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

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Abstract

Two new tetranuclear zinc(II) complexes, $[\text{Zn}_4(\text{L}^1)_2(\mu_2\text{-}\eta^1\text{-}\eta^1\text{-CH}_3\text{COO})_4(\mu_{1,1}\text{-N}_3)_2]$ (**1**) and $[\text{Zn}_4(\text{L}^2)_4(\text{CH}_3\text{CH}_2\text{OH})(\text{H}_2\text{O})]$ (**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 (H_2L^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 *St. 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 *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, $[\text{Zn}_4(\text{L}^1)_2(\mu_2\text{-}\eta^1\text{-}\eta^1\text{-CH}_3\text{COO})_4(\mu_{1,1}\text{-N}_3)_2]$ (**1**) and $[\text{Zn}_4(\text{L}^2)_4(\text{CH}_3\text{CH}_2\text{OH})(\text{H}_2\text{O})]$ (**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 (H_2L^2 ; Scheme 1, right), is reported.

Scheme 1. The Schiff base ligands.

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 HL¹ and H₂L² 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.

HL¹: Yield 77%. Anal. Calcd. for C₁₃H₁₁N₂O: C 67.82, H 4.82, N 12.17. Found: C 67.71, H 4.93, N 12.26. IR data (KBr, cm⁻¹): 3327, 1622, 1585, 1571, 1513, 1473, 1438, 1389, 1346, 1285, 1220, 1205, 1153, 1140, 1112, 1034, 960, 877, 830, 797, 762, 723, 710, 633, 620. UV-Vis data in ethanol [$\lambda_{\max}$ (nm), ϵ (L mol⁻¹ cm⁻¹): 250, 14570; 280, 17530; 300, 18150; 380, 7637.

H₂L²: Yield 83%. Anal. Calcd. for C₁₄H₁₂FNO₂: C 68.56, H 4.93, N 5.71. Found: C 68.67, H 5.02, N 5.63. IR data (KBr, cm⁻¹): 3341, 3243, 1626, 1570, 1485, 1447, 1387, 1355, 1321, 1257, 1201, 1141, 1103, 1034, 955, 870, 795, 767, 716, 667, 626, 575, 535, 466. UV-Vis data in ethanol [$\lambda_{\max}$ (nm), ϵ (L mol⁻¹ cm⁻¹): 230, 19310; 265, 14220; 347, 13150.

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

An ethanolic solution (20 mL) of HL¹ (0.20 mmol, 0.046 g) was mixed with an ethanolic solution (30 mL) of Zn(CH₃COO)₂·2H₂O (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 CaCl₂. Yield 56%. Anal. Calcd. for C₃₄H₃₂F₂N₁₀O₁₀Zn₄: C 39.26, H 3.10, N 13.46. Found: C 39.05, H 3.18, N 13.33. IR data (KBr, cm⁻¹): 2080, 1640, 1598, 1480, 1437, 1395, 1289, 1213, 1154, 1044, 874, 815, 769, 667, 617, 561, 490, 456. UV-Vis data in ethanol [$\lambda_{\max}$ (nm), ϵ (L mol⁻¹ cm⁻¹): 232, 19150; 250, 18110; 280, 12560; 370, 5570.

A small amount of the complex was recrystallized from ethanol, affording colorless single crystals suitable for X-ray analysis.

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

An ethanolic solution (20 mL) of H₂L² (0.20 mmol, 0.049 g) was mixed with an ethanolic solution (30 mL) of Zn(CH₃COO)₂·2H₂O (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 CaCl₂. Yield 43%. Anal. Calcd. for C₅₈H₄₈F₄N₄O₁₀Zn₄: C 53.64, H 3.73, N 4.31. Found: C 53.45, H 3.91, N 4.25. IR data (KBr, cm⁻¹): 3641, 1609, 1536,

1460, 1382, 1306, 1241, 1198, 1139, 1026, 979, 874, 816, 752, 673, 624, 564, 513, 443. UV-Vis data in ethanol [$\lambda_{\max}$ (nm), ϵ (L mol⁻¹ cm⁻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 α radiation (λ = 0.71073 Å). A preliminary orientation matrix and cell parameters were determined from three sets of ω scans at different starting angles. Data frames were obtained at scan intervals of 0.5° with an exposure time of 10 s frame⁻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.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 ₃₄ H ₃₂ F ₂ N ₁₀ O ₁₀ Zn ₄	C ₅₈ H ₄₈ F ₄ N ₄ O ₁₀ Zn 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	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.4606(9)	14.0120(11)
<i>b</i> (Å)	10.8780(11)	14.1500(10)
<i>c</i> (Å)	11.0332(11)	15.1470(10)
α (°)	84.734(2)	101.189(1)
β (°)	86.041(2)	103.022(1)
γ (°)	88.243(2)	93.211(1)
<i>V</i> (Å ³)	1008.43(18)	2854.7(4)
<i>Z</i>	1	2
<i>D</i> _{calc} (g cm ⁻³)	1.713	1.511
μ (Mo K α) (mm ⁻¹)	2.427	1.734
<i>F</i> (000)	524	1320
Number of measured reflections	9913	15426
Number of observations (<i>I</i> > 2 σ (<i>I</i>))	3748	9251
Unique reflections	3175	5361
Parameters	273	722
Number of restraints	0	0
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0273, 0.0641	0.0640, 0.1841
<i>R</i> ₁ , <i>wR</i> ₂ (all data) ^a	0.0360, 0.0687	0.1182, 0.2252
Goodness of fit of <i>F</i> ²	1.034	1.013

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^3]^{1/2}$.

