Hydrogen Bonds within an Ionic Environment: The Remarkable Behavior of the Zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$

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Summary: The organometallic zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ forms a hydrogen-bonded supramolecular adduct with the cationic acid $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$ in the solid state and shows self-organization around K^+ cations in the mixed system $\{[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2\}[K]^+[PF_6]^-$.

The combination of polyfunctional ligands with the variable oxidation (hence charge and spin) states of transition-metal atoms is one of the attractive reasons for the utilization of organometallic building blocks in molecular crystal engineering.[1] The capacity of a molecule or ion to form noncovalent bonds with other molecules allows design of one-, two-, and three-dimensional arrays.[2] The hydrogen bond (HB) is the interaction of choice in molecular crystal engineering because it combines strength (a prerequisite of stability) with directionality (a prerequisite of reproducibility).[3] These properties may be altered if the HB is immersed in the electrostatic field generated by ions in the solid state.[4] It has been demonstrated, for example, that O−H- - -O and C−H- - -O HB interactions between anions ought to be described as “supramolecular organizers” rather than stable bonds.[5,6] We have successfully used polycarboxylic acids to prepare a number of organometallic solids with predefined architectures and structural features.[4] In our quest for new supramolecular synthons,[7] designed for use in the synthesis of crystalline materials carrying either the same metal atom[6] or different metal atoms[8] in different oxidation/spin states, we have directed our interest toward the preparation and study of the HB behavior of the unusual cationic cobaltocenium dicarboxylic acid $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$ (see Chart 1).[9] In the following we shall discuss self-assembly and HB interactions in crystalline $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+[PF_6]^-$ (**1**) and in the cocrystalline salt of the zwitterionic form $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ (see Chart 1), namely $\{[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)][Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]\}^+[PF_6]^-$ (**2**). Finally, we will discuss the intriguing interactions between zwitterions and K^+ cations in $\{[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2\}[K]^+[PF_6]^-$ (**3**).[10]

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(9) (a) The synthesis of $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$ is based on a modified version of the synthesis of 1,1′-dimethylcobaltocenium (**a**) described by Robbins et al.,[9b] starting with 10 mL of methylcyclopentadiene. 1,1′-Dicarboxylic cobaltocenium acid, $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$, was obtained as $\{[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)][Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]\}^+[PF_6]^-$ (**2**) by oxidizing **a** with $KMnO_4$ in a basic solution as described by Sheats et al.[9c] A 0.3 mmol (0.209 g) portion of $\{[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)][Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]\}^+[PF_6]^-$ was then dissolved in 20 mL of a 6 M HCl solution. The solution was extracted three times with a total of 70 mL of nitromethane. Evaporation of the nitromethane solution gave yellow crystals of $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+[PF_6]^-$ (**1**), while crystals of $\{[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2\}[K]^+[PF_6]^-$ (**3**) were obtained from the water residue. Crystals suitable for X-ray diffraction were selected from the solid residues. Correspondence between the structures determined by single-crystal X-ray diffraction and the bulk materials was confirmed by powder diffraction. (b) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882. (c) Sheats, J. E.; Rausch, M. D. *J. Org. Chem.* **1970**, *35*, 3245.

(10) (a) Crystal data are as follows. **1**: $C_{12}H_{10}CoF_6O_4P$, $M_r = 422.10$, monoclinic, $C2/m$, $a = 10.99(2)$ Å, $b = 9.930(10)$ Å, $c = 7.462(8)$ Å, $\beta = 120.480(10)°$, $V = 702(2)$ Å^3, $Z = 2$, $d_c = 1.997$ g cm^{-3}, $\mu = 1.426$ mm^{-1}, θ range 3−23°, 522 measured reflections, 495 independent reflections, 64 parameters, R1($I > 2\sigma(I)$) = 0.0782, wR2(all data, F^2) = 0.2535. **2**: $C_{24}H_{19}Co_2F_6O_8P$, $M_r = 698.22$, triclinic, $P\bar{1}$, $a = 6.953(2)$ Å, $b = 11.856(9)$ Å, $c = 11.862(5)$ Å, $\alpha = 86.98(5)°$, $\beta = 80.55(2)°$, $\gamma = 82.69(4)°$, $V = 1198(11)$ Å^3, $Z = 2$, $d_c = 1.935$ g cm^{-3}, $\mu = 1.550$ mm^{-1}, θ range 3.0−25.0°, 4172measured reflections, 3997 independent reflections, 349 parameters, R1($I > 2\sigma(I)$) = 0.0472, wR2(F^2, all data) = 0.1607. **3**: $C_{12}H_9CoF_3K_{0.5}O_4P_{0.5}$, $M_r = 368.16$, triclinic, $P\bar{1}$, $a = 5.951(2)$ Å, $b = 7.864(1)$ Å, $c = 14.298(8)$ Å, $\alpha = 74.40(3)°$, $\beta = 78.22(3)°$, $\gamma = 74.45(2)°$, $V = 614.6(4)$ Å^3, $Z = 2$, $d_c = 1.989$ g cm^{-3}, $\mu = 1.682$ mm^{-1}, θ range 3.0−28.0°, 3242 measured reflections, 2931 independent reflections, 188 parameters, R1($I > 2\sigma(I)$) = 0.0688, wR2(F^2, all data) = 0.1999. Common to all species: X-ray diffraction data collected on a Nonius CAD4 diffractometer equipped with an Oxford Cryostream liquid-N_2 device, $T = 223(2)$ K, Mo Kα radiation, $\lambda = 0.710\,69$ Å, monochromator graphite, ψ-scan absorption correction. The SHELX-97[10b] package was used for structure solution and refinement based on F^2. All non-H atoms were refined anisotropically. H_{CH} atoms were added in calculated positions. SCHAKAL97[10c] was used for all graphical representations. The PF_6^- anions in **2** and **3** were found to be disordered over two orientations. (b) Sheldrick, G. M. SHELX-97, Program for Crystal Structure Determination; University of Gottingen: Göttingen, Germany, 1997. (c) Keller, E. SCHAKAL97 Graphical Representation of Molecular Models; University of Freiburg, Freiburg, Germany, 1997. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center.

