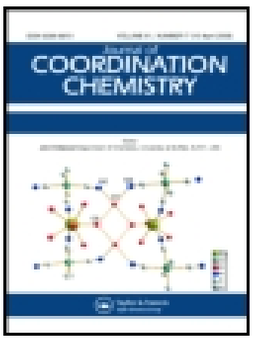

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Synthesis, crystal structures and antimicrobial activity of azido and isocyanato Zn(II) complexes with the condensation product of 2-quinolinecarboxaldehyde and Girard's T reagent

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Synthesis, crystal structures and antimicrobial activity of azido and isocyanato Zn(II) complexes with the condensation product of 2-quinolinecarboxaldehyde and Girard's T reagent

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Two Zn(II) complexes with the condensation product of 2-quinolinecarboxaldehyde and trimethylammonium acetohydrazide chloride (Girard's T reagent) (**HL**Cl) and monodentate pseudohalides (azide and cyanate) have been synthesized and characterized by elemental analysis, IR and NMR spectroscopy and single-crystal X-ray diffraction. In both complexes, the coordination surroundings of the Zn(II) ions consist of a deprotonated hydrazone ligand coordinated through an NNO set of donor atoms and two monodentate pseudohalides (N_3^- or NCO^-) at the remaining coordination sites. The Zn(II) complexes showed low to moderate activity against laboratory control strains of pathogenic bacteria and fungi.

Keywords: Zn(II) complexes; Hydrazones; Crystal structure; Antimicrobial activity; Pseudohalides

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1. Introduction

Pseudohalides (azide and cyanate) are versatile ligands which can be coordinated as monodentate species [1-3] or as bridges between metal centers [4-7]. The homoatomic azido ligand 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, $\mu_{1,1,2,2}$-N_3, and $\mu_{1,1,1,3,3,3}$-N_3 [8]. Cyanate as an ambidentate ligand exhibits linkage isomerism and may coordinate through nitrogen or oxygen donor atoms as a monodentate or bridging ligand (end-on $\mu_{1,1}$-κ_N and $\mu_{1,1}$-κ_O or end-to-end $\mu_{1,3}$) [9]. Zinc naturally occurs as the non-redox active divalent cation Zn(II). Due to its d^{10} electronic configuration, the Zn(II) ion has a zero ligand field stabilization energy, so the bonding energies and repulsions among the ligands determine the coordination geometry in its complexes [10]. Pseudohalide Zn(II) complexes attract attention due to their structural and luminescent properties [11-14]. Zinc, as one of the most important bio-elements, takes a significant part in metabolic pathways and regulation of gene expression [15]. A low concentration of Zn(II) ion is necessary for normal metabolism of bacteria, while at high concentration Zn(II) inhibits bacterial growth [16]. Schiff base complexes containing a quinoline pharmacophore showed significant antitumor and antimicrobial activity [17-21]. As a part of our investigations of hydrazone metal complexes with pseudohalide ligands [3, 22-28], we have previously synthesized and characterized a dinuclear end-on azido bridged Ni(II) complex with the condensation product of 2-quinolinecarboxaldehyde and trimethylammonium acetohydrazide chloride (Girard's T reagent) (**HL**Cl) [29]. In this study we extend our work to examine reactions of Zn(II) with the **HL**Cl ligand and pseudohalides (azide and cyanate). The mononuclear azido and isocyanato Zn(II) complexes obtained, *i.e.* [Zn**L**$(N_3)_2$] (**1**) and [Zn**L**$(NCO)_2$] (**2**), were structurally characterized and their antimicrobial activity was tested.

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). ^1H (500 MHz), ^{13}C (125 MHz) and 2-D NMR spectra of ligand **HL**Cl and Zn(II) complexes were recorded on a Bruker Avance 500 spectrometer at room temperature using TMS as internal standard in methanol−d^4 in the case of

HLCl and DMSO−d^6 in the case of Zn(II) complexes. Chemical shifts are expressed in ppm (δ) values and coupling constants (*J*) in Hz. Elemental analyses (C, H, and N) were performed by standard micro-methods using the ELEMENTARVario ELIII C.H.N.S.O analyzer.

