Scientific paper

Synthesis, Crystal Structures and Urease Inhibition of Zinc Complexes Derived from 4-Chloro-2-(((2-(pyrrolidin-1-yl) ethyl)imino)methyl)phenol

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Received: 12-20-2022

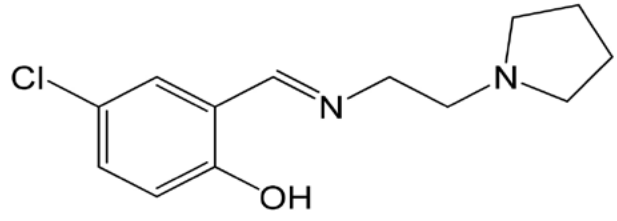
Abstract

Three new zinc(II) complexes, $[Zn_3(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}OAc)_2(\mu_2\text{-}\eta^2\text{:}\eta^0\text{-}OAc)_2L_2]$ (**1**), $[Zn_3(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}OAc)_2(\mu_{1,1}\text{-}N_3)(N_3)L_2]$ (**2**), $[Zn_2(\mu_{1,3}\text{-}N_3)(N_3)(H_2O)L_2]$ (**3**), with the Schiff base ligand 4-chloro-2-(((2-(pyrrolidin-1-yl)ethyl)imino)methyl)phenol (HL) have been synthesized and characterized by elemental analysis, IR and UV-Vis spectroscopic studies. Crystal structures of the complexes were confirmed by single crystal X-ray diffraction. Complex **1** is a bidentate acetato, monoatomic bridging acetato, and phenolato co-bridged trinuclear zinc compound. The Zn atoms are in octahedral and square pyramidal coordination. Complex **2** is a bidentate acetato, end-on azido, and phenolato co-bridged trinuclear zinc compound. The Zn atoms are in trigonal bipyramidal and square pyramidal coordination. Complex **3** is an end-to-end azido bridged dinuclear zinc compound. The Zn atoms are in square pyramidal and trigonal bipyramidal coordination. The Schiff base ligands in the complexes coordinate to the Zn atoms through the phenolate oxygen, imino nitrogen and pyrrolidine nitrogen. The complexes have interesting inhibitory activity on *Jack bean* urease, with IC_{50} values of 7.1–15.3 μmol·L^{-1}.

Keywords: Schiff base; zinc complex; crystal structure; urease inhibition

1. Introduction

Urease catalyzes the rapid hydrolysis of urea to form ammonia, which is harmful for environment, agriculture and human health.[1] In the last few years, urease inhibitors have attracted much attention and numerous urease inhibitors have been reported.[2] Among the known urease inhibitors, hydroxamic acids, phosphoramides and thiols are the best recognized species. Because the low efficiency and negative side effects of the present urease inhibitors, the discovery of new and more efficient urease inhibitors is of high urgency. Schiff bases constitute a class of important ligands that have attracted much attention for their versatile coordination behavior toward various metal ions,[3] and wide applications especially in biological fields such as antibacterial,[4] antitumor,[5] anti-inflammatory[6] and cytotoxic,[7] *etc*. Interestingly, Schiff base compounds have been reported to have urease inhibitory activities.[8] Metal complexes with Schiff base ligands are reported to show effective biological activities, like antibacterial and urease inhibitory aspects.[9] Zinc is an important biological element, its complexes play important roles in various enzymatic processes.[10] In addition, acetate and azide anions are interesting bridging blocks in the construction of polynuclear complexes.[11] In this work, three new zinc complexes, $[Zn_3(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}OAc)_2(\mu_2\text{-}\eta^2\text{:}\eta^0\text{-}OAc)_2L_2]$ (**1**), $[Zn_3(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}OAc)_2(\mu_{1,1}\text{-}N_3)(N_3)L_2]$ (**2**), $[Zn_2(\mu_{1,3}\text{-}N_3)(N_3)(H_2O)L_2]$ (**3**), with the Schiff base ligand 4-chloro-2-(((2-(pyrrolidin-1-yl)ethyl)imino)methyl)phenol (HL, Scheme 1), are presented.



Scheme 1. The Schiff base HL

2. Experimental

2. 1. Materials and Methods

5-Chlorosalicylaldehyde and 1-(2-aminoethyl) pyrrolidine with analytical grade were purchased from TCI. All other chemicals were obtained from Xiya Chemical Co. Ltd. All the starting materials were used as received. Elemental analyses (CHN) were performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra were recorded on a Jasco FT/IR-4000 spectrophotometer in the region 4000–400 cm^{-1} using KBr pellets. Electronic absorption spectra were recorded with a Lambda 35 spectrophotometer. Single crystal X-ray diffraction was carried out with a Bruker SMART 1000 CCD diffractometer.

