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Synthesis and crystal structures of decamethylferrocenium salts of anilate anions derived from bromanilic acid, chloranilic acid and cyananilic acid

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Abstract

Four complexes were synthesized using bis(pentamethylcyclopentadienyl)iron $Fe(C_5Me_5)_2$ as an organometallic donor and three anilic acids (2,5-dibromo-3,6-dihydroxy-1,4-benzoquinone; BA, 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone; CA and 2,5-dicyano-3,6-dihydroxy-1,4-benzoquinone; CNA) as an organic acceptor. The molecular-based structures with different stoichiometric ratios [1:1, 1:1:1(H_2O) and 2:1] of these complexes have been determined by X-ray crystallographic analysis and elemental analysis. These complexes have a one-dimensional alternated stacking arrangement as $\cdots D^+A^-D^+A^-\cdots$ type. Close contacts between the bromine atoms and oxygen atoms of the BA units are observed in the structure $[Fe(C_5Me_5)_2](BA)$ (**1**) of 1:1 composition. Interestingly, the structures $[Fe(C_5Me_5)_2](CA)(H_2O)$ (**2**) and $[Fe(C_5Me_5)_2](CNA)(H_2O)$ (**3**) of 1:1:1(H_2O) ratio contain one-dimensional molecular tape structures with the combination of the CA or the CNA units and water molecules via O–H···O hydrogen bonds. Different stoichiometric ratios and structures are found from the CNA complexes $[Fe(C_5Me_5)_2](CNA)(H_2O)$ (**3**) and $[Fe(C_5Me_5)_2]_2(CNA)$ (**4**). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structures; Ferrocene complexes; Anilic acid complexes

1. Introduction

Bis(pentamethylcyclopentadienyl)iron $Fe(C_5Me_5)_2$, i.e. decamethylferrocene, is well demonstrated as metallocenium donor (D) and combines with cyanocarbon acceptors (A) to afford charge-transfer complexes composed of $\cdots D^+A^-D^+A^-\cdots$ type alternated stackings [1]. These complexes exhibit cooperative magnetic phenomena, that is, ferro-, antiferro-, ferri-, and metamagnetism, which depend on stacking arrangements and the inter- and intra- molecular interactions in the crystal structure. Moreover, controlling of non-covalent interactions between organometallic molecules and organic components provides a path in transmitting the spin and charge along the supramolecular structures [2–4]. Thus crystal engineering with organometallic and/or organic molecules has played a major role in developing new molecular-based magnets [1–5].

Our strategy is to synthesize crystals containing organic and organometallic molecules or ions with intra- and intermolecular interactions to explore novel building blocks in organometallic crystal engineering. In organic–organometallic systems the non-covalent intermolecular bonding capacity of the organic molecules [6] can be combined with the coordination geometry, variable ionic charges, oxidation and spin states typical of organometallic complexes [7]. As organic counter part with organometallic $Fe(C_5Me_5)_2$, we have chosen anilic acids, which possess electron accepting abilities with multi-stage deprotonation and protonation processes, to form characteristic intermolecular hydrogen-bonded networks [8,9]. First we have examined the complexation of $Fe(C_5Me_5)_2$ with chloranilic acid (CA), and

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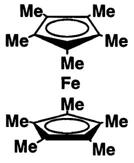
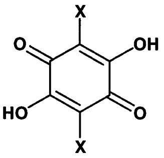
observed an infinite one-dimensional molecular tape structure via hydrogen bonding between CA and water molecules. This preliminary result was reported in our recent communication [9]. As an extension of this work, it is of interest to investigate the complexes derived from other anilic acids.

In this paper we report the synthesis and structural characterization of the crystalline complexes $[Fe(C_5Me_5)_2](BA)$ (**1**), $[Fe(C_5Me_5)_2](CA)(H_2O)$ (**2**), $[Fe(C_5Me_5)_2](CNA)(H_2O)$ (**3**) and $[Fe(C_5Me_5)_2]_2(CNA)$ (**4**), obtained by using bis(pentamethylcyclopentadienyl)iron $Fe(C_5Me_5)_2$ as organometallic donor and anilic acids [2,5-dibromo-3,6-dihydroxy-1,4-benzoquinone (bromanilic acid); BA, 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid); CA and 2,5-dicyano-3,6-dihydroxy-1,4-benzoquinone (cyananilic acid); CNA] as organic electron acceptors with proton donating hydroxyl groups.



