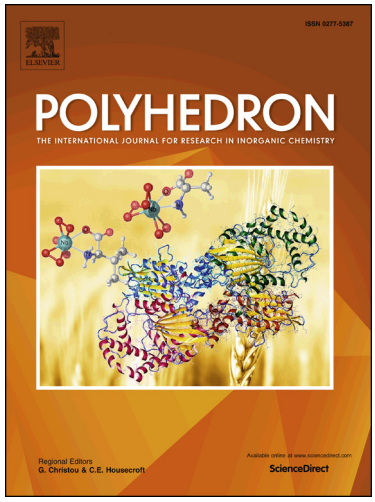

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Crystal structures, magnetic properties and DFT study of cobalt(II) azido complexes with the condensation product of 2-quinolinecarboxaldehyde and Girard's T reagent

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Abstract

A tridentate NNO condensation product of 2-quinolinecarboxaldehyde and Girard's T reagent (**HL**Cl) in the presence of azide ions coordinates with cobalt(II) giving mononuclear azido Co(II) complex [Co**HL**$(N_3)_3$] (**1**) as a main product and dinuclear end-on azido bridged Co(II) complex [Co_2**L**$_2$(μ-$_{1,1}$-$N_3)_2(N_3)_2$] (**2**) in traces. Crystal structures of both complexes were determined. Variable temperature magnetic susceptibility measurement studies of complex **1** showed that Co(II) cation is in the low-spin state with $t_{2g}^6 e_g^1$ (S = 1/2) configuration. DFT-BS calculations for complex **2** anticipated ferromagnetic type interaction between paramagnetic centers (J = 53 cm^{-1}).

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Keywords: Hydrazones; Cobalt(II) azido complexes; Single crystal structures; DFT calculations; Magnetic properties

1. Introduction

Investigation of azido bridged polynuclear d-metal complexes is an attractive field of research due to their interesting structural, spectroscopic and magnetic properties [1]. The azido ligand is one of the most extensively used pseudohalide building block for preparation of mono- [2] and polynuclear d-metals coordination compounds of different dimensionalities [3]. It can acts as monodentate [2] or exhibits many bridging coordination modes: single and double $\mu_{1,3}$-N_3 (end-to-end, EE) and $\mu_{1,1}$-N_3 (end-on, EO), $\mu_{1,1,3}$-N_3, $\mu_{1,1,1}$-N_3, $\mu_{1,1,1,1}$-N_3, $\mu_{1,1,3,3}$-N_3, and $\mu_{1,1,1,3,3,3}$-N_3 [1a,4]. A relatively large number of dinuclear azido bridged Cu(II), Ni(II) and Mn(II) [3,5] complexes have been reported, while the end-on azido bridged Co(II) complexes are rare [6], probably due to the synthetic problems to obtain good quality single crystals and oxidation to Co(III) complexes. DFT calculations on EO and EE azido bridged dinuclear transition metal complexes provide good predictions of their magnetic properties. Also, these systems are excellent examples for theoretical analysis of exchange coupling [7]. Low spin Co(II) complexes are very rare. In contrast to octahedral Co(II) complexes, the number of the reported square-planar and five coordinated Co(II) complexes is higher. Very strong-field ligands are required to undergo spin pairing in Co(II) complexes. The Jahn-Teller effect favorizes the loss of some ligand to give four- or five- rather than six-coordinate complexes [8,9]. Complexes of d-metals with the condensation product of 2-quinolinecarboxaldehyde and trimethylammonium acetohydrazide chloride (Girard's T reagent) (**HL**Cl) and pseudohalides have recently been the subject of study of our research group [10,11]. The ligand (**HL**Cl) is a quaternary ammonium salt, which acts as a potentially tridentate ligand and can be coordinated via quinoline nitrogen, azomethine nitrogen and carbonyl oxygen atoms. Also, this ligand exhibits keto-enol tautomerism and can coordinate metal ions in non-deprotonated positively charged form or deprotonated formally neutral zwitter-ionic form. Recently, we reported the synthesis and characterization of dinuclear end-on azido bridged Ni(II) complex $[Ni_2\mathbf{L}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]$ [10] and mononuclear azido Zn(II) complex $[Zn\mathbf{L}(N_3)_2]$ [10] with this ligand. Here, we present synthesis, structural characterization and magnetic properties of mononuclear azido Co(II)

complex [Co**HL**$(N_3)_3$] (**1**) and dinuclear end-on azido bridged Co(II) complex [Co_2**L**$_2$(μ-$_{1,1}$-$N_3)_2(N_3)_2$] (**2**) with the same ligand.

