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New types of hydrogen bonds

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Abstract

Since 1990, several new types of hydrogen bonding have been identified involving transition metals or their complexes, for example, X–H···H–M, X–H···M and M–H···l.p. types. In addition, conventional X–H···l.p. hydrogen bonding has also been used in a number of contexts. Although the area is at an early stage of development, it already holds the promise of providing useful applications in inorganic chemistry and homogeneous catalysis. © 1998 Elsevier Science S.A. All rights reserved.

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Hydrogen bonding [1] plays a key role in determining the physical properties of materials, the packing in crystals, the conformation of biopolymers, and in molecular recognition. In many enzymes, selective binding of the transition state by H-bonding within the protein is thought to account for the large rate accelerations seen. In our work we have therefore tried to apply hydrogen bonding concepts to the fields of homogeneous catalysis and inorganic chemistry. In this review we gather together the leading features of some of the main new types of hydrogen bonds that have emerged from recent work in the field by our group and by others, emphasizing examples involving metals and M–H bonds.

1. General types of hydrogen bonds

Looking first at hydrogen bonding as a whole, Table 1 lists the three fundamentally different types of hydrogen bonds that each employ the same weakly acidic X–H proton donor groups (X = N, O..) but that differ in the nature of the proton acceptor. In the classical hydrogen bond (X–H···l.p type; l.p. = lone pair), the proton acceptor is a lone pair of a weakly basic, electron rich element, typically N, O or halide ion. This type has been recognized since the 1930s and is of most importance in biochemistry [1]. Very recently, π-electrons, such as those of arene rings or CC multiple bonds, have been shown [2] to be able to act as weak proton acceptors in hydrogen bonding. This X–H···π type is weaker than the X–H···l.p. type, probably because π bonding electrons are in general much less basic than lone pairs.

In view of the decrease in hydrogen bond strength on going from X–H···l.p. to X–H···π types, one would have expected to find that if any X–H···σ type of hydrogen bond existed it would be even weaker than the X–H···π type and so neither be readily detectable nor have significant effects on physical properties, σ-bonding electrons being even less basic than π-bonding ones. In fact, it is now clear [3,4] that such hydrogen bonds can in certain cases be much stronger than the

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Table 1
General types of hydrogen bond

Type	Geometry[a]	Strength (kcal mol^{-1})[b]	Nature of proton acceptor
X-H···l.p.	Linear	2–8	Lone Pair of electronegative atom (N, O, Hal)
X-H···π	Side-on	2–3	Pi Bond involving electropositive atom (arene)
X-H···σ	Side-on	4–7	X-H σ bond (X = electropositive atom {B, Tr. Mtl.})

[a] Of approach of the proton acceptor.
[b] For X = N, O.

X–H···π type and comparable in strength with the classical X–H···l.p. type.

2. X–H···σ or dihydrogen bonding

The condition that allows X–H···σ hydrogen bonds to be strong is that the proton acceptor, YH, is an element-hydrogen bond, where the element or fragment Y is electropositive. In such a case, two hydrogens are involved in the interaction a short H···H distance is allowed. Possible Y elements currently known are boron and the transition metals; other cases will no doubt be discovered in the future. The electropositive character of Y is expected to impart strong hydridic character to the YH hydrogen. The oppositely charged hydridic hydrogen of YH and the protonic hydrogen of XH can now interact attractively and a surprisingly strong hydrogen bond can be formed. Because two hydrogens are involved in this type, we have called them 'dihydrogen bonds'. The same type of electronegativity condition applies to the X–H···π hydrogen bond case, where the π bond involves electropositive elements, preferably carbon, for an interaction to be observed.

The first proposal (1990) of an attractive interaction between a hydridic and protonic hydrogen in a metal complex was based on the neutron diffraction structure of $[(Me_3P)_4Ir(OH)H]$ where the Ir–H and O–H hydrogens are syn to one another and separated by 2.4 Å [5], which was described as being 'too long for the interaction to be considered a normal hydrogen bond'. This distance is equal to the sum of the van der Waals radii of two hydrogen atoms and the interaction can indeed therefore be seen as being of a weak dipole–dipole type. A very short H···H distance (1.86 Å), found in the neutron diffraction structure of $[(Et_2PhP)_3Fe(H_2)H_2]$, was identified as resulting from an attraction between a hydridic Ir–H and a *cis* protonic H_2 ligand and was called a '*cis*-effect' [6]. This H···H distance is entirely comparable with the ones later seen in X–H···σ hydrogen bonds in general and it can now be considered ([4]a) as a particular case of a true dihydrogen bond.

