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Inorganic–organometallic crystal synthesis. The role of charge-assisted C–H...O and C–H...Cl hydrogen bonds in crystalline $[(\eta^5\text{-}C_5H_5)_2Co][H_2PO_4]\cdot 3H_2O$ and $[(\eta^6\text{-}C_6H_5Me)_2Cr][Cl]$[1]

Dario Braga [a,*], Sylvia M. Draper [b], Elise Champeil [b], Fabrizia Grepioni [a]

[a] *Dipartimento di Chimica G. Ciamician, Università di Bologna, Via Selmi 2, 40126 Bologna, Italy*
[b] *Chemistry Department, Trinity College, Dublin 2, Ireland*

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Abstract

The organometallic dihydrogen phosphate $[(\eta^5\text{-}C_5H_5)_2Co][H_2PO_4]\cdot 3H_2O$ has been obtained by direct reaction of phosphoric acid with the organometallic hydroxide $[(\eta^5\text{-}C_5H_5)_2Co][OH]$ prepared in situ by oxidation of $[(\eta^5\text{-}C_5H_5)_2Co]$ in water. The role of negatively charged O–H...O$^{(-)}$ and neutral O–H...O hydrogen bonds between the $H_2PO_4^-$ anions and water molecules and that of charge-assisted C–H$^{\delta+}$...O$^{\delta-}$ hydrogen-bonds between organometallic and inorganic components has been investigated. The crystal structure of the chloride $[(\eta^6\text{-}C_6H_5Me)_2Cr][Cl]$ has also been used to analyse charge assisted C–H$^{\delta+}$...Cl$^-$ interactions. The results have been compared with data retrieved from the Cambridge Crystallographic Database. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cobaltocenium salts; Hydrogen bonding; Structural analysis

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1. Introduction

We have recently begun a systematic investigation of the effect of weak hydrogen bonds on the cohesion of organometallic and inorganic crystalline materials [1]. We have shown that weak hydrogen bonds such as C–H...O and C–H...F can be reinforced if the donor belongs to a cation and the acceptor to an anion [2] thus taking advantage of the essentially electrostatic nature of these interactions. Since many organometallic and inorganic building blocks are ions, the ‘charge assistance’ phenomenon is particularly important in organometallic crystal engineering. This consideration has been exploited for the preparation of organic–organometallic crystalline aggregates by means of co-operative strong O–H...O and weak C–H...O hydrogen bonds [3]. The synthetic procedure is founded on the reaction between organic or inorganic molecules possessing acidic protons and organometallic molecules that can be easily oxidized to yield organometallic hydroxides, such as $[(\eta^6\text{-arene})_2Cr][OH]$ (arene = η^6-C_6H_6, η^6-C_6H_5Me) and $[(\eta^5\text{-}C_5H_5)_2Co][OH]$. The result of this acid–base reaction are supramolecular salts formed via hydrogen bonding interactions. The design criteria can be summarised as follows: (i) the presence of strong donor/acceptor hydrogen bonding groups on the acidic molecules but not on the organometallic fragments leads to selective self-assembling of the anions obtained from the deprotonated acids in O–H...O hydrogen bonded anionic frameworks around the organometallic cations; (ii) a large number of acidic C–H groups on the organometallic moiety such as those carried by arene and cyclopentadienyl ligands make use of the ‘free’ hydrogen bonding acceptor sites on the O–H...O hydrogen bonded framework; (iii) the

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* Corresponding author. Tel.: +39 51 259555; fax: +39 51 259456; e-mail: dbraga@ciam.unibo.it

[1] Dedicated to Professor Brian F.G. Johnson on the occasion of his 60th birthday for his enthusiastic support to younger scientists.

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opposite charges reinforce the C–H...O hydrogen bonding interactions between the anionic superstructure and the organometallic cations. According to this crystal synthesis strategy several organic–organometallic aggregates have been obtained. The most relevant aspect is that one can utilize enantiomerically pure polycarboxylic acids to obtain chiral organic networks in which the organometallic cations can be accommodated. Examples of this type are provided by the crystalline materials obtained with L-tartaric acid and L-benzoyl tartaric acid [4]. These results open up a convenient route to the engineering of chiral crystals containing organometallic ions or molecules carrying delocalized electron systems and/or aligned spin systems.

