

Intermolecular interactions and supramolecular organization in organometallic solids

Dario Braga and Fabrizia Grepioni

Dipartimento di Chimica G. Ciamician, Università degli Studi di Bologna, Via F. Selmi 2, Bologna, Italy

Structural variability and flexibility are distinctive properties of organometallic molecules which are reflected in the patterns of intermolecular interactions established by mononuclear and polynuclear coordination complexes in the solid state. The study of van der Waals interactions, hydrogen bonding, and anion–cation interactions allows us to understand how organometallic molecules self-recognize and self-organize and to gain insight into the relationship between molecular and supramolecular crystal structures. This establishes a basis on which a strategy of organometallic crystal engineering can be developed.

*'Warum ist es so dunkel, Mondenkind?'. fragte er,
'Der Anfang ist immer dunkel, mein Bastian'†*

Introduction

The field of organometallic solid-state chemistry is relatively young, but now that materials chemistry is becoming a new frontier field, the interest in organometallic systems is growing rapidly. In spite of the similarities between organic and organometallic systems, little has been done thus far to understand the influence of the presence of metal atoms and of the bonding between organic fragments and metal centres on the properties of organometallic solids. The design of crystalline materials based on the relationship between function and structural organization requires a profound knowledge of those properties that govern orientation, recognition and assembly of the components in the solid state.¹

Over the last few years, at Bologna, we have been studying organometallic solids with the aim of understanding the factors that control crystal formation, stability and molecular organization in relation to the structure of the component molecules or ions.² Before beginning a discussion of this work we would like to acknowledge the many scientists from various countries who share the authorship of the papers quoted throughout this review and who have contributed greatly with their imagination and hard work.

Structural variability and flexibility

Organometallic compounds are those in which the carbon atoms of organic groups are bound to metal atoms *via* two-electron σ bonds or *via* π interactions of unsaturated groups with metal orbitals of appropriate orientation and symmetry. Ionic compounds of electropositive alkali metals also fall into this class of compounds.³ The organic residue bound to the metal centres is often a molecule itself, that is to say a stable and isolable chemical entity. Many organometallic molecules can be constructed by *assembling* (with the tricks of chemistry) ligands and metal atoms by means of donor–acceptor interactions. This process is illustrated in Fig. 1 where a typical organic molecule, benzene, and a typical inorganic molecule, carbon monoxide, are *combined* with a metal atom, chromium, to generate complex molecular systems such as dibenzene chromium, chromium hexacarbonyl, and the mixed-ligand species benzene chromium tricarbonyl. In a broad sense, these are *super-molecules* in which the component molecules are held together by basically non-covalent interactions. More complex systems

can be obtained by increasing, for example, the number of metal atoms, or by adding other σ or π ligands. This purposefully oversimplified representation of organometallic chemistry serves, in this context, to emphasize one of the most important characteristics of organometallic compounds (and coordination complexes, of course), namely *structural variability*. Several factors contribute to this structural variability, for example the number and type of ligands and their combinations, the coordination geometry and the number of metal atoms (the nuclearity of the complex), and the presence of ionic charge.

Structural variability is intimately associated with another typical property of organometallic systems, namely *structural flexibility*. Most organometallic molecules are structurally non-rigid because of two distinctive features of the bonding between the metal centre(s) and the ligands, *viz.* the availability of *almost* isoenergetic, though geometrically different, bonding modes for the same ligand (CO, phosphines, arsines, NO^+ , CN^- , *etc.*) and the delocalized nature of the bonding interactions between unsaturated π systems (aromatic rings, alkenes, alkynes, *etc.*) and the metals. Many organometallic molecules exist in several isomeric forms which can interconvert *via* low-energy processes (*viz.* reorientation, scrambling, fluxionality) both in the gas phase and in the condensed state.^{4,5} It is thus essential to take structural variability and flexibility into account when approaching organometallic solids.

Internal versus external interactions

The assembling of molecules to form stable three-dimensional aggregates is the quintessence of the self-recognition and self-aggregation processes which are supramolecular chemistry paradigms.⁶ A crystal is a supermolecule which possesses *collective* properties that differ from those of the isolated (gas phase) molecule and from those of the same molecule in a solution or melt. The understanding of these collective properties requires a profound knowledge of the interactions acting among molecules and ions in the solid state.⁷ Chemical functionality can be used to develop a strategy to control and predict nucleation and growth of molecular crystals as well as to study solid-state reactivity, and to prepare solids for non-linear

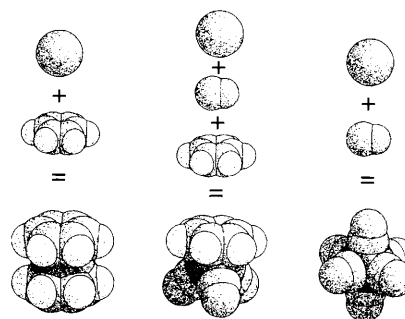


Fig. 1 An example of structural variability in organometallic chemistry: benzene, carbon monoxide and a chromium atom are *combined* to generate dibenzene chromium (left), benzene chromium tricarbonyl (centre) and chromium hexacarbonyl (right)

optics, conductivity, and magnetism.⁸ This is the ground on which crystal engineering can be approached as clearly laid out in the pioneering studies of M. Etter: 'Organizing molecules into predictable arrays is the first step in a systematic approach to designing (organic) solid-state materials.'⁹

The combination of intra- and inter-molecular bonding features of the ligands with the variable valence state and magnetic behaviour of transition-metal atoms can be utilized to devise solids with predefined physical and chemical features such as nanoporous materials, low-dimensional solids, and gas sensors.¹⁰ Strong and directional hydrogen bonding can also be exploited to fix the building blocks in rigid skeletons leaving channels and cavities.¹¹

It is along this way of thinking that we have recently been able to (partially) mimic the behaviour of the cyclamer host-guest system prepared by Etter¹² upon crystallization of cyclohexane-1,3-dione [CHD] from benzene [see Fig. 2(a)] by engineering a 1:4 co-crystal formed by the cation $(C_6H_6)_2Cr^+$ and a complex tetramolecular anion formed by three molecules of CHD and by one $[CHD]^-$ anion obtained by deprotonation of a fourth molecule [see Fig. 2(b)].¹³ The cover picture of the issue shows a space-filling representation of the *pseudo*-cyclamer formed by two $[(C_6H_6)_2Cr][CHD_4]$ units held together by O-H...O and C-H...O interactions.

