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Solid-state structure of a tetrazole-substituted ferrocenium salt with weak intermolecular C–H···N hydrogen bonds

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ABSTRACT

A perchlorate salt of ferrocenylphenyltetrazole has been prepared and characterized crystallographically. In the crystal, tape-like one-dimensional molecular arrangements are formed by weak CH···N intermolecular hydrogen bonds between the tetrazole moieties (H···N distance: 2.49 Å). A layer-like structure was formed, composed of neutral layers of phenyltetrazole moieties and ionic layers of ferrocenium moieties and anions.

Keywords: Crystal Engineering; Ferrocenium salt; Tetrazole; Crystal structure; Weak hydrogen bond

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1. Introduction

Crystal engineering of organometallic crystals has attracted considerable attention in recent years [1]. C–H \cdots X intermolecular interactions, where X is an electronegative atom such as oxygen, nitrogen, and halogens, are regarded as weak hydrogen bonds [2,3], and their importance in crystal engineering is well recognized [1,4,5]. As part of our continuous investigation into ferrocene-based organometallic supramolecular assemblies [6,7], we have previously prepared tetrazoles and triazoles with ferrocenyl substituents, and investigated their structures and properties [8]. X-ray crystallography revealed that short intermolecular C–H \cdots N contacts are formed between the azole moieties. Ferrocenyl-tetrazoles and -triazoles exhibit one-dimensional molecular arrangements via these interactions (Fig. 1). The H \cdots N distances are about 2.3 Å and are 0.4 Å shorter than the sum of the van der Waals radii. Intermolecular C–H \cdots N contacts have been found in tetrazole [9] and related compounds [5], and play an important role in their crystal architectures. Although heteroaryl ferrocenes form a variety of organometallic supramolecular complexes when reacted with metal salts [10], only a few complexes of ferrocenylazoles have been reported [11], despite the versatile metal coordination properties of triazole and tetrazole [12].

In this study, we isolated and determined the crystal structure of a perchlorate salt of ferrocenylphenyltetrazole, [Fe(C₅H₅)(C₅H₄PhN₄CH)](ClO₄) (**1**; Fig. 2), to investigate the intermolecular interactions of ferrocenylazole salts. Ferrocenium salts with conjugated heterocyclic substituents are interesting because of their optical and electronic properties, and several have been characterized crystallographically [13]. Here, we report the X-ray crystal structure of **1**, which exhibits weak C–H \cdots N interactions between the tetrazole moieties and Coulombic interactions between the cations and anions. The structure is compared with those of ferrocenyl- and ferrocenylphenyl-azolium salts [14], which have been prepared as part of our studies on ferrocene-based ionic liquids [15]. To our knowledge, this is the first example of the structural characterization of an azole-substituted ferrocenium salt, whereas there is a report on a carbazole derivative of a ferrocenium salt [16].

2. Result and discussion

A small amount of the crystalline salt of **1** was produced by the reaction of ferrocenylphenyltetrazole and $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in methanol followed by vapor diffusion of ether. Considering the redox potential of ferrocenylphenyltetrazole ($E^{1/2} = 0.09$ V, vs. $\text{FeCp}_2/\text{FeCp}_2^+$ [8]), $\text{Fe}(\text{III})$ species formed by air oxidation might be acting as an oxidant.

The molecular structure of **1** determined at 100 K is shown in Fig. 3 and its crystallographic parameters are listed in Table 1. The average intramolecular Fe–C distance in the ferrocenium moiety (2.083 Å) corresponds to the value for the ferrocenium cation (2.095 Å) [17], and is longer than in neutral ferrocenylphenyltetrazole (2.034 Å) [8]. Among the Fe–C bonds, the bond involving the carbon connected to the phenylene ring is the longest [2.112(5) Å]. The dihedral angles between the Cp–Cp, Cp–phenylene, and phenylene–tetrazole rings are $1.8(4)^\circ$, $14.7(3)^\circ$, and $19.7(3)^\circ$, respectively. The Cp rings in the cation adopt a staggered conformation. The bond lengths in the azole moiety are almost the same as those observed for ferrocenylphenyltetrazole [8] and *N*-aryl-tetrazoles [5a, 18], which is consistent with the charge localization in the ferrocenium moiety.

