



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

### RESULTS AND DISCUSSION

Table I is the data of elemental analysis for the complexes prepared. Fe(II) (dibz)<sub>2</sub>-Py<sub>2</sub> and Fe(II) (sdibz)<sub>2</sub>Py<sub>2</sub> are stable in solid, but the crystal of Fe(II) (acac)<sub>2</sub>Py<sub>2</sub> 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.

Table I. Data of Elemental Analysis

Complex	Color	C(%)		H(%)		N(%)		S(%)	
		Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
monothiodibenzoyl-methane	red	74.29	74.97	5.12	5.04			13.51	13.34
Fe(II) (acac) <sub>2</sub> Py <sub>2</sub>	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) <sub>2</sub> Py <sub>2</sub>	dark green	69.53	69.36	4.77	4.66	4.34	4.05		

Table II. Mössbauer Data of Iron(II) Complexes

Complex	Temp.	I. S	Q. S.
Fe(II) (acac) <sub>2</sub> Py <sub>2</sub>	R. T.	1.08	2.40
	~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) <sub>2</sub> Py <sub>2</sub>	R. T.	1.02	2.48
	~110K	1.13	2.50

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 shows the absorption spectra and the band maxima are listed in Table III. Acetylacetonone does not exhibit any absorption band in the visible region. Therefore, the bands of Fe(II) (acac)<sub>2</sub>Py<sub>2</sub> at 349 and 442 nm are probably classified to charge-transfer band. The absorption bands of Fe(II) (dibz)<sub>2</sub>Py<sub>2</sub> 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>9)</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>-

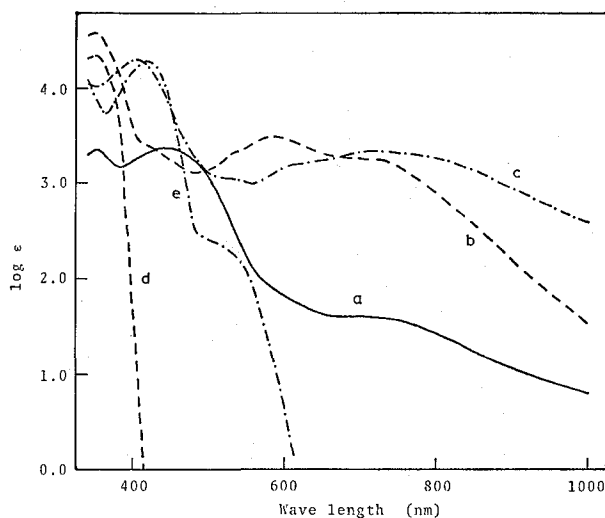
Characterization of Fe(II) Complexes with  $\beta$ - and Monothio- $\beta$ -diketones


Fig. 1. Absorption spectra of iron(II)- $\beta$ -diketone complexes, a: Fe(II) (acac)<sub>2</sub>Py<sub>2</sub>, b: Fe(II) (dibz)<sub>2</sub>Py<sub>2</sub>, c: Fe(II) (sdibz)<sub>2</sub>Py<sub>2</sub>, d: dibenzoylmethane, e: monothiodibenzoylmethane

Table III. Absorption Maxima of Iron(II) complexes

Complex	Absorption Maxima nm( $\epsilon$ )				
dibenzoylmethane	346(22, 100)				
monothiodibenzoylmethane	415(19, 100)	500 <sup>a</sup> ( 262)			
Fe(II) (acac) <sub>2</sub> Py <sub>2</sub>	349( 2, 249)	442 (2, 447)	673 (42. 4)		
Fe(II) (dibz) <sub>2</sub> Py <sub>2</sub>	346(37, 270)	420 <sup>a</sup> (2, 520)	530 <sup>a</sup> (2, 030)	582(3, 080)	680 (1, 900)
Fe(II) (sd bz) <sub>2</sub> Py <sub>2</sub>	403(20, 470)	529 (1, 120)	626 <sup>a</sup> (1, 600)	720(2, 160)	800 <sup>a</sup> (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 monothiothenoyltriuroacetone 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 *o*-phenanthroline or bathophenanthroline in sensitivity. Thus, another method using trioctylphosphine oxide instead of pyridine was proposed in order to improve the sensitivity.<sup>9</sup>

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

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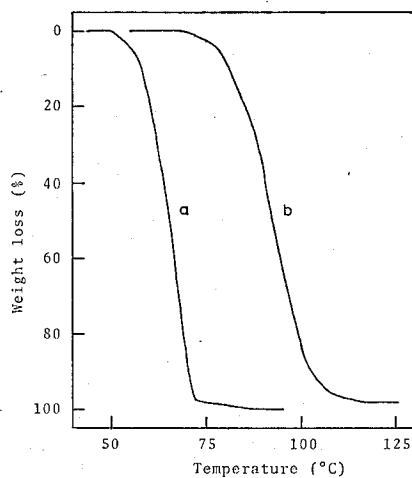


Fig. 2. Thermogravimetric curves of iron(II)- $\beta$ -diketone complexes.  
 a: Fe(II)(acac)<sub>2</sub>Py<sub>2</sub>, b: Fe(II)(dibz)<sub>2</sub>Py<sub>2</sub>

bauer measurements. The author is grateful to Mr. K. Fukui for supplying monothio-dibenzoylmethane.

#### REFERENCES

- (1) R. K. Y. Ho and S. E. Livingstone, *Aust. J. Chem.*, **21**, 1987 (1968).
- (2) M. Cox, J. Darken, B. W. Fitzsimmons, A. W. Smith, L. F. Larkworthy, and K. A. Rogers, *J. Chem. Soc. Dalton Trans.*, 1192 (1972).
- (3) B. Emmert and R. Tarczynski, *Chem. Ber.*, **64**, 1072 (1931).
- (4) B. Emmert and H. Gsottschneider, *ibid*, **66**, 1871 (1933).
- (5) E. Uhlemann and P. Thomas, *Z. Naturfor.*, **23b**, 275 (1968).
- (6) H. Kawamoto and H. Akaiwa, *Nippon Kagaku Zasshi*, **89** 585 (1968).
- (7) H. Akaiwa, H. Kawamoto, and M. Hara, *Anal. Chim. Acta*, **43**, 297 (1968).
- (8) H. Akaiwa, H. Kawamoto, and E. Hiyamuta, *Japan Analyst (Bunseki Kagaku)*, **28**, 477 (1979).
- (9) W. Chikuma, A. Yokoyama, Y. Ooi, and H. Tanaka, *Chem. Pharm. Bull.*, **23**, 507 (1975).
- (10) T. Honjo, Y. Fujioka, H. Itoh, and T. Kiba, *Anal. Chem.*, **49**, 2241 (1977).
- (11) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, and V. A. Pickles, *Aust. J. Chem.*, **18** 673 (1965).