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Hydrogen-Bonding Interactions with the CO Ligand in the Solid State

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Carbon monoxide is the prototype of all π-acid ligands and the ligand *par excellence* in organometallic chemistry.[1] Although carbonyl complexes are known by the thousands, the participation of CO in intermolecular interactions has only recently begun to be appreciated.[2] This is the subject matter of this Account with a focus on the capacity of CO of establishing hydrogen bonds with suitable donor groups. Hydrogen-bonding networks play a fundamental role in the three-dimensional organization of molecules in the solid state,[3] and studies of hydrogen bonds are relevant to supramolecular[4] and materials chemistry[5] as well as to crystal engineering.[6]

In a conventional MO picture the Tr−CO (Tr = transition metal) bond results from the σ-donation from the more basic C atom to the metal and from back-donation from metal d-orbitals to the π^*-orbitals of the ligand. The back-donation is very efficient so that the polarity of metal-coordinated CO is very small and the basicity of the oxygen is very weak. The basicity increases on passing from terminal to doubly and to triply bridging bonding modes as the ketonic nature of the bonding between C and O increases. This is understood as a consequence of the increased back-donation from the metal onto the ligand π^*-orbitals which causes the CO stretching frequency to move to lower wavenumbers, the C−O distance to lengthen, and the polarity of CO to increase.

Before discussing the participation of CO in hydrogen bonding, we shall consider some fundamental manifestations of the Tr−CO system basicity, namely, the formation of end-on (isocarbonyl) species when CO ligands interact with Lewis acids[7] and the formation of tight ion pairs when carbonyl anions interact with alkali metal cations.[8] It is worth recalling that the interaction with the oxygen atoms of CO is important in the alkyl migration ("CO insertion") and CO cleavage reactions. This is the frame in which the hydrogen-bonding acceptor capacity of the CO ligand needs to be approached.

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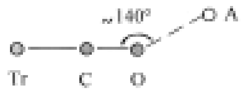
Chart 1. Bending of the Tr−C−O···A System with the Angle at the O Atom of about 140°



Carbonyl basicity has been extensively discussed in a series of seminal papers by Shriver and collaborators.[9] Several structures of isocarbonyl complexes containing electropositive early-transition metal or lanthanide atoms (A) along with a CO ligand coordinated to a low-valent metal are known.[10] In these complexes the Tr−C−O···A system is generally bent; *viz*., the angle at the O atom is usually around 140° (see Chart 1). Since end-on complexes are generally formed with hard acids, the oxygen end of the CO ligand apparently behaves as a hard base, although Shriver pointed out[9] that the hard and soft concept has to be used with some caution since examples are available for both types of behavior.

Examples are also available of the direct interaction between the small hard acid H^+ and the CO ligand. ^1H and ^{13}C NMR data showed that protonation with fluorosulfuric acid of $HFe_3(CO)_{11}^-$ gives $HFe_3(CO)_{10}(COH)$ in which the proton attaches directly onto a bridging CO (see Figure 1a).[12] Protonation of the carbonyl ligand has also been obtained for $HRu_3(CO)_{11}^-$ although the initial protonation at CO is rapidly followed by migration onto the cluster and rearrangement to $H_2Ru_3(CO)_{11}$.[13] This mechanism has been often invoked to explain cluster hydride formation.[14] The higher basicity of the face-bridging

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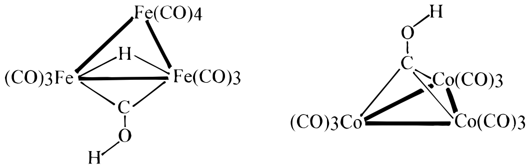
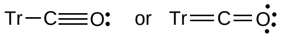


FIGURE 1. Example of CO protonation of bridging and face-capping ligands: the structures of $HFe_3(CO)_{10}(COH)$ (a, left) in which the proton attaches a bridging μ_2-CO and that of $Co_3(CO)_9CO$-H (b, right) where protonation occurs on the face-capping μ_3-CO.

ligand allows formation of the complex $Co_3(CO)_9CO{-}H$ (see Figure 1b) when $[Co_3(CO)_{10}]^-$ is reacted with HCl.[15] In the absence of CO the complex decomposes readily to $HCo_3(CO)_9$, showing that the initial CO protonation is most often followed by migration of the hydrogen onto the cluster. However, the CO-protonated species is sufficiently stable to be isolated and characterized in the solid state.[16]