Later work established the generality of the phenomenon in both intra- and intermolecular cases. The H···H distances, determined by neutron diffraction, and (less accurately) by T_1 measurements, were found [3] to be in the 1.7–1.9 Å range for the interaction of a series of OH and NH donors with transition metal hydrides. This H···H distance is to be compared with the sum of the van der Waals radii of two H atoms: 2.4 Å. The preferential side-on binding of the X–H proton donor to the Y–H proton acceptor was confirmed by a Cambridge Crystallographic Database search of borane-amines which suggested a preferred B–H···H angle of 110°. The N–H···H angle is close to linear, however.

As an example [7], the polyhydride, $[ReH_5(PPh_3)_3]$ was found to cocrystallize with indole to give a 1:1 adduct with an H···H distance of 1.73 Å (neutron diffraction). An interesting feature of this system is the very high quality of the crystals of the adduct compared to the poor crystals formed by the Re complex in the absence of indole. Addition of indole to the recrystallizing medium may be a useful strategy for forming high quality crystals of a potential proton acceptor which crystallizes poorly on its own. Epstein and Berke and coworkers have obtained IR and NMR evidence for the formation of adducts in the case of the interaction of $[WH(CO)_2(NO)L_2]$ with a variety of acidic alcohols; for this system, $-\Delta H°$ was found to be in the range of 4–7 kcal mol^{-1} [8].

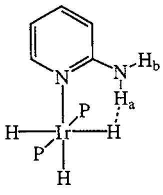
The energetics of the intramolecular dihydrogen bond were established by studies of 2-aminopyridine complexes such as **1** ($P = PPh_3$) [9], where the C–N bond rotation could be observed by proton NMR via the resulting exchange of H_a and H_b. In the transition state for the rotation the H...H bond is broken and the partial CN double bonding due to exocyclic resonance is prevented. The resonance effect was estimated both by experimental and theoretical studies and after subtraction the H···H bond energy could be obtained. In a series of complexes of type **2**, the nature of the ligand X *trans* to H was shown to have a strong effect on the NH···HIr bond strength determined in the same way. When X is hydride, the hydrogen bond strength is as much as 5 kcal mol^{-1} but

Table 2
Some specific types of hydrogen bond involving metal complexes

Category	Geometry[a]	Type	Nature of proton donor	Nature of proton acceptor
X–H···M	Linear	X–H···l.p.	OH, NH, CH[b]	d^8 metal
M–H···l.p.	Linear	X–H···l.p.	M–H[c]	MCO, $OPPh_3$
M–H···H–M′	Bent	X–H···σ	M–H[c]	M–H[d]

[a] Of approach of the proton acceptor.
[b] Intramolecular cases predominate.
[c] A cationic hydride is expected to be the preferred proton donor.
[d] A neutral or anionic hydride is expected to be preferred.

when X is an electronegative atom or group such as F or CO, the hydrogen bond strength falls to ca. 3 kcal mol^{-1} presumably because the trans hydride is no longer so hydridic in character.



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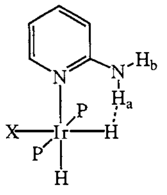
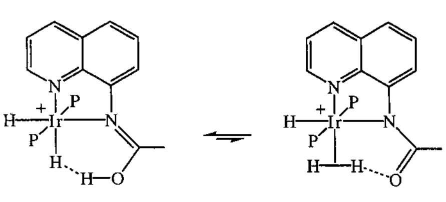


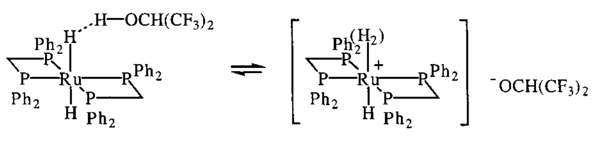
2

Complexes **1** and **2** also showed H···H coupling in the proton NMR spectrum, where J(HH) was in the 2–4 Hz range. The presence of a coupling may indicate that there is a small covalent contribution to the H···H bond strength.