In this paper we report on the preparation and structural characterization of two novel salts, namely $[(\eta^5\text{-}C_5H_5)_2Co][H_2PO_4]\cdot 3H_2O$ and $[(\eta^6\text{-}C_6H_5Me)_2Cr][Cl]$. $[(\eta^5\text{-}C_5H_5)_2Co][H_2PO_4]\cdot 3H_2O$ has been obtained by reacting the hydroxide with phosphoric acid in water solution, whereas $[(\eta^6\text{-}C_6H_5Me)_2Cr][Cl]$ has been obtained by treating neutral $[(\eta^6\text{-}C_6H_5Me)_2Cr]$ with diluted HCl.

C–H...Cl hydrogen bonds have been analysed in the light of a Cambridge Database analysis [5] of organometallic crystal structures containing chloride ions. The Database does not contain organometallic phosphate salts, hence $[(\eta^5\text{-}C_5H_5)_2Co][H_2PO_4]\cdot 3H_2O$ is also the first example of such compounds.

2. Experimental

2.1. Preparation of the crystalline materials

Brown powder of $(C_5H_5)_2Co$ (4.73 mg, 0.025 mmol) was added to 10 ml of bidistilled water at room temperature. Oxygen was bubbled to completely oxidize cobaltocene to bright yellow $[(C_5H_5)_2Co]^+$. The resulting solution of $[(C_5H_5)_2Co][OH]$ is strongly basic (pH > 10). An equimolar solution of phosphoric acid was then added. Bis-toluene chromium (15 mg, 0.06 mmol) was added to 10 ml of a dilute water solution of HCl at room temperature and stirred in the air for 30 min obtaining a bright yellow solution. Crystals suitable for X-ray diffraction of $[(\eta^5\text{-}C_5H_5)_2Co][H_2PO_4]\cdot 3H_2O$ and of $[(\eta^6\text{-}C_6H_5Me)_2Cr][Cl]$ were obtained directly from the evaporation of the solutions.

2.2. Crystal data

$[(\eta^5\text{-}C_5H_5)_2Co][H_2PO_4]\cdot 3H_2O$: $C_{10}H_{18}CoO_7P$, $T = 223(2)$ K, $M = 340.14$, monoclinic, $C2/c$, $a = 16.523(4)$, $b = 11.188(4)$, $c = 7.654(9)$ Å, $\beta = 97.14(5)$, $V = 1404(2)$ Å^3, $Z = 4$, $d_c = 1.609$ g cm^{-3}, $F(000) = 704$, $\mu = 1.360$ mm^{-1}, θ-range 3.0–25°, 1328 reflections measured, 1231 of which independent, refinement on F^2 for 116 parameters, wR (F^2, all reflections) = 0.0753, R_1 (reflections with $I > 2\sigma(I)$) = 0.0282). The Cp rings are disordered over two positions, with occupancy factors of 0.55 and 0.45, respectively. The Co and P atoms and one of the two independent O atoms lay on crystallographic symmetry elements, while the second water molecule is in general position.

$[(\eta^6\text{-}C_6H_5Me)_2Cr][Cl]$: $C_{14}H_{16}ClCr$, $T = 253(2)$ K, $M = 271.72$, triclinic, $P\bar{1}$, $a = 6.174(5)$, $b = 9.620(10)$, $c = 11.99(2)$ Å, $\alpha = 76.40(9)$, $\beta = 73.79(9)$, $\gamma = 71.40(8)°$, $V = 589.9(13)$ Å^3, $Z = 2$, $d_c = 1.538$ g cm^{-3}, $F(000) = 282$, $\mu = 1.169$ mm^{-1}, θ-range 3.0–25°, 2173 reflections measured, 2053 of which independent, refinement on F^2 for 178 parameters, wR (F^2, all reflections) = 0.1584, R_1 ($I > 2\sigma(I)$) = 0.0532. The Cl anion is in general position, while two half independent cations are present in the asymmetric unit, with the Cr atoms on two different crystallographic centres of inversion. Residual peaks are located in the proximity of the metal atom.

