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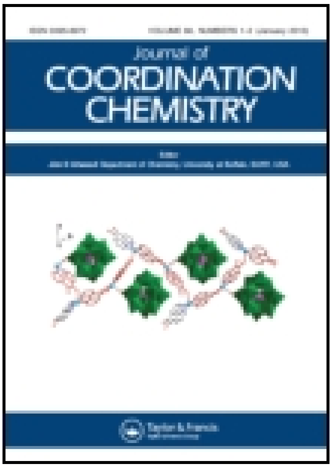

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# Synthesis, structures, and fluorescent properties of two oxalato-bridged dinuclear zinc(II) complexes with tridentate and tetradentate polybenzimidazole ligands

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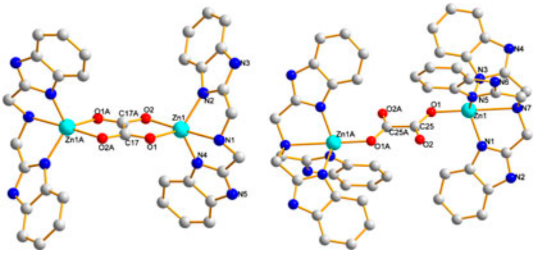

Two dinuclear oxalato-bridged zinc(II) complexes, $[Zn_2(bbma)_2(\mu_2\text{-}\eta^4\text{-ox})](ClO_4)_2$ (**1**) and $[Zn_2(ntb)_2(\mu_2\text{-}\eta^2\text{-ox})](ClO_4)_2 \cdot 4CH_3OH$ (**2**), containing tridentate and tetradentate polybenzimidazole ligands were synthesized, where bbma is bis(benzimidazol-2-yl-methyl)amine and ntb is tris(2-benzimidazolylmethyl)amine. They were characterized by single-crystal X-ray diffraction, elemental analysis, IR, and fluorescence spectroscopy. Zinc(II) complexes in **1** and **2** are five-coordinate in distorted trigonal bipyramidal geometry. Oxalate bridges two zinc(II) ions as a bis-bidentate chelate in **1,** while bis-monodentate in **2**. The Zn···Zn distances are 5.318(1) Å for **1** and 7.1295(5) Å for **2**, respectively. 1-D chain structures are formed in **2** by intermolecular hydrogen bonds. The solid state fluorescence spectra have been studied for **1** and **2**.

*Keywords*: Dinuclear zinc(II) complex; Benzimidazole; Oxalic acid; Crystal structure

## 1. Introduction

Oxalate is a versatile ligand which can adopt many coordination modes [1]. It binds zinc(II) to form mononuclear, dinuclear, polymeric 1-, 2-, and 3-D frameworks [2–17]. Many oxalato-bridged zinc(II) complexes have been prepared and structurally characterized. Only a few oxalato-bridged dinuclear zinc(II) complexes were obtained with auxiliary ligands. In most cases, oxalate is bis-bidentate as in the structures of $[Zn_2(L)_2(\mu\text{-}C_2O_4)(H_2O)_2](ClO_4)_2 \cdot CH_3OH$ [3], $[\{Zn(bpy)_2\}_2(\mu\text{-}C_2O_4)][Zn(bpy)_2(\mu\text{-}C_2O_4)NbO(C_2O_4)_2]_2 \cdot 0.5bpy \cdot 7H_2O$ [4] $[Zn_2(L)_2(ox)]_2ClO_4 \cdot 2DMF$ [5], $[Zn_2(C_2O_4)(C_{10}H_8N_2)_2(H_2O)_4](C_8H_6N_3O_2)_2 \cdot 6H_2O$ [6],

