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Organometallic building blocks for crystal engineering. Synthesis, structure and hydrogen bonding interactions in $[Fe(\eta^5\text{-}C_5H_4\text{–}CH_2(CH_3)OH)_2]$, $[Fe(\eta^5\text{-}C_5H_3(CH_3)COOH)_2]$, $[Fe(\eta^5\text{-}C_5H_4CH(CH_3)NH(\eta^5\text{-}C_5H_4CH(CH_3))]$ and in the diaminecyclohexane salt $[Fe(\eta^5\text{-}C_5H_4COO)_2]^{2-}[(1S,2S)\text{-}(NH_3)_2C_6H_{10}]^{2+}\cdot 2[H_2O]$

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Abstract

The novel ferrocene-based compounds $[Fe(\eta^5\text{-}C_5H_4\text{–}CH(CH_3)OH)_2]$ (**1**), $[Fe(\eta^5\text{-}C_5H_3(CH_3)COOH)_2]$ (**2**), $[Fe(\eta^5\text{-}C_5H_4CH(CH_3)NH(\eta^5\text{-}C_5H_4CH(CH_3))]$ (**3**) and the diaminecyclohexane salt $[Fe(\eta^5\text{-}C_5H_4COO)_2]^{2-}[1S,2S\text{-}(NH_3)_2C_6H_{10}]^{2+}\cdot 2[H_2O]$ (**4**) have been synthesised and their molecular and supramolecular structures determined by single-crystal X-ray diffraction. The hydrogen bonding networks established by the –COOH, $CH(CH_3)OH$, and $\text{–}COO^{(-)}$ groups have been studied and the structural parameters compared with those available for the prototypical dicarboxylic acid $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Crystal engineering; Organometallic complexes; Polycarboxylic acids; Hydrogen bonds

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1. Introduction

The hydrogen bond [1] is the interaction of choice in molecular crystal engineering [2] because it combines strength (a prerequisite of stability) with directionality (a prerequisite of reproducibility). Strength and directionality can be *tuned* by varying the polarity and the geometry of the acceptor and donor groups. The classical O–H···O hydrogen bonds formed by –COOH and –OH groups are among the strongest neutral bonds and are widely employed to construct crystal edifices [3]. It is well known, however, that the O–H···O bond can be further strengthened if the polarity of the acceptor systems is increased via deprotonation [4].

While hydrogen bonds between organic molecules have been extensively studied and there is a vast literature available on the subject [5], this is not so for organometallic molecules. While it is true, on the one hand, that 'organic type' ligands behave very much in the same way in the formation of hydrogen bridges as the corresponding organic molecules, differences arise in the topology of the systems and, often, in the polarity of the HB donor/acceptor systems that depend on the type of metal, on its oxidation state and on the ionic charge carried by the complex [6].

Much of the current interest in the utilisation of metal complexes in crystal engineering stems from the potentials inherent to the utilisation of crystal construction strategies, developed in the neighbouring field of

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organic crystal engineering, to assemble molecules by controlling the non-covalent interactions between the ligands. Indeed, the ultimate goal of the inorganic branch of crystal engineering is that of preparing novel materials in which the characteristics of transition metal coordination chemistry (e.g. variable valence, oxidation and spin states of the metal atoms) are brought in the crystals [7].

In the recent past, we have successfully used commercially available polycarboxylic acids to prepare a number of complex organic and organometallic superstructures [8,9] with predefined architectures and structural features by means of the simultaneous use of neutral O–H···O and negatively charged $O–H···O^{(-)}$ bonding interactions [8]. More recently, we have begun to synthesise new building blocks in an attempt to enlarge the library of synthons available for crystal construction [10].

Herein we report that the novel ferrocene-based compounds $[Fe(\eta^5\text{-}C_5H_4\text{–}CH(CH_3)OH)_2]$ (**1**), $[Fe(\eta^5\text{-}C_5H_3(CH_3)COOH)_2]$ (**2**), $[Fe(\eta^5\text{-}C_5H_4CH(CH_3)NH\text{-}(\eta^5\text{-}C_5H_4CH(CH_3))]$ (**3**) and $[Fe(\eta^5\text{-}C_5H_4COO)_2]^{2-}[(1S,2S)\text{-}(NH_3)_2C_6H_{10}]^{2+}\cdot 2[H_2O]$ (**4**) have been synthesised and their molecular and supramolecular structures determined by single-crystal X-ray diffraction. The hydrogen bonding networks established by the –COOH, CH(Me)OH, and $–COO^{(-)}$ groups have been studied and the structural parameters compared with those available for the prototypical dicarboxylic acid $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ [11].