Fe(C₅Me₅)₂



BA: X = Br
CA: X = Cl
CNA: X = CN

2. Experimental

2.1. Materials

Bis(pentamethylcyclopentadienyl)iron $Fe(C_5Me_5)_2$ was commercially obtained and purified by recrystallization followed by sublimation in vacuum. 2,5-Dibromo- and 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinones (BA and CA) were used without further purification. 2,5-Dicyano-3,6-dihydroxy-1,4-benzoquinone (CNA) was synthesized via five steps starting from 1,4-dimethoxybenzene [10].

2.2. Preparation of crystalline complexes

2.2.1. Synthesis of complex 1

A solution of BA (14.9 mg, 0.05 mmol) in distilled hot acetonitrile (6–8 ml) was mixed with a solution of $Fe(C_5Me_5)_2$ (16.4 mg, 0.05 mmol) in distilled hot acetonitrile (5–6 ml). Within a day the solution became brown and solids appeared in the flask. Black crystals suitable for X-ray crystallographic analysis were grown at room temperature by slow evaporation for 4 weeks. D.p. 218–219°C. *Anal.* Calc. for $(C_{20}H_{30}Fe)(C_6HBr_2O_4)$: C, 50.11; H, 5.01; N, 0.00. Found: C, 49.95; H, 5.02; N, 0.00%.

2.2.2. Synthesis of complex 2

Complex **2** was prepared by a diffusion method. In the method, CA (10.5 mg, 0.05 mmol) and $Fe(C_5Me_5)_2$ (16.4 mg, 0.05 mmol) were placed at the bottom of the H-shaped tube and then the tube was filled with dry acetonitrile. After 20–25 days dark brown crystals were formed. D.p. 213–215°C. *Anal.* Calc. for $(C_{20}H_{30}Fe)(C_6HCl_2O_4)(H_2O)$: C, 56.54; H, 6.02; N, 0.00. Found: C, 56.59; H, 5.91; N, 0.00%.

2.2.3. Synthesis of complexes 3 and 4

A solution of CNA (9.6 mg, 0.051 mmol) in 10 ml of dry acetonitrile was added to a solution of $Fe(C_5Me_5)_2$ (16.3 mg, 0.050 mmol) in 8 ml of dry hot acetonitrile. Slow evaporation of the dark brown solution during a month gave two types of crystals, dark red crystals of **3** (D.p. 264–265°C) and dark green crystals of **4** (D.p. 244–245°C). *Anal.* Calc. for $(C_{20}H_{30}Fe)(C_8HN_2O_4)(H_2O)$ for **3**: C, 63.05; H 6.24; N, 5.25. Found: C, 63.11; H, 5.99; N, 5.38%. *Anal.* Calc. for $(C_{20}H_{30}Fe)_2(C_8N_2O_4)$ for **4**: C, 68.58; H, 7.19; N, 3.33. Found: C, 68.36; H, 7.19; N, 3.72%.

2.3. X-ray crystallographic studies

Single crystals of **1**–**4** were individually mounted on the end of a glass fiber and optically centered in the X-ray beam. The intensity data for complexes **1**, **2** and **4** were collected on an Enraf-Nonius CAD4 diffractometer using Cu Kα radiation ($\lambda = 1.54178$ Å) at 296 K. In this case, absorption corrections were applied using empirical procedures based on azimuthal ψ scans of seven reflections having an Eulerian angle, χ, near 90°. On the other hand, intensity data for complex **3** was collected on a Rigaku AFC-7R diffractometer using Mo Kα radiation ($\lambda = 0.71069$ Å) at 296 K and no absorption and decay correction was applied. All structures were solved using direct methods with SHELXS-97 [11] and refined by full-matrix least-squares on F^2 with SHELXL-97 [12]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined by using a riding model. The data for collected parameters and details of measurements for complexes **1**, **3** and **4** are summarized in Table 1.

3. Results and discussion

This paper focuses on three anilic acids that act as proton donor and electron acceptor, and are useful for building novel organic–organometallic crystalline complexes [8,9][2]. The complexes of $Fe(C_5Me_5)_2$ with the

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[2] Detail of the magnetic properties of the complexes **1**–**4** will be reported elsewhere.