In general, organometallic molecules form solids that resemble typical organic solids,¹⁴ in which strong electrostatic interactions (of the type occurring in alkali-metal salts, for example) as well as extended covalent arrays (as in many inorganic systems) are absent. When the organometallic species is flexible, however, molecular structure and crystal packing influence each other in a manner which is much more complex than for the majority of organic crystals or inorganic solids.¹⁵ The cohesion of the solid formed in this case depends on the interplay between *internal* and *external* interactions. Internal interactions, of both the *bonding* and *non-bonding* type, arise from direct orbital overlap between atoms as well as from (steric) inter-atomic repulsions *and* attractions operating at the molecular level. These interactions determine the minima and the low energy regions of the molecular potential energy hypersurface. External interactions operate at the crystal level and are mostly non-covalent in nature. Van der Waals and Coulombic interactions (both between ionic charges and between polar groups) lack directionality, whereas hydrogen bonds are more directional. Clearly, both internal and external interactions are *simultaneously* at work in the crystal (any crystal) and, although to a different extent, *both contribute to determine the structure of the molecule in the solid state.*

Shape, size and dynamics

Organic molecules, such as benzene, hexamethylbenzene, thiophene, or larger aromatic carbocyclic compounds, undergo

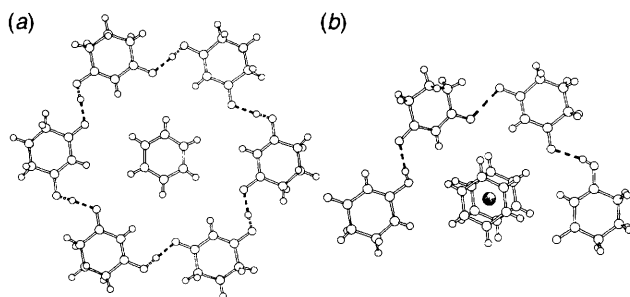


Fig. 2 (a) The cyclamer formed by cyclohexane-1,3-dione [CHD] with benzene;¹² note how the benzene molecule is surrounded by six CHDs linked by O-H...O interactions; (b) the 1:4 co-crystal of the cation $(C_6H_6)_2Cr^+$ with the anion $[CHD_4]^-$; note how the CHD molecules interact with $(C_6H_6)_2Cr^+$ via C-H...O interactions (a space-filling representation of the *pseudo*-cyclamer formed by two $[(C_6H_6)_2Cr][CHD_4]$ is shown as cover picture of this issue)

reorientational jumping motions in the solid state with low or very low activation energies or potential barriers (in the range 15–30 kJ mol⁻¹).⁵ The more the molecular shape approximates that of a disc, an ellipsoid, or a sphere, which cannot be efficiently blocked in the crystal structure, the easier it is for the rigid-body reorientational motion to take place.

What happens when molecules of this type are then 'turned into ligands' and are bound to metal centres in a delocalized fashion? Fig. 3 shows a comparison of the solid-state reorientational barriers (and/or energies of activation) for some organic molecules and for the corresponding organometallic complexes.^{5,16} Since the internal barrier contribution is very small because of the delocalized ligand-metal π bonding, *the crystal packing exerts the same control over the motion in the two types of crystals, and therefore this control depends on the shape of the reorienting fragment.* This is confirmed by the change in the ease of reorientation on changing the overall shape of the ligand: less discoidal or less symmetric ligands cannot reorientate unless the crystal structure is relaxed (usually through a phase transition) as in $(\eta^6-C_6H_4Me_2-1,3)Cr(CO)_3$ and $(\eta^6-C_6H_3Me_3-1,3,5)Cr(CO)_3$.^{16a} Recent ¹³C CP MAS NMR evidence has also indicated a $2\pi/3$ jumping motion of the tricarbonyl unit in solid $(\eta^6-C_6Me_5H)Cr(CO)_3$ at room temperature.^{16e}

Carbonyl ligands in polynuclear systems can adopt terminal, double or triple bridging bonding geometries that differ little in energy. In most cases the barrier to interconversion between these bonding modes is low and the ligands can move from one metal atom to a neighbouring one *via* the 'merry-go-round' or related processes.¹⁷ Whether this is possible in the solid state is still a matter of debate. Spectroscopic, theoretical and, more recently, crystallographic evidence is available for carbonyl clusters such as $Fe_3(CO)_{12}$ ¹⁸ and its analogue $Fe_2Os(CO)_{12}$ ¹⁹ in which reorientational motion of the metal triangle is taking place in the solid state.

