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Hydrogen Bonds Involving Transition Metal Centres – A Brief Review

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Abstract

Hydrogen bonding is a topic which has received much attention over the years and continues to do so as the importance of such interactions is established in all areas of chemistry. The class of hydrogen bonds that directly involves electron-rich transition metal centres in the three-centre interaction has received little attention until quite recently. Such interactions are of importance in understanding intermolecular interactions between organometallic molecules and are particularly relevant to understanding proton transfer reactions that directly involve transition metal centres. Hydrogen bonds in which transition metal centres serve as the hydrogen-bond acceptor, *i.e.* X—H···M (X = C, N, O, S), can be identified on the basis of geometric and spectroscopic criteria which confirm: (i) that such interactions should be classified alongside conventional hydrogen bonds (X—H···X'), and (ii) that these three-centre four-electron interactions can be distinguished from the better known three-centre two-electron X—H···M (X = B, C, Si, P, S) interactions. In salts of the type $R_3NH^+Co(CO)_3L^-$, where L = CO, $P(OR)_3$ or PR_3, it is shown that increasing the basicity of the hydrogen-bond acceptor $[Co(CO)_3L^-]$ by changing L leads to strengthening of the N—H···Co hydrogen bond. Furthermore, in reactions where the products were dictated by a competition between N—H···N and N—H···Co hydrogen-bond formation, results suggested that N—H···N were formed preferentially, inferring that those hydrogen bonds involving metal centres are the weaker hydrogen bonds. Some initial results that point towards the construction of larger hydrogen-bonded assemblies involving X—H···M hydrogen bonds are also discussed.

Introduction

A vast literature exists on the topic of hydrogen bonding (for reviews, see: Hadzi, 1959; Pimental & McClellan, 1960; Hamilton & Ibers, 1968; Green, 1974; Schuster, Zundel & Sandorfy, 1976; Taylor & Kennard, 1984; Deakyne, 1987; Desiraju, 1991; Jeffrey & Saenger, 1991). The importance of hydrogen bonds in organic chemistry and biochemistry is well established. In inorganic chemistry the past emphasis on hydrogen bonding has been primarily on topics such as the hydration of inorganic salts, and interligand hydrogen bonding in coordination complexes. Thus, hydrogen bonds typically have been considered to be confined to the interaction of non-metals (Y) possessing lone pairs of electrons, such as nitrogen, oxygen, sulfur or halogens, with H atoms that are covalently bound to one of these same electronegative elements (or to carbon), X. This accounts for the predominant electrostatic component of these $X^{\delta-}$—$H^{\delta+}\cdots Y^{\delta-}$ interactions, particularly when Y is an anionic species. More recently, it has also been recognized that the π-electron clouds of aromatic rings and alkyne $C\equiv C$ bonds can act as hydrogen-bond acceptors. Excellent examples of such hydrogen bonds have been described by Mootz & Deeg (1992) and Deeg & Mootz (1993).

Hydrogen bonding is one example of a situation in which H atoms might be described as having a coordination number greater than one. The other well established instances of such increased hydrogen coordination numbers arising in molecular chemistry are those of (i) metal complexes with bridging hydride ligands (Teller & Bau, 1981), (ii) so-called σ-bond complexes (Brookhart, Green & Wong, 1988; Crabtree, 1993) in which three-centre two-electron X—H···M bonds are formed (X = B, C, Si, P, S, Ge, Sn; M = transition metal), and (iii) complexes with molecular hydrogen ligands, η^2-H_2 (Kubas, 1988; Crabtree, 1990; Jessop & Morris, 1992; Heinekey, 1993), which can be considered as a special class of σ-bond complexes.

In the past few years examples of interactions that are analogous to conventional hydrogen bonds but directly involve transition metal centres have been identified. These involve an electron-rich transition metal as the hydrogen-bond acceptor. Our work in this area began with a low-temperature neutron diffraction study of the unusual diplatinum salt $[NPr_4^n]_2[PtCl_4]$.*cis*-$[PtCl_2(NH_2Me)_2]$ (1; Brammer, Charnock, Goggin, Goodfellow, Koetzle & Orpen, 1991). The dianion of (1), shown in Fig. 1, consists of two square-planar d^8-platinum centres held together by short intermolecular N—H···Pt and N—H···Cl interactions [H···Pt 2.262 (11) and H···Cl 2.318 (12) Å]. The latter is readily identified as an N—H···Cl hydrogen bond.

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The two interactions, however, share many common features, notably the amine N—H group and the geometry of the three-centre interaction. The near linear N—H· · ·Pt geometry [167.1 (9)°] is consistent with its description as a three-centre four-electron (3*c*–4*e*) interaction. Furthermore, the presence of the filled Pt d_{z^2}-orbital oriented towards the amine N—H group suggests that a 3*c*–4*e* description is more appropriate than a 3*c*–2*e* description. The latter would of course require interaction of the N—H σ-bonding orbital with a vacant metal orbital.* A qualitative description of the bonding in 3*c*–2*e* and 3*c*–4*e* *X*—H· · ·*M* interactions is presented in Fig. 2.

