Scientific paper

Syntheses, Crystal Structures, and Antibacterial Activity of New Tetranuclear Zinc(II) Complexes with Schiff Base Ligands

Heng-Yu Qian

Key Laboratory of Surface & Interface Science of Henan, School of Material & Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou, 450002 P.R. China

* Corresponding author: E-mail: hengyu_qian@126.com

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Abstract

Two new tetranuclear zinc(II) complexes, \([\text{Zn}_4(L^1)_2(\mu_2-\eta^1-\text{CH}_3\text{COO})_4(\mu_{1,1}-\text{N}_3)_2]\) (1) and \([\text{Zn}_4(L^2)_4(\text{CH}_3\text{CH}_2\text{OH})(\text{H}_2\text{O})]\) (2), where \(L^1\) and \(L^2\) are the deprotonated forms of 4-fluoro-2-((pyridin-2-ylmethylimino)methyl)phenol (HL\(^1\)) and 4-fluoro-2-((2-(hydroxymethyl)phenylimino)methyl)phenol (HL\(^2\)), have been synthesized and characterized by elemental analysis, IR and UV-vis spectroscopy, and single crystal X-ray diffraction. X-ray crystal structural study indicated that the distances between the adjacent Zn atoms are 3.160(1)–3.353(1) Å in 1 and 3.005(1)–3.168(1) Å in 2. All zinc atoms in 1 are pentacoordinated in trigonal bipyramidal geometry, and those in 2 are in square pyramidal and octahedral geometry. The complexes and the Schiff bases were assayed for antibacterial activities against three Gram-positive bacterial strains (\(B.\) subtilis, \(S.\) aureus, and \(S t.\) faecalis) and three Gram-negative bacterial strains (\(E.\) coli, \(P .\) aeruginosa, and \(E.\) cloacae) by MTT method.

Keywords: Tridentate Schiff base; crystal structure; zinc complex; tetranuclear structure; antibacterial property

1. Introduction

Zinc is an important element for biological processes of human beings.\(^1\) However, the mechanism of action of zinc in physiology and pathology are poorly understood. Zinc is also an essential cofactor in six classes of enzymes as well as in several families of regulatory proteins.\(^2\) Its importance in DNA synthesis, control of gene expression, and induction of cell apoptosis is becoming better understood.\(^3\) Schiff bases derived from substituted salicylaldehyde with various organic amines are important ligands in coordination chemistry,\(^4\) and show various biological properties such as antitumor,\(^5\) antibacterial,\(^6\) anti-fungi,\(^7\) and enzyme inhibition.\(^8\) It was reported that the compounds containing one or more halo-atoms on the aromatic ring have improved biological properties, especially for the antibacterial activities.\(^9\) Rai \textit{et al}. reported a series of fluoro, chloro, bromo and iodo-substituted compounds, and found that they have significant antimicrobial activities.\(^10\) Acetate, azide anions and the phenolate group of Schiff base ligands usually act as flexible bridging ligands, which bind different metal atoms to form interesting polymeric structures.\(^11\) In the present work, two new tetranuclear zinc(II) complexes, \([\text{Zn}_4(L^1)_2(\mu_2-\eta^1-\text{CH}_3\text{COO})_4(\mu_{1,1}-\text{N}_3)_2]\) (1) and \([\text{Zn}_4(L^2)_4(\text{CH}_3\text{CH}_2\text{OH})(\text{H}_2\text{O})]\) (2), where \(L^1\) and \(L^2\) are the deprotonated forms of 4-fluoro-2-((pyridin-2-ylmethylimino)methyl)phenol (HL\(^1\)); Scheme 1, left) and 4-fluoro-2-((2-(hydroxymethyl)phenylimino)methyl)phenol (HL\(^2\)); Scheme 1, right), is reported.

