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Hydrogen bonding in substituted-ammonium salts of the tetracarbonylcobaltate(− I) anion: some insights into potential roles for transition metals in organometallic crystal engineering

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Abstract

This review examines the supramolecular structures of substituted-ammonium salts of the tetracarbonylcobaltate(− I) anion, $Co(CO)_4^-$. The salts discussed contain cations of increasing complexity, ranging from simple tertiary ammonium cations, through cations consisting of dimeric or trimeric units, to a protonated tetraamine. Across the series distinct changes in the supramolecular structure are apparent. For the simplest cations the principal cation–anion interaction is a short (strong) direct N–H···Co hydrogen bond, which is augmented by longer (weaker) C–H···O hydrogen bonds. The availability of amine acceptor sites results in competition with the metal center for the available N–H donors and leads to the formation of dimeric, trimeric, and even polymeric $N–H^+···N$ hydrogen-bonded ammonium/amine cations. Such cations typically utilize all N–H donors, leaving cation–anion links to be formed solely through C–H···O hydrogen bonds. In the extreme case of the protonated tetraamine, a strong $N–H^+···N$ hydrogen bonded cation network is formed, the anions reside in channels and few cation–anion links are present. The $Co(CO)_4^-$ anion is revealed as a rich source of hydrogen bond acceptor sites. Three types are identified and discussed in detail, namely the metal center (Co), the carbonyl oxygens, and the carbonyl π-system. Further, in determining the overall supramolecular arrangement, it is clear that a balance exists between the effect of hydrogen bonds of different types (strengths) depending upon their relative populations. The observations presented in the review are discussed in the context of organometallic crystal engineering, and the potential roles for metal-mediated hydrogen bonding are illustrated.

Keywords: Crystal engineering; Supramolecular organometallic chemistry; Hydrogen bonding; Metal carbonyl compounds

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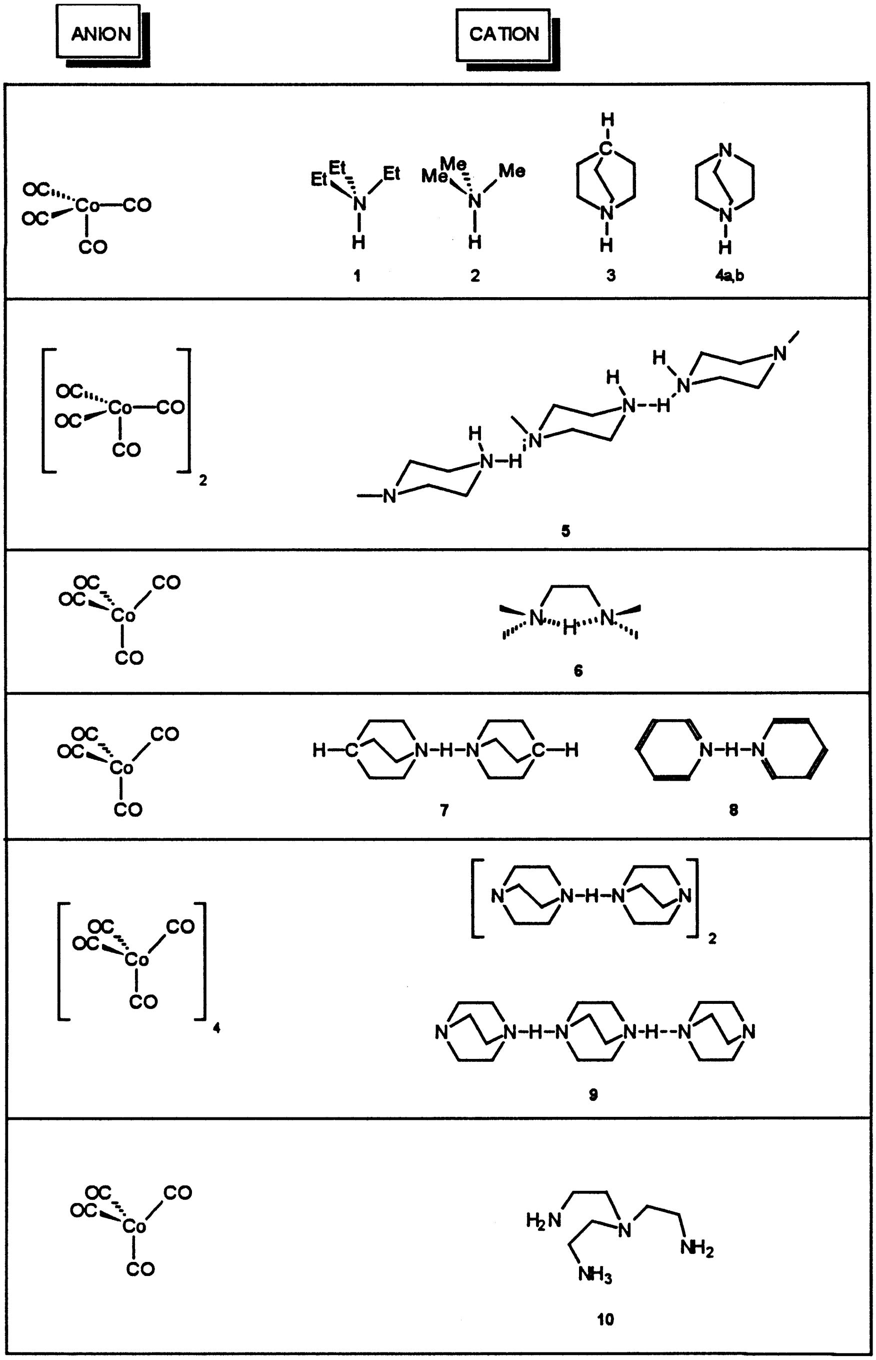
1. Introduction

Elucidation of the molecular structure of chemical compounds has been, and still is, the main objective in the large majority of the crystallographic studies. Until the 1960s the dependence of solid state properties upon both the molecular structure and crystal structure (or supramolecular structure) was not really appreciated [1]. It was then that Schmidt and coworkers [2] demonstrated that not only the distribution of atoms in a molecule, but also the distribution of molecules in a crystal, play an important role in the chemical and physical properties of the solid material. This work is generally regarded as marking the origin of what is now the exciting and emerging field of crystal engineering [3]. The aim of crystal engineering is the rational use of intermolecular interactions to design the supramolecular structure of crystalline materials. The ability to achieve controlled molecular self-assembly promises exciting applications in that it should allow the design of solid-state materials with predefined physical and chemical properties [4]. Such crystal design relies greatly on an understanding of the interactions taking place at the supramolecular level. However, traditionally such interactions have been included under the general and therefore quite uninformative classification of packing forces [5]. As we progressively increase our knowledge of these types of interactions, we should aim to be able to identify them and provide a more precise nomenclature [6]. Also, as our understanding of molecular self-recognition in crystals increases [7] so do our chances of achieving the actual crystal design. This summarizes the main objectives in crystal engineering, namely the understanding and exploitation of intermolecular interactions.

Crystal engineering must clearly rely substantially upon crystallography for the characterization of supramolecular arrangements in the solid state. However, although tens of thousands of crystal structures are determined annually relatively few are examined in great detail, at least beyond intramolecular geometries. The advancement of crystal engineering as a discipline will certainly require such analyses to become more commonplace.

The strength of hydrogen bonding interactions relative to other intermolecular interactions is well established. Therefore, it seems reasonable to expect that the distribution of molecules in crystals is often strongly dependent on the number and strength of inter- and intramolecular hydrogen bonding interactions. In spite of the increasing efforts to use hydrogen bonding interactions in the crystal engineering of organic systems (e.g. see Refs. [3,8]), comparatively less effort has been devoted to the role that metal centers can play in hydrogen bonding interactions that control the supramolecular structure of organometallic species. The first step towards possible extensive use of metal-influenced hydrogen bonding interactions in inorganic/organometallic crystal engineering is the systematic investigation of such interactions (see Section 1.1.1). With this in mind, in recent years our research and that of others has explored different types of hydrogen bonds in which metal centers play a role.

In this review the supramolecular structures of ten substituted-ammonium salts of the tetracarbonylcobaltate($-$I) anion, $Co(CO)_4^-$, will be discussed (Scheme 1). Each is prepared by the proton-transfer reaction between $HCo(CO)_4$ and the appropriate amine. It will be shown that the anion is a rich source of hydrogen bond acceptor sites. The metal can play a role in hydrogen bonding, either directly, as the acceptor atom, or indirectly through influence of the ligand hydrogen bonding sites. Further, in determining the final supramolecular arrangement, there is interplay between different types of hydrogen bonds, including that between stronger but less prevalent and weaker but more prevalent hydrogen bonds.



Scheme 1. Substituted-ammonium salts of tetracarbonylcobaltate(− I), **1**–**10**.

1.1. Brief survey of non-conventional hydrogen bonds

Historically, hydrogen bonds were considered to be confined to the interaction with a hydrogen atom of two strongly electronegative atoms, a donor D and an acceptor A, (D and A typically N, O, halogens), visualized as $D^{\delta-}-H^{\delta+}\cdots A^{\delta-}$ [9]. Such hydrogen bonds can be described as hard acid/hard base interactions, where the attractive force involved is primarily Coulombic; they are typically at least moderately strong hydrogen bonds (>5 kcal mol^{-1}). These are by far the most studied types of hydrogen bonds and hereafter in this review will be referred to as conventional hydrogen bonds.

However, the number of interactions being classified under the term 'hydrogen bond' continues to increase, with both new donor and new acceptor sites being identified. This is, in part, a consequence of the still uncertain definition of the term hydrogen bond itself [9]. Thus, on the donor side, it is now widely accepted that some C-atoms can act as hydrogen bond donors (soft acid/hard base type of hydrogen bond). It is also largely accepted that π-electrons can be acceptors and even that metals can serve either as donor or acceptor groups. For the purpose of the present review we will refer to all of these interactions as non-conventional hydrogen bonds.

1.1.1. Participation of transition metals in hydrogen bonding interactions

The participation of a metal in hydrogen bonding interactions can be essentially divided into two categories based on the domain at which those interactions operate. Firstly, there are hydrogen bonding interactions where the metal plays a direct role in the hydrogen bond. These interactions operate in what has been described elsewhere as the metal domain [10]. In organometallic and/or inorganic molecules the metal domain is the core of the molecule, therefore the domain containing the metal or metals. Secondly, there are numerous cases of hydrogen bonding interactions where the metal participates indirectly. Hydrogen bonding involving indirect participation of a metal primarily takes place in the following two domains:

1. the so-called *ligand domain*, defined as the region delimited by the atoms at the immediate surrounding of the metal (metal domain), i.e. the atoms directly bound to the metal. Some of these atoms may be potential hydrogen bond donors and/or acceptors.
2. the *periphery domain* or region formed by the peripheral atoms or functional groups of the metal-bound ligands which in some cases can participate in hydrogen bonding (Fig. 1).

The direct participation of the metal in hydrogen bonding can be divided into two subclasses. Thus, the metal can serve as the hydrogen bond acceptor, $D-H\cdots M^{\delta-}$ ($D=$ hydrogen bond donor), typically requiring low oxidation-state metals and/or late transition metals (Fig. 2). Such interactions have received recent attention in our own work [11] and that of others [12] and have been the subject a short review ([11]d).

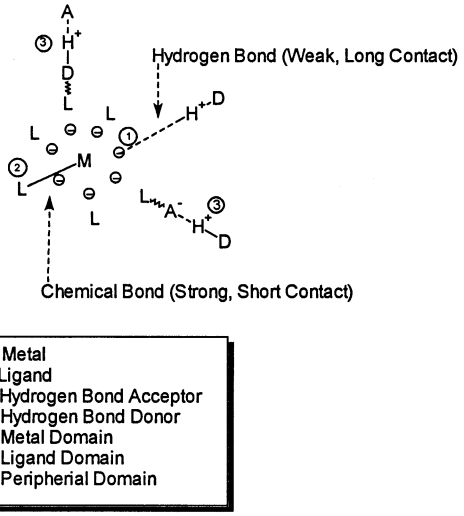


Fig. 1. Illustration of hydrogen bonding interactions showing metal participation in the different domains.

