

Dichlorobis(thiourea)zinc(II)  
bis(4,5-diazafluoren-9-one)Zhi-Yong Wu,<sup>a</sup> Duan-Jun Xu<sup>a\*</sup>  
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## Key indicators

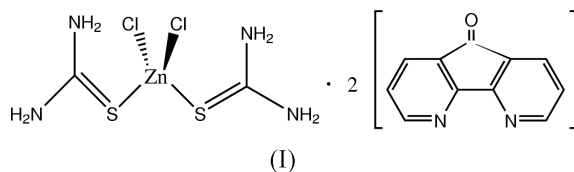
Single-crystal X-ray study  
 $T = 295\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$   
 $R$  factor = 0.033  
 $wR$  factor = 0.103  
Data-to-parameter ratio = 15.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $[\text{ZnCl}_2(\text{CH}_4\text{N}_2\text{S})_2] \cdot 2\text{C}_{11}\text{H}_6\text{N}_2\text{O}$ , consists of the tetrahedral  $\text{ZnCl}_2$ -thiourea complex and hydrogen-bonded 4,5-diazafluoren-9-one (dafone). The  $\text{N} \cdots \text{N}$  distance in dafone when not involved in metal coordination is significantly larger than when it is metal chelating. Neighboring zinc(II) complex molecules hydrogen bond to each other, forming supramolecular chains.  $\pi$ - $\pi$  stacking is observed between neighboring dafone rings.

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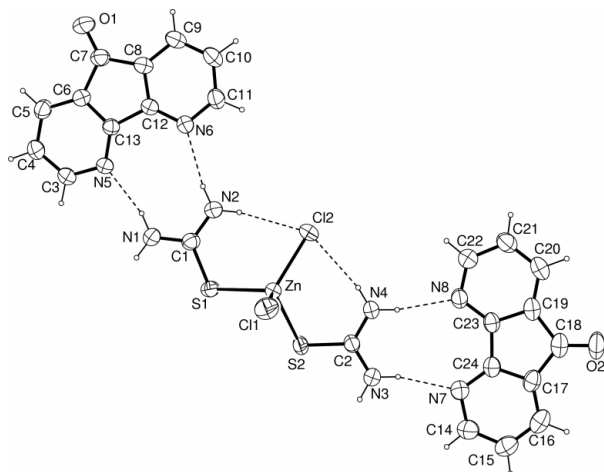
## Comment

4,5-Diazafluoren-9-one (dafone) is structurally similar to phenanthroline and plays the role of chelating ligand in some metal complexes (Xiong *et al.*, 1996; Shi *et al.*, 1994); however, in most cases, X-ray structure determination showed that dafone does not coordinate to first-row transition metal ions (Ravikumar & Lakshmi, 1994; Wu, Xu, Wu & Chiang, 2002). The structure of the title compound, (I), is presented here to enable comparison of the structure of dafone with the structures of dafone-chelating complexes reported previously.



The structure of (I) is shown in Fig. 1. The crystal consists of the zinc(II) complex and uncoordinated dafone in a 1:2 ratio. The Zn complex has a distorted tetrahedral coordination geometry, formed by two thiourea molecules and two  $\text{Cl}^-$  anions, coordination bond angles at the  $\text{Zn}^{\text{II}}$  atom ranging from  $98.40(3)$  to  $114.11(3)^\circ$  (Table 1). The amine groups are intramolecularly hydrogen bonded to atom Cl2 (Table 2). Dafone is linked to the zinc complex *via* hydrogen bonding; this structure agrees with the situation found in the  $\text{Co}^{\text{II}}$  analogue (Wu, Xu & Yin, 2002) and in bis(thiourea)chloro-copper(I) di(4,5-diazafluoren-9-one) (Wu, Xu, Wu & Chiang, 2002). These structures imply that the thiourea S atom is the preferred metal-coordinating ligand in the presence of dafone.