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). Elemental analyses (C, H, and N) were performed by standard micro-methods using the ELEMENTARVario 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 of (E)-N,N,N-trimethyl-2-oxo-2-(2-(quinolin-2-ylmethylene)hydrazinyl)ethan-1-aminium chloride (**HL**Cl)*

The ligand *(E)-N,N,N*-trimethyl-2-oxo-2-(2-(quinolin-2-ylmethylene)hydrazinyl)ethan-1-aminium chloride (**HL**Cl), was obtained in the condensation reaction of 2-quinolinecarboxaldehyde and Girard's T reagent (Scheme 1) according to the previously described method [10].

*2.3. Synthesis of Co(II) complexes [Co**HL**$(N_3)_3$] (**1**) and [Co_2**L**$_2$(μ-$_{1,1}$-$N_3)_2(N_3)_2$]·H_2O·CH_3OH (**2**)*

The ligand **HL**Cl (90 mg, 0.30 mmol) was disolved in methanol/acetonitrile mixture (20 mL MeOH, 20 mL CH_3CN) and solid $Co(BF_4)_2{\cdot}6H_2O$ (100 mg, 0.30 mmol) was added. Sodium azide (80 mg, 1.20 mmol) was added after complete dissolution of $Co(BF_4)_2{\cdot}6H_2O$ in reaction mixture. The reaction solution was refluxed for 5 h. After slow evaporation of solvent in refrigerator (~ 4 ^oC) during ten days, two kinds of red crystals, were obtained. The main fraction corresponds to compound **1**, while only few crystals of complex **2** were obtained.

Yield of complex **1**: 59 mg (43%). Elemental analysis for complex **1** calcd for $C_{15}H_{19}N_{13}CoO$: C 39.48 %, H 4.20 %, N 39.90 %, found: C 39.52 %, H 4.34 %, N 38.61 %. IR for complex **1** (cm^{-1}): 3277 (m), 3037 (m), 2363 (w), 2030 (s), 2006 (s), 1591 (w), 1552 (w), 1504 (m), 1477 (m), 1443 (m), 1398 (w), 1358 (w), 1332 (m), 1292 (m), 1231 (w), 1152 (w), 1078 (w), 962 (w), 920 (w), 759 (w), 675 (w), 589 (w), 507 (w), 401 (w).

2.4. X-ray Crystallography

The molecular structures of complexes **1** and **2** were determined by single-crystal X-ray diffraction methods. Crystallographic data and refinement details are given in **Table 1**. The X-ray intensity data for **1** were collected at room temperature with Agilent SuperNova dual source diffractometer using an Atlas detector and equipped with mirror-monochromated CuKα radiation (λ = 1.54184 Å). The data were processed using CRYSALIS PRO [12]. The X-ray intensity data for **2** were collected at room temperature with Nonius Kappa CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) and processed using DENZO-SMN [13]. The structures were solved by direct methods (SIR–92) [14] and refined by full-matrix least-squares procedures based on F^2 (SHELXL–2016) [15]. All non-hydrogen atoms were refined anisotropically. The C10 and N3 bonded hydrogen atoms in **1** and C10 and C25 bonded hydrogen atoms in **2** were located in a difference map and refined with the distance restraints (DFIX) with C–H = 0.98 and N–H = 0.86 Å and with U_{iso}(H) = 1.2U_{eq}(C) and U_{iso}(H) = 1.2U_{eq}(N), respectively. All other hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The hydrogen atoms for water oxygen in **2** were not found in a difference map. CCDC 1560081 (for **1**) and 1560082 (for **2**) contain the

supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Table 1

Crystal data and structure refinement details for **1** and **2**.

	1	**2**
formula	$C_{15}H_{19}CoN_{13}O$	$C_{31}H_{42}Co_2N_{20}O_4$
Fw (g mol^{-1})	456.36	876.70
crystal size (mm)	0.60 × 0.20 × 0.18	0.23 × 0.23 × 0.15
crystal color	red	red
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	9.4878(2)	15.8722(4)
b (Å)	13.2977(2)	11.4252(3)
c (Å)	15.1344(3)	22.6649(4)
β (º)	91.401(2)	109.5360(10)
V (Å^3)	1908.87(6)	3873.51(16)
Z	4	4
calcd density (g cm^{-3})	1.588	1.503
F(000)	940	1816
no. of collected reflns	11893	16476
no. of independent reflns	3889	8827
R_{int}	0.0621	0.0240
no. of reflns observed	3263	6403
no. parameters	281	528
$R[I > 2\sigma(I)]^a$	0.0532	0.0434
wR_2 (all data)^b	0.1368	0.1308

Goof , S^c	1.026	1.049
maximum/minimum residual electron density (e Å^{-3})	+0.69/–0.51	+0.61/–0.40

