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Hydrogen bonds and other intermolecular interactions in organometallic crystals †

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Organometallic compounds have been studied with X-ray crystallography from their very discovery. Yet structural organometallic chemists were almost exclusively concerned with the molecular structure and stereochemistry of organometallic compounds and clusters rather than with their crystal structures and packing characteristics. The growing importance of crystal engineering and supramolecular chemistry, however, led to interest in the nature of the interactions that bind organometallic molecules into crystals. In part, these interactions are similar to those found in purely organic crystals because the peripheries of these molecules often contain organic residues. Yet molecular features peculiar to organometallic compounds also do lead to distinctive supramolecular characteristics. Most notable among these intermolecular interactions are hydrogen bonds. Organometallic compounds contain a wealth and diversity of hydrogen bonds that are without counterpart in the organic world. These include C–H · · · O bonds to M–C≡O acceptors, and hydrogen bonds wherein the metal atom itself acts as a donor or as an acceptor. Even more exotic is the dihydrogen bond M^1–H · · · H–M^2. Despite this variety, all these weak interactions have properties that resemble those of the more familiar hydrogen bonds such as O–H · · · O, N–H · · · O, O–H · · · N and N–H · · · N. Other interactions that are distinctive to organometallic compounds are the agostic interaction to electron deficient metals (C–H) · · · M and the aurophilic interaction Au · · · Au. The Cambridge Structural Database (CSD) is an essential tool in the analysis of weak intermolecular interactions. Since the number of organometallic crystal structures in the CSD is very large, the weakest of intermolecular interactions may be studied with ever-increasing degrees of reliability. Through such analysis one is able to obtain a more complete idea of organometallic crystal architecture. Crystal engineering must pass through the stage of analysis before crystal synthesis can be attempted and organometallic crystal engineering is still in its infancy. However, the progress made so far in understanding the nature of intermolecular interactions in these crystals indicates that one may expect rapid progress in the engineering of organometallic crystals with desired structures and properties.

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Introduction

Organometallics constitute the largest and possibly the most important category of metal-atom-containing molecular crystals.[1] The growth of organometallic chemistry during the second half of the 20th century is closely intertwined with the progress of X-ray crystallography, beginning with the very important crystal structure determination of ferrocene.[2] Given that the molecular structures of organometallic and metal-cluster compounds are often both unpredictable and novel, and also given that many of these compounds are moisture- and/or air-sensitive, X-ray crystallography continues to be the method of first choice for determining these structures. Of the 215 403 entries in the April 2000 release of the Cambridge Structural Database (CSD),[3] 55 045 correspond to compounds that contain a C–M bond.

Despite this wealth of structural information available, the almost exclusive interest of the structural organometallic chemist was, until very recently, confined to the molecular structure and stereochemistry of these compounds. Molecular structure was the ruling paradigm in inorganic chemistry right through until the late 1980s.[4] Such an emphasis was fortified by the dominance of ligand field theory which focussed attention on single metal atoms and their immediate surroundings, mostly organic ligands. Gradually, however, this purely molecular view of inorganic chemistry gave way to newer concepts and paradigms that explored more extended domains. The first of these innovations arose from interest in the structures and properties of metal oxides and other related infinite structures.[5] A second arose from the application of supramolecular ideas to inorganic molecular solids.[6,7] It is with this second aspect of inorganic solid state chemistry that I shall be concerned with in this article.

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Discussion

Crystal engineering is the planning and synthesis of a crystal structure from its molecular constituents.[8] The assembly of these constituents, that is the nucleation and growth of a molecular crystal, is one of the most fundamental and yet most impressive examples of supramolecular recognition. This assembly is mediated by intermolecular interactions, rightly termed supramolecular glue. An understanding of the nature and properties of the large numbers of intermolecular interactions that are found in molecular crystals is therefore of the utmost importance in developing strategies and methodologies of crystal synthesis.[9] Crystal engineering, like other forms of synthesis, may conceptually be divided into analytical and synthetic components.[10,11] Analysis consists in understanding intermolecular interactions through a dissection of already known crystal structures. This exercise is most conveniently carried out by either: (1) carrying out the crystal structure determinations of a family of closely related compounds followed by subsequent analysis of the crystal packing; or (2) charting out general trends with the CSD. These approaches have been employed independently or in conjunction. Synthesis consists in using information on intermolecular interactions in various strategic operations to obtain structures with predesired architectures associated with properties of choice. Synthesis then necessarily follows analysis. In organometallic crystal engineering, a subject that is still nascent, synthetic efforts are still in a fledgling state. The emphasis in this article is therefore largely on the analytical component of organometallic crystal engineering; I have attempted to provide a brief overview of hydrogen bonding and other interactions in organometallic crystals, and wherever possible, in the context of crystal design and synthesis.