Common to both compounds: Mo–Kα radiation, $\lambda = 0.71069$ Å, monochromator graphite, psi-scan absorption correction. All non-H atoms were refined anisotropically. (O)H atoms directly located from Fourier maps and not refined. H atoms bound to C atoms were added in calculated positions. The computer programs SHELX86 [6](a) and SHELXL92 [6](b) were used for structure solution and refinement. The computer program SCHAKAL92 [6](c) was used for all graphical representations. In order to evaluate the C–H...O bonds the C–H distances were normalized to the neutron derived value of 1.08 Å and the program PLATON was used [6](d).

2.3. Intermolecular searches of C–H...Cl interactions

Searches were made with version 5.14 of the CSD (October 1998), by using the program QUEST3D, on organometallic salts containing a C–H fragment, directly bound to one transition metal atom, and one chloride anion [6](e). Structures affected by disorder or for which no coordinates of the H atoms were available were excluded. Intermolecular contacts of the C–H...Cl$^-$ type with H...Cl distances less than 3.2 Å were accepted and subsequently examined with the VISTA package. C–H distances were all normalized to the neutron derived values (1.08 Å). An intermolecular search of C–H...Cl contacts involving metal bound C–H fragments and chlorine atoms in neutral complexes has also been carried out for comparison.

3. Results and discussion

The crystal structure of $[(\eta^5\text{-}C_5H_5)_2Co][H_2PO_4]\cdot 3H_2O$ is based on a network of O–H...O hydrogen bonded dihydrogen phosphate monoanions, which also interact with water molecules as shown in Fig. 1. The interaction between the $[H_2PO_4]^-$ anions is based on hydrogen bond rings of the type commonly observed for organic and organometallic carboxylic acids [7]. The O...O separation of 2.575(2) Å (see Table 1) is indicative of a strong hydrogen bonding interaction. This interaction occurs twice by symmetry and links the monoanions in $\{[H_2PO_4]^-\}_n$ chains formed by negatively charged hydrogen bonds between one –OH group and O-atom of the phosphate. The O...O separation is shorter than the values usually observed for neutral O–H...O hydrogen bonds, while they are comparable to those in crystalline $[PhCH_2NH_3][H_2PO_4]$ (O...O separations 2.630(4) and 2.568(4) Å) which has been studied for its non-linear optical properties [8]. There is no disorder of the phosphate hydrogen atoms and the two chemically distinct P–O bonds are clearly recognizable on the basis of the bond distances [1.501(2) and 1.572(2) Å, respectively]. Fig. 1 also shows how the water molecules form a distinct network which is hydrogen bonded to the $\{[H_2PO_4]^-\}_n$ chain via the available lone pairs on the phosphate anions. The inter-water bonds are such as to form tetrameric units. Hydrogen bond tetramers and hexamers are commonly observed with –O–H groups belonging to alcohols or water molecules [9]. The hydrogen atoms of the water molecules are disordered. However, thanks to the high quality of the diffraction data, separate positions corresponding to two and three orientations of the –OH groups in the two independent water molecules (see Section 2) could be observed in the Fourier map. The different types of O–H...O bonds are all recognizable from the O...O separations with the negatively charged O(phosphate)...O(water) bonds being slightly shorter than neutral O(water)...O(water) (2.737(2) versus 2.796(2), and 2.810Å) (see Table 1).

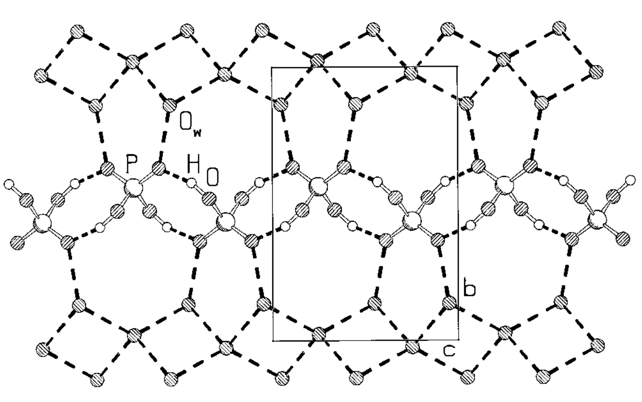

Fig. 1. Hydrogen bond network in crystalline $[(\eta^5\text{-}C_5H_5)_2Co][H_2PO_4]\cdot 3H_2O$. Note how the $[H_2PO_4]^-$ monoanions form chains via hydrogen bond rings, and the water molecules form hydrogen bonded tetrameric units. The water hydrogen atoms are omitted for clarity.

