

**4-*tert*-Butyl-2,6-bis[(imidazolium-1-yl)-methyl]phenol tetrachlorozincate(II)****Gang Xu, Yu-Bo Cui, Wei Huang\* and Shao-Hua Gou**

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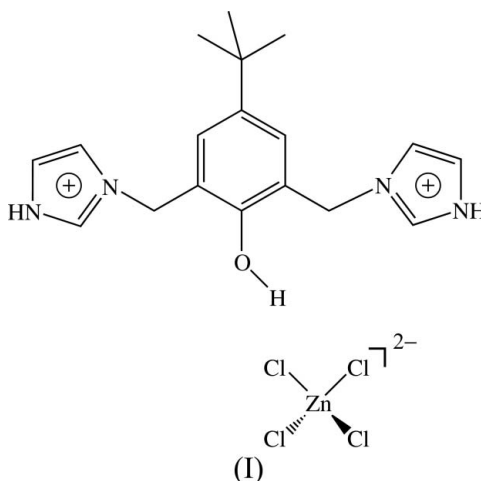
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**Key indicators**Single-crystal X-ray study  
 $T = 291$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.008$  Å  
 $R$  factor = 0.057  
 $wR$  factor = 0.116  
Data-to-parameter ratio = 15.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

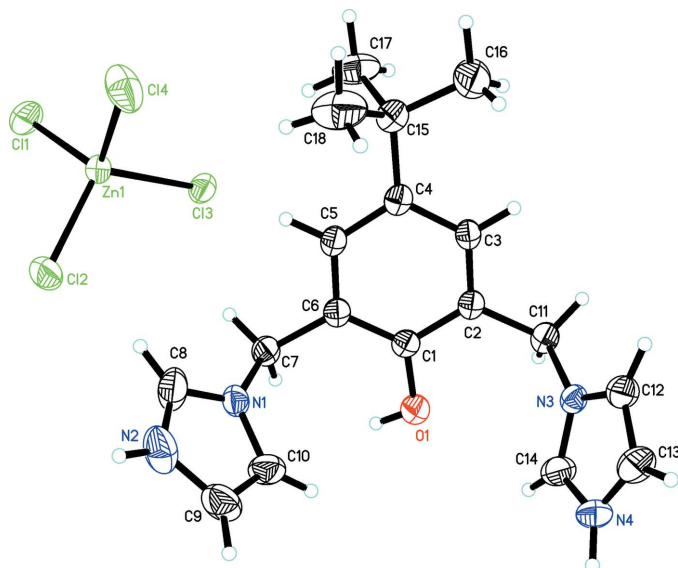
The title compound,  $(\text{C}_{18}\text{H}_{24}\text{N}_4\text{O})[\text{ZnCl}_4]$ , a tetrachlorozincate(II) salt of 4-*tert*-butyl-2,6-bis[(imidazol-1-yl)methyl]phenol, has the phenol H atom linked to one of the Cl atoms. The two imidazole rings adopt *cis* configurations with respect to the phenol plane. In the crystal structure, a hydrogen-bond-sustained three-dimensional supramolecular network is formed.

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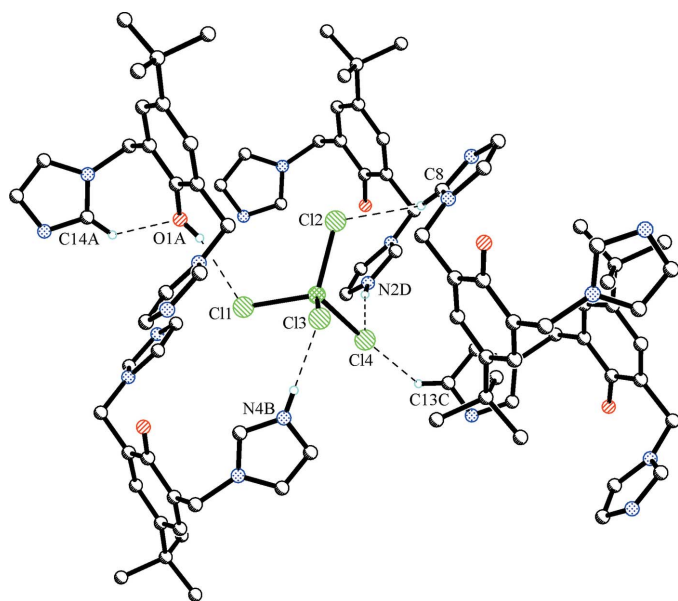
Recently, the rational design and preparation of novel functional materials has become one of the highlights in supramolecular chemistry and crystal engineering (Carlucci *et al.*, 1995; Fujita *et al.*, 1995; Kawata *et al.*, 1996). How to control the molecular structure and topology in the process of self-assembly has attracted considerable attention (Lehn, 1990; Piguet *et al.*, 1995). Imidazolium salts have been used as building blocks (Sato *et al.* 1999; Ramirez *et al.* 2002; Yao *et al.*, 2003) to assemble a variety of compounds where forces at the supramolecular level play an important role. On the other hand, some of them can serve as ionic liquids for many applications (Fei *et al.*, 2004; Moret *et al.*, 2005). To date, there have been many studies on metal complexes bearing the 1,3-di[(imidazol-1-yl)methyl]benzene group; however, by checking the Cambridge Structural Database (Version 5.26; Allen, 2002), it was found that the title compound, (I), is the first single-crystal structural report where the 1,3-di[(imidazol-1-yl)methyl]phenol unit is involved.



