

Self-Assembly of 1-D Chains of Different Topologies Using the Hydrogen-Bonded Inorganic Supramolecular Synthons N–H···Cl₂M or N–H···Cl₃M

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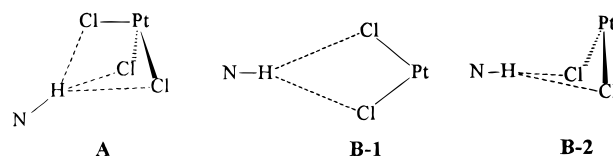
Crystal Engineering^{1,2} has as its ultimate goal the synthesis of crystalline solids from molecular units connected in such a way as to convey desirable macroscopic physical properties.

Achieving this goal requires not only choice of the right molecular building blocks but an understanding, and ultimately some degree of control, of the interactions between molecules. Thus, the common types of intermolecular interactions and geometries, termed “supramolecular synthons” by Desiraju,³ must be identified and studied carefully in conjunction with the energetics of these interactions. Hydrogen bonds, regarded as the strongest and most directional of intermolecular interactions, have been widely exploited in organic crystal engineering,⁴ but less so in systems involving organometallic or coordination compounds.⁵ Nevertheless, transition metal-containing systems offer a wide selection of ligands with available hydrogen bond donor and/or acceptor sites.⁶ The range of accessible metal oxidation states also leads to the ready availability of anionic and cationic species, which have been shown to be advantageous^{2a,4d} (but are less accessible) in hydrogen-bonded organic systems.

Recently we have demonstrated the dramatic enhancement of the acceptor capability⁷ of chlorine imparted by coordination to metal centers, relative to organochlorine, and the anisotropy of the metal chloride acceptor group, which shows strong preference for H···Cl–M angles of 90–130°.⁸ Van Koten has reported a 1-D zigzag chain arrangement based upon O–H···Cl–Pt hydrogen bonds.^{9a} Crabtree has reported a bifurcated N–H···Cl₂M hydrogen bond in the salt 2,6-diphenylpyridinium tetrachloroaurate(III) and suggested basicity of the Cl p-lone pairs favors this arrangement.^{9b} Bernstein has also noted that such bifurcated hydrogen bonds are relatively common,^{9c} based upon a CSD^{9d} search. With this background in mind we have sought to explore the application of double (Cl₂M) or triple (Cl₃M) metal chloride

acceptors and suitable donors in the construction of transition metal-containing hydrogen bonded networks.

In this paper we report the successful application of trifurcated N–H···Cl₃M (A) and bifurcated N–H···Cl₂M hydrogen bonds (B) (here M = Pt) as *inorganic* supramolecular synthons in the construction of linear and zigzag assemblies in the solid state.



Our design strategy was to choose simple systems containing only (strong) metal chloride acceptors and (strong) N–H and (weak) C–H groups as potential donors. The three systems studied, [(DABCO)H₂][PtCl₆] (1), [(DABCO)H₂][PtCl₄] (2), and PtCl₃{(DABCO)H} (3) (DABCO = 1,4-diazabicyclooctane), were prepared from common starting materials and stoichiometry, but under different solution conditions,¹⁰ and characterized by elemental analysis and X-ray crystallography.¹¹ The crystal structures show that 1-D self-assembly of either linear or zigzag chains has been achieved through the dominance of hydrogen bonds formed between strong donors and acceptors using the aforementioned supramolecular synthons. Weaker C–H donors provide cross-linking between the chains using chloride ligand acceptors, as well as the sterically accessible Pt acceptors in 2 and 3.

