Hydrogen bonding in organometallic crystals – a survey

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Abstract

Patterns of hydrogen bonding in organometallic crystals and the relationship with the hydrogen bonding patterns in organic solids have been discussed. It has been shown, inter alia, that organometallic systems provide new types of hydrogen bonding donor and acceptor groups, such as the M-H system and the CO ligand in its various bonding modes, which have no counterpart in organic crystals. Emphasis is given to the recognition of packing motifs and to the importance of hydrogen bonds in the construction of crystalline materials based on co-crystallization of organic and organometallic molecules chosen on the basis of complementarity of shape and size. © 1997 Elsevier Science B.V.

1. Introduction

The knowledge of the intermolecular interactions controlling the organization of molecules or ions in the solid state is a necessary prerequisite for the construction of materials with pre-defined chemical and physical properties [1]. We have recently undertaken a study of hydrogen bonding in organometallic crystals. Our research has been aimed at the understanding of the major cohesive forces in inorganic and organometallic solids in the context of crystal engineering [2] and supramolecular synthesis [3]. Attention has been initially directed to the most important patterns of hydrogen bonding in organometallic crystals and to the relationship with similar patterns in organic solids. Hydrogen bonding complementarity, for example, as well as the recognition of recurring packing motifs can be used to project the synthesis of crystalline materials based on co-crystallization of organic and organometallic molecules chosen on the basis of complementarity of shape, size, and structural functionality [4]. While an analysis of the structures deposited in the Cambridge Structural Database (CSD) [5] provides a means for the statistical analysis, it is from a direct comparison of selected examples that one can best appreciate similarities and differences in hydrogen bonding patterns and geometry between organic and organometallic crystal structures.

In keeping with the theme of this special issue we take the opportunity to stress the importance of hydrogen bonds in the emerging area of organometallic crystal engineering. Hydrogen bonds between conventional donors and acceptors, such as -COOH, -OH, -CONR$_2$ groups etc., will be discussed first, while the second part of the paper will be devoted to interactions more specific to the organometallic chemistry field. In all cases use will be made of CSD REFCODES [6], which shall permit the interested reader to access easily the reference to the original structural papers. Unless otherwise stated, all bond distances and angles discussed in the following have been calculated on the basis of geometrically positioned hydrogen atoms or of 'normalized' X–H bonds based on observed hydrogen atom coordinates.

2. The hydrogen bonded carboxylic ring in crystalline complexes [7]

One of the strongest hydrogen bonds is that established by -COOH groups [8]. While mono-carboxylic acids generally form isolate 'rings' via interactions between carboxylic groups belonging to different molecules, and only rarely form extended catemer-type structures, di-carboxylic acids form chains of molecules

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linked by the carboxylic rings. This is a fundamental packing motif that is maintained on going from organic to organometallic solids.

A striking example of the analogy between organic and organometallic crystals is afforded by fumaric acid and its iron complex (η^2-fumaric acid)Fe(CO)$_4$. Two polymorphs are known for fumaric acid (FUMAAC, α-form [6]a and FUMAAC01, β-form [6]b). Both contain molecular chains interlinked via hydrogen bonded carboxylic rings (see Fig. 1a and b). In crystalline FUMAAC, however, the molecular ribbons are not coplanar. Two polymorphic modifications are known also for the complex (η^2-fumaric acid)Fe(CO)$_4$(FECAFA02 [6]c and FEFUMR10 [6]d) in which 'Fe(CO)$_4$' groups are coordinated to the unsaturated C=C bonds. In FECAFA02 the fumaric acid ligands form an intermolecular pattern of the type seen in the dimorphs of fumaric acid, i.e. ribbons of ligands joined by carboxylic rings. This is shown in Fig. 2a. The arrangement of the Fe(CO)$_4$ groups can be appreciated from Fig. 2b which also shows how the fumaric acid molecules form chains parallel to the ab-plane. In this respect the crystal of FECAFA02 can be viewed as derived from crystalline FUMAAC01 (and FUMAAC) by 'intercalation' of Fe(CO)$_4$ units.

In the second form of the fumaric acid complex the carboxylic ring coexists with a catemer-type pattern. FEFUMR10 contains three crystallographically independent molecules in the asymmetric unit which form both large ring systems (see Fig. 3) as well as ribbons interlinked by carboxylic rings.

