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Design of organometallic molecular and ionic materials☆

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Contents

Abstract

Organometallic crystal engineering is the modeling, synthesis, characterization and evaluation of crystalline materials constituted by organometallic molecules and ions. The properties

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of solids containing transition metal complexes are distinct and diverse from those of purely organic systems as well as from those of inorganic materials. In particular, while the periphery of (most) organometallic molecules are ‘organic’ in nature, since the outer atoms are usually those of the ligands, the ‘cores’ are formed by transition metal atoms in their (often variable) spin and charge states. These characteristics can be exploited to make crystalline materials with predefined physical properties as well as to organize organometallic molecules in complex supramolecular structures for absorption and desorption of solvent molecules. The possibility of utilizing the same building blocks in different ionic conditions (including neutral, e.g. in molecular crystals) permits tuning of the intermolecular bonding capacity via acid-base reactions. Organometallic polymorphism is discussed as a possibility for preparing and interconverting crystalline isomers. Pseudo-polymorphism is shown to be advantageous for the preparation of elusive crystal forms.

Keywords: Organometallic materials; Organometallic crystal engineering; Hydrogen bonds; Organometallic polymorphism

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1. Introduction

1.1. Crystal engineering: from molecules and crystals to materials

The possibility of designing, modeling, synthesizing and exploiting solids with predefined aggregation of molecules or ions is attracting an increasing number of scientists [1]. The most appealing areas of application are in materials chemistry, in particular in optoelectronics [2], conductivity and superconductivity [3], charge-transfer and magnetism [4], nano-porous materials [5] and biomimetic materials [6]. The construction of materials with predefined physical properties or destined to predefined applications and uses is based on a fundamental paradigm: the utilization of crystal-directed synthetic strategies.

However, on approaching the construction of crystalline solids a distinction needs to be made between covalent solids, coordination networks and molecular solids. While covalent or coordination solids are ‘held together’ by strong two-electron bonds (whether covalent or dative), molecular materials owe their stability to the network of (generally weak) non-covalent interactions between molecular building blocks [7]. Since the cohesion of covalent and coordination solids depends on interactions that, generally speaking, require much more energy to be broken and formed than in the case of molecular solids, the synthetic strategies that can be adopted to make covalent (and coordination) crystalline materials are different from those required when molecules or molecular ions are involved.

Another fundamental distinction is between neutral and ionic systems. The role of Coulombic forces arising from the presence of ions in the crystal structure is, obviously, extremely relevant in determining crystal cohesion [8].

This article will deal essentially with the engineering of crystals based on molecular building blocks, e.g. molecular crystal engineering. The epithet ‘molecular' will be used in a broad sense, encompassing both neutral and ionic systems based on the working assumption that are 'molecular' all those aggregates of atoms that have their own identity in gas-phase or solution. On this premise we will call intermolecular all those types of secondary inter-ionic or inter-molecular non-covalent interactions that do not imply two-electrons σ-bonds (e.g. electrostatic, EL, hydrogen bonds, HB, and van der Waals, vdW, interactions).

Conceptually, the engineering of a molecular solid is closely related to the construction of a supermolecule whose collective functions depend on the aggregation via intermolecular bonds of two or more component units. This analogy is only conceptual, certainly not practical, as one needs a very large number of building blocks to obtain crystalline materials with useful supramolecular properties.

If a molecular crystal is perceived as a periodical supermolecule thus the properties of the bulk solid are supramolecular properties. Though näive it may appear, many basic physical properties of molecular solid aggregates, such as melting point, vapor pressure, solubility, etc. depend on the type and number of intermolecular interactions, and may thus be regarded as supramolecular properties (after all single molecules do not boil and do not melt). The fact that ammonia is a gas while water is liquid at thermodynamic STP conditions, and that their melting points differ by about 80° (195.45 and 273.15 K, respectively), depends on the difference in free energy, topology and number of $N-H\cdots N$ and $O-H\cdots O$ interactions between solid ammonia and ice, hence on differences in intermolecular bonding. The two structures are shown in Fig. 1.

2. Organometallic crystal engineering with ionic building blocks

The utilization of organometallic building blocks, whether molecules or ions, allows one to take advantage of the valence and spin states of transition metal atoms as well as of metal–ligand bonding [11]. One particularly useful combination is that between metal atom oxidation state and charge of the ligand. An example is provided by the dicarboxylic acid $[(\eta^5\text{-}C_5H_4COOH)_2Co(II)]$ which is readily oxidized in air to the cation $[(\eta^5\text{-}C_5H_4COOH)_2Co(III)]^+$ [12]. These two complexes provide a grand total of six synthons [13] potentially useful in crystal engineering. These are grouped in Fig. 2. It is easy to appreciate that by controlling the oxidation state and/or the pH this relatively simple chemical system can afford complexes that can be diamagnetic or paramagnetic [Co(III), and Co(II)], neutral, cationic or anionic [from $+1$ to -2], hydrogen bonding donor or acceptor [$-COOH$ and $-COO^{(-)}$], or a combination of these characteristics. Some examples of the utilization of these building blocks in crystal engineering applications will be provided below.

Organometallic ions have been utilized by Fagan and Ward to prepare crystalline materials for charge-transfer applications [14]. The strategy is based on the so called 'electrostatic templating' method which takes advantage of the constraints to the crystal build-up sequence arising from the need to pack anions and cations while

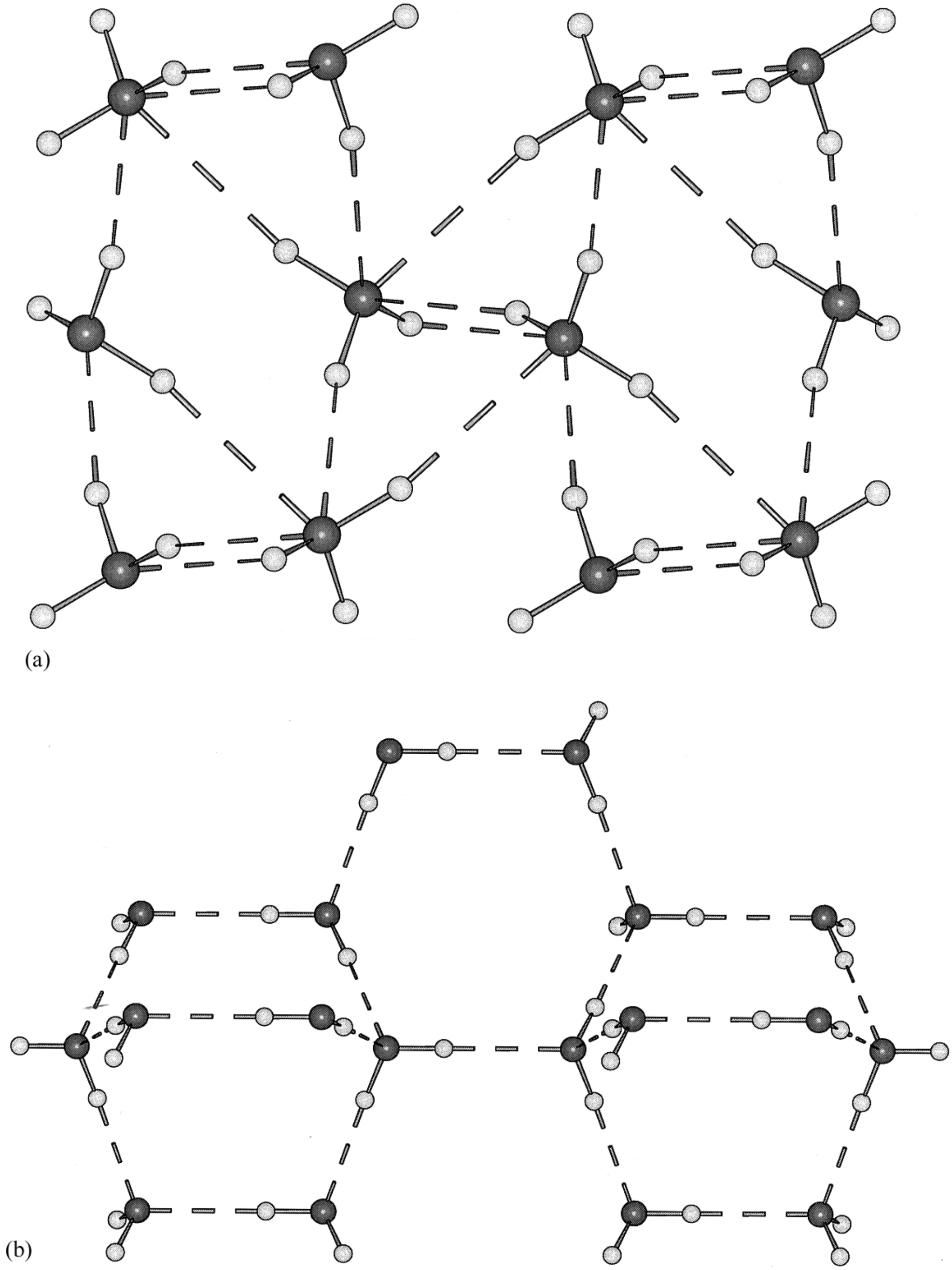

Fig. 1. A comparison of the hydrogen bond networks in crystalline ammonia [9] and in ice ($P6_3/mmc$ form) [10].