A second large category of complexes in which metal bound CO ligands act as Lewis bases is that of the transition metal carbonylates in which the interaction is between a mononuclear or polynuclear carbonyl anion and a strong Lewis acid such as alkali metal or main group cations. As pointed out by Darensbourg,[8] most of these complexes show that the Tr−CO···A interaction is not linear but angular as in the cases of most end-on carbonyl complexes. The angularity of the $CO\cdots M^{n+}$ interaction implicates a directional electrostatic potential dependent on the relative contribution of the valence bond structures pertinent to metal bound CO:



$$\mathrm{Tr{-}C{\equiv}\ddot{O}} \quad \text{or} \quad \mathrm{Tr{=}C{=}\ddot{O}}$$

(a) (b)

While structure (a) should favor a “straight” interaction, structure (b) has the oxygen lone pairs in ketonic directions and is therefore consistent with the angularity of the interaction. Structure (b) is also in agreement with the lowering of the ν(CO) stretching frequency associated with the Tr−CO···A interaction. It has been argued, however, that structure (a) might still allow good interaction with the electron density in both σ- and π-orbitals.[8]

The C−O distances, in principle, provide direct assessment of the effect of these interactions, because they are, as well as the stretching frequencies, very sensitive to the strength of the C−O bond. Unfortunately these distances are affected by the model of crystallographic data treatment (data collection cutoff[17a] and/or refinement of the C and O displacement parameters[17b]), and a direct correlation between ν(CO) and C−O distance cannot be used with confidence. However, we will see in the following that similar conclusions about the dominance of structure (b) over structure (a) can be reached from an alternative direction, namely, the geometry of weak intermolecular interactions in the solid state.

Table 1 shows the results of a Cambridge Structural Database[18] (CSD) survey of the solid state structures containing the $Tr{-}CO\cdots M^{n+}$ (Tr = transition metal, M^{n+} = metal cations of the IA and IIA groups) or the $Tr{-}CO\cdots AlR_3$ systems.[19] The number of alkali salts and AlR_3 derivatives showing close contact between metal bound CO ligands and the cations is not very large but well defined. The $CO\cdots M^{n+}$ distances fall within fairly narrow ranges, the shorter values being generally associated with bridging CO ligands. Interestingly, $CO\cdots AlR_3$ distances appear to be slightly shorter than $CO\cdots Li^+$ ones. The size of the cations is well reflected in the increase of the distance on going from Na^+ to Cs^+. As an example, the structure of the bisadduct $[Al(Et)_3][(C_5H_5)_2Fe_2(\mu\text{-}CO)_2(CO)_2]$ is shown in Figure 2. To the best of our knowledge there is only one structurally characterized example of interaction with IIA metals, $Mg(C_5H_5N)_4[(C_5H_5)Mo(CO)_3]_2$, which also shows a bent $Mo\text{-}CO\cdots Mg^{2+}$ interaction.[16]

CO Ligands in a Strong Hydrogen-Bonding Environment

Let us now move, conceptually, from Lewis acidity to Brønsted acidity. The presence of strong hydrogen bond donor and acceptor groups (such as carboxylic (COOH), amido (CONHR), and hydroxyl (OH) groups)[20] on the metal bound ligands has essentially the same effect on the intermolecular organization as in the corresponding organic solids where the ligands exist as free molecules. Common patterns such as the carboxylic dimer, the −OH ring, the amide dimer, and the “catemer” are maintained in organometallic crystals. The CO ligand is rarely involved in interactions with such donors, and the packing patterns are determined by strong donor−acceptor bonds. Intermediate situations begin to appear when the −OH group is considered because CO ligands may offer alternative hydrogen-bonding acceptor sites toward the donor −OH groups, which in turn may accept donation from neighboring C−H systems.

