Hydrogen Bonding in Organometallic Crystals. 6.[†] X−H---M Hydrogen Bonds and M---(H−X) Pseudo-Agostic Bonds

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The intermolecular interactions between X−H groups (X = C, N, and O) and metal atoms in crystalline organometallic complexes have been investigated. Molecular and crystal structures determined by neutron and/or X-ray diffraction data have been retrieved from the Cambridge Structural Database. The comparative analysis of intermolecular H---M and X---M distances as well as that of the X−H---M angles allows a discrimination between the behavior of electrophilic and nucleophilic metal centers. Two novel types of interactions have been characterized: (i) the intermolecular multicenter hetero-acceptor (IMH) hydrogen bond formed when the X−H donor group interacts with $M-X'_n$ systems where M is an electron-rich metal and X′ a metal-coordinated electronegative atom (X′ = S, N, O, Cl); (ii) the intermolecular pseudo-agostic (IPA) interaction in which the X−H bond can donate electron density to electron deficient metal atoms M---(H-X) as observed in intramolecular agostic interactions. Hydrogen bonding to metal centers in neutral complexes (X−H---M) have been compared with charge assisted ($X-H^+$---M^-) hydrogen bonds involving electron-rich anionic complexes.

Introduction

The great structural diversity of organometallic systems, arising from the variability of the ligands and from the ligand−metal(s) bonding, is reflected in the types and patterns of hydrogen bonding and other intermolecular interactions established by organometallic molecules and ions in the solid state.[1] In our systematic approach to supramolecular interactions we have recently investigated the hydrogen bonds formed by strong donor/acceptor groups such as −COOH and −OH systems,[2a] as well as by primary $-CONH_2$ and secondary amido −CONHR groups belonging to metal−coordinated ligands.[2b]

With organometallic species, however, the capacity to form hydrogen bonds is not confined to the traditional common acceptor and donor groups of organic molecules. Indeed, organometallic systems afford "new" bases and acids which have no counterpart in the organic chemistry field. In previous papers we have investigated by means of the Cambridge Structural Database[3] two specific cases: (i) the basicity of the CO ligand and its the participation in hydrogen bonds of the C−H---O type;[4] (ii) the acidity of hydrogen atoms bound to transition metal clusters and their capacity to establish M−H---O(C) bonds comparable in length to those formed between C−H groups and CO ligands.[5]

Metal atoms show an amphoteric behavior. Pearson and Shriver have pointed out on separate occasions[6] that the M−H bond is chemically very similar to the C−H bond. Indeed, both systems undergo reactions as H^+, $H^•$, and H^- depending on the relative stability of the resulting species. These earlier studies lend a picture of the H---M interaction as an extremely soft and polarizable bonding system, with the M−H group able to act both as hydrogen bonding donors or acceptors depending on a number of factors such as electronic configuration, oxidation state, and electronegativity of the metal and the type and distribution of ligands.

The Lewis basicity of metal atoms in coordination complexes is an issue which is receiving increasing attention. Epstein, Shubina and co-workers have found IR evidence for the formation of intermolecular O−H---M hydrogen bonds between phenols and para-substituted phenols and metallocenes $(\eta^5\text{-}C_5H_5)_2M$ (M = Fe, Ru, and Os).[7a] The equilibrium between molecular and ionic hydrogen-bonded complexes has also been inves-

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[†] Part 5: Reference 13.

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tigated by IR and UV spectroscopy.[7b] Kazarian and Polyakoff have measured IR spectra in the ν(C−O) and ν(O−H) region to investigate the hydrogen-bonding interaction between fluoroalcohols and organometallic complexes (η^5-C_5Me_5)$_2$M(L)$_2$ (M = Co, Rh, Ir, L = CO, C_2H_4, N_2, PMe_3) in hydrocarbons, nobles gases, and supercritical fluid solutions.[7c,d]

Clear-cut solid-state structural evidence for the existence of intermolecular hydrogen bonds of the X−H---M type have been provided by the early work of Calderazzo and co-workers[8] and by the systematic investigation of the basicity of the anion $Co(CO)_4^-$ by Brammer.[9]

Recently, there have been several reports on the existence of the "dihydrogen bond" M−H---H−X between two hydrogen atoms one of which bound to a metal atom and the second bound to an electronegative main group atom (C, N, O, S). This intriguing type of interaction is being intensively investigated by means of spectroscopic[10] and structural methods.[11] The intramolecular Ir−H---H−N interaction in the ionic complex [Ir{H(η^1-SC_5H_4NH)(PCy_3)}$_2$]$^+$ has also been analyzed by extended Hückel methods.[12]

In this paper we investigate the Lewis acid−base behavior of transition metal atoms by studying intermolecular interactions between metal centers and C−H, N−H, and O−H groups belonging to the ligands or to the counterions in the case of organometallic salts. In order to do so, the CSD has been searched for those complexes showing intermolecular H---M separations below predefined cut-off values (see below). This approach can be used not only to obtain information on hydrogen bond donation to a metal center, X−H---M, but also on the *reverse* situation, *i.e.* on the electron donation from an electron-rich system carrying one or more hydrogen atoms to an electron deficient metal, M---(H-X). A similar relationship has been used to investigate intramolecular agostic interactions with respect to the interactions between electron deficient Li atoms and C−H systems.[13] M---(H-X) interactions have been previously detected, for example, in the ion-pair adducts between anionic Lewis acids and electron deficient and coordinatively unsaturated zirconocene compounds prepared by Marks and co-workers.[14]

This analysis amounts to the assessment, *via* solid-state data, of the acid−base behavior of transition metal atoms. We shall demonstrate in the following not only that *intermolecular hydrogen bond* formation with an electron-rich metal center is a common phenomenon, observed with all traditional donor groups, but also that *intermolecular electron donation* from covalent bonds to satisfy the electronic requirements of electron deficient metal atoms is also a well-defined phenomenon. In the context of this discussion the notations X−H---M and M---(H−X) have been chosen so that the flow of electron density is, in both cases, from right to left, i.e. from Lewis base to acid.

Methodology

As in previous papers in this series we have investigated the distribution and geometry of intermolecular X−H---M interactions (X = O, N, C) by searching the CSD.[3] Data were retrieved from the April 1996 update version of the CSD for all crystal structures with an exact match between chemical and crystallographic connectivity. Both neutral and charged species were considered. Only entries presenting atomic coordinates, including those of the hydrogen atoms, and where $R < 0.10$ for X = N and O and $R < 0.05$ for the more abundant X = C were considered. The results of the CSD searches are discussed below and presented in tabular form. O−H---M, N−H---M, C−H---M interactions were searched, and separate subsets of the CSD were created in order to run comparative analyses. Crystal structures discussed in the following are identified by their respective CSD REFCODES. Unless stated otherwise, all structural parameters are calculated on the basis of X−H distances normalized to the corresponding neutron diffraction values in order to cope with the well-known shortening of O−H, N−H, and C−H bond lengths in X-ray diffraction experiments.[15a] Selection criteria, beside those on the quality of the structural data, have been based on H---M interatomic separations falling below a predefined cutoff value of 3.2 Å corresponding to a maximum van der Waals radius of *ca.* 2.1 Å for the metal atoms. This value is large enough to guarantee that all relevant interactions are included in the search. Geometrical questions for X = C are given in the Supporting Information as representative examples. Key examples were selected from the search outputs and investigated by computer graphics.[15b] The computer program PLATON[15c] was used to analyze the metrical features of the hydrogen-bonding patterns.

As anticipated in the Introduction, a criterion based on intermolecular X---M distance is critical in coordination chemistry since many metal-coordinated molecules (such as water or other solvent molecules) are coded as separate molecules in the crystal although they are well within the first coordination sphere of a metal complex. The problem can be circumvented by analyzing X---M and H---M distances and X−H---M angles simultaneously. Chart 1 shows the possible geometrical relationships between these three parameters and the different types of interactions that arise in each of the following cases.