The packing diagram of **1** projected along the *b*-axis is shown in Fig. 4. The ionic moieties and the neutral moieties form layer-like structures. The perchlorate anions are located between the ferrocenium cations, exhibiting a short $\text{C}_{\text{Cp}}\text{H} \cdots \text{O}_{\text{anion}}$ contact [$\text{H} \cdots \text{O}$ distance: 2.365(8) Å]. The cations and anions form ionic layers, in which π – π interactions exist between the Cp rings of the neighboring ferrocenium unit. The ionic layers are separated by the neutral layers of phenyltetrazole moieties. The azole moieties form a tape-like one-dimensional arrangement via weak $\text{C}–\text{H} \cdots \text{N}$ hydrogen bonds (Fig. 5). The molecular arrangement closely resembles those of ferrocenyl-tetrazole and -triazole (Fig. 1), whereas the arrangement in ferrocenylphenyl-tetrazole and -triazole are somewhat different [8]. The $\text{C}–\text{H} \cdots \text{N}$ distance of 2.485(4) Å in **1** is 0.27 Å shorter than the sum of the van der Waals radii (2.75 Å). The distance is comparable to those in ferrocenylphenyl-tetrazole and -triazole (2.5 Å), but longer than those in ferrocenyl-tetrazole and -triazole (2.3 Å) [8]. The ferrocenylphenyl moieties are arranged as pendants with respect to the one-dimensional tape structure of the neutral moieties, and adjacent

phenylene-tetrazole moieties overlap via π – π interactions.

Ferrocenyl- and ferrocenylphenyl-azolium salts also generally exhibit layer-like structures [14]. The azolium cations and anions form ionic layers, with the azole hydrogens interacting with the anion and the ferrocenyl moieties aggregating to form neutral layers. Hence, despite the different location of the cation within the molecules, the azolium salts and **1** have similar structures.

In summary, the importance of weak C–H \cdots N hydrogen bonds in the salt of ferrocenylazole has been revealed. This study may lead to the future construction of magnetic organometallic supramolecules involving ferrocenium cations.

3. Experimental

Ferrocenylphenyltetrazole [4-(4-ferrocenylphenyl)-1*H*-tetrazole] was prepared according to the literature [8]. Other chemicals were commercially available. Vapor diffusion of ether into a methanol solution of ferrocenylphenyltetrazole and Fe(ClO₄)₂·6H₂O produced a small amount of black crystals of **1** together with uncharacterizable powders. X-ray diffraction data for **1** was collected on a Bruker SMART APEX II Ultra CCD diffractometer using MoK α radiation (λ = 0.71073 Å). Crystal data, data collection parameters, and analysis statistics for these compounds are listed in Table 1. All calculations were performed using SHELXL [19]. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were inserted at calculated positions. Empirical absorption corrections (SADABS) [20] were applied. The packing diagrams were drawn using ORTEP-3 [21]. CCDC 832625 contains the supplementary crystallographic data for this paper.

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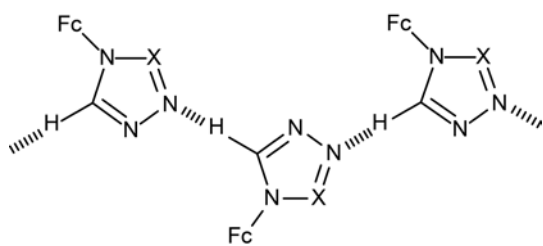


Fig. 1. Schematic illustration of weak C–H···N hydrogen bonds in azole derivatives (X = CH or N).

