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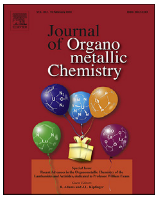

Structures of 1,1′,3,3′-tetra(2-methyl-2-nonyl)ferrocenium(1+) salts of $CB_{11}H_{12}^{-}$, $B_{12}F_{12}^{2-}$, BF_4^{-}, PF_6^{-}, and ClO_3^{-}

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DEDICATION: We dedicate this paper to our friend and fellow boron cluster chemist Narayan S. Hosmane on the occasion of his 70th birthday

Keywords:
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ABSTRACT

The interdigitated and layered structures of the tetraalkylferrocenium salts [DEC][$CB_{11}H_{12}$], $[DEC]_2[B_{12}F_{12}]$, [DEC][BF_4], [DEC][PF_6], and [DEC][ClO_3] were determined by single-crystal X-ray diffraction (DEC^{+} = 1,1′,3,3′-tetrakis(2-methyl-2-nonyl)ferrocenium(1+)). The structures of the salts of the two smaller anions were similar to the previously published oxoanion structures of [DEC][XO_n^{-}] ($XO_n^{-} = NO_3^{-}$, ClO_4^{-}, and ReO_4^{-}), with layers of trigonal-pyramidal ClO_3^{-} or tetrahedral BF_4^{-} anions stuffed between layers of interdigitated ferrocenium ions. The DEC^{+} cations in structures with the more highly charged and/or larger anions $B_{12}F_{12}^{2-}$, $CB_{11}H_{12}^{-}$, and PF_6^{-} are also layered but the interdigitation is not as regular and not as complete as in the structures with relatively small 1− anions. Other differences and similarities of the eight $[DEC]_n[X]$ structures ($n = 1, 2$) are discussed.

1. Introduction

Interactions between derivatized ferrocenes and ferrocenium ions, and/or with co-crystallized solvent molecules or counterions, continues to be of interest, including $C-H\cdots O$, $C-H\cdots\pi$, and $\pi\cdots\pi$ interactions and alkyl-group interdigitation [1–13]. Such interactions can control electrochemical recognition [1,13], ionic liquid melting points [6,8], and magnetic [3–5,7], spectroscopic [2,3], or ion-exchange properties [9–12].

We previously developed an ATR-FTIR technique for the quantitative determination of IR detectable (i.e., polyatomic) aqueous monoanions at ppb levels within minutes with no sample pretreatment [10,14–16]. The key to this methodology was the rapid and selective anion exchange of, for example, aqueous ClO_4^{-}, BF_4^{-}, PF_6^{-}, and $CB_{11}H_{12}^{-}$ with the NO_3^{-} counterion in a thin film of the lipophilic organometallic extractant [DEC][NO_3] coated on a silicon ATR crystal (DEC^{+} = 1,1′,3,3′-tetrakis(2-methyl-2-nonyl)ferrocenium(1+)). For example, the ten-minute limit of detection of aqueous ClO_4^{-} using this methodology was found to be 0.03 μM (3 ppb). Some ClO_4^{-}, BF_4^{-}, PF_6^{-}, and $CB_{11}H_{12}^{-}$ ion-exchange ATR-FTIR spectra adapted from Refs. [10] and [16] are shown in Fig. S1 in the ESI.

In 2012 we published the structures of DEC, [DEC][NO_3], [DEC][ClO_4], and [DEC][ReO_4] [9]. The monovalent oxoanion salts formed unprecedented structures that clearly facilitated the ion-exchange process, with alternating ionic and alkane-like domains tilted 60–80° with respect to layers of XO_n^{-} anions stuffed between two-dimensional layers of the interdigitated ferrocenium cations. In this work we report the structures of five new DEC^{+} salts of anions with a greater range of size, shape, and charge: trigonal-pyramidal ClO_3^{-}, tetrahedral BF_4^{-}, octahedral PF_6^{-}, and icosahedral $CB_{11}H_{12}^{-}$ and $B_{12}F_{12}^{2-}$. There are recent structures of ferrocenium salts other than DEC^{+} with BF_4^{-} [3,17] or PF_6^{-} [3] counterions, but this work represents the first examples of salts of any metallocenium cation and an icosahedral anion.

