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Novel Organometallic Building Blocks for Crystal Engineering. Synthesis and Structural Characterization of the Dicarboxylic Acid $[Cr^0(\eta^6\text{-}C_6H_5COOH)_2]$, of Two Polymorphs of Its Oxidation Derivative $[Cr^I(\eta^6\text{-}C_6H_5COOH)_2]^+[PF_6]^-$, and of the Zwitterionic Form $[Cr^I(\eta^6\text{-}C_6H_5COOH)(\eta^6\text{-}C_6H_5COO)]$[†]

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The synthesis and structural characterization of the neutral diamagnetic organometallic dicarboxylic acid $[Cr^0(\eta^6\text{-}C_6H_5COOH)_2]$ (**1**) is reported. Oxidation of **1** by oxygen leads to formation of the paramagnetic dicarboxylic acid cation $[Cr^I(\eta^6\text{-}C_6H_5COOH)_2]^+$ (**2**), which has been isolated as the $[PF_6]^-$ salt in two crystalline polymorphic modifications, a monoclinic form α and a triclinic form β. The neutral zwitterionic form $[Cr^I(\eta^6\text{-}C_6H_5COOH)(\eta^6\text{-}C_6H_5COO)]$ (**3**) has been obtained in a cocrystal with $[NH_4][PF_6]$ upon treatment of the acid salt $[Cr^I(\eta^6\text{-}C_6H_5COOH)_2]^+[PF_6]^-$ with ammonia. The hydrogen bonding interactions established by the neutral and cationic acids are discussed and compared with those observed in the zwitterionic form and in the related complexes $[Fe^{II}(\eta^5\text{-}C_5H_4COOH)_2]$ and $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+[PF_6]^-$.

Introduction

Organometallic crystal engineering is a rapidly developing interdisciplinary field of research at the intersection of organometallic and inorganic supramolecular and materials chemistries.[1] The interest in this new area stems from the enormous potentials arising from the possibility of combining, inter alia, the electronic and magnetic characteristics of metal-bound ligands with those of metal atoms. Coordination and organometallic complexes can be used to obtain novel solid-state properties for applications in the fields of magnetism, conductivity, and nonlinear optics.[2] A distinction needs to be made on the basis of the nature of the interactions utilized in the construction of the desired superstructure. In the case of coordination networks the backbone interaction is the co-coordinative bond between multidentate ligands and metal centers,[3] whereas in molecular networks the interactions of choice are van der Waals[4] and hydrogen bridges[5] between building blocks that possess a defined structure in solution. Since van der Waals interactions and hydrogen bonds are generally weaker than coordination bonds, the synthesis of the two types of materials requires substantially different synthetic strategies than those required when coordination networks and covalent bonds are involved. Clearly, there is no precise borderline between the two

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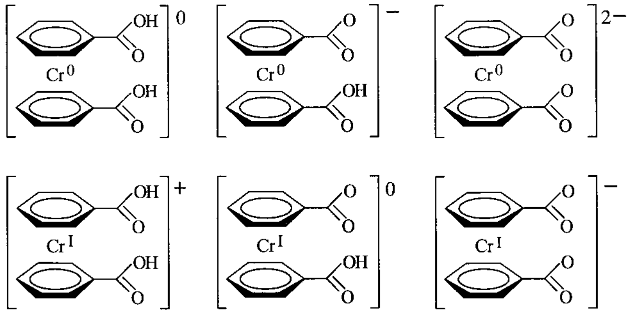
areas, as interesting results are being obtained also by combining coordination and noncovalent interactions.[6]

Our strategy is based on the utilization of hydrogen bridges between adequately fictionalized organometallic and/or organic molecules and ions.[7] Hydrogen bonding interactions are highly reproducible and easily transferable from packing to packing because of their high directional properties.[8] Directionality and robustness of the interactions are fundamental prerequisites for a successful supramolecular synthesis, whether directed to supramolecular assemblies[9] or to periodic supermolecules.[10] In the case of ionic crystals the effect of the Coulombic field generated by the ions on the noncovalent interactions needs to be taken into account if one wants to understand the factors responsible for crystal cohesion and the many physical properties typical of ionic crystals, such as solubility in polar solvents, high melting points, and hardness. On the other hand the presence of hydrogen bonding donor and acceptor groups on the component ions generates directional hydrogen bonding interactions that contribute to crystal stability. Hence, hydrogen bonds between ions represent a way to combine the highly reproducible topology of hydrogen bonds with the strength of ionic forces.[11]

