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## Note

# Characterization of Iron(II) Comoplexes with $\beta$ -Diketones and Monthio- $\beta$ -diketone

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### KEY WORDS : β-Diketones/ Monothiodibenzoylmethane/ Iron(II) complexes/ Characterization/

 $\beta$ -Diketones and monothio- $\beta$ -diketones are well-known and frequently used ligands. Change of a donor atom from oxygen to sulfur often gives rise to different properties in complexes formed. For example, the tris complexes of iron(III) with  $\beta$ -diketones are high-spin, but the tris complexes with some monothio- $\beta$ -diketones exhibit an anormalous magnetic behavior ascribed to a spin-equilibrium between  ${}^{5}A_{1}{}^{2}T_{2}$  states.<sup>1,2)</sup> The ligands are capable of forming stable adducts with iron(II) in the presence of Lewis bases. Emmert *et al.* synthesized bis(acetylacetonato)dipyridineiron(II), Fe(II)(acac)\_2Py\_{2}, and bis(oxo-1, 3-diphenylprop-2-en-1-onato)dipyridineiron(II), Fe(II)(dibz)\_2Py\_{2},^{3,4)} Uhlemann and Thomas isolated bis(thioxo-1, 3-diphenylprop-2-en-1-onato)dipyridineiron(II), Fe(II) (sdibz)\_2Py\_{2},^{5)} These complexes are soluble in organic solvents. Therefore, it is possible to extract iron(II) into organic solvents containing these ligands synergistically and determine it spectrophotometrically.<sup>6-10)</sup> The author characterized Fe(II)(acac)\_2Py\_{2}, Fe(II)(dibz)\_2Py\_2 and Fe(II)(sdibz)\_2Py\_2 through spectroscopic and thermogravimetric measurements and will report the results in this paper.

#### EXPERIMENTAL

Monothiodibenzoylmethane synthesized according to the literature was offered by Fukui.<sup>11)</sup> Acetylacetone, dibenzoylmethane, pyridine and Mohr's salt were obtained commercially and pyridine was purified by distillation. Fe(II)  $(acac)_2Py_2$  was prepared by the addition of acetylacetone (1.0g) and pyridine (7ml) to an aqueous solution (15ml) of Mohr's salt (2.0g). The solution upon recrystallization from pyridine gave black crystals. Fe(II)  $(dibz)_2Py_2$  and Fe(II)  $(sdibz)_2Py_2$  were prepared by using dibenzoylmethane and monothiodibenzoylmethane instead of acetylacetone, respectively.

Optical absorption measurements were made on a Hitachi 323 automatic recording spectrophotometer. Pyridine (10%)—reagent grade benzene (90%) was used as solvent. Mössbauer spectra were obtained with a scanning velocity spectrometer in the time

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mode. The valocity scale was calibrated with metallic iron. Thermogravimetric curves were obtained with a Schimazu thermal balance.

#### **RESULTS AND DISCUSSION**

Table I is the data of elemental analysis for the complexes prepared.  $Fe(II) (dibz)_2$ -Py<sub>2</sub> and  $Fe(II) (sdibz)_2 Py_2$  are stable in solid, but the crystal of  $Fe(II) (acac)_2 Py_2$  changes color from black to red after a week. The color of the complexes in pyridine (10%) benzene (90%) solvent changes completely after a day.

Complex	Color	C(%)		H(%)		N(%)		S(%)	
		Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
monothiodibenzoy- lmethane	red	74.29	74.97	5.12	5.04			13. 51	13.34
$Fe(II)(acac)_2Py_2$	black	57.38	58.25	5.85	5.87	6.63	6.80		
Fe(II)(dibz) <sub>2</sub> Py <sub>2</sub>	dark blue	72.34	72.70	4.70	4.93	4.37	4.24		
$Fe(II)(sdibz)_2Py_2$	dark green	69.53	69.36	4.77	4.66	4.34	4.05		

Table I. Data of Elemental Analysis

Complex	Temp.	I. S	Q. S.	
$Fe(II)(acac)_2Py_2$	R. T.	1.08	2.40	Γ
	~110K	1.12	2.44	
Fe(II) (dibz) <sub>2</sub> Py <sub>2</sub>	R. T.	1.00	2.25	
	~110K	1.06	2.28	
$Fe(II)(sdibz)_2Py_2$	R. T.	1.02	2.48	
	~110K	1.13	2.50	

#### Table II. Mössbauer Data of Iron(II) Complexes

unit: mm/s

The Mössbauer parameters are shown in Table II. The parameters are consistent with characteristic values observed in high-spin iron(II) complexes. In the present complexes, change of a donor atom from oxygen to sulfur does not give rise to a sharp difference in the electronic ground state of the central iron(II).

