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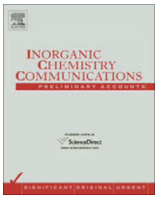

Influence of the steric effects of the Schiff bases and the hydrogen bonds on the bridging modes of the azide groups: Syntheses and crystal structures of three azide-bridged Schiff base zinc(II) complexes

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ABSTRACT

Three polymeric zinc(II) complexes, derived from the end-on azide ($\mu_{1,1}$-N_3) and end-to-end azide ($\mu_{1,3}$-N_3) bridges and similar tridentate Schiff base ligands, have been synthesized and structurally characterized. The zinc(II) atom in each complex is in a midway between trigonal–bipyramidal and square–pyramidal coordination. The slight difference of the steric effects of the Schiff bases and the hydrogen bonds can influence the bridging modes of the azide groups.

Polynuclear complexes with bridging groups are currently attracting attention for their interesting molecular topologies and crystal packing motifs, as well as the fact that they may be designed with specific functionalities [1]. As is well known, the azide ligand can adopt end-on ($\mu_{1,1}$-N_3), end-to-end ($\mu_{1,3}$-N_3), and many other coordination modes when it links different metal atoms, forming versatile polynuclear structures [2]. However, given the present state of knowledge, it is not possible to determine which coordination mode will be adopted by the azide group and what structures will finally be formed. Although Schiff base complexes with azide bridges have been extensively studied, Schiff base zinc(II) complexes involving azide bridges have seldom been reported [3]. Study the influence of the Schiff base ligands and the hydrogen bonds on the coordination modes of the azide groups may help us better understand and control the topologies of the azide-bridged complexes. In this paper, three new azide-bridged polymeric zinc(II) complexes with similar Schiff bases, $[ZnL1(\mu_{1,1}\text{-}N_3)ZnL1(\mu_{1,3}\text{-}N_3)]_n$ (**1**), $[ZnL2(\mu_{1,1}\text{-}N_3)ZnL2(\mu_{1,1}\text{-}N_3)]_n$ (**2**), and $[ZnL3(\mu_{1,3}\text{-}N_3)ZnL3(\mu_{1,3}\text{-}N_3)]_n$ (**3**) (L1 = 1-[(2-propylamino-ethylimino)methyl]naphthalen-2-olate, L2 = 2-bromo-4-chloro-6-[(2-propylaminoethylimino)methyl]phenolate, and L3 = 2-bromo-4-chloro-6-[(2-piperidin-1-ylethylimino)methyl]phenolate; see Scheme 1), have been synthesized to investigate the influence of the Schiff bases and the hydrogen bonds on the bridging modes of the azide. The three Schiff bases in this paper are very similar tridentate ligands, which can coordinate to the metal atoms through the phenolic oxygen, imine nitrogen and amine nitrogen atoms [4]. The mere difference lies in the steric effects of the terminal groups. It is notable that the Schiff bases HL2 and HL3 were newly synthesized and the metal complexes of them have never been reported previously. For HL1, only one mononuclear copper(II) complex has been reported [5]. The complexes showed weak inhibitory activity against urease.

The three Schiff bases were prepared by reaction of the corresponding aldehydes with the amines in methanol solutions and subsequent evaporation of the solvent [6]. All the complexes were synthesized according to the same method: A methanol solution (2 ml) of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 mmol, 27.1 mg) was added with stirring to a methanol solution (10 ml) of NaN_3 (0.1 mmol, 6.5 mg) and the corresponding Schiff base (0.1 mmol). The mixture was stirred at room temperature for 30 min to give a colorless solution. X-ray quality colorless block-shaped single crystals were formed by slow evaporation of the solution in air for a few days. Yield: 73% (**1**), 81% (**2**), and 65% (**3**) [7].

X-ray crystallography [8] reveals that the structures of the complexes are similar one-dimensional chains, except for the different coordination modes of the azide bridges. Complex **1** (Fig. 1) is an alternate end-on and end-to-end azide-bridged polymeric zinc(II) compound. Complex **2** (Fig. 2) is a pure end-on azide-bridged polymeric zinc(II) compound. And complex **3** (Fig. 3) is a pure end-to-end azide-bridged polymeric zinc(II) compound.

