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The Preparation and Some Properties of Potassium Tris(1,1′-ferrocenedicarboxylato)ferrate(III)

Tomoko Nomura
Department of Chemistry, Faculty of Science and Engineering, The Aoyama Gakuin University,
Shibuya, Shibuya-ku, Tokyo 150

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The $K_3[Fe(1,1'\text{-ferrocenedicarboxylato})_3]$ complex was synthesized. The infrared absorption bands of the ligand (parent) acid, its potassium and barium salts, and the complex were assigned in studying the nature of the oxygen-to-metal bond in the complex. The electronic absorption spectra of the ligand acid and the complex were also measured. The techniques of thermogravimetry (TG) and differential thermal analysis (DTA) were used to establish the thermal decomposition of the complex.

There are some complexes in which ferrocenyl groups are introduced into the ligand,[1,7,9] but no complexes with 1,1′-ferrocenedicarboxylic acid (H_2fdc) as ligands have yet been reported. The $K_3[Fe(1,1'\text{-ferrocenedicarboxylate})_3]$ ($K_3[Fe(fdc)_3]$) complex was synthesized by using iron(III) sulfate and barium 1,1′-ferrocenedicarboxylate. Its properties was investigated in the present study.

Experimental

Preparation of Ligand. H_2fdc was prepared according to Rausch and Ciappenelli.[2] The product recrystallized from glacial acetic acid was orange and melted, with decomposition, at *ca.* 246 °C (lit: decomposition over 240 °C). The product was identified by means of IR[3] and NMR measurments. Calcd for $C_{12}H_{10}O_4Fe$: Fe, 20.38%. Found: Fe, 20.1%.

Preparation of the Complex. The $K_3[Fe(fdc)_3]$ complex could not be synthesized by the following procedure:

$$2Fe(OH)_3 + 3H_2fdc \longrightarrow Fe_2(fdc)_3 + 6H_2O,$$

$$Fe_2(fdc)_3 + 3K_2fdc \longrightarrow 2K_3[Fe(fdc)_3].$$

However, the procedure of Bailar and Jones[4] could be successfully applied:

$$Fe_2(SO_4)_3 \cdot nH_2O + 3Bafdc \longrightarrow Fe_2(fdc)_3 + 3BaSO_4,$$

$$Fe_2(fdc)_3 + 3K_2fdc \longrightarrow 2K_3[Fe(fdc)_3].$$

$Fe_2(SO_4)_3$ (0.55 g), Bafdc (2.2 g) (prepared from $Ba(OH)_2 \cdot 8H_2O$ (3.15 g) and H_2fdc (2.74 g)), and K_2fdc (1.6 g) (prepared from K_2CO_3 (1.38 g) and H_2fdc (2.74 g)) were placed in water (400 cm^3) and digested for 3 h on a water bath. A crystalline substance then began to precipitate. After centrifugation, the filtrate was evaporated to *ca.* 70 cm^3, at which point crystals precipitated. The product, which formed after standing for 1 h, was filtered with suction and washed with 50% ethanol several times. Yellowish brown, flat crystals of $K_3[Fe(fdc)_3]$ were thus prepared in a nearly quantitative yield . The complex was stable in air, decomposed at 284 °C, and was insoluble in most organic solvents. It was dried *in vacuo* over silica gel at room temperature. Found: C, 44.86; H, 2.95; Fe, 22.1%. Calcd for $K_3[Fe(fdc)_3]$: C, 43.70; H, 2.42; Fe, 22.6%. Attempted recrystallizations with water and *N,N*-dimethylformamide were unsuccessful. In the case of a protogenic solvent such as acetic acid or an amphiprotic solvent such as water, the $K_3[Fe(fdc)_3]$ was changed to H_2fdc. In an organic solvent such as *N,N*-dimethylformamide, a slight decomposition was observed after one week.

Measurements. The electronic spectra were measured with a Shimadzu UV-200 spectrophotometer in cells with a 1-cm light path. The infrared spectra were measured with a JASCO IRA-1 spectrophotometer in the range of 650—4000 cm^{-1} on KBr pellets. The TG and DTA measurements were made with a Shimadzu DTA-20B differential thermal microbalance under two conditions, in static N_2 and air at the heating rate of 10 °C/min. The sample amounts taken in the TG runs were *ca.* 5 mg, and in the DTA runs, *ca.* 2 mg.