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- (10) Compound 1 can be prepared from a 1:1 mixture of DABCO and K₂[PtCl₄] in 12 M aqueous HCl solution but is most readily prepared from a 1:1 molar mixture of aqueous [(DABCO)H₂]Cl₂ and K₂[PtCl₆]. Yellow crystals of 1 suitable for X-ray diffraction were grown by evaporation of the solvent (25 °C) after preparation by the latter method. Compounds 2 and 3 were prepared from addition of 1 equiv of [(DABCO)H₂]Cl₂ to an aqueous solution of K₂[PtCl₆]. This results in precipitation of 2 as a pink-cream-colored solid, which upon recrystallization yields red crystals. Over periods of days the initial product 2 is converted in solution into 3 by reaction of [(DABCO)H₂]²⁺ with [PtCl₄]²⁻ with loss of HCl. This conversion can be accelerated by heating the suspension of 2, to remove HCl from solution. Yellow crystals of 3, with crystalline 2 as a minor product, were obtained by evaporation of water from such a heated (80 °C) solution. Elemental analyses concur with expected values.
- (11) Crystal data: **1**, *M* = 521.98, rhombohedral, *R* $\bar{3}m$, *a* = 9.286(1) Å, α = 67.85(1)°, *U* = 660.81(1) Å³, *Z* = 2, *D_c* = 2.623 Mg m⁻³, *R*₁(*F*) = 0.0178, *wR*₂(*F*²) = 0.0547, *S*(*F*²) = 1.68 for 722 *F*² > 2 σ (*F*²). **2**, *M* = 451.08, triclinic, *P* $\bar{1}$, *a* = 6.7139(1) Å, *b* = 6.8680(1) Å, *c* = 13.4628(1) Å, α = 79.000(1)°, β = 83.517(1)°, γ = 71.672(1)°, *U* = 577.53(1) Å³, *Z* = 2, *D_c* = 2.594 Mg m⁻³, *R*₁(*F*) = 0.0241, *wR*₂(*F*²) = 0.0545, *S*(*F*²) = 1.083 for 3008 *F*² > 2 σ (*F*²). **3**, *M* = 414.62, monoclinic, *P*2₁/*n*, *a* = 6.5973(1) Å, *b* = 11.8324(2) Å, *c* = 13.6331(1) Å, β = 102.035(1)°, *U* = 1040.83(2) Å³, *Z* = 4, *D_c* = 2.646 Mg m⁻³, *R*₁(*F*) = 0.0281, *wR*₂(*F*²) = 0.0552, *S*(*F*²) = 1.051 for 3052 *F*² > 2 σ (*F*²). Distances and angles involving hydrogen atoms are calculated assuming N–H and C–H bond lengths normalized to neutron values of 1.01 and 1.08 Å, respectively.

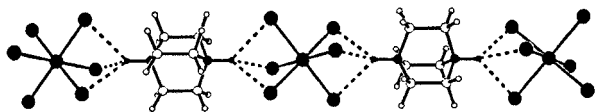


Figure 1. View of **1** perpendicular to linear chains based upon N-H...Cl₃Pt hydrogen bonds (synthon **A**): H...Cl, 2.535, 2.565 Å; N-H...Cl, 132.4, 132.8°; H...Cl-Pt, 78.3, 78.6°; Cl...H...Cl, 79.6, 78.9°. Atoms comprising synthon **A** are shaded. View along the [111] direction showing columnar arrangement provided in the Supporting Information.

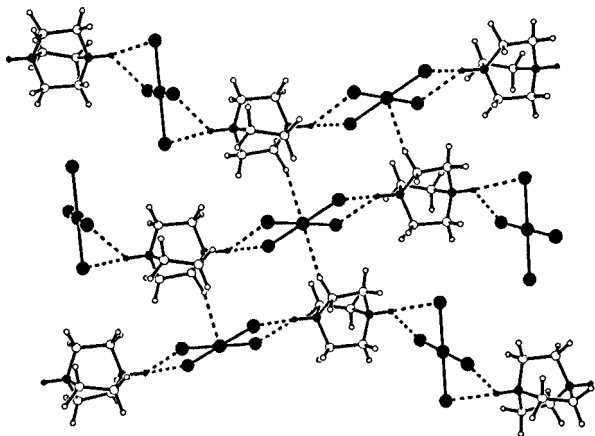


Figure 2. View of **2** showing layers comprising zigzag chains based upon N-H...Cl₂Pt hydrogen bonds. Synthon **B-1**: H...Cl, 2.218, 2.844 Å; N-H...Cl, 152.7, 125.0°; H...Cl-Pt, 104.1, 87.1°. Cl...H...Cl, 78.4°. Synthon **B-2**: H...Cl, 2.480, 2.475 Å; N-H...Cl, 141.7, 127.2°; H...Cl-Pt, 78.8, 78.7°; Cl...H...Cl, 81.3° and cross-linked by C-H...Pt hydrogen bonds (see text). Atoms of synthons **B-1** and **B-2** are shaded.

Compound **1** crystallizes in the uncommon space group $R\bar{3}m$ as linear chains of alternating cations and anions linked via trifurcated N-H...Cl₃Pt hydrogen bonds (synthon **A**) along the crystallographic 3-fold axis (Figure 1). Cations and anions are staggered with respect to each other, necessitating a staggered configuration of consecutive cations. The set of three mutually orthogonal chloride ligands are optimally positioned for interaction with the ammonium hydrogen (H...Cl-Pt ca. 80°). Each chain is surrounded equidistantly by six other chains in a columnar manner, but without short or directional interactions. Interchain H...Cl separations lie in the range 2.78–3.10 Å.