Maleic acid (MALIAC11 [6]e) forms an intramolecular hydrogen bond as well as an intermolecular interaction [8]. Fig. 4a shows the chains of molecules related by translational symmetry as well as the intramolecular bonds. The donor–acceptor separation within the intramolecular ring is shorter than in the intermolecular ring (2.50 vs. 2.64 Å). The difference can be attributed to resonance. The intermolecular bond also attains a more linear geometry (O–H $\cdots$ A 178.6 vs. 171.50). When maleic acid is coordinated to a Fe(CO)$_4$ unit the complex (η^2 maleic acid)Fe(CO)$_4$ (KAMKAK [6]f is obtained. The complex crystallizes with two independent molecular units. The hydrogen bonding pattern is shown in Fig. 4b. As in crystalline maleic acid, each molecule of (η^2-maleic acid)Fe(CO)$_4$ establishes one intra- and one inter-molecular hydrogen bond. Notably, the intermolecular pattern is the same in both crystals with the maleic acid ligands forming chains. The donor–acceptor distances in KAMKAK are of similar length (2.56 and
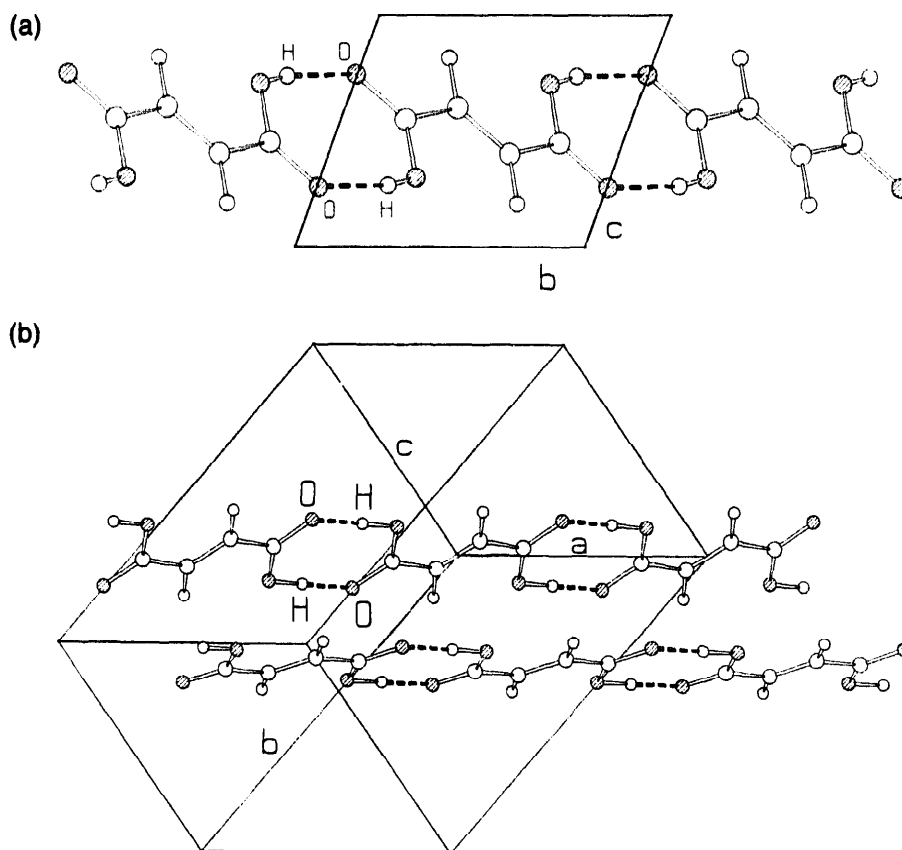
(a)

(b)

Fig. 1. The two polymorphic modifications of fumaric acid. a: P-1 crystal with only one centrosymmetric molecule in the cell (FUMAAC01); b: P2$_1$/c crystal with 6 molecules in the cell (FUMAAC).
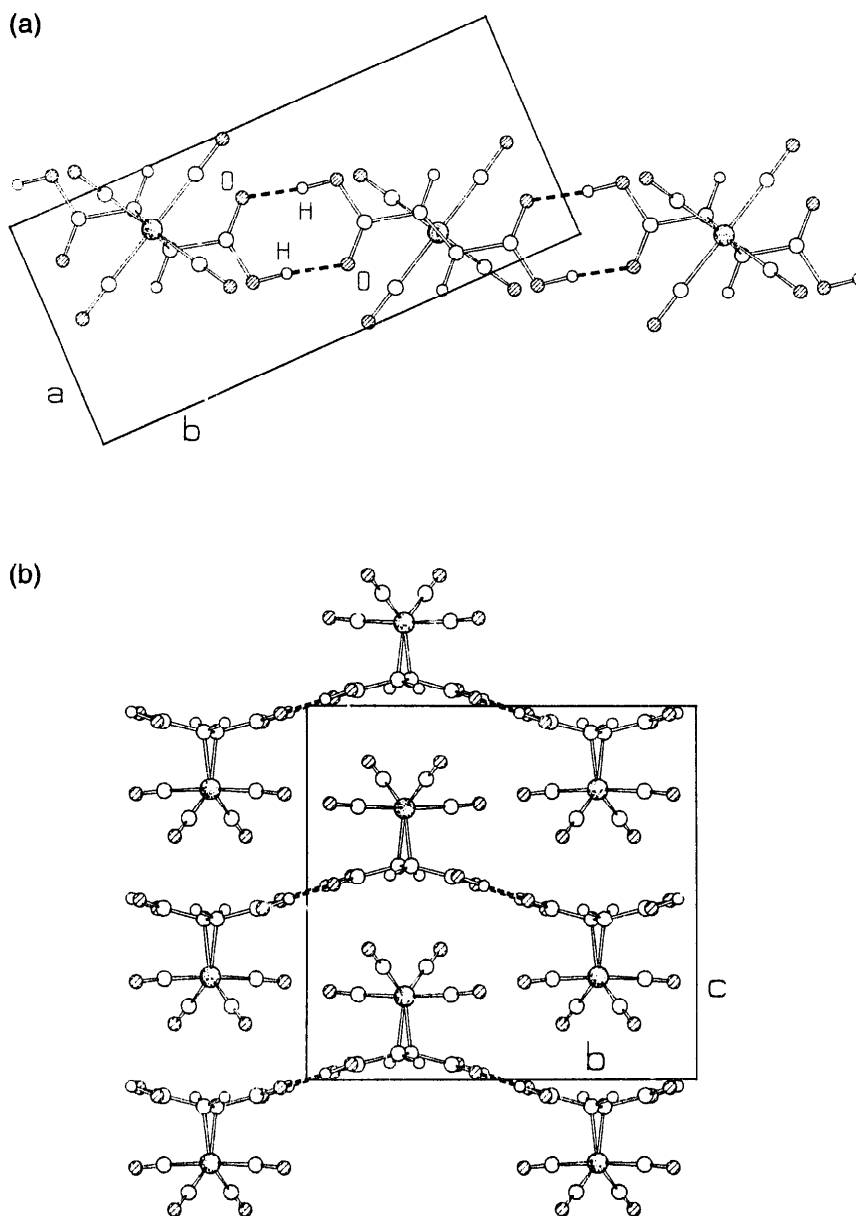
(a)

(b)

Fig. 2. a: the hydrogen bonding network in form FECAFA02 of (η^2-fumaric acid)Fe(CO)$_4$. Note how the fumaric acid ligands are linked via carboxylic rings as in crystalline FUMAAC and FUMAAC01. b: view down the a-axis of the molecular organization in FECAFA02.

2.55 Å for the inter- and intramolecular bond respectively). As in the case of fumaric acid the C=C double bond in maleic acid is π-coordinated to the metal, this probably causes a partial loss of the resonance within the ring.

