Coordination Chemistry Reviews
183 (1999) 19–41

Organometallic crystal engineering: prospects for a systematic design☆

Dario Braga *, Fabrizia Grepioni*

Dipartimento di Chimica G. Ciamician, University of Bologna, Via Selmi 2, 40126 Bologna, Italy

Received 25 September 1997

Contents

Abstract

Crystal engineering is a bridge between supramolecular and materials chemistry. The use of organometallic molecules or ions in the construction of crystals with predefined architectures is a means to introduce into the crystals the variable oxidation and spin states of metal

---

* Corresponding authors. E-mail: dbraga@ciam.unibo.it (D. Braga), grepioni@ciam.unib.it (F. Grepioni).

☆ This review article is largely based on conferences given by the authors in 1997: INDABA-II (Skukuza, South Africa); ECM17 (Lisbon, Portugal); Annual SCI Inorganic Chemistry Congress (Alessandria, Italy).

PII S0010-8545(98)00172-6

atoms as well as the specific topological requirements of coordination bonds. The perspective of an emerging organometallic crystal engineering discipline has been discussed. It has been shown through a number of examples that the presence of metal atoms makes organometallic crystal engineering distinct from organic crystal engineering. The effect of ligand topology, the ability to tune the acid/base behavior of ligands by means of ligand–metal(s) coordination, the direct participation of metal atoms in extramolecular interactions in the solid state, as well as the consequence of the ionic charges on the strength of weak and strong intermolecular hydrogen bonds have been discussed. In particular, a design strategy to obtain organic–organometallic crystals by means of a selective use of strong hydrogen bonds between the organic component and of weak hydrogen bonds between organic and organometallic components is illustrated with emphasis on the role of charge-assisted $C–H^{\delta+}\cdots O^{\delta-}$ hydrogen bonds.

Keywords: Crystal engineering; Intermolecular interactions; Organometallics

1. Introduction

The last few years have seen a true explosion of interest in the modeling, synthesis and evaluation of crystalline materials [1–6]. At Bologna, we have taken advantage of the experience accumulated in the investigation of intermolecular interactions involving organometallic molecules [7–9] to initiate a project focused on the engineering of organometallic solids [10–12].

Crystal engineering was born in the field of solid-state organic chemistry [13,14]. The term “crystal engineering” was put forward by Schmidt in the context of the study of the solid-state photodimerization of cinnamic acid [15–17]. The original idea was the design of crystals in which organic molecules could adopt a relative orientation suitable for topochemical reactions. Since then the field has developed enormously, nowadays encompassing all branches of vertical division of chemistry, namely organics, organometallics and inorganics.

However, the use of the word ‘engineering’ still causes some confusion and is accepted with diffidence by some structural chemists. In our perception, modern crystal engineering is a strategy to construct crystals with a purpose. A utilitarian crystal engineering strategy implies the utilization of design principles to synthesize predefined crystal structures in the laboratory, i.e. to make crystals with desired characteristics and properties.

Clearly, there is a substantial methodological and energetic difference if the crystal synthesis involves only non-covalent interactions or if covalent bonds are broken and formed [18]. In the construction of non-covalent crystals, use is predominantly made of molecular or ionic building blocks held together via extramolecular interactions which are weaker than the covalent bonds between the atoms constituting the building blocks. In covalent crystal engineering, in contrast, use is made of covalent bonds between components which do not have a chemical identity on their own (i.e. those which are most often impossible to isolate as stable species). Although the design principles (namely the choice of adequate building blocks to achieve a predesired crystal architecture) are conceptually identical in the two cases, breaking and forming extramolecular non-covalent interactions requires much less energy than breaking and forming covalent bonds. Covalent and non-covalent crystal engineering admit an intermediate situation, i.e. coordination crystal engineering, where the link between building blocks is provided by (polydentate) ligands which can join together coordination complexes in a three-dimensional network [19–23]. In terms of energy, breaking and forming dative bonds (formed via the well-known Lewis acid–base mechanism of coordination) requires less energy than with covalency and more energy than for hydrogen bonds or other weaker extramolecular interactions. The relationship between non-covalent, covalent and coordination crystal engineering is represented schematically in Fig. 1.

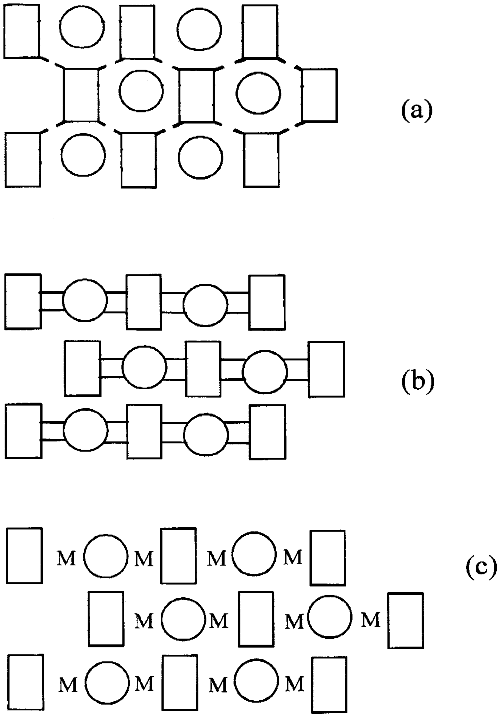


Fig. 1. Schematic representation of the relationship between (a) non-covalent, (b) covalent and (c) coordination crystal engineering.

2. Crystal engineering as a bridge between supramolecular and materials chemistry

Non-covalent crystal engineering conforms strictly to the paradigm of supramolecular chemistry [24,25], i.e. the intelligent utilization of non-covalent interactions to make aggregates which function differently from the individualcomponents [26]. Since materials chemistry is concerned with the function of solids [27], crystal engineering can be viewed as a bridge between supramolecular and materials chemistry.

The development of synthetic strategies to make crystals does not differ conceptually from the development of reaction paths to obtain products from reactants. In the synthesis of non-covalent crystals, the reactants are most often stable molecules or ions whose covalent bonding systems pass though the synthetic process almost unaffected. The first step of any crystal synthesis (as of any molecular synthesis for that matter) is the recognition stage between reactants. Even the simplest crystallization process, namely the nucleation of a molecular crystalline solid from solution or melt, implies an initial molecular recognition stage and intermolecular bond formation. With multi-component systems (viz. cocrystallization of different molecules or aggregation of ions of opposite sign), the process of extramolecular bond-breaking and forming, although slightly more complicated, is conceptually the same. The supermolecule–crystal analogy can be stretched even further: crystal polymorphism [28,29] can be viewed as a manifestation of intermolecular isomerism, i.e. of the existence of isomeric forms of the same gigantic supermolecule [30,31].

3. Perspective of organometallic crystal engineering. The role of metal atoms

Why organometallic crystal engineering? The answer to this question comes to mind if one looks at the periodic table. Organic crystal chemistry concentrates basically on the behavior of a few, albeit important, atoms on the top left- and top right-hand sides of the periodic table with some limited involvement of heavier atoms. Organometallic crystal chemistry, on the contrary, encompasses almost the whole periodic table. This statement is admittedly quite naive, but the consequences are enormous when applied to crystal engineering. The number of possible combinations of ligands, metals and assisting molecules or ions to make crystals is virtually unlimited. Clearly, one needs an objective to pursue, a kind of thin Ariadne's thread which may lead the way through the multiple choice of a combinatory approach.

One may object that the non-covalent bonding capacity of organometallic molecules must not differ much from that of organic molecules because the peripheral atoms are the same. Indeed, most ligands are organic-type fragments, at times 'whole molecules' turned into ligands. Such is the case, for example, of benzene and other carbocycles, of alkynes and alkenes π-bonded to one or more metal centers, or of inorganic molecules such as water, ammonia, or the ubiquitous CO molecule and other similar Lewis bases. All these ligands maintain their

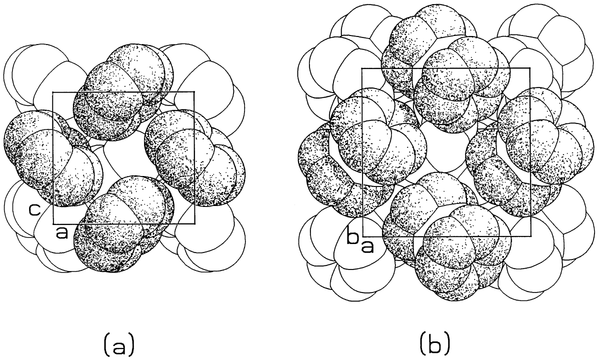


Fig. 2. The peripheral atoms in (a) benzene and (b) dibenzene chromium are the same and the molecules pack in a similar manner.

structural and chemical identity upon coordination to metal(s), and hence it can be expected that they also behave in very much the same way in the formation of intermolecular bonds.

