-based *d*-orbitals (CAS(8,5)). These calculations resulted in following ZFS parameters: $D = + 10.1 \text{ cm}^{-1}$ and E/D = 0.21 for **1** and $D = +2.1 \text{ cm}^{-1}$ and E/D = 0.24

for **2**. The contributions of excited states to ZFS terms are tabulated in Tables S2–S3 (Supplementary Information). Thus, in both complexes **1** and **2** the positive *D*-parameter was found and also significant rhombicity.

The axes of calculated ZFS and *g*-tensors together with molecular structures are visualized in Fig. 4. In both cases, *g*-tensor and ZFS-tensor axes almost coincide, with following g-tensor parameters: $g_1 = 2.173$, $g_2 = 2.233$, $g_3 = 2.264$ for **1** and $g_1 = 2.181$, $g_2 = 2.193$, $g_1 = 2.200$ for **2**. *Z*-axes of ZFS tensor lies along O–Ni–O bonds, while other two axes (X and Y) lies along N–Ni–N bonds in **1**. In compound **2**, the *Z*-axis of ZFS tensor is approximately located along N1–Ni–O2 bonds, that means, along bonds which are the longest within given chromophore, and X and Y axis are found in plane defined by N2N3N4O1 atoms, but not strictly located along donor–acceptor bonds (Fig. 4).

3.4. Magnetic data

The temperature dependence of the effective magnetic moment for **1** is shown in Fig. 5 on the left. On cooling it starts to decrease at 150 K which is a fingerprint of the exchange interaction of an antiferromagnetic nature. The susceptibility passes through a round maximum at ca 20 K that matches the antiferromagnetic coupling and S = 0 ground state. Small hook at the lowest temperature of the data taking is attributed to a paramagnetic impurity. Also the magnetization measurements agree with J < 0 since the magnetization increases with temperature (the excited S = 1 and S = 2 states being populated).

The magnetic data of **1** was interpreted in terms of the spin Hamiltonian appropriate to an exchange coupled dinuclear unit (*J*) with $S_1 = S_2 = 1$ and single-ion zero-field splitting (*D*).

$$\hat{H}_{m}(\vartheta,\varphi) = -J\hbar^{-2}(\vec{S}_{1}\cdot\vec{S}_{2}) + \sum_{A=1}^{2}D\hbar^{-2}(\hat{S}_{Az}^{2}-\hat{S}_{A}^{2}/3) + \sum_{A=1}^{2}\mu_{B}\hbar^{-1}B g_{A}\hat{S}_{A}$$
(9)

The final calculated molar magnetization was calculated as an integral average in order to properly simulate powder sample signal as

$$M_{\rm mol} = 1/4\pi \int_0^{2\pi} \int_0^{\pi} M_a \sin\theta d\theta d\phi \qquad (10)$$

First, the fitting procedure was done for positive *D*-parameter following results from ab initio calculations and resulted in this set of magnetic parameters: $J/hc = -13.0 \text{ cm}^{-1}$, $g_{iso} = 2.093$, $D/hc = +11.2 \text{ cm}^{-1}$, mole fraction of the paramagnetic impurity



Fig. 4. The CASSCF/NEVPT2 calculated principal axes of ZFS tensors labeled DX,DY,DZ and axes of g tensors labeled as g1,g2, g3 visualized together with molecular structures [Ni(HCOO)(b2)₄(H₂O)]⁺ of 1 and [Ni(tren)(HCOO)₂] of 2.



Fig. 5. Magnetic functions for **1**. Temperature dependence of the effective magnetic moment (inset: molar magnetic susceptibility) and field dependence of the magnetization per formula unit. Lines – fitted. Left: fit with *D* > 0, right – fit with *D* < 0.



Fig. 6. Magnetic functions for **2**. Temperature dependence of the effective magnetic moment (inset: molar magnetic susceptibility/magnetization) and field dependence of the magnetization (T = 2 and 4.6 K) scaled per one Ni(II) ion. Blue lines – fitted, red line – Brillouin function. Left: fit with Eqs. (11, 12), right – fit with Eqs. (13, 14). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

 $x_{\text{PI}} = 1.07\%$. Both crucial fitted parameters, *J* and *D*, are in very good agreement with the calculate ones. Next, we also tried to fit the magnetic data for negative *D*-parameter, which resulted in: $J/hc = -12.8 \text{ cm}^{-1}$, $g_{\text{iso}} = 2.096$, $D/hc = -16.3 \text{ cm}^{-1}$, and $x_{\text{PI}} = 1.30\%$. Both fits describe experimental data in similar quality, thus this emphasize the importance of theoretical methods in magnetic analysis.