2. 2. Synthesis of $[Zn_3(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}OAc)_2(\mu_2\text{-}\eta^2\text{:}\eta^0\text{-}OAc)_2L_2]$ (1)

5-Chlorosalicylaldehyde (0.16 g, 1.0 mmol) was dissolved in 10 mL methanol, to which was added 10 mL methanol solution of 1-(2-aminoethyl)pyrrolidine (0.11 g, 1.0 mmol). The mixture was stirred for 10 min at room temperature. Then, zinc acetate dihydrate (0.44 g, 2.0 mmol) was added to the mixture. The final mixture was stirred at room temperature for 30 min to give a colorless solution. The solution was kept in air for several days to give colorless block-shaped single crystals of the complex. Yield: 0.18 g (38%). Anal. Calcd for $C_{34}H_{44}Cl_2N_4O_{10}Zn_3$: C, 43.64; H, 4.74; N, 5.99. Found: C, 43.47; H, 4.83; N, 6.12%. FT-IR data (KBr, cm^{-1}): ν(C=N) 1646; 1585, 1526, 1463, 1436, 1387, 1310, 1293, 1185, 1126, 1071, 1023, 902, 868, 797, 673, 613, 545, 469. UV-Vis data [10^{-3} mol L^{-1} in methanol, λ/nm (ε/L mol^{-1} cm^{-1})]: 235 (16,370), 265 (5,725), 360 (3,130). Λ_M (10^{-3} M in methanol): 26 Ω^{-1} cm^2 mol^{-1}.

2. 3. Synthesis of $[Zn_3(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}OAc)_2(\mu_{1,1}\text{-}N_3)(N_3)L_2]$ (2)

5-Chlorosalicylaldehyde (0.16 g, 1.0 mmol) was dissolved in 10 mL methanol, to which was added 10 mL methanol solution of 1-(2-aminoethyl)pyrrolidine (0.11 g, 1.0 mmol). The mixture was stirred for 10 min at room temperature. Then, zinc acetate dihydrate (0.44 g, 2.0 mmol) and sodium azide (0.13 g, 2.0 mmol) were added to the mixture. The final mixture was stirred at room temperature for 30 min to give a colorless solution. The solution was kept in air for several days to give colorless block-shaped single crystals of the complex. Yield: 0.23 g (51%). Anal. Calcd for $C_{30}H_{38}Cl_2N_{10}O_6Zn_3$: C, 39.96; H, 4.25; N, 15.53. Found: C, 40.12; H, 4.33; N, 15.41%. FT-IR data (KBr, cm^{-1}): ν(N_3) 2093, 2063; ν(C=N) 1646; 1595, 1466, 1439, 1385, 1296, 1180, 1123, 1074, 1054, 897, 827, 798, 709, 667, 645, 615, 573, 538, 465, 440. UV-Vis data [10^{-3} mol L^{-1} in methanol, λ/nm (ε/L mol^{-1} cm^{-1})]: 238 (15,230), 265 (6,850), 360 (3,345). Λ_M (10^{-3} M in methanol): 31 Ω^{-1} cm^2 mol^{-1}.

2. 4. Synthesis of $[Zn_2(\mu_{1,3}\text{-}N_3)(N_3)(H_2O)L_2]$ (3)

5-Chlorosalicylaldehyde (0.16 g, 1.0 mmol) was dissolved in 10 mL methanol, to which was added 10 mL methanol solution of 1-(2-aminoethyl)pyrrolidine (0.11 g, 1.0 mmol). The mixture was stirred for 10 min at room temperature. Then, zinc nitrate hexahydrate (0.60 g, 2.0 mmol) and sodium azide (0.13 g, 2.0 mmol) were added to the mixture. The final mixture was stirred at room temperature for 30 min to give a colorless solution. The solution was kept in air for several days to give colorless block-shaped single crystals of the complex. Yield: 0.23 g (51%). Anal. Calcd for $C_{26}H_{34}Cl_2N_{10}O_3Zn_2$: C, 42.41; H, 4.65; N, 19.02. Found: C, 42.26; H, 4.58; N, 18.89%. FT-IR data (KBr, cm^{-1}): ν(N_3) 2140, 2069; ν(C=N) 1643; 1595, 1528, 1467, 1390, 1308, 1245, 1173, 1131, 1047, 901, 826, 795, 706, 647, 605, 521, 472, 435. UV-Vis data [10^{-3} mol L^{-1} in methanol, λ/nm (ε/L mol^{-1} cm^{-1})]: 233 (16,110), 265 (5,473), 370 (4,125). Λ_M (10^{-3} M in methanol): 36 Ω^{-1} cm^2 mol^{-1}.

2. 5. X-Ray Crystallography

The X-ray data of the three complexes were collected at 298(2) K on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (0.71073 Å) from a classical sealed tube. The intensity data were reduced with SAINT.[12] The multi-scan absorption correction was performed with SADABS.[13] Structures of the complexes were solved with SHELXTL by direct methods and refined against F^2 by full-matrix least-squares method.[14] All non-hydrogen atoms of the compounds were refined anisotropically. The water H atoms in complex **3** were located from a difference Fourier map and refined with O–H and H···H distances restrained to 0.85(1) and 1.37(2) Å, respectively. All other hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The group C21-C22-N4-C23-C24-C25-C26 in complex **2** is disordered over two sites, with occupancies of 0.47(2) and 0.53(2), respectively. The low bond precision on C-C bonds of complex **1** may be due to the poor diffraction quality of the crystal. In complexes **2** and **3**, the large differences of atoms N2, C8-C13 (for **2**) and N7, N8, C22 (for **3**) are due to the slight disorder of the groups. Crystallographic data for the complexes are summarized in Table 1.