In the structure of the *exo*-form of $\{(C_6H_4(C_5H_4MeOH)\}$-$Cr(CO)_3$,[21] for example, O−H···O(C) and C−H···O(H) bonds have similar donor−acceptor separations (2.29, 2.44, and 2.27 Å, respectively; see Figure 3), showing that there is competition for hydrogen bond formation between −OH itself and other acceptors, such as the CO ligand. Involvement of the CO ligand in hydrogen-bonding networks is also observed in crystalline $[(\mu\text{-}H)_2\text{-}\{(\eta^3\text{-}2\text{-}MeC_3H_4)(CO)_2\text{-}3,5\text{-}Me_2\text{-}pyrazole)\}_2Mo_2]$.[22] As shown in Figure 4, the H atoms bound to the bridging oxygen

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Table 1. Survey of the Tr−CO···IA$^+$ and Tr−CO···AlR$_3$ Structural Parameters from a CSD Search

acceptor (cutoff)	no. of compds	no. of hits	CO···A range (Å) [mean (sample std)][18]	C−O···A range (deg) [mean (sample std)][18]
Li (2.0)	4	5	1.90−1.94 [1.92(2)]	145−180 [155(14)]
Na (3.2)	13	22	2.31−2.87 [2.50(17)]	100−178 [144(23)]
K (3.4)	14	185	2.57−3.36 [2.91(18)]	85−176 [118(21)]
Rb	2	10	2.86−3.33 [2.97(16)]	86−164 [140(30)]
Cs (3.4)	7	45	2.96−3.32 [3.18(10)]	86−163 [121(42)]
Al (2.6)	12	18	1.75−1.98 [1.82(5)]	109−176 [136(18)]

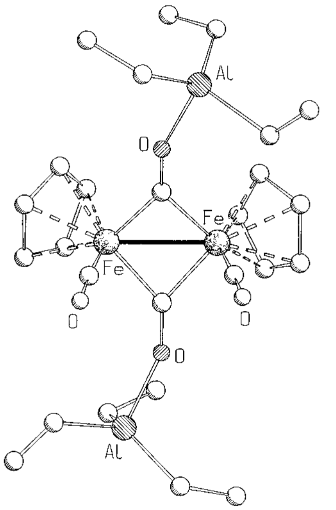

FIGURE 2. Molecular structure of the bisadduct [Al(Et)$_3$][(C$_5$H$_5$)$_2$Fe$_2$(μ-CO)$_2$(CO)$_2$].

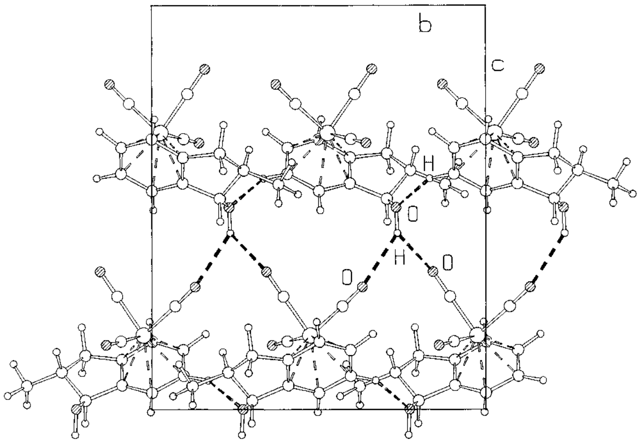

FIGURE 3. Hydrogen-bonding network in solid {(η^6-C$_6$H$_4$(C$_5$H$_4$MeOH)}-Cr(CO)$_3$ (note the direct involvement of the CO ligands in the Cr−CH···HO hydrogen bonding and the existence of C−H···OH interactions).

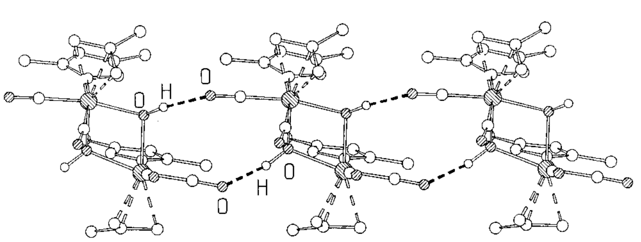

FIGURE 4. Hydrogen-bonding network in the crystal of the dinuclear complex [(μ-H)$_2${(η^3-2-MeC$_3$H$_4$)(CO)$_2$-3,5-Me$_2$-pyrazole)}$_2$Mo$_2$] (note the direct involvement of the CO ligands in the −OH···OC−M hydrogen bonding).

