

## Halogeno(triazoly)zinc complexes as molecular building blocks for metal-organic frameworks

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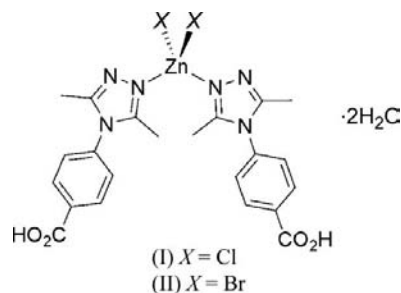
The isomorphous title complexes, dichlorido[4-(3,5-dimethyl-4*H*-1,2,4-triazol-4-yl)benzoic acid- $\kappa N^1$ ]zinc(II) dihydrate,  $[\text{ZnCl}_2(\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2)_2] \cdot 2\text{H}_2\text{O}$ , and dibromido[4-(3,5-dimethyl-4*H*-1,2,4-triazol-4-yl)benzoic acid- $\kappa N^1$ ]zinc(II) dihydrate,  $[\text{ZnBr}_2(\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2)_2] \cdot 2\text{H}_2\text{O}$ , were synthesized and crystallized by slow evaporation of the solvent from a solution of the ligand and either zinc chloride or zinc bromide, respectively, in water/ethanol. The  $\text{Zn}^{\text{II}}$  ions occupy twofold axes in the noncentrosymmetric orthorhombic space group *Fdd2*. The metal ion is approximately tetrahedrally coordinated by two monodentate triazole groups of the ligands and additionally by two halide ions. The water molecules incorporate the complexes into a three-dimensional framework made up by hydrogen bonds. Furthermore, each complex possesses two hydrogen-bond-donor sites represented by the carboxy groups and two acceptor sites at the noncoordinating N atoms of the triazoles.

### Comment

Typically, metal-organic frameworks (MOFs) consist of inorganic building blocks, e.g. metal ions, or more complex secondary building blocks connected by bridging organic linkers. Knowledge of hydrogen bonding as well as of self-assembly is essential for understanding the underlying processes of MOF formation, and for the design of coordination polymers. The complexes reported herein, namely dichlorido[4-(3,5-dimethyl-4*H*-1,2,4-triazol-4-yl)benzoic acid- $\kappa N^1$ ]zinc(II) dihydrate, (I), and dibromido[4-(3,5-dimethyl-4*H*-1,2,4-triazol-4-yl)benzoic acid- $\kappa N^1$ ]zinc(II) dihydrate, (II), containing additional noncoordinating water molecules, are excellent examples for investigating these principles.

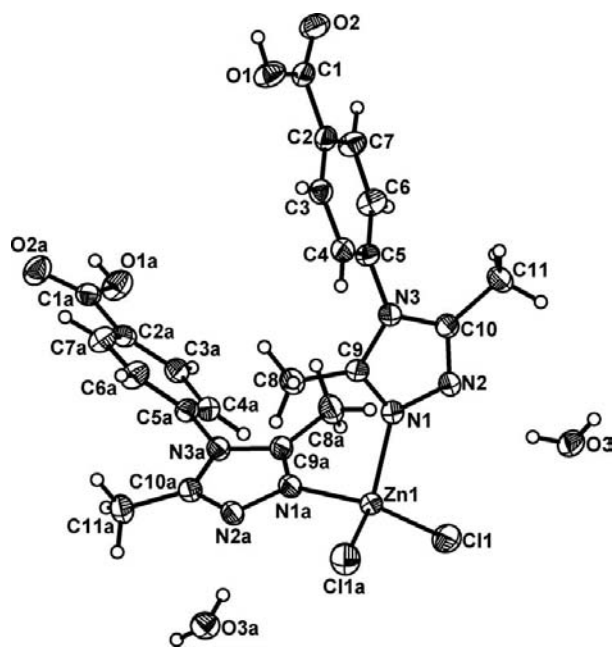
Lukashuk *et al.* (2007) and Zou *et al.* (2005) reported the hydrogen-bonding behaviour of 4-(1,2,4-triazol-4-yl)benzoic acid. Depending on the reaction conditions, varying coordination behaviour of the ligand was observed. We synthesized 3,5-dimethyl-4-(1,2,4-triazol-4-yl)benzoic acid [ $\text{H}(\text{Me}_2\text{trzpba})$ ],

