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Double inclusion of ferrocene within a doubly interpenetrated three-dimensional framework based on a resorcin[4]arene

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Abstract

Co-crystallization of *C*-methylcalix[4]resorcinarene (**1**) and 4,4′-bipyridine (**2**) from ethanol in the presence of ferrocene affords single crystals of **3h**·2.15 (ethanol)·0.85 (ferrocene) that consist of a doubly interpenetrated 3D hydrogen-bonded framework, **1**·1.5(**2**) (**3h**). The 3D framework **3h** is a supramolecular isomer of a reported 2D framework **3g** and possesses box-shaped cavities that include two molecules of ferrocene as a guest.

Keywords: Ferrocene; Host–guest chemistry; Hydrogen bonds; Isomerism; Interpenetration

1. Introduction

Although organometallic sandwich-type complexes (e.g. ferrocenes) are attractive guests for studies of crystalline solids where a molecular receptor serves as a host, such inclusion behavior remains largely unexplored [1,2]. Indeed, the ability to decorate metals of organometallic sandwich complexes with a variety of organic ligands means that a virtually unlimited number of such organometallics may be studied as guests [3]. Despite this realization, however, the relatively large sizes and diverse functionalities of such sandwich compounds—factors that make such complexes attractive targets as guests—have largely hindered studies of their inclusion behavior. Moreover, the systematic design of solid state materials involving molecular receptors as hosts and organometallic sandwich-type compounds as guests may lead to the construction of crystalline materials [4] wherein properties of a receptor (e.g. recognition) and sandwich complex (e.g. optical) may be engineered in a solid [5].

In this context, we, and others, have demonstrated the ability of cavity-containing organic materials based on *C*-methylcalix[4]resorcinarene (**1**) and 4,4′-bipyridine (**2**) to include organometallic sandwich compounds as guests [6,7]. Specifically, we have demonstrated the ability of ferrocene, and acylated derivatives, to assemble within a one-dimensional (1D) wave-like hydrogen-bonded framework **1**·2(**2**) (**3a**) [6] while Coppens et al. have recently revealed the ability of a ruthenocene to assemble within a 2D symmetrical brick framework **1**·2(**2**) (**3b**) [7], a net which is a supramolecular isomer of the 1D material [8]. In the former, 1,1′-diacetylferrocene was observed to adopt a conformation within **3a** not adopted by the free complex in the solid state while, in the latter, decamethylruthenocene was observed to exhibit an excited state lifetime within **3b** greater than that of the free sandwich compound.

A remarkable feature of such resorcin[4]arene-based solids is an ability of the components to form a variety of cavity-containing frameworks. The ability of **1** to function as a multiple hydrogen bond donor, combined with the conformational flexibility of **1** and the hydrogen bonds that link the molecular components, has meant that **1** and **2** may assemble in the solid state to form cavities of diverse sizes, shapes, and functionalities, as well as of various stoichiometries. In addition to **3a** and **3b**, the components of **1**·2(**2**), for example, may form two supramolecular isomers which define a 0D capsule **3c** [9] and a 1D linear array **3d** [10] (Scheme 1).

