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The Remarkable Behavior of Crystalline $[Fe(\eta^5\text{-}C_5H_4CHO)_2]$: Two Solid-to-Solid Phase Transitions and a Solid-State Reaction[†]

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The crystal architecture, stability, and behavior with temperature of bis(formyl)ferrocene, $[Fe(\eta^5\text{-}C_5H_4CHO)_2]$, have been investigated by variable-temperature X-ray diffraction experiments, differential scanning calorimetry, and thermogravimetry experiments. $[Fe(\eta^5\text{-}C_5H_4CHO)_2]$ is present with two independent molecules with *cisoid* and *transoid* relative orientations of the two formyl groups in the crystals obtained from the reaction sequence (phase RT-1). The role of C−H- - -O interactions involving the formyl groups has been examined. When RT-1 is heated, the first *irreversible* phase transition to a plastic phase (phase HT) is observed at ca. 38 °C (311 K). When it is cooled, phase HT transforms into a new room-temperature phase (RT-2). Once RT-2 has been formed, the system switches *reversibly* between HT and RT-2 (transition temperature in the heating cycles ca. 35 °C), while RT-1 can no longer be obtained. Further heating of phase HT shows the occurrence of an exothermic reaction at ca. 150 °C (423 K) leading to the formation of a ferrocene-based polymer.

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Introduction

The use of organometallic building blocks in the engineering of crystalline materials permits bringing to the solid the characteristics of transition metals such as variable oxidation and spin states and ionic charges.[1] The implications of utilizing these features to prepare novel materials are substantial.[2]

One of our lines of research is devoted to the preparation and characterization of novel building blocks and of their precursors for the construction of crystalline materials via cooperative strong and weak hydrogen bonds.[3] Thus far we have concentrated our efforts on the exploitation of the multiple extramolecular bonding capacity of organic and organometallic polycarboxylic acids. We have prepared a number of supramolecular crystalline systems (supersalts[3]) containing transition-metal atoms in different oxidation and spin states.[4] The prerequisites of our candidate building blocks are essentially 3-fold: (a) chemical stability to yield robust materials, (b) specific and predictable capacity for the formation of a large number of extramolecular interactions, in particular of the O−H- - -O and C−H- - -O types,[5] and (c) suitable *shape* for molding the intermolecular H-bond networks to achieve highly organized superstructures.

Previous work with ferrocene and cobaltocene dicarboxylic acids has taught us how to utilize the −COOH groups, and the deprotonated $-COO^-$ units, successfully.[6] In an attempt to expand our knowledge of the factors controlling stability of organometallic crystals, we have investigated the solid-state structure of crystalline bis(formyl)ferrocene $[Fe(\eta^5\text{-}C_5H_4CHO)_2]$ (**1**), a useful starting material in the synthesis of many ferrocene-based compounds. We have discovered that **1** shows an intriguing behavior under variable-temperature conditions, undergoing a phase transition and an exothermic reaction in a fairly limited temperature range. In the following we report the results of the investigation of **1** by single-crystal and powder X-ray diffraction as well as by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Results and Discussion

Although the main focus of this paper is on the supramolecular structural features of **1** and on the

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[†] This contribution is dedicated to Professor Dirk Walther on the occasion of his 60th birthday.

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(1) (a) Braga, D.; Grepioni, F. *Chem. Commun.* **1996**, 571. (b) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375.

(2) See, for example: (a) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690. (b) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21. (c) Marder, S. R. *Inorg. Mater.* **1992**, 115. (d) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690. (e) Miller, J. S.; Epstein, A. J. *Chem. Commun.* **1998**, 1319. (f) Müller, A.; Peters, F.; Pope, M. T.; Gatteschi, D. *Chem. Rev.* **1998**, *98*, 239.

(3) Braga, D.; Grepioni, F. *J. Chem. Soc., Dalton Trans.* **1999**, 1.

(4) Braga, D.; Grepioni, F.; Maini, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 2240.

(5) (a) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **1997**, *30*, 81. (b) Braga, D.; Grepioni, F. *Coord. Chem. Rev.* **1999**, *183*, 19.