![Scheme 1. The Schiff base ligands.](image)

2. Experimental

2.1. Material and Measurements

All chemical reagents and solvents were of analytical grade and were obtained from Sigma-Aldrich. Elemental analyses were performed on a Perkin-Elmer 2400 II elemental analyzer. Infrared spectra were recorded on a Per-
kin-Elmer RX I FT-IR spectrophotometer with KBr discs. Electronic spectra were obtained with Lambda 35 spectrophotometer.

2. 2. Synthesis of the Schiff Bases

The Schiff bases HL\textsuperscript{1} and H\textsubscript{2}L\textsubscript{2} were synthesized by refluxing hot ethanolic solution (30 mL) of 5-fluorosalicylaldehyde (0.002 mol, 0.280 g) with 2-aminomethylpyridine (0.002 mol, 0.216 g) and 2-aminophenylmethanol, respectively, for 1 h. The precipitate formed during reflux was filtered, washed with cold EtOH, and recrystallized from hot EtOH.

HL\textsuperscript{1}: Yield 77%. Anal. Calcd. for C\textsubscript{13}H\textsubscript{11}FN\textsubscript{2}O: C 67.82, H 4.93, N 12.17. Found: C 67.71, H 4.82, N 12.26. IR data (KBr, cm\textsuperscript{-1}): 3641, 1609, 1536, 1513, 1473, 1438, 1387, 1355, 1321, 1257, 1201, 1141, 1034, 955, 870, 795, 767, 716, 667, 626, 575, 535, 466. UV-Vis data in ethanol [\(\lambda_{\text{max}}\) (nm), \(\varepsilon\) (L mol\textsuperscript{-1} cm\textsuperscript{-1})]: 230, 1930; 250, 14570; 280, 17530; 300, 18150; 380, 7637.

H\textsubscript{2}L\textsubscript{2}: Yield 83%. Anal. Calcd. for C\textsubscript{14}H\textsubscript{12}FNO\textsubscript{2}: 1.713 1.511

2. 3. Synthesis of the Zn(II) Complex 1

An ethanolic solution (20 mL) of HL\textsuperscript{1} (0.20 mmol, 0.046 g) was mixed with an ethanolic solution (30 mL) of Zn(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O (0.50 mmol, 0.11 g) and an aqueous solution (1 mL) of sodium azide (0.20 mmol, 0.013 g), and refluxed in a water bath for 1 h. The separated complex was filtered, washed thoroughly with water, ethanol, ether, and finally dried in a vacuum over fused CaCl\textsubscript{2}. Yield 43%. Anal. Calcd. for C\textsubscript{34}H\textsubscript{32}F\textsubscript{2}N\textsubscript{10}O\textsubscript{10}Zn\textsubscript{4}: C 39.26, H 3.10, N 13.46. Found: C 39.05, H 3.18, N 13.33. IR data (KBr, cm\textsuperscript{-1}): 2080, 1640, 1598, 1480, 1437, 1395, 1289, 1213, 1154, 1044, 874, 815, 769, 667, 626, 575, 535, 466. UV-Vis data in ethanol [\(\lambda_{\text{max}}\) (nm), \(\varepsilon\) (L mol\textsuperscript{-1} cm\textsuperscript{-1})]: 232, 19150; 250, 14220; 347, 13150.

2. 4. Synthesis of the Zn(II) Complex 2

An ethanolic solution (20 mL) of H\textsubscript{2}L\textsubscript{2} (0.20 mmol, 0.049 g) was mixed with an ethanolic solution (30 mL) of Zn(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O (0.50 mmol, 110 mg) and refluxed in a water bath for 1 h. The separated complex was filtered, washed thoroughly with water, ethanol, ether, and finally dried in a vacuum over fused CaCl\textsubscript{2}. Yield 56%. Anal. Calcd. for C\textsubscript{58}H\textsubscript{48}F\textsubscript{4}N\textsubscript{4}O\textsubscript{10}Zn\textsubscript{4}: C 53.64, H 3.73, N 4.31. Found: C 53.45, H 3.91, N 4.25. IR data (KBr, cm\textsuperscript{-1}): 3641, 1609, 1536, 1460, 1382, 1306, 1241, 1198, 1139, 1026, 979, 874, 816, 752, 763, 624, 564, 513, 443. UV-Vis data in ethanol [\(\lambda_{\text{max}}\) (nm), \(\varepsilon\) (L mol\textsuperscript{-1} cm\textsuperscript{-1})]: 238, 17270; 281, 11450; 399, 8760. A small amount of the complex was recrystallized from ethanol, affording colorless single crystals suitable for X-ray analysis.