3. Results and Discussion

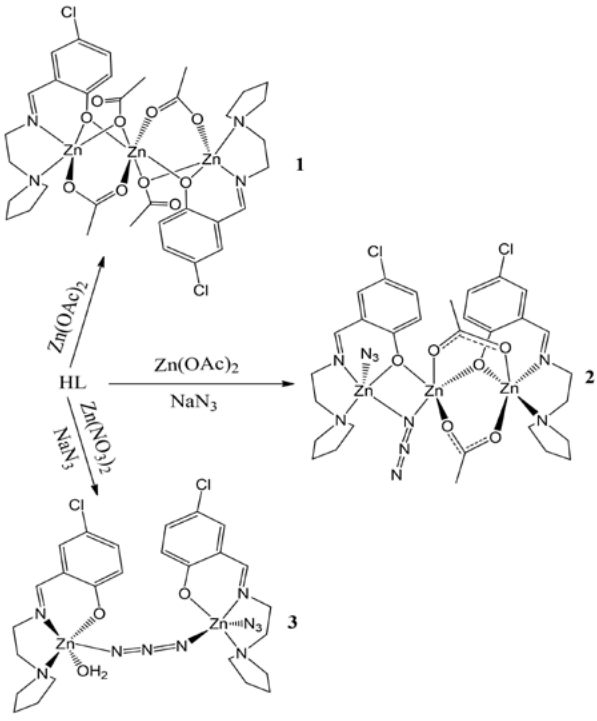
3. 1. Synthesis

The complexes **1**-**3** were facile prepared by reaction of the newly formed Schiff base with zinc acetate (**1**), zinc acetate and sodium azide (**2**), zinc nitrate and sodium azide (**3**), respectively in methanol. Single crystals of the

Table 1. Crystal data for the complexes

	1	**2**	**3**
Formula	$C_{34}H_{44}Cl_2N_4O_{10}Zn_3$	$C_{30}H_{38}Cl_2N_{10}O_6Zn_3$	$C_{26}H_{34}Cl_2N_{10}O_3Zn_2$
FW	935.74	901.71	736.27
Crystal shape/colour	block/colorless	block/colorless	block/colorless
Crystal size /mm	0.15´0.13´0.13	0.19´0.18´0.15	0.26´0.23´0.21
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	24.5043(12)	12.9152(11)	8.9470(7)
b (Å)	8.4919(6)	17.0982(14)	12.9416(11)
c (Å)	21.1838(13)	17.0597(15)	14.5580(12)
α (°)	90	90	79.583(1)
β (°)	115.138(1)	93.113(2)	89.490(1)
γ (°)	90	90	74.624(1)
V (Å^3)	3990.6(4)	3761.7(6)	1597.2(2)
Z	4	4	2
λ(MoKα) (Å)	0.71073	0.71073	0.71073
T (K)	298(2)	298(2)	298(2)
μ(MoKα) (cm^{-1})	1.980	2.094	1.714
T_{min}	0.7555	0.6917	0.6642
T_{max}	0.7828	0.7441	0.7148
R_{int}	0.0406	0.0344	0.0415
Reflections	20735	19896	17089
Parameters	481	508	394
Unique reflections	7410	7011	5892
Observed reflections [$I \geq 2\sigma(I)$]	5263	4926	4542
Restraints	0	106	43
Goodness of fit on F^2	1.147	1.020	1.096
R_1, wR_2 [$I \geq 2\sigma(I)$][a]	0.0724, 0.1990	0.0439, 0.1074	0.0818, 0.2496
R_1, wR_2 (all data)[a]	0.1008, 0.2118	0.0720, 0.1240	0.1006, 0.2637

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



Scheme 2. The synthetic procedure for the complexes

complexes were formed by slow evaporation method. Molar conductivity of the zinc complexes in methanol with concentrations of about 10^{-3} mol·L^{-1} is 26–36 Ω^{-1}·cm^2·mol^{-1}, indicating the non-electrolytic nature of the complexes.[15]

3. 2. Structure Description of Complex 1

Molecular structure of the trinuclear zinc complex **1** is shown in Figure 1. Selected bond lengths and angles are given in Table 2. There are two independent molecules in the compound. Both molecules possess crystallographic inversion center symmetry, with the centers located at the Zn2 and Zn4 atoms. The Zn1···Zn2 and Zn3···Zn4 distances are 3.091(2) and 3.070(2) Å, respectively. The Schiff base ligand coordinates to the Zn atoms through the phenolate O, imino N, and pyrrolidine N atoms, generating a five- and a six-membered chelate rings with bite angles of 80.5(3)° and 88.0(3)°, respectively for Zn1, and 81.8(3)° and 87.1(2)°, respectively for Zn3. The Zn1 and Zn3 atoms are in coordination geometry between square pyramidal and trigonal bipyramidal, as evidenced by the index factor τ (0.50 for Zn1 and 0.47 for Zn3).[16] Three donor atoms come from a Schiff base ligand, and the other two come