The widespread occurrence of isolable isomeric forms which differ marginally in *internal* bonding energy is another manifestation of structural flexibility. It is often possible to *compensate* the energy difference between most and least (thermodynamically) stable isomers with *external* interactions in the solid state. Although a discrimination between the effects of internal and external interactions would be highly desirable in crystal engineering, the problem of separating the relative contributions is not an easy one. The comparison of the isomer energies on a scale of relative (enthalpic) stability with the energies of cohesion of the corresponding crystals would be a reasonable approach. In principle, one should be able to evaluate the contribution of external interactions to the stabilization of less stable isomeric forms if the difference in internal energy can be estimated. However, even the most up-to-date theoretical tools are generally not well suited for the complexity of organometallic molecules and solids. We have found that some insight can be obtained by combining a molecular orbital analysis based on extended-Hückel theoretical calculations²⁰ with an analysis of the intermolecular

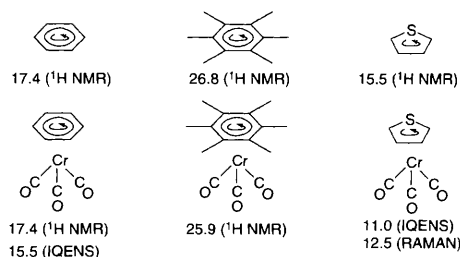


Fig. 3 Reorientational freedom is a function of molecular (or ligand) shape. The solid state reorientational barriers/activation energies (kJ mol⁻¹) are compared for some organic molecules and for the corresponding organometallic complexes (IQENS = incoherent quasi-elastic neutron scattering).

bonding based on packing potential energy calculations.²¹ The following section will focus on some key examples.

Organometallic Solids

Clearly, the factors responsible for cohesion in molecular crystals of identical neutral molecules (A–A systems) will differ from those in crystals formed by cations and anions (A⁺–B[–] systems) or from those in co-crystals containing two different molecules (A–B systems), although the type and energetics of the non-covalent interactions will be basically the same. Some examples will now be described.

Molecular crystals of neutral molecules (A–A system)

The arene clusters $\text{Ru}_5\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)$ and $\text{Ru}_5\text{C}(\text{CO})_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$, $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)_2$ and $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ form two pairs of isomers that are sufficiently stable to be isolated and characterized in the solid state.²² The apical (η^6) isomers in both penta- and hexa-nuclear systems are the most stable isomeric forms. In terms of crystal cohesion the crystals containing facial isomers are as cohesive as those formed by the apical isomers, although intermolecular hydrogen bonds of the C–H...O type are established preferentially between apical arenes and CO ligands. This is quite a general behaviour and, as will become evident later, the presence of this type of interaction is recurrent in organometallic solids formed by molecules carrying a large number of CO ligands and CH groups.²³

This aspect has been further elaborated in a comprehensive investigation²⁴ of the family of clusters of the type $(\text{Cp}^R)_3\text{M}_3(\text{CO})_3$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}; \text{Cp}^R = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5, \text{C}_5\text{H}_4\text{Me}$). These molecules differ at the molecular level mainly in the number and type of CO bridges in the structure. The back-donation component of the bonding between bridging CO ligands and the clusters involves a metal–metal antibonding orbital. This effect is less important for Co, which has more contracted d orbitals, than for Ir, for which the structure with only terminal COs becomes favoured. For Rh intermediate solutions are possible. It has been shown that the difference in stability between the two isomers $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\mu_2\text{-CO})_3$ and $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\mu_2\text{-CO})_2(\text{CO})$ is related to the difference in cohesion between the respective crystal structures: the latter least stable isomer crystallizes in the most stable crystal form, and *vice versa*. As in the cases of the arene clusters, the CO ligands form intermolecular hydrogen bonds of the C–H...O type (see Fig. 4). The length of the C–H...O interactions follows roughly the trend face-capping (μ_3) > edge-bridging (μ_2) > terminal, which corresponds to the well known trend of decreasing basicity of the CO ligand.²⁵

The electronic reason for the CO bonding mode and the involvement of this ligand in intermolecular hydrogen bonds has also been investigated in $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_9(\mu_3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$, which carry only terminal COs, and in $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})_3(\mu_3\text{-S}_3\text{C}_3\text{H}_6)$ which carries three bridging COs.^{26a} Since bridging COs are more efficient π acceptors than terminal ones, their presence in $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})_3(\mu_3\text{-S}_3\text{C}_3\text{H}_6)$ is required in order to compensate for the substitution of the σ -donor ligand ($\mu_3\text{-S}_3\text{C}_3\text{H}_6$) for three axial ligands in the structure of $\text{Ru}_3(\text{CO})_{12}$; this is not so in $\text{Ru}_3(\text{CO})_9(\mu_3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ where the facial C_6H_6 ligand takes the place of the axial COs as a π acceptor and stabilizes the all-terminal structure. Although the terminal ligands participate in C–H...O bonding in both $\text{Ru}_3(\text{CO})_9(\mu_3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ and $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})_3(\mu_3\text{-S}_3\text{C}_3\text{H}_6)$, the shortest interactions are observed between the ($\mu_3\text{-S}_3\text{C}_3\text{H}_6$) hydrogen atoms and the bridging COs in this latter complex, as expected. The participation of the thioether hydrogens in intermolecular links has been assessed recently by examining a number of crystalline cobalt clusters carrying this type of ligand.^{26b}

Molecular co-crystals formed by neutral molecules (A–B system)

Different crystalline forms containing molecules of identical compositions and geometry are called polymorphs.²⁷ In the case of conformational isomers, the structural differences at the molecular level between conformers are usually minor since the distribution of chemical bonds is maintained (*conformational polymorphism*).²⁷ With flexible organometallic systems, however, the bonding mode of the ligands may change in fluxional processes. The above definitions are clearly inadequate and crystals formed by structural isomers related by a low-energy interconversion pathway should be regarded as *crystal isomers*. Crystal polymorphs or isomers may (or may not) interconvert *via* a phase transition. Furthermore, there is the intriguing possibility of changing the *chemical composition* without changing the distribution of chemical bonds by isoelectronic replacement of one or more metal atoms with other metals in the same group. Crystals of isoelectronic and isostructural species may crystallize in the same space group, thus being isomorphous, or in different space groups, forming *pseudo-polymorphs*.