(6) (a) Takusagawa, F.; Koetzle, T. F. *Acta Crystallogr.* **1979**, *B35*, 2888. (b) Braga, D.; Grepioni, F.; Maini, L. *Organometallics*, in press.

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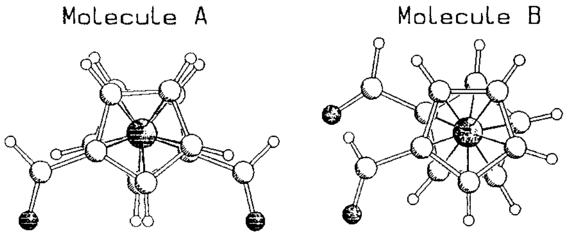

Figure 1. The two independent molecular units in the asymmetric unit of crystalline **1** (phase RT-1). The two molecules possess different rotameric conformations; in molecule **A** the two Cp rings are eclipsed, with the two −CHO groups in a *transoid* conformation, while in molecule **B** the Cp rings are almost staggered and the two −CHO groups adopt a *cisoid* conformation (mean Fe−C = 2.046(13) Å; mean $C_{Cp}-C_{CHO}$ = 1.454(8) Å; mean C−O = 1.205(14) Å).

Table 1. Relevant C−H- -O Interactions in the Room-Temperature Crystalline Form (RT-1) of 1 (distances in Å, Angles in deg, Esd's in the Range 2−4)[a]

C−H- - -O	(C)H−O	C- - -O	C−H- - -O
C_{Cp}−H- - -O	2.452	3.458	154.4
	2.592	3.540	146.1
	2.592	3.606	156.1
	2.773	3.708	144.7
	2.355	3.385	158.9
	2.666	3.453	129.4
	2.663	3.469	131.0
	2.524	3.382	135.7
	2.669	3.435	127.5
C_{CHO}−H- - -O	2.486	3.413	143.2
	2.351	3.430	177.6
	2.797	3.552	126.9

[a] C−H distances were normalized to the neutron diffraction value of 1.08 Å.

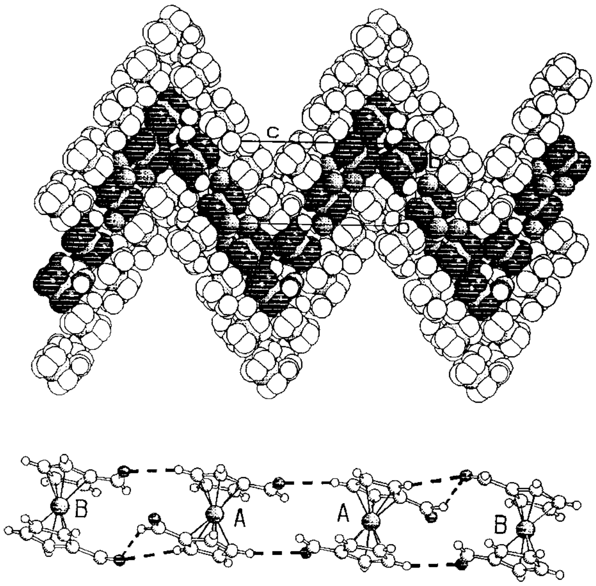

Figure 2. (a, top) Relative orientations of molecules **A** and **B** in phase RT-1. Note how the packing within the layer can be described as a zigzag sequence of repeating units constituted of four molecules. (b, bottom) Ball and stick representation of the repeating unit, with two *transoid* molecules in the middle and two *cisoid* molecules on the exterior. Dashed filled lines represent the C−H- - -O interactions involving the formyl groups in the "tetrameric" unit.

behavior with temperature of its crystals, it is still useful to point out some molecular characteristics which bear on the overall solid-state molecular organization. Crystalline **1** contains two independent molecular units in the asymmetric unit. The two molecules possess different rotameric conformations: in molecule **A** the two Cp rings are eclipsed, with the two −CHO groups in a *transoid* relative conformation (dihedral angle 138°), while the Cp rings are almost staggered in molecule **B**, with the two −CHO groups in a *cisoid* conformation (dihedral angle 43°) (see Figure 1). Furthermore, the relative orientations of the two formyl groups within each molecular unit are different: on (ideally) rotating the two formyl groups into eclipsed geometry, one notices that in **A** the two oxygen atoms point in opposite directions, while in **B** they point in the same direction. Crystalline **1** is, therefore, more adequately described as a *cocrystal* of conformational isomers rather than as a more conventional crystal containing two independent molecules of the same type in the asymmetric unit.