In each complex, the coordination of the Zn atom may be regarded as midway between trigonal–bipyramidal and square–pyramidal as described by the τ parameters, an index of the degree of trigonality [9]. The τ values calculated for the complexes are

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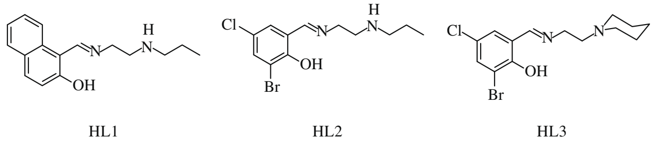

Scheme 1. Schematic views of the Schiff bases.

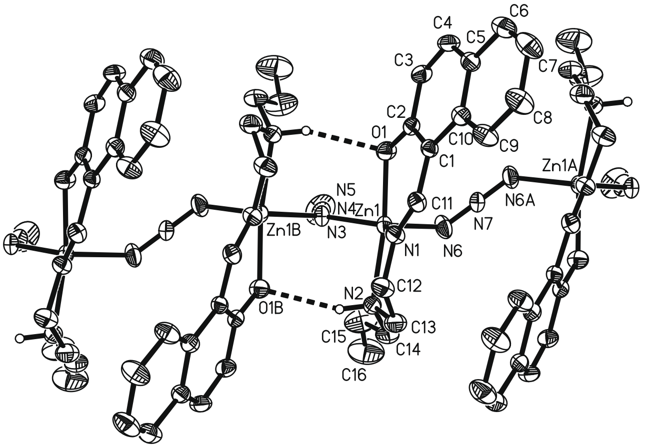

Fig. 1. Molecular structure of **1** and the atomic numbering scheme. Intermolecular hydrogen bonds are shown as dashed lines. Selected bond lengths (Å) and bond angles (°): Zn1–O1 2.033(2), Zn1–N1 2.028(3), Zn1–N2 2.185(3), Zn1–N3 2.043(2), Zn1–N6 2.020(3), N6–Zn1–N1 117.3(2), N6–Zn1–O1 96.8(2), N1–Zn1–O1 85.6(1), N6–Zn1–N3 113.0(2), N1–Zn1–N3 129.6(2), O1–Zn1–N3 90.0(1), N6–Zn1–N2 97.0(2), N1–Zn1–N2 81.9(1), O1–Zn1–N2 164.5(2), N3–Zn1–N2 91.1(1).

