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# Hydrogen Bonding in Organometallic Crystals. 1. From Carboxylic Acids and Alcohols to Carbonyl Complexes[†]

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The molecular organization in crystals of selected transition metal complexes and clusters containing hydrogen bond donor and acceptor groups such as —COOH, —OH, and —COOR as well as CO ligands has been investigated. Strict analogies have been found between the hydrogen bonding patterns in the organometallic crystals and those present in the corresponding organic crystals. It has been possible to show that CO participates in hydrogen bonding when other stronger acceptors are not in competition.

## Introduction

The hydrogen bond has always constituted a subject of major interest in organic solid state chemistry. A number of excellent review articles, books, and regular papers over the last 40–50 years deal specifically with hydrogen bond geometry and energetics in organic crystals.[1] Even some 10 years ago Kennard and Taylor pointed out that the number of references dealing specifically with hydrogen bonding must run into "the tens of thousands" at that time.[2]

It is surprising, then, that comparatively little has been done in the neighboring field of organometallic solid state chemistry. In contrast to simple organic compounds[3] the rules governing the crystal packing of organometallic and cluster compounds are still to be established firmly. In our earlier studies of organometallic systems, we have been mainly interested in comparing the respective roles of the "metal" and "organic" portions of an organometallic compound in determining crystal structures. In certain cases, metal atoms are actively involved in the pattern of intermolecular forces.[4] In several others, the metal centers are situated deep within the molecular core and are well-shielded from neighboring molecules. A typical example would be the crystal structure of bis(benzene)chromium which resembles the crystal structure of benzene itself.[5] Effectively, the outer portions of these molecules—the rims or peripheries—are "organic" in nature and the packing problem reduces to the organic case. These ideas are concerned more generally with the hitherto unexplored field of *organometallic supramolecular chemistry*.

Our efforts have been, thus far, directed to the understanding of the intermolecular interactions acting among organometallic molecules, on their control of the molecular arrangement in the crystal,[6] and on their effect on the structure of the individual molecule.[7] The understanding of the first two aspects is of relevance to the appreciation of organometallic crystals as materials, *viz.* for the appreciation of the physical (diffusion of molecules, reorientational phenomena, second harmonic generation and nonlinear optics, magnetic susceptibility, and conductivity) and chemical properties (solid state reactivity, racemization, occurrence of phase transitions, etc.) that a crystalline material can show. These properties, besides depending on the nature of the component particles, depend on the way molecules and ions are organized in the crystal structure. Furthermore, it is well-known that molecules possessing very little structural rigidity may be greatly affected by the optimization of the crystal structure. In these cases the appreciation of the interplay between molecular and crystal structure is another goal of great relevance. It is not always possible to attribute unequivocally the minimum enthalpy structural arrangement of a flexible organometallic molecule to the one observed in the solid state.[7]

In the course of these studies we have found, *inter alia*, that carbon monoxide ligands act as acceptor in C—H---O hydrogen bonding[8] as well as in strong bonds

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[†] Dedicated to the memory of Professor Margaret C. Etter.

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with water molecules in alkali metal solvate salts of transition metal cluster anions.[9] We are currently investigating this type of hydrogen bond in organometallic crystals in which there are usually a large number of CO ligands as well as groupings and ligands carrying acidic C—H groups.[10]

This paper focuses on O—H---O hydrogen bond linkages in organometallic crystals. The hydrogen bond patterns established by neutral complexes carrying CO ligands as well as —COOH and —OH groups are compared with those formed by organic molecules carrying the same potential donor and acceptor groups with the exception of the CO ligand. As a matter of fact, there is no organic analogue (apart from the —CN group) of the CO ligand terminally bound to metal center(s).

The purpose of this report is to address the following questions: (i) Does CO, the most common $\pi$-acid ligand, take part in the formation of hydrogen bonds; *i.e.* is the CO ligand a competitive acceptor in organometallic crystals with respect to organic ones, such as —COOH, and —OH? (ii) Do the most common organic hydrogen bonding donor groups (such as —COOH and —OH) establish different types of intermolecular interactions when present in metal-bound ligands or in the corresponding non-metal containing compounds? (iii) Do organometallic molecules participate in hydrogen bonding networks of the same type as do organic molecules? (iv) Are there recurring packing motifs that can be used to develop a theory of hydrogen bonding in organometallic materials to parallel that of organic crystals?

In order to address these questions we have selected from the Cambridge Structural Database (CSD)[11] mono- and polynuclear organometallic complexes containing —COOH and/or —OH donor groups, and carrying at least two metal coordinated CO ligands. This representative sample will be analyzed in some detail in this paper. To the best of our knowledge these problems have never been systematically investigated.

## Methodology

In order to disentangle hydrogen bonding patterns and to compare networks in organic and organometallic crystals, we have adopted the method of graph-set assignments put forward by Etter and Bernstein.[12] We have used graph sets as shorthand descriptors of the most representative hydrogen bonding networks. This graph-set notation is the first systematic attempt at classifying these often complex patterns. There is a considerable interest in this approach to hydrogen bonding decoding. As presently defined, however, the graph-set notation has a qualitative descriptive value but not a quantitative or mathematical meaning. For instance the notations for substructural motifs cannot be easily combined to yield the notation for larger networks in the same structure. The need for an improvement of the graph-set language to make it more straightforward and consistent so as to be coded in widely available computer programs has been recently pointed out, and progress in this direction is being made.[13]

Graph-set assignment requires the identification of the donor and acceptor atoms in the structure under investigation. This task is generally quite straightforward with organic substances since the positions of the H atoms, in spite of their weaker diffracting strength, are usually determined in X-ray diffraction experiments. This is not so for organometallic molecules where the H atoms are, most often, completely obscured by the presence of one or more strongly diffracting metal atoms.[14] It should be stressed that in these conditions, only a neutron diffraction study can afford an accurate positioning of the H atoms.

When H-atom positions are not accessible directly, the identification of the hydrogen bonded atoms must rely on an analysis of the donor—acceptor distances. In the case of O—H---O bonds, these distances are diagnostically shorter than expected on the basis of normal van der Waals interactions. The computer program PLATON[15a] is well suited for this type of analysis and allows generation of symmetry related molecules in the crystal structure so as to perform a complete screen-out of all possible intermolecular interactions and thus of the intermolecular hydrogen bonds. Alternatively, the search can be done with (commonly available) molecular and crystal graphics software[15b] or with the aid of atom—atom pairwise potential energy calculations.[16]

Graph sets are attributed by means of three intermolecular designators, namely C (chain), R (ring), and D (dimer or other finite sets). The number of donors (d) and acceptors (a) used in each motif are written as superscript and subscript, respectively, whereas the number of atoms forming the repeating unit (the "size" of the hydrogen bonding motif) is indicated in parentheses. The S designator is instead used to identify intramolecular hydrogen bonding. For a detailed description of the graph-set assignment the reader is addressed to the original papers.[12]

Crystal structures were obtained from the CSD.[11] Structures were selected which contained at least one —COOH or one —OH group, at least two metal-bound CO ligands, and one or more transition metal atoms. The sample was manually screened: ionic complexes, as well as structures in which the donor groups belonged to solvent molecules were not considered. Complexes containing very bulky ligands were also left out. These limitations were adopted in order to confine the sample to representative cases. It should be pointed out that this sampling has no pretensions of being exhaustive. The main objective of our analysis was not to obtain information on a statistical basis. Rather we attempted

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**Table 1. Structural Features of the Hydrogen Bonding Networks in Crystalline Complexes Containing One —COOH Group**

| —COOH | accept. | D—H, Å | H- - -A, Å | D- - -A, Å | D—H- - A deg | type | space group | *Z* | fig. | ref |
|---|---|---|---|---|---|---|---|---|---|---|
| BTCRBZ | —COOH | 0.74 | 1.91 | 2.65 | 169.5 | $R_2^2(8)$ | $P2_1/c$ | 4 | 1a | 19 |
| BONLOF butylbenzoic acid | —COOH | 0.94 | 1.72 | 2.64 | 168.1 | $R_2^2(8)^a$ | $P\bar{1}$ | 8 | 1b | 20 |
| | | 0.83 | 2.64 | 2.62 | 172.9 | | | | | |
| | | 0.81 | 1.91 | 2.69 | 164.3 | $R_2^2(8)^a$ | | | | |
| | | 0.74 | 1.89 | 2.61 | 168.7 | | | | | |
| SORBFE | —COOH | 1.10 | 1.58 | 2.63 | 156.7 | $R_2^2(8)^b$ | $P2_1/n$ | 4 | 2 | 21 |
| | | 1.12 | 1.53 | 2.64 | 169.0 | $R_2^2(8)^b$ | | | | |
| CPCMFE10 | —COOH | | | 2.49 | | $R_2^2(8)$ | $P\bar{1}$ | 2 | 3a | 22 |
| CPCMMO10 | —COOH | | | 2.65 | | $R_2^2(8)$ | $P2_1/n$ | 4 | 3b | 22 |
| FIWCOD | —COOH | | | 2.57 | | $R_2^2(8)$ | $P2_1/c$ | 4 | 4a | 23 |
| MCERUC10 | —COOH | | | 2.61 | | $R_2^2(8)$ | $P2_1/c$ | 2 | 4b | 24 |