There are also cases where the polarity of the M–H bond allows the metal to behave as the hydrogen bond donor (acidic behavior), visualized as $M^{\delta-}-H^{\delta+}\cdots A^{\delta-}$ [13] (A = hydrogen bond acceptor) (Fig. 3). It is important to point out that the importance of hydrogen bonds in which the metal participates directly goes beyond their potential applications in crystal engineering of non-organic crystals. Thus, we have previously suggested the possible role of interactions of D–H···M

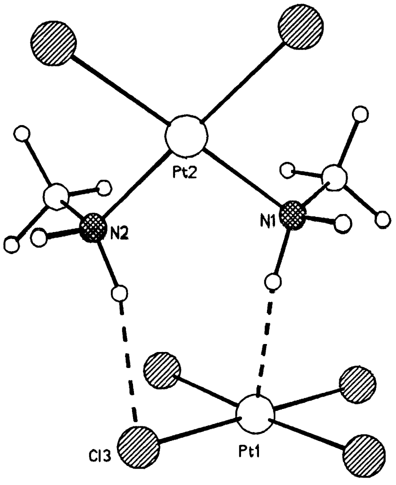


Fig. 2. Illustration of an intermolecular N–H···Pt (and N–H···Cl) hydrogen bond in $[NPr^n_4]_2[PtCl_4]\cdot$*cis*-$[PtCl_2(NH_2Me)_2]$. Drawn using coordinates from Ref. ([11]a).

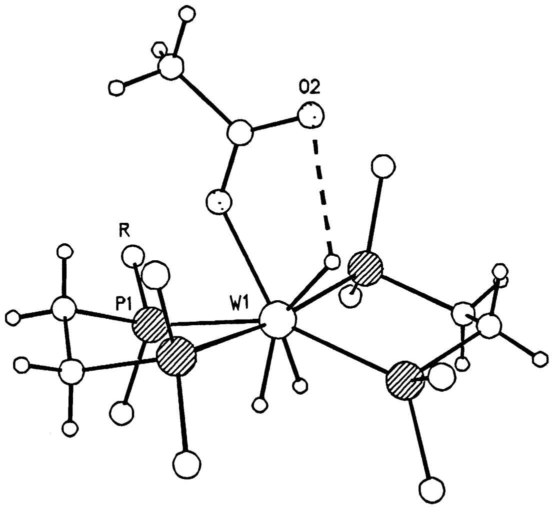


Fig. 3. Illustration of the W–H···O hydrogen bond in the compound [$WH_3(\eta^1$-OCOMe)(dppe)$_2$] {dppe, 1,2-bis(diphenylphosphinoethane)}. Drawn using coordinates form Ref. ([13]b).

hydrogen bonds in oxidative addition reactions at some metal centers ([11]d). It is also reasonable to anticipate that D–H···M and M–H···A hydrogen bonds may play a role in the protonation/deprotonation of metal centers.

The cases of hydrogen bonding in which the metal participates indirectly are interactions between metal-bound ligands. The influence of the metal upon these hydrogen bonds will depend upon the domain in which the hydrogen bond donor or acceptor lies. For donors and acceptors in the ligand domain, the metal can exert an electronic influence on the donor or acceptor through the electron donation/back-donation involved in metal–ligand bonding. This will in some cases affect the availability of ligand lone pairs, i.e. the strength of the hydrogen bond acceptors, while in other cases, the effect will be on the polarity or acidity of the donor–hydrogen (D–H) bond, i.e. the strength of the hydrogen bond donors [14]. Moreover, in some instances, it is found that the coordination of a particular atom or molecule to a metal results in a dramatic enhancement of its ability to participate in hydrogen bonding interactions. A good example is presented in a recent survey of the Cambridge Structural Database (CSD) [15] that compares the geometries of hydrogen bonding interactions involving metal-bound chlorine, the chloride ion and carbon-bound chlorine as the H-bond acceptors. This work clearly demonstrates that M–Cl groups are excellent acceptors (likewise Cl^- ions) while the C–Cl moieties (conventional organic system) are poor acceptors [16]. Similarly while organic hydrogen atoms (C–H groups) are clearly unsuited to be hydrogen bond acceptors, it has been shown, remarkably, that their metal-bound counterparts, M–H, can serve as hydrogen bond acceptors, viz. $D^{\delta-}-H^{\delta+}\cdots H^{\delta-}-M^{\delta+}$ [17]. Particularly pertinent to the present review is the enhancement of the acceptor capability of carbonyl ligands upon coordination to metal centers [18], vide infra.

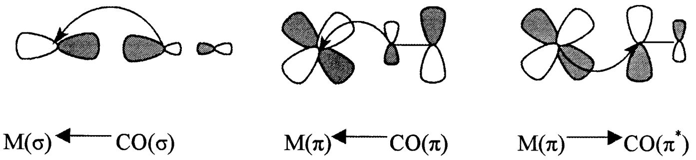


Fig. 4. Schematic representation of a molecular orbital (MO) description of the M–CO bonding interaction.

1.1.2. Carbonyl ligands as Lewis bases

Carbon monoxide is a classical example of a π-acid ligand. Thus, bonding between the CO and the transition metal in metal carbonyl complexes involves (i) σ-donation of electron density from a CO σ-molecular orbital (which has predominant C-character) to an empty σ-orbital on the transition metal, and (ii) π-back-donation from filled π-orbitals on the metal to the empty π^*-molecular orbital of the CO ligand (also of predominant C-character) (Fig. 4). The extent to which the π-back-donation occurs determines the basicity of the O-atom and polarity of the C≡O bond, and therefore the capability of the oxygen to act as a Lewis base. It is important to note that the extent to which the π-back-donation occurs depends on several factors associated both with the metal and its coordination environment. Thus, the basicity of the CO ligand depends among other factors on the oxidation state and the number of electrons in the d-orbitals of the metal, as well as on the characteristics of the other ligands present in the coordination sphere of the metal. The basicity of the electron pairs located at the O-atom leads to interactions where the metal-bound CO behaves as a Lewis base [18,19]. The species that interact with the CO in an acid–base fashion include hard acids such as alkali and alkaline-earth metals [19] as well as hard acid hydrogen bond donors, e.g. O–H groups ([18]b). However, it is also common in organometallic crystal structures to find interactions with soft acids such as C–H groups ([18]c).

These interactions show a remarkable directional preference. The Lewis acid species tend to approach the carbonyl O-atoms at angles closer to the ketonic directions than end-on ([18]b,c). This suggests an M–CO bonding interaction more in agreement with the valence bond (VB) description of M–CO bonding illustrated on the right hand side of Fig. 5.

1.1.3. Importance of C–H···O hydrogen bonding interactions in crystals

The idea of C–H···O hydrogen bonding interactions is not new, and in fact is attributed to Glasstone in 1937 [20]. The experimental observation that in some cases the ν(CH) was shifted considerably to lower wavenumbers in the presence of

Fig. 5. Simple valence bond (VB) description of the M–CO bond showing the expected direction of approach of Lewis acids.

electronegative atoms or potential hydrogen bond acceptors led spectroscopists to suggest and accept the idea of C–H···O interactions as hydrogen bonds [21]. Moreover, a shift to lower wavenumbers in the ν(CH) is not indispensable and there are cases where the existence of C–H···O hydrogen bonds is not accompanied by such a shift [22]. However, possibly the first attempts at a systematic crystallographic investigation of this type of interactions can be attributed to Sutor [23]. Sutor suggested that C–H···O hydrogen bonds might play an important role in determining the structures of organic crystals. Although at that point these suggestions were considered speculations, following the work of Taylor and Kennard [24] they are generally accepted as being correct. The topic of C–H···O hydrogen bonding has been the subject of recent reviews [25].

Indeed, nowadays, it is accepted that in some cases the C–H···O hydrogen bonds can be important in stabilizing unfavorable molecular conformations [26] and even useful in supramolecular design and crystal engineering [27]. The reason for the importance of these C–H···O hydrogen bonds both in the molecular and supramolecular structural features of organic crystals is surely not the strength of such attractive interactions but rather their abundance in organic compounds (both C–H and CO groups are very common in organic species). Clearly the analogue in organometallic chemistry is the large number of known metal carbonyl complexes. In many cases in such complexes the CO ligands are accompanied by ligands containing C–H groups. Therefore, one can anticipate, assuming a similarity with organic crystals, that C–H···OC–M hydrogen bonding interactions play an important role in determining the supramolecular structure of metal carbonyl complexes. In fact the importance of these interactions in solid state structures of transition metal carbonyl complexes is a topic which has been recently reviewed by Braga and Grepioni ([18]b).

1.1.4. C–H···π hydrogen bonds and their importance

Recent work has shown that the π-electrons of multiple bonds (and aromatic rings) can act as hydrogen bond acceptors in organic systems [28–30]. Examples include simple systems, such as the crystal structure of acetylene ([29]a) or the adduct of alkynes and arenes with HCl ([29]b,c), as well as inclusion compounds ([30]a,b,f). However, D–H···π interactions are still relatively uncommon in the literature, although a contributing factor is that until recently they have been often overlooked. Of such interactions, perhaps greatest the controversy exists for C–H···π hydrogen bonds, which can be regarded as interactions between a soft acid and a soft base. While C–H···π hydrogen bonds in highly activated systems such as terminal acetylenes are unambiguously attractive interactions ([29]a, [30]c,d), recent studies show, to quote the authors, that "the grey area between the weak (C–H···π) hydrogen bonds and the herringbone interaction (common in arene structures) is gradually diminishing" ([30]f).

In organic chemistry C–H···π hydrogen bonds can be important in determining molecular conformation, which leads in some cases to reaction selectivity ([28]a). An important role in molecular recognition of biological molecules has also been ascribed to C–H···π interactions ([28]b) (and to N–H···π interactions [31]). Similar

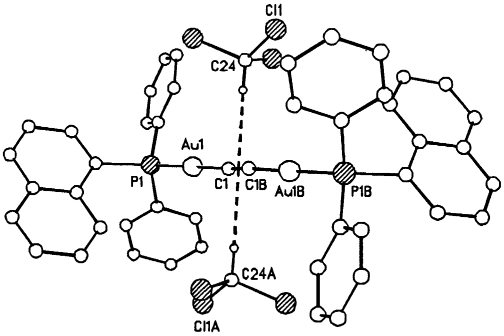


Fig. 6. C–H···π interactions in an organometallic complex described in Ref. ([32]a), from which the atomic coordinates were also taken.

to the case of C–H···O hydrogen bonds, the importance of C–H···π interactions is due to their abundance rather than their strength. Moreover, recent efforts suggest that in selected systems C–H···π interactions may be useful in crystal engineering ([30]d).

To the best of our knowledge, reports in the literature of C–H···π hydrogen bonds for inorganic and organometallic species are rare [32] and in any case much less common than for organic compounds. However, an illustration of the potentially important role of transition metals in the strength of such hydrogen bonds is found in the metalloalkyne compound shown in Fig. 6. Here the C–H···π interaction adopts the theoretically predicted T-shaped geometry and the H···π separation (2.42 Å) was found to be significantly shorter than that observed in related organic species ([32]a). As the authors point out, the hydrogen bond is strengthened due to the back-donation from the metal to the C≡C bond. In a forthcoming article we will discuss the occurrence of D–H···π hydrogen bonds (D = C, N, O) in which the acceptor π system is that of a carbonyl ligand [33]. Examples of this latter hydrogen bond in the salts pertinent to this review are discussed in Section 4.3.

1.2. The $[Co(CO)_4]^-$ anion as a source of multiple hydrogen bond acceptor sites

As mentioned previously, the basicity of the lone pairs at the oxygen in metal carbonyl complexes largely depends on the metal d-orbital population. Considering this and the fact that most hydrogen bonds are primarily electrostatic interactions, the simplest terminal metal carbonyl complex and arguably one of the most suited to yield strong D–H···O hydrogen bonds is the tetracarbonylcobaltate(– I) anion, $[Co(CO)_4]^-$. With filled metal d-orbitals (Co(– I) is a d^{10} system) and an overall negative charge one can expect a substantial π-back-donation from the Co to the CO ligand (as noted by IR spectroscopy, viz. ν(CO) 1890 cm^{-1}). The increased basicity of the lone pairs at the O-atoms, and the fact that hydrogen bonding interactions involving this anion in salts of the type $[R_3NH][Co(CO)_4]$ will be charge-assisted ([12]k) might be expected to lead to networks involving D–H···OC–M hydrogen bonds as a major cohesive force in the observed crystal structures.

