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Crystal Engineering and Organometallic Architecture

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I. Introduction

A recent feature in the development and progress of chemical research has been the concern with molecular assemblies, ensembles, and all manner of structured aggregates.[1] Since group properties of molecules are often different from those of individual molecules, such trends have the prospects of leading to exciting discoveries[2] and have resulted in the growth of the new, burgeoning areas of supramolecular chemistry[3,4] and solid-state chemistry.[5] These areas are examples of the new, horizontal divisions of chemistry itself, divisions that unify rather than separate as did the traditional vertical divisions of chemistry. While the origins of supramolecular chemistry lie in organic chemistry,[4] solid-state chemistry has been traditionally concerned with inorganic compounds[6] with more recent developments in the domain of molecular solids.[7,8] The present article is concerned with crystal engineering, a young and rapidly growing subject that lies at the intersection of solid-state chemistry and supramolecular chemistry.[9,10]

Interestingly, the formal development of crystal engineering occurred through organic rather than through inorganic solid-state chemistry.[11,12] Why this should have been the case is not entirely clear, considering that the structural systematics of inorganic solids[13] were established long before similar developments took place for organic solids.[14,15] Nonetheless, crystal engineering today has a predominantly organic outlook that is likely to persist for some time to come. The present review attempts to modify this outlook by a discussion of the state-of-the-art of what may be termed “organometallic crystal engineering”.

Crystal engineering was concerned originally with the design of more efficient topochemical reactions[16] but has now greatly increased its scope to the design of molecular crystals for a wide variety of physical and chemical purposes. Crystal engineering consists of two main components, analysis and synthesis, and because of this, its resemblance to classical organic chemistry is so marked.[17] Reason and imagination come into play simultaneously in the quest for new,

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functionalized solids while experiment and computation are of equal significance in the prediction and design of crystal structures.[18]

Organometallic chemistry, as the name suggests, is a bridge between organic and inorganic chemistry. The earliest example of an organometallic crystal structure determination was the crystal structure of ferrocene.[19] Since then X-ray crystallography has always played an unusually important role in the development of this subject. A torrent of subsequent crystallographic work has meant that more than half the Cambridge Structural Database (CSD)[15] now consists of organometallic and metal–organic compounds. The importance of X-ray crystallography in organometallic chemistry arose because the complex structural features of organometallic complexes and clusters (many of which are air- and moisture-sensitive) could not be determined by any other known means.[20] Despite this activity, or arguably because of it, the almost exclusive interest of organometallic chemists lay in the *molecular* structure and stereochemistry of organometallic compounds and clusters rather than in their *crystal* structures and packing characteristics.[21,22] However, crystals of organometallic complexes and clusters are molecular in nature, and so they must be held together by interactions that are, at least, similar to the interactions responsible for the assembly of purely organic molecular crystals.[23]

By the term “organometallic” is meant a compound which contains a C–M bond,[24] and we have largely retained this convention here. Barring some organolithium compounds, we will deal exclusively with complexes and clusters of the transition metals. In a few cases, we describe metal coordination compounds because of certain obvious similarities with previously discussed organics. However, the limits we have set ourselves exclude a discussion of coordination polymers, a large and diverse group of compounds that are of current interest in the crystal engineering context and that have been extensively reviewed in a recent book and elsewhere.[25] Coordination polymers are quite distinct from organometallics. They are not molecular crystals, if the term “molecular” is used in the traditional, three-dimensional way[26] and their crystal chemistry, and especially topology, is more reminiscent of inorganic solids.

Crystal engineering is then the planning and execution of a crystal structure synthesis from the constituent molecules.[27] The ultimate constituents are molecules and ions chosen on the basis of their size, shape, and extramolecular bonding capacity, a kind of supramolecular valence as it were. The assembly of these constituents, that is the nucleation and growth of a molecular crystal, is one of the most basic processes in solid-state chemistry. This process is also one of the most impressive examples of molecular recognition. Additionally, just as the chemistry of a supermolecule is governed by weak intermolecular interactions, so are the chemical and physical properties of molecular crystals controlled by the intermolecular, and where appropriate interionic, interactions. Accordingly, a molecular crystal may be viewed as a solid supermolecule—a hard supermolecule no doubt in contrast to the softer supramolecular species that exist in solution but nevertheless, in the words of Dunitz, a supermolecule *par excellence*.[28]

The following discussion is organized in sections. Each section will provide the reader with entry points in the most recent literature on the subject matter. While many important review articles and books are available for all major aspects of organic solid-state chemistry and crystal engineering as well as for organic and inorganic materials, this is not so when organometallic systems are considered. All previously published review-type articles on crystalline organometallic systems (see, for example, ref 23) deal with specific aspects. We concluded our 1996 *Chemical Communications* feature article[23b] on intermolecular interactions in organometallic crystals by stating that the field was mature to give birth to a new discipline called “organometallic crystal engineering” as the result of interdisciplinary interactions across the traditional divisions of chemistry. A characteristic of crystal engineering is that the development of methodological, strategic, and application-oriented aspects occur concurrently. This feature is particularly marked in organometallic crystal engineering. So, even while the nature of some of the intermolecular interactions involving organometallic species is subject to speculation and dispute, there has already been progress in the design of materials for various applications and functions (see section VIII). There is no contradiction in this type of development, rather it has made for rapid scientific achievements. This Review represents the first attempt to examine in a systematic manner the progress made in the design, synthesis, and application of organometallic solids.

II. Intermolecular Interactions and Organometallic Crystal Architecture

Many factors that influence and guide organic crystal packing are also important in the crystal engineering of organometallic compounds. This is because the metal centers in these compounds are mostly situated in the molecular cores and are well-shielded from neighboring molecules. Effectively, the outer portions of these molecules—the rims or peripheries are "organic" in nature. Since these peripheries are crucial in determining crystal structures, the packing problem reduces to the organic case. An illustrative example is obtained when one compares[29] the molecular organization in the crystal structures of benzene[30] and dibenzenechromium.[31] These structures are shown in Figure 1. The peripheral, that is crystal-structure-determining, features of the two molecules are the same. The benzene molecule is quasi-spherical or discoid in shape and adopts a quasi face centered cubic structure (actually orthorhombic with nearly equal cell edges). Dibenzenechromium is more nearly spherical; accordingly the space group is now accurately cubic but still quasi face centered because the tilting of neighboring molecules permits the formation of herringbone C···H interactions.

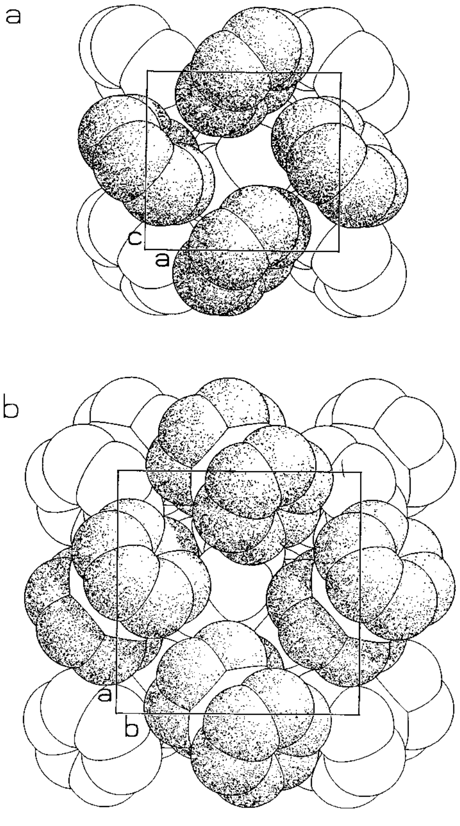


Figure 1. Space-filling representation of the crystal structures of benzene (a) and dibenzenechromium (b) showing the similarity between the two packing arrangements.

In most cases organometallic crystals are more like organics than like inorganics because they are composed of distinct molecules or ions. Of course, lower-dimensional molecularity may also be defined for inorganic substances[26] but the principles governing the packing of inorganic crystals is quite different. There are "fuzzy" areas of course between these three large groups of compounds and organometallics form a natural bridge between organic and inorganic crystals.[32]

A. The Role of Ligands and of Metal Atoms

The properties of organometallic molecules show dependence on the interplay between the electronic nature of the metal(s), and the intermolecular bonding capacity of the ligands, most often organic molecules or fragments.

The coordinative bond between ligands and metals provides an additional tool in organometallic crystal engineering since metal coordination can be used to preorganize in space intermolecular bonding functionalities and to tune the extramolecular bonding capacity of the ligands by the varying nature of the metal, their coordination geometry, and their oxidation states.

i. Coordination Stereogeometry around the Metal Centers. The Nature and Characteristics of the Ligands. The ligand geometry can be combined with metal coordination site (e.g., cis and trans in octahedral complexes) to preorganize complementary hydrogen bonding acceptor and donor groups in space. The intermolecular bonding capacity can also be varied by placing one or more highly polar ligands ($-CN^-$, $-NO^+$, $-SCN^-$, $-Cl^-$, $-Br^-$) among less polar ones (CO, for instance). Another important feature is ligand chirality which can be exploited to form chiral complexes. Ligands can be selected to form dipolar electronic structures in the ground state (organometallic zwitterions) or in easily accessible excited states.

ii. Tuning of Extramolecular Bonding Capacity via Electronic Effects on the Ligands. The polarity (acid base behavior) of any given ligand, and in particular π-acceptor or π-donor ligands, can be tuned by changing the oxidation state of the metal(s). The metal itself can be changed allowing a wide variety of situations from electron-deficient early transition metals to electron-rich late transition metals. The different Lewis acid−base behavior of the metal atoms arising from the electronic configuration of the metal influences the $\sigma-\pi$ bonding interaction between ligand and metal centers.

iii. Ionic Charge. While the chemistry of ions per se does not constitute a large portion of organic chemistry, this is not so for organometallic systems where metal atom oxidation states and the interaction with nonneutral ligands make ions extremely abundant. Examples of complexes that have been isolated in the solid state both as ions and as neutral molecules, are numerous. It should be stressed, however, that the effect of the ionic charge depends very much on the size of the complex ion. The aggregational requirements of large ions (e.g., transition metal cluster anions) carrying a small ionic charge are essentially the same as those of neutral van der Waals objects (with the obvious additional requirement of electroneutrality).

iv. Direct Participation of Metal Atoms in Extramolecular Interactions. It is here that organic and organometallic systems differ the most, since metal atoms may participate directly in extramolecular bonds (see below). Electron-deficient metal atoms, e.g., early transition metal complexes, may accept electron donation via extramolecular interactions into empty or partially filled low-lying orbitals. Conversely, electron rich metals, e.g., late transition metals, may utilize lone pairs to interact intermolecularly with suitable electron acceptors, including hydrogen bonding donor systems. Direct interactions between metal atoms are also of relevance.

v. Structural Flexibility versus Delocalized Bonding Interactions. Ligand Fluxionality in the Solid State. Most organometallic molecules are structurally nonrigid. The typical degrees of (structural) freedom of organic molecules are integrated by the presence of delocalized bonding interactions (e.g., ligand−metal π bonding) and by the possibility of different bonding modes for the same ligand (e.g., terminal and bridging carbonyls, phosphines, hydrides, etc.). What is more, they relate to changeable structures with little cost in terms of energy. These factors have important consequences on the dynamic behavior of organometallic species in solution as well as in the solid state.[33] It has been well-demonstrated that organic fragments such as benzene, hexamethylbenzene, thiophene, or larger aromatic carbocycles bound to metal centers in a delocalized fashion undergo reorientational jumping motion in the solid state depending on the shape of the reorientating fragment.[33−35]

The occurrence of solid-state CO−ligand motion, of the type observed in solution,[36] is still debated. Spectroscopic, theoretical, and, more recently, crystallographic evidence is available for carbonyl clusters such as $[Fe_3(CO)_{12}]$[37] and its analogues $[Fe_2Os(CO)_{12}]$,[38] and $[Fe_2Ru(CO)_{12}]$ and $[FeRu_2(CO)_{12}]$[39] for which reorientational motion of the metal triangle is taking place in the solid state.

vi. Structural Flexibility and Isomerism. The aggregation in the solid state of flexible organometallic molecules depends critically on the compromise between intramolecular bonding and intramolecular nonbonding interactions (internal interactions) and intermolecular interactions in the crystal (external or extramolecular interactions). These energetic terms need not be convergent, i.e., may not necessarily lead to a unique solution. Consequently organometallic molecules can often be isolated in isomeric forms. Indeed, it is often possible to account for 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 probably impossible today. Insights can be obtained, however, by combining a molecular orbital analysis based on extended-Hückel theoretical calculations with an analysis of the intermolecular bonding based on packing potential energy calculations.[40] More recently the same strategy has been adopted by using DFT calculations.[41]

B. Polymorphism, Crystal Isomerization, and Phase Transition

At first glance, it would appear that the web of intermolecular interactions that generate packing arrangements could be organized in many ways. It is well-known that alternative packing modes, which are still chemically and crystallographically acceptable, differ very little in terms of free energy. Different crystalline forms containing molecules of identical compositions and geometry are called polymorphs.[42] Polymorphism is of major industrial importance today. While much money and energy is being invested in the study of polymorphic modifications of drugs, a systematic investigation of organometallic polymorphism has never been carried out this far. Only a few scattered examples are available in the literature.

Polymorphism is, in reality, crystal isomerism and yet the phenomenon is still not fully understood. For instance, its occurrence is probably not as widespread as was conjectured formerly and this would indicate that the sequence of events in crystallization are far more efficient and selective than might have been anticipated. Incidentally, the proportion of polymorphic structures for organometallic compounds in the Cambridge Structural Database (CSD)[15] is slightly lower than that for the pure organics. There are roughly the same number of organics and metal organics (that is, organometallics and coordination complexes) in the CSD. However, among polymorphic forms, the pure organics occur to the extent of 63% while the metal organics account for the remaining 37%.

Structural flexibility plays a particularly important role in organometallic polymorphism. The consequence is that structurally nonrigid organometallic molecules are likely candidates for the formation of conformational polymorphs. *Conformational polymorphism* refers to the crystallization of conformers that differ little in structure since the distribution of chemical bonds is maintained.[43] With flexible organometallic systems, however, the bonding mode of the ligands may change in the course of reorientational or migrational (fluxional) processes.[44] Crystals formed by structural isomers related by a low-energy interconversion pathway are referred to 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

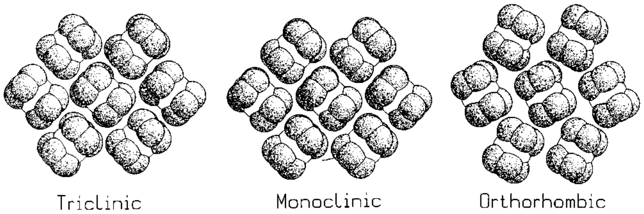


Figure 2. Space-filling representations of the molecular organizations in the structures of the three polymorphic forms of ferrocene: (a) triclinic, (b) monoclinic, and (c) orthorhombic phase.

and isostructural species may crystallize in the same space group, thus being isomorphous, or in different space groups, forming pseudo polymorphs (see later).

A classical example of organometallic conformational polymorphism is provided by ferrocene, for which one room-temperature disordered[45] and two low-temperature ordered crystalline forms are known.[46] At the molecular level the ferrocene molecules differ only in the relative orientation of the two cyclopentadienyl rings. At the crystal level they differ in the relative orientation of the molecules (see Figure 2), so that the phase transition mechanism requires only low-energy reorientation of the rings and a limited motion of the molecules in the crystal structure.[47,48]

Ferrocenedicarboxylic acid affords an intriguing case of crystal polymorphism associated with the presence or absence of orientational disorder. The crystal structure of the monoclinic form was initially determined at room temperature.[49] This was later redetermined by neutron diffraction as also that of the triclinic form.[50] The major difference between the two crystals lies in the −COOH group which is ordered in the triclinic form and disordered in the monoclinic one. Interestingly, this latter form can only be obtained from hot solutions, whereas the ordered form is obtained at room temperature. Differences in entropy have been invoked to explain the phenomenon.

Examples of organometallic pseudo polymorphs in which the structures differ for the ligand distributions are the three crystal forms of $[Ru_6C(CO)_{17}]$,[51] Co-, Rh-, and Ir-clusters of the form $[(Cp^R)_3M_3(CO)_3]$ ($Cp^R = C_5H_5$, C_5Me_5, C_5H_4Me),[52] as well as the pair of molecules $[Fe_3(CO)_{12}]$[53] and $[Fe_2Os(CO)_{12}]$.[38]

Polymorphism is also related to the phase transitional behavior of the crystalline organometallic material depending on whether the polymorphic modifications belong to enantiotropic systems (i.e., the solid−solid transition between polymorphs is below the solid−liquid transition and the polymorphs interconvert before melting) or to monotropic systems (i.e., the polymorphs melt before the solid−solid transition can occur). Many crystals of globular organometallic molecules have been shown to undergo phase transitions, and, for some, the formation of plastic phases characterized by short-range orientational disorder and long range order is known.[54] The change in crystal structure associated with a phase transition, in which intermolecular bonds are broken and formed, is the crystalline equivalent of an isomerization at the molecular level. The chemical and physical properties of the crystalline material can change dramatically with the solid-state transformation.

Substituted ferrocene derivatives $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CHO)Fe]$[55] and $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CMeO)Fe]$[56] as well as salts of the type $[(\eta^5\text{-}FC_6H_5)(\eta^5\text{-}C_5H_5)Fe][A]$ [A = AsF_6, PF_6, SbF_6, and BF_4][57,58] are all known to undergo order−disorder phase transitions. Other examples are afforded by the crystalline salts $[(\eta^5\text{-}C_5H_5)_2M][PF_6]$ (M = Co, Fe) which have been shown by variable-temperature X-ray diffraction experiments and differential scanning calorimetry to undergo two fully reversible phase changes.[59,60c] In the case of the cobalt complex, diffraction experiments were carried out at 243, 293, and 313 K on the same crystal specimen.[59] The room temperature ordered monoclinic crystal (form I) transforms, below 252 K, into another ordered monoclinic crystal (form II) with different relative orientation of the two independent $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations, and into a semiplastic system (form III) containing ordered PF_6^- anions and orientationally disordered $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations above 314 K (see Figure 3). From DSC thermograms the enthalpy differences associated with the two transitions have been estimated to be 1.30 and 3.05 kJ mol^{-1}, respectively. Although isomorphous at room temperature with crystalline $[(\eta^5\text{-}C_5H_5)_2Co][PF_6]$, the ferricinium salt $[(\eta^5\text{-}C_5H_5)_2Fe][PF_6]$[60a,b] shows a different phase transitional behavior with the two phase transitions taking place at 213 and 347 K,[60c] i.e., 39°

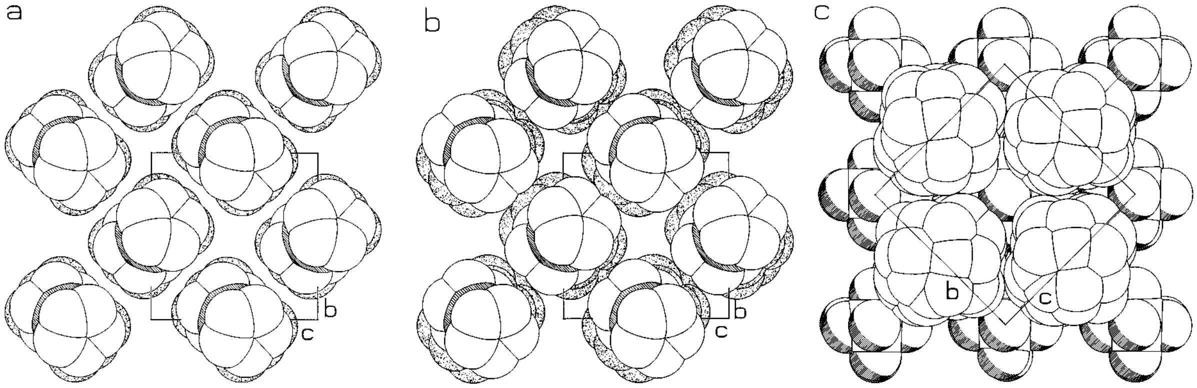


Figure 3. Space-filling representation of the low temperature (a) and room temperature (b) monoclinic ordered forms and of the disordered high temperature monoclinic form (c) of crystalline $[(\eta^5\text{-}C_5H_5)_2Co][PF_6]$. In a and b, PF_6 anions are omitted for clarity. (Reprinted from ref 59b. Copyright 1998 American Chemical Society.)

and 33° deg below and above those of crystalline $[(\eta^5\text{-}C_5H_5)_2Co][PF_6]$.