[a] Each ring is originated from two of the four independent molecules. [b] Each ring is generated from one of the two independent molecules *via* a crystallographic inversion center.

to focus on selected examples and examine them in detail, seeking, whenever possible, a correlation with the corresponding organic crystals. This approach has been previously applied with success to the study of the relationship between organic and organometallic crystals in which intermolecular interactions were only of the van der Waals type.[5]

All crystalline complexes used for this analysis are listed in Tables 1–3 with their corresponding REFCODES and references to the original structural papers.[19-41] The donor and acceptor groups involved in hydrogen bond formation as well as the salient geometric features such as donor---acceptor distances (D---A), O—H bond lengths, and donor—H—acceptor angles (D—H---A) are also listed. H-atom coordinates were taken directly from the CSD and were not normalized. The hydrogen bonding patterns are described with graph sets. Since this work is aimed at a correlation between relatively simple organic and organometallic molecules, the assignment of high order patterns has not been attempted.[12a] Space groups and the number of molecules in the unit cell (*Z*) are reported. A full listing of all REFCODES with the corresponding chemical formulas is provided as supplementary material.

## From Carboxylic Acids to Carboxylic Acid Complexes

The hydrogen bonding networks and molecular structure organization in crystalline carboxylic acids have been exhaustively investigated by Leiserowitz.[17] The subject has also been recently revisited by Gavezzotti and Filippini[18] within an ample study of the geometrical features of intermolecular hydrogen bonds in organic systems aimed at calibrating empirical atom—atom potential parameters for H atoms.

It has been shown that monocarboxylic acids R—COOH preferentially form rings *via* interaction of the OH donor with the C=O acceptor of another molecule; the O—H---O bond is usually linear, and the ring is planar. In graph-set notation such a ring is denoted as $R_2^2(8)$. Dicarboxylic acids of the type HOOC—R—COOH preferentially form extended zigzag chains of $R_2^2(8)$ ring systems of the same type as those observed for monocarboxylic acids. The separation and relative orientation of the rings depend on the nature of the organic residue.

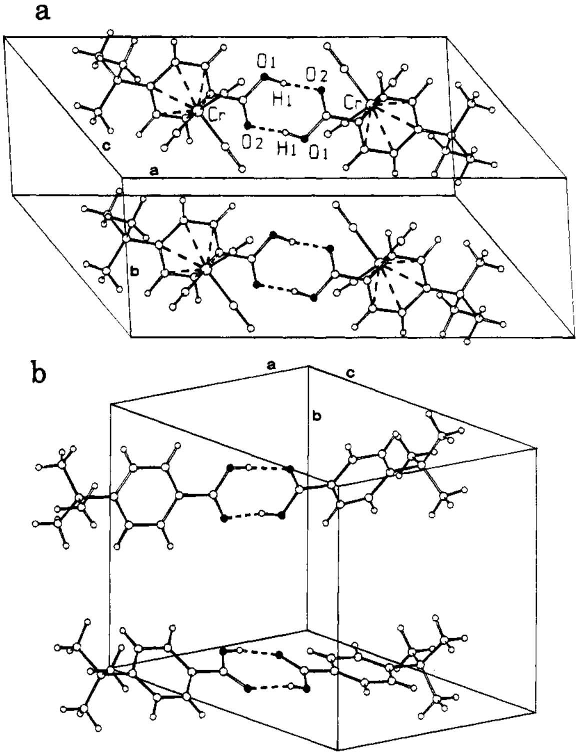

**Figure 1.** (a) Molecular organization in crystalline ($\eta^6$-$^t$BuC$_6$H$_4$COOH)Cr(CO)$_3$ (BTCRBZ). Two molecules are joined by a $R_2^2(8)$ hydrogen bonded ring. (b) Distribution in the crystal structure of the four independent molecules of the carboxylic acid $^t$BuC$_6$H$_4$COOH (BONLOF). Note how the $R_2^2(8)$ rigns are twisted with respect to BTCRBZ.

Both mono- and dicarboxylic acids are found in metal coordinated organic fragments. Selected examples of carboxylic complexes and clusters will now be discussed with reference to the information grouped in Table 1.[19-24]

**Transition Metal Complexes with One—COOH Group.** All monocarboxylic acids adopt the $R_2^2(8)$ structure, irrespective of the type of ligand carrying the organic function and the nuclearity of the complex.

The crystalline ($\eta^6$-$^t$BuC$_6$H$_4$COOH)Cr(CO)$_3$ (BTCRBZ) offers the first strict analogy between organic and organometallic crystals. The $^t$BuC$_6$H$_4$COOH acid ligand forms hydrogen bonding rings of the $R_2^2(8)$ type. The ring joins two molecular units in the crystal, as shown in Figure 1a. The two Cr(CO)$_3$ units $\eta^6$-coordinating the C$_6$ rings in the "dimer" are located *trans* with respect to the $R_2^2(8)$ ring. Due to the near planarity of the ring and to the conjugation between the aromatic systems

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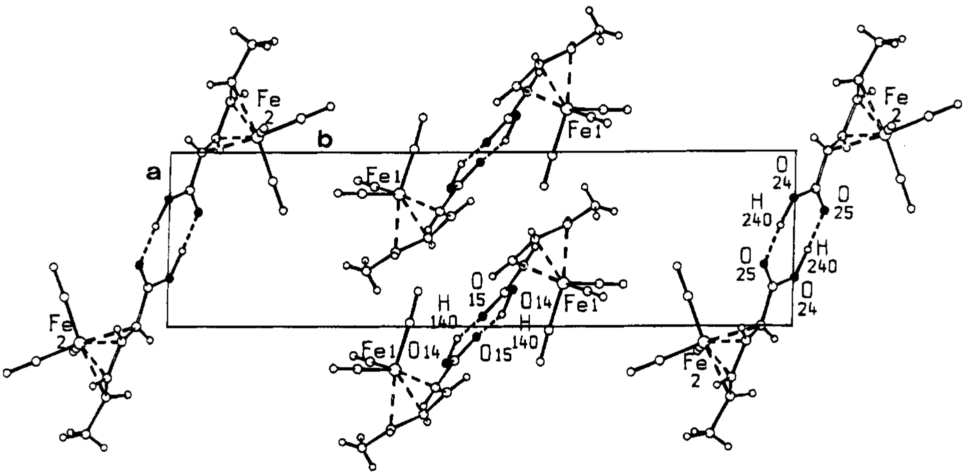

**Figure 2.** Two "dimers" formed by the two crystallographically independent molecules present in crystalline ($\eta^6$-$CH_3C_4H_4$-$COOH$)$Fe(CO)_3$ (SORBFE).

and the —COOH groups, the system formed by the sequence phenyl—$R_2^2$—phenyl is almost exactly planar. An analogous bonding pattern is present in benzoic acid.

The uncomplexed acid $^tBuC_6H_4COOH$ (BONLOF) crystallizes with four independent molecules in the asymmetric unit of space group $P\bar{1}$. These four molecules form two dimeric pairs *via* $R_2^2(8)$ rings, as shown in Figure 1b. The $C_6$ rings are rotated in opposite directions with respect to the $R_2^2(8)$ system. The difference in planarity of the phenyl—$R_2^2(8)$—phenyl system between the organometallic crystal and the organic one is most certainly due to the optimization of other intermolecular interactions besides hydrogen bonding. In terms of donor---acceptor separations the two systems are also strictly comparable: in crystalline $^tBuC_6H_4$-COOH the D---A separation ranges between 2.61 and 2.69 Å, and the D—H---A angle between 164.3 and 172.9°, whereas in BTCRBZ the D--A distance is 2.65 Å and the angle 169.5°.

The molecular organization in crystalline BONLOF is closer to that of the complex of $Fe(CO)_3$ with sorbic acid, ($\eta^6$-$CH_3C_4H_4COOH$)$Fe(CO)_3$ (SORBFE), where two crystallographically independent molecules dimerize *via* information of $R_2^2(8)$ rings, as shown in Figure 2. The two dimers differ in the torsion of the sorbic acid moieties with respect to the $R_2^2(8)$ ring although in both dimers the $Fe(CO)_3$ fragments are in *trans* configuration, as observed in BTCRBZ. There is no information on sorbic acid stored in the CSD; information is available from ref 17. However, this acid adopts the *syn* conformation and forms $R_2^2(8)$ networks as in SORBFE. Neither in BTCRBZ nor in SORBFE do the CO ligands participate in the hydrogen bond network. The structural parameters within the two $R_2^2(8)$ rings (see Table 1) are comparable to those of BTCRBZ irrespective of the difference in the nature of the organic acid.