2. Experimental

2.1. Synthesis of $[Fe(\eta^5\text{-}C_5H_4\text{-}CH(CH_3)OH)_2]$ (1)

(*R*,*R*)-bis(α-hydroxyethyl)ferrocene was prepared using the procedure described by Knochel et al. [12] through bis-acetylation of ferrocene followed by asymmetric reduction of 1,1-diacetylferrocene with $H_3B\cdot SMe_2$ catalysed by (*S*)-oxaborolidine derived from (*S*)-2-(diphenylhydroxymethyl)pyrrolidine and methylboronic acid. Crystals of **1** suitable for X-ray diffraction were obtained by slow evaporation of the nitromethane solution.

2.2. Synthesis of $[Fe(\eta^5\text{-}C_5H_3(CH_3)COOH)_2]$ (2)

Compound **2** was prepared using the procedure described by Rausch et al. [13], which consisted of double metalation of dimethylferrocene by *n*-buthyllithium in the presence of TMEDA, followed by carbonation and hydrolysis. Crystallisation from nitromethane afforded orange crystals of 1,1′-dimethylferrocene-3,3′dicarboxylic acid.

2.3. Synthesis of [(R,S)-bis(1-cyclopentadienyleth-1-yl)-amine]iron $[Fe(\eta^5\text{-}C_5H_4CH(CH_3)NH(\eta^5\text{-}C_5H_4CH\text{-}(CH_3))]$ (3)

To a solution of **1** (0.78 g, 2.87 mmol) in anhydrous Py (4 ml), Ac_2O (1.5 ml) was added and the mixture was stirred at room temperature (r.t.) for 24 h. All volatile materials were then removed in vacuum and the residue was dissolved in CH_3CN (24 ml). A 37% aqueous NH_3 solution (4.8 ml) was added, and the reaction was continued at r.t. for 24 h. An aqueous solution of 10% HCl (24 ml) was then added, the mixture was filtered to remove solid materials and made basic with 20% NaOH (24 ml). The amine was extracted with ether (3 × 20 ml), dried, concentrated and crystallised from ether–hexane (8:2) to afford 0.50 g of a yellow solid (65% yield). ^1H-NMR ($CDCl_3$, 300 MHz, δ ppm): 3.94–3.96 (m, 8H); 3.48 (q, 2H, $J = 6.9$ Hz); 1.34 (d, 6H, $J = 6.9$ Hz).

2.4. Synthesis of $[Fe(\eta^5\text{-}C_5H_4COO)_2]^{2-}[(1S,2S)\text{-}(NH_3)_2C_6H_{10}]^{2+}$ (4)

$[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ (100 mg, 0.36 mmol) was dissolved in 25 ml of THF, $[(1S,2S)\text{-}(NH_2)_2C_6H_{10}]$ (41 mg, 0.36 mmol) was added and suddenly an orange precipitate was formed. The precipitate was filtered and recrystallised from water to yield crystals suitable for X-ray diffraction.

2.5. Crystal structure characterisation

All X-ray diffraction data collections were carried out on a NONIUS CAD-4 diffractometer equipped with an Oxford Cryostream liquid-N_2 device. Crystal data and details of measurements are reported in Table 1. Diffraction data were corrected for absorption by azimuthal scanning of high-χ reflections. SHELXL-97 [14a] was used for structure solution and refinement based on F^2. SCHAKAL-97 [14b] was used for the graphical representation of the results. Common to all compounds: Mo–K_α radiation, $\lambda = 0.71069$ Å, monochromator graphite. All non-H atoms were refined anisotropically in **1**–**3**. In **4** only Fe, O and N were refined anisotropically. The structure of **2** was found affected by disorder in the positions of the methyl group, the disordered images being related by the mirror plane bisecting the cyclopentadienyl rings and the carboxylic groups. The computer program PLATON [14c] was used to analyse the geometry of the hydrogen bonding patterns.