The peripheral atoms in benzene and bis-benzene chromium [Fig. 2(a) and (b)], for example, are the same and the molecules pack in a similar manner in their respective crystals. The hydrogen bond carboxylic rings formed by fumaric acid in its crystals are maintained unchanged in crystals of the corresponding iron complex [Fig. 3(a) and (b)]. Similarly the intra- and intermolecular hydrogen bonds formed by maleic acid are transferred to the corresponding organometallic crystal [Fig. 3(c) and (d)]. Tetrameric $(-O-H)_4$ and hexameric $(-O-H)_6$ hydrogen bond rings typically formed by organic alcohols are also maintained when the –O–H group belongs to metal coordinated ligands [Fig. 4(a) and (b)].

Based on these examples, one may be tempted to think that there is no great scope in expanding from organic to organometallic crystal engineering. Since the extramolecular bonding capacity of organic molecules is essentially the same whether as free molecules or as ligands, all knowledge of ‘organic’ non-covalent interactions will be transferable with little additional effort. No great surprise could be expected from the study of organometallic solids. This would be the end of the story and, probably, of this paper.

However, the interplay between ligand supramolecular bonding capacity and ligand–metal(s) coordination is responsible for distinct features of organometallic crystal architectures. The presence of one or more metal atoms, though embedded within the ligand shell, has several effects on crystal design strategies: (i) the effect of spatial geometry (topological effect); (ii) the effect of coordination on the acid/base behavior of the ligands; (iii) the direct participation of the metal atoms in extramolecular bonding; and (iv) the effect of ionic charge. Obviously, steric and electronic components cannot easily be pried apart and the separate discussion of the four terms is purely utilitarian.

3.1. Topological effect

Ligand geometry can be combined with coordination geometry around the metal center(s) to preorganize in space non-covalent linkages. For example, Mingos and

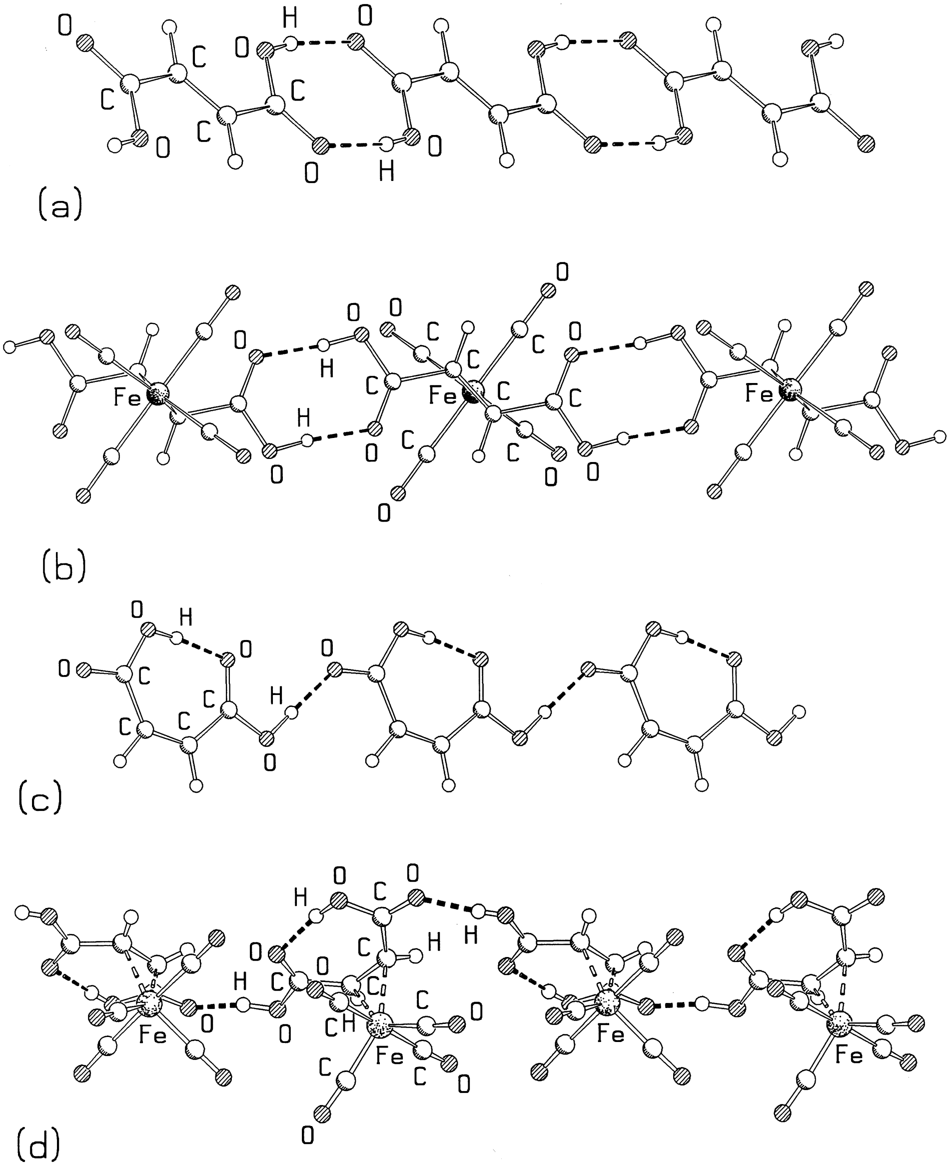


Fig. 3. The hydrogen bond carboxylic rings formed by fumaric acid (a) are maintained unchanged in crystals of the corresponding iron complex (b). The intra- and intermolecular hydrogen bonds formed by maleic acid (c) are transferred to the corresponding organometallic crystal (d).

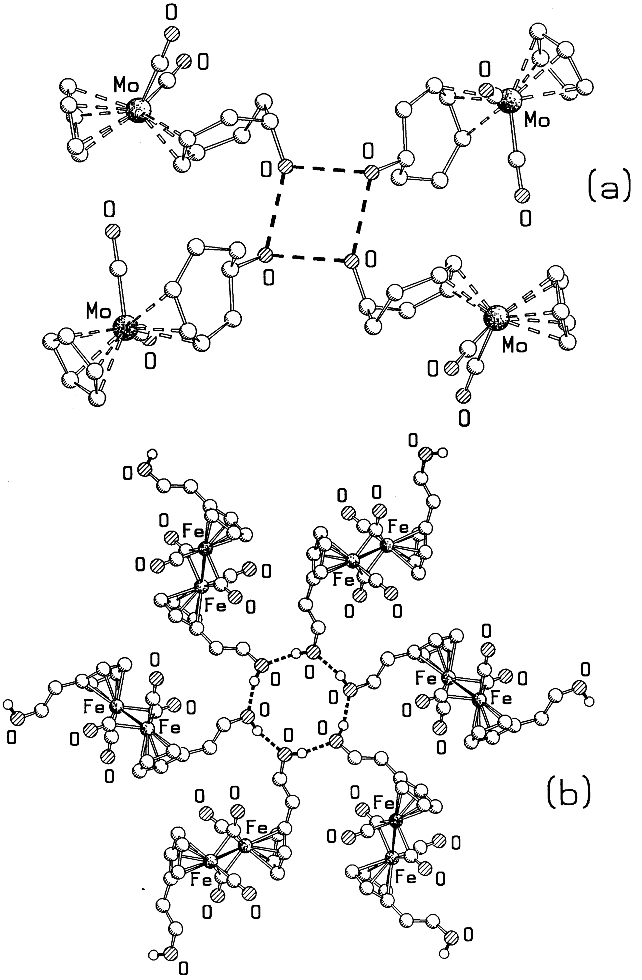


Fig. 4. Tetrameric $(\text{–O–H})_4$ (a) and hexameric $(\text{–O–H})_6$ (b) hydrogen bond rings are observed also for metal coordinated ligands.

coworkers [32] have constructed solid state sheets and tapes via co-crystallization of bifunctional transition-metal complexes and organic bases by using complementary hydrogen bonds. More recently, an interesting example of interaction between chloroform solvate molecules and the C≡C triple bond of a gold ethynide complex has been reported by the same group [33,34]. The solid-state structure results from the spatial organization of four solvent molecules around a straight P–Au–C≡C–Au–P system with the C–H vectors pointing towards the midpoint of the C≡C π-system. Density functional theory calculations have shown that the interaction energy is ca. $\sim 25\,\text{kJ mol}^{-1}$, i.e. comparable to relatively strong hydrogen bonds.