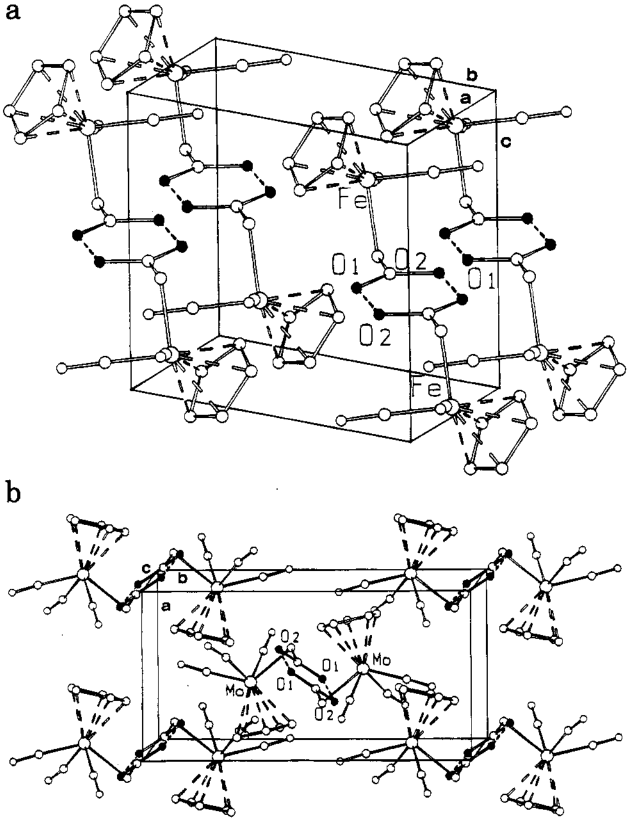

**Figure 3.** Molecular distribution and hydrogen bonded $R_2^2(8)$ rings in ($\eta^5$-$C_5H_5$)$Fe(CO)_2$($\sigma$-$CH_2COOH$) (CPCMFE10) (a) and ($\eta^5$-$C_5H_5$)$Mo(CO)_3$($\sigma$-$CH_2COOH$) (CPCMMO10) (b). (H atom coordinates not available from CSD.)

Eight-atom rings are also formed by —COOH residues carried by ligands $\sigma$-bound to the metal centers. This is the case for the crystalline complexes ($\eta^5$-$C_5H_5$)$Fe(CO)_2$($\sigma$-$CH_2COOH$) (CPCMFE10) and ($\eta^5$-$C_5H_5$)-$Mo(CO)_3$($\sigma$-$CH_2COOH$) (CPCMMO10) shown in Figure 3a,b, respectively. From a comparison of the two drawings it is easy to appreciate the similarities between the molecular arrangements in the two crystals. In spite of the different number of CO ligands, both complexes adopt a chairlike arrangement about the $R_2^2(8)$ system with the ($\eta^5$-$C_5H_5$)$Fe(CO)_2$ and ($\eta^5$-$C_5H_5$)-$Mo(CO)_3$ units in a transoid orientation related by a crystallographic inversion center. In neither case are

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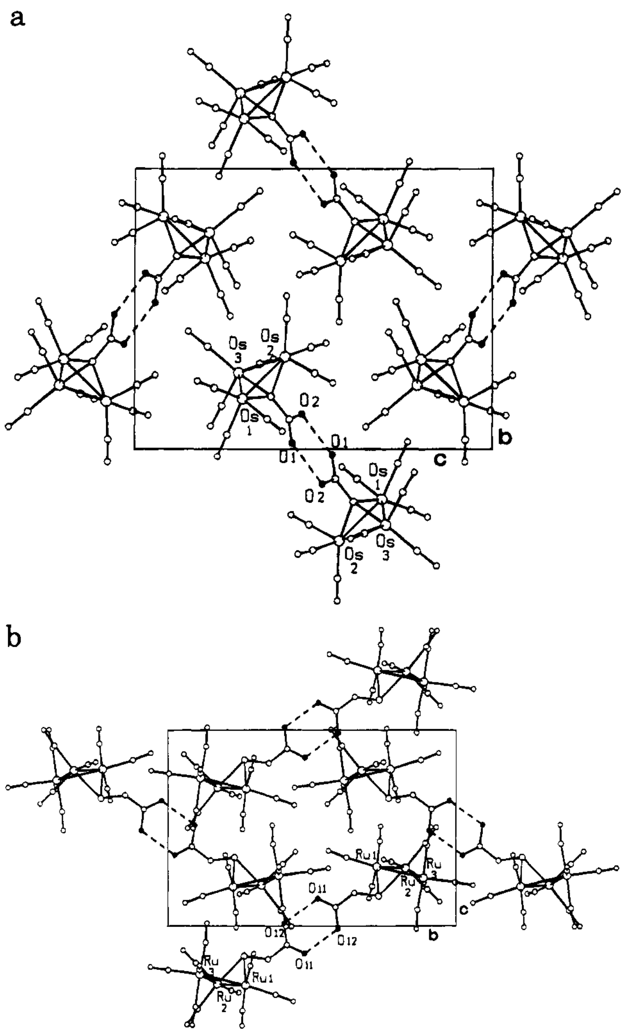

**Figure 4.** Hydrogen bonded dimolecular units in crystalline transition metal hydride clusters: (a) $H_3Os_3(CO)_9(\mu\text{-}CCOOH)$ (FIWCOD) and (b) $HRu_3(CO)_{10}(\mu\text{-}SCH_2COOH)$ (MCERUC10). (H atom coordinates not available from CSD).

the CO ligands involved to any extent in the hydrogen bond network. Whereas the D--A separation in CPCMMO10 (2.65 Å) is comparable to that observed in the other cases described above and to that found in other common organic acids (2.631 Å in acetic acid, 2.58 Å in formic acid, 2.655 Å in $\beta$-tetrolic acid[17]), this separation is appreciably shorter (2.49 Å) in CPCMFE10.

To conclude this section, it is relevant to observe that $R_2^2(8)$ systems, generated by dimerization of $-COOH$ residues, are present also in crystals of transition metal cluster species such as $H_3Os_3(CO)_9(\mu\text{-}CCOOH)$ (FIWCOD) and $HRu_3(CO)_{10}(\mu\text{-}SCH_2COOH)$ (MCERUC10), as shown in Figure 4a,b, respectively. In neither case is information on the H-atom positions available. Interestingly though, the donor---acceptor distances (2.57 and 2.61 Å, respectively) are relatively short with respect to the other species, indicating that $R_2^2(8)$ ring formation is not sterically hindered by the approach of the two cluster systems. The position of the H(hydride) atoms is also unknown, thus preventing an analysis of the interactions involving these ligands. CO⋯H interactions between CO ligands and H(hydride) atoms have, for instance, been observed in the Fe clusters $HFe_4(CO)_{12}(\mu_4\text{-}CH)$[42a,b] and $HFe_4(CO)_{11}(PPh_3)(\mu_4\text{-}CH)$.[42c]

In all these examples, it is clear that the carboxyl groups form hydrogen bonded dimers rather than catemers, chains, and so on. In general for R—COOH acids, dimer stability is not influenced by the steric bulk of R whereas catemer stability is.[17] Only acids with very small R groups, like formic and acetic acid, form catemers. Therefore it is not surprising that the organometallic carboxylic acids considered here, with their bulky substituent groups, should form dimers. Similarly, the absence of catemer motifs in these structures also stands explained. Perhaps because of this factor there are close analogies between the intermolecular organization of organic and organometallic carboxylic acids.

**Transition Metal Complexes with Two —COOH Groups.** This section will be devoted to the discussion of the hydrogen bonding networks present in crystalline organometallic systems containing dicarboxylic acid ligands. The information on the selected examples is summarized in Table 2.