Table 1
Crystallographic data for $[Fe(C_5Me_5)_2](BA)$ (**1**), $[Fe(C_5Me_5)_2](CNA)(H_2O)$ (**3**) and $[Fe(C_5Me_5)_2]_2(CNA)$ (**4**)[a]

	1	**3**	**4**
Formula	$C_{26}H_{31}O_4Br_2Fe$	$C_{28}H_{34}O_5N_2Fe$	$C_{48}H_{60}O_4N_2Fe_2$
Molecular weight	623.18	532.41	840.68
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$ (no. 14)	$Imm2$ (no. 44)	$C2/m$ (no. 12)
a (Å)	9.942(1)	13.703(2)	14.672(1)
b (Å)	14.505(1)	10.566(1)	14.543(1)
c (Å)	17.739(2)	9.300(2)	9.731(1)
β (°)	98.17(1)		90.62(1)
V (Å^3)	2532.3(3)	1346.5(3)	2076.2(2)
Z	4	2	2
ρ_{calc} (g cm^{-3})	1.635	1.313	1.345
Crystal size (mm^3)	$0.20 \times 0.15 \times 0.08$	$0.35 \times 0.10 \times 0.02$	$0.25 \times 0.20 \times 0.05$
$F(000)$	1260	560	892
μ (mm^{-1})	8.715 (Cu Kα)	0.599 (Mo Kα)	5.964 (Cu Kα)
Measured 2θ range (°)	7.90–148.46	4.86–54.96	8.56–148.36
Number of reflections measured	5467	830	2338
Number of independent reflections	5164	830	2209
Number of reflections with $I>2\sigma(I)$	3229	612	1568
Parameters, restrains	308, 0	108, 33	150, 10
R_1 [a] $[I>2\sigma(I)]$	0.0607	0.0572	0.0604
wR_2 [b] $[I>2\sigma(I)]$	0.1527	0.1519	0.1544
Goodness-of-fit S [c] on F^2	1.022	1.098	1.040

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$.
[b] $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.
[c] $S = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/(N_{reflns} - N_{param})\}^{1/2}$.

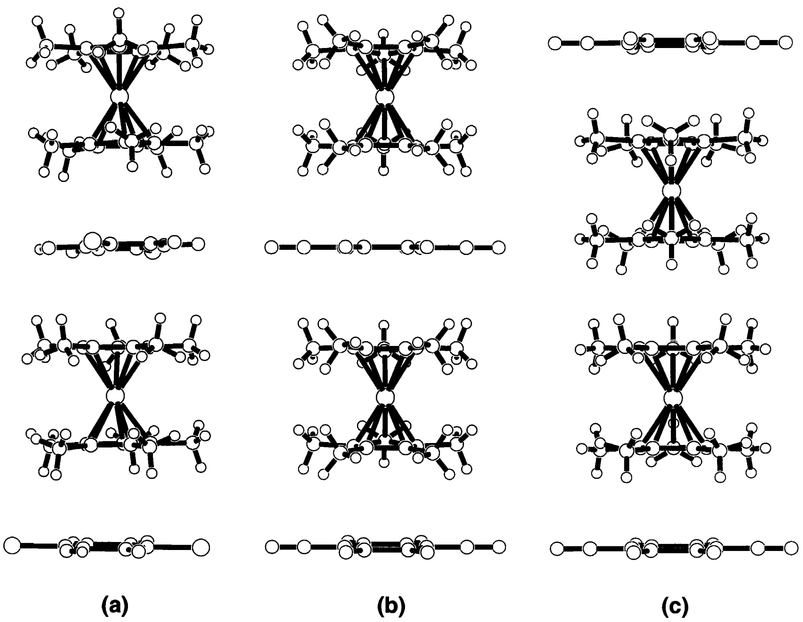


Fig. 1. One-dimensional alternated stacking structure of (a) $[Fe(C_5Me_5)_2](BA)$ (**1**), (b) $[Fe(C_5Me_5)_2](CNA)(H_2O)$ (**3**) and (c) $[Fe(C_5Me_5)_2]_2(CNA)$ (**4**).

anilic acids have been prepared from dry solvent. The D–A ratios of the complexes **1**, **2**, **3** and **4** were determined by both of elemental analyses and X-ray crystallographic analyses. Even if a water-free solvent was used for preparation of the crystals, the complexes **2** and **3** containing water molecules were obtained. The complexes **3** and **4** were obtained from the same batch. In all the crystalline complexes, a one-dimensional alternated stacking of D and A molecules was observed (Fig. 1).

