Two-dimensional supramolecular networks via C–H···Cl and N–H···Cl interactions utilizing bidentate neutral pyridine amide coordinated Mn^{II}Cl$_2$ tectons

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Abstract. Reaction of *N*-(phenyl)-2-pyridinecarboxamide (HL^1) and *N*-(*p*-tolyl)-2-pyridinecarboxamide (HL^2) ligands with MnCl$_2$·4H$_2$O affords complexes [(HL^1)$_2$MnCl$_2$] **1** and [(HL^2)$_2$MnCl$_2$] **2**. The structures of **1** and **2** were determined by three-dimensional X-ray crystallography revealing that the Mn^{II} ions assume distorted octahedral geometry with coordination by two HL^1/HL^2 ligands providing two pyridine N and two amide O and two chloride ions. Notably, secondary interactions [C–H···Cl (pyridine 3-H hydrogen) and N–H···Cl (amide NH hydrogen)] triggered by Mn^{II}-coordinated chloride ions acting as hydrogen bonding acceptors generate self-complementary dimeric tectons, which lead to 2D supramolecular architectures.

Keywords. Mn^{II}Cl$_2$-containing coordination compounds; neutral pyridine amide ligands; crystal structures; non-covalent (C–H···Cl and N–H···Cl) interactions; 2D supramolecular networks.

1. Introduction

The basis of crystal engineering,[1–11] a sub-discipline of supramolecular chemistry, is the identification and exploration of reliable synthons[4] that can control the dimensionality of the molecular assembly and thereby lead to controlled supramolecular architectures. In the context of inorganic crystal engineering,[6–11] the combination of coordination chemistry of metal–ligand coordination units with non-covalent interactions, such as hydrogen bonding,[12] provides a powerful method for generating supramolecular architectures from simple building blocks (synthons/tectons). The advantage of using transition metal complexes is that the geometry of the central metal ion controls the shape of the synthon. A typical geometry can then be extended throughout the crystal if suitable ligands are chosen/designed that carry sites suitable for participation in non-covalent interactions with nearest neighbours. In addition to the bench marked C–H···N/O/S hydrogen bonds,[1,12] the existence of C–H···Cl hydrogen bonds[13,14] triggered by terminal M–Cl bonds[8,9,14] have been well recognized in recent times. It is noticeable that terminal M–Cl bonds are distinctly directional acceptors of hydrogen bonds.

Because of our continued interest in both exploration of coordination chemistry with pyridine amide ligands[15–17] and inorganic crystal engineering focusing in the creation of interesting supramolecular architectures of various dimensionality using M^{II}Cl/M^{II}Cl$_2$/M^{III}Cl$_3$-containing simple coordination compounds as tectons *via* primarily C–H···Cl hydrogen bonding interactions[18,19] we were motivated to focus our attention to mononuclear pyridine amide complexes [(HL^1)MnCl$_2$] **1**, [(HL^2)MnCl$_2$] **2** and [(HL^3)MnCl$_2$] **3** [HL^1, *N*-(phenyl)-2-pyridinecarboxamide; HL^2, *N*-(*p*-tolyl)-2-pyridinecarboxamide; HL^3, *N*-(3-chlorophenyl)-pyridine-2-carboxamide] (figure 1).[15,17,20,21] In these complexes the ligands coordinate in their neutral form providing coordination by pyridine nitrogen and amide oxygen.[17] In this report, we demonstrate the existence of C–H···Cl and N–H···Cl interactions as six-coordinate motifs of **1**–**3** act as tectons leading to self-complementary dimers, which eventually afford interesting 2D network assemblies. To look for generalization of observed non-covalent interactions and also for possible rationalization, in this work we have analysed the secondary interactions of the reported complex [(HL^3)$_2$MnCl$_2$] **3**.[21]

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2. Experimental

2.1 Materials

All reagents were obtained from commercial sources and used as received. Solvents were dried/purified as reported previously.[15–19] The ligands HL^1 and HL^2 were synthesized as before.[15,17,20]

