

	Experiment title:	Experiment number: CH-2417
Beamline: ID18	Date of experiment: from: 04/07/2007 to: 10/07/2007	Date of report: 22/08/2007
Shifts: 15	Local contact(s): A. I. Chumakov	<i>Received at ESRF:</i>
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Report:

The Michael reaction ([1], Fig. 1) is one of the most important C–C bond forming reactions in organic chemistry. When carried out in the presence of Fe(III) salts, conversion takes place under relatively mild conditions [2]. A mechanism for the underlying catalytic cycle was proposed and corroborated by kinetic studies and *ab initio* density functional calculations ([3] and Fig. 2). Combined studies using XAS, UV/VIS and Raman spectroscopy [4] revealed that the compound formed in the first reaction step (i.e. when $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ or $\text{Fe}(\text{ClO}_4)_3 \cdot 9 \text{H}_2\text{O}$ is dissolved in the Michael donor 2-oxocyclopentanecarboxylate) can be described as a bis-diketonato-iron(III) unit probably coordinated with two water molecules. Information on the precise geometry and bonding strengths is now mandatory in order to proceed towards understanding the nature of the species undergoing further reaction. Moreover, in addition to the FeCl_4^- anion, which acts as an iron sink and therefore decreases the efficiency of the reaction, the existence of other chloroferrate species is under debate [5]. In the present experiment, we have used nuclear inelastic scattering (NIS) to monitor selectively the bonding around the central iron atom [6].

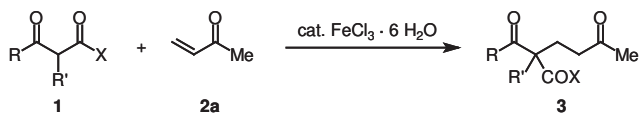


Fig.1: Scheme of the Michael reaction

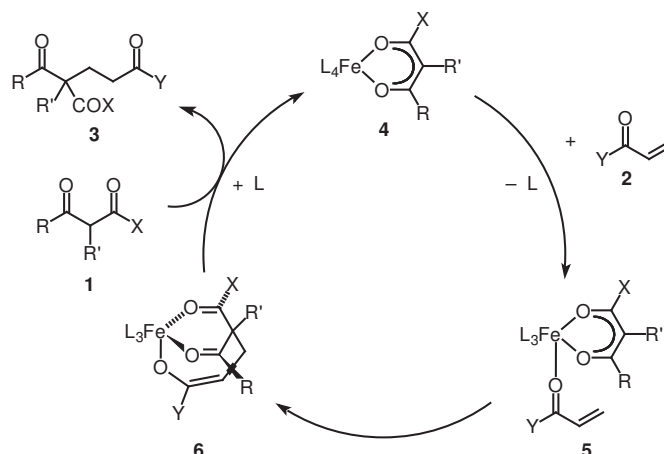


Fig.2: Proposed mechanism according to [3]

We have carried out NIS experiments at the ID18 beamline using an inline-geometry high-resolution monochromator [7] (outer crystals: Si (4 4 0), outer crystals: Si (10 6 4)) yielding an overall energy resolution of about 1.0 meV or 8 cm⁻¹ and high spectral flux. The powder samples were pressed into disk shape (8 mm diameter), sealed into copper holders with kapton windows and placed nearly horizontally with 5° inclination to the beam, in order to ensure maximum count rate. The liquid samples were prepared *ex situ* and injected into copper holders coated with parylene (so as to avoid corrosion of the copper) sealed with kapton windows. Measurements were done at around 70 K on three solid reference compounds – N(CH₃)₄⁺ FeCl₄⁻, Fe(acac)₃, and FeCl₃*6H₂O – and on the frozen solutions of FeCl₃*6H₂O dissolved in **1** both without and with methyl vinyl ketone added.

Fig. 3 shows the complementarity of Raman spectroscopy and NIS at the example of solid tetramethyl ammonium tetrachloroferrate (where the normal vibrations of the FeCl₄⁻ unit known from literature are marked by vertical arrows). The tetrachloroferrate ion was shown to be formed in equimolar amounts with the di-ketoester complex when FeCl₃*6H₂O is added to the ketoester **1** [4]. Fig. 4 depicts the vibrational density of states (VDOS) of the iron atoms in four different samples studied by NIS. An additional spectrum (not shown) was measured of the reaction mixture where also the reactant methyl vinyl ketone was added. Within the experimental accuracy, this spectrum was identical to the one of ferric chloride hexahydrate dissolved in **1**, with however a very slight shift of the 385 cm⁻¹ band of FeCl₄⁻ towards lower frequencies.

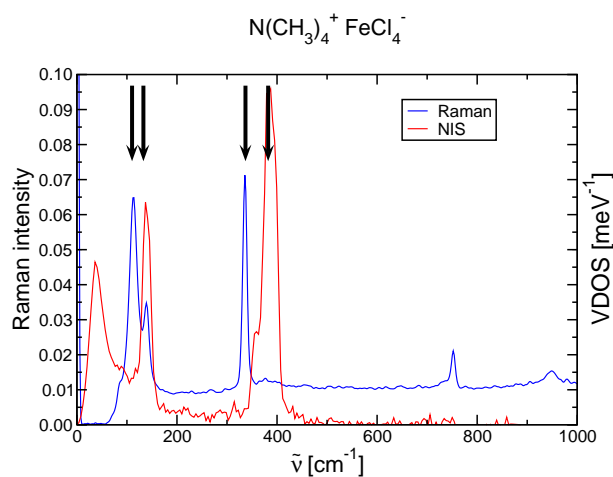


Fig. 3

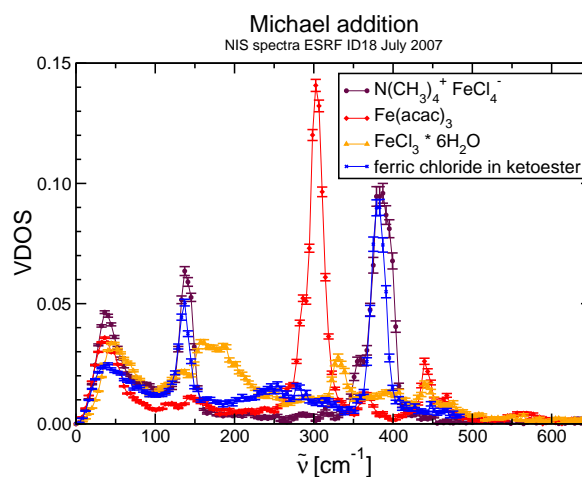


Fig. 4

Obviously, the frozen solution exhibits the two spectral bands at 133 and 385 cm⁻¹ that can be assigned to the tetrachloroferrate species, corroborating the EXAFS and Raman findings [4]. Additionally, various weak features between 210 and 300 cm⁻¹ can be seen. Most probably, these bands can be assigned to the di-ketoester complex. Whether the two ketoester groups in this complex are coordinated equatorially or facially to the Fe atom can only be decided after careful studies both of the frozen solution using a higher spectral resolution and even better statistics and of theoretical studies of the two complexes.

Our study demonstrates for the first time that NIS is not only a valuable tool in biochemistry but also helps to shed light on organic reactions in homogeneous solution at specific metal centres.

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