Commonalities between organic and organometallic crystal packing

Many factors that influence and guide organic crystal packing are also important in the crystal engineering of organometallic compounds. This is because the metal centres in these compounds are mostly situated in the molecular cores and are well shielded from neighbouring 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. The crystal structures of benzene[12] and dibenzenechromium[13] are similar because the two molecules are chemically and geometrically similar.[14] The benzene molecule is quasi-spherical or discoid in shape and adopts a quasi-face centred cubic structure (actually orthorhombic with nearly equal cell edges). Dibenzenechromium is more nearly spherical and the space group can now be accurately cubic but still quasi-face centred because the tilting of neighbouring molecules permits the formation of herringbone C···H interactions. What is noteworthy is that the Cr atoms are well screened by the benzene rings and play a negligible role in stabilising the crystal structure of dibenzenechromium.[15]

In general, organometallic crystals resemble organic rather than inorganic crystals because they are composed of distinct molecules.[16] The close-packing principle is as important as it is for organics but since the molecular peripheries in organometallic molecules do not show the diversity that is seen in the pure organics, with groups such as phenyl and CO tending to occur frequently, a more limited variety of overall packing type is observed. On occasion, however, the metal atoms are particularly exposed in the molecular structure. In such instances the crystal packing behaviour of organometallics could diverge from that of simple organics.[17,18] Polymorphism is prevalent but is generally less frequent than in organics (from CSD statistics), as is pseudopolymorphism. However, these observations could be the result of limited experimentation into these matters rather than indicative of any fundamental difference in behaviour. As in organic crystals, the few polar functional groups that decorate the molecular surface form directional interactions and these interactions have a greater or lesser influence on the overall packing arrangement. Surely the most important of these directional interactions is hydrogen bonding.

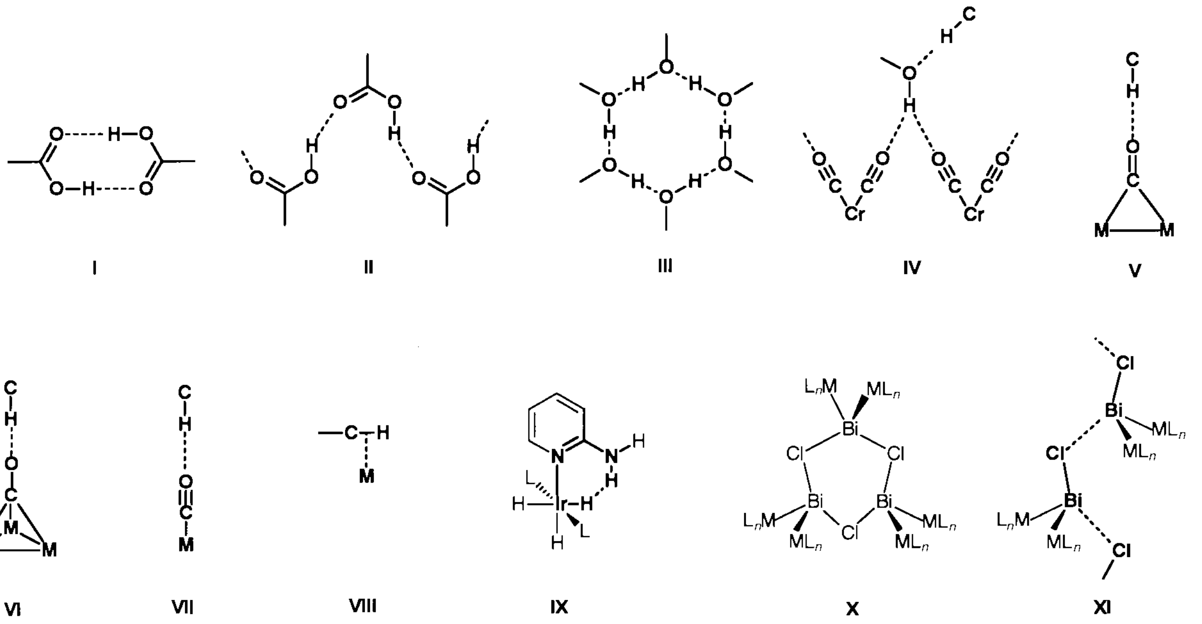
Strong and weak hydrogen bonds common to organic and organometallic crystals

The hydrogen bond may most generally be considered as a three-centre four-electron interaction that is stabilising and directional with certain spectroscopic attributes, structure-defining effects and reproducibility of occurrence.[19] The energy of the hydrogen bond is dominated by electrostatic factors. However, polarisation, charge transfer and exchange repulsion are also important. Hydrogen bonds may be classified as very strong, strong and weak. This classification is somewhat subjective and often parallels the appearance of non-conventional donors and acceptors (which render the hydrogen bonds weak). However, in the end, there is no real phenomenological difference between hydrogen bonds of varying strength. More significantly, and in the context of crystal engineering, there seems to be little distinction between these categories. It is their directionality that makes all hydrogen bonds important as crystal structure directors.