Type 1: (X)H---M > X---M and a small X−H---M angle (<100°) most often correspond to metal-coordinated ligands interacting *via* lone pair dative bonds. The proximity of the

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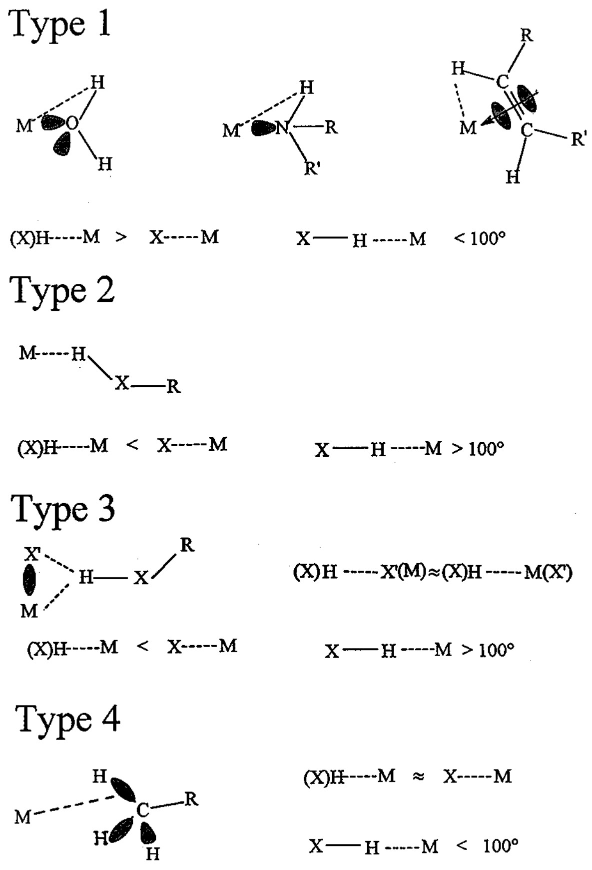
Chart 1



donor atom to the metal brings some of the ligand H atoms at a distance below cutoff. In these cases, short (X)H---M distances are not indicative of hydrogen bond formation ("false" hydrogen bonds).

Type 2: (X)H---M < X---M and a large X−H---M angle (>100°) may indicate the existence of a true hydrogen bond interaction. Such a bond implies that the H atom points directly toward the metal atom. This interaction is observed only with very electronegative metal atoms and, in the case of ionic species, is reinforced by charge difference between anion and cation.

Type 3: This is as above, *i.e.* (X)H---M < X---M and X−H---M > 100°, but with the additional condition (X)H---X′(M) ≈ (X)H---M(X′). In this situation the X−H donor group is at hydrogen bond distance not only from the electron-rich metal atom but also from one or more of the metal-coordinated electronegative atom X′ (X′ = S, N, O, Cl). We call this arrangement an intermolecular multicenter hetero-acceptor (IMH) hydrogen bond. In terms of geometry this is rather similar to type 2; hence, each case must be individually checked on the X−H---X′ versus X−H---M distances. IMH interactions require the presence of electron-rich metal atoms bound to electronegative main group elements, thus forming an electron-rich system capable of accepting H-bond formation from suitable donors. This interaction is analogous to that established by C−H donors with C=C multiple bonds or π-systems.[16]

Type 4: (X)H---M ≈ X---M and an X−H---M angle < 100° might indicate an electron donation from the X−H bond of a ligand to an electron deficient metal atom (*viz.* the behavior of a Lewis base) which brings the H atom in the proximity of the metal. We call this an interaction of the "pseudo-agostic" type (IPA). This condition should not be confused with type 1. As in true agostic interactions,[17] IPA interactions require an electron deficient metal atom capable of accepting electron density from X−H bonds belonging to another molecule or ion. IPA interactions appear also to be reinforced by charge difference.

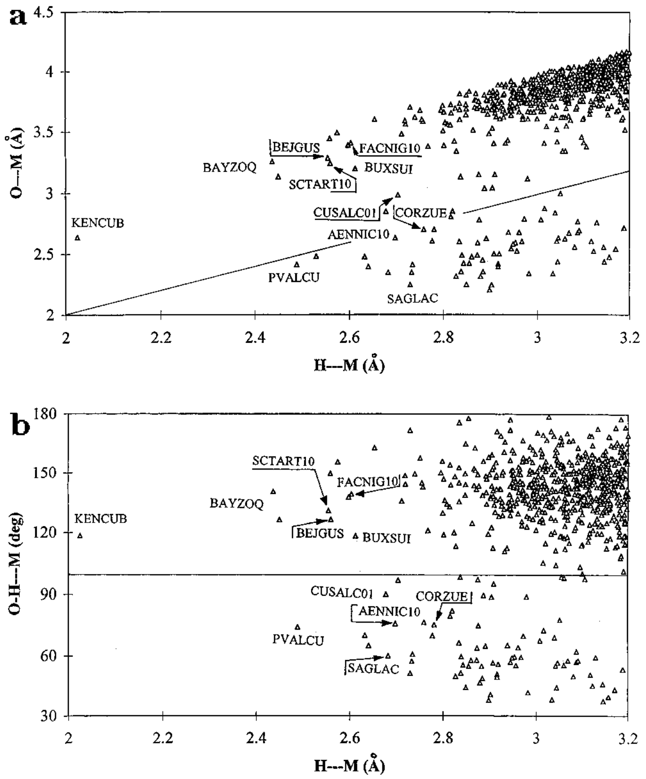


Figure 1. Scattergrams of O---M versus (O)H---M (a) and of O−H---M versus (O)H---M (b). The diagonal line in (a) indicates the separation between type 1 [(O)H---M > O---M] and the other interactions, while the horizontal line in (b) marks the separation between types 1 and 4 (<100°) and types 2 and 3 (>100°) geometries shown in the Chart 1. CSD REFCODES of most relevant compounds discussed in the text are indicated.

Results and Discussion

The first part of this section will be devoted to the description of the CSD analysis results, while specific examples of the different types of interactions will be discussed in the second part.

O−H---M and M---(H−O) Interactions. There are 483 compounds in the (O)H---M search for a total of 708 interactions. The −OH donor groups most often belong to hydration water molecules incorporated in the crystal lattice by networks of H-bonds. Few examples are also found of RO−H---M/X bonds. Scattergrams of O---M versus (O)H---M distances and of O−H---M angles versus (O)H---M distances are shown in Figure 1a,b, respectively.

Figure 1a shows two populations of O---M distances, the gap line being roughly at 3.0−3.2 Å. The majority of complexes are concentrated in the top part where O---M > 3.2 and H---M > 2.6 Å. There are, however, eight interactions with H---M shorter than 2.6 Å and O---M longer than 3.0 Å, thus satisfying the condition for type 2 interaction (true hydrogen bonds). Some of

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these will be discussed below. The bottom part of the scattergram generally contains complexes with O---M < H---M. These are chiefly aquo complexes where H_2O---M coordination brings the water hydrogens close to the metal, *i.e.* "false" hydrogen bonds. These complexes can be of interest for the hydrogen-bonding patterns they form with neighbors *via* the water molecules. This area contains also a couple of intriguing cases for which H---M ≈ O---M (see below) which may correspond to IPA interactions. We shall see that this particular area will become more populated with C−H---M situations where pseudo-agostic interactions are more abundant.