2.2 Physical measurements

Elemental analyses were obtained using Thermo Quest EA1110 CHNS-O, Italy. Conductivity measurements were done with an Elico type CM–82T conductivity bridge (Hyderabad, India). Spectroscopic measurements were made using the following instruments: IR (KBr, 4000–600 cm^{-1}), Bruker Vector 22; electronic, Perkin Elmer Lambda 2 and Agilent 8453 diode-array spectrophotometer. Magnetic susceptibility measurements on solid samples of **1** and **2** were done with a locally-built Faraday balance[15,16] equipped with an electromagnet with constant-gradient pole caps (Polytronic Corporation, Mumbai, India), Sartorius balance M-25-D/S (Göttingen, Germany), a closed-cycle refrigerator, and a Lake Shore temperature controller (Cryo Industries, USA). All measurements were made at fixed main field strength of 6 kG. Solution-state magnetic susceptibilities were obtained by the NMR technique of Evans,[22a] in MeCN with a PMX-60 JEOL (60 MHz) NMR spectrometer. Corrections underlying diamagnetism were applied with the use of appropriate constants.[22b]

2.3 Synthesis of complexes

2.3a *[(HL^1)$_2$MnCl$_2$] (1):*
To a stirred solution of HL^1 (0·05 g, 0·25 mmol) in dry MeCN (3 ml), solid

R = R' = H; HL^1
R = Me, R' = H; HL^2
R = H, R' = Cl; HL^3

Figure 1. The ligands used for the synthesis of [(HL^1)$_2$MnCl$_2$] (**1**) and [(HL^2)$_2$MnCl$_2$] (**2**). The complex [(HL^3)$_2$MnCl$_2$] (**3**) is reported in the literature.[21]

$MnCl_2 \cdot 4H_2O$ (0·025 g, 0·125 mmol) was added portion-wise. The light yellow solution that resulted was magnetically stirred for an hour. The light yellow precipitate that formed was filtered, washed with a mixture of MeCN and diethyl ether and air-dried. X-ray quality single crystals were grown by vapour diffusion of diethyl ether into a solution of the complex in EtOH (yield: 0·059 g, ~91%). Anal. calcd. for $C_{24}H_{20}N_4O_2Cl_2Mn$ **1**: C 55·14, H 3·83, N 10·72%. Found: C 54·90, H 3·52, N 10·97%. IR (KBr, cm^{-1}, selected peaks): 3345 ν(N–H), 1640 ν (amide I) and 1550 ν(amide II). Molar conductance, Λ_M (MeCN, ~ 1 mol dm^{-3}, 298 K) = 22 Ω^{-1} cm^2 mol^{-1} (expected range[23] for 1 : 1 electrolyte: 120–160 Ω^{-1} cm^2 mol^{-1}). Absorption spectrum [λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1})]: 240 (26 850), 290 (18 400) (in EtOH). μ_{eff} (solid, 300 K) = 5·95 μ_B. μ_{eff} (MeCN, 300 K) = 5·85 μ_B.

2.3b *[(HL^2)$_2$MnCl$_2$] (2):*
The complex **2** was synthesized following a closely similar methodology as described for the synthesis of **1** (yield: 0·06 g, ~90%). Anal. calcd. for $C_{26}H_{24}N_4O_2Cl_2Mn$ **2**: C 56·70; H 4·36; N, 10·18%. Found: C 57·12; H 4·18, N, 10·67%. IR (KBr, cm^{-1}, selected peaks): 3340 ν(N–H), 1630 ν(amide I) and 1540 ν(amide II). Molar conductance, Λ_M (MeCN, ~ 1 mol dm^{-3}, 298 K) = 8 Ω^{-1} cm^2 mol^{-1} Absorption spectrum [λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1})]: 250 (26 200), 280 (17 700) (in EtOH). μ_{eff} (solid, 300 K) = 5·92 μ_B. μ_{eff} (MeCN, 300 K) = 5·90 μ_B.

2.4 X-ray crystallography

Single crystals of suitable dimensions were used for data collection. Diffracted intensities were collected on a Bruker SMART APEX CCD diffractometer, with graphite-monochromated Mo-K$_\alpha$ (λ = 0·71073 Å) radiation at 100(2) K. For data reduction the 'Bruker Saint Plus' program was used. Empirical absorption correction (SADABS) was applied to data sets. The structures were solved by SIR-97, expanded by Fourier-difference syntheses and refined with the SHELXL-97 package incorporated in the WinGX 1·64 crystallographic collective package.[24] The positions of the hydrogen atoms were calculated assuming ideal geometries, but not refined. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedure on F^2. Intermolecular contacts of the C–H···Cl and N–H···Cl type were examined with the DIAMOND package.[25]

Table 1. Data collection and structure refinement parameters for $[(HL^1)_2MnCl_2]$ (**1**) and $[(HL^2)_2MnCl_2]$ (**2**).

