Metals and hydrogen bonds

Lee Brammer *

*Department of Chemistry, University of Sheffield, Sheffield, UK S3 7HF.
E-mail: lee.brammer@sheffield.ac.uk*

The hydrogen bond is commonly considered to lie within the domain of organic or biological chemistry, involving interactions of a hydrogen atom with two electronegative p-block elements. However, recent work, particularly in the past decade, has highlighted the role of metal centres in hydrogen bonding, the inorganic and organometallic sides of hydrogen bonding. This Perspective provides a personal view of the varied roles that metals, particularly transition metals, can play in hydrogen bonding and the potential importance and applications of metal involvement. It draws upon work in this area conducted in my research group over the past decade as well as related work from the literature.

1 Introduction

Hydrogen bonds have an almost ubiquitous presence in chemistry and molecular biology, with roles that range from a structural one, permitting directional aggregation of molecules *via* self-assembly, through selective molecular recognition to facilitating proton transfer. Metallic elements typically are not included in discussions of hydrogen bonding, the presumption being that these typically electropositive elements are uninvolved or have no significant role to play.[1] However, it has become increasingly evident that metals can play a considerable and varied role in hydrogen bonding. This role ranges from direct participation in the three-centre interaction that defines the hydrogen bond to exertion of an indirect electronic influence or a sterically directing role upon hydrogen bonds.[2] The importance of these metal-containing or metal-influenced hydrogen bonds is far reaching in inorganic chemistry, from organometallic chemistry and bond activation through supramolecular and materials chemistry to bioinorganic chemistry.[3]

This Perspective will focus on the participation of transition metals in hydrogen bonding. Their involvement will be discussed within a conceptual framework wherein a domain model for the description of metal complexes is used. This model, adapted from that proposed by Dance for more general consideration of the supramolecular chemistry of metal complexes,[4] and depicted schematically in Fig. 1, comprises three principal domains. The *metal domain* consists of the central
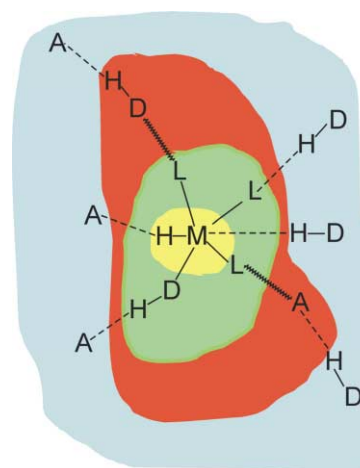

Fig. 1 Domain model for hydrogen bonding interactions involving metal complexes. Metal domain (yellow); ligand domain (green); periphery domain (red); environment (cyan). Adapted from ref. 2*a*, with permission from John Wiley & Sons.

metal atom in a mononuclear complex, or all metal atoms for a dinuclear or metal cluster complex. Surrounding the metal domain is the *ligand domain*, which consists of those ligand atoms that are directly bonded to the metal centre or have a strong electronic interaction with the metal. The *periphery domain*, as its name suggests, consists of those parts of the ligands that are more remote from and have only a weak electronic interaction with the metal centre. Surrounding the periphery domain is the *environment*, which may consist of neighbouring molecules in the solid state, solvent molecules in solution or may be absent entirely in the gas phase.

It is worth reminding ourselves at this point that a hydrogen bond in its simplest form contains three components, the hydrogen bond (proton) donor, D, the hydrogen bond acceptor, A, and the all important hydrogen atom. The donor atom forms a covalent bond with the hydrogen atom, D–H, and the acceptor typically forms a weaker, predominantly electro-static interaction with the hydrogen atom, H · · · A, leading to an overall three-centre, four-electron (3c–4e) interaction,

Lee Brammer was born in Barnsley, England in 1963. He graduated with a First Class Honours degree in Chemistry in 1983 and Ph.D. in Inorganic Chemistry in 1987 from the University of Bristol, where he worked with A. Guy Orpen on crystallographic studies of metal hydrides and related systems. He was awarded a NATO Postdoctoral Fellowship to work with Edwin D. Stevens at the University of New Orleans on experimental charge density analysis of bonding in organometallic compounds and subsequently was a postdoctoral associate at Brookhaven National Laboratory, working with Thomas F. Koetzle on neutron diffraction studies of organic and organometallic compounds and with the late Richard K. McMullan on clathrate hydrates. From 1990–2001 he was Assistant and then Associate Professor of Inorganic Chemistry at University of Missouri–St. Louis and in 2001 he accepted a Readership at the University of Sheffield. In 1990 he received the S. S. Sidhu Award, a North American early career award presented by the Pittsburgh Diffraction Society for contributions to the field of crystallography or diffraction. He is a co-editor for Acta Crystallographica, Section B and chair of the Editorial Board of the RSC journal CrystEngComm. His research interests include supramolecular inorganic chemistry; crystal engineering; intermolecular interactions, particularly hydrogen bonding; organometallic chemistry involving metal–hydrogen interactions; cryo-crystallography and charge density analysis.

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D–H ⋯ A. D is generally an electronegative main group element (*e.g.*, N, O, F) that gives rise to a polar bond $D^{\delta-}–H^{\delta+}$. A is often a similar electronegative main group element bearing a lone pair, but can in principle be any significant accumulation of electrons such as that found in the π-systems of arene rings or other types of multiple bonds. Significantly, the donor group, D, can also be a carbon atom, leading to a weakly polar C–H bond and a correspondingly weaker C–H ⋯ A hydrogen bond.[1e]

Hydrogen bonding in the metal domain implies direct involvement of a metal atom (M) in the hydrogen bond itself. Thus, the metal serves as either the hydrogen bond donor, M–H ⋯ A, or acceptor, D–H ⋯ M. In the ligand domain, the hydrogen bond may be viewed as M–D–H ⋯ A or D–H ⋯ A–M, such that M–D or M–A bonding permits indirect electronic influence over the (D–H ⋯ A) hydrogen bond. When hydrogen bond donor or acceptor groups are located in the periphery domain the metal can exert only a more limited electronic influence over hydrogen bonds formed. However, the metal centre can exert a spatial influence over hydrogen bond formation (Fig. 2).
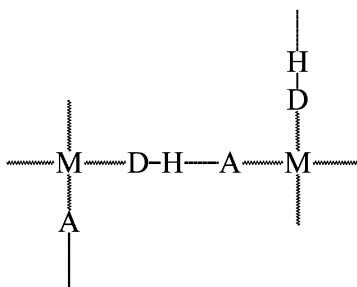

Fig. 2 Spatial influence of metal centres on hydrogen bond formation involving donors and/or acceptors located in the periphery domain (D = hydrogen bond donor; A = hydrogen bond acceptor).

Our own work on hydrogen bonds has evolved over the past decade from studies of systems in which transition metals play a direct role in hydrogen bonding (metal domain) to encompass projects focussed on systems in which the metal plays an indirect role in the hydrogen bonds (ligand and periphery domains). This Perspective will unfold in a manner that parallels this development of our own research. It will also liberally incorporate work from a number of other groups in providing examples, illustrating concepts and indicating potential applications.

2 The metal domain

2.1 M–H ⋯ A hydrogen bonds

Hydrogen bonds in which transition metals serve as hydrogen bond donors, *i.e.* M–H ⋯ A, are uncommon. This should be anticipated given that the polarisation, $D^{\delta-}–H^{\delta+}$, found in a conventional hydrogen bond is not found in a typical metal–hydride bond, *viz.* $M^{\delta+}–H^{\delta-}$. Nevertheless, a number of examples have been confirmed by spectroscopic and/or crystallographic means.[5]

Epstein *et al.* reported[5b] in 1993 that combining [Os-(η⁵-C₅Me₅)₂H]PF₆ with PPh₃O (or related phosphine oxides) in CH₂Cl₂ solution gives rise to an Os–H ⋯ O(=P) hydrogen-bonded adduct (Fig. 3(a)) as evidenced by IR bands for Os–H and P=O stretches occurring at lower wavenumbers relative to individual measurements for [Os(η⁵-C₅Me₅)₂H]PF₆ and PPh₃O, respectively ($\Delta\nu_{O–H}$ = 20 cm⁻¹; $\Delta\nu_{P–O}$ = 26 cm⁻¹). Peris and Crabtree have reported similar findings in studies of cationic iridium hydrides as potential hydrogen bond donors.[5d] The study by Pickett and co-workers[5c] of WH₃(dppe)₂{OC(Me)=O} indicated the presence of the intramolecular W–H ⋯ O(=C) interaction through crystallographic characterisation (H ⋯ O
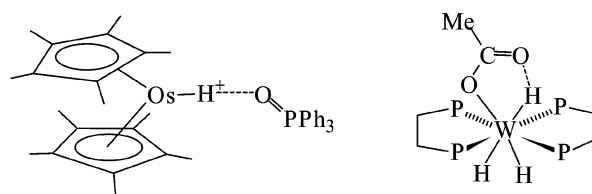

Fig. 3 M–H ⋯ A hydrogen bonds in (a) [Os(η⁵-C₅Me₅)₂H]PF₆· PPh₃O[5b] and (b) WH₃(dppe)₂{OC(Me)=O}.[5c] Reproduced from ref 2*b* with permission from Kluwer Academic Publishers.

2.33(6) Å). In CD₂Cl₂ solution, ¹H NMR data show substantial deshielding for the key hydride ligand (δ 2.92) relative to that for the non-interacting hydrides (δ −2.78), as is typical of hydrogen atoms engaging in hydrogen bonds.[6]

In a study by Braga, Grepioni, Desiraju and co-workers[5e] using the Cambridge Structural Database (CSD),[7] geometric criteria were applied to crystal structure data in order to identify likely M–H ⋯ O hydrogen bonds. The authors concluded that such interactions, while uncommon, have comparable metrics and, by inference, comparable strengths to C–H ⋯ O hydrogen bonds. A major unanswered question is whether M–H bonds that participate in M–H ⋯ A hydrogen bonding are polarised $M^{\delta-}–H^{\delta+}$. If not, then further explanation of the nature of such hydrogen bonds involving *neutral* metal hydrides as hydrogen bond donors is clearly warranted.