the corresponding dimethylated triazole ligand. The methyl groups lead to a greater dihedral angle of  $59.44(4)^\circ$  between the benzene ring and the triazole unit in the neat ligand  $\text{H}(\text{Me}_2\text{trzpba})$  in comparison to the unsubstituted 4-(1,2,4-triazol-4-yl)benzoic acid [ $33.79(7)$  and  $20.77(6)^\circ$ , two independent molecules]. This leads to enhanced solubility due to reduced  $\pi$ - $\pi$  stacking interactions (Lässig *et al.*, 2009).

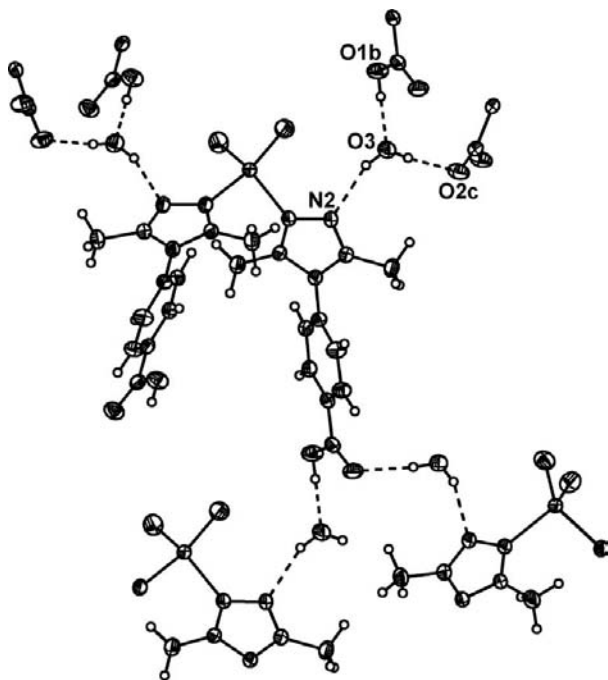


The crystal structures of two isomorphous zinc halide complexes incorporating this new ligand are reported here. The synthesis of both complexes was performed by reacting the ligand with the respective zinc halide in water/ethanol (1:1 v/v). While the pure ligand is only slightly soluble in water/ethanol, the addition of zinc halide significantly increases the solubility. A clear solution resulted, from which single crystals of (I) and (II) were obtained by slow evaporation of the solvent.

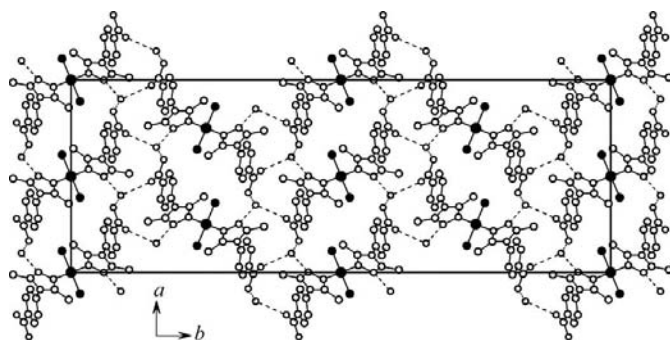
The asymmetric unit is represented by half of the complex where the Zn ions reside on twofold axes in the achiral noncentrosymmetric orthorhombic space group *Fdd2* (No. 43). The Zn ion is approximately tetrahedrally coordinated by



**Figure 1**  
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (a)  $1 - x, 1 - y, z$ .]



**Figure 2**  
Hydrogen bonding between the metal complex and water molecules of (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (b)  $-\frac{1}{2} + x, y, -\frac{3}{2} + z$ ; (c)  $-\frac{1}{4} + x, \frac{5}{4} - y, -\frac{5}{4} + z$ .]



**Figure 3**  
Packing diagram along [001], showing the hydrogen-bonded three-dimensional network of (I). H atoms have been omitted for clarity.

two monodentate triazole units and two halide ions (see scheme and Fig. 1). The Zn1—N1 distance of 2.055 (2) Å in (I) correlates quite well with a typical Zn—N(triazole) bond length, for example, in Zn(dmatrz)<sub>2</sub>Cl<sub>2</sub> (dmatrz = 4-amino-3,5-dimethyl-1,2,4-triazole; Du, 2004).