In the unit cell of **1** there is a crystallographically independent pair of $Fe(C_5Me_5)_2$ and BA. Each

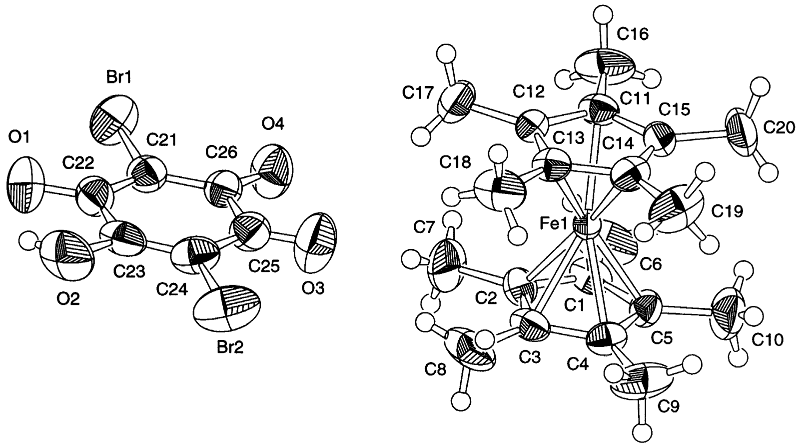


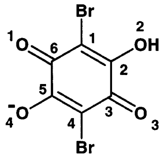
Fig. 2. Molecular structure of [Fe(C_5Me_5)$_2$](BA) (**1**) with atomic labeling scheme. Selected bond lengths (Å): Fe(1)–C(3) 2.090(5), Fe(1)–C(4) 2.096(5), Fe(1)–C(5) 2.099(5), Fe(1)–C(2) 2.099(5), Fe(1)–C(15) 2.100(5), Fe(1)–C(14) 2.102(5), Fe(1)–C(13) 2.103(5), Fe(1)–C(12) 2.103(5), Fe(1)–C(1) 2.106(5), Fe(1)–C(11) 2.106(5), O(1)–C(22) 1.253(7), O(2)–C(23) 1.316(7), O(3)–C(25) 1.201(8), O(4)–C(26) 1.225(7), Br(1)–C(21) 1.902(6), Br(2)–C(24) 1.888(7), C(1)–C(2) 1.416(8), C(1)–C(5) 1.445(8), C(1)–C(6) 1.493(8), C(2)–C(3) 1.423(8), C(2)–C(7) 1.503(8), C(3)–C(4) 1.406(9), C(3)–C(8) 1.505(8), C(4)–C(5) 1.419(7), C(4)–C(9) 1.508(8), C(5)–C(10) 1.490(8), C(11)–C(15) 1.421(8), C(11)–C(12) 1.426(7), C(11)–C(16) 1.495(7), C(12)–C(13) 1.423(7), C(12)–C(17) 1.488(8), C(13)–C(14) 1.424(8), C(13)–C(18) 1.497(7), C(14)–C(15) 1.436(8), C(14)–C(19) 1.498(8), C(15)–C(20) 1.507(8), C(21)–C(22) 1.384(8), C(21)–C(26) 1.403(9), C(22)–C(23) 1.500(10), C(23)–C(24) 1.341(10), C(24)–C(25) 1.439(9), C(25)–C(26) 1.554(9).

molecule was not located on the special positions. The atomic labeling scheme is shown in Fig. 2. No hydrogen atom of the BA unit was found in the Fourier map. Thus to determine the ionicity of the BA unit we have calculated the bond lengths of the BA monoanion. The experimental data for the BA unit are consistent with the calculated values of the BA monoanion (see Table 2) and those of partially deprotonated BA monoanion [13]. On the other hand, the bond lengths of Fe(C_5Me_5)$_2$ unit in **1** are almost similar to those of Fe(C_5Me_5)$_2$ molecules (Table 3) reported previously [14]. These facts suggest that the charges on the BA and Fe(C_5Me_5)$_2$ unit in **1** are − 1 and + 1, which supports the 1:1 ratio of **1**. The close intermolecular contacts (3.24 Å) between the bromine atom and the oxygen atom of the BA unit were observed. The ribbon type structure of the BA units formed with the Br···O contacts is shown in Fig. 3.

