Sonochemical Reaction of $[Fe(CO)_5]$ with 1-Methylimidazole in An Ionic Liquid: Formation of $[(1\text{-Methylimidazole})_6Fe^{II}](PF_6)_2$

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The ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, $(BMI^+)(PF_6^-)$, has been used as a solvent in the sonochemical reaction of 1-methylimidazole and $[Fe(CO)_5]$ at 40–50 °C under air. The reaction afforded $[(1\text{-methylimidazole})_6Fe^{II}](PF_6)_2$, the structure of which was determined at 293 K by single-crystal X-ray diffraction methods. The salt crystallizes in the trigonal space group $P\bar{3}$ with unit-cell parameters of a = 11.4603(16) Å, c = 8.0172(11) Å, and Z = 1. The crystals showed twinning by merohedry, which was accounted for in the structure determination and refinement calculations. All the 1-methylimidazole ligands are equivalent, with a Fe–N bond length of 2.204(3) Å. Mössbauer spectroscopy confirmed the presence of Fe^{2+}.

Introduction

Ionic liquids are generally considered to be noncoordinating green solvents in organic synthesis and catalysis.[1] However, there are few examples where ionic liquids behave as templates or charge-compensating groups in the reactions. Xiao et al.[2] were the first to report the in situ formation of 1-butyl-3-methylimidazole-2-ylidene (bmiy) complexes of palladium $[Br(\mu\text{-}Br)(bmiy)Pd]_2$ and $[Br_2(bmiy)_2Pd]$ in 1-butyl-3-methylimidazolium bromide ionic liquid. Welton et al.[3] have studied the in situ formation of the mixed phosphane imidazolylidene palladium complexes $[(PPh_3)_2Pd(bmimy)X](BF_4^-)$ at room temperature in 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid (where X = Cl, Br). These references show the solvent incorporation behavior of the ionic liquid in the final product. Aggarwal et al.[4] have reported unexpected side reaction of imidazole-based ionic liquids in the base-catalysed Baylis−Hillman reaction. Zaworotko et al.[5] synthesized *trans*-$[(1\text{-Meim})_4F_2Fe]BF_4$ in 1-methylimidazolium tetrafluoroborate ionic liquid as a reactant. In the solvothermal synthesis of the coordination polymer $[Cu^I(bpp)]$-BF_4, using 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid as solvent, Li et al.[6] found that BF_4^- anions entered the final structure as a charge-compensating species.

Although ionic liquids have several important properties that could make them useful in various chemical processes,[1,7−16] experimental evidence is lacking in the field of coordination chemistry, wherein ionic liquids act as clean, effective solvents for the crystallization of complexes. To explore the reactions in ionic liquids, we report here the inorganic synthesis of (1-methylimidazole)iron complex in ionic liquid (as solvents) under sonochemical conditions.

Transition metals and imidazole play an important role as an active centre of metalloproteins, as well as in many other biological systems such as hemoglobin, vitamin B_{12},[17] and F_{430}. The interaction between imidazole ligand and transition metal ions[17−20] forms well-defined complexes whose stoichiometry is $M(Im)_6X_2$, M = Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} ions.[18,19] The structures of known *N*-substituted imidazole complexes of transition metal ions have been studied extensively.[21] An $[(1\text{-methylimidazole})_6Fe^{II}]^{2+}$ complex has been prepared using iron(II) salts as precursors for iron.[21b,21c]

A further literature survey revealed a reaction of ferrocene and cyclopentadienyl irondicarbonyl with imidazole

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(unsubstituted), yielding $\text{Fe(N}_2\text{C}_3\text{H}_3)\cdot0.71\text{N}_2\text{C}_3\text{H}_4$ with fourfold, as well as sixfold, coordinated metal ions.[22] For substituted imidazole, only a fourfold coordinated iron is detected.[22]