The hydrogen-bonding interactions are discussed for (I). There are three types of hydrogen bonds (Fig. 2), all involving the water molecule (O3). As a result, a three-dimensional network (Fig. 3) is formed. A strong hydrogen bond is found between O1 and O3 with a donor–acceptor distance of 2.605 (3) Å. Furthermore, the water molecule (O3) acts as a donor in two further hydrogen-bonding interactions; one involves carbonyl atom O2 of a neighbouring complex, with an O···O distance of 2.787 (3) Å, while the second (weaker)

hydrogen bond is directed to atom N2 of the triazole, with an O···N distance of 2.971 (3) Å.

The observation that H(Me<sub>2</sub>trzpba) is soluble in the presence of zinc halides led us to the conclusion that (I) and (II) already exist in solution. This shows impressively the ability of this ligand to competitively replace coordinating water and the dramatic change in solubility due to coordination.

## Experimental

All chemicals and solvents were available commercially and were used without further purification. The H(Me<sub>2</sub>trzpba) ligand was synthesized according to the method of Lässig *et al.* (2009). In a typical procedure for the preparation of (I) and (II), the ligand (21.7 mg, 0.1 mmol) was suspended in ethanol (2 ml), a solution of zinc halide (0.1 mmol) dissolved in distilled water (2 ml) was added and the mixture was stirred for 5 min at room temperature. Colourless prismatic crystals of (I) and (II) were obtained after 3–4 d by slow evaporation of the solvent under ambient conditions. For (I): yield 13.3 mg, 22.0 μmol, 44% of theory (based on the ligand). IR (KBr) (cm<sup>-1</sup>): 3085 (*m*), 2968 (*w*), 1679 (*s*), 1610 (*s*), 1548 (*s*), 1513 (*m*), 1418 (*s*), 1387 (*m*), 1340 (*m*), 1313 (*m*), 1274 (*s*), 1179 (*m*), 1131 (*m*), 1066 (*w*), 1044 (*m*), 1014 (*s*), 871 (*m*), 805 (*m*), 793 (*m*), 770 (*m*), 701 (*m*), 632 (*w*), 558 (*m*), 528 (*m*). For (II): yield: 7.5 mg, 10.8 μmol, 22% of theory (based on the ligand). IR (KBr) (cm<sup>-1</sup>): 3081 (*m*), 2973 (*w*), 1698 (*m*), 1607 (*m*), 1546 (*s*), 1510 (*m*), 1416 (*s*), 1381 (*m*), 1335 (*m*), 1300 (*m*), 1259 (*s*), 1173 (*m*), 1124 (*m*), 1062 (*w*), 1037 (*m*), 1011 (*s*), 871 (*m*), 807 (*m*), 788 (*m*), 764 (*m*), 698 (*m*), 629 (*w*), 555 (*m*), 525 (*m*).

## Compound (I)

### Crystal data

[ZnCl<sub>2</sub>(C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>)<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O  
*M<sub>r</sub>* = 606.76  
 Orthorhombic, *Fdd2*  
*a* = 15.893 (3) Å  
*b* = 44.480 (5) Å  
*c* = 7.3582 (10) Å

*V* = 5201.7 (14) Å<sup>3</sup>  
*Z* = 8  
 Mo *K*α radiation  
 μ = 1.21 mm<sup>-1</sup>  
*T* = 180 K  
 0.50 × 0.32 × 0.15 mm

### Data collection

Stoe IPDS-2T diffractometer  
 Absorption correction: numerical  
 (*X-RED*; Stoe & Cie, 2006)  
*T<sub>min</sub>* = 0.417, *T<sub>max</sub>* = 0.583

3974 measured reflections  
 2189 independent reflections  
 2157 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.023

### Refinement

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.025  
*wR*(*F*<sup>2</sup>) = 0.068  
*S* = 1.09  
 2189 reflections  
 180 parameters  
 4 restraints