2.2 D–H ⋯ M hydrogen bonds

That metals can serve as hydrogen bond acceptors was first proposed some 40 years ago based upon solution-phase IR spectroscopic studies of ferrocenyl alcohols.[8] Further IR work on metallocenyl alcohols by Epstein and co-workers supported these early suppositions,[2d,9] though little attention to metal involvement in hydrogen bonding in the broader literature was accorded prior to *ca.* 1990.[10,11]

Our own entry into this field resulted from our neutron diffraction study[12] of the salt (NPrⁿ₄)₂[PtCl₄]·[PtCl₂(NH₂Me)₂], which established the presence of short intermolecular N–H ⋯ Pt and N–H ⋯ Cl interactions [H ⋯ Pt 2.262(11) and H ⋯ Cl 2.318(12) Å] between the neutral [PtCl₂-(NH₂Me)₂] and the dianion [PtCl₄]²⁻ (Fig. 4), as well as a weaker C–H ⋯ Pt interaction [H ⋯ Pt 2.768(9) Å; C–H ⋯ Pt l64.4(7)°] involving an α-C–H group of one of the cations and the [PtCl₂(NH₂Me)₂] molecule. The near linear N–H ⋯ Pt geometry [167.1(9)°] suggested that description as a three-centre, four-electron (3c–4e) interaction may be appropriate, *i.e.*, a hydrogen bond. This was reinforced by the
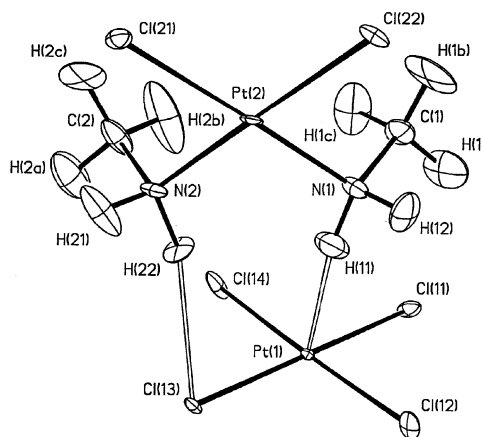

Fig. 4 Crystal structure of (NⁿPr₄)₂[PtCl₄]·[PtCl₂(NH₂Me)₂] with cations omitted shown with all atoms represented as 50% probability ellipsoids (from neutron diffraction study at 20 K). N–H ⋯ Pt and N–H ⋯ Cl hydrogen bonds are indicated by hollow bonds Reproduced from ref. 12.

orientation of the *filled* Pt d$_{z^2}$ orbital towards the amine N–H group. The alternative, a 3c–2e bonding description appropriate for so-called σ-bond complexes and agostic interactions,[13] would require interaction of the N–H σ-bonding orbital with a *vacant* metal orbital.† Both 3c–4e D–H · · · M and 3c–2e X–H · · · M interactions can be viewed as Lewis acid–Lewis base interactions, wherein the metal centre in the former serves as the Lewis base while in the latter it adopts the role of the Lewis acid. A qualitative description of the bonding in such 3c–2e and 3c–4e interactions is presented in Fig. 5.
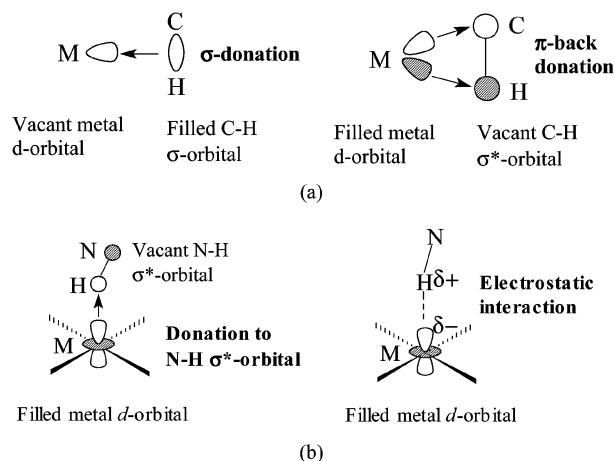

Fig. 5 Qualitative bonding descriptions for (a) 3c–2e C–H · · · M interactions and (b) 3c–4e N–H · · · M interactions. Adapted from ref. 2c with permission of the International Union of Crystallography.

Having recognised that the N–H · · · Pt interaction in (N^{n}Pr$_4$)$_2$[PtCl$_4$]·[PtCl$_2$(NH$_2$Me)$_2$] was not only distinct from the more well established 3c–2e X–H · · · M interactions (*e.g.*, X = B, C, Si) but was consistent with being a hydrogen bond, we sought to establish criteria by which other 3c–4e D–H · · · M interactions (hydrogen bonds) could be identified and distinguished from 3c–2e interactions. We also sought to compare hydrogen bonds containing metals with conventional hydrogen bonds (D–H · · · A; D = N, O; A = N, O) found in organic compounds.

The results of these comparisons can be summarised, thus, as the *characteristic features of D–H · · · M hydrogen bonds*:

• The bridging hydrogen atom is protonic (acidic) in nature. This is consistent with other types of hydrogen bond, but not a requirement for 3c–2e X–H · · · M interactions (most notably when X = B, Si).

• The metal atom (M) is electron-rich (typically a late transition metal) with filled d-orbitals suitably oriented to facilitate the hydrogen bond.

• The ^{1}H NMR chemical shift of the bridging hydrogen atom is shifted downfield (deshielded) as a result of the hydrogen bond interaction. This is of course characteristic of conventional hydrogen bonds and indeed is noted for the W–H · · · O hydrogen bond in WH$_3$(dppe)$_2$\{OC(Me)=O\}[5c] (*vide supra*). Coupling between the hydrogen atom and the metal centre can also be observed in some cases.

• The IR stretching frequency, $ν$(D–H), is decreased upon formation of the D–H · · · M hydrogen bond. This is again consistent with well-established observations for conventional hydrogen bonds and is also noted for the Os–H · · · O hydrogen bond in [Os(η^5-C$_5$Me$_5$)$_2$H]BF$_4$·PPh$_3$O[5b] (*vide supra*).

• Intermolecular interactions have approximately linear geometries, as observed for all other hydrogen bonds, consistent with the 3c–4e nature of the interaction.

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† The vacant Pt 6p orbital is of suitable symmetry to serve as such an acceptor orbital but is rather high in energy and at best plays a very minor role in the three-centre interaction.[14]

• D–H · · · M hydrogen bonds can involve electronically saturated (*i.e.* 18-electron) metal centers, unlike 3c–2e interactions for which electronic unsaturation at the metal centre is a requirement.

• Energy decomposition analyses (using Morokuma[15a,b] and Restricted Variational Space[15c] partition schemes) of the calculated interaction energy for O–H · · · M hydrogen bonds[16] suggest:

(a) charge transfer occurs predominantly from M → H–O, consistent with other types of hydrogen bond.

(b) electrostatics are not as dominant a contribution to the interaction energy as found for conventional hydrogen bonds.

(c) polarisation is a more important contributor to the inter-action energy than is the case in conventional hydrogen bonds. Particularly important is polarisation of the metal-containing moiety.

In relation to these points, D–H · · · M hydrogen bonds have been clearly established for low oxidation state metal complexes with d^6, d^8 or d^{10} metal centres, the most common metal coordination geometries being d^6 metallocene,[17] d^8 square-planar[18] or CpML$_2$,[19] and d^{10} tetrahedral.[20] The distribution of D–H · · · M geometries observed in crystal structures has been examined in a study using the CSD by Braga *et al.*[21] Observations on the downfield shift in the ^{1}H NMR signal for the bridging hydrogen atom are best documented in square-planar d^8 systems, as noted by Forniés and co-workers in for the intramolecular O–H · · · Pt hydrogen bond in [Pt(8-hydroxy-2-methylquinoline)(C$_6$F$_5$)$_3$]$^-$ (Fig. 6(b)).[18c] In this system the shift relative to the free ligand signal (Δδ) is 0.76 ppm. Further examples can be found in the summary by Crabtree and co-workers.[22] In platinum(II) square-planar complexes appreciable coupling between the hydrogen atom and the metal centre (J_{PtH}) has been observed in some cases, *e.g.* 88 Hz for the above compound reported by Forniés and co-workers and as high as 180 Hz for the N–H · · · Pt hydrogen bond in the zwitterionic system [PtBr(*C,N*-8-dimethylaminonaphthyl)(*C*-8-diethyl-amoniumnaphthyl)] reported by van Koten and co-workers (Fig. 6(a)).[18b]
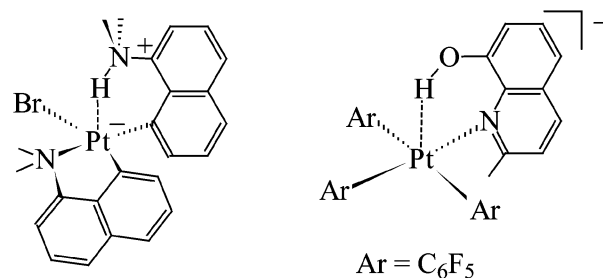
Fig. 6 Intramolecular N–H · · · Pt and O–H · · · Pt hydrogen bonds in (a) [PtBr(*C,N*-8-C$_{10}$H$_7$NMe$_2$)(*C*-8-C$_{10}$H$_7$NMe$_2$H)][18b] and (b) [Pt(8-hydroxy-2-methylquinoline)(C$_6$F$_5$)$_3$]$^-$.[18c]

A definitive account of the effect on O–H stretching frequency upon formation of O–H · · · M hydrogen bonds is provided in an outstanding IR spectroscopic study by Poliakoff and co-workers on the interaction of perfluoro alcohols with d^8 CpML$_2$ compounds (M = Co, Rh, Ir) in non-polar or supercritical fluid solvents.[19a] The study not only identifies the hydrogen-bonded complexes that are present, but establishes that the O–H · · · M hydrogen bonds are of comparable strengths to conventional hydrogen bonds (*e.g.* O–H · · · O hydrogen bonds between water molecules). Furthermore, the study demonstrates that hydrogen bond strength increases when the basicity of the hydrogen bond acceptor (M) is increased, either by introducing more electron donating ligands or by moving down the period, *viz.* Co → Rh → Ir (Table 1).