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.
[c] $S = \{\sum[(F_o^2 - F_c^2)^2]/(n/p)\}^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

2.5. Computational methodology

Full geometry optimizations of the crystal structures of Co(II) complexes were carried out using Gaussian 09 program package [16] at the B3LYP/6–31G [17–20] level of theory, in the gas phase. The partial atomic charges for investigated compounds at the ground state geometry were calculated using the natural bond orbital analysis (NBO) [21] incorporated in the Gaussian09. Magnetic couplings in binuclear complexes were calculated using ORCA software package [22] with the broken symmetry approach developed by Noodleman et al [23,24]. In calculations B3LYP functional coupled with common basis sets TZVPP/TZV for Co atoms and with one set of first polarization functions (SVP basis set) for N, C, H and O are used. The exchange coupling constant, *J*, is estimated according to the Yamaguchi approach using equation (2): $J = (E_{HS} - E_{BS})/[\langle S^2\rangle_{HS} - \langle S^2\rangle_{BS}]$, where E_{HS} is the energy of the high spin, E_{BS} is the energy of the broken-symmetry, and $\langle S^2\rangle_{HS}$ and $\langle S^2\rangle_{BS}$ are the expectation values of the high spin and broken symmetry spin operators [25]. If the metal centers are ferromagnetically coupled, *J* is positive because the highest spin state lies lower in energy. On the contrary, antiferromagnetic coupling yields the negative value of *J* and the lowest spin state is the ground state.

3. Results and discussion

3.1. Synthesis

The ligand *(E)-N,N,N*-trimethyl-2-oxo-2-(2-(quinolin-2-ylmethylene)hydrazinyl)ethan-1-aminium chloride (**HL**Cl), was obtained in the condensation reaction of 2-quinolinecarboxaldehyde and Girard's T reagent using the previously described method, **Scheme**

1 [10]. Reaction of the ligand **HL**Cl with $Co(BF_4)_2 \cdot 6H_2O$ and NaN_3 in molar ratio 1 : 1 : 2 in methanol/acetonitrile mixture results in formation of mononuclear octahedral azido Co(II) complex (**1**) with composition [Co**HL**$(N_3)_3$]. In the reaction of **HL**Cl with $Co(BF_4)_2 \cdot 6H_2O$ and NaN_3 in molar ratio 1 : 1 : 4 in the same mixture of solvents, a dinuclear double end-on azido bridged Co(II) complex (**2**), with composition $[Co_2\mathbf{L}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2] \cdot H_2O \cdot CH_3OH$ was obtained in traces together with complex **1**.

<Scheme 1.>

3.2. Crystal structures

The molecular structure of **1** is shown in **Fig. 1**. Selected bond distances and angles are given in **Table S1**. Two nitrogen atoms (N1, N2) and one oxygen atom (O1) of the tridentate ligand **HL** in combination with three nitrogen atoms (N5, N8, N11) of three different azides in a meridional alignment complete octahedral coordination of the cobalt(II) ion. The tridentate NNO coordination of **HL** to Co(II) ion generates two five-membered chelation rings that are almost planar (maximum deviation from the average ring skeleton including the metal = 0.04 Å). The Co−N (azido) distances of 1.951(3) −1.967(3) Å are shorter than those found in [Co(4-benzoylpyridine)$_4(N_3)_2$] [26]: Co−$N_{(azido)}$ = 2.252(2), 2.091(2) and [Co(tedmpza)(N_3)]$ClO_4 \cdot H_2O$ [27] (tedmpza = tris(3,5-dimethyl-ethyl-pyrazol-1H-yl)amine: Co−$N_{(azido)}$ = 2.058(2) Å, and are similar to that found in $[Co(tbta)N_3]ClO_4 \cdot 3CH_3CN$ [28] (tbta=[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]-amine): Co−$N_{(azido)}$ = 1.964(3) Å. The chelating ligand is strongly coordinated to metallic center through imine nitrogen (Co−N(imine) = 1.854(2) Å) and weakly through quinoline nitrogen (Co−N(quinoline) = 2.003(2) Å). One of the measures of the octahedral strain is average ΔO_h value, defined as the mean deviation of 12 octahedral angles from ideal 90°. The distorted octahedron formed around Co1 in **1** exhibits average ΔO_h value of 4.1°. The N−N−Co bond angles are between 120.7(2) and 122.0(2)° showing bent coordination of the anionic terminals. The terminal azido ligands are nearly linear and slightly asymmetric [N5−N6 = 1.179(4)Å and N6−N7=1.142(4)Å; N8−N9 = 1.188(4)Å and N9−N10=1.152(4)Å; N11−N12