The magnetic data of the 1D chain compound **2** shows again antiferromagnetic exchange among paramagnetic Ni(II) atoms supported by maximum of susceptibility found at 18 K (Fig. 6) and data were analyzed by two approaches. First, the spin Hamiltonian for a 1D uniform chain (Haldane chain) with $S_i = 1$ reads.

$$\hat{H} = -J\hbar^{-2}\sum_{i=1}^{\infty} (\vec{S}_i \cdot \vec{S}_{i+1}) + \mu_{\rm B}\hbar^{-1}B\sum_{i=1}^{\infty} g_i \hat{S}_{iz}$$
(11)

for which the susceptibility formula exists [46].

$$\chi_{\rm mol} = \frac{N_{\rm A}\mu_0\mu_{\rm B}^2 g^2}{k_{\rm B}T} [0.125 \exp(-0.451x) + 0.564 \\ \times \exp(-1.793x)]$$
(12)

The calculated values, $J/hc = -11.0 \text{ cm}^{-1}$, g = 2.158, $x_{\text{Pl}} = 1.98\%$, confirm an intermediate antiferromagnetic coupling between Ni ions (x_{Pl} is molar fraction of monomeric paramagnetic impurity).

In order to be able to interpret also the isothermal magnetization data, the spin Hamiltonian for the decanuclear ring was postulated as

$$\hat{H}^{\text{ring}} = -J\hbar^{-2} \left[\sum_{i}^{9} \vec{S}_{i} \cdot \vec{S}_{i+1} + \vec{S}_{10} \cdot \vec{S}_{1} \right] + \mu_{\text{B}}\hbar^{-1}g \ \vec{B} \sum_{i}^{10} \vec{S}_{i}$$
(13)

The exchange coupling of ten Ni(II) centers leads to the number $N = 3^{10} = 59049$ magnetic states; such large interaction matrix cannot be efficiently diagonalized. In a simplified way (strong exchange limit), having the energy levels labeled as $\varepsilon_i(\alpha SM_S) = \varepsilon_{0,k}(\alpha S) + \mu_{\rm B}gBM_S$, the molar magnetization can be easily calculated as

$$M_{\rm mol} = N_{\rm A} \mu_{\rm B} g \frac{\sum_{i} M_{\rm S} \exp\left[-\varepsilon_{i} (\alpha S M_{\rm S})/kT\right]}{\sum_{i} \exp\left[-\varepsilon_{i} (\alpha S M_{\rm S})/kT\right]}$$
(14)

The fitting procedure resulted in the following set of magnetic parameters: $J/hc = -10.8 \text{ cm}^{-1}$, g = 2.166, $x_{Pl} = 1.96\%$, so that the coupling constant agrees well with the Haldane chain approach. As both approaches describes the experimental data reliably without including ZFS terms, we can suppose that strong exchange limit holds ($|J| \gg |D|$) as found by ab initio calculations and detection of *D*-parameter cannot be pursuit from magnetic data alone, as we discussed in depth for similar system recently [47].

The exchange coupling in dinuclear Ni(II) complexes can be of ferromagnetic as well as antiferromagnetic nature, as documented by a few examples in Table 4. The single-ion zero-field splitting parameter D has been reported either positive or negative. According to the spin-Hamiltonian theory for hexacoordinate Ni(II) complexes, D > 0 are expected for an elongated tetragonal bipyramid whereas D < 0 is typical for the compressed form [63].

Apparently, the exchange coupling constants vary in a broad range. The structure of the complex plays a key role, as it is shown in Table 4 and this finding is supported also by literature sources [52–62]. For instance, magnetic exchange interactions mediated by azido ligands in complexes depend upon a bridging mode: for

Table 4

Examples of magnetic data for dinuclear Ni(II) complexes, tetranuclear Ni(II) pseudohalido complexes and polynuclear Ni(II) complexes.