Walther and coworkers, in collaboration with the present authors, have investigated the architecture of crystalline alkynol and alkynediol transition metal complexes of Pt and Ni [35,36] in relation to that of crystalline organic alcohols [37]. As an example, the molecular row connected via $(-O-H)_4$ hydrogen bond rings on either side of the metal centers in the case of the crystalline complexes bis(*t*-butyl-ethyl-alkynol)M(0) (M = Ni, Pt) is shown in Fig. 5.

van Koten and coworkers have obtained one-dimensional aggregation in the solid state of square-planar Pt complexes linked by intermolecular hydrogen bonds of the $-O-H\cdots Cl$ [38] or $-C\equiv C-H\cdots Cl$ types [39].

Zaworotko and coworkers have used cubane-like molecules such as $[M(CO)_3(OH)_4]$ (M = Mn, Re), which possess groups capable of hydrogen-bond formation directed towards the vertices of a tetrahedron, to synthesize superdiamantoids networks [40] with large empty space available for enclathation.

3.2. Effect of coordination on the acid/base behavior of ligands

The acid/base behavior of ligands, and hence their participation in hydrogen bonding interactions, can be tuned by changing the ligand-to-metal coordination mode(s), which, in turn, depends on the electronic nature of the metal. This change is reflected in the metric of the intermolecular hydrogen bonding interactions established in the solid state.

For example, the hydrogen atoms belonging to metal coordinated methylidyne (μ_3-CH) and methylene (μ_2-CH_2) ligands have been shown to participate in intermolecular C–H–O hydrogen bonding networks [41]. The acceptor atom belongs, in most cases, to CO ligands. The average length of the H–O separations suggests that the μ_2-CH_2 ligand is less acidic than the μ_3-CH one. This is in keeping with experimental [42–45] and theoretical [46–48] evidence indicating (though with some controversy) sp^2 ($=CH_2$) and sp ($\equiv CH$) hybridization for the C atom in the two types of coordination geometries. Hence, the hydrogen bonding capacity of the methylidyne and methylene ligands recalls that of organic $\equiv C-H$ and $=CH_2$ hydrogen bond donors which have been shown to be amongst the most acidic C–H systems [49,50].

The hydrogen bond accepting capacity of metal bound CO has also been extensively studied [51–53] and discussed in a recent review article [54]. For this

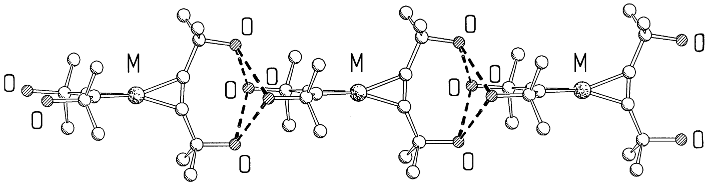
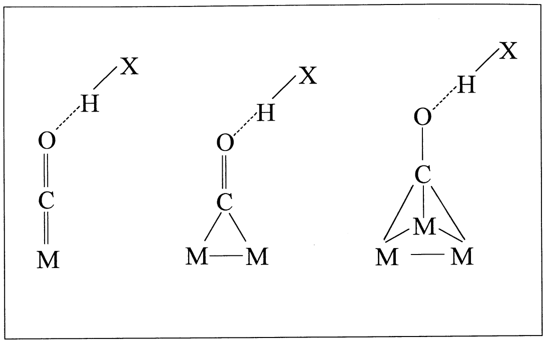
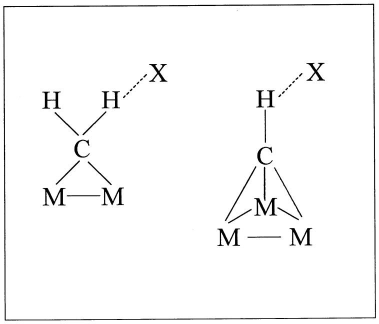


Fig. 5. An example of metal coordination topological effect: a molecular row connected via $(-O-H)_4$ hydrogen bond rings on either side of the metal centers in the case of the crystalline complexes bis(*t*-butyl-ethyl-alkynol)M(0) (M = Ni, Pt).



(a)



(b)

Fig. 6. Scheme of the hydrogen bonding interactions of the terminal CO···H, μ_2-CO···H, and μ_3-CO···H type (a) and of the μ_2-CH_2···O and μ_3-CH···O type (b).

reason we need only to recall that the CO ligand can adopt terminal, doubly (μ_2-CO) and triply (μ_3-CO) bridging coordination modes in transition metal complexes and clusters. The propensity of the CO ligand to adopt bridging bonding modes decreases on descending along groups and increases on moving from left to right in the periodic table according to the increasing need of electron delocalization, but also to the contraction of the d-orbitals on increasing atomic number. Theoxygen atom participates in acid–base interactions with Lewis acids (such as electropositive metal atoms in isocarbonyls and carbonylate anions) or Brønsted acids (such as water, –OH and C–H groups). The order of basicity is terminal $< \mu_2$ bridge $< \mu_3$ bridge, in keeping with the shift of stretching frequencies towards lower wavenumbers. The average length of the Tr–C–O–A interaction (where A is a Lewis or a Brønsted acid) follows the reverse trend, viz. bridging ligands form shorter intermolecular bonds, and/or tighter ion pairs with metal cations, than terminal ligands. In crystalline salts, Tr–C–O···H–X interactions, usually between carbonyl anion species and organic-type cations [55], follow the same trend as above, though reinforced by the difference in charge (see below).

The hydrogen bonding interactions of the terminal CO···H, μ_2-CO···H, and μ_3-CO···H are schematically represented in Fig. 6(a), while those of the μ_2-CH_2···O and μ_3-CH···O types are shown in Fig. 6(b).

Another distinctive type of non-organic extramolecular interaction is that involving the Tr–H system (Tr = transition metal). Depending on the type of metal and on the nuclearity of the complex, the M–H system can behave as a hydrogen bond donor or acceptor (see below). It has been shown that edge- and face-bridging hydrogen atoms in transition metal clusters can be donated to form hydrogen bonds with 'soft' bases such as the CO ligand [56]. In spite of the large number of hydride clusters characterized to date, the formation of an intermolecular M–H···O hydrogen bond is evident only in few cases because the hydrogen ligands are usually sterically screened from the neighboring molecules by the other bulkier ligands.

Non-classical H_2 ligands [57–60] can also take part in intermolecular interactions. This has been observed, for example, in the case of the recently reported complex *cis*-$Ir(H)Cl_2H_2(P^iPr_3)_2$ [61] where the H_2 ligand participates in a hydrogen bonding interaction with a chlorine atom of a neighboring molecule.

3.3. Effect of the direct participation of the metal atoms in extramolecular bonds

The direct involvement of metal atoms in extramolecular interactions is, rather obviously, one of the major differences between organic and organometallic crystal engineering [62]. Once again, the reference to the periodic table is immediate: electron-deficient metal atoms on the left-hand side are able to accept electron density both intra- and intermolecularly from suitable Lewis bases (which could even be a C–H σ-bond in the case of agostic [63–65] or *pseudo*-agostic [62] interactions), while electron-rich metal atoms on the right-hand side of the periodic table will be able to donate electron density, and are hence able to act, for example, as hydrogen bond acceptors towards organic or inorganic bases (see Fig. 7).

Examples of both types of behavior are available. After the first report by Calderazzo et al. [66] of a short N–H···Co interaction in crystalline $[NMe_3H^+][Co(CO)_4^-]$, Brammer has investigated several three-center four-electron N–H···Co hydrogen bonds formed by the carbonyl anion $Co(CO)_4^-$ with counterions of the NR_3H^+ type (R = Me, Et) [67]. Other examples of three-center four-electron interactions are available [68,69]. This matter has recently been reviewed [70].