A classical example of *organometallic conformational polymorphism* is provided by ferrocene, for which one room-temperature disordered²⁸ and two low-temperature ordered crystalline forms are known.²⁹ At the molecular level the ferrocene molecules differ only in the relative orientation of the two cyclopentadienyl rings (see Fig. 5). At the crystal level they differ in the relative orientation of the molecules, so that the phase-transition mechanism requires only low-energy re-orientation of the rings and a limited motion of the molecules in the crystal structure.³⁰ Some of the $(\text{Cp}^R)_3\text{M}_3(\text{CO})_3$ clusters discussed above as well as the pair $\text{Fe}_3(\text{CO})_{12}$ and $\text{Fe}_2\text{Os}(\text{CO})_{12}$ are examples of organometallic *pseudo-polymorphism*.

Co-crystallization of organometallic molecules possessing different chemical compositions has not been studied in a systematic manner. The situation is complicated further when different isomers are present in the same crystal, as independent molecules in the asymmetric unit, thus forming a co-crystal of isomers.

The two known forms³¹ of $\text{Ru}_6\text{C}(\text{CO})_{17}$ contain a total of three isomers that differ in the rotameric conformation of the tricarbonyl units above and below the equatorial plane contain-

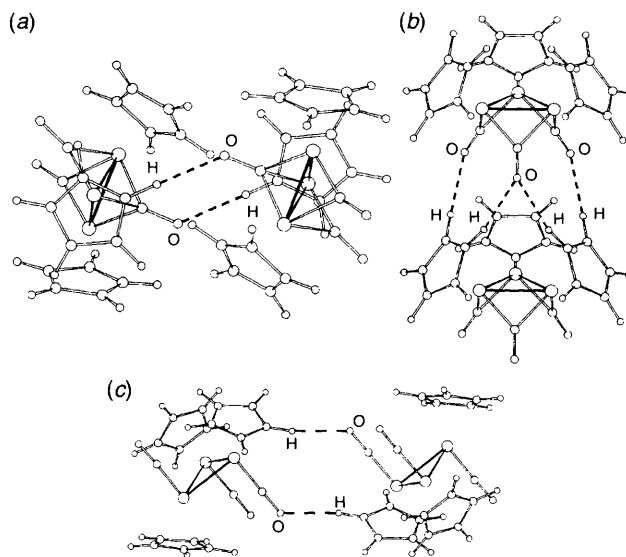


Fig. 4 Networks of C–H...O interactions. Centrosymmetric pairing in $(\eta\text{-C}_5\text{H}_5)_3\text{Co}_3(\mu_3\text{-CO})(\mu_2\text{-CO})_2$ (a); C–H...O interactions are formed between H($\eta\text{-C}_5\text{H}_5$) atoms and the face-capping CO; bifurcated C–H...O(CO) interactions in crystalline $(\eta\text{-C}_5\text{H}_5)_3\text{Rh}_3(\mu_2\text{-CO})_3$; (b) involving the edge-bridging ligands; (c) C–H...O interactions formed by the terminal ligands in crystalline $(\eta\text{-C}_5\text{H}_5)_3\text{Ir}_3(\text{CO})_3$ (only the shortest are shown).

ing the bridging ligands, and in the pattern of terminal, bridging, and semibringing COs around the molecular equator. The existence of these rotamers indicates that the carbonyl units lie on a flat potential energy surface, so that the conformational choice is chiefly under *intermolecular control* in agreement with molecular mechanics calculations.³² Similarly, the hydridoborido cluster $\text{HRu}_6\text{B}(\text{CO})_{17}$ ³³ is known in two crystalline forms whose molecules differ in the orientation of the tricarbonyl units above and below the equatorial plane as well as in the location of the H(hydride) atom over the cluster surface.

The structure of the 1 : 1 co-crystal formed by the two clusters $\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_4\text{Me}_2\text{-1,3})$ and *trans*- $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_4\text{Me}_2\text{-1,3})_2$ is strictly related to those of the respective *homomolecular* crystals.³⁴ The co-crystal can be described as being composed of homomolecular crystals of $\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_4\text{Me}_2\text{-1,3})$ and of homomolecular crystals of *trans*- $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_4\text{Me}_2\text{-1,3})_2$, both extending for only two layers (see Fig. 6). The AABBA layered structure allows molecules of each type to interact on one side with molecules of the same type and on the opposite side with molecules of the other type. Empirical packing energy calculations indicated that the dimolecular A + B system is slightly more cohesive than that formed by A with A and by B with B.

Molecular salts: choice of counter ions and isolation of isomers

The isolation of different structural isomers on changing the counter ion is another manifestation of organometallic structural flexibility. A key example is that represented by neutral

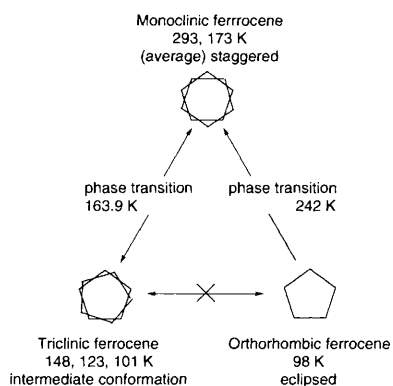


Fig. 5 Conformational isomers of ferrocene and the phase transitions relating the orthorhombic and triclinic phases to the disordered room-temperature monoclinic phase

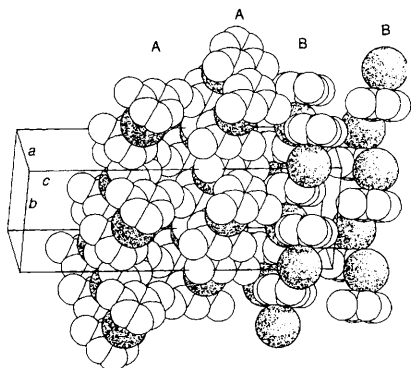


Fig. 6 The AABBA layered structure present in the co-crystal formed by the two clusters $\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_4\text{Me}_2\text{-1,3})$ (A) and *trans*- $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_4\text{Me}_2\text{-1,3})_2$ (B); this molecular arrangement is a combination of those observed in crystalline $\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_4\text{Me}_2\text{-1,3})$ and *trans*- $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_4\text{Me}_2\text{-1,3})$. CO ligands and H atoms are omitted for clarity; shaded atom spheres represent the octahedral metal frames.