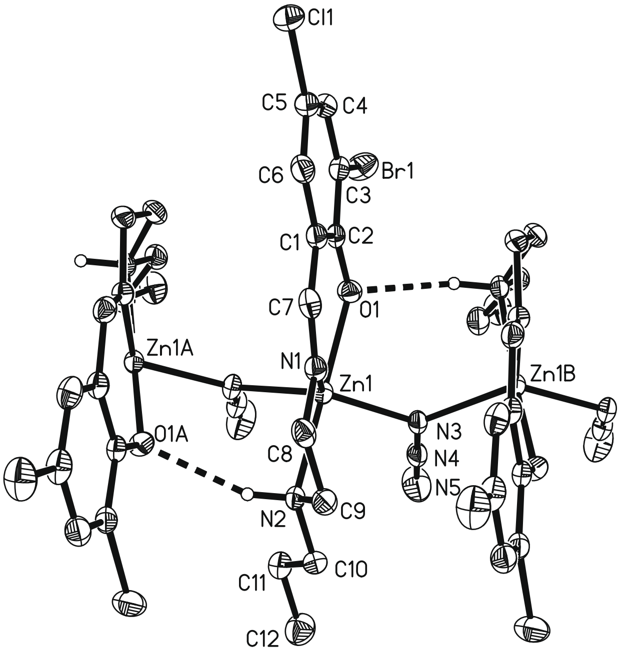

Fig. 2. Molecular structure of **2** and the atomic numbering scheme. Intermolecular hydrogen bonds are shown as dashed lines. Selected bond lengths (Å) and bond angles (°): Zn1–O1 2.037(2), Zn1–N1 2.049(2), Zn1–N2 2.181(2), Zn1–N3 2.092(2), Zn1–N3^i 2.118(2), O1–Zn1–N1 87.4(1), O1–Zn1–N3 89.2(1), N1–Zn1–N3 120.1(1), O1–Zn1–N3^i 94.5(1), N1–Zn1–N3^i 117.2(1), N3–Zn1–N3^i 122.7(2), O1–Zn1–N2 167.8(1), N1–Zn1–N2 80.5(1), N3–Zn1–N2 95.8(1), N3^i–Zn1–N2 92.1(1). Symmetry code for *i*: *x*, 1/2 − *y*, −1/2 + *z*.

0.582 for **1**, 0.752 for **2**, and 0.433 for **3**, respectively. It can be seen that the coordination of the Zn atoms in **1** and **2** is close to distorted trigonal-bipyramidal, while that in **3** is close to distorted square pyramidal.

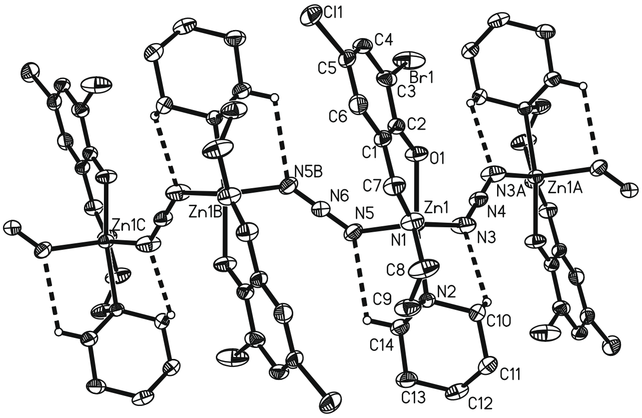

Fig. 3. Molecular structure of **3** and the atomic numbering scheme. Intramolecular hydrogen bonds are shown as dashed lines. Selected bond lengths (Å) and bond angles (°): Zn1–O1 2.008(3), Zn1–N1 2.032(4), Zn1–N2 2.219(3), Zn1–N3 2.013(4), Zn1–N5 2.073(4), O1–Zn1–N3 91.8(2), O1–Zn1–N1 87.3(2), N3–Zn1–N1 140.2(2), O1–Zn1–N5 97.2(2), N3–Zn1–N5 106.6(2), N1–Zn1–N5 113.0(2), O1–Zn1–N2 166.2(2), N3–Zn1–N2 91.1(2), N1–Zn1–N2 81.9(2), N5–Zn1–N2 94.9(2).

In **1** and **2**, the basal plane of the trigonal–bipyramid is furnished by one imine nitrogen atom of the Schiff base ligand and two nitrogen atoms from two azide groups, and the axial positions are occupied by one phenolic oxygen and one amine nitrogen atoms of the Schiff base ligand. The Zn atoms deviate by 0.016(2) Å in **1** and 0.014(2) Å in **2**, respectively, from the least-squares plane defined by the three basal donor atoms. In **3**, the basal plane of the square pyramid is furnished by one phenolic oxygen, one imine nitrogen and one amine nitrogen atoms of the Schiff base ligand and one nitrogen atom of an azide group, and the apical position is occupied by one nitrogen atom of another azide group. The Zn atom deviates by 0.051(2) Å in **3** from the least-squares plane defined by the four basal donor atoms. Close examination of the structures revealed that the Zn–O and Zn–N bond lengths are comparable to each other, and can be considered as normal by comparison with those reported in the literatures [3,4a].