Our own work on D–H · · · M hydrogen bonds in the 1990s centred primarily upon the salts of the type R$_3$NH$^+$Co(CO)$_3$L$^-$ (L = CO, triarylphosphine)[20b–f] first prepared by Calderazzo

Table 1 IR spectroscopic studies of $(CF_3)_3CO–H \cdots MCpL_2$ hydrogen-bonded adducts in liquid xenon solution at 173 K [19a]

Compound	Wavenumber		$\Delta H^{\circ b}$/kcal mol^{-1}
	$\nu(OH)^a$	$\Delta\nu(OH)^a$	
CpRh(CO)PMe$_3$	3080	510	−6.91
Cp*Ir(CO)$_2$	3090	500	−6.84
Cp*Rh(CO)$_2$	3130	460	−6.57
CpIr(CO)$_2$	3190	400	−6.12
Cp*Co(CO)$_2$	3195	395	−6.09
CpCo(CO)$_2$	3330	260	−4.92
Free (CF$_3$)$_3$COH	3590	—	—

^{a} (H-bonded adduct)− (free (CF$_3$)$_3$COH). ^{b} Interaction energy calculated according to formula ΔH°/kcal mol$^{-1} = -5.35(\Delta\nu)^{1/2}$ as prescribed by Iogansen *et al.*[23]

and co-workers (R = Me, Et; L = CO).[11a,24] Our initial effort involved preparation of large crystals of Et$_3$NH$^+$Co(CO)$_4^-$ and establishment by low-temperature neutron diffraction of the presence of an N–H $\cdots$ Co hydrogen bond, with a well-localised proton, a linear N–H $\cdots$ Co geometry and an elongated N–H bond ‡ [N–H 1.054(1), H $\cdots$ Co 2.613(2) Å; N–H $\cdots$ Co 180.0 ° at 15 K;[20b] see Fig. 7].
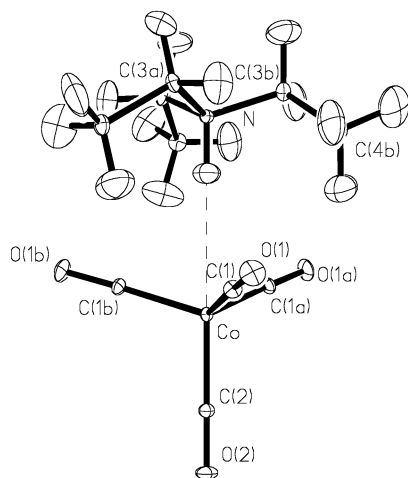

Fig. 7 Structure of Et$_3$NH$^+$Co(CO)$_4^-$ determined by neutron diffraction at 15 K, showing the N–H $\cdots$ Co hydrogen bond. All atoms are represented as 70% probability ellipsoids.

The R$_3$NH$^+$Co(CO)$_3$L$^-$ system proved a versatile one for manipulation of the charge-assisted N$^+$–H $\cdots$ Co$^-$ hydrogen bond, wherein both steric and electronic aspects (acidity) of the hydrogen bond donor (N–H) could be readily modified through the choice of ammonium cation. Manipulation of the basicity of the acceptor (Co) also proved feasible through substitution of one carbonyl ligand by a triarylphosphine. Of particular interest are the pair of compounds (DABCO)H$^+$Co(CO)$_3$L$^-$ (DABCO = 1,4-diaza[2.2.2]bicyclooctane; L = CO, PPh$_3$)[20d] which, consistent with Poliakoff's studies of CpML$_2$ compounds (*vide supra*), demonstrate the increased basicity at the acceptor (*i.e.* L = PPh$_3$) leads to strengthening of the (N–H $\cdots$ Co) hydrogen bond.§ This is evident not only from

‡ The mean length for an N–H bond determined by neutron diffraction is 1.009 Å based upon structures presently in the CSD.[7]
§ It should be noted that it is in fact dangerous to infer the strengthening of individual hydrogen bonds based upon comparisons of geometries found in only a small number of crystal structures, since hydrogen bonds are subject to accomodation of all other packing forces in the crystal structure. This is evident from the structures of (DABCO)H$^+$Co(CO)$_3$L$^-$ (L = PPh$_2$(p-tol), P(p-tol)$_3$; p-tol = *para*-tolyl), which exhibit H $\cdots$ Co separations greater than that of the corresponding salt with the less basic anion Co(CO)$_3$PPh$_3^-$.[20e]

low-temperature crystal structure determinations but also from solution-phase spectroscopic studies. In the solid state, H $\cdots$ Co separations [2.39 Å (L = CO) and 2.25 Å (L = PPh$_3$)] are substantially reduced relative to that of Et$_3$NH$^+$Co(CO)$_4^-$. Not only does the more basic metal centre participate in the shortest hydrogen bond, but shortening (strengthening) of the hydrogen bond is also accompanied by distortion of the anion away from tetrahedral geometry through decreasing of the angle between the axial ligand (L) and the three equatorial carbonyl ligands. Thus, these structures can be thought of as sequentially representing the progress of proton transfer from an ammonium cation to the metalate anion. This idea is expanded upon in the next section. Solution phase IR spectroscopic studies indicate that the N–H $\cdots$ Co hydrogen-bonded ion-pair is retained in non-polar solvents. ^{1}H NMR studies of (DABCO)H$^+$Co(CO)$_3$L$^-$ (L = CO, PPh$_3$) in toluene solution indicate that the adduct is fluxional, rendering the two ends of the cation equivalent on the NMR timescale at room temperature. However, while the Co(CO)$_4^-$ salt remains fluxional at 188 K, the Co(CO)$_3$(PPh$_3$)$^-$ salt is only fluxional above 233 K indicating that the barrier to interconversion is greater in the presence of the phosphine ligand. The interconversion mechanism (Fig. 8) must of course involve cleavage of the hydrogen bond, either directly (pathway **I**) or *via* proton transfer to the metal centre (pathway **II**, **III**). *Ab initio* calculations on the model systems Me$_3$NH$^+$Co(CO)$_3$L$^-$ (L = CO, PH$_3$) indicate that pathway **II,III** would be more facile for L = phosphine supporting the assertion that pathway **I** instead must be active in the interconversion process.¶
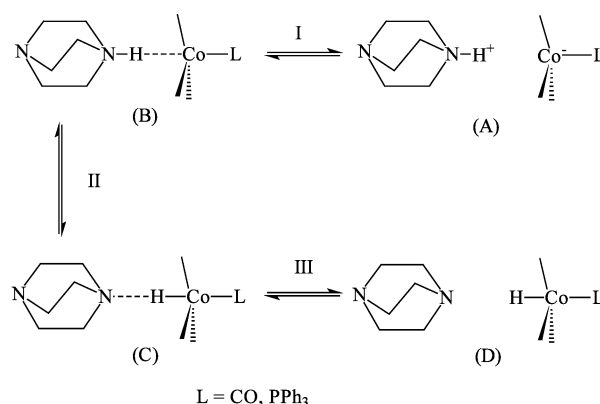

Fig. 8 Possible interconversion pathways considered in accounting for fluxional behaviour of (DABCO)H$^+$Co(CO)$_3$L$^-$ (L = CO, PPh$_3$). Reproduced from ref. 20*d* with permission of the American Chemical Society.

2.3 Applications: reactions in which D–H $\cdots$ M hydrogen bonds are implicated

Protonation and deprotonation of metal centres. While hydrogen bonds are often discussed in static structural terms, an important way to recall the important dynamic aspect of hydrogen bonds is to regard them as an incipient proton transfer reaction. Both Epstein and Shubina[2d] and Poliakoff and coworkers[19a] have demonstrated that D–H $\cdots$ M hydrogen bonds can lead to proton transfer to the metal centre. Consider-

¶ After cleavage of the N–H $\cdots$ Co hydrogen bond, the ammonium proton may either shuttle to the free nitrogen within the same cation or be involved in an intermolecular proton shuttle with other (DABCO)H$^+$ cations (possibly mediated by undetected small amounts of free diamine, DABCO). An alternative structure (a polymorph or possibly a solvate containing unresolved highly disordered solvent) has been observed for (DABCO)H$^+$Co(CO)$_4^-$ in which the cations form an infinite N–H $\cdots$ N hydrogen bonded chain. This arrangement lends credence to the idea of a proton shuttle between (DABCO)H$^+$ cations. (See: J. C. Mareque Rivas, Ph.D. Dissertation, University of Missouri–St. Louis, 1999).
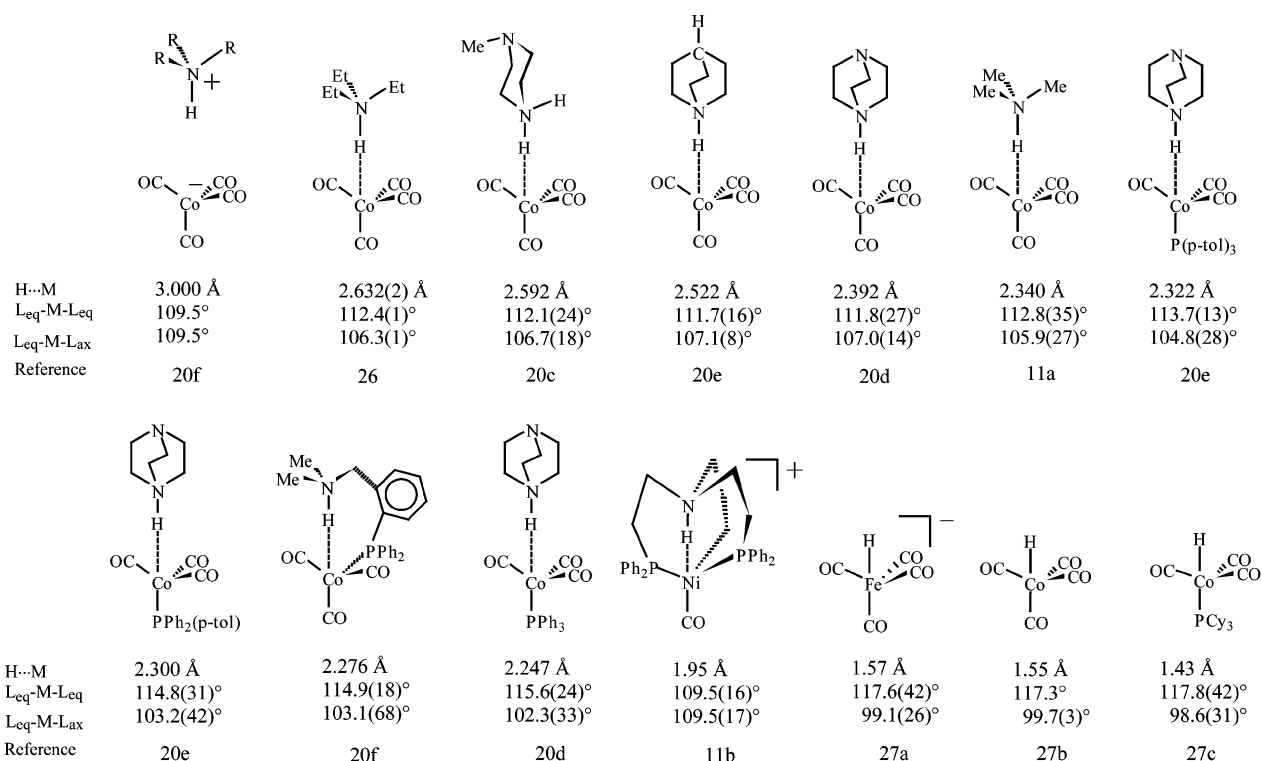
H···M	3.000 Å	2.632(2) Å	2.592 Å	2.522 Å	2.392 Å	2.340 Å	2.322 Å
L_{eq}-M-L_{eq}	109.5°	112.4(1)°	112.1(24)°	111.7(16)°	111.8(27)°	112.8(35)°	113.7(13)°
L_{eq}-M-L_{ax}	109.5°	106.3(1)°	106.7(18)°	107.1(8)°	107.0(14)°	105.9(27)°	104.8(28)°
Reference	20f	26	20c	20e	20d	11a	20e