In both crystals, C—H···F hydrogen bonding interactions between the C_5H_5 ligands and the PF_6^- anions appear to play an important role.[59b] C—H···F bonds, although weaker than the conventional O—H···O type hydrogen bonds, are of comparable length (hence, most likely, strength) with respect to the C—H···O interactions (see also below).[61]

Variable-temperature diffraction experiments have shown that all members of the family of trinuclear cluster molecules $[Fe_3(CO)_{12}]$,[53,62] $[Fe_2Ru(CO)_{12}]$ and $[Fe_2Os(CO)_{12}]$,[38,63] and $[FeRu_2(CO)_{12}]$[64] show dynamic disorder in the solid-state arising from reorientational jumping motion of the metal triangle within the ligand sheath.

III. Modeling of Organometallic Crystal Structures

The design of crystals for magnetic, conductivity, superconductivity, or nonlinear optical applications would become much easier and efficient if one could model crystal structures computationally from molecular structures. This is what is often referred to as “crystal structure prediction”.[65] The molecular or ionic structure needs not necessarily to be determined with crystallography. Spectroscopic techniques or ab initio methods may be just as satisfactory. Indeed, the generation of hypothetical crystal structures is logically connected to ab initio calculations of molecular structures. The prerequisite for the construction of a molecular crystal is the ability to model intermolecular interactions correctly and this can only be done with a good knowledge of the factors that control molecular recognition and crystal cohesion.

A. Evaluation of Crystal Cohesion

The atom−atom potential energy method[66a] and its variation, molecular mechanics,[66b] have been used by organic and physical chemists for more than 50 years. This method still represents the simplest and most transferable way to estimate noncovalent interactions of the van der Waals type in molecular crystals.[67] Portability makes it a method of choice for the estimate of the cohesive energy of molecular crystals; it has been shown in a number of instances that, with very small changes, the method can be applied to a great variety of crystalline systems including crystalline organometallic molecules and clusters. In the organometallic case there are, of course, limitations arising chiefly from the lack of suitable parameters for the metal atoms, although the problem can be circumvented by attributing to metal atoms the potential parameters of the corresponding noble gases.[68] This seemingly severe approximation does not seriously affect the calculations because the periphery of organometallic complexes is, in most cases, constituted with the nonmetallic atoms C, H, N, and O for which potential parameters are available and well-tested.

Packing energy calculations have been successfully applied to several families of organometallic crystals, such as the binary transition metal carbonyls,[69] and the metallocene complexes.[47] In all these cases, the atom−atom method has afforded insights into the way molecules self-assemble in the solid state and has helped in the identification of the most frequent interlocking motifs between ligands or groups of ligands. Such an analysis is based on the inspection of the enclosure shell formed by the molecules in the immediate neighborhood of the one molecule chosen for reference. The process by which the most important packing motifs in observed crystal structures are identified has been called crystal structure decoding (see Figure 4). Decoding can be achieved either by studying in detail the metrics (distances and spatial relationships) of the next-neighbor intermolecular interactions or by calculating the intermolecular interactions energies via atom−atom potentials and by ranking the molecules in order of decreasing contribution to the total cohesive energy of the crystal. In this way, similarities and differences between crystals can be appreciated more easily.

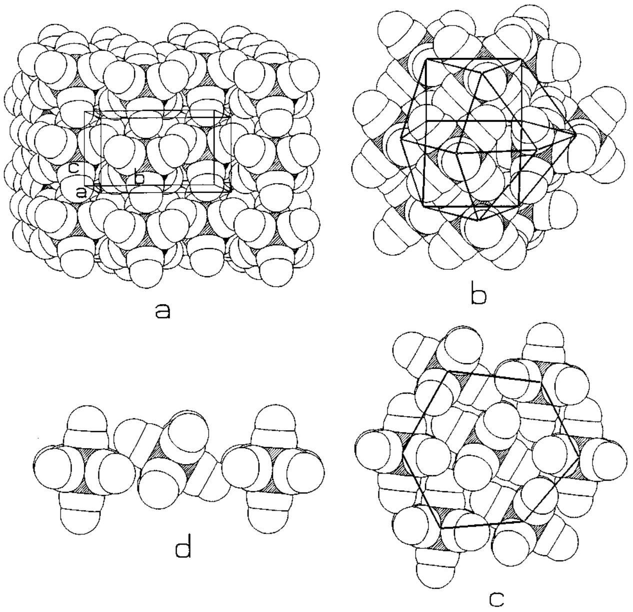


Figure 4. A schematic representation of the crystal structure decoding process: from three-dimensional packing distribution of molecules (a), to the “enclosure shell” of first neighbors (b), to a molecular layer (c), and to a molecular row (d).

The second level of the packing decoding is concerned with the interlocking of atomic groupings belonging to neighboring molecules. The crystal is reconstructed starting from pairs of molecules generated via most common symmetry operators. This energy analysis allows recognition of the most relevant structural subunits in the experimental crystal structures. Information of this type is useful for the investigation of recognition and nucleation processes, and it is transferable to other molecules containing similar structural subunits.

B. Space Group Frequency and Crystal Packing Generation

Theoretical crystal structure generation constitutes a fundamental component of crystal engineering strategies. To construct crystals computationally one also needs to know the most likely symmetry arrangements of molecules that might be expected.

Table 1. Space Group Frequencies

space group	pure organic	%	organometallics	%
$P2_1/c$	23339	100	30395	100
$P\bar{1}$	10399	44.6	17948	59.1
$P2_12_12_1$	10673	45.7	3650	12.0
$P2_1$	6810	29.2	2079	6.8
$C2/c$	3732	16.0	6725	22.1
Pbca	2855	12.2	3014	9.9
$Pna2_1$	1100	4.7	1240	4.1
Pbcn	522	2.2	834	2.7
*P*1	937	4.0	505	1.7

Clearly, if all 230 space groups were to be taken into account, the task would become extremely difficult. Fortunately, this is not necessary because most organic and organometallic molecules tend to crystallize in a very small subset of packing arrangements.[70] Space group frequencies in organic and organometallic crystals have been obtained (see Table 1) by analyzing the structures deposited in the CSD.

From Table 1 it is immediately obvious that there is no need to worry about all 230 space groups. The relative majority of organometallic crystals crystallize in the monoclinic space group $P2_1/c$, whereas the second best choice is the centrosymmetric triclinic space group $P\bar{1}$. Just these two space groups account for almost 60% of all known organometallic crystal structures characterized to date. Interestingly, the number of noncentrosymmetric crystal structures for organometallics in the CSD is lower than that for organics probably because of the lower incidence of chiral molecules in the former class of substances.

The problem of computational crystal structure generation (or crystal structure prediction[71]) has been tackled in different ways. Gavezzotti's so-called static approach[72] is based on an elaboration of Kitaigorodsky's aufbau process. The molecular crystal is constructed by translation in the three-dimensional space of a nucleus formed by molecules which are related by symmetry operators such as a screw axis, an inversion center or a glide plane. Both the nucleus energy and the crystal energy are optimized under the action of atom−atom potential functions of the type described above.[72] What is new is the combination of computation with Kitaigorodsky's ideas of close packing; in other words, larger modular units are used for the calculations. This simplifies the problem. An organometallic example of this approach is discussed below.

Alternatively, crystal structure generation can be attempted by using Monte Carlo simulated annealing.[73] This is the so-called dynamical approach and it has the advantage that no particular crystallographic assumption is necessary. The method relies solely on a brute force computation in which a collection of randomly oriented molecules are moved in space until the energy minimum is reached. The crystal structures of benzene, ethylene, and hexamethylbenzene[73] have been correctly reproduced by this method and progress has been made for more polar molecules.[74]

The method put forth by Williams is based on a combination of molecular dynamics and packing analysis.[75] The packing arrangements of hydrogen-bonded molecules has also been modeled by atom−atom potential force fields and Monte Carlo simulated annealing techniques.[76] A design strategy based on the predictable aggregation of molecules via strong hydrogen bonding interactions has been developed to generate two-dimensional layered structures of a series of dicarboxylic-urea derivatives.[77] Hydrogen-bonded structures will be discussed more extensively in section V.

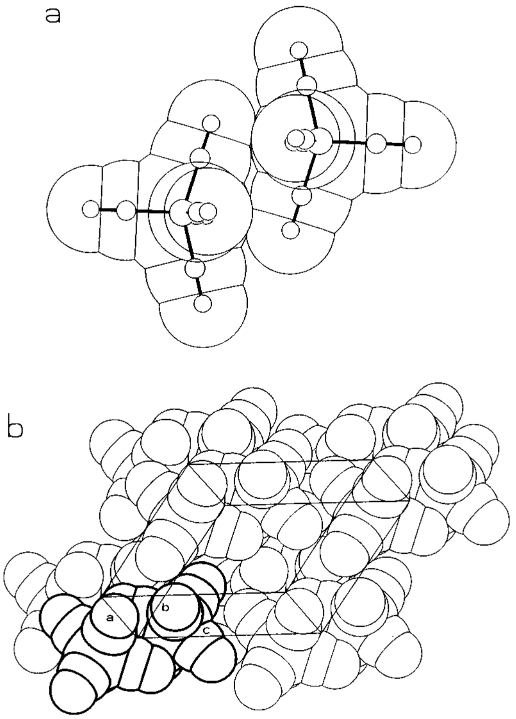


Figure 5. Space-filling representation of the crystal construction process from an hypothetical molecule of square-pyramidal [Fe(CO)$_5$] to a dimolecular nucleus (a) which is then translated in the three directions of space to generate a calculated crystal structure (b) in space group $P\bar{1}$. (Reprinted from ref 79a. Copyright 1994 American Chemical Society.)

To the best of the authors' knowledge, neither the Monte Carlo simulated annealing or molecular dynamics methods have been applied to organometallic systems, while lattice energy minimization starting from random molecular arrangements have been successfully used to generate unknown crystal structures of some metallocene and substituted metallocene complexes.[78] Some useful results have been obtained by applying Gavezzotti's approach to transition metal binary carbonyls such as [Ni(CO)$_4$], [Fe(CO)$_5$],[79a] and [Cr(CO)$_6$][79b] taken as representative of the classes of tetrahedral, trigonal-bipyramidal, and octahedral complexes. In all these cases, it was possible to retrace the experimentally determined crystal structures among other solutions of similar cohesive energy. The method was also applied to calculate hypothetical crystal packings for the model structure of square-pyramidal [Fe(CO)$_5$],[79a] i.e., for the intermediate of the Berry pseudo rotation mechanism that accounts for the fluxional behavior of [Fe(CO)$_5$] and many other trigonal bipyramidal complexes. This process can be assimilated to an ab initio crystal structure generation (see Figure 5).

In the cases of the dinuclear complexes [Co$_2$(CO)$_8$] and [Fe$_2$(CO)$_9$][80] the method was used to demonstrate that the similarity between the molecular arrangements in the crystals of the two species arises from the stereoactivity of the lone pairs on the Co atoms which occupy the space taken by the two additional carbonyl ligands in the structure of the Fe complex. When the approach is extended to higher nuclearity complexes, however, the limitations inherent to the description of the metal atoms become more and more severe. In the case of crystalline $[Fe_3(CO)_{12}]$[81a] and $[Ru_3(CO)_{12}]$[81b] the experimental crystal structures could also be retraced and compared with other computational ones, although the packing energies of the computed crystals were found to be invariably higher than those of the observed structures.

In all cases, however, rigid molecules have been used as input. This is a major drawback because most organometallic molecules possess internal degrees of structural freedom. The consequence is clear—very often there is no unique solution to the problem of minimizing the global energy of the molecule-crystal systems. Ideally the minimization should take into account the simultaneous optimization of molecular *and* crystal structure because each affects the other implicitly for organometallic crystals.[82] However, the lack of a sufficiently general intramolecular force field and the necessity of combining and scaling intramolecular versus intermolecular energy terms is the limit of organometallic crystal structure generation for structurally nonrigid systems. It may be anticipated that computational experiments that attempt to rationalize, model, and predict crystal structures and properties will almost routinely accompany laboratory experiments in crystal engineering in the future.

IV. The Cambridge Structural Database (CSD): An Essential Tool for Crystal Engineering

The Cambridge Structural Database (CSD) is an essential tool in the analysis of known crystal structures.[15] The need for a crystallographic database such as the CSD was articulated very early in the development of X-ray crystallography.[83] It is a testimony to the far-sightedness of Bernal[84] that he was able to confidentially predict more than 60 years ago that crystallographic databases would not only be useful but would also become necessary—and this at a time when the total number of crystal structure determinations was less than 100! Today, the CSD contains more than 160 000 entries and constitutes an enormous storehouse of accurate crystallographic data. Unlike most other databases, crystallographic databases contain “hard” or numerical data.[85] In contrast to “soft” or bibliographic data, such numerical data can be further manipulated and analyzed, ultimately leading to diverse and yet certain crystallographic and chemical conclusions.[86] The capacity of extracting information from a variety of structures stored in the CSD constitutes, for example, the conceptual basis of the structural correlation method of Dunitz and Bürgi which relies on the examination of the perturbation of a given fragment geometry within different crystal environments.[87]

The power of the CSD in the context of crystal engineering lies in the statistical approach it permits in the analysis of crystal structures.[88a] The underlying principle is that a range of geometries will be obtained from which the most probable geometry is chosen to be the representative one. Observed geometries that are very far from this most probable geometry correspond to extreme deformations and in the limit may even be outlier points, where different and possibly other chemical effects are important. As the number of crystal structures in the sample increases, weaker intermolecular interactions may be reliably examined; essentially, weaker signals may be discerned from the crystallographic noise.[88b] Quite apart from the fact that it is impossible today to exhaustively peruse the crystallographic literature manually, the sorts of *chemical* conclusions that a CSD analysis permits cannot be obtained from *any* manual reading of the journals, howsoever detailed. As for the future of database research, it may be reasonably anticipated that with the rapid strides in the theory and practice of crystallography, there will be a vast increase in the sizes of the various databases. It is conservatively estimated that the CSD will contain 500 000 entries by the year 2010.[89] Another likely development is that it will be possible to access all the crystallographic databases through a common platform. Already, the CSD software may be used to access the Protein Data Bank.[90] There are obvious implications for organometallic chemistry if the CSD and the Inorganic Crystal Structure Database[91] are similarly conjoined.

V. Hydrogen Bonding

Hydrogen bonding in organic and biological systems has been investigated and reviewed thoroughly.[92] However, the phenomenon has not been discussed systematically in the context of organometallic systems.[93]

The hydrogen bond is the master-key interaction in crystal engineering because it combines directionality with strength.[94] This is what makes it the interaction of choice in many crystal engineering studies. The use of hydrogen bonding has become, in the past few years, a major element in the quest for controlled supramolecular synthesis. Such studies have depended largely on crystallographic databases such as the CSD.[95]

The hydrogen bond may most generally be considered to be a three-center four-electron interaction that is attractive and directional with certain spectroscopic attributes, structure-defining effects, and reproducibility of occurrence. The energy of this bond is dominated by electrostatic factors. However, polarization, charge transfer and exchange repulsion are also important. As one obtains strong and weak covalent bonds, one obtains strong and weak hydrogen bonds and there is no real demarcation between the different kinds of hydrogen bonds. The strongest of the weak hydrogen bonds are comparable to the weakest of the strong hydrogen bonds (~ 20 kJ mol^{-1}) and in terms of crystal structure directing effects, there seems to be little difference between these categories. The distinction between strong and weak is, therefore, purely conventional. The effect of charge, for example, needs also to be taken into account as it has a great influence on the strength of these interactions since they are essentially electrostatic in nature. Negatively charge assisted,[96] positively charge assisted,[97] as well as resonance assisted[98] hydrogen bonds have been identified. It is therefore for reasons of convenience only that we discuss strong and weak hydrogen bonds separately in this section.

A. O—H···O Hydrogen Bonds Formed by Carboxyl Groups

The hydrogen-bonded carboxylic ring established by −COOH groups is the prototype of strong hydrogen-bonding systems in crystalline complexes.[92] This is a fundamental packing motif that is maintained on going from organic to organometallic solids.[99] As in the corresponding organic solids, complexes carrying one −COOH group generally form rings via interactions between two $-CO_2H$ groups, while dicarboxylic acids form chains of molecules linked by a sequence of carboxylic rings. Catemer-type chain structures are only rarely observed. Unsurprisingly, these types of hydrogen bonds are widely used in crystal engineering studies.

The organometallic complexes $[(\eta^2\text{-fumaric acid})Fe(CO)_4]$ and $[(\eta^2\text{-maleic acid})Fe(CO)_4]$ afford an educative example of the transferability of the carboxylic ring from organic to organometallic crystals. Two polymorphic modifications are known for the complex $[(\eta^2\text{-fumaric acid})Fe(CO)_4]$ (forms I and II). In form I, the fumaric acid ligands form ribbons of ligands joined by carboxylic rings (Figure 6a). This arrangement is the same as that observed in crystalline fumaric acid which also possesses two polymorphic forms both based on molecular chains interlinked via hydrogen bonded carboxylic rings (see Figure 6b). In form II of $[(\eta^2\text{-fumaric acid})Fe(CO)_4]$ both carboxylic ring and chains are found extending in a catemer-type pattern.[99]

In crystalline $[(\eta^2\text{-maleic acid})Fe(CO)_4]$ there is simultaneous presence of an intra- and of an intermolecular hydrogen bond as in crystalline maleic acid (see Figure 6c and 6d, respectively).While the two O···O distances in crystalline $[(\eta^2\text{-maleic acid})Fe(CO)_4]$ are of similar length (2.56 and 2.55 Å, respectively), in maleic acid the intermolecular O···O distance is appreciably longer than the intramolecular one (2.64 versus 2.50 Å) in keeping with the strengthening via resonance of the intramolecular ring system.