2. 5. Single Crystal X-Ray Diffraction

X-ray data for the complexes were collected on a Bruker APEX II diffractometer equipped with graphite-monochromated Mo K\textalpha radiation (\(\lambda = 0.71073 \text{ Å}\)). A preliminary orientation matrix and cell parameters were determined from three sets of \(\omega\) scans at different starting angles. Data frames were obtained at scan intervals of 0.5\(^\circ\) with an exposure time of 10 s frame\textsuperscript{-1}. The reflection data were corrected for Lorentz and polarization factors. Absorption corrections were carried out using SADABS. The structures of the complexes were solved by direct method and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-H atoms with the SHELXTL.\textsuperscript{12} All H atoms were calculated at idealized positions and refined with the riding models. Crystallographic data for the complexes are summarized in Table 1.

Table 1. Crystal and refinement data for the complexes

| Parameter | 1 | 2 |
|-----------|---|---|
| Empirical formula | C\textsubscript{34}H\textsubscript{32}F\textsubscript{2}N\textsubscript{10}O\textsubscript{10}Zn\textsubscript{4} | C\textsubscript{58}H\textsubscript{48}F\textsubscript{4}N\textsubscript{4}O\textsubscript{10}Zn\textsubscript{4} |
| Formula weight | 1040.2 | 1298.5 |
| Crystal size (mm) | 0.20 × 0.20 × 0.15 | 0.16 × 0.15 × 0.15 |
| Temperature (°C) | 298(2) | 298(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | triclinic | triclinic |
| Space group | P \(\bar{T}\) | P \(\bar{T}\) |
| \(a\) (Å) | 8.4606(9) | 14.0120(11) |
| \(b\) (Å) | 10.8780(11) | 14.1500(10) |
| \(c\) (Å) | 11.0332(11) | 15.1470(10) |
| \(\alpha\) (°) | 84.734(2) | 101.189(1) |
| \(\beta\) (°) | 86.041(2) | 103.022(1) |
| \(\gamma\) (°) | 88.243(2) | 93.211(1) |
| \(V\) (Å\textsuperscript{3}) | 1008.43(18) | 2854.7(4) |
| \(Z\) | 1 | 2 |
| \(D\textsubscript{calc}\) (g cm\textsuperscript{-3}) | 1.713 | 1.511 |
| \(\mu\) (Mo K\textalpha\textsuperscript{1}) (mm\textsuperscript{-1}) | 2.427 | 1.734 |
| F(000) | 524 | 1320 |
| Number of measured reflections | 9913 | 15426 |
| Number of observations | 3748 | 9251 |
| \((I > 2\sigma(I))\) \(a\) | 3175 | 5361 |
| Unique reflections | 273 | 722 |
| Parameters | | |
| Number of restraints | 0 | 0 |
| \(R\textsubscript{1}, wR\textsubscript{2}\) (all data) \(a\) | 0.0273, 0.0641 | 0.0640, 0.1841 |
| \(R\textsubscript{1}, wR\textsubscript{2}\) (all data) \(a\) | 0.0360, 0.0687 | 0.1182, 0.2252 |
| Goodness of fit of \(F^2\) | 1.034 | 1.013 |

\(a\) \(R\textsubscript{1} = \sum||F_o|| - ||F_c||/\sum||F_o||, wR\textsubscript{2} = \sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{1/2}\).
2.5. Antibacterial Activity