In terms of intermolecular interactions the system is capable of forming intermolecular hydrogen bonds of the C−H- - -O type. Although it is by now well accepted and demonstrated in crystal engineering practices[1,3] that interactions involving C−H donors play a fundamental role in determining molecular packing,[7] it has been argued that short C−H- - -O contacts involving formyl hydrogens might arise primarily from electrostatic interactions between the carbonyl carbon and the carbonyl oxygen atom.[8] We have examined the geometrical features of the C−H- - -O contacts in **1** after normalization of the C−H distances to neutron-derived values (1.08 Å; see Table 1). The data in Table 1 indicate that both the formyl and the cyclopentadienyl hydrogen atoms participate in C−H- - -O interactions. In particular, the formyl C−H group is involved in a fairly short and linear interaction (2.351 Å, 177.6°). Although great care should be exerted in assigning hydrogen-bond character to this interaction without independent verification, it is worth noting that not only is the formyl C−H- - -O interaction is close to linear but also the (C)H- - -O contact distance falls toward the lower limits for such weak bonds.[7a−c]

The molecular organization in **1** can be rationalized by looking at the molecular layer shown in Figure 2a. It can be seen that both the **A** and **B** molecules lie with the Cp ligands almost perpendicular to this plane. The packing within the layer can be described as a zigzag sequence of repeating units constituted of four molecules, linked via C−H- - -O interactions, with two *transoid* molecules in the middle and two *cisoid* molecules to close up the "tetrameric" unit (see Figure 2b).

With the aim of checking whether the bulk of the solid material obtained from the reaction had the same structure as determined from the single-crystal diffraction experiment, we ground the powder in order to

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(7) (a) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441. (b) Steiner, T. *Chem. Commun.* **1997**, 727. (c) Braga, D.; Grepioni, F.; Biradha, K.; Pedireddi, V. R.; Desiraju, G. R. *J. Am. Chem. Soc.* **1995**, *117*, 3156. (d) Braga, D.; Scaccianoce, L.; Grepioni, F.; Draper, S. M. *Organometallics* **1996**, *15*, 4675. (e) Grepioni, F.; Cojazzi, G.; Draper, S. M.; Scully, N.; Braga, D. *Organometallics* **1998**, *17*, 296.

(8) Chaney, J. D.; Goss, C. R.; Folting, K.; Santarsiero, B. D.; Hollinsgworth, M. D. *J. Am. Chem. Soc.* **1996**, *118*, 9432.

