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Jian-Ge Wang and Weizhou Wang*

Crystal structure of halogen-bonded 2-chloro-1,10-phenanthroline—1,4-diiodotetrafluorobenzene (2/1), $C_{30}H_{14}Cl_2F_4I_2N_4$

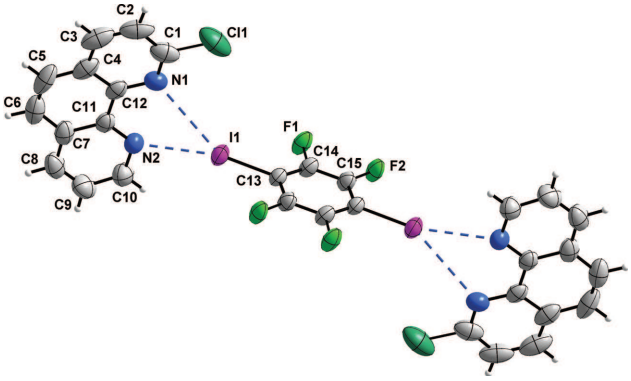

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.32 × 0.23 × 0.21 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.1 cm^{-1}
Diffractometer, scan mode:	SuperNova, ω-scans
$2\theta_{max}$, completeness:	58.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9674, 3412, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2878
$N(param)_{refined}$:	190
Programs:	CrysAlis^{PRO} [8], SHELX [9], OLEX2 [10]

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Abstract

$C_{30}H_{14}Cl_2F_4I_2N_4$, monoclinic, $I2/a$ (no. 15), $a = 17.3143(9)$ Å, $b = 8.7081(4)$ Å, $c = 19.6795(8)$ Å, $\beta = 101.795(4)°$, $V = 2904.5(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0340$, wR_{ref} $(F^2) = 0.0890$, $T = 293$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

2-Chloro-1,10-phenanthroline, 1,4-dichlorotetrafluorobenzene and dichloromethane were purchased from Aldrich Chemical Co., and used as received. The halogen bond donor and halogen bond acceptor in a molar ratio of 1:1 were dissolved in 50 mL of dichloromethane with gentle stirring at room temperature. The undissolved materials were removed by filtration. The filtrate was set aside for crystallization at 6–10 °C. After a few days, yellow crystals of title compound were obtained.

Experimental details

All H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with $U_{iso}(H)$ set to $1.2U_{eq}(C)$.

Discussion

The halogen bond is the noncovalent interaction involving halogen atom as acceptor of electron density [1]. In recent years, the important role of the halogen bond in crystal growth and design has been revealed both experimentally and theoretically [2–4]. Besides the mono-coordinate halogen bond, the bifurcated halogen bond was also frequently found in the crystal structures [5–7]. In fact, among the halogen bond supramolecular synthons proposed by Desiraju, the robustness of the bifurcated halogen bond synthons are outstanding [5]. The compounds 2-chloro-1,10-phenanthroline and 1,4-dichlorotetrafluorobenzene are good candidates for the formation of the bifurcated halogen bond.

***Corresponding author: Weizhou Wang,** College of Chemistry and Chemical Engineering, and Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang 471934, China, e-mail: wzw@lynu.edu.cn
Jian-Ge Wang: College of Chemistry and Chemical Engineering, and Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang 471934, China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
I1	0.464018(14)	0.84114(3)	0.653802(12)	0.05959(11)
Cl1	0.29627(10)	0.4627(2)	0.58798(8)	0.1215(6)
F1	0.59263(13)	0.7692(3)	0.56108(13)	0.0799(7)
F2	0.61909(14)	0.8892(3)	0.44490(14)	0.0803(7)
N1	0.33559(18)	0.5813(4)	0.71058(16)	0.0606(8)
N2	0.43706(18)	0.7782(4)	0.79387(15)	0.0589(7)
C1	0.2844(3)	0.4934(5)	0.6723(2)	0.0784(13)
C2	0.2199(3)	0.4198(5)	0.6937(3)	0.0883(16)
H2	0.1841	0.3588	0.6637	0.106*
C3	0.2138(3)	0.4444(6)	0.7608(3)	0.0918(16)
H3	0.1733	0.3968	0.7774	0.110*
C4	0.2657(2)	0.5375(5)	0.8045(2)	0.0697(11)
C5	0.2609(3)	0.5687(6)	0.8747(3)	0.0845(15)
H5	0.2219	0.5205	0.8932	0.101*
C6	0.3106(3)	0.6647(6)	0.9147(2)	0.0797(14)
H6	0.3057	0.6816	0.9604	0.096*
C7	0.3703(2)	0.7409(5)	0.88866(19)	0.0633(10)
C8	0.4206(3)	0.8459(5)	0.9276(2)	0.0776(13)
H8	0.4152	0.8690	0.9726	0.093*
C9	0.4777(3)	0.9154(6)	0.9009(2)	0.0858(14)
H9	0.5114	0.9865	0.9268	0.103*
C10	0.4847(3)	0.8785(5)	0.8343(2)	0.0743(11)
H10	0.5245	0.9254	0.8164	0.089*
C11	0.3799(2)	0.7099(4)	0.81990(18)	0.0521(8)
C12	0.3272(2)	0.6068(4)	0.77691(19)	0.0536(8)
C13	0.48665(19)	0.9366(4)	0.56225(17)	0.0492(7)
C14	0.5461(2)	0.8851(4)	0.53199(19)	0.0524(8)
C15	0.55938(19)	0.9463(4)	0.47132(18)	0.0514(8)

All bond lengths and angles in the title crystal structure are in normal ranges. One 1,4-dichlorotetrafluorobenzene molecule and two 2-chloro-1,10-phenanthroline molecules are linked by two asymmetric bifurcated halogen bonds with $d(I1\cdots N1) = 3.511$ Å, $d(I1\cdots N2) = 2.940$ Å, $<(C13—I1\cdots N1) = 140.55°$ and $<(C13—I1\cdots N2) = 167.13°$. According to the interatomic distances, the halogen C13—I1$\cdots$N2 is much stronger than the very weak halogen-nitrogen contact C13—I1$\cdots$N1, which reproduces the van-der-Waals distance. The four fluorine atoms of 1,4-dichlorotetrafluorobenzene are not involved in the formation of C—H$\cdots$F hydrogen bonds, as the H$\cdots$F distances reflect the van-der-Waals distances. At the same time, the $\pi\cdots\pi$ stacking interactions between 2-chloro-1,10-phenanthroline and 1,4-dichlorotetrafluorobenzene and the $\pi\cdots\pi$ stacking interactions between two 2-chloro-1,10-phenanthroline molecules are also formed. All these non-covalent bonds cooperate to construct the 3-D connected crystal structure.

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