3. O–H · · · O hydrogen bonds in complexes carrying -OH groups

Another common hydrogen bonding donor–acceptor pair is that afforded by the -OH group [9]. Generally -OH groups form chain or rings. Tetramers and hexamers are quite common in crystals of organic alcohols as well as in crystals of organometallic complexes. For example, the basic packing motif in crystalline (1,2-bis(1-hydroxyethyl)-η^6 benzene)-tricarbonyl-chromium (BENGLY) [6]g is constituted of four molecules forming a ring as shown in Fig. 5a. The donor–acceptor separations within the ring are 2.82 and 2.78 Å, respectively, O–H · · · O angles are 146.4 and 151.5°. The hydroxyl ring is also the hydrogen bonding pattern established by molecules of (η^5-C$_5$H$_5$)-(1-3-η^3-5-exo-hydroxycycloheptenyl)Mo(CO)$_2$ (JEZMUW) [6]h as shown in Fig. 5b. A large hydrogen bonded hexameric unit is present in crystalline trans-bis(μ2-CO)-di-carbonyl-bis(η^5-(2-hydroxyethyl)cyclopentadienyl)-di-iron (JOFJET) [6]j and is shown in Fig. 5c. A twelve-membered ring formed by six molecules of (η^5-C$_5$H$_4$C$_2$H$_4$OH)$_2$Fe$_2$(CO)$_4$ via O–H · · · O bonds (O–O
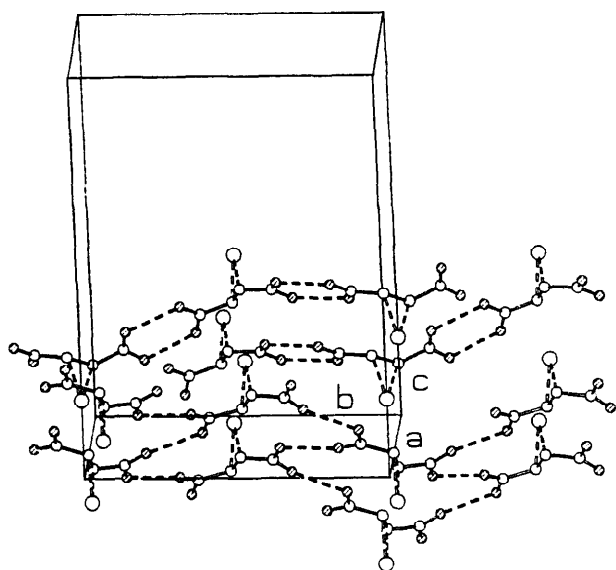
Fig. 3. The three layers of molecules in form FEFUMR10 of (η^2-fumaric acid)Fe(CO)$_4$. CO ligands are not shown for clarity.

2.66 Å, O–H $\cdots$ O 147.1°) between the CH$_2$CH$_2$OH groups.

4. Hydrogen bonding in crystalline amido-complexes [10]

The manganese complex (cyclopentadienyl)-carbonyl-nitrosyl-carbamoylmanganese (η^5C$_5$H$_5$)-carbonyl-nitrosyl-carbamoyl-manganese (CPCNMN) [6]j is a good example of cyclic amide ring systems. The manganese atom is coordinated to one formamide moiety via a M-C σ-bond. Fig. 6a shows how a cyclic amide dimer is established via the interaction of one amide hydrogen with the amide oxygen of a second molecule (N $\cdots$ O, 2.95, (N)H $\cdots$ O 1.93 Å, N–H $\cdots$ O 176.5°). Fig. 6b shows the similar packing motif present in crystalline formamide. The N $\cdots$ O separation is shorter in formamide (2.88 Å) than in the CPCNMN complex. The second amide hydrogen in CPCNMN does not participate in intermolecular interactions but points towards the N-atom of the NO-ligand. The amide oxygen, on the contrary, establishes an additional link (which probably takes the place of the second N–H $\cdots$ O interaction commonly observed in primary amides [11]) with an H-atom belonging to the Cp-ligand (C $\cdots$ O 3.33, (C)H $\cdots$ O 2.39 Å, C–H $\cdots$ O 145.2°).

A dimethylformamide molecule co-crystallizes with the Cu-complex (bis(oxamido)trisulfane-*N,N',O,O'*)-copper(II) (GEHRAM) [6]k. The dimethyl formamide molecule 'bridges' two molecules of the complex in the crystal via NH $\cdots$ O(formamide) interactions (N $\cdots$ O 2.89, and 2.91 Å). In addition, there are two primary

amido groups, belonging to a large macrocycle, which interact directly with the metal atom via the two amido oxygens as shown in Fig. 7. In the amide ring the donor acceptor separation is 2.99, while the separation is shorter within the larger ten-membered ring (2.84 Å).

5. The CO-ligand as C–H $\cdots$ O hydrogen bond acceptor

We have shown that the CO-ligand, so abundant in organometallic chemistry, can be regarded as a new hydrogen bonding acceptor in crystalline complexes and clusters. What is more the ligand is capable of changing its hydrogen bonding accepting capacity by varying the bonding modes with the metal centers. The basicity of CO increases as the ketonic nature of the bonding between C and O increases on passing from terminal to doubly and to triply bridging bonding mode. The basicity of the carbonyl oxygen is, however, small in comparison to the oxygen atom in stronger polar conditions. Thus it is not surprising that CO is able to participate in hydrogen bonding only when stronger acceptor groups are absent and prefers interactions with acidic C–H groups. The order of basicity of CO follows the order $\mu_3 > \mu_2 >$ terminal, which is the reverse order of C–H $\cdots$ O lengths.

Indeed, the abundance of acidic C–H groups on the ligands and of basic sites (oxygen, nitrogen and other typical acceptor atoms) renders C–H $\cdots$ O hydrogen bonding a common feature in organometallic crystals [12]. The role played by C–H $\cdots$ O interactions in determining crystal structure stability is now well established [13] and there is converging evidence of C–H $\cdots$ X (X = O, N, S, etc.) acting as 'crystal sieves' in the nucleation process of stable crystal nuclei. Bonds of this type, although much weaker than those of O–H $\cdots$ O or N–H $\cdots$ O types, become far more important on passing from organic to organometallic crystals because of the profusion of donor and acceptor groups. A large number of organometallic complexes and clusters carry *both* π-acid ligands such as CO and hydrogen bonding C–H donors such as arenes, cyclopentadienyl ligands, phenyls, methylidine and methylidyne groups [14] which add stabilization and directionality to the van der Waals cohesion of organometallic molecular crystals.