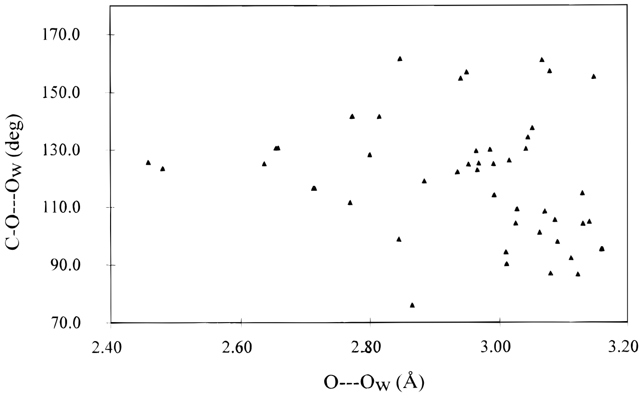

FIGURE 5. Scatter gram of O···O$_w$ distances (*x*-axis) versus the C−O···O$_w$ angles (*y*-axis).

atoms interact directly with the carbonyl oxygens, thus forming a chain of ring systems, each ring being made of two hydrogen-bonded molecules.

In general, CO ligands within a strong hydrogen-bonding environment follow the empirical rule that less basic sites are used only when more basic sites are not sterically accessible or when there is compensation *via* participation of the weaker base in polyfurcated bonds.

Hydrogen Bonding of CO Ligands with Water

A CSD survey reveals the existence of 25 crystalline hydrates in which metal bound CO ligands interact with water molecules. These complexes provide a total of 49 Tr−CO···O$_w$ interactions for which O···O$_w$ distances are less than 3.2 Å. Twenty-two interactions involve bridging CO ligands. Since no information on the hydrogen atom location is available, the geometric analysis has to be confined to CO···O$_w$ distances and C−O···O$_w$ angles whose distribution is shown in Figure 5. It can be appreciated that CO···O$_w$ distances can be as short as 2.46 Å [in the range 2.46−3.16 Å, average 2.94(18) Å], *i.e.*, comparable to relatively "strong" O−H···O interactions, and that at short distance Tr−C−O···O$_w$ angles tend toward 120−130° while diverging with increasing separation.

Kubas *et al.*[24] reported the crystal structure of W(CO)$_3$(p-^{i}Pr)$_2$(H$_2$O)(THF) in which a metal-coordinated water molecule bridges *via* its H atoms one THF molecule and a CO ligand of a neighboring molecule as shown in Figure 6. The two O···O separations are comparable in length [O$_w$···O$_{thf}$, 2.739; O$_w$···O$_{CO}$, 2.792 Å].

Rare examples of crystalline cluster salt hydrates are afforded by the hexacobalt species [Co$_6$(CO)$_{14}$]K$_4$·6H$_2$O[25a] and [Co$_6$(CO)$_{15}$]Cs$_2$·3H$_2$O[25b] (see Figures 7 and 8, respectively). Both crystals present two key features: (i) in addition to water−water hydrogen bonds (O$_w$···O$_w$, 2.982, 2.846 and 2.881, 2.936 Å, for the potassium and the cesium salts, respectively), the H$_2$O solvate molecules are bound to the cluster anions *via* O$_w$···O$_{CO}$ hydrogen bonds

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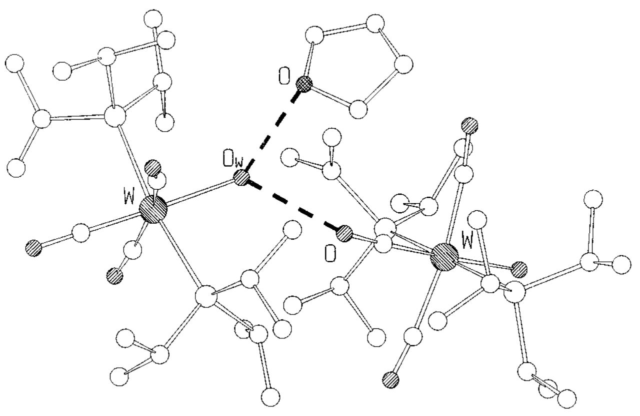

FIGURE 6. Crystal structure of $W(CO)_3(p\text{-}^iPr)_2(H_2O)(THF)$ in which a metal-coordinated water molecule is H-bridged to one THF molecule and a CO ligand of a neighboring molecule.

