

Synthesis of Cyclodextrin Inclusion Complexes with (η -Cyclopentadienyl)iron Derivatives as Potential Nonlinear Optics Materials*

A. R. Dias¹, M. H. Garcia^{1,2}, M. P. Robalo^{1,3}, A. P. S. Tekheira^{1,3},
L. A. Bulygina⁴, and V. I. Sokolov⁴

¹ Structural Chemistry Center, High Institute of Technology, Lisbon, Portugal

² University of Lisbon, Portugal

³ University of Evora, L. A. Verney College, Portugal

⁴ Institute of Organometallic Chemistry, Russian Academy of Sciences,
ul. Vavilova 28, Moscow, 117813 Russia

Received October 25, 2000

Abstract—Dicarbonyl(η -cyclopentadienyl)iron tetrafluoroborates containing aromatic nitriles as ligands were synthesized. These and other (η -cyclopentadienyl)iron derivatives were used to obtain intercalation compounds with β -cyclodextrin.

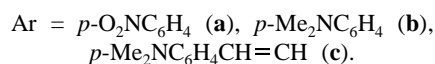
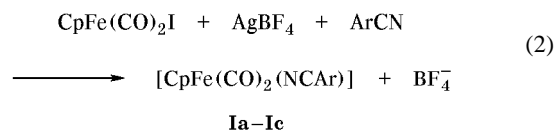
A promising line in the development of material science is synthesis of new compounds possessing nonlinear optical properties [1–3]. High-intense light flux (E) generated by laser produces nonlinear dependence of the induced molecular polarizability P :

$$P = \alpha E + \beta E^2 + \gamma E^3 + \dots \quad (1)$$

The second-order nonlinear polarizability coefficient is also called first hyperpolarizability. The emission frequency $n\nu$ is a multiple of the initial laser frequency ν ; it is called n th harmonic of the base frequency. As a result, each laser gives rise to a certain set of frequencies, which is of practical importance. From the viewpoint of stereochemistry, it is essential that even harmonics are characterized by nonzero coefficient only when the molecular crystal lacks symmetry center. Therefore, chiral molecules should necessarily have the second harmonic, but the magnitude of the nonlinear effect, i.e., the value of β , is difficult to predict. A universal way of making any molecule chiral is its incorporation into a chiral matrix, e.g., by obtaining complexes with natural optically active cyclodextrins [4, 5].

Among organometallic compounds there are many kinds of molecules possessing nonlinear optical properties. Specifically, such compounds are substituted ferrocenes [6–9] and dicarbonyl(η -cyclopentadienyl)iron derivatives [10]. The presence of donor and acceptor groups in these molecules favors charge separation which enhances nonlinear polarizability. Cyclodextrin complexes are well known for a number of transition metals [11, 12]. Nonzero values of β were found for complexes formed by intercalation of ferrocene and other achiral molecules into a chiral matrix [13].

The goal of the present study was to synthesize cyclodextrin complexes with some cationic dicarbonyl(η -cyclopentadienyl)iron complexes containing an aromatic nitrile as ligand. Such derivatives should be characterized by a nonzero second harmonics. They were prepared from dicarbonyl(η^5 -cyclopentadienyl)iron iodide by reaction (2).



* This study was financially supported by the European Program “Supramolecular Chemistry” (1995–1997).

Cyclodextrin complexes of water-soluble compounds are usually prepared by joint crystallization from hot aqueous solution on cooling. We applied the same procedure to obtain the above salt-like complexes. With less soluble compounds it is necessary to resort to a heterogeneous procedure, according to which a solid organometallic complex or organic ligand is added to a hot aqueous solution of β -cyclodextrin and the resulting suspension is stirred for several hours. After cooling, the precipitate is filtered off and is thoroughly washed with water to remove free cyclodextrin. The product is dried under reduced pressure, and excess of the "guest" compound is removed by extraction with hexane or methylene chloride. This treatment does not cause decomposition of the inclusion compounds which can be dissolved in dimethyl sulfoxide. The products were characterized by the IR and NMR spectra and elemental analyses.