Complex	Chromophore	Bridge	<i>J/hc</i> /cm ^{-1**}	$D/hc \ /cm^{-1}$	g _{av}	Ref.
Dinuclear Ni(II) complexes						
$[Ni_2(trpn)_2(\mu_{1,3}-N_3)_2](ClO_4)_2^e$	${NiN_4N'_2}$	N_3^-	-64		2.34	[48]
$[Ni_2(L^2)(CH_3COO)(H_2O)_2](CIO_4)_2^b$	{NiN ₃ OO'O'}	CH₃COO ⁻	-43.3		2.24	[49]
		alkoxido of L ²				
$[Ni_2(L^2)(OPr)(H_2O)_2](ClO_4)_2.H_2O^b$	{NiN ₃ OO′O′}	$C_2H_5COO^-$	-34.4		2.09	[49]
		alkoxido oxygen				
$[Ni_2(HCOO)(bz)_8(H_2O)_2](HCOO)_3 \cdot 4H_2O$	{NiN400′}	HCOO-	-13.0	11.2	2.093	This work
			-12.8	-16.3	2.096	This work
$\{[NI(L')(\mu_{1,1}-NCS)NI(L')(NCS)(OH_2)\}$	$\{N_1^*N_3OO'N'\}$	phenoxido oxygen	-3./	0.07	2.27	[50]
$[NI(L^{*})(\mu-CH_{3}COO)NI(L^{*})(NCS)(OH_{2})]\}^{**}$	$\{NI^2N_2O_2O'N'\}$	SCN				
	$\{N_1, N_2, O_2, O, O'\}$					
$[Ni_{\mu}(\mu_{trian})(trian)_{\mu}](C[0_{\mu})_{\mu}$	$\{N_1 N_3 0 0 0\}$	trien pod	1.68	0.0	2 10	[44]
$[Ni_2(\mu-men)(men)_2](ClO_4)_4$ $[Ni_2]_2(N(CN)_2)_2(H_2O)]^c$	$\{NiN_2O_2N'_2\}$	N(CN)	-1.00	9.85	2.10	[51]
$[{Ni(dnt)(N(CN)_2)}_2]$	$\{NiN_2N'_2\}$	$N(CN)_{2}$	-0.58	2.58	2.14	[52]
$[Ni_2(HL^3)_4(H_2O)]^d$	$\{NiN_2OO'_2O''\}$	nhenoxido oxygen	3 46	-3.84	2.122	[53]
[2//4/2/]	(****2==2=)	H ₂ O				[]
$[Ni_2(HL^2)_4(H_2O)]^d$	{NiN ₂ 00' ₂ 0"}	phenoxido oxygen	3.72	-3.56	2.12	[53]
	/	H ₂ O				
$[{Ni(teta)(tcm)}_2](ClO_4)_2$	$\{NiN_4N_2'\}$	$C(CN)_3^-$	3.75		2.119	[54]
$[Ni_2(HL^1)_4(H_2O)]^d$	{NiN ₂ OO' ₂ O"}	phenoxido oxygen	4.92	-2.11	2.091	[53]
		H ₂ O				
$[{Ni_2(en)_4Cl_2}]Cl_2$	${NiN_4Cl_2}$	Cl-	9.66	-4.78	2.242	[55]
$[Ni(L^1)(\mu_{1,1}-NCO)Ni(L^1)(NCO)(OH_2)] \cdot H_2O^h$	${Ni^1N_2O_2O'N'}$	phenoxido oxygen	12.4	-0.22	2.19	[50]
	{Ni ² N ₃ OO'N'}	OCN ⁻				
$[Ni_2(L^1)(N_3)_4]^a$	${NiN_4N'_2}$	N_3^-	43.6		2.28	[56]
$[Ni_2L_2(o-(NO_2)C_6H_4COO)_2(H_2O)]^4$	$\{NiN_2OO'O_2''\}$	phenoxido oxygen	25.4	3.20	2.27	[57]
		H ₂ O	26.2	0.17	2.21	1011
$[NI_2L_2(PIICH_2COO)_2(H_2O)]^2$	$\{NIN_2O_2O'O''\}$	H ₂ U	20.2	0.17	2.21	[51]
		phenoxido oxygen	20.1	2 80	2 22	[57]
$[10_{2}L_{2}(p-(10_{2})C_{6}H_{4}COU)_{2}(11_{2}U)] \cdot 0.5CH_{3}OH$	{ININ20002}		20.1	2.80	2.23	[57]
$[Ni_{\alpha}(I^{1})_{\alpha}(u_{\alpha}, -N_{\alpha})(N_{\alpha})(H_{\alpha}O)].CH_{\alpha}CH_{\alpha}OH^{g}$	{Ni ¹ N ₂ OO'N'}	nhenovido ovvgen	33.2	_73	22	[58]
	$\{N_1^2 N_2 O_2 O' N'\}$	N ₂	55.2	-7.5	2,2	[50]
$[Ni_2(L^2)_2(\mu_{1,1}-N_3)(CH_3CN)(H_2O)](ClO_4)\cdot H_2O\cdot CH_3CN^g$	$\{N_1^1 N_3 OO'N'\}$	phenoxido oxygen	33.84	-6.41	2.2	[58]
[2(=)2(Pi,1:3)(3)(2)(2)(4)(2)	$\{Ni^2N_2O_2O'N'\}$	N3				[]
$[Ni(L^{1})(\mu_{1,1}-N_{3})Ni(L^{1})(N_{3})(OH_{2})]\cdot H_{2}O^{h}$	{NiN ₂ O ₂ O'N'}	phenoxido oxygen	51.2	6.8	2.20	[50]
		N_3				
$[Ni(L^2-OMe)(\mu_{1,1}-N_3)(N_3)]_2^i$	${NiN_4N'_2}$	N_3^-	78.0	7.3	2.27	[50]
Tetranuclear Ni(II) pseudohalide complexes						
$[N_{12}(dpk.OH)(dpk.CH_{3}O)(N_{3})(H_{2}O)]_{2}(ClO_{4})_{2}\cdot 2H_{2}O^{j}$	{NiN ₂ O ₂ N'O'}	u-1.1-N ₃	$J_1 = J_2 = +11.2$	5.6	2.03	[59]
	(22)	μ-0	$J_3 = +23.6$			1.1.1
[Ni ₂ (dpk.OH)(dpk.CH ₃ O)(NCO)(H ₂ O)] ₂ (ClO ₄) ₂ ·2H ₂ O ^j	{NiN ₂ O ₂ N'O'}	μ-1,1-NCO	$J_1 = J_2 = +11$	5.6	2.03	[59]
		μ-0	$J_3 = +24.0$			
[Ni ₂ (dpk.OH)(dpk.CH ₃ O)(NCO)(H ₂ O)] ₂ (NO ₃) ₂ ·2H ₂ O ^j	${NiN_2O_2N'O'}$	μ-1,1-NCO	$J_1 = J_2 = +12.6$	6.2	2.21	[59]
		μ-0	$J_3 = +9.8$			
$[Ni_4(dpk.OH)_3(dpk.CH_3O)_2(NCO)](BF_4)_2 \cdot 3H_2O^3$	${Ni^{1}N_{3}N'O'_{2}}$	μ-1,1-NCO	+13.8	4.8	2.06	[59]
	$\{Ni^2N_2O'_4\}$	μ-0	+14.0			
	$\{NI^3N_3U_3\}$		+30.4			
	$\{NI^{*}N_{2}N^{*}U^{*}_{3}\}$					
Polynuclear Ni(II) complexes						
$[Ni(HCOO)_2(4,4'-bpy)]\cdot 5H_2O$	${NiN_2O_2O'_2}$	HCOO-	-19.4		2.23	[12]
$\{[Ni(phen)(H_2O)(H_2P_2O_7)] \cdot H_2O\}_n^{\kappa}$	$\{NiN_2OO'_3\}$	$H_2P_2O_7^{-}$	-1.88		2.09	[60]
$c_{13} = [N_1(Me_6 trien)(\mu_{1,3} - N_3)]_n (ClO_4)_n \cdot nH_2O^{\circ}$	$\{NiN_4N'_2\}$	N ₃	-26.8		2.36	[48]
$\{[N_{12}(\mu-\text{tren})_2(\text{tren})](CIO_4)_4 \cdot 3.25H_2O\}_{h}^{h}$	$\{N_1N_4N_2\}$	tren pod $C O^{2-}$	-1.19		2.16	[44]
$[Ni(\mu - 0X)(pyOH)_2]_n$	$\{\text{ININ}_2\text{U}'_4\}$	$C_2 U_4^2$	-28.0		2.23	[0]]
$\lim_{n \to \infty} \frac{1}{(1 \le \frac{1}{2})_n} = \lim_{n \to \infty} \frac{1}{(1 \le \frac{1}{2})_n} = \lim_{n \to \infty} \frac{1}{(1 \le \frac{1}{2})_n}$	$\{N_1N_2\cup 4\}$	C ₂ O ₄	-21.2		2.13	[01]
$c_{13} - 1$	1111141N 23	143	-55. 4 -63.7		2,33	[40]
{[Ni2(11,1-N2)(11,2-N2)(1)2(MeOH)2]}. ^p	$\{NiO_2N_2N'\}$	N_2^-	-74.2		2.15	[62]
$[Ni(tren)(HCOO)]ClO_4 H_2O$	$\{NiN_4O_2\}$	HC00 ⁻	-10.8		2.166	This work
	(1010		2.100	1110 1.01K

