A Structural Investigation of the D$_2$O Solvated, Acetone Solvated and Nonsolvated 1,4-Diazabicyclo[2.2.2]octane Complexes of the Half Sandwich Moiety [(η^5-C$_5$H$_5$)(CO)$_2$Fe]

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ABSTRACT

Two new solvates of the dinuclear salt {(η^5-C$_5$H$_5$)(CO)$_2$Fe}$_2$(μ-DABCO)](BF$_4$)$_2$ (DABCO = 1,4-diazabicyclo[2.2.2]octane); **1** (D$_2$O solvate) and **2** (acetone solvate), and the mononuclear salt [(η^5-C$_5$H$_5$)(CO)$_2$Fe(DABCO)]BF$_4$, **3**, have been synthesized and structurally characterized. The D$_2$O solvate, **1** forms crystals in the triclinic space group $P\bar{1}$, the acetone solvate forms crystals in the monoclinic $P2_1/c$ space group, while the unsolvated mononuclear salt, **3**, forms crystals in the orthorhombic $P2_12_12_1$ space group. The respective unit cell parameters are: Compound **1**, a = 7.66300(10) Å, b = 12.3133(2) Å, c = 13.9629(2) Å, α = 69.179(1) °, β = 77.114(1) ° and γ = 84.282(1) °; Compound **2**, a = 17.3633(3) Å, b = 14.1688(3) Å, c = 11.3542(2) Å, β = 99.344(1) °; Compound **3**, a = 8.9936(2) Å, b = 10.8949(3) Å, c = 15.3417(4) Å. The DABCO ligand adopts a twisted conformation with N-C-C-N torsion angles ranging between –21.05(12) to –19.31(12) ° and 15.3(2) –15.7(2) ° in **1** and **2**, respectively, whereas in **3**, the CH$_2$ groups of each NCH$_2$CH$_2$N moiety are almost eclipsed, the torsion angles ranging from –2.89(18) to –1.50(16) °.

KEYWORDS

Cyclopentadienyliron dicarbonyl complex, 1,4-diazabicyclo[2.2.2]octane (DABCO), X-ray crystallography.

1. Introduction

1,4-Diazabicyclo[2.2.2]octane (DABCO) and its derivatives have been widely investigated due to their good catalytic activity in organic synthesis[1–5] and ability to form non-metallic salt.[6,7] DABCO is a bicyclic amine with a rigid and compact cage-like structure of nearly-spherical shape which constitutes an unusually favourable characteristic that effectively minimizes the steric hindrance to coordination, which in tertiary aliphatic amines arises from the flexibility of the nitrogen-bonded alkyl groups. Thus, DABCO has also been widely utilized as a ligand in preparation of metal complexes and several structures of metal-DABCO compounds have been reported.[8–12] However, to the best of our knowledge there is only one crystal structure of iron carbonyl with the DABCO ligand that has been previously reported.[11] There are no reports on crystal structures of iron-DABCO compounds in which both cyclopentadienyl and carbonyls are present. Herein we report three crystal structures of DABCO complexes of the half sandwich cyclopentadienyliron dicarbonyl moiety,[(η^5-C$_5$H$_5$)(CO)$_2$Fe (**1**, **2** and **3** in Scheme 1).

2. Experimental

2.1. General Methods

All chemicals were of analytical grade and were used without purification. The compounds [{(η^5-C$_5$H$_5$)(CO)$_2$Fe}$_2$(μ-DABCO)](BF$_4$)$_2$ and [(η^5-C$_5$H$_5$)(CO)$_2$Fe(DABCO)]BF$_4$ were prepared following the procedure described in literature.[13] Crystals of compounds **1–3** were obtained as described below:

[{(η5-C$_5$H$_5$)(CO)$_2$Fe}$_2$(μ-DABCO)](BF$_4$)$_2$.(D$_2$O), 1

A solution of [{(η^5-C$_5$H$_5$)(CO)$_2$Fe}$_2$(μ-DABCO)](BF$_4$)$_2$ in D$_2$O

was placed in an aluminium-wrapped Schlenk tube and the solution evaporated slowly under reduced pressure. Brown block-shaped crystals developed after three days and a quality single crystal was carefully selected and subjected to single crystal X-ray diffraction. Anal. Calc. for C$_{20}$H$_{22}$D$_2$B$_2$F$_8$Fe$_2$N$_2$O$_5$: C, 36.41; H, 3.97; N, 4.25. Found: C, 36.45; H, 4.02; N, 4.58 %. ^{1}H NMR (400 MHz, CD$_3$CN): δ 5.35 (s, 5H, C$_5$H$_5$), 2.99 (s, 12H, CH$_2$), 2.08 {O(CH$_3$)$_2$}. IR (solid state): $ν$(CO) 2053, 2000 cm^{-1}.