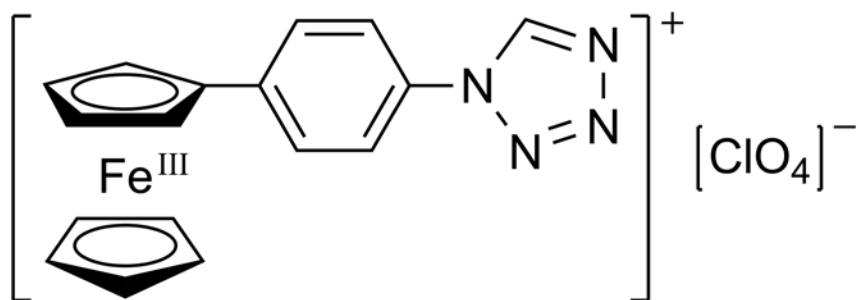


Fig. 2. Chemical diagram of $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{PhN}_4\text{CH})](\text{ClO}_4)$ (**1**).

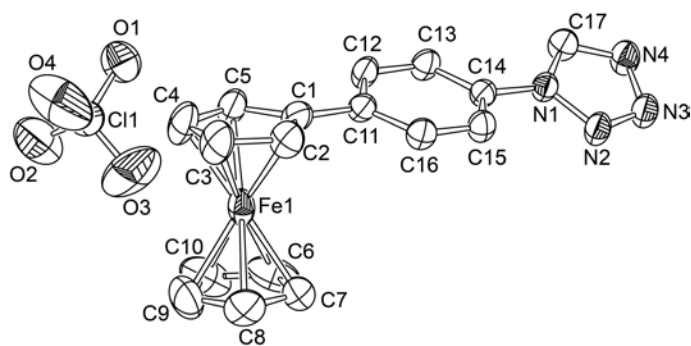


Fig. 3. ORTEP drawing of the molecular structure of **1** with the numbering scheme. Thermal ellipsoids are shown at the probability level of 50%.

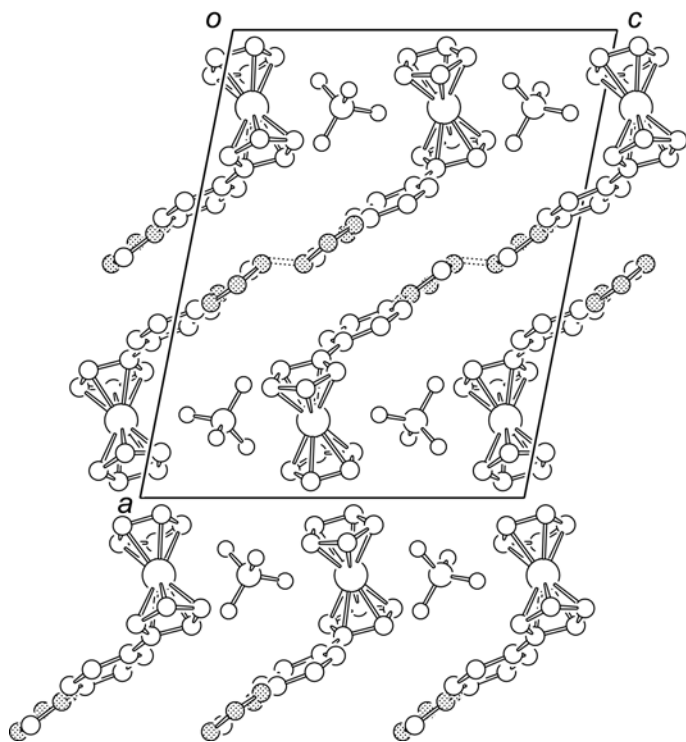


Fig. 4. Packing diagram of **1** viewed along the *b*-axis. Hydrogen atoms are omitted for clarity. C–H...N contacts are indicated by dashed lines.