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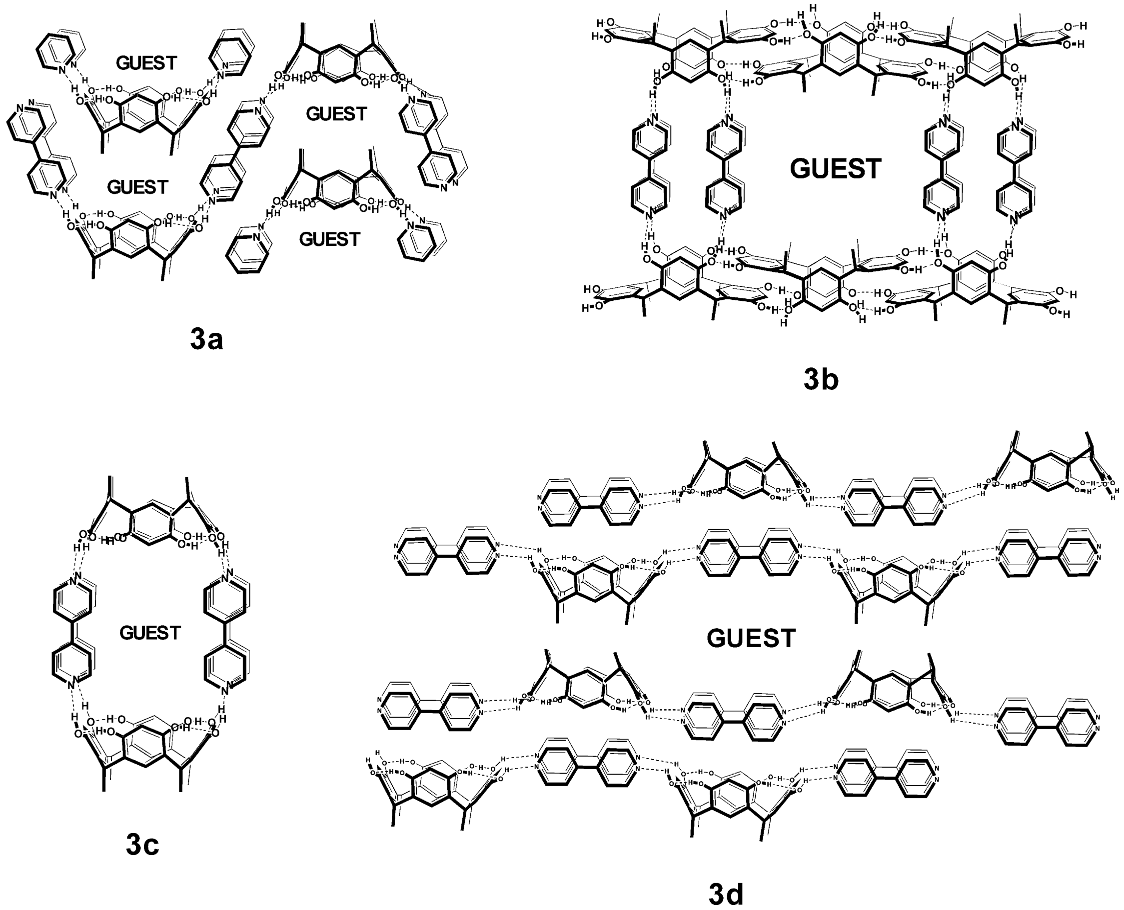


3a **3b** **3c** **3d**

Scheme 1.

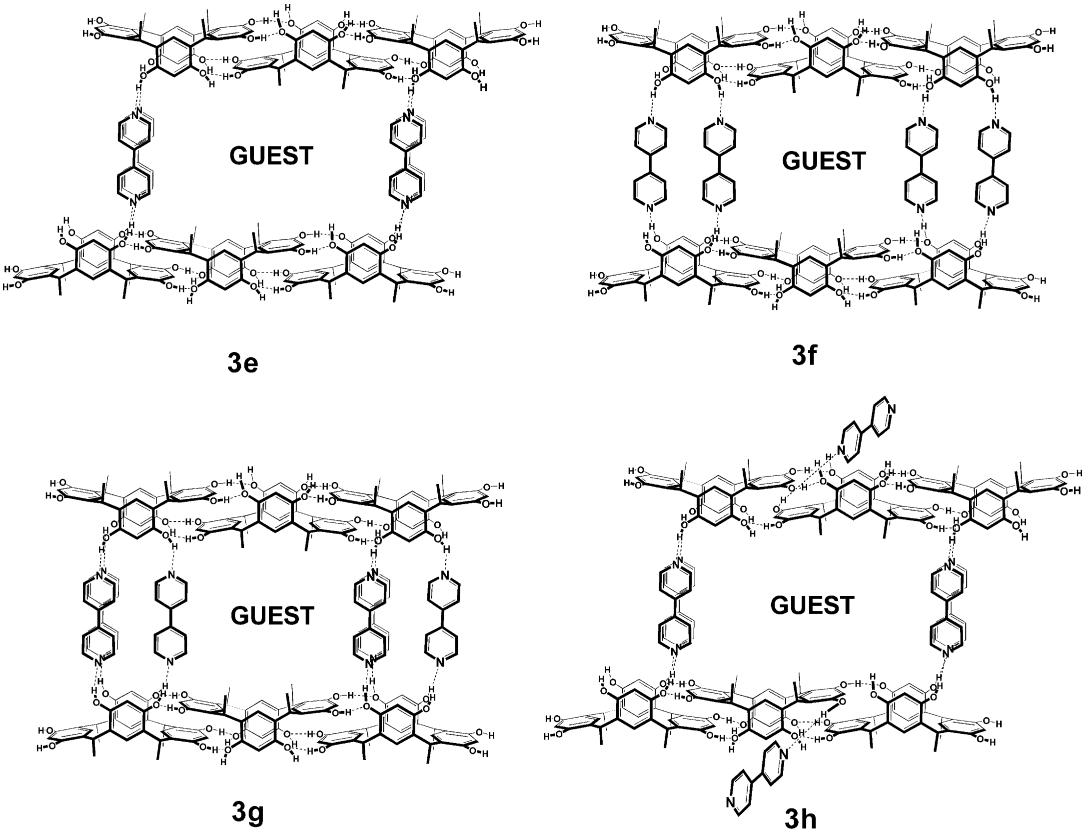
Template effects involving single and multiple guests have been used to rationalize the formation of each structure [11]. Notably, three brick frameworks, of composition **1**·**2** (**3e** and **3f**) [12–14] and **1**·1.5(**2**) (**3g**) [12], with cavities larger than **3b**, have been described (Scheme 2). Whereas the cavities of **3a**–**3d** are lined with aryl and alkyl groups and are therefore hydrophobic, the cavities of **3e**–**3g** are partly lined with hydroxyl groups and therefore may be both hydrophobic and hydrophilic. Together, these observations suggest that such resorcin[4]arene-based solids may be considered 'soft materials' capable of entrapping a wide range of guest molecules [10,15].