The alternated stacking of the structure **1** along the [− 1 0 1] direction is shown in Fig. 1(a). The distances and the angles between the least-squares planes of the BA unit and the two C_5Me_5 rings are 3.64 and 3.68 Å and 2.2 and 2.3°, respectively, which are similar to those in [Fe(C_5Me_5)$_2$][A] [A = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and tetracyanoethylene (TCNE)] [15]. The C_5Me_5 rings are almost eclipsed by the BA rings in the stacking. The interstacking Fe–Fe distances are within the range of 8.5–9.0 Å.

When Fe(C_5Me_5)$_2$ was reacted with CNA (cyananilic acid) in MeCN at room temperature, two types of crystalline complexes, **3** and **4**, were produced at the same time. The different stoichiometric ratios were observed with a dramatic change in the crystal structure, which are also reflected in a different color of the crystalline complexes. The colors of **3** with the ratio of 1:1:1(H_2O) and **4** with the ratio of 2:1 are dark red and dark green, respectively. On the other hand, Yamochi et al. have obtained a different crystal of [Fe(C_5Me_5)$_2$](CNA) with the ratio of 1:1 [8]. Interestingly, the black crystal of [Fe(C_5Me_5)$_2$](CNA), which was obtained from a benzene–MeCN solution, is crys-

Table 2
Calculated and observed bond lengths for BA monoanion[a]



Bond	Obsd. in **1** (Å)	Calc., PM3 [a] (Å)	Calc., 3-21G* [b] (Å)
C6–O1	1.201	1.216	1.211
C2–O2	1.316	1.353	1.338
C3–O3	1.253	1.240	1.252
C5–O4	1.225	1.228	1.222
C1–C2	1.342	1.342	1.322
C2–C3	1.499	1.519	1.524
C3–C4	1.384	1.394	1.370
C4–C5	1.403	1.416	1.416
C6–C1	1.554	1.542	1.551
C1–Br	1.888	1.866	1.889
C4–Br	1.902	1.867	1.895

[a] Ref. [20].

[b] Ref. [21].

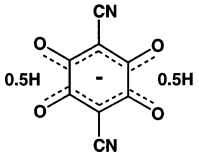
Table 3
Summary of average bond lengths for $[Fe(C_5Me_5)_2]$ units[a]

	Fe–C	C–C	C–Me	Fe–C_5Me_5 ring[a]	Ref.
$[Fe(C_5Me_5)_2]$	2.050	1.419	1.502	1.656	[15]
$[Fe(C_5Me_5)_2][C(CN)_3]$	2.092	1.423	1.498	1.710	[15]
$[Fe(C_5Me_5)_2](TCNE)$	2.086	1.418	1.499	1.700	[15]
$[Fe(C_5Me_5)_2]_2\{Mo[S_2C_2(CF_3)_2]_3\}$	2.086	1.400	1.504		[18]
$[Fe(C_5Me_5)_2](BA)$ (**1**)	2.100	1.423	1.498	1.715	this work
$[Fe(C_5Me_5)_2](CA)(H_2O)$ (**2**)	2.080	1.387	1.510	1.710	[9]
$[Fe(C_5Me_5)_2](CNA)(H_2O)$ (**3**)	2.067	1.484	1.493	1.705	this work
$[Fe(C_5Me_5)_2]_2(CNA)$ (**4**)	2.087	1.405	1.502	1.710	this work

[a] The average distance between the least-squares plane of the C_5Me_5 ring and the iron atom.

tallographically isomorphous with the BA complex **1**, and the intermolecular close –HO···NC– contacts (2.80 Å) between the oxygen atom and the nitrogen atom of the CNA unit were observed in the structure of $[Fe(C_5Me_5)_2](CNA)$ [16].[3]