H···M	2.300 Å	2.276 Å	2.247 Å	1.95 Å	1.57 Å	1.55 Å	1.43 Å
L_{eq}-M-L_{eq}	114.8(31)°	114.9(18)°	115.6(24)°	109.5(16)°	117.6(42)°	117.3°	117.8(42)°
L_{eq}-M-L_{ax}	103.2(42)°	103.1(68)°	102.3(33)°	109.5(17)°	99.1(26)°	99.7(3)°	98.6(31)°
Reference	20e	20f	20d	11b	27a	27b	27c

Fig. 9 Crystal structures used in the Structure Correlation study. H ··· M distances for $Co(CO)_3L^-$ salts are calculated after normalising the X-ray determined N–H distance to 1.054 Å, as determined by neutron diffraction in $Et_3NH^+Co(CO)_4^-$. L_{eq}–M–L_{eq} = average angle** between equatorial ligands. L_{eq}–M–L_{ax} = average angle** between axial and equatorial ligands. Adapted from ref. 20f with permission of Elsevier Science S. A.

ing the N–H ··· Co hydrogen bonds of salts $R_3NH^+Co(CO)_3L^-$ (vide supra) the proton transfer reaction in question is from the ammonium cation to the cobaltate anion, the product of which would be $HCo(CO)_3L$. We were able to prepare and crystallographically characterise a series of $R_3NH^+Co(CO)_3L^-$ salts, the structure of each of which may be viewed as a snapshot of the reaction pathway for protonation of the cobaltate anion by the ammonium cation. Taken collectively and in sequence these structures can then map out the geometric pathway for proton transfer.[25] In addition to following the path of the proton it is also instructive to consider the change in geometry occurring at the metal centre during the reaction. This is readily monitored by the interligand angles and shows a progression from tetrahedral $Co(CO)_4^-$ (C–Co–C 109.5°) to distorted trigonal bipyramidal $HCo(CO)_3L$ (C_{eq}–Co–L_{ax} ca. 99°). Fig. 9 depicts the structures used in this Structure Correlation study and includes a model for the isolated ion pair and structures that describe the product metal hydride. Fig. 10 shows the predicted pathway (**A** ⟶ **D**) for protonation of the metal centre by an ammonium ion. The pathway begins with the separated ions (**A**) and progresses via the N–H ··· M hydrogen-bonded species **B** through to the product metal hydride **D**. The pathway suggests that only slight deformation of the anion geometry occurs at H ··· M distances greater than ca. 2.4 Å, though this deformation is accentuated by more sterically demanding ammonium ions (viz. $Et_3NH^+Co(CO)_4^-$). Between H ··· M distances of ca. 2.4 to 2.2 Å, strengthening of N–H ··· Co hydrogen-bond is accompanied by substantial deformation of the anion resulting in a $Co(CO)_3L$ geometry closely resembling that in the product $HCo(CO)_3L$. Thus, one could argue that at this stage the metal center is geometrically (and presumably electronically) prepared for facile proton transfer. This may explain the absence of Co–H ··· N hydrogen-bonded species (**C**).‖

Oxidative addition of D–H groups (D = O, N). We have previously suggested that D–H ··· M hydrogen bond formation may in some systems facilitate oxidative addition of the D–H bond at the metal centre.[2b,c] Our proposed mechanism was one in which the hydrogen bond facilitates proton transfer to the metal centre followed by coordination of the conjugate base, D⁻. †† This idea is illustrated by our suggested involvement of D–H ··· M hydrogen bonds (D = N, O) in the reactions reported by van Koten and co-workers[18b] and Merola and co-workers,[29] and shown in Fig. 11. Our proposed mechanism for the van Koten system (Fig. 11(a)) is supported by the recent observation by Vedernikov and Caulton of an equilibrium between the N–H ··· Pt(II) hydrogen-bonded complex Pt(κ²-LH)(Ph)₂ with its Pt(IV) hydride tautomer Pt(κ³-L)(Ph)₂H (L = [2.1.1]-2,6-pyridinophane).[30] The proposed mechanism in each case would constitute a heterolytic cleavage of the D–H bond and a stepwise addition to the metal centre. This contrasts with the homolytic cleavage and concerted addition mechanism operative for oxidative addition via 3c–2e interactions such as agostic C–H ··· M or for oxidative addition of dihydrogen.[13] Until very recently D–H ··· M hydrogen bond facilitation of D–H bond oxidative addition had not been unambiguously demonstrated. However, Parkin and co-workers were able to characterise the compound {η⁶-C₆H₅C₆H₃(Ph)OH}Mo(PMe₃)₃, which forms an O–H ··· Mo hydrogen bond to the 18-electron d⁶ metal centre, as confirmed by X-ray crystallography and ¹H NMR spectroscopy (Δδ = 3.0 ppm).[31] Upon

‖ Norton, Sweany and co-workers examined the possibility of trapping such Co–H ··· N hydrogen-bonded species in inert matrices at very low temperature, but found no evidence for such (metal-donor) hydrogen bonds.[28] This is attributed to the ground state polarisation, $Co^{\delta+}$–$H^{\delta-}$, of the metal–hydride bond. The point at "C" that is displaced substantially form the proposed geometric pathway is [Ni(CO){(P3N)-H}]BF₄, where P3N is tris(2-diphenylphosphino)amine. P3N forms a cage in which the proton is encapsulated.[11b]

** Esds, σ (in parentheses) denoted for the average angles <a> for the angles represent the scatter in the set of angles used to calculate the average (i.e. $\sigma = [\Sigma_i(<a> - a_i)^2/(n - 1)]^{1/2}$, where r_i = ith observation, n = no. of observations). These esds do not necessarily correlate with those for the individual angles.

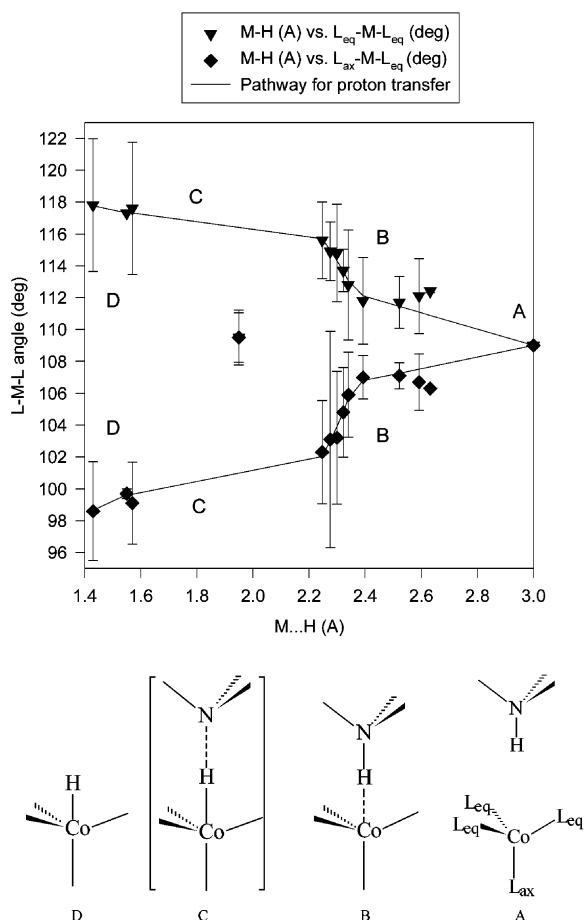†† Accompanied by loss of another ligand in the case of 18e complexes.

Fig. 10 Structure Correlation study modelling the pathway for protonation of $Co(CO)_3L^-$ anion at the metal centre. Error bars on L–M–L angles at the 1σ level. ** Reproduced from ref. 20*f* with permission of Elsevier Science S. A.
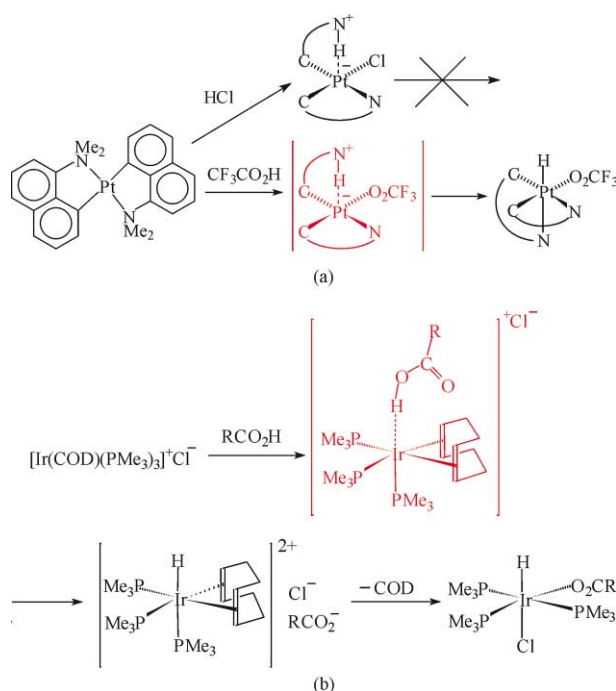

Fig. 11 Proposed mechanisms for the oxidative addition of (a) an N–H bond at a 16e PtL_2R_2 centre, based upon an interpretation of work by van Koten and co-workers,[18b] and (b) an O–H bond at an 18e $[Ir(COD)L_3]^+$ centre based upon an interpretation of work by Merola and co-workers.[29] (see text). Experimentally observed species are depicted in black.[18b,29] Species in black have been observed by the authors. Species in red are proposed D–H ··· M hydrogen-bonded species that may facilitate D–H bond cleavage.

