

Formation of acetylacetonato iron complexes in acetonitrile and their resonance Raman spectra

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Abstract

Formation of acetylacetonato iron complexes in acetonitrile, $\text{Fe}(\text{acac})^{2+}$, $\text{Fe}(\text{acac})_2^+$ and $\text{Fe}(\text{acac})_3$, (the expression represents the solvated species: acac^- is the 2,4-pentanedionate ion), were spectrophotometrically studied. On addition of Hacac to an acetonitrile solution of $\text{Fe}(\text{ClO}_4)_3$, $\text{Fe}(\text{acac})^{2+}$ was quantitatively formed. When excess Hacac was added, only $\text{Fe}(\text{acac})_2^+$ was obtained without forming $\text{Fe}(\text{acac})_3$. On the other hand, $\text{Fe}(\text{acac})_2^+$ was quantitatively obtained by adding HClO_4 to an acetonitrile solution of $\text{Fe}(\text{acac})_3$, and $\text{Fe}(\text{acac})^{2+}$ was also formed by adding an excess of HClO_4 . All the species of acetylacetonato complexes: $\text{Fe}(\text{acac})^{2+}$, $\text{Fe}(\text{acac})_2^+$ and $\text{Fe}(\text{acac})_3$ were formed in the system of $\text{Fe}(\text{ClO}_4)_3$ with an addition of tetraethylammonium acetylacetonate. The resonance Raman spectra of the obtained solutions of $\text{Fe}(\text{acac})^{2+}$ and $\text{Fe}(\text{acac})_2^+$ and of the solution of $\text{Fe}(\text{acac})_3$ were measured. The peaks mainly associated with $\nu(\text{Fe}-\text{O})$ and $\nu(\text{C}-\text{O})$ are observed near 450 and 1600 cm^{-1} , respectively. The order of $\nu(\text{Fe}-\text{O})$ is $\text{Fe}(\text{acac})^{2+}$ (474 cm^{-1}) > $\text{Fe}(\text{acac})_2^+$ (462 cm^{-1}) > $\text{Fe}(\text{acac})_3$ (451 cm^{-1}) and that of $\nu(\text{C}-\text{O})$ is $\text{Fe}(\text{acac})^{2+}$ (1554 cm^{-1}) < $\text{Fe}(\text{acac})_2^+$ (1578 cm^{-1}) < $\text{Fe}(\text{acac})_3$ (1603 cm^{-1}). These results indicate that the coordination strength of acac^- to Fe becomes weaker, because the Lewis acidity of the metal decreases as the number of coordinated acac^- increases.

Introduction

β -Diketonato complexes have been widely studied because of their interesting properties [1]. For example, the β -diketones are famous as reagents of the solvent extraction of metals [2, 3]. By using some β -diketones, radioactive elements have been successfully separated from mixtures [4, 5]. Most of the complexes show volatility: some examples have been reported [6–9]. Mixed-ligand β -diketonato complexes are of interest [10], and investigations of some octahedral metal complexes with two kinds of β -diketonates have been carried out [11–14]. From the point of view of electrochemistry, cobalt(III) complexes with two different β -diketonates, one of which is an unsymmetrical ligand [15], and mixed-ligand β -diketonato complexes of ruthenium [16, 17] have been studied.

Recently, Sato and coworkers reported methods of preparation of bis(β -diketonato)bis(acetonitrile)-ruthenium(III) complexes, which were useful intermediates for the synthesis of mixed-ligand β -diketonato ruthenium(III) complexes of the $[\text{Ru}^{\text{III}}\text{L}_2\text{L}']$ type [18, 19]. Kasahara *et al.* [19] reported that bis(β -diketonato)bis(acetonitrile)ruthenium(III) was readily formed through the reaction of the corresponding tris(β -diketonato)ruthenium(III) with perchloric, sulfuric or hydrochloric acid in acetonitrile. The reaction was quantitative, and no further replacement occurs.

In this study, the method by Kasahara *et al.*, which is for an inert Ru^{III} system, was applied to a labile Fe^{III} system. In the Fe^{III} system, two kinds of species, $\text{Fe}(\text{acac})_2^+$ and $\text{Fe}(\text{acac})^{2+}$, (the expression represents the solvated species: acac^- is the 2,4-pentanedionate ion, acetylacetonate ion), were obtained unlike the Ru^{III} system. The most favorable conditions for the formation of $\text{Fe}(\text{acac})_2^+$ or $\text{Fe}(\text{acac})^{2+}$ were investigated and their resonance Raman spectra were studied together with $\text{Fe}(\text{acac})_3$.