[{(η5-C$_5$H$_5$)(CO)$_2$Fe}$_2$(μ-DABCO)](BF$_4$)$_2$.(CH$_3$COCH$_3$), 2

A concentrated solution of [{(η^5-C$_5$H$_5$)(CO)$_2$Fe}$_2$(μ-DABCO)](BF$_4$)$_2$ in acetone was layered with dry diethyl ether. The resulting mixture was kept in the dark undisturbed for two days after which brown block-shaped crystals developed. A quality crystal was selected for single crystal analysis. Anal. Calc. for C$_{23}$H$_{28}$B$_2$F$_8$Fe$_2$N$_2$O$_5$: C, 39.59; H, 4.04; N, 4.01. Found: C, 39.70; H, 3.97; N, 3.74 %. ^{1}H NMR (400 MHz, CD$_3$CN): δ 5.33 (s, 5H, C$_5$H$_5$), 3.00 (s, 12H, CH$_2$), 2.08 {OC(CH$_3$)$_2$}. IR (solid state): $ν$(CO) 2054, 2001 cm^{-1}.

[η^5-C$_5$H$_5$)(CO)$_2$Fe(DABCO)]BF$_4$, 3

Crystals of compound **3** were grown in a similar manner as described for compound **2**. Anal. Calc. for C$_{13}$H$_{17}$BF$_4$FeN$_2$O$_2$: C, 41.49; H, 4.52; N, 7.45. Found: C, 41.98; H, 4.77; N, 7.37 %. ^{1}H NMR (600 MHz, D$_2$O): δ 5.39 (s, 5H, C$_5$H$_5$), 3.14 (CH$_2$), 2.84 (CH$_2$). ^{13}C NMR (600 MHz, D$_2$O); δ 86.75 (C$_5$H$_5$), 58.31 (CH$_2$), 46.00 (CH$_2$), 210.60 (CO) IR (solid state): $ν$(CO) 2050, 1996.

2.2. X-ray Crystallographic Analysis

Suitable single crystals of **1–3** were carefully selected under an optical microscope and glued to thin glass fibre with epoxy resin. Data collection was performed on a Bruker SMART APEXII CCD

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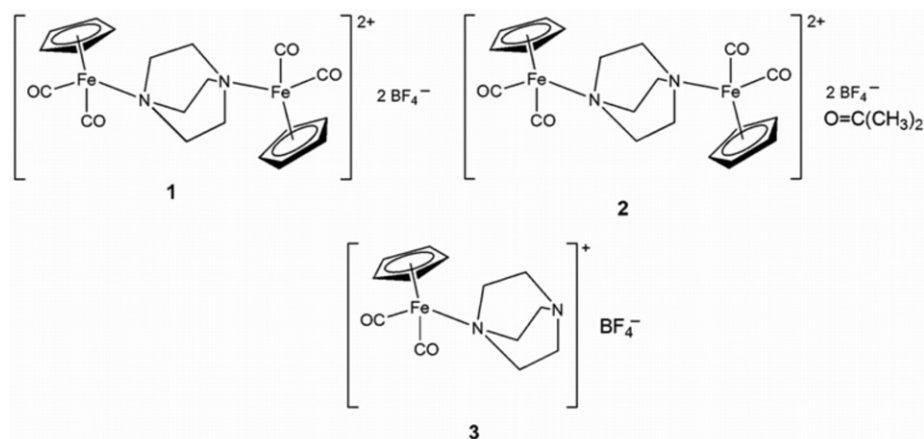
Scheme 1
Line drawings for compounds **1**, **2** and **3**.

single crystal X-ray diffractometer at 173(2) K using Mo K_α radiation (λ = 0.71073A °, 50 kV, 30 mA) using the APEX 2[14] data collection software. The cell matrix was obtained from 36 frames collected at intervals of 0.5 ° and exposure time of 10 seconds per frame and the reflections indexed by an automated indexing routine built in the *APEX*II program suit.[14] The data collection method involved ω scans of width 0.5 °. Data reduction was carried using the program *SAINT+*.[14] The structures were solved by direct methods using Bruker *SHELXS*[15] and refined using Bruker *SHELX*.[14] Non-H atoms were first refined isotropically and then by anisotropic refinement with full-matrix least-squares calculations based on F^2 using Bruker *SHELXS*. Carbon-bound H atoms were placed in calculated positions [C–H = 0.98 Å for methine H atoms and 0.97 Å for Methylene H atoms for compounds **1** and **2**, and C–H = 1.00 Å for methine H atoms and 0.99 Å for methylene H atoms for compounds **3**; U_{iso}(H) = 1.2U_{eq}(C) and were included in the refinement in the riding model approximation. In the structure of compound **1**, an isolated deuterated water molecule (O1W) was refined isotropically with an occupancy of 0.3. Disorder was found for the fluorine atoms of one of the tetrafluoroborate anions in compound **2**. The disorder was modelled for the F atoms using PART instructions while keeping the total occupancy at each atom site at 1 during refinement. The F atoms involved were refined isotropically. Disorder was also found for one of the O atoms of a carbonyl group. The disorder was treated in a similar fashion as described above but refined anisotropically. The F atoms involved were refined anisotropically. Further details for data collection and refinement are summarized in Table 1. The crystallographic data for compounds **1**, **2** and **3** were deposited to the Cambridge Crystallographic Data Centre (entry nos. CCDC-903054, 903055 and 903056, respectively) and are available free of charge upon request to CCDC, 12 Union Road, Cambridge, UK (Fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