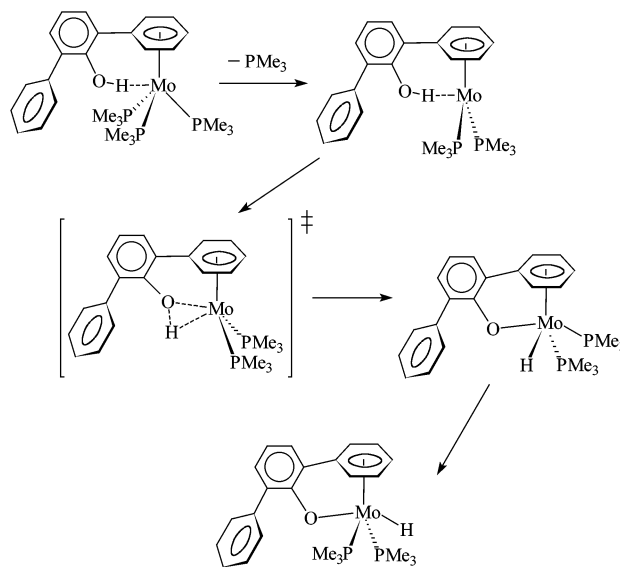**Fig. 12** Mechanism for intramolecular oxidative addition of the phenol O–H bond in $\{\eta^6\text{-}C_6H_5C_6H_3(Ph)OH\}Mo(PMe_3)_3$, showing the sequential involvement of a 3c-4e O–H ··· Mo interaction (hydrogen bond) and a 3c–2e O–H ··· Mo (agostic) interaction.[31]

heating, oxidative addition of the O–H bond occurs with loss of one PMe_3 ligand to give the aryloxy–hydride complex $\{\eta^6,\eta^1\text{-}C_6H_5C_6H_3(Ph)O\}Mo(PMe_3)_2H$. Extensive DFT calculations permitted four alternative reaction pathways to be evaluated and the most probable mechanism to be elucidated (Fig. 12). Interestingly, the calculations implicate the O–H ··· Mo hydrogen bond not only in stabilising the ground state but also the 16e intermediate that follows from loss of PMe_3. Oxidative addition of the O–H bond then occurs *via* an 18e transition state involving an agostic (*i.e.* 3c–2e) O–H ··· Mo interaction. Clearly further examples are needed to establish whether the mechanism operative in this system is more generally applicable (*viz.* the 3c–4e D–H ··· M hydrogen bond plays an important stabilising role, but a 3c–2e D–H ··· M interaction is ultimately required for D–H bond cleavage) or whether our earlier suggested mechanism, in which the hydrogen bond is directly responsible for the D–H bond cleavage *via* proton transfer, is also viable in some instances.

2.4 C–H ··· M interactions. Hydrogen bonds, agostic, pregostic or repulsive?

But what of C–H ··· M hydrogen bonds? C–H groups are now well established as weak hydrogen bond donors, most commonly participating in C–H ··· O and C–H ··· N hydrogen bonds.[1e,32] So why not C–H ··· M hydrogen bonds? Geometric data from crystal structures certainly support the assignment of C–H ··· M hydrogen bonds in a number of systems.[12,33,34] However, the situation is not entirely straightforward, particularly in the case of 16e metal centres as found in square-planar d^8 systems, where in principle axial C–H ··· M interactions

could in principle be either 3c–4e and 3c–2e in nature. Crabtree and co-workers examined the available experimental evidence for square-planar d^8 systems and concluded that the nature of axial C–H ··· M interactions was still ambiguous, unlike that of analogous N–H ··· M and O–H ··· M interactions, which are clearly hydrogen bonds (3c–4e).[22] Extensive NMR studies on weak C–H ··· M[35] and N–H ··· M[36] interactions led Venanzi and Pregosin to refer to these interactions as "pregostic", meaning either pre-agostic or weakly agostic.[35] Despite the implication in this term that such interactions are 3c–2e in nature (*cf.* agostic), the authors conclude their articles[35,36] with statements suggesting that the C–H ··· M and

N–H $\cdots$ M interactions are most likely 3c–4e in nature (*i.e.* hydrogen bonds). Axial intramolecular C–H $\cdots$ M interactions in square-planar d^8 systems have also been described as repulsive,[37,38] wherein the observed C–H $\cdots$ M geometry is suggested to arise from a minimization of the four-electron repulsion between the filled metal d_{z^2} orbital and the C–H bond σ-orbital.[37]

Further experimental work involving well-designed systems is needed to more clearly understand the nature of these interactions. Appropriate high-level theoretical calculations may also shed light on the situation. It seems plausible that polar C–H bonds should be able to engage in C–H $\cdots$ M hydrogen bond formation, but the situation for interactions involving very weakly polar C–H bonds is likely to remain somewhat difficult to discern, as in the case for interactions of such C–H groups with other classes of weak hydrogen bond acceptor. However, the recent work by Parkin and co-workers, in which conversion of an O–H $\cdots$ M hydrogen bond (3c–4e) to an O–H $\cdots$ M σ-bond complex (3c–2e) affording O–H oxidative addition (*vide supra*),[31] certainly prompts the question of whether such a mechanism could ever be active for oxidative addition of (polar) C–H bonds.

3 The ligand domain

3.1 Metal influence on coordinated hydrogen bond donors and acceptors

Hydrogen bonding in the ligand domain is exemplified by the effect that electronic interaction with the metal centre has upon the acidity of hydrogen bond donors or the basicity of hydrogen bond acceptors.

A simple and well-known case is that of coordinated water molecules, which show greater acidity and hydrogen bonding ability than their uncoordinated counterparts. Thus, the hydrogen bond donor capability of the water molecule is being tuned (here accentuated) through the electron-withdrawing effect of coordination to a metal centre. Turning to hydrogen bond acceptors, the hydrogen bonding capability of carbonyl ligands has been examined extensively by Braga, Grepioni, Desiraju and co-workers,[39] particularly with respect to the prevalent formation of C–H $\cdots$ O≡C–M hydrogen bonds. Of specific relevance here is the fact that average hydrogen bond distances (H $\cdots$ O) decrease in the order $M(CO) > M_2(\mu\text{-}CO) > M_3(\mu_3\text{-}CO)$ (Fig. 13). Thus, bridging of the carbonyl ligand increases π-back donation from the metal(s) to the CO π* orbital, which is predominantly associated with the oxygen atom. The resulting increase in basicity of the carbonyl oxygen atom therefore enhances the hydrogen bond acceptor capability of the CO ligand.
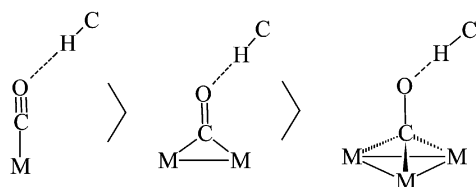

Fig. 13 Relative strengths of C–H $\cdots$ O hydrogen bonds involving carbonyl ligands.[39]

3.2 Hydrogen bond influence on the metal centres

Not only can the metal centre influence the hydrogen bonding capability of donor and acceptor groups within the ligand sphere, but hydrogen bonding in the ligand sphere can have an electronic influence on the metal centre. This is particularly important in the context of metalloproteins and illustrative of this are the studies of Walters and co-workers.[40,41] Thus, their studies of model thiolate coordination complexes show

that hydrogen bonding to the coordinated sulfur atom of the thiolate groups has a significant effect on M–S bonding and on the redox potential of the complex, mimicking similar effects seen in metalloproteins containing cysteine residues.

3.3 Metal halides as hydrogen bond acceptors

Our own work on ligand domain hydrogen bonds has focussed on halide ligands, which we have shown to be good hydrogen bond acceptors. Specifically, using the CSD, the geometries of many thousands of D–H $\cdots$ X–M interactions (D = C, N, O; X = F, Cl, Br, I) have been examined alongside their counterparts in which metal halide groups (X–M) are replaced by halocarbon groups (X–C) or halide ions (X$^-$).[42] Significantly, X–M acceptor groups form substantially shorter (stronger) hydrogen bonds than the corresponding X–C acceptor groups. This illustrates the influence of the metal centres on the hydrogen bonding capability of the halogens, which arises here through the greater polarity of the $M^{\delta+}$–$X^{\delta-}$ bond compared to the C–X bond. After correcting for the difference in size of the halogens, mean H $\cdots$ X distances can be directly compared cross the halogens. Thus, it can be deduced that the relative *strength* of the D–H $\cdots$ X–M hydrogen bonds lie in the series:

$$D–H \cdots F–M \gg D–H \cdots Cl–M \geq D–H \cdots Br–M > D–H \cdots I–M$$
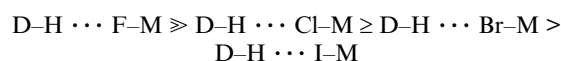
for D = C, N and O. This trend shows remarkably good qualitative agreement with the trend in the energies determined by Crabtree, Eisenstein and co-workers using a combination of NMR spectroscopy and *ab initio* calculations for intramolecular N–H $\cdots$ X–Ir hydrogen bonds (X = F, Cl, Br, I) in the series of compounds of formula $IrH_2X(PPh_3)_2(pyNH_2)$ (Fig. 14).[43]
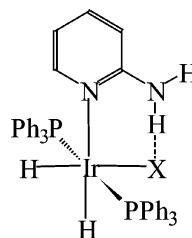