^{*} Abbreviation for ligands: 4,4'-bpy = 4,4'-bipyridine; *bz* = benzimidazole; *teta* = triethylenetetramine (abbr. also *tta*); *tcm* = C(CN)₃, tricyanomethanide; *en* = 1,2-diaminopropane (ethylenediamine); ^aL¹ = hexadentate Schiff base ligand made from the reaction of 2 mol of 2-benzoyl pyridine and 1 mol of triethylenetetramine; ^bHL² = N,N,N',N'-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-l,3-diaminopropane; ^bOPr = propionate anion; ^cHL = 1-[(3-dimethylamino-propylimino)-methyl]-naphthalen-2-ol; ^dH₂L¹ = Schiff base ligand from 5-amino-1-pentanol and salicylaldehyde, H_2L^2 = 5-bromo salicylaldehyde, H_2L^3 = 3-methoxy salicylaldehyde; ^e*trpn* = tris(3-aminopropyl)amine; ^fHL = 1-[(3-dimethylamino-propylimino)-methyl]-naphthalen-2-ol; ^gHL¹ and HL² = are the [1 + 1] condensation products of 3-methoxysalicylaldehyde and 1- (2-aminoethyl)-piperidine (for HL¹)/4-(2-aminoethyl)-morpholine (for HL²); ^bL¹ = Me₂N(CH₂)₂NCHC₆H₃(O⁻)(OCH₃); ⁱL² = Me₂N(CH₂)₂NCHC₆H₃N; ⁱdpk = di-2-pyridylketone, dpk.OH and dpk.CH₃O result from solvolysis and deprotonation of dpk in water and methanol; ^kphen = 1,10-phenanthroline; ⁱpyOH = 3-hydroxypyridine; ^misq = isoquinoline; ⁿabap = N-(2-aminoethyl)-N,N-bis(3-aminopropyl)amine; ^oMe₆trien = 1,1,4,7,10,10-hexamethyltriethylene tetramine; ^pL⁻ = 1,1,1-trifluoro-7-(dimethylamino)-4-methyl-5-aza-3-hepten-2-onato).

