Structure and properties of a ferrocenylpyrimidine-bromanilic acid hydrogen-bonded supramolecular complex

Mochida, Tomoyuki

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Note

Structure and properties of a ferrocenylpyrimidine–bromanilic acid hydrogen-bonded supramolecular complex

Tomoyuki Mochida

Department of Chemistry, Graduate School of Science, Kobe University, Rokkodai, Nada, Hyogo 657-8501, Japan

Abstract

A hydrogen-bonded assembly composed of ferrocenylpyrimidine (FcPM) and bromanilic acid (BA), represented as [FcPM](BA)(acetone)$_{0.5}$, was prepared and crystallographically characterized. The asymmetric unit of the crystal contained two crystallographically independent molecules of FcPM and BA, which were alternately connected to form one-dimensional zigzag chains via OH···N hydrogen bonds. The BA molecules were stacked to form one-dimensional columns. No charge transfer was observed between FcPM and BA. Acetone molecules, which were located in channels, were desorbed at 433 K.

Keywords: Hydrogen bond; Supermolecule; Ferrocenylpyrimidine; Crystal structure

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Tel/fax: +81-78-803-5679, *E-mail address: tmochida@platinum.kobe-u.ac.jp*

1. Introduction

The construction of supramolecular assemblies has attracted considerable interest in recent decades [1]. In particular, the combined use of hydrogen bonds and coordination bonds has produced many interesting molecular architectures [2]. Recently, we have been systematically preparing organometallic supermolecules using ferrocene-based ligands [3–5]. One of these, ferrocenylpyrimidine (FcPM), is a versatile ligand that affords various supramolecular metal complexes [4] and hydrogen-bonded architectures with hydrogen-bond donors such as carboxylic acids and aromatic alcohols [5]. Because ferrocenes are useful electron donors [6, 7], we investigated the reactions of FcPM with organic acceptors such as benzoquinone and TCNQ derivatives to form supramolecular charge-transfer complexes.

Among benzoquinone derivatives, bromanilic acid (BA) and chloranilic acid (CA) are versatile hydrogen-bond donors [8]. The reaction of decamethylferrocene with BA produces an ionic complex composed of a decamethylferrocenium cation and a deprotonated anion of BA [9], while the reaction of decamethylferrocene with CA produces a neutral complex in which CA forms a hydrogen-bonded supramolecular structure via solvated water molecules [9]. Here we report the preparation and characterization of the FcPM–BA complex **1**, an acetone solvate represented as [FcPM](BA)(acetone)$_{0.5}$ (Fig. 1). It was found that FcPM and BA were alternately connected to form 1-D zigzag chains via OH···N hydrogen bonds, and the BA molecules were stacked to form one-dimensional columns. No charge-transfer bands were observed between FcPM and BA. Acetone molecules were located in channels formed between BA and FcPM, and were desorbed at 433 K.

2. Results and Discussion

2.1. Crystal structure

Complex **1** was obtained by slow evaporation of an acetone solution of a mixture of FcPM

and BA. In the crystal, FcPM and BA form an alternating zigzag hydrogen-bonded tape structure with ferrocenyl pendants, as shown in Fig. 2. The chain contains two pairs of crystallographically independent molecules of FcPM and BA (molecules I and II). The intramolecular geometries are almost identical to those observed for FcPM [3a] and BA [10], indicating that both components are neutral. The two molecules of FcPM differ in their Cp–PM torsion angles, which are 18.6° (molecule I) and 50.6° (molecule II). The BA molecules contain intramolecular O···HO hydrogen bonds (O···O distances: 2.66–2.69 Å), and there are intermolecular N···HO hydrogen bonds between FcPM and BA (N···O distances: 2.65–2.71 Å); thus, strong bifurcated hydrogen bonds are formed (Table 1). In addition, CH···O contacts that are shorter by 0.2–0.5 Å than van der Waals distances (C···O distances: 2.97 Å and 3.08 Å) exist between FcPM and BA (except between FcPM I and BA I); these can be regarded as non-classical hydrogen bonds [11]. A packing diagram determined at 90 K is shown in Fig. 3. The complex crystallized in space group $P2_1/c$. BA molecules are stacked along the *b*-axis to form one-dimensional columns via π–π interactions, while no direct π–π interaction exists between FcPM and BA. The acetone molecules are located in one-dimensional channels formed between FcPM and BA, and do not form hydrogen bonds.