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 (**HL**Cl)**.** The ligand **HL**Cl was synthesized in the reaction of 2-quinolinecarboxaldehyde and Girard's T reagent according to the previously described method [29]. IR and NMR spectra of **HL**Cl are given in the Supplementary Material.

2.2.2. Synthesis of diazido (E)-N,N,N-trimethyl-2-oxo-2-(2-(quinolin-2-ylmethylene)hydrazinyl)ethan-1-aminium zinc(II) complex ([ZnL(N_3)$_2$]) (1). The ligand **HL**Cl (92.0 mg, 0.30 mmol) was dissolved in methanol (30 mL) and solid $Zn(BF_4)_2{\cdot}6H_2O$ (104.1 mg, 0.30 mmol) was added. After complete dissolution of $Zn(BF_4)_2{\cdot}6H_2O$ in the reaction mixture, NaN_3 (39.0 mg, 0.60 mmol) was added. The reaction solution was stirred at room temperature for 4 h. After slow evaporation of solvent in a refrigerator (~ 4 °C) for 48 h, yellow crystals were obtained. Yield 39.7 mg (32%). Elemental analysis calcd for $C_{15}H_{18}N_{10}OZn$: C 42.92 %, H 4.32 %, N 33.37 %, found: C 43.03 %, H 4.56 %, N 33.35 %.

IR (cm^{-1}): 3310 (w), 3027 (w), 2939 (w), 2817 (w), 2169 (w), 2067 (s), 1923 (w), 1748 (w), 1645 (w), 1612 (w), 1566 (s), 1535 (s), 1398 (m), 1344 (w), 1300 (s), 1232 (w), 1125 (w), 1086 (s), 1032 (w), 972 (w), 925 (m), 873 (w), 833 (w), 785 (w), 757 (m), 632 (w), 589 (w). ^{1}H NMR (500 MHz, DMSO−d^6), (numbering of atoms according to scheme 1), δ (ppm) 3.28 (s, 9H, C12-H), 4.17 (s, 2H, C11-H), 8.38 (s, 1H, C9-H), 7.71 (d, 1H, $^3J_{C3\text{-}H/C4\text{-}H}$ = 10 Hz, C3-H), 8.09 (d, 1H, $^3J_{C3\text{-}H/C4\text{-}H}$ = 10 Hz, C4-H), 8.70 (d, 1H, $^3J_{C5\text{-}H/C6\text{-}H}$ = 10 Hz, C5-H), 7.91(m, 1H, C6-H), 7.91 (m, 1H, C7-H), 8.70 (d, 1H, $^3J_{C7\text{-}H/C8\text{-}H}$ = 10 Hz, C8-H). ^{13}C NMR (125 MHz, DMSO−d^6), (numbering of atoms according to scheme 1), δ (ppm) 53.5 (C12), 66.4 (C11), 128.04 (C9), 148.9 (C2), 128.3 (C3), 128.6 (C4), 129.3 (C4a), 140.5 (C5), 122.5 (C6), 131.7 (C7), 143.6 (C8), 145.4 (C8a), 172.5 (C10).

2.2.3. Synthesis of diisocyanato (E)-N,N,N-trimethyl-2-oxo-2-(2-(quinolin-2-

ylmethylene)hydrazinyl)ethan-1-aminium zinc(II) complex ([ZnL(NCO)$_2$]) (2). To a solution of **HL**Cl (92.0 mg, 0.30 mmol) in methanol (30 mL), solid $Zn(BF_4)_2 \cdot 6H_2O$ (104.1 mg, 0.30 mmol) was added. After complete dissolution of the zinc(II) salt in the reaction solution, NaOCN (78.0 mg, 1.20 mmol) was added. The reaction mixture was stirred for 3 h at room temperature. After slow evaporation of solvent in a refrigerator (~ 4 °C) for 48 h, yellow crystals were obtained. Yield 71.2 mg (56%). Elemental analysis calcd for $C_{17}H_{18}N_6O_3Zn$: C 48.64 %, H 4.32 %, 20.02 N %, found: C 48.73 %, H 4.47 %, N 19.98 %.