Antibacterial activity of the Schiff base ligands and the complexes was tested against *B. subtilis*, *S. aureus*, *S. faecalis*, *P. aeruginosa*, *E. coli*, and *E. cloacae* using MTT medium. The minimum inhibitory concentrations (MICs) of the compounds were determined by a colorimetric method using MTT dye. A stock solution of the compounds (50 μg mL⁻¹) in DMSO was prepared and quantities of the compounds were incorporated in specified quantity of sterilized liquid medium. A specified quantity of the medium containing the compounds was poured into micro-titration plates. Suspension of the microorganism was prepared to contain approximately 10⁵ cfu mL⁻¹ and applied to micro-titration plates with serially diluted compounds in DMSO to be tested, and incubated at 37 °C for 24 h for bacteria. After the MICs were visually determined on each micro-titration plate, 50 μL of phosphate buffered saline (PBS 0.01 mol L⁻¹, pH 7.4: Na₂HPO₄·2H₂O 2.9 g, KH₂PO₄ 0.2 g, NaCl 8.0 g, KCl 0.2 g, distilled water 1000 mL) containing 2 mg mL⁻¹ of MTT was added to each well. Incubation was continued at room temperature for 4–5 h. The content of each well was removed, and 100 μL of isopropanol containing 5% 1 mol L⁻¹ HCl was added to extract the dye. After 12 h of incubation at room temperature, the optical density (OD) was measured with a microplate reader at 570 nm.

3. Results and Discussion

3.1. Synthesis of the complexes

Complex 1 was prepared by the reaction of 4-fluoro-2-((pyridin-2-yl)methyl)imino)methyl)phenol, zinc acetate and sodium azide in methanol, and complex 2 was prepared by the reaction of 4-fluoro-2-(2-(hydroxymethyl)phenylimino)methyl)phenol and zinc acetate in methanol. When compared with the zinc complexes with similar Schiff base ligands but different zinc salts, we found that the acetate and azide ligands are interesting bridging groups, which are readily participate in the construction of polynuclear complexes.

3.2. Crystal Structure Description of Complex 1

The molecular structure of complex 1 is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. The complex is a phenolate oxygen, nitrate, and end-on azide co-bridged tetranuclear zinc(II) species, with a crystallographic inversion center symmetry. The inversion center is located at the midpoint of the Zn2 and Zn2A atoms (symmetry code for A: −x, 1 − y, 1 − z). Zn2 forms distances of 3.160(1) and 3.353(1) Å, respectively, with Zn1 and Zn2A. All the zinc atoms are penta-coordinated in trigonal bipyramidal geometry. For the outer zinc atoms, Zn1 and Zn1A, the equatorial plane is defined by the imino nitrogen (N1) of the Schiff base ligand, and two ac etate oxygen (O3, O5), and the axial positions are defined by the phenolate oxygen (O1) and pyridine nitrogen (N2) of the Schiff base ligand. For the inner zinc atoms, Zn2 and Zn2A, the equatorial plane is defined by the phenolate oxygen (O1), one acetate oxygen (O4), and one azide nitrogen (N3A), and the axial positions are defined by one acetate oxygen (O2) and one azide nitrogen (N3). The trigonal bipyramidal coordination is distorted, which can be observed from the bond angles related to the zinc atoms. The bond angles of the equatorial planes range from 112.70(8) to 125.55(8)º for Zn1 and from 108.97(7) to 131.25(9)º for Zn2. In addition, the perpendicular angles are 166.31(7)º for Zn1 and 169.41(7)º for Zn2. The coordination bond lengths are also deviate from the ideal values of trigonal bipyramidal geometry, but they are within normal values as compared to other Schiff base zinc(II) complexes. Zn1 and Zn2 atoms deviate from the best coordination planes defined by the equatorial donor atoms by 0.120(1) Å and 0.155(1) Å, respectively.

