



# Crystalline Inclusion Compounds Derived from 1,1'-Bis(ethenyl-2-pyridyl)ferrocene and ( $\pm$ )-1,1'-Bi-2-naphthol in Different Solvents

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**Abstract.** Crystallization of organometallic dipyrindine (1,1'-bis(ethenyl-2-pyridyl)-ferrocene) (**1**) with ( $\pm$ )-1,1'-bi-2-naphthol (**2**) from EtOH, *i*-PrOH, ( $\pm$ )-2-BuOH, and MeOH forms crystalline inclusion compounds of stoichiometries **1** · **2** · C<sub>2</sub>H<sub>5</sub>OH (**3**), **1** · **2** · C<sub>3</sub>H<sub>7</sub>OH (**4**), **1** · **2** · C<sub>4</sub>H<sub>9</sub>OH (**5**), and **1** · **2** · CH<sub>3</sub>OH · H<sub>2</sub>O (**6**), respectively. The crystalline species **3**, **4**, and **5** are isostructural with the three molecular components interlinked by hydrogen bonds to form a columnar structure. In **6**, the four molecular components are interlinked by hydrogen bonds to form a two-dimensional framework structure.

**Keywords:** crystalline inclusion compounds, hydrogen bonding, X-ray structure determination, dipyrindine, naphthol

**Supplementary Data Available:** Hydrogen bonding networks in **4**, **5**, and **6**, and network of C—H ···  $\pi$  interactions in **3**, tables of atomic coordinates and isotropic thermal parameters, a complete list of bond lengths and angles, anisotropic thermal parameters, hydrogen parameters for **3–6** have been deposited with the British Library at Boston Spa, Wetherby, West Yorkshire, U.K., as Supplementary Publication No. SUP 82272 (29 pages).

## 1. Introduction

Self-assembly represents a powerful mean for the spontaneous and programmed generation of architectures [1]. The basis of self-assembly is the presence of information in the interacting components. In supramolecular structures, information is expressed by a component's potential to interact with its partners to form non-covalent bonds and by its steric requirement. Sometimes solvent molecules can act as one of components or a glue connecting components in building-up of an architecture [2]. The participation of solvent molecules in the construction of the crystals can introduce some unique features.

We have been interested in the construction of the organic-organometallic hybrid supramolecular architectures derived from organic diols and organometallic

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dipyridines [3]. Recently, we found that solvent molecules were incorporated into the supramolecular architectures to give rise to the unique structures. Herein we report the self-assembly of stable hydrogen-bonded supramolecular aggregates derived from 1,1'-bis(ethenyl-2-pyridyl)ferrocene (**1**) and ( $\pm$ )-1,1'-bi-2-naphthol (**2**) in MeOH, EtOH, *i*-PrOH, and ( $\pm$ )-2-BuOH.

## 2. Experimental

### 2.1. GENERAL

All solvents were purified by standard methods, and the synthesis of **1** was carried out under a nitrogen atmosphere. Reagent grade chemicals were used without further purification.

Elemental analyses were done at the Chemical Analytic Center, College of Engineering, Seoul National University and Inter-University Center Natural Science Facilities, Seoul National University.  $^1\text{H}$  NMR spectra were obtained with a Bruker 300 MHz instrument. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer.

#### 2.1.1. Synthesis of **1**

To the lithium carbanion solution, derived from 2-picoline (1.6 mL, 16.2 mmol) and LDA (16.4 mmol) in 30 mL of THF, was added 1,1'-ferrocenedicarboxaldehyde (1.5 g, 6.20 mmol) at  $-78\text{ }^\circ\text{C}$ . The resulting solution was stirred at  $-78\text{ }^\circ\text{C}$  for 30 min and quenched with water (50 mL). Excess  $\text{CH}_2\text{Cl}_2$  (30 mL) was added and the  $\text{CH}_2\text{Cl}_2$  layer was separated and evaporated. The residue was dissolved in 15 mL of pyridine and cooled to  $0\text{ }^\circ\text{C}$ . To the cold solution was added 1 mL of  $\text{POCl}_3$ . The reaction mixture was stirred at room temperature for 1.5 h and quenched by ice. After removal of pyridine, the residue was dissolved in 10 mL of water and basified by 4 M NaOH solution to give a precipitate. After filtration, the precipitate was dissolved in 15 mL of  $\text{CH}_2\text{Cl}_2$  and evaporated to dryness. The residue was chromatographed on a silica gel column by eluting with  $\text{Et}_2\text{O}$ /hexane (v/v, 2 : 1) to give **1** in 61% yield (1.48 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.45 (d, 4.8 Hz, 2 H), 7.44 (t, 7.7 Hz, 2 H), 7.21 (d, 16.0 Hz, 2 H), 7.03 (m, 4 H), 6.64 (d, 16.0 HZ, 2 H), 4.49 (s, 4 H), 4.31 (s, 4 H) ppm; Anal. Calcd. for  $\text{C}_{24}\text{H}_{20}\text{FeN}_2$ : C, 73.48; H, 5.14; N, 7.14. Found: C, 73.43; H, 5.20; N, 7.21.