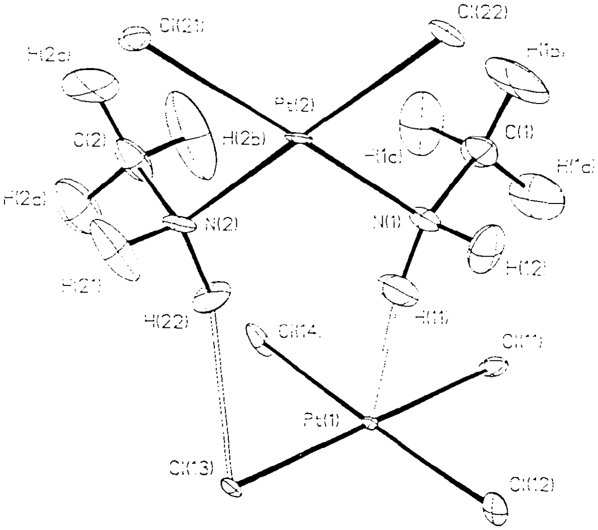

Fig. 1. Molecular structure of the [$PtCl_4$].*cis*-[$PtCl_2(NH_2Me)_2$] dianion, shown with 50% probability ellipsoids [from the neutron diffraction study of 1 at 20 K; from Brammer, Charnock, Goggin, Goodfellow, Orpen & Koetzle (1991)].

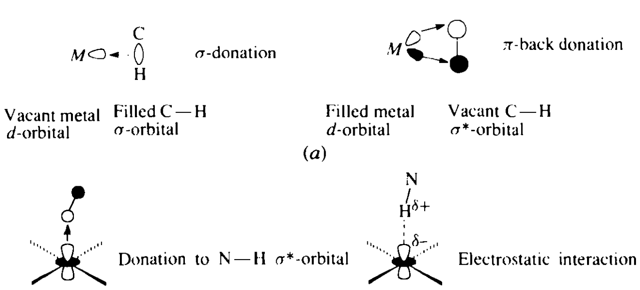

Fig. 2. (*a*) Representation of the orbital interactions involved in coordination of a σ-bond to a transition metal centre (*M*), through a 3*c*–2*e* interaction. Shown here for the interaction of a C—H σ-bond. (*b*) Representation of the orbital and electrostatic componenets of a 3*c*–2*e* N—H· · ·*M* interaction (hydrogen bond), where *M* is a d^8 metal centre with a square-planar coordination environment, *e.g.* Pt^{II}.

Table 1. ^{1}H *chemical shifts* (*p.p.m.*) *illustrative of* 3*c*–4*e* *X*—H· · ·Pt *interactions* (*X* = C,N)

Compound	δ *X*—H· · ·Pt	δ free ligand	Reference
(2)	11.0	8.7	Hedden *et al.* (1986)
(3)	13.1	11.5	Albinati, Anklin *et al.* (1987)
(4)	9.7	9.5	Albinati, Arz *et al.* (1987)
(5)	15.8	—	Wehman-Ooyevaar, Grove, Kooijman *et al.* (1992)

Examination of the literature revealed a number of square-planar d^8-Pt^{II} and -Pd^{II} complexes which have N—H· · ·*M* or C—H· · ·*M* interactions similar to that observed in (1). Compounds (2)–(5) shown in Fig. 3 are representative examples (Hedden, Roundhill, Fultz & Rheingold, 1986; Albinati, Anklin, Ganazzoli, Rüegg & Pregosin, 1987; Albinati, Arz & Pregosin, 1987; Wehman-Ooyevaar, Grove, Kooijman, van der Sluis, Spek & van Koten, 1992). While (2)–(5) have thus far been structurally characterized only by X-ray diffraction, yielding approximate H-atom positions, it is clear in each case that a C—H or N—H group lies close enough to the metal to permit an interaction of the type described above. However, perhaps the most interesting feature that these compounds have in common is that the proton in close proximity to the metal has a chemical shift substantially downfield of TMS (see Table 1). Furthermore, these protons are deshielded relative to the corresponding free ligands.*

These findings led us to suggest a series of criteria by which to characterize 3*c*–4*e* *X*—H· · ·*M* interactions, namely:

(i) the bridging hydrogen is reasonably protonic in nature, facilitating an electrostatic component to the

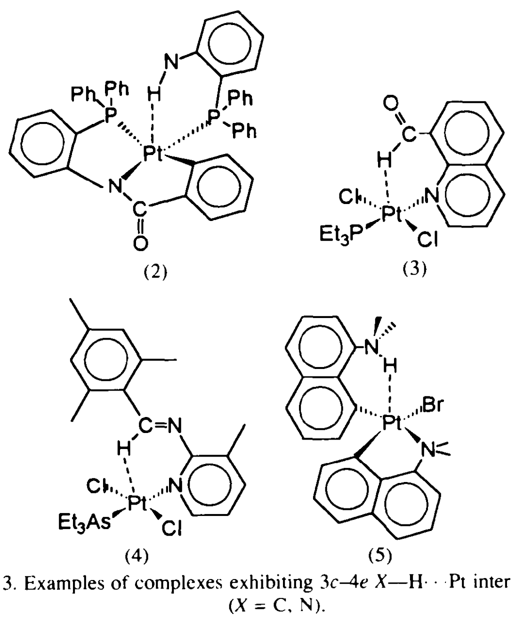

Fig. 3. Examples of complexes exhibiting 3*c*–4*e* *X*—H· · ·Pt interactions (*X* = C, N).

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* The vacant Pt 6*p*-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 (Wehman-Ooyevaar, Grove, de Vaal, Dedieu & van Koten, 1992).