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Experimental

Chemicals

Tetraethylammonium perchlorate (TEAP) of special polarographic grade and tetraethylammonium hydroxide (TEAOH) were obtained from Nakarai Chemical Ltd. and Aldrich Chemical Co., Inc., respectively. Iron(III) perchlorate hexahydrate was purchased from Kanto Chemical Co., Inc. Hacac was purchased from Wako Pure Chemical Ltd. High purity acetonitrile for high-pressure liquid chromatography (Wako Pure Chemical Ltd.) was used for the measurement of UV-Vis and Raman spectra. TEA(acac) acetonitrile solution was prepared by neutralization of Hacac with TEAOH.

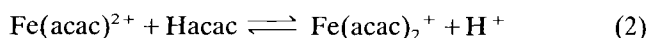
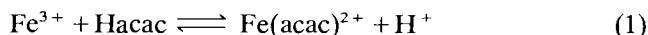
Measurements

Resonance Raman spectra were recorded on a Jobin Yvon U-1000 spectrometer with a capillary cell, the exciting line (514.5 nm) being provided by an NEC Ar⁺ ion laser GLG 3200.

A Hitachi U-3400 spectrophotometer was used for spectrophotometric titrations. An Fe(acac)₃ acetonitrile solution of 0.5 mmol dm⁻³ was titrated with an 11.6 mmol dm⁻³ HClO₄ solution which was prepared from commercial perchloric acid diluted with the Fe(acac)₃ acetonitrile solution. An Fe(ClO₄)₃ acetonitrile solution of 1.0 mmol dm⁻³ was titrated with 20 mmol dm⁻³ Hacac solution containing 1.0 mmol dm⁻³ Fe(ClO₄)₃ in order to keep the same concentration of Fe³⁺. Similarly, a 0.5 mmol dm⁻³ Fe(ClO₄)₃ solution was titrated with 10 mmol dm⁻³ TEA(acac) solution instead of the Hacac solution. All the titrated solutions contained 50 mmol dm⁻³ TEAP.

Results and discussion

Spectral changes of the Fe(ClO₄)₃ solution with additions of Hacac are shown in Fig. 1(a). The mole ratio plot (Fig. 1(b)) indicates that the first species was stoichiometrically formed at mole ratio Fe(ClO₄)₃:Hacac=1:1, followed by the formation of the second one by adding excess Hacac. The reactions are shown by the following equations



The first species, Fe(acac)₂⁺, was quantitatively produced as shown in Fig. 1(b), unlike the second one. When excess Hacac was added, the peak height increased but did not shift. Therefore the third species, Fe(acac)₃, was not formed even if excess Hacac was added.

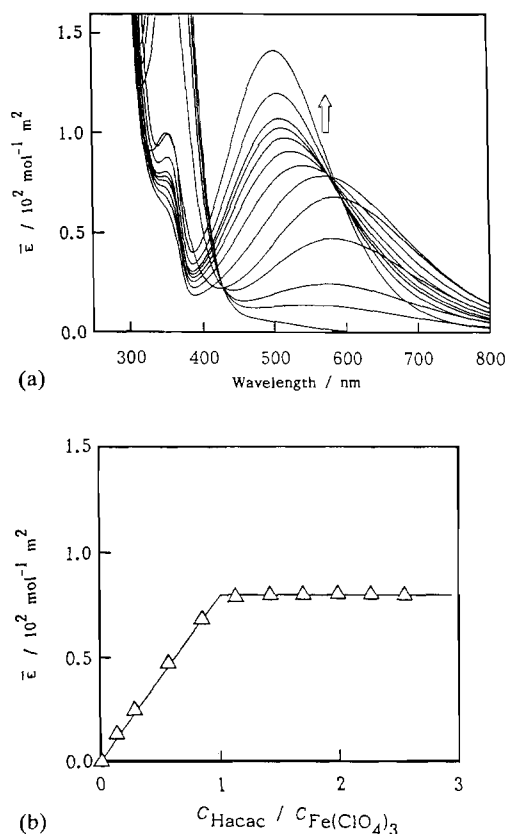
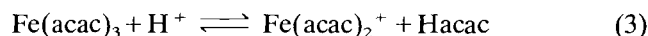


Fig. 1. Spectrophotometric titration of Fe(ClO₄)₃ with Hacac in acetonitrile solutions. (a) Spectral change. (b) Mole ratio plot at 575 nm. C: Concentration (mmol dm⁻³), C_{Fe(ClO₄)₃} = 1.0 mmol dm⁻³.