#### 2.1.2. Synthesis of **3**

Compounds **1** (20 mg, 0.051 mmol) and **2** (14.6 mg, 0.051 mmol) were dissolved in 10 mL of ethanol. The resulting solution was allowed to be evaporated in air at room temperature. After 7 days, a red plate-shaped crystalline **3** was obtained quantitatively. IR (KBr)  $\nu_{\text{O—H}}$  3053, 2967  $\text{cm}^{-1}$ ; Anal. Calcd. for  $\text{C}_{44}\text{H}_{34}\text{FeN}_2\text{O}_2\cdot\text{C}_2\text{H}_5\text{OH}$ : C, 76.24; H, 5.56; N, 3.87. Found: C, 76.18; H, 5.74; N, 3.77.

### 2.1.3. Synthesis of **4**

The same procedure as the synthesis of **3** was employed except for isopropyl alcohol instead of ethanol. After 10 days, a red plate-shaped crystalline **4** was obtained quantitatively. Anal. Calcd. for  $C_{44}H_{34}FeN_2O_2 \cdot C_3H_7OH$ : C, 76.42; H, 5.73; N, 3.79. Found: C, 76.28; H, 5.77; N, 4.00.

### 2.1.4. Synthesis of **5**

The same procedure as the synthesis of **3** was employed except for ( $\pm$ )-2-butanol instead of ethanol. After 10 days, a red plate-shaped crystalline **5** was obtained quantitatively. Anal. Calcd. for  $C_{44}H_{34}FeN_2O_2 \cdot C_4H_9OH$ : C, 76.59; H, 5.89; N, 3.72. Found: C, 76.47; H, 5.61; N, 4.03.

### 2.1.5. Synthesis of **6**

The same procedure as the synthesis of **3** was employed except for methanol alcohol instead of ethanol. After 7 days, a deep red cube **6** was obtained in 72.4% yield. IR (KBr)  $\nu_{O-H}$   $3020\text{ cm}^{-1}$ ; Anal. Calcd. for  $C_{44}H_{34}FeN_2O_2 \cdot CH_3OH \cdot H_2O$ : C, 74.18; H, 5.53; N, 3.84. Found: C, 74.40; H, 5.31; N, 4.00.

## 2.2. CRYSTAL STRUCTURE DETERMINATIONS OF **3–6**

Crystals of **3–6** were grown by slow evaporation of the solvent. Diffraction was measured by an Enraf-Nonius CAD4 automated diffractometer with a  $\omega/2\theta$  scan method. Unit cells were determined by centering 25 reflections in the appropriate  $2\theta$  range. Other relevant experimental details are listed in S1 in the Supplementary Data. The structure was solved by direct methods using SHELXS-86 [4] and refined by full-matrix least-squares with SHELXL-93 [5]. All non-hydrogen atoms were refined anisotropically; H(01) and H(017) in **3**, H(02), H(11), H(12), H(18), and H(19) in **4**, H(01), H(02), H(18), and H(19) in **5**, and H(02), H(1\*), H(1'), H(2'), and H(07) in **6** were found in the Fourier map and refined isotropically. The remaining H atoms were located on ideal positions using riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached.