A recent example of deliberate *engineering* of a supramolecular arrangement with target magnetic properties is provided by crystalline $[Cr^{I}(\eta^6\text{-}C_6H_6)_2]^+[HC_4O_4]^-$, obtained by reacting squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, $H_2C_4O_4$) with $[Cr^{I}(\eta^6\text{-}C_6H_6)_2]$.[12] The anion $[HC_4O_4]^-$ self-assembles into chains linked by $^{(-)}O{-}H\text{- - -}O^{(-)}$ interactions and intercalates between the benzene ligands forming a π-stacking interaction. The presence of a charge-transfer transition was detected in the reflectance spectrum, while magnetic measurements showed that the weak, but appreciable, antiferromagnetic interaction between the $[Cr^{I}(\eta^6\text{-}C_6H_6)_2]^+$ cations could be attributed to the anion−cation π-stacking interaction. Magnetic materials based on organometallic open-shell complexes are extensively studied.[13] Exchange interactions mediated by $O{-}H\text{- - -}O$ hydrogen bonds have been investigated previously in the EPR study of the paramagnetic complex $[V(\eta^7\text{-}C_7H_7)(\eta\text{-}C_5H_4COOH)]$.[14]

Scheme 1. Differently Charged Building Blocks that Can Be Obtained from the Neutral and Cationic Dicarboxylic Acid $[Cr^0(\eta^6\text{-}C_6H_5COOH)_2]$ and $[Cr^{I}(\eta^6\text{-}C_6H_5COOH)_2]^+$ upon Deprotonation



We have undertaken a systematic study of the synthesis and preparation of polycarboxylic organometallic acids whose metal centers may possess different oxidation states. The goal is that of *combining* in a controlled manner the charge states that can be varied via a redox process with the hydrogen bonding capacity that can be varied via an acid−base reaction. We now report the synthesis of the neutral dicarboxylic acid $[Cr^0(\eta^6\text{-}C_6H_5\text{-}COOH)_2]$ (**1**) and of its oxidation product $[Cr^{I}(\eta^6\text{-}C_6H_5\text{-}COOH)_2]^+$ (**2**). The two complexes have different magnetic properties, as **1** is diamagnetic while **2** is a 17-electron paramagnetic complex, and offer a large number of combinations of hydrogen bonding donor/acceptor capacity together with different ionic charges.

Removal of protons from neutral **1** (see Scheme 1) leads to sequential formation of a monoanion and of a dianion, while deprotonation of **2** leads first to formation of the neutral sandwich zwitterion $[Cr^{I}(\eta^6\text{-}C_6H_5COOH)(\eta^6\text{-}C_6H_5COO)]$ (**3**), with one −COOH and one $-COO^{(-)}$ system. A related species, namely, the zwitterion $[Cr^{I}(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_5COO)]$, has been described previously, although in that paper the interest was mainly focused on the redox properties of the complex.[15]

Further deprotonation of **3** leads to the dicarboxylate monoanion $[Cr^{I}(\eta^6\text{-}C_6H_5COO)_2]^-$ (**3**) with two $-COO^{(-)}$ groups. Hence, the bis-benzene chromium system can be regarded as composed of a fundamental building block, namely, "$Cr(\eta^6\text{-}C_6H_5COO)_2$", which can participate, depending on the extent of protonation and on the metal atom oxidation state, in hydrogen bonding networks as a monocation, a neutral species, and as a mono- and dianion building block.

In this paper, besides reporting the synthesis and crystal structure characterization of the complexes, we will discuss the hydrogen bonding interactions formed in the solid state by the two neutral compounds **1** and **3** and by the cationic complex **2**. The $[PF_6]^-$ salt of **2** has been isolated in two polymorphic modifications: the monoclinic form α and the triclinic form β. Organometallic polymorphism has been recently reviewed.[16] A comparison will also be carried out with the almost isostructural complexes based on ferrocene, namely,

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Table 1. Crystal Data and Details of Measurement for Compounds 1, 2[PF$_6$]α, 2[PF$_6$]*β*, and 3·[NH$_4$][PF$_6$]