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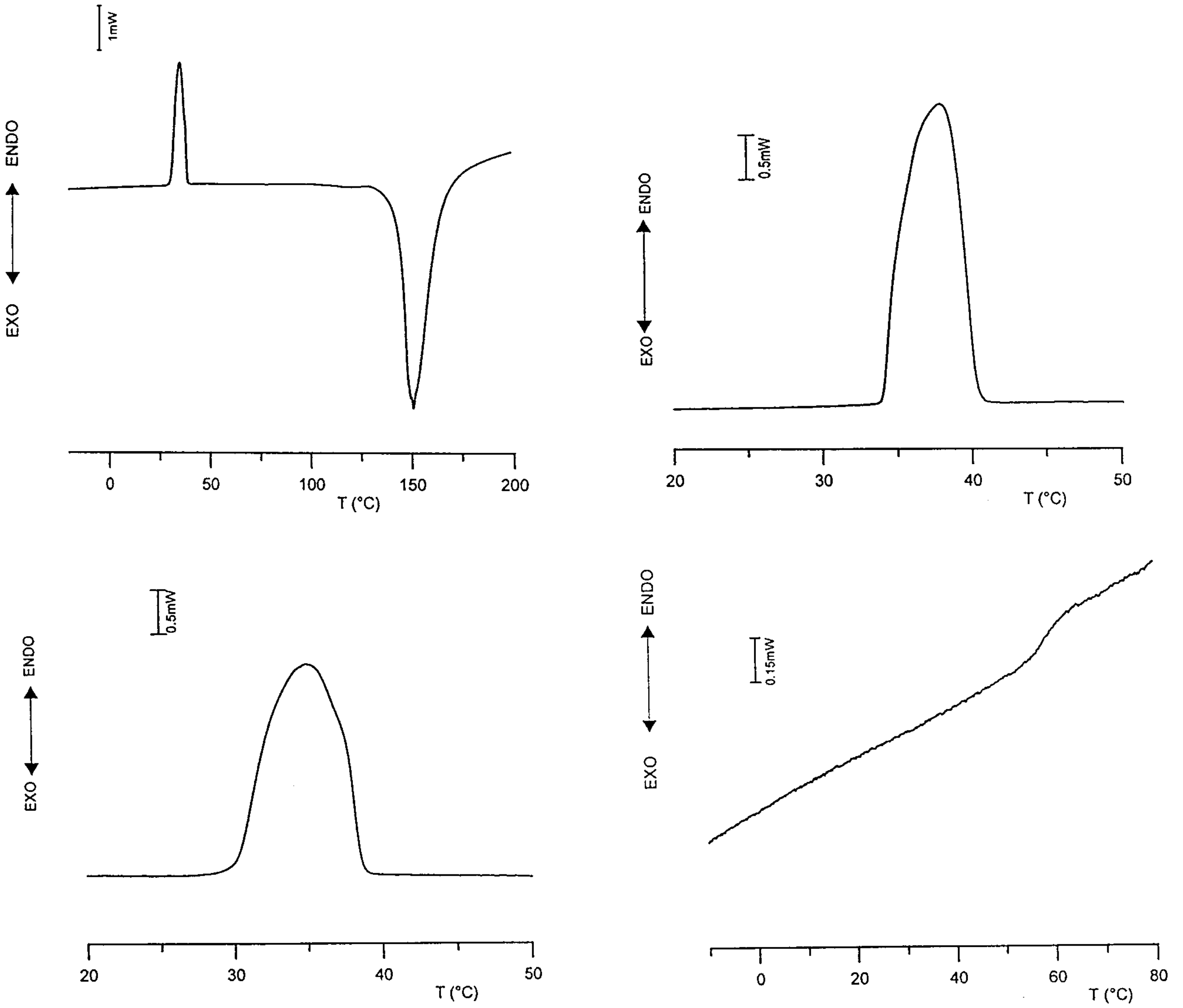

Figure 3. DSC thermograms for crystalline **1**: (a, top left) the first DSC scan showing both the irreversible RT-1 → HT phase transition (38 °C, 311 K) and the exothermic reaction (150 °C, 423 K); (b, top right) heating cycle on another sample of **1** (without passing through the exothermic process) showing the endothermic peak for the RT-1 → HT phase transition; (c, bottom left) heating of RT-2 through the new phase transition temperature (35 °C, 308 K); (d, bottom right) amorphous → liquid transition at ca. 60 °C (333 K) observed after the exothermic reaction in (a) has taken place. Note how (b) and (c) plots differ not only in the temperature of the peaks but also in the onset temperatures.

prepare a sample for a powder diffraction experiment. To our surprise, the dark red sample turned, on grinding, into a slimy and darker material unsuitable for diffraction. This observation prompted us to undertake a calorimetric investigation. The DSC graph obtained from a continuous heating scan of a sample of pure crystalline **1** between −20 and 200 °C is shown in Figure 3a. There are two clearly distinct processes that need to be examined: (i) the endothermic transition at ca. 38 °C (311 K) and (ii) the exothermic process taking place at ca. 150 °C (423 K). The investigation of these two processes required separate DSC experiments as described in the following.