3. Results and discussion

3.1. Crystal and molecular structure of $[Fe(\eta^5\text{-}C_5H_4\text{–}CH(CH_3)OH)_2]$ (1)

Compound **1** is enantiomerically pure and crystallises in the chiral space group $P2_1$. The asymmetric unit contains two independent molecules (A and B) in general position. In both molecules the cyclopentadienyl rings have an almost eclipsed conformation stabilised by the intramolecular O–H···O hydrogen bond shown in Fig. 1a. The two molecules form chains along the *b*-axis in the unit cell. The two OH groups generate two types of hydrogen bridges, an intra- and an intermolecular bond, respectively. The two types of bonds are approximately of the same length (see figure caption). The distribution of OH groups is such that the two independent molecules form independent chains in the crystal (see Fig. 1b). The 1-D network for alcohols is not a common supramolecular motif, because molecules with C–OH functions tend to form fourfold or sixfold O–H···O rings [5b]. In the case of **1**, however, the size of the organometallic complex and the need to optimise simultaneously the intra- and the intermolecular interactions appear to favour the alternative chain-like arrangement. Fig. 1c shows how the chains are neatly placed parallel to each other so that the packing can be seen as formed only of parallel 1-D networks.

Table 1
Crystal data and details of measurements for **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{14}H_{18}FeO_2$	$C_{14}H_{10}FeO_4$	$C_{14}H_{17}FeN$	$C_{18}H_{28}FeN_2O_6$
Formula weight	274.13	302.10	255.14	424.27
Temperature (K)	223(2)	293(2)	293(2)	223(2)
Crystal system	monoclinic	monoclinic	monoclinic	orthorombic
Space group	$P2_1$	$C/2m$	$P2_1/n$	$P2_12_12_1$
Unit cell dimensions				
a (Å)	9.915(2)	9.584(4)	11.150(10)	7.428(3)
b (Å)	6.110(4)	11.356(7)	7.400(10)	9.320(4)
c (Å)	20.890(4)	7.040(4)	14.650(10)	27.600(10)
β (°)	93.00(2)	122.80(4)	105.980(10)	90
V (Å^3)	1263.8(9)	644.0(6)	1162(2)	1910.7(13)
Z	4	2	4	4
μ(Mo–K$_\alpha$) (mm^{-1})	1.180	1.177	1.267	0.827
F(000)	576	312	536	896
θ Range	3–27	3–25	3–23	3–28
Measured reflections	3278	656	1531	2641
Unique reflections	2342	601	1318	2630
Min/max transmission	0.42–1.00	0.70–1.00	0.38–1.00	0.6–1.00
Refined parameters	271	54	127	136
Goodness-of-fit on F^2	1.072	1.029	0.920	0.843
R_1 (on F, $I > 2\sigma(I)$)	0.0358	0.0951	0.0838	0.0880
wR_2 (F^2, all data)	0.1013	0.2966	0.2161	0.3130

3.2. The dicarboxylic acid [Fe(η^5-$C_5H_3(CH_3)COOH)_2$] (**2**)

The most interesting feature of the crystal structure of [Fe(η^5-$C_5H_3(CH_3)COOH)_2$] (**2**) is the molecular organisation in the solid state, even though the molecule *per se* is affected by disorder of the methyl substituent over two positions (Section 2). In particular, it is worth comparing the supramolecular organisation in the crystal of **2** with that known for the two polymorphic modifications of the congener dicarboxylic acid [Fe(η^5-$C_5H_4COOH)_2$]. Organometallic polymorphism presents some unique features that arise from the topology and conformational adaptability of organometallic molecules. The subject of organometallic polymorphism has been recently reviewed [15]. Both the crystalline forms of [Fe(η^5-$C_5H_4COOH)_2$] are characterised by the presence of dimers of molecules joined directly by a twin hydrogen bonding system involving the two –COOH groups (see Fig. 2a). The difference between the two crystal structures, in spite of the closeness between the two molecular structures, is quite large: the carboxylic dimers present in [Fe(η^5-$C_5H_4COOH)_2$] are replaced by the alternative arrangement based on hydrogen bonded chains in **2** (see Fig. 2b). The structural parameters concerning the hydrogen bridges are strictly comparable in the two systems; O···O distances are in the range 2.593(2)–2.635(2) and 2.620–2.671(2) Å, respectively, for the monoclinic and triclinic forms of the ferrocene dicarboxylic acid, while the O···O distance is 2.602(9) Å in **2**. The difference in hydrogen bonding motif between [Fe(η^5-$C_5H_4COOH)_2$] and **2** might be due to the fact that the methyl groups in this latter compound are better accommodated in the crystal structure if the cyclopentadienyl rings are staggered, and the –COOH groups are in *transoid* conformation. It is also possible, however, that alternative structures, i.e. new polymorphic modifications either based on O–H···O chains or on dimers, for both acids are still ‘waiting to be discovered’. This is admittedly very speculative but it is interesting to mention here that the neutral acid [Cr(η^6-$C_6H_5COOH)_2$] [10] also forms dimers as [Fe(η^5-$C_5H_4COOH)_2$], whereas chains have been observed for the cationic acids [Co(η^5-$C_5H_4COOH)_2]^+$ [16] and [Cr(η^6-$C_6H_5COOH)_2]^+$ in their PF_6^- salts [10], this latter system being also known in two polymorphic forms.