Let us discuss first cases where similar hydrogen bond patterns occur in organometallic and organic crystals. Both strong and weak hydrogen bonds may be considered. Strong hydrogen bonds include interactions of the type O–H···O, N–H···O, O–H···N and N–H···N. These originate commonly from molecular functionalities such as NH_2, OH, CO_2H, $CONH_2$ and CONHR. Such hydrogen bonds are sufficiently strong and directional so that the structural motifs formed by them, say dimer **I** and catemer **II**, formed by carboxylic acid groups and the $(O–H\cdots)_n$ loops, such as **III**, formed by alcohols and phenols are also observed in crystal structures of organometallic molecules that contain these functional groups (Scheme 1).[20] Take for instance, the organometallic complex tetracarbonyl(η^2-fumaric acid)iron. This is a good example of the transferability of the carboxylic dimer synthon from organic to organometallic crystals. In the complex the fumaric acid ligands form corrugated ribbons that are constituted with carboxylic dimer synthons (Fig. 1a). This arrangement nearly replicates what is observed in crystalline fumaric acid (Fig. 1b). Analogous relationships between organic molecules and organometallic complexes are seen when primary and secondary amido groups are present on the ligands.[21,22]

Strong hydrogen bonds dominate the crystal packing in both organometallic and organic systems because of the possibility of forming ring systems that confer additional stabilisation to the hydrogen bond network. This is maintained even in the presence of weaker acceptors such as the CO ligand, which is peculiar to organometallic compounds. There is also the possibility of the formation of weak C–H···O≡C hydrogen bonds. In general, there is a competition between the various donors and acceptors based on their number, strength and steric availability. A nice example is crystalline $[Cr(CO)_3\{\eta^6\text{-}C_6H_4\text{-}(C_3H_4(CH_3)OH)\}]$, in which (Fig. 2) the OH groups participate in a bifurcated interaction with two CO ligands and accept hydrogen bonds from the arene C–H group, to form a linear array as shown in **IV**.[23]

Among the weak hydrogen bonds, the C–H···O variety is ubiquitous and occurs in most molecular crystals, which contain the atoms, C, H and O.[24,25] The role of C–H···O interactions in determining crystal structures is by now well established as is an acceptance of their hydrogen bond nature.[19,26] In almost all cases, short and linear C–H···O geometries correspond to stabilising electrostatic contacts. In a very small number of cases, notably for contacts formed by unactivated



Scheme 1 Structures and supramolecular synthons.

alkyl C–H groups, C–H ··· O geometries are repulsive in nature and could be the forced consequences of packing. C–H ··· O hydrogen bonds are pervasive in crystalline organometallic transition metal complexes and clusters because of the profusion of C(sp^2)–H groups[27] and CO ligands.[28] An interesting feature of C–H ··· O hydrogen bonds 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 the harder O–H ··· O and N–H ··· O hydrogen bonds. The hydrogen bond character of these interactions is borne out by the fact that their length (strength) parallels acceptor basicity. Bridging CO ligands, $M_2(CO)$ and $M_3(CO)$, form contacts to C–H groups, **V** and **VI**, that are shorter than those formed to terminal CO ligands, M(CO), **VII**. C–H ··· O hydrogen bonds in organometallic compounds are also quite directional, with the φ angle around the O atom being around 140°, irrespective of the mode of bonding. In other words, both terminal and bridging ligands are approached in ketone-like directions.[27]

It is pertinent to comment about the CO ligand as a hydrogen bond acceptor in organometallic crystal chemistry.[28] There are several reasons that make hydrogen bonding to the CO ligand important. (1) Weak donor groups are abundant. Most organometallic complexes carry ligands such as arene, cyclopentadienyl, phenyl, methylidene and methylidyne, all of which are capable of hydrogen bond donation from C–H groups of greater or lesser acidity. Hydrogen bonding involving M–H donor groups is also possible (see below). (2) Other common acceptors could be absent. Ligands with organic-type acceptors are not very common in organometallic chemistry. The stabilisation of low oxidation states requires neutral π-acid ligands such as C≡O, that are capable of interacting with the metal in the electron σ donation/π back donation synergistic ligand–metal interaction. (3) The basicity of the CO ligand is tunable with metal co-ordination and increases with the ketone nature of the C≡O (see above).