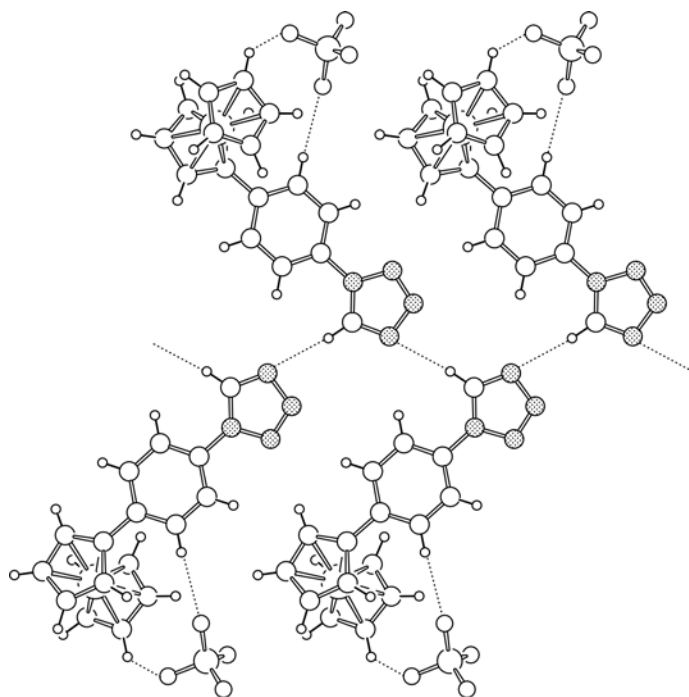


Fig. 5. Molecular tapes joined by C–H⋯N interactions in **1**, extending along the *b*-axis. Nitrogen atoms are hatched. Intermolecular contacts that are 0.2 Å shorter than the sum of the van der Waals radii are indicated by dotted lines.

Table 1.Crystallographic parameters for **1**

| | |
|----------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------|
| Formula | C ₁₇ H ₁₄ Cl Fe N ₄ O ₄ |
| Formula weight | 429.62 |
| <i>T</i> (K) | 100 |
| Crystal system | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> (Å) | 16.311(5) |
| <i>b</i> (Å) | 8.053(3) |
| <i>c</i> (Å) | 13.118(4) |
| β (°) | 101.229(4) |
| <i>V</i> (Å ³) | 1690.0(9) |
| <i>Z</i> | 4 |
| <i>D</i> _{calc} (g cm ⁻³) | 1.688 |
| μ (mm ⁻¹) | 1.084 |
| Reflections collected | 7986 |
| Independent reflections | 3190 |
| <i>F</i> (000) | 876 |
| Parameters | 244 |
| Final <i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2 σ) | 0.0643, 0.1659 |
| Final <i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data) | 0.0918, 0.1883 |

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$$

Table 2. DSC data for ferrocene-based CT complexes

| | Heating run | | | Cooling run | | | ΔT (K) |
|----------------------------------------------------------------------------------------------------|---------------------|--------------------------------------|-----------------------------------------------------|--------------|--------------------------------------|-----------------------------------------------------|----------------|
| | <i>T</i> (K) | ΔH (kJmol ⁻¹) | ΔS (JK ⁻¹ mol ⁻¹) | <i>T</i> (K) | ΔH (kJmol ⁻¹) | ΔS (JK ⁻¹ mol ⁻¹) | |
| [Fe(C ₅ HMe ₄) ₂][Cl ₂ -naphthoquinone] (3) | 174.6 | 0.46 | 2.65 | 155.1 | 0.59 | 3.83 | 19.5 |
| | 426.2 ^{a)} | 63.0 | 146.05 | 408.9 | 9.63 ^{b)} | 23.94 ^{b)} | 17.3 |
| [Fe(Cp*) ₂][TCNQ] (1-D phase) | 215.9 | 0.66 | 3.02 | 214.2 | 0.61 | 2.90 | 1.7 |
| [Fe(C ₅ HMe ₄) ₂][TCNQ] | 226.5 | 0.28 | 1.23 | 181.7 | 0.24 | 1.33 | 44.8 |
| | 395.4 ^{a)} | 7.70 | 19.4 | 390.6 | 7.52 | 19.4 | 4.8 |

^{a)} Melting. ^{b)} Smaller due to decomposition.

