Iron(II), Cobalt(II), Nickel(II) and Copper(II) Chelates of 1,1'-Dibenzoylacetylferrocene

Ho-Hsiang Wei* and Dang-Ming Horng

Department of Chemistry, Tamkang University, Tamsui, Taiwan

Summary

1,1'-Dibenzoylacetylferrocene (DBAFc) complexes of iron(II), cobalt(II), nickel(II) and copper(II) have been prepared and characterized. The physical properties of the complexes are discussed on the basis of uv-visible, Mössbauer spectra and magnetic measurements.

Introduction

It is of interest to investigate the behavior and properties of the chelates of ferrocene-substituted β-diketones such as acetoacetylferrocene and benzoylacetylferrocene in which the β-position in the β-diketone is substituted by a ferrocenyl group. So far, few reports have appeared dealing with the metal chelates of the first transition metal series with ferrocene-substituted β-diketones[1-4], and the properties of 1,1'-dibenzoylacetylferrocene (DBAFc) dihydrate complexes of the type $M^{II}(DBAFc) \cdot 2 H_2O$ where M^{II} = iron, cobalt and nickel do not seem to have been described.

The main aim of this investigation was to obtain information concerning the electronic state of the iron atom in the ferrocene site in 1,1'-dibenzoylacetylferrocene chelates of iron(II), cobalt(II), nickel(II) and copper(II) employing the Mössbauer ^{57}Fe effect. In addition, the electronic state of chelated iron(II) in Fe(DBAFc) $\cdot$ 2 H_2O is also compared with that of iron(II) in Fe(DBM)$_2 \cdot$ 2 H_2O (where DBM = dibenzoylmethane) by means of Mössbauer spectroscopy.

The configuration and physico-chemical properties of the complexes in the present work are discussed by means of molecular weight, solubility, magnetic moment measurement and uv-visible or i.r. spectra.

Experimental

Synthesis of ligand

The ligand was made by the previously described procedure[3].

Preparation of chelates

A solution of the ligand (1 mmole) in MeOH (25 cm^3) was added to the M^{II} acetate hydrate (1 mmole) in H_2O (20 cm^3). The precipitate obtained was filtered, washed with H_2O and dried *in vacuo*. The whole preparative operation was carried out under a N$_2$ atmosphere.

Physico-chemical measurements

Molecular weights were determined by Rast's method in camphor. I.r. spectra were recorded as KBr pellets or nujol

mulls with a Beckman 5250 spectrophotometer. Uv-visible spectra were recorded with Shimatzu UV-200 and QV-50 spectrophotometers in CHCl$_3$ solution (*ca.* 10^{-3} M).

Magnetic moments of the complexes in the solid state at 298 K were measured with a Newport Gouy balance.

The Mössbauer spectra of the complexes at 298 K and 78 K were measured with a Austin s-600 constant acceleration type Mössbauer spectrometer, using a $^{57}Co(Pd)$ source. The isomer shift (I.S.) was taken with respect to the centroid of the sodium nitroprusside.

Results and Discussion

Analytical data and the most notable characteristic i.r. bands in the 1500–1600 cm^{-1} region [ν(C=O)] are given in Table 1.

Two configurations for $M^{II}(DBAFc) \cdot$ 2 H_2O, *(1)* and *(2)*, are possible:

(1)   *(2)*
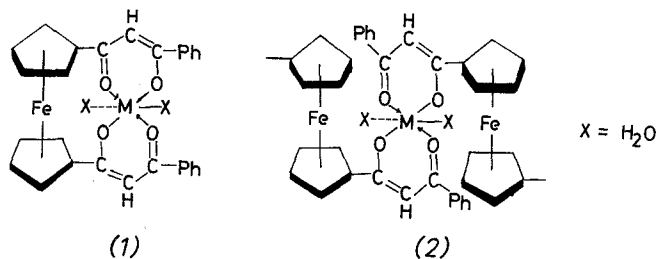
A structure of type *(1)* has been found for copper adducts[3]. The present molecular weight measurement results also suggest a monomeric structure for Cu(DBAFc) (Found 545; calcd. 538.3). On the other hand, molecular data, obtained for the other metal chelates by Rast's method, seem to exclude a similar configuration, and suggest a polymeric structure such as *(2)*. It should be noted that the Cu(DBAFc) complex is fairly soluble in some organic solvents (*e.g.* CHCl$_3$, CH$_2$Cl$_2$ or C$_6$H$_6$), whereas the corresponding complexes of iron, cobalt and nickel are only slightly soluble (*ca.* 10^{-3} M).