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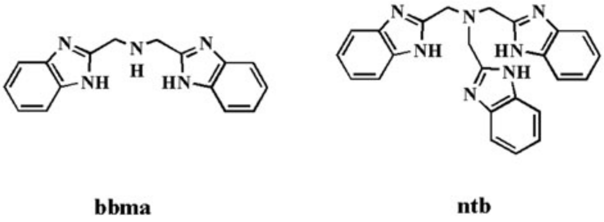
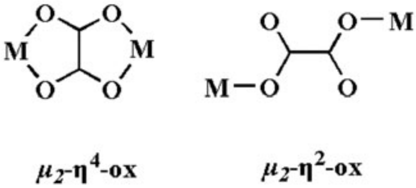
$[Zn_2(C_2O_4)_2(C_3N_2H_4)_2]_n$ [12], etc. Structurally characterized dizinc complexes with oxalate binding the two zinc ions in bis-monodentate mode are rare. Only two zinc(II) complexes reported by the Kim group with a tetraazamacrocycle as the main ligand exhibit an unusual twisted bis-monodentate coordination [7, 8].

Tridentate and tetradentate polybenzimidazole bbma and ntb have long been used in coordination and supramolecular chemistry. Bis(benzimidazol-2-yl-methyl)amine (bbma) is a linear tridentate ligand with two aromatic benzimidazole side arms, while tris(2-benzimidazolylmethyl)amine (ntb) is a tripodal ligand with three benzimidazole side arms. These two ligands are widely used to prepare metal complexes. Compared to other metal complexes, zinc complexes of ntb and bbma are less reported. Only three mononuclear zinc complexes, $[Zn(bbma)Cl_2]\cdot CH_3OH$ [18], $[Zn(bbma)Cl(H_2O)]ClO_4\cdot H_2O$ [19], and [Zn(bbma)(POP)] [20], have been established by X-ray analysis. There is one 1-D zigzag chain structure of $\{[Zn_2(BMA)_2(\mu\text{-ta})(\mu_{1,5}\text{-dca})]ClO_4\cdot CH_3OH\}_n$ [21] in which zinc(II) ions are bridged alternately by terephthalate and $\mu_{1,5}$-dicyanamide ligands. For ntb, several zinc(II) complexes [22–30] containing diorganophosphate, diethyl thiophosphate, water, azide, $SCN^-$, chloride, and monocarboxylates as coligands have been characterized via X-ray diffraction. All these zinc complexes of ntb are mononuclear with five-coordinate zinc(II).

We are interested in the preparation of zinc(II) oxalato-bridged complexes containing bbma and ntb for the following two reasons. First, we would like to see how the structural change of the main ligand from linear tridentate bbma to tetradentate tripodal ntb (scheme 1) affects the coordination mode of oxalate. Since reported zinc(II) complexes of tridentate ligand bbma and tetradentate ligand ntb are all five-coordinate in distorted trigonal bipyramidal geometry, oxalate may have to adopt different coordination when zinc(II) ions are coordinated with bbma and ntb. Second, uncoordinated NH of bbma or ntb on the benzimidazole rings may act as hydrogen donors to the uncoordinated oxygen of oxalate and the counter anions as hydrogen acceptors. Hydrogen bonds and strong $\pi$–$\pi$ interactions may afford interesting supramolecular coordination. Here, we report $[Zn_2(bbma)_2(\mu_2\text{-}\eta^4\text{-ox})](ClO_4)_2$ (**1**) and $[Zn_2(ntb)_2(\mu_2\text{-}\eta^2\text{-ox})](ClO_4)_2\cdot 4CH_3OH$ (**2**), in which oxalate bridges zinc(II) in the



Scheme 1. Chemical diagram of bbma and ntb.



Scheme 2. Bonding modes of oxalate in this article.

prevalent bis-bidentate coordination mode in **1**, while the unusual bis-monodentate mode in **2** (scheme 2).

## 2. Experimental setup

### 2.1. *Reagents and measurements*

All chemicals used in this study were purchased from commercial sources. Ligands bbma and ntb were synthesized according to literature procedures [31, 32]. Infrared spectra were recorded on a Bruker TENSOR 27 FT-IR spectrophotometer with KBr pellets from 4000 to 400 cm$^{-1}$. Elemental analyses (C, H, N) were performed by a Perkin-Elmer 240 elemental analyzer.