The two independent dafone molecules have a similar planar structure. The  $\text{N}5 \cdots \text{N}6$  [ $3.064(3)\text{ \AA}$ ] and  $\text{N}7 \cdots \text{N}8$  [ $3.065(3)\text{ \AA}$ ] distances are not significantly different from the values of  $3.068(3)$  and  $3.064(3)\text{ \AA}$  found in the  $\text{Co}^{\text{II}}$  analog, and  $3.055(2)\text{ \AA}$  found in the crystal structure of dafone itself (Fun *et al.*, 1995), but are much longer than the  $\text{N} \cdots \text{N}$  distances ( $2.880$  and  $2.841\text{ \AA}$ ) found in a Co complex and a Ni complex, both with a chelating dafone ligand (Xiong *et al.*, 1996; Shi *et al.*, 1994). The  $\text{C}12-\text{C}13$  [ $1.481(3)\text{ \AA}$ ] and  $\text{C}23-$



**Figure 1**  
The molecular structure of (I), with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds.

C24 [1.475 (4) Å] bonds are also significantly longer than the values of 1.457 and 1.441 Å found in Co and Ni complexes with chelating dafone.

Neighboring Zn<sup>II</sup> complex molecules are linked to each other *via* hydrogen bonding between amine groups and Cl atoms, and between amine groups and S atoms, forming a supramolecular chain (Fig. 2) along the [1 $\bar{1}$ 0] direction.

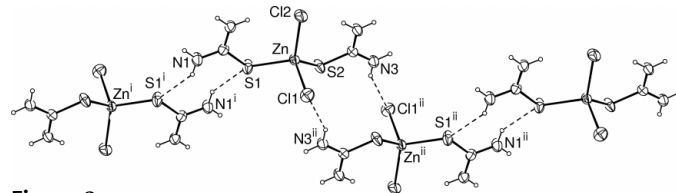
The C7-ring and C9-ring of dafone are partially overlapped with the N8<sup>iii</sup>-ring of a neighboring dafone [symmetry code: (iii)  $-1 + x, 1 + y, z$ ; Fig. 3], which suggests  $\pi$ - $\pi$  stacking interactions between the dafone rings. The  $\pi$ - $\pi$  stacking interactions involving the nearly parallel dafone rings can be better defined by the ring-centroid separation (DC), the interplanar average spacing (DP), the centroid shifts (SH) and the interplanar dihedral angle (DA). The numerical values of these parameters are DC = 3.526 (4) Å, DP = 2.91 (2) Å, SH = 1.99 (3) Å and DA = 3.33 (11)° for the C7- and N8<sup>iii</sup>-rings, and DC = 3.668 (4) Å, DP = 2.86 (2) Å, SH = 2.30 (2) Å and DA = 3.47 (10)° for the C9- and N8<sup>iii</sup>-rings.

## Experimental

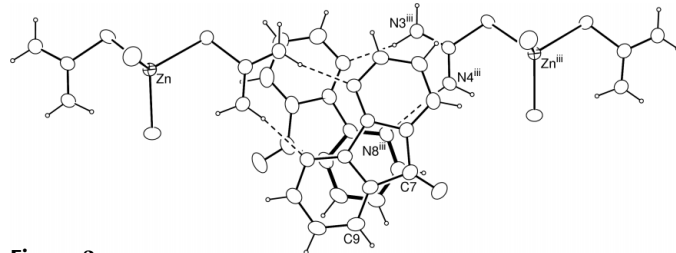
Dafone was prepared according to a previously reported method (Henderson *et al.*, 1984). ZnCl<sub>2</sub> (34 mg, 0.25 mmol), thiourea (38 mg, 0.5 mmol) and dafone (91 mg, 0.5 mmol) were dissolved in acetone (15 ml). The solution was refluxed for 2 h and filtered after cooling to room temperature. Yellow single crystals were obtained after 5 d. Analysis calculated for C<sub>24</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>2</sub>S<sub>2</sub>Zn: C 44.15, H 3.09, N 17.16%; found: C 43.6, H 3.09, N 16.65%.