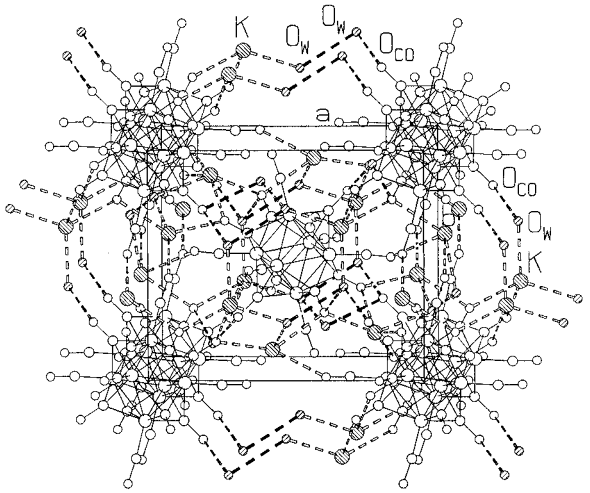

FIGURE 7. Ion arrangement in crystalline $[Co_6(CO)_{14}]K_4{\cdot}6H_2O$. The alkali metal cations carry the H_2O solvate molecules bound to the cluster anions *via* $O_w{\cdots}O_{CO}$ hydrogen bonds.

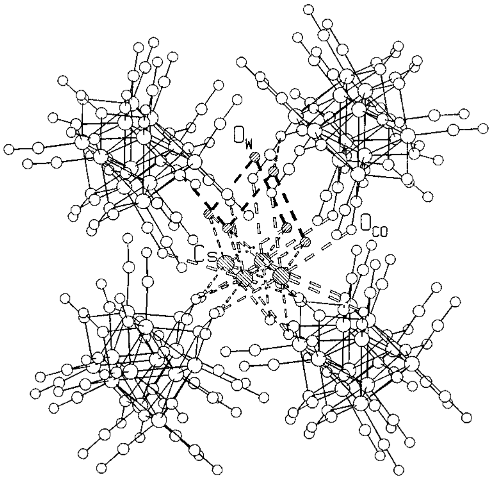

FIGURE 8. View along the *b*-axis of the ion arrangement in crystalline $[Co_6(CO)_{15}]Cs_2{\cdot}3H_2O$. The alkali metal cations carry the H_2O solvate molecules bound to the cluster anions *via* $O_w{\cdots}O_{CO}$ hydrogen bonds.

($O_w{\cdots}O_{CO}$, 2.857, 2.941, 2.882 and 2.815, 2.964 Å for the potassium and the cesium salts, respectively) and (b) both water molecules and the CO ligands interact with the alkali cations. Therefore, these complexes provide an example of the interaction of CO with both hard (the K^+ and Cs^+ cations) and soft (the H_2O molecule) acids.[26] It is interesting to note that, in both salts, the O_{CO} atoms involved in the interactions with the water molecules belong to triply bridging CO molecules, *i.e.*, to the most basic CO ligands.

CO Ligands in a Weak Hydrogen-Bonding Environment

The C−H···O interaction established by C−H donor groups and metal bound CO acceptors is the most abundant hydrogen-bonding interaction in organometallic systems.[27]

The role played by C−H···O interactions in determining crystal structure stability is now well established,[28] and there is converging evidence of C−H···X (X = O, N, S, etc.) acting as "crystal structure sieves" in the nucleation process of stable crystal nuclei. The importance of C−H···O hydrogen bonds in supramolecular chemistry has been recently assessed in a comprehensive Account by G. R. Desiraju.[29] It has also been demonstrated that C−H···O interactions are able to restrain the thermal displacement of H-bonded atoms in crystals, hence acting as true intermolecular bonds.[30] Bonds of this type, although much weaker than those of O−H···O or N−H···O types, become far more important on passing from organic to organometallic crystals because of the profusion of donor and acceptor groups. As a matter of fact, a large number of organometallic complexes and clusters carry *both* π-acid ligands such as CO and organic-type fragments among which hydrogen-bonding C−H donors such as arenes, cyclopentadienyl ligands, phenyls, and methylidine and methylidyne groups abound. These groups offer a large number of potential donor and acceptor sites which can all be utilized to afford additional stabilization to the van der Waals cohesion of organometallic molecular crystals.[31]