However, the electron-rich and sterically uncrowded metal center can also become directly involved as the acceptor in hydrogen bonding interactions. Such hydrogen bonds in the family of salts $[R_3NH][Co(CO)_4]$ are of the type N–H···Co, and often form the closest link between anions and cations.

Finally, the tetracarbonylcobaltate(− I) anion provides one further type of unconventional hydrogen bond acceptor site, namely the π-electrons of the C≡O multiple bonds. The role of this type of interaction in organometallic compounds will be discussed in greater detail in a forthcoming article [33].

Hydrogen bonding interactions dominate the arrangements of anions and cations in the salts discussed in this review. The general patterns and typical geometries of these hydrogen bonds will be discussed as well as effects upon molecular geometry and conformations. While the examples presented are not intended to comprise a systematic effort to engineer crystals based upon the $[R_3NH][Co(CO)_4]$ salts, analysis of the hydrogen bonding interactions in which they participate provides a useful illustration of the range of possibilities available for application in organometallic crystal engineering.

1.3. Criteria for identifying hydrogen bonds from crystal structure data

Crystallography is the most powerful technique for directly determining accurate interatomic geometries in the solid state. Identification of hydrogen bonds from crystallographic data must, of necessity, rely upon the use of distance cutoffs to assess the presence of hydrogen bonds. The use of distance criteria in assessing hydrogen bonds is clearly most applicable when examining geometric data by statistical means for a large number of hydrogen bonds. For individual structures, such distance information should of course be used with care in the absence of corroborating evidence from other experimental (e.g. IR spectroscopy) or theoretical techniques, since the crystal structure necessarily represents a balance of all intermolecular interactions. Nevertheless, some guidance based upon distances (and by inference angles) in identifying hydrogen bonds important in supramolecular arrangements of molecules is essential in studying hydrogen bonding.

An early suggestion made by Hamilton and Ibers ([9]b) was that a D···A separation less than the sum of van der Waals radii should be a necessary but not sufficient condition for a hydrogen bond. However, hydrogen bonds, particularly weaker (longer) examples, arise due to a predominantly electrostatic attraction, which has an r^{-1} dependence (assuming primarily monopole–monopole and monopole–dipole interactions) ([9]d). Thus, hydrogen bonds can be attractive to distances greater than the sum of van der Waals radii of the donor and acceptor groups, and indeed to distances beyond the sum of van der Waals radii of H + A. This topic has been addressed by a number of authors {for example ([9]d, [24,25])} and has been the source of a lively exchange in the very recent literature [34].

In this present review, we adopt we discuss a variety of hydrogen bond types in the series of salts examined. Where distance criteria alone are used, a upper limit for the H···A separation equal to the sum of van der Waals radii of H + A and an angle at the hydrogen of $> 110°$ has been adopted. Specifically, for D–H···O and

D–H···π hydrogen bonds (D = C, N) an upper limit of 2.7 Å for H···O or H···π (midpoint) has been used throughout.

2. Hydrogen bonding involving cobalt as the acceptor

The preparation and characterization of salts of the type $[R_3NH][Co(CO)_4]$ were first reported by Calderazzo and coworkers ([12]a) (for R = Et **1**, Me **2**). However, the room temperature X-ray diffraction studies of these salts left open the interpretation of the cation–anion interaction. Later, Horwitz and Shriver [19] suggested that these salts posses an N–H···Co hydrogen bond, whereas Creutz and Sutin [35] suggested that N–H···O hydrogen bond(s) may be involved. A neutron diffraction study of $[Et_3NH][Co(CO)_4]$ **1** finally clearly established the position of the ammonium hydrogen and identified an N–H···Co hydrogen bond as the primary cation–anion link ([11]b). The N–H bond is slightly elongated at 1.054(1) Å, and the interaction is linear.

In order to examine factors affecting the strength of this 'novel' type of hydrogen bond, other amines with different steric requirements (size) and electronic properties (basicity) were used to prepare three additional analogues **3**, **4a**, **5**. Further analogues in which cobalt basicity has been increased by replacing CO by phosphine ligands have also been prepared ([11]e, [36]a) but will not be discussed in this review. The N–H···Co hydrogen-bonded salts were investigated by both spectroscopic and crystallographic means.

2.1. Spectroscopic studies

Compounds **1**, **2**, **3**, and **4a** have been characterized in solution by NMR and IR methods, with variable temperature ^{1}H- and ^{13}C-NMR experiments being conducted for **3** ([36]a) and **4a** ([11]e).

NMR studies clearly demonstrate the persistence of the N–H···Co hydrogen bonding interaction in non-polar solvents. The N–*H* protons appear in the range δ 7–13 ppm, depending upon the compound in question, solvent and temperature. C–*H* protons are shielded in non-polar solvents relative to polar solvents, an effect that is enhanced upon lowering the temperature. This is consistent with the fact that the ions exist as ion pairs linked via the N–H···Co hydrogen bond in non-polar solvents, but as solvent separated ions in polar solvents. The shielding of the C–*H* protons is most probably explained in terms of their proximity to the electron density of the carbonyl groups due to the short cation–anion separation.

Although the N–H IR bands could not unambiguously be assigned for these salts, indirect evidence of the presence of N–H···Co hydrogen bonds in non-polar solvents, and their absence in polar solvents, comes from the number and position of the carbonyl IR bands (Table 1). The N–H···Co interaction expresses itself geometrically by distorting the geometry of the tetracarbonylcobaltate(– I) anion from tetrahedral (T_d) to pyramidal (C_{3v}), a fact confirmed by crystallographic studies (vide infra). In polar solvents where the salts exist as solvent separated ions, the anion is undistorted (T_d), leading to only one IR active carbonyl stretch (T_2 band). In non-polar solvents distortion of the anion to C_{3v} symmetry as a result of the hydrogen bond leads to three IR-active carbonyl bands ($2A_1 + E$). Furthermore, the hydrogen bonded salt shows ν(CO) bands shifted to lower wavenumbers relative to $HCo(CO)_4$ (also of C_{3v} symmetry), an indication of the increased π-back-donation from the Co to the carbonyl ligands in the hydrogen bonded salts compared to the hydride.

2.2. Crystallographic studies

The strength of the N–H···Co hydrogen bonds in the resulting solid-state structures is inferred from the geometry of the salt, which has been analyzed on the basis of three structural features: (i) the Co···N (Co···H) separation, (ii) the N–H···Co angle, and (iii) the CO_{eq}–Co–CO_{eq} angles (where CO_{eq} is an equatorial carbonyl). Table 2 summarizes this structural information.

From these structural data it can be seen that in the crystalline state the strength of the N–H···Co hydrogen bond, as inferred by the N···Co (or H···Co) separation, is sensitive both to the steric requirements of the cation and electronic effects (i.e. acidity of the ammonium ion or basicity of the amine). On electronic grounds, the strongest hydrogen bond should be expected when the acidity of the ammonium ion is most similar to that of $HCo(CO)_4$ (estimated pK_a of zero in aqueous solution). Thus, considering the acidity of the ammonium ion as the only factor affecting the strength of the N–H···Co hydrogen bond the expected sequence of hydrogen bond lengths should be $\mathbf{3} \approx \mathbf{1} > \mathbf{2} \approx \mathbf{4} > \mathbf{5}$ (consistent with increasing acidity of the ammonium ion). On the other hand, based exclusively on the steric requirements of

Table 1
IR bands for the carbonyl region of salts of general formula $X^+Co(CO)_4^-$ (X^+ = alkylammonium, alkylphosphonium or alkali metal) and $HCo(CO)_4$

Compound	ν(CO) (cm^{-1})	Solvent	Type of cation–anion interaction	Anion symmetry
$HCo(CO)_4$[a]	2117, 2054, 2023	CH_3CN	n.a.	C_{3v}
$Et_3NH^+Co(CO)_4^-$ **1**	2015, 1931, 1895	$C_6H_5CH_3$	N–H···Co	C_{3v}
$Et_3NH^+Co(CO)_4^-$ **1**	1892	CH_3CN	Solvent separated	T_d
$DabcoH^+Co(CO)_4^-$ **4a**	2020, 1935, 1898	$C_6H_5CH_3$	N–H···Co	C_{3v}
$DabcoH^+Co(CO)_4^-$ **4a**	1892	CH_3CN	Solvent separated	T_d
$QuinH^+Co(CO)_4^-$ **3**	2020, 1931, 1896	$C_6H_5CH_3$	N–H···Co	C_{3v}
$QuinH^+Co(CO)_4^-$ **3**	1891	CH_3CN	Solvent separated	T_d
$Na^+Co(CO)_4^-$[a]	1890	Diglyme	Solvent separated	T_d
$Me_3PH^+Co(CO)_4^-$[b]	2002, 1901, 1886	THF	P–H···Co	C_{3v}

[a] See Ref. [49].

[b] See Ref. ([12]e).

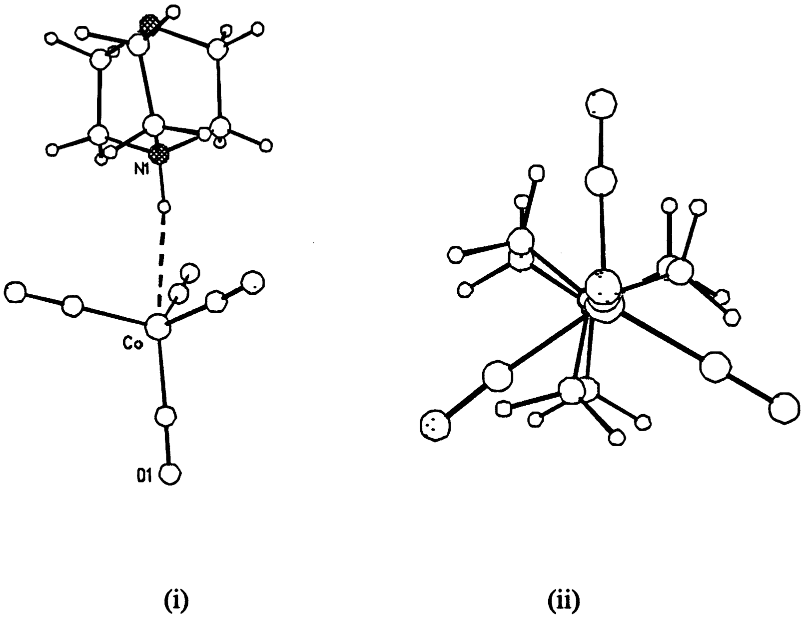
Table 2
Geometries of the N–H···Co hydrogen bonds[a] for the different alkylammonium salts of $Co(CO)_4^-$

Cation	N···Co (Å)	H···Co (Å)	N–H···Co (°)	CO_{eq}–Co–CO_{eq} (°)
Et_3NH^+ (**1**)	3.684	2.632	180	112.4
[(*N*-Methylpiperazine)$_3H_2]^{2+}$ (**5**)	3.639	2.592	175.5	112.1
(Quinuclidine)H^+ (**3**)	3.563	2.519	172.4	111.7
(Dabco)H^+ (**4a**)	3.437	2.392	173	111.2
Me_3NH^+ (**2**)	3.389	2.340	179.6	112.7

[a] N–H distances extended to 1.05 Å as observed by neutron diffraction in **1**.

the cation the sequence should be $\mathbf{1} > \mathbf{2} \approx \mathbf{3} \approx \mathbf{4} \approx \mathbf{5}$. Therefore, combining the two effects one might estimate the N–H···Co hydrogen bond length sequence to be $\mathbf{1} > \mathbf{3} > \mathbf{4} \approx \mathbf{2} > \mathbf{5}$. From the experimental crystallographic data the actual sequence turns out to be $\mathbf{1} > \mathbf{5} > \mathbf{3} > \mathbf{4} > \mathbf{2}$. This indicates that the experimental and expected sequences agree very well, the only major exception being the anomalous behavior of compound **5**. The N–H···Co hydrogen bond in **5** is longer (weaker) than expected. However, this can be attributed to the fact that the secondary ammonium center that forms the N–H···Co hydrogen bond is also involved in N–H···N hydrogen bonding through its second hydrogen.

Another interesting observation is the unexpected magnitude of the difference between **3** and **4a** despite their chemical similarity. The N–H···Co hydrogen



(i) (ii)

Fig. 7. Molecular structure of **4a.** (i) The short cation–anion contact via the N–H···Co hydrogen bond from a perpendicular view. (ii) The staggered cation–anion conformation.