Table 1
Hydrogen bonding parameters (distances in Å, angles in deg) for $[(\eta^5\text{-}C_5H_5)_2Co][H_2PO_4]\cdot 3H_2O$ and $[(\eta^6\text{-}C_6H_5Me)_2Cr][Cl]$

D–H...A	D...A	D–H	H...A	D–H...A
$[(\eta^5\text{-}C_5H_5)_2Co][H_2PO_4]\cdot 3H_2O$				
O(p)–H...O(p)	2.575(2)	1.026(2)	1.578(2)	162.4(1)
O(w)–H...O(p)	2.737(2)	0.977(2)	1.763(2)	174.9(1)
O(w)–H...O(w)	2.796(2)	0.715(2)	2.102(2)	164.1(1)
O(w)–H...O(w)	2.810(2)	0.852(2)	2.017(2)	154.5(1)
O(w)–H...O(w)	2.810(2)	0.913(2)	1.902(2)	172.7(1)
O(w)–H...O(w)	2.796(2)	0.720(2)	2.109(2)	160.1(1)
First image of disorder				
C–H...O(p)	3.322(3)	1.08	2.515(3)	130.7(1)
C–H...O(p)	3.390(3)	1.08	2.406(3)	150.8(1)
C–H...O(p)	3.658(3)	1.08	2.912(3)	126.5(1)
C–H...O(p)	3.268(3)	1.08	2.381(3)	138.4(1)
C–H...O(w)	3.705(3)	1.08	2.866(3)	134.6(1)
C–H...O(w)	3.645(3)	1.08	2.691(3)	147.0(1)
C–H...O(w)	3.570(3)	1.08	2.851(3)	124.1(1)
Second image of disorder				
C–H...O(p)	3.202(3)	1.08	2.239(3)	147.3(1)
C–H...O(p)	3.568(3)	1.08	2.814(3)	126.9(1)
C–H...O(p)	3.279(3)	1.08	2.300(3)	149.9(1)
C–H...O(p)	3.458(3)	1.08	2.413(3)	162.5(1)
C–H...O(w)	3.672(3)	1.08	2.868(3)	131.3(1)
C–H...O(w)	3.506(3)	1.08	2.598(3)	141.2(1)
C–H...O(w)	3.677(3)	1.08	2.870(3)	131.6(1)
$[(\eta^6\text{-}C_6H_5Me)_2Cr][Cl]$				
C–H...Cl	2.875(3)	1.08	3.738(3)	137.0(1)
C–H...Cl	2.914(3)	1.08	3.603(3)	121.9(1)
C–H...Cl	2.808(3)	1.08	3.534(3)	124.5(1)
C–H...Cl	2.614(3)	1.08	3.646(3)	159.7(1)
C–H...Cl	2.919(3)	1.08	3.744(3)	133.4(1)
C–H...Cl	2.928(3)	1.08	3.600(3)	120.6(1)
C–H...Cl	2.721(3)	1.08	3.538(3)	132.2(1)
C–H...Cl	2.740(3)	1.08	3.660(3)	142.9(1)

An O–H...O hydrogen bonded layer is generated by joining together water and dihydrogen phosphate strings. The O-atoms on the layers accommodate the interactions with the cobalticinium cations. As observed in the case of the mixed organic–organometallic crystals prepared by using polycarboxylic acids, the interaction between anions and cations is controlled by C–H...O hydrogen bonds between the cyclopentadienyl C–H groups and the dihydrogen phosphate and water molecules. As expected, the C–H...O hydrogen bonds between the organometallic cation and the inorganic anion ('charge-assisted' by the difference in charge) are appreciably shorter (five distances in the range 2.239(3)–2.413(3) Å) than those involving the water molecules (see Table 1). The network of C–H...O bonds is shown in Fig. 2 for the Cp rings of the main image of disorder (see Section 2), while a space filling representation of the alternate stacking of cobalticinium cations and hydrated dihydrogen phosphate anions is shown in Fig. 3.