and ionic derivatives of the clusters $\text{M}_4(\text{CO})_{12}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) which are known in two isomeric forms: one containing only terminally bound CO ligands ('all-terminal' form for $\text{M} = \text{Ir}$) and the 'bridged' form with three bridging CO ligands for all three metals.³⁵ The difference in energy between the two forms is generally small and for some ligands (such as SCN^- and $\mu_3\text{-S}_3\text{C}_3\text{H}_6$ in iridium clusters) isolation of the isomers is possible. In crystals of ionic species the distribution of anions and cations is controlled primarily by the relative size and shape of the component ions, although more directional, though weak, interactions such as those between CO ligands or other acceptor ligands, such as the SCN ligand in $[\text{Ir}_4(\text{CO})_{11}(\text{SCN})]^-$, and C–H donors on the cations, also play an important role. The effect of hydrogen-bonding interactions between anion and cation has been well illustrated in the case of $[\text{Fe}_3(\text{CO})_{11}]^-$ which has been characterized with different hydrogen-bonding donor $[\text{H}_2\text{NR}_2]^+$ cations.³⁶

In another study the molecular and crystal structure of the complexes $[(\mu\text{-Cl})_3\{\eta^6\text{-areneRu}\}_2][\text{BF}_4]$ (arene = C_6H_6 , $\text{C}_6\text{H}_5\text{Me}$) has been investigated³⁷ showing the importance of C–H...Cl between cations and C–H...F interactions between cations and anions in the stabilization of the crystalline edifice.

The platinum cluster $[\text{Pt}_9(\text{CO})_{18}]^{2-}$ has been isolated as both its $[\text{PPh}_4]^+$ and its $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$ salts. This cluster belongs to the family of pillared $[\text{M}_3(\text{CO})_6]_n^{2-}$ ($\text{M} = \text{Ni}, \text{Pt}; n = 1\text{--}5$) clusters³⁸ which have been shown to undergo rotational motion around the cluster axis in solution. This degree of freedom is preserved upon crystallization. The two stacks of Pt_3 clusters have different relative orientations in the two crystalline salts as shown in Fig. 7.

Organometallic salts or co-crystals?

Organometallic anions and cations are often crystallized with large organic-type counter ions. 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 counter ion size and shape is the determinant for the anion aggregation in the crystal. The general rule is relatively simple: *small cations favour one- or two-dimensional aggregation of the anions*.³⁹ 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 to engineer anisotropic arrangements of the particles in the solid state. The size of the cations becomes a critical factor as the dimension of the anion increases; this is one of the reasons, for instance, why high nuclearity clusters can be isolated more easily in stable and ordered 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 this way space is used more efficiently and crystal cohesion is

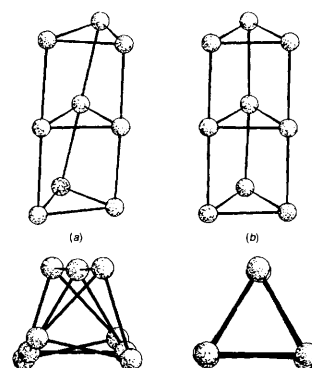


Fig. 7 Comparison of the metal frame conformations in crystalline $[\text{Pt}_9(\text{CO})_{18}]^{2-}$ as its $[\text{PPh}_4]^+$ (a) and $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$ salts (b); top: front views, bottom: projections perpendicular to the metal triangle planes

guaranteed.⁴⁰ In some cases, solvent of crystallization is also required in order to fill in interstices in the crystals.

When the homogeneous charge distribution over the surface of a polycarbonyl anion is perturbed by the presence of hetero-ligands, such as halides, cyanates or thiocyanates, additional factors come into play.⁴¹ The distribution of the ions in the crystal tends towards the insulation of the more polar groups either by direct *ion pairing* between the cations and the polar ligand(s), or by *trapping* and *insulating* the polar ligands face-to-face within a cage of counter ions. These two apparently alternative solutions achieve a common result: *the problem of packing soft ions is reduced to that of packing large aggregates of the van der Waals type*. The final aggregate is a dimer of anions plus counter ions or a more complex globular object that can then be packed in a molecular-crystal manner (see Fig. 8).

Can crystal structures be predicted?⁴² Maybe not, but...

Knowledge of the molecular shape allows the investigation of the way molecules self-recognize and self-assemble in the solid state and the identification of the most frequent interlocking motifs between ligands or groups of ligands. Such an analysis, which we call *packing decoding*,⁴³ is based on the inspection of the *enclosure shell* formed by the molecules in the immediate neighbourhood of the one chosen for reference.⁴⁴ Crystal structure decoding can be achieved easily by calculating the intermolecular interactions energies *via* empirical atom-atom potentials and by ranking the molecules in order of decreasing contribution to the total cohesive energy of the crystal. In this way differences and analogies between seemingly very different crystals can be appreciated more efficiently than with *traditional* crystallographic tools. As an example, the *enclosure shells*⁴⁵ of monoclinic ferrocene and orthorhombic decamethylferrocene (space groups $P2_1/a$, $Z = 2$; $Cmca$, $Z = 4$, respectively) are compared in Fig. 9

The second level of the packing decoding is concerned with the interlocking of atomic groupings belonging to neighbouring molecules. The crystal is seen as composed of pairs of

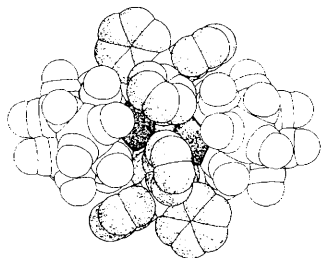


Fig. 8 Trapping of the polar Br ligands in a cage of counter ions (shaded moieties) in crystalline $[\text{Ir}_6(\text{CO})_{14}\text{Br}][\text{PPh}_4]$