The question arises as to whether the coordination polyhedra around the five-coordinated zinc atoms can be described as distorted square pyramid or distorted trigonal bipyramid. Further information can be obtained by determining the relative amount of trigonality (square pyramid, τ = 0; trigonal bipyramid, τ = 1); τ = (β − α)/60º, α and β being the two largest angles around the central atom. The values of τ are 0.68 for Zn1 and 0.636 for Zn2. Therefore, the coordination geometries of the zinc atoms in the complex are best described as severely distorted trigonal bipyramids, instead of square pyramids.

In the crystal structure of the complex, the tetranuclear zinc complex molecules are linked through C8–H8A···O3 hydrogen bonds (Table 3), to form 1D chains along the b axis (Fig. 2).

3.3. Crystal Structure Description of Complex 2

The molecular structure of complex 2 is shown in Fig. 3. Selected bond lengths and angles are listed in Table 2. The complex is a hydroxyl oxygen bridged tetranuclear zinc(II) species. The distances among the Zn atoms are in the range 3.005(1)–3.168(1) Å. The Zn1 and Zn2 atoms are penta-coordinated in square pyramidal geometry, as evidenced by the τ values of 0.38 for Zn1 and 0.40 for Zn2. The basal planes are defined by the phenolate oxygen (O5 for Zn1, O3 for Zn2), imino nitrogen (N3 for Zn1, N2 for Zn2) and hydroxyl oxygen (O6 for Zn1, O4 for Zn2) of one Schiff base ligand, and the hydroxyl oxygen (O8 for Zn1, O2 for Zn2) of another Schiff base ligand. The apical positions are occupied by the hydroxyl oxygen (O4 for Zn1, O8 for Zn2). The Zn1 and Zn2 atoms deviate from the basal planes by 0.415(2) and 0.353(2) Å, respectively. The square pyramidal coordination is distorted, which can
Table 2. Selected bond lengths (Å) and angles (º) for the complexes

|   | Zn1–O1  | 2.048(16) | Zn1–N1  | 2.055(2) |
|---|---------|-----------|---------|----------|
| Zn1–O3  | 1.986(17) | Zn1–N2  | 2.132(19) |
| Zn1–O5  | 1.991(18) | Zn2–O1  | 1.986(17) |
| Zn2–O4  | 1.970(19) | Zn2–N3A | 1.986(2) |
| Zn2–O2  | 2.070(19) | Zn3–O9  | 1.954(2) |
| O3–Zn1–O5 | 112.70(8) | O3–Zn1–O1 | 95.44(7) |
| O5–Zn1–O1 | 97.75(7)  | O3–Zn1–N1 | 125.55(8) |
| O5–Zn1–N1 | 120.69(8) | O1–Zn1–N1 | 87.67(7)  |
| O3–Zn1–N2 | 91.47(7)  | O5–Zn1–N2 | 90.43(7)  |
| O1–Zn1–N2 | 166.31(7) | N1–Zn1–N2 | 78.70(8)  |
| O4–Zn2–O1 | 108.97(7) | O4–Zn2–N3A | 117.91(9) |
| O1–Zn2–N3A | 92.95(7)  | O4–Zn2–O2 | 99.14(8)  |
| O1–Zn2–O2 | 92.32(7)  | N3A–Zn2–O2 | 92.81(8)  |
| O4–Zn2–N3 | 88.25(9)  | O1–Zn2–N3 | 92.42(8)  |
| N3–Zn2–N3A | 76.96(9)  | O2–Zn2–N3 | 169.41(7) |

Table 3. Hydrogen bond distances (Å) and bond angles (º) for the complexes

| D–H···A  | d(D–H)  | d(H···A)  | d(D···A)  | Angle (D–H···A)  |
|---------|---------|-----------|-----------|-----------------|
| O8–H8A···O3  | 0.97  | 2.54  | 3.381(2)  | 145(3)  |
| O21–H21···F1ii | 0.93 | 2.55 | 3.419(5) | 156(6) |
| C38–H38···F4iii | 0.93 | 2.47 | 3.313(5) | 150(6) |