In 1980 a paper reported on the reaction of 1-methyl-, 1-ethyl-, 1,2-dimethyl- and 1,2,3,4-tetramethylimidazole with $[\text{Fe(CO)}_5]$, yielding $(\text{FeIm}_6)[\text{Fe(CO)}_8]$, $(\text{FeIm6})[\text{Fe(CO)}_4]_2$, $(\text{FeIm}_4)[\text{Fe(CO)}_4]$ and Fe(Im)(CO)_2, respectively, (Im = substituted imidazole).[23] The reaction product of $[\text{Fe(CO)}_5]$ with 2-ethylimidazole shows that the anion is $[\text{HFe(CO)}_5]^-$ rather than $[\text{Fe(CO)}_4]^-$, as proposed by Seel et al.[23,24]

The ionic liquid used in our system is composed of an asymmetric 1-butyl-3-methylimidazolium cation (BMI^+) with a bulky hexafluorophosphate (PF_6^-) anion. Ionic liquids exhibit unique properties, including high thermal stability, a large liquid range, and negligible vapour pressure.[25] The latter property could change the characteristics of acoustic cavitation and make ionic liquids potentially attractive for use in sonochemical reactions. Acoustic cavitation, i.e., the formation, growth and implosive collapse of bubbles in a liquid medium, is principally responsible for sonochemistry.[26] The collapse of such bubbles creates hot spots (≈ 5000 °C), high pressures (1000 atm), and very high cooling rates (10^{10} $\text{K}\cdot\text{s}^{-1}$),[27] leading to the extreme conditions responsible for various chemical and physical effects.

Upon cavitational collapse, vapours inside the bubble undergo a gas-phase reaction. It is of great importance that only vapours of the volatile solutes, and not of the solvent, are inside the collapsing bubble, and so low vapour pressure solvents such as decalin, hexadecane, and isodurene are common in sonochemistry.[28] Suslick et al. have shown that sonication of $[\text{Fe(CO)}_5]$ in decane (for 3 h in a dry-ice acetone bath) affords amorphous iron that contains 3% carbon, 2% hydrogen, and 1% oxygen, by weight.[29] The amount of contaminants was reduced sharply upon a shorter sonication time.[30] Such contaminants originate from the small amount of decane vapour found inside the collapsing bubble. The search for low vapour solvents has led recently to the use of diphenylmethane.[31] Ionic liquids are good candidates for this purpose due to their low vapour pressure.

Recently, Suslick et al. have studied the effect of acoustic cavitation on pure ionic liquids sonicated at 20 kHz, and at ca. 60 $\text{W}\cdot\text{cm}^{-2}$ for 3 h at 85−135 °C. The reaction led to the decomposition of the ionic liquid and the products in the headgas were analyzed by gas-chromatography.[32] The ionic liquid decomposed at 1.9−3.8 $\mu\text{mol}\cdot\text{min}^{-1}$, so that after 180 min less than 1% of the ionic liquid had decomposed. $[\text{Fe(CO)}_5]$ yields amorphous iron nanoparticles upon sonication under argon, wheras sonication under air affords nanosized amorphous Fe_2O_3.[33,28] Decalin was used as solvent for both sonications.

The current paper reports an *inorganic* sonochemical reaction carried out in an ionic solvent. $[\text{Fe(CO)}_5]$ (reactant I), and 1-methylimidazole (reactant II) were reactants, while the ionic solvent was 1-butyl-3-methylimidazole hexafluorophosphate (BMI^+)(PF_6^-). The product was composed of iron originating from reactant I, 1-methylimidazole from reactant II, and the PF_6^- anion from the ionic liquid. This product differs from the sonochemical product obtained in the dissociation of $[\text{Fe(CO)}_5]$ in organic solvents such as decalin or hexadecane.[28,29a] Products of all the reactions conducted using transition metal carbonyls were amorphous. This due to the fast cooling rates obtained when the bubble collapses, which prevent crystallization of the product. Here, our focus is on the crystalline product obtained after the sonication reaction. The possibility of producing crystalline products under sonochemical reaction makes our research especially interesting. The structure of the complex was characterized by single crystal and powder X-ray diffraction (XRD) analysis.

Results and Discussion

The single-crystal structure analysis shows that the Fe^{2+} atoms are coordinated by six 1-methylimidazolium groups with an equivalent Fe−N (2.204(3) Å) bond length. This distance is within the range observed for other reported Fe−N distances.[5,21a,21c] Two PF_6^- ions balance the positive charge. The coordination polyhedron around the P atom is slightly disordered and the fluorine atoms were refined with an occupancy factor of 0.333. Figure 1 shows an ORTEP perspective of the $[(1\text{-methylimidazole})_6\text{Fe}^{II}](\text{PF}_6)_2$. Table 1 presents crystal and structure refinement data.