Results and Discussion

Composition of the Chelate. The $K_3[Fe(fdc)_3]$ complex crystals obtained in a solid state could not be recrystallized, and they were too fine for any powder X-ray study. The complex was, however, homogeneous and was found to be composed of single crystals under a polarizing microscope. Therefore it was considered that the complex was pure enough for the structural study. DTA and TG measurements showed that no water molecules existed in the complex. Considering that the majority of Fe(III) complexes are octahedral, like the tris(oxalato) complex, the molar ratio of Fe : H_2fdc (1 : 3) seems to be natural. The molecular weight and conductivity of the complex were not measured, since no suitable solvent could be found.

IR Spectra. A) Assignment of the Observed Frequencies of 1,1′-Ferrocenedicarboxylic Acid and Its Potassium and Barium Salts: The main bands are listed in Table 1. Characteristic bands for the carboxylic acid[3] were observed at 2625, 2545, and 914 cm^{-1} in the spectrum of the H_2fdc, which could be assigned to the OH stretching and out-of-plane OH deformation vibrations. A very strong band at about 1680—1720 cm^{-1} in the H_2fdc spectrum was assigned to the C=O stretching vibrations. Bands at 1492 and 1300 cm^{-1} in the H_2fdc spectrum were assigned to the C–O vibrations, coupled with the in-plane OH deformation vibration. Very strong bands at about 1600 cm^{-1} and other strong band at about 1400 cm^{-1} observed in the spectra of K_2fdc and Bafdc were assigned to the antisymmetric and symmetric OCO stretching vibration respectively. Strong bands at 1465 cm^{-1} in the K_2fdc spectrum and at 1475 cm^{-1} in the Bafdc spectrum were also assigned to the symmetric OCO stretching vibrations.

B) Assignment of the Observed Frequencies of the Potassium Tris(1,1′-ferrocenedicarboxylato)ferrate(III) Complex: On the basis of the reported data on the bands of similar complexes, such as the oxalato,[5] malonato,[6] and 1,1′-diacetylferrocenato complexes,[7] the absorption bands

TABLE 1. IR SPECTRA OF 1,1′-FERROCENEDICARBOXLIC ACID, POTASSIUM, AND BARIUM SALTS[a)]

H_2fdc($\tilde{\nu}$/cm^{-1})	$K_2fdc \cdot xH_2O$($\tilde{\nu}$/cm^{-1})	$Bafdc \cdot H_2O$($\tilde{\nu}$/cm^{-1})	Assignment
	3380 m,b	3380 m,b	$\nu(H_2O)$[b)]
	3070 w	3090 w	$\nu(CH)F_c$
3120 ~ 2860			$\nu(OH)$
2625 vw			$\nu(OH)$
2545 vw			$\nu(OH)$
1720 s,sh 1680 vs,b			$\nu_a(C{=}O)$
	1575 vs,b	1555 vs,b 1525 vs,b	$\nu_a(OCO)$
1492 s			$\nu_s(CO)+\delta(OH)$
	1465 s	1475 s	$\nu_s(OCO)$
1405 m			$\nu(CC)F_c$
1374 w			
	1387 s 1362 s 1340 m,sh	1388 s 1358 m 1346 m	$\nu_s(OCO)$
1300 s			$\delta(OH)+\nu_s(CO)$
1166 m	1187 w 1176 w	1183 w	$\nu_a(CC)$
1025 m	1035 w 1010 w	1028 m	$\delta(CH)F_c$
914 m,b			$\pi(OH)$
823 m,b	808 m 784 m	808 m 780 w,sh	$\delta(OCO)+\pi(CH)F_c$
775 vw			
742 w			

a) The absorption bands: s=strong, w=weak, m=medium, v=very, sh=shoulder, b=broad, *a*=antisym., *s*=sym., F_c=ferrocenyl group, δ=in-plane def., π=out-of-plane def. b) The stretching vibration of H_2O.