3. Results and Discussion

3.1. Molecular Structures of Compounds 1, 2 and 3

Crystals suitable for single crystal X-ray diffraction analysis for compound **1** were obtained from slow evaporation of a solution of [{(η^5-C$_5$H$_5$)(CO)$_2$Fe}$_2$(μ-DABCO)](BF$_4$)$_2$ in D$_2$O. The crystals were isolated and dried under vacuum giving brown crystals of the solvated [{(η^5-C$_5$H$_5$)(CO)$_2$Fe}$_2$(μ-DABCO)](BF$_4$)$_2$.(D$_2$O). Compound **2** was grown by slow evaporation of a solution of [{(η^5-C$_5$H$_5$)(CO)$_2$Fe}$_2$(μ-DABCO)](BF$_4$)$_2$ in acetone resulting in

yellow crystals of [{(η^5-C$_5$H$_5$)(CO)$_2$Fe}$_2$(μ-DABCO)] (BF$_4$)$_2$.(CH$_3$COCH$_3$). *ORTEP* diagrams for the two compounds are shown in Figs. 1 and 2. Selected bond distances and angles are given in Table 2. The structures show that both compounds are dinuclear with two cationic Fe centres and two tetrafluoroborate counter anions. Compound **1** has one-third of a molecule of deuterated water in the asymmetric unit, while compound **2** has one molecule of acetone in its asymmetric unit. In both molecular structures the two Fe^{II} centres are coordinated to two carbonyl ligands each, the cyclopentadienyl rings and to the DABCO ligand through the N atoms resulting in a pseudo octahedral geometry. Three sides of this pseudo-octahedral geometry are occupied by the cyclopentadienyl ligand, while the two carbonyls and DABCO ligand occupy the remaining three sites.

The average Fe–N bond distance in the two compounds is 2.0636(2) Å, slightly shorter than those of the analogous hexamethylenetetramine (HMTA) adduct [{(η^5-C$_5$H$_5$)(CO)$_2$Fe}$_2$(μ-HMTA)](BF$_4$)$_2$ (2.0817(17) and 2.0858(18) Å)[13] and of [(CO)$_4$Fe(DABCO)] (2.092(4) Å),[11] but longer than those of previously reported cyclopentadienylirondicarbonyl amine complexes.[16–19] Interestingly this Fe–N bond distance was found to fall in between a range of other Fe–N distances of Fe complexes with tertiary amines where some were as long as 2.28 Å and others as short as 1.97 Å.[20] Bond distances in the DABCO moiety fall within literature values and range from 1.5396(15) to 1.5461(15) Å for C–C bond lengths[21] and between 1.4982(14) and 1.5027(14) Å for C–N bond lengths. The C–N bond average is 1.5005(5) Å which is longer than the C–N bond distance (1.456–1.472 Å) in an uncoordinated DABCO molecule. Coordination or quaternization of DABCO has an elongating effect of adjacent C–N bonds as also observed in literature.[6,7,22,23]

Crystals of compound **3** were obtained from a solution of the compound in dichloromethane by slow evaporation resulting in yellow crystals. Compound **3** is, however, mononuclear and crystallizes with one cation molecule and an anion molecule in the asymmetric unit and has similar geometry around the Fe centre to compounds **1** and **2** (Fig. 3). Important bond distances and angles are listed in Table 2. The Fe–N and C–C bond distances in the DABCO moiety are similar to those compounds **1** and **2**. The effect of coordination on C–N bond distances in DABCO are best illustrated by the structure of compound **3** in which the C–N bond adjacent to the coordinated nitrogen [average of 1.499(2) Å] are elongated relative to the C–N bond neighboring uncoordinated nitrogen [average of 1.466(2) Å]. The DABCO moiety is slightly distorted from an ideal D_{3h} or $6m_2$ molecular

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Table 1 Crystal data and structural refinement for **1**, **2** and **3**.