	1	**2**[PF$_6$]$_\alpha$	**2**[PF$_6$]$_\beta$	**3**·[NH$_4$][PF$_6$]
formula	$C_{14}H_{12}CrO_4$	$C_{14}H_{12}CrF_6O_4P$	$C_{14}H_{12}CrF_6O_4P$	$C_{14}H_{15}CrF_6NO_4P$
fw	296.24	441.21	441.21	458.24
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	*Cc*	*C*2/*c*	$P\bar{1}$	$P2_1/c$
a, Å	11.482(5)	7.649(4)	7.580(10)	7.518(2)
b, Å	10.035(4)	20.458(6)	7.902(9)	16.289(6)
c, Å	19.669(5)	10.044(3)	7.882(4)	13.791(5)
α, deg	90	90	82.34(7)	90
β, deg	91.13(3)	96.55(3)	66.02(9)	99.79(3)
γ, deg	90	90	65.90(10)	90
vol, Å^3	2265.9(15)	1562(1)	393.5(7)	1664(1)
Z	8	4	1	4
F(000)	1216	884	221	1784
D_{calc}, g/cm^3	1.737	1.877	1.862	1.829
μ, mm^{-1}	1.016	0.922	0.914	1.378
cryst size, mm	0.30 × 0.15 × 0.15	0.22 × 0.20 × 0.18	0.20 × 0.18 × 0.12	0.20 × 0.12 × 0.08
temp, K	253(2)	223(2)	223(2)	223(2)
θ limits, deg	3−30	3−30	3−25	3−26
min/max *h*, *k*, *l*	−16/16,0/14,0/27	−10/10,0/28,0/14	−8/8,−9/9,0/9	−9/9,0/20,0/16
no. of reflns collected	3551	2401	1465	3537
unique reflns	3379	2285	1356	3055
reflns with $I > 2\sigma(I)$	1970	1655	920	955
parameters	344	134	137	137
min and max transmn	0.86−1.00	0.94−1.00	0.85−1.00	0.87−1.00
GOF on F^2	0.983	1.020	0.987	0.784
R_1 (on *F*, $I > 2\sigma(I)$)	0.0381	0.0424	0.0918	0.0876
wR_2 (on F^2, all data)	0.1142	0.1300	0.2971	0.3654

[Fe^{II}(η^5-C_5H_4COOH)$_2$],[17] and on the cobaltocenium cation, namely, [Co^{III}(η^5-C_5H_4COOH)$_2$]$^+$,[18] which are isoelectronic and diamagnetic. The diacid [Fe^{II}(η^5-C_5H_4-COOH)$_2$] is known in two polymorphic modifications.[17]

Experimental Section

General Information. All the experimental manipulations involving the synthesis and crystallization of [Cr^0(η^6-C_6H_5-COOH)$_2$] were carried out under dry oxygen-free nitrogen by employing Schlenk techniques. The solvents (methylcyclohexane, ether) were distilled under a nitrogen atmosphere from K metal. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine was distilled over CaH_2. All other chemicals for synthesis and crystallization of [Cr^I(η^6-C_6H_5COOH)$_2$]$^+$[PF$_6$]$^-$ and the zwitterionic form were purchased from Aldrich (NH_4PF_6, solvents) and used as received. The starting material, bis-benzene chromium, was prepared according to the literature procedure.[19]

1,1′-Bis(carboxyl-η^6-benzene)chromium, [Cr^0(η^6-C_6H_5-COOH)$_2$], 1. A 250 mL flask equipped with a magnetic stirrer was charged with bis-benzene chromium (1.0 g, 4.8 mmol), methylcyclohexane (60 mL), and *N*,*N*,*N*′,*N*′-tetramethylethylendiamine (TMEDA) (1.54 mL, 10.2 mmol). To the resulting mixture was added dropwise *n*-BuLi (6.25 mL, 10.2 mmol, solution 1.6 M in hexane) and refluxed for 4 h. After cooling to ambient temperature, CO_2 was introduced for 1 h. The solvent was evaporated under vacuum, and the residue was dissolved in water; after filtration 20 mL of 1 M HCl was added to the filtrate, yielding a red precipitate, which was filtered and dried under vacuum (yield: 1.1 g, 80%). Red block crystals were obtained by first dissolving the precipitate (100 mg) in hot water, then by adding 0.1 M NaOH (0.5 mL) and layering with ether containing HBF_4 (0.1 mL, solution 58% in ether). MS, *m*/*e*: 122 (100%, $C_6H_5COOH^+$), 105 (93%, $C_6H_5CO^+$), 77 (95%, $C_6H_7{}^+$), 51 (35%, $C_4H_3{}^+$). ^{1}H NMR (300 MHz, THF-d_8): δ 11.18 (s, 2H), 5.13 (d, 4H), 4.54 (m, 6H). Anal. Calcd for $C_{14}H_{12}O_4Cr$ (296.24): C, 56.76; H, 4.08. Found: C, 56.74, H, 4.10.

1,1′-Bis(carboxyl-η^6-benzene)chromium$^+$PF$_6$$^-$, [($\eta^6$-$C_6H_5$-COOH)$_2$Cr^I]$^+$[PF$_6$]$^-$, 2. A 50 mL flask equipped with a magnetic stirrer was charged with bis(carboxyl-η^6-benzene)-chromium (50 mg, 0.17 mmol). A saturated solution of NH_4-PF_6 in water (15 mL) was added, and air was led through the mixture overnight at room temperature; the solution obtained was then dried under vacuum. Yellow crystals of **2**[PF$_6$]α suitable for X-ray diffraction were obtained by ether diffusion into an acetone solution of the salt, while slow evaporation of an acetone solution of the salt yielded yellow crystals of **2**[PF$_6$]*β*.