H atoms treated by a mixture of independent and constrained refinement  
 Δρ<sub>max</sub> = 0.29 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.31 e Å<sup>-3</sup>  
 Absolute structure: Flack (1983)  
 Flack parameter: -0.009 (10)

## Compound (II)

### Crystal data

[ZnBr<sub>2</sub>(C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>)<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O  
*M<sub>r</sub>* = 695.68  
 Orthorhombic, *Fdd2*  
*a* = 16.1158 (12) Å  
*b* = 44.425 (4) Å  
*c* = 7.3861 (5) Å

*V* = 5288.0 (7) Å<sup>3</sup>  
*Z* = 8  
 Mo *K*α radiation  
 μ = 4.01 mm<sup>-1</sup>  
*T* = 180 K  
 0.34 × 0.25 × 0.11 mm

**Table 1**

Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3A $\cdots$ N2	0.843 (18)	2.17 (2)	2.971 (3)	158 (3)
O3—H3B $\cdots$ O2 <sup>i</sup>	0.840 (18)	1.949 (19)	2.787 (3)	176 (4)
O1—H1 $\cdots$ O3 <sup>ii</sup>	0.84	1.77	2.605 (3)	176

 Symmetry codes: (i)  $x - \frac{1}{4}, -y + \frac{5}{4}, z - \frac{5}{4}$ ; (ii)  $x + \frac{1}{2}, y, z + \frac{3}{2}$ .

**Table 2**

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3A $\cdots$ N2	0.855 (19)	2.22 (3)	3.033 (4)	159 (4)
O3—H3B $\cdots$ O2 <sup>i</sup>	0.835 (19)	1.96 (2)	2.788 (4)	169 (5)
O1—H1 $\cdots$ O3 <sup>ii</sup>	0.84	1.80	2.636 (4)	176

 Symmetry codes: (i)  $x - \frac{1}{4}, -y + \frac{5}{4}, z - \frac{5}{4}$ ; (ii)  $x + \frac{1}{2}, y, z + \frac{3}{2}$ .

### Data collection

Stoe IPDS-2T diffractometer  
 Absorption correction: numerical  
 (*X-RED*; Stoe & Cie, 2006)  
 $T_{\min} = 0.396, T_{\max} = 0.713$

8551 measured reflections  
 3189 independent reflections  
 2987 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.052$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.09$   
 $S = 1.01$   
 3189 reflections  
 179 parameters  
 4 restraints

H atoms treated by a mixture of  
 independent and constrained  
 refinement  
 $\Delta\rho_{\max} = 0.62 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.65 \text{ e } \text{Å}^{-3}$   
 Absolute structure: Flack (1983)  
 Flack parameter:  $-0.007 (10)$

Methyl H atoms were located in difference syntheses and thereafter refined as part of rigid rotating groups, with  $C-H = 0.98 \text{ Å}$  and  $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$ . Aromatic H atoms were placed geometrically and refined using a riding model, with  $C-H = 0.95 \text{ Å}$  and  $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ . In each case, the acidic H1 atom on O1 was located in a difference Fourier map and refined as part of a rigid rotating group, with  $O-H = 0.84 \text{ Å}$  and  $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(O)$ . The H atoms of the water molecule in each structure were located from difference Fourier maps and refined using distance restraints [ $O-H = 0.84 (2) \text{ Å}$  and  $H\cdots H = 1.33 (2) \text{ Å}$ ] and with  $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(O)$ .

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2006); cell refinement: *X-AREA*; data reduction: *X-AREA* and *X-RED* (Stoe & Cie, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3026). Services for accessing these data are described at the back of the journal.

### References

- Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.  
 Du, J. Y. (2004). *Transition Met. Chem.* **29**, 699–702.  
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Lässig, D., Lincke, J. & Krautscheid, H. (2009). *Tetrahedron Lett.* Accepted.  
 Lukashuk, L. V., Lysenko, A. B., Rusanov, E. B., Chernega, A. N. & Domasevitch, K. V. (2007). *Acta Cryst.* **C63**, m140–m143.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Stoe & Cie (2006). *X-RED* and *X-AREA*. Stoe & Cie, Darmstadt, Germany.  
 Zou, R.-Q., Cai, L.-Z. & Guo, G.-C. (2005). *J. Mol. Struct.* **737**, 125–129.