* Attempts to obtain NMR spectroscopic information for (1) analogous to that of (2)–(5) have to date been proved unsuccessful due to ^{14}N quadrupolar broadening.

interaction (typically the H atom belongs to an *X*—H or an *X*—C—H group, where *X* is an electronegative element or an electron-withdrawing substituent);

(ii) the metal atom involved is electron-rich, *i.e.* typically a late transition metal, with filled *d*-orbitals that can facilitate the 3*c*–4*e* interaction involving the H atom;

(iii) the ^1H NMR chemical shift of the bridging H atom is downfield of TMS and shifted downfield relative to the free ligand of which the H atom in question is a part;

(iv) intermolecular *X*—H···*M* interactions have an approximately linear geometry;

(v) electronically saturated metal complexes (*e.g.* with 18-electron metal centres) can form such interactions.

These characteristics are analogous to those of conventional hydrogen bonds, but are unlike those of 3*c*–2*e* *X*—H···*M* interactions involving transition metals, such as agostic C—H···*M* interactions (Brookhart *et al.*, 1988). Furthermore, while 3*c*–2*e* *X*—H···*M* interactions are known for both early and late transition metals *M*, the common feature of these interactions is the presence of a vacant metal orbital that can act as an acceptor orbital for electron-donation from the *X*—H σ-bonding orbital. The requirement for 3*c*–4*e* *X*—H···*M* interactions of having an electron-rich metal centre *M*, with available filled orbitals, suggests that such interactions will be mostly confined to the late transition metals.

One might also anticipate that 3*c*–4*e* *X*—H···*M* interactions would lead to weakening of the *X*—H bond, as is observed in conventional hydrogen-bonding interactions. This has been confirmed in elegant work (i) by Pregosin, Albinati, van Koten and coworkers (Wehman-Ooyevaar, Grove, Kooijman *et al.*, 1992; Albinati, Lianza, Pregosin & Müller, 1994), who have quantified the weakening of the N—H bond in (5) and related compounds through the determination of a diminished ^{15}N–^1H coupling constant, and (ii) by Kazarian, Hamley & Poliakoff (1993), who have detected by IR studies a reduction in the O—H stretching frequencies upon O—H···*M* hydrogen bonding of perfluoroalcohols to an extensive series of 18-electron complexes of the Group 9 metals, $(\eta^5\text{-C}_5R_5)ML_2$ (*R* = H, Me; *M* = Co, Rh, Ir; *L* = CO, C_2H_4, N_2, PMe_3). The latter study is also the first documented example of hydrogen bonding to a metal centre which involves a neutral hydrogen-bond donor and acceptor.

There is also emerging evidence that suggests hydrogen bonds to transition metal centres may facilitate the protonation of the metal centre and even oxidative addition of the *X*—H bond to the metal. For example, van Koten and coworkers have isolated not only (5), but also a Pt^{IV}-hydride complex which is related to that which would result from oxidative addition of the N—H bond to the Pt^{II} centre in (5) (Wehman-Ooyevaar, Grove, de Vaal *et al.*, 1992). The Pt^{IV}-hydride and (5) were prepared from similar reactions of the $Pt(1\text{-C}_{10}H_6\text{-NMe}_2\text{-8-}C,N)_2$ precursor, but oxidative addition/reductive elimination of N—H has not been demonstrated. Furthermore, Merola and coworkers have shown that the 18-electron Ir^I species $[Ir(cod)(PMe_3)_3]^+$ can undergo oxidative addition of carboxylic acid and alcohol O—H bonds, which they suggest proceeds *via* initial protonation of the metal centre followed by nucleophilic attack of the carboxylate oxygen (Ladipo, Kooti & Merola, 1993). Consistent with this argument one could reasonably postulate the initial formation of an O—H···Ir hydrogen bond, which weakens the O—H bond and more readily facilitates the protonation step.* Such a proposal is consistent with the observation of *R*O—H···Ir(Cp)L_2 hydrogen bonds by Kazarian *et al.* (1993) (*vide supra*).

There are now a number of examples in the literature in which d^8 metal centres (Ni^{II}, Rh^I, Pd^{II}, Ir^I and Pt^{II}) and d^{10} metal centres (Co^{-1} and Ni^0) exhibit hydrogen-bonding interactions (see discussion in Brammer *et al.*, 1991). Many of these examples predate our studies and those of others in this area. Thus, the nature of the interaction is often either not discussed in these publications or in some cases is incorrectly described in terms of a 3*c*–2*e* agostic interaction. Indeed, there are reports of *X*—H···*M* hydrogen bonds in the literature that date back 20–30 years (for example, see Baker & Bublitz, 1965; Roe, Bailey, Moseley & Maitlis, 1972), although little attention has been paid to such interactions until very recently.

N—H···Co and N—H···N hydrogen bonds in $Z^+Co(CO)_3L^-$ salts (*Z* = substituted ammonium cation, *L* = CO, P*R*$_3$)

In a previous study it has been shown that the salt $Et_3NH^+Co(CO)_4^-$ (6), prepared from the reaction of $HCo(CO)_4$ with NEt_3, exhibits a close anion–cation contact *via* an N—H···Co hydrogen bond (Brammer, McCann, Bullock, McMullan & Sherwood, 1992). This interaction results in a slightly elongated N—H bond, as determined by low-temperature neutron diffraction, and a distortion of the geometry at the metal centre away from the idealized Td symmetry of the isolated anion. Furthermore, studies of the experimentally and theoretically determined charge-density distribution for this salt show features consistent with the formulation of the N—H···Co interaction as a hydrogen bond (Brammer & Sherwood, 1995).

