

# A Study on the Corrosion Inhibition Effects of Sodium Heptanoate for Carbon Steel in Aqueous Solution

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The carboxylates as a corrosion inhibitor has been studied by many researchers because of its environmental safety and low depletion rate. However, conventional test methods of inhibitor such as weight loss measurements, linear polarization resistance and corrosion potential monitoring etc., evaluate uniform corrosion of metals. These methods are unable to evaluate crevice-related corrosions, which are encountered in most of heat exchanging facilities. In order to choose the optimum corrosion inhibitor, the appropriate test methods are required to evaluate their performances in service environment.

From this point of view, polarization technique was used to evaluate the characteristics of sodium heptanoate on corrosion behavior for carbon steel. Especially a thin film crevice sensor technique were applied to simulate the crevice corrosion in this study.

From these experiments, we found that oxygen as an oxidizing agent was required to obtain stable passive film on the metal. Presence of oxygen, however, accelerated crevice corrosion. Potential shift by oxygen depletion and weakened inhibitive film inside the crevice were responsible for such accelerated feature. It is shown that film for corrosion inhibition is a mixture of sodium heptanoate and iron (II) heptanoate as reaction product of iron surface and sodium heptanoate. The iron (II) heptanoate which has been synthesized by reaction of heptanoic acid and ferrous chloride in methanol solution forms bidentate complex.

**Keywords** : *corrosion, inhibitor, crevice, carboxylate, inhibition film.*

## 1. Introduction

There have been many studies on carboxylic acids as corrosion inhibitors, but they have evaluated corrosion inhibition efficiencies with the carbon chain length and pH variation, etc. Most of these studies were on the chemical point of views, but few researches were done on the metal corrosion point of view.<sup>1),2),3)</sup>

Straight chain aliphatic carboxylates shows good corrosion inhibition efficiency for carbon steel and other metals. These days there have been many researches on carboxylates as a corrosion inhibitor because of their low toxicity and biodegradability. Among many carboxylates, sodium heptanoate were selected as a corrosion inhibitor for carbon steel in aqueous solution because it has shown superior corrosion efficiency to others.<sup>4)</sup>

In fields, we occasionally found various kind of localized corrosions such as crevice corrosion, under-deposit corrosion etc. in inhibitor contained solution. However, most tests have estimated by weight loss measurement or electrochemical polarization methods only.<sup>1),2),3)</sup> The corrosion inhibition efficiency by weight loss measure-

ments will be effective only when the type of corrosion is uniform. If the localized corrosions have occurred, the corrosion inhibition efficiency will not effective any more because of its incomplete evaluation of localized attacks.

In this study we have investigated the effects of sodium heptanoate on the corrosion of steel by applying various test methods. And we have applied multiple crevice test method to evaluate the performance of the corrosion inhibitor and have found good agreement with the real conditions. But this method has a weak point in that the test should be performed in the laboratory with accelerated condition. So we have developed the thin film crevice sensor to sense the start of crevice corrosion at the same time. The sensor is made of iron thin film sensor lines deposited on the glass and forms crevices with the sensor holder.<sup>5)</sup> The thin film crevice sensor can detect whether crevice corrosion is occur or not by sensing current variation through the sensor. By applying this method we have evaluated the crevice corrosion inhibition efficiency of the sodium heptanoate.

By utilizing FT-IR spectra we have analyzed that how sodium heptanoate adsorbs on the steel surface and what

kinds of film has formed on the steel surface.

## 2. Experimental

Tests were performed on a carbon steel (A210 Grade A1) of the following composition: 0.87% Mn, 0.30% Si, 0.18% Cu, 0.15% C, 0.122% Cr, 0.07% Ni, and bal. Fe. For electrochemical measurements, they were mounted in epoxy resin and polished to 600 grit before tests. The micro-stop lacquer(The Pyramid Co.) was used along the perimeter of the samples to restrict the exposed area to 1 cm<sup>2</sup>.

The inhibitor tested were sodium heptanoate, which was a reaction products of heptanoic acid and sodium hydroxide. The aggressive solutions of 100 ppm of NaCl were prepared with bidistilled water.

