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Bis{μ-2-[(2-carbamoylhydrazin-1-ylidene)methyl]phenolato}bis[chloridozinc(II)] methanol disolvate, with non-aromatic–aromatic π–π stacking and N—H···Cl—Zn hydrogen bonding

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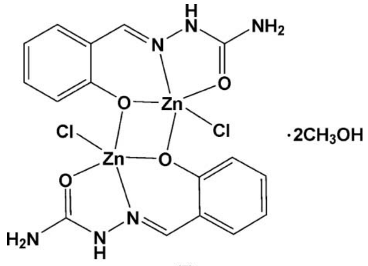
Centrosymmetric dimers of Zn^{II} with singly deprotonated 2-[(2-carbamoylhydrazin-1-ylidene)methyl]phenolate, [$Zn_2(C_8H_8N_3O_2)Cl_2$]·$2CH_3OH$, form an infinite one-dimensional hydrogen-bonded chain which is further aggregated by non-aromatic–aromatic π–π stacking and nonclassical N—H···Cl hydrogen bonding.

Comment

In the past decade, the coordination-driven and conventional hydrogen-bonding-directed self-assembly of high-symmetry conglomerates has been studied extensively (Wei *et al.*, 2009). Noncovalent interactions have also been recognized as playing a substantial role in a variety of chemical and biological phenomena (Nishio, 2004). The understanding and utilization of all types of noncovalent interactions, including π–π stacking, are of fundamental importance for the further development of supramolecular chemistry and the study and prediction of crystal structures (Janiak, 2000). Dance & Scudder (1995) suggested the concept of 'molecular embrace', based on phenyl–phenyl intermolecular interactions, and developed the embrace paradigm as an important and widespread intermolecular motif and crystal engineering tool by analysing the packing of molecules in crystals (Dance & Scudder, 2009). Varied hydrogen-bond patterns, including traditional and nonclassical versions, have been observed in crystal packing, giving diverse supramolecular motifs (Casas *et al.*, 2004). Aullón *et al.* (1998) conducted a study based on the Cambridge Structural Database (Allen, 2002) involving hydrogen bonds containing M—Cl (M = transition metal), C—Cl or Cl$^-$ and either HO or HN. The results indicated that M—Cl moieties are good anisotropic hydrogen-bond acceptors. The D—H···Cl—M (D = O or N) contacts were categorized as short (H···Cl $\leq$ 2.52 Å), intermediate (2.52–2.95 Å) and long (2.95–3.15 Å). It was reported that M—Cl in complexes has the potential to interact with hydrogen-bond donors in both a strong (*i.e.* short) and an anisotropic fashion. To the best of our knowledge, non-aromatic–aromatic π–π stacking has rarely been reported. In this work, the synthesis and structural characterization of the title dinuclear Zn^{II} complex, (I), containing nonclassical N—H···Cl—Zn^{II} hydrogen bonding and π–π interactions that involve non-aromatic groups, are discussed.



(I)

Compound (I) is composed of centrosymmetric [Zn(HSSC)Cl]$_2$ dimers {HSSC is 2-[(2-carbamoylhydrazin-1-ylidene)methyl]phenolate} (Fig. 1). Each HSSC$^-$ ligand has a deprotonated phenol group, which forms a one-atom bridge between the two Zn^{II} centres, and coordinates to one Zn^{II} ion through its N2 and O1 atoms. The Zn1···Zn1^{iv} distance is 3.1317 (13) Å [symmetry code: (iv) $-x + 1, -y + 1, -z + 1$]. Atom Zn1 has a square-pyramidal coordination environment and is situated slightly above the basal plane, which is formed by N2 from azomethine (–CH═N–), O1 from ureido (–NH—CO—NH$_2$) and O2 and O2^{iv} from different phenol groups, with the axial position occupied by one Cl$^-$ ion (Fig. 1). The Zn—O(N,Cl) distances and related angles are all within expected ranges (Casas *et al.*, 2000). However, the structure of

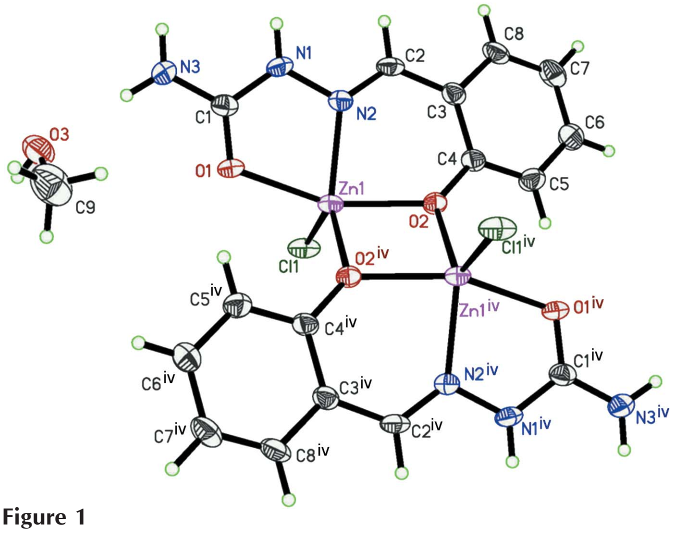


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (iv) $-x + 1, -y + 1, -z + 1$.]