As pointed out by Leiserowitz,[17] hydrogen bonding networks established by 1,2-disubstituted carboxylic acids fall in two main classes: one which contains an intramolecular OH⋯O bond between the two neighboring carbonyl groups and one in which exclusively intermolecular bonds are formed. In the former case the acids

**Table 2. Structural Features of the Hydrogen Bonding Networks in Crystalline Complexes Containing Two —COOH Groups**

| —COOH —COOH | accept. | D—H, Å | H- - -A, Å | D- - -A, Å | D—H- - -A deg | type | space group | Z | fig. | ref |
|---|---|---|---|---|---|---|---|---|---|---|
| MALIAC11 maleic acid | —COOH | 0.99 | 1.66 | 2.64 | 178.6 | C(7) | $P2_1/c$ | 4 | 5a | 25 |
| | intra | 0.91 | 1.60 | 2.50 | 171.5 | S(7) | | | | |
| KAMKAK | —COOH | 0.78 | 1.79 | 2.56 | 174.9 | C(7) | $P2_1/c$ | 8 | 5b | 26 |
| | intra | 0.98 | 1.59 | 2.55 | 164.4 | S(7)[a] | | | | |
| FUMAAC01 fumaric acid, $\beta$-form | —COOH | 0.69 | 2.00 | 2.67 | 166.3 | $R_2^2(8)$ | $P\bar{1}$ | 1 | 6a | 27 |
| FUMAAC fumaric acid, α-form | —COOH | 1.08 | 1.61 | 2.69 | 179.9 | $R_2^2(8)$[b] | $P2_1/c$ | 6 | 6b | 28 |
| | | 1.08 | 1.60 | 2.69 | 180.0 | $R_2^2(8)$[b] | | | | |
| | | 1.08 | 1.60 | 2.68 | 179.9 | | | | | |
| FECAFA02 | —COOH | 0.68 | 1.96 | 2.64 | 175.1 | $R_2^2(8)$ | $Pccn$ | 4 | 7a,b | 26 |
| FEFUMR10 | —COOH | | | 2.68 | | $R_2^2(8)$[c] | $P2_12_12$ | 6 | 8 | 29 |
| | | | | 2.71 | | $R_2^2(8)$[c] | | | | |
| | | | | 2.61 | | $R_4^4(22)$[d] | | | | |
| BIPGIQ10 | —COOH | 0.78 | 1.97 | 2.72 | 160.8 | $R_4^4(22)$ | $P2_12_12_1$ | 4 | 9a | 30 |
| | | 0.71 | 1.99 | 2.62 | 149.4 | | | | | |
| KOKXOX | THF | 1.15 | 1.62 | 2.66 | 146.0 | $D_2^2(12)$ | $P\bar{1}$ | 1 | 9b | 31 |
| | C—H- - -O | 0.95 | 2.34 | 3.25 | 161.4 | | | | | |

[a] Considering the presence of two independent molecules, the repeating chain motif is more appropriately descripted as $C^4_4(16)$. [b] The presence of one and a half independent molecules in the asymmetric unit generates two different rings. [c] Between molecules of types A and C (see Figure 8). [d] Between molecules of type B (see Figure 8).

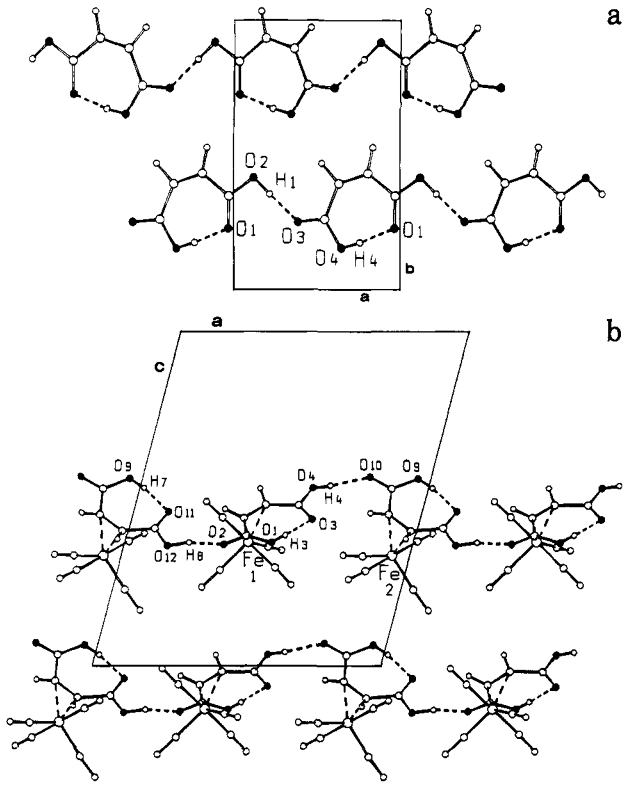

**Figure 5.** Molecular arrangement and hydrogen bonding network in crystalline maleic acid (MALIAC11, a) and in ($\eta^2$-maleic acid)Fe(CO)$_4$ (KAMKAK, b). Note how the dicarboxylic acid molecules form the same C(7)/S(7) patterns in the two crystals but have different relative conformations along the chains.

form chains by linking the acceptor C=O and donor OH groups not involved in the intramolecular ring system. A good example of this type of hydrogen bonding pattern is offered by crystalline maleic acid (MALIAC11 in Table 2). As shown in Figure 5a, maleic acid forms C(7) chains of molecules related by pure translational symmetry along the $a$-axis as well as S(7) intramolecular bonds (the length of the chain is conventionally taken as the shortest repeating unit along the hydrogen bonding network). A comparison of the two types of hydrogen bonds shows that the donor—acceptor separation in the intermolecular network is longer than in the intramolecular ring, where it is shortened by resonance[43] (2.64 *vs* 2.50 Å) whereas the D—H---A angle is closer to 180° (178.6 *vs* 171.5°).

Maleic acid is coordinated to the metal atom in ($\eta^2$-maleic acid)Fe(CO)$_4$ (KAMKAK). The complex crystallizes with two independent molecular units in space group $P2_1/c$. The hydrogen bonding pattern is shown in Figure 5b. From a comparison of parts a and b of Figure 5, it is easy to appreciate differences and similarities between the organometallic and the organic crystals. As in crystalline maleic acid each molecule of KAMKAK establishes one intra- and one intermolecular hydrogen bond. The intermolecular pattern is of the C(7) type in both crystals with the maleic acid ligands forming chains. The ligands, however, are not related by translational symmetry as in MALIAC11 but by a *pseudo* glide plane. The donor—acceptor distances in KAMKAK have similar lengths (2.56 and 2.55 Å for the inter- and intramolecular bonds, respectively). The double bond in maleic acid is $\pi$-coordinated to the metal, and the resonance within the intramolecular ring is seemingly weakened. It is worth recalling that, in general, the $2_1$ axis and the glide plane are favored in 1,2-disubstituted acids when the substituents are large, as in furan-3,4-dicarboxylic acid and in cyclopropane-1,1-dicarboxylic acid.[17]

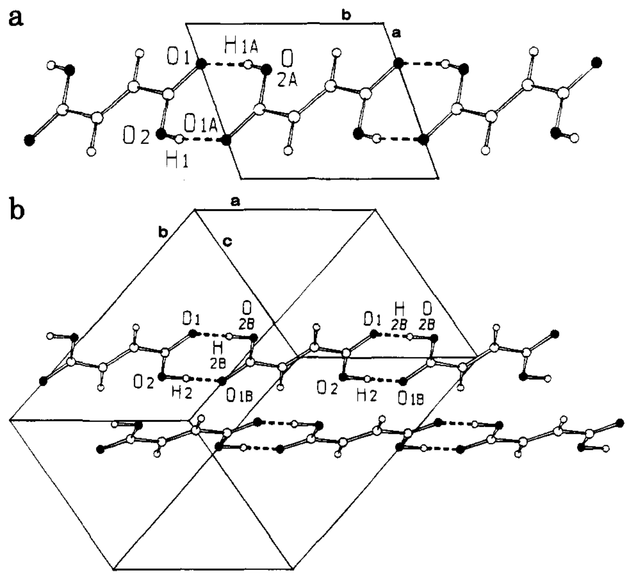

**Figure 6.** Two polymorphic modifications of fumaric acid: (a) $P\bar{1}$ crystal with only one centrosymmetric molecule in the cell (FUMAAC01), and (b) $P2_1/c$ crsytal with six molecules in the cell (FUMAAC). Note that the $b$-axis in the former crystal has almost the same length as the $a$-axis of the latter. Both crystals contain $R_2^2(8)$ rings. (The letter labels indicate symmetry related atoms as obtained from CSD files.[11])

Another, even more striking, analogy between organic and organometallic crystals is offered by fumaric acid and its iron complex ($\eta^2$-fumaric acid)Fe(CO)$_4$. As shown in Table 2, two polymorphic modifications are known for the complex (FECAFA02 and FEFUMR10) as well as two forms for fumaric acids (FUMAAC and FUMAAC01). The molecular arrangement in these crystals will now be compared. Both modifications of fumaric acid contain molecular chains interlinked *via* $R_2^2(8)$ rings. In terms of these gross features the two molecular arrangements are fairly similar, both crystals containing "ribbons" of molecules interlinked *via* hydrogen bonding, as shown in Figure 6a,b. In crystalline FUMAAC, however, the molecular ribbons are not coplanar (see Figure 6b). As shown in Table 2, the structural parameters within the $R_2^2(8)$ rings are comparable.