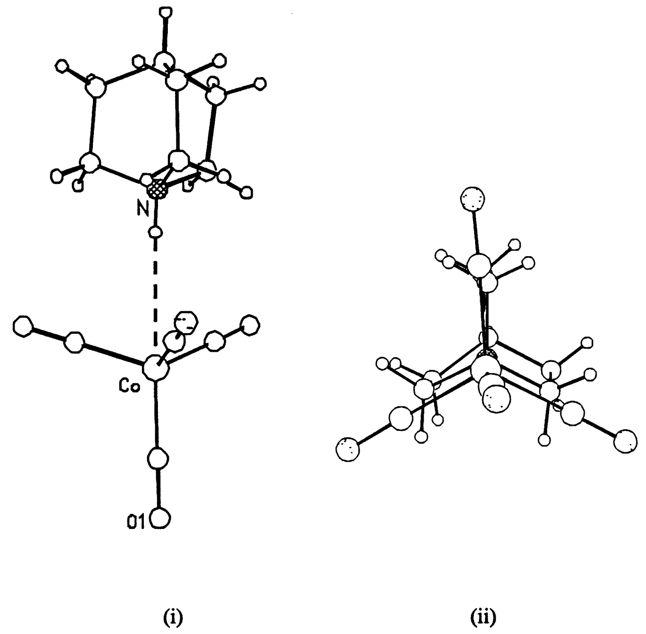


Fig. 8. Molecular structure of **3**. (i) View perpendicular to the N–H···Co hydrogen bond and (ii) View showing the eclipsed cation–anion conformation.

bond in **3** (H···Co 2.519 Å) is substantially longer than that in **4a** (H···Co 2.392). Moreover, the replacement of the amine nitrogen in **4a** by a C–H group in **3** leads to a conformational change of the methylene groups of the cation with respect to the three equatorial carbonyls of the anion (Figs. 7 and 8). Thus, the cation–anion units in **4a** adopt a staggered conformation while in **3** they adopt an eclipsed conformation about the N–H···Co bond.

Compensation for this loss of conformational energy within the hydrogen bonded ion-pair of **3** must therefore be derived from the overall energy associated with the intermolecular interactions that lead to its particular supramolecular architecture. Indeed, there are changes in hydrogen bonding arrangements that affect the supramolecular structure of these two salts, as one might anticipate when replacing a potential hydrogen bond acceptor (N in **4a**) by a potential hydrogen bond donor (C–H in **3**). These changes are discussed in more detail in Section 4.

3. Ionic N–H^{+}···N hydrogen bonds: an alternative to N–H···Co hydrogen bonds

Although N–H···Co hydrogen bonds often provide the closest cation–anion contact, in some cases, the formation of such hydrogen bonds may be prevented by the presence of other electronegative atoms such as N and O that can serve as good hydrogen bond acceptors. This is perhaps not so surprising, as

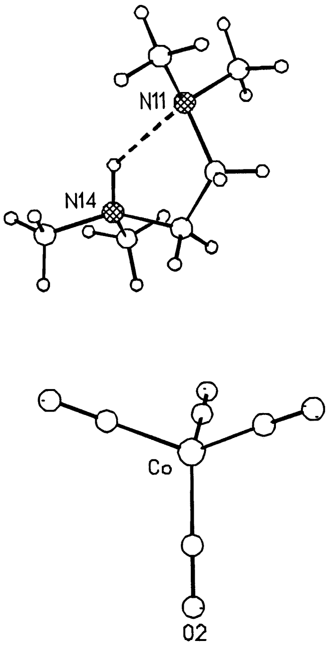


Fig. 9. Molecular structure of **6**, showing the intramolecular $N-H^{+}\cdots N$ hydrogen bond. Coordinates taken from Ref. [37].

$N-H^{+}\cdots N$ and $N-H^{+}\cdots O$ hydrogen bonds often lead to stable ion-molecule complexes in organic and biological systems. In the organometallic salts under discussion here, this situation arises primarily due to $N-H^{+}\cdots N$ hydrogen bond formation, which in turn requires additional amine(N) acceptor sites to compete with the metal center for the ammonium proton. Additional amine(N) sites can arise either: (i) when the salts of monoamines are prepared in the presence of an excess of the amine, or (ii) when salts of polyamines are prepared.

3.1. Intramolecular $N-H^{+}\cdots N$ hydrogen bonds

The major product of the proton transfer reaction between $HCo(CO)_4$ and tetramethylethylenediamine (TMEDA) is the salt **6** shown in Fig. 9. Here the diamine has a flexible backbone, which following protonation allows formation of a five-membered $N-H^{+}\cdots N$ hydrogen bonded ring [37], rather than an $N-H\cdots Co$ hydrogen bonded salt.

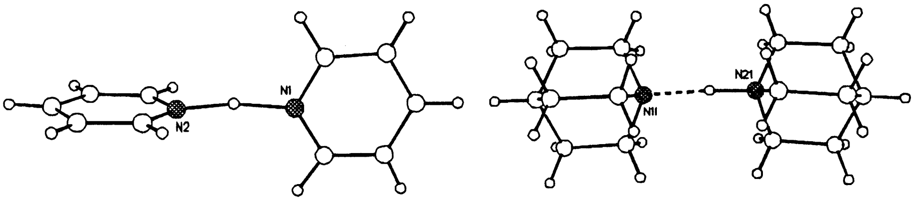
3.2. Formation of ammonium/amine dimers and trimers

In two cases, compounds **7** [36]and **8** [37], the salts were prepared by protonation of a monoamine in the presence of an excess of that amine, quinuclidine and pyridine, respectively. This resulted in the formation of salts,

$[R_nNH\cdots NR_n]^+[Co(CO)_4]^-$ ($n = 2$ or 3), comprising cationic $N–H^+\cdots N$ hydrogen bonded ammonium/amine dimers, which are then linked via weaker $C–H\cdots O$ hydrogen bonds to $Co(CO)_4^-$ anions. The supramolecular structures resulting from the cation–anion links are discussed in greater detail in Section 4. However, it is important to comment on the torsional flexibility of these cationic dimers as it pertains to their potential involvement in, and accommodation of, different supramolecular arrangements. In principal such $[R_nNH\cdots NR_n]^+$ cations have somewhat restricted rotational freedom about the (linear) $N–H^+\cdots N$ linkage (see Fig. 10), with the minimum energy conformations for the isolated cation being a staggered arrangement of the carbon substituents of the two nitrogens. As with all hydrogen bonds, some flexibility of the $N–H^+\cdots N$ hydrogen bond length is also available at an energetic cost. In the solid state, the energetic cost of deviations from the staggered conformation as well as hydrogen bond lengthening can be compensated by formation of new interactions, e.g. other hydrogen bonds. One can speculate that in the $[R_nNH\cdots NR_n][Co(CO)_4]$ salts, such compensation will be associated with the formation of strengthened or perhaps additional $C–H\cdots O$ hydrogen bonds.

Comparison of the $[R_nNH\cdots NR_n]^+$ cations in **7** and **8** illustrates these points. While the pyridinium/pyridine cation in **8** adopts a staggered conformation (interplanar angle 90°) with an $N\cdots N$ separation of 2.634 Å, the quinuclidinium/quinuclidine cation in **7** adopts an eclipsed conformation with a longer $N\cdots N$ separation of 2.689 Å. In these two cases the $C–H\cdots O$ hydrogen bonds that link the cations and anions are different in number as well as mean length (viz. strength), with fewer, but shorter $C–H\cdots O$ hydrogen bonds being formed in **8**. One is thus drawn to the conclusion that it is the greater number of $C–H\cdots O$ hydrogen bonds formed by **7** that provides sufficient energetic compensation to permit the eclipsed conformation and longer $N\cdots N$ separation.

The crystal structure of **9**, $[(DABCO)_3H_2][(DABCO)_2H]_2[Co(CO)_4]_4$ [38], remarkably contains both staggered and eclipsed forms of $N–H^+\cdots N$ bonded dimeric monocations, $[(DABCO)\cdots H\cdots(DABCO)]^+$, as well as trimeric dications,



(i) (ii)

Fig. 10. Illustration of the conformational flexibility about the $N–H^+\cdots N$ hydrogen bond in $[R_nNH\cdots NR_n]^+$ cations (N atoms shaded). (i) Staggered pyridinium/pyridine cation in **8**, and (ii) eclipsed quinuclidinium/quinuclidine cation in **7**.

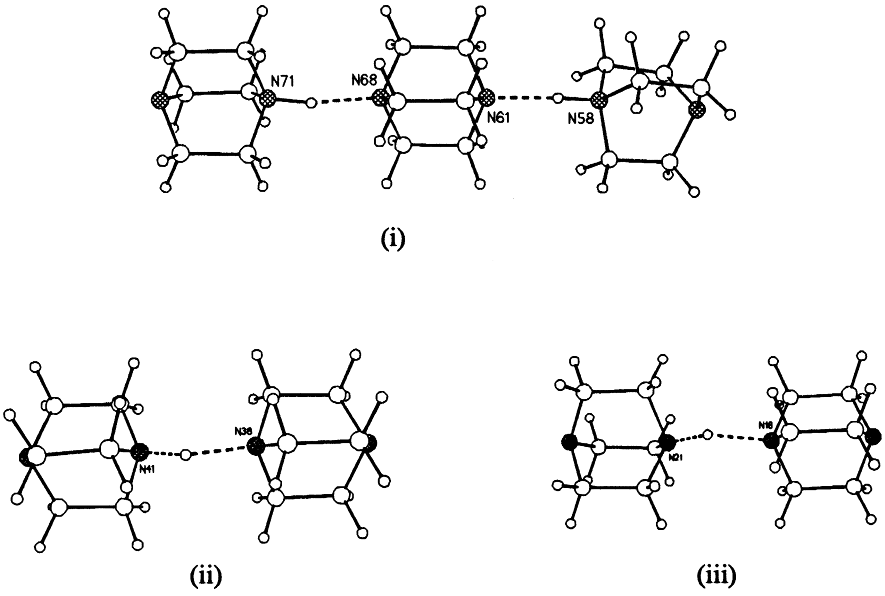


Fig. 11. Molecular structures of the hydrogen bonded cations which comprise **9** (N atoms shaded). (i) $[(DABCO)_3H_2]^{2+}$, (ii) $[(DABCO)_2H]^+$ (eclipsed form), and (iii) $[(DABCO)_2H]^+$ (staggered form).

[(DABCO)···H···(DABCO)···H···(DABCO)]$^{2+}$, linked by two such hydrogen bonds (Fig. 11). Both the staggered and eclipsed forms of the DABCO dimer have approximately symmetrical N···H$^+$···N hydrogen bonds, consistent with the short N···N separations (2.649(9) Å for each dimer). 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. The latter (shorter) separation is between two DABCO moieties that adopt a mutually staggered conformation. The third DABCO moiety [N(51)—N(58)] adopts a conformation intermediate to that of the other two DABCO moieties. Overall this structure further illustrates the conformational flexibility of these dimeric and trimeric hydrogen bonded cations, suggesting their adaptability to a variety of supramolecular arrangements. It should be noted that trimeric units such as that in **9** are uncommon. The only other examples that we are aware of involve further hydrogen bonding to anions, as in the [Br···H···(DABCO)···H···(DABCO)··· H···(DABCO)···H···Br] unit [39] and as observed in compound **5** (vide infra).

[(*N*-Methylpiperazine)$_3$H$_2$][Co(CO)$_4$]$_2$ **5** exists as N–H$^+$···N hydrogen bonded trimers of *N*-methylpiperazine/piperazinium, which are capped at each end by Co(CO)$_4^-$ anions that interact via N–H···Co hydrogen bonds as described in Section 2 ([11]c). The pentameric unit is further linked through C–H···O hydrogen bonds (Fig. 12), which also link the pentameric units together as is described in more detail in Section 4.

3.3. Formation of cationic ammonium/amine extended networks

We have already seen structures in which the $Co(CO)_4^-$ anion interacts with a monomeric cation based upon DABCO (**4a**), and with dimeric and trimeric cations derived form the same diamine (**9**). $[DABCO][Co(CO)_4]\cdot THF$ **4b** ([36]b) further extends the range of salts and structures that can be obtained from the reaction of $HCo(CO)_4$ and DABCO. **4b**, in contrast to **4a**, contains infinite parallel cationic chains $[(DABCO)\cdots H^+\cdots]_n$, which are then linked through C–H···O hydrogen bonds to $Co(CO)_4^-$ anions that lie in the channels between these chains (Fig. 13). A structure related to **4b** containing $[(DABCO)\cdots H^+\cdots]_n$ chains has been observed for $(DABCO)H^+ClO_4^-$ [40].