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.¹³ A stock solution of the compounds ($50 \mu\text{g mL}^{-1}$) 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 10^5 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, $50 \mu\text{L}$ of phosphate buffered saline (PBS 0.01 mol L^{-1} , pH 7.4: $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ 2.9 g, KH_2PO_4 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 $100 \mu\text{L}$ 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-ylmethylimino)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,¹⁴ 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 $3.353(1) \text{ \AA}$, 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 acetate 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 $125.55(8)^\circ$ for Zn1 and from $108.97(7)$ to $131.25(9)^\circ$ for Zn2. In addition, the perpendicular angles are $166.31(7)^\circ$ for Zn1 and $169.41(7)^\circ$ for Zn2. The coordinate 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.¹⁵ Zn1 and Zn2 atoms deviate from the best coordination planes defined by the equatorial donor atoms by $0.120(1) \text{ \AA}$ and $0.155(1) \text{ \AA}$, 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 structural index τ which represents the relative amount of trigonality (square pyramid, $\tau = 0$; trigonal bipyramid, $\tau = 1$); $\tau = (\beta - \alpha)/60^\circ$, α and β being the two largest angles around the central atom.¹⁶ 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 $3.005(1)$ – $3.168(1) \text{ \AA}$. 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 $0.353(2) \text{ \AA}$, respectively. The square pyramidal coordination is distorted, which can

Table 2. Selected bond lengths (Å) and angles (°) for the complexes

1			
Zn1–O1	2.0484(16)	Zn1–N1	2.055(2)
Zn1–O3	1.9866(17)	Zn1–N2	2.1321(19)
Zn1–O5	1.9915(18)	Zn2–O1	1.9864(17)
Zn2–O4	1.9707(19)	Zn2–N3A	1.986(2)
Zn2–O2	2.0707(19)	Zn2–N3	2.290(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	131.25(9)	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)
2			
Zn1–O5	1.942(6)	Zn1–O4	2.021(5)
Zn1–N3	2.054(8)	Zn1–O6	2.061(5)
Zn1–O8	2.156(5)	Zn2–O3	1.987(6)
Zn2–O8	2.003(5)	Zn2–N2	2.021(7)
Zn2–O2	2.069(5)	Zn2–O4	2.118(5)
Zn3–O7	1.968(5)	Zn3–O8	2.086(5)
Zn3–N4	2.094(7)	Zn3–O2	2.112(5)
Zn3–O6	2.133(5)	Zn3–O9	2.255(6)
Zn4–O1	1.943(6)	Zn4–O2	2.083(5)
Zn4–N1	2.119(6)	Zn4–O6	2.119(5)
Zn4–O4	2.173(5)	Zn4–O10	2.265(6)
O5–Zn1–N3	92.2(3)	O5–Zn1–O6	167.0(2)
N3–Zn1–O6	89.9(3)	O5–Zn1–O8	91.4(2)
N3–Zn1–O8	144.4(3)	O6–Zn1–O8	79.58(19)
O4–Zn1–O8	84.1(2)	O4–Zn1–O6	84.6(2)
O5–Zn1–O4	103.8(2)	O4–Zn1–N3	129.1(3)
O3–Zn2–O8	101.2(2)	O8–Zn2–N2	123.4(2)
O8–Zn2–O2	87.20(19)	O8–Zn2–O4	85.5(2)
O3–Zn2–N2	91.0(3)	O3–Zn2–O2	93.6(2)
N2–Zn2–O2	147.5(2)	O3–Zn2–O4	170.9(2)
N2–Zn2–O4	90.5(3)	O2–Zn2–O4	80.4(2)
O7–Zn3–O8	176.1(2)	O7–Zn3–N4	89.2(3)
O8–Zn3–N4	91.2(2)	O7–Zn3–O2	95.8(2)
O8–Zn3–O2	83.95(19)	N4–Zn3–O2	174.9(2)
O7–Zn3–O6	96.5(2)	O8–Zn3–O6	79.6(2)
N4–Zn3–O6	99.7(3)	O2–Zn3–O6	81.1(2)
O7–Zn3–O9	95.2(3)	O8–Zn3–O9	88.7(2)
N4–Zn3–O9	91.2(3)	O2–Zn3–O9	87.1(2)
O6–Zn3–O9	164.1(2)	O1–Zn4–O2	177.2(2)
O1–Zn4–N1	88.9(3)	O2–Zn4–N1	88.5(2)
O1–Zn4–O6	100.5(2)	O2–Zn4–O6	82.1(2)
N1–Zn4–O6	170.6(3)	O1–Zn4–O4	100.4(2)
O2–Zn4–O4	78.8(2)	N1–Zn4–O4	99.5(2)
O6–Zn4–O4	79.61(19)	O1–Zn4–O10	95.9(3)
O2–Zn4–O10	85.4(2)	N1–Zn4–O10	92.7(2)
O6–Zn4–O10	85.7(2)	O4–Zn4–O10	159.8(2)