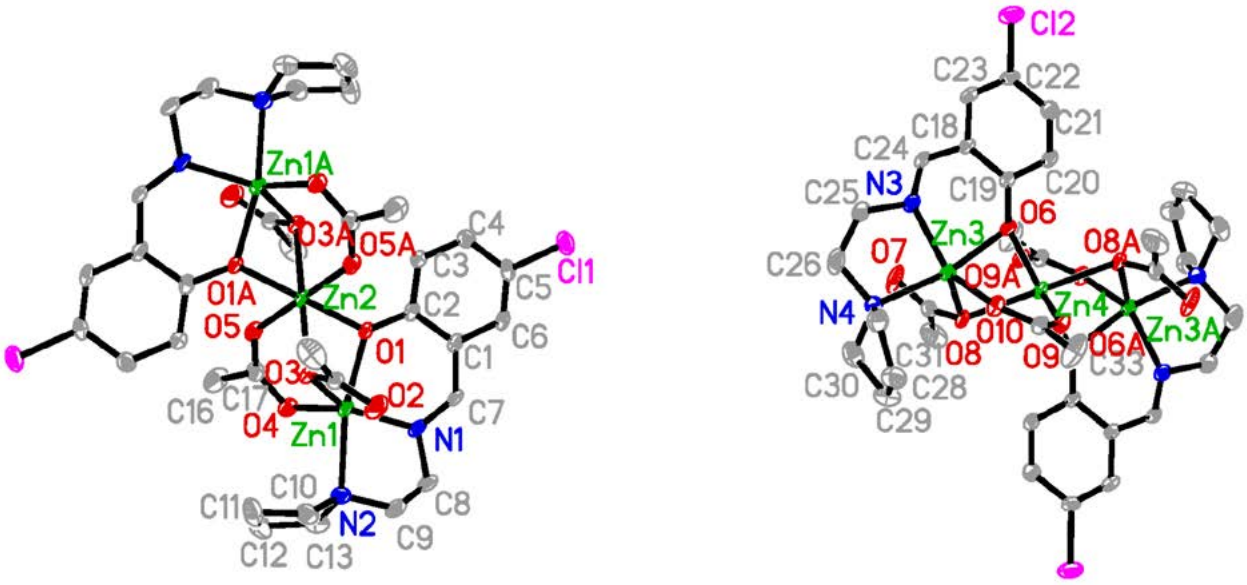


Figure 1. Molecular structure of complex **1**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Unlabeled atoms are related to the symmetry operations 1 – *x*, 1 – *y*, – *z* (left) and – *x*, 1 – *y*, 1 – *z* (right). Hydrogen atoms are omitted for clarity.

respectively from a bidentate acetate and a monoatomic acetate ligands. The Zn2 and Zn4 atoms are in octahedral coordination, with the two phenolate O atoms from two Schiff base ligands and two O atoms from two bidentate acetate ligands defining the equatorial plane, and with the two O atoms from two monoanionic acetate ligands occupying the axial positions. The bond lengths around the Zn atoms are within normal values with the reported zinc(II) complexes derived from Schiff base ligands.[17]

The neighboring molecules of the complex are connected by intermolecular C7–H7···O2 and C24–H24···O7 hydrogen bonds (Table 3), to form one-dimensional chains running along the *c* axis (Figure 2).

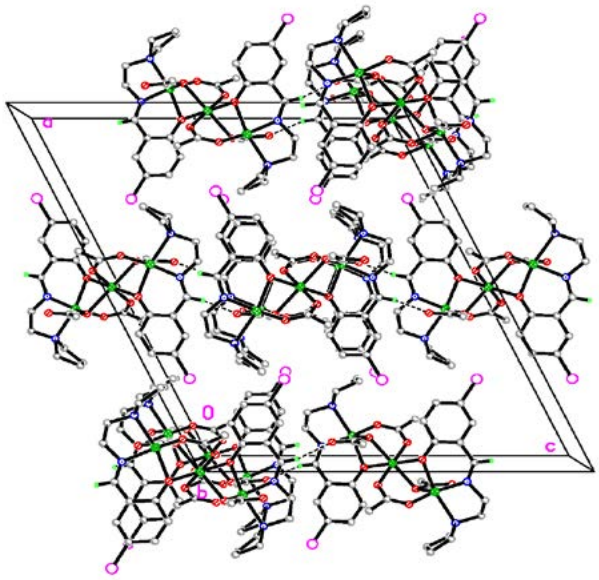


Figure 2. Molecular packing structure of complex **1**, viewed down the *b* axis. Hydrogen bonds are drawn as dotted lines.