Parameter	1	2	3
Empirical formula	$C_{20}H_{22}B_2F_8Fe_2N_2O_{4.3}$	$C_{23}H_{22}B_2F_8Fe_2N_2O_5$	$C_{13}H_{17}BF_4FeN_2O_2$
Formula weight	644.52	699.86	375.95
Temperature (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
a (Å), α (°)	7.66300(10), 69.1790(10)	17.3633(3)	8.9936(2)
b (Å), β (°)	12.3133(2), 77.1140(10)	14.1688(3), 99.3440(10)	10.8949(3)
c (Å), γ (°)	13.9629(2), 84.2820(10)	11.3542(2)	15.3417(4)
Volume	1200.14(3)	2756.26(9)	1503.25(7)
Z	2	4	4
$\sigma_{calc.}$ (Mg m^{-3})	1.784	1.636	1.661
Absorption coefficient (mm^{-1})	1.304	1.146	1.056
$F(000)$	648.8	1419.6	768
Crystal size (mm^3)	$0.53 \times 0.18 \times 0.10$	$0.43 \times 0.33 \times 0.2$	$0.37 \times 0.29 \times 0.24$
Theta range for data collection (°)	1.77–28.62	1.19 –28.33	2.29–28.32
Index ranges	$-9 \to 10$ $-16 \to 16$ $-18 \to 18$	$-23 \to 23$ $-18 \to 18$ $-15 \to 15$	$-11 \to 12$ $-14 \to 14$ $-20 \to 20$
Reflections collected	29733	80540	46367
Independent reflections	6068 [R(int) = 0.0260]	6731 [R(int) = 0.0175]	3741 [R(int) = 0.0159]
Completeness to theta = 28.00 °	98.3	98.0	100.0
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and Min. transmission	0.5448; 0.8806	0.6386; 0.7786	0.6961; 0.7857
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6068/0/352	6731/0/392	3741/0/263
Goodness of fit on F^2	1.04	1.031	1.049
Final R indices [I > 2σ(I)]	R1 = 0.0226, wR2 = 0.0617	R1 = 0.0356, wR2 = 0.0955	R1 = 0.0177, wR2 = 0.0471
R indices (all data)	R1 = 0.0241, wR2 = 0.0630	R1 = 0.0395, wR2 = 0.0995	R1 = 0.0181, wR2 = 0.0473
Largest diff. peak and hole (e. Å^{-3})	0.427 and –0.397	1.014 and –0.655	0.273 and –0.201
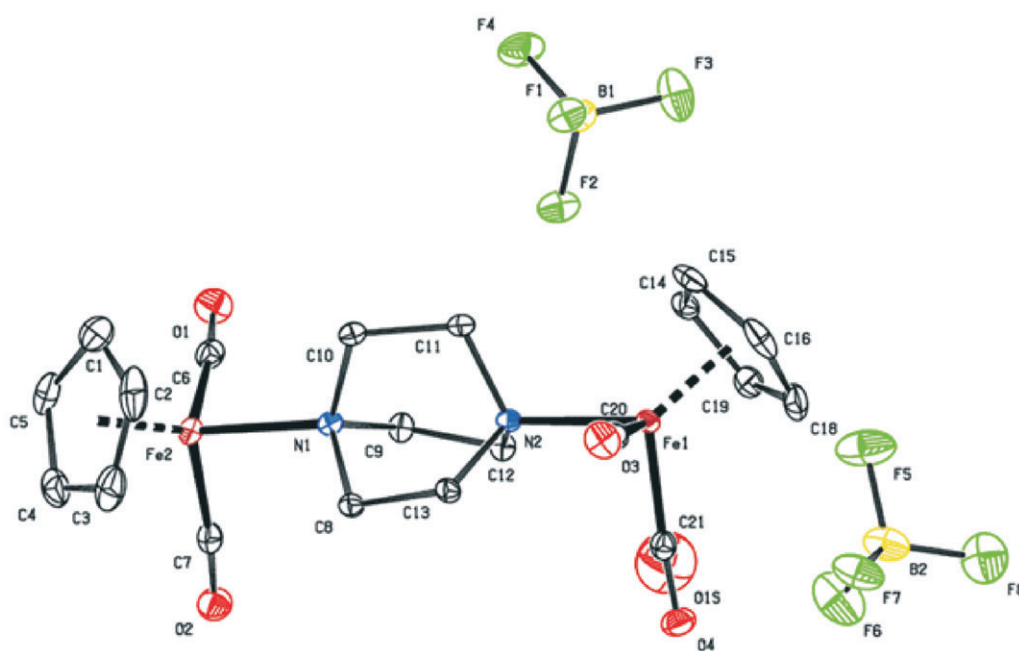
Figure 1 Molecular structure of [{(η^5-C$_5$H$_5$)(CO)$_2$Fe}$_2$(μ-DABCO)](BF$_4$)$_2$.(D$_2$O), **1**, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level with H atoms omitted for clarity.
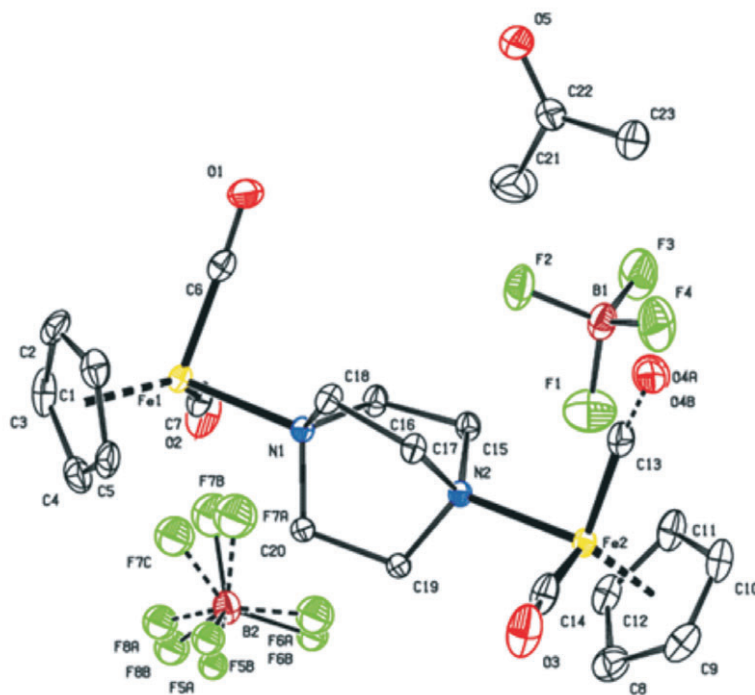
Figure 2 The molecular structure of $[\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}_2(\mu\text{-}DABCO)](BF_4)_2 \cdot (CH_3COCH_3)$, **2**, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level with H atoms omitted for clarity.
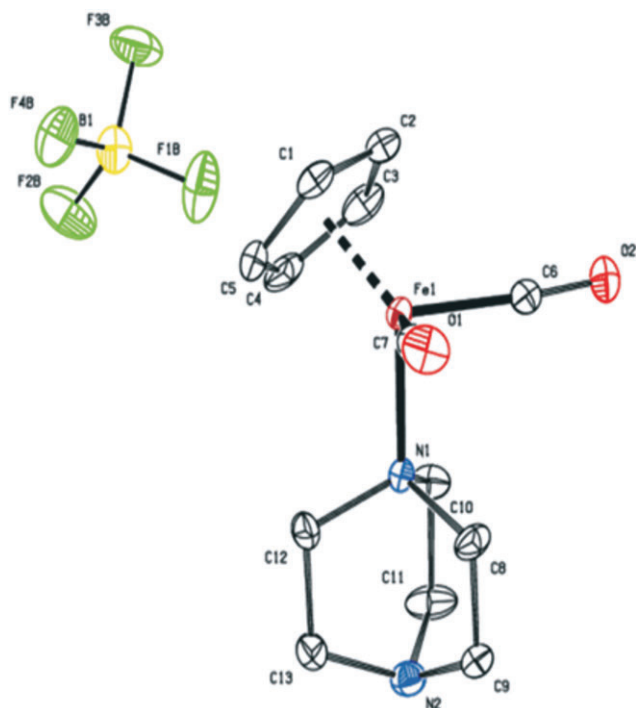
Figure 3 The molecular structure of $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(DABCO)]BF_4$, **3**, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level with H atoms omitted for clarity.
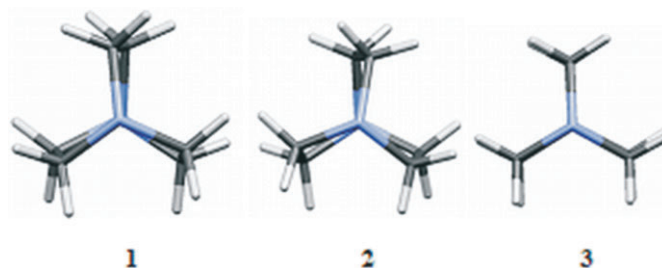