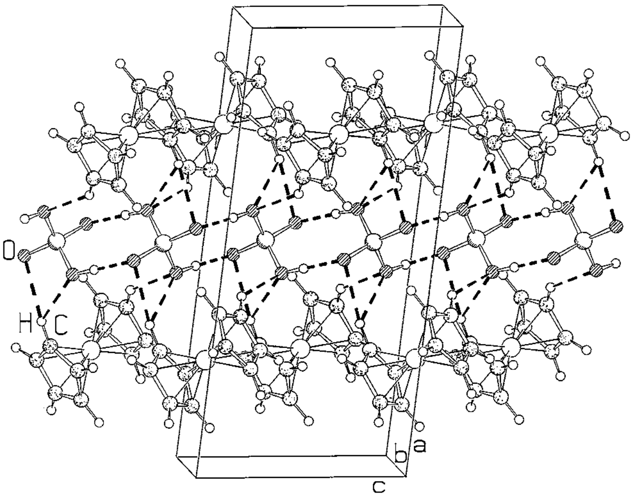

Fig. 2. The network of C–H...O bonds between cobalticinium cations and the $[H_2PO_4]^-$ anions. Only the main image of disorder for the Cp rings is shown for clarity.

A space filling representation of the crystal structure of the chloride $[(\eta^6\text{-}C_6H_5Me)_2Cr][Cl]$ is shown in Fig. 4. The crystal of this simple salt presents some interesting features that deserve examination. The crystal can be described as formed of columns of bis-toluene cations adopting a transoid conformation and of chloride ions. There is a number of C–H...Cl distances (see Table 1) below 2.93 Å thus being appreciably shorter that the sum of the van der Waals radii for the hydrogen and the neutral Cl atoms (ca. 3.0 Å). Two of such distances are ca. 2.72 Å and one is as short as 2.614(3) Å. These data seem to suggest that $C\text{–}H^{\delta+}\ldots Cl^-$ interactions play a role in the stabilization of the crystalline edifice of the chloride. But, how general can this behaviour be? In order to put these data in a somewhat broader perspective (and also in order to prevent objections from the 'unbelievers' of weak hydrogen bonds) we have searched the CSD for the occurrence of C–H...Cl^- interactions involving only chloride ions in organometallic crystals (see Section 2).

The histograms in Fig. 5 compare the distributions of (Tr–C)H...Cl distances (after normalization of the C–H length to the neutron value of 1.08 Å) observed in the case of neutral complexes (Fig. 5, top) with that of charged species (Fig. 5, bottom). The higher proportion of short distances in the latter sample with respect to the former can be appreciated. We have also observed that in both samples the C–H...Cl angles approach linearity as the (Tr–C)H...Cl distances get shorter in keeping with the general behaviour of hydrogen bond interactions.

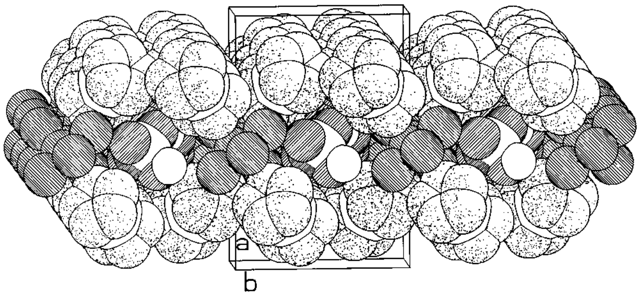

Fig. 3. Space filling representation of the alternate stacking of cobalticinium cations and of hydrated dihydrogen phosphate anions.

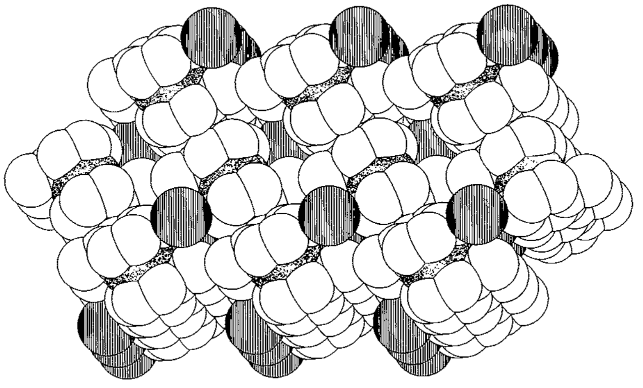

Fig. 4. A space filling representation of the crystal structure of the chloride $[(\eta^6\text{-}C_6H_5Me)_2Cr][Cl]$.