Reference 99 provides several other examples of the transferability of the carboxylic hydrogen bond ring from organic to organometallic crystals. The major problem in using this otherwise extremely powerful linker in organometallic crystal engineering arises from the difficulty of having a relatively strong acidic group carried by a metal-bound ligand. Unless group protection strategies are adopted, the interaction with electropositive metal centers may lead to unwanted formation of oxo ligands engaging the carboxilic groups in metal coordination.

B. N—H···O Hydrogen Bonds Formed by Primary and Secondary Amido Groups

Analogous relationships between organic molecules and coordination complexes are seen when the primary and secondary amido groups are present on the ligands.[100] Although most amido complexes are not strictly organometallic there often being no actual M−C bond, their participation in hydrogen bond networks is well within the scope of this review.

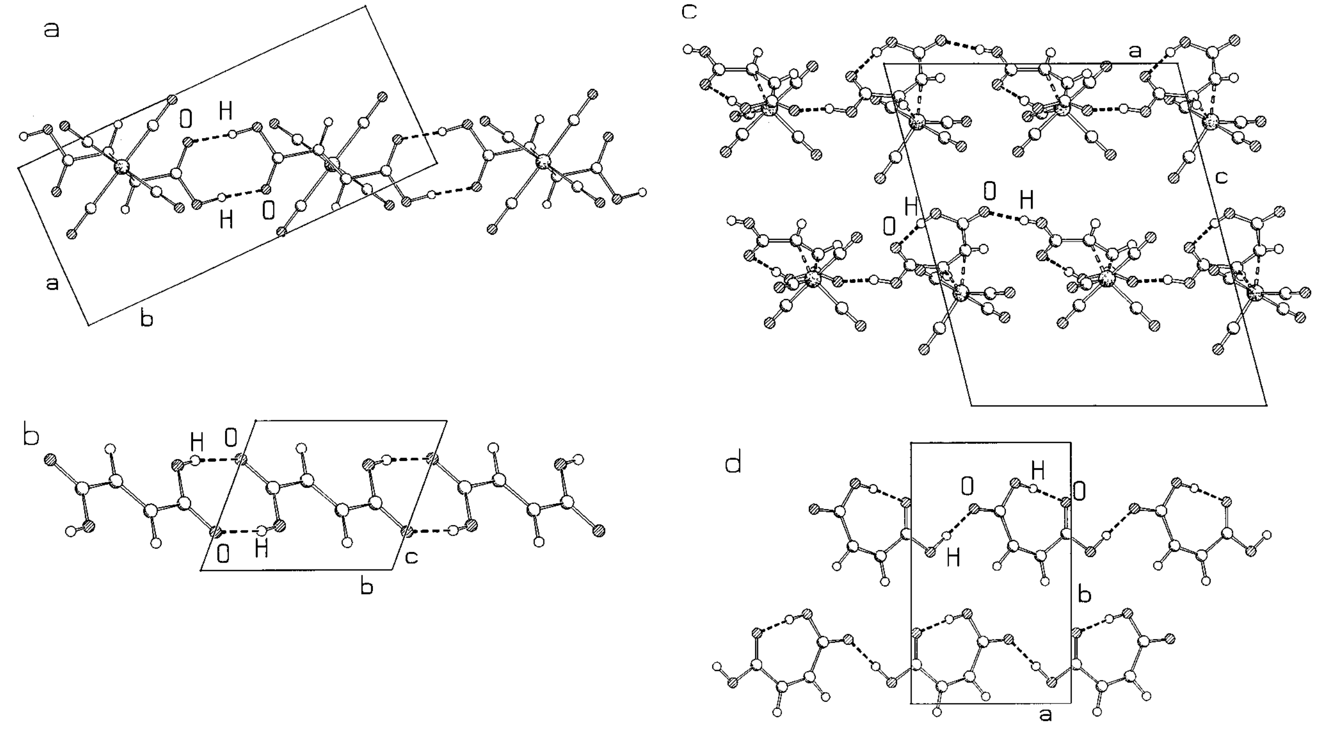
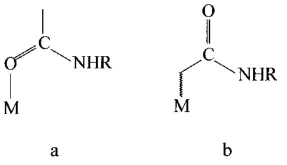


Figure 6. The ribbons of ligands joined by carboxylic rings in crystalline $[(\eta^2\text{-fumaric acid})Fe(CO)_4]$ (a) are compared with those in crystalline fumaric acid (b). The patterns of intra- and intermolecular hydrogen bonds in crystalline $[(\eta^2\text{-maleic acid})Fe(CO)_4]$ (c) and maleic acid (d). (Reprinted from ref 99. Copyright 1994 American Chemical Society.)

Scheme 1. In Metal Coordination Complexes, Primary and Secondary Amido Ligands May Be Either Directly Linked to the Transitional Metal Center(s) via the O Atom Lone Pair (a) or Belong to a Larger Metal-Coordinated Ligand System (b)



In coordination complexes primary and secondary amido groups may be either directly linked to the transitional metal center(s) or belong to a larger metal-coordinated ligand system as shown in Scheme 1.

An example of the similarity in hydrogen bond patterns between organic and organometallic amides is shown in Figure 7. In the complex (cyclopentadienyl)–carbonyl–nitrosyl–carbamoyl–manganese the metal atom is coordinated to one formamide moiety which forms a cyclic amide dimer. The same packing motif in crystalline formamide allows a shorter N···O separation (2.88 Å versus 2.95 Å) than in the complex. The second amide hydrogen of the complex does not participate in intermolecular interactions but points toward the N atom of the NO ligand. In the complex, however, the amide O atom establishes an additional link (which probably takes the place of the second N–H···O interaction commonly observed in primary amides) with an H atom belonging to the Cp ligand [C···O 3.33, (C)H···O 2.39 Å, C–H···O 145.2°].

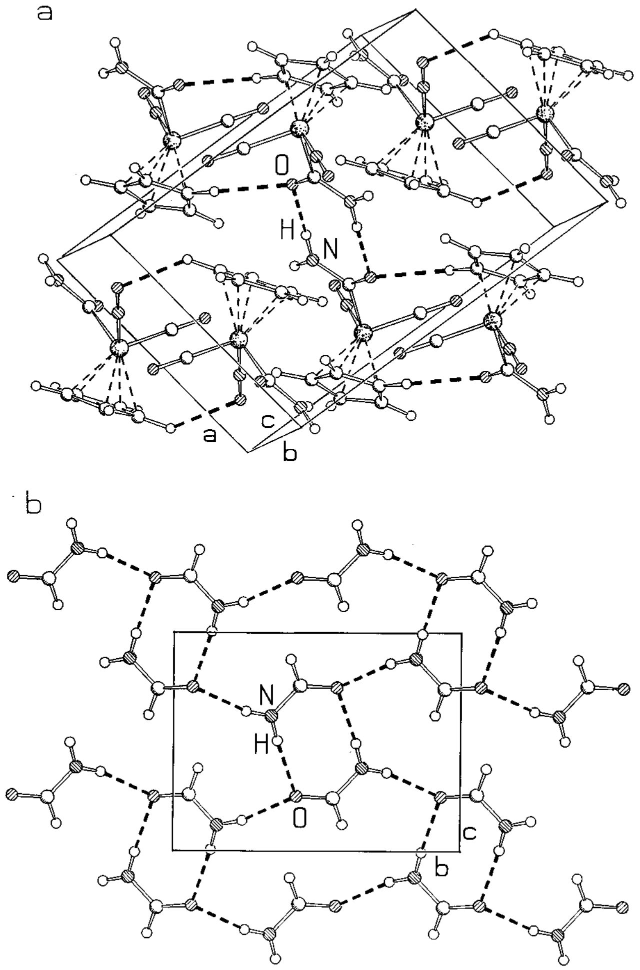


Figure 7. In the complex [(cyclopentadienyl)-carbonyl-nitrosyl-carbamoyl-manganese] (a) the metal atom is coordinated to one formamide moiety which forms a cyclic amide dimer as in crystalline formamide (b). (Reprinted from ref 100. Copyright 1996 American Chemical Society.)

Transition metal complexes, however, form a greater number of hydrogen bonds per molecule because of the more frequent occurrence of bifurcation. In the case of amido complexes a greater proportion of hydrogen bonds tends to linearity, perhaps because of steric factors.[100]

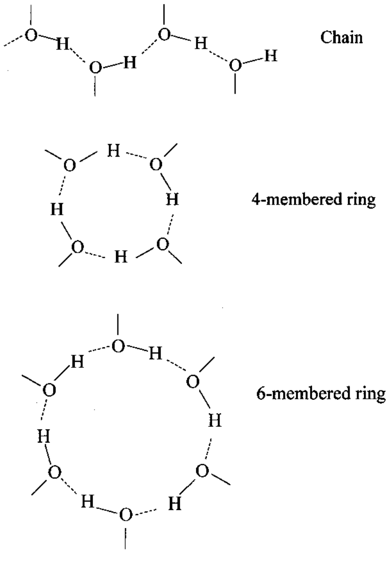
C. O–H···O Hydrogen Bonds Formed by Hydroxyl Groups

Another common hydrogen-bonding donor–acceptor pair is that formed by the –OH group. Recently, the crystal packing of monoalcohols has been investigated with a focus on the occurrence of high-symmetry space groups.[101] Generally –OH groups form chains or rings, and in particular tetramers and hexamers are quite common in crystals of organic alcohols (see Scheme 2).

These packing motifs are often maintained in crystals of organometallic complexes as shown in Figure 8. For example, the basic packing motif in crystalline $[(\eta^3\text{-C}_7\text{H}_{10}\text{OH})(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_2]$ is a tetramer (Figure 8a) while a hydrogen bonded hexameric unit is present in crystalline $[(\eta^5\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{-OH})_2\text{Fe}_2(\text{CO})_4]$ (Figure 8b).[102]

Because of the possibility of forming ring systems that confer additional stabilization to the hydrogen bonding network, strong donor–acceptor systems such as –COOH, –CONH$_2$, and –CONHR dominate the molecular packing in organic as well as in organometallic crystals. This is maintained even in the presence of other, although weaker, acceptors such as the CO ligand. When the donor is –OH, however, this is not so. In crystals of carbonyl complexes this ligand may compete with the –OH

Scheme 2. Hydrogen-Bonding Motifs in Crystalline Organic Alcohols: Chain, Four-Membered Ring, and Six-Membered Ring



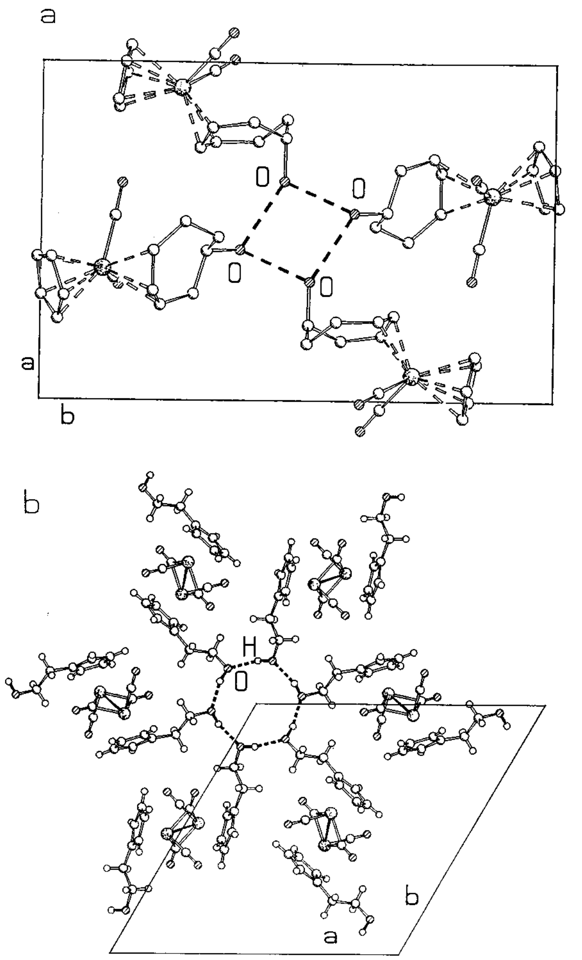


Figure 8. Packing motifs in crystalline transition metal complexes carrying hydroxyl groups: (a) four molecules forming a tetrameric ring in crystalline $[(\eta^3\text{-}C_7H_{10}OH)(\eta^5\text{-}C_5H_5)Mo(CO)_2]$ and (b) the hexameric unit present in crystalline $[(\eta^5\text{-}C_5H_4C_2H_4OH)_2Fe_2(CO)_4]$. (Reprinted from ref 99. Copyright 1994 American Chemical Society.)

group as the hydrogen bond acceptor, especially when steric reasons hinder optimum O—H···O interaction and ring formation. In these cases, the balance between number of acceptors and number of donors may require the participation of C—H groups in the hydrogen bonding scheme. A typical example is crystalline $[\{C_6H_4(C_5H_4MeOH)\}Cr(CO)_3]$,[103] wherein and as shown in Figure 9, the —OH groups participate in a bifurcated interaction with two CO ligands and accept hydrogen-bond donation from the arene C—H group (the two O—H···O(C) bonds and the C—H···O(H) one are comparable in length: 2.29, 2.44, and 2.27 Å, respectively).

The stabilization afforded in the solid state by hydrogen bonds between alkynediols and alkynols groups in metal coordinate alkynes has been elegantly exploited by Walther et al. to isolate zerovalent homoleptic compounds of the composition $[(\text{alkyne})_2Ni]$ and $[(\text{alkyne})_4Ni_3]$ complexes.[104] These complexes are of importance as starting materials for organometallic reactions and in catalytic processes. It has been observed that molecules of the monoalcohol derivatives, such as [(*tert*-butyl-bis(ethyl)-alkynol)$_2$M], and [(*tert*-butyl-cyclohexyl-alkynol)$_2$M] (M = Ni, Pt) are linked in pairs in the solid state via O—H···O hydrogen bonds.[105] The four —OH groups, two on each complex, form a tetrameric arrangement as shown in Figure 10a. Irrespective of the metal type, these tetrameric units are comparable, in terms of geometry, with those formed by the corresponding organic alcohols. The effect of complexation is manifested in an appreciable lengthening of the O···O separations. The complexes [(*tert*-butyl-bis(methyl)-alkynol)$_2$M] (M = Ni, Pt) form chains.

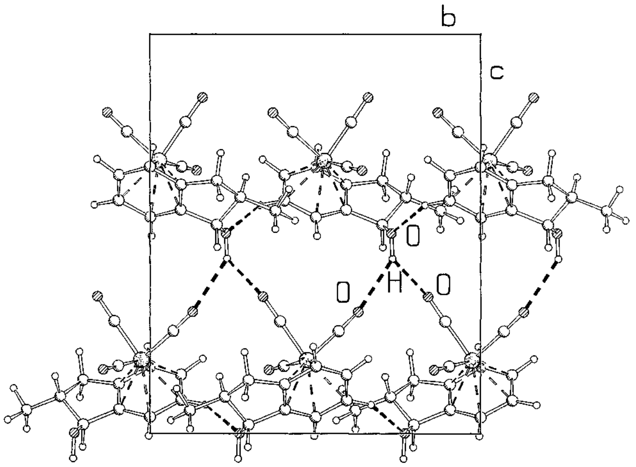


Figure 9. The —OH groups in crystalline $[\{\eta^6\text{-}C_6H_4(C_5H_4\text{-}MeOH)\}Cr(CO)_3]$ participate in a bifurcated interaction with two CO ligands and accept hydrogen bond donation from the arene C—H group. (Reprinted from ref 99. Copyright 1994 American Chemical Society.)

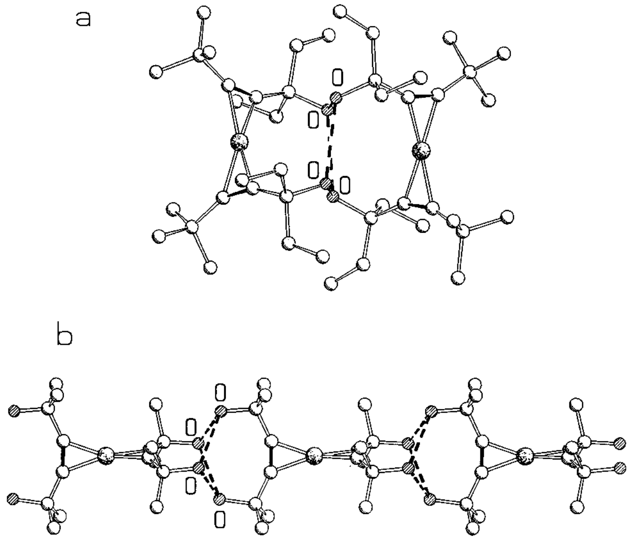


Figure 10. (a) Hydrogen-bonded dimers formed via tetrameric arrangements of the —OH groups in crystalline [(*tert*-butyl-bis(ethyl)alkynol)$_2$M], and [(*tert*-butyl-cyclohexyl-alkynol)$_2$M] (M = Ni, Pt). (b) A row of molecules connected via hydrogen bond rings on either side of the metal centers in the case of the bis-methyl and bis-ethyl alkyndiol derivatives of both nickel and platinum.

It has been pointed out that dimerization via O—H···O bonds not only maximizes O···O approach, but also generates a “protected” system wherein the hydrogen-bonded ring is encapsulated within a sheath of C atoms. In such a way the dimer is, in effect, a van der Waals system (the most polar part is segregated within the organic envelope) and the packing of the complex reduces to that of a larger van der Waals object.[105] Crystals of the bis-methyl and bis-ethyl alkynediol complexes of the same metals, [(alkynediol)$_2$M (M = Ni, Pt)], maintain the fundamental packing motif seen for alkynols with the important difference that the dimer becomes a molecular row connected via two identical sets of hydrogen bond rings on both side of the metal centers. Despite this similarity, however, there is a profound geometric change with respect to the bis-alkynol complexes because the tetrameric O—H···O units are formed by two pairs of O—H groups belonging to the same ligand while they necessarily belong to the two different ligands in bis-alkynol complexes (see Figure 10b).

