Synthesis, crystal structure, magnetic properties and DFT study of dinuclear Ni(II) complex with the condensation product of 2-quinolinecarboxaldehyde and Girard’s T reagent


1. Introduction

Azide anion is a versatile pseudohalide ligand, which can be coordinated monodentately in mononuclear complexes [1–5] or acts as a bridge between metal centers in di- or polynuclear complexes [6–11]. Azido bridged dinuclear Ni(II) complexes have been studied due to their interesting structural and magnetic properties. Among the reported Ni(II) complexes the most common coordination modes of bridging azido ligands are end-to-end (μ-1,3-N₃) and end-on (μ-1,1-N₃) (Scheme 1). Bridging azido ligand mediates different types of magnetic exchange interactions, which magnitude depends on the distance between metal ions, dihedral angle between the planes containing metal ions and metal-bridging ligand bond lengths [12]. Antiferromagnetic coupling is associated with end-to-end (μ-1,3-N₃) coordination of azido ligand [13–15], while end-on (μ-1,1-N₃) coordination mode results in ferromagnetic coupling [16–18], although some exceptions are also reported [19,20]. Quinoline pharmacophore is present in a large number of natural and synthetic compounds possessing wide range of biological activity [21–24]. Schiff base ligands containing the quinoline moiety and their corresponding metal complexes exhibit significant antitumor and antimicrobial activity [25–32]. Delocalised lipophilic cations (quaternary ammonium and phosphonium salts) can penetrate through the hydrophobic biological membranes and accumulate in cells due to the negative inside transmembrane potential [33]. This property can be used for the formulation of new compounds with enhanced biological activity. Condensation products of Girard’s reagents (N-substituted glycine hydrazides) with different mono- and dicarbonyl compounds are water soluble quaternary ammonium salts. Such hydrazones can be coordinated in non deprotonated form as cationic ligands or can be deprotonated forming formally neutral zwitter-ions. The presence of additional donor atoms in these ligands allows formation of stable metal chelates and dictates their geometry [34–37]. The azide anion acts as an inhibitor of cytochrome oxidase, mitochondrial F ATPase [38] and antioxidant enzymes catalase [39], peroxidase [40] and superoxide dismutase [41]. Azido complexes with Schiff base ligands show considerable biological activity [42–44]. Here, we present synthesis, structural characterization and DFT study of a dinuclear double end-on azido bridged Ni(II) complex with the condensation product of 2-quinolinecarboxaldehyde and Girard’s T reagent.
and magnetic properties of dinuclear double end-on azide bridged Ni(II) complex (1) \([\text{Ni}_2\text{L}_2(\mu_1,1-N_3)_2(N_3)_2]\) with the condensation product of 2-quinolinecarboxaldehyde and trimethylammonium acetohydrazide chloride (Girard’s T reagent) (HCl). Experimental results are confirmed and explained by DFT calculations.

2. Experimental

2.1. Materials and methods

2-Quinolinecarboxaldehyde (97%) and Girard’s T reagent (99%) were obtained from Aldrich. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer using the ATR technique in the region 4000–400 cm\(^{-1}\) (s-strong, m-medium, w-weak). \(^1\)H (500 MHz), \(^13\)C (125 MHz), and 2-D NMR spectra of ligand HCl were recorded on a Bruker Avance 500 spectrometer at room temperature in methanol-\(d_4\) using TMS as internal standard. Chemical shifts are expressed in ppm (\(d\)) values and coupling constants (\(J\)) in Hz. Elemental analyses (C, H, and N) were performed by standard micro-methods using the ELEMENTAR Vario ELIII C.H.N.S.O analyzer. The temperature dependence of magnetic susceptibility was measured on the powder sample using a Quantum Design MPMS-XL-5 SQUID magnetometer, from 2 K to 300 K, and in a 1000 Oe magnetic field. The data were corrected for the contributions of the sample holder and for the diamagnetism of the sample estimated from Pascal’s constants.