3. 3. Structure Description of Complex 2

Molecular structure of the trinuclear zinc complex **2** is shown in Figure 3. Selected bond lengths and angles are given in Table 2. The Zn1···Zn2 and Zn2···Zn3 distances are 3.310(2) and 3.195(2) Å, respectively. The Schiff base ligand coordinates to the Zn atoms through the phenolate O, imino N, and pyrrolidine N atoms, generating a five- and a six-membered chelate rings with bite angles of 80.57(16)° and 83.67(14)°, respectively for Zn1, and 82.17(16)° and 86.42(14)°, respectively for Zn3. The Zn1 atom is in distorted square pyramidal coordination, as evidenced by the index factor τ (0.29). The basal plane is defined by the three donor atoms (O1, N1, N2) of the Schiff base ligand, and the N8 atom of the end-on azide ligand, and the apical position is occupied by the N5 atom of the terminal azide ligand. The distortion of the square pyramidal coordination is also indicated by the bond angles. The *cis* and *trans* angles in the basal plane are 76.77(14)-102.38(16)° and 137.59(17)-154.98(14)°, respectively. The bond angles among the apical and basal donor atoms are 101.51(18)-111.32(18)°. The Zn2 atom is in trigonal bipyramidal coordination, as evidenced by the index factor τ (0.72). The equatorial plane is defined by two phenolate O atoms (O1, O2) from two Schiff base ligands, and one O atom (O3) of an acetate ligand, and the two axial positions are occupied by one O atom (O5) of the other acetate ligand and one N atom (N8) of the end-on azide ligand. The three bond angles in the equatorial plane are 110.86(13)-125.86(13)°, and the angles among the axial and equatorial donor atoms are

76.51(14)-96.74(15)°. The Zn3 atom is in trigonal bipyramidal coordination, as evidenced by the index factor τ (0.70). The equatorial plane is defined by the imino N atom (N3) of the Schiff base ligand, and two O atoms (O4, O6) from two acetate ligands, and the two axial positions are occupied by one phenolate O atom (O2) and one pyrrolidine N atom (N4) of the Schiff base ligand. The three bond angles in the equatorial plane are 115.96(15)-126.26(16)°, and the angles among the axial and equatorial donor atoms are 82.17(16)-94.31(13)°. The bond lengths around the three Zn atoms are within normal values with the reported zinc(II) complexes derived from Schiff base ligands.[17]

The neighboring molecules of the complex are connected by intermolecular C7–H7···O3, C8–H8A···O5 and C20–H20···N10 hydrogen bonds (Table 3), to form one-dimensional chains running along the *b* axis (Figure 4). In addition, there are C-H···π interactions in the crystal packing [C9-H9B···*Cg*1$^{\#1}$, 2.76 Å; C18-H18···*Cg*2$^{\#2}$, 2.67 Å; C22-H22A···*Cg*3$^{\#3}$, 2.56 Å; C25-H25A···*Cg*1$^{\#4}$, 2.68 Å; *Cg*1 = C1-C6; *Cg*2 = Zn1-O1-Zn2-N8; *Cg*3 = C14-C19; symmetry codes: #1, 1 – *x*, 1 – *y*, 1 – *z*; #2, *x*, *y*, *z*; #3, 1 – *x*, – *y*, 1 – *z*; #4, 1/2 + *x*, 1/2 – *y*, –1/2 + *z*].

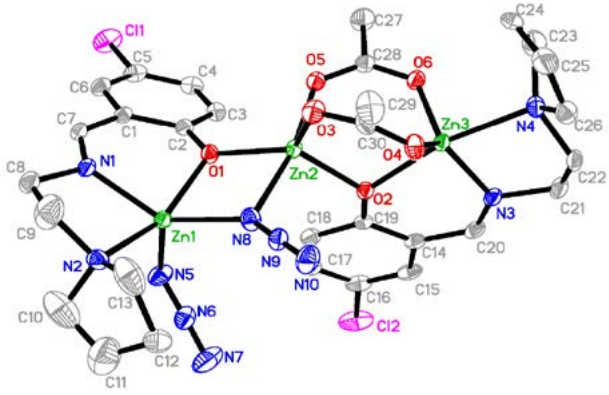


Figure 3. Molecular structure of complex **2**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

3. 4. Structure Description of Complex 3

Molecular structure of the dinuclear zinc complex **3** is shown in Figure 5. Selected bond lengths and angles are given in Table 2. The Zn1···Zn2 distance is 5.797(2) Å. The Schiff base ligand coordinates to the Zn atoms through the phenolate O, imino N, and pyrrolidine N atoms, generating a five- and a six-membered chelate rings with bite angles of 79.1(3)° and 88.9(2)° for Zn1, and 79.3(3)° and 87.0(3)° for Zn2, respectively. The Zn1 atom is in a distorted square pyramidal coordination, as evidenced by the index factor τ (0.37). The basal plane is defined by the three donor atoms of one Schiff base ligand, and one water O atom. The apical position is occupied by one N atom of the bridging azide ligand. The Zn1 atom deviates from the least-squares plane defined by the four basal donor atoms by 0.367(2) Å. The Zn2 atom is in a distorted trigonal-bipyramidal coordination, as evidenced by the index factor τ (0.63). The equatorial plane is defined by the imino N atom of one Schiff base ligand, two N atoms respectively from one bridging and one terminal azide ligands. The two