The Zn3 and Zn4 atoms are hexacoordinated in octahedral geometry. The equatorial planes are defined by the phenolate oxygen (O7 for Zn3, O1 for Zn4), imino nitrogen (N4 for Zn1, N1 for Zn4) and hydroxyl oxygen (O8 for Zn1, O2 for Zn4) of one Schiff base ligand, and the hydroxyl oxygen (O2 for Zn1, O6 for Zn4) of another Schiff base ligand. The axial positions are occupied by the hydroxyl oxygen (O6 for Zn1, O4 for Zn4) and the water oxygen (O9) for Zn3 or ethanol oxygen (O10) for Zn4. The Zn3 and Zn4 atoms deviate from the basal planes by 0.021(2) and 0.003(2) Å, respectively. The octahedral coordination is distorted, which can be observed from the bond angles related to the zinc atoms. The cis and trans bond angles of the equatorial planes range from 93.95(19) to 95.8(2)º and 174.9(2) to 176.1(2)º for Zn3, and from 82.1(2) to 100.5(2)º and 170.6(3) to 177.2(2)º for Zn4. In addition, the perpendicular angles are 164.1(2)º for Zn3 and 159.8(2)º for Zn4. The coordinate bond lengths are within normal values as compared to other Schiff base zinc(II) complexes.

In the crystal structure of the complex, the tetranuclear zinc complex molecules are linked through C–H···F hydrogen bonds (Table 3), to form a 3D network (Fig. 4).

3.3. IR and UV-Vis Spectra

In the IR spectra of complex 1, the strong absorption at 2082 cm⁻¹ is due to the vibration of the azide ligand. The intense absorption at 1622 cm⁻¹ for HL1, 1626 cm⁻¹ for H2L2 is assigned to the azomethine groups, ν(C=N). The bands undergo negative shift of 17 cm⁻¹ for 1 and 13 cm⁻¹ for 2 when compared to the free Schiff bases, which can be attributed to donation of the azomethine nitrogen atom lone pair to the Zn atoms. This conclusion is further supported by the presence of weak bands at low wave numbers, which can be observed from the bond angles related to the zinc atoms.
be assigned to $\nu$(Zn-N) and $\nu$(Zn-O). The phenolic $\nu$(C-O) appears as a medium band at 1213 cm$^{-1}$ for 1 and 1241 cm$^{-1}$ for 2.

3.4. Antibacterial Activity

The complexes and the free Schiff bases were screened for antibacterial property against three Gram-positive bacterial strains (B. subtilis, S. aureus, and St. faecalis) and three Gram-negative bacterial strains (E. coli, P. aeruginosa,

**Table 4.** MICs (μg mL$^{-1}$) of the compounds and related materials

| Tested material | B. subtilis | S. aureus | St. faecalis | P. aeruginosa | E. coli | E. cloacae |
|-----------------|------------|-----------|--------------|---------------|--------|-----------|
| 1               | 0.39       | 6.25      | 3.12         | 25            | 0.78   | > 50      |
| 2               | 0.78       | 3.12      | 6.25         | 25            | 3.12   | > 50      |
| HL$^1$          | 1.56       | 12.5      | 12.5         | > 50          | 3.12   | > 50      |
| H$_2$L$^2$      | 3.12       | 6.25      | 12.5         | > 50          | 6.25   | > 50      |
| NaN$_3$         | 25         | > 50      | > 50         | > 50          | 25     | > 50      |
| Penicillin      | 1.56       | 1.56      | 1.56         | 6.25          | 6.25   | 3.12      |
| Kanamycin       | 0.39       | 1.56      | 3.12         | 3.12          | 3.12   | 1.56      |
and *E. cloacae*) by MTT method. The MICs of the compounds against the bacteria are presented in Table 4. Penicillin and Kanamycin were tested as reference drugs. The complexes show strong activities against the Gram positive bacteria *B. subtilis*, *S. aureus*, *St. faecalis*, and the Gram negative bacteria *E. coli*, medium activity against the Gram negative bacteria *P. aeruginosa*, and no activity against *E. cloacae*. The free Schiff bases show strong activity against the Gram positive bacteria *B. subtilis* and the Gram negative bacteria *E. coli*, and medium activity against *S. aureus* and *St. faecalis*, and no activity against *P. aeruginosa* and *E. cloacae*. In general, the antibacterial activities of the complexes are better than the free Schiff bases. The two complexes have higher activity than the vanadium complexes we reported previously, and the zinc, manganese, cobalt and cadmium complexes with hydrazone ligands.