A fresh sample of **1** was heated to 50 °C, i.e. well below where the exothermic process could begin to take place. Figure 3b shows a broad endothermic peak at ca. 38 °C, corresponding to the first solid-to-solid-phase transition (RT-1 → HT). When HT is cooled back to room temperature, the corresponding exothermic peak appears after a hysteresis of ca. 30 °C. The same sample was then heated again to begin a second heating/cooling cycle. Unexpectedly, the endothermic peak was seen to "move" from ca. 38 to ca. 35 °C (308 K), as shown in Figure 3c. The temperature of this new phase transition (RT-2 ↔ HT) was reproduced in all subsequent cycles (four cycles on the same sample), indicating the occurrence of a fully *reversible* process. In summary, after the first transition takes place (RT-1 → HT), the reverse process leads to the formation of a different, more stable room-temperature phase which interconverts reversibly with HT (HT ↔ RT-2).

The enthalpy differences associated with the transitions from room to high temperature are reported in Table 2. The values are higher than the values observed in the cases of the crystalline salts [M(η^5-$C_5H_5)_2$][PF_6] (3.05 kJ mol^{-1} for M = Co, 4.50 kJ mol^{-1} for M = Fe),[7d,e,9] which have been shown to reversibly *switch* between three phases, two of which are fully ordered,[7d,e] while they are comparable with the value of 12.1 kJ mol^{-1} found for the mono(formyl) derivative

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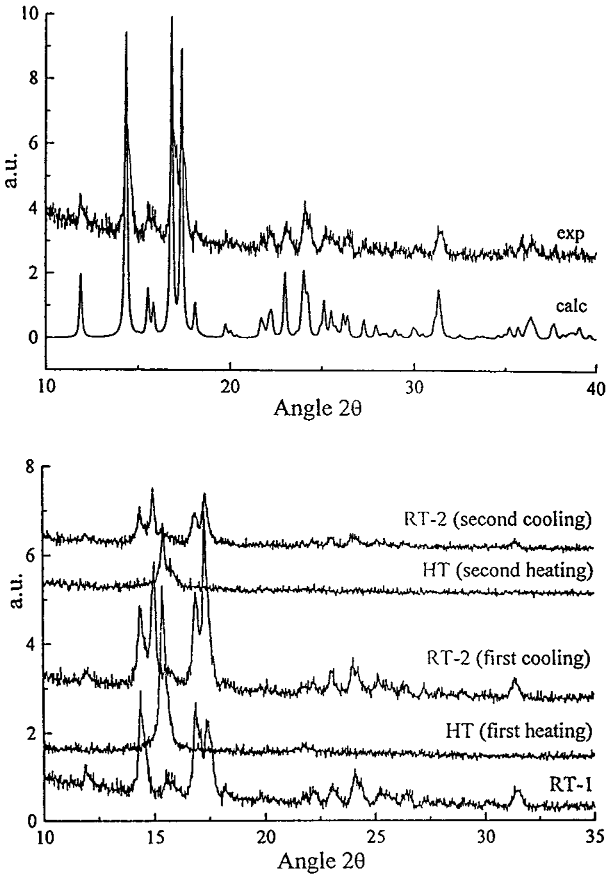

Figure 4. (a, top) Comparison between the diffractograms of **1** (form RT-1) calculated on the basis of the single-crystal determination and measured on the bulk (without grinding). (b, bottom) Comparison of the powder diffraction spectra collected for the *same sample* of powdered **1** in two subsequent cycles of heating and cooling.

Table 2. Thermal Behavior of 1

transition (T, °C [K])	ΔH_{endo} (kJ mol^{-1})	polymerizn T (°C [K]), ΔH_{exo} (kJ mol^{-1})
RT-1 → HT (38 [311])	14.0	150 [423], 72.4
RT-2 → HT (35 [308])	13.3	

[Fe(η^5-C_5H_5)(η^5-C_5H_4CHO)],[10] which shows a mesophase between 316 K and the melting point (396 K). Similar dynamic behavior is shown by the ferrocene methyl ketone [Fe(η^5-C_5H_5)(η^5-C_5H_4CMeO)],[11] which undergoes a reversible phase change before melting.

