derived from squalene cyclization as in the case of bacterial hopanoids.

Experimental Section

A His-tag (6 His residues) was ligated to the N terminus of the SHC cloned from the thermoacidophilic bacterium *Alicyclobacillus acidocaldarius*. This altered enzyme was produced in *Escherichia coli* and purified to homogeneity by complexation chromatography in the last step.[4]

The NMR spectra were recorded on a Bruker WP400 spectrometer in $CDCl_3$ at 300 K; $CHCl_3$ ($\delta = 7.260$) was used as internal standard. The GC-MS measurements were made on a Finnigan TSQ700 spectrometer. Chromatographic conditions were as those previously described.[11] Triterpenes were extracted from the enzymatic reaction mixture with hexane/propan-2-ol (3/2). This crude fraction (229 mg) was separated by flash chromatography (CH_2Cl_2/hexane (1/1) followed by CH_2Cl_2) into a hydrocarbon fraction (179 mg) and diplopterol (31 mg).[27] A further flash chromatography (cyclohexane) yielded a fraction containing all polycyclic triterpenes (112 mg) and unchanged squalene (60 mg). The polycyclic triterpenes were separated by argentation TLC (cyclohexane/toluene (9/1), two migrations),[28] yielding (in order of increasing polarity) a fraction containing neohop-13(18)-ene (**4**, Scheme 1) and apolar hydrocarbons; a mixture of dammara-12,24-diene (**7**), dammara-13(17),24-diene (**6**), and eupha-7,24-diene (**8**); diploptene (**2**); and finally a mixture of dammara-20(21),24-diene (**9**), a hydrocarbon tentatively identified as 17-isodammara-20(21),24-diene (**5**), and some residual **2**. These fractions were further purified by another argentation TLC. Pure **4** ($R_f = 0.70$, 0.3 % yield from the crude reaction mixture) was obtained with cyclohexane as eluent. The mixture of **6**, **7**, and **8** yielded with cyclohexane/toluene (9/1) as eluent a mixture of **6** and **7** in a 54:46 ratio which could not be separated ($R_f = 0.41$, 0.9 % yield) and **8** ($R_f = 0.48$, 0.2 % yield) The most polar fraction was separated with cyclohexane/toluene (60/40) as eluent into **2** ($R_f = 0.64$) and an inseparable mixture of **5** and **9** ($R_f = 0.25$, 0.6 % yield) in a 82:18 ratio. Only spectroscopic data concerning the two new hydrocarbons **5** and **7** are extensively described here.

5 (tentative structure assignment): ^1H NMR: $\delta = 0.803$ (s, CH_3), 0.833 (s, CH_3), 0.845 (s, CH_3), 0.902 (s, CH_3), 0.942 (s, CH_3), 1.618 and 1.684 (2s, 2 × 25-CH_3), 4.87 and 4.91 (2s, 2 × 21-H), 5.11 (brt, $J = 6.7$ Hz, 24-H); GC-MS: m/z (%) = 410 (18, [M^+]), 395 (3, [$M^+ - CH_3$]), 367 (3), 341 (2), 299 (5), 231 (15), 218 (11), 203 (11), 191 (100, cleavage of ring C), 189 (27, cleavage of ring C), 109 (24).

7: ^1H NMR: $\delta = 0.789$ (d, $J = 7.0$ Hz, 20-CH_3), 0.821 (s, 4α-CH_3), 0.867 (s, 10β-CH_3), 0.927 (s, 8β-CH_3), 0.946 (s, 14α-CH_3), 1.606 and 1.643 (2s, 2 × 25-CH_3), 5.10 (brt, $J = 6$ Hz, 24-H), 5.20 (dd, $J = 3$ and 4 Hz, 12-H); GC-MS: m/z (%) = 410 (100, [M^+]), 395 (24, [$M^+ - CH_3$]), 367 (2), 341 (9, allylic cleavage between C22 and C23), 326 (11), 297 (36 [M^+ − side chain − 2H), 284 (21), 218 (32, retro-Diels–Alder reaction induced by the Δ^{12} double bond), 191 (82, cleavage of ring C), 147 (62), 134 (78), 109 (51), 107 (46), 105 (30).