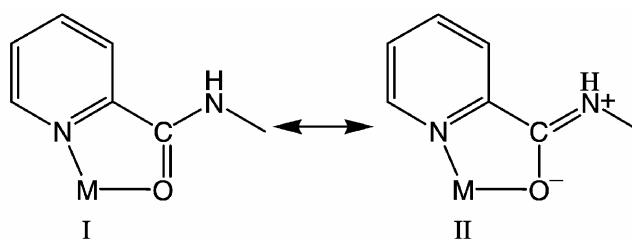|	1	2
Molecular formula	$C_{24}H_{20}Cl_2N_4O_2Mn$	$C_{26}H_{24}Cl_2N_4O_2Mn$
M_r	522·28	550·33
Crystal colour, habit	White, block	White, block
Temperature (K)	100(2)	100(2)
Radiation used (λ/Å)	Mo-K$_\alpha$ (0·71073)	Mo-K$_\alpha$ (0·71073)
Cryst system	Orthorhombic	Orthorhombic
Crystal size (mm)	0·2 × 0·1 × 0·1	0·2 × 0·2 × 0·1
Space group	*Pbcn* (no. 60)	*Pbcn* (no. 60)
a (Å)	13·268(5)	13·318(5)
b (Å)	9·534(5)	9·501(5)
c (Å)	17·368(5)	19·328(5)
V (Å^3)	2197·0(16)	2445·7(17)
Z	4	4
D_c (g cm^{-3})	1·579	1·495
μ (mm^{-1})	0·875	0·791
$F(000)$	1068	1132
No. of reflns collected	13682	15308
No. of indep reflns (R_{int})	2720 (0·0522)	3040 (0·0515)
No. of reflns used ($I > 2\sigma(I)$)	2303	2335
Goodness-of-fit on F^2	1·077	1·141
R (R_w) ($I > 2\sigma(I)$)[a,b]	0·0476, 0·1085	0·0520, 0·1290
R (R_w) (all data)[a,b]	0·0597, 0·1226	0·0779, 0·1669

[a]$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b]$R_w = \{\Sigma[w(|F_0|^2 - |F_c|^2)^2]/\Sigma[w(|F_0|^2)^2]\}^{1/2}$

C–H and N–H distances were normalized along the same vectors to the neutron derived values of 1·083 Å and 1·009 Å, respectively.[12] Pertinent crystallographic parameters are summarized in table 1 and selected metric parameters are presented in table 2. Further details on the CIF files are available from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ quoting the deposition numbers CCDC 648787 **1** and CCDC 648788 **2**.

3. Results and discussion

3.1 *Synthesis and properties*

The complexes $[(HL^1)_2MnCl_2]$ **1** and $[(HL^2)_2MnCl_2]$ **2** were prepared by a straightforward stoichiometric reaction between HL^1/HL^2 and $MnCl_2\cdot4H_2O$ in MeCN. IR spectral data confirm that the ligands have coordinated in their neutral form (scheme 1). In MeCN the complexes behave as non-electrolyte.[23] Micro analytical, solution electrical conductivity and IR spectral data conform to the formulations of **1** and **2**. The μ_{eff} values (~ 5·9 μ_B) of **1** and **2** both in the solid state and in MeCN solution are in conformity with $S = 5/2$ state of manganese(II). As expected, light yellow solutions of **1** and **2** exhibit only metal-perturbed intraligand transitions.

Scheme 1. Resonance forms of metal chelates of pyridine amide ligand coordinated in neutral form.

3.2 *Crystal structures of $[(HL^1)_2MnCl_2]$ 1 and $[(HL^2)_2MnCl_2]$ 2*

Perspective views of the crystal structures of **1** and **2** are shown in figures 2 and 3, respectively. Selected bond distances and angles are collected in table 2. The manganese(II) ion in both complexes sits on a two-fold axis and is coordinated by two chloride ions and two HL^1 ligands in **1** and two HL^2 ligands in **2**. The two bidentate neutral pyridine-2-carboxamide ligands are coordinated to the manganese(II) ion through pyridine nitrogen and amide oxygen. The geometry around the manganese(II) ion is distorted octahedral (table 2). The two chloride ions are mutually *cis* to each other (table 2). The ligand bite angle is 70·93° in **1** and 71·24° in **2**. The Mn–N(pyridine)