Table 1. Crystal and structure refinement data for $[(1\text{-methylimidazole})_6\text{Fe}^{II}](\text{PF}_6)_2$

Empirical formula	$\text{C}_{24}\text{H}_{36}\text{F}_{12}\text{FeN}_{12}\text{P}_2$
Molecular mass	838.44
Temperature	293(2) K
Wavelength	0.71073 Å (Mo-K_α)
Crystal system	trigonal
Space group	$P\bar{3}$ (No.147)
Unit cell dimensions	a = 11.4603(16) Å; a = 90 deg.
b = 11.4603(16) Å; β = 90 deg.	
c = 8.0172(11) Å; γ = 120 deg.	
Volume	911.9(2) Å^3
Z, calculated density	1, 1.527 Mg/m^3
Absorption coefficient	0.599 mm^{-1}
F(000)	428
Color, habit	colorless, needle
Crystal size	0.02 × 0.02 × 0.4 mm
Theta range for data collection	2.05−25.17 deg.
Limiting indices	$-13 \le h \le 12$, $-13 \le k \le 13$, $-9 \le l \le 9$
Reflection collected/unique	5824/1078 [$R_{(\text{int})}$ = 0.0806]
Reflections with $I > 2\sigma$ (I)	890
Absorption correction	none
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	1078/0/116
Goodness-of-fit on F^2	1.116
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0440, $wR2$ = 0.0718
R indices (all data)	$R1$ = 0.0597, $wR2$ = 0.0764
Largest diff. Peak and hole	0.159 and −0.198 Å^{-3}

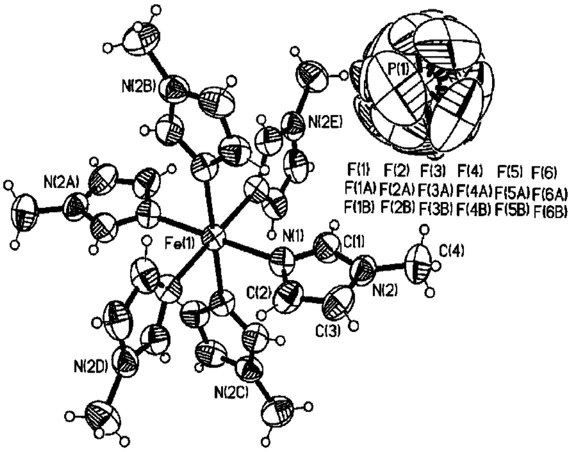

Figure 1. Perspective ORTEP view of $[(1\text{-methylimidazole})_6Fe^{II}](PF_6)_2$ (50% probability displacement ellipsoids); hydrogen atoms omitted for clarity

In parallel, powder XRD (PXRD) structural investigations of the bulk sample reproduced the single crystal results, and confirmed the single-phase purity of the product. Figure 2 illustrates the final agreement between the experimental and calculated PXRD profiles. All observed PXRD peaks are explained fairly well by the refined structure model.

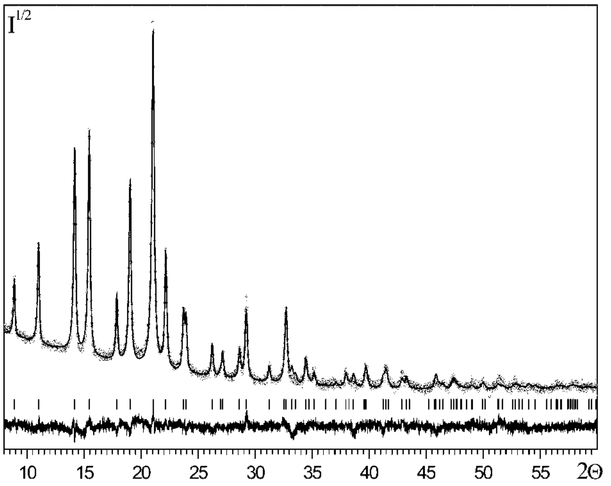

Figure 2. Weighted experimental (circles), calculated (solid line) and difference (bottom curve) PXRD profiles for $[(1\text{-methylimidazole})_6Fe^{II}](PF_6)_2$. Reflection positions are marked by ticks