Strategic concerns regarding crystal architecture have been brought to bear in a recent study wherein suitably chosen π-bonded components are assembled with O–H ··· O hydrogen bonds to generate extended structures. Keeping in mind that both benzene-1,3,5-tricarboxylic acid and $[Cr(CO)_3\{\eta^6\text{-}C_6H_5CO_2H\}]$ form O–H ··· O dimer synthons in their crystal structures, Brammer and co-workers have crystallised $[Cr(CO)_3\{\eta^6\text{-}C_6H_3(CO_2H)_3\text{-}1,3,5\}]$ from di-*n*-butyl ether.[29] Instead of forming the extended hexagonal honeycomb structure as in trimesic acid, the observed structure is more reminiscent of the zigzag ribbon in isophthalic acid derivatives (Fig. 3).[30] The third carboxylic group forms an isolated O–H ··· O hydrogen bond with the ether O atom of the solvent. Whether or not the honeycomb structure was the desired target, and whether it might have been achieved were another recrystallising solvent used, is not clear. However, there is adequate precedent for both honeycomb and zigzag topologies in the organic crystal engineering literature[31,32] and the present example is a case where similar hydrogen bonding interactions are present in organic and organometallic crystals, leading to similar crystal packing arrangements. The fact that trimesic acid generally forms a honeycomb structure while its organometallic counterpart does not reflects the fact that minor molecular modifications can perturb hydrogen bond networks. However, one need not be too critical in such matters, after all, even the honeycomb network in trimesic acid is disrupted in the presence of a strongly hydrogen bonding solvent such as DMSO.[31]

Hydrogen bond types particular to organometallic chemistry

I now discuss hydrogen bonds and related interactions that are distinctive and peculiar to organometallic systems. The identification of transition metal atoms as hydrogen bond donors and acceptors is a fairly recent development.[7,33] The emphasis in hydrogen bond research has remained mostly within the domains of organic and biological compounds[34] where donors and acceptors are constituted with atoms such as O, N, halogen and S, and in the non-conventional or weak case with C. In inorganic systems too attention has largely been directed towards strong bonds formed by the above main group elements, most commonly as ions.[35] In contrast, hydrogen bonds that involve transition metal atoms are usually weak. Certainly, they may be termed non-conventional, at least at the present time.[19] Five major interaction types will be described: (1) hydrogen bonds with metal atom acceptors; (2) hydrogen bonds with M–H group donors; (3) agostic interactions; (4) dihydrogen bonds and (5) inverse hydrogen bonds.

Metal centres that can act as hydrogen bond acceptors (X–H ··· M) are typically late transition metals in low oxidation states and containing a sterically accessible filled metal-bound orbital. Following Brammer, pertinent classes of compounds are given in Scheme 2, with the metal atoms typically being Fe, Co, Ir, Pd, Pt.[36] Database studies by Braga, Desiraju

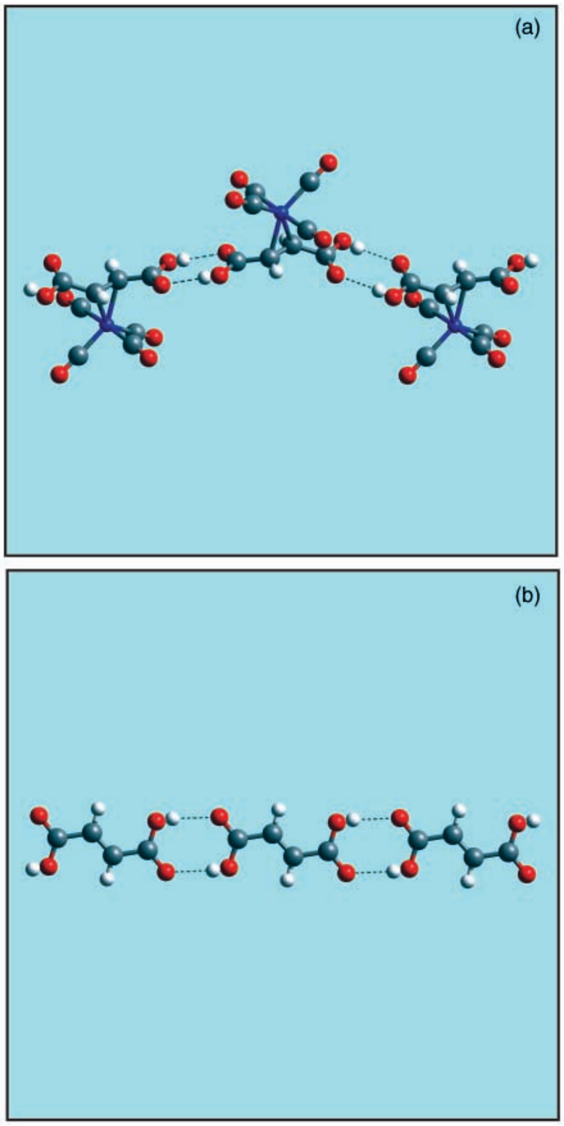
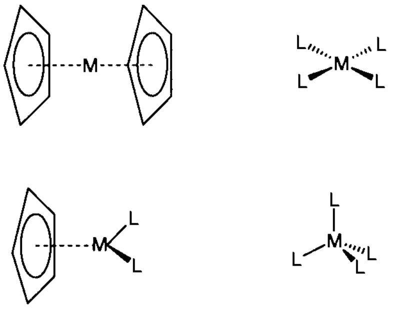


Fig. 1 (a) Fumaric acid as complexed in tetracarbonyl(η^2-fumaric acid)iron. The carboxyl dimer rings lie on centres of inversion with an O–H···O geometry of $d = 1.66$ Å, $\theta = 174°$. (b) O–H···O dimers in crystalline fumaric acid. Notice the same ribbon arrangement of carboxyl dimer rings. Here $d = 1.71$ Å, $\theta = 164°$. Complexation with $Fe(CO)_4$ does not alter the O–H···O hydrogen bond arrangement. The H atom positions are neutron–normalised.