maintaining electroneutrality. The cationic fragment $[(\eta^5\text{-}C_5Me_5)Ru]^+$ in the cations $[(\eta^5\text{-}C_5Me_5)Ru)_2(\text{paracyclophane})]^{2+}$, $[(\eta^5\text{-}C_5Me_5)Ru)_4($*para*-quartpyhenyl$)]^{4+}$, $[(\eta^5\text{-}C_5Me_5)Ru)_6($*para*-sexipyhenyl$)]^{6+}$ and $[\{(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_6H_5)\}_4E]^{4+}$ (E = C, Si, Ge, Sn, Pb) has been employed to form one-, two- and three-dimensional aggregates (see Fig. 3).

The utilization of ionic organometallic acids or bases brings about the intriguing role of hydrogen bonds between ions. Since the hydrogen bond has a fundamentally electrostatic nature [15], the presence of ionic charges on the building blocks can be exploited to strengthen the interaction [16]. Charge assistance to hydrogen bond is the enhancement of donor and acceptor polarity (whether atoms or groups of atoms) by utilizing cationic donors and anionic acceptors instead of neutral systems, i.e. $X\text{–}H^{(+)}\cdots Y^{(-)}$ rather than $X\text{–}H\cdots Y$ [17]. The favorable location of ionic charges enhances proton acidity and acceptor basicity. It should be kept in mind, however, that 'acidity' or 'basicity' are relative concepts and cannot be transferred tout-court to the solid state; other factors may change the polarity of the X–H bond and/or the nucleophilicity of the Y acceptor.

Hydrogen bonds between ions are widely employed to obtain predefined crystalline architectures [18]. There are several reasons for this choice: (i) inter-ionic hydrogen bonds are easily obtained in crystal synthesis via proton transfer in acid–base reactions (see below); (ii) they combine hydrogen bond directionality with the strength of Coulombic forces (which are stronger than ion–dipole or

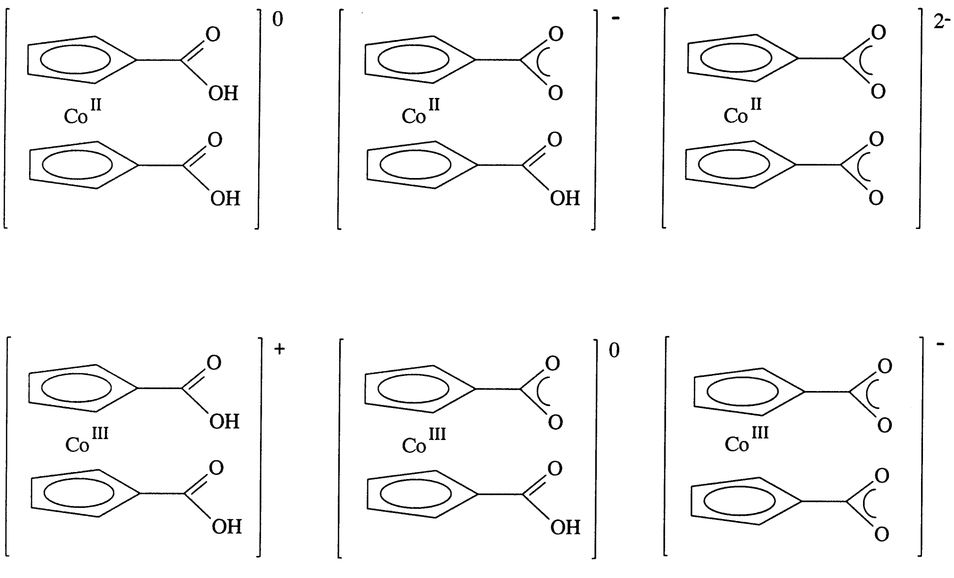

Fig. 2. The six synthons generated by the neutral form of the dicarboxylic acid $[(\eta^5\text{-}C_5H_4COOH)_2Co(II)]$ and its oxidation product $[(\eta^5\text{-}C_5H_4COOH)_2Co(III)]^+$.

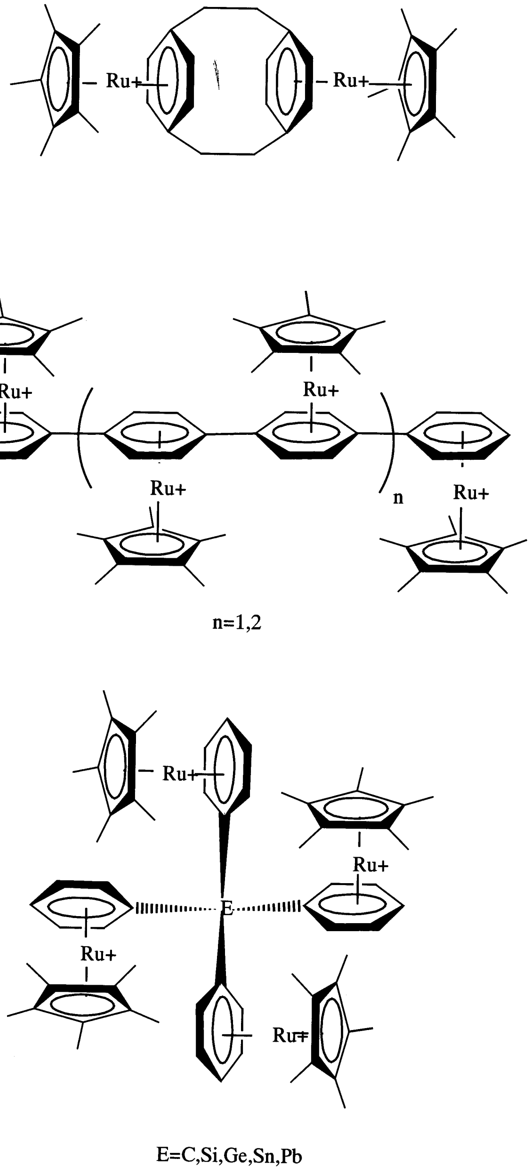

Fig. 3. Schematic representation of the cations $[(\eta^5\text{-}C_5Me_5)Ru)_2(\text{paracyclophane})]^{2+}$, $[(\eta^5\text{-}C_5Me_5)Ru)_4(\textit{para}\text{-quartpyhenyl})]^{4+}$, $[(\eta^5\text{-}C_5Me_5)Ru)_6(\textit{para}\text{-sexipyhenyl})]^{6+}$ and $[\{(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_6H_5)\}_4E]^{4+}$ (E = C, Si, Ge, Sn, Pb).

dipole–dipole forces but less directional and less useful as design tools); (iii) the use of ions permits a much greater choice of components, which, in the case of transition metal complexes, may not only possess different topologies, but also different bonding and electronic characteristics.

Since short intermolecular distances are often a consequence of other truly relevant interactions, such as those between ions in crystalline salts one should keep in mind that (i) even though the stabilizing contribution of the hydrogen bonding interaction is small with respect to the interactions between ions, the directionality is fully operative, and (ii) the common assumption that the intermolecular separation between atoms or groups of atoms reflect the strength of the local interaction is not directly transferable from neutral to ionic environments [19].

An illustrative example of the relationship between charge and hydrogen bonds is afforded by the comparison of the O–H···O interactions established between nearly isostructural organometallic building blocks of the type discussed above (see Table 1). Hydrogen bonds between the neutral dimers present in crystalline $[(\eta^5\text{-}C_5H_4COOH)_2Fe(II)]$ [20] have lengths comparable to those between $[(\eta^5\text{-}C_5H_4COOH)_2Co(III)]^+$ cations [21], while the neutral zwitterion $[(\eta^5\text{-}C_5H_4COO)(\eta^5\text{-}C_5H_4COOH)Co(III)]$ forms hydrogen bonds that are comparable strictly to those between the anionic species $[(\eta^5\text{-}C_5H_4COO)(\eta^5\text{-}C_5H_4COOH)Fe(II)]^-$ and within the supramolecular complex $\{[(\eta^5\text{-}C_5H_4COO)(\eta^5\text{-}C_5H_4COOH)Co(III)][(\eta^5\text{-}C_5H_4COOH)_2Co(III)]\}^+$ [21]. The hydrogen bonding networks are shown in Fig. 4.