On closing this section, it should be stressed that all these interactions are much weaker than conventional O–H···O and N–H···O hydrogen bonds. Calculations and experiments indicate for C–H···X and M–H···X, as well as for agostic or *pseudo*-agostic type bonds, the order of a few kJ mol^{-1} [56,71]. Although interactions of this strength are not able to control the crystal construction process, they can still act as 'crystal sieves', selecting those crystal architectures which, besides providing efficient van der Waals interlocking of molecules, can make use of the additional stabilization provided by these weak but more directional interactions.

3.4. The effect of the ionic charge

The role of the ionic charge in organometallic and inorganic crystal engineering is naturally relevant due to the fact that many organometallic building blocks are ions with variable metal atom oxidation states and/or non-neutral ligands. The crystal engineering effect of charge depends on the number of atoms forming the ions. While the aggregation of large molecular ions (e.g. many transition metal clusters) carrying a small ionic charge essentially follows the same criteria as those of co-crystals (though formed by species of different polarity), this is not so with low-nuclearity complexes, where the charge is 'shared' by a smaller number of atoms [72–74]. Contrary to hydrogen bonding interactions, electrostatic interactions are non-directional and active at long range as they fall off very smoothly with distance.

Organometallic anions and cations are often crystallized with large organic-type counterions, such as PPh_4^+, PPN^+, BPh_4^-, etc. The ionic charge is usually small (-1 or -2, rarely higher) and is distributed over a large number of atoms. Carbonyl cluster anions, for example, form crystals in which the counterion size and shape is determinant for the anion aggregation in the crystal. The general rule is relatively simple: small cations favor one-dimensional or two-dimensional aggregation of the anions (see Fig. 8). When both ions have comparable size and nearly spherical shape, the crystal is constructed as a mixed system in which anions and cations are distributed as van der Waals particles. This information can be utilized

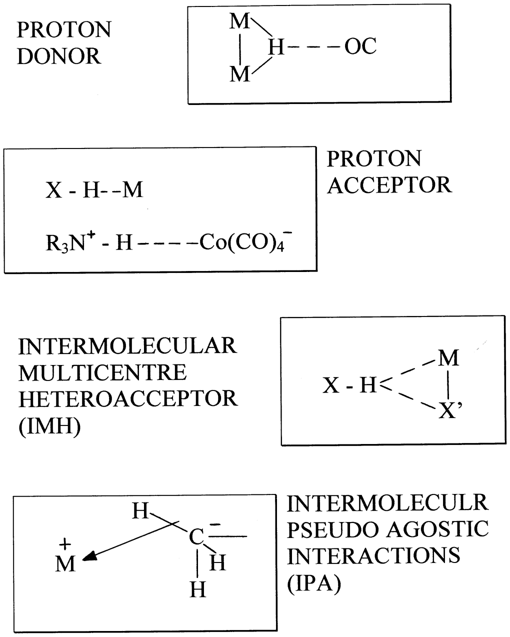


Fig. 7. Schematic representation of the involvement of metal atoms in hydrogen bonding.

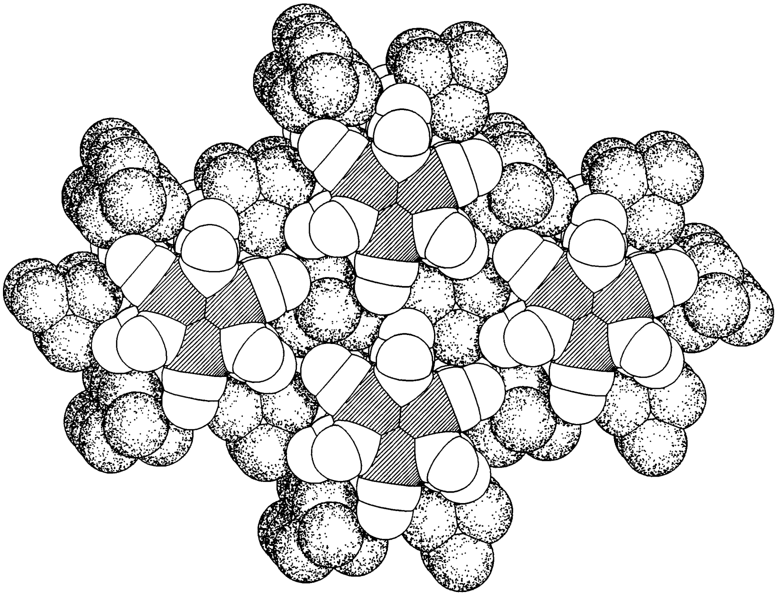


Fig. 8. An example of the effect of the counterion choice on crystal packing: the small Me_4N^+ cation leads to one-dimensional aggregation of the $[Ni_6(CO)_{12}]^{2-}$ anions in the crystal (see Ref. [75] for the determination of the anion structure).

to engineer anisotropic arrangements of the particles in the solid state. It has been shown that the size of the cations becomes a critical factor as the dimension of the anion increases. In fact, high-nuclearity transition metal clusters can be more easily isolated as crystalline materials when the anion charge is high (viz. when a large number of cations are 'brought' into the crystal by a single anion). In some cases, solvent of crystallization is also needed to fill in interstices in the crystals and improve cohesion [75].

Fagan and Ward have utilized ionic charges in organometallic crystals to prepare crystalline materials for charge transfer applications [76,77]. 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 for packing anions and cations while maintaining electroneutrality. The spatial geometry of the template depends on the shape and geometry of cations and anions as well as on the spatial arrangements of the positive and negative charges. The cations $[(\eta^5\text{-}C_5Me_5)Ru]^+$, $[((\eta^5\text{-}C_5Me_5)Ru)_2(\text{paracyclophane})]^{2+}$ and $[\{(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_6H_5)\}_4E]^{4+}$ ($E = C$, Si, Ge, Sn, Pb) have been employed to form one-, two- and three-dimensional aggregates.

The effect of charge becomes crucial when hydrogen-bond donor/acceptor groups are present. This particular aspect will be developed in more detail in Section 4.

4. Organic–organometallic crystal synthesis via charge-assisted hydrogen bonds

The hydrogen bond provides the most efficacious non-covalent infrastructure to crystalline architectures. The interaction is basically electrostatic in nature, and hence all factors influencing the charge distribution on the donor/acceptor system affect the strength of the hydrogen bond [78–80].

This consideration constitutes the basis of our strategy for the preparation of organic–organometallic crystalline aggregates by means of cooperative strong O–H···O and weak C–H···O hydrogen bonds. The synthetic procedure is founded on the reaction between organic or inorganic molecules possessing acidic protons and organometallic molecules which can easily be oxidized to yield organometallic hydroxides, such as $[(\eta^6\text{-arene})_2\text{Cr}][\text{OH}]$ (arene = η^6-C_6H_6 and η^6-C_6H_5Me) and $[(\eta^5\text{-}C_5H_5)_2\text{Co}][\text{OH}]$ prepared in situ. The result of this reaction is supramolecular salts formed via hydrogen bonding interactions [81].

In our ‘recipe’, the prerequisites of the organic acidic species are the presence of strong donor/acceptor hydrogen bonding groups (–COOH, –OH, –POOH, etc.), together with a number of acceptors which is larger than the number of donor sites. The organometallic partners, in contrast, must not possess strong hydrogen bonding donor/acceptor systems which may compete with the organic fragments, but rather a large number of acidic C–H groups, such as those bound to sp- or sp^2-hybridized C atoms in arene, cyclopentadienyl, alkene and alkyne ligands. This is necessary to drive the organic/inorganic acid to selectively self-assemble into large hydrogen-bonded superanions which can then interact with the organometallic system via numerous, though weaker, interactions.

The acid–base reaction on which the crystal synthesis is based generates three different types of interactions: (i) conventional strong O–H···O hydrogen bonds as well as (ii) negatively charged [82–84] $\text{O–H}\cdots\text{O}^-$ hydrogen bonds between the organic/inorganic components, and (iii) charge assisted $\text{C–H}^{\delta+}\cdots\text{O}^{\delta-}$ bonds between the organic/inorganic component and the organometallic template. This synthetic strategy has been applied, until now, to prepare supramolecular aggregates of 1,3-cyclohexanedione [81,85,86] and dicarboxylic acids [87,88] with bis-arene chromium and cobalticinium cations, respectively.

