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Synthesis and Crystal Structures of a Pair of Isostructural Azido-Bridged Polynuclear Schiff Base Zinc(II) Complexes

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Abstract A pair of novel isostructural azido-bridged polynuclear zinc(II) complexes, $[Zn_2(L1)_2(\mu_{1,1}-N_3)(\mu_{1,3}-N_3)]_n$ (1) and $[Zn_2(L2)_2(\mu_{1,1}-N_3)(\mu_{1,3}-N_3)]_n$ (2) (HL1 = 2-bromo-4-chloro-6-[(2-isopropylaminoethylimino)methyl]phenol, HL2 = 2,4-dibromo-6-[(2-isopropylaminoethylimino)methyl]phenol), have been synthesized and structurally characterized by elemental analysis, IR spectra and single crystal X-ray diffraction. Both complexes crystallize in the orthorhombic space group *Pcca*. Crystal data for (1): a =22.567(4) Å, b = 8.414(2) Å, c = 17.268(3) Å, V = 3279.0(11) Å³, Z = 8, $R_1 = 0.0441$, and $wR_2 = 0.0846$. Crystal data for (2): a = 22.536(4) Å, b = 8.409(2) Å, c =17.531(3) Å, V = 3322.2(11) Å³, Z = 8, $R_1 = 0.0538$, and $wR_2 = 0.0906$. X-ray structure determination revealed that each zinc(II) atom in the complexes is in a trigonalbipyramidal coordination, with one imine N atom of a Schiff base ligand and two N atoms from two bridging azide ligands defining the basal plane, and one phenolate O and one amine N atoms of the Schiff base ligand occupying the two axial positions.

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Introduction

Polynuclear complexes have been widely investigated due to their versatile molecular structures and interesting functionalities [1-3]. The prime strategy for designing the polynuclear complexes is to use suitable bridging ligands, such as azide, thiocyanate, cyanide, and so on [4-7]. Among the bridging groups, azide is the preference. Depending upon the steric and electronic demand of the co-ligands, the azido group has been shown to be able to link two or more metal ions in various bridging modes such as $\mu_{1,3}$, $\mu_{1,1}$, $\mu_{1,1,1}$, $\mu_{1,1,3}$, etc. to give birth to a variety of one-, two-, and three-dimensional species using Schiff bases or other polydentate organics as auxillary ligands [8-11]. The versatile features of metal-azido systems in coordination chemistry may lead to novel topologies that are difficult to achieve with other bridging ligands, but a major obstacle is impossible to predict which coordination modes will be adopted by the azide ligand. For the zinc(II) complexes, the azide bridges usually adopt $\mu_{1,1}$ mode [12–16]. It is surprising that the $\mu_{1,3}$ mode is not observed for the azidobridged zinc(II) complexes through the CSD search, except for one sample containing both $\mu_{1,1}$ and $\mu_{1,3}$ azido bridges [17]. In this article, a pair of novel azido-bridged polynuclear zinc(II) complexes, $[Zn_2(L1)_2(\mu_{1,1}-N_3)(\mu_{1,3}-N_3)]_n$ (1) and $[Zn_2(L2)_2(\mu_{1,1}-N_3)(\mu_{1,3}-N_3)]_n$ (2) (Scheme 1; HL1 = 2-bromo-4-chloro-6-[(2-isopropylaminoethylimino)methyl]phenol, HL2 = 2,4-dibromo-6-[(2-isopropylaminoethylimino)methyl]phenol), have been synthesized and structurally characterized by elemental analysis, IR spectra and single-crystal

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Scheme 1 X = Cl for (1), X = Br for (2)

X-ray diffraction. The results indicates that the hydrogen bonds can influence the bridging modes of the azide ligands.

Experimental

Materials and Measurements

3-Bromo-5-chlorosalicylaldehyde, 3,5-dibromosalicylaldehyde and *N*-isopropylethane-1,2-diamine were purchased from Lancaster. All other chemicals (reagent grade) were commercially available and were used without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Nicolet AVATAR 360 spectrophotometer as KBr pellets in the 4000–400 cm⁻¹ region.

Synthesis of the Schiff Bases HL1 and HL2

HL1 and HL2 were synthesized by the condensation of equimolar quantities of *N*-isopropylethane-1,2-diamine with 3-bromo-5-chlorosalicylaldehyde and 3,5-dibromo-salicylaldehyde, respectively, in methanol solutions at room temperature. Yield: 92% for HL1 and 97% for HL2. (Found: C, 45.5; H, 5.4; N, 8.6. Calc. for HL1: C, 45.1; H, 5.1; N, 8.8%. Found: C, 39.3; H, 4.5; N, 7.9. Calc. for HL2: C, 39.6; H, 4.4; N, 7.7%).