*Caution!* Perchlorate salts are potentially explosive and should only be handled in small quantities.

### 2.2. *Synthesis of the complexes*

**2.2.1. Synthesis of [Zn$_2$(bbma)$_2$($\mu_2$-η$^4$-ox)](ClO$_4$)$_2$ (1).** Zn(ClO$_4$)$_2$·6H$_2$O (0.186 g, 0.5 mM) in 5 mL of methanol was dropped carefully to a stirred methanol solution (7 mL) containing bbma (0.139 g, 0.5 mM); to this solution, a methanol solution (5 mL) of oxalic acid (0.032 g, 0.25 mM) and triethylamine (0.051 g, 0.5 mM) was added. After stirring for 4.5 h, the filtrate of the resulting solution was allowed to stand for five days to give colorless crystals of **1**. Yield: 72.1%. FT-IR (KBr pellet, cm$^{-1}$): 3341(s), 1665(s), 1626(m), 1542(w), 1500(w), 1473(w), 1458(s), 1436(w), 1282(m), 1121(vs), 1045(m), 748(m), 625(m). Anal. Calcd for $C_{34}H_{30}Zn_2N_{10}O_{12}Cl_2$: C, 42.00; H, 3.11; N, 14.40. Found: C, 41.75; H, 3.18; N, 14.84.

**2.2.2. Synthesis of [Zn$_2$(ntb)$_2$($\mu_2$-η$^2$-ox)](ClO$_4$)$_2$·4CH$_3$OH (2).** Zn(ClO$_4$)$_2$·6H$_2$O (0.073 g, 0.2 mM) in 5 mL of methanol was dropped carefully to a stirred methanol solution (20 mL) containing ntb (0.204 g, 0.5 mM); to this solution, a methanol solution (5 mL) of oxalic acid (0.060 g, 0.5 mM) and triethylamine (0.102 g, 1 mM) was added. After stirring for 1.5 h, the filtrate of the resulting solution was allowed to stand for two days to give colorless crystals of **2**. Yield: 66.4%. FT-IR (KBr pellet, cm$^{-1}$): 3441(s), 1645(s), 1545(w), 1493(w), 1474(w), 1455(s), 1390(w), 1317(m), 1278(m), 1108(vs), 1049(m), 750(m), 630(m). Anal. Calcd for $C_{54}H_{58}Zn_2N_{14}O_{16}Cl_2$: C, 47.66; H, 4.29; N, 14.41. Found: C, 47.45; H, 4.31; N, 14.36.

### 2.3. *X-ray crystal analysis*

Crystals of **1** and **2** were mounted on Bruker P4 and Saturn 724+ diffractometers, respectively. Determination of unit cell parameters and data collection were performed with Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and Fourier difference techniques and refined by full-matrix least-squares methods using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogens were located on calculated positions and refined isotropically. The perchlorate in **1** is disordered over two positions with occupancy of 0.973(3) for O3, O4, O5, O6, and 0.073(3) for O3′, O4′, O5′, and O6′. The perchlorate in **2** is also disordered with occupancy of 0.50 for O4 and O5 and 0.50 for

Table 1. Crystallographic data and structure refinements for **1** and **2**.