bond length is longer than Mn–O(amide) oxygen bond length by 0·063 Å in **1** and 0·054 Å in **2**. Shortening of M^{II}–O(amide) bond lengths must be due to better stabilization of positive charge on the amide N atom and in turn gain of electron density (and formal negative charge) on the carbonyl O atom (scheme 1, resonance form II). This is supported by C–N and C–O bond lengths (table 2).[17,21,26] For a given ligand the angle between a pyridine ring and a phenyl ring is 12·791(9)° for **1** and 12·347(8)° for **2**. Thus the bidentate ligand is almost planar. The bond lengths and angles in **1** and
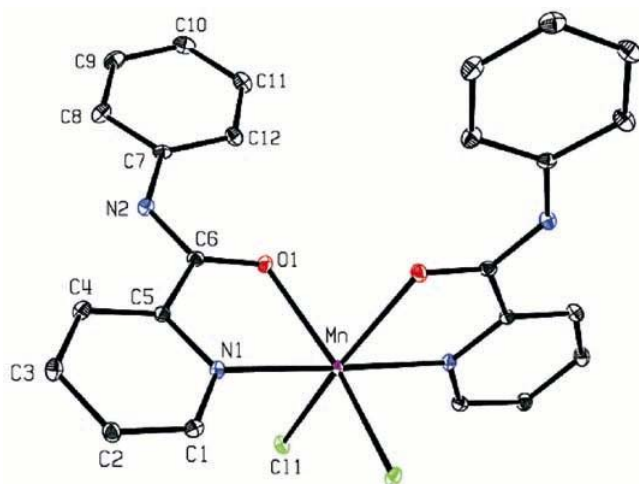

Figure 2. Perspective view of $[(HL^1)_2MnCl_2]$ (**1**). Hydrogen atoms are omitted for clarity.
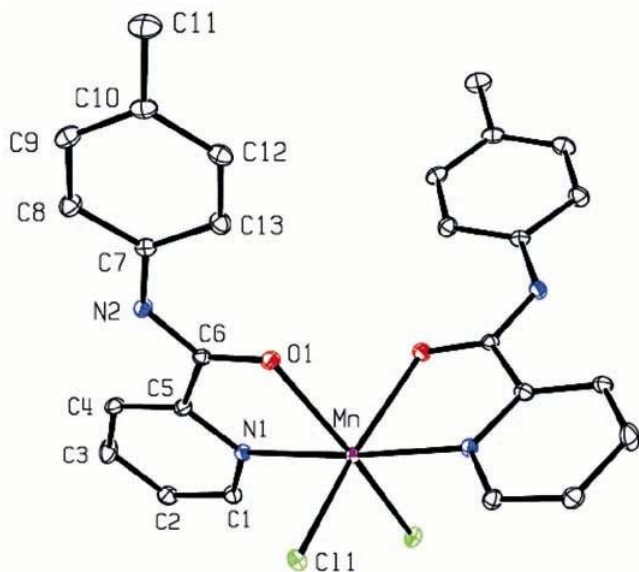

Figure 3. Perspective view of $[(HL^2)_2MnCl_2]$ (**2**). Hydrogen atoms are omitted for clarity.

2 are comparable with similar kind of complexes reported in the literature,[21,26] including the structures reported by us very recently.[17] It should be mentioned here that the structure of $[(HL^3)_2MnCl_2]$ **3** $[HL^3 = N$-(3-chlorophenyl)-pyridine-2-carboxamide] is reported in the literature.[21] Within the complexes **1**, **2** and **3** the Mn–O(amide) [2·244 for **1**, 2·234 for **2** and 2·2158(14) for **3**] and Mn–N(pyridine) [2·306 for **1**, 2·291 for **2** and 2·2821(15) for **3**] bond lengths (Å) follow the trend: **1** > **2** > **3**. Thus the amide oxygen in **3** carries maximum negative charge and hence the C–O bond lengths (Å) [1·238(3) for **1**, 1·234(4) for **2** and 1·234(2) for **3**] follow the trend **3** ≈ **2** > **1**. In line with this the C–N bond lengths (Å) [1·344(3) for **1**, 1·341(4) for **2** and 1·336(2) for **3**] follow the trend **1** > **2** > **3**.