IR (cm^{-1}): 3536 (w), 3063 (w), 2966 (w), 2203 (s), 1611 (w), 1563 (m), 1530 (s), 1482 (w), 1400 (w), 1343 (w), 1305 (w), 1242 (w), 1203 (w), 1124 (w), 1080 (w), 1026 (w), 995 (w), 972 (w), 931 (w), 830 (w), 807 (w), 785 (w), 752 (w), 629 (w). ^{1}H NMR (500 MHz, DMSO−d^6), (numbering of atoms according to scheme 1), δ (ppm) 3.27 (s, 9H, C12-H), 4.15 (s, 2H, C11-H), 8.34 (s, 1H, C9-H), 7.71 (d, 1H, $^3J_{C3\text{-}H/C4\text{-}H}$ = 10 Hz, C3-H), 8.09 (d, 1H, $^3J_{C3\text{-}H/C4\text{-}H}$ = 10 Hz, C4-H), 8.66 (d, 1H, $^3J_{C5\text{-}H/C6\text{-}H}$ =10 Hz, C5-H), 7.91 (m, 1H, C6-H), 7.91 (m, 1H, C7-H), 8.66 (d, 1H, $^3J_{C7\text{-}H/C8\text{-}H}$ =10 Hz, C8-H). ^{13}C NMR (125 MHz, DMSO−d^6), (numbering of atoms according to scheme 1), δ (ppm) 53.5 (C12), 66.3 (C11), 127.5 (C9), 149.0 (C2), 127.9 (C3), 128.4 (C4), 125.4 (C4a), 140.0 (C5), 122.4 (C6), 131.7 (C7), 144.0 (C8), 145.5 (C8a), 172.3 (C10), 129.1 (OCN^-).

2.3. *Crystallographic structure determination*

The molecular structures of **1** and **2** were determined by single-crystal X-ray diffraction methods. Crystallographic data and refinement parameters of **1** and **2** are listed in table 1. The X−ray intensity data for all complexes were collected at room temperature with a Nonius Kappa CCD diffractometer with graphite-monochromated Mo−K_α radiation (λ = 0.71073 Å). The data were processed using DENZO-SMN [30]. The structures were solved by direct methods using SIR-92 [31] and refined by full-matrix least-squares based on F^2 with SHELXL-97 [32]. All non-hydrogen atoms were refined anisotropically. Hydrogens bonded to C9 in both structures were visible in the last stages of the refinement and were refined with the distance restraints (DFIX) with C–H = 0.98 Å and isotropic thermal parameters (1.2 times the thermal parameter of the attached carbon atom). All other C–H hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. ORTEP-3 for Windows was used to prepare drawings [33]. Crystallographic data for the structures have been deposited at the

Cambridge Crystallographic Data Centre as supplementary publication CCDC 1546080 and 1546081 for **1** and **2**, respectively. Copies of the structures can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif.

2.4. *Antimicrobial activity*

Antimicrobial activity was investigated against eight laboratory control strains of bacteria *i.e.*, Gram-positive: *Staphylococcus aureus* (ATCC 6538), *Enterococcus faecalis* (ATCC 29212), *Bacillus subtilis* (ATCC 6633); Gram-negative: *Escherichia coli* (ATCC 10536), *Klebsiella pneumoniae* (ATCC 13883), *Pseudomonas aeruginosa* (ATCC 9027), and *Salmonella enterica* subsp. *abony* (ATCC 6017) and one strain of yeast *Candida albicans* (ATCC 10231). In order to determine minimum inhibitory concentrations (MIC) of the tested compounds, a broth microdilution method was used according to Clinical and Laboratory Standards Institute guidelines CLSI (2016) [34] with some modifications. Tests were performed in Müller-Hinton broth for the bacterial strains and in Sabouraud dextrose broth for *Candida albicans*. The tested compounds were dissolved in 1% dimethyl sulfoxide (DMSO) and then diluted to the highest concentration. Twofold serial concentrations of the compounds were prepared in a 96-well microtiter plate (ranging from 62.5–1000 μg/mL) with addition of 0.05% 2,3,5-triphenyl-2*H*-tetrazolium chloride (TTC, Sigma-Aldrich, USA) as a growth indicator. All of the MIC determinations were performed in duplicate, and two positive growth controls were included (wells containing only the microorganisms in the broth). Each test was repeated three times. Identical MIC values were obtained in all experiments for a particular substance and strain.