The scattergram in Figure 1b also shows a double population: although most complexes concentrate in the area defined by (O)H---M > 2.6 Å and O−H---M > 100°, there are few cases of small (<100°) O−H---M angles and short (<2.6 Å) (O)H---M distances corresponding to those for which H---M ≈ O---M in scattergram 1a. There are only very few systems characterized by short (O)H---M < 2.6 Å and O−H---M angles > 100°; these are of major structural interest as we shall see later since they correspond to intermolecular H-bonds, chiefly of the IMH type.

N−H---M and M---(H−N) Interactions. There are 166 compounds in the nitrogen search, for a total of 237 interactions. Those compounds for which either the N---M or the H---M distances are very short will be discussed below in detail. Some "false" hydrogen bonds arising from close proximity of the H atoms bound to coordinated ligands is also observed in some cases (distance N---M < (N)H---M). Scattergrams of N---M distances versus (N)H---M distances and of N−H---M angles versus (N)H---M distances are shown in Figures 2a,b, respectively. Figure 2a allows identification of the four types of interactions. Figure 2b shows that most complexes, however, cluster at N−H---M angles above 120° and only few are at smaller N−H---M angles which are indicative of either "false" hydrogen bonds or of IPA interactions. The strong interionic $M^{(-)}$---$HNR_3^{(+)}$ interaction between carbonyl anions and quaternary amino cations reported by Calderazzo[8] and Brammer[9] are those for which "true" hydrogen bonds are observed [distance N---M > (N)H---M, N−H---M *ca.* 180°].

C−H---M and M---(H−C) Interactions. The number of organometallic ligands containing C−H groups is *per se* much larger than that of the ligands containing O−H or N−H groups. There are 2085 compounds in the CSD search for a total of 3000 observations (H---M < 3.2 Å). On the other hand the acidity of C−H is in general smaller than of O−H and N−H groups; hence, as usually observed with organic C−H---X (X = O, N, Cl) interactions, the donor−acceptor distances tend to be much longer than with stronger donors. The C−H donors are, therefore, less easy to identify.

In general, the distribution of the C−H---M interactions follow the same trend as in the O−H---M and N−H---M cases. There are a number of examples of C−H---M hydrogen bonds, also of the IMH type, as well as several M---(H−C) IPA interactions. Such interactions are usually, though not always, associated with the presence of tight ion pairs formed by an electron deficient metal cation and the counterion carrying methyl or phenyl groups. In both searches, there is a significant number of structures for which the (C)H---M separation is shorter than 2.5 Å which, in the case of "organic" C−H---X bonds, is usually taken as indicative of fairly strong C−H---X interactions. Some of the very short (C)H---M distances will be examined in detail.

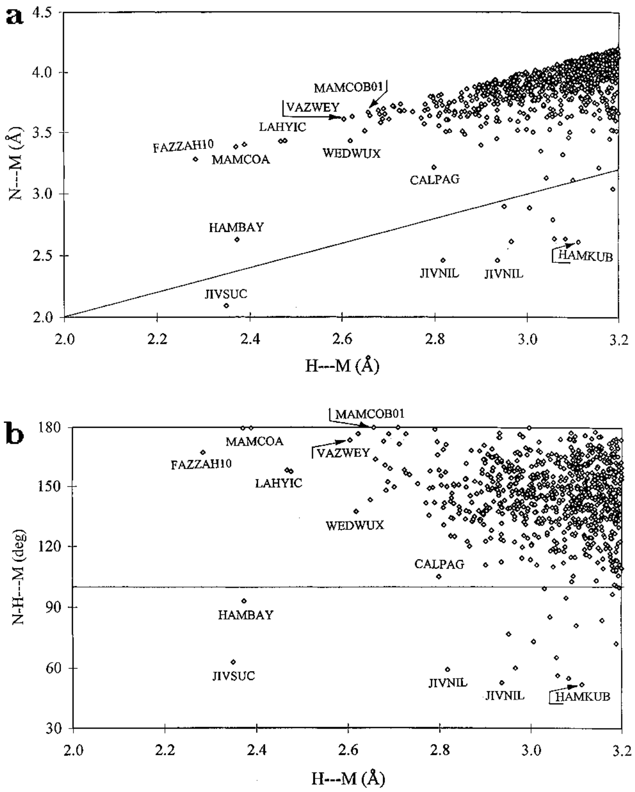

Figure 2. Scattergrams of N---M versus (N)H---M (a) and of N−H---M versus (N)H---M (b). The diagonal line in (a) indicates the separation between type 1 [(N)H---M > N---M] and the other interactions, while the horizontal line in (b) marks the separation between types 1 and 4 (<100°) and types 2 and 3 (>100°) geometries shown in the Chart 1. CSD REFCODES of most relevant compounds discussed in the text are indicated.

The scattergrams of C---M versus (C)H---M distances and of C−H---M angles versus (C)H---M distances are shown in Figures 3a,b. It can also be seen that there are some complexes for which the H---M and C---M separations have comparable length, *i.e.* most likely IPA interactions. Furthermore, there appear to be several cases of "short" (C)H---M separations associated with large C−H---M angles, which most likely correspond to C−H---M hydrogen bonds.

The examples selected from the searches for the O−H---M, N−H---M, and C−H---M interactions are listed in Tables 1−3, respectively, and will be discussed in detail in the following. References to the original structural papers quoted in the tables are also given.

Intermolecular Multicenter Hetero-Acceptor (IMH) Hydrogen Bond Involving Oxygen. The square planar copper complex BEJGUS, $CuL_2L'_2{\cdot}2[H_2O]$ (L = *N*-acetyl-α-alaninato, L′ = *N*-methylimidazole), crystallizes with two water molecules per formula unit. These water molecules are hydrogen bonded to two complexes as shown in Figure 4. The IMH interaction is clear to see: the water molecules fill in the coordination around the metal with H15 participating in a bifurcated link with the copper atom and with one O atom of the ligand thus constituting a five-membered

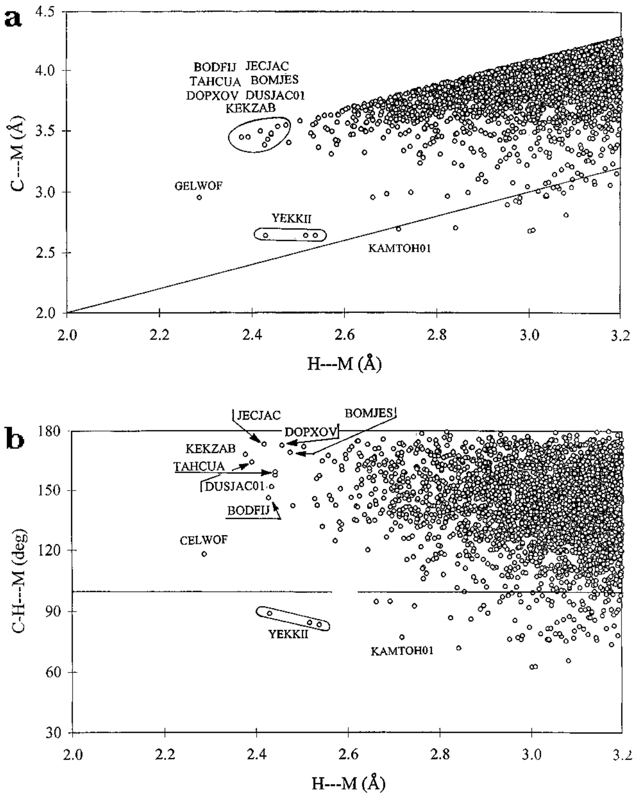

Figure 3. Scattergrams of C---M versus (C)H---M (a) and of C−H---M versus (C)H---M (b). The diagonal line in (a) indicates the separation between type 1 [(C)H---M > C---M] and the other interactions, while the horizontal line in (b) marks the separation between types 1 and 4 (<100°) and types 2 and 3 (>100°) geometries shown in the Chart 1. CSD REFCODES of most relevant compounds discussed in the text are indicated.