| Complex | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{34}H_{30}Zn_2N_{10}O_{12}C_{12}$ | $C_{54}H_{58}Zn_2N_{14}O_{16}Cl_2$ |
| Formula weight | 972.32 | 1360.82 |
| Color | Colorless | Colorless |
| Temperature/K | 153 (2) | 296 (2) |
| Wavelength/Å | 0.71073 | 0.71073 |
| Crystal system | Orthorhombic | Triclinic |
| Space group | *Pbca* | *P-1* |
| *a*/Å | 14.454 (3) | 10.5775 (10) |
| *b*/Å | 9.0745 (16) | 12.0407 (11) |
| *c*/Å | 29.639 (6) | 12.4968 (11) |
| *α*/° | 90 | 75.277 (5) |
| *β*/° | 90 | 76.528 (5) |
| *v*/° | 90 | 77.160 (5) |
| Volume/Å³ | 3887.6 (12) | 1474.3 (2) |
| *Z* | 4 | 2 |
| $D_c$/mg m$^{-3}$ | 1.661 | 1.533 |
| Absorption coefficient/mm$^{-1}$ | 1.448 | 0.985 |
| *F* (0 0 0) | 1976 | 702 |
| Crystal size/mm | 0.31 × 0.23 × 0.22 | 0.32 × 0.21 × 0.18 |
| Theta range for data collection/° | 1.97–29.14 | 1.72–25.01 |
| Limiting indices | $-14<=h<=19$<br>$-12<=k<=11$<br>$-37<=l<=40$ | $-12<=h<=12$<br>$-14<=k<=14$<br>$-14<=l<=14$ |
| Reflections collected/unique | 25,284/5233 | 16,876/5158 |
| *R*(int) | 0.0426 | 0.0252 |
| Completeness to *θ* | 29.14, 99.8% | 25.01, 99.3% |
| Max. and min. transmission | 0.7412 and 0.6584 | 0.6664 and 0.7456 |
| Data/restraints/parameters | 5233/10/287 | 5158/76/419 |
| Goodness-of-fit on $F^2$ | 1.001 | 1.056 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1 = 0.0486$<br>$wR_2 = 0.1259$ | $R_1 = 0.0446$<br>$wR_2 = 0.1246$ |
| *R* indices (all data) | $R_1 = 0.0620$<br>$wR_2 = 0.1364$ | $R_1 = 0.0502$<br>$wR_2 = 0.1295$ |
| Largest diff. peak and hole (eÅ$^{-3}$) | 0.459 and −0.453 | 0.627 and −0.558 |

O4′ and O5′. The crystal parameters and the details of data collection and refinement for the two complexes are listed in table 1.

## 3. Results and discussion

### 3.1. *Description of the crystal structures*

**3.1.1. Structure of [$Zn_2$(bbma)$_2$($\mu_2$-$\eta^4$-ox)]($ClO_4$)$_2$ (1).** The molecule consists of a centrosymmetric dinuclear [$Zn_2$(bbma)$_2$($\mu_2$-$\eta^4$-ox)]$^{2+}$ and two perchlorates. In the structure of **1**, bbma is tridentate and oxalate, as a bis-bidentate chelating ligand, bridges two Zn(II) ions to form a dinuclear complex, as shown in figure 1. Selected bond parameters are given in tables 2 and 3. The two zinc(II) ions are in identical coordination environments, five-coordinate in a distorted trigonal bipyramid with $\tau = 0.891$ ($\tau = 0$ for square pyramidal and $\tau = 1$ for trigonal bipyramidal geometry) [33]. O(1) of the bridging oxalate [Zn(1)–O(1) = 2.0063(18) Å] and the two nitrogens N2, N4 of bbma determine the equatorial plane of Zn(1) [Zn(1)–N(4) = 1.983(2) Å and Zn(1)–N(2) = 1.995(2) Å]. The axial coordination sites

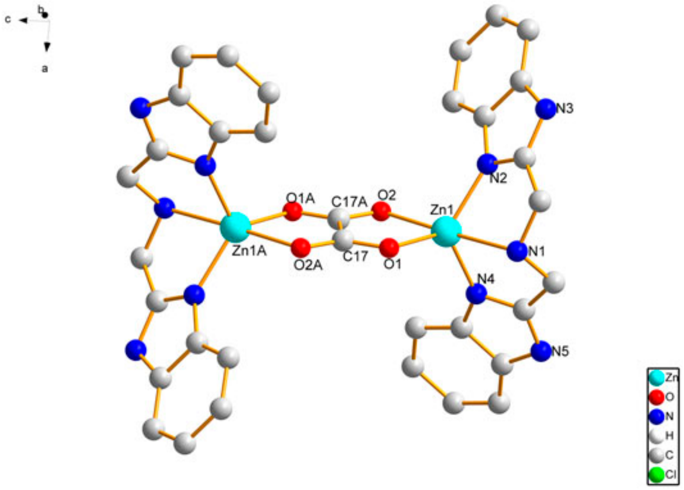


Figure 1. Perspective view of the cation structure of **1**.