Figure 4 DABCO fragment showing distortion from ideal D_{3h} symmetry about N…N vector in compounds **1**, **2** and **3**.

Table 2 Selected bond distances (Å) and angles (°) for compounds **1**, **2** and **3**.

	1	2	3
Fe–N	2.0624(9)	2.0658(15)	2.0591(10)
Fe–N	2.0650(10)	2.0611(15)	–
N–C	1.5027(14)	1.500(2)	1.5000(15)
N–C	1.4983(14)	1.495(2)	1.5025(15)
N–C	1.5005(14)	1.498(2)	1.4983(15)
N–C	1.4982(14)	1.495(2)	1.4693(18)
N–C	1.5026(14)	1.499(2)	1.4628(18)
N–C	1.5009(14)	1.497(2)	1.4665(17)
Fe–Cg [1]	1.719	1.721	1.727
Fe–Cg	1.731	1.733	–
N–C–C–N	–20.65(12)	15.7(2)	–2.56(15)
N–C–C–N	–21.03(12)	15.4(2)	–2.89(18)
N–C–C–N	–19.31(12)	15.3(2)	–1.50(16)

[1] Cg is the centroid of the atoms forming the cyclopentadienyl ring (e.g. C1, C2, C3, C4 and C5)

symmetry (which requires full eclipse of CH_2 groups within each NCH_2CH_2N fragment) about a vector along the two nitrogen atoms in compounds **1** and **2**, but less in compound **3** (Fig. 4). The average N–C–C–N torsion angle is –20.3(1) ° in **1** and 15.5(2) ° in **2** as compared to an average of –2.32(2) ° in **3**. The large deviation can be attributed to steric strain by the cyclopentadienyl dicarbonyl moieties in **1** and **2**. The intramolecular N…N distance is 2.615 Å in **3**, which is slightly shorter than the 2.640

and 2.638 Å observed in compounds **1** and **2**, respectively, but slightly longer than the 2.573–2.580 Å observed in free DABCO molecules, implying that the distance between the two nitro-

Table 3 Molecular interaction geometry for compounds **1**, **2** and **3** (Å, °).

