Supporting Information

for

First Systematic Investigation of C-H ... Cl Hydrogen Bonding Using Inorganic Supramolecular Synthons: Lamellar, Stitched Stair-Case, Linked-Ladder, and Helical Structures

By

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Figure S1. $^1$H NMR spectrum (400 MHz) of [(L$_2$)CoCl$_2$] (1) in CD$_3$COCD$_3$ (only relevant portion is shown). Assignments are indicated.

Figure S2. $^1$H NMR spectrum (400 MHz) of [(L$_1$)ZnCl$_2$] (4) in (CD$_3$)$_2$SO (only relevant portion is shown). Assignments are indicated.

Figure S3. $^1$H NMR spectrum (400 MHz) of [(L$_3$)ZnCl$_2$] (5) in (CD$_3$)$_2$SO (only relevant portion is shown). Assignments are indicated.
Figure S4. $^1$H NMR spectrum (400 MHz) of [(L$^5$)ZnCl$_2$] (6) in (CD$_3$)$_2$SO (only relevant portion is shown; NMe signal (not shown) appears at 3.55 $\delta$). Assignments are indicated.

Figure S5. X-ray structure of [(L$^2$)CoCl$_2$] (1); selected bond lengths [Å] and angles [$^\circ$]: Co-N(1) 2.049(2), Co-N(3) 2.002(2), Co-Cl(1) 2.2249(12), Co-Cl(2) 2.2194(14), N(1)-Co-N(3) 92.64(9)$^\circ$, N(1)-Co-Cl(1) 107.70(7)$^\circ$, N(1)-Co-Cl(2) 111.50(7)$^\circ$, N(3)-Co-Cl(1) 115.56(7)$^\circ$, N(3)-Co-Cl(2) 111.01(7)$^\circ$, Cl(1)-Co-Cl(2) 115.94(4)$^\circ$.

Figure S6. View of lamellar structure with two different alternate channels present in the solid-state structure of [(L$^2$)CoCl$_2$] (1). All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity.

Figure S7. A perspective view of [(L$^4$)CuCl$_2$] (3) showing the presence of intramolecular C-H $\cdots$ Cl hydrogen bonds. Hydrogen bonding parameters: $D - H \cdots A$: C6 $-$ H6A $\cdots$ Cl; H $\cdots$ A: 2.666 Å; $D \cdots A$: 3.380 Å; $D - H \cdots A$: 130.80$^\circ$.

Figure S8. X-ray structure of [(L$^1$)ZnCl$_2$] (4); selected bond lengths [Å] and angles [$^\circ$]: Zn-N(1) 2.066(8), Zn-N(3) 2.045(7), Zn-Cl(1) 2.193(3), Zn-Cl(2) 2.222(3), N(1)-Zn-N(3) 91.0(3)$^\circ$, N(1)-Zn-Cl(1) 110.4(2)$^\circ$, N(1)-Zn-Cl(2) 110.1(2)$^\circ$, N(3)-Zn-Cl(1) 114.1(2)$^\circ$, N(3)-Zn-Cl(2) 110.9(2)$^\circ$, Cl(1)-Zn-Cl(2) 117.31(11)$^\circ$.

Figure S9. X-ray structure of [(L$^3$)ZnCl$_2$] (5); selected bond lengths [Å] and angles [$^\circ$]: Zn-N(1) 2.058(3), Zn-N(3) 2.499(3), Zn-N(5) 2.067(3), Zn-Cl(1) 2.3727(13), Zn-Cl(2) 2.2247(13), N(1)-Zn-N(3) 81.38(12)$^\circ$, N(1)-Zn-N(5) 113.95(13)$^\circ$, N(1)-Zn-Cl(1) 94.31(10)$^\circ$, N(1)-Zn-Cl(2) 118.69(10)$^\circ$, N(3)-Zn-N(5) 79.79(12)$^\circ$, N(3)-Zn-Cl(1) 167.64(7)$^\circ$, N(3)-Zn-Cl(2) 88.68(8)$^\circ$, N(5)-Zn-Cl(1) 91.54(10)$^\circ$, N(5)-Zn-Cl(2) 123.42(9)$^\circ$, Cl(1)-Zn-Cl(2) 103.50(5)$^\circ$.

Figure S10. X-ray structure of [(L$^5$)ZnCl$_2$] (6); selected bond lengths [Å] and angles [$^\circ$]: Zn-N(1) 2.242(8), Zn-N(2) 2.157(8), Zn-N(3) 2.232(8), Zn-Cl(1) 2.271(2), Zn-Cl(2) 2.270(2), N(1)-Zn-N(2) 86.9(4)$^\circ$, N(1)-Zn-N(3) 162.9(3)$^\circ$, N(1)-Zn-Cl(1) 97.8(2)$^\circ$, N(1)-Zn-Cl(2) 97.8(2)$^\circ$, N(1)-Zn-Cl(2) 97.8(2)$^\circ$. 
91.9(2)°, N(2)-Zn-N(3) 77.1(4)°, N(2)-Zn-Cl(1) 114.3(2)°, N(2)-Zn-Cl(2) 124.4(2)°, N(3)-Zn-
Cl(1) 94.3(2)°, N(3)-Zn-Cl(2) 92.3(2)°, Cl(1)-Zn-Cl(2) 120.89(10)°.

**Figure S11.** X-ray structure of [(bpc)CoCl₂] (bpc = bis(picolylamino)cyclohexane), showing
intramolecular C-H…Cl hydrogen bonding interactions (ref.29). All the hydrogen atoms
except those involved in hydrogen bonding have been omitted for clarity. Hydrogen bonding
parameters: \( D - H \ldots A \): C16 – H16A... Cl1; \( D \ldots A \): 2.898 Å; \( D - H \ldots A \): 121.81°. Symmetry codes: (i) - x, y, 1/2 - z.

**Figure S12.** Crystal packing diagram of [(Me-Bz-dpa)CoCl₂] (Me-Bz-dpa = dipicolylamine,
pyridine ring 6-substituents: Me, aliphatic amine N has Bz substituent), showing C-H…Cl
hydrogen bonding interactions (ref. 29). All the hydrogen atoms except those involved in
hydrogen bonding have been omitted for clarity. Hydrogen bonding parameters: \( D - H \ldots A \):
C54 – H54 ... Cl2 ; \( D \ldots A \): 3.048Å; \( D - H \ldots A \): 136.36°. \( D - H \ldots A \): C57
– H57A... Cl1 ; \( D \ldots A \): 2.831 Å; \( D - H \ldots A \): 143.32°. \( D - H \ldots A \): C67 –
H67C ... Cl1 ; \( D \ldots A \): 2.860 Å; \( D - H \ldots A \): 138.48°. Symmetry codes: (i) –
1 + x , y, z.
Figure S1
Figure S2
Figure S4
Figure S7
Figure S8