Table 2. The bond lengths (Å) and angles (°) of **1** and **2**.

| | | | | | |
|---|---|---|---|---|---|
| Complex **1** | | | | | |
| Zn(1)–N(1) | 2.294 (2) | Zn(1)–N(2) | 1.995 (2) | Zn(1)–N(4) | 1.983 (2) |
| Zn(1)–O(1) | 2.0063 (18) | Zn(1)–O(2)#1 | 2.0844 (17) | | |
| | | | | | |
| N(4)–Zn(1)–N(2) | 117.74 (9) | N(4)–Zn(1)–O(1) | 115.93 (9) | N(2)–Zn(1)–O(1) | 123.88 (9) |
| N(4)–Zn(1)–O(2)#1 | 102.92 (9) | N(2)–Zn(1)–O(2)#1 | 100.83 (8) | O(1)–Zn(1)–O(2)#1 | 81.97 (7) |
| N(4)–Zn(1)–N(1) | 79.74 (10) | N(2)–Zn(1)–N(1) | 77.80 (8) | O(1)–Zn(1)–N(1) | 96.87 (8) |
| O(2)#1–Zn(1)–N(1) | 177.34 (9) | | | | |
| Complex **2** | | | | | |
| Zn(1)–O(1) | 1.992 (2) | Zn(1)–N(1) | 2.026 (3) | Zn(1)–N(3) | 2.026 (3) |
| Zn(1)–N(5) | 2.037 (3) | Zn(1)–N(7) | 2.504 (3) | | |
| | | | | | |
| N(1)–Zn(1)–N(3) | 119.82 (11) | N(1)–Zn(1)–N(5) | 121.27 (11) | N(1)–Zn(1)–N(7) | 75.78 (10) |
| N(3)–Zn(1)–N(5) | 101.68 (11) | N(3)–Zn(1)–N(7) | 76.33 (10) | N(5)–Zn(1)–N(7) | 76.08 (10) |
| O(1)–Zn(1)–N(1) | 102.14 (10) | O(1)–Zn(1)–N(3) | 99.67 (10) | O(1)–Zn(1)–N(5) | 110.14 (10) |
| O(1)–Zn(1)–N(7) | 173.35 (9) | | | | |

are occupied by O(2) of oxalate and amine N(1) of bbma [Zn(1)–O(2)#1 = 2.0844(17) Å; Zn(1)–N(1) = 2.294(2) Å]. The dihedral angle between two benzimidazole side arms of bbma is 121.24°, typical for zinc(II) complexes. The bridging oxalate is planar. The bridging oxalate is the prevalent bis-bidentate with a Zn···Zn distance of 5.318(1) Å, in accord with other published similar dinuclear complexes with bis-bidentate oxalate bridges [2–6]. Each perchlorate forms three H-bonds with three different bbma through its NH resulting in a 3-D network.

**3.1.2. Structure of $[Zn_2(ntb)_2(\mu_2\text{-}\eta^2\text{-ox})](ClO_4)_2\cdot 4CH_3OH$ (2).** The molecular structure of **2** consists of a $[Zn_2(ntb)_2(\mu_2\text{-}\eta^2\text{-ox})]^{2+}$, two perchlorates, and four lattice methanols. A view of the binuclear unit is presented in figure 2. Selected bond distances, bond angles, and hydrogen bond information are listed in tables 2 and 3.