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 synthesized in the reaction of 2-quinolinecarboxaldehyde and Girard's T reagent as described previously [29] and used for the synthesis of complexes $[Zn\mathbf{L}(N_3)_2]$ (**1**) and $[Zn\mathbf{L}(NCO)_2]$ (**2**) (scheme 1). Complex **1** was obtained in the reaction of **HL**Cl with $Zn(BF_4)_2{\cdot}6H_2O$ and NaN_3 in the molar ratio 1 : 1 : 2 in methanol. Reaction of **HL**Cl with $Zn(BF_4)_2{\cdot}6H_2O$ and NaOCN in the molar ratio 1 : 1 : 4 in methanol results in formation of **2**. In both complexes, the hydrazone ligand is coordinated in the deprotonated formally neutral,

zwitterionic form. Deprotonation of the ligand was facilitated by the presence of basic OCN^- and N_3^- anions in the reaction solution. In **1** and **2**, Zn(II) is five coordinate with quinoline nitrogen, azomethine nitrogen and carbonyl oxygen atoms from hydrazone ligands and two N-coordinated monodentate pseudohalide ligands.

3.2. *Spectroscopy*

3.2.1. IR spectra. IR spectra of **1** and **2** confirm coordination of the **HL**Cl ligand in the deprotonated α-oxyazine form. The new band at 1535 cm^{-1} in the spectrum of **1** and at 1530 cm^{-1} in the spectrum of **2**, corresponding to ν($^-$O–C=N) vibration of the deprotonated hydrazine moiety, appeared instead of the band of carbonyl group of non-coordinated hydrazonic form of **HL**Cl at 1699 cm^{-1}. In the IR spectrum of **1** a strong band at 2067 cm^{-1} corresponds to the vibration of coordinated azide ions. Coordination of cyanate ions in **2** was confirmed from the appearance of a strong band at 2203 cm^{-1} [35].

3.2.2. NMR spectra. The signal of a hydrazide NH is not observed in the ^{1}H NMR spectra of **1** and **2**, indicating that the ligand is coordinated in the deprotonated zwitterionic form. Coordination of the azomethine nitrogen in **1** and **2** can be confirmed from the position of the signal of proton C9-H (8.38 ppm in **1**, 8.34 ppm in **2**), which is shifted downfield in comparison with the corresponding signal in **HL**Cl at 8.17 ppm. The downfield shift of the carbonyl carbon (C10) from 167.0 ppm in the spectrum of **HL**Cl to 172.5 ppm and 172.3 ppm in the spectra of **1** and **2**, respectively, indicates coordination of the carbonyl oxygen atom. Coordination of the quinoline nitrogen atom results in the upfield shift of the C2 atom signal from 154.4 ppm in the spectrum of **HL**Cl to 148.9 ppm and 149.0 ppm in the spectra of **1** and **2**, respectively. The signal of the azomethine carbon atom (C9) at 146.9 ppm in the spectrum of **HL**Cl is shifted upfield in the spectra of **1** and **2** (127.5 ppm in spectrum of **1** and 128.0 in the spectrum of **2**). In the ^{13}C NMR spectrum of **2** the signal of a coordinated OCN^- ion was observed at 129.1 ppm which is in accord with the previously published ^{13}C NMR results for isocyanato complexes of Zn(II) [36].

3.3. *Description of the crystal structures*

Compounds **1** and **2** crystallize in the same space group $P2_1/c$ with almost the same lattice

parameters. The structures of both compounds are displayed in figures 1 and 2, respectively. Selected bond lengths and angles of **1** and **2** are given in table 2. The zinc(II) central ion is coordinated with a tridentate ligand **L** and with two N_3^- ligands in the case of **1** and two NCO^- ligands in the case of **2**. The tridentate ligand **L** is coordinated to the zinc ion with a NNO set of donor atoms forming two five-membered chelate rings. The largest deviation from the best plane that contained the condensed five-membered chelate rings is found for the carboxyl O1 atom in both **1** and **2**. The values are 0.08840(21) Å and 0.1197(15) Å out of the plane for **1** and **2**, respectively.