A large number of α-ferrocenyl alcohols has been synthesized by Glidewell et al. and the packing in the solid-state investigated in terms of hydrogen bonded interactions.[106]

D. Weak Hydrogen Bonds. The Organometallic C—H···O Hydrogen Bond

The role played by C—H···O interactions in determining crystal structure stability is now well-established, and there is converging evidence of C—H···X (X = O, N, S, Cl, maybe F) acting as crystal structure sieves in the nucleation process of stable crystal nuclei.[59b,107–109] It has also been demonstrated that C—H···O interactions are able to restrain the thermal displacement of H-bonded atoms in crystals, thus behaving like true intermolecular bonds.[110] Such evidence is important because there is still skepticism as to whether some of these short contacts are actually repulsive in nature and are stabilized by other attractive interactions in the crystal, in other words that they are the forced consequences of packing rather than packing directors. Hydrogen bonds of the C—H···O type are pervasive in crystalline organometallic transition metal complexes and clusters where C—H groups (mainly in sp^2- and sp-hybridized systems) and the CO base are abundant.[111]

An intriguing feature of C—H···O hydrogen bonding in organometallic complexes is that the C—H group matches the CO ligand in softness. Accordingly, C—H···O bonds to such ligands may be formed in preference to stronger O—H···O and N—H···O hydrogen bonds that must be formed with the harder O—H and N—H groups. C—H···O bonds in organometallic compounds are also quite directional, with the C—O···H angle around 140°, irrespective of the mode of bonding, i.e., both terminal and bridging ligands are approached in ketonic-like directions. This observation indicates that at least in the solid state and in the presence of C—H donors, there is O atom lone pair electron density in ketonic directions even when the CO ligand is in the terminal bonding mode. An example of the participation of terminal ligands in several hydrogen bonds of the C—H···O type is shown in Figure 11.

There are several reasons that make hydrogen bonding to the CO ligand important for crystal cohesion:

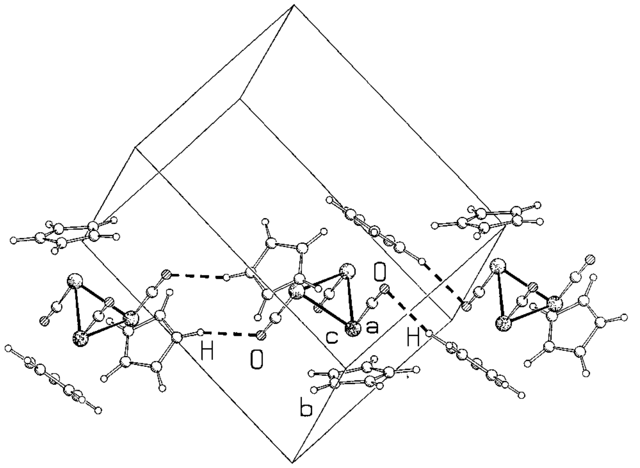
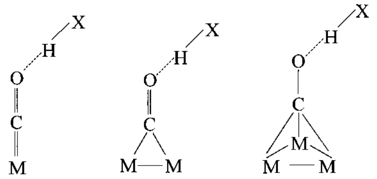


Figure 11. Terminal CO ligands in crystalline [Cp$_3$Ir$_3$(CO)$_3$] participate in several interactions of the C—H···O type with the hydrogen atoms of the Cp ligands. (Reprinted from ref 52. Copyright 1995 American Chemical Society.)

Scheme 3. Schematic Representation of the M—CO···H Interactions in the Cases of Terminal, Doubly, and Triply Bridging CO Ligands



i. A Profusion of Weak Donors. Most organometallic complexes carry ligands such as arenes, cyclopentadienyl ligands, phenyls, methylidine, and methylidyne groups, which are all capable of hydrogen bond donation via acidic C—H groups; hydrogen bonding involving the M—H donor (see below) is also possible.

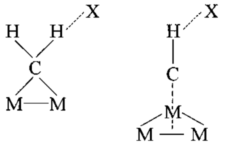
ii. The Absence of Other Commoner Acceptor Sites. Ligands carrying organic-type acceptors are not very common in organometallic chemistry. The stabilization of low oxidation states requires neutral π-acid ligands such as C≡O, capable of interacting with the metal in the electron σ-donation/π back-donation synergistic ligand—metal interaction.[24]

iii. Tunable Basicity. The basicity of the CO ligand increases with the increase in the ketonic nature of the C≡O bond on passing from the terminal to the doubly and finally to the triply bridging bonding mode (see Scheme 3). The basicity of the O atom here is, however, small in comparison to the O atoms in more polar compounds. The CSD study afforded a scale of CO ligand basicity purely on the basis of crystallographic data, an approach similar to that used to correlate C—H···O distances and C—H acidity in organic crystals.[112]

iv. Bifurcation. Such interactions are also quite common as might be expected in donor-rich systems.

Molecules belonging to the family of clusters [(Cp^R)$_3$M$_3$(CO)$_3$] (M = Co, Rh, Ir; Cp^R = C$_5$H$_5$, C$_5$Me$_5$, C$_5$H$_4$Me) provide examples of C—H···O bonds involving μ_3, μ_2, and terminal ligands (see also Figure 11).[52] The relative acidity of C—H groups belonging to facially bound benzene and trithiane ligands (trithiane = μ_3-S$_3$C$_3$H$_6$) has been assessed by comparing C—H···O bonds in crystalline [Ru$_3$(CO)$_9$(μ_3:η^2:η^2:η^2-C$_6$H$_6$)] and [Ru$_3$(CO)$_6$(μ-CO)$_3$(μ_3-S$_3$C$_3$H$_6$)]. In this latter crystal, the bridging CO ligands form short bonds with the trithiane ligand (H···O distances in

Scheme 4. Schematic Representation of μ_2-CH_2···OC and μ_3-CH···OC Interactions in Crystalline Complexes



the range 2.262–2.538 Å) while $[Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ forms several bonds involving the facially bound benzene ligands and the CO ligands, the shortest distances being 2.416 and 2.372 Å.[113] The trithiane ligand has also been found to form shorter C–H···O interactions with bridging than with terminal CO ligands in crystals of the two isomers $[Ir_4(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}S_3C_3H_6)]$ and $[Ir_4(CO)_9(\mu_3\text{-}S_3C_3H_6)]$.[114] Tetranuclear Co clusters carrying the trithiane ligand or its derivatives have also been synthesized and structurally characterized with a focus on the intermolecular organization in their crystals.[115]

Other chemically and structurally relevant manifestations of CO ligand basicity are the formation of end-on (isocarbonyl) species when CO ligands interact with Lewis acids[116] and the formation of tight ion pairs when carbonyl anions interact with alkali metal cations.[117] It has been argued,[117] in the context of these studies, that the need of optimizing the interaction with the electron density in both σ- and π-orbitals of terminal CO ligands may be responsible for the observed angularity of the interaction with electrophiles. The manifestation of CO basicity in the solid state, including M–C–O···HOH hydrogen-bonding interactions with water and $M\text{–}C\text{–}O^{\delta-}\cdots H^{\delta+}$ interactions between carbonyl anion species (usually carbonyl clusters) and organic-type cations has been recently discussed.[118]

Methylidyne (μ_3-CH) and methylene (μ_2-CH_2) ligands bound to transition metal clusters also form hydrogen bonds of the C–H···O type with O atoms of CO ligands.[119] The order of acidity judged from the average length of the hydrogen bonding interactions is μ_3-CH > μ_2-CH_2; the interactions are comparable in length to those established by alkyne and alkene hydrogens in organic systems hence methylidyne and methylene C atoms behave as sp and sp^2-hybridized C atoms, respectively (see Scheme 4). These observations are in keeping with a model of ligand–metal bonding based on σ donation from the ligand and retrodonation from metal atom d orbitals of suitable orientation into empty π^* orbitals on the ligand, rather than as distorted sp^3 hybrids. As pointed out above, in the case of ionic systems the charge difference between anions and cations reinforces the hydrogen bonding interactions leading to shorter (C)H···X separations than in the case of neutral species.

The cluster $[Co_3(\mu_3\text{-}CH)(CO)_9]$ carries three terminal CO ligands on each Co atom, while the methylidyne ligand is bound to the metal triangle. The methylidyne ligand participates in a trifurcated interaction (Figure 12a) with two neighboring molecules forming a centrosymmetric dimer based on a 10 atom ring and a chain motif involving two axial CO ligands. The neutron diffraction H···O distances are in the range 2.50–2.63 Å.[120] As an example of hydrogen bonding between the methylene hydrogen and carbonyl oxygens the crystal structure of $[Cp_2Mn_2(CO)_4(\mu_2\text{-}CH_2)]$ is shown in Figure 12b. The molecules are held together in piles along the *c* axis by two HCH···O and two H(Cp)···O interactions of comparable length (2.56 and 2.50 Å, respectively).[121]

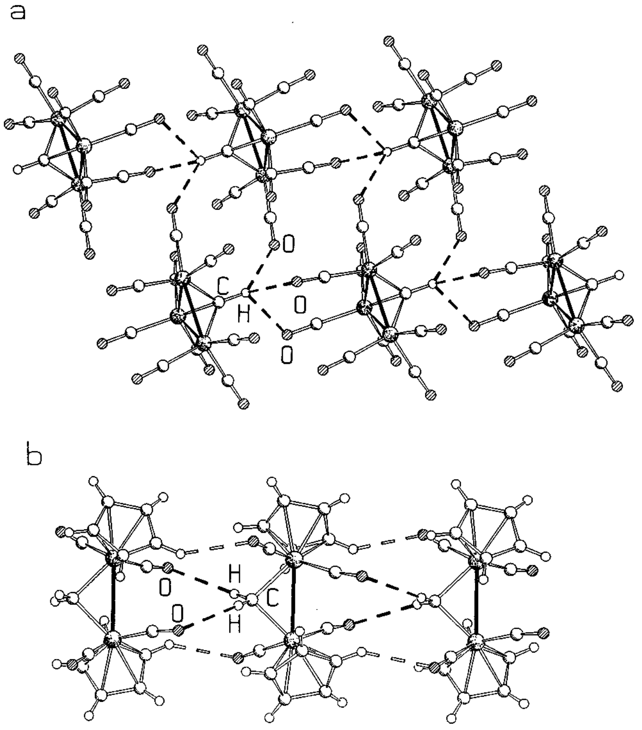


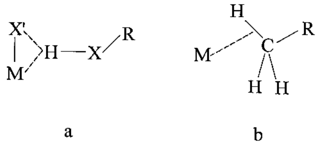
Figure 12. (a) Hydrogen bonding network in crystalline $[Co_3(\mu_3\text{-}CH)(CO)_9]$, note how the methylidyne ligand participates in a trifurcated interaction with two neighboring molecules and (b) hydrogen bonding in crystalline $[Cp_2Mn_2(CO)_4(\mu_2\text{-}CH_2)]$. The molecules form piles along the *c* axis and are held together by two HCH···O and two Cp–H···O interactions of comparable length.

In 1981 Muetterties recognized the structural importance of intermolecular hydrogen bonding interactions involving CO. He was able to show that the agostic C–H system in the tetranuclear methylidyne cluster $[HFe_4(\eta^2\text{-}CH)(CO)_{12}]$ is sufficiently acidic so as to form a C–H···OC interaction between a terminal CO ligand and the H atom of the C–H group.[122] An intermolecular μ_3-CH···O bond involving the methylidyne group is present also in the phospine derivative of the same cluster species.[123]

E. Hydrogen Bonds Involving Transition Metal Atoms

Metal atoms in coordination complexes and clusters are amphoteric. It has been shown[124] that the bond between a transition metal and a hydrogen atom is highly polarizable and can undergo reactions as H^+, $H^\cdot$, and H^- depending on the relative stability of the resulting species. The behavior depends on a number of factors, such as electronic configuration, oxidation state, and electronegativity of the metal as well as the type and distribution of ligands. This amphoteric behavior is reflected in the capacity of a metal atom

Scheme 5. Schematic Representation of the Intermolecular Multicenter Hetero-Acceptor (IMH) Hydrogen Bond (a) and of the Intermolecular Pseudo Agostic (IPA) Interaction (b)



in a coordination complex of accepting or donating electron density, i.e., in the Lewis acid/base character. The intramolecular three-center two-electron agostic interactions[125] between an electron-deficient metal atom and a C−H σ bond of a ligand M···(H−C) has long since being recognized as a manifestation of metal atom Lewis acidity. M···(H−C) interactions still elicit much research interest because of the possible connection with C−H bond activation by metal atoms.[126] Metal atom hydrogen bonding accepting capacity, in other words the formation of three-center four-electron interactions in which an electron-rich metal atom is capable of accepting hydrogen bond donation from a suitable donor, has also been observed. For example, O−H···M interactions in solution have been the subject of a number of spectroscopic studies.[127,128]

Recently, the manifestation of acid−base behavior of transition metal atoms in the solid state has been investigated by means of the CSD.[129] It has been demonstrated that formation of intermolecular hydrogen bond with an electron-rich metal center is a common phenomenon, observed with all traditional hydrogen-bonding donor groups. It has also been shown that *intermolecular* electron donation from covalent bonds, to satisfy the electronic requirements of electron deficient metal atoms, is a well-defined phenomenon.

Two novel types of interactions have been characterized: (i) the intermolecular multicenter hetero-acceptor (IMH) hydrogen bond formed when the X−H donor group interacts with $M{-}X'_n$ systems, where M is an electron-rich metal and X′ a metal coordinated electronegative atom (X′ = S, N, O, Cl), and (ii) the intermolecular pseudoagostic (IPA) interaction in which the X−H bond can donate electron density to electron-deficient metal atoms M···(H−X), as observed in intramolecular agostic interactions (see Scheme 5). M···(H−X) interactions have been previously detected in the ion-pair adducts between anionic Lewis acids and electron-deficient and coordinatively unsaturated zirconocene compounds prepared by Marks and co-workers.[130] Hydrogen bonding to metal centers in neutral complexes (X−H···M) have been compared with charge assisted ($X{-}H^{+}\cdots M^{-}$) hydrogen bonds involving electron-rich anionic complexes. The notations X−H···M and M···(H−X) indicate a flow of electron density from right to left, i.e., from Lewis base to acid.

Scattergrams of X···M versus (X)H···M distances and versus X−H···M angles have been obtained for X = C, N, and O. The reader is referred to ref 129 for a detailed discussion. In this context only the scattergrams for X = C are reported (see Figure 13) because the number of organometallic ligands containing C−H groups is much larger than that of the ligands containing O−H or N−H groups. The distribution of the C−H···M interactions, however, follows the same trend as in the O−H···M and N−H···M cases. There are many examples of C−H···M hydrogen bonds, also of the IMH type, as well as several M···(H−C) IPA interactions. Such interactions are usually, although not always, associated with the presence of tight ion pairs formed by an electron-deficient metal cation and the counterion carrying methyl or phenyl groups. There is also a significant number of structures for which the (C)H···M separation is shorter than 2.5 Å which, in the case of organic C−H···X bonds, is taken as indicative of fairly strong C−H···X interactions. It can also be seen that there are several cases for which H···M ≅ C···M, i.e., falling under the condition for IPA interactions, as well as cases of short (C)H···M separations associated with large C−H···M angles corresponding to C−H···M hydrogen bonds.

In the case of X = O, there are cases for which H···M < 2.6 Å, O···M > 3.0 Å, and O−H···M angles > 100°, i.e., corresponding to the geometrical requirements of a hydrogen bond. Some of these are bonds of the IMH-type (see below). The distributions discussed above for O atom donors are also observed for N with the important difference that some of the strongest interactions correspond to inter-ionic $M^{(-)}\cdots HNR_3^{(+)}$ interaction between carbonyl anions and quaternary amino cations [distance N···M > (N)H···M, N−H···M ca. 180°], i.e., to charge assisted hydrogen bonds.

An example of intermolecular multicenter heteroacceptor (IMH) interaction is provided by the square-planar copper complex $[CuL_2L'_2]\cdot 2[H_2O]$ (L = N-acetyl-α-alaninato, L′ = *N*-methylimidazole).[131] The water molecules of crystallization are hydrogen bonded to two complexes filling in the coordination around the metal. Figure 14 shows how the water H atom participates in a bifurcated link with the Cu atom and one O atom of the ligand, constituting a five-membered metallacycle. The (O)H···Cu and (O)H···O separations are 2.568 and 2.027 Å, respectively.

A charge-assisted, three-center four-electron, ($N{-}H^{\delta+}\cdots M^{\delta-}$) hydrogen bond is formed by the anion $[Co(CO)_4]^-$ and counterions of the $[NR_3H]^+$ type (R = Me, Et).[132] The structure of the $[NMe_3H]^+$ salt represents probably the first example of a direct interaction between an acid proton and a carbonyl anion (see Figure 15). The two independent N···Co separations are 3.379 and 3.398 Å, while the (N)H···Co distances are 2.371 and 2.389 Å, and the angles N−H···Co are 179.5° and 179.7°, respectively. In the crystal structure of the $[NEt_3H]^+$ salt determined by neutron diffraction at 15 K, the N···Co and (N)H···Co distances are 3.666 and 2.611 Å, respectively.[133] Pt···H−N intramolecular interactions have been observed in the complex formed between square planar $[NPr^n_4]_2[PtCl_4]$ and *cis*-$[PtCl_2(NH_2Me_2)]$.[134] Other examples of three center four electron interactions are known.[135] It is however, worth mentioning

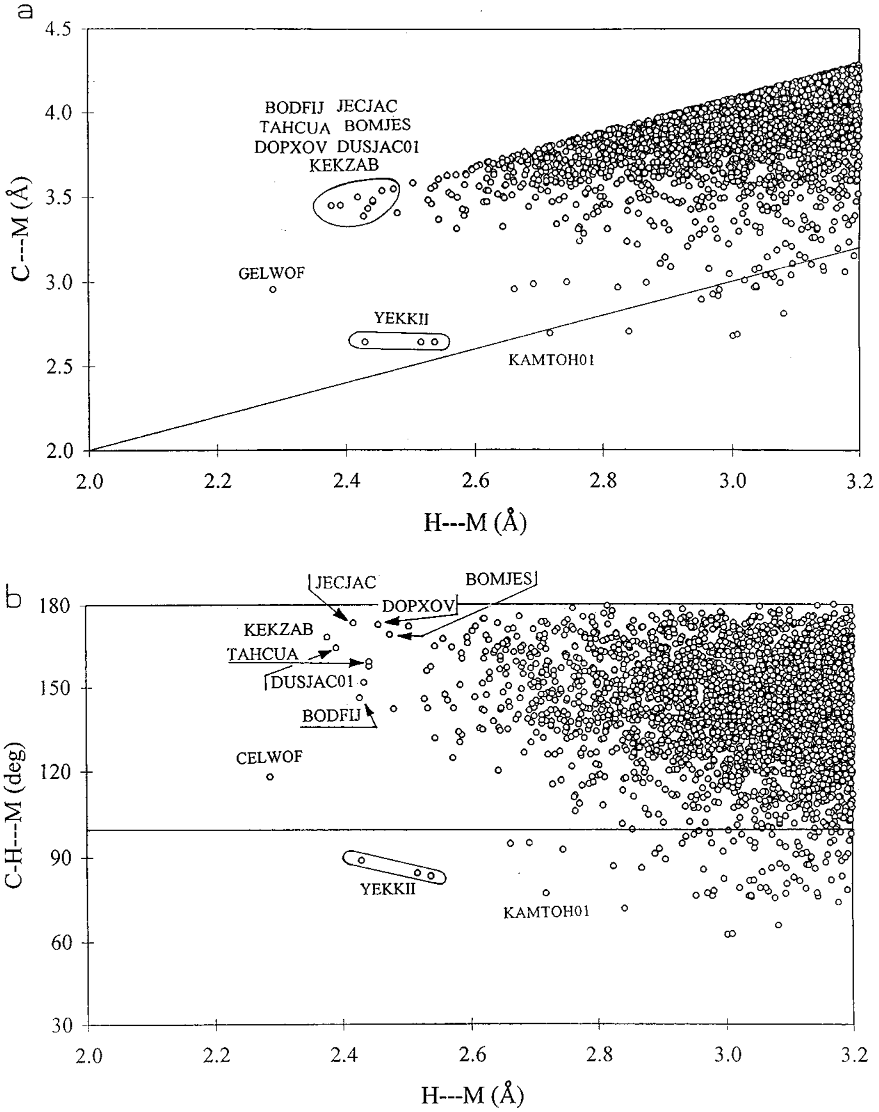


Figure 13. Scattergrams of C···M versus (C)H···M (a); and of C—H···M versus (C)H···M (b). The diagonal line in a indicates the separation between IPA and other interactions, while the horizontal line in b marks the separation between interactions with C—H···M < 100° and C—H···M > 100°. (Reprinted from ref 129. Copyright 1997 American Chemical Society.)