| D–H...A	D–H	H...A	D...A	D–H...A	Symmetry operator
1.[BF$_4$]					
C2–H2...F2	0.98	2.50	3.380(2)	149	1+x, y, z
C10–10b...F4	0.97	2.30	3.2584(15)	170	1-x, -y, 1-z
C16–H16...F3	0.98	2.30	3.2595(19)	166	1-x, 1-y, 1-z
C19–H19...F5	0.98	2.33	3.2017(16)	147	x, y, z
2.[BF$_4$]					
C1–H1...O5	0.98	2.33	3.270(3)	161	x, 3/2- y, -½+z
C4–H4...O5	0.98	2.36	3.185(3)	141	x, y, -1+z
C2 –H2...F3	0.98	2.48	3.431(3)	164	1-x, 1-y, 1-z
C11–H11...F4	0.98	2.40	3.311(2)	155	x, y, z
C12–H12...F4	0.98	2.23	3.156(3)	158	x, ½-y, -½+z
C16–H16b...F3	0.97	2.48	3.358(3)	151	x, ½-y, -½+z
C19–H19b...F4	0.97	2.49	3.458(3)	172	x, ½-y, -½+z
3.[BF$_4$]					
C3–H3...F2b	0.98	2.44	3.328(4)	151	1-x, ½+y, ½-z
C13– H13b...F3	0.97	2.41	3.348(4)	161	-x, ½+y, ½-z

gens in *trans* position stretches out upon coordination, probably to minimize steric crowding as nitrogen donates a pair of electrons to the metal, thus weakening the adjacent C–N bond. Furthermore, although the angles round the nitrogen atom N2 do not differ significantly from 109.5 °, the values round N1 show a significant trend in the direction expected for a lone pair of electrons occupying the orbital directed towards iron; the mean Fe–N1–C angle at 111.59 ° is 4.32 ° larger than the mean C–N1–C angle.