For five-coordinate complexes, the angular structural parameter (τ) is used to describe the degree of trigonality, within the structural continuum between trigonal bipyramidal and square based pyramidal geometry. The value of τ is defined by an equation represented by $\tau = (\beta - \alpha)/60$, where β is the greatest basal angle and α is the second greatest angle; τ is 0 for regular square based pyramidal geometry and 1 for regular trigonal bipyramidal geometry [37]. The τ values for **1** and **2** of 0.31 and 0.34, respectively, indicate that the Zn(II) ion has a distorted square based pyramidal coordination geometry. In **1** and **2**, the Zn(II) ion is lifted out of the plane of the four in-plane ligand atoms (N1, N2, N5 and O1) by a distance ρ of 0.6165(5) and 0.6462(4) Å, respectively (table 3). The angular structural parameters (τ) of **1** and **2** have been compared with those of structurally related five-coordinate Zn(II) complexes with Schiff base ligands (table 3). In complexes **3**-**8** [38-42], Schiff base ligands are coordinated to Zn(II) ion through an NNO set of donor atoms forming two fused five-membered chelate rings. The other two coordination sites are supplemented by monodentate ligands (Cl^-, Br^- or DMSO). All five-coordinate Zn(II) complexes which have been considered here adopt a distorted square based pyramidal coordination geometry, as indicated by τ values ranging from 0.13 to 0.40. The greatest trigonal distortion from the square based pyramidal coordination geometry was observed for **3** [38] in which two coordination sites are occupied by Cl^- anions. For this complex the parameter τ is 0.40. The smallest parameter τ of 0.13 is calculated for **8** [41] which also includes two Cl^- anions in the coordination sphere. In **1**-**8**, the greatest basal angle (β), that is, $N_{heteroaromatic}$–Zn–O_{amide} spans the range from 143.18(9) to 149.56(7)°, while the second greatest angle (α), that is, N_{imine}–Zn–X (X = monodentate ligand) covers the range from 123.36(5) to 135.35(8)°.

In the crystal structures of **1** and **2**, quinoline rings are involved in intermolecular π–π interactions around the center of inversion at ½, 0, ½. The distances between the centers of gravity of the pyridine fragments are 3.381(2) and 3.420(2) Å, with a slippage of 0.553 and 0.655 Å, for **1** and **2**, respectively. The centers of gravity of pyridine and arene fragments are separated by 4.089(3) and 3.980(2) Å in **1** and **2**, respectively.

3.4. *Antimicrobial activity*

In vitro antimicrobial activity of **HL**Cl ligand, Zn(II) complexes **1** and **2**, and previously reported dinuclear azido bridged Ni(II) complex with **HL**Cl [29], was examined against laboratory control strains of Gram-positive and Gram-negative bacteria and one strain of yeast *C. albicans*. The results (table 4) indicated that the investigated complexes were less active than the standard drugs. The dinuclear azido bridged Ni(II) complex with **HL**Cl was inactive against the tested bacterial strains and showed activity only against *C. albicans* (MIC value 0.571 mM). **HL**Cl showed noteworthy activity only against *E. faecalis*. Complexes **1** and **2** showed low to moderate antimicrobial activity. The best activity of **1** and **2** was observed against *B. subtilis* and *K. pneumoniae* (0.148 mM). Complex **2** showed better activity than **1** against most of the tested microbial strains. With the exception of the case of *S. aureus*, the activity of **2** was better than the activity of Zn(II) salt, NaOCN and **HL**Cl. A literature survey shows that complexation with ligands frequently improves antimicrobial activity of Zn(II) ion. Previously reported results indicate that antimicrobial activity of Zn(II) complexes depends on their liphophilicity, stability, steric and electronic properties, which are determined by the nature of coordinated ligand [28, 43-45].