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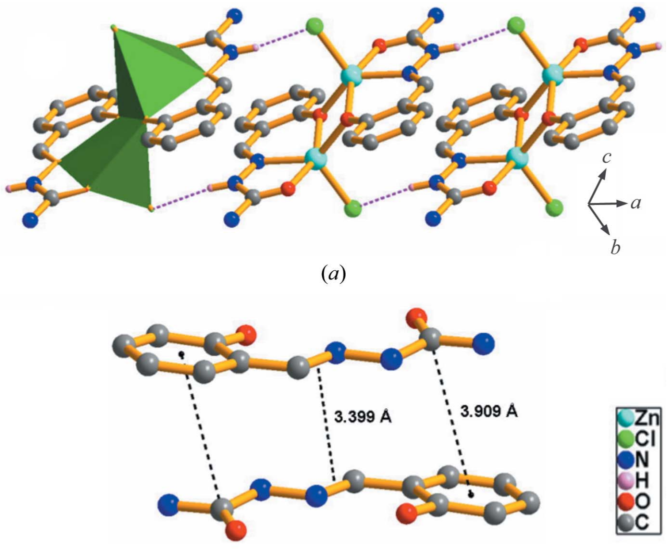

(*a*)

(*b*)

Figure 2
(*a*) The one-dimensional staircase structure of (I) formed by N1—H1···Cl1(x − 1, y, z) hydrogen bonds and extending along the *a* axis. Hydrogen-bonding interactions are represented by dashed lines. For clarity, H atoms not involved in hydrogen bonding have been omitted. (*b*) A drawing of the non-aromatic–aromatic π–π contacts between adjacent dimers in the one-dimensional staircase chain.

the HSSC$^-$ ligand is slightly twisted, with an angle of 13.5 (3)° between the ureido plane (C1/O1/N1/N3) and the benzene group (C3–C8) to accommodate the geometric requirements of coordination about Zn^{II}, and to accommodate noncovalent interactions.

The π-electron density is delocalized in neutral H$_2$SSC, especially when an aromatic group is bound to the azomethine C atom (Casas *et al.*, 2000). Compared with free H$_2$SSC, the related bond lengths of the C2—N2—N1—C1—O1—N3 backbone are almost unvaried in the dimer of (I) (Table 1). In addition, compared with conventional localized bond lengths of C—N = 1.472 (5) Å in RNH$_2$, N—N = 1.451 (5) Å in R_2NNH$_2$ and C=O = 1.145 (10) Å in carbonyls (Dean 1999), the corresponding single bonds are shorter and the double bonds are longer in (I). Thus, it is reasonable to conclude that HSSC$^-$ maintains a considerably delocalized π system in the dimer of (I).

The dimers of (I) are assembled through intermolecular N1—H1···Cl1^{iii} interactions [Table 2; symmetry code: (iii) x − 1, y, z] and non-aromatic–aromatic π–π interactions to form an infinite one-dimensional hydrogen-bond-supported chain. This one-dimensional chain has the form of a staircase propagating in the direction of the shortest lattice parameter (*a* axis; Fig. 2*a*). According to the study of Aullón *et al.* (1998), the H1···Cl1^{iii} distance of 2.33 Å indicates strong hydrogen-bonding interactions in the one-dimensional chains. Within one staircase-like chain, the HSSC$^-$ ligand is in contact with that at ($-x$, $-y + 1$, $-z + 1$) in a head-to-tail fashion, with π–π interactions that appear to extend the entire length of the ligand (Fig. 2*b*). Specifically, non-aromatic ureido and azomethine and aromatic phenol groups participate in π-stacking. The best planes of the two contacting ligands are parallel, being related by a centre of symmetry, and are at a distance of 3.618 (7) Å.

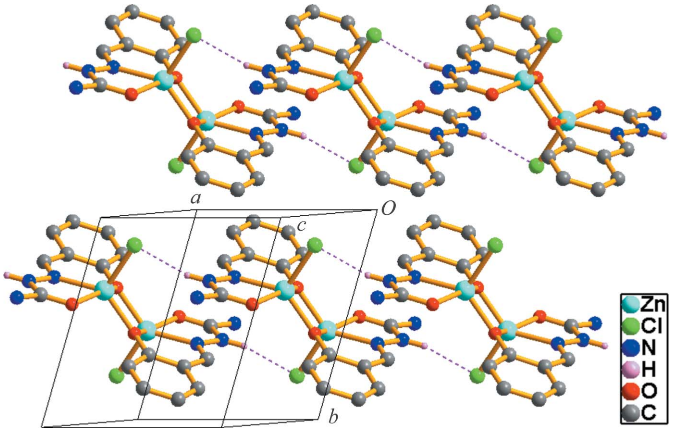

Figure 3
The arrangement of one-dimensional staircase chains in the *ab* plane. Hydrogen-bonding interactions are represented by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