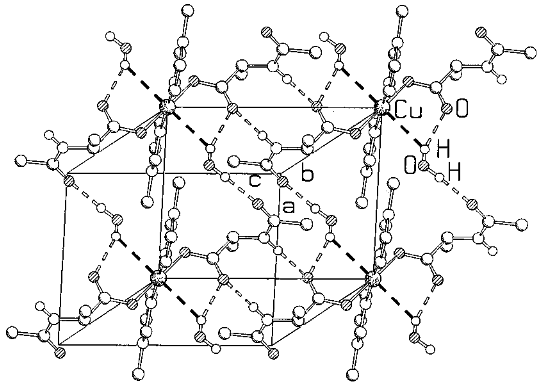


Figure 14. Intermolecular multicenter hetero-acceptor interaction in crystalline $[CuL_2L'_2]\cdot2[H_2O]$ (L = *N*-acetyl-α-alaninato, L′ = *N*-methylimidazole). (Reprinted from ref 129. Copyright 1997 American Chemical Society.)

that a three center four electron $Pt^{(II)}\cdots(H-N)$ interaction has been observed in the zwitterionic complex $[PtX(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)]$ (X = Cl, Br).[136] This interaction has also been investigated theoretically.[137]

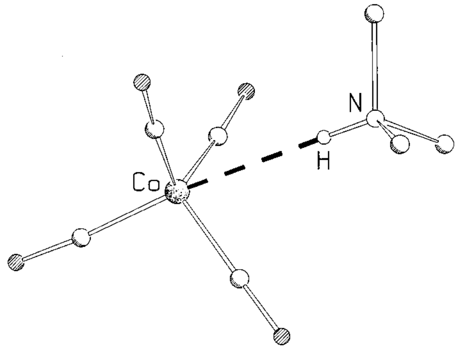


Figure 15. The N—H···Co hydrogen bond in crystalline $[NMe_3H][Co(CO)_4]$.

The structure of $[(Cp^*)_2ZrMe][(C_6F_5)_3BMe]$ (Figure 16) represents a prototype[138] of a number of electron-deficient coordinatively unsaturated cationic zirconocene complexes which participate in intermolecular pseudoagostic (IPA) interactions. These interactions are characterized by the presence of short Zr···H and Zr···C interactions due to the close approach of the B atom bound CH_3 group to the

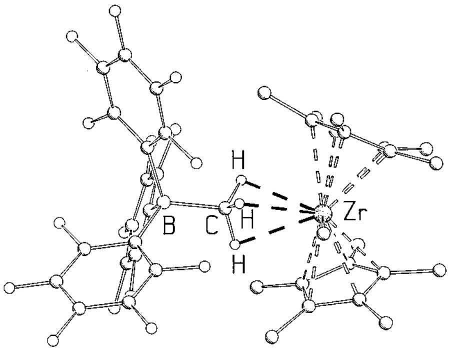


Figure 16. Intermolecular pseudo agostic (IPA) interactions in crystalline $[(Cp^*)_2ZrMe][(C_6F_5)_3BMe]$. (Reprinted from ref 129. Copyright 1997 American Chemical Society.)

electron deficient Zr atom. IPA interactions can be identified in Figure 13a and 13b (C···M ≈ H···M and C—H···M <100°).

1. The M—H···O≡C Intermolecular Hydrogen Bond

If transition metal atoms and metal-bound CO ligands can be seen as nontraditional hydrogen bond acceptors the M—H group is a nontraditional hydrogen bond donor.[139] It has been demonstrated[140] that metal-bound hydrogen atoms (metal hydrides[141]) in polymetallic complexes can form hydrogen bonds with suitable bases (usually CO), provided that the hydrogen ligand is not sterically hindered. When the approach is not forbidden by the encapsulation of the H ligand within the ligand shell, the H atoms form intermolecular bonds comparable in length with those of the C—H···O≡C type discussed above. Needless to say, the electronic nature of the metal plays a fundamental role in *tuning* the polarity of the M—H system. In general, a positive polarization of the metal-bound H atom is observed in neutral polynuclear cluster complexes where the hydrogen atom is most often present in μ_2 or μ_3 bonding fashion. As a matter of fact, polynuclear hydrides are most often obtained by protonation with acids of carbonylate anions of group VIII transition metals.[142]

A good example is afforded by the structure of $[(\mu\text{-H})(\mu\text{-NCHCF}_3)Os_3(CO)_{10}]$[143a] which has been determined by neutron diffraction. As shown in Figure 17a each cluster molecule participates in two types of hydrogen-bonding interactions. The hydrogen bond involving the H(hydride) effectively links molecules via a direct interaction with a terminally bound CO [(Os)H···O 2.594 Å]. Dimers of molecules are also formed via C—H···O bonds [(C)H···O 2.571 Å] forming a ring of the type observed in the case of strong hydrogen bonding situations. Crystalline $[(\mu\text{-H})_3Os_3Ni(CO)_9(C_5H_5)_2]$[143b] also shows the cooperative effect of Os—H···O and C—H···O hydrogen bonds, the former links molecules in chainlike fashion while a C—H group belonging to a C_5H_5 ring and a terminally bound forms a ring with two molecules related by a center of inversion (see Figure 17b).

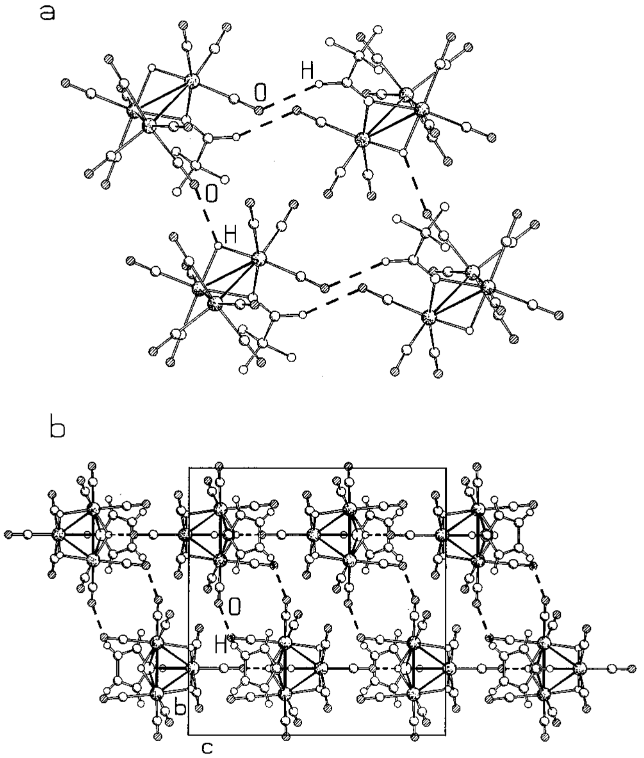


Figure 17. Intermolecular M—H···OC interactions. (a) In crystalline $[(\mu\text{-H})(\mu\text{-NCHCF}_3)Os_3(CO)_{10}]$ each cluster molecule participates in two types of hydrogen bonding interactions. (b) The cooperative effect of Os—H···O and C—H···O hydrogen bonds in crystalline $[(\mu\text{-H})_3Os_3Ni(CO)_9(C_5H_5)_2]$. (Reprinted from ref 140. Copyright 1996 American Chemical Society.)

2. Intramolecular Agostic Interactions M···(H—C)

It is important to address, in the context of this section, the similarities and differences between intramolecular agostic interactions and hydrogen bonds. In contrast to hydrogen bonds that can be formally designated as three-center four-electron interactions, an agostic interaction is of the three-center two-electron type wherein an electron-deficient metal makes a close approach to an electron-rich C—H bond. Metals such as Zr and Ta are typically involved. Interestingly, the electron-deficient Li atom also participates in an agostic interaction.[144] Figure 18 shows the tribridged structure of $[LiBMe_4]$ wherein the BMe_4 units are linked by one tri- and two dibridged C—H···Li contacts to form a linear chain. Such cases are not surprising because of the high Lewis acidity of Li^+.

In summary, X—H···M hydrogen bonding interactions are quite common when donors such as nitrogen, oxygen, and carbon can approach the nucleophilic (electron-rich) metal center. Enhanced basicity is usually associated with late transition metals in

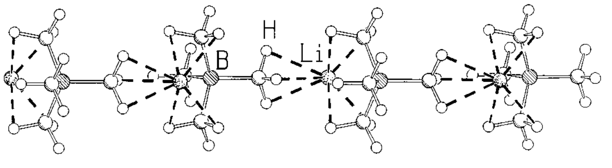


Figure 18. In crystalline $[LiBMe_4]$ the $[BMe_4]$ units are linked by one tri- and two dibridged C—H···Li contacts to form a linear chain.

low oxidation states. When the metal atom acceptor carries a ligand with electronegative atoms, polyfurcated hydrogen bonding is formed between the donor atom and those forming the electron-rich system. On the other hand, when the metal atom is electron-deficient, as in the case of some early transition metals, the metal can act as an acid accepting electron density *intermolecularly* from suitable donors, including σ bonds belonging to the counterions. This acid−base behavior is analogous to that present in intramolecular agostic interactions. IMH and IPA intermolecular interactions are specific to organometallic systems and have no counterpart in organic chemistry.

3. Intermolecular and Intramolecular Interactions of the M−H···H−X Type

We have seen that the polarity of the M−H bond can be tuned from $M^{\delta-}-H^{\delta+}$ to $M^{\delta+}-H^{\delta-}$ depending on the mode of coordination of the H atom, on the electronic state of the metal, and on the nature of the other ligand(s) bound to the metal centers. In view of this amphoteric behavior it is thus not surprising that the $M^{\delta+}-H^{\delta-}$ system may attractively interact with groups of opposite polarization $H^{\delta+}-X^{\delta-}$, such as those usually acting as H-bond donors. The existence of attractive M−H···H−X interactions further demonstrates the duality of the M−H system with regard to its participation in hydrogen-bonding interactions.

The intramolecular interaction between two hydrogen atoms in M−H···H−X systems (X = C, N, O, S) can be weakly attractive in nature as demonstrated by spectroscopic,[145,146] and diffraction[147] experiments and discussed in theoretical studies.[148] These interactions in general involve terminally bound H atoms. The crystalline complexes *cis*-$[IrH(OH)(PMe_3)_4][PF_6]$[149a] and *cis*-$[IrH(SH)(PMe_3)_4][PF_6]$[149b] represent an interesting comparative case. The hydrogen atom bound to the metal coordinated oxygen in the first complex establishes an intramolecular interaction with the hydride ligand (Ir−H···H−O 2.334 Å). In the isoelectronic SH derivative, the orientation of the SH group is such that the sulfur-bound hydrogen atom points outward far away from the hydride ligand but directed toward the F atoms of the $[BF_4]^-$ anions (see Figure 19).

An important role of $C-H\cdots F(BF_4^-)$ interactions has also been observed in crystalline $[(\eta^5-C_5H_5)(PMe_3)_2RuH_2][BF_4]$ where H···F distances in the range 2.3−2.5 Å between cyclopentadienyl hydrogens and the counterion have been observed by neutron diffraction at 20 K.[150] The existence of C−H···F hydrogen bonds is being actively debated today. In question is the actual van der Waals radius of the F atom and whether geometrical criteria alone are meaningful in identifying this sort of putative hydrogen bond. Good evidence of the role in crystal structure cohesion of "charge assisted" $X-H^{\delta+}\cdots F^{\delta-}$ interactions (X = C, N, O) involving the PF_6^- and BF_4^- anions have been obtained by comparing the ion organization and the phase transitional behaviors of cationic metallocene and bis-benzene complexes.[59b]

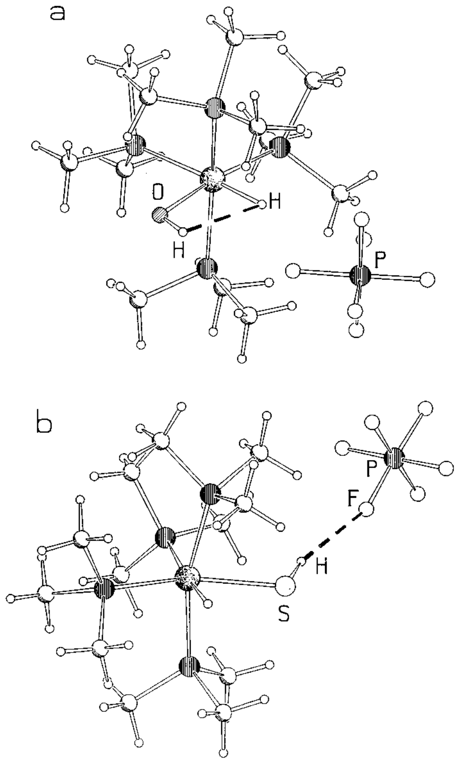


Figure 19. Hydrogen bonding interactions involving the −OH and −SH groups in crystalline *cis*-$[IrH(OH)(PMe_3)_4][PF_6]$ (a) and *cis*-$[IrH(SH)(PMe_3)_4][PF_6]$ (b).

F. The Hydrogen Bond in Organometallic Crystal Engineering

We have shown evidence that hydrogen bonds of the traditional and nontraditional types are ubiquitous in organometallic crystals. The nontraditional types include the weak "organic" C−H···O and N−H···O bonds and also the distinctively organometallic bonds involving metal atoms such as M−H···O, O−H···M, N−H···M, and the H···H bond. The metal atom has, at least potentially, a manifold role. It may simply act as a coordination center around which donor and acceptor groups are organized in a given way, or it can exert an electronic effect on the donor or acceptor site because of the oxidation state and the possible presence of ionic charge. More importantly, it can participate directly in hydrogen bonding interactions either as a donor or as an acceptor system. Most crystal engineering applications to date have chiefly made use of the two former characteristics of coordination complexes, namely the possibility of preorganizing donor and acceptor sites and of controlling the acid/base behavior by tuning the electronic state of the metal atom.

Organometallic building blocks for the preparation of one-dimensional hydrogen-bonded polymeric structures have been synthesized by van Koten et al.[151] The key structural motif is constituted of square-planar Pt complexes carrying hydrogen bonding donors and acceptors at either end of the molecule separated by a rigid aryl spacer as shown in Figure 20. These structural features allow intermolecular hydrogen bonds of the O−H···Cl[151a] or C≡C−H···Cl.[151b] type between molecules to be formed leading to one-dimensional aggregation in the solid state. In crys-

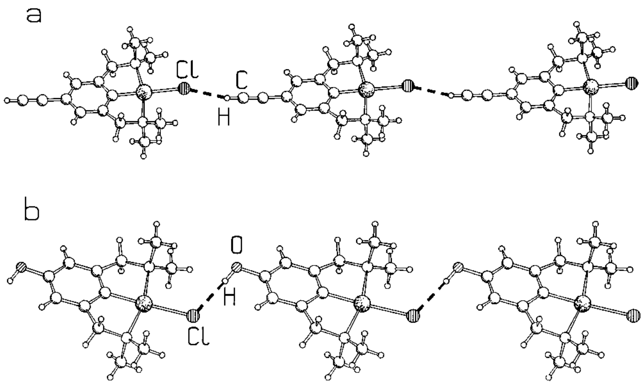


Figure 20. Intermolecular interactions in crystalline [PtCl{$C_6H_2(CH_2NMe_2)_2$-2,6-(C≡CH)-4}] (a) and [PtCl{$C_6H_2(CH_2NMe_2)_2$-2,6-(OH)-4}] (b). (Redrawn from original coordinates with permission from the authors.)

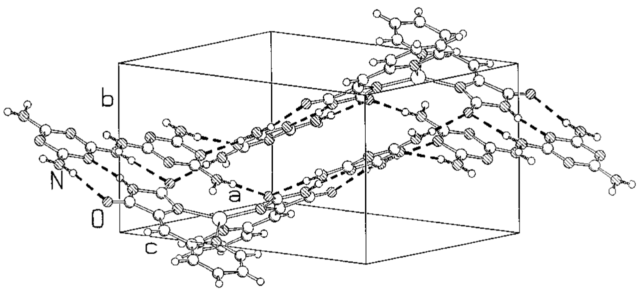


Figure 21. The result of the cocrystallization of [Cu(pyhy)$_2$] with two melamine molecules. Note how the interlink via hydrogen bonds forms corrugated sheets in the crystal.

talline [PtCl{$C_6H_2(CH_2NMe_2)_2$-2,6-(C≡CH)-4}] the molecular chain is held by C≡C—H···Cl interactions, (C)H···Cl 2.60(17) Å, C—H···Cl 157(14) Å. Hydrogen bond distances within the [PtCl{$C_6H_2(CH_2NMe_2)_2$-2,6-(OH)-4}] systems are O—H 0.84(13) Å, (O)H···Cl(Pt) 2.32(13) Å, the O—H···Cl angle is 161(15)°.

Complementary triple hydrogen bonds have been employed to synthesize bifunctional transition metal complexes that could be cocrystallized with organic bases in order to construct solid-state sheet and tape structures.[94c] The reference system is that of the cytosine-guanine base pair which are held together by a twin N—H···O and a single N—H···N interactions. Such complementary triple hydrogen bonds are very strong and could well constitute highly selective and transferable packing motifs when applied to coordination compounds. For example, the bidentate ligand 5-(2-pyridylmethylene)hydantoin forms stable complexes with transition metals in which the ability to form complementary hydrogen bonds with nucleotide-type bases is retained. This has been exploited to cocrystallize the coordination complex Cu(pyhy)$_2$ with two melamine molecules (see Figure 21) which then interlink via hydrogen bonds forming corrugated sheets.[152] Similar three-point recognition via C—H···O hydrogen bonds has only been discussed recently and its application to organometallic systems is still awaited.[153]

Other examples of hydrogen bonding directed cocrystallization are provided by the Ni, Pd, and Pt complexes of the biureto $[C_2N_3O_2H_3]^{2-}$ and dithiobiureto $[C_2N_3S_2H_3]^{2-}$ ligands which possess an arrangement of donor and acceptor sites capable of base pairing with complementary organic bases such as 1,8-naphthalimide and uracil.[154,155]

Cocrystallization of tetramethylethylenediamine with Pd(II) arenethiolate complexes via N—H···S hydrogen bonds has also been achieved. Importantly, this interaction can now be recognized as being of the IMH type, as the hydrogen atom of the donor N—H system interacts simultaneously with the S atom of the thiolate ligand and with the square-planar Pd center [(N)H···S 3.256, (N)H···Pd 3.11 Å].[156]

In summary, it may be stated that systematic organometallic crystal engineering will probably begin with the use of traditional hydrogen-bond interactions if previous developments in organic crystal engineering are to be any guide. The use of nontraditional hydrogen bonding interactions will be much more difficult especially because of their soft, cooperative nature. However, it must be realized that strong and weak hydrogen bonds *jointly* control crystal structure and this is much more valid for organometallics than it is for the pure organics. This poses a real challenge for the future of organometallic crystal engineering.