TABLE 2. IR SPECTRA OF POTASSIUM TRIS(1,1′-FERROGENEDICARBOXYLATO)FERRATE(III)

$K_3[Fe(fdc)_3]$ ($\tilde{\nu}$/cm^{-1})	Assignment
3100 vw, b	$\nu(CH)F_c$
1677 vs	$\nu_a(C{=}O)$
1586 m 1542 m	$\nu_a(OCO)$
1465 s,b	$\nu_s(OCO)$
1380 m 1353 w 1325 w	$\nu_s(OCO)$
1280 vs,b	$\nu_s(CO)+\delta(OCO)$
1160 m	
1025 w	$\delta(CH)F_c$
905 vw	
816 w 775 w	$\delta(OCO)$
724 w,b	

of $K_3[Fe(fdc)_3]$ were assigned; they are shown in Table 2 and Fig. 1 (——). The bands at 2860—3120, 2625, and 2545 cm^{-1} assignable to the OH stretching vibration were not observed. The very strong C=O stretching vibration at 1680—1720 cm^{-1} in the ligand was shifted to a lower frequency, 1677 cm^{-1}, in the complex. New bands were observed at 1586 and 1542 cm^{-1}; they were assigned to the antisymmetric OCO stretching vibrations corresponding to the bands at 1555 and 1525 cm^{-1} respectively present in the spectrum of Bafdc. The band at 1465 cm^{-1} corresponded to the bands of symmetric OCO stretching vibration in the K_2fdc and Bafdc spectra. The band at 1380 cm^{-1} and new weak bands at 1353 and 1325 cm^{-1} assigned to the symmetric OCO stretching vibrations corresponded to the bands at 1387, 1362, and 1340 cm^{-1} respectively in the K_2fdc spectrum and to the bands at 1388, 1358, and 1346 cm^{-1} in the Bafdc spectrum. The nature of the metal-to-ligand

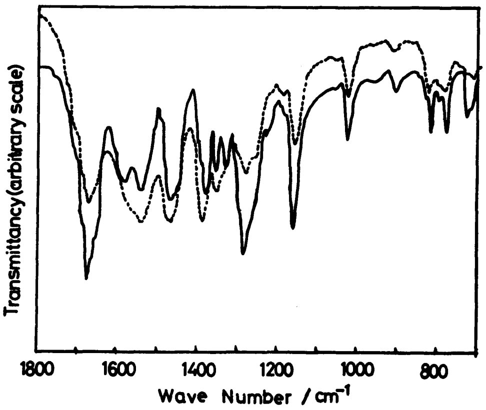

Fig. 1. IR spectra of $K_3[Fe(fdc)_3]$ (——) and the thermal decomposition product of $K_3[Fe(fdc)_3]$ after heating at 290 °C in N_2 in the DTA procedure (------).

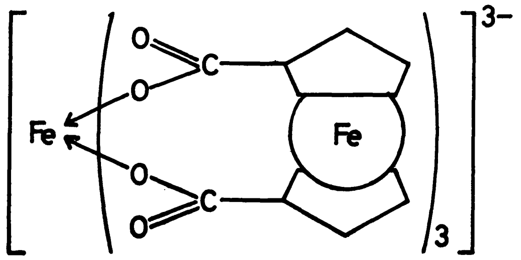

Fig. 2. The structure of $K_3[Fe(fdc)_3]$.

TABLE 3. ELECTRONIC SPECTRAL DATA FOR LIGAND AND COMPLEX

Compound	Solvent	$\tilde{\nu}/10^3$ cm^{-1} (logϵ)		
H_2fdc	95% EtOH	32.4(3.12),	28.6(2.58),	22.3(2.47)
	H_2O	32.3sh,		22.1
	DMSO	32.3sh(3.13),	28.6(2.60),	22.2(2.46)
$K_3[Fe(fdc)_3]$				
	95% EtOH	32.3sh,	28.6sh,	22.3
	H_2O	32.3sh,		22.0sh
	DMSO	32.3sh(3.63),	28.6sh(3.25),	22.0(2.95)

The ligand did not dissolve enough in H_2O, and the complex, in 95% EtOH and H_2O, to enable us determine the extinction coefficients. sh=shoulder.

