Synthesis of novel heterobimetallic complexes of 1,5-bis(2-carboxyphenyl)-3-ferrocenylformazan

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Abstract

1,5-Bis(2-carboxyphenyl)-3-ferrocenylformazan (BFF) has been synthesized by the coupling reaction of the diazonium salt of 2-aminobenzoic acid and ferrocenealdehyde-2-carboxyphenylhydrazone (FFH). FFH was obtained from the condensation reaction of ferrocenealdehyde with 2-carboxyphenylhydrazine. The Cu(II) and Co(III) complexes of BFF have been isolated. The structures of the formazan and its complexes were confirmed on the basis of elemental analysis, proton and ^{13}C NMR, IR and UV–Vis spectral data.

Introduction

Formazans and their metal complexes are of interest in the field of dyes, medicine and biochemistry [1–3]. The pharmaceutical effects of azo groups are known to be important [4]. In addition, the oxidation product of formazans, namely tetrazolium salts, have attracted attention as bio-indicators. The formazans themselves have found application in dyeing various textile fibers [5]. The structure of the formazans, bearing the $-N{=}N-C{=}N-NH$ skeleton, was first determined by Bamberger and Weelwright [6]. According to the number of formazans groups in the molecule, these compounds are named as formazan or bis(formazan). Two important aspects of these structures are the strong tautomerism due to the existence of more-than-one conjugation or intramolecular hydrogen bonding [7, 8]. Although organometallic and coordination chemistry are regarded to be closely related, there are relatively few examples of compounds for which both the attributes coordination and organometallic can be used. In recent years, there has been much interest in binuclear complexes [9]. This is partly due to the relevance of binuclear compounds to bioorganic systems [10].

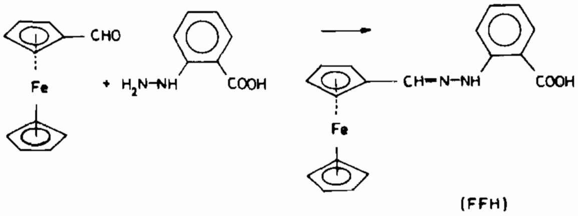
Metal complex formation by tetradentate groups has been investigated by Tobel and Wizinger [11] who studied the reactions of these compounds and their transition metal complexes.

We have previously studied the synthesis and chracterization of bis(formazan) [12] and the effects of the substitution of a crown ether ring on the properties of the compound [13].

We describe here the results of a study on the changes in the donor properties of formazan and carboxy groups due to an attachment to the ferrocene ring system. To achieve this, the hydrazone of ferrocenealdehyde with 2-carboxyphenylhydrazine (FFH) and a formazan derived from FFH and the 2-carboxyphenyl diazonium salt and its complexes with Cu(II) and Co(III) were investigated.

Results and discussion

Ferrocenealdehyde-2-carboxyphenylhydrazone (FFH) was prepared from the addition reaction of ferrocenealdehyde with 2-carboxyphenylhydrazine (Scheme 1). In the ^{1}H NMR spectrum of FFH, the signals from the α and β protons of cyclopentadienyl appeared as two discrete singlets at $\delta = 4.38$ and 4.21 ppm, and those of free cyclopentadienyl as a singlet



Scheme 1.

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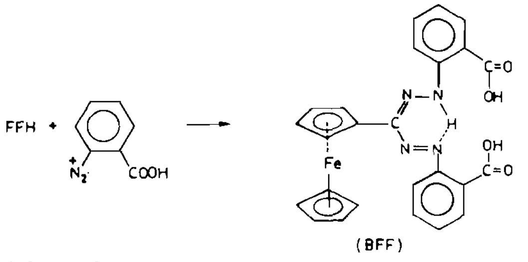
at $\delta = 3.58$ ppm. The D_2O exchangeable NH proton of the hydrazine group appeared at $\delta = 7.44$ ppm, as a singlet. In the ^{13}C NMR spectrum of this compound the carbon resonances of the cyclopentadienyl ring were assigned according to the literature [14]. The bridgehead carbon, α- and β-carbons of the cyclopentadienyl rings showed their resonances at 131.15, 69.09 and 62.76 ppm, respectively. The resonances of the phenyl ring were shifted upfield as expected.

In the IR spectrum of FFH, the bands due to $\nu(N-H)$, $\nu(O-H)$, $\nu(C=O)$, $\nu(C=N)$ and $\delta(O-H)$ stretchings appear at 3280, 3100, 1680, 1640 and 1430 cm^{-1}, respectively; and these values are comparable to those of similar compounds [15]. The C−H out-of-plane bending vibrations of the ferrocene group gave a resonance at 810 cm^{-1}.

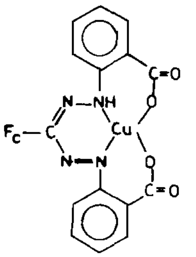
BFF has been obtained by the reaction of FFH with the diazonium salt of 2-aminobenzoic acid in strong alkali media (Scheme 2). The ^1H NMR spectrum of BFF was very similar to that of FFH, lacking only the C−H (aldehydic) signal which disappears after formazan formation. The ^{13}C NMR spectrum of BFF was also similar to that of FFH. However, new carbon resonances, which belong to the new 2-carboxyphenyl azo group, appeared. These new carbon resonances are observed in a similar position for both FFH and BFF.