The crystals of **2** and **3** have the orthorhombic crystal system with space groups *Pnnm* and *Imm*2, respectively. Thus, the crystal of **2** contains a crystallographically independent fourth part of the CA unit and fourth part of the $Fe(C_5Me_5)_2$, whereas the crystal of **3** contains a crystallographically independent half of CNA unit and fourth part of the $Fe(C_5Me_5)_2$. The cell parameters, the stacking arrangement and the pattern of the one-dimensional molecular tape structure of **2** and **3**, however, are approximately similar. The structure of **2** can be viewed in our preliminary communication [9] and is not shown here. The atomic labeling scheme of **3** is shown in Fig. 4. The CNA unit of 3 has two crystallographically independent C–O bonds [C(8)–O(1) 1.247(7) Å and C(9)–O(2) 1.245(7) Å]. These bond lengths are almost equivalent and are similar to those of the CA anion of **2**. Other bond lengths in the CNA unit of **3** are consistent with the geometry of the reported CNA monoanion (Table 4). Thus, the following resonance valance structure can be proposed to contribute to the CNA monoanion structure of **3**. Similarly to the complex **2**, each oxygen atom in the CNA anions of **3** is coordinated to the water molecules and constructs the one-dimensional molecular tape structure along the *c* axis. The tape structure through an infinite O–H···O linkage in **3** is shown in Fig. 5. The characteristic feature of the tape structure in **3** is that the CNA units and water molecules are linked via two different O···O distances (2.60 and 2.77 Å) within the tapes, in contrast with the case of **2**.



In complexes **2** and **3** the C_5Me_5 rings have eclipse conformation with the CA or CNA rings and the one-dimensional alternated unistackings as ···DADA··· type along the *b* axis are formed (Fig. 1(b)). The distances between the least-squares planes of the C_5Me_5 rings and the CA or the CNA rings within the stackings are 3.59 Å for **2** and 3.57 Å for **3**.

The crystal of **4** contains a crystallographically independent half of $Fe(C_5Me_5)_2$ and fourth part of the CNA unit. The CNA unit of **4** lies on a mirror plane with an inversion center (Fig. 6) and has the only independent C–O bond [C(14)–O(1) 1.217(6) Å]. The

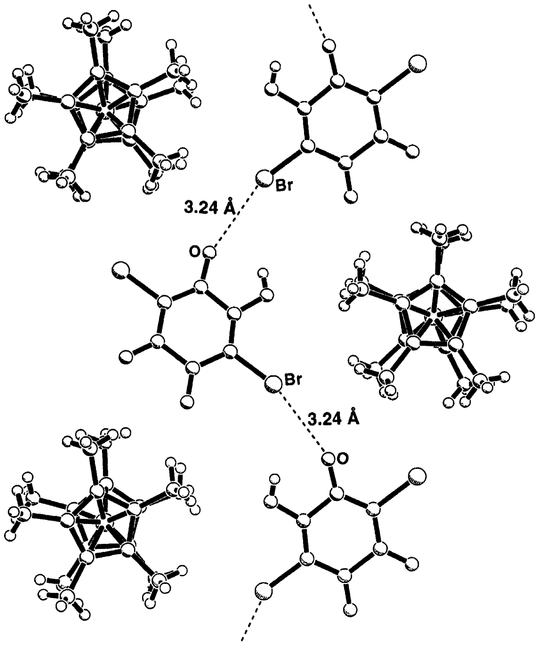


Fig. 3. Crystal structure of $[Fe(C_5Me_5)_2](BA)$ (**1**) viewed perpendicular to the [1 0 −1] plane. Dotted lines show close intermolecular Br···O contacts.

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[3] Crystal data of the 1:1 complex, $[Fe(C_5Me_5)_2](CNA)$: monoclinic, space group $P2_1/n$, $a = 9.915(2)$, $b = 14.572(3)$, $c = 17.671(2)$ Å, $\beta = 96.21(1)°$, $V = 2538.7(8)$ Å^3, $Z = 4$. Data obtained from [16].