Some insight into the phase transition process comes from powder diffraction measurements. Figure 4a shows a comparison between the diffractograms calculated on the basis of the single-crystal determination of **1** and measured on the bulk (without grinding). Figure 4b shows a comparison of the powder diffractograms collected for the *same sample* of powdered **1** (form RT-1) in two subsequent cycles of heating and cooling. The first diffractogram (form RT-1) was measured at room temperature; then the powder was heated above the phase transition, and data were collected on form HT. Clearly, the high-temperature phase retains some degree of crystallinity: the presence of only two major peaks in the diffractogram (form HT, first heating) suggests that the crystal is in a plastic phase which has retained some long-range order but has lost local ordering. This is in keeping with the idea that, when the crystals are heated, the weak C−H- - -O bonds are broken and the four C_5H_4CHO groups reorientate. When the sample is cooled below the transition temperature, one obtains a third powder diffractogram (form RT-2, first cooling) characterized by the presence of an additional intense peak in a previously empty region (2θ = ca. 15°). This difference is indicative of the formation of a different crystalline form (RT-2) that is stable at room temperature. In keeping with the DSC results, the subsequent cycle of heating and cooling showed that the sample reversibly switches between RT-2 and HT without "going back" to RT-1. This behavior suggests that form RT-1 is a kinetic product of the crystallization process: when it is heated, the sample undergoes an order → disorder phase transition to the plastic phase HT, which trasforms on cooling to the thermodynamically more stable form RT-2. Once RT-2 is formed, RT-1 can no longer be obtained, except via recrystallization from solution. The process can be summarized as

$$\text{form RT-1} \xrightarrow{\text{heating}} \text{form HT} \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftarrows}} \text{form RT-2}$$

$$\text{form RT-1} \neq \text{form RT-2}$$

$$\text{form HT/form RT-2} \xrightarrow[\text{crystallization}]{} \text{form RT-1}$$

It is worth stressing that, under these conditions, form RT-2 can be obtained only from the high-temperature phase. All attempts to obtain single crystals of form RT-2 suitable for single-crystal experiments from the RT-2 powder have been, so far, unsuccessful.

A further point of interest in the behavior of crystalline **1** with temperature is the appearance of an appreciable *exothermic* peak at ca. 150 °C (423 K), when the sample is heated above the phase transition temperature. This temperature was reported as the melting point,[12] but melting of the sample would appear on a DSC plot as an enthalpy absorption, not as a release. Exothermic peaks are usually associated with chemical reactions. After reaction the sample becomes rubbery and viscous and the color changes from deep red to lustrous black. When it is cooled to room temperature, the sample solidifies into an amorphous phase, which on heating shows on the DSC a typical amorphous → liquid transition at ca. 60 °C (333 K; see Figure 3d). These observations suggest the occurrence of a polymerization reaction in the solid state. The polymer is dark brown and is soluble in organic solvents such as $CHCl_3$ and CCl_4. Thermogravimetric measurements on a fresh sample of RT-1 under an N_2 atmosphere indicate a weight loss of ca. 5% at about 155 °C (428 K), due to the release of two water molecules every three bis(formyl)ferrocene units, as shown by mass spectrometric measurements on the evolved gas. The ^{1}H NMR spec-

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(9) (a) Webb, R. J.; Lowery, M. D.; Shiomi, Y.; Sorai, M.; Wittebort, R. J.; Hendrickson, D. N. *Inorg. Chem.* **1992**, *31*, 5211. (b) Sorai, M.; Shiomi, Y. *Thermochim. Acta* **1986**, *109*, 29.

(10) (a) Sato, K.; Iwai, M.; Sano, H.; Konno, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 634. (b) Daniel, M. F.; Leadbetter, A. J.; Mazid, M. A. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 1837.

(11) Sato, K.; Katada, M.; Sano, H.; Konno, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2361.