2.2. Synthesis

2.2.1. Synthesis of (E)-N,N,N-trimethyl-2-oxo-2-(2-(quinolin-2-ylmethylene)hydrazinyl)ethan-1-aminium chloride (HCl)

2-Quinolinecarboxaldehyde 0.31 g (2.00 mmol) was dissolved in ethanol (25 mL) and Girard’s T reagent 0.34 g (2.00 mmol) was added. The mixture was refluxed for 3 h. After cooling to the room temperature, a white precipitate was filtered and washed with ethanol. M.p. 210 °C. Yield: 0.39 g (63%). Elemental analysis calculated for C\(_{15}\)H\(_{19}\)ClN\(_4\)O: C 58.73%, H 6.24%, N 18.26%, found: C 58.96%, H 6.13%, N 18.02%. IR (cm\(^{-1}\)): 3414 (m), 3062 (m), 2970 (m), 2939 (m), 2831 (m), 1699 (s), 1595 (m), 1562 (w), 1497 (m), 1414 (m), 1379 (w), 1340 (w), 1301 (m), 1230 (m), 1135 (m), 989 (w), 950 (w), 916 (w), 868 (w), 832 (w), 758 (m), 656 (w), 633 (w), 533 (w).

\(^1\)H NMR (500 MHz, CD\(_3\)OD), (numbering of atoms according to Scheme 2 a), \(d\) (ppm) 3.47 (s, 9H, C\(_{12}\)-H), 4.94 (s, 2H, C\(_{11}\)-H), 8.17 (s, 1H, C\(_{9}\)-H), 8.18 (d, 1H, \(J\)\(\text{C3-H/C4-H} = 10\) Hz, C\(_{3}\)-H), 8.36 (d, 1H, \(J\)\(\text{C3-H/C4-H} = 10\) Hz, C\(_{4}\)-H), 7.94 (d, 1H, \(J\)\(\text{C5-H/C6-H} = 5\) Hz C\(_{5}\)-H), 7.62 (t, 1H, \(J\)\(\text{C5-H/C6-H/C7-H} = 5\) Hz, C\(_{6}\)-H), 7.78 (t, 1H, \(J\)\(\text{C6-H/C7-H/C8-H} = 5\) Hz, C\(_{7}\)-H), 8.03 (d, 1H, \(J\)\(\text{C7-H/C8-H} = 5\) Hz, C\(_{8}\)-H).

\(^13\)C NMR (125 MHz, CD\(_3\)OD), (numbering of atoms according to Scheme 2 a), \(d\) (ppm) 55.0 (C\(_{12}\)), 64.4 (C\(_{11}\)), 146.9 (C\(_{9}\)), 154.4 (C\(_{2}\)), 119.2 (C\(_{3}\)), 138.7 (C\(_{4}\)), 130.1 (C\(_{4a}\)), 129.3 (C\(_{5}\)), 129.0 (C\(_{6}\)), 131.7 (C\(_{7}\)), 129.7 (C\(_{8}\)), 148.9 (C\(_{8a}\)), 167.0 (C\(_{10}\)).

2.2.2. Synthesis of Ni(II) complex (1)

Into the mixture of 0.09 g (0.30 mmol) Ni(BF\(_4\))\(_2\)-6H\(_2\)O and 0.10 g (0.30 mmol) of the ligand HCl in methanol (20 mL) 0.08 g (1.20 mmol), of NaN\(_3\) was added. The solution was refluxed for 4 h. After refrigeration of reaction solution at \(-8\) °C for two weeks, the red crystals suitable for X-ray analysis were formed. Yield: 0.08 g (31%). Elemental analysis calculated for C\(_{31}\)H\(_{42}\)N\(_2\)O\(_4\) Ni\(_2\): C 42.50%, H 4.83%, N 31.97%, found: C 42.27%, H 4.68%, N 31.68%. IR (cm\(^{-1}\)): 3578 (w), 3518 (w), 3342 (w), 3034 (w), 2956 (w), 2823 (w), 2059 (s), 2030 (s), 1644 (w), 1591 (w), 1556 (w), 1530 (m), 1479 (w), 1433 (w), 1400 (w), 1362 (w), 1334 (w), 1301 (m), 1200 (w), 1188 (w), 1086 (m), 1024 (w), 974 (w), 913 (w), 829 (w), 808 (w), 785 (w), 757 (w).