C–H...Cl interactions are expected to be weak because of the low acidity of the C–H system. However, the number of potential donors and the fact that a single chloride ion may act as a multi-acceptor system may well result in an important collective contribution

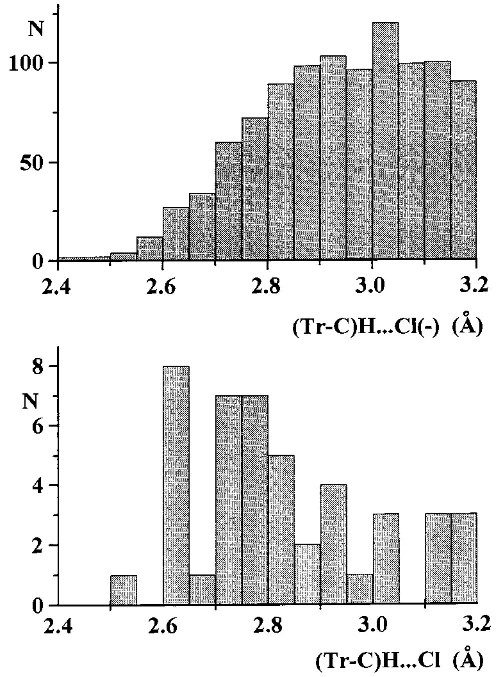

Fig. 5. Histograms showing the distribution of (Tr–C)H...Cl distances (after normalization of the C–H length to the neutron value of 1.08 Å) in the case of neutral (top) and charged systems (bottom). Note how, in spite of the different population, there is a much higher proportion of short distances in the latter sample.

to cohesion. These observations have been compared with the results of an analogous search carried out on neutral complexes. Although distances below 2.9 Å are still observed the percentage of short contacts decreases from ca. 69 to ca. 39% on passing from charged chloride ions to neutral complexes. The sequence of acceptor strength $Cl^- < Cl–M$ or Cl–C is in agreement with the general trend established in a recent paper by Aullon et al. [10].

4. Conclusions

The hydrogen bond provides the most efficacious and robust non-covalent infrastructure to complex architectures and, for this reason, is being widely employed in crystal engineering. The interaction is basically electrostatic in nature, hence all factors influencing the charge distribution on the donor/acceptor system affect the strength of the hydrogen bond.

In this paper we have shown that our synthetic strategy based on the direct deprotonation of a polyprotic acid by means of a non-coordinating base produced in situ can be extended to inorganic acids such as phosphoric acid. The structural result is predictable on the basis of the knowledge accumulated on the interplay between strong and weak hydrogen bonds. Once deprotonated the inorganic acid forms the maximum number of strong hydrogen bonds that is achievable, thus constituting the backbone of the crystal structure. The unused O-atoms lone-pairs are stabilized by the interaction with the weaker hydrogen bond donors on the cyclopentadienyl (or arene) ligands. These interactions, though weak, are numerous and are reinforced by the opposite polarity of the two components thus yielding an overall 'Gulliver effect' (the combination of several weak links) that stabilizes the crystalline edifice.

The 'charge assistance' effect plays a strong influence also on C–H...Cl interactions involving chloride ions, thus reproducing the trend observed in organometallic salts crystallized with the PF_6^- or BF_4^- anions [2](b). These seemingly 'innocent anions', so widely used to crystallize organic or organometallic cations, are involved in a profusion of weak hydrogen bonds in the crystal. One may object that these interactions, in the end, still amount to a very tiny fraction of the overall Coulombic energy of a crystalline salt of the type discussed herein. This is indeed so, but anion–cation Coulombic interactions are non-directional. Weak hydrogen bonds couple some of the Coulombic strength to directionality and provide sieves to drive crystallization.

The use of inorganic polyprotic acids opens a route towards the construction of novel inorganic–organometallic crystalline materials. It is possible to envisage the preparation of systems in which transition metal complexes (with their variable valence and spin states) are encapsulated, and possibly aligned, within robust hydrogen bond networks.

Acknowledgements

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