Vibrational bands in the Raman and IR absorption spectra of the complex (Figure 3) are assigned in Table 2. The vibrational bands of the ligands are shifted, as reported previously by Reedijk,[34] Perchard and Novak.[35] M–N vibrations in the Raman spectrum below 300 cm^{-1} are in accordance with the literature values.[34] The intense Raman line at 739 cm^{-1} is assigned to the symmetric ν_1 mode of the PF_6^- ion.[36]

NMR studies of ^{31}P and ^{19}F confirm the presence of PF_6^- anions (Figure 4). The ^{31}P NMR spectrum shows septet with respect to fluorine and the ^{19}F NMR spectrum shows the doublet with respect to phosphorus (where $I_P = 1/2$ and $I_F = 1/2$).

Table 2. Raman and IR vibration bands (cm^{-1}) for $Fe^{II}(1\text{-methylimidazole})_6(PF_6)_2$ (w = weak, m = medium, s = strong and br. = broad)

Assignments	Vibration frequency $[(C_4H_6N_2)_6Fe](PF_6)_2$ IR (cm^{-1})	Raman (cm^{-1})
C–H stretching	3139 m	3153 m
CH_3 stretchings	2971 m	2970 m
Combination bands	1614 w	–
Ring stretching (R^1)	1533 s	1531 m
Ring stretching (R^2)	–	1513 m
CH_3 bending	1465 w	–
CH_3 bending	1425 m	1425 m
Ring stretching (R^3)	–	1346 s, br.
Ring stretching (R^4)	1335 w	–
In plane C–H bending	1287 s	1281 m
Ring stretching (R^5) + CN stretch	1233 s	1229 m
In plane C–H bending	1092 s	1087 m, br.
CH_3 deformation	1029 m	1024 s
Ring stretching (R^6)	939 s	933 m
Out-of-plane C–H bending	845 s, br.	–
Out-of-plane C–H bending	760 m	–
Ring stretching and CN stretching	661 m	666 s
Ring deformation	618 m	–
C–N deformation	–	368 m
C–N deformation	–	237 m

Mössbauer spectroscopic data confirm the +2 oxidation state of iron with an isomeric shift (IS) = 1.041 mm s^{-1} and a quadrupole splitting (QS) = 0.769 mm s^{-1}, which agree with the literature values.[19,23] The Mössbauer spectrum does not show Fe^{III} impurities. The mass spectrum of the complex, obtained by desorption chemical ionization (DCI) using methane, shows the 1-methylimidazole peak at $m/z = 82$. The PF_6^-anion of the complex appears at $m/z = 145$ under fast atom bombardment (FAB)-glycerol in methanol. Elemental analysis for $[(1\text{-methylimidazole})_6Fe^{II}](PF_6)_2$ also matches the calculated theoretical values.

Following previous sonochemical experiments,[29] we assume that the first stage of the current reaction involves the decomposition of $[Fe(CO)_5]$ to Fe and CO. The CO is then released from the sonication cell, while the Fe(0) is oxidized by air to Fe^{2+} ions in the $(BMI^+)(PF_6^-)$ ionic liquid. Sonication of $[Fe(CO)_5]$ under the same conditions in decalin gave amorphous Fe_2O_3.[28] Unlike the reaction in decalin, here the surrounding environment of the 1-methylimidazole and the ionic liquid $(BMI^+)(PF_6^-)$ prevented complete oxidation of the iron. Our first assumption is, following earlier reports,[2–6] that the ionic liquid is the source of the imidazole ring and the counterion (PF_6^-) in the product, while losing a 1-butyl group during the reaction. This assumption might also agree with the decomposition product of the sonication of $(BMI^+)(PF_6^-)$ under argon[32] where the cation of the ionic liquid $(BMI^+)(PF_6^-)$ loses a butyl/methyl group. ^1H and ^{13}C NMR analysis of the product of the ionic liquid reaction indicates the presence of a 1-methylimidazole, but no butyl group. This means that the 1-meth-