=1.185(4)Å and N12−N13= 1.143(5)Å. As for the other metal complexes with terminal azido ligands, the shorter $N_{(azido)}$ $-N_{(azido)}$ bonds are more remote from the metal atom [26]. The molecular structure of **2** is shown in **Fig. 2**. Selected bond distances and angles are given in **Table S1**. The two azido N_3^- groups bridge the two cobalt centers in a μ-$_{1,1}$ fashion with metal – metal separation of 3.3409(5) Å. In the previously reported dinuclear hexacoordinated μ-$_{1,1}$ azido bridged Co(II) complexes [29–31] the distance between metal centers is shorter than that in **2** and range from 3.168 to 3.276 Å, which may be attributed to the specific bridging coordination of the corresponding organic ligands. In the isostructural $[Ni_2\mathbf{L}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot H_2O\cdot CH_3OH$ complex [10] the metal–metal separation is somewhat smaller and sums 3.2814(6) Å. The bridged Co–N distances are unequal (2.091(2) – 2.167(3) Å) showing a parallelogram pattern. In the isostructural Ni(II) complex the Ni–N distances within the parallelogram pattern span the range from 2.082(2) to 2.140(2). The cobalt(II) centers in **2** are six coordinate comprising the tridentate NNO ligand (**L**) and three azido groups, two of which are end-on azido bridges, while the third is a terminal azido group, forming an octahedral coordination. The octahedral coordination geometries of both metallic centers are more distorted than in **1**, as evidenced by the ΔO_h values of 8.9° and 8.6° for Co1 and Co2, respectively. The two planar five-membered chelation rings originated from coordination of the ligand **L** to the metallic center have slightly increased deviation from the average ring skeleton including the metal than in complex **1** (0.13 and 0.14 Å, respectively). The Co–N(imine) and Co–N(quinoline) bond lengths in **2** are considerably longer than that in **1** but retain the same fact that metallic center is strongly coordinated through imine nitrogen atom and weakly through quinoline nitrogen atom. The Co–O and Co–N(terminal azido) bond lengths in **2** are also longer than those found in **1**. The N–N–Co bond angles in **2** are in accordance with those found in **1**. The terminal and bridging azido ligands in **2** are also slightly asymmetric in bond lengths as in the case of compound **1**. Each of the binuclear complexes, $[Co_2\mathbf{L}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot H_2O\cdot CH_3OH$ and $[Ni_2\mathbf{L}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot H_2O\cdot CH_3OH$, has almost the same M^{II}–$N_{azido(end\text{-}on)}$–M^{II} bond angles within $M^{II}{}_2N_{2(azido(end\text{-}on))}$ parallelogram pattern, that sum ≈103° and ≈102°, respectively. Crystal packing of **2** is comparable with that of isostructural $[Ni_2\mathbf{L}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot H_2O\cdot CH_3OH$ [10] complex. In the crystals of **1**, complex molecules linked through intermolecular contacts of π···π and C-H···π(ring) type extend along the direction parallel with [1 0 0]. Geometric parameters describing

π···π and C–H···π(ring) interactions are given in the Supplementary material together with graphical presentation of crystal packing.

< Fig. 1. >

< Fig. 2. >

*3.3. Magnetic properties of complex **1***

Measured data were corrected for the contributions of the sample holder, for the diamagnetism of the sample estimated from Pascal's constants (χ_d = –207 × 10^{-6} emu/moleOe), as well as for temperature independent paramagnetism of Co^{2+} ion (450 × 10^{-6} emu/moleOe) [28].

Results of magnetic measurements are shown in **Fig. 3**, where temperature dependence of χT and inverse magnetic susceptibility ($1/\chi$) per mol of Co (II) complex, are depicted. It can be seen that between 50 and 300 K, the χT remains almost constant with the value of about 0.34 emuK/moleOe, which is near the spin-only value (0.374 emuK/moleOe) for an uncoupled S = 1/2 Co(II) ion. On lowering of the temperature, the χT value decreases rapidly to a value of 0.28 emuK/moleOe at 5 K. Also, inverse magnetic susceptibility, in the same temperature range, obeys the Curie-Weiss law (χ = C/(T – θ)) with a Curie constant C = 0.34 emu/ molOe (μ = 1.65 μ_B), as well as small Weiss constant of +4.7 K.