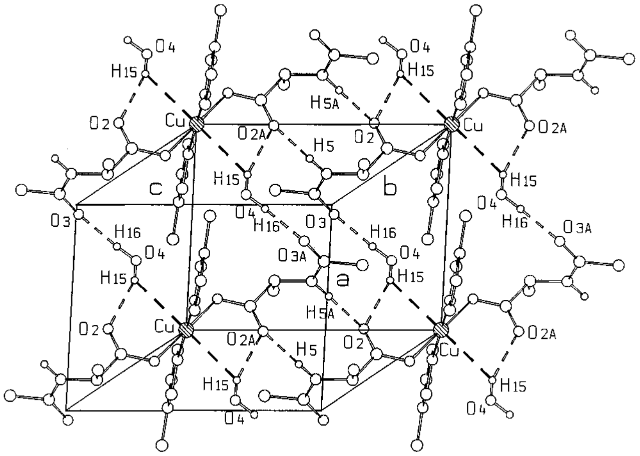

Figure 4. Intermolecular multicenter hetero-acceptor (IMH) interaction in crystalline BEJGUS. Note how the water molecules fill in the coordination around the metal with H15 linking simultaneously the Cu atom and one O atom of the ligand. Only H atoms bound to oxygen are shown for clarity.

metallacycle. The (O)H---Cu and (O)H---O separations are 2.568 and 2.027 Å, respectively. Two *N*-acetyl-α-alaninato ligands also establish a 10-membered ring *via* C−H---O interactions.

Similar IMH interactions are present in crystalline BAYZOQ, $Cu_2(\mu\text{-L})Cl_2(\mu\text{-Cl})(\mu\text{-OH})\cdot 1.5H_2O$ (L = (2-pyridylamino)phthalazine-N^1,N^3,N^4,N^6), with a water hydrogen pointing toward the copper atom and the available lone pair on the bridging O−H group. H---Cu distances and O−H---Cu angles are 2.448 and 2.458 Å and 140.6 and 126.4°, respectively.

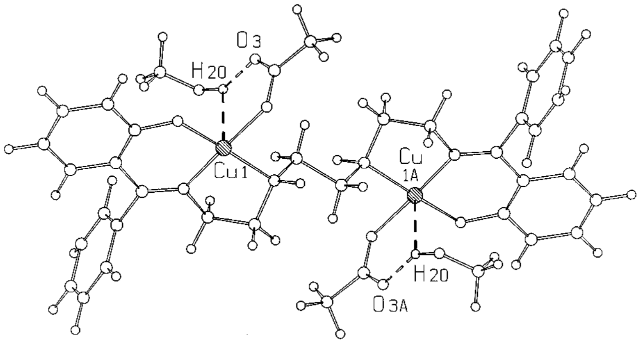

Figure 5. IMH interaction in crystalline BUXSUI involving a methanol molecule. The H atom of the −OH group bridges the copper and the O atom of the ligand.

Hydrogen bonds of the IMH type are not confined to water molecules as it can be seen in crystalline BUXSUI, $Cu_2L(CH_3COO)_2\cdot 2CH_3OH$ (L = μ-*N*,*N*′-bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl). Figure 5 shows how a methanol molecule takes part in an interaction of the type discussed above with the H atom of the −OH group bridging the copper and the O atom of the acetate ligand (H---Cu 2.619 Å, H---O 1.752 Å). As in the case of BEJGUS, the H atom is part of a five-membered ring including the Cu atom. In crystalline KENCUB, $CuL_2(C_6H_5O)_2$ (L = μ-1,3-bis(hydroxymethyl)-2-imidazolidinethione-*O*,*O*,*S*), on the other hand, the IMH interaction involves one copper atom of the binuclear complex [Cu---O 2.639, (O)H---Cu 2.025 Å, O−H---Cu 118.5°] and the copper-bound sulfur [(O)H---S 2.580 Å]. In the bicopper complex SCTART10, $Na_4[Cu_2L_2]\cdot 10H_2O$ (L = μ-D,L-tartrato-*O*,*O*′,*O*″,*O*‴), three water molecules point one H atom toward copper and one of the copper-bound oxygen atoms [H(3)---Cu 2.564 Å, H(1)---Cu 2.824 Å, H(11)---Cu 2.940 Å]. The O atoms of the water molecules point toward the Na^+ cations.

In crystalline CUSALC01, $CuL_2(H_2O)_2\cdot 2H_2O$ (L = salicylato-*O*), the water molecules manifest their dual behavior as both Lewis bases and proton acids. Contrary to the copper complexes discussed thus far CUSALC01 presents two salicylato-*O* ligands coordinated *via* oxygen *trans* with respect to the copper atom (Cu-O 1.938 Å); the square planar coordination is then satisfied by two water molecules (Cu-O 1.915 Å) as clearly shown in Figure 6. Two metal-coordinated water molecules direct the H atoms toward the Cu−O (salicylato-*O* ligand) bonds (Cu---O 2.854, H---Cu 2.678 Å, O−H---Cu 90.1°). Two additional water molecules in the crystal form hydrogen bonds with the metal-coordinated molecules as well as with other acceptor sites on the ligand.

Intermolecular Multicenter Hetero-Acceptor (IMH) Hydrogen Bonds Involving Nitrogen. Crystalline LAHYIC, $[Ni(NH_2Et)_3][NiL_2]$ (L = maleonitriledithiolato), and WEDWUX, $PdClL\cdot 1.5H_2O$ (L = glycyl-L-histidine-*N*,*N*′,*N*″), offer two examples of IMH interactions involving nitrogen donors. Other metal atoms as well as other acceptors (S and Cl, for example) can be used in the bonding. In LAHYIC the interaction between anion and cation occurs through an IMH link with the N−H system pointing toward the center of the square planar Ni complex and the surrounding S atoms bound to Ni as shown in Figure 7. The H---Ni and

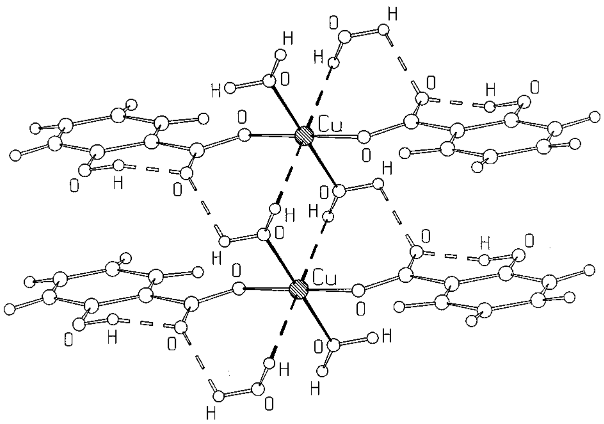

Figure 6. Crystalline CUSALC01 showing water molecules in both their dual behaviors as Lewis bases and of proton acids. The water hydrogen atoms interact with the copper and with the O atom of the ligand involved in an intramolecular O---H−O bond.

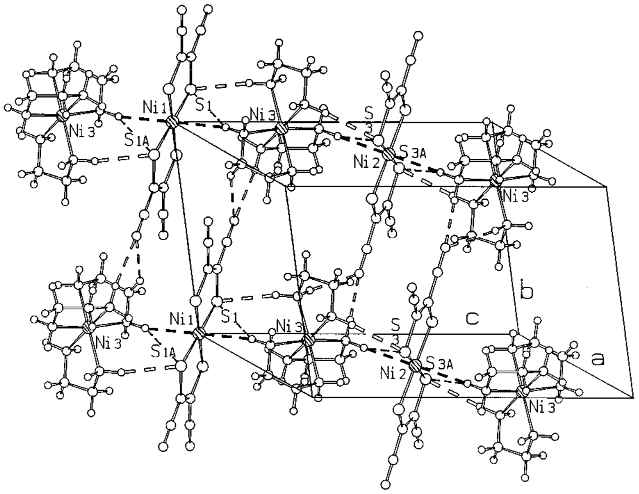

Figure 7. IMH interaction in crystalline LAHYIC. The N−H systems point toward the Ni and the surrounding S atoms.