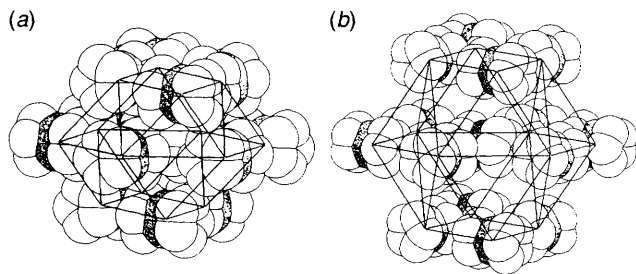


Fig. 9 The 'enclosure shell' molecules in monoclinic ferrocene (a) and permethylferrocene (b) showing the close similarity between the two crystal structures; the hydrogen atoms in both structures as well as the methyl carbons in permethylferrocene are not shown for clarity; note how these latter groups would fill in the space between layers without changing molecular distribution and relative orientation with respect to monoclinic ferrocene

molecules (dimolecular nuclei, DMN) and the interlocking of the reference molecule with each first neighbour is analysed both geometrically and energetically. The scope of this exercise is to find which are the most relevant structural subunits and how molecules stick one to another. Information of this type is fundamental to the investigation of self-recognition and nucleation processes, since it is often transferrable to different molecules that contain similar structural subunits regardless of the molecular complexity.⁴⁶

This approach will now be illustrated briefly for the binary carbonyl complexes $\text{Ni}(\text{CO})_4$,⁴⁷ $\text{Fe}(\text{CO})_5$,⁴⁷ and $\text{Cr}(\text{CO})_6$,⁴⁸ representing the classes of tetrahedral, trigonal bipyramidal, and octahedral complexes. Their molecular structures can be easily *partitioned* into $\text{M}(\text{CO})_n$ subunits, where n is a small integer (2, 3, 4); the interlockings of highest cohesion in the experimental crystal structures are shown in Fig. 10. The key motif in crystalline $\text{Ni}(\text{CO})_4$ consists of two tetrahedral $\text{Ni}(\text{CO})_4$ molecules interlocked along one threefold axis bringing the two metal atoms to a distance of 4.61 Å [see Fig. 10(a)]. In crystalline $\text{Fe}(\text{CO})_5$, the trigonal-bipyramidal molecules interact *via* $\text{Fe}(\text{CO})_3 \cdots \text{Fe}(\text{CO})_3$ interlocking parallel to the molecular axis [Fig. 10(b)]. In crystalline $\text{Cr}(\text{CO})_6$ the most cohesive DMNs are obtained either *via* interlocking of one CO with a trigonal unit formed by two equatorial and one axial CO of a neighbouring molecule or by embracing one axial CO with two equatorial carbonyl ligands.

This type of analysis has also been carried out on polynuclear systems. In the cases of $\text{Co}_2(\text{CO})_8$ and of $\text{Fe}_2(\text{CO})_9$ it has been possible to rationalize the relationships between the two molecular structures and those of the respective crystals.⁴⁹ The latter molecule allows extremely cohesive packing thanks to a perfect match of the carbonyl subunits in the crystal structure. This accounts for the very high packing coefficient and for the well known insolubility in most common solvents. In the case of $\text{Co}_2(\text{CO})_8$, on the other hand, it has been possible to detect the stereoactivity of the lone-pair electrons on the metal atoms pointing towards the site of the ninth ligand in the partner $\text{Fe}_2(\text{CO})_9$ structure.

This approach has also been applied to crystalline $\text{Fe}_3(\text{CO})_{12}$ ⁵⁰ and $\text{Ru}_3(\text{CO})_{12}$ ⁵¹ and to crystals of small⁵² and high nuclearity carbonyl-arene clusters.⁵³

Recent developments⁴² in the methods for generating theoretical crystal structures from those of known molecules have been applied to most of the above-mentioned species and the results compared with the packing arrangements present in the experimental crystal structures.

In retrospect, while we essentially agree with Gavezzotti that crystal structures cannot be *predicted*, we believe that the investigation of how molecules can be linked together in the solid by optimizing intermolecular cohesion (even if confined to oligomolecular units) is a worthwhile exercise. In doing so we

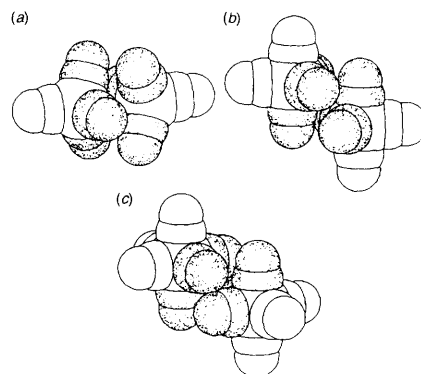


Fig. 10 Molecular interlocking in simple binary carbonyls; (a) $\text{Ni}(\text{CO})_4$: two tetrahedra interlock along one threefold axis; (b) $\text{Fe}(\text{CO})_5$: the trigonal-bipyramidal molecules interact *via* $\text{Fe}(\text{CO})_3 \cdots \text{Fe}(\text{CO})_3$ subunits; (c) $\text{Cr}(\text{CO})_6$: one CO is embraced by two equatorial carbonyl ligands

gain access to information on the factors responsible for crystal stability and cohesion as well as on the interplay between molecular shape and crystal organization.