In **1**, there exists two intermolecular N–H$\cdots$O hydrogen bonds (Table 1) between the adjacent two complex moieties, which made the two Zn atoms close to each other, and the azide group adopts end-on bridging mode, with the Zn$\cdots$Zn distance of 3.362(2) Å. While the adjacent two complex moieties without hydrogen bonds are deviate from each other, with the azide group has no choice but adopts end-to-end bridging mode, the Zn$\cdots$Zn distance between them is 5.371(2) Å. In **2**, there exists equivalent intermolecular N–H$\cdots$O hydrogen bonds between each adjacent moieties, which made the two Zn atoms close to each other, and the azide groups adopt end-on bridging mode, with the Zn$\cdots$Zn distances of 3.681(2) Å. And in **3**, there are no intermolecular hydrogen bonds

Table 1
Hydrogen bond distances (Å) and bond angles (°) for the complexes.

D–H$\cdots$*A*	*d*(*D*–H)	*d*(H$\cdots$*A*)	*d*(*D*$\cdots$*A*)	*Angle* (*D*–H$\cdots$*A*)
1				
N2–H2$\cdots$O1$^{\#1}$	0.899(10)	2.23(2)	3.079(4)	158(4)
2				
N2–H2$\cdots$O1$^{\#2}$	0.896(10)	2.191(18)	3.042(3)	159(4)
N2–H2$\cdots$Br1$^{\#2}$	0.896(10)	3.08(3)	3.714(2)	130(3)
C6–H6$\cdots$N5$^{\#3}$	0.93	2.57	3.359(3)	144(3)
3				
C10–H10B$\cdots$N3	0.97	2.47	3.053(3)	118(3)
C14–H14B$\cdots$N5	0.97	2.62	3.092(3)	110(3)

Symmetry transformations used to generate the equivalent atoms: #1: 1/2 − *x*, −1/2 − *y*, *z*; #2: *x*, 1/2 − *y*, −1/2 + *z*; #3: 1 + *x*, 1/2 − *y*, −1/2 + *z*.

Table 2
Inhibition of urease by the tested materials.

Tested materials	IC_{50}[a] (μM)
1	>100
2	72.19 ± 0.70
3	77.36 ± 0.53
HL1	>100
HL2	>100
HL3	>100
Zinc acetate	31.45 ± 0.39
Acetohydroxamic acid	45.32 ± 0.27

[a] All IC_{50} values were expressed as mean ± S.D. values of the three parallel tests.

between the adjacent moieties as those in **1** and **2**, instead, there exists intramolecular C–H···N hydrogen bonds. The lack of intermolecular hydrogen bonds, as well as the large steric effects of the cyclohexyl groups in **3** lead to the two adjacent moieties deviate from each other, and the azide groups adopt end-to-end bridging mode. The Zn···Zn distances are 5.879(2) and 5.545(2) Å, respectively.

It can be seen that the hydrogen bonds in **1** and **2** influence the bridging modes of the azide groups, while that in **3**, the steric effects of the terminal cyclohexyl group appears more convincing.

The measurement of *jack bean* urease inhibitory activity was carried out for three parallel times according to the literature phenol-red method [10]. The acetohydroxamic acid was used as a positive reference. The results are summarized in Table 2. Complex **1** shows no activity, while **2** and **3** show weak activity against the enzyme. The results in this paper are accordance with those reported previously, that the zinc(II) complexes have much weak urease inhibitory activities [11].

In summary, the present study reports the synthesis, structures and urease inhibitory activity of three azide-bridged polymeric Schiff base zinc(II) complexes. The steric effects of the Schiff bases and the hydrogen bonds can influence the bridging modes of the azide groups. The urease inhibitory activities of the zinc(II) complexes are not very satisfactory.

Acknowledgement

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Appendix A. Supplementary material

CCDC 719165 (**1**), 719166 (**2**), and 719167 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.03.009.