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Crystal Engineering of Organometallic Compounds through Cooperative Strong and Weak Hydrogen Bonds: A Simple Route to Mixed-Metal Systems**

Dario Braga,* Lucia Maini, and Fabrizia Grepioni*

Crystal engineering of organometallic compounds is an emerging field of research.[1] Much of the excitement arises from the idea of being able to combine the plethora of characteristics provided by functional groups of organic molecules[2] with the coordination geometry, variable ionic charges, and valence and spin states typical of organometallic complexes to obtain novel crystalline materials.[3] An intelligent choice of the building blocks may yield materials with magnetic, conducting, superconducting, and nonlinear optical properties.

We now report our success in synthesizing new organometallic crystalline materials by allowing a (rather unconventional) polycarboxylic acid—namely, the neutral organome-

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tallic complex $[(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2\text{Fe}]$ (FeACH_2)[4]—to react with $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]$ and $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}]$ in THF in the presence of oxygen. As previously discussed for the case of polyprotic organic acids,[5] our crystal engineering strategy is based on the self-assembly of the species carrying strong hydrogen bond donor/acceptor systems, (e.g. FeACH_2 with its two carboxylic groups) around the Cr and Co sandwich complexes. The reaction sequence proceeds by 1) oxidation in the air of solutions of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]$ and $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}]$ in THF and initial formation of the strongly basic anion O_2^-; 2) deprotonation of FeACH_2 to yield the anion FeACH^- (or FeAC^{2-}); 3) precipitation of the organometallic salts formed through self-aggregation of the partly deprotonated acid. The precipitates are then recrystallized from nitromethane. Crystalline **1** and **2** have been prepared. The two species contain different electronic and spin states for the metal centers: Fe^{II} and Co^{III} with 18 electrons are present in **1**, whereas Fe^{II} and a paramagnetic Cr^{I} center with 17 electrons are present in **2**. The two crystalline edifices are held together by the complementary contribution of strong neutral O-H···O and/or negatively charged $\text{O-H}\cdots\text{O}^{(-)}$ hydrogen bonds between the acid moieties as well as charge-assisted $\text{C-H}^{\delta+}\cdots\text{O}^{\delta-}$ bonds between cations and anions.[6]

$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+[(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})\text{Fe}]^-$ **1**

$[(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}]^+\{[(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})\text{Fe}][(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2\text{Fe}]_{0.5}\}^-$ **2**

In crystalline **1** the FeACH^- anions form chains (Figure 1 a) through symmetric O-H-O interactions between ligands in *transoid* conformation. The O–O distances are much shorter than in the O-H···O bonds present in neutral crystalline FeACH_2 (2.453(3) versus 2.606 Å). Charge-assisted $\text{C-H}^{\delta+}\cdots\text{O}^{\delta-}$ hydrogen bonds link the cobalticinium cations to the FeACH^- chains. Figure 1 b shows how the two sets of three $\text{C-H}^{\delta+}\cdots\text{O}^{\delta-}$ hydrogen bonds on both sides of the cations are directed precisely towards the "unused" lone pairs on the carboxylic oxygen atoms. There are two very short (C)H–O distances (2.192 and 2.254(3) Å) and a longer one (2.523(3) Å) in the bifurcated bond.