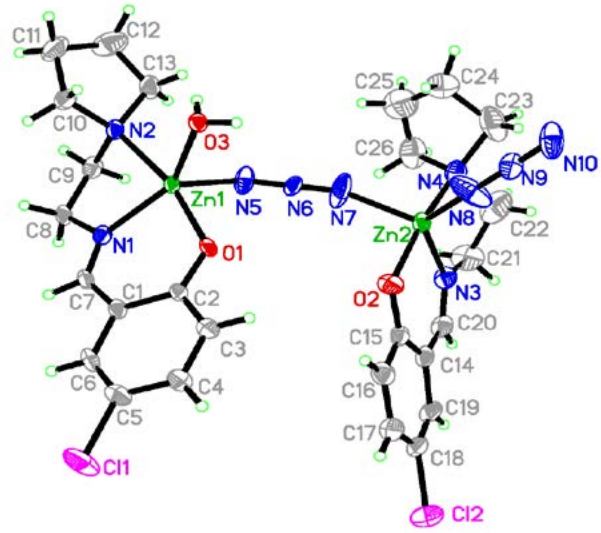


Figure 5. Molecular structure of complex **3**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

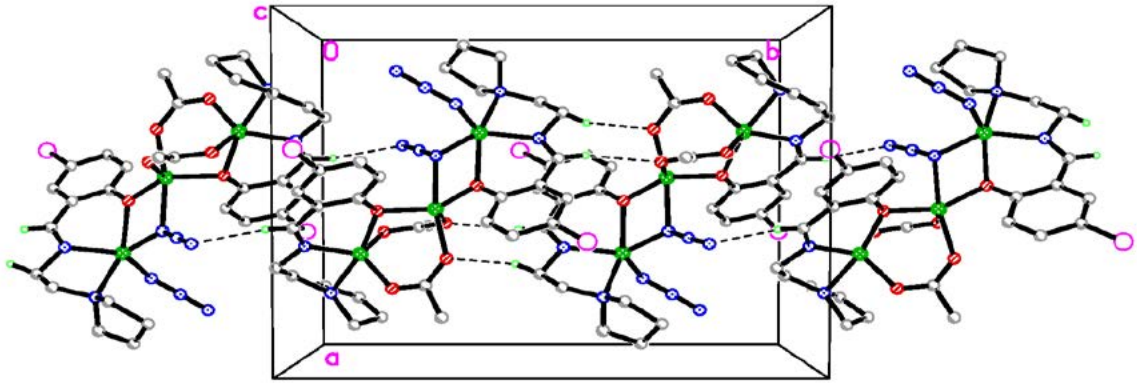


Figure 4. Molecular packing structure of complex **2**, viewed down the *c* axis. Hydrogen bonds are drawn as dotted lines.

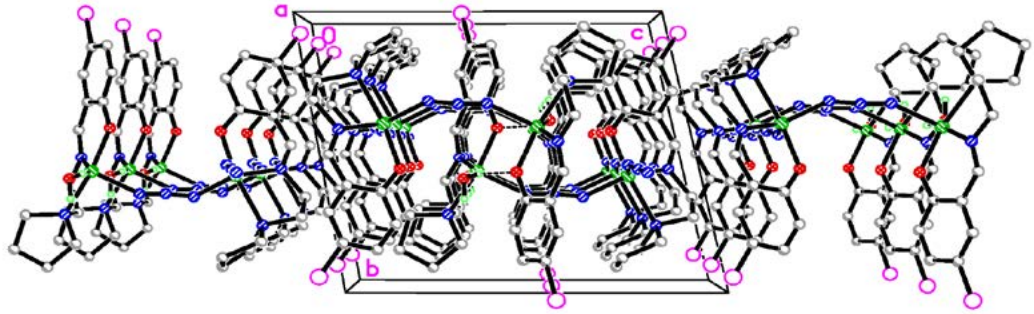


Figure 6. Molecular packing structure of complex **3**, viewed down the *a* axis. Hydrogen bonds are drawn as dotted lines.

axial positions are occupied by one phenolate O and one pyrrolidine N atoms of the Schiff base ligand. The Zn2 atom deviates from the least-squares plane defined by the three equatorial donor atoms by 0.023(2) Å. The bond lengths around the Zn1 and Zn2 atoms are within normal values with the reported zinc(II) complexes derived from Schiff base ligands.[17]

The neighboring molecules of the complex are connected by intermolecular O3–H3B···O1^{v} hydrogen bonds (Table 3), to form dimeric structure (Figure 6). In addition, there are C-H···π interactions in the crystal packing [C9-H9A···*Cg*4$^{\#5}$, 2.77 Å; C24-H24A···*Cg*4$^{\#1}$, 2.97 Å; *Cg*4 = C1-C6; symmetry codes: #5, 2 – *x*, 1 – *y*, 1 – *z*].