Table 3. Hydrogen bond geometry for **1** and **2**.

| D–H···A | d(H···A)/Å | ∠(DHA)/(°) | d(D···A)/Å | Symmetry codes |
|---|---|---|---|---|
| Complex **1** | | | | |
| N(1)–H(1)···O(5) | 2.15 | 141 | 2.926(4) | |
| N(3)–H(3)···O(3) | 2.16 | 159 | 2.996(4) | $1/2+x, y, 3/2-z$ |
| N(3)–H(3)···O(6) | 2.44 | 139 | 3.162(4) | $1/2+x, y, 3/2-z$ |
| N(5)–H(5)···O(4) | 2.34 | 133 | 3.012(4) | $x, 1+y, z$ |
| N(5)–H(5)···O(3) | 2.45 | 140 | 3.012(4) | $1/2-x, 1/2+y, z$ |
| Complex **2** | | | | |
| N(2)–H(2B)···O(5) | 1.93 | 175 | 2.792(9) | $1-x, 1-y, 1-z$ |
| N(4)–H(4B)···O(8) | 2.00 | 153 | 2.795(5) | |
| N(6)–H(6A)···O(7) | 1.97 | 147 | 2.734(4) | |
| O(7)–H(7)···O(2) | 1.92 | 173 | 2.737(4) | $1-x, -y, 2-z$ |
| O(8)–H(8)···O(2) | 2.36 | 141 | 3.042(4) | $x, 1+y, z$ |
| O(8)–H(8)···O(1) | 2.33 | 149 | 3.059(4) | $1-x, 1-y, 1-z$ |

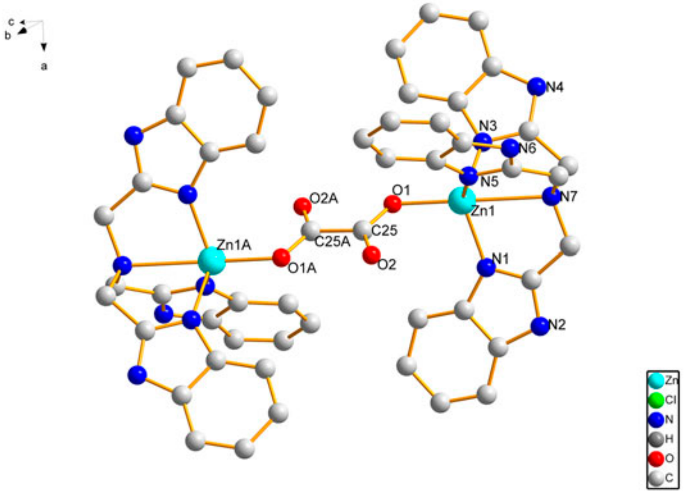


Figure 2. Perspective view of the cation structure of **2**.

The binuclear cation has an inversion center at the midpoint of the two carbons of the bridging oxalate. In the dinuclear unit $[Zn_2(ntb)_2(\mu_2\text{-}\eta^2\text{-ox})]^{2+}$, both zinc(II) ions are five-coordinate with a $N_4O$ donor set. The coordination geometries around the two zinc ions are the same and very close to trigonal bipyramidal ($\beta$ = ∠O(1)–Zn(1)–N(7) = 173.35(9)°, $\alpha$ = ∠N(1)–Zn(1)–N(5) = 121.27(11)°, $\tau = 0.868$), with the basal plane formed by N1, N3, and N5 of benzimidazole groups of ntb [Zn(1)–N(1) = 2.026(3) Å, Zn(1)–N(3) = 2.026(3) Å, Zn(1)–N(5) = 2.037(3) Å] and the axial positions occupied by O1 and N7 [Zn(1)–O(1) = 1.992(2) Å, Zn(1)–N(7) = 2.504(3) Å]. The oxalate links the two zinc ions through the rare bis-monodentate coordination as shown in scheme 2. This is very different from the bis-bidentate coordination as in most oxalate-bridged zinc(II) complexes [3–6, 9–17]. The strain imposed on the metal coordination environment by tripodal ligand and the bulkiness of the benzimidazole is responsible for the coordination of oxalate. This indicates that the enforcing quality of tripodal ligand ntb is strong enough to make the oxalate bis-monodentate. The

Zn···Zn distance across the oxalate is 7.1295(5) Å, significantly longer than those published for dinuclear complexes with bis-bidentate oxalate bridges [3–6, 9–17].