2.3. X-ray structure determinations

Crystal data and refinement parameters of 1 are listed in Table 1. The X-ray intensity data were collected at room temperature with an Agilent SuperNova dual source diffractometer using an Atlas detector and equipped with mirror-monochromated Cu K\(_{\alpha}\) radiation (\(\lambda = 1.54184\) Å). The data were processed using CRYSTALS PRO [45]. The structure was solved by direct methods implemented in SHELXS–2013 [46] and refined by a full-matrix least-squares procedure based on \(\chi^2\) using SHELXL-2016 [46]. All non-hydrogen atoms
were refined anisotropically. The C9A- and C9B-bound hydrogens and water hydrogen atoms were located in a difference map and refined with the using distance restraints (DFIX) of C–H or O–H = 0.98 and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $U_{iso}(H) = 1.5U_{eq}(O)$, respectively. All other hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

### 2.4. Computational details

Within the present study the density functional theory (DFT) was employed for quantum-chemical modeling of the compounds. For geometry optimizations hybrid exchange-correlation functional B3LYP [47] with Becke’s exchange component [48] and the Lee–Yang–Parr correlation functional [49] was used in combination with Pople’s group split-valence 6-311G(d,p) basis set extended with polarization functions on non-hydrogen atoms. Molecular model exactly matching ligand $HLCl$ and coordination compound $1$ were used. Geometry optimizations were done without any symmetry constrains. The energy minima for all optimized structures were verified by vibration frequency calculations and no vibrations with imaginary frequency were found. Program package GAUSSIAN’03 was employed for calculations [50]. Exchange interaction parameter was evaluated within broken symmetry approximation (DFT-BS) by Ginsberg, Noodleman, Yamaguchi and others [51–53].

We employed three formulas that were proposed and widely used to extract exchange parameter $J$ value from the energies of high-spin (HS) and broken symmetry (BS) states, namely spin-projected formula (1) by Noodleman [52], theoretically justified for the case of strong localization of the magnetically active molecular spin–orbitals (SOMOs), non-spin projected formula (2) of Ruiz and others [54,55], justified for delocalized SOMOs and Yamaguchi formula (3) [53] which is considered to be a “compromise” one.

### Table 1
Crystal data and structure refinement details for $1$.

<table>
<thead>
<tr>
<th>Formula</th>
<th>$\text{C}<em>{31}\text{H}</em>{42}\text{N}<em>{2}\text{O}</em>{4}\text{Ni}_{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_w$ (g mol$^{-1}$)</td>
<td>876.26</td>
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<tr>
<td>Crystal size (mm)</td>
<td>$0.25 \times 0.20 \times 0.10$</td>
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<tr>
<td>Crystal color</td>
<td>red</td>
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<tr>
<td>Radiation, Wavelength ($\AA$)</td>
<td>Cu Kα, 1.54184</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td>$a$ ($\AA$)</td>
<td>15.6460(3)</td>
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<tr>
<td>$b$ ($\AA$)</td>
<td>11.9586(2)</td>
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<tr>
<td>$c$ ($\AA$)</td>
<td>22.3571(5)</td>
</tr>
<tr>
<td>$\beta$ ($^\circ$)</td>
<td>107.206(2)</td>
</tr>
<tr>
<td>$V$ ($\AA^3$)</td>
<td>3995.90(14)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>$D_{calc}$ (g cm$^{-3}$)</td>
<td>1.457</td>
</tr>
<tr>
<td>$R_{int}$</td>
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</tr>
<tr>
<td>No. of collected reflections</td>
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</tr>
<tr>
<td>No. of independent reflections</td>
<td>7812</td>
</tr>
<tr>
<td>No. of parameters</td>
<td>540</td>
</tr>
<tr>
<td>$R$ and $R_{int}$ values</td>
<td>$R = \sum</td>
</tr>
<tr>
<td>$R_{int}$</td>
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<tr>
<td>$wR_{2}$ (all data)</td>
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</tr>
<tr>
<td>Goodness-of-fit (GOF)</td>
<td>1.037</td>
</tr>
<tr>
<td>Maximum/minimum residual electron density (e Å$^{-3}$)</td>
<td>$+0.384/-0.346$</td>
</tr>
</tbody>
</table>