In the i.r. spectra of these complexes, the ν(C=O) absorption of the β-diketone ligand shifts slightly towards low wave numbers on going from free to the coordinated ligand. This suggests that the β-diketonate ion may be chelated to the divalent metal atoms in the complexes.

Electronic spectra

Absorption bands of each complex in the 20000–40000 cm^{-1} and 8000–20000 cm^{-1} regions are given in Table 2. Two bands at 28000–33000 cm^{-1} and 20000–22000 cm^{-1} are due to the absorptions of β-diketone and ferrocenyl respectively[2, 5].

The absorption bands in the 8000–20000 cm^{-1} region may be assigned to d–d transitions of the divalent metal ions in the complexes in which the ligand field of iron(II), cobalt(II) and nickel(II) chelates are assigned as octahedral tetragonal sym-

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* Author to whom all correspondence should be directed.

Table 1. Analytical and i.r. data for the complexes.

Compound	Found (calcd.) % C	H	Fe	Other	ν(C=O) (cm⁻¹)
					ν(C=O) (cm^{-1})
DBAFc	70.1(70.5)	4.08(4.22)	11.6(11.8)		1530
Fe(DBAFc) · 2 H₂O	58.8(59.1)	4.30(4.24)	20.4(19.6)		1525
Co(DBAFc) · 2 H₂O	59.0(58.8)	4.25(4.21)	9.9(9.8)	Co: 10.4(10.3)	1520
Ni(DBAFc) · 2 H₂O	58.6(58.8)	4.20(4.21)	9.5(9.8)	Ni: 10.1(10.3)	1518
Cu(DBAFc)	61.6(62.2)	3.80(3.72)	10.6(10.4)	Cu: 11.2(11.8)	1525

Table 2. Electronic spectra data for the complexes.

Compound	Absorption bands[a] (cm⁻¹)	(log ε)	Assignment
Fe(DBAFc) · 2H₂O	29 100	(4.65)	Ligand
	20 600	(3.60)	
	14 900	(0.90)	$^5A_{1g} \leftarrow {}^5E_g$
	9 100	(1.00)	$^5B_{1g} \leftarrow$
Co(DBAFc)· 2H₂O	28 300	(4.56)	Ligand
	21 000	(3.66)	
	15 500	(1.15)	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$
	14 000	(0.74)	$^4A_{2g} \leftarrow$
	8 900	(0.97)	$^4T_{2g}$
Ni(DBAFc)· 2H₂O	28 400	(4.60)	Ligand
	20 700	(3.67)	
	16 100	(0.54)	$^1E_g(D) \leftarrow {}^3A_{2g}(F)$
	14 200	(1.17)	$^3T_{1g}(F) \leftarrow$
	9 100	(0.90)	$^3T_{2g}(F) \leftarrow$
Cu(DBAFc)	28 200	(4.81)	Ligand
	20 500	(3.74)	
	16 000	(1.70)	$B_{2g}(D) \leftarrow B_{3g}$ or $A_g \leftarrow$

[a] Extinction coefficient in parentheses.

metry (D_{4h}) and copper(II) is assigned as having distorted square planar symmetry $(C_{2h})^{[6, 7]}$. In addition, the two absorption bands, 14880 and 9050 cm^{-1}, for Fe(DBAFc) · 2 H₂O may be compared with those of 14260 and 8600 cm^{-1} for Fe(DBM)₂ · 2 H₂O reported previously by Jorgensen[8]. This would imply that the field strength of DBM is weaker than that of DBAFc.