VI. Other Interactions in Organometallic Crystals

The hydrogen bond is not the only interaction sufficiently strong and selective to envisage crystal engineering applications. Intermolecular interactions between closed-shell atoms and between given classes of molecular fragments or ligands have attracted the attention of several investigators.

The subject of strong interactions between closed-shell atoms has been reviewed recently[157] and will not be discussed in any great detail here. The reader can find in this article examples of interactions between main group d^8, d^{10}, and s^2 metal cations with interaction energies in the range 0.1−0.4 eV (2.3−9.2 kcal mol^{-1}). These values are smaller than covalent bonds but stronger than most van der Waals interactions. It has been pointed out that there is a continuum of bonding from donor−acceptor interactions to the purely covalent bond. Theoretical treatment has shown that the strength of Au···Au interactions, the so-called aurophilic effect, depends on the type of ligand bound to the Au atom, increasing, for example, on going from Cl to Br to I.[158] Here, we only summarize some recent applications of these sorts of interactions in the crystal engineering context.

The geometries of these Au···Au interactions have been investigated with the CSD showing that intermolecular Au···Au contacts are observed in the vast majority of Au-containing compounds.[159] Au is the most electronegative metal and it has been suggested that its tendency to form short Au···Au contacts is reminiscent of the well-known behavior of the halogens (X = Cl, Br, I) to form short X···X contacts. Furthermore, the orientations of the Au atoms in crystals appear to be characterized by specific angular requirements.[159]

Examples of Au···Au interactions are afforded by the crystals obtained by reaction of *tert*-butyl or mesityl isocyanide gold chloride with sodium thiosal-

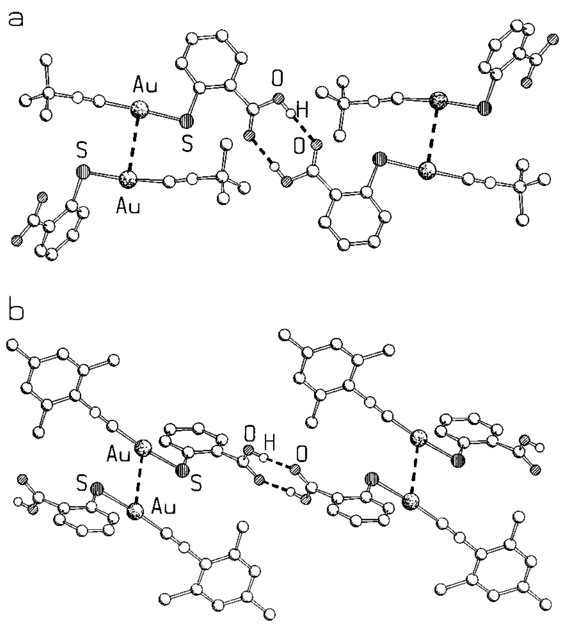


Figure 22. (a) Tetrameric unit aggregated via Au···Au interactions and hydrogen bonds. (b) Extended chains formed via Au···Au interactions and O—H···O hydrogen bonds. (Reprinted from ref 160. Copyright 1996 American Chemical Society.)

icylate, which show the cooperative effect of supramolecular Au···Au interactions and of hydrogen bonds.[160] The energy of the individual Au···Au interaction is estimated to lie in the range 6−11 kcal mol^{-1}, i.e., in the range of medium strength hydrogen bonds.[161] Au···Au interactions form zigzag structures in the crystal architecture of diphenylmethanimine complexes of Au.[162] As in the cases illustrated in Figure 22, Au···Au interactions are combined with hydrogen bonds (in these cases of the N—H···Cl type).

The supramolecular chemistry of coinage metals in general and of Au complexes in particular has been reviewed.[163] Au···Au interactions have also been used to produce extended solid-state structures of long-chain [(AuI)$_2$(bis(diphenylphosphino)hexane)].[164] The chains are interwoven to produce discrete layers, the gold atoms being at ~3.5 Å. Polymers of the type [$C_6H_3(C{\equiv}CAuL)_3$-1,3-5]$_n$ are formed via Au···Au bonding (in the range 3.234 and 3.316 Å) when L = isocyanide, phosphite, or phosphine.[165]

The crystal structure of *cis*-[PtCl$_2$(CO)$_2$], a prototypical organometallic molecule first reported by Schützenberger in 1870,[166a] has been recently determined.[166b] It has been found that the molecules stack in the crystalline edifice with the Pt atoms forming chains at Pt···Pt distances of 3.378(1) Å (see Figure 23). Another interesting feature is the interaction between the Cl ligands and the C atoms of the CO ligands along the stack.

Intermolecular interactions of phenyl rings, arene ligands, or condensed polycycles are also a common features of organometallic crystals.[167,168] For instance, high nuclearity transition metal carbonyl clusters carrying one or more arene fragments (arene clusters)[168] show the occurrence of two basic packing motifs: the arene ribbon and the arene−arene graphitic interaction. With mono-arene derivatives packing optimization is achieved by forming arene ribbons or layers through the lattice, while with bis-arenes this is better achieved by placing the ligands face-to-face. In this latter case the distance between arene planes is always comparable to that between carbon sheets in graphite. Arene ribbons are present in crystalline [H$_2$Os$_4$(CO)$_{10}$(η^6-C$_6$H$_6$)] and [H$_2$Os$_4$(CO)$_{10}$(η^6-C$_6$H$_5$Me)], while face-to-face interactions are present in crystals of the bis-benzene cluster isomers [Ru$_6$C(CO)$_{11}$(η^6-C$_6$H$_6$)(μ_3-η^2:η^2:η^2-C$_6$H$_6$)] and]Ru$_6$C(CO)$_{11}$(η^6-C$_6$H$_6$)$_2$].[169a,b]

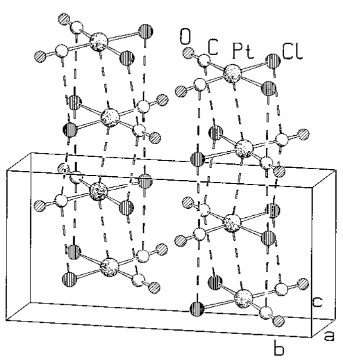
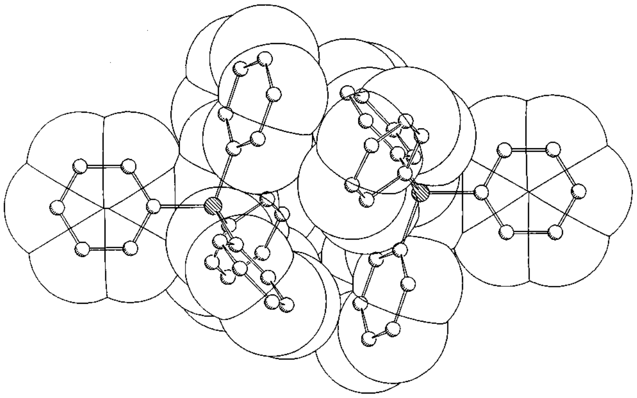


Figure 23. Molecules of *cis*-[PtCl$_2$(CO)$_2$] are stacked in the solid state (Pt···Pt distance 3.378(1) Å) in such a way that the Cl ligands are eclipsed with the C atoms of the CO ligands. (Redrawn from original coordinates with permission from the authors.)

Scheme 6. Interlocking of PPh$_3^+$ Cations: The Offset Face-to-Face Interaction (Also Observed in Arene Clusters), the Edge-to-Face Interaction and the Vertex-to-Face Interaction



Somewhat related to the interlocking of arene fragments is the so-called "phenyl embrace". It has been recently shown by Dance et al. on the basis of a CSD analysis that molecules containing PPh$_3$ ligands (as well as crystalline salts containing the [PPh$_3$]$^+$ cations) commonly associate in crystals in supramolecular motifs named sextuple phenyl embraces.[170] This motif arises because three phenyls groups of each neighbor in the crystal interlock with other three phenyls. The energy of the interaction has been estimated in 60−85 kJ mol^{-1}, the source of attraction being the interaction between phenyl groups. Three basic motifs have been identified (see Scheme 6), the offset face-to-face interaction (also observed in arene clusters), the edge-to-face interaction, and the vertex-to-face interaction.[171]

Another common van der Waals interaction in crystalline complexes is that established by the CO ligand. This ligand is common in coordination chem-

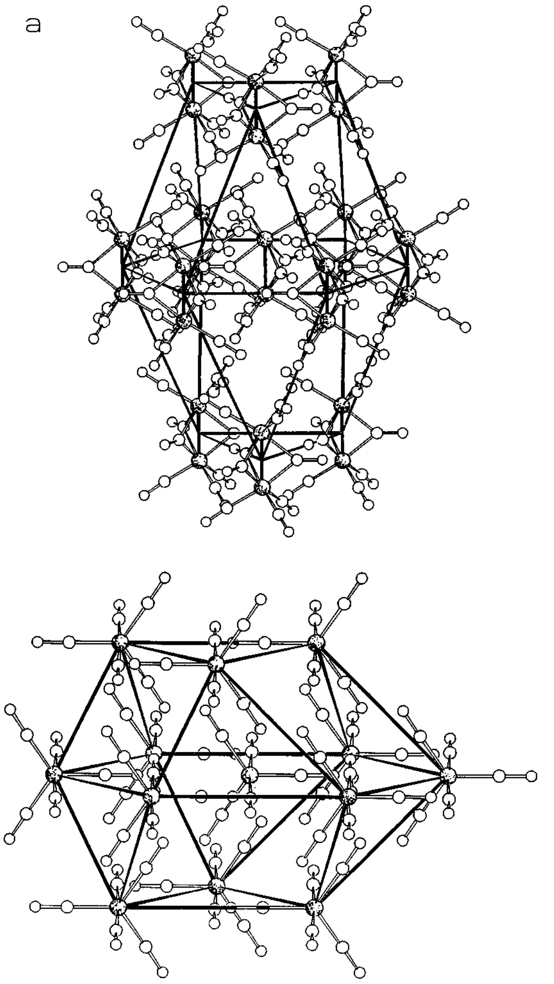


Figure 24. The quasi anticubo- and cubooctahedral packing polyhedra in crystalline [$Fe_2(CO)_9$] (a) (A/B/A sequence of layers), and [$Fe(CO)_5$] (b) (A/B/C sequence of layers).

istry and is almost invariably present in transition metal clusters where its bonding features (terminal, edge-bridging, and face-bridging) are coupled with the tendency toward formation of closed metal atom polyhedra which maximize the intrametal bonding.[21d] Since the external shape of carbonyl complexes is that of a bumpy object with the O atoms protruding from the surface, crystal cohesion depends on the way CO ligands belonging to neighboring molecules take advantage of the niches and bumps available on the surface of the complex. An analysis of the packing motifs in the family of neutral binary carbonyls has demonstrated that these molecules pack essentially in accord with the close-packing principle.[69] [$V(CO)_6$], [$Cr(CO)_6$], as well as [$Fe_2(CO)_9$] and [$Co_2(CO)_8$] pack in quasi cubooctahedral fashion (A/B/C sequence of layers) while [$Fe(CO)_5$] and [$Mn_2(CO)_{10}$] form quasi anticubooctahedral structures (A/B/A sequence of layers), see Figure 24.

It is worth stressing that the analysis of molecular interlocking may help to understand how molecules recognize each other before reacting. A representative example is shown in Figure 25; the interaction between two [$Fe(CO)_5$] might well represent the initial step of the reaction 2[$Fe(CO)_5$] (l) → [$Fe_2(CO)_9$] (s) + CO.[80] The generation of the [$Fe_2(CO)_9$] dimer requires elimination of one CO molecule and CO bridge formation. Interestingly, [$Fe_2(CO)_9$] possesses a structure of high symmetry extremely well-suited for close packing with neighboring molecules. The resulting high packing cohesion is probably the reason for the well-known insolubility of [$Fe_2(CO)_9$] in most common solvents.

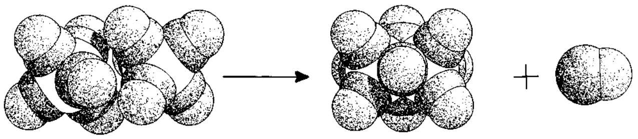


Figure 25. Space-filling representation of an (hypothetical) initial "recognition" step in the reaction 2[$Fe(CO)_5$] (l) → [$Fe_2(CO)_9$] (s) + CO.

VII. Supramolecular Architecture

This section is devoted to the discussion of design strategies to obtain organometallic crystal architecture with cavities, channels, and interpenetrating frameworks.

The emphasis will be on the engineering of supramolecular structures by means of ionic species and electrostatic templates. The context, however, is much broader than the phrase "ionic species" can convey. In organometallic chemistry, ions play a far more important role than in organic chemistry, if for no other reason because the variable oxidation states of metals often stabilizes charged species. On the other hand, organometallic molecules are, roughly speaking, more "organic" than "inorganic" because the majority of the typical organometallic molecule is usually composed of organic fragments (the ligands) with the metal atom(s) completely embedded within the ligand envelope. Care should be exercised therefore when referring to "ions" in structural organometallic chemistry. Generalizations are not easy and should only be attempted with caution. When the actual ionic charge is distributed over a large fragment, Coulombic effects in the crystal organization sequence are very limited and other factors such as shape and size or optimization of assisting interactions become important. Still, the facile utilization of mutual interactions between anions and cations adds an important extra dimension to crystal engineering. Electrostatic forces are long-range in nature and can control crystal packing effectively.

A. Crystal Engineering with Organic Alkali Metal Salts

Organometallic compounds of alkali metals generally exist as supramolecular aggregates with a great variety of often surprising structural typologies such as rings, cubes, chains, and layers. The structure investigation of alkali metal compounds began in 1963 with ethyllitium[172] followed by that of methyllithium in 1964.[173] Both compounds form tetrameric cubane-like Li_4C_4 aggregates in the solid state (see Figure 26a). Each tetramer interacts with eight neighbors. It is noteworthy that as the number of carbon atoms increases in this series, volatility increases and melting points decrease so that butyllitium is a liquid at ambient temperatures.[174] The relevance of such an observation in the context of this

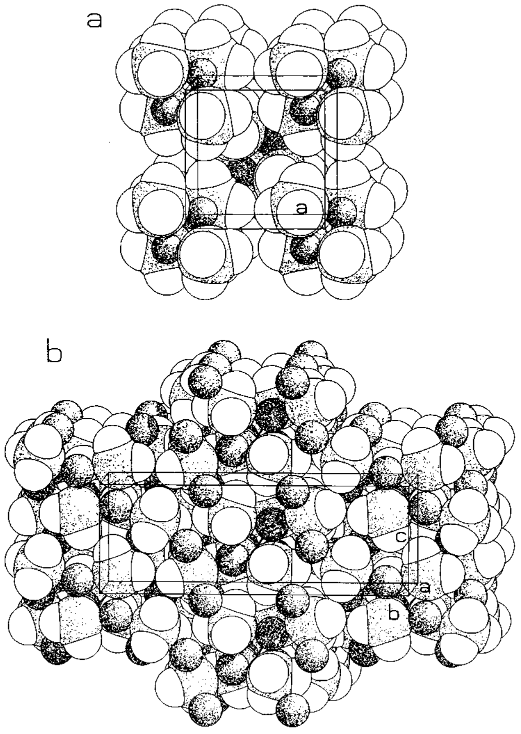


Figure 26. Space-filling representation of the organization in crystalline methyllithium (a) and methylsodium (b).

review is to be stressed. Such supramolecular aggregates are held together by a central polar core but as the size of the outer organic residues increases, the inner polar interactions are no longer sufficient to hold the material together. Methylsodium[175] shows the transition from the cubane-type structures of the small lithium compounds to that of the larger alkali metal compounds ([$\mathrm{KCH_3}$], [$\mathrm{CsCH_3}$], and [$\mathrm{RbCH_3}$]) which have a NiAs-type structure (Figure 26b).[176] In this structure, half of the ions have the same structure as [$\mathrm{(LiCH_3)_4}$] while the other half connect the tetramers via Na···C contacts which are longer than within the tetramer. When [$\mathrm{NaCH_3}$] is prepared by exchange with [$\mathrm{LiCH_3}$], mixed crystals are obtained. In crystalline [$\mathrm{NaCH_3}$-$\mathrm{LiCH_3}$], the [$\mathrm{NaCH_3}$] forms a supernetwork leaving large cavities that accommodate the [$\mathrm{LiCH_3}$].[177]

Following these initial studies, the structural chemistry of organo alkali compounds has been thoroughly investigated. The reader is referred to the relevant references for exhaustive reviews of the field.[176,178] The largest structural diversity is found with the lithium compounds which show almost all important structural motifs from monomers, dimers, trimers, cubes, hexamers, linear chains, and layers. The heavier alkali metals allow for interaction with multiple-bond systems.