Scheme 2 Metal centres that can act as hydrogen bond acceptors.

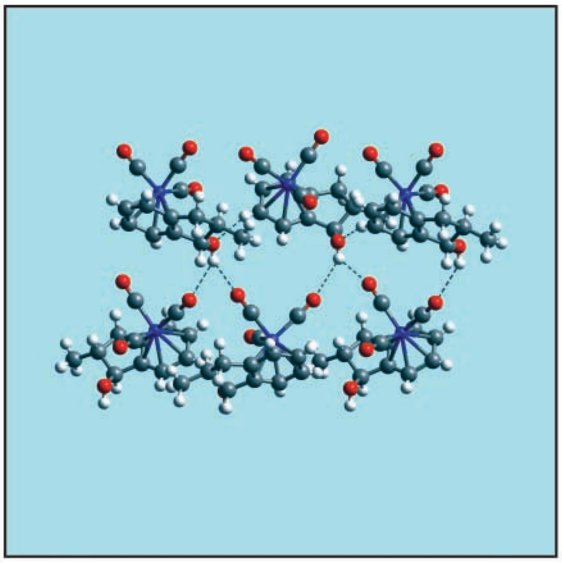


Fig. 2 Structure of crystalline $[Cr(CO)_3\{\eta^6\text{-}C_6H_4(C_3H_4(CH_3)OH\}]$. The OH groups participate in a bifurcated interaction with two CO ligands ($d = 2.42$, 2.27 Å, $\theta = 144$, $131°$) and accept hydrogen bond donation from the arene C–H group ($d = 2.26$ Å, $\theta = 153°$). The hydrogen bond pattern is shown schematically in **IV**. Note that the O–H···O and C–H···O interactions are part of a co-operative network and are of similar lengths. The H atom positions are normalised.

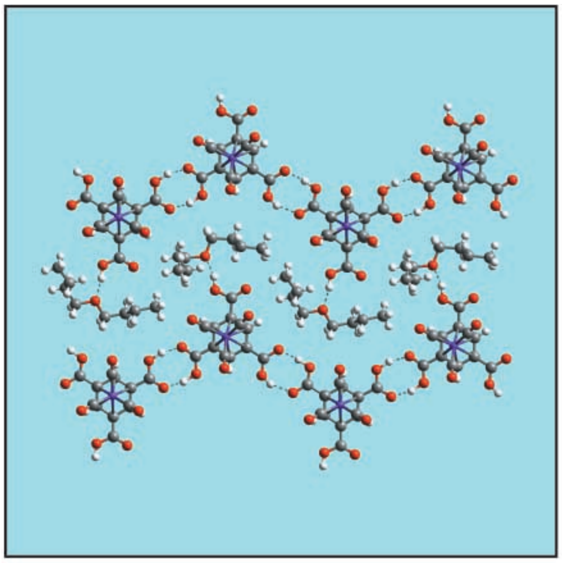


Fig. 3 Zigzag ribbons of carboxylic acid O–H···O dimer rings (range $d = 1.64$ to 1.70 Å, $\theta = 154$ to $164°$) in $[Cr(CO)_3\{\eta^6\text{-}C_6H_3(CO_2H)_3\text{-}1,3,5\}]$. The third carboxyl group is hydrogen bonded ($d = 1.73$ Å, $\theta = 164°$) to the solvent di-*n*-butyl ether, which fills the spaces between acid ribbons. Notice that the hexagonal cavity structure of trimesic acid is not realised here. The H atom positions are normalised.

and co-workers show that the formation of intermolecular hydrogen bonds to such electron rich metals is a common phenomenon, observed for all traditional and non-traditional hydrogen bonding donor groups.[37] Hydrogen bonding to metal centres in neutral complexes has been compared with charge assisted hydrogen bonds (X^+–H···M^-) involving electron rich anionic complexes. Inter-ionic hydrogen bonds of the type N^+–H···M^- were originally noticed by Calderazzo *et al.* with the anion $[Co(CO)_4]^-$ and counter ions of the $[NR_3H]^+$ type.[38] As an example, the structure of the $[NMe_3H]^+$ salt is shown in Fig. 4. Brammer and co-workers examined related crystal structures from the structure correlation viewpoint.[36] These workers also carried out neutron diffraction studies.[39] In $[NEt_3H]^+$-$[Co(CO)_4]^-$, for example, the N–H···Co distances *d* and *D* were found to be 2.61 and 3.67 Å, respectively, at 15 K. Other recent examples of N–H···Pt,[40] O–H···Pt[41] and C–H···Pd[42] hydrogen bonds may be mentioned in this context. To summarise, X–H···M hydrogen bonding interactions are common when donors such as N–H, O–H and C–H are able to approach a nucleophilic metal centre.