As part of a program of study aimed at determining the ability of solid state hosts based on **1** and **2** to entrap organometallic sandwich compounds as guests, we describe here the ability of **1** and **2** to form a hitherto unobserved 3D framework of composition **1**·1.5(**2**) (**3h**), in **3h**·2.15(ethanol)·0.85(ferrocene), that includes ferrocene as a guest. The 3D host, which is a supramolecular isomer of the 2D net **3g** [8], forms a doubly interpenetrated framework structure that involves box-shaped cavities, of nanometer-scale dimensions [14], which accommodate two ferrocenes as guests. In addition to providing a new structure type for hosts based on **1** and **2**, **3h**·2.15(ethanol)·0.85(ferrocene) represents, to our knowledge, the first example in which more than one organometallic complex has been included within a closed molecular cavity in the solid state. Such observations provide insight into factors that lead to inclusion of multiple guests within closed solid-state cavities, which is of emerging interest [16].

2. Results and discussion

Cooling of a solution of **1**, **2**, and ferrocene in ethanol yielded, upon slow cooling, light yellow crystals of **3h**·2.15(ethanol)·0.85(ferrocene) suitable for single-crystal X-ray analysis within ca. 1 day. The formulation of **3h**·2.15(ethanol)·0.85(ferrocene) was confirmed by single-crystal X-ray diffraction, thermal gravimetric analysis, and ^{1}H-NMR spectroscopy.

A view of the X-ray crystal structure of **3h** is shown in Fig. 1. In a similar way to **3e** [12,14], **1** adopts a T-shaped conformation wherein two molecules of **2** form two O–H···N hydrogen bonds [O···N separations (Å): O(1)···N(1) 2.693(5), O(5)···N(2) 2.657(5)] along the upper rim of **1** while neighboring resorcin[4]arenes self-assemble as chains via O–H···O forces [O···O separa-



3e 3f

3g 3h

Scheme 2.

tions (Å): O(2)···O(4) 2.809(4), O(3)···O(6) 2.883(4), O(7)···O(1) 2.729(4), O(8)···O(5) 2.699(4)]. In this arrangement, the components of **3h**, similar to **3e**, form a 2D skewed-brick framework that possesses box-shaped cavities of dimensions ca. 1.1 × 1.0 × 0.4 nm (based on van der Waals radii) and an internal volume of ca. 1.0 nm^3. In contrast to **3e**, however, a third molecule of **2**, which sits around a crystallographic center of inversion, has assembled alongside **1** such that the bipyridine is oriented approximately orthogonal to the plane of the brick framework. In this arrangement, the bipyridine joins, in an alternating fashion above and below the brick framework, neighboring brick nets via O–H···N forces [O···N separation (Å): O(4)···N(3) 2.804(7)]. Thus, the components of **3h** have assembled to form a 3D framework in which the third bipyridine, in effect, serves as a pillar, cross-linking the 2D brick structures. To our knowledge, **3h**, which is a supramolecular isomer of the 2D framework **3g** [12], has not been observed.