3.3 *Secondary interactions*

As part of our continued activity in inorganic crystal engineering[18,19] involving C–H···Cl hydrogen bonding interactions we have investigated the noncovalent interactions in the crystal packing of **1** and **2** and also for the reported complex $[(HL^3)_2MnCl_2]$ **3**.[21] For all three complexes **1–3** we have identified discrete dimeric units, formed due to bifurcated[8] C–H···Cl [C–H of pyridine ring 3–H] and N–H···Cl [N–H of amide group] contacts. The case of **1** is displayed in figure 4. In these dimers, the Mn···Mn distances are 8·1691(25) Å (for **1**), 8·1798(25) Å (for **2**) and 8·1940(19) Å (for **3**). Notably, out of two Mn-coordinated chloride ions only one is involved in this dimer formation. These dimers form 2D-network structures, utilizing similar C–H···Cl and N–H···Cl

Table 2. Selected bond distances (Å) and angles (°) in $[(HL^1)_2MnCl_2]$ **1** and $[(HL^2)_2MnCl_2]$ **2**.

	1	2
Mn–N1	2·306(2)	2·291(3)
Mn–O1	2·244(2)	2·234(2)
Mn–Cl1	2·4582(10)	2·460(11)
C6–N2	1·344(3)	1·341(4)
C6–O1	1·238(3)	1·235(4)
N1–Mn–O1	70·93(7)	71·25(9)
N1*–Mn–O1	107·75(7)	105·23(9)
N1–Mn–Cl1	88·80(6)	89·64(7)
N1–Mn–Cl1*	92·26(6)	93·21(7)
O1–Mn–Cl1	91·61(6)	91·24(7)
O1–Mn–Cl1*	156·37(5)	157·73(6)
Cl1–Mn–Cl1*	101·48(9)	101·42(9)

*Denotes the symmetry operator: $-x + 1$, y, $-z + 1/2$

Table 3. Hydrogen bonding parameters for $[(HL^1)_2MnCl_2]$ **1**, $[(HL^2)_2MnCl_2]$ **2** and $[(HL^3)_2MnCl_2]$ **3**.

$D–H···A$	$H···A$, Å	$D···A$, Å	$D–H···A$
$[(HL^1)_2MnCl_2]$ (**1**)			
C4–H4···Cl1	2·3993(6)[i]	3·4819(9)[i]	178·698(21)[ii]
N2–H5···Cl1	2·3506(8)[i]	3·4003(12)[i]	162·809(18)[ii]
$[(HL^2)_2MnCl_2]$ (**2**)			
C4–H4···Cl1	2·5137(6)[i]	3·4636(9)[i]	179·041(23)[ii]
N2–H5···Cl1	2·5739(9)[i]	3·3899(12)[i]	167·077(21)[ii]
$[(HL^3)_2MnCl_2]$ (**3**)			
C4–H4···Cl1	2·5246(6)[iii]	3·4536(21)[iii]	176·81(12)[iv]
N2–H2···Cl1	2·5102(8)[iii]	3·3468(18)[iii]	164·365(98)[iv]

Symmetry code: (i) $0·5 + x$, $–0·5 + y$, $0·5 – z$; (ii) $–0·5 + x$, $0·5 + y$, $0·5 – z$; (iii) $1·5 – x$, $0·5 + y$, z; (iv) $1·5 – x$, $–0·5 + y$, z
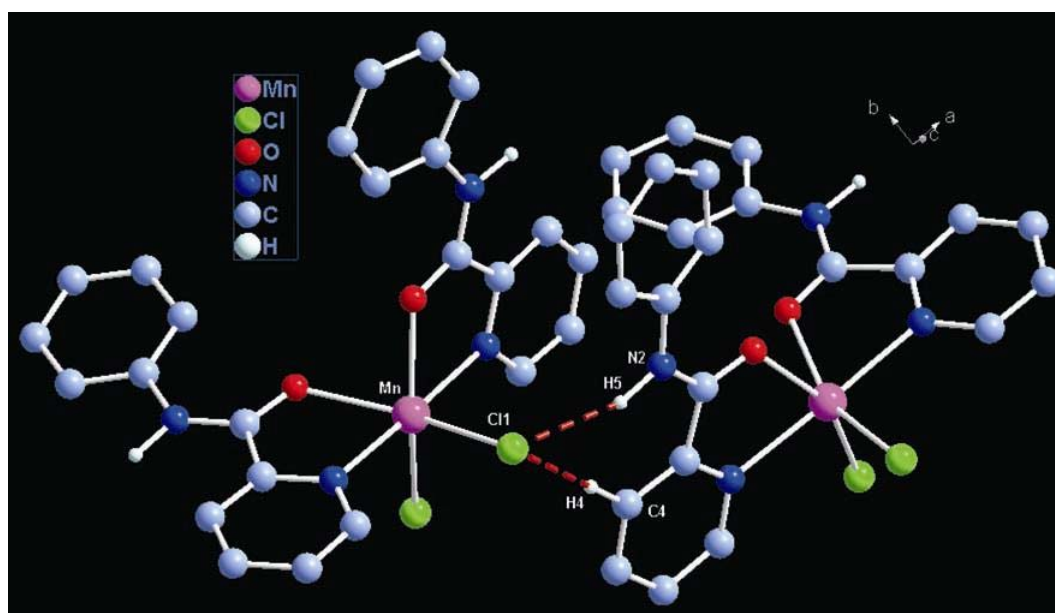