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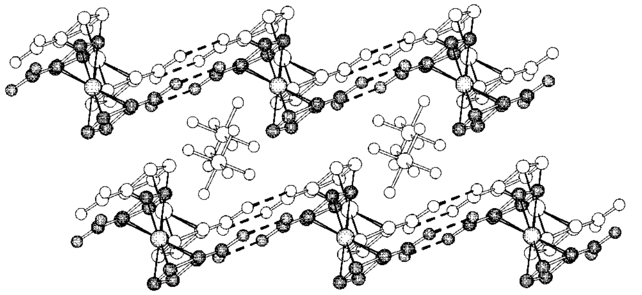
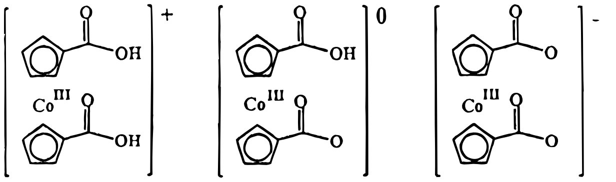


Figure 1. (a) The hydrogen-bonded chain formed by $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$ cations in crystalline **1**. Note how the cations form typical R2,2(8) hydrogen-bonded rings. Parallel chains form a stepladder two-dimensional cationic superstructure by aligning side-by-side $\{[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+\}_n$ chains with the PF_6^- anions accommodated between the steps. H atoms are omitted for clarity.

Chart 1



The acid $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$ is isoelectronic and isostructural with the neutral complex $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$, which is known in two polymorphic modifications,[11] both containing eight-membered HB carboxylic rings (R2,2(8) in graph set[12] notation). In its fully protonated form, however, the cobaltocenium acid is a *cation* (see Chart 1), which poses an intriguing question as to the effect of the positive charge on the donor and acceptor HB systems.[13] As a matter of fact, the O- - -O separation within the R2,2(8) rings (2.600(2) Å) in crystalline **1** is strictly comparable with the value of 2.606 in $[Fe^{II}(\eta^5\text{-}C_5H_4COOH)_2]$ and slightly shorter than in the monosubstituted acid $[Co^{III}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COOH)]^+$ (2.625 Å).[14] Figure 1 shows how the cations form $\{[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+\}_n$ HB chains based on R2,2(8) dicarboxylic rings and how side-by-side chains form a stepladder two-dimensional cationic superstructure with the PF_6^- anions accommodated between the steps.

Crystalline **2** and **3** contain the *zwitterionic form* $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$. **2** is a mixed supramolecular salt in which the cationic unit $\{[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)][Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]\}^+$ results from the aggregation of the cationic dicarboxylic acid $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$ (present in **1**) with the zwitterionic species $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$; crystalline **3** contains dimers of the zwitterionic species $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ templated electrostatically around the K^+ cations (see below).

A focus on the number of protons available for O−H- - -O bonds allows an easy comparison of the two systems: the acceptor/donor ratio is 5:3 and 6:2 in **2** and **3**, respectively. In **2** there are three O−H- - -O HB's, the two outer O- - -O bonds being longer than the inner one (2.594(5) and 2.609(5) Å versus 2.488(5) Å). This sequence of HB results in a kind of "S" sewing together the four −COO groups, which are tilted with respect to the C_5 plane in order to accommodate the three HB's, as shown in Figure 2.