(12) Edwards, J. W.; Kington, G. L.; Mason, R. *J. Chem. Soc., Faraday Trans.* **1959**, *55*, 660.

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trum shows three very broad bands (centered at ca. 2.2, 4.6, and 10 ppm) which indicate that the formyl and cyclopentadienyl hydrogens are still present in the polymer with an integration ratio of 1:10 (1:4 in the bis-formyl complex). Work is in progress to envisage a possible reaction mechanism for the condensation/polymerization of **1**. Ferrocene-based polymers are of great interest because they are expected to possess a range of interesting and potentially useful physical properties.[13]

Conclusions

With this paper we have investigated the crystal structure and behavior with temperature of the bis-(formyl)ferrocene complex. The main *supramolecular* difference between this kind of system and ferrocene or other metallocenes[14] resides in the simultaneous presence of CO acceptor groups and of a profusion of C−H donors. These interactions, though weak, may play a crucial role in controlling the packing arrangement of the two complexes. The main outcomes of this work can be summarized as follows.

(i) Compound **1** is present in the crystals obtained from the reaction sequence (form RT-1) with two different conformations (*cisoid* and *transoid*) with respect to the orientation of the formyl groups. In form RT-1 there are several C−H- - -O hydrogen-bonding interactions comparable in length and angles to those usually observed in organometallic crystals containing O-acceptors and cyclopentadienyl C−H donors.

(ii) Compound **1** in its form RT-1 undergoes one irreversible (38 °C) and one reversible (35 °C) solid-to-solid-phase transitions according to the sequence RT-1 → HT ↔ RT-2.

(iii) Crystals of form RT-1 appear to represent a metastable ordered phase[15] (probably formed under kinetic control) which transforms, upon heating, into a disordered high-temperature phase, HT. HT transforms *reversibly* to the thermodynamically more stable room-temperature phase RT-2.

(iv) Crystalline **1** undergoes a high-temperature reaction with likely formation of a ferrocene-based polymeric phase whose full characterization requires further study.

It is worth recalling, however, that metallocene-based polymers are attracting considerable interest for their potential applications in materials chemistry.[13,16]

Besides these chemical and structural findings, our work also carries a small caveat. Since the reaction products in crystal engineering are solids for which routine laboratory analytical and spectroscopical tools are much less useful than in the case of solution chemistry, the utilization of powder diffraction is, sometimes, the only way to ascertain whether the whole solid material has the *same structure as* that characterized by single-crystal diffraction. It is therefore useful to keep in mind that a common method of sample preparation (powder grinding) may lead to solid-state transformations and to formation of new polymorphic modifications.[15] For instance, we have recently reported that the crystals of the supersalt [Fe(η^5-C_5H_4COO)(η^5-C_5H_4COOH)][Co(η^5-C_5H_5)$_2$] undergoes stoichiometric hydration with formation of the pseudo-polymorph [Fe(η^5-C_5H_4COO)(η^5-C_5H_4COOH)][Co(η^5-C_5H_5)$_2$]·H_2O upon grinding.[18] Of some importance is, therefore, the notion that the crystallization product may not represent the most stable (thermodynamic) system. In principle, any new solid material should be subjected routinely to a DSC run in order to ascertain the phase transition behavior and the possibility of solid-state reactivity. This is not so much relevant for solution chemistry but may be crucial for the success of crystal engineering and solid-state chemistry processes.

Experimental Section

Compound **1** was synthesized following the procedure reported by Edwards et al.[12] The dark red powdered product (yield 70%) was recrystallized from hexane, yielding crystals suitable for the X-ray diffraction experiments.

The ^{1}H NMR spectrum of the polymer obtained above 150 °C was recorded in $CDCl_3$ solution on a Varian Gemini 300 at 300 MHz with TMS as internal standard.

Differential Scanning Calorimetry (DSC). DSC thermograms of compound **1** were measured on a Perkin-Elmer DSC-7 in sealed Al pans. A 2.720 mg portion of crystalline **1** was taken from the same crystal batch used for the single crystal and powder diffraction experiments. Repeated cycles of cooling and heating were run at a scanning rate of 5.0 °C min^{-1}.