By searching the CSD, it has been possible to show that bridging CO ligands establish preferential interactions with respect to the terminal ligands; *i.e.*, the μ_3-bridge is more basic than the μ_2-bridge, while the terminal CO is the least basic.[27] This trend is reproduced in the average lengths of the H···O separations (2.44, 2.57, and 2.62 Å for triply bridging, doubly bridging, and terminal CO ligands, respectively). Bifurcated acceptor interactions are also quite common as would be expected in donor-rich systems. The CSD survey also revealed that the C−H···OC bonds are quite directional, with the C−O···H angle around 140° irrespective of the mode of bonding; *i.e.*, *both* terminal and bridging ligands are approached in ketonic-like directions. This observation indicates that in the solid state and in the presence of C−H donors there is oxygen lone pair density in ketonic directions also when CO is in the terminal bonding mode. Molecules belonging to the

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family of clusters $(Cp^R)_3M_3(CO)_3$ (M = Co, Rh, Ir; Cp^R = C_5H_5, C_5Me_5, C_5H_4Me) provide examples of all three types of links.[32]

In yet another study[33] the crystal structures of the carbonyl clusters $Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$[34a] and $Ru_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}S_3C_3H_6)$[34b,c] have been compared, showing that in the latter crystal the bridging CO ligands form short CO···H bonds with the μ_3-$S_3C_3H_6$ ligand (H···O separations in the range 2.262−2.538 Å). $Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ forms several bonds involving the facially bound benzene ligands and the CO ligands, the shortest distances being 2.416 and 2.372 Å. The μ_3-$S_3C_3H_6$ ligand has also been found to form shorter C−H···O interactions with bridging than with terminal CO ligands in crystals of the two isomers $Ir_4(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}S_3C_3H_6)$ and $Ir_4(CO)_9(\mu_3\text{-}S_3C_3H_6)$.[35]

Muetterties[36a] showed that the agostic C−H system in the tetranuclear methylidene cluster $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ is sufficiently acidic so as to form a C−H···OC interaction between a terminal CO ligand and the H atom of the C−H group. The participation of methylidene (μ_3-CH) and methylene (μ_2-CH_2) ligands in intermolecular hydrogen-bonding networks has been recently investigated,[36b,c] showing that methylidene forms shorter C−H···O hydrogen bonds than methylene and that the two sets of interactions are comparable to those established by hydrogen atoms bound to sp and to sp^2 hybridized carbon atoms.

Hydrogen Bonds Involving CO Ligands in Crystalline Molecular Salts

When electron-rich metal atoms are sterically accessible, hydrogen bonding to metal centers (and not to O_{CO} atoms) is preferred in the interaction with organic cations. Structurally characterized examples are rather uncommon. The $(Me_3NH)^+$ and $(Et_3NH)^+$ salts of $[Co(CO)_4]^-$ where a hydrogen atom bridges the ammonium N and Co atoms have been studied.[37,38a] Pt···H−N intramolecular interactions have been observed by neutron diffraction in the complex formed between square planar $[NPr^n{}_4]_2PtCl_4$ and *cis*-$[PtCl_2(NH_2Me_2)]$.[38b] This matter has been recently reviewed.[39]

More commonly, however, the access to the metal atoms is obstructed by the ligand envelope. In such cases the organic cations tend to interact with the most basic CO ligands available on the surface of the complex. For example, the $[^iPr_2NH_2]^+$ cation forms N−H···OC hydrogen bonds with the unique bridging CO and one terminal ligand of the cluster anion $[HFe_3(CO)_{11}]^-$ in the crystal structure.[40]

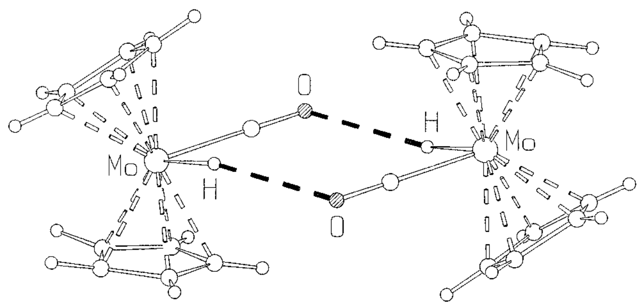

FIGURE 9. M−H···OC hydrogen-bonded cycle in crystalline $[(C_5H_5)_2Mo(H)CO][(C_5H_5)Mo(CO)_3]$.