3.3. The crystalline [Fe(η^5-$C_5H_4CH(CH_3)$-$NH(\eta^5$-$C_5H_4CH(CH_3))$] (**3**)

The amino complex **3** was prepared by bis-acetylation of **1** followed by treatment of the diacetate with

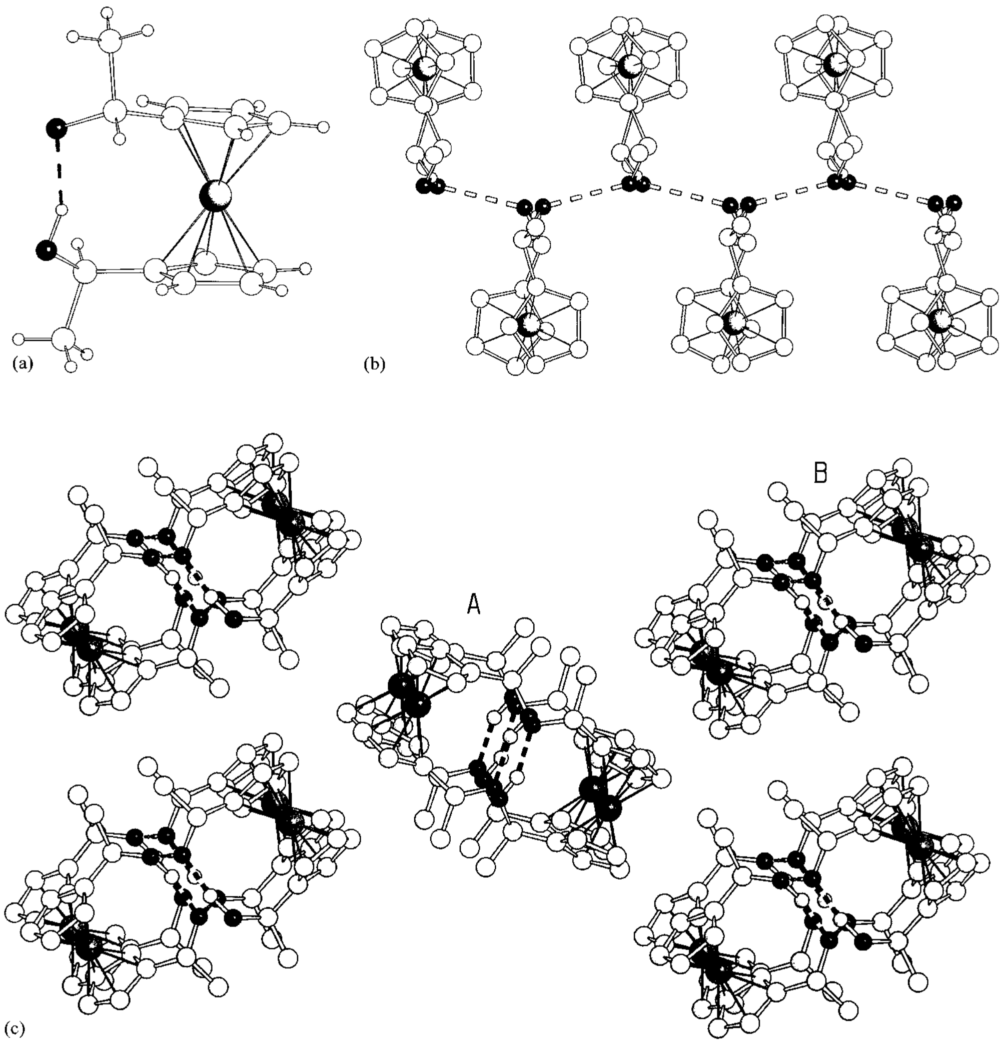

Fig. 1. (a) The molecular structure of [Fe(η^5-C_5H_4–CH(CH_3)OH$)_2$] (**1**) showing how the cyclopentadienyl rings have a near eclipsed conformation resulting from the intramolecular O–H···O hydrogen bonds. (b) The molecules are joined in chains via O–H···O intermolecular interactions. (c) The two independent molecules in crystalline **1** form independent and parallel 1-D networks (A and B) in the crystal. Hydrogen bonding O···O distances are: intramolecular bonds 2.679(5), 2.693(5); intermolecular bonds 2.696(5), 2.708(5) Å.

ammonia in CH_3CN–H_2O [17]. Since **3** derives from intramolecular S_N2 reaction of an intermediate amminoacetate, *meso*-**3** is obtained starting from (*R*,*R*)-**1**. The structure is that of a bent-metallocene (Fig. 3), the angle formed by the planes of the two Cp ligands is 8.08°. The N atom is 'segregated' between the two methyl groups and cannot participate in hydrogen bonding interactions. The crystal of **3** is therefore a van der Waals crystal where specific, highly directional, intermolecular interactions are absent.

3.4. The crystalline salt [Fe(η^5-$C_5H_4COO)_2]^{2-}$[(1S, 2S)-$(NH_3)_2C_6H_{10}]^{2+}\cdot 2H_2O$ (4)

We previously used anions derived from the dicarboxylic acid [Fe(η^5-$C_5H_4COOH)_2$] to prepare mixed-metal organometallic crystalline materials, such as $[(\eta^5$-$C_5H_5)_2Co]^+[(\eta^5$-$C_5H_4COOH)(\eta^5$-$C_5H_4COO)Fe]^-$ and $[(\eta^6$-$C_6H_6)_2Cr]^+[(\eta^5$-$C_5H_4COOH)(\eta^5$-$C_5H_4COO)$-$Fe]^-\cdot H_2O$ [18]. The strategy adopted to construct these crystals was such that the hydrogen bridges could only be formed between the organometallic acid moieties since the counterions could not compete in the formation of hydrogen bonding interactions with the –COOH and $COO^{(-)}$ groups. In these compounds the interactions between anions and cations was mainly based on a large number of weaker C–H···O hydrogen bonding interactions.