Thermogravimetric Analysis (TGA). Thermogravimetric curves were measured on a Perkin-Elmer TGA-7 in open Al pans under an N_2 atmosphere.

Crystal Structure Determination. Diffraction intensities for compound **1** were collected at 223 K on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo Kα radiation, $\lambda = 0.710\ 69$ Å) and an Oxford Cryosystem device. The phase transition from the room-temperature to the high-temperature phase was observed also on single crystals on the diffractometer, although, as is usually the case, the temperature at which the transition occurred was higher than the one observed in the DSC experiment. During the heating process, at a rate of about 5 °C min^{-1}, we monitored a few strong reflections, whose intensity rapidly dropped and disappeared as an effect of the transition after the nominal temperature of 323 K. A new search on the high-temperature phase showed the presence of few diffraction peaks at a very low θ angle. No low-temperature transition was observed on the diffractometer on cooling various crystals of **1** down to 100 K.

Crystal Data. 1 (room-temperature form, RT-1): $C_{12}H_{10}FeO_4$, $M_r = 242.05$, monoclinic, space group $P2_1/n$, $a = 5.933(5)$ Å, $b = 11.404(2)$ Å, $c = 29.459(7)$ Å, $V = 1985(2)$ Å^3, $Z = 8$, $T = 223(2)$ K, $d_c = 1.620$ g cm^{-1}, $\mu = 1.491$ mm^{-1}, 3536 reflections measured, refinement on F^2 (3468 independent reflections) for 251 parameters; $R_w(F^2$, all reflections$) = 0.1434$, R1 = 0.0449, $S = 1.015$; crystal size 0.18 × 0.14 × 0.13 mm, $F(000) = 992$; θ range 3.0−25.0°. The computer program SHELXL97[17a] was used for structure solution and refinement. All non-H atoms were treated anisotropically. The H atoms of

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[13] Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602. Manners, I. *Chem. Commun.* **1999**, 857.

[14] (a) Seiler, P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1982**, *B38*, 1741. (b) Takusagawa, F.; Koetzle, T. F. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1074. (c) Seiler, P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1068. (d) Seiler, P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2255.

[15] Dunitz, J.; Bernstein, J. *Acc. Chem. Res.* **1995**, *28*, 193.

[16] See, for example: (a) Altmann, M.; Friederich, J.; Beer, F.; Reuter, R.; Enkelmann, V.; Bunz, U. H. *J. Am. Chem. Soc.* **1997**, *119*, 1472. (b) Southard, G. E.; Curtis, M. D. *Organometallics* **1997**, *16*, 5618.

[17] (a) Sheldrick, G. M. SHELXL97, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1997. (b) Keller, E. SCHAKAL97 Graphical Representation of Molecular Models; University of Freiburg, Freiburg, Germany, 1997. (c) Spek, A. L. PLATON. *Acta Crystallogr., Sect. A* **1990**, *A46*, C31.

[18] Braga, D.; Grepioni, F.; Maini, L. *Chem. Commun.* **1999**, 937.

the CHO groups were located directly from difference Fourier maps and refined. The H atoms of the Cp rings were added in calculated positions and refined riding on their respective C atoms. For all molecular representations the graphic program SCHAKAL97[17b] was used. The program PLATON[17c] was used to calculate the hydrogen-bonding interactions of the C—H- - -O type. For these calculations all C—H distances were normalized to the neutron-derived value (1.08 Å). Crystal data and details of measurement and tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles are all available as Supporting Information and have been deposited with the Cambridge Crystallographic Data Centre.

Powder spectra were measured on an automated PW 1100 powder diffractometer, with monochromatic Cu Kα radiation. To measure the HT diffractogram of compound **1**, the crystalline material was heated above the phase transition temperature and then exposed to diffraction at room temperature: due to the large hysteresis range the sample was still present as form HT. The HT → RT-2 process was then ensured by cooling the sample below 273 K.

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Supporting Information Available: Details about the X-ray crystal structures, including ORTEP diagrams and tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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