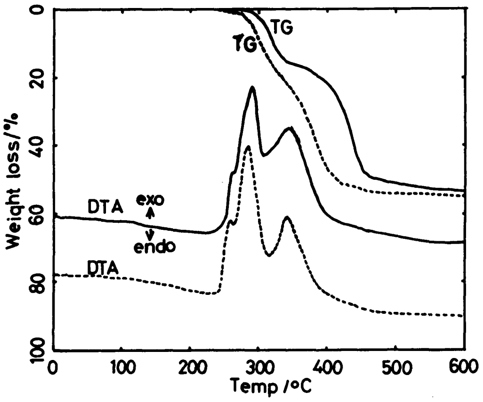

Fig. 3. TG and DTA curves of $K_3[Fe(fdc)_3]$ in N_2 (——) and in air (------).

bond (M–O) could thus be studied indirectly from the value of the CO stretching frequency, without determining the M–O stretching vibration, which appears at a much lower frequency. The structure deduced from these data is shown in Fig. 2.

Electronic Spectra. The electronic spectra of H_2fdc and its complex was measured in three solvents: 95% ethanol (EtOH), dimethyl sulfoxide (DMSO), and H_2O. The absorption bands in the (12.5—33.5)$\times 10^3$ cm^{-1} region are given in Table 3. In these spectra, a broad low-intensity band around 440 nm, which is identified as a forbidden d-d transition localized on the iron atom, and another band at 325 nm, which is identified as a N–Q transition or as a symmetry-forbidden N–V transition, are characteristic. In comparison with the absorption bands of ferrocene (325 nm (ε, 49), 440(91)) and ferrocenemonocarboxylic acid (342^{sh}-(361), 445(223)) in 95% EtOH,[8] the spectrum of the H_2fdc showed a bathochromic shift. These bands shifted with substitution on the cyclopentadienyl ring, and the intensity increased in such derivatives where a ferrocene was conjugated with COOH. In the spectrum of the complex, the positions of the absorption bands were negligibly changed, while the intensities increased. Interestingly, the change in the electronic spectrum was not so pronounced as would be expected when COOH groups substituted on ferrocene are coordinated to Fe^{III}. The H_2fdc ligand has a strongly aromatic nature with π electrons. When such ligands are coordinated to a metal, the spectrum of the complex is almost the same as that of a free ligand. Therefore the electronic spectrum of the complex showed the absorption bands based on the ligand.

TG and DTA. The data for $K_3[Fe(fdc)_3]$ are shown in Fig. 3. They show that the thermal-decomposition process of $K_3[Fe(fdc)_3]$ proceeds in two stages, corresponding to the exothermic peaks at 284 and 339 °C in air and at 289 and 343 °C in N_2. The H_2fdc ligand is decomposed with an exothermic peak at 246 °C in air. In the investigation of the thermal decomposition of $K_3[Fe(fdc)_3]$ in N_2, the solid residue obtained at 290 °C (loss in weight 12%) was identified by means of its IR spectra. Figure 1 (------) shows that the strong absorption band at 1677 cm^{-1} assigned to the C=O stretching vibration and that at 1280 cm^{-1} assigned to the C=O stretching and the O–C$\cdots$O deformation vibrations were both very much reduced. The weak absorption bands at 1586, 1325, and 730 cm^{-1} disappeared. These spectral changes show that the Fe–O bonds are partially dissociated by heating. After the extraction of this solid residue with *N,N*-dimethylformamide, ferrocene or its derivative was not found by studying IR spectra of the extract. It seems that such an organic compound is sublimed in the thermal decomposition process, as has been described in the literature.[9] The solid residue obtained at 360 °C (loss weight in 49.8%) was identified by means of its IR spectra; it was found to be potassium carbonate. A comparison of the thermal decomposition of the chelate of H_2fdc and that of the chelate of oxalic acid[10] shows that the thermal stability rises a little upon the introduction of the carboxyl groups into ferrocene, which is thermally stable.

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