The two crystalline forms of the complex ($\eta^2$-fumaric acid)Fe(CO)$_4$ show more substantial differences. In FECAFA02 the fumaric acid ligands form an intermolecular pattern of the type seen in both forms of fumaric acid, *i.e.* ribbons of ligands joined by $R_2^2(8)$ rings, as

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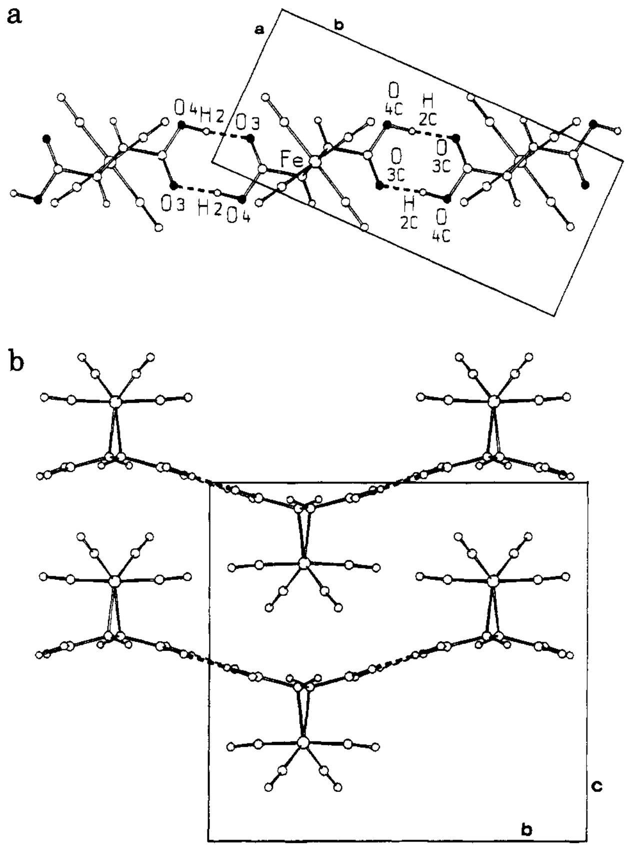

**Figure 7.** Hydrogen bonding network in form FECAFA02 of ($\eta^2$-fumaric acid)Fe(CO)$_4$ (a). Note how the fumaric acid ligands are linked *via* $R_2^2(8)$ rings as in crystalline FUMAAC and FUMAAC01; (b) View down the *a*-axis of the molecular organization in FECAFA02. (The letter labels indicate symmetry related atoms as obtained from CSD files.[11])

shown in Figure 7a. The "Fe(CO)$_4$" groups are coordinated to the unsaturated C=C bonds in an alternating fashion, as observed in the maleic complex described above. The distribution of the Fe(CO)$_4$ groups is easier to appreciate from Figure 7b which also allows us to see how the fumaric acid chains form waves 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. As previously noted with monocarboxylic acids, the donor—acceptor distances of the $R_2^2(8)$ rings in the organic (FUMAAC and FUMAAC01) and organometallic (FECAFA02) crystals are strictly comparable.

The second form of the fumaric acid complex represents an interesting case in which the $R_2^2(8)$ pattern coexists with a catemer-type pattern. FEFUMR10 contains three crystallographically independent molecules in the asymmetric unit. Molecules of type A [Fe(3)] form extended two-dimensional networks, which can be described as adjacent $R_4^4(22)$ large ring systems formed by four molecules, as shown in Figure 8. Molecules of types B and C [Fe(1) and Fe(2)] form ribbons of the type observed in crystalline FECAFA02 with acid ligands interlinked by $R_2^2(8)$ rings. These ribbons and the corrugated sheets formed by molecules A stack up along the *c*-axis. The O---O distances are shorter in the $R_4^4(22)$ systems (2.61 Å) than in the smaller $R_2^2(8)$ rings (2.68 and 2.71 Å). No information is available on hydrogen atoms. The presence of different patterns within the crystal structure of FEFUMR10 as well as the difference between the two polymorphic forms (FECAFA02 and FEFUMR10) can be taken as indicative that these hydrogen bonding networks are isoenergetic or differ only slightly in energy.

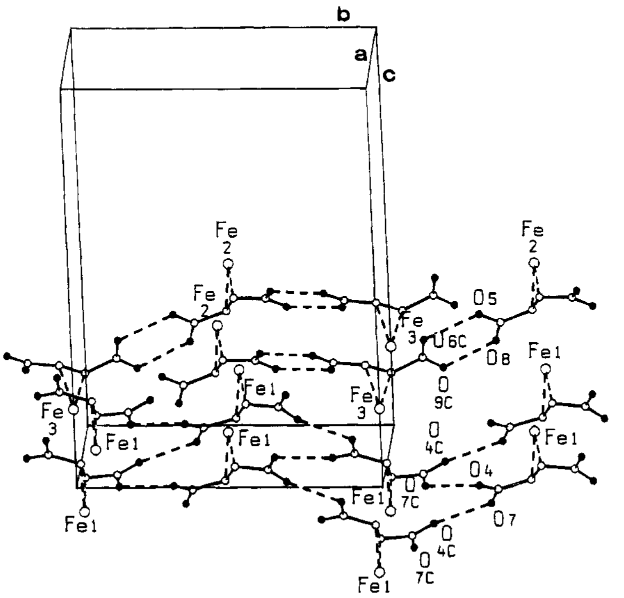

**Figure 8.** Three layers of molecules in form FEFUMR10 of ($\eta^2$-fumaric acid)Fe(CO)$_4$: molecules B [Fe2] and C [Fe3] form ribbons of $R_2^2(8)$ fumaric acid ligands as in crystalline FECAFA02, whereas molecules A [Fe1] form two-dimensional networks which can be described either as cross-linked chains of type C(4) or as large $R_2^2(22)$ rings. (H atom coordinates not available from CSD. CO ligands not shown for clarity. The letter labels indicate symmetry related atoms as obtained from CSD files.[11])

In crystalline {$\mu$-$\eta^2$-C$_2$(COOH)$_2$}Co$_2$(CO)$_6$ [BIPGIQ10], the steric hindrance of the Co$_2$(CO)$_6$ group and the "folding" of the acid ligand upon $\mu_2$-$\eta^2$, $\eta^2$-coordination to the two metal atoms very likely forbids ring closure and is the driving force toward the formation of large rings of the $R_4^4(22)$ type, as observed in crystalline FEFUMR10 (see Figure 9a). The two—COOH groups in each molecule act as donors and acceptors with two neighboring molecules, thus resulting in a network of joined ring systems linked by two independent O—H---O interactions [O(1)—H(10)---O(4) 2.72 Å; O(3)—H(30)---O(2) 2.62 Å].

An alternative solution to the optimization of van der Waals interactions in the presence of a strong hydrogen bond donor such as the carboxylic group is that observed in crystalline ($\eta^5$-C$_5$H$_4$COOH)$_2$W$_2$(CO)$_6$ (KOKXOX) where the —COOH groups form finite clustes (D) with two molecules of solvated tetrahydrofuran (see Figure 9b). A very similar pattern is present in one of the polymorphic forms of cyanoacetic acid.[13]

## From Alcohols to Hydroxy Complexes

This section will concentrate on hydrogen bonding between complexes carrying the —OH function bound to a metal coordinated ligand(s). The examples selected

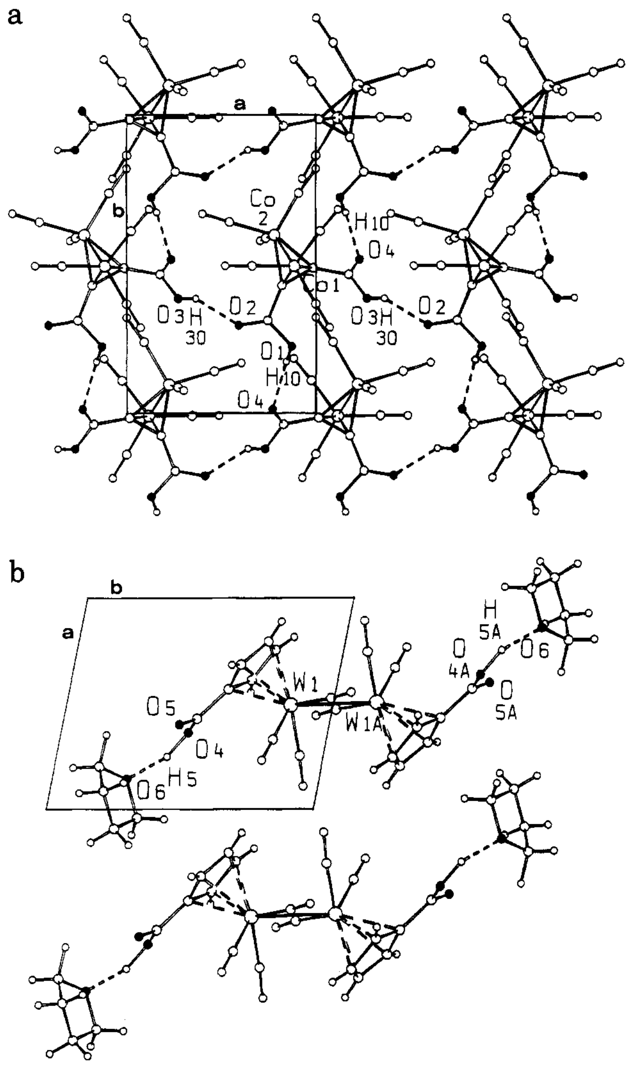

**Figure 9.** (a) $R_4^4(22)$ rings of hydrogen bonded molecules of [$\mu$-$\eta^2$-$C_2(COOH)_2$]$Co_2(CO)_6$] [BIPGIQ10]. (b) Hydrogen bonding interactions with thf molecules in crystalline [$(C_5H_4COOH)_2W_2(CO)_6$](thf)$_2$ (KOKXOX).

from the CSD are listed in Table 3. It can be anticipated that these complexes, due to the variable orientation of the O—H vector, will show a variety of hydrogen bonding patterns greater than observed for the stronger —COOH donors. It will also be seen in some cases that CO ligands can compete as hydrogen bonding acceptors with the —OH groups.