The data in Table 1 demonstrates that the difference in O···O separation between COOH···OC(OH) and COOH···$^{(-)}$OOC interactions does not depend on the neutral or ionic nature of the complex. This observation suggests that, at least in the solid state, proton removal from COOH groups leaves the extra-electron localized on the deprotonated group. A possible rationale is that the electron localization on the deprotonated groups, e.g. $-COO^{(-)}$, allows one to take full advantage of the stabilizing contribution arising from the O–H···O$^{(-)}$ interaction even though the building blocks carry the same charge (which is 'dealt with' by the counterions). The corollary of this argument is, however, that the stabilization afforded by the O–H···O$^{(-)}$ interaction cannot offset the repulsive forces between like charges next to each other and is not sufficient per se to keep the anions together in the absence of counterions [19]. This conclusion has been challenged recently [22]. However,

Table 1
A comparison of the O–H···O hydrogen bonding interactions in some bis-metallocene dicarboxylic acid molecules, anions and cations

Complex	O(H)···O distance (Å)
$[(\eta^5\text{-}C_5H_4COOH)_2Fe(II)]$	2.606
$[(\eta^5\text{-}C_5H_4COOH)_2Co(III)]^+$	2.600(2)
$[(\eta^5\text{-}C_5H_4COO)(\eta^5\text{-}C_5H_4COOH)Co(III)]$	2.456(2)
$[(\eta^5\text{-}C_5H_4COO)(\eta^5\text{-}C_5H_4COOH)Fe(II)]^-$	2.453(3)
$\{[(\eta^5\text{-}C_5H_4COO)(\eta^5\text{-}C_5H_4COOH)Co(III)][(\eta^5\text{-}C_5H_4COOH)_2Co(III)]\}^+$	2.594(5), 2.609(5), 2.488(5)

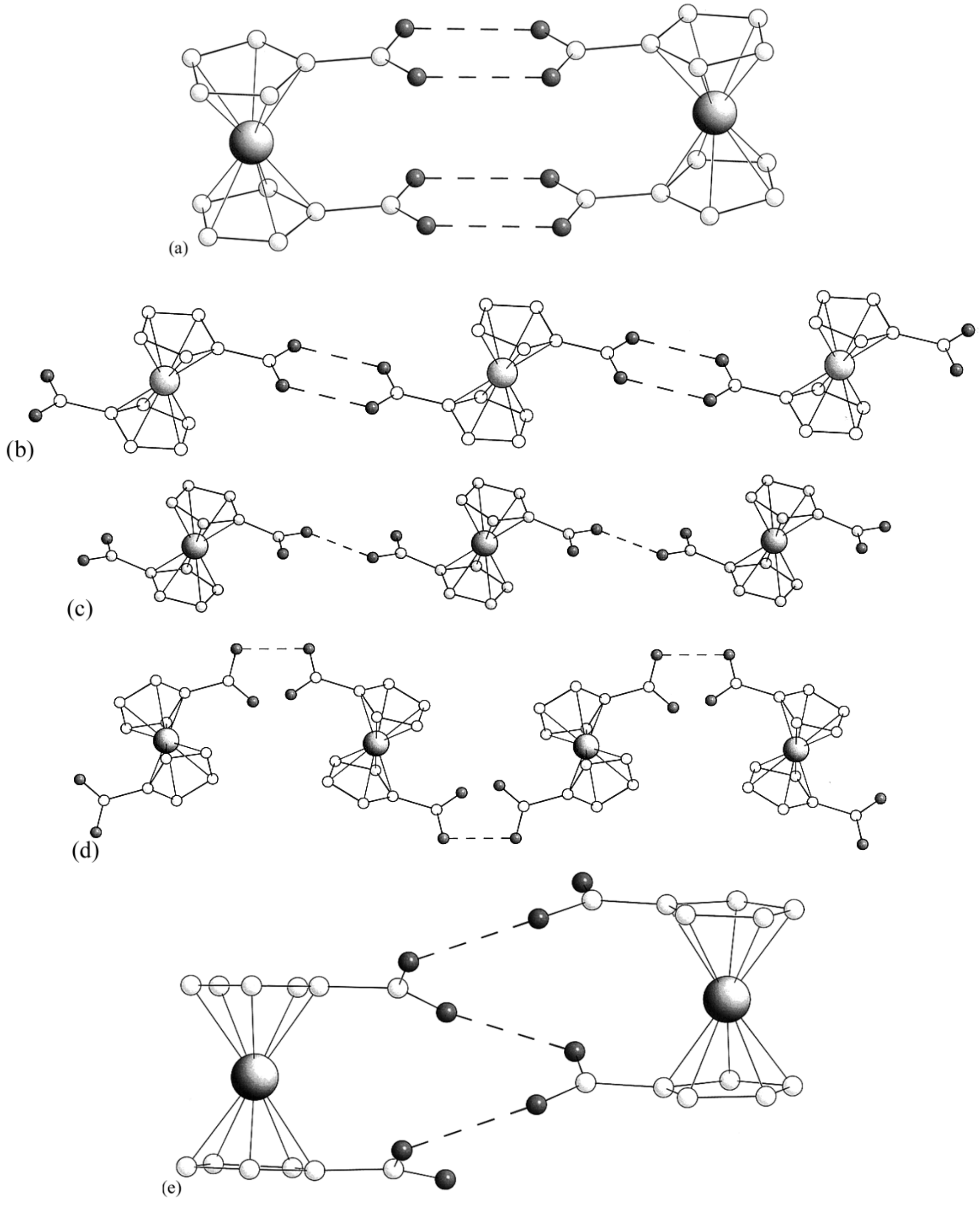

Fig. 4. The neutral dimer present in crystalline $[(\eta^5\text{-}C_5H_4COOH)_2Fe(II)]$ (a) and the cationic chain formed by $[(\eta^5\text{-}C_5H_4COOH)_2Co(III)]^+$ cations (b); the chain formed by the anionic species $[(\eta^5\text{-}C_5H_4COO)(\eta^5\text{-}C_5H_4COOH)Fe(II)]^-$ (c); the neutral zwitterion $[(\eta^5\text{-}C_5H_4COO)(\eta^5\text{-}C_5H_4COOH)Co(III)]$ (d); and the aggregate formed by one cationic unit and one zwitterionic unit within the supramolecular complex $\{[(\eta^5\text{-}C_5H_4COO)(\eta^5\text{-}C_5H_4COOH)Co(III)][(\eta^5\text{-}C_5H_4COOH)_2Co(III)]\}^+$ (e).

relevant to the understanding of supramolecular bonding, the controversy is somewhat 'academic' because the precondition 'in the absence of the counterions' is physically meaningless in the solid state. Crystal cohesion is guaranteed by hetero-ionic $+/-$ attractions that overcompensate for the homo-ionic $+/+$ and $-/-$ repulsions with the additional stabilizing contribution arising from hydrogen bonding interactions.

3. π-Stacking can be used to preorganize ions

Other non-covalent interactions, beside the hydrogen bond, are sufficiently strong and selective to be of use in crystal engineering applications: (i) graphitic-like π-stacking of metal bound arene ligands is a recurrent motif in crystalline environments [23]; (ii) closed-shell atoms form strong intermolecular interactions with energies of the order of 10–40 kJ mol^{-1} [24], i.e. weaker than covalent bonds but stronger than most vdW interactions; gold atoms in coordination complexes form 'aureophilic' interactions [25]; (iii) intermolecular hypervalent interactions involving heavy p-block elements allow formation of extended networks in the solid state with many geometrical features in common with hydrogen bonding interactions [26].

We have used π-stacking interactions in conjunction with charge-assisted hydrogen bonding interactions to prepare novel crystalline materials in which co-ordination compounds interact primarily via face-to-face contact of flat, aromatic-type, ligands irrespective to the charged or neutral nature of the fragments [27]. The relevance of π–π interactions in the crystal packing of organic [28], organometallic and inorganic [29] systems as well as in biological systems is well established [30].