A view of the included guests of **3h**·2.15(ethanol)·0.85(ferrocene) is shown in Fig. 2. The 3D framework **3h** exhibits twofold interpenetration wherein the bipyridines that run orthogonal to the brick nets are threaded through the box-shaped cavities. Despite this interpenetration [8], however, the cavities of **3h**, as in the case of **3e**·4(acetone) and **3e**·3.5(ethanol)·H_2O [12,14], are filled with multiple guests. In particular, in addition to the pillar **2**, two ferrocenes, each of which exhibits static disorder with a solvent ethanol molecule (occupancies: 85:15) [17], occupy the two hydrophobic corners of each cavity while four ethanols, two of which lie disordered across two sites (occupancies: 60:40), occupy the two hydrophilic corners, participating in O–H···O forces with each other [O···O separation (Å): O(9)···O(10) 2.728(8)] and the walls of the host [O···O separations (Å): O(6)···O(9) 2.659(6), O(10)···O(2) 2.780(6)]. Similar to **3b**·0.5(decamethylruthenocene)·(ethanol)·(H_2O) [7], the Cp rings of each included ferrocene, which lie eclipsed [6], exhibit a 'tongue-in-groove' fit with the lower rim of **1** such that the principal rotation axis of the guest runs approximately perpendicular to that of **1**. Thus, each box-shaped cavity of **3h** accommodates seven guests involving three different components wherein the included bipyridine, in effect, serves to segment each cavity into two identical compartments [12,14,18,19]. In the present case, each compartment is filled with one hydrophobic and two hydrophilic guests, the multiple ferrocene guests, presumably, playing a role in directing the formation of **3h** [6]. To our knowledge, such multiple inclusion of an organometallic guest within a closed cavity in the solid state has not been observed [16].