N---Ni separations (2.448 and 3.425 Å) are comparable to the (O)H---Cu and Cu---O distances discussed above. However, the N−H---(Ni−S) interaction is not the only hydrogen bond established by N−H donors; another N−H group also forms a short bond with another S-acceptor on the molecule (H---S 2.664 Å). A similar IMH geometry is present in WEDWUX with an N−H---(Pd−Cl) interaction: the H atom links a Pd atom [(N)H---Pd 2.603 Å] and a Cl atom (H---Cl 2.395 Å) as shown in Figure 8.

The possibility of a Pt−Br bond acting as an intramolecular hydrogen bond acceptor from an N−H bond of the ligand has been discussed by van Koten *et al.* in the case of a zwitterionic Pt(II)$^-$---H−N$^+$ complex.[46]

Charge-Assisted (N−H$^{\delta+}$---M$^{\delta-}$) Hydrogen Bonds. It is well-known that electron-rich metal atoms may accept hydrogen bond donation from N−H systems. These interactions are of great importance for the understanding of hydrogen transfer reactions. The earliest example in this class of compounds is the anion $Co(CO)_4^-$ which forms a tight ion pair in the solid state when crystallized with NR_3H^+ counterions. The structure of the $[NMe_3H]^+$ salt (MAMCOA) represents probably the first example of a direct interaction between an acid proton and a carbonyl anion. In crystalline MAMCOA there are two independent structural units; the N---Co separations are 3.379 and 3.398 Å, while the (N)H---Co distances are 2.371 and 2.389 Å, and the angles N−H---Co are 179.5 and 179.7°, respectively. When the small $[NMe_3H]^+$ cation in MAMCOA is replaced by the more sterically demanding $[NEt_3H]^+$ (MAMCOB), the approach between anion and cation is made more difficult and the N---Co and (N)H---Co separations lengthen (3.719 and 2.689 Å in MAMCOB), the N−H---Co angle being 180.0°. The crystal structure of MAMCOB was later redetermined by neutron diffraction at 15 K, confirming the results obtained at room temperature [N---Co 3.666, (N)H---Co 2.611 Å]. N−H---Co interactions of the same type are also present in crystalline LEVBAP where an *N*-methylpiperazine ligand joins two $Co(CO)_4^-$ ions [N---Co 3.641 and 3.631 Å, (N)H---Co 2.641 Å, 2.602 Å, N−H---Co 163.9 and 176.8°].

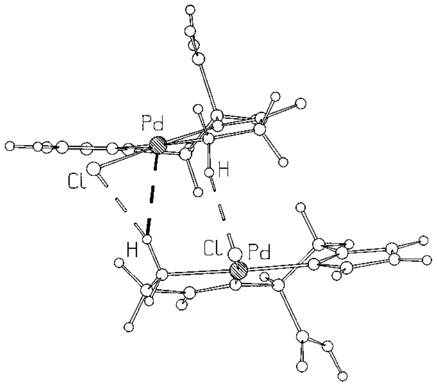

Figure 8. N−H---(Pd−Cl) interaction in crystalline WEDWUX.

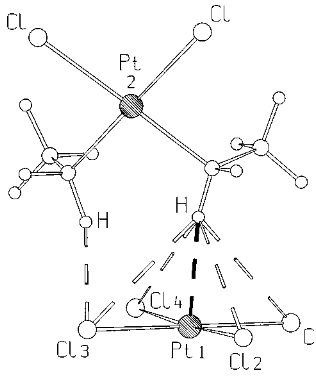

Figure 9. N−H---Pt interaction between anion and cation in crystalline FAZZAN. Note how the N−H vector points directly toward the Pt atom of the $PtCl_4^-$ complex.

After these initial findings, other examples of transition metal anions acting as hydrogen bond acceptors toward cation donors were investigated. This work is very well documented and does not need to be reexamined in the context of this paper. The reader is addressed to Brammer's recent review article.[9c] For the sake of completeness, however, and in order to allow comparison with previously discussed cases of IMH interactions, the case of the Pt complex FAZZAH10, $[PtCl_2(NH_2Me)_2][NPr^n_4]_2[PtCl_4]$, needs to be, though briefly, discussed. Figure 9 shows the N−H---Pt interaction (N---Pt 3.276; H---Pt 2.263 Å, N−H---Pt 167.3°) between anion and cation as ascertained by neutron diffraction at 20 K. The N−H vector points directly toward the filled d_{z^2} orbital that serves as Pt atom lone

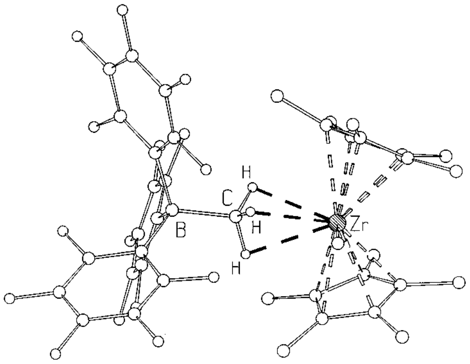

Figure 10. Intermolecular pseudo-agostic (IPA) interactions in crystalline YEKKII.

pair, while a secondary hydrogen bond is established between another N−H system and one Cl ligand. Alternatively, FAZZAH10 can be seen as an extreme case of IMH interaction of the type discussed above: the Pt-bound H atom is indeed in the middle and almost equidistant from four Cl ligands [H---Cl(1) 3.287, H---Cl(2) 2.895, H---Cl(3) 3.162, H---Cl(4) 3.435 Å].

Electron Deficient Complexes and Intermolecular Pseudo-Agostic (IPA) Interactions. A number of electron deficient coordinatively unsaturated cationic zirconocene complexes have been prepared and characterized by Marks' group.[14] These complexes are highly active catalysts for the polymerization of ethylene and α-olefin. The activity of such complexes is dependent upon that of the cocatalyst, usually a strong Lewis acid, such as the $[CH_3B(C_6H_5)_3]^-$. The cocatalyst is capable of selectively interacting with the electron deficient metal *via* ion-pairing or adduct formation. The molecular and crystal structures of several complexes have been determined and described. These complexes in the solid state share a common feature, the presence of short Zr---H and Zr---C interactions due to the close approach of the boron bound methyl group to the electron deficient Zr atom. These distances have been shown to depend on the bulk of the substituents on the Cp ligands coordinated to Zr as well as on the electronic characteristics of the metal center; *viz.* more basic Zr atoms are associated with shorter Zr---C distances. The reason for bringing up this subject in the context of this paper is clear: these compounds fall in the area of IPA interactions, which can be easily identified because C---M ≈ H---M and C−H---M < 100°. The case of YEKKII, $[(Cp^*)_2ZrMe][(C_6F_5)_3BMe]$, will be used as a prototype. Figure 10 shows the ion-pair formation: the Zr---C separation is 2.640 Å, and the three hydrogen of the methyl group are at 2.517, 2.430, and 2.538 Å from the Zr center, forming Zr---H−C angles of 84.3, 88.8, and 83.3°. Structural data for other examples are given in Table 3. Importantly, solution ^1H and ^{13}C as well as solid-state ^{13}C CPMAS NMR data are consistent with the ion-pair nature of these complexes and point to the fact that the interaction is through the hydrogen atoms of the methyl groups rather than directly with the carbon atom.