4. Conclusion

The synthesized Zn(II) complexes contain a common tridentate ligand, the condensation product of 2-quinolinecarboxaldehyde and trimethylammonium acetohydrazide chloride (Girard's T reagent), coordinated in the deprotonated zwitterionic form via quinoline nitrogen, imine nitrogen and carbonyl oxygen atoms and two monodentate pseudohalides (azide or cyanate) in the remaining two coordination sites. The investigated Zn(II) complexes showed low to moderate antimicrobial activity against a range of Gram-positive and Gram-negative bacteria and one strain of yeast *C. albicans*.

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

	1	**2**
Formula	$C_{15}H_{18}N_{10}OZn$	$C_{17}H_{18}N_6O_3Zn$
Fw (g mol^{-1})	419.76	419.74
Crystal size (mm)	0.20 × 0.10 × 0.05	0.10 × 0.10 × 0.05
Crystal color	Yellow	Yellow
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	7.9427(2)	8.2977(2)
b (Å)	22.0751(9)	21.6627(4)
c (Å)	10.7922(4)	10.8121(3)
β (°)	98.681(2)	99.1360(10)
V (Å^3)	1870.58(11)	1918.83(8)
Z	4	4
Calcd density (g cm^{-3})	1.491	1.453
F(000)	864	864
No. of collected reflns	8122	8342
No. of independent reflns	4206	4363
R_{int}	0.0194	0.0332
No. of reflns observed	2773	2699
No. parameters	250	250
$R[I > 2\sigma(I)]^a$	0.0549	0.0434
wR_2 (all data)^b	0.1753	0.1090
Goof, S^c	1.030	1.017
Max/min residual electron density (e Å^{-3})	+0.86/–0.52	+0.26/–0.24

[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.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Zn1–N1	2.298(4)	Zn1–N1	2.344(2)
Zn1–N2	2.049(3)	Zn1–N2	2.051(2)
Zn1–N5	1.975(4)	Zn1–N5	1.931(2)
Zn1–N8	1.982(5)	Zn1–N6	1.935(3)
Zn1–O1	2.204(3)	Zn1–O1	2.197(2)
N2–N3	1.369(4)	N2–N3	1.380(3)
N2–C9	1.265(5)	N2–C9	1.274(3)
O1–Zn1–N1	147.68(10)	O1–Zn1–N1	146.98(8)
O1–Zn1–N2	73.47(11)	O1–Zn1–N2	73.79(8)
O1–Zn1–N5	98.70(15)	O1–Zn1–N5	100.60(9)
O1–Zn1–N8	98.8(2)	O1–Zn1–N6	98.32(12)
N5–Zn1–N8	111.9(2)	N5–Zn1–N6	117.64(13)
N5–N6–N7	176.3(4)	N5–C15–O2	178.2(4)
N8–N9–N10	173.0(8)	N6–C16–O3	176.4(5)

Table 3. Structural parameters correlating coordination geometry of structurally related five-coordinated Zn(II) complexes.

Complex	β (°)	α (°)	τ	ρ (Å)	References
[Zn**L**$(N_3)_2$] (**1**)	147.68(10)	129.4(2)	0.31	0.6165(5)	This work
[Zn**L**$(NCO)_2$] (**2**)	146.98(8)	126.41(10)	0.34	0.6462(4)	This work
[Zn(L^2)Cl_2]·0.5H_2O[a] (**3**)	147.07(6)	123.36(5)	0.40	0.6453(3)	[38]
[Zn(L^3)Cl_2][b] (**4**)	146.03(7)	126.09(5)	0.33	0.6715(2)	[39]
[Zn(L^4)Br_2][c] (**5**)	146.06(9)	129.81(8)	0.27	0.6677(4)	[40]
[Zn(L^5)Cl(DMSO)][d] (**6**)	149.56(7)	134.73(6)	0.25	0.5025(3)	[41]
[Zn(L^6)Cl_2][e] (**7**)	144.88(7)	133.36(6)	0.19	0.6438(3)	[42]
[Zn(L^7)Cl_2][f] (**8**)	143.18(9)	135.35(8)	0.13	0.6503(4)	[41]