When the organic acids 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid, $H_2C_4O_4$, H_2SQA hereafter) is reacted with $[(\eta^5\text{-}C_5H_5)_2Co]$, the co-ordination complex $\{[Co(HSQA\text{–}HSQA)_2(H_2O)_4]^{2-}\}\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2$ can be isolated, while reaction of the acid pyridine-2,6-dicarboxylic (dipicolinic acid, $H_5NC_7O_4$, H_2DPA hereafter) with $[(\eta^6\text{-}C_6H_6)_2Cr]$ affords the complex $\{[(\eta^6\text{-}C_6H_6)_2Cr(I)]^+\}_2$ $\{[(DPA)_2Cr(III)]^-\}\cdot 2H_2O$ [31].

In the case of $\{[Co(HSQA\text{–}HSQA)_2(H_2O)_4]^{2-}\}$ $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2$ (Fig. 5) the 'free' O-atom termini on the outer hydrogen squarate anions form hydrogen bonds with the water molecules co-ordinated to the Co-centers in such a way that each squarate unit acts as a bridge between two complexes. The result is that dimeric (HSQA–HSQA) units interdigitate forming a two-dimensional layered structure with O-atoms protruding above and below the plane, the stacking separations being 3.28 and 3.36 Å. The cations are accommodated in between the anions forming an alternating sequence of negative and positive layers.

The structure of the complex $\{[(\eta^6\text{-}C_6H_6)_2Cr^I]^+\}_2$ $\{[(DPA)_2Cr(III)]^-\}\cdot 2H_2O$ is shown in Fig. 6. The organic ligands are deprotonated, thus formally behaving

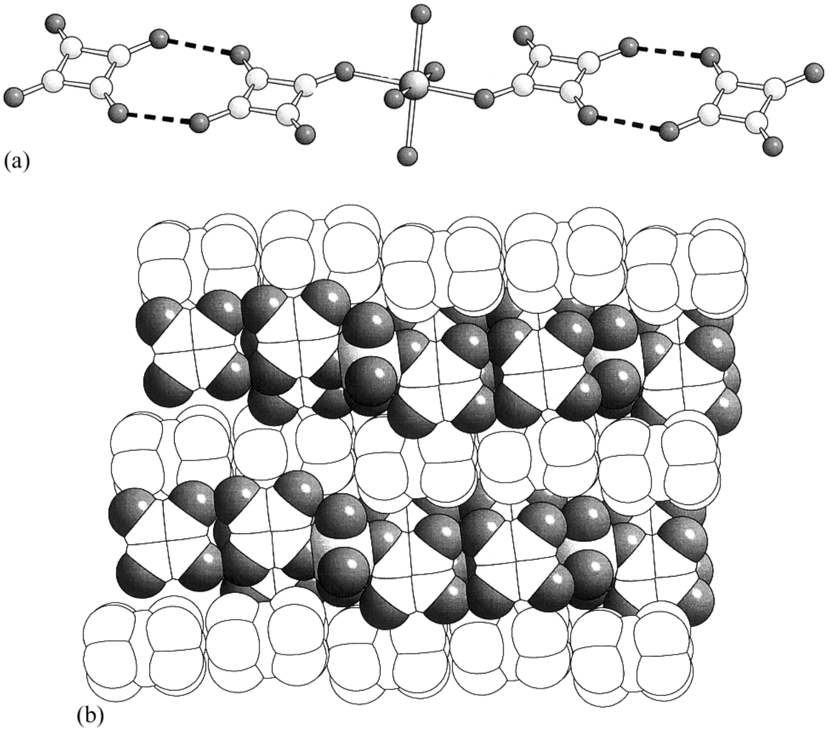

Fig. 5. Ball and stick representation of the supramolecular arrangement of the dianion $[Co(HSQA-HSQA)_2(H_2O)_4]^{2-}$ showing the HSQA–HSQA interdigitation. Space filling representation of the alternating sequence of negative layers carrying the $[Co(HSQA-HSQA)_2(H_2O)_4]^{2-}$ units and positive layers formed by the cations $[(\eta^5-C_5H_5)_2Co]^+$.

as dianionic units interacting with the Cr(III) metal ion. The space filling shows how the complexes are interdigitated with formation of an anionic pile. The separation between the flat ligands varies between 3.35 and 3.40 Å. The piles of $[(DPA)_2Cr(III)]^-$ anions interact in graphitic-like fashion also laterally, thus forming a wavy two-dimensional sheet in which the non-covalent interactions between anions are only of the π-stacking type. Neighboring sheets are 'linked' by O–H···O hydrogen bonds involving the outer O-atoms of the DPA ligands and the water molecules H_2O [O···O separations 2.863(2) and 2.918(2) Å] while the $[(\eta^6-C_6H_6)_2Cr]^+$ cations are accommodated between the sheets and interact, as usual, with a large number of charge assisted C–H···O interactions.

4. Hydrogen bonds between ions can be used to construct crystals

There are essentially two distinct strategies that utilize acid–base reactions to construct crystals based on charge assisted hydrogen bonds between ions:

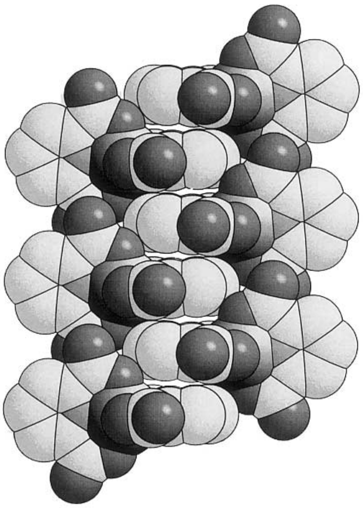

Fig. 6. Space filling representation of the interdigitation between the chromium complexes with formation of an anionic pile extending along the a-axis in crystalline $\{[(\eta^6\text{-}C_6H_6)_2Cr^I]^+\}_2$ $\{[(DPA)_2Cr(III)]^-\}\cdot 2H_2O$

1. The base forms charge assisted HB interactions [32]. This is the case, for instance, of nitrogen containing bases (amines, aminidines etc.) which are protonated upon reaction with polycarboxylic acid molecules, e.g. $RCOOH + NR_3 \rightarrow RCOO^{(-)}\cdots{}^{(+)}HNR_3$, leading to formation of strong $N\text{–}H^{(+)}\cdots O^{(-)}$ interactions, hence an anion–cation pairing in the solid state. Depending on the acid:base stoichiometric ratio $N\text{–}H^{(+)}\cdots O^{(-)}$ and $O\text{–}H\cdots O^{(-)}$ HB interactions may be present simultaneously [33].
2. The base cannot form HB interactions with the acid moiety [17]. This is the case of the reaction between polycarboxylic acids with inorganic or organometallic hydroxides that do not carry strong acceptor/donor hydrogen bond groups. Partial deprotonation of the –COOH groups leads to self-assembly of acid anions via $O\text{–}H\cdots O^{(-)}$ and ${}^{(-)}O\text{–}H\cdots O^{(-)}$ interactions [34]. By choosing the number of carboxylic groups (hence the number of potential donor/acceptor systems) and the stoichiometric ratios in the acid–base reactions, one can control the formation of $O\text{–}H\cdots O^{(-)}$ and/or ${}^{(-)}O\text{–}H\cdots O^{(-)}$ interactions hence homo-ionic self-assembly. We shall now illustrate this strategy by means of three examples coming from our own work.

