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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 $[Ni_2(HCOO)(bz)_8(H_2O)_2](HCOO)_3{\cdot}4H_2O$ (**1**) and $[Ni(tren)(HCOO)]ClO_4{\cdot}H_2O$ (**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.

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 $Ni(HCOO)_2(H_2O)_2$ 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 $M(HCOO)_2{\cdot}2H_2O$ 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 $[Ni_2(HCOO)(bz)_8(H_2O)_2](HCOO)_3{\cdot}4H_2O$ (**1**) and a polynuclear compound $[Ni(tren)(HCOO)]ClO_4{\cdot}H_2O$ (**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 $Ni(HCOO)_2{\cdot}2H_2O$ (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. $[Ni_2(HCOO)(bz)_8(H_2O)_2](HCOO)_3{\cdot}4H_2O$ requires N, 16.6; C, 53.4; H, 4.78; Ni, 8.7%.

From water–methanol solution the compound of composition $[Ni(tren)(HCOO)]ClO_4{\cdot}H_2O$ (**2**) has been prepared. To dissolved $Ni(ClO_4)_2{\cdot}6H_2O$ (0.50 g) in 10 cm^3 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 $Ni(HCOO)_2{\cdot}2H_2O$ (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 cm^3 of methanol was added and then 30 cm^3 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. $[Ni(tren)(HCOO)]ClO_4{\cdot}H_2O$ 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 [O1,C1,O2]/[O1i,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 $[Ni_2(HCOO)(bz)_8(H_2O)_2]^{3+}$ 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.

Table 1
Crystallographic data for **1** and **2**.

Chemical formula	$C_{57}H_{53}N_{16}Ni_2O_4\ (HCO_2)_3\ 4H_2O$[a]	$C_7H_{19}N_4NiO_2{\cdot}(ClO_4){\cdot}(H_2O)$
M_r	1374.10[b]	367.44
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
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
Z	4	4
λ (Mo Kα)/Å	0.71037	0.71037
μ (mm^{-1})	1.13	1.583
Crystal size (mm)	0.44 × 0.28 × 0.20	0.20 × 0.14 × 0.06
ρ_{calc} (g cm^{-3})	1.121	1.710
S	0.984	1.184
R_1 [$I > 2\sigma(I)$]	0.1138	0.0584
wR_2 [all data]	0.3426	0.1484
$\Delta\rangle_{max}, \Delta\rangle_{min}$ (e Å^{-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.

Table 2
Selected bond lengths (Å) of **1** and **2**.

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–O1	2.010(10)	Ni2–O2	2.023(10)
Ni1–O1I	2.061(12)	Ni2–O2I	1.966(13)
Ni1–O1W	2.134(5)	Ni2–O2W	2.204(6)
2			
Ni1–N1	2.110(5)	Ni1–N4	2.104(5)
Ni1–N2	2.076(5)	Ni1–O1	2.045(4)
Ni1–N3	2.086(5)	Ni1–O2	2.116(4)

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

Temperature dependence of the magnetic susceptibility was taken using SQUID magnetometer (MPMS, Quantum Design) at the applied field of B_{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: $\mu_{eff}/\mu_B = 798\ (\chi' T)^{1/2}$ 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/J and def2-SVP/J Coulomb fitting basis set or def2-TZV/C and def2-SVP/C auxiliary basis sets for correlation calculations together with