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Chlorobis(thiourea-*κS*)copper(I) bis(4,5-diazafluoren-9-one) monohydrate

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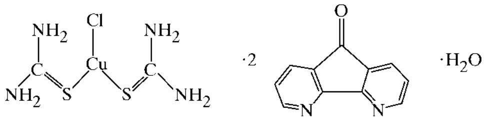
The title compound, $[CuCl(CH_4N_2S)_2]\cdot 2C_{11}H_6N_2O\cdot H_2O$, consists of molecules of a Cu^I–thiourea complex, free 4,5-diazafluoren-9-one (dafone) and crystalline water. The planar complex molecule has trigonal coordination geometry around the Cu^I atom. The dafone and water molecules, which are hydrogen bonded to the Cu^I complex, are approximately coplanar with this complex. The crystal displays a sheet structure and π–π stacking is observed between neighbouring sheets.

Comment

The structural study of transition metal complexes containing sulfur coordination is helpful for catalysis (Stiefel & Matsumoto, 1996) and medicinal chemistry (Jurisson *et al.*, 1993). As a ligand containing an S atom, thiourea is an interesting reagent, having several possible modes of bonding to a metal ion.

A thiourea–Cu^I complex has been reported previously (Spofford & Amma, 1970) in which the thiourea acted as a bridging ligand, with the S atom bonding to neighbouring Cu^I atoms, resulting in a spiral structure. Recently, during an investigation of the coordination ability of 4,5-diazafluoren-9-one (dafone), a new thiourea–Cu^I complex, (I), in which thiourea displays a different coordination mode from that reported, was obtained in our laboratory.



(I)

The molecular structure of (I) is illustrated in Fig. 1. Selected hydrogen-bonding parameters are listed in Table 1. The asymmetric unit consists of molecules of the Cu^I complex, free dafone and crystalline water. The Cu^I atom lies in a planar trigonal coordination environment, with a deviation of 0.0456 (9) Å from the plane formed by atoms Cl, S1 and S2. Two monodentate thiourea molecules coordinate to the Cu^I atom through their S atoms, with normal Cu—S distances of 2.2084 (10) and 2.2158 (10) Å. A Cl atom coordinates to the Cu^I atom at a distance of 2.2429 (10) Å, which is much shorter than the distances of 2.828 (5) and 3.164 (4) Å found in the Cu^I complex cited above (Spofford & Amma, 1970). Intramolecular hydrogen bonding between the chlorine and amine groups stabilizes the planar structure of the Cu^I complex.

The dafone and water molecules link the Cu^I complex through hydrogen bonds, as shown in Fig. 1. Both dafone and the water O atom are approximately coplanar with the Cu^I complex, the maximum atomic deviation from the mean plane of the complex being 0.858 (6) Å for O1. The planar dafone molecule is structurally similar to phenanthroline (phen), but the carbonyl bridge in dafone distorts the bipyridine portion. The average bond angle of 126.7 (3)° for N6—C12—C13 and N5—C13—C12 results in the longer N$\cdots$N separation of 3.075 (4) Å, while the average bond angle of 126.6 (3)° for N8—C23—C24 and N7—C24—C23 results in a similar N$\cdots$N separation of 3.066 (4) Å. The N$\cdots$N separations in the present structure are in agreement with the values of 3.055 and