All the electrochemical tests were performed at 25 °C. The reference electrode was a saturated calomel electrode(S.C.E.). All reported potential values were referred this type of electrode. A platinum wire was used as the auxiliary electrode. Square sheets of the carbon steel (1.2 cm by 1.2 cm by 0.2 cm), which exposed 1cm<sup>2</sup> surface to the test solution, were used as the working electrode.

To investigate the effect of dissolved oxygen on the polarization behavior, the concentration of dissolved oxygen was controlled by aerating N<sub>2</sub> balanced gas with O<sub>2</sub> for 3.6x10<sup>3</sup> sec with flow rate of 100 ml/min before test. The concentration of dissolved oxygen was measured by dissolved oxygen meter(model 880, ORION).

The effects of dissolved oxygen on the crevice corrosion were tested by applying the iron thin film crevice sensor. The pattern of the thin film crevice sensor was shown in Fig. 1. The crevice formation was made by the sensor holder. All the crevice corrosion test were performed in accelerated condition of 88°C and 100 ppm of NaCl solution. In order to sense the time of crevice corrosion begins, we applied 10 mV of potential between the electrical contacts and recorded their current variation with time.

Characterization of the inhibitor films was done by use of Fourier transform infrared spectrometry (FT-IR, Bomem DA8). To identify the inhibitor film composition, we formulated iron (II) heptanoate, which is a reaction product with 380 mg FeCl<sub>2</sub> and heptanoic acid 781 mg in methanol solution at room temperature, N<sub>2</sub> atmosphere.

## 3. Results and discussion

### 3.1 Influence of sodium heptanoate concentration

Anodic polarization behaviors are shown in Fig. 2 for the carbon steel (A210 Grade A1) in aerated sodium heptanoate solution containing 100 ppm of Cl<sup>-</sup> at 25°C.

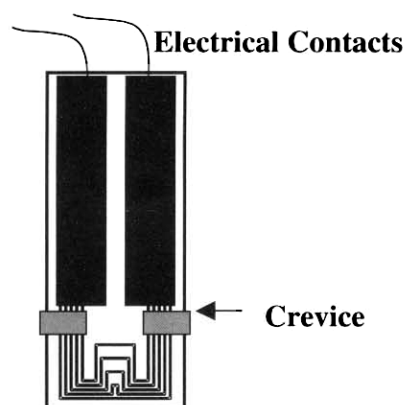


Fig. 1. Schematics of the pattern for thin film crevice sensor.

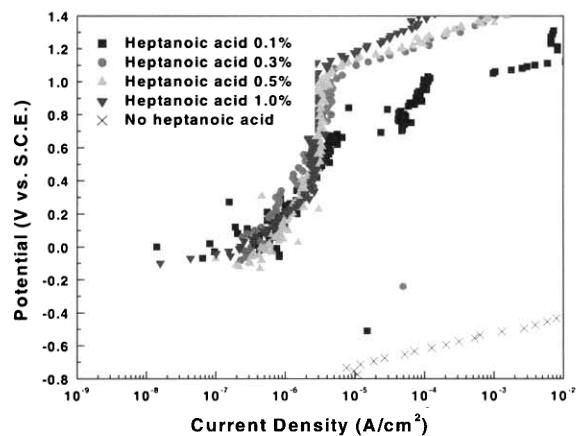


Fig. 2. Polarization behavior of A210 Grade A1 with sodium heptanoate concentration in the aerated solution containing 100 ppm of Cl<sup>-</sup> at 25°C.

When it contains no sodium heptanoate, corrosion potential( $E_{corr}$ ) was near -700 mV(S.C.E) and current density increased suddenly with potential. However, when small amount of sodium heptanoate(0.1%) introduced,  $E_{corr}$  shifted to more positive potentials than that of uninhibited solution and the passive region was appear with no active region. At high potential the stability of passive film is unstable for 0.1% sodium heptanoate. But above 0.3% of sodium heptanoate they showed stable passive film behaviors upto high potential(1000 mV(S.C.E)).

After experiment we found the hydrophobicity on the tested specimen at high concentration, which means some inhibitor film was formed on the surface.