Subsequent work has shown that the reaction of a number of different amines with $HCo(CO)_4$ leads to hydrogen-bonded salts, such as (7)–(11) (Scheme 1). A number of these compounds have been described elsewhere (8, Brammer, Zhao, Ladipo, Braddock-Wilking & Sherwood, 1995; 9, Brammer & Zhao, 1994; 10 and 11, Brammer & Zhao, 1995*a*) and $[(DABCO)_3H_2][(DABCO)_2H]_2[Co(CO)_4]_4$ (7; DABCO = 1,4-diazabicyclo[2.2.2]octane) will be

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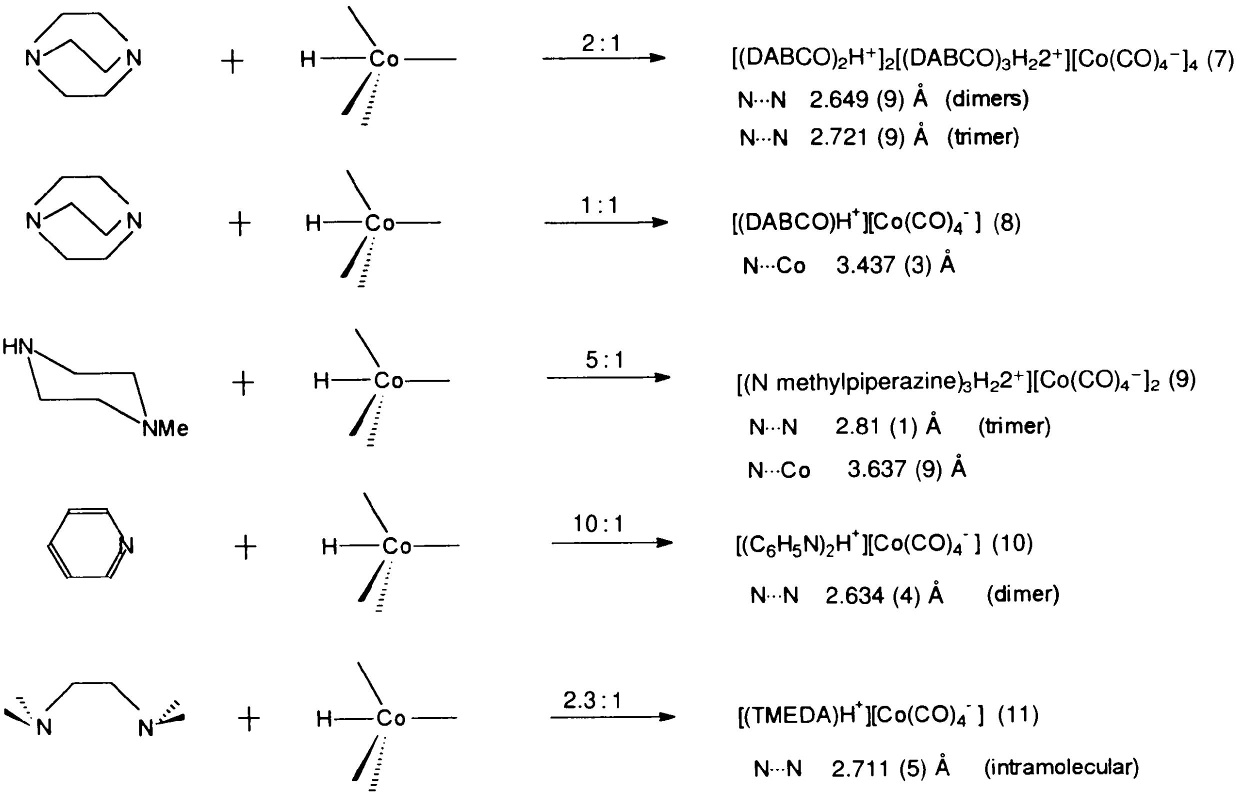
* Such a postulate is not put forward in this article.



Scheme 1. Preparation of salts containing N—H···Co and/or N—H···N hydrogen bonds with the indicated distance between the heavy atoms (N···N, N···Co) determined from low-temperature X-ray diffraction studies.

described in greater detail in a future article (Brammer & Zhao, 1995*b*).

N—H···Co *versus* N—H···N *hydrogen-bond formation in* $[(DABCO)_3H_2][(DABCO)_2H]_2[Co(CO)_4]_4$ *and* $[(DABCO)H][Co(CO)_4]$

Although the reaction of DABCO with $HCo(CO)_4$ (Scheme 1) was initiated primarily to prepare the N—H···Co hydrogen-bonded analogue of (6) using a less sterically demanding amine (DABCO), the study was initiated with the knowledge that DABCO was known to form a variety of different hydrogen-bonded salts. In particular, the mono- and dihydrochloride salts are known (Brammer, Zhao, Kwiatkowski & Schultz, 1995; Kennedy, Schultz, Slade & Tiekink, 1987), as is the salt formulated as $[(DABCO)H][ClO_4]$ in which an infinite N···H···N hydrogen-bonded chain is present (Glowiak, Sobczyk & Grech, 1975). Reaction of DABCO with $HCo(CO)_4$ in a 1:1 molar ratio yields $[(DABCO)H][Co(CO)_4]$ (8), which has been characterized by a low-temperature X-ray diffraction study (Fig. 6*a*). Compound (8) exists as a hydrogen-bonded salt similar to the previously reported $Et_3NH^+Co(CO)_4^-$ (Brammer *et al.*, 1992) in which the shortest cation–anion contact is *via* an N—H···Co linkage, with the methylene groups of the cation adopting a staggered conformation with respect to the three 'equatorial' CO ligands of the anion. Although the bridging hydrogen is located and refined [N—H 0.94 (4), Co···H 2.50 (4) Å], perhaps the most informative comparison with the neutron diffraction study of $Et_3NH^+Co(CO)_4^-$ is the N···Co separation which is 3.437 (3) in (8) and 3.684 (2) Å in $Et_3NH^+Co(CO)_4^-$ at 123 K (Brammer, McCann, Bullock, McMullan & Sherwood, 1995). The marked shortening of the cation–anion separation in (8) relative to $Et_3NH^+Co(CO)_4^-$ suggests a stronger N—H···Co interaction, presumably arising from the fact that the ethyl groups in Et_3NH^+ exhibit a greater steric interaction than $(DABCO)H^+$ with the $Co(CO)_4^-$ moiety. Nevertheless, the anions of (8) and $Et_3NH^+Co(CO)_4^-$ exhibit similar C_{3v} geometries intermediate between that of the metal–carbonyl framework of $HCo(CO)_4$ (McNeill & Scholer, 1977) and that of an undistorted $Co(CO)_4^-$ anion (of T_d symmetry).