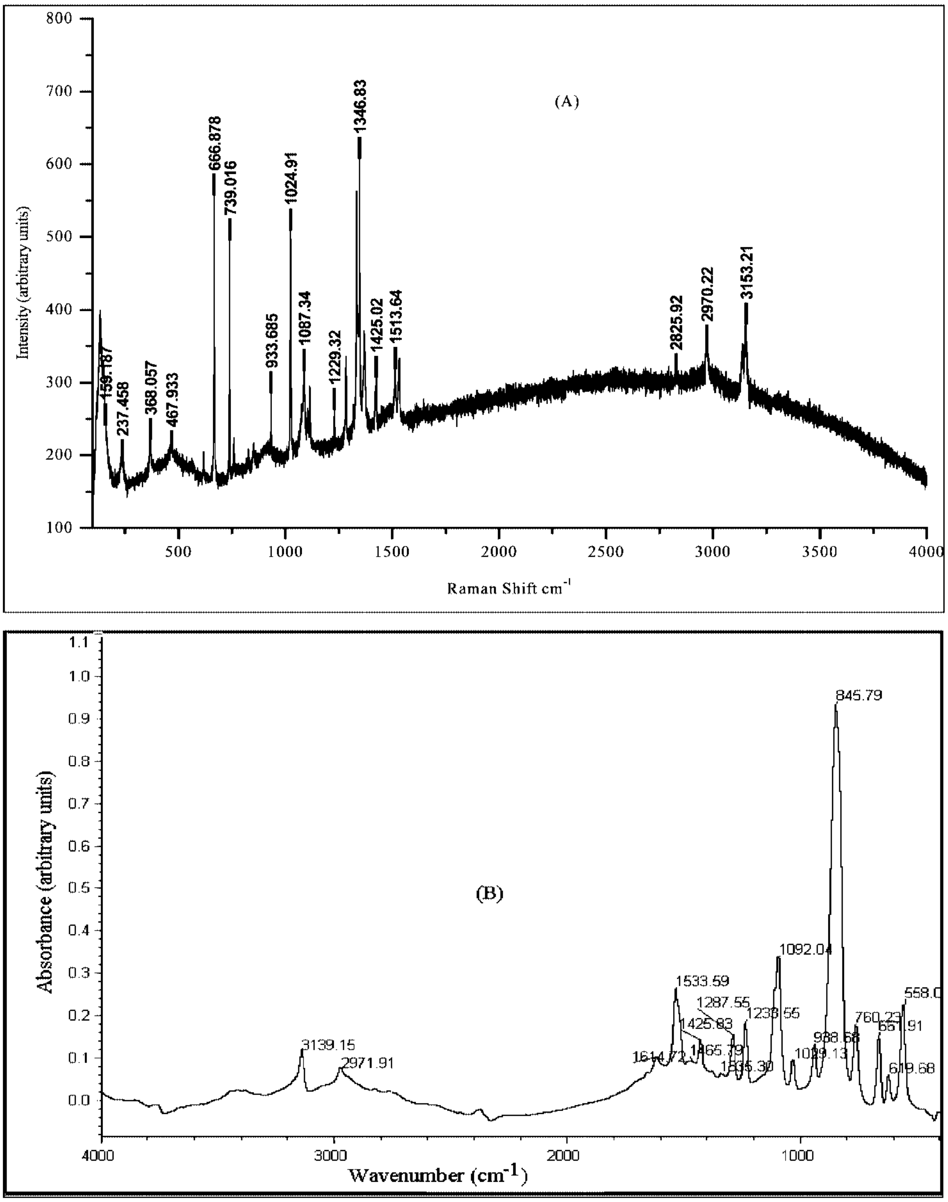

Figure 3. Raman (A) and IR (B) absorption spectrum of [(1-methylimidazole)$_6$Fe^{II}](PF$_6$)$_2$

ylimidazole source is not the ionic liquid, but the reactant II. Conversely, the anions in the product originate from the ionic liquid.