IPA interactions, however, are not confined to the zirconocene cations but appear to be a general feature of electron deficient metal complexes provided that the access to the metal is not obstructed by bulky ligands. IPA bonding is, for instance, observed in crystalline KAMTOH01, where a C−H system of the Ag-coordinated μ-salicylato-*O,O′* ligand interacts directly with the Ag atoms of the Ag_2 dimer as shown in Figure 11. Ag---C and Ag---H distances are 2.695 and 2.718 Å, respectively. Further contribution to crystal cohesion arises from a C−H---O hydrogen bond between the ligands (O---H 2.343 Å).

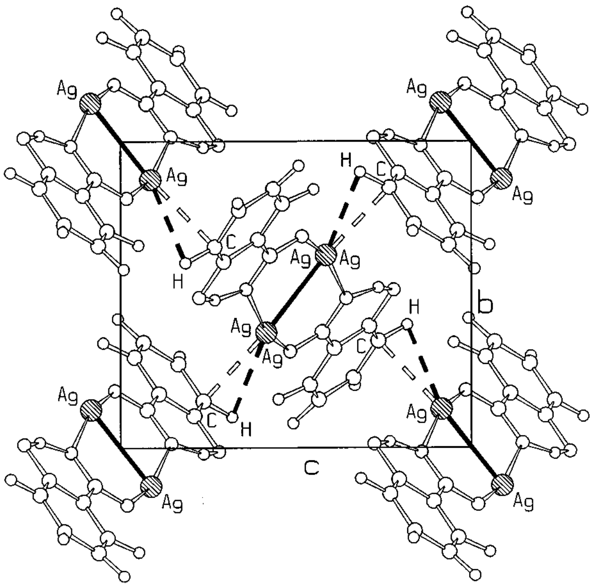

Figure 11. IPA bonding of the Ag---(H−C) type in crystalline KAMTOH01.

Crystalline compounds showing distances X---M ≈ H---X and angles X−H---M < 100° are present also in the oxygen and nitrogen scatterplots and are listed in Tables 1 and 2. These situations are, however, less clear-cut than in the case of carbon because of the presence of lone pairs on the donor atoms which are

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Table 1. Compound Formula, REFCODES, and Relevant Geometrical Parameters for M---H−O Intermolecular Interactions for Transition Metals with Intermolecular M---H < 3.2 Å and Comparison with M---O Interactions

compd	REFCODE	O---M (Å)	H---M (Å)	O−H---M (deg)	ref
O---M > (O)H---M, O−H---M > 100°					
$PdL_2(P(n\text{-}Bu)_3)_2CH_3OH$ (L = adeninato)	ADBPPD	3.462	3.099	103.6	18
$CuL_2(HCOO)_2{\cdot}H_2O$ (L = amidonicotinato)	ANCTCU	3.391	2.809	119.1	19
$Cu(H_2O)_3L_2{\cdot}5H_2O$ (L = *p*-hydroxybenzoato)	BAPHEF	3.425	2.831	120.1	20
$Cu_2(\mu\text{-}L)Cl_2(\mu\text{-}Cl)(m\text{-}OH){\cdot}1.5H_2O$ (L = (2-pyridylamino)phthalazine-N^1,N^3,N^4,N^6	BAYZOQ	3.257, 3.135	2.448, 2.458	140.6, 126.4	21
$CuL_2L'_2{\cdot}2H_2O$ (L = *N*-acetyl-α-alaninato; (L′ = *N*-methylimidazole)	BEJGUS	3.243	2.568	126.5	22
$Cu_2L(CH_3COO)_2{\cdot}2[CH_3OH]$ (L = μ-*N*,*N*′-bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl))	BUXSUI	3.200	2.619	118.5	23
$CuL_2(C_6H_5O)_2$ (L = μ-1,3-bis(hydroxymethyl)-2-imidazolidinethione-*O*,*O*,*S*)	KENCUB	2.639	2.032	118.5	24
$K_2[ZnL]{\cdot}3H_2O$ (L = *o*-phenylenediaminetetraacetato-*N*,*N*′,*O*,*O*′,*O*″,*O*‴	DORGOG	3.408	2.911	112.6	25
$Na_2[CuL]{\cdot}4H_2O$ (L = *o*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetato-*N*,*N*′,*O*,*O*′,*O*″,*O*‴	DUYJEM	3.436	2.942	112.5	26
$K_4[Pt_2L]{\cdot}6H_2O$ (L = μ-methylenebis(phosphonito)-*P*,*P*′	FACNIG10	3.392	2.608	137.9	27
$Cu(H_2O)L_2$ (L = (2-fluorophenoxyacetato)pyridyl-*O*)	FADZUF	3.422	3.037	104.4	28
$Na_4[Cu_2L2]{\cdot}10H_2O$ (L = μ-D,L-tartrato-*O*,*O*′,*O*″,*O*‴	SCTART10	3.286	2.564	131.1	29
$CuL_2(H_2O)_2{\cdot}2H_2O$ (L = salicylato-O)	CUSALC01	2.854	2.678	90.1	30
O---M ≈ (O)H---M, O−H---M < 100°					
$[CuL_2][CuL_2\text{-}Ni_2L_4]{\cdot}4H_2O$ (L = ethylenediamine)	AENNIC10	2.635	2.695	75.8	31
$Cu(\beta\text{-}Ala)_2{\cdot}4[H_2O]$	CORZUE	2.609	2.773	69.9	32
$[CuL_2]$[D-tartrate]$\cdot 2H_2O$ (L = *N*-methylethylenediamine)	ECUTAR	2.630	2.886	64.9	33
$[CuL_2][PF_6]_2{\cdot}H_2O$ (L = mthylenediamine)	JIRCIW	2.397	2.635	65.0	34
$[CuL_2(CH_3COO)_2][H_2O$ (L = 3,4-dimethylpyridine)	MEPCUA	2.809	2.813	79.6	35
$CuL(H_2O){\cdot}[H_2O$ (L = pyruvidene-alaninato)	PVALCU	2.413	2.486	74.2	36
$CuL(H_2O){\cdot}4H_2O$ (L = N-salicylideneglycinato)	SAGLAC	2.352	2.677	60.0	37

better bases than the O−H or N−H bonds and thus should favor coordination to the metal centers rather than IPA bonding. Some examples of this type are discussed in the following.

The species AENNIC10, $[CuL_2][CuL_2\text{-}Ni_2L_4]{\cdot}4H_2O$ (L = ethylenediamine), SAGLAC, $CuL(H_2O){\cdot}4H_2O$ (L = *N*-salicylideneglycinato), and PVALCU, $CuL(H_2O){\cdot}2H_2O$ (L = pyruvidenealaninato), show O---M ≈ (O)H---M distances. They are all complexes with ligands coordinated in square-planar geometry *via* nitrogen and/or oxygen. Both SAGLAC and PVALCU carry two types of water molecules, one coordinated to the metal center (Cu---O 1.965 and 1.946 Å, in SAGLAC and PVALCU, respectively) while the second water molecule is placed "side on" with the oxygen and hydrogen atoms almost equidistant from the Cu-centers (SAGLAC, Cu---O 2.352, Cu---H 2.677 Å; PVALCU, Cu---O 2.413, Cu---H 2.486 Å). In both crystals a third water molecule is hydrogen bonded to the other two but does not interact with the Cu atom. Similar bonding of a water molecule is present in crystalline AENNIC10. These water molecules are in the second coordination sphere and not strongly bound to the metal; the orientation of the O−H vectors may be dictated by the directionality of the H-bonds with the neighbors.