Table 3. Redox potentials of ferrocenes and quinones, and CT energies observed in powders obtained by solvent-drop grinding.

| Donor | Acceptor | E_D / V^a | E_A / V^a | $\Delta E_{\text{redox}} / V^b$ | $h\nu_{\text{CT}} / \text{eV}$ |
|------------------------------------------------------|--------------------|--------------------|----------------------|---------------------------------|--------------------------------|
| [Fe(Cp*) ₂] | F ₄ BQ | −0.08 ^c | 0.02 ^{e, f} | −0.10 | 1.59 |
| | Cl ₄ BQ | −0.08 | 0.05 ^g | −0.13 | 1.60 |
| | Br ₄ BQ | −0.08 | 0.00 ^h | −0.18 | 1.59 |
| | Cl ₂ BQ | −0.08 | −0.18 ^h | 0.10 | 1.60 |
| [Fe(C ₅ HMe ₄) ₂] | F ₄ BQ | −0.04 ^c | 0.02 | −0.06 | 1.66 |
| | Cl ₄ BQ | −0.04 | 0.05 | −0.09 | 1.64 |
| | Br ₄ BQ | −0.04 | 0.00 | −0.04 | 1.65 |
| | Cl ₂ BQ | −0.04 | −0.18 | 0.14 | 1.64 |
| [Co(Cp*) ₂] | F ₄ BQ | −1.47 ^d | 0.02 | −1.45 | 2.14 ⁱ |
| | Cl ₄ BQ | −1.47 | 0.05 | −1.52 | 2.66 ⁱ |
| | Br ₄ BQ | −1.47 | 0.00 | −1.47 | 2.48 ⁱ |
| | Cl ₂ BQ | −1.47 | −0.18 | −1.65 | 2.10 ⁱ |

^a) Half-wave redox potentials of donors (E_D) and acceptors (E_A) vs. SCE in CH₃CN, ^b) $\Delta E_{\text{redox}} / V = E_D - E_A$, ^c) ref. 25, ^d) ref. 26, ^e) ref. 27, ^f) Potentials referenced to SCE, ^g) ref. 28, ^h) ref. 29, ⁱ) shoulder.

Table 4. Redox potentials of the components and CT energies of ferrocene-based CT complexes.

| Complex | E_D / V^a | E_A / V^a | $\Delta E_{\text{redox}} / V^b$ | $h\nu_{\text{CT}} / \text{eV}$ |
|----------------------------------------------------------------------------------------------------|--------------------|-----------------------|---------------------------------|--------------------------------|
| [Fe(Cp*) ₂][Cl ₂ -naphthoquinone] (1) | −0.08 ^h | −0.45 ⁱ | 0.37 | 1.98 |
| [Fe(Cp*) ₂][Br ₂ -naphthoquinone] (2) | −0.08 | −0.30 ⁱ | 0.22 | 1.94 |
| [Fe(C ₅ HMe ₄) ₂][Cl ₂ -naphthoquinone] (3) | −0.04 ^h | −0.45 | 0.41 | |
| [Fe(Cp*) ₂][acenaphthenequinone] ^c | −0.08 | −0.98 ^{j, k} | 0.90 | 1.5–2.0 ^o |
| [Fe(Cp*) ₂][CN ₂ -naphthoquinone] ^d | −0.08 | 0.20 ^l | −0.28 | |
| [Fe(Cp*) ₂][TCNQ] (1-D phase) ^e | −0.08 | 0.21 ^m | −0.29 | 1.41 |
| [Fe(C ₅ HMe ₄) ₂][TCNQ] ^f | −0.04 | 0.21 | −0.25 | 1.43 |
| [Fe(Cp*) ₂][DMDCNQI] ^g | −0.08 | 0.06 ⁿ | −0.14 | 1.83 |

^a) Half-wave redox potentials of donors (E_D) and acceptors (E_A) vs. SCE in CH₃CN except for acenaphthenequinone, ^b) $\Delta E_{\text{redox}} / V = E_D - E_A$, ^c) ref. 17a, ^d) ref. 18a, ^e) ref. 14, ^f) ref. 15, ^g) ref. 16, ^h) ref. 25, ⁱ) ref. 30, ^j) ref. 31, ^k) Potentials referenced to SCE in DMF, ^l) ref. 32, ^m) ref. 33, ⁿ) ref. 34, ^o) broad, ref. 14a.

TOC