### Table 2
Selected bond lengths ($\AA$) and angles ($^\circ$) for $1$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$d$ ($\AA$)</th>
<th>Angle</th>
<th>$\psi$ ($^\circ$)</th>
</tr>
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<tbody>
<tr>
<td>Ni1A–N1A</td>
<td>2.1850(18)</td>
<td>O1A–Ni1A–N1A</td>
<td>153.82(6)</td>
</tr>
<tr>
<td>Ni1A–N2A</td>
<td>1.9948(17)</td>
<td>O1A–Ni1A–N2A</td>
<td>76.80(7)</td>
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<tr>
<td>Ni1A–N3A</td>
<td>2.0851(17)</td>
<td>O1A–Ni1A–N3A</td>
<td>93.33(7)</td>
</tr>
<tr>
<td>Ni1A–N4A</td>
<td>2.1400(19)</td>
<td>O1A–Ni1A–N4A</td>
<td>92.17(7)</td>
</tr>
<tr>
<td>Ni1A–N1ZA</td>
<td>2.063(2)</td>
<td>O1A–Ni1A–N1ZA</td>
<td>91.58(8)</td>
</tr>
<tr>
<td>Ni1A–O1A</td>
<td>2.0997(15)</td>
<td>O1B–Ni1B–N1B</td>
<td>152.96(7)</td>
</tr>
<tr>
<td>Ni1B–N1B</td>
<td>2.1793(19)</td>
<td>O1B–Ni1B–N1B</td>
<td>75.77(7)</td>
</tr>
<tr>
<td>Ni1B–N2B</td>
<td>1.9962(18)</td>
<td>O1B–Ni1B–N2B</td>
<td>93.13(7)</td>
</tr>
<tr>
<td>Ni1B–N1Z</td>
<td>2.1339(18)</td>
<td>O1B–Ni1B–N1Z</td>
<td>97.39(7)</td>
</tr>
<tr>
<td>Ni1B–N4Z</td>
<td>2.0819(18)</td>
<td>O1B–Ni1B–N4Z</td>
<td>90.37(8)</td>
</tr>
<tr>
<td>Ni1B–N1ZB</td>
<td>2.064(2)</td>
<td>O1B–Ni1B–N1ZB</td>
<td>102.11(7)</td>
</tr>
<tr>
<td>Ni1B–O1B</td>
<td>2.1373(16)</td>
<td>O1B–Ni1B–O1B</td>
<td>102.01(8)</td>
</tr>
</tbody>
</table>

![Fig. 1. Graphical representation of 1. Non-coordinated water and methanol molecules have been left out for clarity.][1]

![Fig. 2. Temperature dependences of $\chi T$ and inverse susceptibility. Solid line is the best fit of the experimental data using Eq. (4) and Curie-Weiss law.][2]
between first two. For the case of two interacting spin-centers with equal local spins $S$ these formulas are written as follows:

$$f = \frac{(E_{BS} - E_{HS})}{4S^2}$$  \hspace{1cm} (1)

$$f = \frac{E_{BS} - E_{BS}}{4S^2 + 2S}$$  \hspace{1cm} (2)

$$f = \frac{(E_{BS} - E_{BS})}{(S_{BS}^2)} - \frac{(S_{HS}^2)}{S_{BS}^2}$$  \hspace{1cm} (3)

where $E_{BS}$, $E_{HS}$, $(S_{BS}^2)$, $(S_{HS}^2)$ – energies of the broken symmetry (BS), high spin (HS) states, expectation values of spin squared for BS and HS states, correspondingly.

Accuracy of DFT-BS approximation is known to be strongly dependent on the DFT functional used, thus it seems important to employ several functionals to calculate $f$ values for comparison purposes and in the order to test the stability of the obtained results. Accounting of the exact Hartree–Fock exchange is well understood to be vital to obtain meaningful quantitative results with DFT-BS [56–58], so for calculations we chose series of hybrid exchange-correlation functionals: B3LYP, modified B3LYP [59] (differing from the original by reducing exchange HF admixture from 20% to 15%), TPSSH [60] and PBEO [61].