Symmetry code for A: $-x, 1-y, 1-z$.

be observed from the bond angles related to the zinc atoms. The *cis* and *trans* bond angles of the basal planes range from 79.58(19) to 92.2(3)° and 84.1(2) to 129.1(3)° for Zn1, and from 80.4(2) to 93.6(2)° and 85.2(2) to 123.4(2)° for Zn2.

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)° and 174.9(2) to 176.1(2)° for Zn3, and from 82.1(2) to 100.5(2)° and 170.6(3) to 177.2(2)° for Zn4. In addition, the perpendicular angles are 164.1(2)° for Zn3 and 159.8(2)° for Zn4. The coordinate bond lengths are within normal values as compared to other Schiff base zinc(II) complexes.¹⁵

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).

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

<i>D</i> –H... <i>A</i>	<i>d</i> (<i>D</i> –H)	<i>d</i> (H... <i>A</i>)	<i>d</i> (<i>D</i> ... <i>A</i>)	Angle (<i>D</i> –H... <i>A</i>)
1				
O8–H8A...O3 ⁱ	0.97	2.54	3.381(2)	145(3)
2				
C21–H21...F1 ⁱⁱ	0.93	2.55	3.419(5)	156(6)
C38–H38...F4 ⁱⁱⁱ	0.93	2.55	3.186(5)	126(6)
C47–H47...F2 ^{iv}	0.93	2.47	3.313(5)	150(6)

Symmetry codes: i: $-x, 2-y, -z$; ii: $-x, 1-y, -z$; iii: $-1+x, y, z$; iv: $1-x, 1-y, -z$.

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, 1598 cm^{−1} for **1** and 1609 cm^{−1} for **2** is assigned to the azomethine groups, $\nu(\text{C}=\text{N})$.¹⁷ 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

Fig. 1. ORTEP diagram of complex **1** with 30% thermal ellipsoids for all non-hydrogen atoms. Hydrogen atoms are omitted for clarity. Atoms with the suffix A are related to the operate position $-x$, $1 - y$, $1 - z$.

Fig. 2. Hydrogen bond (dashed lines) linked 1D chains of complex **1**, viewed along the c axis.

be assigned to $\nu(\text{Zn}-\text{N})$ and $\nu(\text{Zn}-\text{O})$. The phenolic $\nu(\text{C}-\text{O})$ 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*,

Fig. 3. ORTEP diagram of complex **2** with 30% thermal ellipsoids for all non-hydrogen atoms. Hydrogen atoms are omitted for clarity.

Fig. 4. Hydrogen bond (dashed lines) linked 3D network of complex **2**, viewed along the b axis.

Table 4. MICs ($\mu\text{g mL}^{-1}$) of the compounds and related materials

Tested material	Gram positive			Gram negative		
	<i>B. subtilis</i>	<i>S. aureus</i>	<i>St. faecalis</i>	<i>P. aeruginosa</i>	<i>E. coli</i>	<i>E. cloacae</i>
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*, 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,¹⁸ and the zinc, manganese, cobalt and cadmium complexes with hydrazone ligands.¹⁹

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*, and medium activity against the Gram negative bacteria *P. aeruginosa*. 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/const/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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Povzetek

Sintetizirali smo dva nova štirijedna cinkova(II) kompleksa, $[\text{Zn}_4(\text{L}^1)_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-CH}_3\text{COO})_4(\mu_{1,1}\text{-N}_3)_2]$ (**1**) in $[\text{Zn}_4(\text{L}^2)_4(\text{CH}_3\text{CH}_2\text{OH})(\text{H}_2\text{O})]$ (**2**), kjer sta L^1 in L^2 deprotonirani obliki 4-fluoro-2-((piridin-2-ilmetilimino)metil)fenola (HL^1) in 4-fluoro-2-((2-(hidroksimetil)fenilimino)metil)fenol (H_2L^2) ter ju okarakterizirali z elementno analizo, IR in UV-vis spektroskopijo ter rentgensko monokristalno analizo. Rentgenska strukturna analiza razkriva, 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**. Vsi 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*, and *E. cloacae*) z MTT metodo.

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