Rather than discussing organometallic C–H $\cdots$ O bonds at length, we have decided to focus on two examples in which C–H $\cdots$ O interactions *prove* their bonding nature by restraining atomic displacement in the solid state. This approach follows that used by Steiner [15] in a recent study of C–H $\cdots$ O bonded alkyne C=C–H groups. He was able to demonstrate that the ADPs (atomic displacement parameters) of the

terminal alkyne C-atom are generally smaller than those of the internal alkyne C-atom with the ratio of these parameters being correlated with the C $\cdots$ O distance thus showing that C–H $\cdots$ O interactions are able to restrain the thermal displacement of linked atoms in crystals.

The C–H $\cdots$ O bond network in crystalline [(μ_3-H)Co$_3$Fe(CO)$_9$\{P(OMe)$_3$\}$_3$] HMPCIC0161 [6]] (see Fig. 8) shows the participation of both terminal and bridging CO-ligands in both intra- and intermolecular hydrogen bonds. The structure of HMPCI01 has been determined by neutron diffraction at 90 K, so that hydrogen atom positions are very reliable. An analysis of the anisotropic displacement parameters available for these atoms afford important additional information on the bonding nature of C–H $\cdots$ O interactions. The basic assumption is that a strong C–H $\cdots$ O bonding would affect the

thermal vibration of the atoms involved in the bond. In particular, we concentrated on the U_{eq} values for the C and O atoms of the ligand. Our results (discussed in detail in Ref. [12]) indicate clearly that there is lower relative motion of O with respect to C for bridging carbonyl ligands as compared to terminal ones as might be expected since these latter protrude more from the surface and have a larger soft bending motion. Interestingly, there is a very good correlation between the ratio of the observed Us and the H $\cdots$ O distances. This demonstrates clearly that as the C–H $\cdots$ O bond gets stronger, the Oatoms are able to vibrate less.

Another interesting manifestation of the effect of C–H $\cdots$ O bonding on solid state dynamical behavior is shown by crystalline *cis*-, and *trans*-$(\eta^5$-C$_5$H$_5$)$_2$Fe$_2$(CO)$_2$(μ-CO)$_2$. These complexes carry both terminal and bridging CO ligands which participate in
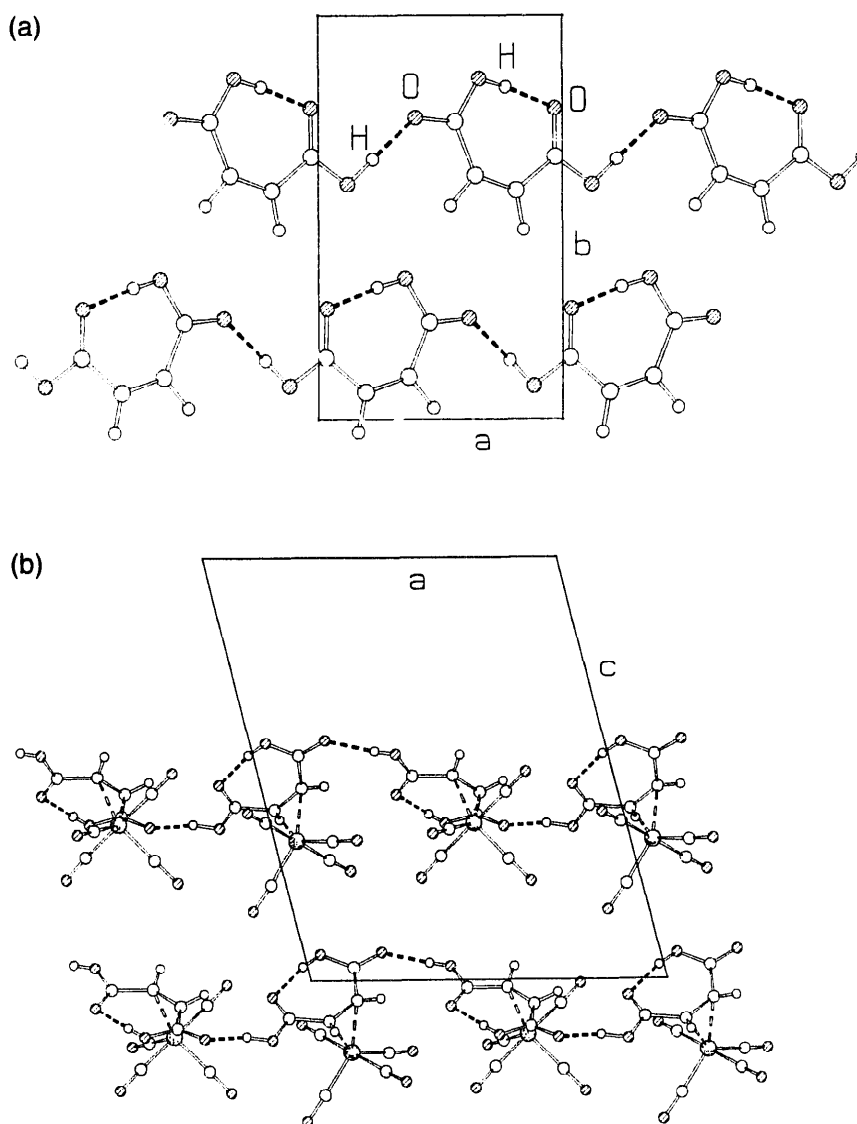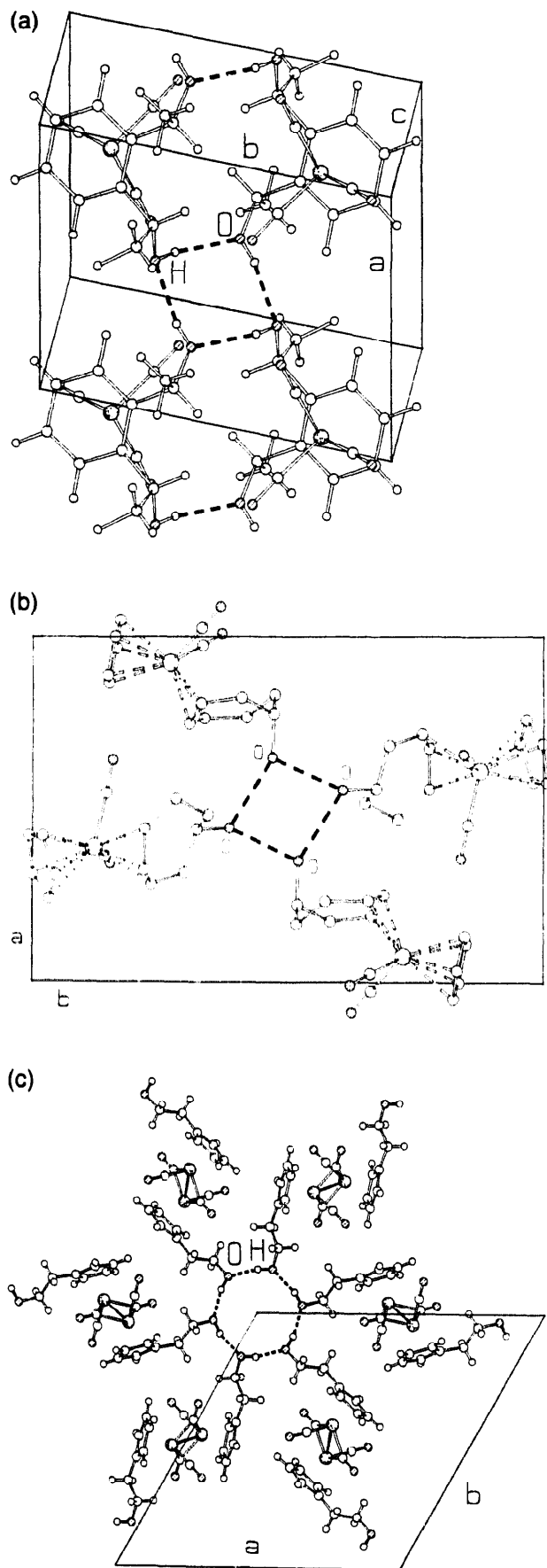