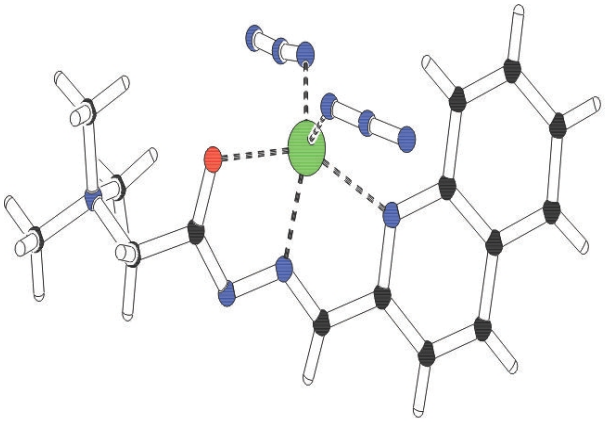
[a] L^2 = 2-hydroxyimino-*N*′-[1-(2-pyridyl)ethylidene]propanohydrazide;
[b] L^3 = (*E*)-4-(dimethylamino)-*N*′-(pyridin-2-ylmethylene)benzohydrazide;
[c] L^4 = di-2-pyridyl ketone N^4-phenyl-3-semicarbazone;
[d] L^5 = 2-formylpyridine-*para*-nitro-phenyl hydrazone;
[e] L^6 = 2-formylpyridine isonicotinoyl hydrazone;
[f] L^7 = 2-formylpyridine-*para*-chloro-phenyl hydrazone

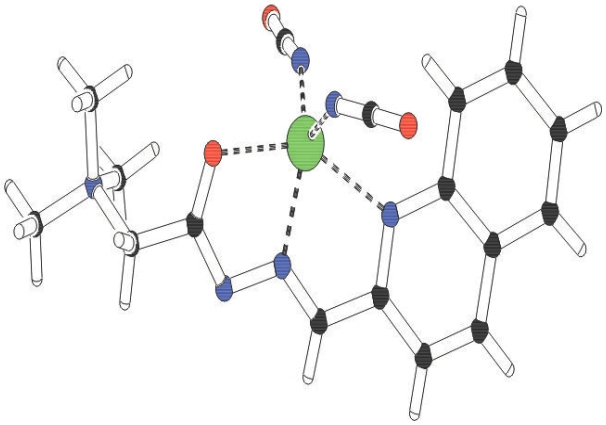
Table 4. Antimicrobial activity of investigated compounds.

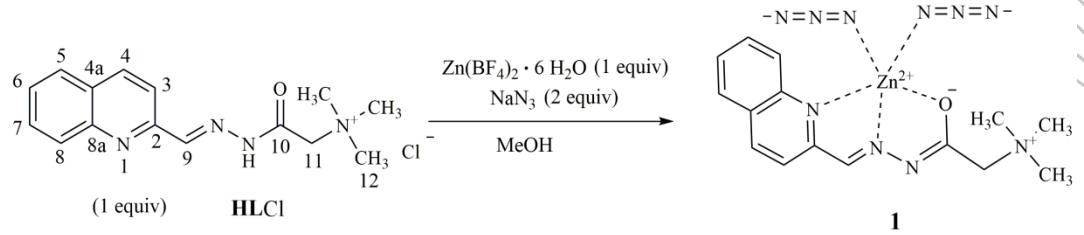
Microorganisms	MIC (mM)									
	HLCl	$Zn(BF_4)_2 \cdot 6H_2O$	NaN_3	NaOCN	**1**	**2**	meropenem*	amikacin*	ampicillin*	amphotericin*
S. aureus ATCC 6538	1.630	0.180	3.846	>15.385	1.191	0.297	0.004	0.005	0.008	n.t.
E. faecalis ATCC 29212	0.407	0.360	0.961	15.385	1.191	0.297	0.003	0.005	0.002	n.t.
B. subtilis ATCC 6633	3.260	0.360	0.961	>15.385	0.148	0.148	0.005	n.t.	0.003	n.t.
E. coli ATCC 10536	>3.260	2.881	3.846	>15.385	0.297	0.148	0.006	0.004	0.010	n.t.
K. pneumoniae ATCC13883	1.630	1.440	1.923	>15.385	0.148	0.148	0.008	0.006	0.012	n.t.
P. aeruginosa ATCC 9027	>3.260	>2.881	7.692	>15.385	1.191	2.382	0.010	0.009	n.t.	n.t.
S. enterica ATCC 6017	>3.260	0.720	3.846	>15.385	1.191	0.297	0.006	0.008	0.014	n.t.
C. albicans ATCC 10231	>3.260	>2.881	0.961	>15.385	1.191	0.297	n.t.	n.t.	n.t.	0.0005