4.1. 1,3-Cyclohexanedione and bis-arene chromium

1,3-Cyclohexanedione (CHD) has been used to generate organic anionic frameworks in which the paramagnetic cations $[(\eta^6\text{-arene})_2\text{Cr}]^+$ (arene = η^6-C_6H_6 and η^6-C_6H_5Me) can be encapsulated. Crystalline aggregates of the type $[(\eta^6\text{-}C_6H_6)_2\text{Cr}]^+[(\text{CHD})_2]^- \cdot (\text{CHD})_2$ and $[(\eta^6\text{-}C_6H_5\text{Me})_2\text{Cr}]^+[(\text{CHD})_2]^-$ have been obtained. The formation of the superanions $[(\text{CHD})_2]^- \cdot (\text{CHD})_2$ and $[(\text{CHD})_2]^-$ is attained by deprotonation of one dione molecule by reaction between the bis-arene chromium hydroxides and the dione in THF.

The molecular organization, hydrogen bonding and dynamics in the solid state of CHD was extensively studied by Etter et al. [89]. When CHD is crystallized from THF, molecular chains are formed. The CHD molecules are linked head-to-tail via

O–H···O=C hydrogen bonds [O···O distance = 2.561(4) Å], whereas if crystallization is carried out from benzene, CHD is crystallized as a hexamer formed by a ring of six CHD molecules (a cyclamer) linked by hydrogen bonds in *syn–anti* configuration [O···O distance = 2.579(1) Å] and enclosing a benzene molecule.

We were very much inspired by Etter's work and attempted the preparation of similar aggregates using bis-arene chromium complexes. The organic–organometallic crystals $[(\eta^6\text{-}C_6H_6)_2Cr]^+[(CHD)_2]^- \cdot (CHD)_2$ and $[(\eta^6\text{-}C_6H_5Me)_2Cr]^+[(CHD)_2]^-$ are held together by strong hydrogen bonds of the O–H···O$^-$ and O–H···O type within the superanions $[(CHD)_2]^- \cdot (CHD)_2$ and $[(CHD)_2]^-$ and by a number of C–H$^{\delta+}$···O$^{\delta-}$ hydrogen bonds between these anions and the organometallic cations (see Fig. 9).

In the course of the same experiments, the hydrated crystalline species $[(\eta^6\text{-}C_6H_6)_2Cr][OH] \cdot 3H_2O$ and $[(\eta^6\text{-}C_6H_6)_2Cr][CHD] \cdot 3H_2O$ were also obtained. They provide useful examples of the role which water oxygen atoms can play as C–H···O hydrogen bonding acceptor systems. The hydroxide is particularly fascinating and affords a remarkable example of the supermolecule–crystal analogy: the non-covalent aggregation of water and of two simple ions such as OH$^-$ and $[(C_6H_6)_2Cr]^+$ generates a highly specialized and polar superstructure in which layers of opposite sign alternate and result in a system with sides of completely different chemical composition. Furthermore, $[(C_6H_6)_2Cr][OH] \cdot 3H_2O$ shows the importance of C–

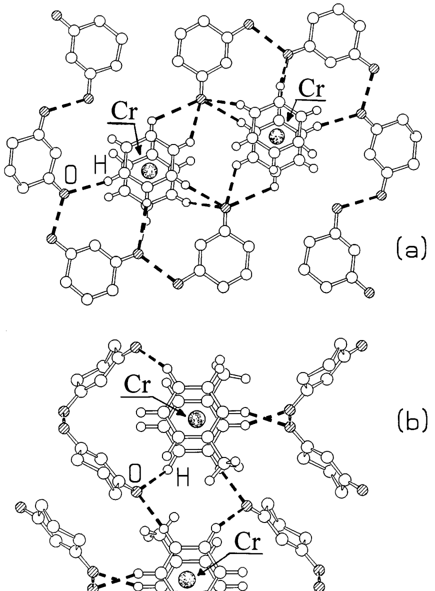
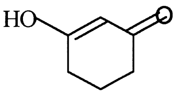


Fig. 9. A view of the hydrogen bonding systems in crystalline $[(\eta^6\text{-}C_6H_6)_2Cr]^+[(CHD)_2]^- \cdot (CHD)_2$ (a) and $[(\eta^6\text{-}C_6H_5Me)_2Cr]^+[(CHD)_2]^-$ (b) (CHD = 1,3-cyclohexandione).

Table 1
Relevant hydrogen bonding parameters in crystals of 1,3-cyclohexandione and of the mixed organic–organometallic systems (distances are in Å, negatively charged O–H···O$^-$ bonds in bold)

 1,3-Cyclohexandione (CHD)	$O_{OH}\cdots O^-$	$O_{OH}\cdots O_{CO}$
$(CHD)_6.(C_6H_6)$ [89]		2.579(1)
CHD (chain) [89]		2.561(4)
$[(\eta^6\text{-}C_6H_6)_2Cr][(CHD)_2]^- \cdot (CHD)_2$	**2.469(2)**	2.544(2)
		2.570(2)
$[(\eta^6\text{-}C_6H_5Me)_2Cr][(CHD)_2]$	**2.437(5)**	
$[(\eta^6\text{-}C_6H_6)_2Cr][OH] \cdot 3H_2O$		$O_W\cdots O_W$
		2.815(4)
		2.963(4)
		2.967(4)
		2.985(4)
$[(\eta^6\text{-}C_6H_6)_2Cr][CHD] \cdot 3H_2O$		2.742(6)
		2.758(6)
		2.784(6)
		$O\cdots O_W$
		2.754(5)
		2.770(5)
		2.764(5)

H···O(water) interactions. The hydrated hydroxide is constituted of a stacking sequence of layers containing $[(C_6H_6)_2Cr]^+$ cations intercalated with layers of water molecules and OH^- groups. The $\{[OH] \cdot 3H_2O\}_n$ layer is formed of a slightly puckered hexagonal network containing three water molecules and one OH^- group per formula unit, with the O atoms hydrogen-bonded to three neighbors. The interlayer link is provided by three C–H···O interactions between each crystallographically independent oxygen atom and the benzene ligands above and below the hydrated layers.

Some relevant hydrogen bonding parameters of the bis-arene chromium crystals are listed in Table 1 and compared with the data available for CHD (see below) [89].

4.2. Dicarboxylic acids and cobalticinium cation

An approach similar to that employed to produce the CHD crystals has been utilized with dicarboxylic acids and cobaltocene. Cobaltocene is readily oxidized by oxygen, in water or THF solution, to the yellow cobalticinium cation. If the oxidation, and the consequent formation of the hydroxide $[(\eta^5\text{-}C_5H_5)_2Co]^+[OH]^-$, occurs in the presence of an organic acid, a neutralization process takes place with formation of organic salts of the $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cation [85,86]. The type and stoichiometry of the solid product depend on several factors, such as the acid pK, the relative solubility of the organic acid and of the salt (hence depends on the solvent in use), and the molar ratio between acidic protons and hydroxide.

The crystalline products of chemical formulae $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\text{D,L-HTA})(\text{D,L-}H_2TA)]^-$ and $[(\eta^5\text{-}C_5H_5)_2Co]^+[\text{L-HTA}]^-$ have been obtained by utilizing D,L-tartaric acid and L-tartaric acid, respectively. The two crystalline materials are respectively constituted of hexagonal and tetragonal superanions molded around the cobalticinium cations, as shown in Fig. 10. As in the case of the CHD crystals, the organic frameworks are held together by (i) negatively charged $O\text{–}H\cdots O^-$ bonds formed between two carboxylic groups which have lost one proton upon reaction with the hydroxide and (ii) $O\text{–}H\cdots O$ hydrogen bonds between neutral carboxylic groups, with the additional contribution of $O\text{–}H\cdots O$ hydrogen bonds involving the oxydrilic –OH groups and the –COOH groups. The interaction between the organic framework and the organometallic cations is based on a profusion of charge-assisted $C\text{–}H^{\delta+}\cdots O^{\delta-}$ hydrogen bonds between the C–H groups of the cyclopentadienyl ligands and the free O atom accepting sites on the acid. The combination of weak and strong hydrogen bonds in crystalline $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\text{D,L-HTA})(\text{D,L-}H_2TA)]^-$ is represented schematically in Fig. 11. The metric of these interactions is reported in Table 2.