The M–H group, nominally hydridic in character, can sometimes act as a non-conventional hydrogen bond donor (M–H···X). This is because metal atoms in co-ordination

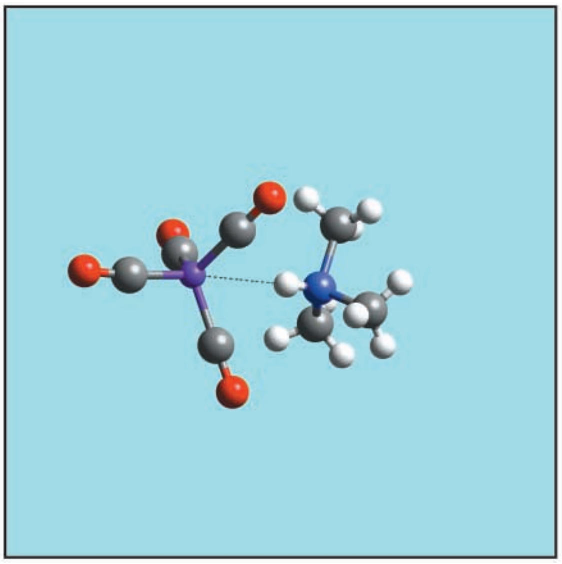


Fig. 4 The N–H···Co hydrogen bond in crystalline $[NMe_3H][Co(CO)_4]$. There are two symmetry-independent interactions with $d = 2.37$, 2.39 Å; $\theta = 179.5$, 179.7°. The H atom positions are normalised.

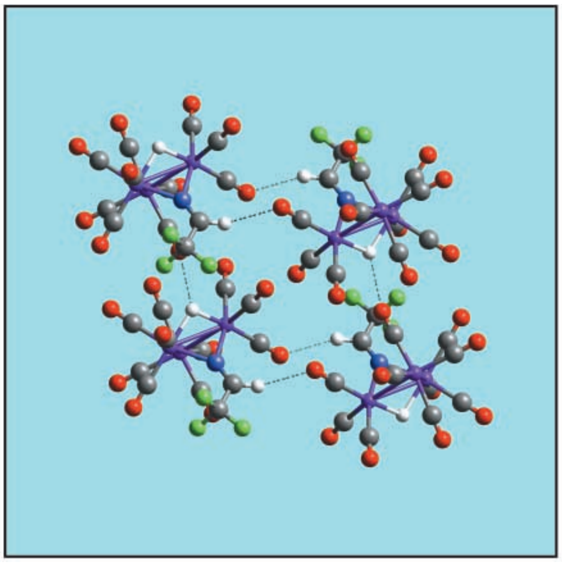


Fig. 5 Os–H···O≡C and C–H···O≡C hydrogen bonds in $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-NCHCF}_3)]$. Notice that both types of C–H groups are activated. The metrics are: Os–H···O, $d = 2.59$ Å, $\theta = 116$, 136° (not normalised); C–H···O, $d = 2.57$ Å, $\theta = 159°$ (normalised).

complexes and clusters are amphoteric depending on their electronic configuration, oxidation state and electronegativity, as well as the type and distribution of ligands.[43] Metal-bound H atoms in metal clusters, the so-called metal hydrides, can form hydrogen bonds with suitable bases provided that the hydrogen ligand is not sterically hindered.[44] When the approach is not forbidden by the encapsulation of the H ligand within the ligand shell, the H atoms can form intermolecular bonds comparable in length with those of the C–H···O≡C type.[45] Needless to say, the electronic nature of the metal plays a fundamental role in tuning the polarity of the M–H system. In general, an accumulation of positive charge on the metal-bound H atom is observed in neutral polynuclear cluster complexes where the H atom is often present in a μ or in a μ_3 bonding fashion. A good example with μ-H atoms is afforded by $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-NCHCF}_3)]$, the structure of which has been determined by neutron diffraction (Fig. 5).[46] Each cluster molecule participates in two types of hydrogen bonds. The first is of the Os–H···O type ($d = 2.59$ Å) while the other is a more traditional C–H···O bond ($d = 2.57$ Å). Note though that the two interactions are nearly of the same length.