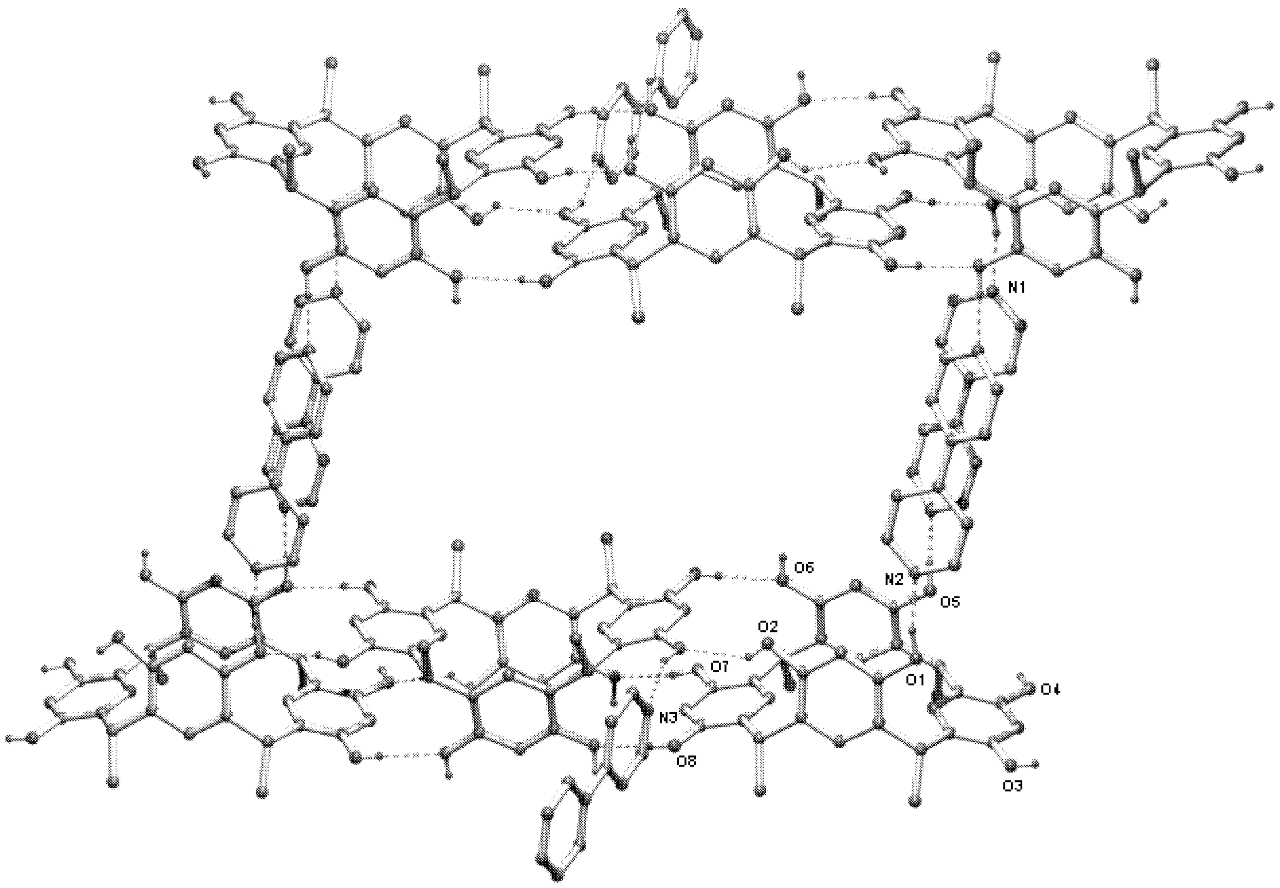


Fig. 1. Ball-and-stick representation of the X-ray crystal structure of **3h**·2.15(ethanol)·0.85(ferrocene) showing the framework **3h**. Selected interatomic distances (Å): O(1)···N(1) 2.693(5), O(5)···N(2) 2.657(5), O(2)···O(4) 2.809(4), O(3)···O(6) 2.883(4), O(7)···O(1) 2.729(4), O(8)···O(5) 2.699(4), O(4)···N(3) 2.804(7).

3. Conclusion

In this report, we have demonstrated the ability of **1** and **2** to assemble in the solid state to form a doubly interpenetrated 3D framework, **3h**, which is a supramolecular isomer [8] of a reported 2D framework **3g** [12], that hosts multiple ferrocenes as guests. With such observations achieved, efforts are underway to investigate the ability of **1** and **2** to assemble with additional organometallic sandwich molecules, where the size, shape, and functionality of the organometallic guest may be employed to induce the formation of additional solid state structures [7,11]. Our current study augurs well for **1** and **2** to yield additional cavity-containing hosts involving such organometallic complexes.

4. Experimental

All reactions were performed in air under ambient pressure and temperature using sealed 10 g sample vials as reaction vessels. NMR spectra were recorded on a Bruker DX-300 (300 MHz). The thermal analysis was conducted under nitrogen using a heating range of 28–600 °C with a heating rate of 10 °C min^{-1} using a TA Instruments TGA 2950 thermogravimetric analyzer. All reagents were purchased from Aldrich Chemical Company and were used as received unless otherwise stated. Compound **1** was prepared according to a literature procedure [20].

*4.1. Preparation of **3h**·2.15(EtOH)·0.85(ferrocene)*

Cooling of a solution of **1** (0.011 g), **2** (0.005 g) and ferrocene (0.004 g) in 2 ml of EtOH yielded, within a day, light yellow crystals of **3h**·2.15(EtOH)·0.85(ferrocene), suitable for single-crystal X-ray analysis (yield: 70%). ^{1}H-NMR (Me$_2$SO-d_6, 300 MHz, δ ppm): 1.05 (s, CH$_3$), 1.28 (s, CH$_3$), 3.44 (m, CH$_2$), 4.16 (s, C–H aromatic), 4.46 (s, C–H methine), 6.14 (s, C–H aromatic), 6.77 (s, C–H aromatic), 7.84 (d, C–H aromatic), 8.52 (s, O–H), 8.73 (d, C–H aromatic). Thermal analysis of **3h**·2.15(EtOH)·0.85(ferrocene) reveals that the material decomposes in four steps. The first two steps occur between 29–70 °C and 70–100 °C, respectively, and can be ascribed to the loss of EtOH (7.8%). The third step occurs between 180 and 227 °C and can