## 3. Results and Discussion

### 3.1. COCRYSTALLIZATION OF **1** AND **2** IN ETHANOL, *i*-PrOH, AND ( $\pm$ )-2-BuOH

Cocrystallization of equimolar amounts of **1** with a racemic mixture of **2** in ethanol led to a red plate-shaped crystalline **3** quantitatively. In the same way, **4** and **5** were obtained in *i*-PrOH, and ( $\pm$ )-2-BuOH, respectively. The formulas obtained by the crystal structure analysis were confirmed by microanalyses. These analyses confirmed the formulas of compounds **3** (**1** : **2** : EtOH = 1 : 1 : 1), **4** (**1** : **2** : *i*-PrOH =

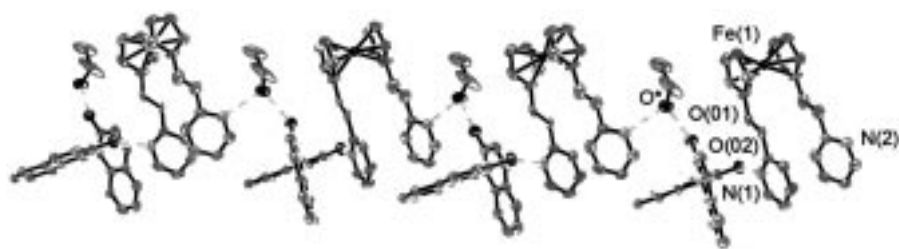


Figure 1. Extended chain structure in **3**. Solvent molecules (EtOH) intercede between two asymmetric units with opposite chiralities.

1 : 1 : 1), and **5** (1 : 2 : ( $\pm$ )-2-BuOH = 1 : 1 : 1). Inclusion crystal structures of **3**, **4**, and **5** display quite similar molecular structures and hydrogen-bonding networks (Figure 1 and Table I: see supplementary data S1 and S2). Thus, we discuss only the structure of **3**.

X-ray crystallographic analysis of **3** reveals the formation of a columnar superstructure (Figure 1), in which **1**, **2**, and EtOH are self-assembled through the hydrogen bonds and the aromatic C-H  $\cdots \pi$  interactions [6]. The repeated unit consists of **1**, **2**, and EtOH in the ratio of 1 : 1 : 1 and EtOH intercedes in the hydrogen bond between **1** and **2** (O\*—O(01), 2.692(0.008) Å; O\*—N(2), 2.805(0.010) Å; O(01)—N(1), 2.705(0.008) Å). The two cyclopentadienyl rings of **1** in the superstructure are almost eclipsed, two pyridyl groups are  $\pi$ -stacked with each other, and the N(1) and N(2) atoms direct opposite directions to form hydrogen-bonds. The distance and angle between the two pyridyl rings of **1** in **3** are 3.787 Å and 16.6(0.4)°, respectively, and the angle between the naphthalene rings of **2** in **3** is 83.4(0.3)°. Ethanol acts as a hydrogen-acceptor from naphthol in an asymmetric unit and donor to pyridyl group in other asymmetric unit with relation of  $-0.5 + x$ ,  $0.5 - y$ ,  $-0.5 + z$ . Thus, a naphthalene ring in a chain contacts with the nearest neighboring naphthalene ring in the other chain by a T-geometry, which leads to a herring-bone structure [7]. The distance between the centroid of the closest aromatic ring of the binaphthol in a chain and the nearest C-atom of the binaphthol of the nearest chain is 3.692 Å (H-centroid 2.755 Å; C—H  $\cdots$  centroid 175.8°; interplanar angle: 85.2(0.3)°). Thus, aromatic C—H  $\cdots \pi$  interactions resulted in a folded curtain structure.

### 3.2. COCRYSTALLIZATION OF **1** AND **2** IN METHANOL

Cocrystallization of equimolar amounts of **1** and a racemic mixture of **2** in methanol afforded deep red cubic-shaped crystalline **6** in 72% yield. The crystal morphology of **6** was different from those of **3–5**. X-ray crystallographic determination of **6** shows that in addition to solvent molecule a water molecule is included in an asymmetric unit. The involvement of water molecules was also confirmed by microanalyses.