Treatment of $HCo(CO)_4$ with a 2:1 excess of DABCO leads to the salt $[(DABCO)_3H_2][(DABCO)_2H]_2[Co(CO)_4]_4$ (7) as the major product. Compound (7) has a remarkable structure (Fig. 4) consisting of two N—H···N hydrogen-bonded dimers $[(DABCO)\cdots H\cdots(DABCO)]^+$ (one of staggered conformation, one eclipsed), one N—H···N hydrogen-bonded trimer $[(DABCO)\cdots H\cdots(DABCO)\cdots H\cdots(DABCO)]^{2+}$, and four independent $Co(CO)_4^-$ anions per asymmetric unit. In this case no unusually short contacts between anions and cations are present. To our knowledge, this is the first crystallographic characterization of a hydrogen-bonded DABCO dimer and suggests that both the staggered and eclipsed forms have approximately symmetrical N···H···N hydrogen bonds, consistent with the short N···N separations of 2.649 (9) Å for each dimer (for related examples of short N···H···N hydrogen bonds, see Roziere, Belin & Lehmann, 1982; Glidewell & Holden, 1982). The trimeric unit comprises three DABCO molecules linked by asymmetric N—H···N hydrogen bonds, as suggested by the longer N···N separations of 2.754 (9) and 2.709 (9) Å.

Table 2. ^{1}H *NMR chemical shifts* (*p.p.m.*) *of DABCO*, (7) *and* (8) *in toluene-*d_8 *and acetone-*d_6

Temperature	Toluene			Acetone		
(K)	DABCO	7	8	DABCO	7	8
298	2.4	2.4	2.18	2.64	3.02	—
273	2.4	2.4	—	—	—	3.29
233	2.4	2.4	2.03	2.62	3.01	3.27
−60	2.4	2.4	1.87	—	2.99	3.22
−80	2.4	2.4	1.74	2.59	2.98	3.21

The ^{1}H NMR spectrum of (8) demonstrates that the N—H···Co interaction remains intact in toluene solution, as indicated by the fact that methylene hydrogens in (8) are shielded by the carbonyl groups, yielding a chemical shift which lies upfield relative to that of the free diamine in toluene. The ^{1}H spectrum of (8) in acetone indicates that the N—H···Co interaction is broken to yield solvated (DABCO)H$^+$ and Co(CO)$_4$$^-$ ions; the methylene protons are deshielded relative to the free diamine in acetone solution, as would be anticipated for protonation of an amine. The NMR spectra of Et$_3$NH$^+$Co(CO)$_4^-$ and of the related salt Me$_3$NH$^+$Co(CO)$_4^-$ show the same trends, indicating that these hydrogen-bonded salts show the same general behaviour as each other in polar and non-polar solvents.

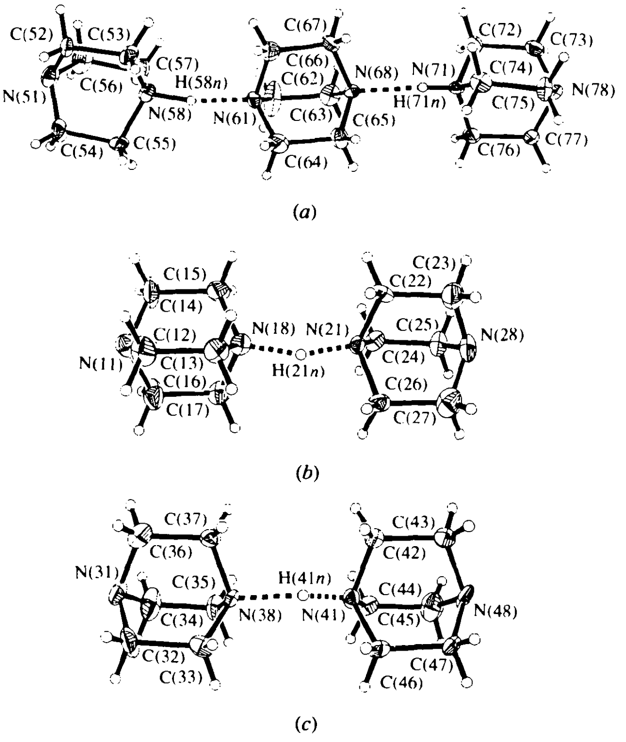


Fig. 4. Molecular structures of the hydrogen-bonded cations which comprise (7), shown with 50% probability ellipsoids for non-H atoms. (*a*) [(DABCO)$_3$H$_2$]$^{2+}$; (*b*) [(DABCO)$_2$H]$^+$ (staggered form); (*c*) [(DABCO)$_2$H]$^+$ (eclipsed form).