** All *J*-parameters conform the Hamiltonian term $\hat{H}_{ij} = -J_{ij}\hbar^{-2}(\vec{S}_i \cdot \vec{S}_j)$.

 μ -N₃(N₁, N₁) type of bridging the ferromagnetic exchange is typical, while in μ -N₃(κ -N₁, N₃) type the antiferromagnetic exchange interaction prevails [56]. This is also the reason why the *I*-values vary seriously (from -74.2 to +78.0 cm⁻¹). In addition, bridging modes of formato and azido ligands are similar and this fact could be essential in building up new complexes. The azido ligand along with CN^- , $C_2O_4^{2-}$ and $N(CN)_2^-$ ones are responsible for presence of either a strong ferromagnetic or a strong antiferromagnetic coupling. This is also the reason why there is a growing interest in this group of ligands [12]. In many cases Schiff bases were embodied into the complexes, creating phenoxido bridges with some coligands. There is an obvious benefit in use of Schiff bases to achieve new structures with interesting magnetic, catalytic or bioactive properties [53]. The polynuclear Ni(II) complexes, however, display only the antiferromagnetic exchange with *I*/*hc* ranging from -1.19 cm^{-1} for the tren bridge to -74.2 cm^{-1} for the azido coligand.

It must be mentioned that in considering the variability of the *I* values some qualitative as well as quantitative magnetostructural *I*-correlations have been proposed for Ni(II) complexes [64,65]. Recently, the quantitative magnetostructural D-correlation in hexacoordinate Ni(II) complexes also has been outlined [63].

4. Conclusion

The formato-bridged assemblies of formula [Ni₂(HCOO)(bz)₈ (H₂O)₂](HCOO)₃·4H₂O (**1**) and [Ni(tren)(HCOO)]ClO₄·H₂O (**2**) were prepared. The X-ray analysis revealed dinuclear structure in case of compound (1), while polymeric complex (2) was formed in both compounds with formate bridges. The magnetic analyses confirmed antiferromagnetic nature of exchange (1) among paramagnetic Ni(II) atoms as also proposed by DFT method based on B3LYP functional. Moreover, theoretical calculation using CASSCF/ NEVPT2 were helpful in identifying the correct sign of D-parameter in compound **1** and also in supporting negligible role of *D*-parameter in magnetic analysis of polymeric compound 2.

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Appendix A. Supplementary data

CCDC 1005076 and 1005077 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html. or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10. 1016/j.poly.2015.04.010.

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