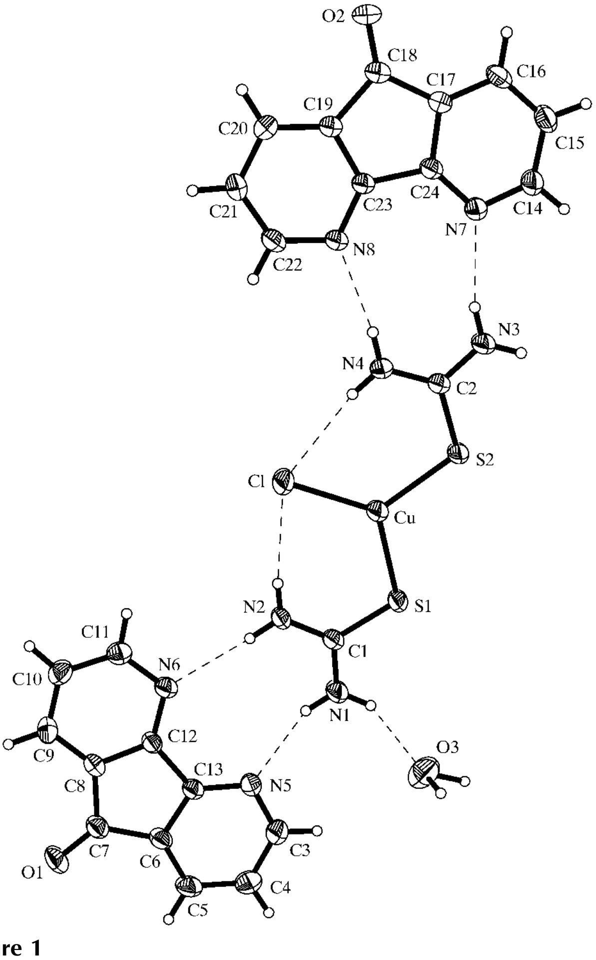


Figure 1
The structure of (I), shown with 30% probability displacement ellipsoids. Dashed lines show hydrogen bonds between the complex and dafone molecules.

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3.064 Å found in reported structures containing free dafone (Fun *et al.*, 1995; Luo *et al.*, 2002), but much longer than the N···N distance of 2.724 Å in free phen (Nishigaki *et al.*, 1978). The longer N···N separation in dafone reduces overlap of the nitrogen–metal orbitals (Henderson *et al.*, 1984) and results in a weaker chelating ability of dafone compared with phen. In fact, several complex structures with uncoordinated dafone (Menon *et al.*, 1994; Chen, 1998; Kulkarni *et al.*, 2001), dafone coordinated as a monodentate ligand (Lu *et al.*, 1996) or dafone as an asymmetric chelate (*i.e.* one normal bond and another much longer bond) (Menon & Rajasekharan, 1998; Balagopalakrishna *et al.*, 1992) have been reported previously. Structures with dafone symmetrically chelating to a metal ion have also been reported. It is interesting that significantly shorter N···N distances of 2.850 and 2.806 Å were found in the symmetrically chelating structures (Xiong *et al.*, 1996; Menon & Rajasekharan, 1997). These facts imply that the structure of dafone is rather flexible and the distortion of the bipyridine portion in dafone may be self-adjusting when dafone chelates a metal ion.

With the aid of hydrogen bonds between dafone, water and thiourea, the asymmetric units link to each other to form planar chains. The chains self-assemble to form a two-dimensional sheet structure, as shown in Fig. 2. The centrosymmetric N—H···S hydrogen-bonded dimer observed in the present structure has also been found in both a free thiourea structure (Truter, 1967) and a thiourea complex (Johnson & Steed, 1998).

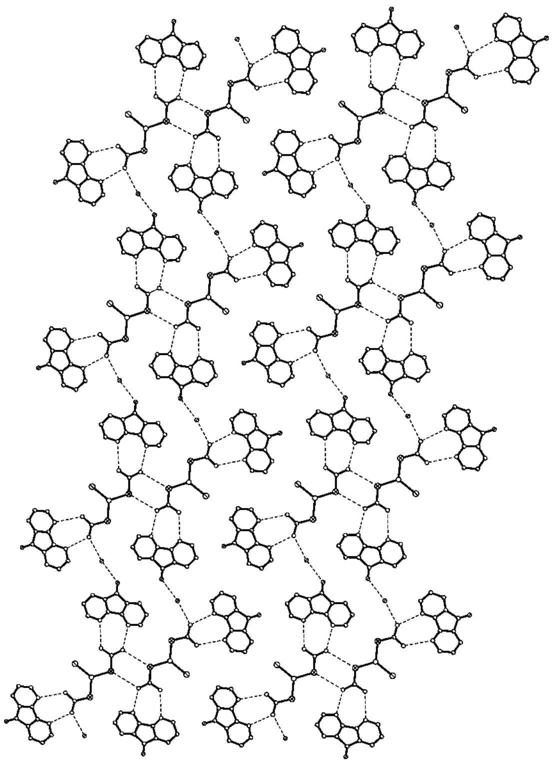

Figure 2
A view of the sheet structure in (I) assembled by planar supramolecular chains.