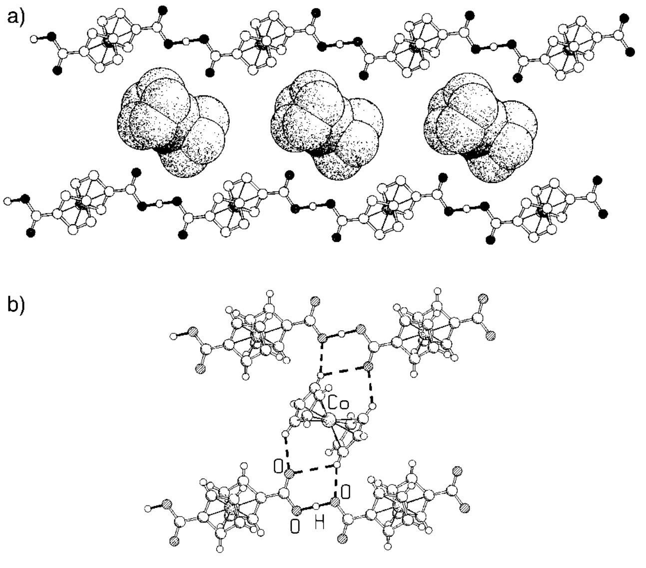

Figure 1. a) In crystalline **1** the FeACH^- anions form parallel chains that enclose the $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+$ cations (space-filling representation). The H atoms bound to C atoms are omitted for clarity. b) Schematic representation of the patterns of O-H-O interactions connecting the FeACH^- anions and of charge-enhanced $\text{C-H}^{\delta+}\text{--O}^{\delta-}$ hydrogen bonds (dashed lines) between the FeACH^- anions and the cobalticinium cations. The two sets of three $\text{C-H}^{\delta+}\cdots\text{O}^{\delta-}$ hydrogen bonds are directed precisely towards the "unused" lone pairs on the carboxylic oxygen atoms.

Crystalline **2** contains one neutral FeACH_2 molecule for every two FeACH^- anions. The neutral molecule acts as a bridge between hydrogen-bonded dimers formed by two FeACH^- anions. The two $\text{O-H}\cdots\text{O}^{(-)}$ hydrogen bonds (see the bifurcated interaction in Figure 2) are comparable in length (2.570(5) and 2.569(5) Å); they are longer than in **1**, but still shorter than in the neutral acid. All "unused" acceptor sites on the oxygen atoms are directed outwards along the chain to attain the maximum number of $\text{C-H}^{\delta+}\cdots\text{O}^{\delta-}$ interactions with the $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}]^+$ cations. There are as many as six (C)H–O distances shorter than 2.5 Å, with one as short as 2.072(5) Å. These values are again indicative of a substantial electrostatic reinforcement of the weak bonds.[7]

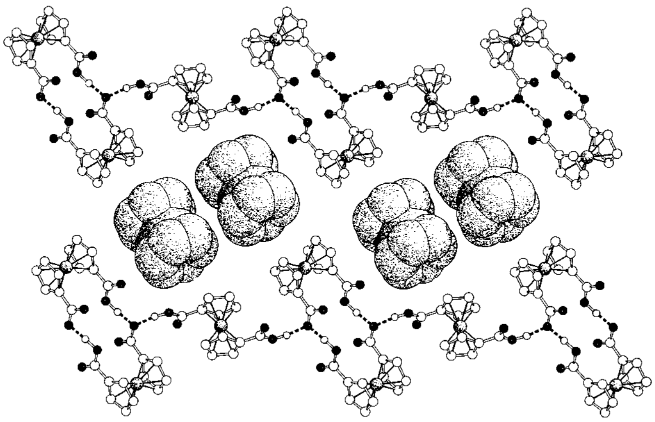

Figure 2. In crystalline **2** neutral FeACH_2 molecules form bridges between dimers of FeACH^- anions linked through negatively charged $\text{O-H}\cdots\text{O}^-$ hydrogen bonds. A space-filling representation is used for the $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}]^+$ cations. The H atoms bound to C atoms are omitted for clarity.

Crystallization from water of the cobaltocene/FeACH_2 system prepared in 2:1 ratio leads to complete deprotonation of the dicarboxylic acid and formation of **3**. The presence of a large number of water molecules had been previously observed in crystalline $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+\}_2[\text{L-BTA}]^{2-}\cdot 11\,\text{H}_2\text{O}$ (BTA = 1*H*-benzotriazole) obtained from complete deprotonation of dibenzoyl-L-tartaric acid.[5b] This behavior suggests that extra donors are required when hydrogen bonds between the acid molecules are not possible owing to a lack of COOH donors.

$\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+\}_2[(\eta^5\text{-C}_5\text{H}_4\text{COO})_2\text{Fe}]^{2-}\cdot 7.75\,\text{H}_2\text{O}$ **3**

We have shown here that novel hydrogen-bonded organometallic architectures can be obtained by utilizing organometallic carboxylic acids as building blocks for the construction of anionic hydrogen-bonded frameworks. The acid $[(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2\text{Fe}]$ is very versatile not only because it can participate in hydrogen-bonded networks as neutral, mono-, and diprotonated species, but also because the conformational freedom allows optimum orientation in space of the functional groups. The acid–base reaction allows a conception for the preparation of a great variety of hydrogen-bonded organometallic crystalline compounds in which metal atoms in different oxidation and spin states can be combined within robust hydrogen-bonded superstructures. Furthermore, the abundance of polarized C–H groups on metal-coordinated ligands, such as C_5H_5 and C_6H_6, make the use of C-H$\cdots$O hydrogen bonds also profitable, in particular since they may be reinforced when hydrogen donors and acceptors belong to cations and anions, respectively.[6]