However, (8) differs from Et$_3$NH$^+$Co(CO)$_4^-$ and Me$_3$NH$^+$Co(CO)$_4$$^-$ in that a free amine centre is available. Proton transfer between the ammonium centres and the amine centres occurs rapidly in solution, leading to fluxionality observed in the NMR spectra. The fluxionality of (8) in toluene solution leads to temperature-dependent singlet resonances for the methylene protons and carbons, in the ^{1}H and ^{13}C NMR spectra, respectively. It is not evident at this stage whether the fluxionality arises from an inter- or intramolecular process. A broad ^{1}H resonance assigned to the N—H proton is observed at δ 10.2 only in the lowest temperature spectrum. The cation that results from solvation of (8) in acetone, (DABCO)H$^+$, also exhibits only a single ^{1}H NMR resonance for the methylene group. Here fluxionality again arises from proton transfer between nitrogen sites and is presumably readily mediated by the solvent in this case.

Spectroscopic characterization of (7) in solution is not as straightforward. Dissolution in toluene yields only a single temperature-independent resonance in the ^{1}H and ^{13}C NMR spectra at frequencies characteristic of the free diamine, DABCO. The most probable explanation is that an equilibrium exists between (7) and its dissociation products, the free diamine and the salt (8); the diamine being very soluble in toluene should drive the equilibrium strongly in favour of the dissociation. A ^{1}H NMR spectrum showing the same features as that of (7) is obtained by adding 0.5 equivalents of the free diamine to a toluene solution of (8). This suggests that although (8) is still present in solution, its signal is very weak compared with that from the diamine and is thus not observed. Evidence that the hydrogen-bonded salt (8) is present in solution despite the absence of the NMR signal comes from comparison of the IR spectra of (7) and (8) in toluene. Both yield only carbonyl bands at 1897 (*s*), 1936 (*m*) and 2019 cm^{-1} (*w*) ($2A_1 + E$ bands), characteristic of the C_{3v} symmetry of the Co(CO)$_4$$^-$ anion present in (8) (and very similar to that observed for 6).

The ^{1}H NMR spectrum of (7) in acetone-d_6 is also temperature-independent and shows a single resonance for the methylene protons at a frequency between those recorded for DABCO and for (8) in acetone. Recall that the ^{1}H NMR spectrum of (8) in acetone is really the spectrum of the solvated cation (DABCO)H$^+$. In fact, the ^{1}H chemical shift (δ) for (7), at 3.0 p.p.m., can be estimated as $\frac{3}{7}\delta$ [DABCO] + $\frac{4}{7}\delta$ [(DABCO)H$^+$], which is the correct ratio of products assuming (7) is completely dissociated by acetone. Thus, rapid proton transfer between the amine nitrogen sites makes the CH_2 groups of the DABCO and (DABCO)H$^+$ species equivalent on the NMR timescale.

These NMR results are summarized in Table 2 and the solution behaviour of (7) and (8) is summarized in Scheme 2.

In toluene solution

Dissolution of (7)

$[(DABCO)_7H_4][Co(CO)_4]_4 \rightarrow 3\,DABCO + 4\,DABCO\text{-}H^+\;Co(CO)_4^-$

(7) v soluble (8) (sparingly soluble)

^1H & ^{13}C NMR: Only singlet for DABCO observed. No signal for (8). IR: ν_{CO} confirms C_{3v} anion

Dissolution of (8)

The N-H· · ·Co hydrogen-bonded salt (8) remains intact.

^1H & ^{13}C NMR: Singlet resonance shifted upfield for CH_2 groups confirms (8) is present.

IR ν_{CO} confirms C_{3v} anion

In acetone solution

Dissolution of (7)

$[(DABCO)_7H_4][Co(CO)_4]_4 \rightarrow 3\,DABCO + 4\,DABCO\text{-}H^+ + 4\,Co(CO)_4^-$

soluble soluble soluble

^1H NMR Singlet resonance for weighted average of DABCO and DABCO-H$^+$

IR ν_{CO} confirms T_d $Co(CO)_4^-$ anion

Dissolution of (8)

$DABCO\text{-}H^+\;Co(CO)_4^- \rightarrow DABCO\text{-}H^+ + Co(CO)_4^-$

soluble soluble

^1H NMR Singlet resonance for DABCO-H$^+$ IR ν_{CO} confirms T_d $Co(CO)_4^-$ anion

Scheme 2. The dissolution of (7) and (8) in toluene and in acetone.

Formation of supramolecular architectures containing both conventional and X—H· · ·M hydrogen bonds

The structures of (7) and (8), when considered together, suggest the opportunity to build more extensive hydrogen-bonded architectures which incorporate both conventional hydrogen bonds, such as N—H· · ·N interactions, and those incorporating transition metal centres (*X*—H· · ·*M*).

As indicated in Scheme 1, to date we have been able to characterize one example of such a system, $[(NMP)_3H_2][Co(CO)_4]_2$ (9; NMP = *N*-methylpiperazine), which is depicted in Fig. 5. $HCo(CO)_4$ was reacted with an excess of the diamine *N*-methylpiperazine, which contains both a tertiary and a secondary amine site. As in the reaction to produce (7), an excess of the diamine appears to promote species with N—H· · ·N hydrogen bonds, which we believe to be stronger than the N—H· · ·Co interactions. However, when *N*-methylpiperazine is used, the resultant secondary ammonium sites can form two hydrogen bonds, N—H· · ·N and N—H· · ·Co, as occurs in (9). Thus, (9) is a five-component hydrogen-bonded chain consisting of three diamine units and two transition metal moieties linked by a series of four hydrogen bonds. This example merely illustrates the possibilities of designing larger hydrogen-bonded networks that directly involve transition metal centres in the hydrogen-bonding interactions.