Formation of a dihydrogen bonded adduct can precede proton transfer, as shown in the intramolecular case of Eq. 1 ([9]a) where this transfer allows intramolecular exchange between the OH and IrH hydrogens. An intermolecular case found by Chaudret and coworkers is shown in Eq. 2 [10], where the proton transfer leads to the formation of an intermediate dihydrogen complex.



(1)



(2)

It is likely that adduct formation precedes proton transfer whenever an acid interacts with a hydride compound. Indeed the facile loss of H_2 normally observed in such systems may have been the key factor that prevented discovery of the dihydrogen bond prior to the 1990s.

The crystal structure of $[ReH_5(PPh_3)_3]$·indole [7] also illustrates a common feature of polyhydrides: the presence of close (ca. 1.9 Å) C–H···H–M contacts between the phosphine substituents and the metal hydride bonds. We regard these as weak dihydrogen bonds because they have so far only been found in intramolecular cases and no evidence has yet been published for any intermolecular examples of such an interaction ([7]b).

3. X–H···M hydrogen bonding

There are also several unconventional hydrogen bonds that are specific to metal complexes, although their chemistry is only beginning to be studied (Table 2). Brammer [11] was the first to suggest that the close N–H···M contacts seen in certain crystal structures of d^8 square planar species and once ascribed to agostic C–H···M interactions are in fact better described as hydrogen bonds. In these complexes an NH bond is located above the square plane of the complex to give a quasi-linear N–H···M arrangement. Had the system been agostic [12], the N–H would have approached side-on, not end-on, and the square planar metal would have distorted to a sawhorse structure to direct an empty orbital on the metal towards the incoming ligand. In these X–H···M cases, it is not a lone pair on the metal but a non-bonding electron pair that takes the role of proton acceptor. In a later Cambridge Crystallographic Database search of d^8 square planar systems [13], we found that although N–H···M interactions are close to linear, C–H···M interactions were more nearly bent. At the time we were uncertain whether to interpret this as a tendency towards agostic binding for the CH cases. Because the ML_4 square planar ligand array shows no tendency to distort, we now believe that these C–H···M cases represent true hydrogen bonds but in which the tendency to adopt a linear geometry is less strong because of the low dipole of the CH bond. The energetics of these types of interactions remain to be determined. Another example of the same type of interaction was found by Kazarian, Hamley and Poliakoff in the interaction of fluorinated alcohols with $CpIrL_2$ complexes, where the presence of O–H···Ir hydrogen bonds was proposed on spectroscopic grounds [14].

4. M–H···l.p hydrogen bonding

In another type of hydrogen bond specific to metal complexes, an M–H bond takes on the role of proton donor to a conventional base, such as $OPPh_3$ or pyridine. This type was first suggested by Epstein [15] Other examples, indirectly detected more recently by Peris et al. [16] involve cationic iridium hydrides and $OPPh_3$. The bond strength was estimated from IR studies as 2–3 kcal mol^{-1} and so these interactions are rather weak. Of the examples studied, only cationic and not neutral hydrides showed any observable interaction, so this type of hydrogen bond is presumably favored by delocalization of the positive ionic charge onto the 'hydride' ligand, which has thereby lost any true hydridic character. Related to this type of adduct, Braga and Grepioni [17] have shown how M–H···OCM interactions are common in the crystal structures of metal carbonyl hydrides, as in the case of $[Cp_2MoH(CO)][CpMo(CO)_3]$ where the cation self-associates via this type of interaction.