Organocesium crystalline materials are still a rarity. Bock has been able to prepare cesium contact ions with tetraphenylethanediyl [$\mathrm{(Ph_2C\text{-}CPh_2)^{2-}(Cs^+(diglyme)_2}$] and 1,1,4,4,-tetraphenylbutadiene-2,3-diyl [$\mathrm{(Ph_2C{=}(CHCH){=}CPh_2)^{2-}}$ ($\mathrm{Cs^+(diglyme)(Cs^+OCH_2CH_2OCH_3)_2}$] π-dianions. In the black crystals of [$\mathrm{(Ph_2C\text{-}CPh_2)^{2-}(Cs^+(diglyme)_2}$], the $\mathrm{Cs^+}$ cations participate in interactions with four phenyl rings of two tetraphenylethanediyl dianions as well as with three O atoms of one diglyme molecule while in the violet

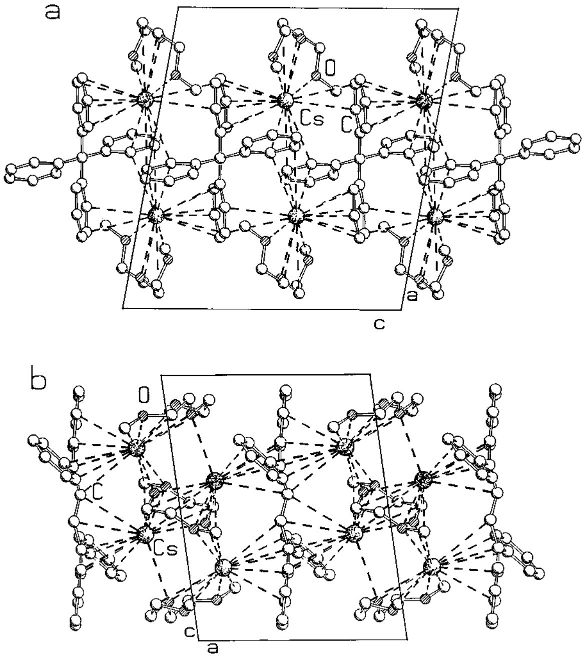


Figure 27. Packing arrangement in crystalline [$\mathrm{(Ph_2C\text{-}CPh_2)^{2-}(Cs^+(diglyme)_2}$] (a) and [$\mathrm{(Ph_2C{=}(CHCH){=}CPh_2)^{2-}(Cs^+(diglyme)(Cs^+OCH_2CH_2OCH_3)_2}$] (b). (Reprinted from ref 179. Copyright 1996 American Chemical Society.)

blue crystals of [$\mathrm{(Ph_2C{=}(CHCH){=}CPh_2)^{2-}(Cs^+(diglyme)(Cs^+OCH_2CH_2OCH_3)_2}$], each $\mathrm{Cs^+}$ cation is η^6- or η^7-bonded to one dianion, η^3-bonded to one diglyme molecule and η^2-bonded to two 2-methoxyethanolate anions.[179] Despite the presence of different components, the two packing arrangements are very similar (see Figure 27) and show the ability of $\mathrm{Cs^+}$ in acting as a multihapto coordinating cation capable of combining π interactions with ion pairing. It is suggested that because of the large size of $\mathrm{Cs^+}$, polymeric systems are formed by multiple interactions with suitable electron-rich species.

A large number of alkali metal ion aggregates and of intriguing crystal architectures has been obtained by reducing phenyl-substituted hydrocarbons with alkali metals. Radical contact ion pairs and polycation salts have also been studied and the results summarized in a recent review article.[180] Despite this massive structural investigation, however, the conditions to obtain suitable crystalline materials are still unknown to the point that Bock and collaborators conclude their review by stating that "we cannot disguise our dissatisfaction with regard to the question 'what crystallizes, how, and why?' ".[180]

A recent development of the alkali metal structural chemistry which falls in the realm of supramolecular studies is the preparation of so-called "lipophilically wrapped polyion aggregates" which are composed of a cluster nucleus of cations (or anions) surrounded but a predominant and largely impenetrable hydrocarbon skin. This latter coverage affords kinetic stability to the system, whereas the inner cluster provides thermodynamic stability. The reason for discussing this particular result here is that these materials are obtained directly via self-organization in crystalline form. Polyions such as {$\mathrm{[Ba_6Li_3O_2]^{11+}[OC(CH_3)_3]^-_{11}{\cdot}(OC_4H_8)_3)}$} and {$\mathrm{[Na]^{6+}}$-

$[H_{120}C_{144}O_{24}(OP)_2N]^-\}$ have been isolated and characterized.[181]

B. Ionic Systems and Electrostatic Templates

The strategy chosen by Fagan and Ward and their collaborators for the engineering of ionic networks is based on the development of ions that could serve as electrostatic templates for the self-assembly of molecules into crystalline molecular salts.[182] The idea of electrostatic templating stems from the recognition that the shape of a molecule as well as of a molecular ion defines possible interlocking motifs.

As discussed above the packing of neutral molecules is a multisolution problem because of the presence of numerous but relatively weak intermolecular interactions between molecules in the solid state. The van der Waals interactions are active at short range but are essentially nondirectional. Even when more directional bonds are involved, say in hydrogen bonding, molecules will tend to pack in a manner that optimizes space filling, that is by compromising between optimization of van der Waals and electrostatic interactions. Electrostatic templating introduces constraints to the crystal build-up sequence since anions and cations need to organize in a way that maintains electroneutrality. The topology 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. This is fundamental if one wants to synthesize crystals with manipulable properties such as conductivity and magnetism. Molecules with localized charges are better suited for this goal than flexible molecules with charge delocalization because the behavior of structurally nonrigid systems is less predictable. Another important prerequisite is that of attaining control on the spacing between charges in order to fit anions and cations into a predefined crystal architecture avoiding at the same time network interpenetration. Charge-transfer complexes are commonly prepared by in situ electron transfer between donor and acceptor or by electrochemical crystallization, this latter method permitting the preparation of high quality crystals.[183]

The organometallic fragment $[(\eta^5\text{-}C_5Me_5)Ru]^+$ has been used as precursor because of its great ability to bind to arenes. By using this building block one-, two-, and three-dimensional systems have been constructed. A zero-dimensional topology is obtained in the adduct formed by $[(\eta^5\text{-}C_5Me_5)Ru]^+$ with benzene.[182] Higher degrees of organization are attained by synthesizing polycations. Binding of multiple $[(\eta^5\text{-}C_5Me_5)Ru]^+$ fragments to arene ligands constrained to a linear array leads to monodimensional aggregates, as in the case of the paracyclophane complex $[((\eta^5\text{-}C_5Me_5)Ru)_2(\text{paracyclophane})]^{2+}$, or in other similar polycations with different charges. Two-dimensional geometry has been attained with *p*-quaterphenyl and *p*-sexiphenyl as arene ligands. These provide zigzag arrangements of four and six positive charges. The extension to three dimensions has been attained by using tetrahedral tetraphenyl complexes of group 14 of the type $[\{(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_6H_5)\}_4E]^{4+}$ (E = C, Si, Ge, Sn, Pb) while an octahedral array of charges has been obtained by reaction of the $[(\eta^5\text{-}C_5Me_5)Ru]^+$ fragment with hexa(*p*-methoxyphenoxy)benzene. Eight positive charges arranged in an almost cubic structure are present in the triflate salt of the polycation $[\{(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}p\text{-}MeC_6H_4)\}_8Si_8O_{12}]^{8+}$.

C. Architecture of Transition Metal Cluster Salts

Most high nuclearity transition metal carbonyl clusters are ions. This is not surprising since the solubility of neutral species of high nuclearity is very limited. Isolation and characterization of neutral species is hampered by the difficulty of obtaining good quality crystals. As a consequence, a large portion of the structural chemistry of transition metal clusters is based on salts. These materials have characteristics somewhat halfway between those of true Kitaigorodsky molecular crystals (those formed with molecular entities that can be distinguished on the basis of interatomic separations) and those of ionic salts (those constituted with small ions surrounded by counterions and held together by Coulombic forces). For instance, it has been reported that high nuclearity cluster anions of Os, Pt, and Pd show magnetic properties that are intermediate between those of dispersed metals and those of bulk metals.[184]

The terms “molecular salt” or “soft salt” have been suggested[23] to designate materials in which the component particles are ions of opposite sign but which interact essentially via van der Waals interactions. Interestingly, the crystal engineering concept is implied in the work of Basolo who recognized the importance of crystal stabilization long ago. He stated that large cations are stabilized by large anions possibly of the same but opposite charge and that “better results (in the crystallization) are expected if the counterion has a compact spherical shape similar to that of the metal complex to be stabilized”.[185]

Carbonyl cluster anions form crystals in which the counterion size and shape determines the type of anion aggregation. These molecular salts can be regarded essentially as mixed molecular crystals whose components are packed in the lattice according to the same rules which govern the packing of neutral molecules in single component systems. Since the ionic charge is usually small (−1 or −2, rarely higher) the large dimension of the cluster anions, together with a homogeneous ligand distribution, leads to effective delocalization of the charge, so that repulsion between neighboring anions is seemingly irrelevant to the packing. The general rule is relatively simple: small cations favor one-dimensional or two-dimensional aggregation of the anions, whereas when both ions have comparable sizes and nearly spherical shapes, the crystal is constructed as a mixed system in which anions and cations are distributed as van der Waals particles.[186] When the homogeneous charge distribution over the surface of a polycarbonyl anion is perturbed by the presence of more polar ligands (halides, cyanates, thiocyanates), the distribution of the ions in the crystal tends toward the insulation of the 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 counterions. 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.[187]

D. Organic–Organometallic Crystal Engineering

We have discussed at length how some degree of control on the aggregation process of organometallic ions to yield predetermined packing arrangements can be attained by using strong and possibly multiple hydrogen bonding. When the hydrogen-bonding interactions are not strong enough (as in the case of C—H···O bonds, for example) or when the shape of the molecules or ions are not suited for efficient interlocking then crystal design becomes more difficult and the results often unpredictable. One way to circumvent these difficulties is to reinforce the electrostatic component of weak hydrogen bonds by using ions of opposite charges.

These ideas have been exploited in devising mixed systems constituted of supramolecular organic anions and organometallic cations. Organo-organometallic crystals have been constructed by utilizing two basic concepts of molecular modeling: (i) the shape analogy between organic molecules and those organometallic molecules which carry the same organic fragments as ligands and (ii) the complementary role of strong and directional hydrogen bonds (such as O—H···O) to selectively and tightly link together organic molecules and of diffuse networks of weak C—H···O hydrogen bonds and anion—cation interactions to link the organic and organometallic fragments in the crystal.

The design, synthesis, and characterization of supramolecular aggregates between the paramagnetic cations $[(\eta^6\text{-arene})_2Cr]^+$ (arene = benzene and toluene) and 1,3-cyclohexanedione (CHD) has been reported.[188] The aggregation of the CHD system in superanions and/or in extended hydrated aggregates are based on strong hydrogen bonds, whereas the interaction between organic aggregates and the organometallic complexes is based on weak C—H···O hydrogen bonds reinforced by the different polarity.[189] In the cases of $[(\eta^6\text{-}C_6H_6)_2Cr][(CHD)_4]$ and of $[(\eta^6\text{-}C_6H_5Me)_2Cr][(CHD)_2]$ the crystals are held together by O—H···O hydrogen bonds between the supramolecular $[(CHD)_2]^-\cdot(CHD)_2$ and $[(CHD)_2]^-$ anions and by C—H···O hydrogen bonds between the anions and the organometallic cations as shown in Figures 28 and 29, respectively. The bis-benzene chromium aggregate bears a close relationship with the CHD cyclamer prepared by Etter by crystallization of the dione from a benzene solution.[190]

The participation of a third partner, namely the water used as solvent in the crystallization process led to other supramolecular aggregates.[188,189] The crystal of the hydroxide $[(\eta^6\text{-}C_6H_6)_2Cr][OH]\cdot 3H_2O$ shows the importance of C—H···O$_{\text{water}}$ interactions and affords a remarkable example of the supermolecule—crystal analogy: the noncovalent aggregation of water and of two simple ions such as OH^- and $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ generates a highly specialized superstructure in which layers of opposite sign alternate and result in a system with *sides* of completely different chemical composition. The hydrated hydroxide is constituted with a stacking sequence of layers containing $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations intercalated between layers of water molecules and OH^- groups (see Figure 30a). 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.[189b] The structure of the hydrated $[(\eta^6\text{-}C_6H_6)_2Cr][CHD]\cdot 3H_2O$ salt is related to that of the hydroxide $[(\eta^6\text{-}C_6H_6)_2Cr][OH]\cdot 3H_2O$. The CHD system terminates the hexagonal water layers via O(water)H···O(CHD) links. The resulting packing arrangement is reminiscent of that of the hydroxide, being composed of a stacking sequence of cations and of strings containing water and CHD^- anions (see Figure 30b).

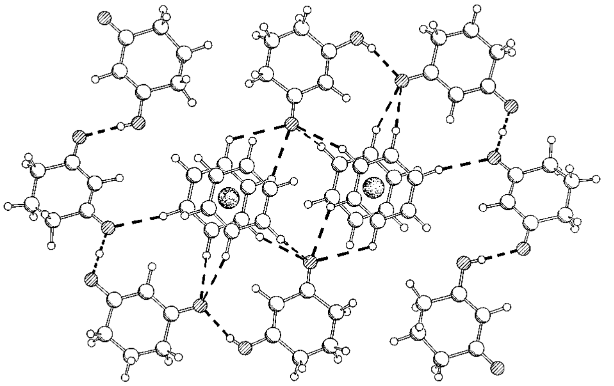


Figure 28. The network of O—H···O and C—H···O hydrogen bond interactions in crystalline $[(\eta^6\text{-}C_6H_6)_2Cr][(CHD)_4]$. Note how two organometallic $[(\eta^6\text{-}C_6H_6)_2Cr^+]$ cations are encapsulated between two “horseshoe”-shaped supramolecular $[(CHD)_2]^-\cdot(CHD)_2$ anions.

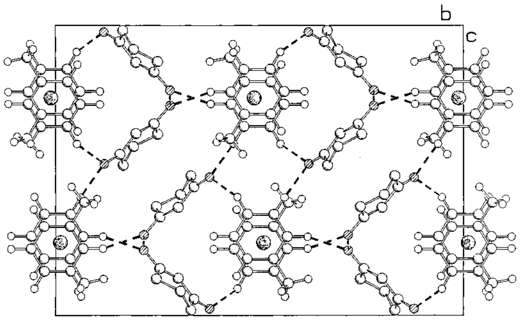


Figure 29. The network of C—H···O hydrogen bond interactions in crystalline $[(\eta^6\text{-}C_6H_5Me)_2Cr][(CHD)_2]$. (Reprinted from ref 188. Copyright 1997 American Chemical Society.)

An analogous crystal synthesis strategy has been used to build honeycomb-type organic frameworks around the organometallic cation $[(\eta^5\text{-}C_5H_5)_2Co]^+$. D,L-tartaric acid, for example, affords different crystalline materials depending on the stoichiometric ratio $[(\eta^5\text{-}C_5H_5)_2Co]$/tartaric acid and on the solvent of crystallization.[191a] The architecture of crystalline $[(\eta^5\text{-}C_5H_5)_2Co]^+[(D,L\text{-tartaric acid})_2]^-$ is constitued of an hexagonal superanion molded around the cobal-

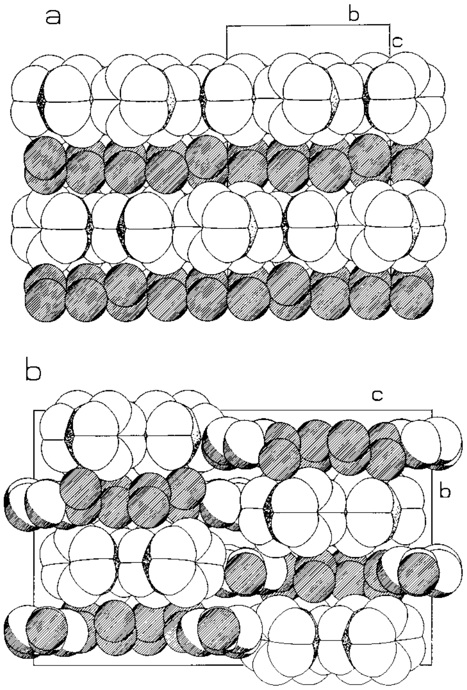


Figure 30. (a) The stacking sequence of layers formed by $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations intercalated with layers of $\{[OH]\cdot 3H_2O\}_n$ in the crystalline hydroxide $[(\eta^6\text{-}C_6H_6)_2Cr][OH]\cdot 3H_2O$ (a). Intercalation of $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations with strings of $[CHD]\cdot 3H_2O$ (b). (Reprinted from ref 188. Copyright 1997 American Chemical Society.)

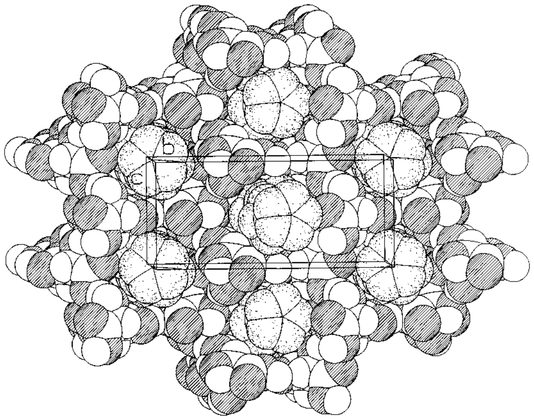


Figure 31. Space-filling representation of the anionic honeycomb framework formed by tartaric acid in crystalline $[(\eta^5\text{-}C_5H_5)_2Co]^+[(D,L\text{-tartaric acid})_2]^-$, the cobalticinium cations pile inside the channels. (Reprinted from ref 191a. Copyright 1997 Royal Society of Chemistry.)

ticinium cation as shown in Figure 31. When enantiomerically pure L-tartaric acid or L-benzoyltartaric acid are used, chiral frameworks are obtained, thus opening the way to the engineering of chiral crystals containing organometallic ions or molecules carrying delocalized electron systems and/or aligned spin systems.[191b]

The design criteria utilized to obtain both cyclohexanedione and tartaric acid aggregates can be summarized as follows: (i) strong donor/acceptor hydrogen bonding groups on the organic but not on the organometallic fragments for the selective self-assembling of the former fragments; (ii) a large number of acidic C−H groups, such as those carried by arene and cyclopentadienyl ligands, to make use of the "free" hydrogen-bonding acceptor sites on the organic framework; (iii) opposite charges on the two types of fragment to reinforce the C−H···O hydrogen-bonding interactions which hold together the organic superstructure around the organometallic cations.

VIII. Materials

This section will review some important results obtained in the construction of 'organometallic crystals with a purpose', i.e., of those systems in which the molecular or ionic organization is related to physical properties of the crystalline material. Many of these systems were devised at a time when crystal engineering and materials chemistry (of molecular aggregates) were rather separated fields of research with very little mutual awareness. As pointed out in the Introduction, the two fields were awaiting the cultural bridge now provided by supramolecular chemistry.

A. Molecular-Based Magnetic Materials and Charge-Transfer Salts

The construction of molecular-based magnetic materials is one of the most attractive areas of investigation. The term "molecular" here also serves to indicate that use is made of the synthetic methods of solution chemistry.[192] The magnetic behavior of a crystalline material depends on the ability of assembling molecular building blocks in low-dimensional aggregates with a nonzero resulting spin in the ground state and by coupling these aggregates in two- or three-dimensional systems in a ferromagnetic fashion. Although there are many important review articles available that provide a detailed treatment of magnetism and meta-magnetism, it is useful to briefly discuss this subject in the present context because magnetism depends on the arrangements of ions in the crystal structure.[193,194]

In general, the stabilization of ferromagnetic interactions within donor/acceptor complexes requires the formation of a one-dimensional (D+A-D+A···) structure comprised of alternating cation donor (D) and anion acceptors (A) (the so-called linear-chain paradigm). Ever since the observation that various TCNQ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) salts form conducting linear chains, many organometallic materials based on this anion have been isolated and the magnetic and electrical conductivity behaviors were established. The first report of high electrical conductivity of 1:2 ferrocene complexes of TCNQ goes back to 1962.[195] Experimental evidence for bulk ferromagnetic behavior in molecular based crystals has been accumulated over the past 20 years on a number of electron-transfer salts based on TCNQ, or TCNE (tetracyanoethylene) anions. In 1979 $[(\eta^5\text{-}C_5Me_5)_2Fe][TCNQ]$ was shown to exhibit a high-moment ferromagnetic state above 1600 Oe and the crystal structure was shown to be composed of linear chains.[196,197] For the first time, bulk ferromagnetic behavior has been observed below the critical (Curie) temperature Tc of 4.8 K for $[(\eta^5\text{-}C_5Me_5)_2Fe][TCNE]$.[198]

Another interesting acceptor system is hexacyanotrimethylenecyclopropanide $[C_3(C(CN)_2)_3]^-$ that has

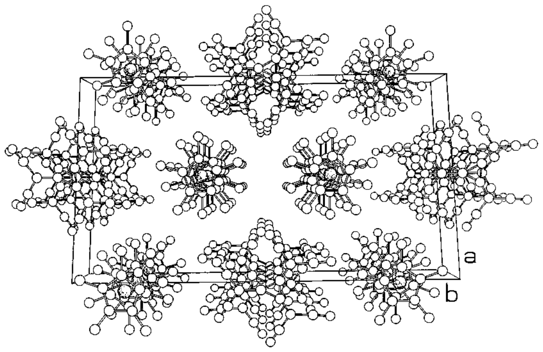


Figure 32. Perspective projection of the ion organization in the crystal of $[C_3(C(CN)_2)_3]^-[(\eta^6\text{-}C_6H_3Me_3)_2Fe]^{2+}$.