For each functional geometry optimizations were performed separately for both HS and BS spin-states without any constrains.

3. Results and discussion

3.1. Synthesis

The ligand (HLCl), $(E)$-N,N,N-trimethyl-2-oxo-2-(2-(quinolin-2-ylmethylene)hydrazinyl)ethan-1-aminium chloride, was obtained in the condensation reaction of 2-quinolinecarboxaldehyde and Girard’s T reagent (Scheme 2a). In the reaction of the ligand HLCl with Ni(BF$_4$)$_2$·6H$_2$O and NaN$_3$ in molar ratio 1:1:4 in methanol dinuclear double end-on azido bridged Ni(II) complex (1), with composition [Ni$_2$L$_2$(μ−1,1-N$_3$)$_2$(N$_3$)$_4$], was obtained (Scheme 2b).

3.2. Spectroscopy

From the IR spectrum of complex 1 it can be seen that the ligand is coordinated in deprotonated form since the new band at 1530 cm$^{-1}$ corresponding to ν(O−C−N) vibration of deprotonated hydrazide moiety appeared instead of the band of carbonyl group in the free ligand HLCl at 1699 cm$^{-1}$. Coordination of the azomethine nitrogen results in red shift of ν(C=N) group, from 1595 cm$^{-1}$ in the spectrum of HLCl ligand to 1591 cm$^{-1}$ in the spectrum of complex 1. In the IR spectrum of complex 1 two strong bands appeared at 2060 cm$^{-1}$ and 2030 cm$^{-1}$ which can be attributed to the $\nu_{asym}$ stretch of the terminal and end-on azido ligands, respectively [62].
The selected bond distances and angles of the Ni(II) complexes range from 2.0819 to 2.1400 Å, which are close to the values reported in the other end-on azido Ni(II) complexes [3,63,64]. All of the Ni–N (bridging azido) bonds in the molecule range from 2.0819 to 2.1400 Å, which are close to the values reported in the other end-on azido Ni(II) complexes [3,63,64].

Quinoline fragments are involved in intra- and intermolecular π⋯π interactions and intermolecular interactions of C–H⋯π (quinoline ring) type. The π⋯π interactions between quinoline rings comprise arene-arene, arene-πydine and pyridine-πydine contacts. Solvent water molecule serving as double hydrogen bond donor (toward N62 and N3B at x, 3/2, y, −1/2+z) mediate in joining the dimeric units into infinite chains running parallel to c direction. The neighboring infinite chains are linked through intermolecular π⋯π interactions of pyridine-πydine and arene-πydine type and C–H⋯π (quinoline ring) interactions. Geometric parameters describing π⋯π, C–H⋯π (ring) and hydrogen bonding interactions are given in the Supplementary material together with graphical presentation of crystal packing.

### 3.3. Description of crystal structure

The structure of 1 with atom numbering is shown in Fig. 1. The selected bond distances and angles of 1 are listed in Table 2. Complex 1 with formula [Ni₂L₂(μ-1,1-N₃)]₂[N₂]₂ crystallizes in the monoclinic space group P2₁/c with space group P2₁/c and composition of the L₁L₂C₁(C₅H₅)₂Ni₃[N₂]₂[62] crystallizes in the monoclinic space group P2₁/c. Each Ni(II) atom is octahedrally coordinated by two N atoms from one terminal azido ligand and two N atoms from two azido bridging ligands. The terminal azido ligands are coordinated trans to each other. The Ni–N bond lengths in the range from 1.9948 to 2.1850 Å, in which the bond lengths to the quinoline nitrogen atoms N1A and N1B are the longest. Both of the Ni–O distances (2.0997 Å and 2.1373 Å, respectively) are comparable to the corresponding values observed for the Ni–O bond length in similar complexes [3]. All of the Ni–N (bridging azido) bonds in the molecule range from 2.0819 to 2.1400 Å, which are close to the values reported in the other end-on azido Ni(II) complexes [3,63,64].