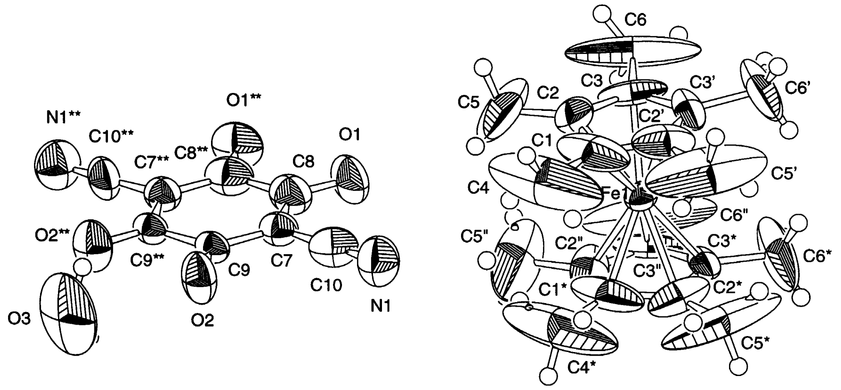


Fig. 4. Molecular structure of $[Fe(C_5Me_5)_2](CNA)(H_2O)$ (**3**) with atomic labeling scheme. Selected bond lengths (Å): Fe(1)–C(1) 2.04(2), Fe(1)–C(1*) 2.04(2), Fe(1)–C(3) 2.047(10), Fe(1)–C(3′) 2.047(10), Fe(1)–C(3*) 2.047(10), Fe(1)–C(3″) 2.047(10), Fe(1)–C(2*) 2.113(16), Fe(1)–C(2″) 2.113(16), Fe(1)–C(2) 2.113(16), Fe(1)–C(2′) 2.113(16), N(1)–C(10) 1.136(13), O(1)–C(8) 1.247(7), O(2)–C(9) 1.245(7), C(1)–C(2) 1.384(6), C(1)–C(2′) 1.384(6), C(1)–C(4) 1.50(2), C(2)–C(3) 1.384(7), C(2)–C(5) 1.498(17), C(3)–C(3′) 1.385(8), C(3)–C(6) 1.480(14), C(7)–C(9) 1.411(7), C(7)–C(8) 1.412(7), C(7)–C(10) 1.410(12), C(8)–C(8**) 1.527(7), C(9)–C(9**) 1.526(7). Symmetry operations: (*) $-x, -y, z$; (′) $-x, y, z$; (″) $x, -y, z$; (**) $-x+1, -y, z$.

Table 4
Summary of average bond lengths for CNA units [a]

	Charge of CNA	C–O	C–C in ring	C–N	Ref.
$(CNA)(H_2O)_6$	0	1.242	1.415, 1.533	1.149	[19]
$(TMTTF)_2(CNA)$ [a]	−1	1.257	1.407, 1.532	1.140	[8]
$[Fe(C_5Me_5)_2](CNA)$	−1	1.240	1.407, 1.530	1.139	[16]
$[Fe(C_5Me_5)_2](CNA)(H_2O)$ (**3**)	−1	1.246	1.411, 1.527	1.136	this work
$[Fe(C_5Me_5)_2]_2(CNA)$ (**4**)	−2	1.217	1.425, 1.556	1.139	this work

[a] TMTTF = tetramethyltetrathiafulvalene.

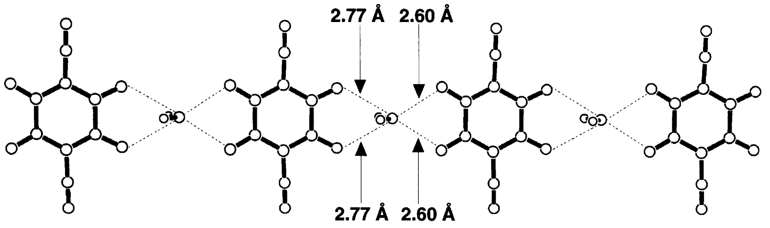
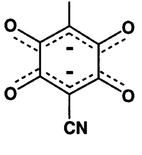


Fig. 5. One-dimensional molecular tape structure in $[Fe(C_5Me_5)_2](CNA)(H_2O)$ (**3**). Dotted lines show intermolecular O···O linkages.

C–O bond length is shorter than those in other CNA dianion structures [17]. The bond lengths for the two independent C–C bonds in the six-membered ring are 1.425(6) Å for C(13)–C(14) and 1.556(12) Å for C(14)–C(14*). Therefore, the following resonance valance structures can be proposed to depict the CNA dianion structures of **4**.



In the crystal structure of **4**, the alternated stackings consist of two $Fe(C_5Me_5)_2$ cations and one CNA dianion. The one-dimensional ···DDADDA··· type stackings are parallel to the [−1 0 1] direction (Fig. 1(c)). The intracolumnar short distances between the least-squares planes of the two C_5Me_5 rings, the C_5Me_5 ring and the CNA unit, and the two iron atoms are 3.91, 3.48 and 7.31 Å, respectively. To the best of our knowledge, the complex, $[Fe(C_5Me_5)_2]_2\{Mo[S_2C_2(CF_3)_2]_3\}$ is the only example of decamethylferrocenium salts with the ratio of 2:1 [18].[4]

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[4] $Mo[S_2C_2(CF_3)_2]_3$ = tris[bis(trifluromethyl)ethylene-1,2-dithiolato]-molybdate.