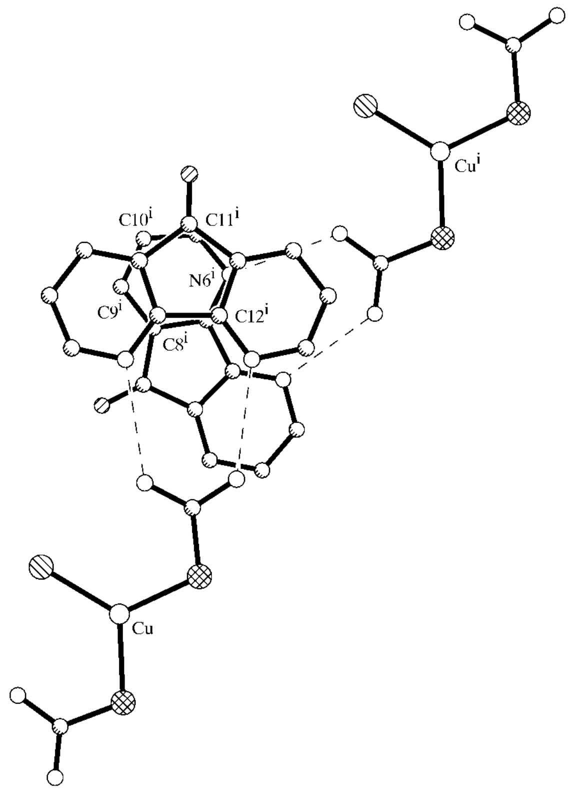

Figure 3
A view showing the aromatic π–π interactions between neighbouring dafone molecules. [Symmetry code: (i) x, y, $-1 + z$.]

Between neighbouring sheets, the dafone rings are approximately parallel [dihedral angle 1.13 (10)°] and partially overlap each other, as shown in Fig. 3. Atoms of the N6^{i}-pyridine ring deviate from the mean plane of the N7-dafone molecule with relatively short distances ranging from 3.354 (4) (C8^{i}) to 3.455 (4) Å (C11^{i}), which suggests the existence of aromatic π–π-stacking interactions between neighbouring dafone molecules [symmetry code: (i) x, y, $-1 + z$].

Experimental

Dafone was prepared according to the method of Henderson *et al.* (1984). An aqueous solution (15 ml) containing $CuCl_2 \cdot 2H_2O$ (0.85 g, 0.5 mmol) was mixed with an aqueous solution (15 ml) containing

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N5	0.86	2.12	2.937 (4)	158
N1—H2···O3	0.86	2.08	2.864 (5)	152
N2—H3···N6	0.86	2.20	3.052 (4)	171
N2—H4···Cl	0.86	2.48	3.337 (3)	172
N3—H5···N7	0.86	2.11	2.930 (4)	160
N3—H6···S2^{i}	0.86	2.64	3.468 (4)	161
N4—H7···N8	0.86	2.20	3.053 (4)	172
N4—H8···Cl	0.86	2.48	3.331 (3)	169
O3—H21···S1^{ii}	0.86	2.54	3.247 (4)	140
O3—H22···O2^{iii}	0.86	1.98	2.848 (4)	176

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

thiourea (0.076 g, 1 mmol) at room temperature. Thiourea reduced Cu^{II} to Cu^{I} (Perrin, 1970) and a large amount of white precipitate of a Cu^{I} compound appeared. Dafone (0.182 g, 1 mmol) was introduced to the solution containing the precipitate. The solution was refluxed for about 2 h until the white precipitate had completely disappeared. Then the yellow solution was filtered and the filtrate kept in a thermostat at 338 K. Yellow crystals of the title compound were obtained after 2 d. Analysis (Carlo–Erba 1160 instrument) calculated for $C_{24}H_{22}ClCuN_8O_3S_2$: C 45.50, H 3.48, N 17.60%; found: C 45.12, H 3.41, N 17.14%.

Crystal data

$[CuCl(CH_4N_2S)_2]\cdot 2C_{11}H_6N_2O\cdot H_2O$
$M_r = 633.64$
Triclinic, $P\overline{1}$
$a = 8.3016$ (9) Å
$b = 11.8473$ (18) Å
$c = 14.3024$ (9) Å
$\alpha = 93.896$ (8)°
$\beta = 99.206$ (7)°
$\gamma = 100.562$ (10)°
$V = 1358.1$ (3) Å^3
$Z = 2$
$D_x = 1.549$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 4.6$–9.9°
$\mu = 1.10$ mm^{-1}
$T = 298$ (2) K
Prism, yellow
0.44 × 0.40 × 0.38 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.617$, $T_{\max} = 0.659$
5608 measured reflections
5336 independent reflections
3411 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\max} = 26°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = -17 \rightarrow 17$
3 standard reflections every 100 reflections intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.132$
$S = 1.02$
5336 reflections
352 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.5579P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.81$ e Å^{-3}
$\Delta\rho_{\min} = -0.57$ e Å^{-3}

H atoms were placed in calculated positions, with C—H distances of 0.93 Å, N—H distances of 0.86 Å and O—H distances of 0.86 Å (Nardelli, 1999). All H atoms were included in the final cycles of least-squares refinement; water H atoms were refined with fixed coordinates and $U_{\rm iso}$ values of 0.08 Å^2, while the other H atoms were refined as riding on their parent non-H atoms with $U_{\rm iso}$ values 1.2 times the $U_{\rm eq}$ values of the parent atoms.

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: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1373). Services for accessing these data are described at the back of the journal.

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