DABCO is known for its strong interaction with neutral molecules possessing hydrogen-bond donors leading to adducts linked by hydrogen bonding in which the DABCO nitrogen acts as hydrogen bond acceptor.[22,24–26] Interestingly, although in the compound [{(η^5-C$_5$H$_5$)(CO)$_2$Fe}$_2$(μ-DABCO)](BF$_4$)$_2$, the nitrogen is not available for hydrogen bonding, it interacts strongly with the D$_2$O and CH$_3$COCH$_3$ molecules. Thus, in crystals of compounds **1** and **2** packing is governed mainly by a set of strong and weak C–H...F intermolecular interactions (Table 3). In the crystal structure of **1**, there are four C–H F intermolecular interactions [C9–H9B F8, C16–H16 F3, C2–H2 F2 and C19–H19 F5] that connect the cations and anions along all crystallographic axes (Fig. 5a). The H atoms of the deuterated 1/3 H$_2$O molecule could not be located in the difference map. No strong hydrogen bonding interaction is observed for **2**. The crystal structure of compound **2** has five fairly strong C–H...F intermolecular interactions and two C–H...O hydrogen bond interactions, in which the O atom of the acetone molecule acts as the hydrogen bond acceptor (Fig. 5b). The two C–H...O intermolecular interactions connect the cationic molecules resulting in chains down the crystallographic *c*-axis (Fig. 5c). In contrast the mononuclear complex [(η^5-C$_5$H$_5$)(CO)$_2$Fe(DABCO)]BF$_4$ does not trap any solvent molecule in its crystal lattice, although the single crystal was grown under similar conditions to those of compound **2**. However, the crystal structure of compound **3** exhibited two C–H...F intermolecular interactions which contribute to the packing of the molecules in the crystal lattice.
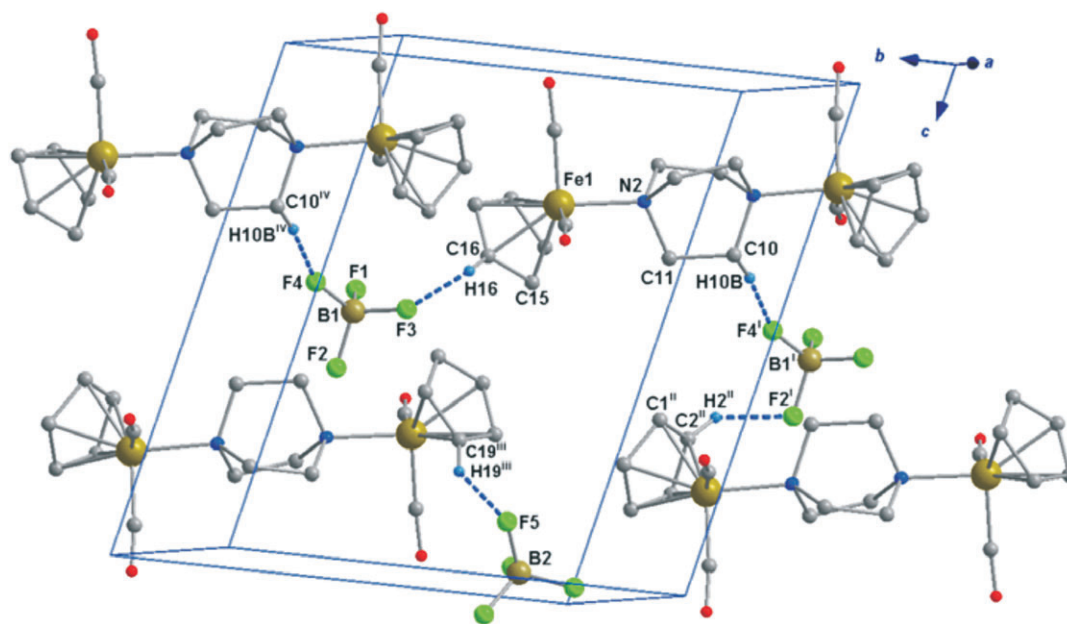
Figure 5a A perspective of **1** showing C–H...F intermolecular interactions blue dashed lines. Symmetry operators: i = x, -1+y, z; ii = x, ½-y, ½+z; iii = 2-x, -y, 1-z; iv = x, 1+y, z. H atoms of the 1/3 deuterated water molecule could not be located on the difference map and as such the O atom (O1s) is omitted from this figure for clarity.
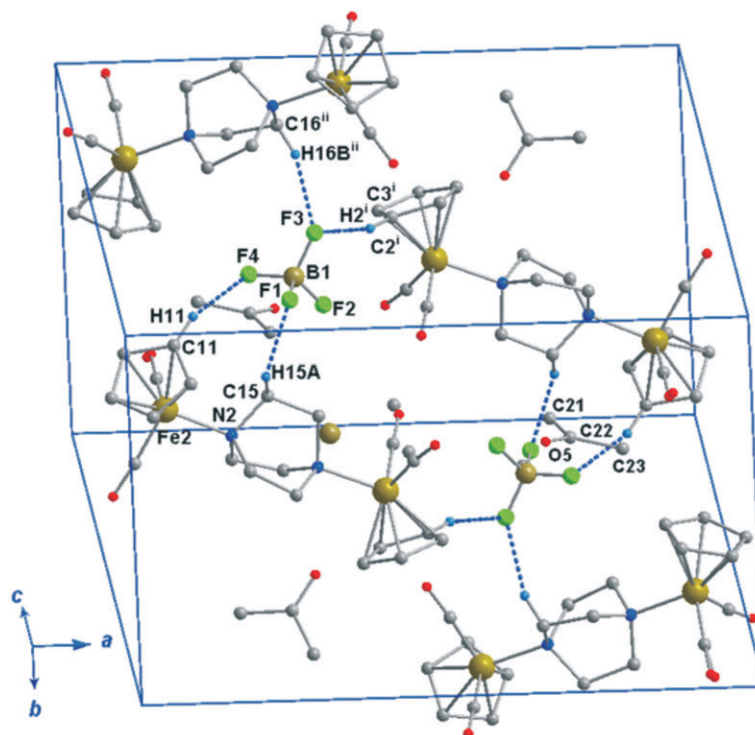
Figure 5b A perspective of **2** showing C–H…F intermolecular interactions blue dashed lines. Symmetry operators: i = 1-x, 1-y, 1-z; ii = x, ½-y, ½+z.
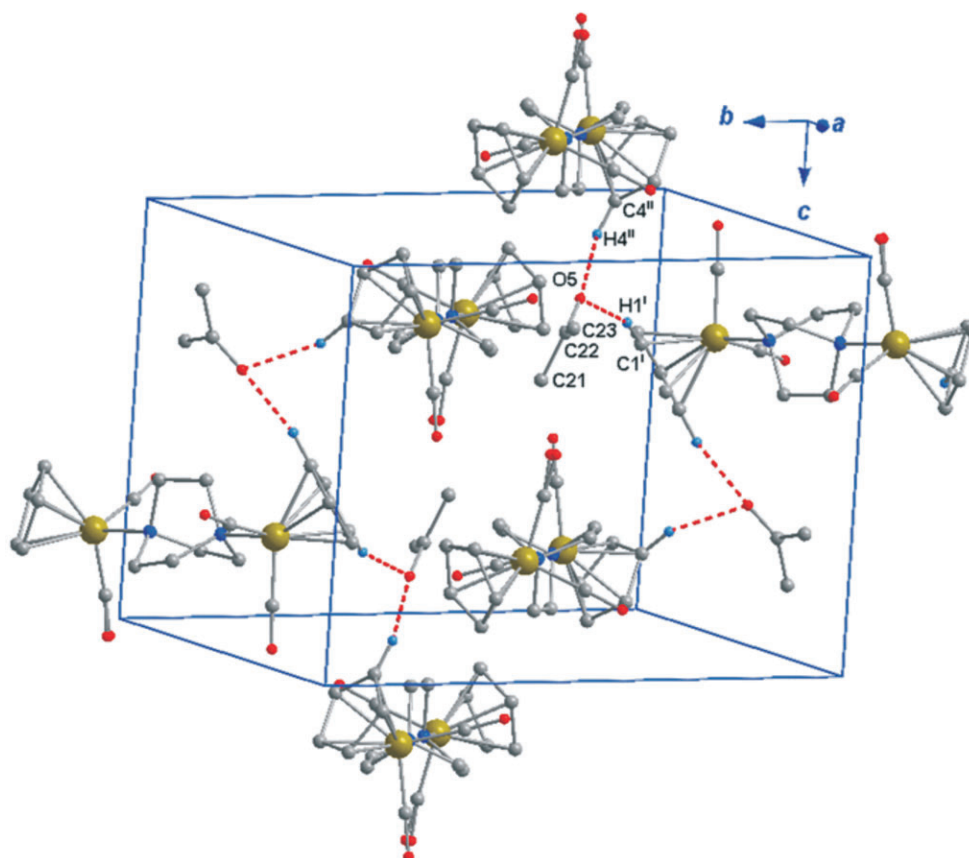
Figure 5c A perspective of **2** showing C–H…O intermolecular interactions red dashed lines. Symmetry operators: i = 1-x, -½-y, ½-z; ii = 1-x, 1-y, -z.