4. Conclusion

Two new tetranuclear zinc(II) complexes with fluoro-containing Schiff base ligands have been prepared and structurally characterized. The Zn atoms are in trigonal bipyramidal, square pyramidal and octahedral coordination. The complexes show strong activities against the Gram positive bacteria *B. subtilis*, *S. aureus*, *St. faecalis*, and the Gram negative bacteria *E. coli*, medium activity against *S. aureus* and *St. faecalis*, and no activity against *P. aeruginosa* and *E. cloacae*. The antibacterial assay of the free Schiff bases and the complexes indicate that they are potential antibacterial agents for *B. subtilis* and *E. coli*.

5. Supplementary Material

CCDC 967151 (1) and 2063585 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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6. References

1. (a) A. Lupo, E. Cesaro, G. Montano, D. Zurlo, P. Izzo, P. Costanzo, *Curr. Genomics* 2013, 14, 268; DOI:10.2174/13892029113149990002
(b) L. P. Huang, S. Tepaamorndech, *Mol. Aspects Med.* 2013, 34, 548; DOI:10.1016/j.mam.2012.05.008
(c) S. Tabassum, A. Asim, F. Arjmand, M. Afzal, V. Bagchi, *Eur. J. Med. Chem.* 2012, 58, 308; DOI:10.1016/j.ejmech.2012.09.051
2. E. Roscioli, R. Hamon, S. Lester, C. Murgia, J. Grant, P. Zalewski, *Biometals* 2013, 26, 205; DOI:10.1007/s10534-013-9618-2
3. K. L. Cooper, B. S. King, M. M. Sandoval, K. J. Liu, L. G. Hudson, *Toxicol. Appl. Pharm.* 2013, 269, 81; DOI:10.1016/j.taap.2013.03.008
4. (a) Z. You, H. Yu, Z. Li, W. Zhai, Y. Jiang, A. Li, S. Guo, K. Li, C. Lv, C. Zhang, *Inorg. Chim. Acta* 2018, 480, 120; DOI:10.1016/j.ica.2018.05.020
(b) Y.-T. Li, J.-W. Dong, Y.-T. Gu, C.-N. Shang, F.-Y. Liu, Y. Xin, C.-L. Jiang, Z.-L. You, *Chinese J. Inorg. Chem.* 2018, 34, 1192;
(c) J. Wang, D. Qu, J.-X. Lei, Z.-L. You, *J. Coord. Chem.* 2017, 70, 544; DOI:10.1080/00958972.2016.1262538
5. (a) V. C. D. Silveira, J. S. Luz, C. C. Oliveira, I. Graziani, M. R. Ciriolo, A. M. da Costa Ferreira, *J. Inorg. Biochem.* 2008, 102, 1090; DOI:10.1016/j.jinorgbio.2007.12.033
(b) C. Liang, J. Xia, D. Lei, X. Li, Q. Yao, J. Gao, *Eur. J. Med. Chem.* 2014, 74, 742; DOI:10.1016/j.ejmech.2013.04.040
6. (a) R. M. Ramadan, A. K. Abu Al-Nasr, A. F. Nourelddeen, *Spectrochim. Acta A Mol Bio.* 2014, 132, 417; DOI:10.1016/j.saa.2014.04.015
(b) J. R. Anacona, N. Noriega, J. Camus, *Spectrochim. Acta A Mol Bio.* 2015, 137, 16; DOI:10.1016/j.saa.2014.07.091