4. Conclusion

In this study three anilic acids (bromanilic acid, chloranilic acid and cyananilic acid) have been used to prepare crystalline complexes with organometallic decamethylferrocene. This combination could afford various and unique crystal structures because of the electron accepting abilities with multi-stage deprotonation and protonation processes of anilic acids. There are three important structural features obtained from these complexes: (i) in the structure of the 1:1 complex **1**, the BA monoanion units form the ribbon type structure through close Br···O contacts. The –HO···NC– contacts were found in the complex $[Fe(C_5Me_5)_2](CNA)$ [8] and the intermolecular interactions of these two complexes are geometrically similar. (ii) In $1:1:1(H_2O)$ complexes, **2** and **3**, the CA or the CNA units and water molecules are linked via O–H···O hydrogen bonds and form the one-dimensional molecular tape structure. (iii) The 2:1 complex **4** contains alternated stackings of ···DDADDA··· type that are rare and attractive. The structural units with intermolecular interactions in (i) and (ii) may be useful for constructing crystalline materials with anilic acids. Studies on the characterization of physical properties of the complexes **1**–**4** and the construction of novel structures using anilic acids are now in progress.

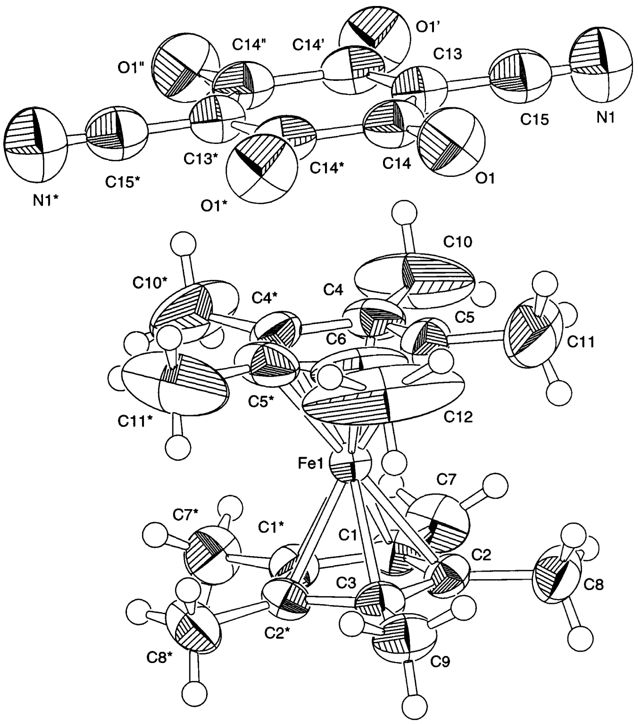

Fig. 6. Molecular structure of $[Fe(C_5Me_5)_2]_2(CNA)$ (**4**) with atomic labeling scheme. Selected bond lengths: Fe(1)–C(4) 2.084(4), Fe(1)–C(4*) 2.084(4), Fe(1)–C(5) 2.077(5), Fe(1)–C(5*) 2.077(5), Fe(1)–C(6) 2.080(7), Fe(1)–C(3) 2.089(6), Fe(1)–C(1) 2.094(4), Fe(1)–C(1*) 2.094(4), Fe(1)–C(2) 2.094(4), Fe(1)–C(2*) 2.094(4), O(1)–C(14) 1.217(6), N(1)–C(15) 1.139(11), C(1)–C(2) 1.426(6), C(1)–C(1*) 1.432(9), C(1)–C(7) 1.504(6), C(2)–C(3) 1.413(5), C(2)–C(8) 1.513(6), C(3)–C(2*) 1.413(5), C(3)–C(9) 1.494(9), C(4)–C(5) 1.380(8), C(4)–C(4*) 1.400(11), C(4)–C(10) 1.501(8), C(5)–C(6) 1.389(8), C(5)–C(11) 1.500(9), C(6)–C(5*) 1.389(8), C(6)–C(12) 1.500(11), C(13)–C(14) 1.425(6), C(13)–C(14′) 1.425(6), C(13)–C(15) 1.426(12), C(14)–C(14*) 1.556(12). Symmetry operations: (*) $x, -y, z$; (′) $-x+2, y, -z$.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 158468–158470 for complexes **1**, **3** and **4**, respectively. The crystal data for complex **2** was deposited previously with the Cambridge Crystallographic Data Centre, CCDC no. 1350/6 and will not be reported here. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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