The Zwitterion [Cr^I(η^6-C_6H_5COOH)(η^6-C_6H_5COO)] in Its Cocrystal with [NH$_4$][PF$_6$], 3·[NH$_4$][PF$_6$]. A 50 mL flask equipped with a magnetic stirrer was charged with bis-(carboxyl-η^6-benzene)chromium$^+$PF$_6$$^-$ (105 mg, 0.24 mmol), water (15 mL), and 2.4 mL of NH_3 0.1 N. The yellow solution obtained was cooled at 0 °C, and NH_4PF_6 (10 mg) was added. The precipitate obtained was filtered and dried under vacuum. Yellow crystals suitable for X-ray diffraction were obtained by recrystallization in methanol.

Crystal Structure Characterization of Compounds 1, 2[PF$_6$]α, 2[PF$_6$]*β*, and 3·[NH$_4$][PF$_6$]. X-ray diffraction data were collected on a NONIUS CAD-4 diffractometer equipped with a liquid nitrogen Oxford-Cryostream device. Crystal data and details of measurements are summarized in Table 1. Common to all compounds: Mo Kα radiation, $\lambda = 0.71073$ Å, monochromator graphite, ψ-scan absorption correction. All non-H atoms refined anisotropically in **1**, **2**[PF$_6$]α, and **2**[PF$_6$]*β*, while, due to the low observed data-to-parameter ratio, only Cr, O, P, and F atoms were refined anisotropically in **3**·[NH$_4$]-[PF$_6$]. Arene H atoms were added in calculated positions and refined riding on their respective C atoms. All carboxyl H atoms were located from the Fourier map in **1** but not refined. Only one of the two carboxyl H atoms was found in **2**[PF$_6$]α, and two of the four ammonium H atoms were located in **3**·[NH$_4$][PF$_6$]. Due to the presence of a 2-fold axis the atom was given a site occupancy factor of 0.5. The [PF$_6$]$^-$ anions in all structures were found to be disordered over two orientations, with occupancy ratios of 50:50 for all the F atoms in **2**[PF$_6$]α

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Table 2. Relevant Hydrogen Bonding Interactions [(C)H- -O, (C)H- -F, and (N)H- -F < 2.600 Å] in Crystalline 1, 2[PF$_6$]α, 2[PF$_6$]β, 3·[NH$_4$][PF$_6$], 4α, 4β, and a Comparison with the Cobalt Complex [Co^{III}(η^5-C$_5$H$_4$COOH)$_2$]$^+$[PF$_6$]$^-$, 5[PF$_6$][a]

parameter type	**1**	**2**[PF$_6$]α	**2**[PF$_6$]β	**3**·[NH$_4$][PF$_6$]	**4**α	**4**β	**5**[PF$_6$]
O- - -O	2.638 2.643 2.558 2.603	2.629 2.634	2.618	2.477	2.593 2.635	2.625 2.671 2.620 2.643	2.600
O- - -N				2.909 2.860 2.818 2.841			
(O)H- - -O, O−H- - -O	1.60 170 1.77 162 1.63 164 1.90 152	1.71 161				1.73 172 1.78 174 1.82 172 1.86 172	
(C)H- - -O, C−H- - -O	2.47 142 2.52 155 2.40 148 2.46 155 2.50 139 2.52 155	2.59 135		2.48 138	2.23 142 2.40 151 2.50 133	2.26 154 2.32 151 2.53 150 2.53 128 2.58 143	2.54 139
(N)H- - -F				2.45 128 2.52 112 2.21 130			
(C)H- - -F, C−H- - -F		2.56 151 2.36 153 2.49 142 2.42 162 2.42 127 2.51 137 2.59 145 2.55 126	2.42 140 2.48 128 2.41 136 2.43 128 2.39 149 2.42 148 2.48 158 2.55 156 2.52 137 2.54 127 2.39 142 2.57 127	2.36 120 2.47 135 2.42 135 2.33 163 2.59 125 2.54 134 2.59 118 2.55 120			2.542 110.88 2.554 136.53

[a] Distances in Å, angles in deg, esd's values for O- -O and O- -N distances are 0.002 for **1**, **2**[PF$_6$]α, **4**α, **4**β, and **5**[PF$_6$]; 0.004 for **2**[PF$_6$]β and **3**·[NH$_4$][PF$_6$]). C−H distances normalized to the neutron value (1.08 Å) except for neutron structures 4α and 4β.

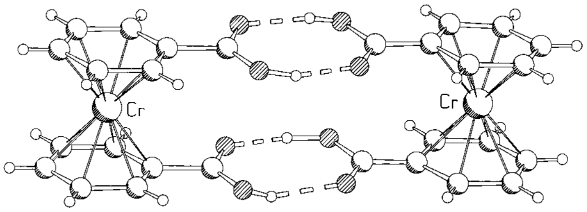

Figure 1. Ball-and-stick representation of the dimers formed by molecules of **1** in the solid state. Shaded atoms represent O atoms.

and **2**[PF$_6$]β and for four out of six F atoms in **3**·[NH$_4$][PF$_6$]. The SHELX97[20a] package was used for structure solution and refinement based on F^2. SCHAKAL99[20b] was used for all graphical representations. Due to the small amount of substance available, correspondence between the structure determined by single-crystal X-ray diffraction and the bulk material was confirmed by powder X-ray diffraction only in the case of **2**[PF$_6$]β.