Porphyrin sponges have been extensively investigated by Strouse's group.[42,43] About 200 such complexes have been prepared and structurally characterized. Some of these complexes have been shown to form efficient host structures able to trap many different types of guest molecules. Compounds JIVNIL, JIVSUC, HAMBAY, and HAMKUB (see Table 2 for chemical formulas), for example, all capture N-donor guests to fill in the Zn^{2+}, Fe^{2+}, and Co^{2+} coordination sites. The coordination of the guests *via* the N atom brings the H atoms close to the metal centers. In JIVNIL, JIVSUC, and HAMKUB (see Table 2) the Zn---N distances are either shorter than or almost equal to Zn---H distances, whereas in the Co complex HAMBAY the H atom is closer to the metal than the N atom (2.372 and 2.628 Å, respectively).

Further work, mainly theoretical, is necessary before it can be assessed whether these M---(H−O) and M---(H−N) interactions are determined solely by the coordinative bond with the metal centers or present a definite contribution of the IPA type.

Intermolecular Multicenter Hetero-Acceptor (IMH) Hydrogen Bonds Involving Carbon. IMH

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Table 2. Compound Formulas, REFCODES, and Relevant Geometrical Parameters for N−H---M Intermolecular Interactions for Transition Metals with Intermolecular M---H < 3.2 Å and Comparison with N---M Interactions

compd	REFCODE	N---M (Å)	H---M (Å)	N−H---M angle (deg)	ref
$[PtCl_2(NH_2Me)_2][NPr_4n]_2[PtCl_4]$	FAZZAH10	3.276, 3.893	2.263, 2.927	167.3, 154.6	38,39
$[NMe_3H][Co(CO)_4]$	MAMCOA	3.379, 3.398	2.506, 2.523	179.5, 179.7	8
$[NEt_3H][Co(CO)_4]$	MAMCOB	3.719	2.689	180.0	8
$[NEt_3H][Co(CO)_4]$	MAMCOB01	3.666	2.611	180.0	9a
$L_2L'[Co(CO)_4]$ (L = *N*-methylpiperazinium; L′ = *N*-methylpiperazine)	LEVBAP	3.641, 3.631	2.641, 2.602	163.9, 176.8	9c
$[Ni(NH_2Et)_3][NiL_2]$ (L = maleonitriledithiolato)	LAHYIC	3.425, 3.431	2.448, 2.457	158.2	40
$PdClL\cdot 1.5[H_2O]$ (L = glycyl-L-histidine-*N*,*N*′,*N*″)	WEDWUX	3.431	2.603	137.5	41
$ZnLL'_2$ clathrate (L = tetraphenylporphyrinato; L′ = *o*-chloroaniline)	JIVNIL	2.460, 2.460	2.828, 2.949	59.2, 52.7	42
$ZnLL'_2$ clathrate (L = tetraphenylporphyrinate; (L′ = 1,5-diaminoanthraquinone)	HAMKUB	2.614	3.112	52.0	43
CoLL′ clathrate (L = (*R*)-(phenethylamino)tetraphenylporphyrin (L′ = (*R*)-phenethylamine)	HAMBAY	2.628	2.372	93.1	43
$FeLL'_2$ clathrate·$C_6H_5CH_3$ (L = tetraphenylporphyrinato; L′ = piperidine)	JIVSUC	2.093	2.359	62.9	42
$Hg_2Cl_4(urea)_2$	CALPAG	3.213	2.794	105.1	44
$PtCl_2L_2$ (L = pyrazole-N)	VAZWEY	3.610	2.585	173.7	45

Table 3. Compound Formulas, REFCODES, and Relevant Geometrical Parameters for C−H---M Intermolecular Interactions for Transition Metals with Intermolecular M---H < 3.2 Å and Comparison with C---M Interactions

compd[a]	REFCODE	C---M (Å)	H---M (Å)	C−H---M (deg)	ref
NiL_2 (L = malonenamidoximato)	BODFIJ	3.382	2.431	146.2	47
$CuClL_2$ (L = tetrahydro-1*H*-pyrimidine-2-thione	BOMJES	3.545	2.478	169.2	48
CuL_2 (L = cyclodecane-1,3-dionato)	CELWOF	2.955	2.289	118.0	49
CuL (L = 2-(bis(pyrazolylethyl)amino)phenolato-*N*,*N*′,*N*″,*O*)	DOPXOV	3.893, 3.534	2.887, 2.460	155.0, 172.7	50
Ag_2L_2 (L = μ-salicylato-*O*,*O*′)	KAMTOH01	2.695	2.718	77.3	51
$NiMe(C_6H_5O)(PMe_3)_2[C_6H_5OH]$	JECJAC	3.497	2.422	173.3	52
$PtL.[CHCl_3]$ (L = 2,2′-Bis(5,6-dihydro-4*H*-1,3-thiazine-*N*,*N*′)-diphenyl	KEKZAB	3.445	2.381	168.2	53
$Pt(NH_3)_2L$ (L = 5-oxoprolinato)	TAHCUA	3.477	2.446	159.3	54
$[Cu(CN)_3][CuL_2]\cdot 2[H_2O]$ (L = 1,4,7-triazacyclononane-*N*,*N*′*N*″)	DUSJAC	3.522	2.564	147.3	55
$[Cu(CN)_3][CuL_2]\cdot 2[H_2O]$ (L = 1,4,7-triazacyclononane-*N*,*N*′*N*″)	DUSJAC01	3.428	2.438	151.8	55
$[(Cp^*)_2ZrMe][(C_6F_5)_3BMe]$	YEKKII	2.640	2.517, 2.430, 2.538	84.3, 88.8, 83.3	14
$[(Cp^*)_2ZrMe][(C_6F_5)_3BMe]^a$	SOBTIM10	2.549	2.254, 2.298, 2.720	95.8, 93.7, 69.6	14
$[(Cp^*)_2ZrMe][(C_6F_5)_3BMe]^b$	YEKKOO	2.625	2.437, 2.373, 2.645	87.7, 91.1, 77.1	14
$[(Cp^*)_2ZrMe][(C_6F_5)_3BMe]^c$	YEKKUU	2.624	2.490, 2.422, 2.602	89.9, 92.0, 78.5	14

[a] Not found in the CSD intermolecular search because the Zr---C interaction is coded as an intramolecular bond. [b] M---H distances based on calculated hydrogen atom positions for the Me group. [c] Not obtained from the CSD search because R-factor > 0.05 (see Methodology).

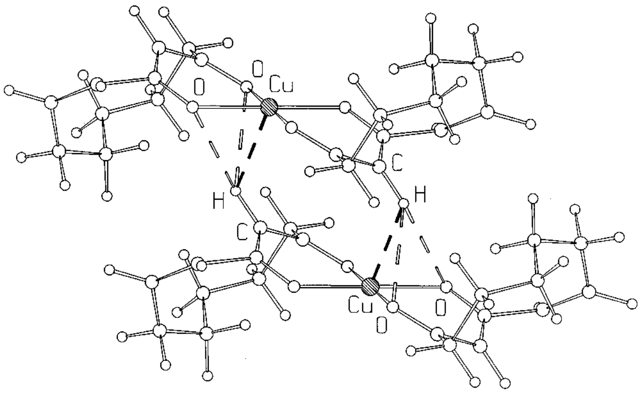

Figure 12. "Dimer" formed by two centrosymmetry related neutral Cu complexes in solid CELWOF linked together *via* IMH interactions.

interactions are observed in crystalline CELWOF, CuL_2 (L = cyclodecane-1,3-dionato), and some other complexes that will now be discussed. Figure 12 shows the "dimer" formed by two centrosymmetrically related neutral Cu complexes in solid CELWOF *via* the unique H atom bound to the metallacycle. As in the case of some IMH interactions discussed above, the C−H system points toward the Cu atom and the two nearby oxygens of the ligand (H---Cu 2.289 Å, H---O 2.643 and 2.694 Å).