In the IR spectrum of BFF, the formation of formazan is further confirmed by N=N vibrations at 1400 cm^{-1}. As the $-N=N-$ group in the proposed structure of BFF (Scheme 2) is unsymmetrical, it gives rise to an IR band due to the stretching mode in the 1400–1450 cm^{-1} region, the characteristic range for azo groups [16]. Skeletal vibrations of the $C-N=N-C$ or $C=N-N-C$ groups appear at 1000 cm^{-1} [17]. In addition to this, the $\nu(N-H)$ vibration at 3300 cm^{-1} indicates that there is an NH··N intramolecular hydrogen bonding in the molecule. Since one of the azonitrogens is involved in the hydrogen bonding a noticeable downward shift of the azo band [18] is observed.



Scheme 2.

Reaction of BFF with copper(II) acetate was carried out in ethanol. The solution gradually turned black upon addition of a solution of BFF to the solution of the metal salt. Elemental analysis data indicate a 1:1 metal/ligand ratio (Fig. 1). Even if excess Cu(II) salt was added to complex with the tetradentate donor groups of the formazan, only one type of complex was obtained [19]. The suggested structure of the Cu(II) complex of BFF is confirmed by IR data. The existence of the $\nu(N-H)$ band at 3340 cm^{-1} in the IR spectrum is as expected. The absence of $\nu(O-H)$ bands, which belong to the carboxyl groups, indicates that the suggested structure for the complex is likely to be that given in Fig. 1.



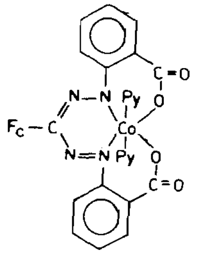


Fig. 1. The Cu(II) complex.

Fig. 2. The Co(III) complex.

The reaction of BFF with cobalt(II) acetate was carried out in ethanol and in oxidizing conditions. Elemental analysis results show a 1:1 metal/ligand ratio. The IR spectrum of trivalent cobalt which forms a tricyclic complex with tetradentate formazan indicates the structure which is illustrated in Fig. 2. The absence of $\nu(N-H)$ bands, which belong to the hydrazine group, suggests that the structure of the Co(III) complex is probably that shown in Fig. 2.

The absorption bands corresponding to the d–d transition of ferrocene appeared at longer wavelengths (455–451 nm) for FFH and BFF than that of the ferrocene itself (440 nm) [20, 21]. A further bathochromic shift takes place after complexation with Cu (468 nm) or Co (472 nm). The absorption bands at 434, 442 and 431 nm indicate the transition which belongs to the formazan structure [22]. The charge-transfer transitions are observed at 614 and 553 nm.

Experimental

^1H and ^{13}C NMR spectra and elemental analysis were recorded on a Bruker AC-200 FT-NMR spectrophotometer and Perkin-Elmer 240C elemental analyzer. IR and UV–Vis spectra were recorded on Perkin-Elmer 1600 FT-IR and GBC 911 spectrophotometers, respectively. Ferrocenealdehyde and 2-carboxyphenyl hydrazine hydrochloride (Aldrich) and 2-aminobenzoic acid (Koch-Light) were used without further purification.

Ferrocenealdehyde-2-carboxyphenylhydrazone (FFH)

To a solution of free 2-carboxyphenylhydrazine (0.7612 g, 5 mmol), which was prepared by mixing an ethanolic solution of 2-carboxyphenylhydrazine-hydrochloride (0.943 g, 5 mmol) in absolute ethanol (40 ml) with a solution of NaOH (0.2 g, 5 mmol) in absolute ethanol (30 ml), ferrocenealdehyde (1.07 g, 5 mmol) was added in small portions. The mixture was refluxed and stirred for 5 h and then filtered. The filtrate was evaporated until no ethanol could be detected. The red residue was continuously extracted with hot n-heptane. The extract was cooled in the refrigerator at 0 °C. The red crystals formed were filtered off, washed with cold n-heptane and then dried under vacuum. Yield 1.250 g (71.8%), m.p. 185 °C. The product was soluble in ethanol, acetone, and DMF. ^{1}H NMR (DMSO-d$_6$): δ 3.98 (s, 5H), 4.21 (s, 2H), 4.38 (s, 2H), 6.74 (m, 2H), 7.44 (s, 1H), 7.56 (m, 2H), 7.89 (s, 1H), 8.65 (s, 1H) ppm. ^{13}C NMR (DMSO-d$_6$): δ 131.1 (C_b), 69.1 (C_β), 62.7 (C_α), 169.6, 147.13, 141.13, 134.2, 133.2, 116.6, 112.7, 109.4, 80.4, 70.16, 69.33, 68.83, ppm. IR (KBr): 3280, 3100, 3040, 2980, 2900, 2840, 1680, 1640, 1595, 1565, 1500, 1430, 1400, 1375, 1310, 1250, 1220, 1200, 1150, 1100, 940, 810, 750, 480 cm^{-1}. UV–Vis (DMF): λ 489 (ϵ 4614), 451 (3340), 407 (2923), 372 (2300), 355 (8908), 331 (6264). *Anal.* Found: C, 61.81; H, 4.42; N, 7.73. Calc. for $C_{18}H_{16}N_2O_2Fe$: C, 62.06; H, 4.59; N, 8.04%.