Hydrogen bonding in organometallic crystals

Our knowledge (ignorance?) of hydrogen bonding in organometallic systems with respect to organic systems parallels that of the less directional intermolecular interactions discussed so far. Hydrogen bonding is by far the major interaction in biological materials,⁵⁴ as well as in supramolecular chemistry and in molecular crystal engineering.⁵⁵

Following the same conceptual approach discussed above, we have first investigated to what extent 'classical' hydrogen bonding patterns established by donors/acceptors such as $-\text{CO}_2\text{H}$, $-\text{OH}$, $-\text{CONH}_2$ and $-\text{CONHR}$ are transferred to organometallic crystals when the organic molecule is 'turned into' a metal-coordinated ligand.⁵⁶ Generally speaking, *organic molecules such as carboxylic acids, alcohols, or amides form the same type of hydrogen bonding whether as 'free' molecules or as ligands.* An example of this analogy is shown in Fig. 11. Common patterns,⁵⁷ such as the carboxylic dimer, the $-\text{OH}$ ring, and the 'catemer', are maintained in organometallic crystals.

In weak hydrogen-bonding situations and/or when steric factors do not permit an efficient approach, the CO ligand, almost ubiquitous in transition-metal coordination chemistry, can become a competitive base and accept hydrogen bonds from donors such as $\text{O}-\text{H}$, $\text{N}-\text{H}$ and (mainly) $\text{C}-\text{H}$ groups.²³ With respect to the hard $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond, we have shown that the $\text{C}-\text{H}\cdots\text{OC}$ interaction can be regarded as a 'soft' intermolecular interaction. Because of the diffusion of $\text{C}-\text{H}$ units and of the CO ligand, this interaction plays a fundamental role in organometallic crystals. The order of basicity of the ligand depends on the coordination mode and follows the order of increasing back-donation onto oxygen, *i.e.* the μ_3 bridge is more basic than the μ_2 bridge, while the terminal CO is the least basic, this being reflected in the average lengths of the $\text{H}\cdots\text{O}$ separations ($\text{C}-\text{H}\cdots\text{O}$ distances *ca.* in the order 2.44,²⁴ 2.57,²³ 2.62²³ Å). The $\text{C}-\text{H}\cdots\text{OC}$ bonds are quite directional with the $\text{C}-\text{O}\cdots\text{H}$ angle around 120° for both bridging and terminal coordinations. This observation indicates that in the solid state and in the presence of $\text{C}-\text{H}$ donors there is oxygen lone pair density in ketonic directions also when CO is in terminal bonding mode. Bifurcation is also common with several $\text{C}-\text{H}$ groups pointing towards a single O atom. The geometry of the $\text{C}-\text{H}\cdots\text{OC}$ interaction is summarized in Fig. 12.

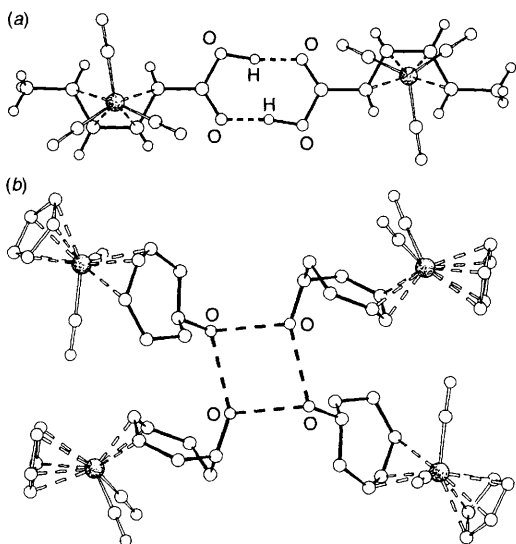


Fig. 11 Organic molecules form the same type of hydrogen bonding whether as 'free' molecules or as ligands: examples of the carboxylic dimer (a) and of the $-\text{OH}$ ring (b)^{56a}

An interesting manifestation of the $\text{C}-\text{H}\cdots\text{O}$ bonding can be seen in crystalline *cis*- and *trans*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$.⁵⁸ This pair of molecules usefully summarizes some of the aspects discussed throughout this review. Both isomers carry two terminal and two bridging CO ligands. The $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds involve both types of ligands and the CH groups of the cyclopentadienyl ligands. Both molecules form dimers which show some resemblance to $\text{O}-\text{H}\cdots\text{O}$ dimers in carboxylic acids. In the crystal of the *trans* isomer each molecule forms $\text{C}-\text{H}\cdots\text{O}$ interactions with the other four surrounding molecules. Because of the site symmetry both C_5H_5 ligands have crystallographically identical surroundings and experience the same type of interaction. In the case of the *cis* isomer there is no crystallographically imposed symmetry, hence the different packing environments around the two C_5H_5 rings are reflected in the presence of different patterns of $\text{C}-\text{H}\cdots\text{OC}$ interactions. This difference accounts for the different librational and reorientational motion of the two C_5H_5 ligands in the solid state as shown in Fig. 13. The two rings not only have a different mean-square librational amplitude of motion about equilibrium positions (302.8 and 62.4 degrees²) but also undergo reorientational jumping motions with different activation energies (7.2 vs. 15.8 kJ mol⁻¹) and different potential energy barriers (7.9 vs. 17.6 kJ mol⁻¹) for the two rings as shown by ¹H spin-lattice relaxation time measurements,⁵⁹ and packing potential energy barrier calculations.⁶⁰ This is a conclusive observation on the effectiveness of $\text{C}-\text{H}\cdots\text{O}$ interactions as bonds, since the ring atoms involved in more and shorter links move less about equilibrium positions and reorientate with a higher cost in energy.

Conclusions and Outlook

The design of solids starting from molecules and ions with predefined shapes and functions has become the forefront of molecular assembly and recognition studies as well as of materials chemistry research. This is witnessed by the rapidly increasing number of publications that deal specifically with intermolecular interactions in organometallic solids.