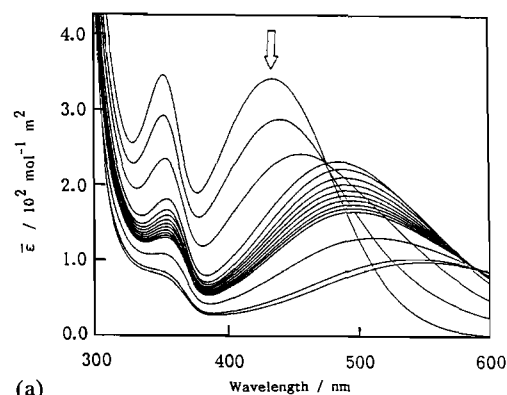
Figure 2 shows the results of the spectrophotometric titration of Fe(acac)₃ solution with HClO₄. From the mole ratio plot (Fig. 2(b)), it is clear that the first species was stoichiometrically formed at mole ratio Fe(acac)₃:HClO₄=1:1, then formation of the second one occurred by adding excess HClO₄. The reaction was quantitative to the extent of mole ratio 1:1 and it shows the formation of Fe(acac)₂⁺



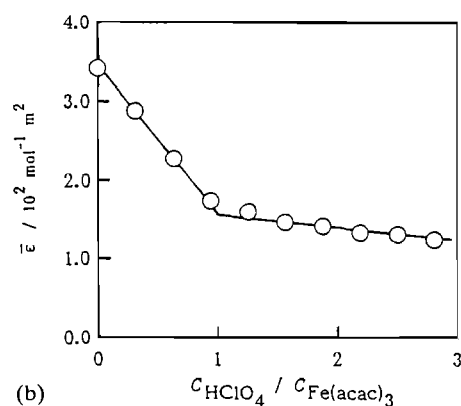
In the region beyond that, the second species, Fe(acac)₂⁺, was formed, and the reaction is not quantitative. Consequently, the stepwise formation constant of Fe(acac)₂⁺ is smaller than that of Fe(acac)₂⁺ in the system. The spectra of Fe(acac)₂⁺ and Fe(acac)₂⁺ agree with those of the corresponding species in Fig. 1(a).

This is different from the case of the Ru^{III} system [19]: in the Ru^{III} system, the reaction was quantitative and no further replacement occurred; that is, only Ru(β-diketonato)₂⁺ was obtained.

Spectral changes of Fe(ClO₄)₃ solution with additions of TEA(acac) are shown in Fig. 3(a) and the mole ratio plot is in Fig. 3(b). As can be seen from the Figures, all the species of acetylacetonato complexes,



(a)



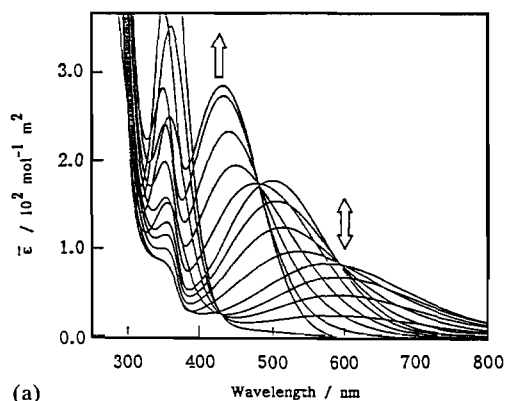
(b)

Fig. 2. Spectrophotometric titration of $\text{Fe}(\text{acac})_3$ with HClO_4 in acetonitrile solutions. (a) Spectral change. (b) Mole ratio plot at 435 nm. C : Concentration (mmol dm^{-3}), $C_{\text{Fe}(\text{acac})_3} = 0.5 \text{ mmol dm}^{-3}$.

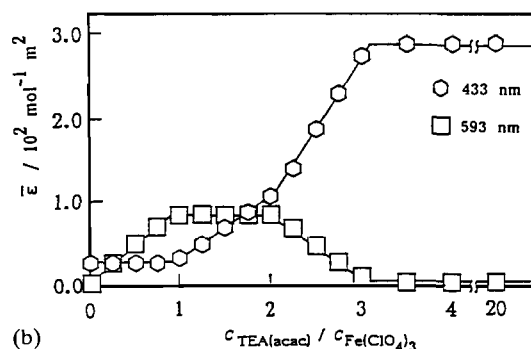
$\text{Fe}(\text{acac})^{2+}$, $\text{Fe}(\text{acac})_2^+$ and $\text{Fe}(\text{acac})_3$ are stoichiometrically formed in this system.