Obtained results show that Co(II) cation is in the low-spin state with $t_{2g}^6e_g^1$ (S = 1/2) configuration. Although it is known that octahedral Co(II) complexes prefer high-spin configuration, there are also some examples where low-spin configuration was observed [32–36]. This configuration can be expected only in a sufficiently strong ligand field which is required to create ^{2}E state of the free ion ($t_{2g}^6e_g^1$ configuration) from ^{2}G state ($t_{2g}^4e_g^3$ configuration). In complex **1** octahedral environment of Co(II) ion consists of two nitrogen atoms (N1 and N2), one oxygen atom (O1) of the tridentate ligand **HL** and three nitrogen atoms (N5, N8, N11) of three different azido ligands in a meridional alignment. It was shown by angular-overlap considerations that octahedral Co(II) complexes with sterically favorable meridional alignment, as is the case for this complex, are preferably in low-spin state [37,38].

Also, Figgis has found that spin-paired octahedral Co(II) complexes show the lowest magnetic moments, with very small orbital contribution, and close to spin-only value for S = 1/2, [39] which is in accordance with the obtained magnetic moment.

Magnetic moments for previously reported octahedral low-spin Co(II) complexes are given in the Table 2.

Table 2

Magnetic moments for octahedral low spin Co(II) complexes

Complex	Magnetic moment (BM)	Reference
[Co**L1**]$(ClO_4)\cdot H_2O$	1.98	[40]
$[Co(NO_2)_6]^{4-}$	1.88	[41]
[Co(**L2**)$_3$]$(ClO_4)_2$	1.92	[41]
[Co**L3**$(H_2O)_2$]	1.85	[42]
[Co**L4**]	1.88	[43]
$K_2Ba[Co(NO_2)_6]$	1.88	[39]
$K_2Pb[Co(NO_2)_6]$	1.81	[39]
[Co(**L5**)](**L6**)$_2$	1.81	[32]
[Co(**L7**)$_2$]$(BF_4)_2$	1.78	[32]
[Co(**L8**)$_3$]$^{2+}$	1.98	[38]

L1 – 30 membered macrocyclic Schiff base; **L2** – diarsine; **L3** – tetradentate macrocyclic bis-bipyridyl (pyrphyrin); **L4** – dithiaalky substituted aryl azo-oxime ligand; **L5** – hexathia-l8-crown-6; **L6** – picrate; **L7** – trithianonane; **L8** – 2-(arylazo)pyridine

Values of magnetic moments of octahedral low spin Co(II) complexes which are higher than the spin only value (1.73 BM) for one unpaired electron can be attributed to the orbital contribution to the ground state [44].

< Fig. 3. >

3.4. DFT study

The ground-state geometries of the complexes **1** and **2** were calculated in the gas phase, starting from the crystal structures. Previous study has shown that B3LYP functional is an acceptable theoretical approach for geometries calculations of similar systems [45,46]. Therefore, the B3LYP/6–31G level was chosen for full geometry optimizations. Experimental and calculated average values of selected bond lengths and angles of **1** and **2** complexes are

listed in **Table S4** and are in a good agreement. The ground state geometries of Co(II) complexes are shown in **Fig. S2**.

Magnetically active single occupied molecular orbitals (SOMOs) for complexes **1** and **2** are shown in **Fig. 4**. The computed spin density indices π antibonding between the Co 3d orbitals and the nitrogen atoms of ligands. The ferromagnetic type of exchange interaction in the complex **2** is predicted in agreement with the experimentally evaluated values for similar hexacoordinated dinuclear complexes that are bridged by two $\mu_{1,1}$-N_3 ligands [10,29–31]. For each metal center of binuclear complex **2** there are two SOMOs $d_{x^2-y^2}$ atomic orbitals lying in the basal plane defined by four nitrogen donor atoms, and d_{xz} oriented along the axial line defined by quinoline nitrogen donor atom and carbonyl oxygen. The $d_{x^2-y^2}$ atomic orbital is more delocalized towards ligands, including bridging azide nitrogens. Due to the orthogonality between the SOMOs and to the small overlap of SOMOs ferromagnetic type interaction between paramagnetic centers is anticipated (J = 53 cm^{-1}).

< Fig. 4. >

Fukui functions were applied in order to study molecular reactivity of cobalt complexes. Based on Parr and Yang theory [47–50], the sites in chemical species with the largest values of Fukui functions *f(r)* are those with higher reactivity. The Fukui *f(r)* function is defined as the change in electron density upon a change in the number of electrons (equation 1), where *ρ(r)* is the total electron density of the molecule, *N* is the number of electrons and *υ(r)* is the external potential exerted by the nucleus. The condensed Fukui function evaluated reactivity of compounds towards nucleophilic and electrophilic attack (eq. 2 and 3 respectively), where q_N, q_{N-1} and q_{N+1} are the partial charge of the atom *A* in neutral, anionic and cationic forms, respectively.