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Table 1
Crystal data and structure refinement parameters.[a]

Compd abbreviation		$[DEC^+]_2[B_{12}F_{12}^{2-}]$	$[DEC^+][CB_{11}H_{12}^-]$	$[DEC^+][BF_4^-]$	$[DEC^+][PF_6^-]$	$[DEC^+][ClO_3^-]$
chemical formula		$C_{100}H_{180}B_{12}F_{12}Fe_2$	$C_{51}H_{102}B_{11}Fe$	$C_{50}H_{90}BF_4Fe$	$C_{50}H_{90}FeF_6P$	$C_{50}H_{90}ClFeO_3$
formula weight, g mol^{-1}		1851.90	890.08	833.90	892.06	830.55
crystal system		triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group, Z		$P\bar{1}$, 1	$P\bar{1}$, 2	$P2/n$, 2	$P2_1/n$, 4	$P2/n$, 2
color of crystal		green	green	green	green	green
unit cell dimensions	a, Å	11.6816(4)	12.739(4)	10.0963(4)	8.9064(3)	9.9951(4)
	b, Å	15.0467(5)	14.991(3)	8.6805(4)	17.8513(5)	8.6933(4)
	c, Å	17.3113(6)	17.380(5)	28.4213(14)	32.268(1)	28.3675(11)
	α, deg	66.018(1)	113.320(6)	90	90	90
	β, deg	70.594(1)	100.994(7)	98.904(1)	97.126(1)	98.131(2)
	γ, deg	80.770(2)	91.522(7)	90	90	90
unit cell volume, $Å^3$		2621.1(2)	2774(1)	2460.9(2)	5090.7(3)	2440.1(2)
temperature, °C		−153(2)	−153(2)	−173(2)	−153(2)	−153(2)
final R indices $[I > 2\sigma(I)]$		$R_1 = 0.0413$, $wR_2 = 0.0971$	$R_1 = 0.0499$, $wR_2 = 0.1244$	$R_1 = 0.0314$, $wR_2 = 0.0843$	$R_1 = 0.0381$, $wR_2 = 0.1506$	$R_1 = 0.0418$, $wR_2 = 0.1125$
goodness-of-fit on F^2		1.027	1.043	1.051	1.182	1.042
CCDC deposition no.		1811819	1811818	1811820	1811822	1811821

[a] $DEC^+ = 1,1',3,3'$-tetra-(2-methyl-2-hexyl)ferrocenium(1+).

2. Results and discussion

2.1. General comments

Crystal data and final refinement parameters for the five single-crystal X-ray structures reported in this work are listed in Table 1. Selected distances and angles are listed in Table 2. Thermal ellipsoid plots of the five structures are shown in Figs. S2–S6 in the ESI.

2.2. Structures of $[DEC^+][BF_4^-]$ and $[DEC^+][ClO_3^-]$

$[DEC][BF_4]$ and $[DEC][ClO_3]$ exhibit the “standard” layered structures previously observed for $[DEC][NO_3]$, $[DEC][ClO_4]$, and $[DEC][ReO_4]$ [9]. This consists of alternating layers of interdigitated DEC^+ cations and BF_4^- (or ClO_3^-) anions, as shown in Fig. 1 for $[DEC][BF_4]$ and in Fig. S7 for $[DEC][ClO_3]$. At an angle of 62.7° to the Fe_n and $[BF_4^-]_n$ layers are layers of cations *and* anions, with the Fe and B atoms forming rigorously planar rectangular arrays, as shown in Fig. 2, with pairs of Fe···B distances of 5.48 and 8.27 Å and with pairs of Fe···Fe (or B···B) distances of 8.68 and 10.10 Å. The corresponding distances and angles for the other [DEC][X] structures with trigonal or tetrahedral anions are listed in Table S1 ($X^- = ClO_3^-$, NO_3^-, ClO_4^-, and ReO_4^-).