For deaerated condition, the results were shown in Fig. 3. In case of aerated condition, they have showed stable passive film with no active region at all concentration of sodium heptanoate solution, but in deaerated condition they need active region to achieve stable passive film. The

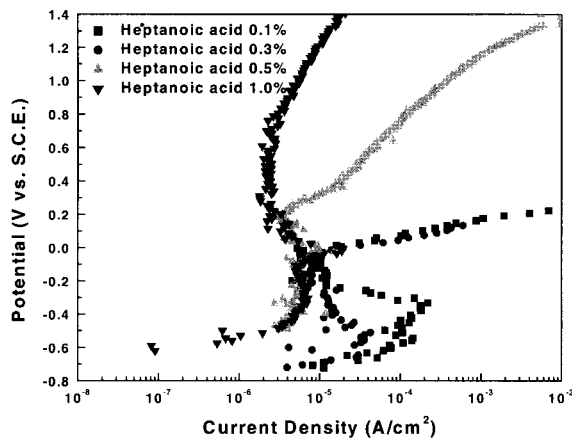


Fig. 3. Polarization behavior of A210 Grade A1 with sodium heptanoate concentration in deaerated solution containing 100 ppm of Cl⁻, at 25°C.

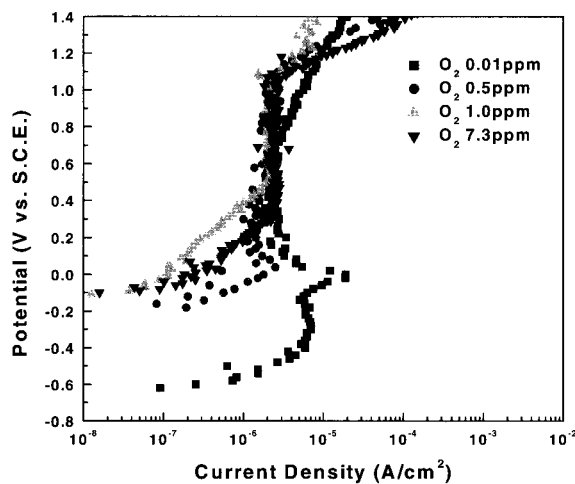


Fig. 4. Polarization behavior of A210 Grade A1 with dissolved oxygen concentration in the 1.0% sodium heptanoate solution containing 100 ppm of Cl⁻ at 25°C.

stable ranges of the passive films were lowered and varied with sodium heptanoate concentration. The corrosion potentials were not increase remarkably upto 1.0% of sodium heptanoate solution. This means that without dissolved oxygen, it needs more concentration of sodium heptanoate and activation energy to form stable passive film.

In order to identify dissolved oxygen effect on the passive film, we have tested anodic polarization behaviors at 1.0% sodium heptanoate with oxygen concentration and showed the results in Fig. 4. At 0.01 ppm of dissolved oxygen concentration the corrosion potential was -620 mV(S.C.E.) and the active region was appeared. However, at 0.5 ppm of the dissolved oxygen concentration, the corrosion potential was increased to -183 mV(S.C.E.) and

the active region was almost disappeared. At the higher concentration the corrosion potential was not increased anymore but the activation region was disappeared completely.

From this we can conclude that the dissolved oxygen is necessary to form stable passive film on the steel surface in sodium heptanoate solution, but the amount is very small to 0.5 ppm. And dissolved oxygen or an oxidizing agent is necessary to form stable passive film in the carboxylate solutions.<sup>6)</sup>

### 3.2 Effects of dissolved oxygen on the crevice corrosion

Then, will the presence of dissolved oxygen promote the inhibition efficiency for crevice corrosion or not? In order to investigate this effect, we developed thin film crevice sensor and tested in deaerated and in aerated condition with sodium heptanoate concentration respectively.

Fig. 5. shows the changes in current of the thin film crevice sensors with time at the potential of +10 mV from corrosion potential in deaerated condition. The decrease of current means the disconnection of sensor line because of the progress of crevice corrosion. The sensor have 5 lines so we can see 5 steps of current variations. In the case of 0.3 and 0.5% of sodium heptanoate concentration all the sensor lines were disconnected around 8 ~ 10 hours by the crevice corrosion. For 1.0% of sodium heptanoate concentration, it lasted a little longer and failed after 14 hours had passed, but no line has disconnected for about 5 hours. From this we founded that the more concentration of sodium heptanoate shows the better resistance to crevice corrosion.