3. 5. Pharmacology Study

The assay of the urease inhibitory activity was in accordance with the literature method.[18] The free Schiff base and zinc acetate have weak activity, with inhibition rates of 15.1% and 22.8% at concentration of 100 μmol·L^{-1}. However, the three zinc complexes have stronger activity than the Schiff base, with IC_{50} values of 15.3 μmol·L^{-1} (**1**), 13.9 μmol·L^{-1} (**2**), and 7.1 μmol·L^{-1} (**3**). It is obvious that the azide coordinated complexes have better activity than those with acetate ligands. However, the sodium azide itself has no activity on urease. Thus, the zinc complexes have better activities than their starting materials. In addi-

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

1			
Zn1–O1	2.120(5)	Zn1–O3	2.020(5)
Zn1–O4	1.979(6)	Zn1–N1	2.021(7)
Zn1–N2	2.259(7)	Zn2–O1	2.097(5)
Zn2–O3	2.177(5)	Zn2–O5	2.038(6)
Zn3–O10	1.992(6)	Zn3–N3	2.051(7)
Zn3–O8	2.058(6)	Zn3–O6	2.105(5)
Zn3–N4	2.248(7)	Zn4–O9	2.045(6)
Zn4–O6	2.086(5)	Zn4–O8	2.196(5)
O4–Zn1–O3	99.0(2)	O4–Zn1–N1	121.8(3)
O3–Zn1–N1	138.5(3)	O4–Zn1–O1	93.7(2)
O3–Zn1–O1	81.8(2)	N1–Zn1–O1	88.0(3)
O4–Zn1–N2	95.3(3)	O3–Zn1–N2	104.6(3)
N1–Zn1–N2	80.5(3)	O1–Zn1–N2	168.0(2)
O5–Zn2–O5A	180	O5–Zn2–O1A	89.9(2)
O5–Zn2–O1	90.1(2)	O1–Zn2–O1A	180
O5–Zn2–O3A	91.1(2)	O5–Zn2–O3	88.9(2)
O1–Zn2–O3A	101.3(2)	O1–Zn2–O3	78.7(2)
O5–Zn2–O3A	91.1(2)	O1–Zn2–O3A	101.3(2)
O3–Zn2–O3A	180		
O10–Zn3–N3	119.2(3)	O10–Zn3–O8	99.7(2)
N3–Zn3–O8	140.3(3)	O10–Zn3–O6	93.1(2)
N3–Zn3–O6	87.1(2)	O8–Zn3–O6	83.2(2)
O10–Zn3–N4	94.2(3)	N3–Zn3–N4	81.8(3)
O8–Zn3–N4	104.0(3)	O6–Zn3–N4	168.7(2)
O9–Zn4–O9B	180	O9–Zn4–O6B	90.1(2)
O9–Zn4–O6	89.9(2)	O6–Zn4–O6B	180
O9–Zn4–O8B	90.8(2)	O6–Zn4–O8B	99.7(2)

O9–Zn4–O8	89.2(2)	O9–Zn4–O8B	90.8(2)
O6–Zn4–O8	80.3(2)	O8–Zn4–O8B	180

Symmetry codes: A: 1 – *x*, 1 – *y*, – *z*; B: – *x*, 1 – *y*, 1 – *z*.

2			
Zn1–O1	2.183(3)	Zn1–N1	2.048(4)
Zn1–N2	2.263(4)	Zn1–N5	1.965(4)
Zn1–N8	2.032(4)	Zn2–O1	1.995(3)
Zn2–O2	1.997(3)	Zn2–O3	2.007(4)
Zn2–O5	2.046(3)	Zn2–N8	2.226(4)
Zn3–O2	2.134(3)	Zn3–O4	1.980(3)
Zn3–O6	1.966(3)	Zn3–N3	2.029(4)
Zn3–N4	2.213(4)		
N5–Zn1–N8	109.28(19)	N5–Zn1–N1	111.32(18)
N8–Zn1–N1	137.59(17)	N5–Zn1–O1	101.51(18)
N8–Zn1–O1	76.77(14)	N1–Zn1–O1	83.67(14)
N5–Zn1–N2	102.28(19)	N8–Zn1–N2	102.38(16)
N1–Zn1–N2	80.57(16)	O1–Zn1–N2	154.98(14)
O1–Zn2–O2	125.86(13)	O1–Zn2–O3	121.73(14)
O2–Zn2–O3	110.86(13)	O1–Zn2–O5	95.54(13)
O2–Zn2–O5	93.99(14)	O3–Zn2–O5	92.62(16)
O1–Zn2–N8	76.51(14)	O2–Zn2–N8	96.74(15)
O3–Zn2–N8	85.46(16)	O5–Zn2–N8	169.09(15)
O6–Zn3–O4	117.78(15)	O6–Zn3–N3	115.96(15)
O4–Zn3–N3	126.26(16)	O6–Zn3–O2	94.31(13)
O4–Zn3–O2	90.56(13)	N3–Zn3–O2	86.42(14)
O6–Zn3–N4	94.11(15)	O4–Zn3–N4	93.10(14)
N3–Zn3–N4	82.17(16)	O2–Zn3–N4	167.97(13)
3			
Zn1–O1	2.020(6)	Zn1–O3	1.982(5)
Zn1–N1	2.042(7)	Zn1–N2	2.246(7)
Zn1–N5	2.063(8)	Zn2–O2	2.052(7)
Zn2–N3	2.049(8)	Zn2–N4	2.310(9)
Zn2–N7	2.025(12)	Zn2–N8	1.975(13)
O3–Zn1–O1	95.8(2)	O3–Zn1–N1	145.3(2)
O1–Zn1–N1	88.9(2)	O3–Zn1–N5	96.8(3)
O1–Zn1–N5	95.4(3)	N1–Zn1–N5	117.0(3)
O3–Zn1–N2	91.9(2)	O1–Zn1–N2	167.3(2)
N1–Zn1–N2	79.1(3)	N5–Zn1–N2	93.7(3)
N8–Zn2–N7	114.6(7)	N8–Zn2–N3	128.9(5)
N7–Zn2–N3	116.5(5)	N8–Zn2–O2	91.6(4)
N7–Zn2–O2	93.7(4)	N3–Zn2–O2	87.0(3)
N8–Zn2–N4	99.2(5)	N7–Zn2–N4	89.8(4)
N3–Zn2–N4	79.3(3)	O2–Zn2–N4	166.0(3)