As a rule, the stoichiometry of the obtained complexes was 1:1. The formation of inclusion compounds is strongly hindered by steric factors. For example, stable β -cyclodextrin complexes were obtained mainly with those monocyclopentadienyliron derivatives which had two CO ligands, though the third ligand (aromatic nitrile) has a larger size than, e.g., methyl group in $\text{CpFe}(\text{CO})_2\text{CH}_3$ for which the formation of an analogous complex with β -cyclodextrin has recently been reported [14]. The presence of bulkier phosphine or phosphite ligands, such as PPh_3 , $\text{P}(\text{OPh})_3$, or dppe , either prevents formation of inclusion complexes with cyclodextrin or strongly reduces their yield, as in the case of iodides **IV** and **V**. It is known that ferrocene derivatives in which one cyclopentadienyl ring is unsubstituted readily form monocyclodextrin complexes. With an aryethylene derivative we previously revealed formation of a double complex containing 1 equiv of β -cyclodextrin per each of the ferrocenyl and aryl fragments [15].

EXPERIMENTAL

All reactions were carried out under nitrogen. β -Cyclodextrin as undecahydrate (Aldrich) was dried under reduced pressure and was used without additional purification. The NMR spectra were recorded on a Varian instrument at 300 MHz for ^1H or 75 MHz for ^{13}C at 23°C in $(\text{CD}_3)_2\text{CO}$ or $(\text{CD}_3)_2\text{SO}$ using tetramethylsilane as internal reference (signals from the cyclodextrin protons are not given). The IR spectra were obtained in KBr on a Perkin-Elmer Paragon 1000 PC spectrophotometer; the frequencies were referenced to the polystyrene line at 1601.4 cm^{-1} .

Compounds of the general formula $[\text{CpFe}(\text{CO})_2\text{L}] \cdot \text{BF}_4$ (**Ia–Ic**) were synthesized by analogy with the procedure reported in [16, 17]. To a solution of 2.0 mmol of $\text{CpFe}(\text{CO})_2\text{I}$ in anhydrous methylene chloride we added at room temperature 2 mmol of AgBF_4 and 2.4 mmol of appropriate nitrile L. The mixture was stirred for 2 h, filtered, and evaporated to dryness. The residue was repeatedly washed with diethyl ether to remove excess nitrile and was recrystallized from methylene chloride–diethyl ether.

Dicarbonyl(η^5 -cyclopentadienyl)(*p*-nitrobenzonitrile)iron tetrafluoroborate (Ia). Yellow crystals, yield 35%. IR spectrum, ν , cm^{-1} : 3111 (Cp), 2269 (CN), 2074 (CO), 2015 (CO), 1524 (NO_2), 1345 (NO_2), 1053 (BF_4), 1033 (BF_4). ^1H NMR spectrum (acetone- d_6), δ , ppm: 5.81 s (5H, Cp), 8.26 d (2H, $J = 9.0$ Hz), 8.44 d (2H, $J = 8.4$ Hz). ^{13}C NMR spectrum (acetone- d_6), δ_{C} , ppm: 88.40 (Cp), 117.32 (C^1), 125.03 (C^3 , C^5), 134.15 (CN), 136.16 (C^2 , C^6), 151.89 (C^4), 209.14 (CO).

Dicarbonyl(η^5 -cyclopentadienyl)(*p*-dimethylaminobenzonitrile)iron tetrafluoroborate (Ib). Orange crystals, yield 60%. IR spectrum, ν , cm^{-1} : 3117 (Cp), 2257 (CN), 2064 (CO), 2018 (CO), 1063 (BF_4), 1035 (BF_4). ^1H NMR spectrum (acetone- d_6), δ , ppm: 3.09 s (6H, NMe_2), 5.73 s (5H, Cp), 6.79 d (2H, 3-H, 5-H, $J = 9.3$ Hz), 7.61 d (2H, 2-H, 6-H, $J = 9.1$ Hz). ^{13}C NMR spectrum (acetone- d_6), δ_{C} , ppm: 39.85 (Me_2N), 87.97 (Cp), 94.74 (C^1), 112.19 (C^3 , C^5), 135.27 (C^2 , C^6), 138.61 (CN), 154.64 (C^4), 209.80 (CO).