2.2. Solid state properties

The redox potentials of FcPM and BA are +0.54 V and –0.12 V (vs. SCE), respectively [4a, 12], which is consistent with the formation of a neutral complex. The spectroscopic data shown below also indicate that the degree of charge transfer from the ferrocenyl moiety of FcPM to BA is small. UV-vis absorption bands in powdered samples of **1** appeared as rather sharp multiple bands at around 401 nm and 766 nm. These are lower energies than those of its precursors (241 nm for FcPM; 244 and 637 nm for BA), but no typical broad and intense charge-transfer band was observed. This is consistent with the crystal structure in which there

is no direct contact between the ferrocenyl moiety of FcPM and BA.

In the IR spectrum of **1**, broad absorption bands representing the hydrogen-bonded OH group were observed at around 2200–3300 cm^{-1}. C=O stretching bands appeared at 1612 and 1664 cm^{-1}, slightly shifted with respect to those of BA (1622 and 1656 cm^{-1}); this is probably due to the additional intermolecular hydrogen bond with FcPM. The C=O stretching band of acetone was observed at 1712 cm^{-1}, which corresponds to free acetone. This is consistent with the absence of hydrogen bonding for this molecule.

Differential scanning calorimetry (DSC) measurements between 103 K and 463 K showed a sharp endothermic peak at 432.5 K (ΔH = 201.9 kJ mol^{-1}) on the heating run, corresponding to the desorption of acetone. No other peak suggestive of a phase transition was observed.

3. Experimental

FcPM was prepared as described in the literature [4a]. BA was purchased from TCI Co. Ltd. Black-brown needle crystals of **1** were obtained in high yield by slow evaporation of an equimolar mixture of FcPM and BA in acetone. IR (KBr, cm^{-1}): 1712 (C=O, acetone), 1664 (C=O, BA), 1612 (C=O, BA), 1408, 1240, 1223, 1352, 1165, 974. Anal. calcd. for $C_{43}H_{34}Br_4Fe_2N_4O_9$: C, 43.69; H, 2.90; N, 4.74, Found: C, 43.26; H, 3.04; N, 4.27. No crystalline complexes were obtained from mixtures of FcPM and CA or tetrahalogenobenzoquinones. IR spectra were recorded using KBr pellets on a JASCO FT-IR 230 spectrometer. Solid-state electronic absorption spectra were measured using a JASCO V-570 UV/Vis/NIR spectrometer equipped with an integrating sphere for diffuse reflectance spectroscopy, and a Kubelka-Munk conversion was applied to the resulting spectra. X-ray diffraction data were collected on a Bruker SMART APEX II CCD diffractometer using MoKα radiation (λ = 0.71073 Å) at 90 K. The structures were solved by the direct method and refined on F^2 using SHELX-97 [13]. Empirical absorption correction was applied

(SADABS [14]). The non-hydrogen atoms were refined anisotropically. The ORTEP-3 program [15] was used for molecular graphics. Crystallographic parameters are listed in Table 2. DSC measurements were performed using a Q100 differential scanning calorimeter (TA Instruments) at a rate of 10 K min^{-1}.

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Appendix A. Supplementary material

CCDC 777264 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be can be found, in the online version, at doi:

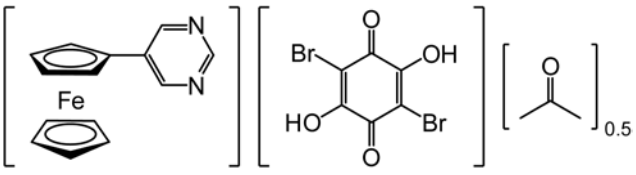

Fig. 1. Structural formula of **1**.