Results and Discussion

The Neutral Acid. Relevant parameters concerning O−H- - -O and C−H- - -O hydrogen bonding interactions are collected in Table 2. The molecular structure of **1** as determined in the solid state is shown in Figure 1. The complex forms a dimer via a pair of typical hydrogen bonding rings involving the two −COOH groups of the acid. Twin intermolecular hydrogen bonding of the type shown by **1** are not commonly observed with organic dicarboxylic acids, because dimer formation requires a degree of structural flexibility that cannot be afforded by molecules based on C−C σ-bonds. In fact, dicarboxylic organic acids tend to form chains in the solid state rather than self-assemble in dimeric units. Compound **1**, and all is congeners, can instead *rotate* around the coordination axis of the carbocyclic ligands to yield the eclipsed conformation of the −COOH groups required for the formation of the dimer. Indeed a strictly comparable situation can be observed in crystalline ferrocene dicarboxylic acid [Fe^{II}(η^5-C$_5$H$_4$COOH)$_2$] (**4** hereafter).[17] As mentioned above, this acid is known in two polymorphic modifications (**4**α and **4**β for the monoclinic and triclinic form, respectively), which contain exactly the same type of dimeric unit, although in different arrangements in the solid state. The space-filling representations of **4**α, **4**β, and **1** (Figure 2) clearly show that the three crystals are formed by layers of dimers arranged in contiguous rows; the packings differ essentially for the angles formed by the dimer “long axes” passing between two Fe or Cr atoms (ca. 90°, 100°, and 165° for **4**α, **4**β, and **1**, respectively) and for the dimer rotation around the same axes within the layer (ca. 0°, 90°, and 90° for **4**α, **4**β, and **1**, respectively).

The carboxylic rings in the two neutral systems have strictly comparable hydrogen bonding parameters [O- - -O 2.558(2), 2.603(2), 2.638(2), 2.643(2) Å in **1**; 2.593(2), 2.635(2) Å in **4**α, and 2.620(2), 2.643(2), 2.625(2), 2.671(2) Å in **4**β (see Table 2)]. In addition to the strong hydrogen bonds, both ferrocene and bis-benzene chromium complexes show in their crystals the presence of a web of intermolecular C−H- - -O interactions between the cyclopentadienyl or benzyl hydrogen atoms and the oxygen atoms of the −COOH groups. Interestingly, despite the differences in crystal structures, the

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(20) (a) Sheldrick, G. M. *SHELX-97, Program for Crystal Structure Determination*; University of Gottingen: Göttingen, Germany, 1997. (b) Keller, E. *SCHAKAL99, Graphical Representation of Molecular Models*; University of Freiburg: Germany, 1999.

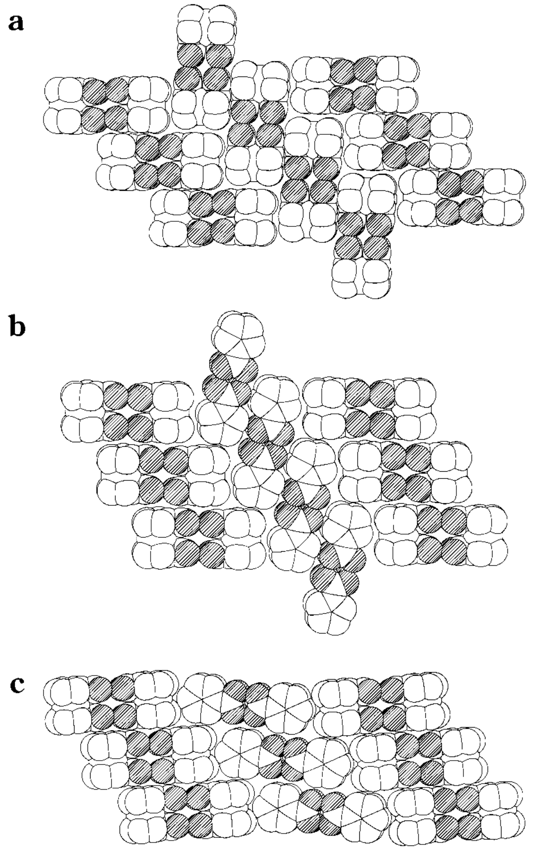

Figure 2. Space-filling representation of the hydrogen-bonded dimers in the two crystalline forms of crystalline [Fe^{II}(η^5-$C_5H_4COOH)_2$] (a, monoclinic **4**α, and b, triclinic **4**β, respectively) and comparison with the hydrogen-bonded dimers in crystalline **1**. H atoms not shown for clarity.