### 3.4. Magnetic measurements

Magnetic data are shown in Fig. 2, where temperature dependence of χT and inverse magnetic susceptibility (1/χ) per mol of Ni(II) are presented. It can be seen that there is a linear behavior of inverse magnetic susceptibility for the temperature above 150 K. Fitting the susceptibility data for T > 150 K to the Curie–Weiss law $\chi = C/(T - \theta)$ (where C and θ present Curie constant and Weiss temperature, respectively), gave C = 1.25 cm³ mol⁻¹ K⁻¹, and $\theta = +24.0$ K. The effective magnetic moment $\mu_{\text{eff}} = 3.16$ μB, obtained from Curie constant C, is slightly higher than the spin-only value for Ni²⁺ ion ($\mu_{\text{eff}} = 2.82$ μB), but it is in a good agreement with literature data for Ni²⁺ in octahedral environment [65,66]. Positive values of Weiss constant speak in favor of strong ferromagnetic coupling between two Ni²⁺ ions. It can be seen that upon cooling χT value increases and shows broad maximum around 23 K (1.89 emu K/mol) indicating the presence of dominant ferromagnetic interaction. Upon further cooling this product decreases sharply to 1.28 emu K/mol at 2 K. This decrease may be due to the intermolecular antiferromagnetic exchange interactions.

In order to evaluate the exchange coupling constants, Eq. (4) was employed [67]:

$$\chi_N = \frac{N\mu_0^2\mu_0^2}{K_B(T - \theta)}\left(\frac{\exp(\beta J/k_BT) + 5 \exp(6J/k_BT)}{1 + 3 \exp(2J/k_BT) + 5 \exp(6J/k_BT)}\right) + Nz$$  (4)

In this equation J is exchange integral between two Ni²⁺ spins (S = 1), Nz is temperature independent paramagnetism and δ is an effective Weiss constant included in equation to take account of inter-dimer interaction. Least-squares fitting of experimental data (Fig. 2) leads to the following parameters: $J = +12.0(2)$ cm⁻¹, $g = 2.3(1)$, $\delta = -0.8(3)$ cm⁻¹ and $Nz = 382.10^{-6}$ emu/mol. R value defined as $R = \sum |\chi_{\text{exp}} - \chi_{\text{calc}}|^2 / \sum |\chi_{\text{exp}}|^2$ was found to be 3.20 · 10⁻⁶. Positive J value confirms significant intra-dimer ferromagnetic coupling. The negative δ value shows inter-dimer antiferromagnetic interactions which causes sharp decrease of χT below 20 K.

It has been shown in the literature, that dinuclear complexes with the azido bridges, exhibit different magnetic behavior, depending upon several parameters like bridging modality, the bridge angles and dimensions of the nuclear centers. The most important is bridging modality which can be twofold: end-to-end (μ₁⁻1,⁻₁-N₃) or end-on (μ⁻₁⁻₁-N₃) (see Scheme 1). As a general rule, the first modality shows, almost exclusively, antiferromagnetic interaction between metallic cations [13–15], while for the later one is characteristic ferromagnetic exchange coupling [16—18]. In investigated complex, end-on coordination mode of the bridging ligands was found (Section 3.3) and thus, obtained ferromagnetic...
interaction is in accordance with the mentioned rule. Found structural parameters (Section 3.3), like the bridging M–N–M angle (102°), the M–N bond distance (2.1 Å) and Ni···Ni separation (3.281 Å), are also very important and affect the strength of the exchange interaction [68]. Determined \( J \) value for complex 1 is comparable with the literature data relating to the similar dinuclear compounds with two \( \mu_1,1 \)-azide bridges. For example, complexes [Ni\(_2\)(L\(_3\))(HL\(_1\))(\(\mu_1,1\)-N\(_3\))] \( \times \) Cl\(_4\) (HL\(_1\) = N,N-bis(2-methyl- pyridyl)-3,5-dimethyl-2-hydroxybenzylamine) with Ni···Ni 3.240 Å, N–Ni–N \( = \) 101.3°, \( J \) = 12.26 cm\(^{-1}\) [69] and [Ni(terpy)(\(\mu_1,1\)-N\(_3\))(N\(_3\))] \( \times \) 2H\(_2\)O with Ni···Ni 3.276 Å, N–Ni–N 101.3°, \( J \) = 20.1 cm\(^{-1}\) [70].