(a)

(b)

Fig. 4. Molecular arrangement and hydrogen bonding network in crystalline maleic acid (MALIAC11, a) and in (η^2-maleic acid)Fe(CO)$_4$ (KAMKAK, b). Note how the dicarboxylic acid molecules form the same patterns in the two crystals but have different relative conformations along the chains.

(a)

(b)

(c)

intermolecular hydrogen bonds of the C–H · · · O type with the CH groups of the cyclopentadienyl ligands. While both isomers form dimers which show some resemblance to O–H · · · O dimers formed by carboxylic acids in the crystal of the *trans*-isomer each molecule forms C–H · · · O interactions with four other surrounding molecules. Because of the site symmetry, both C_5H_5-ligands of the *trans*-isomer have crystallographically identical surroundings and are involved in the same type of interactions. On the contrary, in the case of the *cis*-isomer there is no crystallographically imposed symmetry, hence the different packing environments around the two C_5H_5-rings are reflected in the presence of different patterns of C–H · · · O interactions with the CO-ligands (see Fig. 9). We have been able to show that the difference in hydrogen bonding patterns accounts for the different solid state dynamic behavior of the two C_5H_5-ligands [16]. In fact, the two ligands undergo reorientational jumping motions in the solid state with different activation energies (7.2 vs. 15.8 kJ mol^{-1} from ^1H spin-lattice relaxation time measurements) and different potential energy barriers (7.9 vs. 17.6 kJ mol^{-1} from packing potential energy barrier calculations). What is more, the two ligands possess different mean-square librational amplitude of motion about the axes perpendicular to the ligand planes (302.8 and 62.4 deg^2 from thermal motion analysis). Indeed the ring atoms involved in more and shorter links are those that move less about equilibrium positions and reorientates with a higher cost in energy. This concurrence of evidence coming from different experiments is clearly indicative of the effectiveness of C–H · · · O interactions as bonds.

6. New hydrogen bonding donors

Organometallic systems offer not only new bases, with no parallel in hydrogen bonding in organic chemistry, but also new hydrogen bonding donor systems, i.e. 'new' acids.

We have recently shown [17] that metal-bound hydrogen atoms ('hydrides' [18]) polymetallic complexes, can form hydrogen bonds with suitable bases (usually CO) provided that the hydrogen ligand is not sterically hindered. A good example is afforded by the structure of (μ-H)(μ-NCHCF$_3$)Os$_3$(CO)$_{10}$ (BAJXIT [6]m) which has been determined by neutron diffraction. As shown in Fig. 10 each cluster molecule participates in two types of hydrogen bonding interactions. The hydrogen bond involving the H(hydride) effectively links molecules via a direct with a terminally bound CO