An alternative strategy is that of using cations that *can form hydrogen bonds* with the anions. This approach is widely used also in organic crystal engineering [19]. According to this strategy, we have employed *trans*-diaminocyclohexane allows to construct a crystalline material containing the organometallic dianion $[Fe(\eta^5\text{-}C_5H_4COO)_2]^{2-}$ and the cation $[(1S,2S)\text{-}(NH_3)_2C_6H_{10}]^{2+}$ linked via charge-assisted N–H···O hydrogen bridges. Because we have utilised an enantiomerically pure anion, the resulting crystal is chiral. Each diamine cation interacts directly with two organometallic dianions and with two water molecules by means of $^{(+)}$N–H···O$^{(-)}$ and $^{(+)}$N–H···O hydrogen bonding interactions, respectively. These links are strengthened by the ionic charges carried by the hydrogen bonding donor and acceptor groups, i.e. they are 'charge-assisted'. In **4**, the $^{(+)}$N–H···O$^{(-)}$ interactions are in the range 2.744–2.813. The presence of strong and directional interionic interactions results in the superstructure shown in Fig. 4 which consists of an alternation of cations and anions, with the water molecule occupying a bridging position. The interactions between oxygen atoms are all due to the water molecules donating to the –COO$^{(-)}$ groups and are expectedly shorter than those of the N–H···O type. It is also worth stressing that the utilisation of an enatiomerically pure component, e.g. the cation $[(1S,2S)\text{-}(NH_3)_2C_6H_{10}]^{2+}$ results, as desired, in a chiral crystalline structure in space group $P2_12_12_1$.

4. Conclusions

Crystal engineering [20] is overcoming the stage in which the desired building blocks could be readily available, sometimes commercially available. This is particularly true in the field of organometallic chemistry, where a vast repertoire of combinations of supramolecular functions (e.g. hydrogen bonding groups) and coordination topology can be exploited.