Fig. 6. shows the same results for aerated condition. Even though the resistance of crevice corrosion increased with sodium heptanoate concentration, all the test sensors

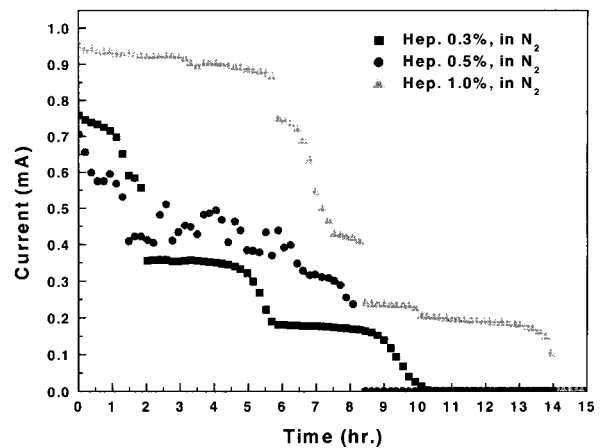


Fig. 5. Change in current of the thin film crevice sensors with time at the potential of 10 mV (deaerated, 88°C).

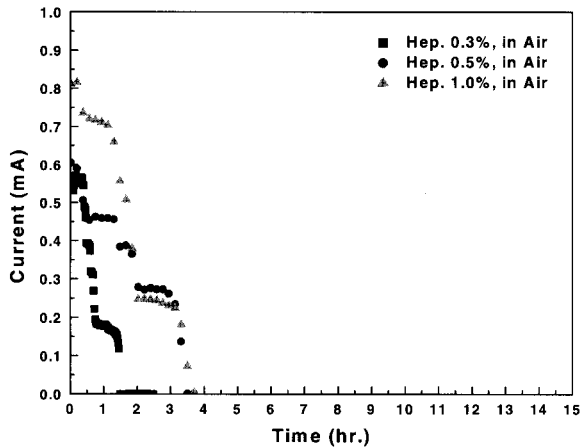


Fig. 6. Change in current of the thin film crevice sensors with time at the potential of 10 mV (aerated, 88°C).

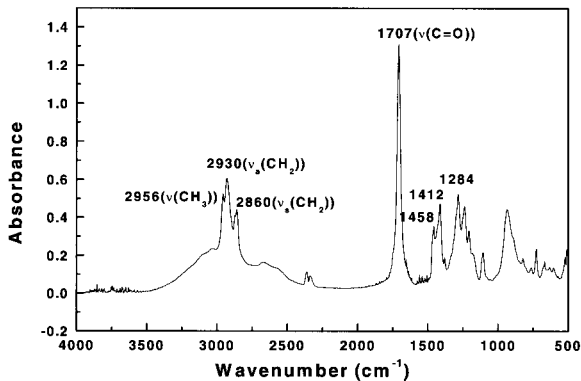


Fig. 7. FT-IR spectrum for heptanoic acid solution.

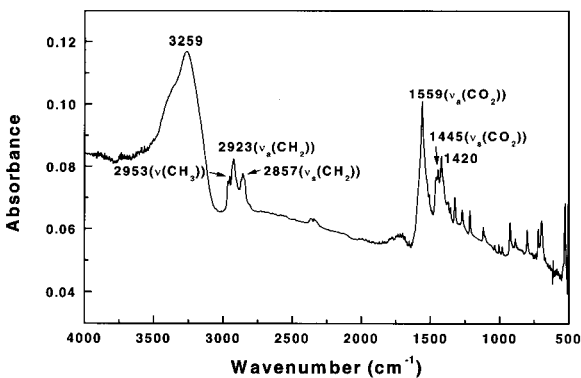


Fig. 8. FT-IR spectrum for sodium heptanoate solution.

were disconnected within 4 hours. It is very short time compared to that of deaerated condition (about 14 hours). As a whole the resistance of crevice corrosion was weakened remarkably with the presence of dissolved oxygen.