In crystalline JECJAC, $NiMe(C_6H_5O)(PMe_3)_2\cdot C_6H_5OH$, the Ni complex forms an adduct with a phenol solvent molecule *via* a "normal" O−H---O hydrogen bond between the phenol hydrogen and the available lone pair on the metal-coordinated phenolate system (O−H---O 1.65 Å) and *via* a Ni---H−C interaction between a C−H group of the C_6 ring and the free coordination site on the Ni atom (see Figure 13). The Ni---H distance (2.422 Å) is very short and comparable to the values usually observed for strong C−H---O bonds.[56]

Solvent inclusion *via* hydrogen bonding at the metal center is also observed in crystalline KEKZAB, PtL·$CHCl_3$ (L = 2,2′-bis(5,6-dihydro-4*H*-1,3-thiazine)diphenyl-*N*,*N*′). As shown in Figure 14 the C−H bond of the chloroform molecule is directed toward the electron-rich Pt center (C---Pt 3.445 Å, H---Pt 2.381 Å, C−H---Pt 168.2°). This in an important example because it shows that the hydrogen bond at the metal center does not necessarily require that donor and acceptor carry opposite ionic charges as in the case of the $Co(CO)_4^-$ ion pairs. Rather the fundamental problem is steric; *i.e.* hydrogen bond formation can be achieved if the electron-rich metal center is accessible.

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(56) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441.

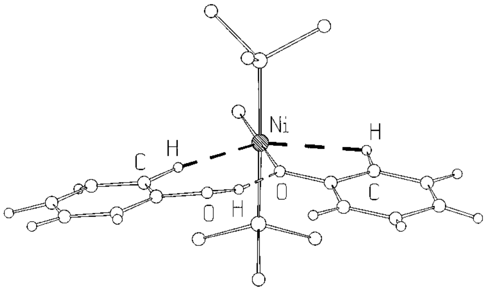

Figure 13. Phenol−complex adduct in crystalline JECJAC. Note how the phenol solvent molecule forms a metallacycle *via* a "normal" O−H---O hydrogen bond and a C−H---Ni interaction between a C−H group of the C_6 ring and the Ni atom. An intramolecular C−H---Ni bond is also formed by the coordinated phenolate ligand.

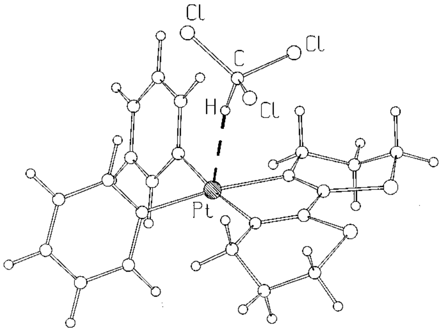

Figure 14. Crystalline KEKZAB. A chloroform molecule points its C−H group directly toward the electron-rich Pt center.

Another example of a C−H---M bond in neutral complexes is afforded by crystalline TAHCUA, $Pt(NH_3)_2L$ (L = 5-oxoprolinato). This Pt complex presents a hydrogen bound "dimer" of the type observed in crystalline CELWOF, *viz*. a C−H group belonging to the coordinated ligand interacts directly with the Pt center (C---Pt 3.477, H---Pt 2.446 Å, C−H---Pt 159.3°). The H atom is also at close distance from the N and O atoms linked to the metal center [3.119 and 3.138 Å, respectively]. There is also a second, much longer, H---Pt interaction of 2.859 Å which appears to be "assisted" by a shorter H---N interaction of 2.845 Å. Of course, as in the case of FAZZAH10 discussed above, the principal interaction certainly involves the Pt atom lone pair perpendicular to the ligand coordination plane.

The crystalline salt DUSJAC, $[Cu(CN)_3][CuL_2]\cdot 2H_2O$ (L = 1,4,7-triaza cyclononane-*N*,*N′*,*N″*), presents a tight C−H---Cu hydrogen bond interaction comparable to those established by some water molecules with electron-rich Cu centers (see above). The crystal contains a $[Cu(CN)_3]^-$ anion which accepts H-donation from the octahedral copper counterion. The data for the solid state structure have been collected at two different temperatures, so that an assessment of the effect of a temperature decrease on the length of the C−H---Cu interactions is possible: at room temperature, C---Cu 3.522, H---Cu 2.561 Å, C−H---Cu 147.3°; at 110 K, C---Cu 3.428, H---Cu 2.435 Å, C−H---Cu 151.8°.

Conclusions

Since we began to investigate hydrogen-bonding interactions in organometallic systems, we have found many structural analogies but also many important differences between organometallic and organic systems. Analogous behaviors, for example, are seen with *typical* hydrogen bond donors such as −COOH, −OH, and −CONHR groups. In comparison to organic solids, however, organometallic solids offer a much greater structural and chemical variability because of the interplay between ligand−metal coordinative bonding and intermolecular noncovalent interactions between molecules or ions.

In this paper we have explored in a systematic manner the acid−base behavior of metal atoms in coordination complexes. Our findings can be summarized as follows:

(i) There is a definite manifestation of X−H---M hydrogen-bonding interactions with donors such as nitrogen and oxygen as well as with carbon donors. In order to be established, X−H---M interactions require sterically available electron-rich metal centers acting as bases toward O−H, N−H, and C−H systems. This is usually observed with late transition metals in low oxidation state.

(ii) In many cases, however, close approach between these donor groups and the metal acceptor center occurs in systems where the ligand, coordinated to the metal center, contains electronegative atoms (chiefly oxygen and nitrogen but also sulfur and chlorine) which are also capable of interacting with acidic protons. In such cases the H atom appears to participate in a polyfurcated interaction with an expanded electron-rich system; the interaction is less directional than in conventional hydrogen bonds, though surely reinforced by the "Gulliver" effect.[57] These (X)H---M(X′) interactions we have named *intermolecular multicenter hetero-acceptor* (IMH) hydrogen bonds.

(iii) Particularly strong, "charge-assisted", (X)H---M hydrogen bonds are observed between anion and cation as in the case of the acidic carbonyl anion $Co(CO)_4^-$. Our analysis, however, provides evidence that the (X)H---M bond does not necessarily require an anionic complex but can be established also by neutral species.

(iv) By investigating hydrogen bonding at the metal center, we have also seen the manifestation of the opposite effect, namely the *acidity* of electron deficient metal atoms. In such cases electron density is provided *intermolecularly* by the interaction with suitable donors analogously to the intramolecular agostic interactions between C−H systems and electron deficient metal centers. The best examples of *intermolecular pseudo-agostic* (IPA) interactions are provided by crystals of electron deficient coordinatively unsaturated complex cations with a strong Lewis base such as $[CH_3B(C_6F_5)_3]^-$. The CSD analysis also shows some intriguing cases in which coordinative bonds with electron deficient metal centers may be assisted by M---(O−H) and M---(N−H) type contributions.

In summary, IMH and IPA interactions represent two novel types of *intermolecular interactions that are specific to organometallic systems* and which have no counterpart in organic chemistry. Though weak, these noncovalent interactions may have important consequences on the solid-state structure of (flexible) organometallic molecules and on the chemical and physical properties of the solid materials. Clearly, even the

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[57] Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991.

smallest step ahead in the understanding of how weak noncovalent interactions can be tuned and controlled when metal atoms are involved might be extremely useful in the field of supramolecular organometallic chemistry as well as in the field of bio-organometallic and metallo-protein biochemistry.

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Supporting Information Available: Geometrical questions for the search of intermolecular X−H---M interactions with X═C and figures for all species listed in Tables 1−3 but not depicted in the paper (18 pages). Ordering information is given on any current masthead page.

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