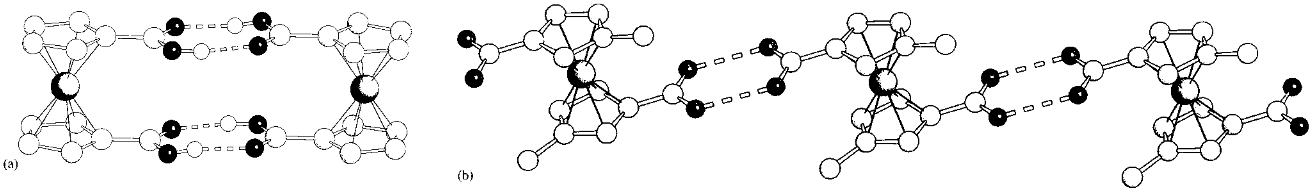

Fig. 2. (a) The hydrogen bonded cyclic dimers in crystalline $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$. (b) Chains of hydrogen bonded molecules in crystalline $[Fe(\eta^5\text{-}C_5H_3(CH_3)COOH)_2]$ (**2**) (only one of the disordered images is shown for sake of clarity). The hydrogen bonding O···O distance in **2** is 2.692(9) Å.

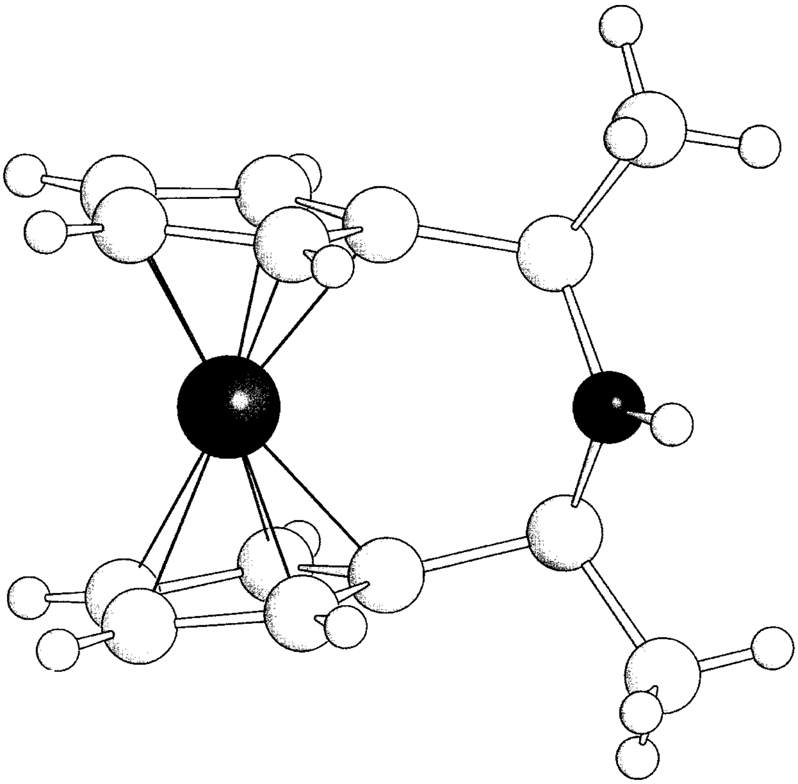

Fig. 3. The molecular structure of $[Fe(\eta^5\text{-}C_5H_4CH(CH_3)NH(\eta^5\text{-}C_5H_4CH(CH_3))]$ (**3**), the angle between the two Cp planes is ca. 8.08°.