Hydrogen bonding chains are present in the complex ($\eta^5$-$C_5H_5$)Mo(CO)$_2$($\eta^3$-$C_8H_{12}OH$) (PACTES), which crystallizes in space group $P2_1/c$ with three independent molecules in the asymmetric unit. These three molecules form a long chain constituted by three C(2) segments. The segments link one by one the three independent OH groups, as shown in Figure 10. In graph-set description this structure corresponds to a $C_3^3(6)$ chain because the actual repeating unit along the chain is made by the three donor and three acceptor groups. No coordinates are available for the H atoms in the bridges; however, the O--O separations fall in a farily narrow range (2.78−2.84 Å). These values are comparable to the donor---acceptor separation in the crystal of the arene complex {$\eta^6$-$C_6H_4Me(CMeEtOH)$}-$Cr(CO)_3$ (RMEBEN, O---O 2.75 Å), where a C(2) chained structure is formed with no involvement of the CO ligands.

In crystalline complex ($\eta^2$,$\eta^2$-$CH_3C_4H_4CCH_3OH$)Fe-(CO)$_3$ (THDOFE) the two independent molecules present in the asymmetric unit form chains of the simple type C(2) by joining —OH groups in the sequence —O—H--O-H--O—H. These hydrogen bonds are almost linear (174.3 and 171.3°) and the two repeating donor---acceptor distances identical (2.71 Å), in this being similar to the values so far discussed for carboxylic acids.

In crystalline BENGLY four molecules form an $R_4^4(8)$ ring (see Figure 11a). The two independent hydrogen bonds are not equivalent in terms of donor—acceptor separations (2.82 *vs* 2.78 Å) and the O—H---O angles deviate appreciably from linearity (146.4 and 151.5°; see Table 3). From Figure 11a it is easy to appreciate the presence of a larger $R_4^2(14)$ ring which involves only the O4—H4---O5 hydrogen bond. The $R_4^4(8)$ ring is also the hydrogen bonding pattern established by molecules of JEZMUW, as shown in Figure 11b. Tetramer formation is quite common in organic crystals: good examples are afforded by the structures of 1-phenylcyclohexanol[44a] and 2-phenyladamantan-2-ol.[44b]

A large hydrogen bonded hexameric unit is present in crystalline JOFJET and is shown in Figure 11c. Six molecules of ($\eta^5$-$C_5H_4C_2H_4OH$)$_2$Fe$_2$(CO)$_4$ are linked *via* direct O—H---O bonds (O---O 2.66 Å, O—H---O 147.1°) between the $CH_2CH_2OH$ groups forming an $R_6^6(12)$ ring. A much larger ring system also joins three molecules by using both $CH_2CH_2OH$ units present on the dinuclear complex. In crystalline ($\eta^5$-$C_5H_4C_2H_4$-$OH$)$_2$Mo$_2$(CO)$_6$ (VIGRAE) the same hydroxyl ligand present in JOFJET forms a $C_2^2(4)$ chain rather than a ring system.

The isomeric pair of compounds JOLNIH and JOLNON [respectively *exo*- and *endo*-{$\eta^6$-$C_6H_4(C_6H_4OH$-$COOMe)$}$Cr(CO)_3$] deserves a close look because they represent an interesting case of the involvement in the hydrogen bonding network of an acceptor group, namely —COOMe, different from the donor itself. As shown in Table 3, both the *exo* and *endo* complex establish hydrogen bonds between the —OH and the —COOMe

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**Table 3. Structural Features of the Hydrogen Bonding Networks in Crystalline Complexes Containing —OH Groups**

| —OH | accept | D—H, Å | H- - -A, Å | D- - -A, Å | D—H- - -A, deg | type | space group | Z | fig. | ref |
|---|---|---|---|---|---|---|---|---|---|---|
| PACTES | OH | | | 2.80 | | $C^3_3(6)$ | $P2_1/c$ | 12 | 10 | 32 |
| | OH | | | 2.78 | | | | | | |
| | OH | | | 2.84 | | | | | | |
| RMEBEN | OH | | | 2.75 | | C(2) | $P2_1/c$ | 4 | | 33 |
| THDOFE | OH | 0.81 | 1.91 | 2.71 | 174.3 | C(2) | $P2_1/c$ | 8 | | 34 |
| | OH | 0.78 | 1.93 | 2.71 | 171.3 | C(2) | | | | |
| | CH- - -OH | 1.05 | 2.45 | 3.41 | 152.9 | | | | | |
| VIGRAE | OH | | | 2.69 | | C(4) | $P2_12_12_1$ | 4 | | 35 |
| | OH | | | 2.72 | | | | | | |
| BENGLY | OH | 0.89 | 2.04 | 2.82 | 146.4 | $R^4_4(8)$ | $P\bar{1}$ | 2 | 11a | 36 |
| | OH | 0.88 | 1.97 | 2.78 | 151.5 | | | | | |
| JEZMUW | OH | | | 2.79 | | $R^4_4(8)$ | $P2_1/c$ | 8 | 11b | 37 |
| | OH | | | 2.74 | | | | | | |
| | CH- - -OC | 0.96 | 2.47 | 3.31 | 145.1 | | | | | |
| JOFJET | OH | 0.96 | 1.80 | 2.66 | 147.1 | $R^6_6(12)$ | $R\bar{3}$ | 9 | 11c | 38 |
| | CH- - -O | 0.95 | 2.51 | 3.39 | 155.5 | | | | | |
| JOLNON | COOMe | | | 2.82 | | $R^2_2(12)$ | $P\bar{1}$ | 2 | 12a | 39 |
| | CH- - -O | 1.10 | 2.47 | 3.40 | 141.8 | | | | | |
| | CH- - -O | 1.09 | 2.39 | 3.46 | 168.4 | | | | | |
| JOLNIH | COOMe | | | 2.63 | | C(6) | $P2_1/c$ | 4 | 12b | 39 |
| | CH- - -OC | 1.10 | 2.45 | 3.39 | 143.3 | | | | | |
| | CH- - -OC | 1.09 | 2.55 | 3.50 | 144.2 | | | | | |
| | CH- - -OH | 1.09 | 2.34 | 3.36 | 154.4 | | | | | |
| EXINCR | CO | 0.89 | 2.50 | 3.27 | 145.2 | $C^1_2(6)$ | Pbca | 8 | 13 | 40 |
| | CO | 0.89 | 2.34 | 3.01 | 132.4 | | | | | |
| | CH- - -OH | 0.88 | 2.46 | 3.27 | 155.5 | | | | | |
| GAMNAJ | CO | 0.69 | 2.33 | 3.00 | 163.7 | $R^2_2(10)$ | $P2_1/c$ | 4 | 14 | 41 |
| | CO | 0.68 | 2.28 | 2.95 | 170.6 | | | | | |

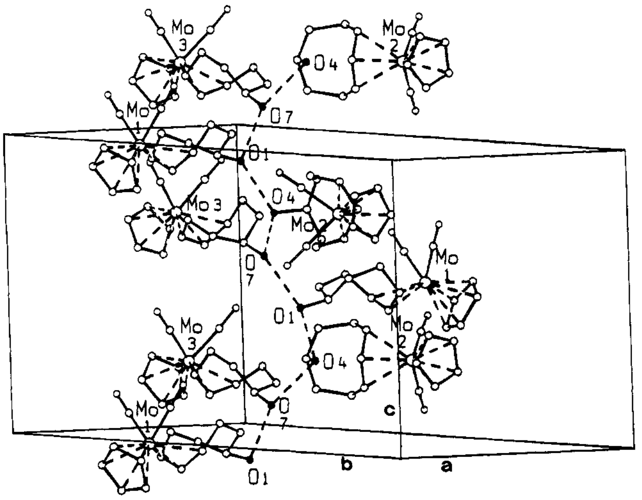

**Figure 10.** $C^3_3(6)$ chain formed by three C(2) segments in crystalline $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_8H_{12}OH)$ (PACTES). The segments are linked by OH···OH bridges. (H atom coordinates not available from CSD.)

groups (D···A 2.82 for JOLNON and 2.63 Å for JOLNIH). Some short C—H···O contacts invovling the O atoms of both the carbonyl ligands and the organic fragment are also observed, indicating the presence of a C—H···O bonding network in the two crystal structures. The molecular organization in the two crystals is shown in Figure 12a,b for JOLNON and JOLNIH, respectively. The hydrogen bonding pattern in JOLNON is of the $R^2_2(12)$ type with large ring systems formed by two molecules in a dimeric fashion. In JOLNIH, on the other hand, C(6) chains are formed in which the repeating unit is the C(=O)—C—C—OH system of the ligand. The donor—acceptor distances are not equivalent in the two patterns: in the chain pattern C---O distances are shorter than with the $R^2_2(12)$ rings (2.63 *vs* 2.82 Å). Perhaps, the formation of the $R^2_2(12)$ rings against that of C(6) chains is due to the different conformations in the two ligands.