Fig. 5. The tetrameric hydrogen bonded rings present in crystalline BENGLY (a) and JEZMUW (b); the ring system present in crystalline JOFJET (c).
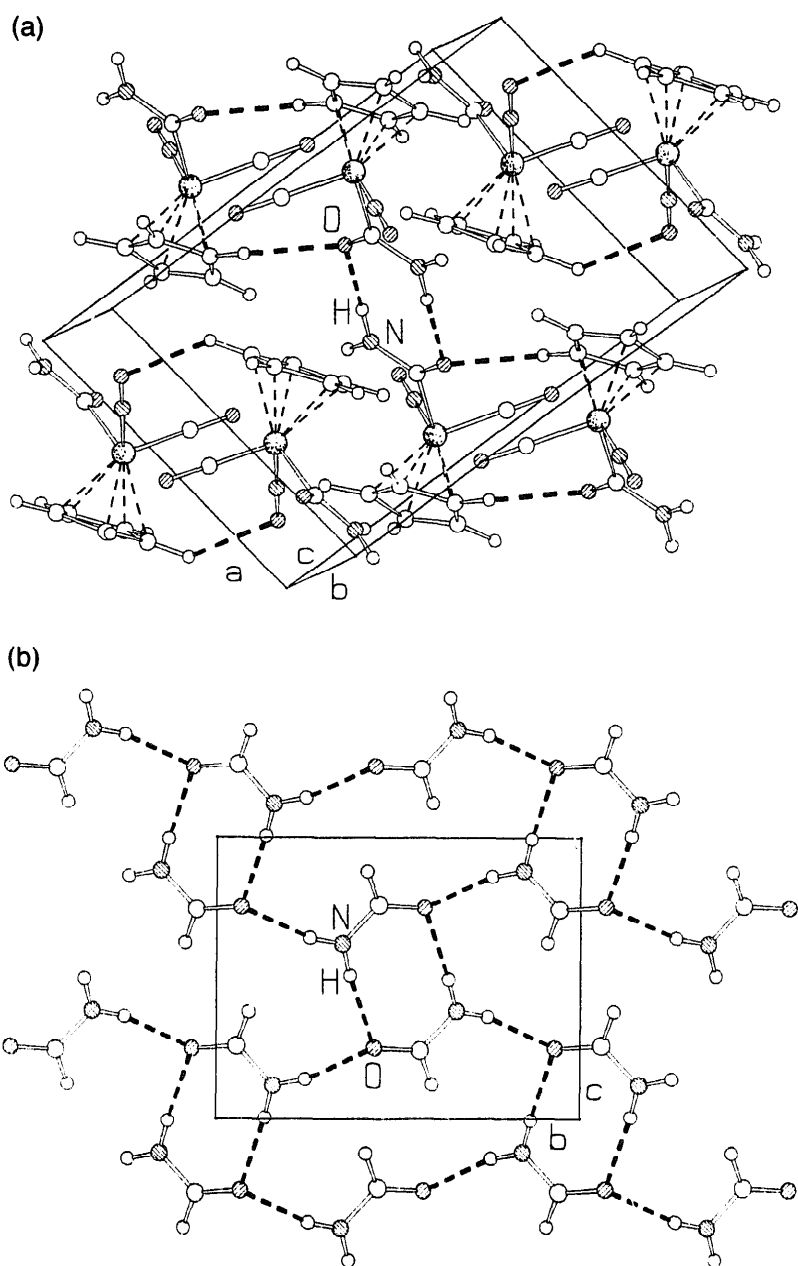
(a)

(b)

Fig. 6. Cyclic amide ring in crystalline CPCNMN (a) and comparison with the cyclic dimers present in crystalline formamide (b). In a, note also the CH · · · O(amide) and CH · · · O(NO) interactions.
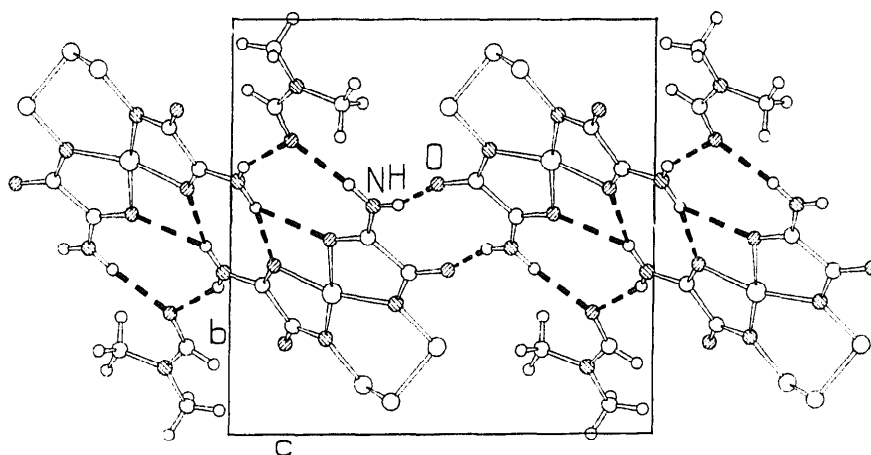

Fig. 7. The two different types of cyclic systems (eight- and ten-membered rings) present in crystalline GEHRAM. Note how the dimethylformammide molecules interact with two molecules of the complex.
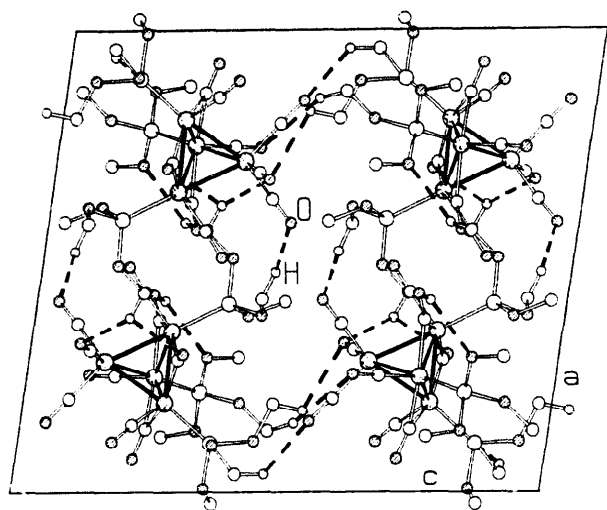
Fig. 8. Hydrogen bonding network in crystalline HMPClCO1. H atoms not involved in hydrogen bonding interactions are omitted for clarity.

((Os)H $\cdots$ O 2.594 Å). Dimers of molecules are also formed via C–H $\cdots$ O bonds between ((C)H $\cdots$ O, 2.571 Å). This kind of ring is reminiscent of the hydrogen bonding patterns discussed above in the case of strong hydrogen bonding situations.