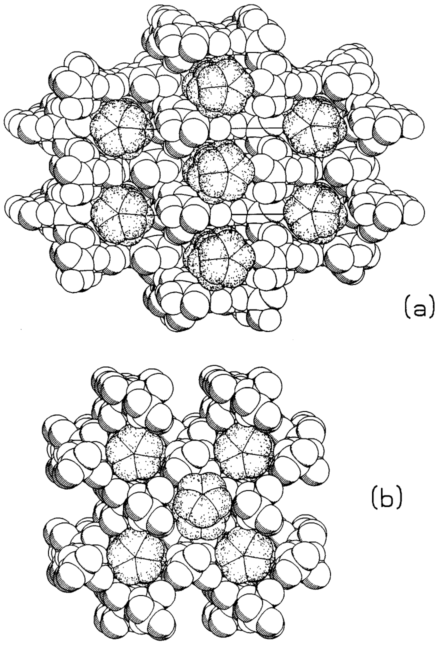


Fig. 10. The hexagonal and tetragonal superanions molded around cobalticinium cations in crystalline $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\text{D,L-HTA})(\text{D,L-}H_2TA)]^-$ (a) and $[(\eta^5\text{-}C_5H_5)_2Co]^+[\text{L-HTA}]^-$ (b) ($\text{D,L-}H_2TA = \text{D,L-}$tartaric acid).

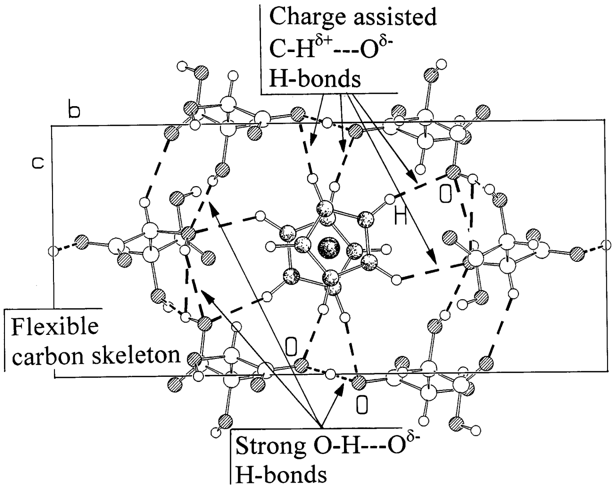


Fig. 11. Schematic representation of the combination of weak and strong hydrogen bonds in crystalline $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\text{D,L-HTA})(\text{D,L-}H_2TA)]^-$ (D,L-H_2TA = D,L-tartaric acid).

On changing the stoichiometric ratio $[(\eta^5\text{-}C_5H_5)_2Co]/(\text{D,L-}H_2TA)$ from 1:2 to 1:1, the crystalline material $[(\eta^5\text{-}C_5H_5)_2Co]^+[\text{D,L-HTA}]^- \cdot H_2O$ is also produced, while the undecahydrate crystalline material $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[\text{L-BTA}]^{2-} \cdot 11H_2O$ is obtained when the organic partner is dibenzoyl(L)tartaric acid (L-H_2BTA) [see Fig. 12(a) and (b)].

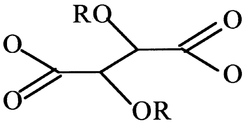
As can be seen from a comparison of the data collected in Tables 1 and 2, in spite of the chemical and structural differences, the dione and the dicarboxylic acids show very similar hydrogen bonding metrics. In particular, the negatively charged $O–H\cdots O^-$ hydrogen bonds, which contribute the strongest interaction and are responsible for the organic superstructure, are strictly comparable in the two systems. The same holds true for the interactions involving water molecules in the four cases of hydrated crystals.

Another important feature shared by the dione and the acids is the ratio between the number of available acceptor sites and the number of –O–H donors. The dione molecule possesses three potential acceptor sites but only one OH donor, while tartaric acid possesses eight potential acceptor sites against four potential O–H donor groups (two in the bis-benzoyl derivative). The number of donor groups reduces further upon deprotonation or if, as in the case of $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\text{D,L-HTA})(\text{D,L-}H_2TA)]^-$, the –O–H groups form intramolecular $O–H\cdots O$ bonds. As mentioned above, the unbalance between acceptor and donor sites is an essential prerequisite to allow formation of a large number of charge assisted $C–H^{\delta+}\cdots O^{\delta-}$ hydrogen bonds between the C–H groups of the arenes or cyclopentadienyl ligands and the free O atom accepting sites on the organic superanions.

Similar approaches have been developed in the organic crystal engineering field. For example, (L)malic acid and substituted benzylamines have been employed by Aakeroy and Nieuwenhuyzen [90,91] to prepare ionic materials via hydrogen bonding interactions of the O–H···O type between the deprotonated acid and of the N–H···O type between anions and cations. The strategy adopted by Hosseini and collaborators to build one-, two-, and three-dimensional networks in mixed organic crystals is also based on the interaction between acids and bases. The building blocks ('tectons' in Hosseini's papers) are chosen so that there is preferential aggregation between the anions and cations rather than forcing self-assembling of the organic part. Bis-cyclic amidines, for example, have been used because their diprotonated form possesses four acidic N–H protons, thus capable of donating four hydrogen bonds. Such a system links tightly with deprotonated organic acids carrying one or two carboxylate groups. In this latter case, the dicarboxylate anion can act as a bridge between aminidine cations forming one-dimensional aggregates (α-networks) [92,93]. Bis-cyclic aminidinium cations have also been assembled in the solid with tosylate dications [94]. More recently, two different types of co-crystals have been obtained by reaction of the same aminidine with fumaric acid [95]. These studies have provided further evidence that the simultaneous use of hydrogen bond and of electrostatic interactions affords reliable and reproducible synthetic strategies for the preparation of crystalline aggregates with predefined arrangements of the ionic components.

It is worth stressing, on closing this section, that the purpose of our organic–organometallic crystal synthesis is that of producing materials for NLO applica-

Table 2
Comparison of hydrogen bond distances in dicarboxylic acid aggregates of the cobalticinium cation (distances in Å, negatively charged O–H···O$^-$ bonds in bold)

	$O_{COO}\cdots O_{COOH}$	$O_{COOH}\cdots O_{OH}$	$O_{COO}\cdots O_{W}$
$[(\eta^5\text{-}C_5H_5)_2Co]^+[(D,L\text{-}HTA)(D,L\text{-}H_2TA)]^-$	**2.434**	intra 2.711	
		2.638	
		2.677	
$[(\eta^5\text{-}C_5H_5)_2Co]^+[L\text{-}HTA]^-$	**2.440**	2.847	
	2.413	2.925	
$[(\eta^5\text{-}C_5H_5)_2Co]^+[D,L\text{-}HTA]^-\cdot H_2O$	**2.479**	2.550	
		2.640	2.725
$\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[L\text{-}BTA]^{2-}\cdot 11H_2O$			2.828
			2.772
			2.802
			2.743
			2.822
			2.757
			2.800

D,L-H_2TA = D,L-tartaric acid; L-H_2TA = L-tartaric acid; L-H_2BTA = dibenzoyl-L-tartaric acid.

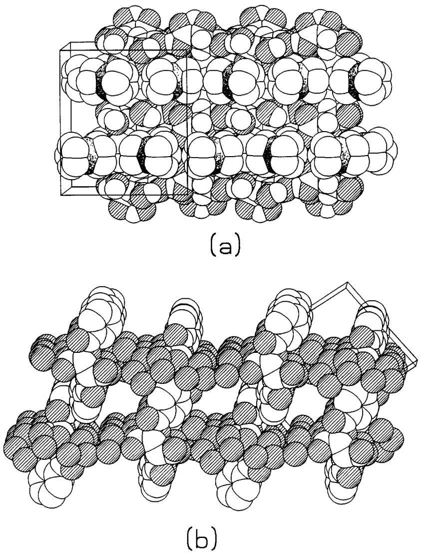


Fig. 12. (a) The hydrated crystalline salt $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+[\text{D,L-HTA}]^- \cdot \text{H}_2\text{O}$ is obtained with a 1:1 $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]/(\text{D,L-H}_2\text{TA})$ stoichiometric ratio ($\text{D,L-H}_2\text{TA} = \text{D,L}$-tartaric acid). (b) The chiral acid dibenzoyl-L-tartaric acid ($\text{L-H}_2\text{BTA}$) gives the undecahydrate crystalline material $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+\}_2[\text{L-BTA}]^{2-} \cdot 11\text{H}_2\text{O}$. Only the anionic/water network is shown for clarity.

tions. The idea that we have currently been exploiting is based on the possibility of functionalizing the organometallic cations (bis-arene chromium, cobalticinium and ferricinium and other related systems) to generate and bring within a non-centrosymmetric superstructure electronic systems suitable for SHG effect. As shown above, the use of enantiomerically pure chiral acids guarantees a simple and cheap access to chiral crystals.