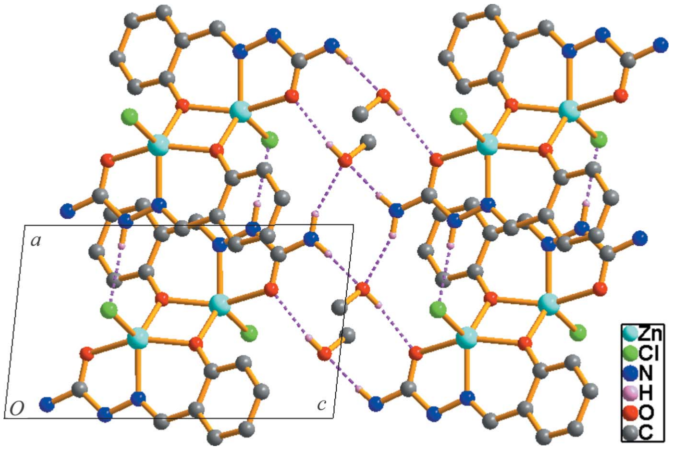

Figure 4
The two-dimensional net structure of (I) formed by hydrogen-bonding interactions (dashed lines), showing the formation of an (010) sheet. For clarity, H atoms not involved in hydrogen bonding have been omitted.

The one-dimensional chains pack into two-dimensional sheets in which neighbouring chains are related by a *b*-axis translation (Fig. 3). Between adjacent chains there are van der Waals contacts between HSSC groups, but their relative disposition is substantially slipped so that no π–π interaction exists.

More significantly, the one-dimensional chains stack in a side-by-side fashion along the *c* axis to form two-dimensional sheets of parallel staircases, which are held together through hydrogen bonds to form aggregates, the basic units of which lie parallel to (010) (Fig. 4). Hydrogen bonding mediates the formation of a chain of fused rings parallel to the *a* axis of the unit cell, with alternating $R_4^4(12)$ and $R_4^2(8)$ rings [see Bernstein *et al.* (1995) for hydrogen-bonding motifs]. These hydrogen-bonded rings also involve the methanol solvent molecules (Table 2).

Experimental

2-[(2-Carbamoylhydrazin-1-ylidene)methyl]phenol (H_2SSC) was prepared by the reaction of semicarbazide hydrochloride with 2-hydroxybenzaldehyde in a 1:1 molar ratio in water. Analysis calculated for H_2SSC: C 53.63, H 5.06, N 23.45%; found: C 53.74, H 5.065, N 22.97%. IR (KBr): ν(OH) 3472 cm^{-1}, ν(C═O) 1697 cm^{-1}, ν(C═N) 1622 cm^{-1}, ν(C—O) 1267 cm^{-1}. H_2SSC (0.179 g, 1 mmol) and $ZnCl_2$ (0.136 g, 1 mmol) were dissolved separately in methanol (20 ml). These solutions were mixed in a flask and stirred for ~3 h. A milky white precipitate was obtained from the resulting reaction solution, separated by filtration, washed with methanol and tetrahydrofuran, and dried. The filtrate was allowed to stand at room temperature and colourless single crystals of (I) were grown by slow evaporation over a period of about four weeks. Analysis calculated for Zn(HSSC)Cl: C 34.44, H 2.89, N 15.06%; found: C 34.32, H 2.91, N 15.02%. IR (KBr): ν(C═O) 1665, ν(C═N) 1600, ν(C—O) 1275 cm^{-1}.

Crystal data

$[Zn_2(C_8H_8N_3O_2)Cl_2]\cdot 2CH_4O$
$M_r = 622.07$
Triclinic, $P\overline{1}$
$a = 6.9061$ (8) Å
$b = 8.3585$ (12) Å
$c = 11.7666$ (16) Å
$\alpha = 75.066$ (1)°
$\beta = 80.565$ (2)°
$\gamma = 76.003$ (1)°
$V = 633.04$ (15) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 2.15$ mm^{-1}
$T = 298$ K
0.38 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.496$, $T_{max} = 0.814$
3291 measured reflections
2179 independent reflections
1602 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.146$
$S = 1.04$
2179 reflections
155 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.78$ e Å^{-3}
$\Delta\rho_{min} = -0.77$ e Å^{-3}

H atoms attached to C, N and O atoms were placed in geometrically idealized positions, with C—H = 0.93 and 0.96 Å for CH and CH_3 groups, respectively, N—H = 0.86 Å and O—H = 0.82 Å, and with $U_{iso}(H) = 1.2U_{eq}$(C,N) or $1.5U_{eq}$(CH_3,O).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Table 1
Selected bond lengths (Å).

C1—N1	1.362 (7)	C1—N3	1.336 (7)
N1—N2	1.391 (6)	C1—O1	1.246 (6)
C2—N2	1.288 (7)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···O3	0.86	2.08	2.929 (7)	170
N3—H3*B*···O3^{i}	0.86	2.27	3.040 (8)	150
O3—H3···O1^{ii}	0.82	2.13	2.923 (6)	163
N1—H1···Cl1^{iii}	0.86	2.33	3.175 (5)	166

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3235). Services for accessing these data are described at the back of the journal.

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