To investigate the purity of the ionic liquid, (BMI$^+$)(PF$_6$$^-$), its thermal decomposition[37] was studied by TGA (Thermo Gravimetric Analysis) between 25 and 1000 °C at 3 °C min^{-1} in a N$_2$ flow. Water, as an impurity, causes the partial decomposition of the ionic liquid, with the formation of phosphate, HF and transition metal fluorides.[38] The (BMI$^+$)(PF$_6$$^-$) was thermally stable at 330 °C and decomposed completely at 516 °C, confirming that it is stable at the reaction temperature, without forming metal fluorides, and that it undergoes a chemical reaction only due to the temperature developed as a result of the bubble collapse.

A control reaction sonicating the same concentration of [Fe(CO)$_5$] in the ionic liquid (BMI$^+$)(PF$_6$$^-$) (without 1-methylimidazole) under an air atmosphere at 40−50 °C yielded a very small amount of an amorphous product (6 mg). A second control reaction, conducted by sonicating [Fe(CO)$_5$] in 1-methylimidazole (no ionic liquid), gave an amorphous product. After crystallization Fe$_2$O$_3$ was identified (PXRD) as the product. This is a main difference between the sonochemical reaction and that in ref.[23], which produces a crystalline product. The time and temperature of the reaction (30 min, 40−50 °C here) also differ (3−6 h, 60−80 °C[23]). The difference between a regular reaction[23] and that of [Fe(CO)$_5$] and imidazole in an ionic liquid is that sonication leads to the loss of CO while the products of a regular reaction contain the carbonyl. Moreover, the