From the investigation, $\text{Fe}(\text{acac})^{2+}$ is stoichiometrically formed at mole ratio $\text{Fe}^{3+}:\text{Hacac} = 1:1$ in the acetonitrile solution, and $\text{Fe}(\text{acac})_2^+$ is at $\text{Fe}(\text{acac})_3:\text{HClO}_4 = 1:1$ in the solution. When acac^- is added to the Fe^{3+} solution, all species, $\text{Fe}(\text{acac})^{2+}$, $\text{Fe}(\text{acac})_2^+$ and $\text{Fe}(\text{acac})_3$, are obtained. In those reactions, H^+ plays an important role.

The formations of $\text{Fe}(\text{acac})^{2+}$ and $\text{Fe}(\text{acac})_2^+$ occur with the generation of H^+ (eqns. (1) and (2)). The progress of the reactions increases the concentration of H^+ , and the state of equilibrium to produce $\text{Fe}(\text{acac})_2^+$ is driven toward the dissociation to form $\text{Fe}(\text{acac})^{2+}$ and acac^- , as shown in eqn. (2). Moreover, even if excess Hacac is added, the formation of $\text{Fe}(\text{acac})_3$ is inhibited for similar reasons. However, if proton free acac^- ($\text{TEA}(\text{acac})$) is added, $\text{Fe}(\text{acac})_3$ is formed instead of Hacac . When HClO_4 was added to the $\text{Fe}(\text{acac})_3$ solution, a ligand replacement reaction occurred and Hacac was formed, because the protonation constant of the acetylacetonate is very large in acetonitrile [20]. In this case, the reaction progresses with adding H^+ ;



(a)



(b)

Fig. 3. Spectrophotometric titration of $\text{Fe}(\text{ClO}_4)_3$ with $\text{TEA}(\text{acac})$ in acetonitrile solutions. (a) Spectral change. (b) Mole ratio plots at 433 nm and 593 nm. C : Concentration (mmol dm^{-3}), $C_{\text{Fe}(\text{ClO}_4)_3} = 0.5 \text{ mmol dm}^{-3}$.

thus $\text{Fe}(\text{acac})^{2+}$ is formed. If the solution containing a large excess of HClO_4 stands for several days, the acac complex is decomposed. Although the mechanism of the replacement reaction with HClO_4 is not yet clear, it is certain that the reaction is initiated by the attack at an $\text{Fe}-\text{O}$ bond by H^+ : if the breakage of the $\text{Fe}-\text{O}$ bond were the first step of the reaction, the reaction would be extremely slow at room temperature, unlike the results of this system. When $\text{TEA}(\text{acac})$ was added to the $\text{Fe}(\text{ClO}_4)_3$ solution, the concentration of H^+ was not changed, different from eqns. (1) and (2), and the reaction progressed to the formation of $\text{Fe}(\text{acac})_3$.

The species of the acetylacetonato- Fe^{III} complexes have absorption bands in the range of 420–500 nm, as shown in Fig. 4(a). Some tris(β -diketonato)-ruthenium(III) complexes also have absorption bands around this wavelength range [21, 22]. Kobayashi *et al.* [21] ascribed three absorption bands of $[\text{Ru}(\text{acac})_3]$ observed in the range of 600–250 nm to the excited states which are the configuration–interaction admixtures of the ligand-to-metal charge-transfer (LMCT) excited states and the ligand (π, π^*) excited triplets and singlets. The absorption band of $[\text{Fe}(\text{acac})_3]$ is also described by a superposition of the LMCT excited states