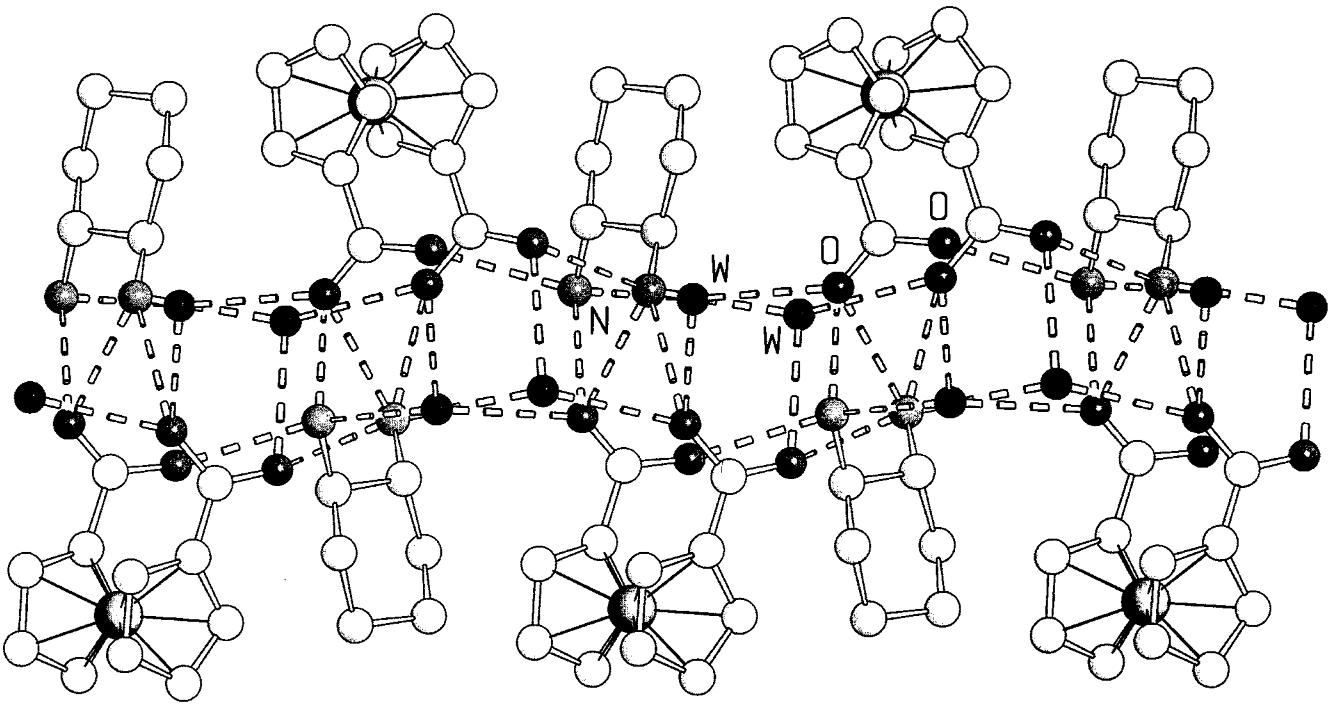

Fig. 4. The intermolecular interactions in the crystalline salt $[Fe(\eta^5\text{-}C_5H_4COO)_2]^{2-}[(1S,2S)\text{-}(NH_3)_2C_6H_{10}]^{2+}\cdot 2[H_2O]$ (**4**); amine nitrogen, carboxylic oxygens and water oxygens are indicated (N, O and W, respectively). Hydrogen bonding parameters are, $O_{COO}\cdots O_{water}$ 2.809, 2.700, 2.686, 2.684(20) Å, $N\cdots O_{water}$ 2.809, 2.813(20), $N\cdots O_{COO}$ 2.781, 2.744, 2.776, 2.790(20) Å, respectively.

Organometallic acids or alcohols, which have not been studied in a systematic manner, offer the possibility of combining molecular features (e.g. oxidation and spin state, ligand topology, ionic charge) with the supramolecular bonding capacity of –COOH and –OH groups. Similar reasoning applies to amines and amides. In an effort to enlarge the *library* of compounds available for the building up of supramolecular organometallic architectures we have prepared and characterised the dihydroxy $[Fe(\eta^5\text{-}C_5H_4-CH(CH_3)OH)_2]$ (**1**), the dicarboxylic acid $[Fe(\eta^5\text{-}C_5H_3(CH_3)COOH)_2]$ (**2**), the amine $[Fe(\eta^5\text{-}C_5H_4CH(CH_3)NH(\eta^5\text{-}C_5H_4CH(CH_3))]$ (**3**) and the cyclohexanediamine salt $[Fe(\eta^5\text{-}C_5H_4COO)_2]^{2-}[(1S,2S)\text{-}(NH_3)_2C_6H_{10}]^{2+}\cdot 2[H_2O]$ (**4**). We have investigated the hydrogen bonding capacity of these species (except in the case of **3**, which does not possess strong hydrogen bonding donor/acceptor groups) and, in the case of **4**, we have provided an example of how to build chiral crystals containing organometallic complexes by using enatiomerically pure organic units capable of strong N–H···O bonds with the ferrocene dicarboxylic acid unit.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 157018, 157019, 157017, 157016 for compounds **1**, **2**, **3** and **4**, respectively. 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; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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