The structure of $[TrenH^+][Co(CO)_4^-]$ (Tren, triethylenetetraamine) **10** [41], has the most elaborate arrangement of cations of the structures discussed in this review. The cation ($TrenH^+$) possesses a primary ammonium center, two primary amine sites and a tertiary amine site. $N–H^+\cdots N$ hydrogen bonds give rise to a 2D network approximately in the *ab* plane (Fig. 14a) that is best described as a buckled sheet (Fig. 14b). The network has small, approximately square, channels perpendicular to the sheet (Fig. 14a), along the *c* direction, as well as channels between layers, along the *b* direction. The anions sit in the latter channels and interact with

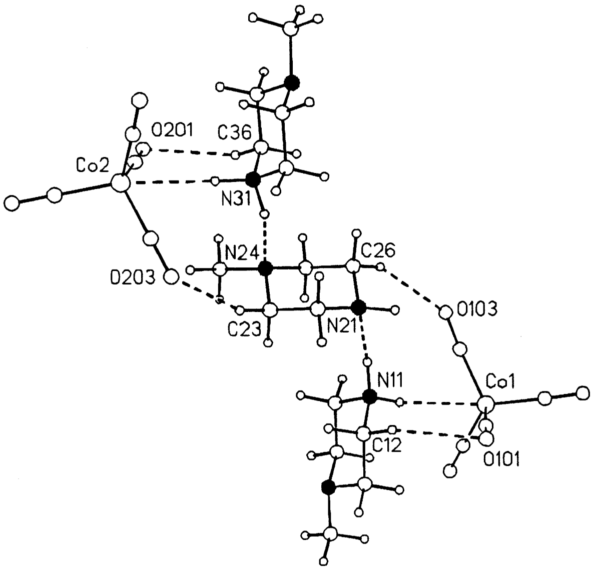


Fig. 12. Molecular structure of one formula unit of **5**, which comprises five moieties linked via N–H···Co, $N–H^+\cdots N$, and C–H···O hydrogen bonds (N atoms shaded).

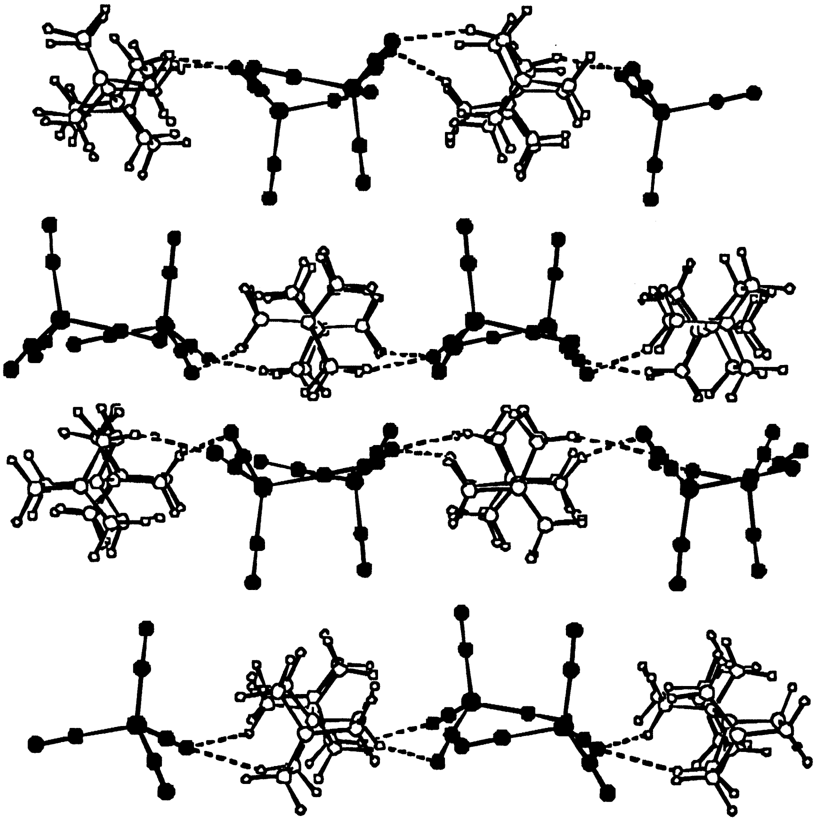


Fig. 13. View of **4b** along the cation (unshaded) chains showing anions (shaded) residing in channels and linked to the cation chains via C–H···O hydrogen bonds.

the cation network via N–H···O and N–H···π, as well as weak C–H···O, hydrogen bonds (see Section 4).

4. Hydrogen bonding involving the carbonyl ligand as the acceptor

As noted in the introduction, the anion $Co(CO)_4^-$ provides a number of potential (non-conventional) hydrogen bond acceptor sites. The case of Co as the hydrogen bond acceptor is described in Section 2. In this section interactions involving the carbonyl group are discussed. The ability of the carbonyl oxygen to serve as a hydrogen bond acceptor has been noted for some time [19], but the abundance of hydrogen bonds involving carbonyl ligands has only recently been recognized ([18]b,c). Indeed, the possibility that the C≡O π-bond can also act as a hydrogen bond acceptor appears to have been overlooked until very recently [33]. The class of salts whose structures are reviewed here presents the opportunity to examine both types of hydrogen bond involving CO ligand acceptors.

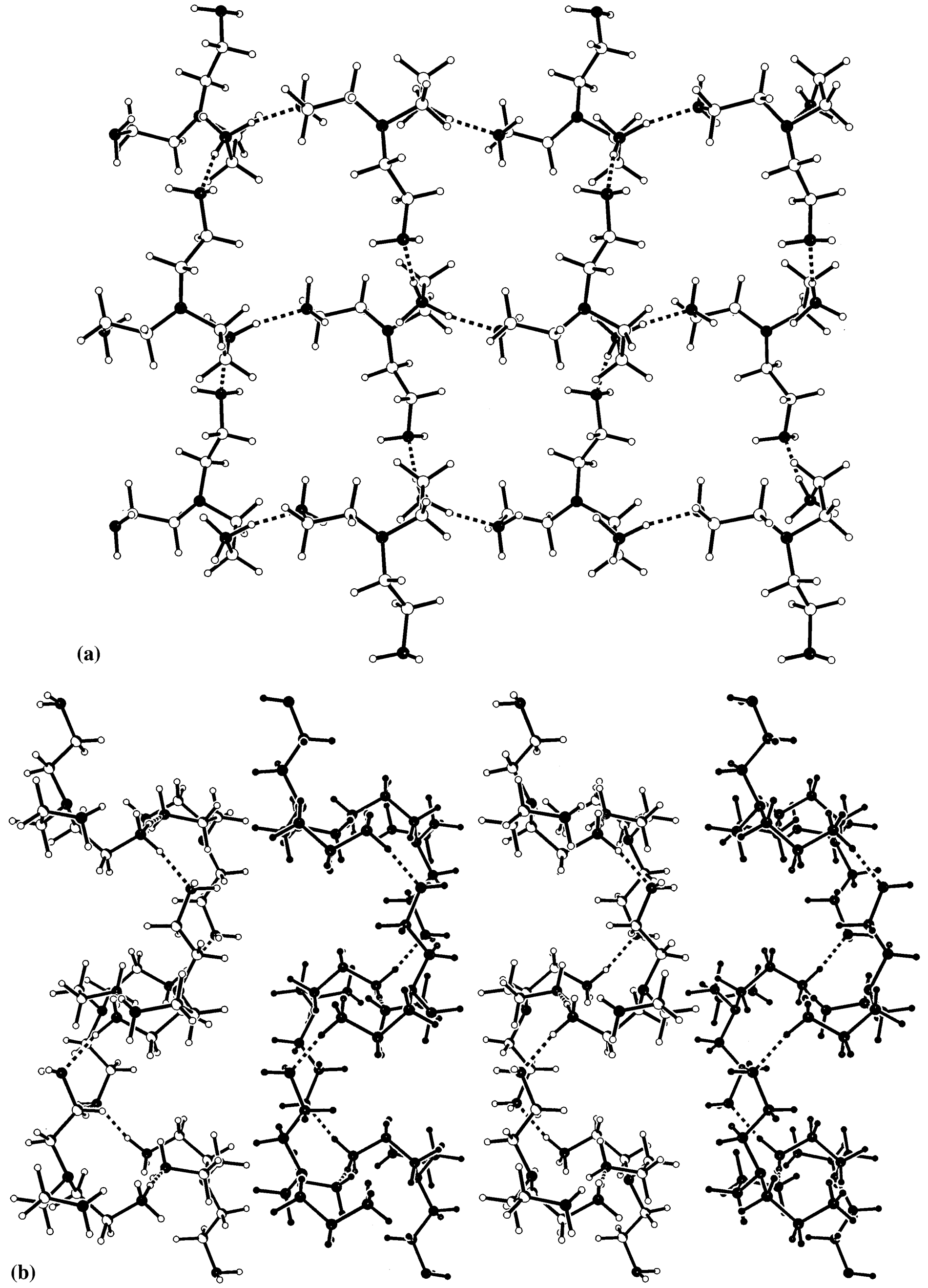


Fig. 14. The cation network in **10**. (a) Viewed down the *c*-axis (*b*-axis horizontal) showing a section of one cation sheet (N atoms shaded). (b) Viewed down the *b*-axis (*c*-axis horizontal) showing four cation layers (alternate layers have all atoms shaded, then only N atoms shaded).

It is to be anticipated that among the cation–anion interactions, D–H···OC(Co) (D = C, N) hydrogen bonding will play a more important role than N–H···Co hydrogen bonding in defining the overall supramolecular architecture of these salts in the crystalline form. The reason for this expectation is straightforward. Despite the lesser strength of the former type (especially *C*–H···OC(Co)), the abundance of (C–H) donor and (CO) acceptor groups compared to those available for N–H···Co hydrogen bonding allows the former to predominate.

4.1. Background

In recent surveys of the Cambridge Structural Database [15], Braga, Grepioni, Desiraju and coworkers have demonstrated the abundance and importance of C–H···OC(M) hydrogen bonds in organometallic compounds of the first transition series ([18]b,c). For further information, the reader is directed to these articles. However, the major conclusions of those studies can be summarized very briefly as follows:

1. bridging CO ligands typically form shorter (stronger) hydrogen bonds than terminal ligands as a result of increased basicity of the oxygen atoms arising from greater metal–ligand π-back-donation. Thus, the average values of the H···O separations in C–H···O hydrogen bonds for the M(μ_3-CO), M(μ_2-CO) and M(CO) (terminal) cases are 2.44, 2.57 and 2.62 Å, respectively.
2. OC(M) hydrogen bonds show directional preference, where angles at the oxygen (H···O–C) are distributed around 140° independent of the M–CO binding mode.

4.2. C–H···O and N–H···O hydrogen bonds in alkylammonium salts of $Co(CO)_4^-$

In all the salts of the $Co(CO)_4^-$ anion discussed in this review the carbonyl groups form hydrogen bonds primarily with C–H groups as the hydrogen bond donors. N–H groups participate only occasionally in hydrogen bonding interactions with the carbonyl oxygen atoms as such donors primarily interact with N or Co acceptors as discussed in Sections 2 and 3.

4.2.1. $[R_3NH][Co(CO)_4]$ salts

In each of these salts (**1**, **2**, **3**, **4a**) the only available N–H donor group is used in forming an N–H···Co hydrogen bond, which is typically the principal (shortest) anion–cation interaction. C–H···O hydrogen bonds, although generally longer (weaker) provide more abundant cation–anion links. Table 3 summarizes the structural information on the C–H···O hydrogen bonds.