The agostic interaction, **VIII**, is a three-centre two-electron interaction between an electron deficient metal atom and a C–H σ bond.[47] Agostic interactions and hydrogen bonds are fundamentally different. As mentioned earlier, hydrogen bonds can formally be designated as three-centre four-electron interactions, and the ideal geometry is linear. In contrast, an agostic interaction is of the three-centre two-electron type, in that an electron deficient metal makes a close approach to an electron-rich C–H bond, and the M···(H–C) geometry is T-shaped.[48] The agostic interaction is therefore a manifestation of metal atom Lewis acidity. Agostic interactions have energies in the range -7 to -15 kcal mol^{-1}. Early transition metals such as Ti, Ta and Zr are typically involved, but also Ni and Fe.[49] In the agostic interaction the position of the H atom can severely be deformed so that neutron diffraction is of particular utility. A nice example is provided by the neutron crystal structure of $[Mo(NC_6H_3Pr^i_2\text{-}2,6)_2Me_2]$ with two highly distorted methyl ligands. This distortion has been ascribed to multiple C–H···Mo agostic interactions.[50] The C–H···Mo angles are around 50° (for a methyl H atom not involved in the agostic interaction the corresponding angle is around 43°) while the H···Mo distances are 2.585 and 2.598 Å, significantly shorter than the distances to the 'free' H atoms (2.755 and 2.760 Å). To summarise then, agostic interactions are formed when an acidic metal atom accepts electron density from C–H σ bonds. Both intramolecular and intermolecular agostic interactions are specific to organometallic systems and have no counterpart in organic crystal chemistry and there has been an increasing appreciation of their importance in crystal packing.[51]

In the dihydrogen bond, X–H···H–M, the element M can be any with the M–H bond having a $M^{\delta+}$–$H^{\delta-}$ polarization.[52,53] Typically, M is a Group III element including B, or a transition metal. The hydridic polarisation $M^{\delta+}$–$H^{\delta-}$ is obtained depending on the mode of co-ordination of the H atom, the electronic state of the central atom and the nature of the other ligand(s) bound. These M–H groups, either Group III or transition metal, may interact attractively with classical $X^{\delta-}$–$H^{\delta+}$ donors. Both cases have attracted much recent attention. Among the former, one might mention N–H···H–B hydrogen bonds in H_3B–NH_3. In a CSD study performed on these interactions it was found that the normalised H···H distances are in the range 1.7–2.2 Å.[54] These are much shorter than the van der Waals distances. It was also found that the N–H···H angles tend to linearity (range 117–171°, average 149°). In most of the examples retrieved the N–H donor is positively charged, as in say ammonium and pyridinium ions. The B–H bonds are typically from boron cage anions, such as aminoboranes or aluminoboranes wherein the B atom is expected to bear at least a partial negative charge. Another recent example of dihydrogen bonds formed by Group III hydrides is cyclotrigallazane $[H_2GaNH_2]_3$, wherein the N–H···H–Ga interaction is estimated to be worth around -3 kcal mol^{-1} of stabilisation.[55]

Dihydrogen bonds of transition metal hydrides are observed intra- and also inter-molecularly. Crabtree *et al.* have provided an estimate of -5 kcal mol^{-1} for the Ir–H···H–N hydrogen bond in $[IrH_3(PPh_3)_2(NC_5H_4NH_2\text{-}2)]$, **IX**, a compound specifically designed to study this unusual phenomenon.[52] The authors conclude that this interaction is strong enough to be considered a full-fledged hydrogen bond, and indeed comparable to a conventional N–H···OH_2 hydrogen bond. While the first examples of intramolecular dihydrogen bonds involving Tr–H (Tr = any transition metal) acceptors were obtained by serendipity, the first *inter*molecular interactions of this kind were constructed deliberately with rhenium polyhydrides.[56] In two examples, that have been studied with neutron diffraction, the shortest H···H distances are around 1.7 Å, and the bonding nature of the interaction has been verified with IR spectroscopy. Dihydrogen bonds formed by C–H donors have been found in some complexes of Ir and Ru.[57]

If X–H groups can have the polarity $X^{\delta+}$–$H^{\delta-}$, it follows that they should be able to form directional interactions of the kind $X^{\delta+}$–$H^{\delta-}\cdots A^{\delta+}$ which obey principles similar to those that hold for normal hydrogen bonds. Indeed such an arrangement would formally fulfil several definitions of a hydrogen bond! Nevertheless, to highlight the reversed distribution of charge, Rozas *et al.* have termed this interaction the inverse hydrogen bond.[58] This seems to be an apt description. It may be noted that the dihydrogen bond described above could also formally be termed as a combination of a normal hydrogen bond $X–H^{\delta+}\cdots{}^{\delta-}H$ and an inverse hydrogen bond $M–H^{\delta-}\cdots{}^{\delta+}H$. In theoretical terms, inverse hydrogen bonds have been treated by several authors but mostly for hypothetical systems.[59]

Whether hydrogen bonds are peculiar to organometallic systems or not, their study derives from a common premise, namely that they are largely electrostatic in nature. One might begin with the archetypical C–H···O hydrogen bond and then, by varying the acceptor, obtain the C–H···M and C–H···π bonds. Alternatively, by varying the donor, one would obtain the M–H···O bond. Modifications in both donor and acceptor moieties result in hydrogen bonds such as O–H···π and X–H···H–M. In all these variations the fundamental properties of the hydrogen bond are maintained. These variations are of further chemical interest because they could also involve changes in hardness or softness. In terms of strength, some of these novel types of hydrogen bond could be significant. The widespread occurrence and diverse geometrical arrangements that characterise these non-conventional hydrogen bonds suggest that they will, in the future, find applications in crystal engineering. At least their role could be a supportive one in the construction of extended hydrogen bonded networks.