When the acid pyridine-2,6-dicarboxylic (dipicolinic acid, H_2DPA) reacts with $[(\eta^5\text{-}C_5H_5)_2Co]$ in the stoichiometric ratio 1:2, the supramolecular salt $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}$ $\{[(HDPA)(H_2DPA)]^-\}$ is formed. The crystalline material contains ribbons of ‘dimers’ $[(HDPA)(H_2DPA)]^-$ joined together by symmetric $O\text{–}H\cdots O$ interactions (see Fig. 7). The ribbons pile up in such a way that the aromatic moieties are stacked in graphitic like fashion (interplanar separation 3.37 Å) leaving large cavities in which the cations are accommodated. The pyridine nitrogen

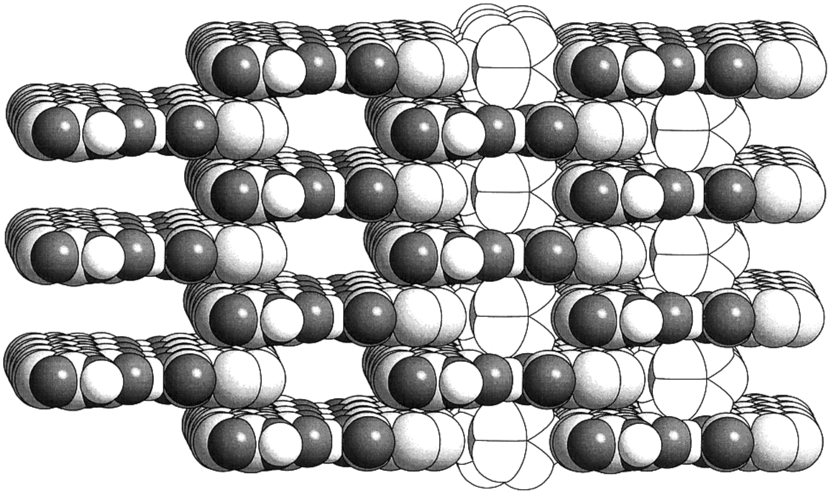

Fig. 7. Space filling representation of the ribbon stacking and of the niches containing the cations $[(\eta^5\text{-}C_5H_5)_2Co]^+$ in crystalline $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}\{[(HDPA)(H_2DPA)]^-\}$. Note how the flat aromatic moieties are stacked in graphitic-like fashion.

participates in a twin C–H···N interaction [(C–)H···N 2.49(2) Å, C–H···N 130.4(1)°].

A related result has been obtained by reacting the cobaltocenium cation with oxalic acid. The crystal structure of $[(\eta^5\text{-}C_5H_5)_2Co(III)]_2[HC_2O_4^-]_2[H_2C_2O_4]\cdot 2H_2O$ can be described as formed by piles of $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations lying next to each other so as to form a layer of cations (see Fig. 8). The cationic layer alternates with anionic layers formed by O–H···O hydrogen bonded neutral oxalic acid molecules and hydrogen oxalate anions in an A/B/A/B stacking sequence. The anionic layers are joined together by O–H···O interactions involving water molecules. Fig. 8b shows the remarkable π-stacking arrangement of the cations in parallel piles.

A recent example of deliberate engineering of a supramolecular arrangement with target magnetic properties is provided by crystalline $[(\eta^6\text{-}C_6H_6)_2Cr(I)]^+[HC_4O_4]^-$ obtained by reacting squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, $H_2C_4O_4$) with $[(\eta^6\text{-}C_6H_6)_2Cr(I)]$ [35]. Because of its flat shape and small dimensions the squarate anion $[HC_4O_4]^-$ was expected to be able to intercalate between the flat benzene ligands of the paramagnetic cation $[(\eta^6\text{-}C_6H_6)_2Cr(I)]^+$. Such intercalation, if achieved, would then lead to the formation of one-dimensional $D^+A^-D^+A^-$ structures comprised of alternating cation donors (D) and anion acceptors (A). As designed, the anion self-assembles into chains linked by $^{(-)}O\text{–}H\cdots O^{(-)}$ interactions and intercalates between the benzene ligands forming the superstructure shown in Fig. 9 (π–π distance 3.375 Å). 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 $S = 1/2$ of the $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations could be attributed to the anion–cation π-stacking interaction. The hydrogen squarate chains thus have the double function of providing the structural framework and of transmitting the magnetic interaction between the paramagnetic cations.

5. Organometallic polymorphism and pseudo-polymorphism

Polymorphism is the property of a substance to exist in different crystalline phases resulting from different arrangements of the molecules in the solid state [36].

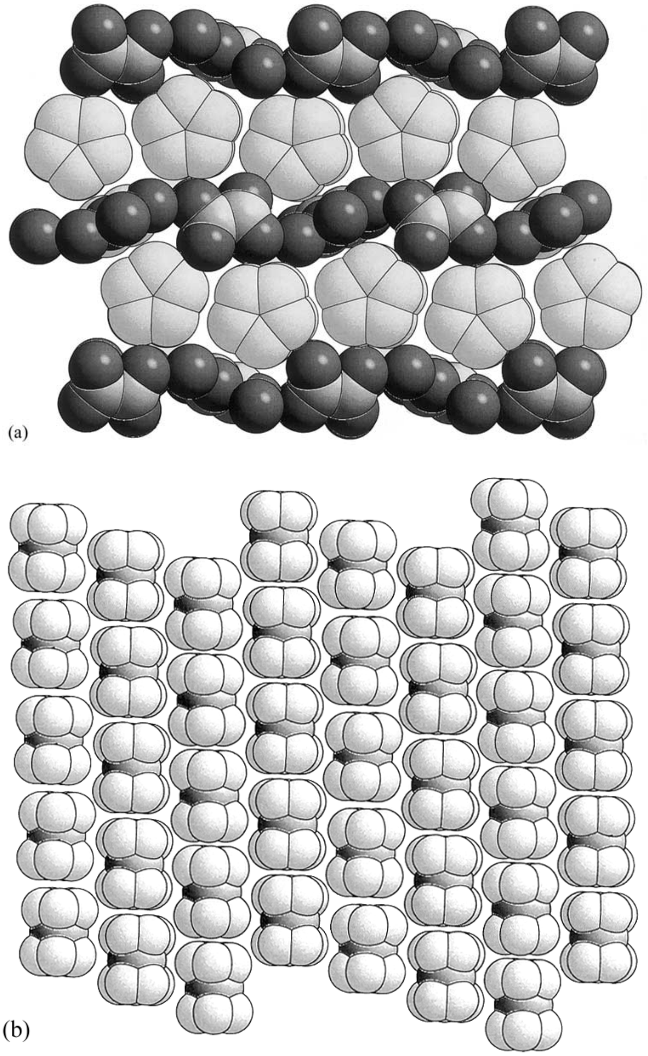

Fig. 8. (a) The cationic layers in cobalticinium hydrogen oxalate alternate with layers of anions and water molecules in an A/B/A/B stacking sequence. (b) Piles of $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations lying next to each other forming a layer of cations.

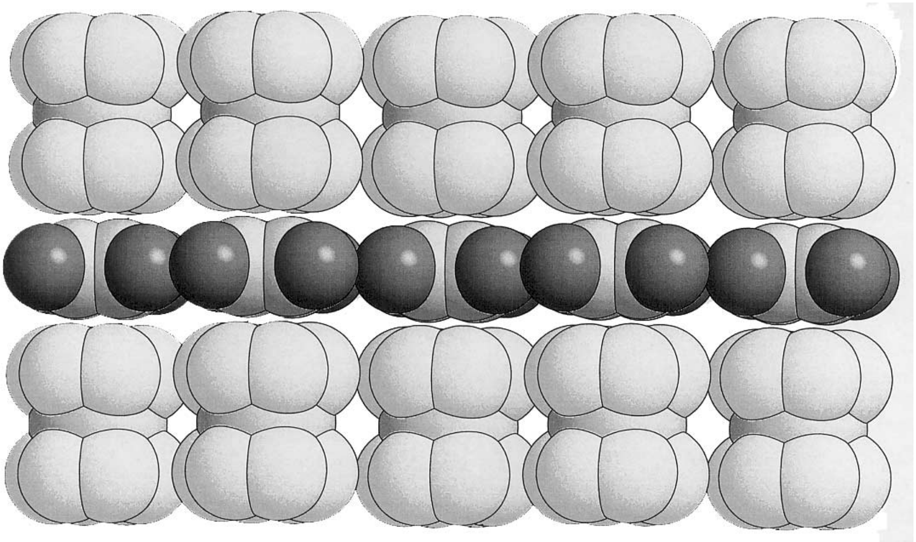

Fig. 9. Two rows of cations $[(\eta^6\text{-}C_6H_6)_2Cr^I]^+$ sandwich a chain of $[HC_4O_4]^-$ anions joined by $^{(-)}O{-}H\cdots O^{(-)}$ interactions.

Within a broad-supramolecular-perception of the nature of a molecular crystal [37], polymorphism can be seen as a form of crystal isomerism: as the different distributions of chemical bonds for molecules of identical composition give rise to structural isomers (e.g. *cis*- and *trans*-isomers), different distributions of intermolecular interactions give rise to structural isomers of the same molecular aggregate. The ideal relationship between supramolecular periodic supermolecules and molecular crystal polymorphism is represented in Scheme 1.

The change in crystal structure associated with an interconversion of polymorphs, i.e. a solid-to-solid phase transition (between ordered phases), in which intermolecular interactions are rearranged, can be regarded as the crystalline equivalent of an isomerization at the molecular level. However, solid to solid phase-transitions imply an extraordinary level of cooperativity and complete conversion of one crystal into the new one without equilibrium mixture of reactant and product [38].