The crystalline complex $\{(\eta^6\text{-}C_6H_4(C_5H_4MeOH)\}Cr(CO)_3$, also known in both an *endo* (ENDICR) and an *exo* form (EXINCR), is also very important in this discussion. Unfortunately, the position of the —OH groups in the former crystalline complex is affected by positional disorder with statistic occupancy of the two sides of the $C_5$ ring. This type of disorder prevents a detailed analysis of the intermolecular interactions. EXINCR, on the contrary, is ordered. What makes this complex remarkable is the direct involvement of CO ligands in the hydrogen bonding interaction with the —OH function. As shown in Figure 13, the carbonyl ligands C(3)O(3) and C(1)O(1) act as acceptor groups toward the donor —OH group. This latter acts, on the other hand, as acceptor with respect to a neighboring C—H system belonging to the $\eta^6$-coordinated arene. It is thus of relevance that in EXINCR both O—H---OC and C—H---OH interactions coexist. These interactions are not very different in terms of donor---acceptor separations: the O(4)—H(9)---O(1) distance is slightly longer than the C(9)—H(4)---O(3) one, whereas the shortest distance is that between the carbonyl O(4) and the hydroxylic O(3) atoms (2.46, 2.50, and 2.34 Å, respectively).

The involvement of CO ligands in hydrogen bonding networks is not confined to crystalline EXINCR. The dinuclear complex GAMNAJ presents an even more straightforward situation. As shown in Figure 14, the H atoms bound to the bridging oxygen atoms interact directly with the carbonyl oxygens O(3) and O(5), thus forming a $R^2_2(10)$ ring system made of two molecules. Each molecule thus participates in four such links. In terms of donor—acceptor separations between the hydroxyl and carbonyl oxygen atoms, these interactions

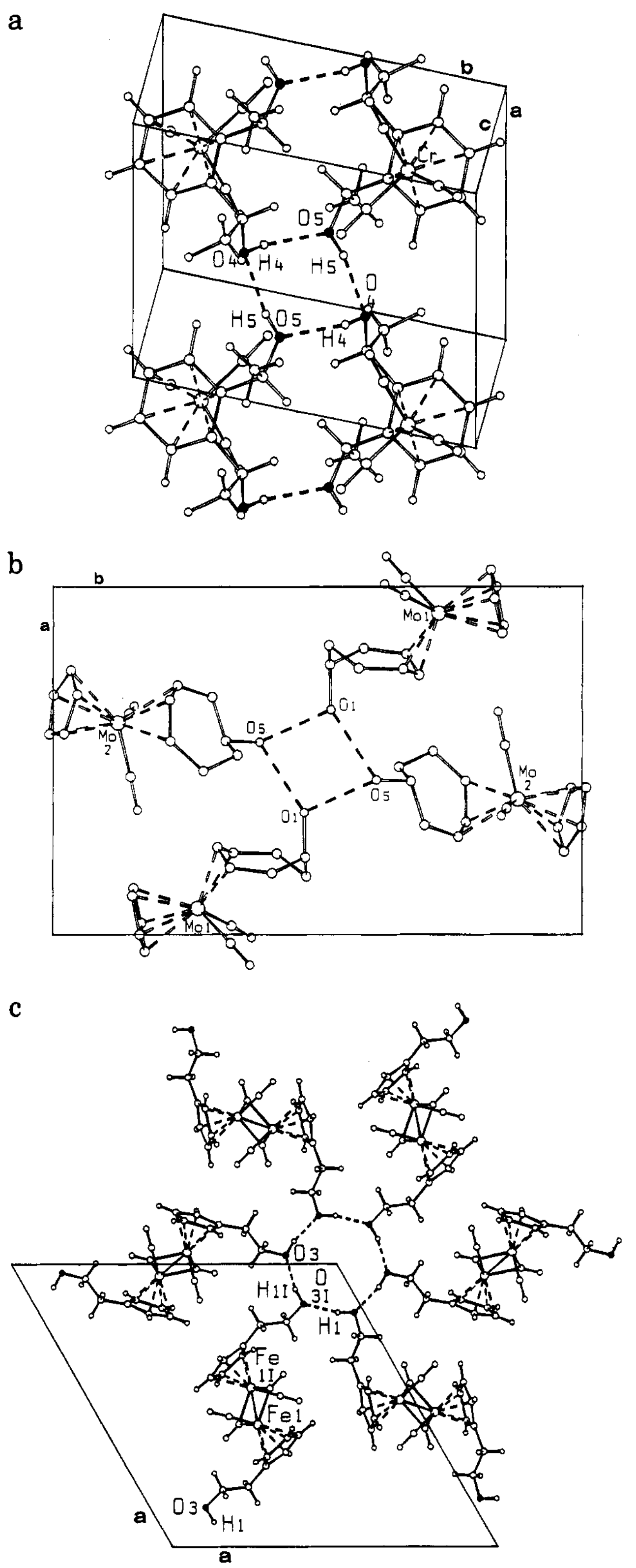

**Figure 11.** The tetrameric hydrogen bonded $R_4^4(8)$ rings present in crystalline BENGLY (a) and JEZMUW (b). (H atom coordinates not available from CSD.) The $R_6^6$ (12) ring system present in crystalline JOFJET (c).(The letter labels indicate symmetry related atoms as obtained from CSD files.[11])

are appreciably long (3.00 and 2.95 Å) although the molecular geometry and the packing arrangement permits the formation of rather linear bonds (163.7 and 170.6°).

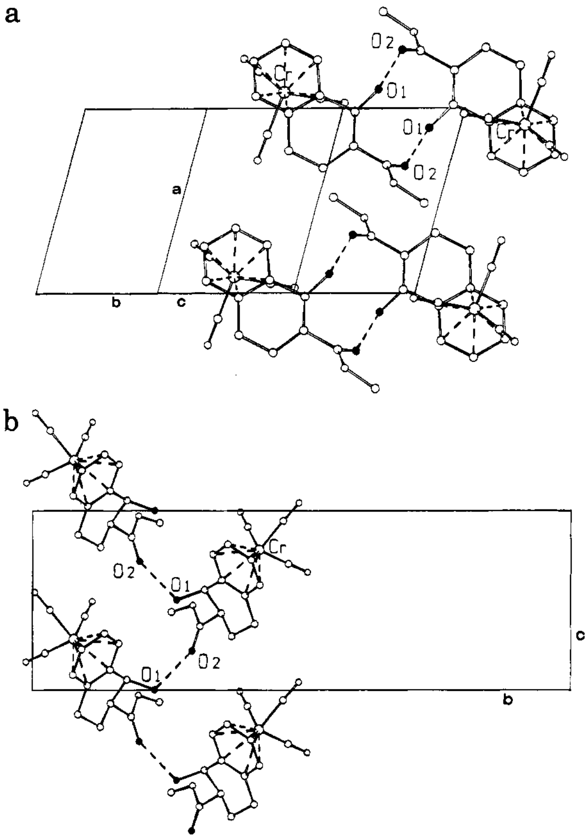

**Figure 12.** Hydrogen bonding network in crystalline JOLNON [*endo*-{$\eta^6$-$C_6H_4(C_6H_4OHCOOMe)$}$Cr(CO)_3$] and JOLNIH [*exo*-{$\eta^6$-$C_6H_4(C_6H_4OH$-$COOMe)$}$Cr(CO)_3$] (a and b, respectively). Note that —OH is a donor only and the esteric (—CCOMe) carbonyl group is the acceptor. In (a) $R_2^2(12)$ rings are clearly recognizable, whereas in (b) the packing is arranged in C(6) chains. [H(OH) atom coordinates not available from CSD. H(CH) atoms omitted for clarity.]