Mean H···O separations are similar to those determined in a survey of cobalt carbonyl complexes ([18]c) (H···OC(Co) 2.61 Å for terminal carbonyls, 2.55 Å for bridging μ_2-carbonyls [42]). However, with the exception of **1**, the present values agree better with means observed for μ_2-CO binding mode, in which oxygen acceptor sites are more basic as a result of greater π-back-donation than to terminal carbonyls. This is consistent with the fact that in the anion $Co(CO)_4^-$ one can expect a greater back donation from the Co(− I) to the CO ligands than in a typical terminal cobalt carbonyl. It also reflects the fact that the C–H···O hydrogen bonds in the salts of $Co(CO)_4^-$, being between cations and anions, can be thought of as charge-assisted. Angular values from Table 3 also agree well with those of the broader distribution of terminal carbonyl compounds ([18]c) (mean C–H···O 140.3°, mean C–O···H 128.3°), the C–O···H angles being consistent with significant metal–ligand π-back-donation (Section 1.1.2; Figs. 4 and 5). The principal outlier is again **1**, which shows much smaller C–H···O angles consistent with the weaker C–H···O hydrogen bonds formed in this compound.

Although the mean geometric features of the C–H···O hydrogen bonds in these four salts appear to be somewhat similar, a closer examination reveals important differences of consequence to the supramolecular structures. Firstly **1** has been identified as an outlier, exhibiting longer H···O distances and C–H···O much further removed from linearity than in **2**, **3** and **4a**. The origin of this difference can be traced to the steric demands of the cation, which substantially restricts access by neighboring cations to the CO ligands of its (N–H···Co bound) anion partner.

2 crystallizes with two anions and two cations per asymmetric unit. C–H···O hydrogen bonds involve only one of the four carbonyls per anion, However, unlike in **1**, steric crowding is not the issue here, consistent with the hydrogen bonds in **2** being shorter and closer to linear than in **1**. The reason, as we have recently proposed [33], appears to be the involvement of four of the eight independent carbonyls of **2** in rather uncommon C–H···π(CO) hydrogen bonds (see Section 4.3 for further discussion).

The supramolecular structures of **3** and **4a** (Figs. 15–17) illustrate the often-difficult task of correctly assessing the geometric and energetic attributes of intermolecular interactions and in particular their manifestation in molecular aggregation. This task is a central one in the field of crystal engineering. As briefly mentioned in Section 2, despite the apparent similarity between the molecular

Table 3
Mean geometric values for C–H···O hydrogen bonds[a] (H···O < 2.7 Å, 110° < C–H···O < 180°) in $R_3NH^+Co(CO)_4^-$ type salts

Compound	No. of C–H···O	No. of CO groups involved	H···O (Å)	C–H···O (°)	C–O···H (°)
1	6 (2 unique)	4 of 4	2.648(17)	117.4(0)	130.2(112)
2	2	2 of 8	2.528(103)	143.4(182)	136.3(352)
3	4	3 of 4	2.517(96)	141.4(152)	121.8(102)
4a	9	7 of 8	2.535(76)	138.6(154)	130.3(119)
Mean values	17 (total)		2.540(76)	138.5(149)	129.3(139)

[a] C–H distances extended to standard neutron diffraction value of 1.08 Å. Standard deviations are calculated according to $\sigma = [\Sigma(d_i - d)^2/(n-1)]^{0.5}$ from the n observations that are averaged. Thus, ca. 67% of observations lie within 1σ of the mean.

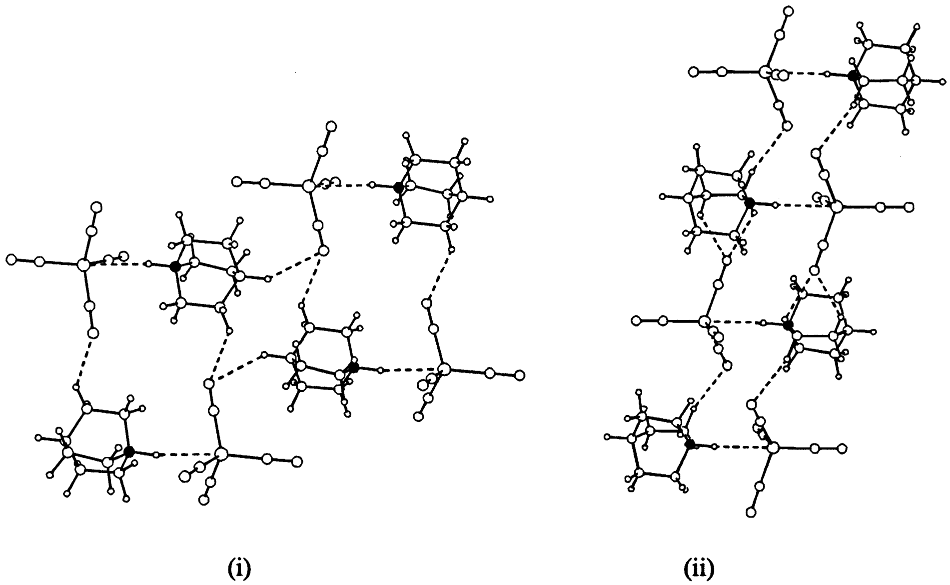


Fig. 15. C–H···O hydrogen bond networks in **3** involving the carbonyl acceptor groups: (i) C(2)O(2), and (ii) C(3)O(3) and C(4)O(4) (N atoms are shaded).

species **3** and **4a**, the N–H···Co hydrogen bond in **3** is substantially longer than in **4a** (H···Co 2.519 vs. 2.389 Å). This lengthening is accompanied by a change from a staggered to an eclipsed conformation of the cation methylene groups relative to the three equatorial carbonyls of the anion. Moreover, in **3** the N–H···Co hydrogen bond no longer provides the shortest cation–anion contact, which instead arises from C–H···O hydrogen bonds as short as 2.428 Å (mean H···O 2.524 Å). At the

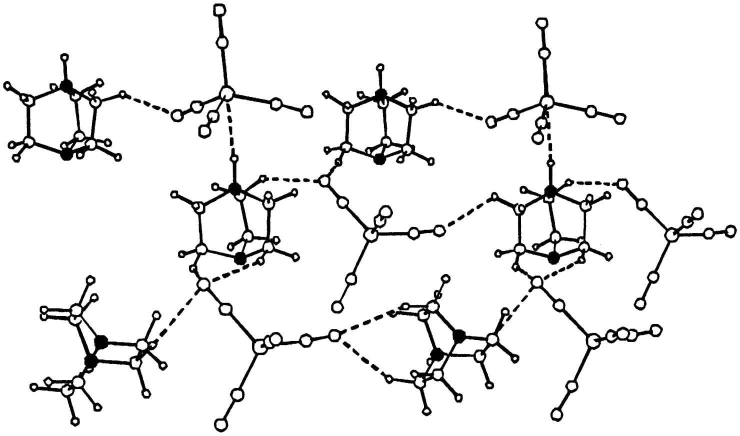


Fig. 16. C–H···O hydrogen bonding network in **4a** (N atoms shaded).

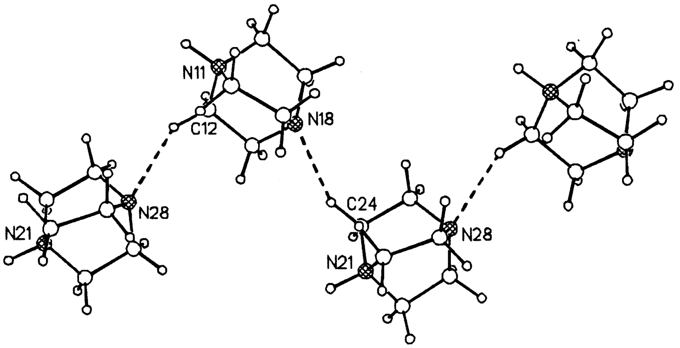


Fig. 17. Illustration of the zigzagged cation chain formed by C–H···N hydrogen bonds in **4a** (N atoms shaded).

molecular level, the major difference between **3** and **4a** is the replacement of a potential hydrogen bond donor (C–H in **3**) by a potential hydrogen bond acceptor (N in **4a**). This necessarily results in different supramolecular structures, as both groups are active in forming C–H···O (**3**, Fig. 15(i)) and C–H···N (**4a**, Fig. 17) hydrogen bonds. It seems reasonable to propose that, at least in part, the C–H···O hydrogen bonded network in **3** compensates energetically for its eclipsed and lengthened N–H···Co bonds.

4.2.2. Salts with ammonium/amine dimer and trimer cations

In Section 3 the main structural features of ionic N–H^{+}···N hydrogen bonds leading to dimeric and trimeric cation units were presented. Such hydrogen bonds occupy all available N–H donors in these salts. In the present section, the role of C–H···O hydrogen bonds in linking these cations to the $Co(CO)_4^-$ anions in the crystal structures is discussed. Table 4 summarizes the geometric features of these C–H···O hydrogen bonds.

Table 4
Mean geometric features for the C–H···O hydrogen bonds[a] (H···O < 2.7 Å, 110° < C–H···O < 180°) in salts **7–9**

Compound	No. of C–H···O	No. of CO groups involved	H···O (Å)	C–H···O (°)	H···O–C (°)
7	8 (4 unique)	3 of 4	2.597(98)	149.5(162)	113.4(152)
8	6	4 of 4	2.548(108)	131.2(107)	114.7(177)
9	16	12 of 16	2.552(109)	143.4(155)	114.4(146)
Mean values	26 (total)		2.558(99)	143.5(159)	113.3(148)

[a] C–H distances extended to standard neutron diffraction value of 1.08 Å. Standard deviations are calculated according to $\sigma = [\Sigma(d_i - d)^2/(n-1)]^{0.5}$ from the n observations that are averaged. Thus, ca. 67% of observations lie within 1σ of the mean.

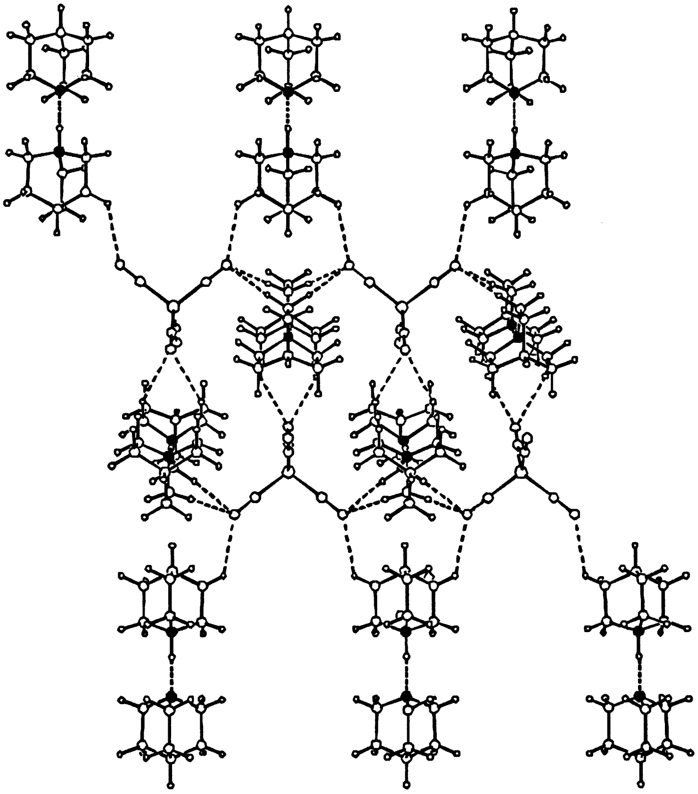


Fig. 18. C–H···O hydrogen bonding network in **7** (N atoms shaded).

The mean geometric values for the C–H···O hydrogen bonds in salts of the type $[R_3N\text{–}H^+\cdots NR_3][Co(CO)_4^-]$ are very similar to those reported in Table 3 concerning salts with the general formula $[R_3NH^+][Co(CO)_4^-]$. The complexity of the hydrogen bonding pattern in **9**, involving three types of cation and four independent anions, prohibits either concise description or illustration. Thus, we will focus on **7** and **8** in order to illustrate graphically how the aforementioned $N\text{–}H^+\cdots N$ dimers are linked to the anions via C–H···O hydrogen bonds.

Fig. 18 shows rows of the dimeric cations of **7** lying with their major axis alternately perpendicular to and parallel with the viewing direction. Cations in a given row form a zigzag arrangement, as is clearly seen for those cations aligned parallel to the viewing direction in Fig. 18. Anion layers intersperse the cation rows linking cations via C–H···O hydrogen bonds. It can be seen that some carbonyl oxygens symmetrically bridge the two quinuclidine units in a given cation, consistent with the eclipsed conformation of these dimeric cations. Fig. 19 shows the staggered conformation of the dimeric cations of **8** linked by alternate anions. All four carbonyl oxygens are used in forming C–H···O hydrogen bonds.