Fig. 14 N–H $\cdots$ X–Ir hydrogen bond in $IrH_2X(PPh_3)_2(pyNH_2)$. Hydrogen bond energies in CD_2Cl_2 solution determined as: X = F 5.2; X = Cl 2.1; X = Br 1.8; X = I <1.3 kcal mol^{-1}.[43]

In our studies of D–H $\cdots$ X–M hydrogen bonds trends in angles were also explored.[42a,c] Notably, examination of the H $\cdots$ X–M angles identified substantial anisotropy in the acceptor behaviour of the metal-bound halogens (Fig. 15), in particular for the heavier halogens (X = Cl, Br, I). The source of this anisotropy can be traced to the electrostatic potential distribution around the terminal halide ligands. Specifically, in calculations on the model systems *trans*-$PdX(CH_3)(PH_3)_2$ the location of minima in the negative potential associated with the chloride (Fig. 16), bromide and iodide ligands is consistent with the observed preference of hydrogen bond donor (D–H) to approach at an H $\cdots$ X–M angle of *ca*. 90–130°. Fluoride ligands, however, exhibit more isotropic acceptor behaviour and favour larger H $\cdots$ F–M angles (*ca*. 120–160°). This is again consistent with the picture that arises from consideration of the electrostatic potential associated with the fluoride ligand in *trans*-$PdF(CH_3)(PH_3)_2$, which shows deeper but less well-defined minima located so as to suggest a greater predicted H $\cdots$ X–M angle than for the heavier halogens.[42a]

Focussing now on metal chlorides, we reasoned that mutually *cis*-dichloride or *fac*-trichloride arrangements might give rise to cooperative enhancement of the electrostatic potential minima observed for the terminal monohalides. The calculated
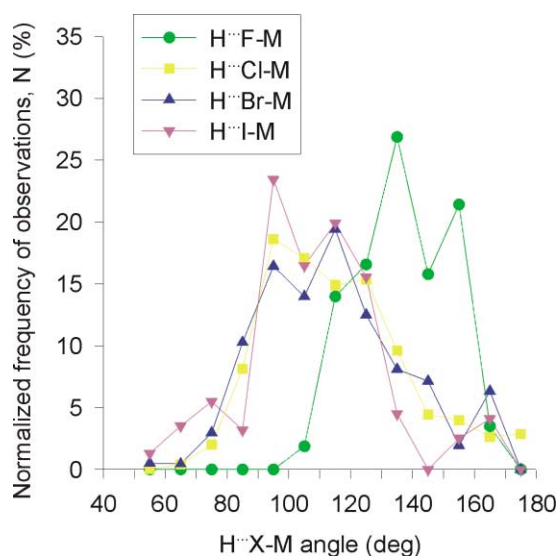
Fig. 15 Cone-corrected [44] (N)H · · · X–M angle distribution based upon crystal structure data.[42a] No. of observations: X = F, 73; Cl, 1341; Br, 205; I 83). Reproduced from ref. 42a with permission of the American Chemical Society.
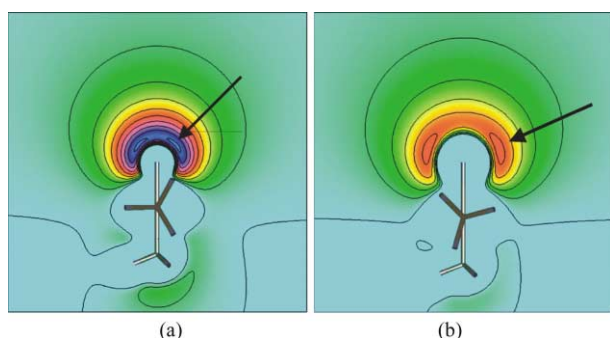

Fig. 16 Calculated negative electrostatic potential contoured at 10 kcal mol^{-1} intervals for model compounds *trans*-PdX(CH$_3$)(PH$_3$)$_2$: (a) X = F; (b) X = Cl.[42a] The preferred angle of approach of a hydrogen bond donor (D–H) is depicted by the arrow.

potentials for the model systems *cis*-PdCl$_2$(PH$_3$)$_2$ and *fac*-RhCl$_3$(PH$_3$)$_3$ confirmed this supposition and suggested the presence of a binding site situated between the chloride ligands (Fig. 17). These binding sites are suitable for formation of bifurcated D–H · · · Cl$_2$M and trifurcated D–H · · · Cl$_3$M hydrogen bonds for *cis*-dichloride or *fac*-trichloride systems, respectively. We have further demonstrated [46] that these hydrogen-bonding interactions can be viewed as (inorganic) supramolecular synthons [47] that may be applied in the construction of hydrogen bonded networks for crystal engineering applications. This view is further supported by the work of Orpen and co-workers [48] and implied, though not explicitly discussed, in work by Crabtree and co-workers [49] and by Dadon and Bernstein.[50] Extending the computational and CSD studies to perchlorometallate ions (Fig. 18), we have identified a series of binding sites for D–H groups associated with square-planar [MCl$_4$]$^{2-}$, tetrahedral [MCl$_4$]$^{2-}$ and octahedral [MCl$_6$]$^{2-}$ ions. These sites can be viewed as second-sphere coordination sites for these anionic complexes and from such a viewpoint one can approach the design of hydrogen-bonded network solids based upon the combination of organic hydrogen bond donor cations and perchlorometalate (more generally perhalometalate) anions. Within such a network the anions serve as nodes, wherein their connectivity is equal to their second-sphere co-ordination number (Fig. 19).[45] This view of a defined second coordination shell is reinforced by recent calculations on the hydration shells of perchlorometallate anions by Naidoo *et al*.[51]

Linear networks, as suggested in Fig. 19(a), can be generated using square-planar anions (*e.g.* [PtCl$_4$]$^{2-}$) in combination with
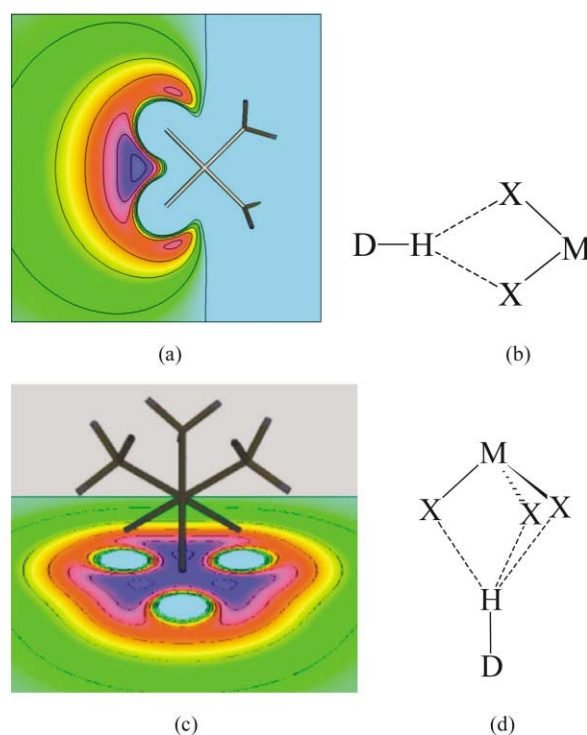

Fig. 17 Calculated negative electrostatic potential contoured at 10 kcal mol^{-1} intervals for model compounds (a) *cis*-PdCl$_2$(PH$_3$)$_2$ and (c) *fac*-RhCl$_3$(PH$_3$)$_3$.[45] Potential minima suggest the presence of (b) bifurcated D–H · · · Cl$_2$M for the dichloride and (d) bifurcated and trifurcated D–H · · · Cl$_3$M hydrogen bond binding sites for the trichloride ‡‡. (Note: colour gradation differs from that used in Fig. 16); (a) and (c) are reproduced from ref. 45 with permission of the National Academy of Sciences.
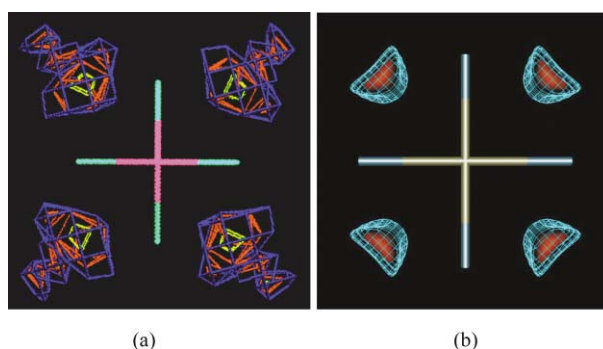

Fig. 18 (a) Experimental population density of hydrogen atoms from N–H groups in the vicinity of square-planar [MCl$_4$]$^{n-}$ anions obtained from crystal structure (CSD) data. Contours: blue 35%, red 55%, yellow 80% of maximum population density. (b) Calculated negative electrostatic potential in the vicinity of the [PdCl$_4$]$^{2-}$ anion. Similar comparisons of experimental distribution with theoretical prediction for tetrahedral and octahedral anions are presented in ref. 45. Reproduced from ref. 45 with permission of the National Academy of Sciences.

topologically linear hydrogen bond donor dications such as (DABCO)H$_2$$^{2+}$ [46] or 4,4′-bipyridinium.[48a] Similar 1D networks can be generated using (DABCO)H$_2$$^{2+}$ with tetrahedral [MCl$_4$]$^{2-}$ and octahedral [MCl$_6$]$^{2-}$ ions, propagated *via* D–H · · · Cl$_2$M and D–H · · · Cl$_3$M hydrogen-bonded synthons, respectively.[45,46] Fig. 20 provides examples of these networks and importantly illustrates their topological and chemical relationship to well known binary metal halide network structures. Reports of square networks, as suggested