Crystalline (μ-H)$_3$Os$_3$Ni(CO)$_9$(C$_5$H$_5$)$_2$, (BOBTAN10) [6]n also shows as both M-H $\cdots$ O and

C–H $\cdots$ O hydrogen bonds are important in determining the molecular arrangements in the crystals (see Fig. 11). The Os-H $\cdots$ O intermolecular bond links molecules in chain-like fashion while a C–H group belonging to a C$_5$H$_5$ ring and a terminally bound form a ring with two molecules related by a center of inversion ((Os)H $\cdots$ O 2.446, (C)H $\cdots$ O 2.434 Å).

7. Agostic interactions C–H $\cdots$ M

It is important to address, in the context of this paper, the analogy and difference between the interaction of electron density donor systems and electron deficient metal atoms ('agostic' interactions [19]) and hydrogen bonds. In contrast to hydrogen bonds that can be formally designated as 3-center/4-electron interactions, an agostic interaction is of the 3-center 2-electron type [20] 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 [21].

Fig. 12 shows the tribridged structure of LiBMe$_4$ wherein the BMe$_4$ units are linked by one tri- and two di-bridged C–H $\cdots$ Li contacts to form a linear chain. Such cases are not surprising because Li + is a very
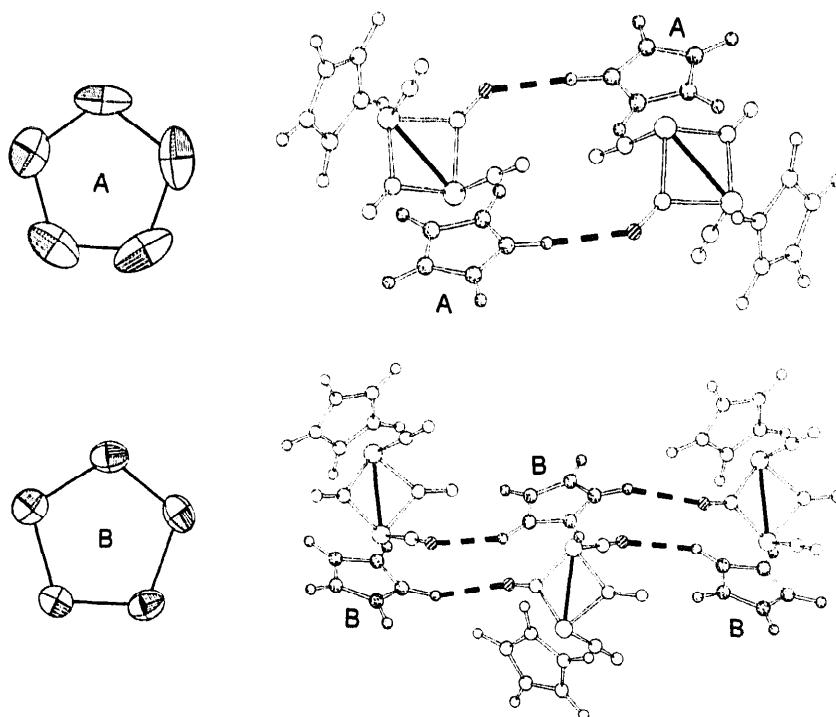

Fig. 9. Both *cis-*, and *trans-*(η^5-C$_5$H$_5$)$_2$Fe$_2$(CO)$_2$(μ-CO)$_2$ form dimers via CH $\cdots$ O hydrogen bonds which show some resemblance to O-H $\cdots$ O dimers in carboxylic acids. The figure shows the effect of the different number of C–H $\cdots$ O hydrogen bonds involving the two crystallographically independent C$_5$H$_5$-rings (A and B) in crystalline cis-(η^5-C$_5$H$_5$)$_2$Fe$_2$(CO)$_2$(μ-CO)$_2$ on the anisotropic displacement parameters of the carbon atoms.
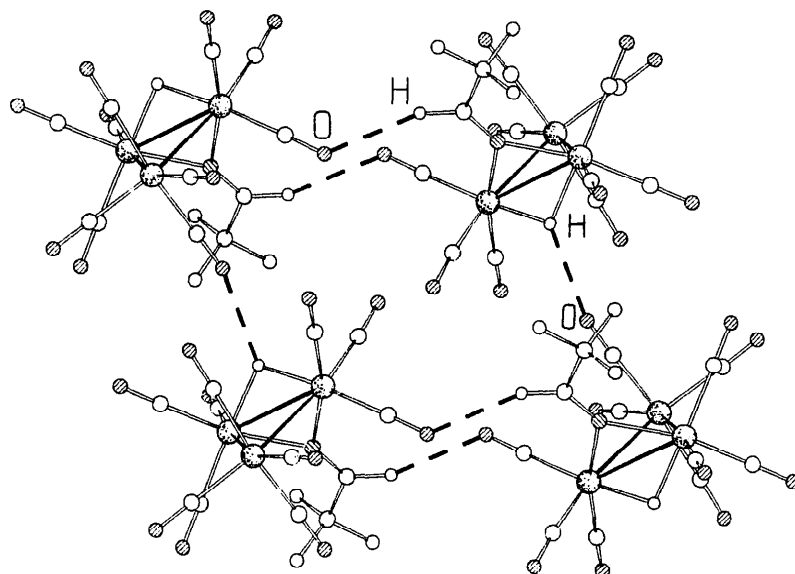
Fig. 10. Crystalline (μ-H)(μ-NCHCF₃)Os₃(CO)₁₀ (BAJX1T). Each cluster molecule participates in hydrogen bonding interactions of the M–H · · · O and CH · · · O types. Note that the hydride · · · CO interactions form molecular rows whereas the C–H · · · O bonds form rings between molecules related by a center of symmetry.

strong Lewis acid which tries to obtain electrons from any available source. C–H · · · Li interactions are expected to lead to C–H activation which is a prerequisite for insertion reactions.