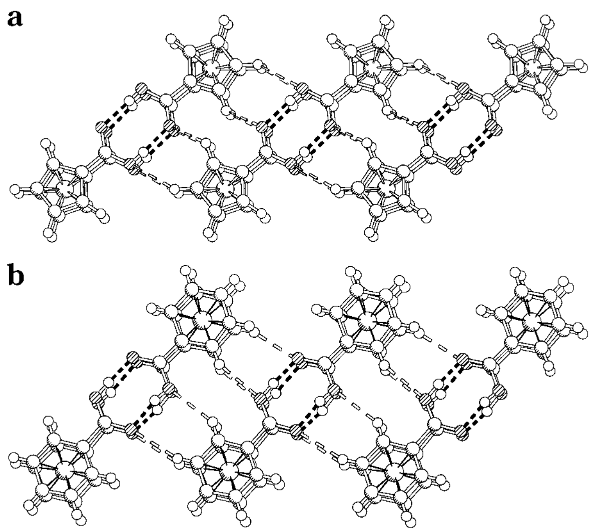

Figure 3. The similarity in the patterns of C−H- - -O interactions in crystalline **4**β (a) and **1** (b).

C−H- - -O interactions in **4**β and **1** possess almost the same pattern, as shown in Figure 3. In both crystals the dimers are aligned and the oxygen atoms interact with the H atoms of the aromatic rings. The alignment of arene moieties with neighboring carboxyl groups through C−H- - -O hydrogen bonding bears some resemblance to that observed for $Cr(CO)_3$ adducts of benzenecarboxylic acids.[6d] In **4**α the pattern is relatively more complex, with C−H- - -O interactions linking four dimers. (C)H- - -O distances and C−H- - -O angles are compared in Table 2 (hydrogen positions were used as such for the neutron structures of **4**α and **4**β), while in the case of **1** the C−H distances were normalized to the neutron diffraction value of 1.08 Å. Some of these values fall in the lower limit for this type of interaction, even if only organometallic molecules are considered.[21]

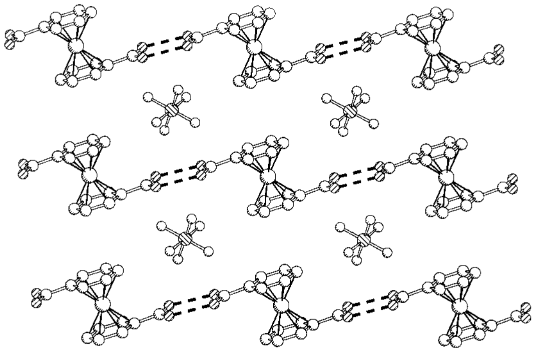

Figure 4. Stepladder hydrogen-bonded superstructure formed by the cationic chains in crystalline **2**[PF_6]α and **2**[PF_6]β, with the [PF_6]$^-$ anions accommodated between the steps. H atoms not shown for clarity.

The Cation. The oxidation product **2** has been crystallized in two polymorphic modifications, **2**[PF_6]α and **2**[PF_6]β, depending on the crystallization conditions (see Experimental Section). The most relevant structural aspects of the two salts can be summarized as follows.

(i) Both **2**[PF_6]α and **2**[PF_6]β contain chains of cations held together by hydrogen bonds between the carboxyl groups, as shown in Figure 4. The O- - -O separations differ slightly in the two crystals [2.629(2), 2.634(2) Å in **2**[PF_6]α and 2.618(4) Å in **2**[PF_6]β] and are comparable to the value of 2.600(2) Å observed for the cationic dicarboxylic acid [Co^{III}(η^5-$C_5H_4COOH)_2$]$^+$[PF_6]$^-$, hereafter **5**[PF_6].[18b] These values are also very similar to those discussed above for the neutral species, thus confirming that the O- - -O separation is a rather “conservative” parameter which does not depend in any appreciable manner on the charged or neutral nature of the complex or on the metal involved.[22]

(ii) Both polymorphs contain cationic chains placed side by side and forming a stepladder superstructure with the [PF_6]$^-$ anions accommodated between the steps, as shown in Figure 4.

(iii) The main difference between the two forms is quite intriguing: the structure of **2**[PF_6]α can be ideally converted into that of **2**[PF_6]β by *sliding* in opposite directions two of every four layers formed by cationic chains and anions. This is easily inferred by looking at Figure 5, which compares packing projections along the cationic chains in both crystals [the cationic chains extend along the *c*-axis in **2**[PF_6]α and along the (*1*−*1*−*1*) diagonal in **2**[PF_6]β]. For sake of clarity the disordered anions are shown as large spheres in the two pictures. It is worth mentioning that the ion arrange-

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[21] (a) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999. (b) Braga, D.; Grepioni, F.; Biradha, K.; Pedireddi, V. R.; Desiraju G. R. *J. Am. Chem. Soc.* **1995**, *117*, 3156

[22] Braga, D.; Grepioni, F., Novoa, J. J. *New J. Chem.* **2001**, *2*, 226.