Table I. Crystal data and refinement details for **3**, **4**, **5**, and **6**

	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Formula	C <sub>46</sub> H <sub>40</sub> FeN <sub>2</sub> O <sub>3</sub>	C <sub>47</sub> H <sub>42</sub> FeN <sub>2</sub> O <sub>3</sub>	C <sub>48</sub> H <sub>44</sub> FeN <sub>2</sub> O <sub>3</sub>	C <sub>45</sub> H <sub>40</sub> FeN <sub>2</sub> O <sub>4</sub>
fw	724.65	738.68	752.70	728.64
Temp., K	293(2)	293(2)	293(2)	293(2)
$\lambda$ (Mo K $\alpha$ ), Å	0.71073	0.71073	0.71073	0.71073
Cryst. syst.	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>a</i>
<i>a</i> , Å	16.201(4)	16.126(2)	16.135(2)	11.428(2)
<i>b</i> , Å	10.491(2)	10.608(2)	10.693(2)	21.295(3)
<i>c</i> , Å	23.175(10)	23.274(3)	23.751(10)	16.170(10)
$\alpha$ , deg.	90	90	90	90
$\beta$ , deg.	107.89(3)	107.260(10)	108.52(3)	110.414(10)
$\gamma$ , deg.	90	90	90	90
<i>V</i> , Å <sup>3</sup>	3749(2)	3802.1(12)	3886(2)	3687.8(8)
<i>Z</i>	4	4	4	4
<i>d</i> (calcd), g/cm <sup>3</sup>	1.284	1.290	1.287	1.312
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	0.446	0.441	0.433	0.456
F(000)	1520	1552	1584	1528
Octants explored				
<i>h</i> <sub>min</sub> / <i>h</i> <sub>max</sub>	0 ≤ <i>h</i> ≤ 19	0 ≤ <i>h</i> ≤ 19	0 ≤ <i>h</i> ≤ 19	0 ≤ <i>h</i> ≤ 13
<i>k</i> <sub>min</sub> / <i>k</i> <sub>max</sub>	0 ≤ <i>k</i> ≤ 12	0 ≤ <i>k</i> ≤ 12	0 ≤ <i>k</i> ≤ 12	0 ≤ <i>k</i> ≤ 25
<i>l</i> <sub>min</sub> / <i>l</i> <sub>max</sub>	-27 ≤ <i>l</i> ≤ 25	-27 ≤ <i>l</i> ≤ 26	-28 ≤ <i>l</i> ≤ 26	-19 ≤ <i>l</i> ≤ 18
No. measd reflns	6761	6925	7081	6849
No. unique reflns	6513	6668	6822	6498
No. params	490	521	525	506
R1	0.0888	0.1123	0.0794	0.0862
wR2	0.1727	0.2577	0.1688	0.2086
GOF on <i>F</i> <sup>2</sup>	0.860	0.896	1.037	0.924

X-ray crystallographic analysis of **6** reveals the formation of a two-dimensional framework structure, in which **1**, **2**, MeOH, and H<sub>2</sub>O are self-assembled through the hydrogen bonds and the aromatic C—H ···  $\pi$  interactions. An asymmetric unit consists of **1**, **2**, CH<sub>3</sub>OH, and H<sub>2</sub>O in the ratio of 1 : 1 : 1 : 1 and each component is linked to each other by hydrogen bonding (O(01)—H(01) ··· N(2), 2.692(0.007) Å; O(02)—H(02) ··· O\*, 2.673(0.006) Å; O\*—H(1\*) ··· O', 2.687(0.008) Å; O'—H(1') ··· N(1), 2.809(0.009) Å; O'—H(2') ··· O(01), 2.887(0.007) Å;  $\angle$ O(02)—H(02)—O(8), 160.7(5.0)°; O\*—H(1\*)—O', 152.4(12.9)°; O'—H(1')—N(1), 173.2(7.0)°; O'—H(2')—O(01), 161.0(7.0)°). Water acts as a hydrogen acceptor to methanol and a hydrogen donor to phenol. The difference in the bond