Mössbauer spectra and magnetic susceptibilities

Mössbauer parameters and magnetic data are given in Table 3. At room temperature, the effective magnetic moments, μ_{eff}, of Fe(DBAFc) · 2 H₂O, Co(DBAFc) · 2 H₂O and Ni(DBAFc) · 2 H₂O in the solid state are 5.37, 4.86 and 3.32 B.M. respectively; these values agree very closely with those for the normal high-spin distorted octahedral structures already adopted. In contrast, Cu(DBAFc) shows a moment of 1.90 B.M., although the μ_{eff} value for copper complexes (theoretical spin only) is 1.78 B.M., and usually is insensitive to ligand field symmetry.

For the Mössbauer data of the compound shown in Table 3, the isomer shifts (I.S. = 0.77 mms^{-1} at 78 K, 0.75 mms^{-1} at 298 K) and quadrupole splittings (Q.S. = 2.14 mms^{-1} at 78 K, 2.10 mms^{-1} at 298 K) for iron in 1,1'-dibenzoylacetylferrocene are slightly lower than those of ferrocene (I.S. = 0.79 mms^{-1} at 78 K, 0.77 mms^{-1} at 298 K; Q.S. = 2.40 mms^{-1} at 78 K, 2.36 mms^{-1} at 298 K). This shows that the benzoylacetyl moiety is electron attracting and this decreases the d-electron population of iron in DBAFc, thus decreasing the isomer shift.

Table 3. Magnetic moment data and Mössbauer parameters for the complexes.

Compound	μ_eff (B.M.) 298 K	Isomer shift 78 K	298 K	Quadrupole splitting 78 K	298 K
Ferrocene		0.79	0.77	2.40	2.36
DBAFc		0.77	0.75	2.14	2.10
Fe(DBAFc)·2H₂O[a]	5.37	(i) 0.78	0.75	2.24	2.17
		(ii) 1.47	1.35	2.88	2.66
Fe(DBM)₂·2H₂O[b]	5.20	1.18	1.09	2.59	2.38
Co(DBAFc)·2H₂O	4.86	0.77	0.76	2.28	2.18
Ni(DBAFc)·2H₂O	3.32	0.79	0.75	2.30	2.19
Cu(DBAFc)	1.90	0.78	0.75	2.32	2.21

[a] (i) For chelating site iron(II), (ii) for ferrocenyl site iron(II);
[b] DBM = Dibenzoylmethane.

Nevertheless, the isomer shifts of the iron atom at the ferrocene site in the DBAFc metal-chelates do not vary much with M = iron(II), cobalt(II), nickel(II) and copper(II). On the other hand, the quadrupole splittings at 78 and 298 K for the complexes do vary with respect to the chelated metal ions and decrease in the order: iron(II) < cobalt(II) < nickel(II) < copper(II). The Mössbauer spectrum of Fe(DBM)₂ · 2 H₂O is presented for comparison with that of Fe(DBAFc) · 2 H₂O. Table 3 shows that the Mössbauer parameters of both Fe(DBM)₂ · 2 H₂O and Fe(DBAFc) · 2 H₂O (chelated site iron) show a characteristic high-spin octahedral configuration for iron(II). Furthermore, the isomer shifts and the quadrupole splittings of Fe(DBM)₂ · 2 H₂O (I.S. = 1.18 mms^{-1} at 78 K, 1.09 mms^{-1} at 298 L; Q.S. = 2.59 mms^{-1} at 78 K, 2.38 mms^{-1} at 298 K)[9] are lower than those of iron(II) in the chelate site of Fe(DBAFc) · 2 H₂O (I.S. = 1.47 mms^{-1} at 78 K, 1.35 mms^{-1} at 298 K; Q.S. = 2.88 mms^{-1} at 78 K. 2.66 mms^{-1} at 298 K). This indicates that the electron attracting power of phenyl group is stronger than that of ferrocenyl, and that the total s-electron density at iron(II) in Fe(DBM)₂·2H₂O is higher than that of Fe(DBAFc)·2H₂O. These results are consistent with the view of an electronic absorption spectral d–d transition of iron(II) described previously.

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