PARADIGM	AGGREGATE
Non-Covalent Interactions	Supermolecule
Periodicity	Crystal
Periodic Non-Covalent Interactions	Molecular Crystal ≡ Periodic Supermolecule
Polymorphs *of a Molecular Crystal*	*Supramolecular Isomers* *of a Periodical Supermolecule*

Scheme 1.

Conformational polymorphism occurs when a molecule may adopt different conformations or relative dispositions of ligands in different crystals [39]. Pseudo-polymorphism refers to cases in which a given substance crystallizes with different amounts or types of solvent molecules [40]. Concomitant polymorphs are those obtained from the same crystallization process [41]. Even though polymorphic modifications contain exactly the same substance, they differ in chemical and physical properties such as density, diffraction pattern, solid state spectroscopy, melting point, stability, reactivity, and mechanical properties.

Traditionally, studies of polymorphism fall into the mainstream of organic solid state chemistry. We are now trying to widen up this perspective [42] and the following section will be used for this purpose. Since structural flexibility is a distinctive characteristic of organometallic molecules (because of the often delocalized nature of the metal–ligand bonding and/or the availability of almost isoenergetic, though geometrically different, bonding modes for the same ligand), the intriguing relationship between molecular non-rigidity and crystalline phase transitional behavior needs to be taken into account when approaching organometallic polymorphism [43]. The reader is addressed to Refs. [42,44] for an up to date review of organometallic polymorphism. Many organometallic molecules exist in different isomeric forms that interconvert via low-energy processes (viz. reorientation, diffusion, scrambling, and fluxionality) both in the gas phase and in the condensed state. Separate crystallization may be attained if the rate at which two isomers interchange in solution is slow with respect to the time required for nucleation. The relationship between the rate of interconversion between isomers and the existence of polymorphic modifications has been discussed [45].

On approaching the relationship between phase transitions and existence of polymorphic forms, one needs to discriminate between polymorphs that interconvert via a solid-to-solid phase transition (enantiotropic systems) and those which do not (monotropic systems). These latter crystals usually melt before interconverting.

Examples of non-interconverting polymorphs are not very common. Ferrocene dicarboxylic acid, $[(\eta^5\text{-}C_5H_4COOH)_2Fe]$ is known in two forms that differ in the relative orientation of the hydrogen bonded molecular pairs [20]. Two polymorphic modifications are also known for the complex $[(\eta^2\text{-fumaric acid})(CO)_4Fe]$ (forms I and II) [46]. In form I, the fumaric acid ligands form ribbons joined by carboxylic rings. Interestingly, the same arrangement is observed in crystalline fumaric acid, which also possesses two polymorphic forms both based on molecular chains interlinked via hydrogen bonded carboxylic rings. In form II of $[(\eta^2\text{-fumaric acid})Fe(CO)_4]$ the carboxylic rings form a chain-type pattern [47]. The relationship between the two forms is shown in Fig. 10.

Interconverting polymorphs, i.e. those for which solid-to-solid phase transitions can be observed, are relatively more common. The two crystalline complexes $[(\eta^5\text{-}C_5H_5)_2M][PF_6]$ ($M = Co$, Fe) are isomorphous at room temperature [48] and have been shown, by variable temperature X-ray diffraction experiments and differential scanning calorimetry, to undergo two reversible phase changes ($M = Fe$, ca. 213 and 347 K, $M = Co$, ca. 252 and 314 K). On heating, $[(\eta^5\text{-}C_5H_5)_2Co][PF_6]$ transforms into a semi-plastic system containing ordered $[PF_6]^-$ anions and orientationally disordered $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations, while $[(\eta^5\text{-}C_5H_5)_2Fe][PF_6]$ goes to a plastic form with both anion and cation orientationally disordered. The crystal structure of $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)Ru]^+$ shows analogies in packing arrangement with crystals of $[(\eta^5\text{-}C_5H_5)_2M][PF_6]$ (M = Co, Fe) [49]. In spite of this, crystalline $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)Ru]^+$ does not undergo a low-temperature phase transition on decreasing the temperature down to 223 K while it shows an order–disorder phase transition on increasing the temperature (332.5 K).The relationship between the room temperature ordered and high temperature disordered structures of $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)Ru]^+$ is shown in Fig. 11.

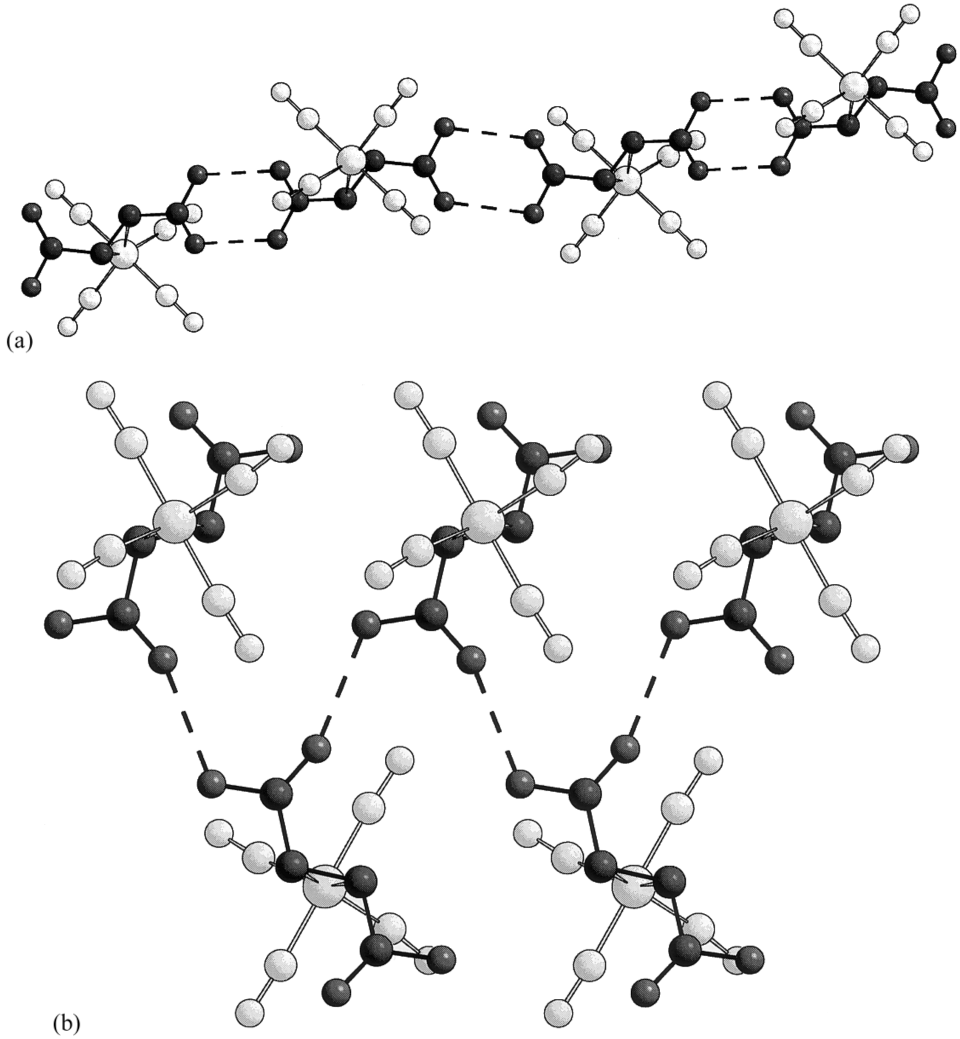

Fig. 10. The relationship between the two forms of $[(\eta^2\text{-fumaric acid})(CO)_4Fe]$. Note how the molecules in form I are joined by O–H···O hydrogen bonded rings while they form catemers in form II.