Dicarbonyl(η^5 -cyclopentadienyl)[β -(*p*-dimethylaminophenyl)acrylonitrile]iron tetrafluoroborate (Ic). Yellow crystals, yield 38%. IR spectrum, ν , cm^{-1} : 3118 (Cp), 2250 (CN), 2076 (CO), 2034 (CO), 1612 (C=C), 1053 (BF_4), 1036 (BF_4). ^1H NMR spectrum (acetone- d_6), δ , ppm: 3.70 s (6H, NMe_2), 5.73 s (5H, Cp), 6.04 d (1H, $J = 16.5$ Hz), 6.75 d (2H, $J = 8.4$ Hz), 7.47 d (2H, $J = 9.3$ Hz), 7.62 d (1H, $J = 16.5$ Hz). ^{13}C NMR spectrum (acetone- d_6), δ_{C} , ppm: 40.36 (Me_2N), 86.97 (C^8), 88.02 (Cp), 112.96 (C^3 , C^5), 122.21 (C^1), 131.04 (C^2 , C^6), 138.25 (CN), 153.76 (C^4), 156.27 (C^7), 209.72 (CO).

Cyclodextrin complexes with uncoordinated nitriles *p*-(CH_3) $_2\text{NC}_6\text{H}_4\text{CN}$ (II) and *trans*-(CH_3) $_2\text{N}-\text{C}_6\text{H}_4\text{CH}=\text{CHCN}$ (III). Finely powdered substituted benzonitrile, 1.3 mmol (1.3 equiv), was added at 60°C to 50 ml of an aqueous solution of 1.0 mmol of β -cyclodextrin, and the mixture was stirred for 24 h

at room temperature and was placed in a refrigerator. The crystals were filtered off, washed with hot water to remove free cyclodextrin, and dried under reduced pressure over P_2O_5 . Excess nitrile was removed by washing with methylene chloride. Complexes **II** and **III** were isolated as light yellow powders. Yield 90–92%. Complex **II**: IR spectrum: $\nu(\text{CN})$ 2212 cm^{-1} . ^1H NMR spectrum (DMSO- d_6), δ , ppm: 2.98 s (6H, NMe_2), 6.74 d (2H, $J = 9.0$ Hz), 7.52 d (2H, $J = 8.4$). Found, %: C 44.10; H 6.70; N 1.76. $\text{C}_{51}\text{H}_{80}\text{N}_2\text{O}_{35} \cdot 6\text{H}_2\text{O}$. Calculated, %: C 44.09; H 6.67; N 2.02.

Complex **III**. IR spectrum: $\nu(\text{CN})$ 2208 cm^{-1} . ^1H NMR spectrum (DMSO- d_6), δ , ppm: 2.96 s (6H, NMe_2), 6.03 d (1H, $J = 16.5$ Hz), 6.69 d (2H, $J = 8.7$ Hz), 7.43 d (1H, $J = 19.8$ Hz), 7.45 d (2H, $J = 6.3$ Hz). Found, %: C 44.88; H 6.79; N 1.75. $\text{C}_{53}\text{H}_{82}\text{N}_2\text{O}_{35} \cdot 6\text{H}_2\text{O}$. Calculated, %: C 44.98; H 6.69; N 1.98.