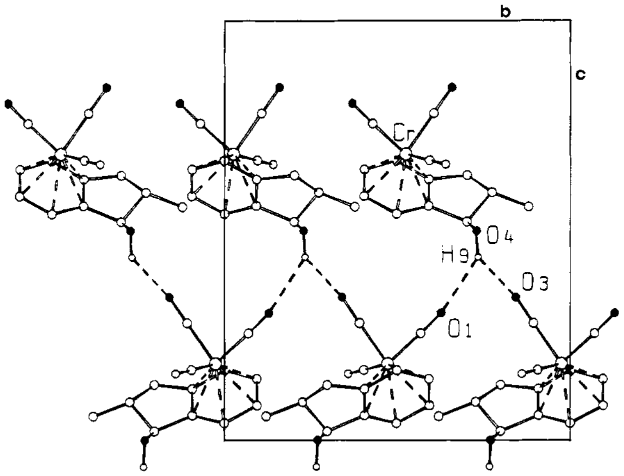

**Figure 13.** Hydrogen bonding network in {($\eta^6$-$C_6H_4(C_5H_4$-$MeOH)$}$Cr(CO)_3$ (EXINCR). Note the direct involvement of the CO ligands in the OH---OC—M hydrogen bonding and the existence of C—H- - -OH interactions. [H(CH) atoms and C—H- - -OH interactions omitted for clarity.]

## Conclusions and Outlook

With this paper we have analyzed the O—H---O hydrogen bonding patterns established by hydrogen bonding donor groups such as —COOH and —OH in crystals of organometallic molecules. These patterns

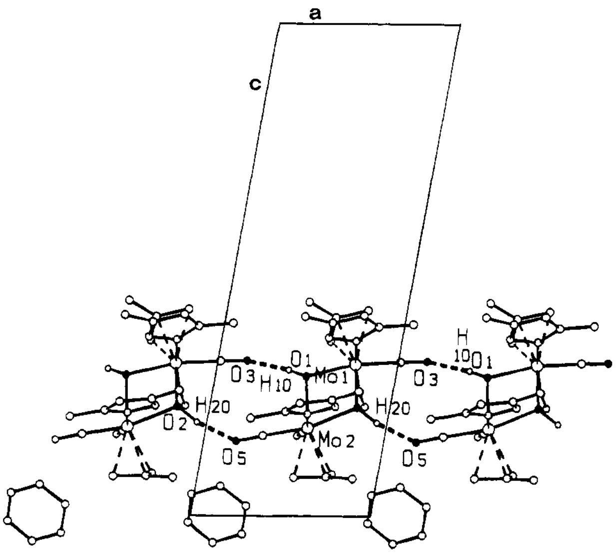

**Figure 14.** Hydrogen bonding network in the crystal of the dinuclear complex GAMNAJ. Note the direct involvement of the CO ligands in the—OH···OC—M hydrogen bonding. [H(CH) atoms omitted for clarity.]

have been compared with those observed in organic crystals. The results of this survey can be summarized as follows.

(i) There is a strict analogy between the hydrogen bonding patterns established in crystals of organic molecules and those established by the same moleculesas metal coordinated ligands in corresponding organometallic complexes.

(ii) Ligands carrying one —COOH group form preferentially $R_2^2(8)$ ring systems in which the —OH group of one ligand binds the carboxylic CO group of a neighboring molecule.

(iii) If two such groups are present within the same ligand, chains are formed either *via* a sequence of $R_2^2$ (8) rings joined by the organic system interacting with the metal center(s) or *via* single OH···OC—interactions. In this latter case the second COOH group is involved in intramolecular hydrogen bonding. This is exactly the behavior observed for the corresponding organic crystals.

(iv) The existence of polymorphic modifications for the carbonyl complexes of fumaric acid is paralleled by the behavior of the native organic material.

(v) Many of the complexes studied here crystallize with more than one independent molecule in the asymmetric unit.

(vi) Catemer formation is never observed with monocarboxylic acid ligands, thus confirming that this motif is formed only by very small and sterically unhindered organic acids such as HCOOH and $CH_3COOH$;[17] the formation of $R_2^2(8)$ systems, on the other hand, is not obstructed by the size of the organometallic molecule and by the nuclearity of the complex.

(vii) Formation of $R_2^2(8)$ systems is not so favorable for bicarboxylic ligands (see Table 2): as the size increases, the complexes seem to form preferentially long chains rather than ring systems. This is probably due to the difficulty of bringing two other molecules close enough to allow formation of two $R_2^2(8)$ ring systems, as observed for monocarboxylic ligands.

(viii) In both mono- and dicarboxylic ligand complexes there is no evidence for the involvement of the CO ligands in the hydrogen bonding network.

(ix) Due to the uncertainty in the determination of the H-atom positions in X-ray diffraction experiments in the presence of heavy metal atoms, the OH distances are spread over a large interval (*ca.* 0.7−1.10 Å) and cannot be commented on. This is not so far the D---A separations (O---O in mono- and dicarboxylic acids) which are fairly constant, clustering about 2.64 for the $R_2^2(8)$ systems. There is no recognizable difference in donor—acceptor distance between organic and corresponding organometallic crystals. This indicates that the carbonyl groups are not affected in their electronic nature (and thus in the polarization of the O—H bonds) when the organic part is coordinated to a metal atom.

(x) Exceptions to this type of behavior are the structures of CPCMFE10 and FIWCOD, where the D···A separations are particularly short (2.49 and 2.57 Å, respectively).

The situation is less clear cut when the donor group is the hydroxyl OH group.

(xi) In most cases the —OH groups form chains in which the group acts both as donor and as acceptor. Given the *caveat* raised above for H-atom positions, it is only possible to note that O···O separations are, as expected, longer than in the networks formed by carboxylic acids.

(xii) Tetramers and hexamers [$R_4^4$ and $R_6^6$] are also common in these systems; similar patterns are established in crystalline organic alcohols, as has been clearly shown in a recent study of crystalline alcohols of the type $C_nH_mOH$.[45]

(xiii) The weakness of the —OH donor with respect to —COOH is also reflected in the competition for hydrogen bond formation between —OH itself and other acceptors. This is very much in keeping with the general observation[12a] that less acidic protons are used for hydrogen bonding only after all of the more acidic protons have been used.

(xiv) With JOLNON and JOLNIH the —COOMe alternative acceptor is preferred, whereas with EXINCR and GAMNAJ it is the CO ligand that comes into play. In these latter cases the donor—acceptor separations appear to be longer than those between hydroxyl groups.

(xv) When the OH function is present, there also appears to be an increase in the number of short C—H···O separations, both involving the —OH group and the carbonyl ligands.

In summary, our analysis provides evidence that carboxylic acids and alcohols establish similar intermolecular hydrogen bonding patterns *whether as free molecules or coordinated to metal centers.* In this respect much of the knowledge on this type of interaction achieved in the field of organic solid state chemistry can be transferred to the neighboring developing area of organometallic crystal chemistry.

In addition to the common organic residues —COOH and —OH investigated in this paper, however, organometallic complexes possess the peculiar "inorganic" CO ligand. The capacity of the oxygen atoms of CO ligands to form intermolecular hydrogen bonds is, though weak, significant. This is in keeping with the well established bonding picture of carbon monoxide to metal centers.

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[45] Brock Pratt, C.; Duncan, L. L. *Org. Solid-State Chem.*, in press.

The good $\sigma$-donation from the more basic C terminus is compensated for by a very efficient back $\pi$-donation from metal to ligand,[46,47] thus leading to the formation of a slightly negatively charged carbonyl ligand. The weak Lewis basicity of CO is, for instance, responsible for the formation of the "end-on" (or isocarbonyl) complexes.[48] The formation of these complexes requires strong Lewis acids such as alkali metal cations or other main group metals or rare earth acceptors. Complexes with transition metal acceptors are also well established, mainly with early transition metals in high oxidation states which are relatively strong Lewis acids. Our analysis provides further evidence that the terminally bound CO is a weak Lewis base which can compete in the participation in hydrogen bonding networks only when stronger acceptor groups are absent.

As the basicity of CO ligands increases on going from the terminal to the bridging bonding geometry, it is conceivable that the involvement of this ligand in hydrogen bonding also increases. The influence of the different CO bonding modes on the formation of hydrogen bonding networks, as well as the participation in networks of other metal coordinated "organic" molecules forming hydrogen bonds (primary and secondary amides, nitroanilines, nucleotides, nucleosides, etc.) and of other potential "inorganic" hydrogen bond acceptors (—NO, CN), will be the subject of future studies.

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**Supplementary Material Available:** Full listing of REFCODES, molecular formulas, and references to the original structural papers for all the species discussed herein (3 pages). Ordering information is given on any current masthead page.

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