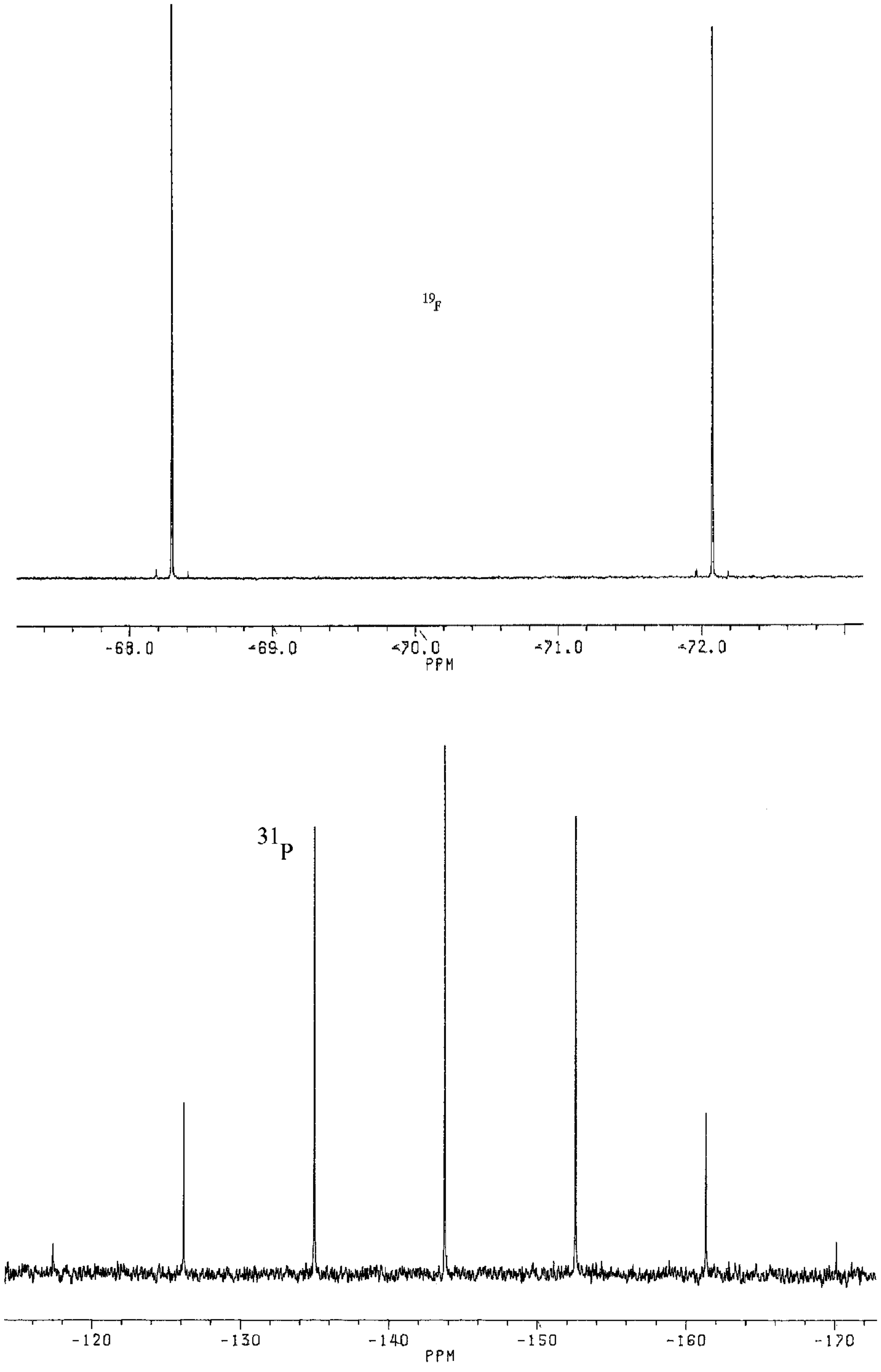

Figure 4. ^{19}F and ^{31}P NMR spectrum of $[(1\text{-methylimidazole})_6Fe^{II}](PF_6)_2$

negative ions originate from the ionic liquid in our reaction, while $[Fe(CO)_5]$ is their source in a regular reaction.[23]

Conclusions

The sonication product of 1-methylimidazole and $[Fe(CO)_5]$ in $(BMI^+)(PF_6^-)$ (which acts as a solvent) gives a complex of $[(1\text{-methylimidazole})_6Fe^{II}](PF_6)_2$ under air. Unlike ref.[2,3,5], where the cation and the anion contribute to the structure of the final product, here only the anion is part of the product, which is similar to ref.[6]. In this sonochemical reaction, Fe^{2+} ion is coordinated octahedrally by six 1-methylimidazole. PF_6^- acts as a charge-stabilizing agent in the formation of the crystal salt, which is characterized by a trigonal crystal lattice with a $P\bar{3}$ space group. To probe the effect of the ionic liquid as a solvent on sonochemical reactions, studies on similar systems using different ionic liquids and transition metal carbonyls are in progress and will be reported soon.

Experimental Section

General Remarks: Ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [(BMI$^+$)(PF$_6^-$)] (Aldrich, 96%), 1-methylimidazole (Aldrich, 99%), and pentacarbonyliron (Strem chemicals, USA, 99.5%, refer to MSDS for safety precaution) were purchased from the Aldrich Chemical Co. and used without further purification.

Synthesis of Complex: Pentacarbonyliron [Fe(CO)$_5$] (1.49 g, 6.08 mmol) and 1-methylimidazole (2 g, 24.3 mmol) were dispersed in the ionic liquid (BMI$^+$)(PF$_6^-$) (5 g, 17.6 mmol) under ultrasonic conditions. Sonication was carried out with a high intensity ultrasonic horn (Sonics and Materials Model VC-600, Ti-horn, 20 kHz, 40 W·cm^{-2}) for 30 min under an air atmosphere. The reaction cell was placed in the exhaust hood so that CO was not released into the laboratory (please refer to MSDS for correct handling of these chemicals). The temperature was maintained at around 40−50 °C using a (Julabo FT 901) acetone cooler bath, as the reaction temperature in ionic liquids rises to about 200 °C without cooling. After completion of the reaction, the ionic liquid changed from clear brown to black. Ethanol was used to precipitate a grey powder and to develop the transparent crystals. The amount of product collected after 30 min of sonication was 1.414 g (1.68 mmol). The yield with respect to iron was 28%.