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{\upsilon(r)} \quad (1)$$

$$f_A^+ = q_N^A - q_{N+1}^A \quad (2)$$

$$f_A^- = q_{N-1}^A - q_N^A \quad (3)$$

The partial atomic charges for investigated compounds were calculated using NBO approach at the ground state geometry in gas-phase. The greatest values of Fukui functions are reported in **Table S5**. The f^- measures reactivity with respect to electrofilic attack, while f^+measures reactivity with respect to nucleophilic attack.

For complex **1**, the highest values of f^+ function occur at N13 and N7, suggesting that these atoms are the most favorable sites for nucleophilic attack (numbering of atoms according to **Fig. 1**).

For complex **2**, the most reactive sites for nucleophilic attack are Co, N20 and N17 atoms of azido bridged groups. Such reactivity may be responsible for breaking link between two metal ions. This is in accordance with the experimental observation where mononuclear complex **1** is obtained as a major component (numbering of atoms according to **Fig. 2**).

Table 3

DFT calculated g tensors for complex **1**.

Compound	g_{xx}	g_{yy}	g_{zz}	g_{iso}*
1 (B3LYP)	1.994	1.995	2.000	1.997
1 (BP86)	1.993	1.998	2.000	1.998

*$g_{iso} = (g_{xx} + g_{yy} + g_{zz})/3$

EPR *g*-values were estimated with BP86 and B3LYP functionals and IGLO-III basis set for all non-metallic atoms and TZVPP basis set for Co atoms. The zeroth-order regular approximation (ZORA) [51] implemented in the ORCA code were used in order to calculate EPR *g*-values.

DFT calculated g-values for Co(II) complex **1** are summarized in Table 3. These results are similar to those reported for low-spin octahedral Co(II) complexes [33,36,43,52].

4. Conclusions

Complex **1** was obtained in the reaction of the condensation product of 2-quinolinecarboxaldehyde and Girard's T reagent **(HL**Cl) with $Co(BF_4)_2 \cdot 6H_2O$ and NaN_3 in molar ratio 1 : 1 : 2 in methanol/acetonitrile mixture. The octahedral Co(II) complex (**1**) with three azido ligands in meridional alignment favors low-spin configuration and the magnetic moment very close to the spin-only value. In the reaction of **HL**Cl with $Co(BF_4)_2 \cdot 6H_2O$ and NaN_3 in molar ratio 1 : 1 : 4 in the same mixture of solvent, a dinuclear double end-on azido bridged Co(II) complex (**2**) was obtained in traces together with complex **1**. Octahedral surrounding around each of the two Co(II) centers in complex **2** consist of NNO coordinated deprotonated hydrazone ligand, one monodentate azido ligand and two azido bridging ligands.

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Scheme caption

Scheme 1. Synthesis of ligand **HL**Cl and complexes **1** and **2**.