We have shown[41] that C−H···O bonds are reinforced in crystalline molecular salts because of the opposite charge of the anions (usually carbonyl clusters) and of the cations (usually phenyl-rich large organic monoanions, such as PPN^+, $PPh_4{}^+$, etc.). In such systems CO ligands and counterions establish direct ion pairs linked by several C−H···O bonds. As a consequence there is the intriguing possibility (at least in the solid state) of stabilizing *via* C−H···OC bonds structures with bridging carbonyls over those with only terminal ligands along fluxional paths. This is the case of several complexes in the family of clusters $[M_4(CO)_{11}L]^-$ (M = Co, Rh, and Ir), many of which are known in two isomeric forms: one containing only terminal and one with three bridging CO ligands.[41] The difference in energy between the two forms is generally small, and for some ligands isolation of the isomers in the solid state is possible. The existence of solution equilibria involving carbonyl complexes hydrogen bonded to donor solvents and the stabilization of bridged isomeric forms of polynuclear carbonyls had been extensively investigated by IR spectroscopy more than 20 years ago,[42] but was never actually put to test in the solid state.

M−H···OC Hydrogen Bonding

A rather novel aspect of the hydrogen bonding in organometallic crystals is the participation of transition metal hydrides (Tr−H) in Tr−H···O intermolecular interactions with CO ligand acceptors.[43] Such a type of bonding has been observed, for example, in crystalline $(\mu_2\text{-}H)Fe_4(\mu\text{-}\eta^2\text{-}CH)(CO)_{11}L$ (L = CO,[36a] PPh_3[36b]) and $[(C_5H_5)_2Mo(H)CO][(C_5H_5)Mo(CO)_3]$.[44] This latter system is particularly remarkable as the hydrogen bond bridges two cations (see Figure 9).

A search of the CSD[45] showed that metal hydrides[46] in mono- and polynuclear systems can indeed act as donors in *intermolecular* hydrogen bonds with the oxygen atoms of the CO ligands. When the approach is not forbidden

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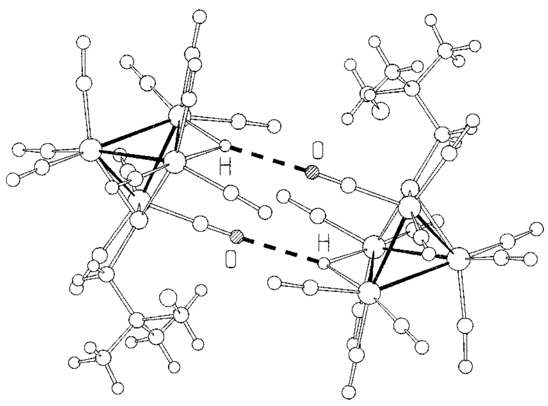

FIGURE 10. Centrosymmetric dimer in crystalline $Os_4(CO)_{13}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)$.

by the encapsulation of the H ligand within the ligand shell, the H atoms form intermolecular bonds comparable in length with those of the C−H···OC type discussed above. Needless to say, the electronic nature of the metal plays a fundamental role in tuning the polarity of the Tr−H system. In general, a positive polarization of the metal bound H atom is observed in neutral polynuclear cluster complexes where the hydrogen atom is most often present in μ_2- or μ_3-bonding fashion. As a matter of fact, polynuclear hydrides are most often obtained by protonation with acids of carbonylate anions of group VIII transition metals.

As an example of a Tr−H···OC bond, the centrosymmetric dimer formed *via* two Os−H···OC interactions (H···O, 2.507 Å; H···O−C, 163.5°) in crystalline $Os_4(CO)_{13}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)$[47] is shown in Figure 10. The similarity between this type of ring system and those formed by organic acids or amides is clear.

The interaction between two hydrogen atoms in Tr−H···H−X systems (X = C, N, O, S) is also attracting great interest. A number of papers dealing with this interaction have been recently published. The weakly attractive nature of the Tr−H···H−X interaction has been demonstrated by spectroscopic,[48ab] and diffraction[48c] experiments and discussed in theoretical[49a] studies. These interactions in general involve terminally bound H atoms. For example, the Ir−H···H−N interaction in the ionic complex $[Ir\{H(\eta^1\text{-}SC_5H_4NH)(PCy_3)\}_2]^+$ has been analyzed by Hoffmann and Liu by extended Hückel methods, showing the interaction is weakly attractive in agreement with the experimental findings of Morris *et al.*[49b]

The existence of Tr−H···H−X interactions provides a further demonstration of the duality of the Tr−H system with regard to its participation in hydrogen-bonding interactions. A survey of the occurrence of these interactions is underway.[50]

Conclusions and Outlook

Organic solids have been studied extensively, and much of the knowledge accumulated on intermolecular interactions stems from investigations of the way organic molecules are organized in the solid state.[51] Comparatively little has been done, thus far, in the neighboring field of organometallic solids. There is great scope in studying these solids, not only in order to enlarge our knowledge of the factors controlling crystal stability and cohesion but also to understand (and learn how to control) the part taken by metal atoms, with their specific electronic and steric requirements, in determining crystal architecture and properties of the solid materials.