‡‡ The electrostatic potential minima for *fac*-RhCl$_3$(PH$_3$)$_3$ lie at bifurcated sites, *i.e.* between pairs of chloride ligands. However, the trifurcated site, *i.e.* in the middle of the three chloride liagnds, differs very little from the bifurcated sites in the value of the electrostatic potential.[45]
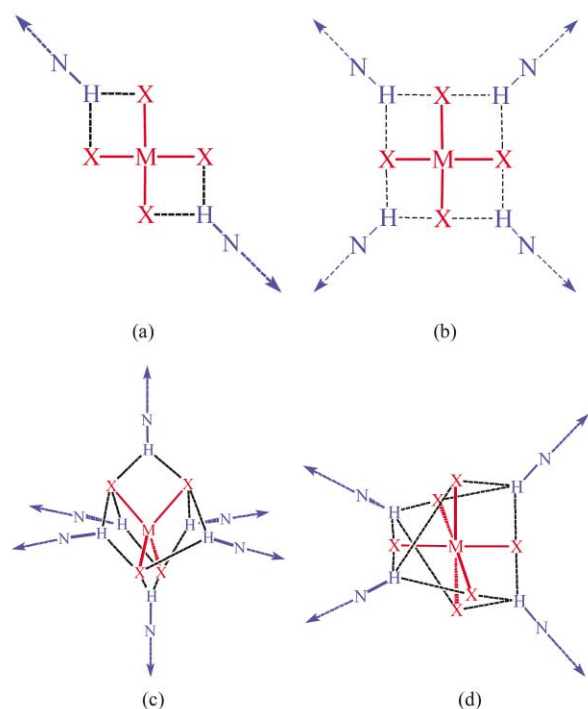
Fig. 19 Second sphere coordination of perhalometalate ions by hydrogen bond donors (N–H). (a) Square-planar $[MCl_4]^{2-}$ with second-sphere coordination number (SSCN) of 2; square-planar $[MCl_4]^{2-}$ with SSCN = 4; tetrahedral $[MCl_4]^{2-}$ with SSCN = 6; octahedral $[MCl_6]^{2-}$ with SSCN = 4. Arrows indicate propagation of hydrogen-bonded networks that could result from the use of such anions as network nodes: (a) linear; (b) square; (c) α-Po; (d) diamondoid. Reproduced from ref. 45 with permission of the National Academy of Sciences.

by Fig. 19(b), are less common to date. A good example is provided by the structure of $(HNC_5H_4CO_2H\text{-}4)_2[PtCl_4]\cdot 2H_2O$, reported by Angeloni and Orpen, in which the tetramolecular self-assembled cation $[(HNC_5H_4CO_2H\text{-}4)_2(H_2O)_2]^{2+}$ provides four roughly orthogonally disposed hydrogen bond donors (two N–H; two O–H) that interact with the four bifurcated binding sites on the $[PtCl_4]^{2-}$ anion.[48c] Designed three-dimensional networks, such as those suggested by Fig. 19(c) and (d) have yet to be realised. We are currently pursuing the strategy described above as a means of providing structural control in two and three dimensions with a view to design of new crystalline materials.

3.4 Metal hydrides as hydrogen bond acceptors

That hydride ligands can serve as hydrogen bond acceptors was clearly demonstrated in the mid-1990s by the work of Crabtree and co-workers[43,52] and Morris and co-workers,[53] though an earlier example from Milstein and Bau suggests this possibility.[54] Such interactions, D–H $\cdots$ H–M (D = N, O), termed either "dihydrogen bonds" or "proton–hydride bonds" involve an interaction between a protic (δ+) hydrogen atom and an hydridic (δ–) hydrogen atom, and are also known in cases where the hydridic hydrogen atom is bonded to an electropositive main group element (*e.g.* B, Al, Ga).[55] N–H $\cdots$ H–M hydrogen bonds have been shown to facilitate protonation of metal hydrides and the reverse reaction, *i.e.* deprotonation of metal dihydrogen complexes.[52a] They have also been used in constructing unusual hydrogen-bonded network structures.[53d,e] Crabtree and co-workers have also noted the propensity of the *ortho* hydrogen atoms in triphenylphosphine ligands to participate in C–H $\cdots$ H–M hydrogen bond formation.[56] We have studied such an interaction in the crystal structure of *cis*-HMn-$(CO)_4PPh_3$, accurately characterising the hydrogen bond geometry by neutron diffraction (Fig. 21) and evaluating the C–H$^{δ+}$ $\cdots$ H$^{δ-}$–M interaction by means of an experimental
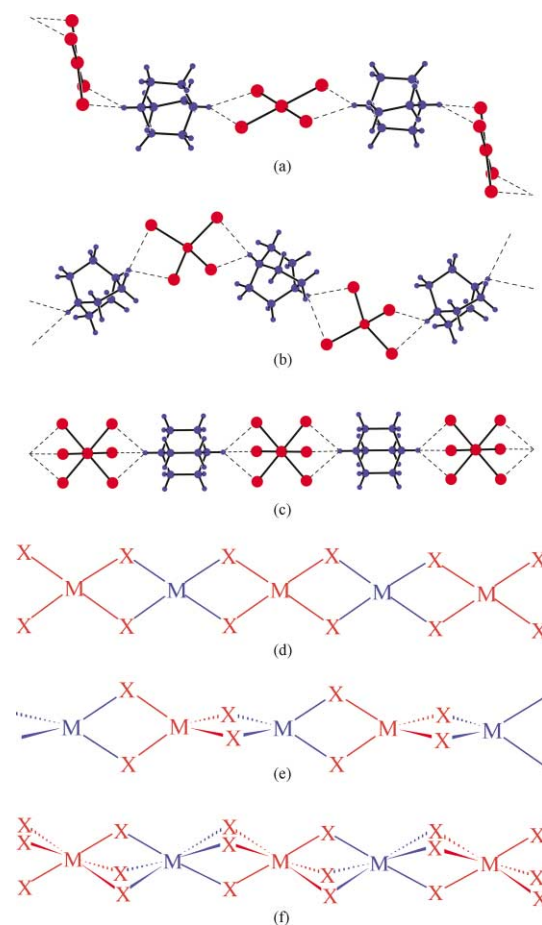
Fig. 20 One-dimensional hydrogen bonded networks for (a) $[(DABCO)H_2][PtCl_4]$,[46] (b) $[(DABCO)H_2][CuCl_4]$[45] and (c) $[(DABCO)\text{-}H_2][PtCl_6]$,[46] using square-planar, tetrahedral and octahedral perchlorometallate ions, respectively and propagated *via* N–H $\cdots$ Cl_2M [(a) and (b)] and D–H $\cdots$ Cl_3M [(c)] hydrogen-bonded synthons. Topologically analogous binary metal halide networks formed using (d) square-planar metal centres in α-MCl_2 (M = Pd, Pt), (e) tetrahedral metal centres in $BeCl_2$, and (f) octahedral metal centres in MX_3 (M = Ti, Zr, Hf; X = Cl, Br, I). The relationship between the hydrogen bonded networks and their binary metal halides analogues can be seen by replacing the organic cation shown in blue in (a), (b) and (c) with the appropriate metal ion to yield (d), (e) and (f) respectively; (a)–(c) are reproduced from ref. 45 with permission of the National Academy of Sciences.

charge density study.[57] In the latter study, the charges associated with the two key hydrogen atoms were determined to be $+0.28(2)$ and $-0.40(5)$ e. The experimental charge distribution was also used to evaluate the electrostatic component of the interaction at 5.7 kcal mol^{-1}.§§

4 The periphery domain

In a series of studies conducted using the CSD, Braga, Grepioni, Desiraju and co-workers established that the common organic functional groups, carboxyl, amide and alcohol, when present in metal complexes, form analogous hydrogen bonding patterns and adopted similar geometries to those established from crystal structures of organic compounds.[58] Implicit in this observation is that these groups typically lie at the periphery of the metal complexes as substituents on an organic ligand. The separation between these hydrogen-bonding groups and the metal centre necessarily mitigates the electronic effects noted within the ligand sphere. Consequently these groups behave largely as expected in organic compounds.

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§§ This is an overestimate of the total interaction energy by a factor of *ca.* 2.
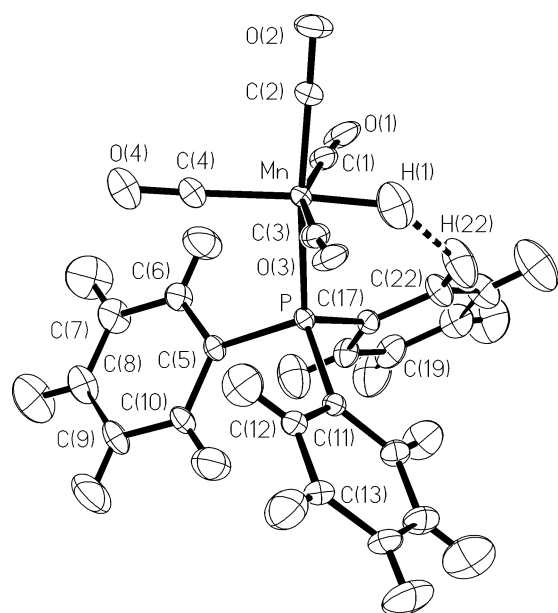
Fig. 21 Molecular structure of *cis*-HMn(CO)$_4$(PPh$_3$) determined by neutron diffraction. H $\cdots$ H 2.101(3) Å; C–H $\cdots$ H 129.0(2)°; Mn–H $\cdots$ H 126.5(1)°. Reproduced from ref. 57 with permission of the American Chemical Society.