Other interaction types

A few other interactions in organometallic crystals should be mentioned for the sake of completeness. The aurophilic interaction, Au···Au, is a new type of linkage for supramolecular assembly and theoretical treatment has shown that its strength depends on the type of ligand bound to the Au atom, increasing for example on going from Cl to Br to I.[60] The aurophilic interaction is observed in the majority of Au-containing compounds and its orientation appears to be characterised by specific angular requirements.[61] It has features that are common to hydrogen bonds.[62] Typical energies lie between −6 and −11 kcal mol^{-1}, in the range for moderate to strong hydrogen bonds.[63] Recent work indicates that the Au···Au interaction competes favourably with other interactions in determining crystal packing preferences, showing that it is both strong and directional. This indicates its potential importance in crystal engineering.[64] A good example of the competing influences of various interactions is given in the analysis of the crystal structure of bis(3-bromopyridine)gold(I) dichloroaurate(I) by Freytag and Jones.[65] The structure of this complex is shown in Fig. 6 wherein it may be seen that the packing is determined by three types of secondary interaction: aurophilic interactions, C–H···Cl hydrogen bonds and Br···Cl interhalogen interactions. The Au···Au distances are 3.268 and 3.311 Å (distance in gold metal is 2.89 Å). This example shows that organometallic crystal structures need to be analysed with care as several weak interactions with varying directionalities may need to be considered.

Orpen and others have outlined secondary bonding to Bi as a potential design tool in crystal engineering.[66] Secondary bonding was defined by Alcock as intermolecular hypervalent interactions to heavy p-block elements (Pb, Bi, Te).[67] These interactions are electronically distinct from systems in which the Lewis acid has no lone pair. Typical ring and chain motifs constituted with such hypervalent Bi···Cl interactions are shown as **X** and **XI**. Other similarities between these interactions and hydrogen bonds have been discussed.

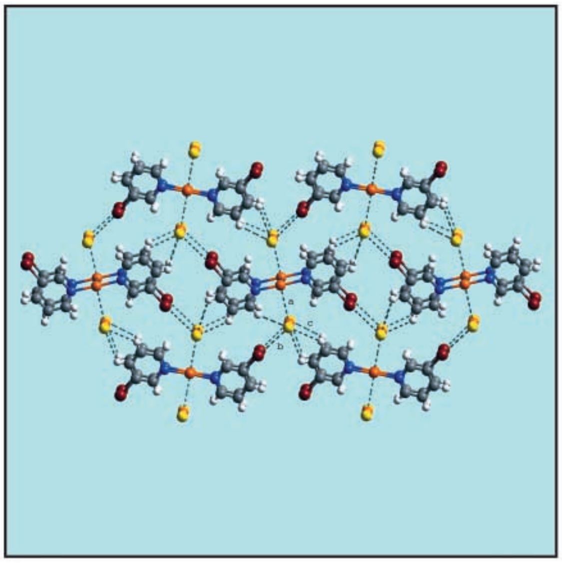


Fig. 6 Au···Au aurophilic interactions (*a*) Br···Cl interhalogen interactions (*b*, 3.38, 3.44 Å) and C–H···Cl hydrogen bonds (*c*, range $d = 2.54$ to 2.91 Å; $\theta = 117$ to 154°) in bis(3-bromopyridine)gold(I) dichloroaurate(I). The aurophilic interactions within the dimeric cation (3.31 Å) and between cation and anion (3.27 Å) are comparable. Only one of the eight distinct C–H···Cl hydrogen bonds is shown. This structure is a nice example of interplay between several weak interactions. The H atom positions are normalised.

Conclusion

In this article I have discussed the properties of the most frequently observed intermolecular interactions in crystal structures of organometallic compounds. If possible, this has been done in the context of crystal engineering, in other words to assess the possibility of using these interactions in crystal design. I have attempted to compare interactions in organometallic crystals with those found in organic crystals. In this connection two situations are prevalent: (1) the same interaction is found in organometallic and organic crystals, either manifested exactly the same way or with some small variations that depend on the organometallic nature of the system; (2) the interactions found in organometallic crystals are entirely different with no organic counterpart.

A few projections regarding organometallic crystal engineering are probably in order. If crystal engineering is to be both interesting and useful, there should be an adequate interplay between molecular and supramolecular synthesis. At a molecular level, synthetic organometallic chemistry is very well developed. Supramolecular organometallic synthesis is still, however, based on interactions that are common to organometallic and organic crystals.[68] What are required are supramolecular synthetic strategies that exploit the unique nature of those intermolecular interactions that are particular to organometallic crystals. Supramolecular synthons based on such interactions need to be identified; this would surely lead to a tremendous increase in the types of crystal architectures and therefore properties that remain to be discovered.[69]

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