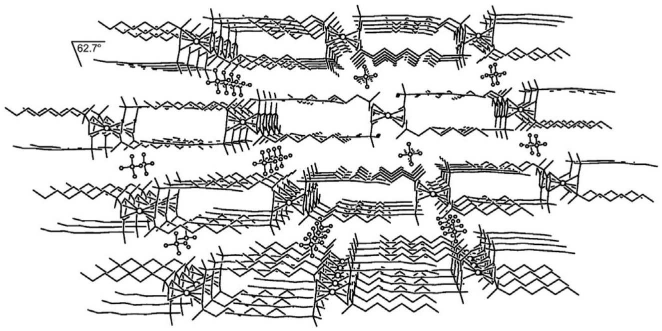

Fig. 1. The structure of $[DEC][BF_4]$. Layers of interdigitated DEC^+ cations are separated by layers of BF_4^- anions. The rigorously co-planar Fe_n planes are 8.97 Å apart. Planes containing both cations and anions, in which the Fe and B atoms are rigorously co-planar, are tilted 62.7° from the first set of planes and have an interplanar separation of 14.04 Å.

Table 2
Selected structural parameters.[a]

compd abbreviation	$[DEC^+]_2[B_{12}F_{12}^{2-}]$	$[DEC^+][CB_{11}H_{12}^-]$	$[DEC^+][BF_4^-]$	$[DEC^+][PF_6^-]$	$[DEC^+][ClO_3^-]$
range of Fe—C distances, Å	2.056(2)–2.159(2)	2.049(2)–2.156(2)	2.075(1)–2.178(1)	2.065(3)–2.171(3)	2.067(1)–2.167(1)
average Fe—C distance, Å	2.110	2.104	2.127	2.115	2.117
Fe···Ct distance(s), Å	1.726, 1.730	1.723, 1.723	1.743	1.734, 1.736	1.734
Ct···Fe···Ct angle, deg	175.1	175.3	174.8	175.7	175.2
Cp···Cp tilt angle, deg	9.4	10.6	10.8	9.3	10.0
shortest Fe···X distance(s), Å	7.08, 7.10[b]	6.69, 6.99	5.48 × 2	5.790, 5.810	5.549 × 2[c]
next shortest Fe···X distance(s), Å	13.61, 13.64	7.39, 8.13	8.27 × 2	7.896, 8.171	8.028 × 2[c]
shortest Fe···X distance(s), Å	8.03, 9.96	8.68, 8.86	8.68 × 2	8.91 × 2	8.851 × 2
next shortest Fe···Fe distance(s), Å	11.68 × 2	10.07, 10.38	10.10 × 2	9.60 × 2[d]	10.458 × 2
Fe_n interplane distance, Å[e]	[12.89]	[15.50]	8.97 [14.04]	[16.30]	9.158 [14.04]
ionic layer offset angle, deg	–	–	62.7	–	61.1

[a] $DEC^+ = 1,1',3,3'$-tetra-(2-methyl-2-nonyl)ferrocenium(1+) cation; Ct = the centroid of each cyclopentadienyl ring; X = the central atom of the BF_4^- or PF_6^- anion, the centroid of the Cl···Cl vector for the disordered ClO_3^- anions in $[DEC^+][ClO_3^-]$, the centroid of the 10 B atoms of the $CB_{11}H_{12}^-$ anion that are not antipodal to the cage C atom in $[DEC^+][CB_{11}H_{12}^-]$, or the centroid of the 12 B atoms of the $B_{12}F_{12}^{2-}$ anion in $[DEC^+][B_{12}F_{12}^{2-}]$.

[b] These are the two distances between Fe2 and the two nearest B_{12} centroids. The two Fe···(B_{12} centroid) distances are nearly the same, 7.08 and 7.09 Å.

[c] These are distances between the Fe atom and the centroid of the disordered Cl atoms (these Cl atoms share the same three O atoms).

[d] The other two Fe···Fe distances that complete the hexagonal array of Fe atoms in $[DEC][PF_6]$ are 10.47 Å.

[e] The distances in square brackets are between Fe_n planes of DEC^+ molecules that are interdigitated.

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