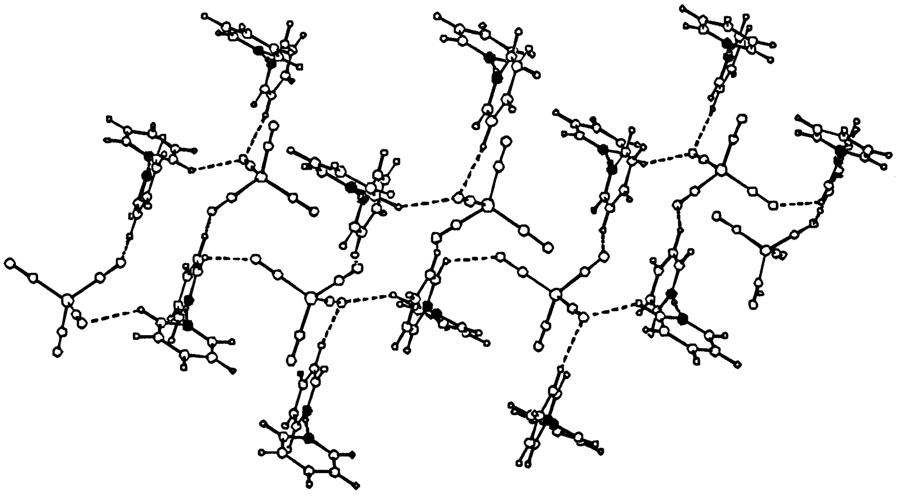


Fig. 19. C–H···O hydrogen bonding network in **8** (N atoms shaded).

*4.2.3. C–H···O and N–H···O hydrogen bonds in **5** and **10***

In previous sections we described hydrogen bonding interactions of the type N–H···Co and N–H$^+$···N as the main intermolecular links in [(NMP)$_3$H$_2$$^{2+}$]-[Co(CO)$_4^-$]$_2$ **5** and the N–H$^+$···N hydrogen bonded cation network in [TrenH$^+$][Co(CO)$_4^-$] **10**. In this section the role of C–H···O and N–H···O hydrogen bonds as cation–anion connections in the supramolecular structures of the two compounds is examined.

Fig. 12 shows the different types of hydrogen bonding interactions involved in linking three *N*-methylpiperazine molecules and two tetracarbonylcobaltate (−I) anions to give the asymmetric unit in the crystal structure of **5**. However, these pentamolecular units are further interlinked by D–H···O hydrogen bonds (D = C, N). The shortest contact between these units occurs via N–H···O hydrogen bonds, giving rise to a hydrogen-bonded decamolecular (5:5) centrosymmetric dimer (Fig. 20). Weaker, but more numerous, C–H···O hydrogen bonds then provide further cation–anion connections. The geometries of these hydrogen bonds are summarized in Table 5.

By contrast short cation–anion interactions are relatively sparse in **10**, which exhibits the most extensive hydrogen bonded cation network of the salts discussed herein (Section 3). As indicated previously, the anions lie in channels that run through the crystal structure. They interact with the cation network via N–H···O and N–H···π(CO) hydrogen bonds (see Fig. 21) as well as weak C–H···O hydrogen bonds. A summary of the D–H···O (D = C, N) hydrogen bonds is given in Table 6. The N–H···π(CO) hydrogen bond is discussed in more detail in the following section.

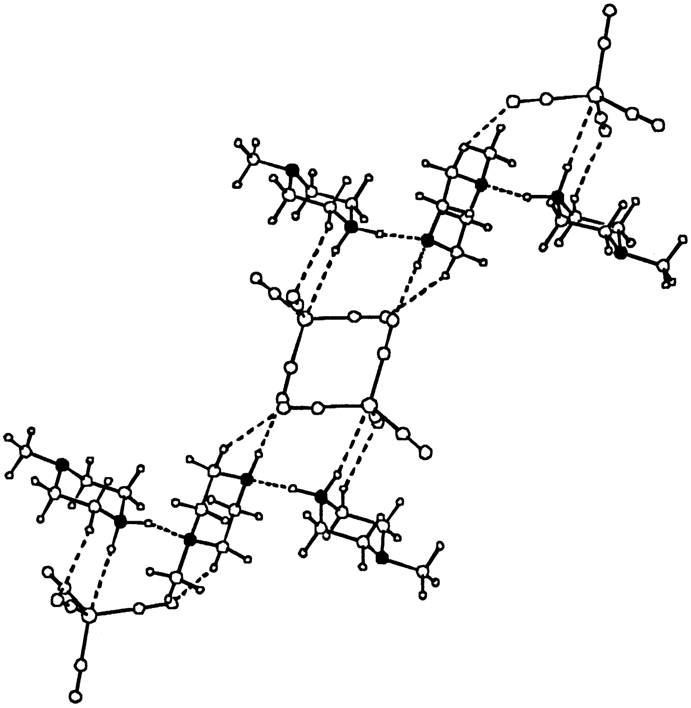


Fig. 20. Decamolecular (5:5) centrosymmetric dimer of **5** (N atoms shaded).

Table 5
Geometries of the D–H···O hydrogen bonds[a] (D = C, N) (H···O < 2.7 Å, 110° < C–H···O < 180°) in **5**

Acceptor	Donor	H···O (Å)	D–H···O (°)	H···O–C (°)
Hydrogen bonds involving $Co(CO)_4^-$ anion I				
O101	C22	2.488	128.0	128.3
O101	C12	2.622	126.8	99.7
O102	C32	2.669	135.0	99.3
O103	C37	2.599	156.1	124.5
O103	C26	2.676	149.9	130.3
Mean Values		2.611	139.2	116.4
O104	N21	2.138	168.6	160.3
Hydrogen bonds involving $Co(CO)_4^-$ anion II				
O201	C36	2.597	127.5	99.9
O201	C37	2.663	142.9	146.6
O202	C27	2.500	163.9	142.2
O202	C16	2.539	122.6	110.2
O203	C23	2.334	157.0	126.7
O203	C17	2.537	163.7	122.4
O204	C37	2.662	140.6	141.8
Mean Values		2.547	145.5	127.1

[a] C–H and N–H distances extended to standard neutron diffraction values of 1.08 and 1.01 Å, respectively.

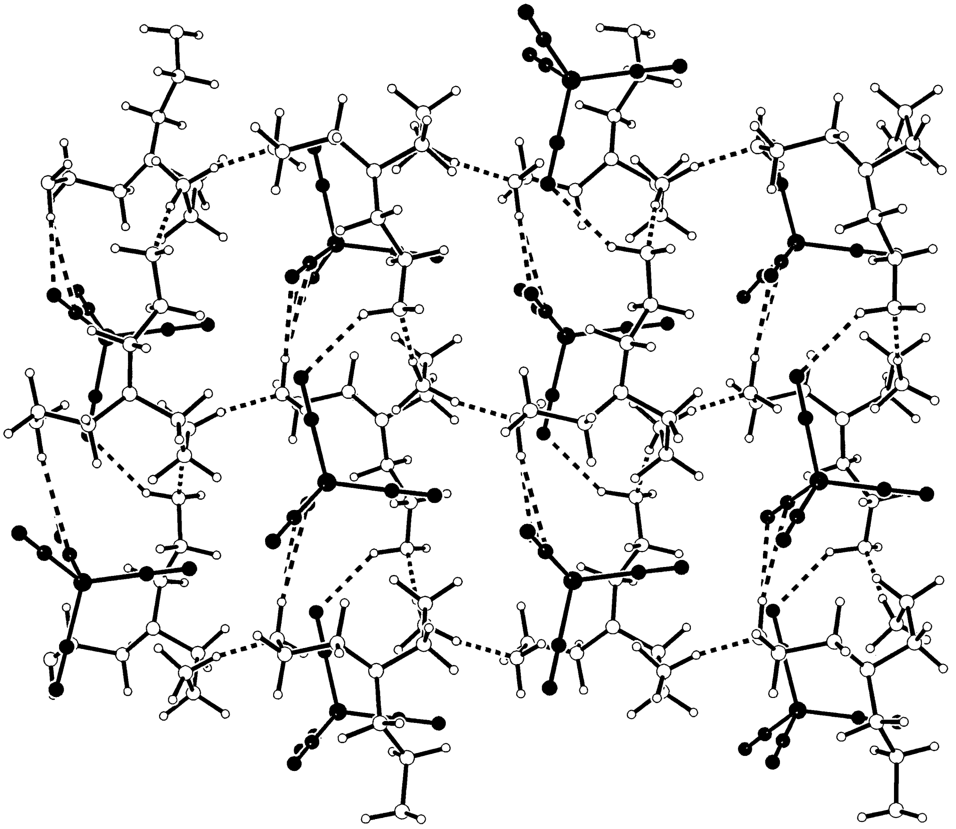


Fig. 21. View of **10** down the *c*-axis (see Fig. 14a) showing anions (shaded) linked to the cation framework (unshaded) via N–H···O and N–H···π(CO) hydrogen bonds.

4.3. *D–H···π(CO) hydrogen bonding (D = C, N)*

In this section, we will discuss the final type of (non-conventional) hydrogen bond able to be investigated in salts of the $Co(CO)_4^-$ anion. Two of the salts, **2** and **10**, show evidence of D–H···π(CO) hydrogen bonds (D = C, N, respectively). As noted previously, a number of cases of hydrogen bonds involving the π-electron density of C≡C bonds are now documented ([29], [30]c,d, [32]), though such reports are still uncommon among organometallic compounds [32]. This area clearly warrants further exploration, especially as it pertains to organometallic systems. Indeed, recently we have recognized that, like C≡C bonds in organic compounds, the asymmetric π-systems in (M)C≡O and (M)C≡N bonds of organometallic compounds can serve as hydrogen bond acceptors [33].

Theoretical studies of the interaction of acidic C–H groups with the π-system of C≡C bonds show that the strongest interaction should arise from an approach of the C–H group perpendicular to the C≡C bond, with the H-atom pointing to the center of the C≡C bond [43]. The observations in **2** and **10** are consistent with this theoretical

Table 6
Geometries of the D–H···O hydrogen bonds[a] (D = C, N) (H···O < 2.7 Å, 110° < C–H···O < 180°) in **10**

Acceptor	Donor	H···O (Å)	D–H···O (°)	H···O–C (°)
O1	C21	2.684	141.2	122.5
O4	C41	2.684	126.7	129.7
O1	N3	2.383	139.4	122.4

[a] C–H and N–H distances extended to standard neutron diffraction values of 1.08 and 1.01 Å, respectively.

description and, respectively, suggest the presence of C–H···π and N–H···π hydrogen bonds involving C≡O ligands [33]. The structural data for these hydrogen bonds are contained in Table 7.

$[Me_3NH][Co(CO)_4]$ **2** crystallizes with two cation–anion pairs that are crystallographically independent ([12]a). Cations and anions of molecule I comprise a remarkable zigzagged chain of alternating anions and cations. Each cation is linked to the adjacent anions in the chain on one side by an N–H···Co hydrogen bond and

Table 7
Geometries of the D–H···π(CO) hydrogen bonds[a] (D = C, N) in **2** and **10** (X = midpoint of CO bond; H···X < 2.7 Å, D–H···X > 130°, D–H···O < 95°)

Donor (D)	Acceptor (A)	D···A (Å)	H···A (Å)	D–H···A (°)	X–A···H (°)
*C–H···π(CO) hydrogen bonds in **2***					
C9	CO(4) [Co(1)]				
	O(4)	3.442	2.526	142.0	79.3
	X(1d)	3.496	2.485	155.5	n.a.
	C(4)	3.649	2.584	168.5	103.2
C10	CO(3) [Co(1)]				
	O(3)	3.519	2.531	151.7	85.3
	X(1c)	3.772	2.549	164.5	n.a.
	C(3)	3.602	2.695	175.1	105.0
C11	CO(1) [Co(1)]				
	O(1)	3.525	2.576	146.2	80.2
	X(1a)	3.572	2.542	159.1	n.a.
	C(1)	3.710	2.638	171.8	104.6
C9	CO(6) [Co(2)]				
	O(6)	3.332	2.525	130.8	87.5
	X(2b)	3.467	2.565	140.4	n.a.
	C(6)	3.688	2.729	147.7	110.3
*C–H···π(CO) hydrogen bonds in **10***					
N4	CO(3) [Co]				
	O(3)	3.533	2.547	165.1	89.6
	X(3)	3.615	2.608	174.1	n.a.
	C(3)	3.785	2.792	167.7	113.1

[a] C–H and N–H distances extended to standard neutron diffraction values of 1.08 and 1.01 Å, respectively.