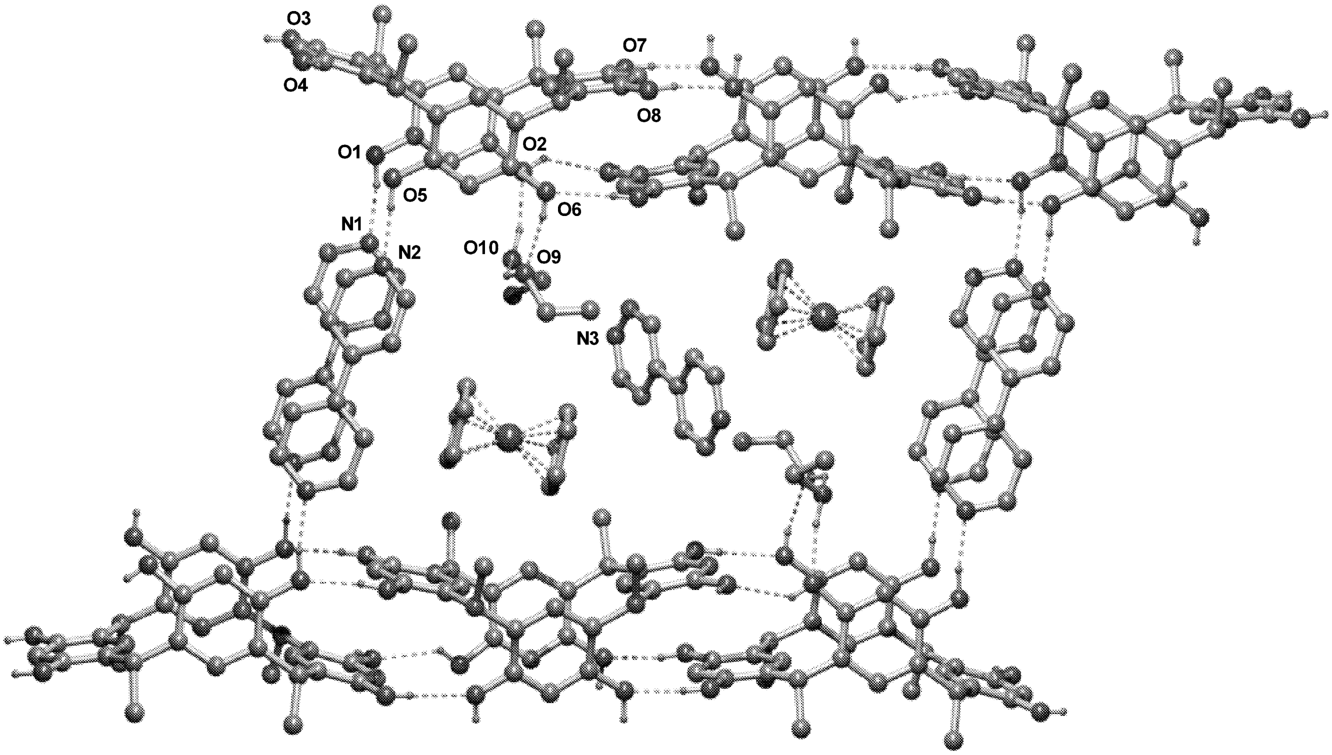


Fig. 2. Ball-and-stick representation of the X-ray crystal structure of **3h**·2.15(ethanol)·0.85(ferrocene) showing the included guests. Selected interatomic distances (Å): O(9)···O(10) 2.728(8), O(6)···O(9) 2.659(6), O(10)···O(2) 2.780(6).

be ascribed the loss of ferrocene and two equivalents of **2** (36.6%). The fourth step occurs above 300 °C and can be ascribed to the decomposition of **1** (55.6%).

4.2. *X-ray crystallography*

Crystal data for **3h**·2.15(EtOH)·0.85(ferrocene): monoclinic, space group *C*2/*c*, $a = 22.244(4)$, $b = 20.968(4)$, $c = 22.382(5)$ Å, $\beta = 93.80(3)°$, $U = 10416(4)$ Å^3, $D_{calc} = 1.33$ g cm^{-3}, Mo–K$_\alpha$ radiation ($\lambda = 0.71070$ Å) for $Z = 8$. Least-squares refinement based on 5394 reflections with $I_{net} > 2.0\sigma(I_{net})$ (out of 9164 unique reflections) led to a final value of $R = 0.076$. A single crystal of **3h**·2.15(EtOH)·0.85(ferrocene) was mounted on the end of a glass fiber and optically centered in the X-ray beam of a Nonius Kappa system for data collection. Cell constants were calculated from reflections obtained from the data collection. The structure was solved using direct methods. After anistropic refinement of all non-hydrogen atoms, aromatic, methine, and hydroxyl hydrogen atoms were placed in idealized positions and allowed to ride on the atom to which they are attached. Structure calculations were conducted using SHELXL-97 [21] locally implemented on a Pentium-based IBM compatible computer.

5. Supplementary material

Crystallography data for the structural analysis have been deposited with the Cambridge Crystallography Data Centre, CCDC no. 191722 for **3h**·2.15(ethanol)·0.85(ferrocene). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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