Figure 1 showes the absorption spectra and the band maxima are listed in Table III. Acetylacetone does not exhibit any absorption band in the visible region. Therefore, the bands of Fe(II)  $(acac)_2Py_2$  at 349 and 442 nm are probably classified to chargetransfer band. The absorption bands of Fe(II)  $(dibz)_2Py_2$  except the band at 346 nm, which is ascribed to the  $\pi$ - $\pi$ \* transition of dibenzoylmethane, are probably assigned to charge-transfer bands as well. Akaiwa *et al.* proposed a method for the spectrophotometric determination of iron(II) extracted into benzene containing dibenzoylmethane and Lewis base.<sup>8)</sup> The absorption spectrum of the pyridine system in the report is different from that in this study, because they employed the benzene used for the extraction of the iron(II)-free solution as a reference. They determined iron(II) spectrophotometrically at 408 nm, but the spectrum in Fig. 1 suggests that it seems good to use the charge-transfer band at 582 nm if the high sensitivity is not required. In Fe(II) (sdibz)<sub>2</sub>- Characterization of Fe (II) Complexes with  $\beta$ - and Monothio- $\beta$ -diketones





Table	III.	Absorption	Maxima	of	Iron(]	II)	compexes

Complex	Absorptio	(ε)			
dibenzoylmethane	346(22,100)		A		
monothodenzoylmethane	415(19, 100)	500° (262)			
Fe(II) (acac) <sub>2</sub> Py <sub>2</sub>	349(2,249)	442 (2,447)	673 (42.4)		
Fe0II) (dibz) <sub>2</sub> Py <sub>2</sub>	346(37,270)	420ª (2, 520)	530ª (2, 030)	582 (3, 080)	680 (1,900)
$Fe(II) (sd bz)_2 Py_2$	403 (20, 470)	529 (1,120)	626 <sup>a</sup> (1,600)	720(2,160)	800ª (1, 830)

a: shoulder

Py<sub>2</sub>, the charge-transfer bands are observed at 620, 720 and 800 nm, and the  $\pi$ - $\pi$ \* band of monothiodibenzoylmethane, at 404 nm. The absorption bands at 720 and 800 nm can be used for the photometric determination of iron(II) extracted.<sup>9)</sup> Chikuma *et al.* and Honjo *et al.* proposed a more sensitive method for the determination of iron(II) with monothiothenoyltriuoroacetone and pyridine, where iron(II) is determined at 810 nm ( $\epsilon$ =5, 590).<sup>9,10</sup> They concluded that the species extracted is the mono-adduct with pyridine. The methods for the determination iron(II) with the  $\beta$ -diketone or the monothio- $\beta$ -diketones are not so good as those with  $\sigma$ -phenanthroline or bathophenan-throline in sensitivity. Thus, another method using trioctylposphine oxide instead of pyridine was proposed in order to improve the sensitivity.<sup>8)</sup>

Figure 2 shows the thermogravimltric curves of  $Fe(II) (acac)_2 Py_2$  and  $Fe(II) (dibz)_2 Py_2$ . 100% Weight loss in the vertical axis is consistent with the calculated decrease in weight when pyridine is perfectly released. Unstable  $Fe(II) (acac)_2 Py_2$  releases pyridine at a lower temperature than  $Fe(II) (dibz)_2 Py_2$  does. Two pyridine molecules are released at the same time in both complexes, suggesting that the mono-adducts are unstable.

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Fig. 2. Thermogravimetric. curves of iron (II)-β-diketone compexes. a: Fe(II) (acac)<sub>2</sub>Py<sub>2</sub>, b: Fe(II) (dibz)<sub>2</sub>Py<sub>2</sub>

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