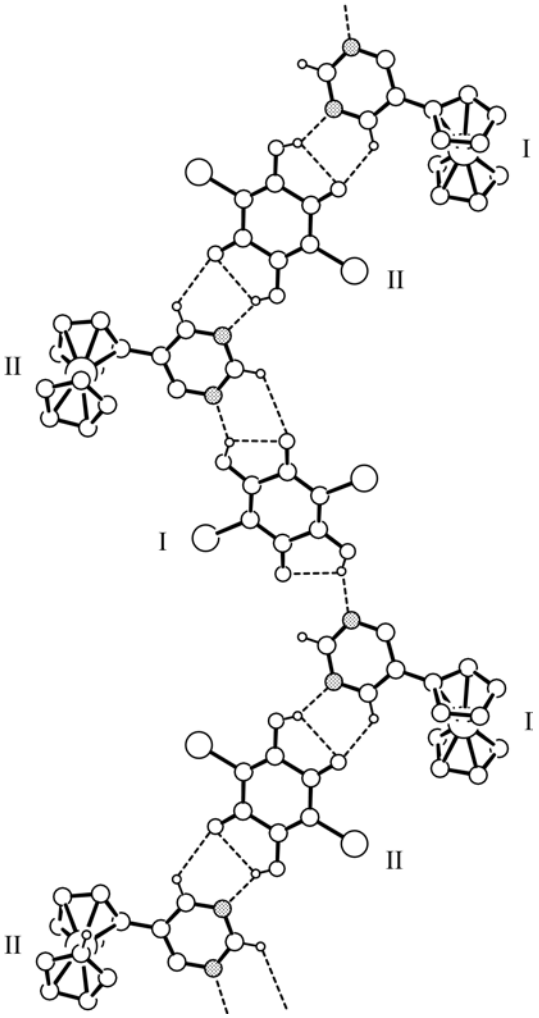

Fig. 2. Hydrogen-bonded zigzag chain structure of **1**. Hydrogen atoms (except for those involved in hydrogen bonding) are omitted for clarity. Hydrogen bonds are represented by dashed lines.

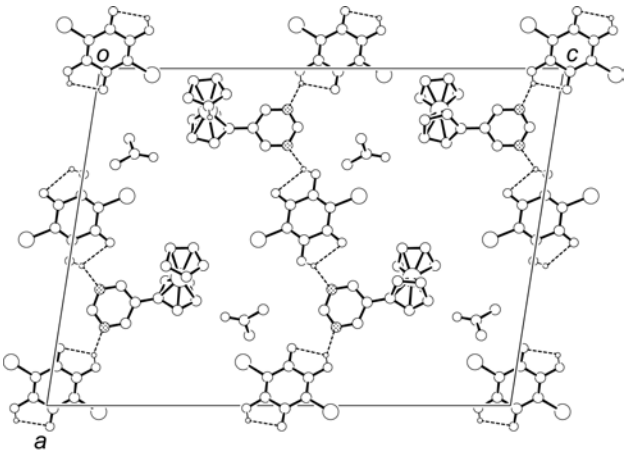

Fig. 3. Packing diagram of **1** viewed along the *a*-axis. Hydrogen atoms (except for the OH hydrogen) are omitted for clarity. Hydrogen bonds are represented by dashed lines.

Table 1
Hydrogen bond distances (Å) in **1**

D–H…A	d (D…A)
Intramolecular hydrogen bond	
O(7)–H…O(8)	2.692(3)
O(5)–H…O(6)	2.686(3)
O(3)–H…O(4)	2.663(3)
O(1)–H…O(2)	2.686(3)
Intermolecular hydrogen bond	
O(7)–H…N(1)	2.675(3)
O(5)–H…N(3)	2.718(3)
O(3)–H…N(4)	2.665(3)
O(1)–H…N(2)	2.651(3)

Table 2

Crystallographic parameters of **1**

Formula	C43 H34 Br4 Fe2 N4 O9
Formula weight	1182.08
T / K	90
Crystal system	Monoclinic
Space group	$P\,2_1/c$
a / Å	20.602(3)
b / Å	7.3147(1)
c / Å	28.044(5)
β / °	99.003(3)
V / Å^3	4174.1(1)
Z	4
ρ_{calcd} / g cm^{-3}	1.881
μ(MoKα) / cm^{-1}	45.87
Data / Parameters	9585 / 565
R_1, R_w	0.0324; 0.0678
Goodness of fit	1.005

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