[23] Le Bideau, F.; Henrique, J.; Samuel, I.; Elschenbroich, Ch. *Chem. Commun.* **1999**, 91.

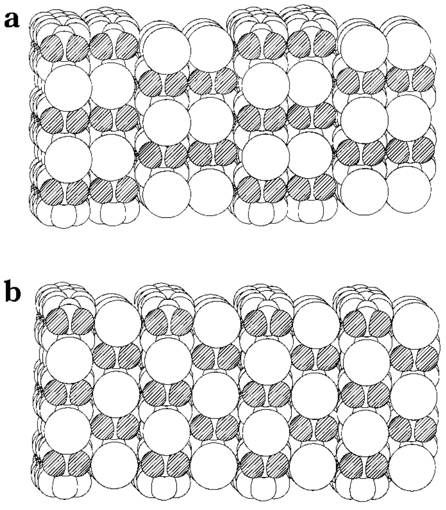

Figure 5. Packing projections along the cationic chains directions in **2**[PF$_6$]α (a) and in **2**[PF$_6$]*β* (b). Large empty spheres represent the disordered [PF$_6$]$^-$ anions. H atoms omitted for clarity.

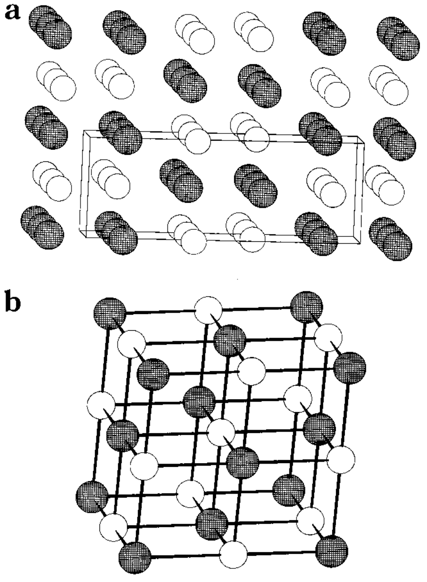

Figure 6. Schematic representation of cations and anions distribution in crystalline **2**[PF$_6$]α (a) and **2**[PF$_6$]*β* (b). Only Cr and P atoms (filled and empty spheres, respectively) are shown for clarity.

ment in crystalline **2**[PF$_6$]*β* is almost the same as that observed in the previously determined, isostructural salt **5**[PF$_6$].[18b]

(iv) In crystalline **2**[PF$_6$]α *pairs* of cationic chains $\{[Cr^I(\eta^6\text{-}C_6H_5COOH)_2]^+\}_n$ (as well as *pairs* of rows of anions) are placed next to each other and extend along the *c*-axis.

(v) Figure 6 shows a schematic comparison of the ion distributions in the two crystals: while **2**[PF$_6$]*β* adopts a nearly cubic NaCl-like structure, **2**[PF$_6$]α shows the presence of twin rows of cations and anions.

The Zwitterion. The zwitterionic form of compound **2**, namely, $[Cr^I(\eta^6\text{-}C_6H_5COOH)(\eta^6\text{-}C_6H_5COO)]$, **3**, was obtained as a cocrystal with ammonium hexafluorophosphate, e.g., **3**·[NH$_4$][PF$_6$]. When studying the possibility of utilizing the isoelectronic cobalticinium zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ to complexate alkali cations and the ammonium cation, we found that the zwitterion could form interesting supramolecular aggregates of the type $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)][MPF_6]$ (M = K$^+$, Rb$^+$, Cs$^+$, NH$_4^+$) if the acid salt $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2][PF_6]$ was reacted with the corresponding metal hydroxides or with aqueous ammonia[18b] As in the case of $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)][NH_4][PF_6]$, the chromium organometallic zwitterion in **3**·[NH$_4$][PF$_6$] forms dimers joined together by two short hydrogen bonding interactions [2.477(2) Å], as shown in Figure 7a. It should be stressed that the difference between the *neutral* dimer formed by **1** and the *neutral* dimer formed by **3** is not trivial: **1** and **3** have metal atoms in different oxidation states, besides involving twice as many hydrogen bonding interactions in the dimer formation. The O- - -O separation in **3**·[NH$_4$][PF$_6$]-ought to be compared with the value of 2.470(5) Å observed in $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)][NH_4][PF_6]$. However, while in the cobalticinium salt the ammonium cation is completely encapsulated within a cage formed by four molecules of $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$, in **3**·[NH$_4$][PF$_6$] the ammonium cation interacts both with the organometallic dimer and with the [PF$_6$] anion, as shown in Figure 7b. The ammonium cation forms two distinct types of hydrogen bonding interactions: those with the oxygen atoms of the carboxylic/carboxylate groups [N−H- - -O 2.818−2.909(2) Å, see Table 2] and those with the PF$_6^-$ anions [N−H- - -F of 2.208−2.517(2) Å, see Table 2].