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[6] Anal. Calc. for $C_{16}H_{22}N_2O$ (HL1): C 74.4, H 8.6, N 10.8%. Found: C 74.7, H 8.5, N 11.0%. Anal. Calc. for $C_{12}H_{16}BrClN_2O$ (HL2): C 45.1, H 5.0, N 8.8%. Found: C 45.5, H 5.2, N 8.7%. Anal. Calc. for $C_{14}H_{18}BrClN_2O$ (HL3): C 48.6, H 5.2, N 8.1%. Found: C 48.1, H 5.2, N 8.3%. Selected IR data (KBr, cm^{-1}): HL1, ν 1632 (s, C=N); HL2, ν 1645 (s, C=N); HL3, ν 1643 (s, C=N). ^{1}HNMR data ($CDCl_3$, ppm): HL1, $\delta = 0.91$ (t, 3H), 1.53 (m, 2H), 2.17 (s, 1H), 2.56 (t, 2H), 2.96 (t, 2H), 3.56 (t, 2H), 7.12 (d, 1H), 7.14 (t, 1H), 7.21 (t, 1H), 7.45 (d, 1H), 7.60 (d, 1H), 7.78 (d, 1H), 8.17 (s, 1H); HL2, $\delta = 0.91$ (t, 3H), 1.53 (m, 2H), 2.16 (s, 1H), 2.56 (t, 2H), 2.96 (t, 2H), 3.57 (t, 2H), 7.14 (s, 1H), 7.51 (s, 1H), 8.19 (s, 1H); HL3, $\delta = 1.43$ (m, 2H), 1.56 (m, 4H), 2.16 (s, 1H), 2.44 (t, 4H), 2.63 (t, 2H), 3.72 (t, 2H), 7.13 (d, 1H), 7.54 (d, 1H), 8.18 (s, 1H).

[7] Anal. Calc. for $C_{16}H_{19}N_5OZn$ (**1**): C 53.0, H 5.3, N 19.3%. Found: C 53.6, H 5.4, N 19.0%. Anal. Calc. for $C_{12}H_{15}BrClN_5OZn$ (**2**): C 33.8, H 3.5, N 16.4%. Found: C 33.4, H 3.6, N 16.6%. Anal. Calc. for $C_{14}H_{17}BrClN_5OZn$ (**3**): C 37.2, H 3.8, N 15.5%. Found: C 37.5, H 4.0, N 15.2%. Selected IR data (KBr, cm^{-1}): 1, ν 2106 (vs, N_3), ν 2066 (sh, vs, N_3), ν 1619 (s, C=N). 2, ν 2100 (vs, N_3), ν 1633 (s, C=N). 3, ν 2145 (s, N_3), ν 2087 (vs, N_3), ν 1632 (s, C=N).

[8] Crystal data for **1** ($C_{16}H_{19}N_5OZn$): $M_t = 362.73$, orthorhombic, space group Pccn, $a = 22.232(2)$, $b = 8.639(2)$, $c = 17.222(3)$ Å, $V = 3307.7(10)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.457$ g cm^{-3}, $\mu(MoK_\alpha) = 1.496$ mm^{-1}, $R_1 = 0.0418$, $wR_2 = 0.1057$ (all data), $T = 298$ K. Crystal data for **2** ($C_{12}H_{15}BrClN_5OZn$): $M_t = 426.02$, monoclinic, space group $P2_1/c$, $a = 9.423(2)$, $b = 22.685(3)$, $c = 7.318(2)$ Å, $\beta = 94.94(3)°$ $V = 1558.5(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.816$ g cm^{-3}, $\mu(MoK_\alpha) = 4.316$ mm^{-1}, $R_1 = 0.0368$, $wR_2 = 0.0884$ (all data), $T = 298$ K. Crystal data for **3** ($C_{14}H_{17}BrClN_5OZn$): $M_t = 452.06$, monoclinic, space group C2/c, $a = 28.679(3)$, $b = 7.039(1)$, $c = 18.881(2)$ Å, $\beta = 117.33(3)°$, $V = 3386.1(12)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.774$ g cm^{-3}, $\mu(MoK_\alpha) = 3.979$ mm^{-1}, $R_1 = 0.0452$, $wR_2 = 0.1038$ (all data), $T = 298$ K.

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