In this review article we have collected some of the most recent results obtained from a study of organometallic crystals. Much we have learned by examining similar molecules in a

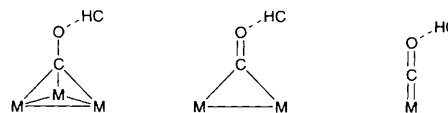


Fig. 12 The geometry of the $\text{C}-\text{H}\cdots\text{OC}$ interactions; the basicity of CO follows the order μ_3 bridge > μ_2 bridge > terminal bonding mode

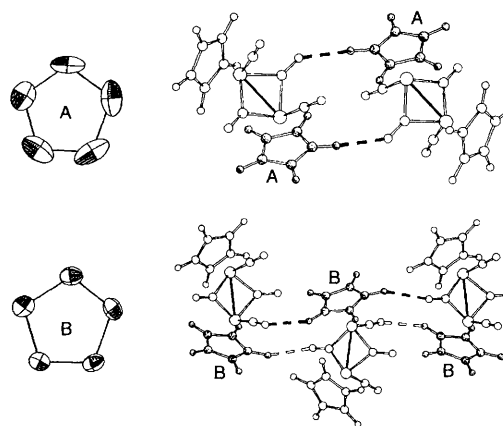


Fig. 13 The effect of the different number of $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds involving the two crystallographically independent C_5H_5 rings (A and B) in crystalline *cis*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ on the anisotropic displacement parameters of the carbon atoms

variety of crystal environments. Throughout this survey we have shown the importance of extracting information from a variety of structures, and for this we have often taken advantage of the abundant information stored in the Cambridge Structural Database. Our approach is similar to the structural correlation method of Dunitz and Bürgi^{57b} based on the examination of the perturbation of a given fragment geometry within different crystal environments. In our approach, however, the crystal field acts on the *soft structural parameters* of coordination compounds, and alterations can be engineered by acting either on the molecule or on the crystal itself. Clearly *there are many ways to compromise internal and external interactions to achieve a free energy minimum for a structurally non-rigid molecule in the solid state*. We have discovered some of these ways: (i) soft molecules can be crystallized in different crystalline forms (crystal isomers) containing different isomeric forms of the same molecule; (ii) structural variations can be induced by changing slightly the electronics of the molecule by changing the type of metal atom, for example, or by changing the ligand shape and size; (iii) structural variations can also be induced *via* co-crystallization of different molecular species; (iv) in ionic crystals the 'degree of freedom' increase because, beside changing the metal and/or changing the substituent, one can play about with the counter ions, enabling the preparation (at least in principle) of a large number of different crystals containing the same anion or cation in different crystal environments.

Extended-Hückel calculations have proved to be applicable to some of these problems, providing reference information on the stability of the isolated molecule at rest (as well as valuable insights into the bonding between molecular fragments). Packing analysis based on packing potential energy calculations within the atom-atom approach allows comparison of different crystal structures in terms of cohesion. Up-to-date graphic software provides a means 'to look inside' the crystal structures which is essential for crystal construction strategies.

In this review we have deliberately spoken only marginally about hydrogen bonding. Emphasis has been given to interactions of the C-H...O type which are almost always found in crystals formed by carbonyl species with ligand substituents that carry C-H groupings. We have also shown how specific aggregational patterns can be obtained by choosing ligands with appropriate hydrogen-bonding donor and acceptor groups. Supramolecular hydrogen bonds between organic and organometallic systems can also be employed in this exercise and we have had some promising initial results. There is still need, however, for some background work to assess to what extent the large body of information available on hydrogen bonding in organic and biological systems can be transferred to organometallic systems in which most molecules participating in intermolecular links are also involved in bonding with metal atoms. Work is progressing in this direction.

We need to concentrate on enlarging our basic knowledge and on extracting chemical information from the study of intermolecular interactions in solids. The goal is that of gaining control of the molecular recognition process which precedes chemical reactivity in molecules, controls solid-state reactivity as well as many other physico-chemical properties, and has important implications for catalytic activity at surfaces.

Clearly, structural variability and flexibility are the beauty and, at the same time, the major obstacle to the development of an organometallic crystal engineering discipline.

*'Mondenkind', flüsterte er, 'ist das nun das Ende?'
'Nein', antwortete sie, 'es ist der Anfang'* ‡

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Footnotes

† 'Why is it so dark, Moonchild?', he asked, 'The beginning is always dark, my Bastian', from Michael Ende, *Die unendliche Geschichte*, Spiegel Buch GmbH, Ulm, Germany.

‡ 'Moonchild', he whispered, 'is this then the end?', 'No' she answered, 'this is the beginning', from Michael Ende, *Die unendliche Geschichte*, Spiegel Buch GmbH, Ulm, Germany.

Dario Braga graduated in Chemistry at the University of Bologna in 1977. He was postdoctoral fellow first at the University of Bologna and then at the University of North London working on the solid-state structures of high-nuclearity transition-metal clusters. He joined the Faculty of Science of the University of Bologna in 1982, where he is currently Associate Professor of General and Inorganic Chemistry. He was awarded the Raffaello Nasini Prize from the Inorganic Chemistry Division of the Italian Society of Chemistry in 1988 for his studies of the factors controlling molecular structure and fluxional behaviours. He received the FEDERCHIMICA Prize for 1995 for his research on the intermolecular interactions in organometallic systems. His major current interests include the static and dynamic structure of organometallic molecules and clusters, the hydrogen bonding in organometallic crystalline materials, and the engineering of organic-organometallic crystals. He is founder Member of the Association for Research and Academic Culture (ARCA) established in 1995.

Fabrizia Grepioni graduated at the University of Bologna in 1985 and received her PhD in Inorganic Chemistry in 1989. She is currently research assistant at the Department of Chemistry of the University of Bologna. Her scientific interests are in the fields of inorganic and organometallic structural chemistry, DataBase analysis, hydrogen bonding, empirical packing-energy calculations and molecular and crystal structure of transition-metal clusters and complexes. She has published more than 100 papers on organometallic solid-state chemistry and intermolecular interactions in organometallic crystals.

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