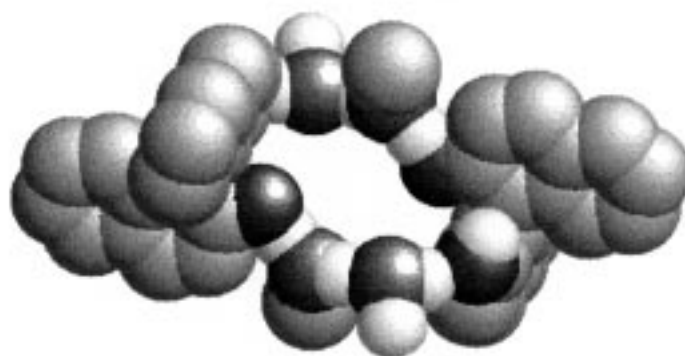
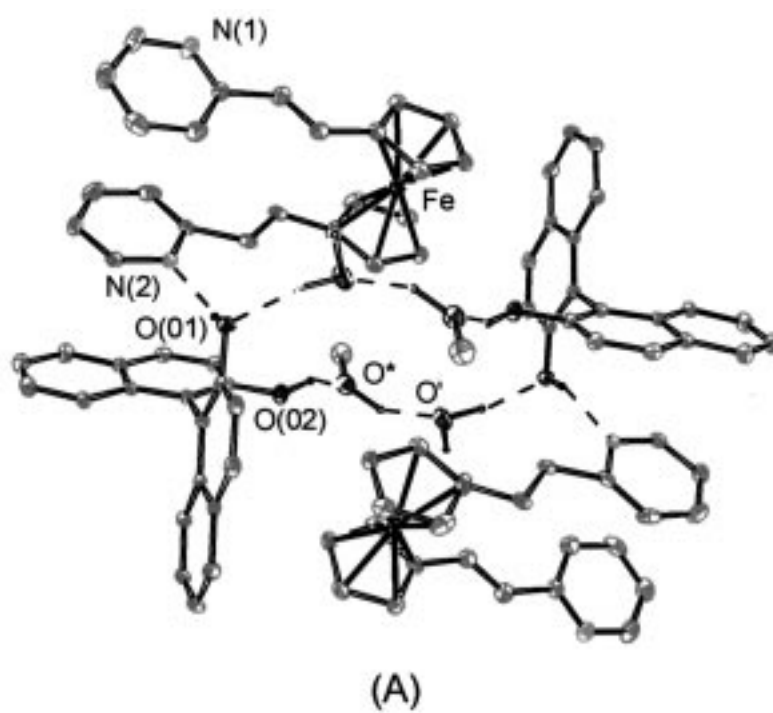
distances of hydrogen bonds with methanol donor (2.687 Å) and with water donor (2.887 Å) is probably due to the difference in the basicity of acceptor groups. The general features of **1** in **6** are not very different from those in **3**. The two cyclopentadienyl rings of **1** in **6** are almost eclipsed, two pyridyl groups are  $\pi$ -stacked with each other, and the N(1) and N(2) atoms direct opposite directions to form hydrogen-bonds. The distance and angle between the two pyridyl rings of **1** in **6** are 3.832 Å and 15.5(0.4)°, respectively. The angle between the naphthalene rings of **2** in **6** is 84.3(0.1)°

Methanol acts as a hydrogen-acceptor from naphthol and a hydrogen-donor to a water molecule. Water molecules are also acting as a hydrogen-acceptor from methanol and a hydrogen-donor to naphthol and pyridine. Hence, water molecules paste three different components at one time to connect three asymmetric units. Thus, the involvement of water molecules may be responsible for the complicated hydrogen-bond networks [8].

Each asymmetric unit is connected to other units in two ways. The first pathway is through hydrogen bonds between the water molecule and O(01) in the other asymmetric unit. Thus, an asymmetric unit is connected to another asymmetric unit with relation of  $-x, -y, -z$  to form roughly a planar cyclic structure surrounded by 24 atoms including six hydrogen atoms and eight oxygen atoms (Figure 2). The cyclic plane is roughly perpendicular to the  $b$  axis and parallel to an  $ac$  plane. The distance between the two irons in the dimeric structure is 8.457(0.002) Å. The eight oxygen atoms linked by hydrogen bonding form a small cavity (size: 6.0–9.3 Å) and each cavity is blocked top and bottom by two ferrocenyl groups. This pattern is quite similar to the binding modes of 1,1'-binaphthyl-2,2'-dicarboxylic acid host/hydroxylic guest inclusions [8]. Crystallization of 1,1'-binaphthyl-2,2'-dicarboxylic acid with ethylene glycol led to a 24-membered pseudo-ring. The second pathway is through hydrogen bonds between the water molecule and N(1) in the other asymmetric unit: Each asymmetric unit is linked with other asymmetric units (with relation of  $0.5 - x, 0.5 + y, 1 - z$ ) by the second pathway and eventually led to a framework structure.

The participation of solvent molecules in the hydrogen bonding led to the construction of the novel structures **3–6**: the crystal structure of **6** is quite different from those of **3–5** although they contain the same organic and organometallic entities. Especially, the participation of water molecules in **6** resulted in a dramatic change in the supramolecular structure. The water molecules in **6** have presumably been captured from the solvent or from the atmosphere during crystallization. The involvement of solvent and water molecules in supramolecular architectures is unpredictable. Hence, structural prediction based only upon the interaction between motifs may not always give rise to the observed structures. On the other hand, if we can manage or control the inclusion phenomenon, the inclusion phenomenon will provide opportunities to study unique architectures.