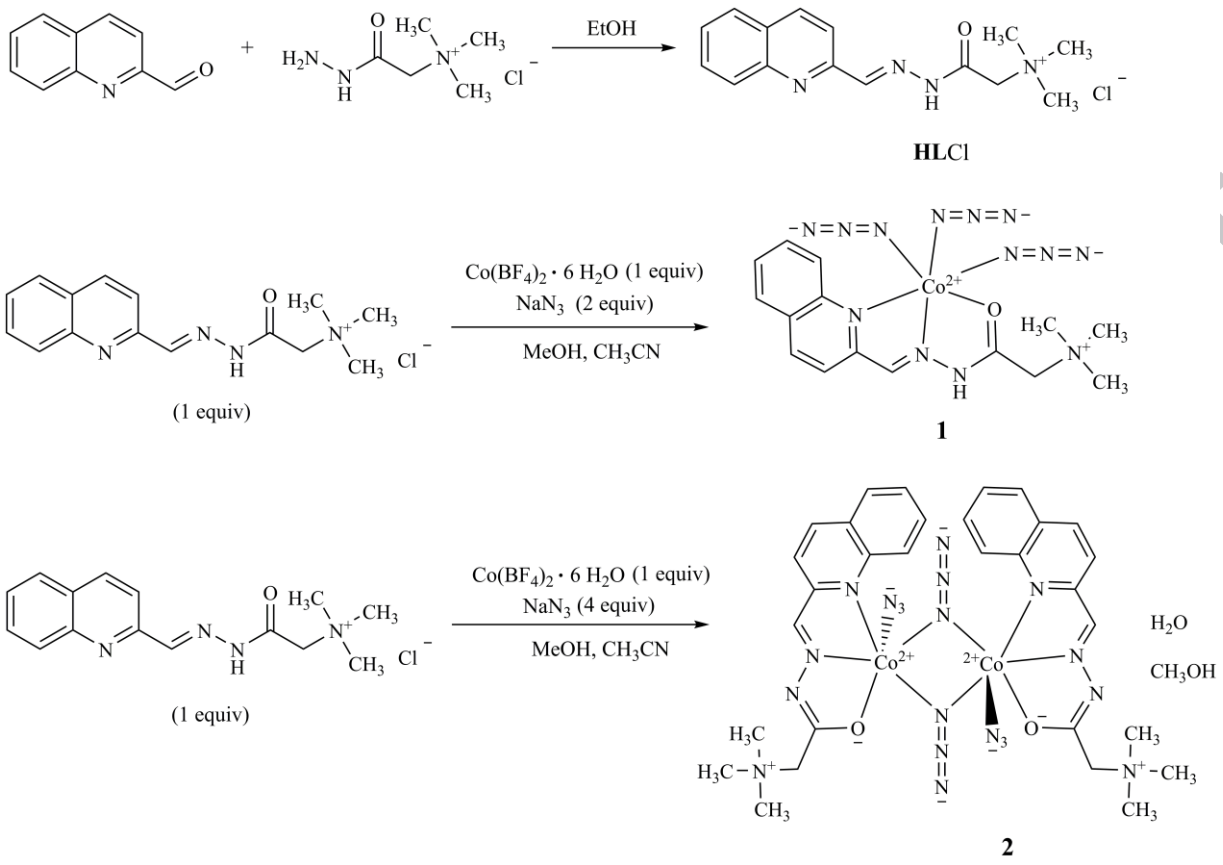
Figure caption

Fig. 1. Graphical representation of **1**.

Fig. 2. Graphical representation of **2**. Methanol and water molecules are omitted for clarity.

Fig. 3. Temperature dependence of χT and inverse magnetic susceptibility ($1/\chi$) per mole of complex **1**. Solid line is the fit to the Curie-Weiss law.

Fig. 4. Magnetic orbitals of complexes **1** (a) and **2** (b).



Scheme 1.

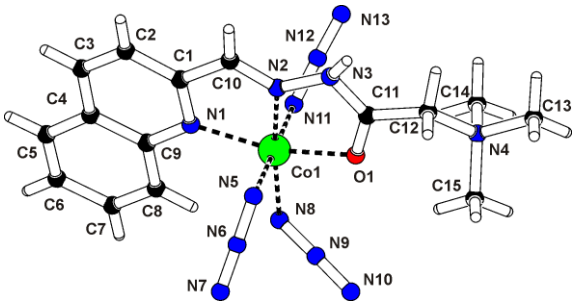


Fig. 1.

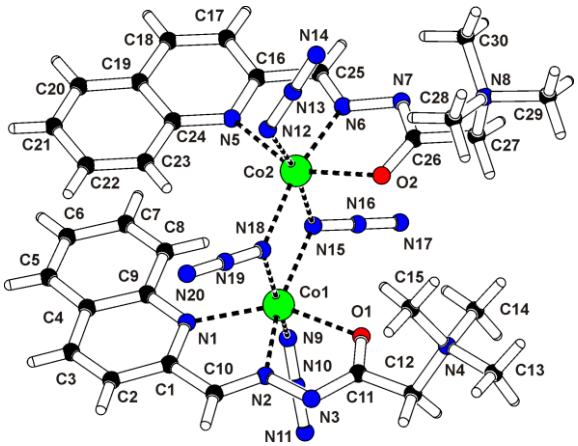


Fig. 2.