3.5. Comparison of structural and magnetic parameters of \( \text{bis}(\mu_{1,1,1}\text{-azido})\text{nickel(II)} \) complexes

The structural parameters correlating the geometry of related ferromagnetically coupled \( \text{bis}(\mu_{1,1,1}\text{-azido})\text{nickel(II)} \) complexes [16,62–64,71–78] are listed in Table 3. In the analyzed dinuclear Ni(II) complexes of octahedral geometry N\(_3\) anions act both as end-on bridging and as terminal ligands. The chelating ligands are tridentate in all cases except in [Ni\(_2\)(L\(_3\))(N\(_3\))\(_4\)] \( \times \) Cl\(_4\) [71] and [Ni (L\(_{1,4}\))*(\(\mu_1\)-N\(_3\))(N\(_3\))] \( \times \) Cl\(_4\) [77] complexes in which ligands L\(_3\) and L\(_{1,4}\) act as bis-tridentate. The complexes presented in Table 3 differ in position of N\(_3\)azido(terminal) atoms with respect to the N\(_2\)N\(_2\)(azido(terminal)) plane, as evidenced by the N\(_3\)azido(terminal)--Ni--N\(_3\)azido(bridging) torsion angles. The analysis of Ruiz et al. performed on \( \text{bis}(\mu\text{-azido}) \) nickel(II) complexes has predicted ferromagnetic interaction on all ranges of Ni--N(N\(_3\))--Ni angles, with \( J \) increasing upon increasing this angle, yielding a maximum at 104° approximately [78]. They have also shown that the bond distance between the metal and bridging atoms has a strong influence on the coupling constant, with the ferromagnetic coupling diminishing upon increasing such distance. The smallest Ni--N\(_3\)azido(bridging)--Ni angles of \( \approx \)98° were found in complexes 2 and 12 and in one moiety of complex 4 which lies at special position in the unit cell. The largest Ni--N\(_3\)azido(bridging)--Ni bond angles within the same N\(_2\)N\(_2\)(azido(terminal)) rhombus are comparable in magnitude, however, the significant difference of +3° has been observed in complex 5. The Ni···Ni separation is relatively large and range from 3.155 to 3.448 Å (Table 3). The [Ni\(_2\)(L\(_2\))(N\(_3\))] \( \times \) Cl\(_4\) complex has the slightly shorter Ni···Ni separation compared with the other complexes listed in Table 3. This may be attributed to the structure of ligand L\(_2\) and its bis-tridentate coordination function.

3.6. Theoretical calculations

Possible isomers of HLCl ligand are geometric isomers (E and Z) related to the azomethine group, keto and enol tautomers (hydrazone and \( \pi \)-oxazine) and rotational isomers (syn and anti). Quantum-chemical calculations of the geometry and total energy of possible isomeric forms of HLCl were performed to give insight into their stability. The results are shown in Fig. 3.

Both in the gas phase and in methanol solution rotamers of hydrazonic tautomers of HLCl (structures a–c) are much more stabilized than \( \pi \)-oxazine ones (structures d, e), more than by 14 kcal/mol. In vacuum the global minimum corresponds to hydrazonic isomer \( a \), stabilized by intramolecular NH···N hydrogen bond between hydrazine fragment and cyclic quinoline nitrogen atom, isomer \( b \) is destabilized by 5.9 kcal/mol. But when methanol media is taken into account, the most stable appeared to be rotamer \( b \), which has energy 1.6 kcal/mol lower, than that of rotamer \( a \). Isomer \( c \) is strongly destabilized both in vacuum and methanol solution. These results were confirmed from the \( ^1 \)H NMR spectrum of HLCI in methanol in which two sets of signals of both a and b isomers were observed with molar ratio 1:4, respectively.