In **2**, neighboring cations are interlinked by two methanols through hydrogen bonding to form a 1-D chain structure as shown in figure 3. Each methanol forms two H-bonds, O(7)–H(7)···O(2) and N(6)–H(6A)···O(7), involving the oxygens of oxalate, oxygen of methanol and the nitrogen of ntb. The 1-D chain is also stabilized by weak $\pi$–$\pi$ stacking interactions from imidazole rings of benzimidazoles with centroid-to-centroid distances of 4.219 Å (Cg1 = Cg2 = C17–C22–N6–C23–N5). In addition, the 1-D chains interact via strong $\pi$–$\pi$ interactions from adjacent imidazole rings of ntb with centroid-to-centroid separation of 3.652 Å (Cg1 = Cg2 = N4–C14–C9–N3–C15) to form a 2-D structure as shown in figure 4. The $\pi$–$\pi$ stacking as well as the hydrogen bonding interactions play an important role in stabilization of the structure of **2**.

## 3.2. *Characterizations of the complexes*

**3.2.1. IR spectra.** The IR spectra of **1** and **2** display broad bands at 3000–3300 cm$^{-1}$, ascribed to $\nu$(N–H) and $\nu$(C–H) of bbma and ntb. The strong absorption bands at 1665 cm$^{-1}$ for **1** and 1645 cm$^{-1}$ for **2** can be assigned to asymmetric ($\nu_{as}$OCO$^{-}$) stretch of oxalate, while the medium absorption bands at 1332 cm$^{-1}$ for **1** and 1317 cm$^{-1}$ for **2** come from the symmetric ($\nu_{s}$OCO$^{-}$) stretch of oxalate. The strong bands centered at 1121 cm$^{-1}$ and a sharp band at 625 cm$^{-1}$ for **1** and 1108 cm$^{-1}$ and 630 cm$^{-1}$ for **2** are due to perchlorate [$\nu$(Cl–O)]. The strong bands at 1100 cm$^{-1}$ split into three bands, indicating that perchlorates are involved in hydrogen bonding as the X-ray structures of the complexes show [34–37].

**3.2.2. Fluorescent properties.** The fluorescent properties of bbma, ntb, **1**, and **2** have been investigated in the solid state at room temperature. Solid bbma exhibits an emission band at 429 nm with excitation wavelength at 372 nm. Complex **1** shows similar emission band with maximum wavelength of 456 nm upon excitation at 387 nm. The ntb displays a broad emission band at 397 nm upon excitation at 335 nm, while **2** displays a similar emission band at 405 nm upon excitation at 356 nm. The emissions of **1** and **2** may be assigned to metal-perturbed intraligand fluorescence [38–41].

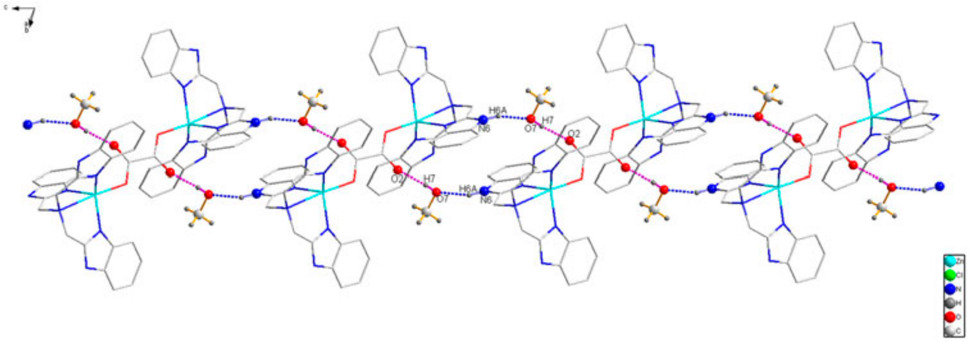


Figure 3. Hydrogen bonding interactions in 1-D chain structure of **2**.