The case of the iron cluster (μ-H)Fe$_4$(η^2-CH)(CO)$_{12}$ (HMYCFE01) [6]o,p is also of great interest, since the methylidyne C–H system bridging the wings of the butterfly cluster participates in both an agostic bond
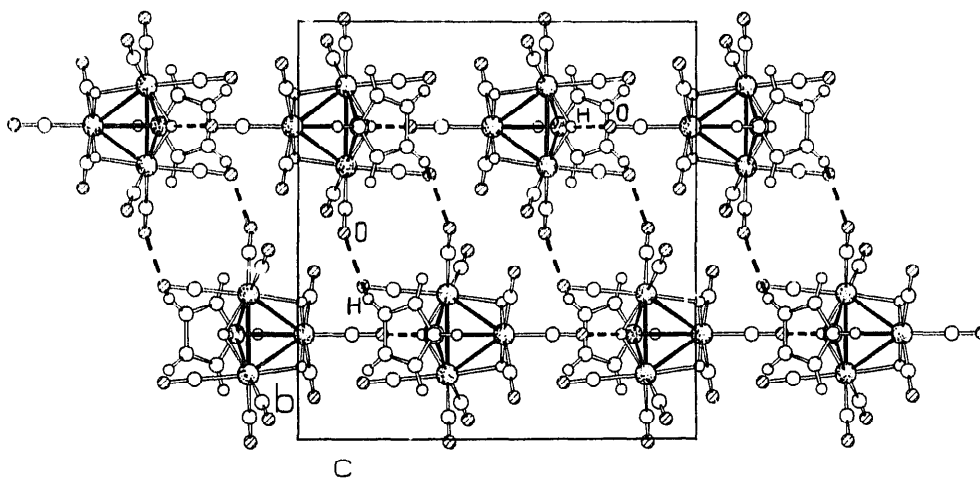

Fig. 11. Molecular rows in crystalline (μ-H)₃Os₃Ni(CO)₉Cp (BOBTAN10). Note how the bonds are formed between terminally CO ligands and bridging H-ligands and between CO ligands and H atoms of the Cp rings.
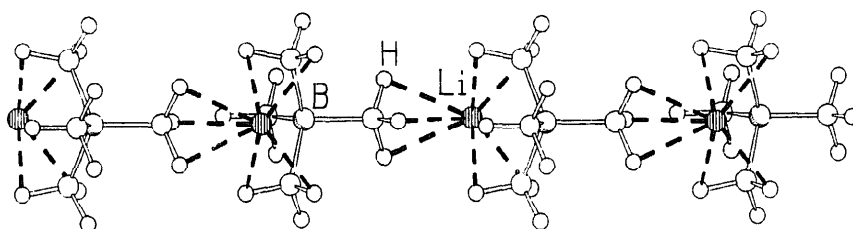

Fig. 12. Plot of the C–H · · · Li agostic bond network in the neutron derived crystal structure of LiBMe₄. Notice the tri- and di-bridged C–H · · · Li geometries.
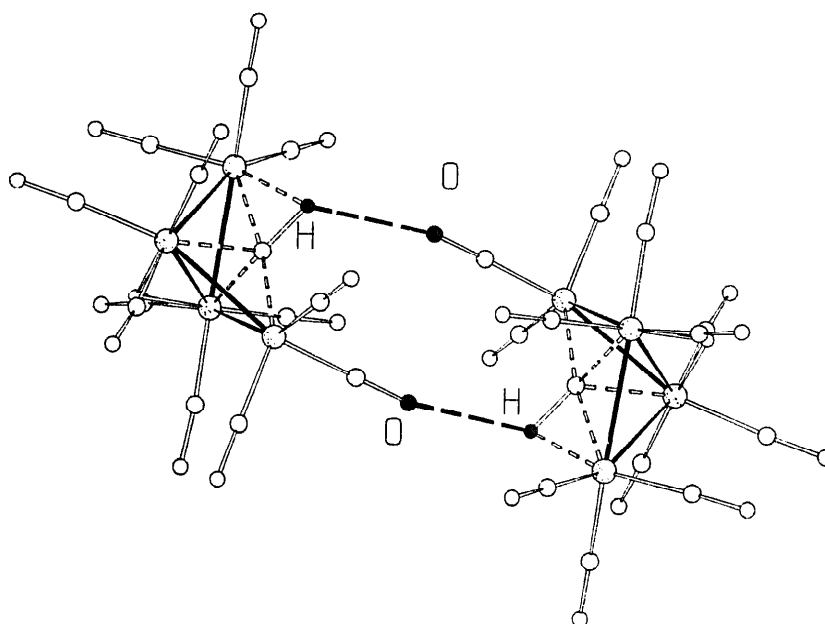
Fig. 13. Intramolecular Fe · · · (H–C) agostic and intermolecular C–H · · · O interactions in crystalline $HFe_4(\eta^2\text{-CH})(CO)_{12}$.

with one wing-tip atom and in short C–H · · · O intermolecular bonds with neighboring molecules (2.58 and 2.48 Å for the two independent molecules in the asymmetric unit) [22]. The C–H system therefore exerts is dual behavior of intramolecular electron density donor towards the electron deficient iron atom and of intermolecular hydrogen bonding donor towards the acceptor CO-ligand. The arrangement of two hydrogen bonded molecules is shown in Fig. 13.

8. Conclusions

In this paper we have provided a brief survey of our recent work on hydrogen bonding in organometallic crystals. We have tried to show to the reader some key examples, selected from the many available from earlier studies, of the most relevant hydrogen bonding interactions and geometric patterns in comparison to those observed in organic crystals. The existence of 'new' hydrogen bond donor and acceptor groups, such as the M–H system in polymetallic complexes and the CO-ligand in its various bonding modes, has been discussed.

Hydrogen bonding is undoubtedly the masterkey interaction in crystal engineering [23] because it is sufficiently strong and directional as to allow choice of intermolecular patterns [24], co-crystallization of organometallic and organic molecules via complementary hydrogen bonding [25], use of chiral organometallic partners to prepare non-centrosymmetric crystals for NLO studies. This approach can also be exploited to prepare bioinorganic and bioorganometallic co-crystals by means of crystallization of functionalized molecules carrying different metal atoms, heterometallic co-crystals

involving transition metal cluster complexes of high nuclearity, small metalloproteins and peptides.

Acknowledgements

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