5. An M–H···M–M′ hydrogen bond?

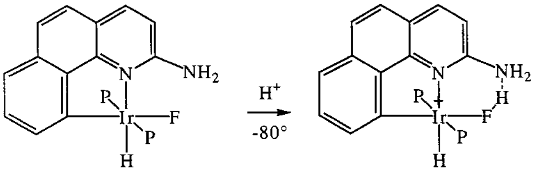
If a pair of metal hydrides were able to take on the proton donor and proton acceptor role in a hydrogen bond, an M–H···M–M′ arrangement would be found. Although this type of hydrogen bond is not yet established, Ibers [18] early work is relevant. He showed that in the crystal of $HMn(CO)_5$, the intermolecular H···H distance is 2.29 Å by neutron diffraction, slightly shorter than the 2.4 Å expected for an H···H contact. We cannot yet distinguish between a number of different possible interpretations. The short H···H distance might be an accident of the crystal packing, but the same H···H distance appears in the other crystal form, having a different packing. The distance may represent a true nonbonding contact, suggesting that 1.15 Å would be a better van der Waals radius for hydrogen in this case. Alternatively, this could be a weak M–H···H–M dihydrogen bond. The experimental Mn–H···H angle of 155° seems appropriate for such an interpretation because it is close to the average (145°) of the angles expected for a proton donor M–H···H (180°) and a proton acceptor M–H···H (110°) in a case like this where the same complex is forced to take on the role of donor and acceptor.

6. X–H···l.p hydrogen bonded interactions in crystals

X–H···l.p hydrogen bonding is also very important in determining the crystal packing of certain metal complexes, as has been shown most notably by the detailed studies of Braga and Grepioni [19] and of Desiraju [20]. These authors have shown how hydrogen bond networks are common in inorganic crystal structures. For example, X–H···OCM (X = O, N, C) and M–H···OCM interactions are found for metal carbonyl complexes. Binding to a metal acidifies such ligands as NH_3 and H_2O, making them more efficient proton donors than in the free state. This fact has been used by various authors in attempts to locate the H atoms of coordinated water, not seen in a crystallographic study, by identifying the proton acceptors to which these OH protons are hydrogen bonded. The OH proton is then assumed to lie on the vector that connects the O of the proton donor to the proton acceptor atom. Neutron diffraction studies have shown that this assumption usually holds quite well. In this way, it is sometimes possible to tell if water adopts the pyramidal (sp^3 O) or planar (sp^2 O) binding mode [21].

Hydrogen bonding involving metal fluorides has also attracted attention recently. In some cases, the fluoride can act as proton acceptor for HF with the result that a bifluoride ($F–H–F^-$) complex is formed. Parkin [22] has reported the formation of $MoH_2(FHF)_2(P)_4$ from $MoH_4(P)_4$ and HF and Perutz [23] has found $[Ru(dmpe)_2(H)(FHF)]$. The crystallography and the J(HF) values of < 30 (Ru and Mo) and 273 Hz (Ru) and 410 Hz (Mo) in the proton NMR suggest the presence of an asymmetric bifluoride ligand of predominant M––F···H–F character.

In recent work, we have looked at the protonation of the fluoride complex **3** at low temperature, which gives an HF complex of type M–F–H, with a J(HF) value of 440 Hz. in the ^{1}H-NMR spectrum. In the absence of the 2-amino group on the ligand, the HF dissociates and a complex is not seen, so we propose that the ligand is bound via an N···HF hydrogen bond as shown in Eq. 3. The fluoride remains attached to the metal in the HF complex, as indicated by the persistence of a ^2J(H–Ir–F) coupling between the fluoride and the *cis*-hydride after protonation. These observations are also relevant to the long-known [24] acid catalysis of substitution in transition metal fluoro-complexes, where HF complexes may be intermediates.



(3)

7. Future prospects

The structural aspects of hydrogen bonding in inorganic chemistry is currently much better understood than the energetic aspects, which may require further solution measurements. In the future we can hope to see a better understanding of the spectroscopic consequences of these types of interactions as well as their applications in reactivity studies. Hydrogen bonds of 4–7 kcal mol^{-1}. should be strong enough to be able to alter the natural selectivity patterns of catalytic reactions in useful ways and alter the conformations of metal hydrides. Asymmetric catalysis seems a particularly promising area for the application of hydrogen bonding ideas. Up to now, steric effects have been used with the result that enantiomeric excesses are normally in the range of 90–99%, but because of the substantial energy involved, a single hydrogen bonding interaction, if properly placed, should be sufficient to give essentially complete enantioselectivity.

8. Conclusion

Since 1990, several new types of hydrogen bonding have been identified involving transition metals or their complexes, for example, X–H···H–M, X–H···M and M–H···l.p. types. In addition, conventional X–H···l.p. hydrogen bonding has also been used in a number of contexts. Although the area is at an early stage of development, it already holds the promise of providing useful applications in inorganic chemistry and homogeneous catalysis.

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