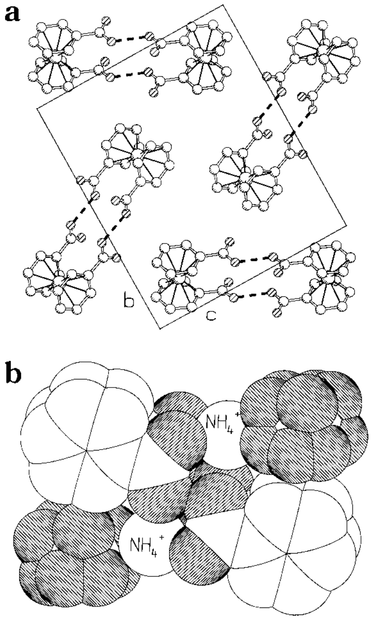

Figure 7. (a) Projection in the *bc*-plane of the dimers formed by zwitterions $[Cr^I(\eta^6\text{-}C_6H_5COOH)(\eta^6\text{-}C_6H_5COO)]$ joined together by two short hydrogen bonding interactions [2.477(4) Å]. (b) Space-filling representation showing how the [NH$_4$]$^+$ cations in crystalline **3**·[NH$_4$][PF$_6$] interact with the zwitterionic dimers and the disordered [PF$_6$]$^-$ anions.

At this stage one may wonder why **3**·[NH$_4$][PF$_6$] and **5**·[NH$_4$][PF$_6$] are not isostructural, while **2**[PF$_6$]*β* is almost isostructural with $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2][PF_6]$. The difference in packing may be due to a subtle difference in size between the two zwitterions (which may prevent a comfortable accommodation of the [NH$_4$]$^+$ cation) but may also indicate the potential existence of an alternative packing available for these complexes, i.e., the existence of polymorphic arrangements.

Conclusions

Organometallic polycarboxylic acids are useful starting materials for the construction of sophisticated superstructures, where the hydrogen bonding capacity of the −COOH groups can be combined with the intrinsic electronic properties of the metal atoms and with the topology of the ligand coordination about the metal centers. In this study we show that the same molecular building block, namely, "$[Cr(\eta^6\text{-}C_6H_5COOH)_2]$", can be used, essentially without structural changes at the molecular level, both as a neutral (diamagnetic) and as a cationic (paramagnetic) system. Both the neutral molecule and the cation can then yield a series of ions depending on the extent of deprotonation. The zwitterionic form $[Cr^I(\eta^6\text{-}C_6H_5COOH)(\eta^6\text{-}C_6H_5COO)]$ is particularly interesting because it can be cocrystallized as a "noninnocent" partner in systems containing simple inorganic salts. In terms of hydrogen bonding interactions it has been noted that the neutral species **1** and the cationic species **2** form hydrogen bonding interactions that are strictly comparable in length, while a much shorter hydrogen bonding interaction is shown by the neutral zwitterionic dimers formed by **3**. This comparison adds further support to the observation[22] that proton removal from a −COOH group leaves the negative charge essentially localized on the deprotonated group, whose hydrogen bonding behavior in the solid state appears to be unaffected by the electronic nature of the metal center.

Besides the crystal engineering interest in the relationship between noncovalent interactions of different nature, the systems discussed in this paper are water soluble and this is not a common characteristic for organometallic molecules.

The 17-electron complexes obtained from oxidation of **1** may provide interesting applications in the construction of magnetic materials. Previous attempts by using paramagnetic $[Cr^I(\eta^6\text{-}C_6H_6)_2]^+$ in the self-assembly with mono-hydrogen squarate anions, $[HC_4O_4]^-$, have been successful.[12] The preparation of hybrid organic−organometallic materials where the two components are joined by hydrogen bonding interactions is a promising line of development of this chemistry. Another interesting application of the organometallic zwitterion **3** would be that of encapsulating open-shell metal cations within a cage of paramagnetic Cr zwitterions.

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Supporting Information Available: Details about the X-ray crystal structures, including tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, ORTEP figures for compounds **1**, **2**$[PF_6]\alpha$, **2**$[PF_6]\beta$, and **3**·$[NH_4][PF_6]$, and X-ray powder diffraction patterns (calculated and experimental) for **2**$[PF_6]\alpha$. This material is available free of charge via the Internet at http://pubs.acs.org. Supporting Information is also available in cif format.

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