The molecular structure of compound (I) is illustrated in Fig. 1. Selected bond distances and bond angles are given in Table 1. The bond distances and angles of the benzene ring, the imidazole rings and the *tert*-butyl group in this structure are in the normal range. The tetrachlorozincate(II) anion



**Figure 1**  
Molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.



**Figure 2**  
A perspective view of the hydrogen-bonding interactions in (I). For clarity, labels are given only for the hydrogen-bond contacts (dashed lines).

adopts a slightly distorted tetrahedral configuration and one of the Cl atoms, Cl1(1 - *x*, 1 - *y*, 1 - *z*), is linked to phenol atom H1, with a Cl···O distance of 2.436 (3) Å (see Table 2). The two imidazole rings adopt *cis* configurations with respect to the plane of the phenol group. The dihedral angles between the phenol ring and the two imidazole rings are 110.1 (2) and 67.5 (2)°, respectively. The two imidazole rings are nearly perpendicular to one another, with a dihedral angle of 83.2 (2)°.

It is worth noting that the hydrogen-bonding interactions involving the tetrachlorozincate(II) anion in the crystal packing are the most important feature in (I). As can be seen in Fig. 2 and Table 2, an O—H···Cl hydrogen bond is

observed between atom Cl1 and the phenol O atom (O1). N—H···Cl hydrogen bonds are found between atom Cl3 and the imidazole atom N4, as well as between atom Cl4 and the other imidazole N atom, N2. A weak C—H···Cl hydrogen-bond contact is also present between an imidazole C atom, (C8) and atom Cl2, as well as between atoms C13 and Cl4. The crystal structure is further stabilized by an intramolecular C—H···O hydrogen bond between the phenol atom O1 and an imidazole C atom (C14). This leads to the formation of a three-dimensional hydrogen-bonding network, as shown in Fig. 3.

In the crystal structure, it can also be seen that all the phenol rings are parallel to one another but the molecules are packed *via* van der Waals interactions. There are no  $\pi$ - $\pi$  stacking interactions between the aromatic rings, although they are parallel to one another (Fig. 3).

## Experimental

All solvents and chemicals were of analytical grade and were used without further purification. 4-*tert*-Butyl-2,6-bis[(imidazol-1-yl)methyl]phenol was prepared *via* a one-step Mannich reaction to give white microcrystals with a 61% yield (Baker *et al.*, 2004). For the synthesis of (I), a solution of ZnCl<sub>2</sub> (0.14 g, 1 mmol) dissolved in water (15 ml) was added to a solution of 4-*tert*-butyl-2,6-bis[(imidazol-1-yl)methyl]phenol (0.31 g, 1 mmol) dissolved in ethanol (20 ml). The mixture was refluxed for 1 h, then cooled to room temperature and filtered. Colorless single crystals suitable for X-ray analysis were grown from the filtrate (pH = 4) by slow evaporation at room temperature. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O, 298 K, TMS):  $\delta$  8.34 (*s*, 2H, Im—H), 7.37 (*s*, 2H, Ar—H), 7.21 (*d*, 4H, Im—H), 5.26 (*s*, 4H, CH<sub>2</sub>), 4.56 (*b*, 1H, OH), 1.14 (*s*, 9H, CH<sub>3</sub>). Elemental analysis calculated for C<sub>18</sub>H<sub>24</sub>C<sub>14</sub>N<sub>4</sub>OZn: C 41.61, H 4.66, N 10.78%; found: C 40.71, H 4.79, N 10.96%. ESI-MS in methanol (*m/z*): 482.7 (100%), [L<sub>1</sub>H<sub>2</sub>ZnCl<sub>3</sub>]<sup>+</sup>.