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

D*–H···*A	***d*(*D*–H)**	***d*(H···*A*)**	***d*(*D*···*A*)**	**Angle (*D*–H···*A*)**
1				
C7–H7···O2^{i}	0.93	2.25	3.1709(2)	169(3)
C24–H24···O7^{ii}	0.93	2.27	3.1649(2)	162(3)
2				
C7–H7···O3^{iii}	0.93	2.56	3.4745(3)	167(4)
C8–H8A···O5^{iii}	0.97	2.37	3.3022(3)	160(4)
C20–H20···N10^{iv}	0.93	2.56	3.4785(3)	170(4)
3				
O3–H3A···O1^{v}	0.85(1)	1.76(2)	2.615(7)	176(11)
O3–H3B···O2^{v}	0.85(1)	1.82(2)	2.593(7)	149(11)

Symmetry codes: (i): 1 – *x*, 1/2 + *y*, 1/2 – *z*; (ii): – *x*, –1/2 + *y*, 1/2 – *z*; (iii): 1 – *x*, 1 – *y*, 1 – *z*; (iv): 1 – *x*, – *y*, 1 – *z*; (v): 1 – *x*, 1 – *y*, 1 – *z*.

tion, the present zinc complexes have stronger activities than the reference drug acetohydroxamic acid (IC_{50} = 28.1 μmol·L^{-1}).

4. Conclusion

In summary, three new acetate and azide coordinated polynuclear zinc complexes have been synthesized. Structures of the complexes have been confirmed with single crystal X-ray diffraction. The Schiff base compound coordinates to the zinc atoms through the phenolate oxygen, imino nitrogen and pyrrolidine nitrogen. The Zn atoms in the complexes are in square pyramidal or trigonal-bipyramidal coordination, or that between them. The complexes have interesting urease inhibitory activity, which may be used as new urease inhibitors.

Supplementary Data

CCDC 2231647 (**1**), 2231648 (**2**) and 2231649 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Povzetek

Sintetizirali smo tri nove komplekse cinka(II), $[Zn_3(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}OAc)_2(\mu_2\text{-}\eta^2\text{:}\eta^0\text{-}OAc)_2L_2]$ (**1**), $[Zn_3(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}OAc)_2(\mu_{1,1}\text{-}N_3)(N_3)L_2]$ (**2**) in $[Zn_2(\mu_{1,3}\text{-}N_3)(N_3)(H_2O)L_2]$ (**3**), z ligandom 4-kloro-2-(((2-(pirolidin-1-il)etil)imino)metil)fenol (HL). Spojine smo karakterizirali z elementno analizo, IR in UV-Vis spektroskopskimi metodami. Kristalne strukture kompleksov smo potrdili z monokristalno rentgensko difrakcijo. Spojina **1** je trijedrna in vsebuje bidentatne acetatne ligande, mostovne acetate in mostovne fenolatne ligande. Tudi kompleks **2** je trijedrn z bidentatnimi acetatnimi, azidnimi in mostovnimi fenolatnimi ligandi. Kompleks **3** je dvojedrn z mostovnimi azidnimi ligandi. Koordinacija okoli cinkovih atomov je kvadratno piramidalna in trigonalno bipiramidalna. Ligandi, ki so Schiffove baze, se na cinkov atom koordinirajo preko kisika iz fenolatne skupine, dušika iz imino skupine in dušika iz pirolidina. Kompleksi delujejo kot inhibitorji na ureazo *Jack bean* z vrednostmi IC_{50} med 7.1 in 15.3 $\mu mol \cdot L^{-1}$.