Synthesis of the Complex $[Zn_2(L1)_2(\mu_{1,1}-N_3)(\mu_{1,3}-N_3)]_n$

To an anhydrous methanol solution (5 mL) of $Zn(CH_3COO)_2 \cdot 2H_2O$ (22.0 mg, 0.1 mmol) was added a methanol solution (10 mL) of HL1 (31.9 mg, 0.1 mmol) and a methanol solution (5 mL) of NaN₃ (6.5 mg, 0.1 mmol) with stirring. The mixture was stirred for 30 min at room

temperature and filtered. Upon keeping the filtrate in air for a week, colorless block-shaped crystals of (1), suitable for X-ray crystal structure determination, formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol and dried in a vacuum desiccator containing anhydrous CaCl₂. Yield 62% on the basis of HL1. (Found: C, 33.2; H, 3.7; N, 16.0. Calc. for $C_{12}H_{15}BrClN_5OZn$: C, 33.8; H, 3.5; N, 16.4%).

Synthesis of the Complex $[Zn_2(L2)_2(\mu_{1,1}-N_3)(\mu_{1,3}-N_3)]_n$

Complex (2) was prepared by the similar procedure as described for (1), with HL1 replaced by HL2 (36.4 mg, 0.1 mmol), resulting colorless block-shaped crystals of (2). Yield 71% on the basis of HL2. (Found: C, 30.9; H, 3.5; N, 14.5. Calc. for $C_{12}H_{15}Br_2N_5OZn$: C, 30.6; H, 3.2; N, 14.9%).

 Table 1
 Crystal data and refinement parameters for the complexes

Complex	1	2	
Molecular formula	C ₁₂ H ₁₅ BrClN ₅ OZn	C ₁₂ H ₁₅ Br ₂ N ₅ OZn	
Molecular weight	426.0	470.5	
Temperature (K)	298(2)	298(2)	
Crystal shape	block	block	
Crystal dimensions (mm); colour	$0.27 \times 0.23 \times 0.20;$ colorless	$0.28 \times 0.27 \times 0.27;$ colorless	
Crystal system	Orthorhombic	Orthorhombic	
Space group	Pcca	Pcca	
a (Å)	22.567(4)	22.536(4)	
<i>b</i> (Å)	8.414(2)	8.409(2)	
<i>c</i> (Å)	17.268(3)	17.531(3)	
Volume (Å ³)	3279.0(11)	3322.2(11)	
Ζ	8	8	
D_{calc} (g cm ⁻³)	1.726	1.881	
Absorption coefficient (mm ⁻¹)	4.103	6.294	
<i>F</i> (000)	1696	1840	
θ range (°)	1.80/27.49	1.81/27.50	
Range/indices (h, k, l)	-28/28, -10/10, -22/22	-29/29, -10/10, -22/22	
Absorption correction	Empirical	Empirical	
T_{\min}	0.404	0.272	
T _{max}	0.494	0.281	
Reflections/Parameters	3760/197	3811/197	
Independent reflections	2069	1707	
Restraints	1	1	
Goodness of fit on F^2	1.000	0.981	
$R_1, wR_2 [I \ge 2\sigma(I)]^a$	0.0441, 0.0846	0.0538, 0.0906	
R_1 , wR_2 (all data) ^a	0.1048, 0.1069	0.1568, 0.1205	

 $\frac{1}{\sigma^2 F_o^2 + (0.0226(F_o^2 + 2F_c^2)/3)^2 + 3.8229(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}, w_1 = [\sigma^2 F_o^2 + (0.0226(F_o^2 + 2F_c^2)/3)^2 + 3.8229(F_o^2 + 2F_c^2)/3]^{-1}, w_2 = [\sigma^2 F_o^2 + (0.0336(F_o^2 + 2F_c^2)/3)^2 + 2.6831(F_o^2 + 2F_c^2)/3]^{-1}$

X-ray Crystallography

X-ray diffraction intensities of the complexes were collected using a Bruker Smart APEXII CCD area detector equipped with graphite-monochromated MoK radiation ($\lambda =$ 0.71073 Å) at 298(2) K. Empirical absorption corrections were applied using the SADABS program [18]. The structures were solved by the direct method and refined by fullmatrix least squares on F^2 using the SHELXTL package [19]. All non-hydrogen atoms were refined anisotropically. Atoms H2 in both (1) and (2) attached to N2 were located in difference Fourier maps and refined isotropically, with N-H distances restrained to 0.90(1) Å. All other H atoms were placed in calculated positions and constrained to ride on their parent atoms, with C-H distances in the range 0.93-0.97 Å, and with U_{iso} (H) set at $1.2U_{eq}$ (C) and $1.5U_{eq}$ (methyl C). The crystallographic data for the two complexes are summarized in Table 1.

Results and Discussion

Selected bond lengths and angles are given in Table 2. The two complexes were synthesized under the same synthetic procedures with similar starting materials.