Cyclodextrin complexes with $\text{CpFe}(\text{CO})_2\text{I}$ (IV) and $\text{CpFe}[\text{P}(\text{OPh})_3](\text{CO})\text{I}$ (V). Finely powdered iron complex, 1.0 mmol, was added with stirring to a solution of 1.0 mmol of cyclodextrin in 30 ml of water, heated to 60°C. The mixture was stirred for 30 h at room temperature and was placed in a refrigerator. After 2 h, the resulting cyclodextrin complex was filtered off, washed with water to remove free cyclodextrin, and dried under reduced pressure over P_2O_5 . Unchanged iron complex was removed by washing with hexane. Complexes **IV** and **V** were isolated as greenish–brown powders.

Complex **IV**. Yield 70%. IR spectrum, ν , cm^{-1} : 2033 and 1988 (CO). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 5.36 s (5H, Cp). Found, %: C 38.47; H 5.74. $\text{C}_{49}\text{H}_{75}\text{FeIO}_{37} \cdot 5\text{H}_2\text{O}$. Calculated, %: C 38.49; H 5.60.

Complex **V**. Yield 11%. IR spectrum, ν , cm^{-1} : 1971 (CO), 1187 and 1159 [$\text{P}(\text{OPh})_3$]. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 4.27 s (5H, Cp), 7.26–7.48 m [15H, $\text{P}(\text{OPh})_3$]. Found, %: C 45.21; H 5.93. $\text{C}_{66}\text{H}_{90}\text{FeIPO}_{39} \cdot 2.5\text{H}_2\text{O}$. Calculated, %: C 44.88; H 5.42.

Cyclodextrin complexes VIa–VIc with dicarbonyl(η^5 -cyclopentadienyl)(nitrile)iron tetrafluoroborates Ia–Ic. An aqueous solution of nitrile complex **Ia–Ic** was added with stirring to an aqueous solution of an equimolar amount of β -cyclodextrin undecahydrate, heated to 40°C (**Ia**) or 80°C (**Ib** and **Ic**). After 15 min, the heating bath was removed, and the mixture was stirred for 20 h at room temperature and was left to stand for several hours in a refrigerator.

The precipitate was filtered off, washed with hot water, and dried under reduced pressure over P_2O_5 .

Complex **VIa**. Light yellow powder, yield 28%. IR spectrum, ν , cm^{-1} : 2267 (CN), 2074 and 2017 (CO), 1524 and 1344 (NO_2). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 5.80 s (5H, Cp), 8.17 d (2H, $J = 8.4$ Hz), 8.38 d (2H, $J = 8.7$ Hz). Found, %: C 40.87; H 5.77; N 1.56. $\text{C}_{58}\text{H}_{85}\text{FeBF}_4\text{N}_2\text{O}_{39} \cdot 6\text{H}_2\text{O}$. Calculated, %: C 40.64; H 5.54; N 1.69.

Complex **VIb**. Light brown powder, yield 13%. IR spectrum, ν , cm^{-1} : 2220 (CN), 2040 and 1990 (CO). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 2.98 s (6H, Me_2N), 5.75 s (5H, Cp), 6.74 d (2H, $J = 9.0$ Hz), 7.53 d (2H, $J = 9.0$ Hz). Found, %: C 40.15; H 5.70; N 1.13. $\text{C}_{58}\text{H}_{85}\text{BF}_4\text{FeN}_2\text{O}_{37} \cdot 10\text{H}_2\text{O}$. Calculated, %: C 40.38; H 6.25; N 1.62.

Complex **VIc**. Brick red powder, yield 26%. IR spectrum, ν , cm^{-1} : 2251 (CN), 2075 and 1988 (CO). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 3.00 s (6H, Me_2N), 5.73 s (5H, Cp), 6.17 d (1H, $J = 16.5$ Hz), 6.72 d (2H, $J = 8.7$ Hz), 7.47 d (2H, $J = 9.0$ Hz), 7.64 d (1H, $J = 16.5$ Hz). Found, %: C 41.23; H 5.51; N 1.31. $\text{C}_{60}\text{H}_{87}\text{BF}_4\text{FeN}_2\text{O}_{37} \cdot 9\text{H}_2\text{O}$. Calculated, %: C 41.58; H 6.10; N 1.62.

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