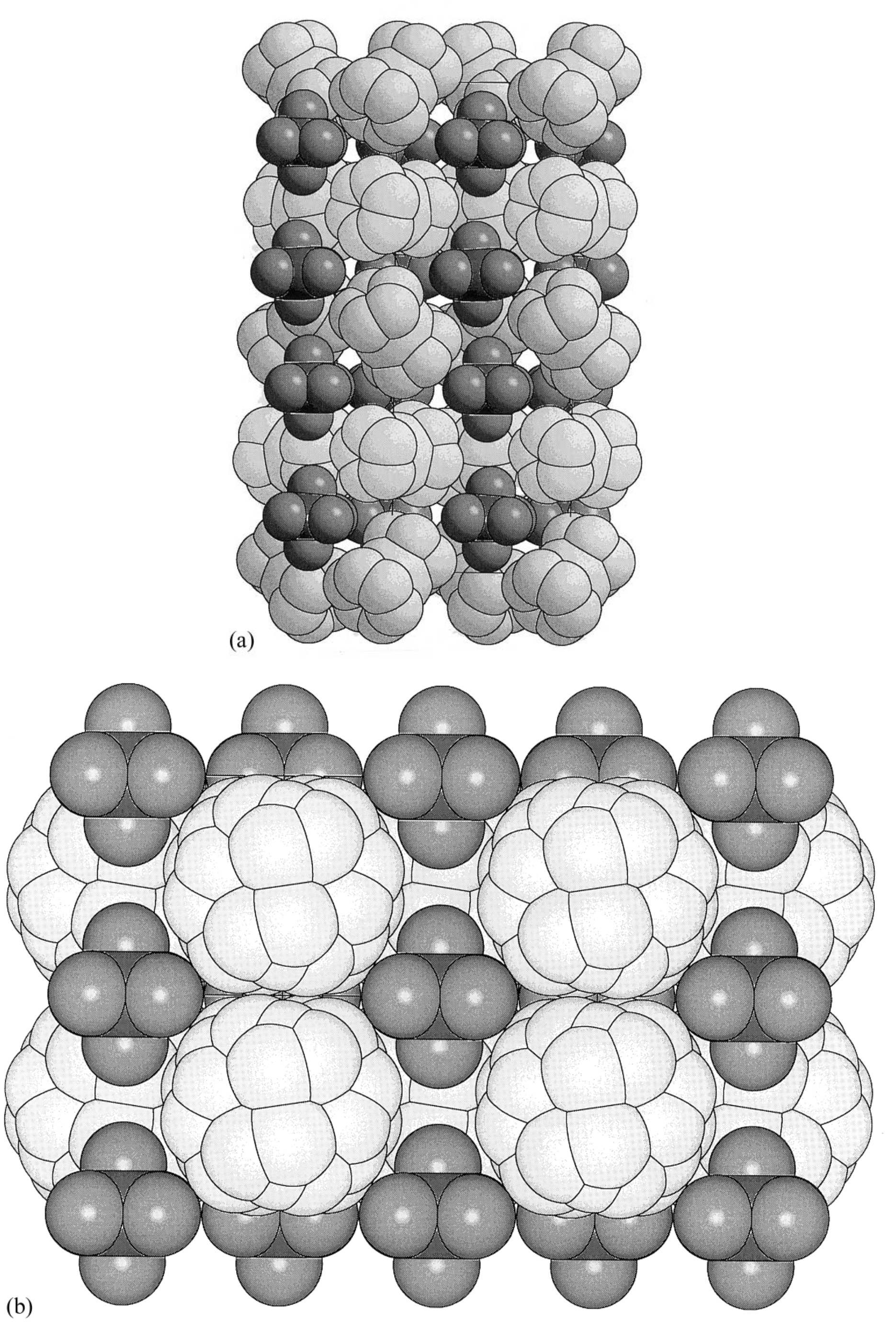

Fig. 11. The relationship between the room temperature ordered and high temperature disordered structures of $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)Ru]^+$. Note the disorder imaged of the cations in the high temperature pseudo-cubic phase.

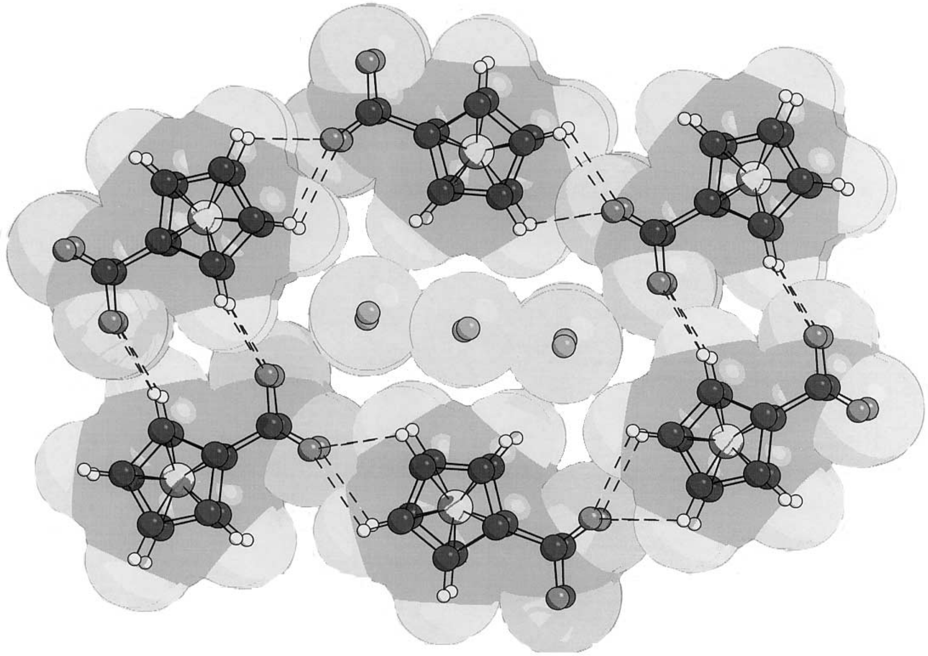

Fig. 12. Ball and stick and space-filling representation of the ‘pipeline’ containing water molecules in the crystal structure of the hydrate species [(η^5-C_5H_4COOH)(η^5-C_5H_4COO)Co(III)].

6. Nano-porous molecular materials and interconversion between pseudo-polymorphs

As mentioned above pseudo-polymorphism is observed when a given substance crystallizes with different amounts and/or types of solvent molecules. One may object that, since the composition of a solvated crystal is not the same as that of an unsolvated crystal (say a hydrated and an anhydrous form), the use of the term polymorphism is not appropriate. While this is true, it is also true, however, that in solution the solvated and unsolvated crystals yield the same chemically relevant species. The problem is clearly rather academic and we will leave it as such. What is more interesting, instead, is the fact that the presence of solvent molecules, which is often an unpredictable event of the crystallization process, may become advantageous when seeking a way to obtain new crystal forms.

This final section of the contribution will be devoted to examples of interconversion between solvated and unsolvated species. In particular, we will show that interconversion can be obtained by removing the solvent molecules of co-crystallization in thermogravimetric experiments. Incidentally, solvent inclusion is one of the classic means to obtain nano-porous, zeolyte-like, materials [5]. Research in the field of nano-porous materials is usually focused on the preparation of robust network structures that can survive to solvent removal without being affected, or with only minor structural change [50].

We have recently reported [51] that the neutral zwitterion [(η^5-C_5H_4COOH)(η^5-C_5H_4COO) Co(III)] crystallizes with three water molecules. The water molecules are accommodated in a channel as shown in Fig. 12. When subjected to a thermogravimetric (TGA) experiment this hydrated form reversibly releases one water molecule at 378 K, while the loss of the two remaining water molecules occurs at ca. 506 K and is immediately followed by a phase transition. Powder diffraction shows that the first dehydration leaves the crystal structure almost unchanged while the phase obtained at the end of the process is markedly different from that of the hydrated form. Crystallization from a water solution of the powder obtained from TGA at 506 K in the presence of seeds (a small portion of the same powder) allows single crystals of the anhydrous species to be obtained. Comparison of the calculated and measured powder diffractograms of the anhydrous phase confirms that the powder obtained at 506 K and the single crystals precipitated at room temperature after seeding possess the same structure.

A related phenomenon has been observed in the case of the hydrated crystalline material $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Fe]^-\cdot H_2O$ [21]. The hydrated form is obtained by simply grinding either the crystalline powder that precipitates from the solvent (THF) on reacting $[(\eta^5\text{-}c_5H_5)_2Co]$ with $[(\eta^5\text{-}C_5H_4COOH)_2Fe]$ or single crystals of the anhydrous salt $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Fe]^-$ obtained by recrystallization of the same powder from nitromethane. Once $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Fe]^-\cdot H_2O$ has been obtained by grinding, its single crystals can be grown from water or nitromethane, while crystals of the anhydrous form are no longer observed. However, on heating at 373 K the hydrated form loses water and reverts to the starting material.