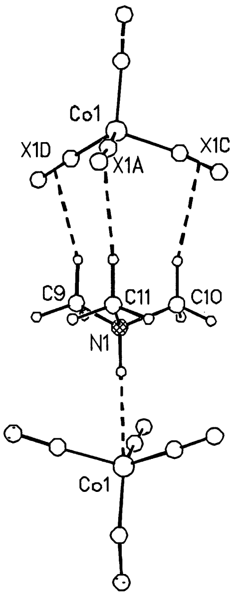


Fig. 22. C–H···π(CO) and N–H···Co hydrogen bonds linking a Me_3NH^+ cation with two adjacent $Co(CO)_4^-$ anions in **2**.

on the other side by three C–H···π(CO) hydrogen bonds [44], as shown in Fig. 22. The ions of molecule II, also mutually linked by an N–H···Co hydrogen bond, lie approximately orthogonal to the chains formed by molecule I and in a stepped arrangement as seen in Fig. 23. Two orthogonally disposed sets of steps adjoin the chain. In one case the cations of molecule II interact with the chain (as shown in Fig. 23). In the second orthogonal set of steps, the anions of molecule II interact with the chain. In both instances anion–cation pairs of molecule II provide a connection between two of the aforementioned chains. This connection between chains is established via two C–H···O hydrogen bonds (from cation II to anion I and from cation I to anion II) and an additional C–H···π(CO) hydrogen bond (from cation I to anion II).

The geometry of the C–H···π(CO) hydrogen bonds, particularly the set of three C–H···π interactions along the zigzagged chain, is consistent with these hydrogen bonds being important in defining the overall supramolecular structure. Thus, the distance between the H-atom and the center of the C≡O bond ranges from 2.48–2.55 Å and the angle at the hydrogen ranges from 155 to 165° (the other C–H···π interaction that links cation I to anion II is apparently weaker at 2.57 Å and 140°). These geometries are comparable to those involving the C≡C bond in organic systems ([30]c–e) and also to values from our recent survey of C–H···π(CO) and C–H···π(CN) hydrogen bonds in organometallic systems [33].

$[TrenH^+][Co(CO)_4^-]$ **10** provides a rare example of an N–H···π(CO) hydrogen bond [41]. This rarity presumably arises because most (hard acid) N–H hydrogen

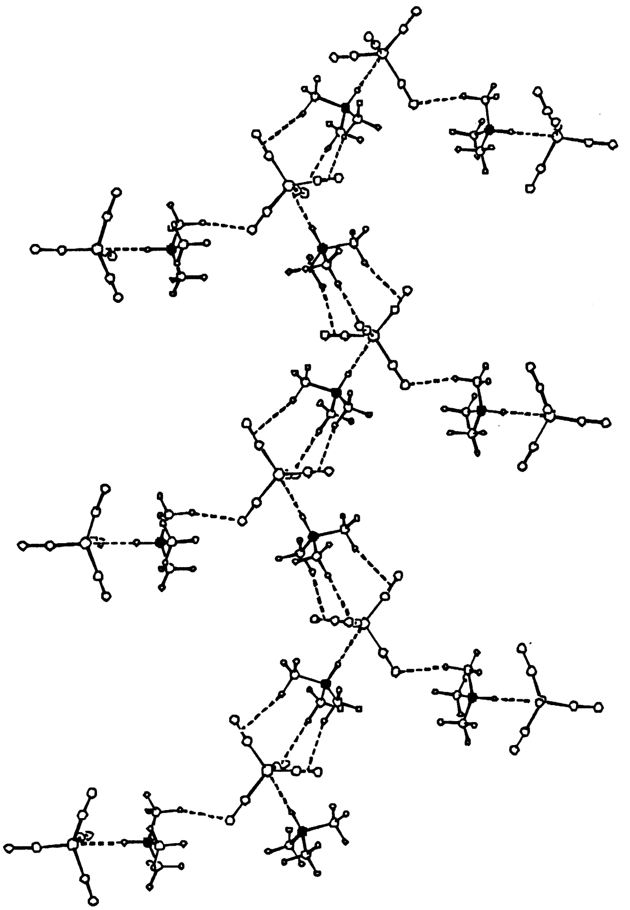


Fig. 23. C–H···π, C–H···O and N–H···Co hydrogen bonding in the supramolecular structure of **2** (N atoms shaded).

bond donors combine with available (hard base) O or N acceptors. That is generally the case here also, and N–H$^+$···N hydrogen bonded cation network in **10** has been discussed previously (Section 3.3). The anions lie in channels within the cation network, and are linked to the cations via the N–H···π(CO) hydrogen bond, and an N–H···O hydrogen bond (shown in Fig. 24) and two rather long C–H···O hydrogen bonds. The positioning of the anions relative to the cation network is illustrated in Fig. 21.

5. Conclusions and prospects for organometallic crystal engineering

In this review we have examined in detail the crystal structures of a group of organometallic salts whose common feature is the presence of $Co(CO)_4^-$, the

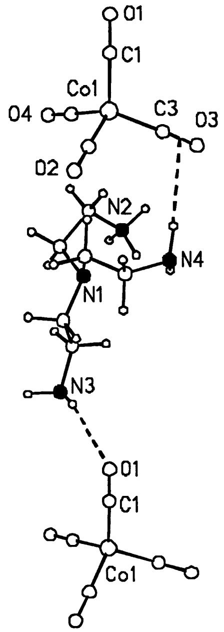


Fig. 24. N–H···π(CO) and N–H···O hydrogen bonds in **10** (N atoms shaded).

simplest homoleptic metal carbonyl anion. Indeed, the rich diversity of hydrogen bond acceptor capability observed belies the simplicity of this anion. This observation is particularly pertinent to the further development of the emerging field of organometallic crystal engineering. Although the geometries and bonding patterns of C–H···O≡C(M) hydrogen bonds in organometallic compounds have been previously surveyed ([18]b,c) using the CSD, and D–H···π(CO) hydrogen bonding (D = C, N) will be the subject of a forthcoming article [33], this is the first systematic analysis of the supramolecular structures of a series of related metal carbonyl compounds.

Remarkably the $Co(CO)_4^-$ anion shows three distinct hydrogen bond acceptor sites, the metal center, the carbonyl oxygens, and the π-bond of the CO ligands. Across this series of salts, the complexity of the ammonium cation has been gradually increased from simple tertiary ammonium cations, through cations consisting of dimeric or trimeric units, to a protonated tetraamine. On traversing this series, features of the supramolecular structure change. For the simplest cations the structure is based upon a short (strong) direct N–H···Co hydrogen bond between the cation and anion augmented by longer (weaker) C–H···O hydrogen bonds. When amine acceptor sites are also available these compete effectively with the metal center of the anion giving rise to dimeric, trimeric, and even polymeric $N–H^+$···N hydrogen-bonded ammonium/amine cations. These cations make use of all the N–H donors, leaving cation–anion links to be formed solely through C–H···O hydrogen bonds. Compound **5** is a hybrid case because of the secondary ammonium centers, which permit features of both the systems described so far, namely $N–H^+\cdots N$ linked ammonium/amine cation trimers and direct $N–H\cdots Co$ hydrogen bonds between cations and anions, in addition to the ubiquitous $C–H\cdots O$ connections. At the other extreme from the salts of the simplest cations is the salt of (Tren)H^+ **10**, which possesses no less than seven N–H donors as well as three amine acceptor sites per cation (and thus per anion). This cation forms an $N–H^+\cdots N$ hydrogen bonded network of buckled sheets that interact directly only through the hydrophobic interlayer contacts of C–H groups. The anions reside in channels in the cation network and also provide links between the cation sheets. The principal cation–anion interaction is through a short $N–H\cdots O$ hydrogen bond and a longer $N–H\cdots \pi(CO)$ hydrogen bond. $C–H\cdots O$ hydrogen bonds are far less numerous and much longer (weaker) than in the other compounds studied.

This series of compounds was not intended to be a crystal engineering study of the $Co(CO)_4^-$ anion, at least not with a view to designing predictable structures based upon these salts. Nevertheless, exploration of the hydrogen bonding capabilities of this simple homoleptic anion provides valuable information for the field of (organometallic) crystal engineering and insight into the potential roles of metal-mediated hydrogen bonding.

Crystal engineering is a complex and ambitious field, one that poses formidable challenges, to among others, chemists and crystallographers. For its development, crystal engineering necessitates a better understanding of extramolecular interactions. This information, which is almost routinely available through crystal structure determinations, often remains overlooked and unused. In order to retrieve such valuable information, more frequent and systematic surveys of the structural features of existing compounds are needed. In the domain of organometallic (and organic) chemistry the primary tool for such investigations is the CSD [15], as illustrated in a recent series of papers by Braga, Grepioni, Desiraju and coworkers that explore a variety of hydrogen bonding interactions in organometallic compounds ([12]k, [13]d, [14], [18]c, [45]). In the future it will become increasingly important to devote more efforts to discussing structural aspects associated with the supramolecular structure. This will require that the careful examination of crystal structures beyond the intramolecular details becomes more a matter of routine. Traditionally it is the weakness of intermolecular interactions that has led to the underestimation of their importance. However, the importance of intermolecular interactions in determining the chemical and physical properties of solid materials is now gaining acceptance. Moreover, intermolecular interactions, in some cases may be the clue to otherwise unexplainable observations.

Turning more specifically to organometallic crystal engineering, it is important to recognize the role that the metal atoms can play. (i) Metals can be harnessed to provide direct intermolecular connections, such as the $N–H\cdots Co$ hydrogen bonds involving the salts of simple ammonium cations of $Co(CO)_4^-$, where the metal serves as an electron-rich Lewis base. Conversely, electron deficient metal centers can play a similar role but serving as Lewis acids in intermolecular σ-bond coordination ([12]k). (ii) Metals can exert an electronic influence upon intermolecular ligand–ligand interactions that occur in the ligand domain. In this review, the strong π-back-donation from Co to the carbonyl ligands can be viewed as contributing to the formation of shorter than typical $C–H\cdots OC(Co)$ hydrogen bonds in most of the salts studied. This point is also clear from other studies [16,18] (iii) The metal can also direct the formation of intermolecular interactions through an extension, via rigid ligands, of the directionality characterized by its coordination geometry. This directionality has been exploited at times with spectacular success in the synthesis of coordination polymers and oligomers [46]. However, to date this role for metals in crystal engineering has been little exploited in organometallic systems linked by hydrogen bonds [47] or other non-covalent interactions. This approach could be used for interactions both in the ligand and periphery domains [10], and falls into the general category of second-sphere coordination [48]. (iv) Finally the presence of metal atoms incorporated in a regular periodic manner into a solid designed by crystal engineering could be used to impart desirable chemical and physical properties to that material. Such properties may arise from the availability or easy generation of a vacant coordination site allowing reaction with an enclathrated guest molecule, or from the electronic, magnetic, and optical properties of the metal,

Organometallic chemistry is a very rich area of chemistry. The synthetic methodology applied to organometallic systems continues to improve rapidly and is leading to the preparation of a large number of new compounds. In the further development of organometallic chemistry, molecular and supramolecular synthesis should complement each other. Thus, a parallel improvement in organometallic/inorganic supramolecular synthesis is needed. The ready availability of ligands, the knowledge of the preferential geometries adopted by a particular metal under a specific crystal field, and the accessibility of various metal oxidation states can lead to numerous metal-based neutral, anionic and cationic species. This can be complemented by the incorporation into these species of, for example, functional groups with potential hydrogen bond donors and acceptors in well-chosen orientations. It should then be possible to link those molecules into more predictable supramolecular arrangements, which is the first step towards designing a system with desirable properties.

At the present it is not known to what extent the supramolecular synthons already identified for organic systems will still be valid in organometallic systems. Early studies have shown that in the right circumstances, great similarities can arise ([27]a, [45]a), but also metals can cause a major departure from behavior seen in purely organic systems [16]. Our present work is geared towards exploring the transferability of organic supramolecular synthons to organometallic systems and understanding those aspects of supramolecular chemistry that are unique to the latter, with the ultimate aim being rational design in supramolecular organometallic chemistry.

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