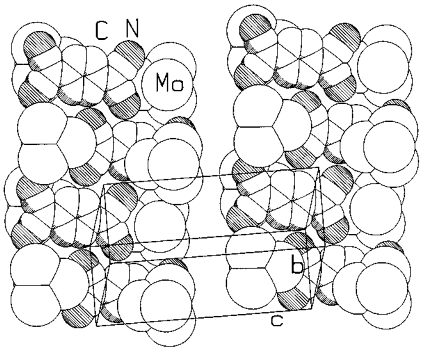


Figure 33. In the crystal structure of the paramagnetic salt of $[Mo_4(\eta^5C_5H_4Pr^i)(S_4)]^+$ the TCNQ anions are arranged in ribbons separated by cluster cations (the ligands on the clusters have been omitted for clarity).

been used in conjunction with $[(\eta^5\text{-}C_5Me_5)_2Fe]^+$ and $[(\eta^6\text{-}C_6H_3Me_3)_2Fe]^{2+}$ to prepare extended linear chain compounds.[199a] This latter compound is isostructural with the ruthenium analogue $[(\eta^6\text{-}C_6H_3Me_3)_2Ru]^{2+}$. Ward[199b] was able to show that the difference in charge-transfer absorption energies between the two complexes is equivalent to the difference in the reduction potentials of the cations in solution. A similar relationship has been observed between salts of the $[\text{iso-}C_4(CN)_6]^{2-}$.[199c] The monoclinic $C2/c$ crystal form of $[(\eta^5\text{-}C_5Me_5)_2Fe]^+$ $[C_3(C(CN)_2)_3]^-$ is shown in Figure 32.[199a]

Two polymorphic forms of the complex $[(\eta^5\text{-}C_5Me_5)_2\text{-}Ru(\eta^6\text{-}C_6Me_6)][TCNQ]$ have been prepared by direct metatesis of an acetonitrile solution of $[(\eta 5\text{-}C_5\text{-}Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+$ with TCNQ.[182] The two crystals have very different packing arrangements of the component ions. The green phase is nearly isomorphous with the crystal structure of the salt $[(\eta^5\text{-}C_5\text{-}Me_5)_2Fe][TCNQ]$[200] in which the ions form a one-dimensional motif ...D+A-D+A-D+A.... The purple phase possesses instead discrete D+A- -A-D+ fragments arranged in a herringbone fashion.

TCNQ has also been used to crystallize metal clusters cations of Mo, Fe, and Cr. In the crystal structure of the paramagnetic salt of $[Mo_4(\eta^5C_5H_4\text{-}Pr^i)(S_4)]^+$ the TCNQ anions are arranged in ribbons separated by cluster cations (see Figure 33). The ribbon arrangement is unusual for TCNQ, which tend to form stacks as seen above for the metallocenium salts. This difference very likely depends on the size of the cluster cations.[201]

The study of the electron-transfer salts based on the structures of $[(\eta^5\text{-}C_5Me_5)_2Fe][TCNQ]$ and $[(\eta^5\text{-}C_5\text{-}Me_5)_2Fe][TCNE]$ has been extended to perfluorinated $[TCNQF_4]$.[202,203] Crystalline $[(\eta^5\text{-}C_5H_5)_2Fe][TCNQF_4]$ and $[(\eta^5\text{-}C_5H_5)_2Fe]_2[TCNQF_4]_3$ have been investigated by ESR and ^{57}Fe Mössbauer spectroscopy.[202]

Recently, recrystallization of the 1:1 precipitate of $[(\eta 5\text{-}C_5Me_5)_2Ni]^+$ with $[TCNQF_4]$ in MeCN has afforded two phases, one of which has been characterized by diffraction, showing the unexpected formation of a polymeric anion constituted of $[HTCNQF_4]^-$ anions linked by a C−H···N hydrogen bond between a protonated C atom of the $TCNQF_4$ unit and the N atom of one of the CN groups.[204]

B. Conductors and Superconductors

As discussed above crystals formed of a stacking sequence of electron donor/acceptor systems are well-suited for magnetism and metamagnetism. However, magnetism and superconductivity are intimately related so that systems of this type are often also conductors and superconductors. One may wonder how the characteristics typical of a metal (conductivity) will mingle with those typical of an organic system (insulation) in an orgametallic system. The majority of organic molecules are electrical insulators (i.e., an electrical conductivity $\sigma < 10-14$ Ω^{-1} cm^{-1}). The conductivity of a small number of organic systems can be thermally activated, while in few cases, low-temperature superconductivity has been observed. Today most organic superconductors are based on chalcogen-containing compounds.[205] Indeed one of the earliest organic metals is the solid-state complex in which the donor is TTF (tetrathiofulvalene) and the acceptor is TCNQ discussed above. The TTF−TCNQ complex was shown in 1973 to possess a high metallic conductivity ($\sim$104 Ω^{-1} cm^{-1} around 55 K).[206] Many materials containing bisthiolene ligands and transition metals have been analyzed in the quest for high conducting molecular materials.[207] Most of these systems are not organometallic complexes strictly speaking, carrying sulfur-bound Ni, Pt, Pd, and Au atoms, but are related to the above discussion in that the physical property depends on the formation of stacks that permit intermolecular or interlayer S···S contacts. The compound $\{\kappa\text{-}(ET)_2Cu[N(CN)_2]Br\}$ is an ambient pressure superconductor with a transition temperature of 12.5 K.[208]

Organometallic molecular conductors based on this approach have also been synthesized. The complexes $[(DIETS)_4M(CN)_4]$ (M = Ni, Pd, Pt; DIETS = diiodoethylenedithiodithiadiselenafulvalene) have been shown to aggregate in the solid state via I−NC interactions. These interactions are responsible for holding together the donor/acceptor system in stacks and for the metallic conductivity property (>80−100 K).[209] A similar behavior has been observed by using IEDT (iodoethylenedithiotetrathiafulvalene) as donor.[210]

The complex of bis(ethylenedithio)tetrathiafulvalenium with $[CuCl_4]$ consists of alternating stacks of organic cations and inorganic anions, the former consisting of side-by-side stacks of BEDT-TTF each bearing the same charge of $^2/_3{}^+$. The crystalline material is metallic from room temperature to 200 mK, without transition to superconducting behavior.[211]

The nonlinear optical response of a solid materials and their crystal architecture are also intimately related. The phenomenon of frequency doubling (or tripling) has become such an important technological issue in solid-state chemistry that many important research groups are actively working on this subject. The relationship between crystal structures and NLO response, in particular the requirements for obtaining a noncentrosymmetric crystal, will be discussed below. In the context of this section, it is only important to mention that many organometallic materials with NLO properties are salts. This is not surprising since Coulombic interactions between counterions in salts can be very effective in stabilizing otherwise unfavorable orientations of the NLO chromophores. Some examples will be discussed below.

C. Organometallic Materials for Nonlinear Optical Applications

The engineering of materials for nonlinear optical applications is one of the major issues of current materials chemistry.[212,213] Among the established design criteria for the construction of molecule-based nonlinear optical materials (polarizable molecules, donor/acceptor asymmetric charge distribution, π-conjugation) the absence of a center of symmetry in the crystal structure is of more direct concern in this review. The design of noncentrosymmetric crystal represents a substantial chemical challenge.

The interaction of an electromagnetic field with matter produces a polarization effect that causes an instantaneous displacement of the electron density away from the nucleus thus resulting in an induced dipole because of the charge separation. With small field the strength of the applied field is proportional to the charge displacement from the equilibrium position and is accounted for by the relationship P (polarization) $= \alpha E$, where E is the electric field, and α the linear polarizability of the molecule or atom. If the field oscillates with a frequency then the induced polarization will have the same frequency and phase if the response is instantaneous. When a molecule is subjected to a laser light, i.e., to a very intense electric field, the polarizability can be taken out of the linear regime. The nonlinear polarization can be expressed by a relationship similar to the one above in which additional terms are introduced, $P = \alpha E + \beta E^2 + \gamma E^3$ where β and γ are the first and second molecular hyperpolarizabilities. Importantly, β is nonzero in the absence of an inversion center. It is not within the scope of this article to review the enormous efforts made in this area. The excellent papers quoted in ref 214 are more than sufficient to provide the necessary input information to the reader.

Organometallic compounds are appealing candidates for the investigation of NLO properties for the following reasons: (i) the diversity of oxidation states allowing for great possibilities for redox ability, a property that leads to large molecular hyperpolarizability; (ii) the presence of low-energy excited states that can be reached simply by electron transfer from the metal centers to the ligands; (iii) structural variability allowing a great diversity of aromatic and π-delocalized systems to be bound to the metals; and (iv) both metal centers and ligands giving chiral centers that would allow crystallization in noncentrosymmetric space groups.

Over the past few years interest in organometallic systems for NLO applications has risen greatly since the report by Green et al. that the ferrocene derivative *cis*-[1-ferrocenyl-2-(4-nitrophenyl)ethylene] has an excellent second harmonic generation efficiency 62 times that of the urea reference.[215] The molecules crystallize in the noncentrosymmetric space group *Cc* and are packed in such a way that preserves the molecular dipole. This initial report caused a surge of interest in ferrocene derivatives also in view of the very extensive organic chemistry of the ligand and of the relative stability of most complexes in air.

Kanis, Ratner, and Marks suggest[213] that the best candidates for high NLO response are organometallic molecules that either possess spectroscopically intense metal-to-ligand or ligand-to-metal charge transfer or complexes where the metal atom is between an electron-donor and an electron-acceptor ligand. Bimetallic compounds exhibiting low-energy charge-transfer bands may also reveal interesting NLO behavior.

The most studied classes of organometallic materials for NLO applications are metallocenes, metal carbonyls, and metal carbonyl pyridine complexes and octahedral and square-planar complexes. In addition several other classes of coordination compounds have been investigated, such as substituted silane complexes, metal-containing organic acetylene complexes, metal dithiolene complexes as well as phthalocyaninato complexes and thiophenes. These systems have been recently reviewed[212b] and only some selected systems, for which a full crystal structure determination has been carried out, will be described in some detail.

Neutral ferrocene and ruthenocene derivatives have been studied extensively[216] because the aromatic character of the cyclopentadienyl ligand and the propensity of the metal center to undergo redox chemistry suggest facile charge-transfer behavior when the metallocene is conjugated with an electron-acceptor system. Indeed one of the most efficient NLO response is shown by the crystalline complex *cis*-1-ferrocenyl-2-(4-nitrophenyl)ethylene mentioned above.[217]

The largest second-harmonic generation powder efficiency of metallocene derivatives is shown by the organometallic salt of formula $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{-}CH{=}CH(4\text{-}C_5H_4N\text{-}1\text{-}CH_3]^+[I^-]$ with an NLO response 220 times that of urea. To ascertain how the change in counterion size and shape could alter the NLO response the anions $[Br^-]$, $[Cl^-]$, $[BF_4^-]$, $[NO_3^-]$, $[PF_6^-]$, $[CF_3SO_3^-]$, $[BPh_4^-]$ were all tested, and second-harmonic generation efficiencies were measured on powder samples. The halide salts were those which gave the largest effect in the order $[I^-] > [Br^-]$ while the $[Cl^-]$ salt is thought to be centrosymmetric because the response is zero. Only the crystal structure of the $[NO_3^-]$ salt could be deter-

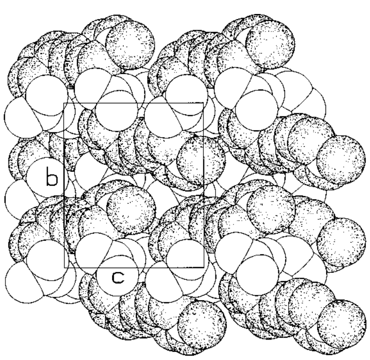


Figure 34. The crystal structure of $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{-}CH{=}CH(4\text{-}C_5H_4N\text{-}1\text{-}CH_3]^+[NO_3^-]$.

mined by single-crystal X-ray diffraction. The crystal is noncentrosymmetric (see Figure 34) and the ferricinium complex packs with the Fe···N vector properly aligned along the *c* axis of the cell. The nitrate salt has a second-harmonic generation efficiency 110 times that of the urea reference. The substitution of ruthenium for iron decreases the NLO efficiency because ruthenium is comparatively less electron rich and therefore a poorer electron donor than iron.[218]

Complexes of the type $[M(PEt_3)_2(X)]$ (M = Pd, Pt, and X = Br and I) have been shown to form polar crystals with NLO response. The structure of the I derivative could be determined by single-crystal X-ray diffraction in the space group $Cmc2_1$ with the dipoles at almost right angle with respect to each other but all pointing in the same direction with respect to the polar axis. Intermolecular I···H interactions of 2.98 Å (i.e., much shorter than the van der Waals radii, 3.25 Å) indicative of the participation of hydrogen bonding in the crystal structure stabilization were also noted.[219] The NLO efficiency of this complexes is 5−8 times that of urea.

D. Organometallic Inclusion Compounds for Nonlinear Optical Applications

Polarizable organometallic molecules such as metal arenes and arene metal carbonyl complexes which crystallize in centrosymmetric space groups can be "forced" in noncentrosymmetric environment by inclusion in a host polar lattice. Inclusion compounds have been extensively studied.[220] Inclusion hosts such as thiourea, tris-*o*-thymotide, deoxycholic acid, as well as clathrate hosts such as cyclodextrins have been shown to be well suited for the formation of host−guest systems with organometallic molecules in noncentrosymmetric space groups.[221] Importantly, neither tris-*o*-thymotide or thiourea are noncentrosymmetric and, in fact, do not shown any NLO response. It is therefore the association of guest and host that leads to noncentrosymmetric aggregation. Eaton et al. indeed observe that while there is statistically ∼30% probability of obtaining a noncentrosymmetric crystal for an organic or organometallic molecules selected at random, the inclusion compounds of the type discussed above crystallize in polar systems in 85% of the cases.[221] The inclusion process seems to favor construction of polar structures.

Thiourea inclusion compounds of $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ and $[(1,3\text{-cyclohexadiene})Fe(CO)_3]$ show an, albeit small, second-harmonic radiation (respectively 2 and 0.4 times that of urea)[222] while ferrocene−thiourea inclusion compound[223] does not have an NLO response. Both Cr and Fe complexes form 3:1 host−guest materials although with different channel structure and packing of the organometallic molecules. The crystal structure of the Cr complex shows hexagonal channels formed by thiourea molecules related by 3-fold axes. The diameter of the channels is 9.3 Å and the $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ molecules are piled in the channels. In the Fe case, although the thiourea channels are identical to the Cr crystal, the orientation of the complexes is completely different. The arrangement is, of course, polar in both crystals (space groups $R3c$ and $Pna2_1$, respectively) but the efficiency of dipole alignment is much greater in the former crystal than in the latter.

The inclusion complex method appears to be an important technique for dipolar alignment. It appears that in the lattice dipoles tend to arrange themselves in a linear, head-to-tail sequence, rather than in an antiparallel sequence (which would cancel the NLO response). The antiparallel arrangement may be prohibited by the channel structure if the molecule carrying the dipole is cylindrical in shape and the size of the channel is adequate. If the dipoles, once included in the channel structure, cannot reorientate then the polar arrangement will be stable.

IX. Prospects for Systematic Design

The study of organometallic solids with a view to systematic design is poised at an interesting stage. Crystal engineering, as has been stated earlier in this article, passes through the stages of analysis, prediction, and experimentation. Although the ethos of the subject is finally experimental, it borrows and uses ideas freely from physical and theoretical chemistry and also from database research which, in turn, goes back to the bedrock of crystallographic findings over the decades. In the context of organometallic crystals, the first of the three stages, that is analysis of structural data is now well-developed and constitutes the major thrust of this article. The second stage, namely the prediction of known and unknown crystal architectures, has still not been researched in a general sense but all indications are that much progress is possible and will be forthcoming. The third stage, or in other words, the use of design principles as obtained in the two first stages to realize predefined crystal structures in the laboratory, is still embryonic.

The analysis of known organometallic crystal architecture is enlivened by the structural variability and flexibility of representative systems. At a certain basic level, concepts that have served well organic crystal chemistry may be used here too. These include the principle of close packing, the varying and contrasting importance of isotropic and directional forces, and the possibility of polymorphism. However, what is more interesting is the manner in which organic and organometallic structures diverge. Concepts such as back-bonding, tunable basicity, the role of metal atoms, both electron-rich and electron-deficient in hydrogen bonding or agostic situations, the diffusion of charge in nominally ionic crystals and the active involvement of uniquely organometallic moieties in crystal cohesion make the subject of organometallic crystal chemistry unique and distinctive. The sufficiently large size of the CSD today contributes in no small measure to the possibility of successful structural analysis that permit conclusions that are at the same time both “diverse and certain”.

The generation of theoretical structures in organometallic crystal engineering follows closely the corresponding developments for organic crystals. Rapid advances in computational techniques including the availability of commercial software that is tailored toward materials science (rather than biological) applications will mean that an increasing number of organometallic systems will be handled with confidence in the future. The generation of model structures is closely linked to polymorphism, a subject that is probably not as mysterious as it was formerly deemed to be, and sustained interest in polymorphism is in turn likely to lead to better methods for structure modeling and computation.

And yet, it is the final stage of crystal engineering, the actual experimentation that leads to a predesired crystal structure (a “crystals with a purpose”) that fully defines and justifies the “engineering” epithet. It is pertinent to ask what could be “predesired” for an organometallic crystal. A crystal may be identified as a target for methodological, aesthetic or, most satisfyingly, utilitarian reasons. The successful development of a distinct organometallic crystal engineering discipline will depend critically on increased interactions between previously separated areas of research. These include organic and organometallic synthesis, crystallography, and computational chemistry. Such a development should also lead to a deeper understanding of the chemistry and physics of materials.

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