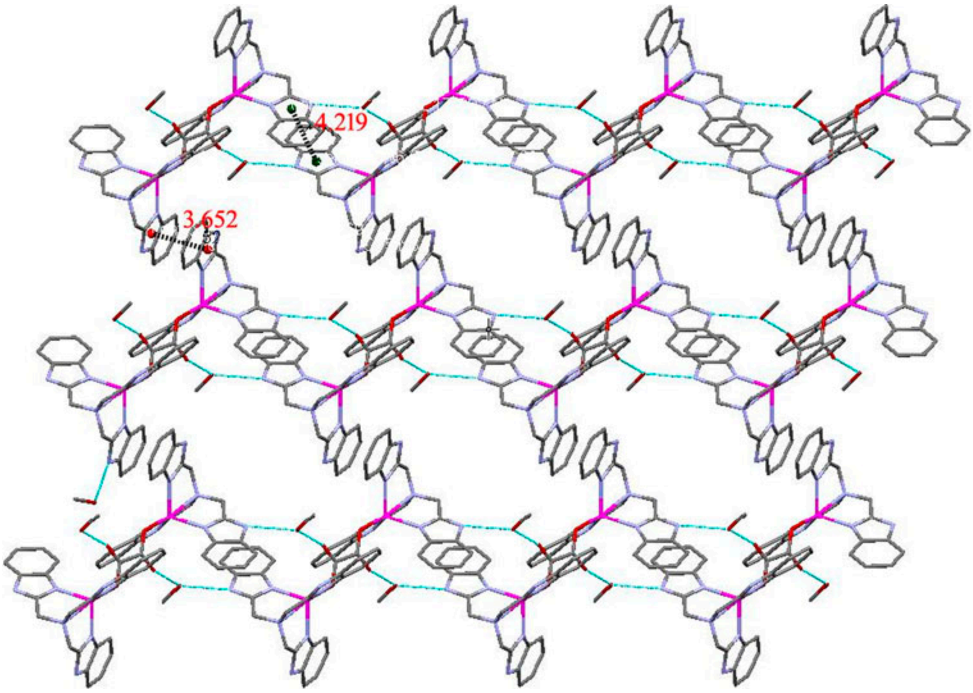


Figure 4. 2-D structure showing H-bonds and $\pi$–$\pi$ stacking interactions in **2**.

## 4. Conclusion

Two new oxalato-bridged zinc(II) complexes, $[Zn_2(bbma)_2(\mu_2\text{-}\eta^4\text{-ox})](ClO_4)_2$ (**1**) and $[Zn_2(ntb)_2(\mu_2\text{-}\eta^2\text{-ox})](ClO_4)_2\cdot 4CH_3OH$ (**2**), with polybenzimidazole tridentate and tripodal tetradentate ligands were synthesized and structurally characterized. Both complexes are dinuclear with Zn···Zn separation of 5.138(1) and 7.1295(5) Å for **1** and **2**, respectively. This is caused by different bridging modes of oxalate. Oxalate bridges the two zinc(II) centers in the prevalent bis-bidentate mode in **1** and the unusual bis-monodentate mode in **2**. The rigidity of tripodal ntb and the bulkiness of the three benzimidazole groups are responsible for the unusual bis-monodentate coordination of oxalate. Both complexes show fluorescent emission in the solid state at room temperature.

## Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 961280 for **1** and No. 961281 for **2**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +441 223 336 033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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## Supplemental data

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