### Crystal data

(C<sub>18</sub>H<sub>24</sub>N<sub>4</sub>O)[ZnCl<sub>4</sub>]  
*M<sub>r</sub>* = 519.58  
 Triclinic, *P* $\bar{1}$   
*a* = 10.051 (1) Å  
*b* = 11.329 (1) Å  
*c* = 11.703 (1) Å  
 $\alpha$  = 62.88 (1)°  
 $\beta$  = 77.54 (1)°  
 $\gamma$  = 82.38 (1)°  
*V* = 1157.3 (2) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 1.491 Mg m<sup>-3</sup>  
 Mo K $\alpha$  radiation  
 Cell parameters from 960 reflections  
 $\theta$  = 2.7–19.9°  
 $\mu$  = 1.54 mm<sup>-1</sup>  
*T* = 291 (2) K  
 Block, colorless  
 0.3 × 0.2 × 0.2 mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
*T<sub>min</sub>* = 0.699, *T<sub>max</sub>* = 0.733  
 5763 measured reflections

4003 independent reflections  
 2999 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.021  
 $\theta_{max}$  = 25.0°  
*h* = -11 → 11  
*k* = -11 → 13  
*l* = 0 → 13

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.057  
*wR*(*F*<sup>2</sup>) = 0.116  
*S* = 1.01  
 4003 reflections  
 257 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 1.9518P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.57 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{min} = -0.39 \text{ e } \text{Å}^{-3}$

**Table 1**  
Selected geometric parameters (Å, °).

Zn1—Cl2	2.2353 (16)	O1—C1	1.361 (5)
Zn1—Cl4	2.2400 (17)	C7—N1	1.467 (6)
Zn1—Cl1	2.2659 (15)	C11—N3	1.477 (5)
Zn1—Cl3	2.2792 (14)		
Cl2—Zn1—Cl4	109.90 (8)	Cl4—Zn1—Cl3	106.59 (6)
Cl2—Zn1—Cl1	109.95 (6)	Cl1—Zn1—Cl3	105.46 (6)
Cl4—Zn1—Cl1	111.25 (8)	N1—C7—C6	111.6 (3)
Cl2—Zn1—Cl3	113.60 (6)	N3—C11—C2	112.9 (4)

**Table 2**  
Hydrogen-bond geometry (Å, °).

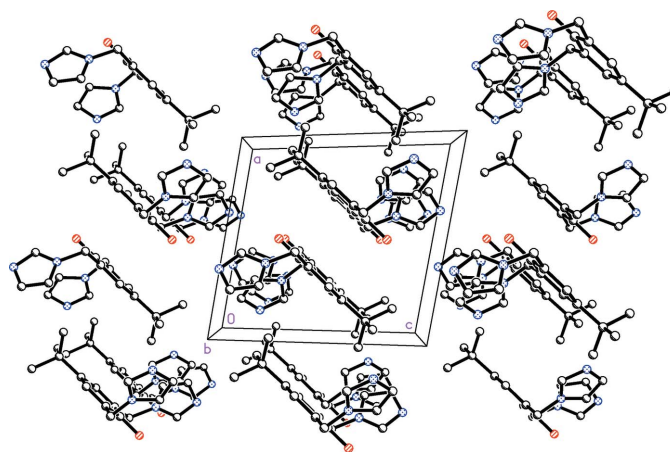
<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C14—H14...O1	0.93	2.56	3.028 (6)	112
C8—H8...Cl2	0.93	2.62	3.452 (6)	149
O1—H1...Cl1 <sup>i</sup>	0.82	2.44	3.159 (4)	148
N2—H2A...Cl4 <sup>ii</sup>	0.86	2.30	3.144 (5)	168
N4—H4...Cl3 <sup>iii</sup>	0.86	2.30	3.155 (5)	173
C13—H13...Cl4 <sup>iv</sup>	0.93	2.80	3.511 (6)	134

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $-x+2, -y+1, -z+1$ ; (iii)  $x, y-1, z+1$ ; (iv)  $-x+2, -y, -z+1$ .

The H atoms were placed in geometrically idealized positions ( $C-H = 0.93-0.97$  Å,  $N-H = 0.86$  Å and  $O-H = 0.82$  Å) and refined as riding atoms, with  $U_{iso}(H) = 1.5U_{eq}[\text{parent N, O and C(methyl) atoms}]$  and  $U_{iso}(H) = 1.2U_{eq}[\text{other C atoms}]$ . Two H atoms were attached to the imidazole N atoms, N2 and N4, to equilibrate the total charge of compound (I), although the charges are believed to be delocalized in the imidazole rings.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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**Figure 3**  
Crystal packing of (I), viewed along the *b* axis, where all the benzene rings are parallel. The tetrachlorozincate(II) anion and the H atoms have been omitted for clarity.

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