The interaction between strong donors (N-H) and acceptors (Cl-Pt) is maximized in **2** (see Figure 2) by the formation of bifurcated N-H...Cl₂Pt hydrogen bonds (synthon **B**). The conformational flexibility of synthon **B** (i.e. pivoting of the N-H bond about the Cl...Cl vector) is illustrated at the two independent anions, where hydrogen bond conformations lie within 12° of the extremes of parallel (**B-1**) and perpendicular (**B-2**), respectively, to the metal coordination plane.¹² This gives rise to a zigzag chain of alternating cations and anions with alternate anions mutually orthogonal (85.5° angle between PtCl₄ mean planes). Compound **2** also exhibits cross-linking of chains into layers via C-H...Pt hydrogen bonds¹³ (H...Pt 2.601 Å; C-H...Pt 157.3°), which comprise a centrosymmetric C-H...M...H-C arrangement involving two hydrogen bond donors with one metal d_{z²} orbital.¹⁴ These layers are further linked by C-H...Cl hydrogen bonds. (Twelve unique, H...Cl range 2.58–2.95 Å.)

(12) Angles are defined between the N-H vector and the normal to the PtL₄ plane.

(13) A CSD^{9d} search (April 1998 version) identified 41 C-H...Pt contacts with H...Pt ≤ 2.8 Å and C-H...Pt ≥ 120°. For discussion of C-H...Pt hydrogen bonds see refs 13b–d. (b) Brammer, L.; Charnock, J. M.; Goggin, P. L.; Goodfellow, R. J.; Koetzle, T. F.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 1789. (c) Gao, Y.; Eisenstein O.; Crabtree, R. H. *Inorg. Chim. Acta* **1997**, 254, 105. (d) Braga, D.; Grepioni, F.; Tedesco, E.; Biradha K.; Desiraju, G. R. *Organometallics* **1997**, 16, 1846.

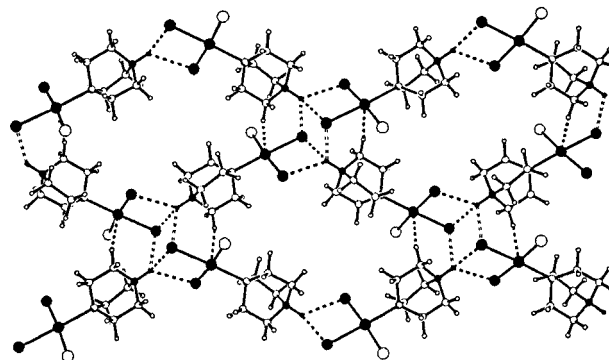


Figure 3. View of **3** perpendicular to the corrugated layers in the (101) plane. Layers comprise zigzag chains based upon N-H...Cl₂Pt hydrogen bonds (synthon **B**, pertinent atoms shaded): H...Cl, 2.602, 2.418 Å; N-H...Cl, 134.2, 128.3°; H...Cl-Pt, 92.8, 98.3°; Cl...H...Cl, 79.4°. Chains are cross-linked by additional longer N-H...Cl hydrogen bonds (H...Cl, 2.901 Å; N-H...Cl, 120.1°) and cross-linked by C-H...Pt hydrogen bonds (see text).

Compound **3** (Figure 3) is a zwitterion with a cationic N⁺-H donor group and three chloride acceptors at the anionic (opposite) end of the molecule (-PtCl₃⁻). Bifurcated N-H...Cl₂Pt hydrogen bonds lead to zigzag chains astride the crystallographic *n*-glide planes. The **B** synthon conformation is intermediate (43.1°) between the **B-1** (0°) and **B-2** (90°) extremes¹² due to weak trifurcation (H...Cl 2.418, 2.602, 2.901 Å) involving a third chloride acceptor from an anion in a neighboring chain. Cross-linking of chains (into corrugated sheets parallel to the (101) planes) also involves short C-H...Pt hydrogen bonds (H...Pt 2.677 Å; C-H...Pt 161.3°).

Thus, we have shown that metal chloride hydrogen bond acceptors, and in particular polychlorometal(ate) compounds, can provide a good basis for supramolecular assembly and crystal engineering of transition metal-containing systems. Specifically, inorganic supramolecular synthons based upon bifurcated and trifurcated hydrogen bonds involving these acceptor groups have been successfully applied to the synthesis of linear and zigzagged 1-D assemblies. These further assemble into columnar stacks (**1**) or sheets (**2** and **3**). In the latter systems, which contain square-planar metal coordination geometries with sterically accessible filled metal orbitals (d_{z²}), intermolecular C-H...Pt hydrogen bonds are involved in assembling the 1-D chains into 2-D sheets.

We are currently exploring the use of the synthons presented herein to develop metal-containing supramolecular systems.

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Supporting Information Available: X-ray crystal structure determination details and figures are available (3 pages), as well as tables of crystal data, atomic coordinates, displacement parameters for **1**, **2**, and **3**, in CIF format, which are available on the Internet only. Ordering and access information is given on any current masthead page.

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