In conclusion, we have shown here that columnar or two-dimensional framework organic-organometallic hybrid architectures can be obtained from organic



(B)

*Figure 2.* Cyclic dimeric structure found in **6**. (A) Two asymmetric units related by the inversion operation constitute the achiral cavity through the first H-bond pathway. Two molecules of **1** block the cavity up and down. (B) Space filling representation. Molecules of **1** are omitted.

diol and organometallic dipyrindine in EtOH, *i*-PrOH, ( $\pm$ )-2-BuOH, and MeOH. In particular, a water molecule can be a versatile motif to introduce a dramatic change in the supramolecular structure.

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### References

- (a) G. R. Desiraju: *Crystal Engineering*, Elsevier (1989). (b) J.-M. Lehn: *Angew. Chem. Int. Ed. Engl.* **29**, 1304 (1990). (c) S. Subramanian and M. Zaworotko: *J. Coord. Chem. Rev.* **137**, 357 (1994). (d) J.-M. Lehn: *Supramolecular Chemistry*, VCH (1995). (e) G. R. Desiraju: *The Crystal as a Supramolecular Entity*, Wiley (1996). (f) in J. L. Atwood (ed.), *Comprehensive Supramolecular Chemistry*, Vol. 6, Pergamon (1996). (g) G. R. Desiraju: *J. Chem. Soc. Chem. Commun.* 1475 (1997). (h) P. J. Stang: *Chem. Eur. J.* **4**, 19 (1998). (i) D. Braga, F. Grepioni, and G. R. Desiraju: *Chem. Rev.* **98**, 1375 (1998). (j) D. Braga and F. Grepioni: *J. Chem. Soc., Dalton Trans.* 1 (1999).
- (a) E. Weber, K. Skobridis, and I. Goldberg: *J. Chem. Soc., Chem. Commun.* 1195 (1989). (b) G. R. Desiraju: *J. Chem. Soc., Chem. Commun.* 426 (1991). (c) I. Csöreg, O. Gallardo, E. Weber, M. Hecker, and A. Wierig: *J. Chem. Soc., Perkin Trans. 2*, 1939 (1992). (d) K. Sada, Y. Hishikawa, T. Kondo, and M. Miyata: *Chem. Lett.* 2113 (1994). (e) F. N. Penkert, T. Weyhermüller, and K. Wieghardt: *J. Chem. Soc. Chem. Commun.* 557 (1998). (f) M. T. Allen, A. D. Burrows, and M. F. Mahon: *J. Chem. Soc., Dalton Trans.* 215 (1999).
- (a) I. S. Lee and Y. K. Chung: *Organometallics* **18**, 5080 (1999).
- G. M. Sheldrick: *Acta Crystallogr. Sect A* **46**, 467 (1990).
- G. M. Sheldrick: SHELXL-93, a computer program for crystal structure refinement, University of Göttingen, 1993.
- (a) J. F. Malone, C. M. Murray, M. H. Charlton, R. Docherty, and A. J. Lavery: *J. Chem. Soc., Faraday Trans.* **93**, 3429 (1997). (b) J. E. Cochran, T. J. Parrott, B. J. Whitlock, and H. W. Whitlock: *J. Am. Chem. Soc.* **114**, 2269 (1992).
- (a) J. Pawliszyn, M. M. Szczesniak, and S. Scheiner: *J. Phys. Chem.* **88**, 1726 (1984). (b) M. F. Perutz, G. Fermi, D. J. Abraham, C. Poyart, and E. Bursaux: *J. Am. Chem. Soc.* **108**, 1064 (1986). (c) G. R. Desiraju: *J. Chem. Soc. Chem. Commun.* 1475 (1997).
- (a) M. Czugler, J. G. Ángyán, G. Náray-Szabó, and E. Weber: *J. Am. Chem. Soc.* **108**, 1275 (1986). (b) G. Ferguson, C. Glidewell, A. J. Lough, G. D. McManus, and P. R. Meehan: *J. Mater. Chem.* **8**, 2339 (1998). (c) D. Braga, S. M. Draper, E. Champeil, and F. Grepioni: *J. Organomet. Chem.* **573**, 73 (1999).