7. (a) G. Saravanan, T. P. Selvam, V. Alagarsamy, S. Kunjiappan, S. D. Joshi, M. Indhumathy, P. D. Kumar, *Drug Res.* 2018, 68, 250; DOI:10.1055/s-0043-120198
(b) M. Patil, R. Hunoor, K. Gudasi, *Eur. J. Med. Chem.* 2010, 43, 2981; DOI:10.1016/j.ejmech.2010.03.025
8. (a) M. Durgun, H. Trukmen, M. Ceruso, C. T. Supuran, *Biorg. Med. Chem. Lett.* 2015, 25, 2377; DOI:10.1016/j.bml.2015.04.007
(b) D. H. Shi, Z. L. You, *Russ. J. Coord. Chem.* 2010, 36, 535; DOI:10.1134/S1070328410070109
9. (a) M. Gopalakrishnan, J. Thanusu, V. Kanagarajan, R. Govindaraju, J. *Enzym. Inhib.* *Mol. Med.* 2009, 24, 52;
(b) L. Shi, H.-M. Ge, S.-H. Tan, H.-Q. Li, Y.-C. Song, H.-L. Zhu, R.-X. Tan, *Eur. J. Med. Chem.* 2007, 42, 558; DOI:10.1016/j.ejmech.2006.11.010
10. (a) N. P. Rai, V. K. Narayananswamy, T. Govender, B. K. Manuprasad, S. Shashikanth, P. N. Arunachalam, *Eur. J. Med. Chem.* 2010, 45, 2677;
(b) N. P. Rai, V. K. Narayananswamy, S. Shashikanth, P. N. Arunachalam, *Eur. J. Med. Chem.* 2009, 44, 4522.
11. (a) M. Fleck, M. Layek, R. Saha, D. Bandyopadhyay, *Trans. Met. Chem.* 2013, 38, 715; DOI:10.1007/s11243-013-9741-5
(b) A. Cingolani, S. Galli, N. Masciocchi, L. Pandolfo, C. Pettinari, A. Sironi, *Dalton Trans.* 2006, 20, 2479; DOI:10.1039/b515630k
(c) Y.-T. Guo, J.-D. Leng, J.-L. Liu, Z.-S. Meng, M.-L. Tong, *Inorg. Chem.* 2012, 51, 405; DOI:10.1021/ic2018314
(d) S. Mukherjee, P. S. Mukherjee, *Dalton Trans.* 2013, 42,
Sintetizirali smo dva nova štirijedrna cinkova(II) kompleksa, [Zn₄(L₁)₂(μ₂-η¹-η¹-CH₃COO)₄(μ₁,₁-N₃)₂] (1) in [Zn₄(L₂)₄(CH₃CH₂OH)(H₂O)] (2), kjer sta L₁ in L₂ deprotonirani obliki 4-fluoro-2-((piridin-2-ilmetilimino)metil)fenoła (HL₁) in 4-fluoro-2-((2-(hidroksimetil)fenilimino)metil)fenoła (H₂L₂) ter ju okarakterizirali z elementno analizo, IR in UV-vis spektroskopijo ter rentgensko monokristalno analizo. Rentgenska strukturna analiza razkrije, da so razdalje med sosednjimi cinkovimi atomi 3.160(1)–3.353(1) Å v 1 in 3.005(1)–3.168(1) Å v 2. Vsii cinkovi atomi v 1 so pentakoordinirani z trigonalno bipiramidalno geometrijo in v 2 s kvadratno piramidalno in oktaedrično geometrijo. Kompleksoma in Schiffovima bazama smo določili antibakterijsko aktivnost proti trem Gram-pozitivnim bakterijskim sevom (B. subtilis, S. aureus, in St. faecalis) in trem Gram-negativnim sevom (E. coli, P. aeruginosa, in E. cloacae) z MTT metodo.