From these results we can conclude that the presence

of dissolved oxygen enhances the corrosion inhibition efficiency of sodium heptanoate but reduce the crevice corrosion efficiency. This is responsible for the positive corrosion potential shift at the present of dissolved oxygen. In case of deaerated condition, the corrosion potential difference between open surface and inside of crevice is small but, in case of aerated condition, it is great. The potential of open surface shifted to noble direction due to the dissolved oxygen but that of inside of crevice shift to base direction with depletion of dissolved oxygen depleted. This potential difference accelerates the crevice corrosion of steel by the large cathode - small anode effect.<sup>7)</sup>

### 3.3 FT-IR spectra

In order to identify the characteristics of the passive film, we have conducted FT-IR spectrum analysis. Fig. 7. shows the FT-IR spectrum of heptanoic acid solution which is raw material to synthesize sodium heptanoate with sodium hydroxide by neutralization. We can see OH stretching bond( $\nu(\text{OH})$ ) at the range of 2500 - 3300  $\text{cm}^{-1}$ ,  $\text{CH}_3$  stretching bond at 2956  $\text{cm}^{-1}$ , asymmetric  $\text{CH}_2$  stretching( $\nu_a(\text{CH}_2)$ ) and symmetric  $\text{CH}_2$  stretching( $\nu_s(\text{CH}_2)$ ) at 2930  $\text{cm}^{-1}$  and 2860  $\text{cm}^{-1}$  respectively. And C=O stretching bond( $\nu(\text{C}=\text{O})$ ) at 1707  $\text{cm}^{-1}$  correspond to carbonyl group.<sup>8)</sup>

Fig. 8. shows the FT-IR spectrum of sodium heptanoate solution. We can see O-H stretching bond( $\nu(\text{O-H})$ ) at the range of 3000 - 3500  $\text{cm}^{-1}$ ,  $\text{CH}_3$  stretching bond at 2953  $\text{cm}^{-1}$ , asymmetric  $\text{CH}_2$  stretching( $\nu_a(\text{CH}_2)$ ) and symmetric  $\text{CH}_2$  stretching( $\nu_s(\text{CH}_2)$ ) at 2923  $\text{cm}^{-1}$  and 2857  $\text{cm}^{-1}$  respectively, strong asymmetric  $\text{CO}_2$  stretching bond( $\nu_a(\text{CO}_2)$ ), weak symmetric  $\text{CO}_2$  stretching bond( $\nu_s(\text{CO}_2)$ ) at 1445 and 1420  $\text{cm}^{-1}$ . It is worthy of notice that the position of C=O stretching bond is shifted from 1707  $\text{cm}^{-1}$  (sodium heptanoate) to 1559  $\text{cm}^{-1}$  (heptanoic acid) by salt formation.

In order to investigate the effect of immersion time to film formation, we immersed the specimen in 2% sodium heptanoate solution with time. At first, we pull out the specimen after 40 minutes immersion and conducted FT-IR spectrum analysis and showed the result in Fig. 9. We can see a symptoms of surface film but the intensity of it was too weak to identify. Only very weak aliphatic  $\text{CH}_3$  and  $\text{CH}_2$  stretching bond can be verified at 2966 and 2929  $\text{cm}^{-1}$  wave number. However, no clear peaks were detected at the band of 1400 - 1600  $\text{cm}^{-1}$  which is correspond to  $\text{CO}_2$  bond of carbonyl group. From this spectrum, we can assume that the corrosion inhibitor film was not formed completely in 40 minutes immersion.

The second result for 10 hours immersion is shown in

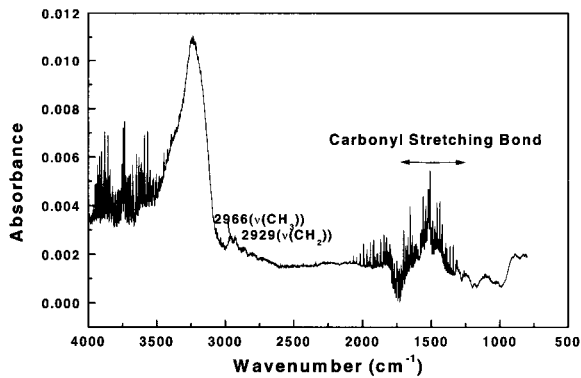


Fig. 9. FT-IR spectrum for the iron surface after 40 minutes immersion in 2.0% sodium heptanoate solution.