X-ray Crystallographic Study

Single Crystal XRD: A needle-shaped crystal (0.02 × 0.02 × 0.40 mm^3) was mounted on the tip of a glass fiber. Diffraction data were recorded on a Stoe imaging plate detector system (IPDS-II). The diffraction symmetry was consistent with Laue group $\bar{3}$. Since no systematically extinct reflections were observed, space groups $P3$ and $P\bar{3}$ were taken into consideration. Subsequent structure determination confirmed the adequacy of the centrosymmetric space group. Due to the low linear absorption coefficient of the material ($\mu = 0.6$ mm^{-1}) for Mo-K_α radiation, no absorption correction has been applied. Data reduction included Lorentz and polarization corrections. The structure was solved by direct methods using the SHELXS-86 program system.[39] Subsequent refinement calculations were also performed with SHELXL-97,[40] using neutral atomic scattering factors. In the initial stages of the structure determination, several models were obtained that were less satisfactory from a crystal chemical point of view. Finally, a possible twinning of the crystal was considered to explain these difficulties. Since the differences between the internal residuals for merging the data in the two Laue groups $\bar{3}$ and $6/m$ were not very pronounced (0.078 and 0.109, respectively), a twinning according to $m_{[001]}$ was assumed. This type of twinning results in an exact superposition of the reciprocal lattices of the two twin domains. The twinning model was introduced into the refinements and resulted in a significant improvement. The volume fraction of the twin component I was refined to 0.438(3). For the final, least-squares cycles, anisotropic displacement parameters were used for the non-hydrogen atoms. Hydrogen atoms were added geometrically, and refined using a riding model with isotropic displacement parameters 1.2 or 1.5 times higher than U_{eq} of the aromatic or methyl carbon atoms.

Powder-XRD: PXRD data were collected in Bragg−Brentano geometry using a DRON-4 diffractometer with graphite secondary monochromator (Cu-K_α radiation) and scintillation counter. Measurements were taken at room temperature in air. The unit cell parameters of the crystalline powder product were determined from the PXRD peak positions. A preliminary structure model was estimated by searching the Cambridge Structure Database.[41] Several structures were found with similar crystal lattice dimensions and cognate structure units to those expected for the studied compound: hexakis(*N*-methylimidazole)ruthenium(II) bis(trifluoromethanesulfonate), hexakis(2-methyltetrazole)nickel(II) bis(tetrafluoroborate), and hexakis(5-methylpyrazole)nickel diperchlorate.[42] Considering the synthesis mixture composition and the analogous structures, the formula of the studied compound was assumed to be hexakis(*N*-methylimidazole)iron(II) bis(hexafluorophosphate). A trial structure model was built based on the atomic coordinates of the analogues. Further full-profile PXRD structure refinement utilizing the Rietveld[43] method confirmed the structure model, which was identical to that obtained from the single-crystal study.

Instrumentation: A Raman absorption spectrum of the title compound was recorded with a Jobin Yvon Horiba Raman spectrometer using a 514.532 nm laser in the range 100−4000 cm^{-1}. An IR absorption spectrum was recorded with a Nicolet (Impact 410) spectrometer in the range 400−4000 cm^{-1}. For IR measurements, a pellet containing 200 mg of KBr and 1 mg of the product was prepared. NMR spectra were recorded with an AC Bruker 200 instrument. Mass spectra were recorded with a VG-autospec instrument.

[(1-Methylimidazole)$_6$Fe^{II}](PF$_6$)$_2$: ^{1}H NMR ([200.1 MHz, [D$_6$]DMSO, ppm): $\delta = 3.59$ [s, 3 H, N−CH$_3$], 6.86 [s, 1 H, H(5)], 7.06 [s, 1 H, H(4)], 7.55 [s, 1 H, H(2)].^{13}C NMR (50.3 MHz, [D$_6$]DMSO, ppm): $\delta = 33.66$ [N−CH$_3$)], 121.61 [C(5)], 128.55 [C(4)], 138.57 [C(2)]. ^{31}P NMR (81.0 MHz, [D$_6$]DMSO, ppm): $\delta = -143.85$ (septet, $J_{\mathrm{PF}} = 709$ Hz). ^{19}F NMR (188.3 MHz, [D$_6$]DMSO, ppm): $\delta = -70.21$ (d, $J_{\mathrm{PF}} = 709$ Hz). $C_{24}H_{36}F_{12}FeN_{12}P_2$ (838.44): calcd. C 34.34, N 20.03, H 4.29; found C 34.61, N 19.98, H 4.33.

CCDC-228751 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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