Exchange interactions in dinuclear complex 1 were modeled within broken symmetry approach (DFT–BS). In Table 4 \( J \) values calculated with formulas (1)(3) (see Section 2) and various hybrid exchange–correlation functionals are given (calculated energies of HS and BS states and other calculation details can be found in Table S.4 of Supplementary material).

The ferromagnetic type of exchange interaction in the complex 1 is predicted in all considered cases. It is seen that while Yamaguchi and spin-projected formulas give virtually the same values and noticeably overestimate the exchange coupling strength, values obtained with Ruiz formula are in reasonably good agreement with the experimental value. Though all DFT functionals give close results (within the 9 cm\(^{-1}\) range), the closest to experimental \( J \) value is obtained with modified B3LYP* functional. Good results with this functional for calculating energies of spin states were reported recently [79,80]. Further the results obtained with this functional will be reported, the values for the other ones are given.
in the Supplementary material. Ni(II) ion with d⁶ electronic configuration in octahedral environment is characterized with local spin S = 1. Shapes of the four localized magnetically active single occupied molecular orbitals (SOMOs) are shown in Fig. 4. For each metal center there are two SOMOs, with predominant input of dₓ²−ᵧ² -like AO (in local coordinate system) lying in the basal plane defined by four nitrogen donor atoms (see Fig. 4, left) and dₓz− ayr-like AO, oriented along the axial line defined by quinoline nitrogen donor atom and carbonyl oxygen (Fig. 4, right).

First two orbitals are more delocalized toward ligands, including bridging azide nitrogens, while latter two are localized on d-AO and axial donors, this difference is illustrated by overlap integral value –0.0305 for first pair and only 0.0067 for latter. Small overlap of SOMOs results in more pronounced partition of α and β-spin electronic density (SD) in broken symmetry state, and is the reason for ferromagnetic type interaction between paramagnetic centers (see Fig. 5 and Table 5 for SD distribution and Mulliken charges/spin populations in complex 1).

It is clearly seen that SD density is strongly localized on the metal centers with only minor delocalization over the nearest donor atoms of the organic ligand, more than 1.6e out of total 2e spin density is localized on Ni centers. On the nitrogen atoms of the bridging N₃ anions SD is very small, even in triplet state –0.025 and 0.015e on nitrogen atoms N1Z and N4Z, correspondingly (see Table 5).

Switching between high and low spin-states have minor influence on charge distribution, leading only to inversion of the spin population sign on one of the two Ni centers and decrease of the spin population on the bridging atoms due to partial α- and β-SD overlap.

4. Conclusion

Complex 1 was obtained in the reaction of the condensation product of 2-quinolinecarboxaldehyde and Girard’s T reagent with Ni(BF₄)₂·6H₂O and NaN₃. In complex 1 octahedral surrounding around each of the two Ni(II) centers consist of NNO coordinated deprotonated hydrazone ligand, one monodentate azido ligand and two azido bridging ligands. Magnetic data for complex 1 showed very intensive intra-dimer ferromagnetic coupling between Ni²⁺ ions and inter-dimer antiferromagnetic interaction. DFT-BS modeling demonstrated that ferromagnetic exchange coupling in complex 1 is determined by small magnetically active SOMOs of the metal centers overlap and their minor delocalization toward nitrogen atoms of the bridging azide anions.

Acknowledgements

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Appendix A. Supplementary data

CCDC 1524733 contains the supplementary crystallographic data for 1. 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.2017.02.039.

References


Table 5

Mulliken spin populations (ρ) and total charges (q) on atoms of the exchange fragment [B3LYP (6-311G(dp))] in high (HS) and low spin states (BS).

<table>
<thead>
<tr>
<th>Spin state</th>
<th>Ni1A</th>
<th>Ni1B</th>
<th>N1Z</th>
<th>N4Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS</td>
<td>1.629/1.360</td>
<td>1.653/1.372</td>
<td>0.025/-0.764</td>
<td>0.015/-0.726</td>
</tr>
<tr>
<td>BS</td>
<td>1.333/1.361</td>
<td>1.656/1.372</td>
<td>-0.012/-0.764</td>
<td>0.000/-0.725</td>
</tr>
</tbody>
</table>

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2017.02.039.