5. Conclusions and outlook

The chemistry of materials is a frontier field of research. The possibility of designing, modeling, synthesizing and exploiting solids with predefined aggregation of molecules or ions is attracting an increasing number of scientists. The most appealing areas of application are those of optoelectronics, in particular SHG generation for optical devices [96–99], conductivity and superconductivity [100,101], charge transfer and magnetism [102,103], nano- and biomimetic materials [104,105]. No matter whether molecular, covalent or coordination solids are required, the construction of materials with predefined physical properties or destined to predefined applications and uses is based on the same concept: the utilization of crystal-directed synthetic strategies.

It is with this awareness that scientists begin to recognize the enormous potential of an organometallic crystal engineering discipline [106]. Efforts need to be directed towards the development of synthetic procedures which may take full advantage of the valence and spin states of transition metal atoms as well as of metal–ligand bonding. The crystallography of these two areas has been separated till recently by a sort of 'generational gap', organic solid state chemistry reached the maturity of organic crystal design long ago whereas organometallic chemistry is only now beginning to overcome the stage of heavy structural characterization and extensive accumulation of data. Though young, organometallic crystal chemistry promises to grow rapidly. The successful development of an organometallic crystal engineering discipline, however, will depend critically on an increased interaction between previously separated areas of research. A crystal engineering team will necessarily be composed of chemists with an interdisciplinary background spanning from organic and organometallic synthesis to crystallography and computational chemistry, and with a deep understanding of the chemistry of materials and of the physics of matter.

Acknowledgements

We acknowledge financial support by the University of Bologna (Project 'Innovative Materials', 1995), MURST, and bilateral exchange projects with Portugal (CNR–JINICT) and Germany (Vigoni Program, DAAR–CRUI), and the Erasmus student exchange program 'Crystallography'. As is evident from the reference list, we have benefited enormously from collaboration with a number of scientists and from the efforts of many students and visiting scientists at Bologna. Finally, we wish to acknowledge invaluable interaction with Gautam R. Desiraju.

References

[1] J. Hulliger, Angew. Chem. Int. Ed. Engl. 33 (1994) 143.
[2] C.L. Bowes, G.A. Ozin, Adv. Mater. 8 (1996) 13.
[3] G.A. Ozin, Acc. Chem. Res. 30 (1997) 17.
[4] O. Khan, in: D.W. Bruce, D. O'Hare (Eds.), Inorganic Materials, Wiley, Chichester, UK, 1992.
[5] T. Bein, G.D. Stucky, Chem. Mater. 8 (1996) 1571.
[6] J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Voegtle, (Eds.), Comprehensive Supramolecular Chemistry, vol. 11, Pergamon, Oxford, 1996.
[7] D. Braga, Chem. Rev. 92 (1992) 369.
[8] D. Braga, F. Grepioni, Acc. Chem. Res. 27 (1994) 51.
[9] D. Braga, F. Grepioni, Commun. Inorg. Chem. 19 (1997) 185.
[10] D. Braga, L. Scaccianoce, F. Grepioni, S.M. Draper, Organometallics 15 (1996) 4675.
[11] D. Braga, F. Grepioni, J.J. Byrne, A. Wolf, J. Chem. Soc. Chem. Commun. (1995) 1023.
[12] D. Braga, A.L. Costa, F. Grepioni, L. Scaccianoce, E. Tagliavini, Organometallics 15 (1996) 1084.
[13] G.R. Desiraju, Organic Solid State Chemistry, Elsevier, Amsterdam, 1987.
[14] G.R. Desiraju, Crystal Engineering: The Design of Organic Solids, Elsevier, Amsterdam, 1989.
[15] J.M. Robertson, Proc. R. Soc. London Ser. A 207 (1951) 101.
[16] G.M.J. Schmidt, Pure Appl. Chem. 27 (1971) 647.
[17] D. Rabinowich, G.M.J. Schmidt, J. Chem. Soc. B (1964) 144.

[18] G.R. Desiraju (Ed.), Perspectives in Supramolecular Chemistry. The Crystal as a Supramolecular Entity, Wiley, Chichester, UK, 1996.
[19] B.F. Abrahams, B.F. Hoskins, R. Robson, J. Am. Chem. Soc. 113 (1991) 3603.
[20] B.F. Abrahams, B.F. Hoskins, D.M. Michail, R. Robson, Nature 369 (1994) 727.
[21] L.R. MacGillivray, S. Subramanian, M.J. Zaworotko, J. Chem. Soc. Chem. Commun. (1994) 1325.
[22] L. Carlucci, G. Ciani, D. Proserpio, A. Sironi, J. Am. Chem. Soc. 117 (1995) 4562.
[23] D.P. Funerin, J.-M. Lehn, G. Baum, D. Fenske, Chem. Eur. J. 3 (1997) 99.
[24] J.M. Lehn, Angew. Chem. Int. Ed. Engl. 29 (1990) 1304.
[25] J.M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim, 1995.
[26] C.V.K. Sharma, G.R. Desiraju, in: G.R. Desiraju (Ed.), Perspectives in Supramolecular Chemistry. The Crystal as a Supramolecular Entity, Wiley, Chichester, UK, 1996.
[27] J.D. Dunitz, in: G.R. Desiraju (Ed.), Perspectives in Supramolecular Chemistry. The Crystal as a Supramolecular Entity, Wiley, Chichester, UK, 1996.
[28] A. Gavezzotti, Acc. Chem. Res. 27 (1994) 309.
[29] J. Dunitz, J. Bernstein, Acc. Chem. Res. 28 (1995) 193 and references cited therein.
[30] D. Braga, L. Scaccianoce, F. Grepioni, S.M. Draper, Organometallics 15 (1996) 4675.
[31] F. Grepioni, G. Cojazzi, S. Draper, N. Scully, D. Braga, Organometallics 17 (1998) 296.
[32] A.D. Burrows, C.-W. Chan, M.M. Chowdry, J.E. McGrady, D.M.P. Mingos, Chem. Soc. Rev. (1995) 329.
[33] T.E. Müller, W.-K.S. Choi, D.M.P. Mingos, D. Murphy, D.J. Williams, W.W.V. Yam, J. Organomet. Chem. 484 (1994) 209.
[34] M.F. Fan, Z. Lin, J.E. McGrady, D.M.P. Mingos, J. Chem. Soc. Perkin. Trans. 2 (1996) 563.
[35] D. Walther, T. Klettke, A. Schmidt, H. Görls, W. Imhof, Organometallics 15 (1966) 2314 and references cited therein.
[36] D. Braga, F. Grepioni, D. Walther, K. Heubach, A. Schmidt, T. Klettke, W. Imhof, H. Görls, Organometallics 16 (1997) 4910.
[37] C.P. Brock, L.L. Duncan, Chem. Mater. 6 (1994) 1307.
[38] P.J. Davies, N. Veldman, D.M. Grove, A.L. Spek, B.T.G. Lutz, G. van Koten, Angew. Chem. Int. Ed. Engl. 35 (1996) 1959.
[39] S.L. James, G. Verspui, A.L. Spek, G. van Koten, J. Chem. Soc. Chem. Commun. (1996) 1309.
[40] S.R. Copp, S. Subramanian, M.J. Zaworotko, J. Am. Chem. Soc. 114 (1992) 8719.
[41] D. Braga, F. Grepioni, E. Tedesco, S. Gebert, H. Wadepohl, J. Chem. Soc. Dalton Trans. (1997) 1727.
[42] P. Hofmann, Angew. Chem. Int. Ed. Engl. 18 (1979) 554.
[43] D.C. Calabro, D.L. Lichtenberger, W.A. Herrmann, J. Am. Chem. Soc. 103 (1981) 6852.
[44] B.E. Bursten, R.H. Cayton, J. Am. Chem. Soc. 108 (1986) 8241.
[45] B.E. Bursten, R.H. Cayton, J. Am. Chem. Soc. 109 (1987) 6053.
[46] D.A. Clemente, B. Rees, G. Bandoli, M.C. Biagini, B. Reiter, W. Herrmann, Angew. Chem. Int. Ed. Engl. 20 (1981) 887.
[47] W.A. Herrmann, Adv. Organomet. Chem. 20 (1982) 159.
[48] M.I. Altbach, F.R. Fronczek, L.G. Butler, Acta Crystallogr. C 48 (1992) 644.
[49] G.R. Desiraju, J. Chem. Soc. Chem. Commun. (1990) 454.
[50] T. Steiner, J. Chem. Soc. Chem. Commun. (1994) 101.
[51] D. Braga, F. Grepioni, H. Wadepohl, S. Gebert, M.J. Calhorda, L.F. Veiros, Organometallics 14 (1995) 5350.
[52] H. Wadepohl, D. Braga, F. Grepioni, Organometallics 14 (1995) 24.
[53] D. Braga, F. Grepioni, K. Biradha, V.R. Pedireddi, G.R. Desiraju, J. Am. Chem. Soc. 117 (1995) 3156.
[54] D. Braga, F. Grepioni, Acc. Chem. Res. 30 (1997) 81.
[55] D. Braga, J.J. Byrne, M.J. Calhorda, F. Grepioni, J. Chem. Soc. Dalton Trans. (1995) 3287, and references cited therein.
[56] D. Braga, F. Grepioni, E. Tedesco, K. Biradha, G.R. Desiraju, Organometallics 15 (1996) 2692.