4. Conclusion

Molecular structures of three DABCO complexes of the half sandwich iron moiety [Cp(CO)$_2$Fe] have been determined by single crystal X-ray crystallography. It has been shown that the dinuclear complex [{Cp(CO)$_2$Fe}$_2$(μ-DABCO)](BF$_4$)$_2$ crystallizes in different crystal systems with solvent molecules trapped in a crystalline lattice. The conformation of the coordinated DABCO in the mononuclear complex [Cp(CO)$_2$Fe(DABCO)]BF$_4$ differs significantly from that of the dinuclear complex.

References

1 M.M. Heravi, R.H. Shoar and L. Pedram, *Mol. Cat. A. Chem.*, 2005, **231**, 89–91.

2 Y. Hon and C. Kao, *Tetrahedron Lett.*, 2009, **50**, 748–751, and references therein.

3 H. Munch, J.S. Hansen, M. Pittelkow, J.B. Christensen and U. Boas, *Tetrahedron Lett.*, 2008, **49**, 3117–3119.

4 F. Zhang, X. Wang, C. Cai and J. Liu, *Tetrahedron*, 2009, **65**, 83–86.

5 B. Baghernejad, *Eur. J. Chem.*, 2010, **1**, 54–60.

6 G. Ferguson, C. Glidewell, R.M. Gregson and P.R. Meehan, *Acta Cryst.*, 1998, B**54**, 129–138.

7 P.R. Meehan, G. Ferguson, C. Glidewell and L.L.J. Patterson, *Acta Cryst.*, 1997, C**53**, 628–631.

8 R.C.E. Durley, D.L. Hughes and M.R. Truter, *Acta Cryst.*, 1980, B**36**, 2991–2997.

9 H. Yuge and T. Iwamoto, *Acta Cryst.*, 1995, C**51**, 374–377.

10 C.A. Ellis, S.W. Ng, E.R.T. Tiekinka, J.L. Wardell, *Acta Cryst.*, 2007, E**63**, m806.

11 R.M. Matos and J.G. Verkade, *J. Braz. Chem. Soc.*, 2003, **14**, 71–75.

12 M. Wei and R.D. Willett, *J. Chem. Crystallogr.*, 2002, **32**, 439–445.

13 C.M. M'thiruaine, H.B. Friedrich, E.O. Changamu and M.D. Bala, *Inorg. Chim. Acta*, 2012, **390**, 83–94.

14 Bruker, *APEX2*, SAINT-*plus*, XPREP and *SADABS*, 2008, Bruker-AXS, Inc., Madison, Wisconsin, USA.

15 G.M. Sheldrick, *Acta Cryst.*, 2008, A**64**, 112–122.

16 C.M. M'thiruaine, H.B. Friedrich, E.O. Changamu and B. Omondi, *Acta Cryst.*, 2011, E**67**, m485.

17 C.M. M'thiruaine, H.B. Friedrich, E.O. Changamu and M.D. Bala, *Inorg. Chim. Acta,* 2011, **366**, 105–115.

18 C.M. M'thiruaine, H.B. Friedrich, E.O. Changamu and M.D. Bala, *Inorg. Chim. Acta*, 2012, **382**, 27–34.

19 C.M. M'thiruaine, H.B. Friedrich, E.O. Changamu and B. Omondi, *Polyhedron*, 2012, **40**, 81–92.

20 (a) H. Schumann, M. Speis, W.P. Bosman, J.M.M. Smits and P.T. Buerskens, *J. Organomet. Chem*, 1991, **403**, 165–182; (b) L. Hewison, S.H. Crook, T.R. Johnson, B.E. Mann, H. Adams, S.E. Plant, P. Sawle and R. Motterlini, *Dalton Trans.*, 2010, **39**, 8967–8975; (c) J.A.S. Howel, A.G. Bell, D. Cunningham, P. McArdle, T.A. Albright, Z, Goldschmidt, H.E. Gottlieb and D. Hezroni-Langerman, *Organometallics*, 1993, **12**, 2541–254.

21 T.C. Lewis and D.A. Tocher, *Acta Cryst.*, 2005, E**61**, o2202.

22 G. Ferguson, W. Bell, P.I. Coupar and C. Glidewell, *Acta Cryst.*, 1997, B**53**, 534–543.

23 R.G. Pritchard, M. Ali, A. Munim and A. Uddin, *Acta Cryst.*, 2006, C**62**, m507–m509.

24 G. Ferguson, P.I. Coupar and C. Glidewell, *Acta Cryst.* 1997, B**53**, 513–520.

25 G. Ferguson, C. Glidewell, R.M. Gregson, P.R. Meehan and I.L.J. Patterson, *Acta Cryst.*, 1998, B**54**, 151–161.

26 Z.-M. Jin, L. Li, B. Tu, M.-L. Hu and M.-C. Li, *Acta Cryst.*, 2005, E**61**, o2939.