n.t. not tested

* reference antimicrobial drugs

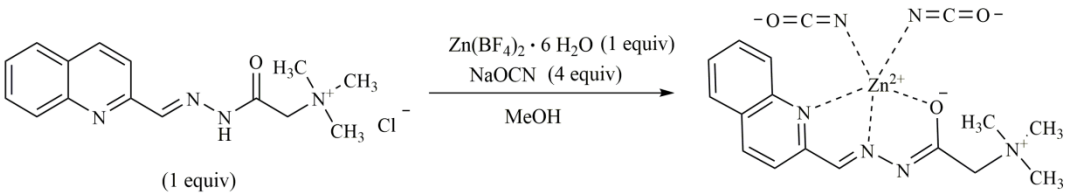






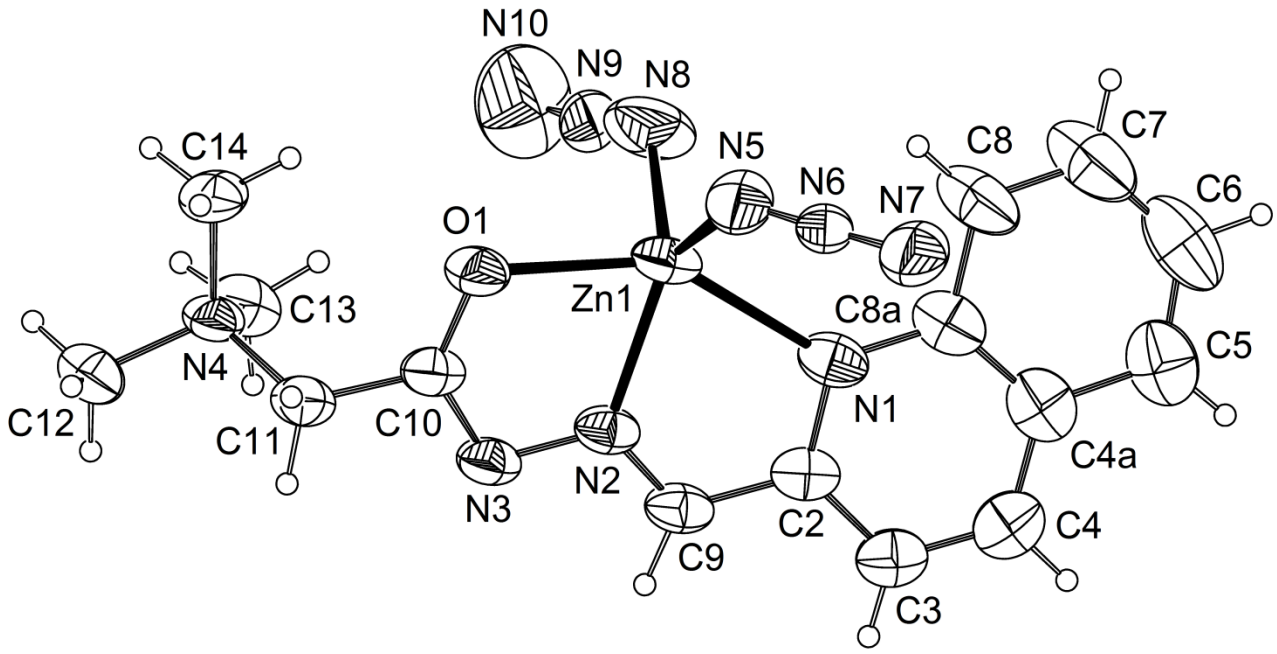
(1 equiv) **HL**Cl

1



(1 equiv)

2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N9
N8
C14
N5
C8
C7
N6
N7
C6
O1
Zn1
C13
C8a
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N4
N1
C12
C11
C10
C4a
N2
N3
C2
C4
C9
C3