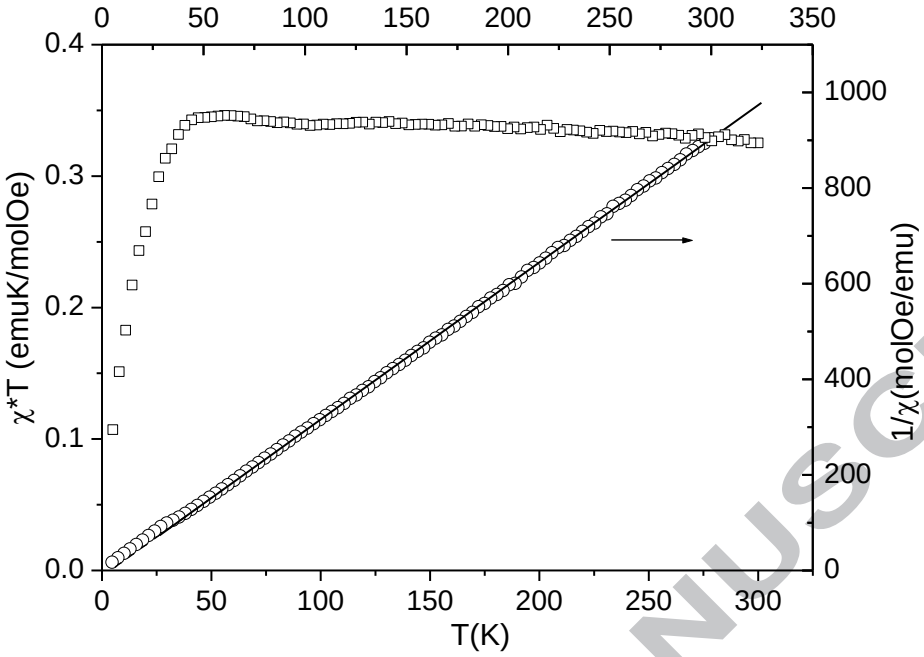


Fig. 3.

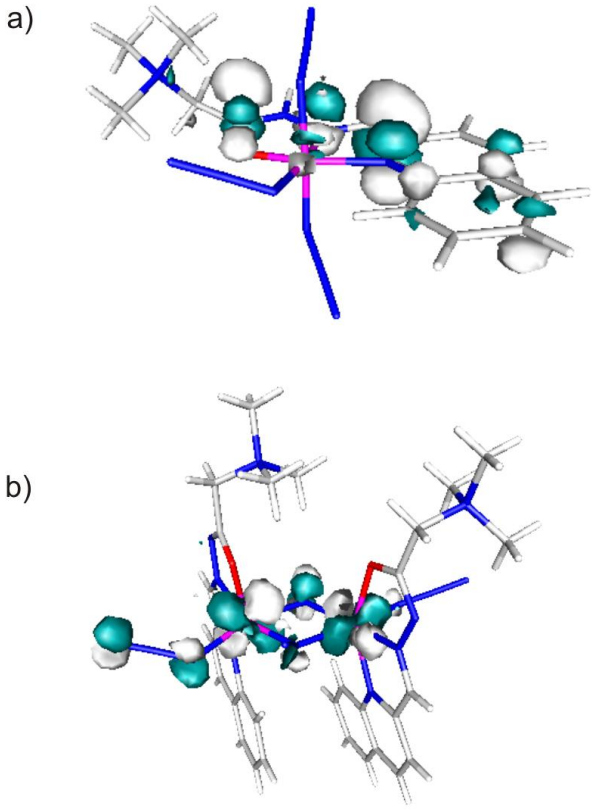
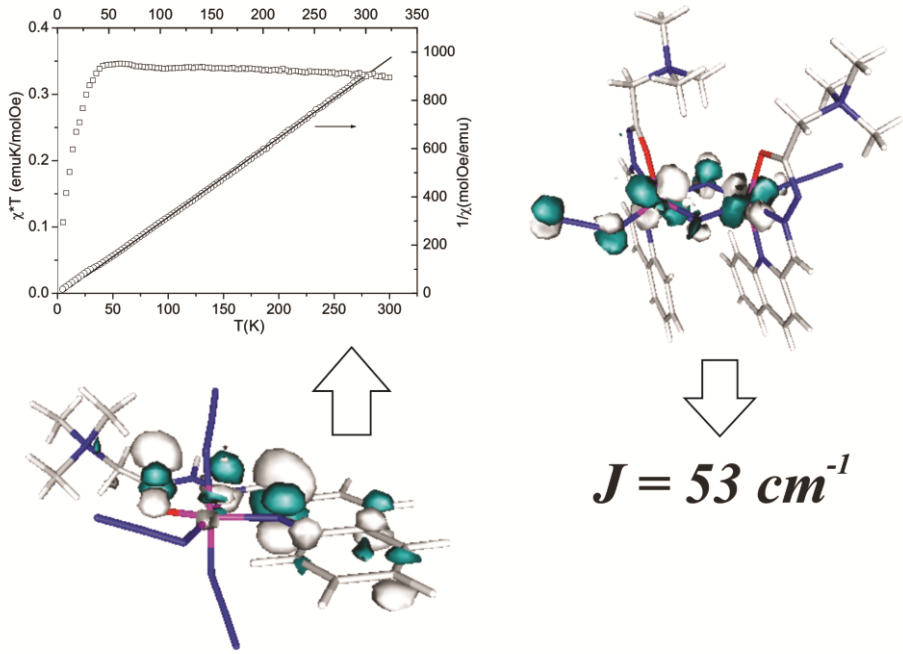


Fig. 4.



Crystal structures of mono- and dinuclear cobalt(II) azido complexes with the condensation product of 2-quinolinecarboxaldehyde and Girard's T reagent. DFT-BS explanation of ferromagnetic exchange coupling in dinuclear Co(II) complex. Magnetic properties of mononuclear Co(II) complex.