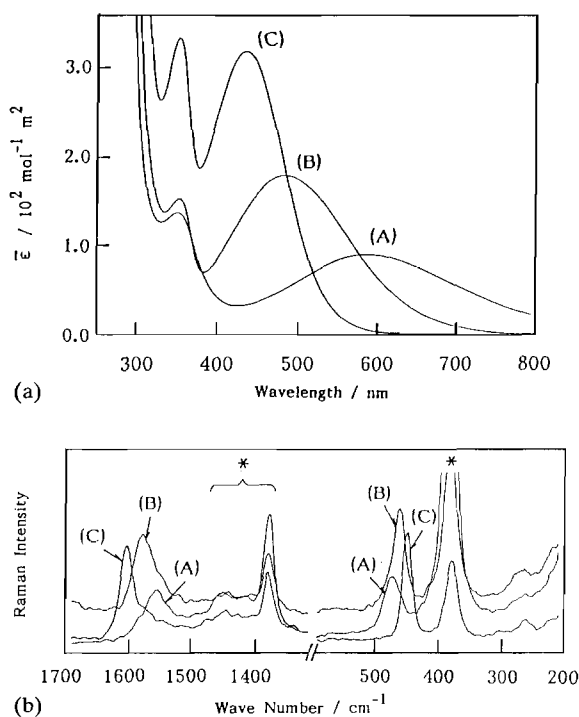


Fig. 4. (a) Absorption spectra and (b) resonance Raman spectra obtained by using 514.5 nm argon ion line, in acetonitrile solutions. (A) $\text{Fe}(\text{acac})_2^+$, (B) $\text{Fe}(\text{acac})_2^+$, (C) $\text{Fe}(\text{acac})_3$. (* acetonitrile: these peaks disappeared by using different solvents.)

and the ligand (π, π^*) excited triplets and singlets. According to the assignment, resonance Raman spectra of the acetylacetonato- Fe^{III} complexes were measured by means of irradiation of the 514.5 nm Ar^+ ion line in order to obtain information about metal-ligand bonding.

Resonance Raman spectra of $\text{Fe}(\text{acac})_3$, $\text{Fe}(\text{acac})_2^+$ and $\text{Fe}(\text{acac})_2^+$ are shown in Fig. 4(b). There is one peak in the range of 600–200 cm^{-1} and also one in 1700–1300 cm^{-1} in each spectrum of the complexes. Infrared (IR) spectra of $\text{M}(\text{acac})_3$ have been assigned [23, 24]: in $[\text{Fe}(\text{acac})_3]$, the 433 cm^{-1} band is a vibration of $\nu(\text{Fe}-\text{O})$, which is coupled by a small amount of $\nu(\text{C}-\text{CH}_3)$, and the 1570 cm^{-1} band is a coupled one, $\nu(\text{C}-\text{C}) + \nu(\text{C}-\text{O})$. The A_1 and E modes in $[\text{M}(\beta\text{-diketonato})_3]$ of D_3 symmetry are Raman active, while the A_2 and E modes are IR active. However, the Raman active modes are not very different in frequencies from those of the IR active modes [21]. Judging from these results, we assign the band around 460 cm^{-1} to the $\nu(\text{Fe}-\text{O})$ dominant vibration and the peak around 1600 cm^{-1} to a coupled one between $\nu(\text{C}-\text{C})$ and $\nu(\text{C}-\text{O})$ in Fig. 4(b).

The band around 460 cm^{-1} shifts toward low frequency with an increase in the number of coordinated acac^- , $\text{Fe}(\text{acac})_2^+$ (474 cm^{-1}) > $\text{Fe}(\text{acac})_2^+$ (462 cm^{-1}) > $\text{Fe}(\text{acac})_3$ (451 cm^{-1}). On the other hand the

band around 1600 cm^{-1} shifts toward high frequency, $\text{Fe}(\text{acac})_2^+$ (1554 cm^{-1}) < $\text{Fe}(\text{acac})_2^+$ (1578 cm^{-1}) < $\text{Fe}(\text{acac})_3$ (1603 cm^{-1}). These facts indicate that the bond strength of $\text{Fe}-\text{O}$ decreases and that of $\text{C}-\text{O}$ increases. The coordination strength of acac^- to Fe becomes weaker because the Lewis acidity of the metal decreases as the number of coordinated anions (acac^-) increases.

The shifts of $\nu(\text{Fe}-\text{O})$ and $\nu(\text{C}-\text{O})$ are proportional to the number of coordinated acac^- . It shows that the influence of acac^- on the iron atom obeys the rule of average environment. The fact agrees with the ligand additivity model of a ligand electrochemical series by Lever [25]: a ligand electrochemical parameter, $E_L(\text{L})$, was described to generate a series which may be used to predict $\text{M}(n)/\text{M}(n-1)$ redox potentials by assuming that all ligand contributions are additive. The parameter is defined as one-sixth that of the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ potential for species RuL_6 in acetonitrile. The availability of the parameters allows one to predict the redox potential of a given metal couple when its structural and spin-state information are available. The ligand additivity model is also confirmed by this work, and further study by means of spectrophotometry and Raman spectroscopy, will enable the model to be generalized.

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