[57] G.J. Kubas, Acc. Chem. Res. 21 (1988) 120.
[58] R.H. Crabtree, Acc. Chem. Res. 23 (1990) 95.
[59] P.J. Jessop, R.H. Morris, Coord. Chem. Rev. 121 (1992) 155.
[60] D.M. Heinekey, W.J. Oldham Jr., Chem. Rev. 93 (1993) 913.
[61] A. Albinati, V.I. Bakhmutov, K.G. Caulton, E. Clot, J. Eckert, O. Eisenstein, D.G. Gusev, V.V. Grushin, B.E. Hauger, W.T. Klooster, T.F. Koetzle, R.K. McMullan, T.J. O'Loughlin, M. Pelissier, J.S. Ricci, M.P. Sigalas, A.B. Vimenits, J. Am. Chem. Soc. 113 (1993) 7300.
[62] D. Braga, F. Grepioni, E. Tedesco, K. Biradha, G.R. Desiraju, Organometallics 16 (1997) 1846.
[63] M. Brookhart, M.L.H. Green, L.-L. Wong, Progr. Inorg. Chem. 36 (1988) 1.
[64] R.H. Crabtree, Chem. Rev. 85 (1985) 245.
[65] R.H. Crabtree, Angew. Chem. Int. Ed. Engl. 32 (1993) 789.
[66] F. Calderazzo, G. Fachinetti, F. Marchetti, P.F. Zanazzi, J. Chem. Soc. Chem. Commun. (1981) 181.
[67] L. Brammer, M.C. McCann, R.M. Bullock, R.K. McMullan, P. Sherwood, Organometallics 11 (1992) 2339.
[68] I.C.M. Wehman-Ooyevaar, D.M. Grove, P. van der Sluis, A.L. Spek, G. van Koten, J. Chem. Soc. Chem. Commun. (1990) 1367.
[69] I.C.M. Wehman-Ooyevaar, D.M. Grove, H. Kooijman, P. van der Sluis, A.L. Spek, G. van Koten, J. Am. Chem. Soc. 114 (1992) 9916.
[70] L. Brammer, D. Zhao, F.T. Ladipo, J. Braddock-Wilking, Acta Crystallogr. B 51 (1995) 632.
[71] D. Braga, P. DeLeonardis, F. Grepioni, E. Tedesco, M.J. Calhorda, Inorg. Chem. 37 (1998) 3337.
[72] D. Braga, F. Grepioni, P. Milne, E. Parisini, J. Am. Chem. Soc. 115 (1993) 5115.
[73] D. Braga, F. Grepioni, P. Marshall, E. Parisini, Inorg. Chim. Acta 213 (1993) 121.
[74] D. Braga, F. Grepioni, E. Parisini, J. Chem. Soc. Dalton Trans. (1995) 287.
[75] J.C. Calabrese, L.F. Dahl, A. Cavalieri, P. Chini, G. Longoni, S. Martinengo, J. Am. Chem. Soc. 96 (1974) 2616.
[76] P.J. Fagan, M.D. Ward, in: G.R. Desiraju (Ed.), The Crystal as a Supramolecular Entity. Perspectives in Supramolecular Chemistry, vol. 2, Wiley, Chichester, UK, 1996, p. 107.
[77] M.D. Ward, M.D. Hollingsworth, Chem. Mater. 6 (1994) 1087.
[78] J. Bernstein, M.C. Etter, L. Leiserowitz, in: H.-B. Bürgi, J.D. Dunitz (Eds.), Structure Correlation, VCH, Weinheim, 1994, p. 431.
[79] G.A. Jeffrey, W. Saenger, Hydrogen Bonding in Biological Structures, Springer, Berlin, 1991.
[80] G.R. Desiraju, Angew. Chem. Int. Ed. Engl. 34 (1995) 2311.
[81] D. Braga, A.L. Costa, F. Grepioni, L. Scaccianoce, E. Tagliavini, Organometallics 16 (1997) 2070.
[82] M. Meot-Ner (Mautner), J. Am. Chem. Soc. 106 (1984) 1257.
[83] M. Meot-Ner (Mautner), L.W. Sieck, J. Am. Chem. Soc. 108 (1986) 7525.
[84] V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, Chem. Eur. J. 2 (1996) 925 and references cited therein.
[85] D. Braga, F. Grepioni, J.J. Byrne, A. Wolf, J. Chem. Soc. Chem. Commun. (1995) 1023.
[86] D. Braga, A.L. Costa, F. Grepioni, L. Scaccianoce, E. Tagliavini, Organometallics 15 (1996) 1084.
[87] D. Braga, A. Angeloni, F. Grepioni, E. Tagliavini, J. Chem. Soc. Chem. Commun. (1997) 1447.
[88] D. Braga, A. Angeloni, F. Grepioni, E. Tagliavini, Organometallics 16 (1997) 5478.
[89] M.C. Etter, Z. Urbonczyck-Lipkowska, D.A. Jahn, J.S. Frye, J. Am. Chem. Soc. 108 (1986) 5871.
[90] C.B. Aakeroy, M. Nieuwenhuyzen, J. Am. Chem. Soc. 116 (1994) 10983.
[91] C.B. Aakeroy, M. Nieuwenhuyzen, J. Mol. Struct. 374 (1996) 223.
[92] M.W. Hosseini, R. Ruppert, P. Schaeffer, A. De Cian, N. Kyritsakas, J. Fisher, J. Chem. Soc. Chem. Commun. (1994) 2135.
[93] O. Félix, M.W. Hosseini, A. De Cian, J. Fisher, Tetrahedron Lett. 38 (1997) 1933 and references cited therein.
[94] G. Brand, M.W. Hosseini, R. Ruppert, A. De Cian, J. Fisher, N. Kyritsakas, New J. Chem. 19 (1995) 9.
[95] O. Félix, M.W. Hosseini, A. De Cian, J. Fisher, Angew. Chem. Int. Ed. Engl. 36 (1997) 102.
[96] S.R. Marder, Inorg. Mater. (1992) 115.
[97] N.J. Long, Angew. Chem. Int. Ed. Engl. 34 (1995) 21.

[98] T.J. Marks, M.A. Ratner, Angew. Chem. Int. Ed. Engl. 34 (1995) 155.
[99] D.R. Kanis, M.A. Ratner, T.J. Marks, Chem. Rev. 94 (1994) 195.
[100] J.S. Miller, A.J. Epstein, Angew. Chem. Int. Ed. Engl. 33 (1994) 385.
[101] J.S. Miller, A.J. Epstein, Chem. Eng. News 73 (1995) 30.
[102] O. Khan, Molecular Magnetism, VCH, New York, 1993.
[103] D. Gatteschi, Adv. Mater. 6 (1994) 635.
[104] S. Mann, J. Chem. Soc. Dalton Trans. (1993) 1.
[105] J. Aizemberg, J. Hanson, T.F. Koetzle, S. Weiner, L. Addadi, J. Am. Chem. Soc. 119 (1997) 881.
[106] D. Braga, F. Grepioni, J. Chem. Soc. Chem. Commun. (1996) 571.