Stronger X—H· · ·M hydrogen bonds; X· · ·H· · ·M and M—H· · ·X hydrogen bonds

In recognizing the commonality between conventional hydrogen bonds and those which directly involve metal centres, it is important to question how far this commonality extends. Some of the issues which need to be addressed are the following:

(1) While it has long been established that symmetric (often called strong or short) hydrogen bonds can be formed, *i.e.* *X*· · ·H· · ·*X*, in which both *X*· · ·H (*X* = N, O, F) separations are substantially longer than covalent bond distances, the equivalent 'symmetric' *X*· · ·H· · ·*ML*$_n$* hydrogen bonds are presently unknown. To achieve the latter presumably both *X* and *ML*$_n$ need to be Brønsted bases of approximately equal basicity.

(2) Can *X*· · ·H—*ML*$_n$ hydrogen bonds be formed, *i.e.* hydrogen bonds in which the covalent interaction is with the metal centre? This issue has been addressed by others, but by no means satisfactorily resolved. Using Raman spectroscopy, Kristjánsdóttir, Norton, Moroz, Sweany & Whittenberg (1991) have investigated the interaction of $HCo(CO)_4$ with a variety of amines in low-temperature matrices. They concluded that interactions of the type Co—H· · ·N were not present. Epstein, Shubina, Krylov, Kreindlin & Rybinskaya

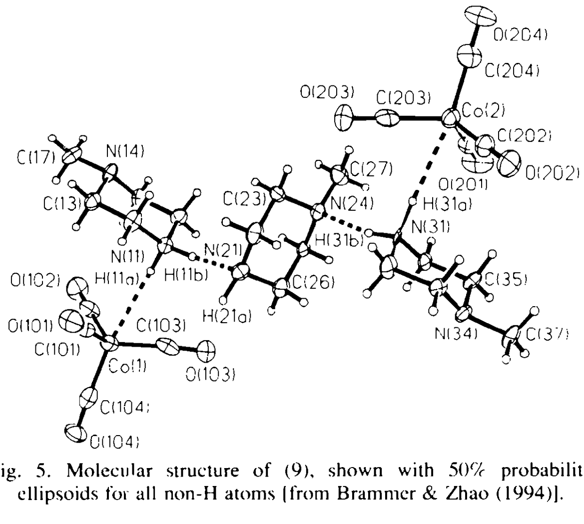


Fig. 5. Molecular structure of (9), shown with 50% probability ellipsoids for all non-H atoms [from Brammer & Zhao (1994)].

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* *ML*$_n$ refers to the fact that the metal centre in question (*M*) is also coordinated by other ligands (*L*).

Table 3. *Comparison of the geometries of* $R_3NH^+Co(CO)_3L^-$ *salts containing* N—H· · ·Co *hydrogen bonds with those of* $HCo(CO)_3L$ (L = CO, PR_3)

Compound	N· · ·Co (Å)	C_{eq}—Co—C_{eq} (°)	C_{ax}—Co—L_{eq} (°)	Temperature (K)	X/N/E*	References
$Et_3NH^+Co(CO)_4^-$ (6)	3.684 (2)	112.4 (1)	106.3 (1)	123.0 (5)	N	(*a*)
$[(NMP)_3H_2][Co(CO)_4]_2$ (9)	3.639 (1)	112.1 (9)	106.7 (7)	135 (5)	X†‡	(*b*)
$(DABCO)H^+Co(CO)_4^-$ (8)	3.437 (3)	111.2 (2)	107.2 (2)	135 (5)	X†‡	(*c*)
$Me_3NH^+Co(CO)_4^-$	3.402 (4)	113 (1)	106 (1)	295	X†§	(*d*)
$(DABCO)H^+Co(CO)_3PPh_3^-$ (12)	3.294 (6)	115 (3)	103 (3)	123 (5)	X†§	(*c*)
$HCo(CO)_4$	n.a.	117.3	99.7 (6)	238	E	(*e*)
$HCo(CO)_3PCy_3$	n.a.	118 (2)	99 (2)	296	X†§	(*f*)

* X = X-ray diffraction, N = neutron diffraction, E = electron diffraction.

† Averaged dimensions, with e.s.d.'s (in parentheses) are calculated according to $[\sum_i (d_i - \langle d\rangle)^2/n(n-1)]^{1/2}$ which thus reflect the scatter in the observed values, rather than e.s.d.'s of the individual values.

‡ All dimensions are averaged values.

§ Interligand angles are averaged values.

(*a*) Brammer *et al.* (1995). (*b*) Brammer & Zhao (1994). (*c*) Brammer, Zhao, Ladipo *et al.* (1995). (*d*) Calderazzo, Fachinetti, Marchetti & Zanazzi (1981). (*e*) McNeill & Scholer (1977). (*f*) Leigh & Whitmire (1989).

(1993) have suggested that such an interaction is present in the system $(\eta^5\text{-}C_5Me_5)_2Os—H^+\cdots O{=}PPh_3$, *i.e.* an Os—H· · ·O hydrogen bond. This assertion is based on solution IR data, which indicate diminished ν(Os—H) and ν(P=O) stretching frequencies. To achieve an *X*· · ·H—ML_n hydrogen bond it is clear that the ML_n fragment needs to be more basic than the *X* fragment.