Experimental Section

$FeACH_2$ (84 mg, 0.3 mmol) was dissolved in anhydrous THF (20 mL), and $(\eta^5\text{-}C_5H_5)_2Co$ (57 mg, 0.3 mmol) was added. $FeACH_2$ (71 mg, 0.26 mmol) was dissolved in anhydrous THF (16 mL), and $(\eta^6\text{-c}_6H_6)_2Cr$ (54 mg, 0.26 mmol) was added. The oxidation of cobaltocene and bis-benzene chromium was almost instantaneous. In both cases an orange precipitate was formed. After 1 h the slurries were filtered, and the orange powders were recrystallized from nitromethane to afford air-stable orange crystals of **1** and **2**.[8] $(\eta^5\text{-c}_5H_5)_2Co$ (57 mg, 0.3 mmol) was dissolved in water (20 mL) and stirred until complete oxidation to yellow $[(\eta^5\text{-c}_5H_5)_2Co][OH]$ had occurred. $FeACH_2$ (8 mg, 0.03 mmol) was added to an aliquot (5 mL) of the solution and stirred for 15 min. The yellow-orange solution was filtered and evaporated to dryness, and the resulting solid was recrystallized from nitromethane to afford well-formed crystals of **3**.[8]

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[6] Hydrogen atoms bound to oxygen atoms in crystalline **1** and **2** were observed in the Fourier maps. To evaluate the C-H$\cdots$O bonds, the C–H distances were normalized to the neutron derived value of 1.08 Å and the program PLATON was used: A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C31.

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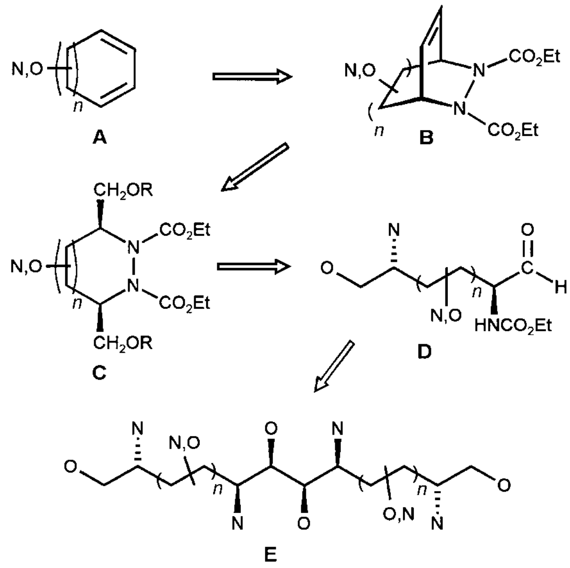
[8] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 101304. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

From Cycloolefins to Linear C_2-Symmetrical 1,4-Diamino-2,3-diol Building Blocks—Peptide Mimetics, Biocatalysis, and Pinacol Coupling of α-Amino Aldehydes**

Joachim Armbruster, Stefan Grabowski, Thomas Ruch, and Horst Prinzbach*

C_2-Symmetrical 1,4-diamino-2,3-diol units of type **E** are central structural elements in numerous bioactive compounds.[1] A variable synthesis of such building blocks, based on the recently reported route to enantiomerically pure amino aldehydes of type **D** from technical cycloolefins **A**,[2] and exemplary applications of this synthetic concept in the area of important bioactive compounds are the subjects of this communication.[1, 3]



The linear, enantiomerically pure C_8 amino aldehyde (+)-**4** (**D**, $n=2$) is prepared by the reaction sequence depicted in Scheme 1:[2] addition of diethyl azodicarboxylate (DEAD) to 1,3-cyclooctadiene (**1**), ozonolysis, reduction (strictly following a temperature program), and enzymatic asymmetrization, either by esterification of the *meso*-diethyl 3,8-bis(hydroxymethyl)-1,2-diazacyclooctane-1,2-dicarboxylate (**2a**) (→(+)-**2c**) or hydrolysis of the diacetate **2b** (→(−)-**2c**); lipozyme IM

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