Early advances in this area were made by Mingos and co-workers who designed a series of chelating ligands with hydrogen bonding groups at their periphery capable of forming double or triple hydrogen bonds in an analogous manner to the DNA bases.[21,59] Despite the spatial separation involved, the metal centre can have a role to play when hydrogen bonding takes place in the periphery domain. We have previously identified and pursued two means by which metal involvement may arise, using coordination compounds and organometallic π-arene compounds. These approaches are illustrated in Fig. 22 for 1D networks.[60]

The approach involving coordination compounds makes use of rigid (typically arene-based) ligands bearing peripheral hydrogen-bonding groups (**III**). These ligands can be thought of as amplifying the metal coordination geometry and serve to direct the interaction, *via* hydrogen bonds, of one coordination compound with its neighbours in the solid state. This approach is a hybrid of those taken to construct organic hydrogen-bonded networks (**II**) and coordination polymers (**I**). In the latter case, linear coordination linkages, N–M–N (**I**), are replaced by hydrogen-bonded linkages such as the dimer recognition synthons formed by carboxylic acids or primary amides, which also effect linear network propagation (**III**). The coordination chemistry approach is exemplified by 1D and 2D hydrogen-bonded networks reported by Aakeröy, Beatty *et al.* (Fig. 23).[61] Our own work in this area has focussed on cationic

coordination complexes of the form [PtL$_4$]X$_2$ (L = nicotinamide or isonicotinamide; X = Cl, PF$_6$),[60,62] as illustrated in Fig. 24. There are now many examples of networks constructed from a combination of coordination chemistry and hydrogen bonds, and this area has recently been reviewed.[2a,n]
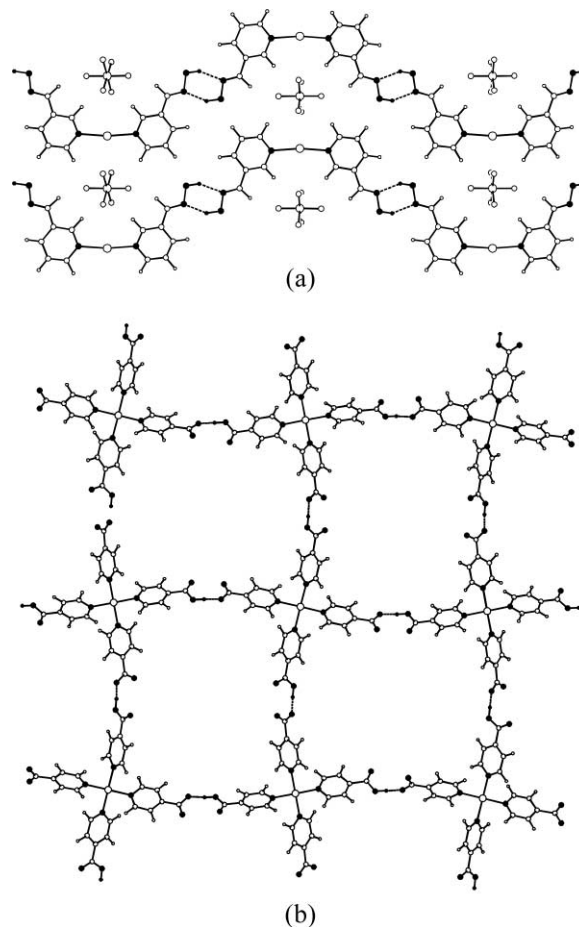

Fig. 23 (a) One-dimensional hydrogen bonded tape formed by the cations of [Ag(3-aldoximepyridine)$_2$]PF$_6$ *via* oxime–oxime hydrogen bonds.[61b] (b) Two-dimensional square grid propagated by O–H $\cdots$ O hydrogen bonds between carboxyl and carboxylate groups in [Pt(L)$_2$(HL)$_2$]·2H$_2$O (L = isonicotinate; water molecules not shown).[61e] Reproduced from ref. 2a with permission of John Wiley & Sons.

Organometallic building blocks based upon [Cr(η^6-C$_6$H$_5$-COOH)$_2$], [Fe(η^5-C$_5$H$_4$COOH)$_2$], [Co(η^5-C$_5$H$_4$COOH)$_2$]$^+$ and closely related complexes have been studied extensively by Braga, Grepioni and co-workers, who have examined hydrogen-bonded network structures formed through carboxyl–carboxyl and carboxyl–carboxylate hydrogen bonding.[63] Some of these systems show interesting polymorphic behaviour[64] and in the
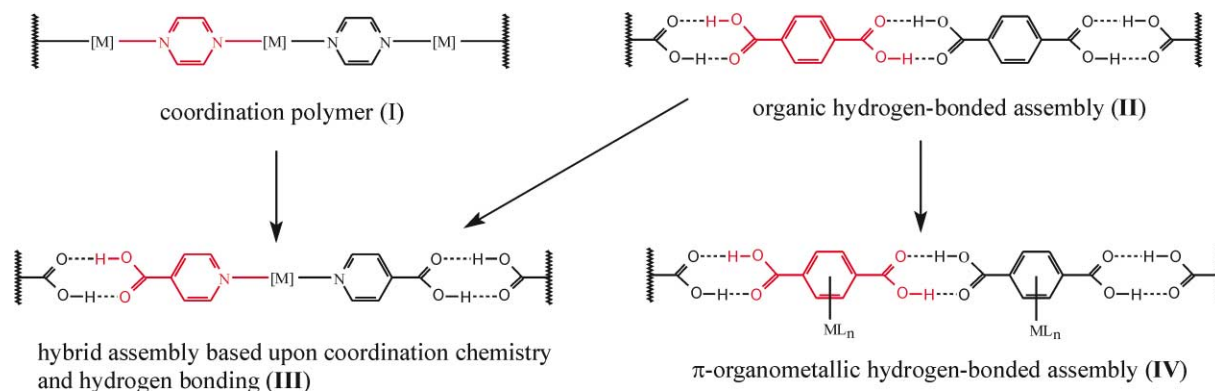

Fig. 22 One-dimensional networks formed *via* hydrogen bonds in the periphery domain of coordination.complexes (**III**) and π-arene organo-metallic complexes (**IV**), showing their relationship to coordination polymers (**I**) and organic hydrogen-bonded networks (**II**). Adapted from ref. 60.
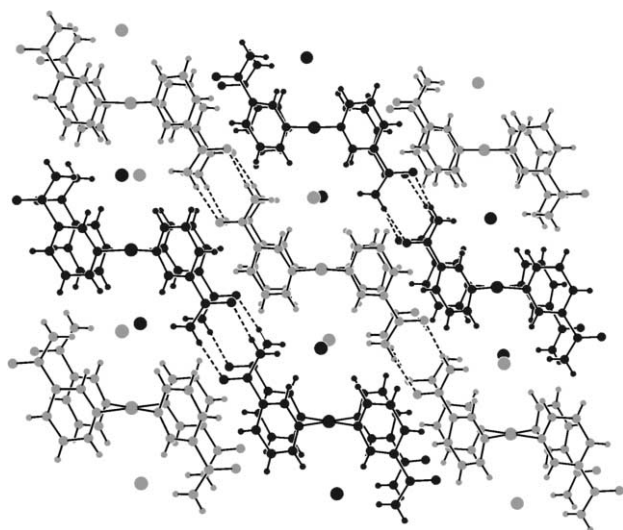
Fig. 24 Hydrogen-bonded tapes comprised of [Pt(nicotinamide)$_4$]$^{2+}$ cations, with chloride ions in channels between tapes. Reproduced from ref. 62.

case of the zwitterion [Co(η^5-C$_5$H$_4$COOH)$_2$(η^5-C$_5$H$_4$COO)] the ability to react with and incorporate simple acids and bases such as HCl and NH$_3$.[65]

Our own efforts in using organometallic building blocks to construct hydrogen bonded networks has focussed on the Cr(CO)$_3$ adducts of benzene carboxylic acids. The aim was effectively to decorate the well-known networks formed by the terephthalic, isophthalic and trimesic acids by addition of the Cr(CO)$_3$ moieties though π-coordination. The building blocks, Cr(η^6-arene)(CO)$_3$, were all able to be prepared,[60] though the electron-withdrawing effect of the carboxyl groups makes π-coordination quite weak, leading to some tendency for decomplexation in solution. [Cr(η^6-C$_6$H$_5$COOH)(CO)$_3$],[66] which was also prepared, forms dimers *via* carboxyl–carboxyl hydrogen bonding in the solid state, in an analogous manner to benzoic acid itself.[67] To date we have only been able to crystallise the complexes of the di- and tri-carboxylic acids as solvates. Interaction of the strongly hydrogen-bonding solvent prevents association *via* carboxyl–carboxyl hydrogen bonds of the metal-containing building blocks in [Cr{η^6-1,3-C$_6$H$_4$-(COOH)$_2$}(CO)$_3$]·2DMF and [Cr{η^6-1,4-C$_6$H$_4$(COOH)$_2$}-(CO)$_3$]·2DMSO.[60] However, in [Cr{η^6-1,3,5-C$_6$H$_3$(COOH)$_3$}-(CO)$_3$]·^{n}Bu$_2$O a 1D zigzag network is propagated *via* hydrogen bonding between two of the three carboxyl groups on each chromium complex. The third carboxyl group binds the ether molecules *via* O–H $\cdots$ O hydrogen bonds (Fig. 25).[60]

Fig. 25 Hydrogen-bonded network in crystal structure of [Cr{η^6-1,3,5-C$_6$H$_3$(COOH)$_3$}(CO)$_3$]·^{n}Bu$_2$O.[59] Reproduced from ref. 2a with permission of John Wiley & Sons.

5 Conclusions and future prospects

The range of involvement of metal atoms in hydrogen bonding, from direct participation to indirect influence has been illustrated in the work presented. Division of metal complexes

into domains provides a convenient and useful classification of the hydrogen bonding interactions in which metal complexes are involved.

While direct metal involvement in hydrogen bonding seems at first unusual, there is now ample definitive evidence of the formation of such hydrogen bonds. Indeed a very recent report even implicates O–H $\cdots$ M hydrogen bonds in the binding of water molecules to Pt(111) surfaces.[68] There remains a need to improve our understanding of M–H $\cdots$ A hydrogen bonds which, while implicated from spectroscopic and crystallographic data, are at present not well understood. There is also much scope to develop and explore the reactions in which D–H $\cdots$ M hydrogen bonds may have an important role to play, namely protonation/deprotonation of metal centres and oxidative addition of polar D–H bonds (D = N, O, *etc.*).

Halometallate ions exemplify the potential for the application of ligand-sphere hydrogen bonds in supramolecular chemistry and in materials design *via* crystal engineering. When hydrogen bond formation takes place in the periphery domain of metal complexes, the metal can have a structure-directing role if suitably rigid ligands are chosen. Alternatively the metal centres can be incorporated *via* coordination into organic hydrogen bonded assemblies, as illustrated by the organometallic π-arene systems described (*vide supra*). While there are many reports of metal complexes linked into networks *via* periphery-domain hydrogen bonds,[2a] in terms of materials design this field is in its infancy and offers a host of opportunities for further development. Although not discussed in any detail in this Perspective it seems clear that ligand and periphery domain hydrogen bonds are likely also to have an important role to play in metalloenzymes and in bioinorganic chemistry in general.

When I present seminars under the same title as this Perspective, I usually conclude by encouraging the audience, when thinking of hydrogen bonds, to look beyond the small number of elements in the top right-hand corner of the periodic table (N, O, F) that are often conveyed as being the only ones of importance. Metals, too, can participate in hydrogen bonds!

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