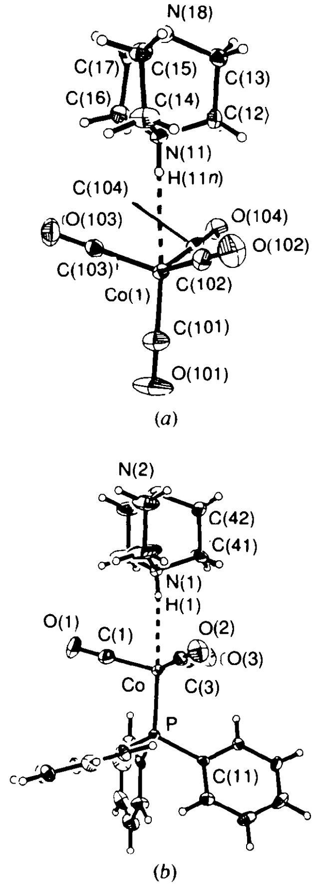

Fig. 6. (*a*) Structure of one independent 'molecule' of (8) and (*b*) structure of (12), with only the major (staggered) orientation of the diamine unit shown. Each structure is shown with 50% probabaility ellipsoids for non-H atoms.

With the possible exception of the work by Epstein *et al.* (1993), all hydrogen bonds observed to date that directly involve the metal centre in the 3*c*–4*e* interaction have been of the type *X*—H· · ·*M*. Working with cobalt salts of the type described above it seemed that we may be able to begin to address questions (1) and (2) and perhaps even provide crystallographic evidence to support the formation of *X*· · ·H· · ·ML_n or *X*· · ·H—ML_n hydrogen bonds. Replacing a CO ligand by a more electron-donating PR_3 or $P(OR)_3$ ligand to yield $R_3NH^+Co(CO)_3L^-$ salts, where L = PR_3 or $P(OR)_3$, should make the metal fragment more basic and lead towards (*a*) stronger hydrogen bonds, and (*b*) hydrogen bonds in which the proton is moved further towards the metal end of the three-centre interaction.

We have recently reported the preparation, variable-temperature NMR study and X-ray crystallographic characterization of $(DABCO)H^+Co(CO)_3PPh_3^-$ (12) (Brammer, Zhao, Ladipo *et al.*, 1995). A comparison of this salt with the related $(DABCO)H^+Co(CO)_4^-$ (8) clearly demonstrates that the N—H· · ·Co hydrogen bond is strengthened upon increasing the basicity at the metal centre. The structures of both salts are depicted in Fig. 6.

The simplest indication of the strengthening of the hydrogen bond is the decrease in the N· · ·Co separation from 3.437 (3) Å in (8) to 3.294 (6) Å in (12). Variable-temperature ^1H and ^{13}C experiments are consistent with this assertion. In toluene solution both salts are involved in a fluxional process which involves breaking and reforming the N—H· · ·Co hydrogen bond (*vide supra* for 8). The barrier to this process is greater for (12) than it is for (8) (Zhao *et al.*, 1995). An indication of the change in geometry that occurs at the metal centre as the hydrogen bond becomes shorter is presented in Table 3. The general trend across this series of compounds suggests that as the N· · ·Co separation decreases, and by inference the H· · ·Co separation decreases, the angle between the equatorial carbonyl ligands increases and a concomitant decrease in the C_{ax}—Co—L_{eq} angle occurs. Thus, this series of compounds could be considered as providing a model for the transfer of a proton from R_3NH^+ to $Co(CO)_3L^-$ in which the equatorial CO ligands move away for the incoming proton in an umbrella motion, ultimately yielding the products R_3N and $HCo(CO)_3L$. This is of course also relevant to understanding the reverse of this reaction, *i.e.* proton transfer by the metal hydride complex $HCo(CO)_3L$ to a substrate (see Bullock, 1991).

Finally, it is also worth mentioning that work by Stevens, Bau, Milstein, Blum & Koetzle (1990), Lee, Rheingold, Müller, Pregosin & Crabtree (1994), Park, Ramachandran, Lough & Morris (1994), Peris, Lee & Crabtree (1994), and Lee, Peris, Rheingold & Crabtree (1995) has shown that hydrogen bonds of the type $N—H\cdots H—M$ and $O—H\cdots H—M$ can be formed. Here the M—H group serves as a Lewis base, unlike proposed interactions of the type $X\cdots H—M$ where the M—H group would be a Lewis acid. Interactions of the type $X—H\cdots H—M$ are of importance in understanding proton transfer from a metal–dihydrogen complex $L_nM(\eta^2\text{-}H_2)$ to a substrate, and the reverse reaction, protonation of a metal hydride to yield a metal–dihydrogen complex.

Concluding remarks

The results described here clearly demonstrate the formation of hydrogen bonds that directly involve electron-rich transition metal centres as the hydrogen-bond acceptor. Criteria based upon NMR spectroscopic data, and geometric data from diffraction experiments, have been used to identify these interactions. Such data combined with orbital arguments show the commonalities between these 3*c*–4*e* interactions and conventional hydrogen bonds (*i.e.* not involving metal centres). Furthermore, these interactions can be distinguished from the more well known 3*c*–2*e* $X—H\cdots M$ interactions by application of the same criteria. The common link between $X—H\cdots M$ hydrogen bonds and conventional hydrogen bonds is further strengthened by the study of $(DABCO)H^+Co(CO)_4^-$ (8) and $(DABCO)H^+Co(CO)_3PPh_3^-$ (12), which shows that increasing the basicity of the hydrogen-bond acceptor (Co) strengthens the $N—H\cdots Co$ hydrogen bond.

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