Table 2 Selected bond distances $({\rm \AA})$ and angles $(^{\rm o})$ for the complexes

(1)			
Bond distances			
Zn1–O1	2.054(3)	Zn1–N1	2.040(4)
Zn1–N2	2.212(4)	Zn1–N3	2.044(3)
Zn1–N6	2.037(4)		
Bond angles			
N6-Zn1-N1	119.8(2)	N6-Zn1-N3	112.2(2)
N1-Zn1-N3	127.9(2)	N6-Zn1-O1	94.4(2)
N1-Zn1-O1	85.9(2)	N3-Zn1-O1	87.4(2)
N6-Zn1-N2	99.3(2)	N1-Zn1-N2	80.8(2)
N3-Zn1-N2	94.4(2)	O1–Zn1–N2	164.4(2)
(2)			
Bond distances			
Zn1–O1	2.059(4)	Zn1–N1	2.049(5)
Zn1–N2	2.208(5)	Zn1–N3	2.034(4)
Zn1–N6	2.032(5)		
Bond angles			
N6-Zn1-N1	119.5(2)	N6-Zn1-N3	112.9(2)
N1-Zn1-N3	127.5(2)	N6-Zn1-O1	94.4(2)
N1–Zn1–O1	86.1(2)	N3-Zn1-O1	87.5(2)
N6-Zn1-N2	98.8(2)	N1–Zn1–N2	80.6(2)
N3-Zn1-N2	94.6(2)	O1–Zn1–N2	164.7(2)



Fig. 1 Molecular structure of (1) at 30% probability displacement. H atoms not involved in the hydrogen bonding have been omitted for clarity. Atoms labeled with the suffix A are at the symmetry position 3/2 - x, 1 - y, z. Hydrogen bonds are shown as *dashed lines*

The elemental analyses are in good agreement with the chemical formulae proposed for the compounds.

Crystal Structure Description of the Complexes

Figures 1 and 2 give perspective views of the complexes (1) and (2) together with the atomic labeling system. Both complexes are one-dimensional zinc(II)-azido chains with alternately end-on and end-to-end azido bridges. The asymmetric unit of each complex consists of one $[ZnL(\mu_{1,1}-N_3)ZnL(\mu_{1,3}-N_3)]$ (L = L1 for (1) and L2 for (2)) moiety. Each Zn^{II} ion in the complexes is in a



Fig. 2 Molecular structure of (2) at 30% probability displacement. H atoms not involved in the hydrogen bonding have been omitted for clarity. Atoms labeled with the suffix A are at the symmetry position 1/2 - x, -y, z. Hydrogen bonds are shown as *dashed lines*

trigonal-bipyramidal coordination, with one imine N atom of the Schiff base ligand and two N atoms from two bridging azido ligands defining the basal plane, and with one phenolate O and one amine N atoms of the Schiff base ligand occupying the axial positions. In both structures, the coordinate bond lengths are typical and comparable with each other, and similar to the corresponding values observed in other Schiff base zinc(II) complexes [20–22]. In (1), the bond angle N1–Zn1–N2 deviates from 90° by 9.2(2)°, and in (2), the bond angle N1–Zn1–N2 deviates from 90° by $9.4(2)^{\circ}$, which are caused by the strain created by the corresponding five-membered chelate rings. The bond angles O1-Zn1-N2 in (1) and (2) deviate from 180° by 15.6(2) and $15.3(2)^{\circ}$, respectively, indicating the distortion of each trigonal-bipyramidal coordination. Each of the azido ligands is nearly linear and shows bent

Fig. 3 Molecular packing arrangement of (1) (X = Cl) and (2) (X = Br). Viewed along the *a* axis



In looking at the unit cell parameters, the only really noteworthy variation between these two structures occurs along the *c*-axis. The *c*-axis for the unit cell in (1) with 17.268(3) Å is shorter than that in (2) with 17.531(3) Å,



which is caused by the shorter bond of C5–Cl1 [1.761(5) Å] in (1) than C5–Br2 [1.893(7) Å] in (2). For the *a* and *b* axes, there are no obvious difference for the bond values between the two structures. The molecular packing diagram for the two complexes is shown in Fig. 3, in which the molecules are linked through bridging azido ligands, forming chains running along the *b* axis.

IR Spectra

The IR spectra of (1) and (2) show strong absorption bands at 2,071 and 2,105 cm⁻¹, respectively, assigned to the vibrations of the end-to-end and end-on azido bridges. The strong absorption bands of the C=N bonds in the complexes are at 1,617 and 1,618 cm⁻¹, respectively. The close resemblance of the shape and the positions of the bands suggest similar coordination modes for the complexes.

Conclusions

A pair of novel azido-bridged polynuclear zinc(II) complexes with similar Schiff bases have been synthesized and structurally characterized. The Schiff bases HL1 and HL2 coordinate to the Zn atoms through the phenolate O, imine N and amine N atoms. The synthesis of the two complexes indicates that the azido ligands are versatile bridging groups, which bridge different Zn atoms through both endto-end and end-on coordination modes.

Supplementary Information

CCDC-715954 and 715955 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at http://www.ccdccam.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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