### Crystal data

[ZnCl <sub>2</sub> (CH <sub>4</sub> N <sub>2</sub> S) <sub>2</sub> ] $\cdot$ 2C <sub>11</sub> H <sub>6</sub> N <sub>2</sub> O	Z = 2
<i>M<sub>r</sub></i> = 652.86	<i>D<sub>x</sub></i> = 1.542 Mg m <sup>-3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> $\alpha$ radiation
<i>a</i> = 7.4059 (17) Å	Cell parameters from 20 reflections
<i>b</i> = 12.973 (2) Å	$\theta$ = 4.5–8.1°
<i>c</i> = 15.184 (3) Å	$\mu$ = 1.25 mm <sup>-1</sup>
$\alpha$ = 89.167 (17)°	<i>T</i> = 295 (2) K
$\beta$ = 78.006 (16)°	Prism, colorless
$\gamma$ = 80.220 (16)°	0.52 $\times$ 0.44 $\times$ 0.18 mm
<i>V</i> = 1405.9 (5) Å <sup>3</sup>	



**Figure 2**  
The hydrogen-bond linkage among Zn<sup>II</sup> complex molecules. [Symmetry codes: (i)  $-x, 1 - y, 1 - z$ ; (ii)  $1 - x, -y, 1 - z$ .]



**Figure 3**  
The partially overlapped arrangement of neighboring dafone rings. [Symmetry code: (iii)  $-1 + x, 1 + y, z$ .]

### Data collection

Rigaku AFC-7S diffractometer  
 $\omega/2\theta$  scans  
Absorption correction:  $\psi$  scan  
(North *et al.*, 1968)  
 $T_{\min} = 0.535, T_{\max} = 0.802$   
5774 measured reflections  
5520 independent reflections  
4070 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$   
 $\theta_{\text{max}} = 26.0^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -15 \rightarrow 0$   
 $l = -18 \rightarrow 18$   
3 standard reflections  
every 150 reflections  
intensity decay: 0.6%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.103$   
 $S = 1.02$   
5520 reflections  
352 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.4107P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.62 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Zn—Cl1	2.2475 (10)	Zn—S2	2.3403 (9)
Zn—Cl2	2.2685 (9)	Zn—S1	2.3619 (10)
Cl1—Zn—Cl2	111.46 (4)	Cl1—Zn—S1	111.10 (4)
Cl1—Zn—S2	107.84 (4)	Cl2—Zn—S1	113.19 (4)
Cl2—Zn—S2	114.11 (3)	S2—Zn—S1	98.40 (3)

**Table 2**

Hydrogen-bonding 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>
N1—H1A...N5	0.88	2.03	2.888 (3)	167
N1—H1B...S1 <sup>i</sup>	0.94	2.83	3.606 (3)	141
N2—H2A...N6	0.89	2.11	2.997 (3)	172
N2—H2B...Cl2	0.93	2.40	3.324 (2)	172
N3—H3A...N7	0.96	1.99	2.939 (3)	167
N3—H3B...Cl1 <sup>ii</sup>	0.94	2.67	3.481 (3)	145
N4—H4A...N8	0.92	2.04	2.953 (3)	173
N4—H4B...Cl2	0.92	2.46	3.344 (2)	163

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

H atoms of amine groups were located in a difference Fourier map and included in structure-factor calculation with fixed positional ( $N-H = 0.877-0.961 \text{ \AA}$ ) and displacement parameters ( $0.08 \text{ \AA}^2$ ); all other H atoms were placed in calculated positions, with  $C-H = 0.93 \text{ \AA}$ , and included in the final cycles of refinement in the riding mode, with  $U_{iso}(H) = 1.2U_{eq}(\text{carrier atom})$ .

Data collection: *MSC/AFC Diffractometer Control Software*. (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *teXsan* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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