Another example of the intriguing relationship between polymorphic and pseudo-polymorphic forms is provided by $[(\eta^6\text{-}C_6H_6)_2Ru][BF_4]_2$. The sandwich cation can be crystallized from nitromethane as the solvated form $[(\eta^6\text{-}C_6H_6)_2Ru][BF_4]_2\cdot MeNO_2$, which, if exposed to air, rapidly converts to a different crystalline material (as ascertained by powder diffraction) [52]. Recrystallization from water of this powder afforded crystals suitable for single crystal X-ray analysis which were characterized as the unsolvated form $[(\eta^6\text{-}C_6H_6)_2Ru][BF_4]_2$. Comparison of the calculated X-ray powder diffractogram of the unsolvated form with that measured for the crystalline powder obtained from the solvated form confirms that the solvated form converts into the unsolvated one. The pseudo-polymorph $[(\eta^6\text{-}C_6H_6)_2Ru][BF_4]_2\cdot MeNO_2$ appears to be kinetically favored when crystallization occurs from nitromethane, while the unsolvated form is more stable thermodynamically. Fig. 13 shows a comparison between the two packings. Even though mechanistic hypotheses on interconversion between crystalline phases have to be considered with great caution, it seems likely that loss of nitromethane, loosely bound to the sandwich cations via C–H···O interactions [53], occurs via the channels in between the anions which can then ‘close around’ the cations without extensive rearrangement.

These three examples suggest that controlled solvation/desolvation may represent a useful ‘non-solution’ method to obtain formation of otherwise elusive solvated or

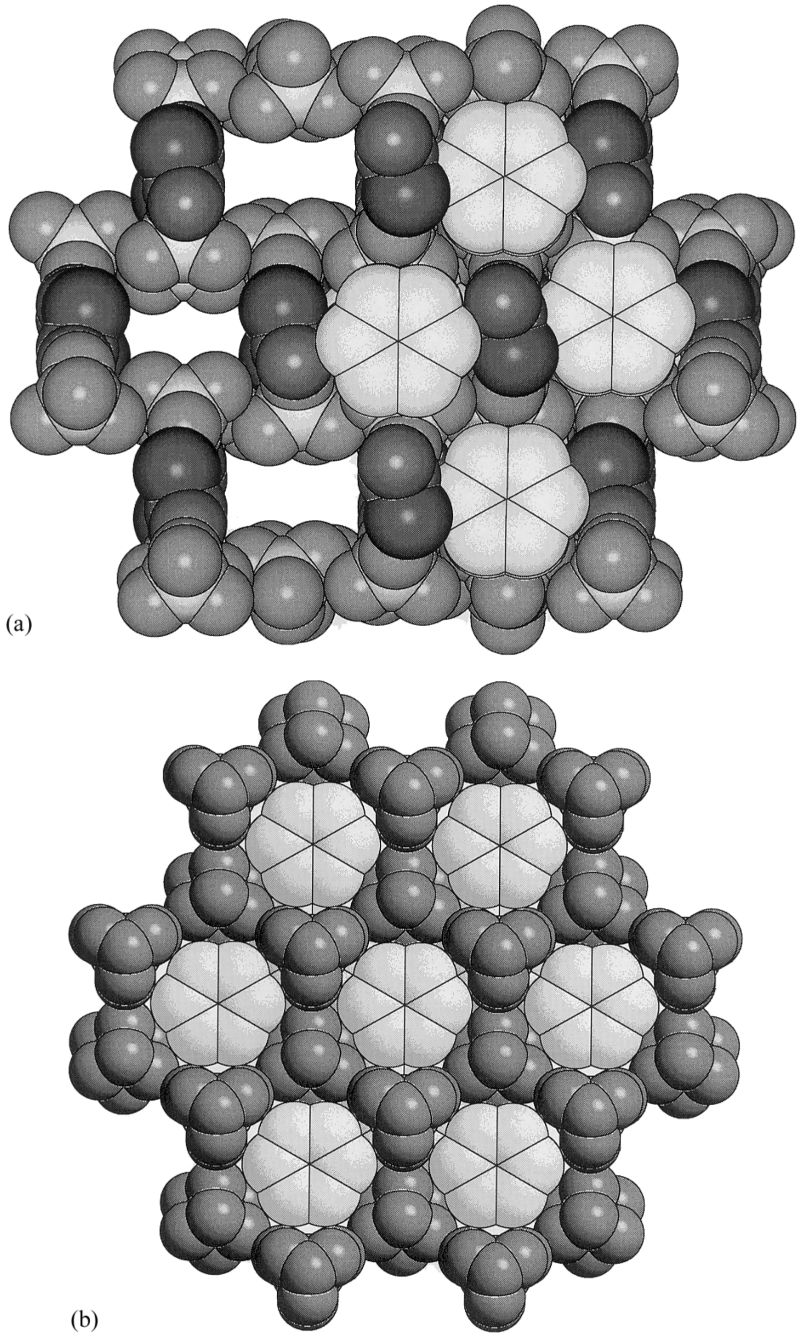

Fig. 13. A space filling representation of the relationship between the structure of the nitromethane solvate species $[(\eta^6\text{-}C_6H_6)_2Ru][BF_4]_2\cdot MeNO_2$ and that of the unsolvated species $[(\eta^6\text{-}C_6H_6)_2Ru][BF_4]_2$.

unsolvated phases. Once a new crystalline powder has been obtained, it is possible to persuade the crystallization process towards the desired phase by seeding.

7. Conclusions and outlook

At the beginning of 2001, it is somewhat surprising that the number of research groups interested in the crystal engineering exploitation of organometallic and coordination compounds is still comparatively small with respect to those interested in organic solids. This seems to contradict the enormous activity in the structural chemistry of these classes of compounds as demonstrated by the Cambridge Structural Database [54] where organic compounds are no longer the majority. Why this should be the case is not entirely clear considering that the structural systematics of inorganic solids [55] were established long before similar developments took place for organic solids [56].

Although this situation is certainly the result of a complex combination of historical, practical, and utilitarian reasons it is now becoming apparent that organometallic and coordination compounds represent an extraordinary deposit of research fuel which is beginning to be exploited in the fields of supramolecular chemistry [57,58], solid state chemistry [59], coordination networks [60], molecular crystal engineering [61], and polymorphism. In order to understand the rapid conversion of many research groups to the chemistry of metal-containing systems, one only needs to look at the periodic table: the number of possible combinations of transition and main group metals atoms, with their variable oxidation, charge, and spin states with the features of the ligands, and with those of other ancillary molecules or ions is virtually unlimited. The development of crystal-oriented synthetic strategies does not differ conceptually from the development of reaction paths to obtain products from reactants. The areas of application are also quite varied and span from nanoporous and mesoporous systems to the 'electrostatic templating' [14], to the preparation of molecular materials for applications in magnetism, in non-linear optics [2], conductivity, solid state sensors etc. which will all be at the forefront of research in materials chemistry in the coming years.

In spite of this optimistic perspective, however, there are some drawbacks that need to be considered by neophytes in the field in order to reduce failure rate and avoid much frustration. Crystal oriented synthetic strategies do not differ, in the essence, from classical chemical experiments in which molecules are modeled, synthetic routes devised, products characterized and their properties measured. In molecular crystal engineering these processes are, in a sense, repeated twice: first in order to prepare the building blocks (whether molecules or ions) and then to arrange the building blocks in a desired way to attain and/or control crystal properties. This latter step invariably requires the characterization of a solid product for which routine analytical and spectroscopic laboratory tools are much less useful than in the case of solution chemistry. Single crystals need to be grown and this may be, per se, an insurmountable problem. As every chemist knows, many materials stubbornly refuse to give decent single crystals for X-ray diffraction. Conversely, ab-initio structure determination from powder diffraction is still far from becoming competitive with single-crystal experiments. Even when single crystals are available, powder diffraction is often the only way to ascertain whether the whole solid material has the same structure as that characterized by single crystal diffraction. Here the notion that sample preparation may alter the structure and lead to a new product becomes quite relevant. Furthermore, that crystal structures may change with temperature and/or pressure has some obvious implication in crystal engineering where the main target is the reproducible synthesis of robust materials. On the other hand, the fact that crystals may be obtained by means of 'non solution methods' offers good opportunities to overcome the perpetual kinetic versus thermodynamic dualism of crystallization. Kinetic products (whether solvated or unsolvated) may interconvert to more thermodynamically stable forms and the interconversion may be activated thermally, but also mechanically to cause loss of trapped solvent molecules. However, thermodynamic products may be 'persuaded' to yield less stable crystal structures if seeds of the desired product can be obtained by other means.

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