Studies of intermolecular interactions fall quite naturally in the realm of supramolecular chemistry and crystal engineering as noncovalent interactions control crystal cohesion and determine the properties of the intermolecular assembly. Our understanding of intermolecular interactions is growing rapidly, mainly thanks to the large body of information available in the CSD and to the progress in software and computing that allow fast intermolecular searches to be made on a very large number of structures.

With organometallics the properties of the solid material depend on the electronic nature of the metals as well as on the characteristics of the ligands, which are, most often, organic molecules or fragments. When we approached the study of organometallic solids with these ideas in mind, we expected to observe many structural analogies between these and organic solids. Indeed this was revealed to be true. As we proceeded, it also became apparent that many new discoveries were awaiting us.

In this Account we have summarized some of our recent findings on the behavior of the ubiquitous CO ligand toward acidic groups *in the solid state*. In particular, we have examined the participation of metal bound CO in intermolecular hydrogen bonding. We have shown this to be pervasive. The CO ligand is sufficiently basic to accept hydrogen bond donation from weak acids such as the water molecule, from −NH and −CH groups, in some cases from −OH donors, and from the M−H system. The donor−acceptor interaction has been examined in light of the more general behavior of the metal bound CO as a base toward electrophilic species, such as alkali metal cations or AlR_3 Lewis acids. We have observed the following.

(i) Intermolecular hydrogen bonds involving CO are usually quite directional: irrespective of the mode of coordination, the CO ligands form C−O···H angles at the O atom in the range 120−140°.

(ii) This is also the angularity of the Tr−C-O···M^{n+} interactions in isocarbonyls as well as that observed in most Tr−C−O···IA^+ carbonylate anions and in Tr−C−O···AlR_3 adducts, as substantiated by a CSD search on these complexes.

(iii) When the donor is water, information on the actual hydrogen atom position within the HOH···OC bond is not

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available; however, the C$-$O$\cdots$O$_w$ interaction is usually bent and the O$\cdots$O$_w$ separation comparable to that observed in ice and crystal hydrates.[52]

(iv) There is a precise relationship between the order of basicity (terminal < μ_2-bridge < μ_3-bridge as reflected by the shift of stretching frequencies toward lower wavenumbers) and the average length of the Tr$-$C$-$O$\cdots$ACID interaction; *viz.*, bridging ligands form shorter intermolecular bonds, and/or tighter ion pairs with metal cations, than terminal ligands.

(v) This all amounts to establishing a scale of CO ligand basicity purely on the basis of crystallographic data, an approach similar to that used to correlate C$-$H$\cdots$O distances and C$-$H acidity in organic crystals.[53]

(vi) In crystalline salts, Tr$-$C$-$O$\cdots$H interactions usually between carbonyl anion species and organic-type cations follow the same trend as above, though reinforced by the difference in charge.

(vii) C$-$H$\cdots$OC bonds are the most abundant interactions. The "Gulliver effect", so well depicted in Jeffrey and Saenger's book,[3c] is at work in most crystals of carbonyl complexes: though weak, C$-$H$\cdots$OC bonds are more abundant than in most organic crystals; hence, they play a far more significant role in determining crystal cohesion.

CO is the ligand of coordination and transition metal cluster chemistry. Although the basicity of metal bound CO attracted attention in the early days, the issue lost some of its original appeal as the chemistry of carbonyl clusters developed toward complexes of ever increasing nuclearity. Now that the chemistry of weak interactions is yielding exciting new results, many coordination chemists are beginning to sense the need for moving from a molecular-based to a supramolecular-based approach to their synthetic and structural work. The perception of the possibilities offered by a molecular system, such as a carbonyl cluster, covered by numerous, though weak, acceptor sites might have important consequences on the way of thinking of synthetic paths as well as on the way of planning construction (and possibly properties) of materials based on organometallic molecules and metal clusters.

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