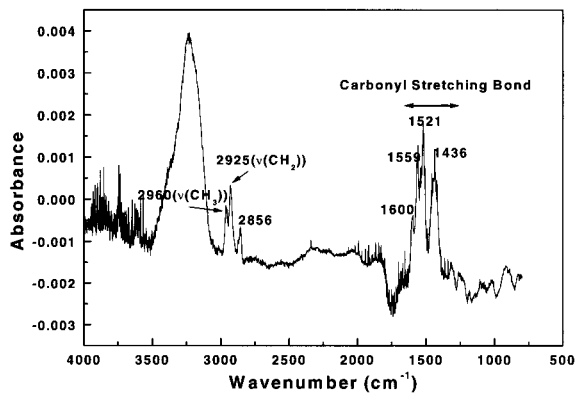


Fig. 10. FT-IR spectrum for the iron surface after 10 hours immersion in 2.0% sodium heptanoate solution.

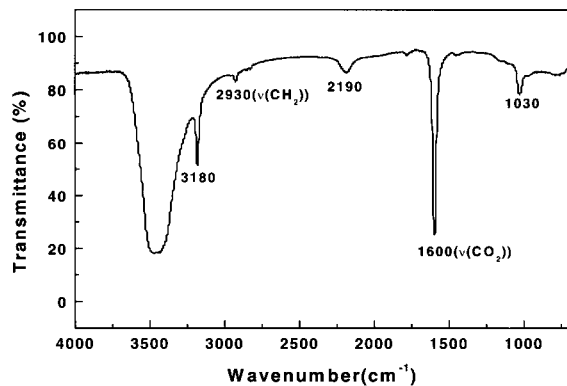
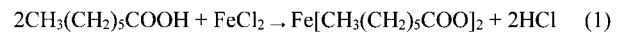


Fig. 11. FT-IR spectrum for reaction product of iron (II) heptanoate.

Fig. 10. The peaks are more clear than that of 40 minutes immersion. We can observe clear CH<sub>3</sub> and CH<sub>2</sub> stretching bond at 2966 cm<sup>-1</sup> and 2929 cm<sup>-1</sup> wave number and carbonyl stretching bonds at 1600, 1559, 1521, 1436 cm<sup>-1</sup> respectively. These carbonyl stretching bonds have not

observed clearly in the early stage of immersion and new peaks of 1600, 1521 cm<sup>-1</sup> wave number are detected newly which were not detected in the spectra of sodium heptanoate. From this we can presume that some new chemical compounds are formed on the steel surface by some reaction.

In order to identify the new peak on the steel surface, we formulated an iron (II) heptanoate by the reaction of FeCl<sub>2</sub> and heptanoic acid in methanol solution. The reaction can be expressed as follows.



The FT-IR spectrum(transmittance) for the reaction product was shown in Fig. 11. We can observe a weak aliphatic C-H stretch at 2930 cm<sup>-1</sup> and a strong peak at 1600 cm<sup>-1</sup>, which is correspond to the peak observed on the inhibitor film on the steel surface. The strong peak at 1600 cm<sup>-1</sup> is the same peak that one of new peaks of 1600, 1521 cm<sup>-1</sup> wave number formed on specimen surface after 10 hours immersion.

From this we can assume that as specimen immersed in the sodium heptanoate solution the adsorption of sodium heptanoate occurs at first and the chemisorbtion of iron (II) heptanoate follows with time.

From the wave number variation consideration, we can assume that iron (II) heptanoate has the bidentate complex structure because it shows single strong peak at 1600 cm<sup>-1</sup> wave number and it is smaller than that of the free ion state C = O stretching bond(ν(C = O), 1707 cm<sup>-1</sup>). This is well agree with the fact that most of carboxylate ion shows strong asymmetric stretching band near 1650 ~ 1550 cm<sup>-1</sup> and weak symmetric stretching band near 1400 cm<sup>-1</sup>.<sup>9)</sup>

#### 4. Conclusions

In conclusion, we have found that the dissolved oxygen is necessary to form stable passive film on the steel surface in sodium heptanoate solution, but the amount of it is very small to 0.5 ppm. And dissolved oxygen or an oxidizing agent is necessary to form stable passive film in the carboxylate solutions.

The presence of dissolved oxygen enhanced the corrosion inhibition efficiency of sodium heptanoate but reduced the crevice corrosion efficiency. This is responsible for the potential difference which accelerates the crevice corrosion of steel by the large cathode - small anode effect.

The passive film of sodium heptanoate is the mixture of sodium heptanoate and the iron (II) heptanoate which is reaction product of iron surface and sodium heptanoate.

The iron (II) heptanoate forms bidentate structure which could have synthesized by the reaction of heptanoic acid and ferrous chloride in methanol solution.

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