1,5-Bis(2-carboxyphenyl)-3-ferrocenylformazan (BFF)

2-Aminobenzoic acid (0.4548 g, 3.318 mmol) was dissolved in 0.75 ml of conc. HCl in an ice-bath, and to this, $NaNO_2$ (0.230 g, 3.332 mmol) was added in small portions while stirring. It was assured by potassium iodide–starch paper that sodium nitrite was in excess. A solution of FFH (0.696 g, 2 mmol) which was dissolved in 50 ml of NaOH solution (5%) at 0 °C, was added to above-mentioned diazonium solution. After stirring for 5 h at 0 °C, the solution was acidified with 0.2 M HCl up to pH = 4.80 and the dark-red formazan was precipitated. The crude product was filtered off, washed with water and then dried under vacuum. The product was purified by dissolving in alkaline media and then reprecipitated with 0.2 M HCl. Yield 0.622 g (62.8%), m.p. 222 °C. The product was soluble in ethanol, acetone and DMF. ^{1}H NMR (DMSO)-d$_6$): δ 3.76 (s, 5H), 4.22 (s, 2H), 4.37 (s, 2H), 6.85 (m, 4H), 7.60 (s, 4H), 7.48 (s, 1H), 8.08 (s, 2H) ppm. ^{13}C NMR (DMSO-d$_6$): δ 131.76 (C_b), 69.21 (C_β), 64.63 (C_α), 169.41, 146.58, 134.25, 132.80, 130.73, 129.12, 116.52, 115.45, 98.40, 85.81, 78.15, 70.29, 68.90, 68.70, 68.51, 66.63 ppm. IR (KBr): 3290, 3120, 3050, 2900, 2850, 1710, 1670, 1590, 1560, 1490, 1445, 1400, 1360, 1300, 1230, 1150, 1100, 1000, 950, 820, 750, 490 cm^{-1}. UV–Vis(DMF): λ 551 (ϵ 4166), 511 (3501), 457 (5158), 434 (7200), 429 (8332), 362 (13 500), 333 (7539), 315 (19 244). *Anal.* Found: C, 60.18; H, 3.83; N, 11.01 Calc. for $C_{25}H_{20}N_4O_4Fe$: C, 60.48; H, 4.03; N, 11.29%.

Cu(II) complex of BFF

A solution of $Cu(CH_3COO)_2 \cdot 2H_2O$ (0.1087 g, 0.5 mmol) in ethanol (15 ml) was added to a solution of BFF (0.248 g, 0.5 mmol) in ethanol (25 ml). The mixture was refluxed with stirring for 3 h. The black precipitate was removed by filtering, washed with water and ethanol. The product was further purified with hot ethanol and then dried in vacuum. Yield 0.269 g (96.5%), m.p. 272 °C. The product was soluble in DMF, DMSO and pyridine. IR (KBr):3340, 3040, 2900, 1690, 1650, 1585, 1550, 1475, 1440, 1430, 1390, 1370, 1280, 1150, 1010, 970, 800, 750, 485 cm^{-1}. UV–Vis(DMF): λ 605 (ϵ 3740), 545 (11700), 452 (7210), 412 (6228), 371 (5420), 333 (6416), 324 (44560). *Anal.* Found: C, 53.57; H, 3.04; N. 9.82. Calc. for $C_{25}H_{18}N_4O_4FeCu$: C, 53.81; H, 3.22; N, 10.04%.

Co(III) complex of BFF

A solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (0.125 g, 0.5 mmol) in ethanol (40 ml) was added to a solution of BFF (0.248 g, 0.5 mmol) in ethanol (25 ml). Pyridine (0.48 g, 6 mmol) in ethanol (10 ml) was added and air was bubbled through the solution for 3 h while refluxing and stirring. The dark-brown precipitate was removed by filtering and washed with water and ethanol. Then the product was purified with hot ethanol and diethyl ether and then dried in vacuum. Yield 0.246 g (89.1%), m.p. > 300 °C. The product was soluble in DMF, DMSO and pyridine. IR (KBr): 3040, 2900, 1710, 1650, 1595, 1590, 1565, 1540, 1485, 1440, 1400, 1390, 1345, 1300, 1225, 1150, 1100, 815, 760, 520 cm^{-1}. UV–Vis (DMF): λ 614 (ϵ 2649), 555 (11 840), 509 (15370), 475 (10 265), 437 (12 163), 340 (6792), 311 (18 458). *Anal.* Found: C, 58.84; H, 3.59; N, 11.57. Calc. for $C_{35}H_{27}N_6O_4FeCo$: C, 59.15; H, 3.80; N, 11.83%.

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