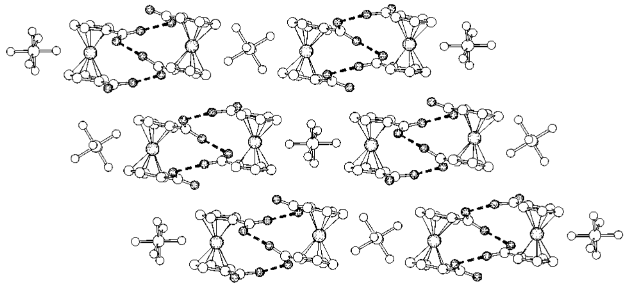


Figure 2. The hydrogen-bonded "dimers" formed between the zwitterionic complex $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ and the cationic complex $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$ in crystalline **2**. Note the "S" type HB pattern. H atoms are omitted for clarity.

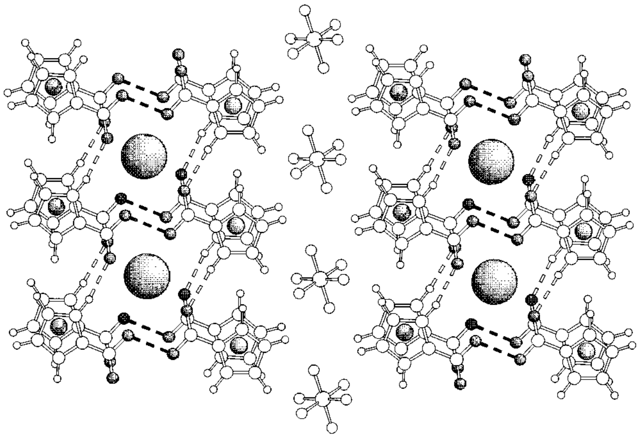


Figure 3. The K^+ cations in crystalline **3** encapsulated, via six K- - -O interactions, within cages formed by four zwitterionic complexes $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO]$ held together by O−H- - -O (dashed filled lines) and C−H- - -O (dashed empty lines) HB interactions. The PF_6^- anions form rows between the zwitterion cages.

The zwitterions in **3** are linked via twin O−H- - -O HB's of the same length (2.454(5) Å), as shown in Figure 3. This separation is *not* what could be expected for an interaction between neutral systems (see above) but rather corresponds to the values observed for most "negative" HB like interactions.[5] The twin-HB pattern is reminiscent of that between $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COOH)]^-$ monoanions (mean O- - -O 2.570(5) Å) in the structure of $[Cr(\eta^6\text{-}C_6H_6)_2]^+\{[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)][Fe(\eta^5\text{-}C_5H_4COOH)_2]_{0.5}\}^-$.[8]

The most remarkable feature of **3**, however, is the zwitterion self-organization around the K^+ cations. As shown in Figure 3, the K^+ cation is encapsulated within the supramolecular aggregate formed by four zwitterionic moieties and interacts directly with six O-atoms of the complexes (K- - -O range 2.792(5)−2.857(6) Å). Electrostatic templating of this sort is unprecedented in organometallic crystal engineering and is reminiscent of crown ether complexation[15a,b] and of the "G-quartets" formed in the presence of K^+ via self-assembly of guanosine monophosphate.[15c] The tetrameric unit in **3** is held together by two sets of O−H- - -O and C−H- - -

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O HB's, these latter arising from the interaction of the H-atoms of the C_5H_4 systems with the "free" lone pairs on the carboxylic oxygens (see Figure 3). Finally, it is worth mentioning that in all species the PF_6^- anions participate in a large number of "charge-assisted" C−H- - -F interactions involving the C−H systems of the acid and zwitterion.[16]

In this communication we have discussed the intriguing hydrogen bond features of the organometallic dicarboxylic cationic acid $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$ and of the zwitterionic form $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4\text{-}COO)]$. All our observations concur to indicate not only that the positive charge in $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$ is not delocalized over the whole cation and does not affect the HB capacity of the −COOH groups but also that in the monodeprotonated zwitterionic species $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ the deprotonated −COO group appears to "retain" the negative charge and behaves very much like a carboxylate $-COO^-$ system. Obviously, an assessment of these features requires quantum chemical calculations.

The difference between the previously used building blocks $[Fe^{II}(\eta^5\text{-}C_5H_4COOH)_2]$ and $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$ is nontrivial: although they possess the same kind of *intermolecular bonding capacity*, the stability of the oxidized Co(III) state allows formation of a robust neutral complex upon monodeprotonation. The possibility of using the same synthon with different interventions of electrostatic interactions promises interesting applications in the preparation of supramolecular aggregates. This strategy is reminiscent of the "electrostatic templating" strategy.[17] Preliminary results obtained from cocrystallization of the zwitterion with complementary HB systems are extremely encouraging.

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Supporting Information Available: Figures giving additional views of compounds **1**−**3** and X-ray crystallographic files, in CIF format, for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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