Figure 4. View of the formation of self-complementary dimer via C–H···Cl and N–H···Cl interaction in $[(HL^1)_2MnCl_2]$ **1**. All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity.

hydrogen bonding contacts of both chloride ions. The case of **2** is shown in figure 5. Relevant hydrogen bonding parameters are collected in table 3.

Compared to unsubstituted phenyl group in **1** and electron-releasing (4-methyl substituted) phenyl group in **2**, due to the presence of 3-chlorophenyl group the amide hydrogen in **3** is most acidic and in turn takes part in strongest N–H···Cl interaction (table 3). Within **1**, **2** and **3** the strongest C–H···Cl interaction observed is also for **3**, implying that pyridine 3-H

hydrogen is most acidic (table 3). In other words, the Mn–N(pyridine) bond distance is strongest in **3**.

The observed C–H···Cl (2·3993–2·5246 Å and 176·81–179·04°) and N–H···Cl (2·3506–2·5739 Å and 162·81–167·08°) hydrogen bonding parameters are in good agreement with literature tabulations (2·569–2·944 Å and 119·3–169·2° for C–H···Cl).[27] Thus compared to literature values, C–H···Cl interactions in these complexes are quite strong (intermediate contacts: 2·52–2·95 Å; distances ≤ 2·52 Å
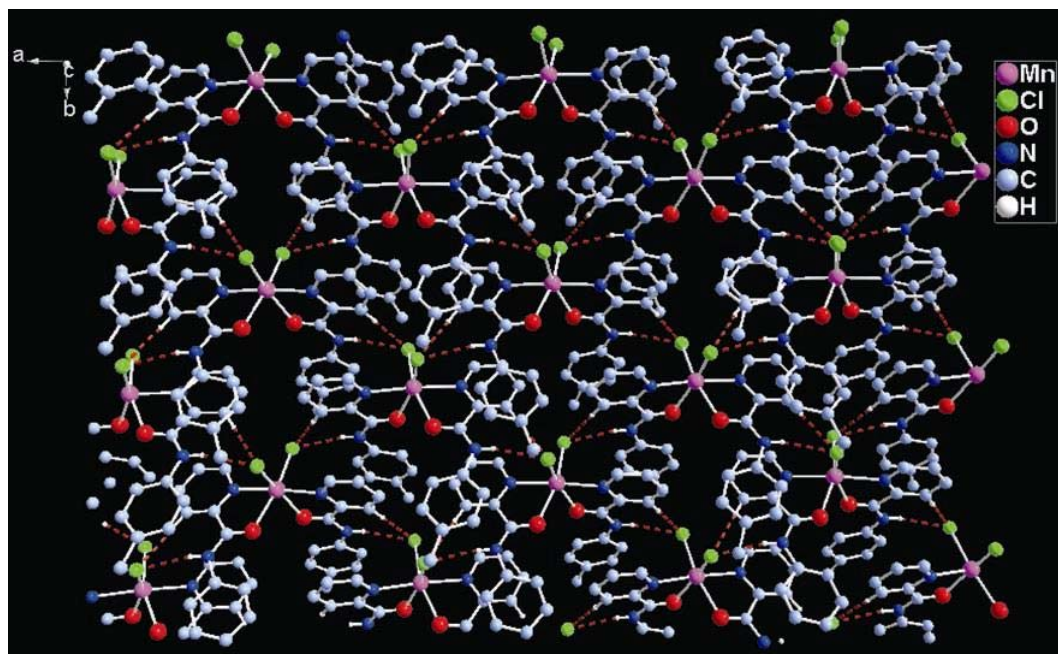
Figure 5. View of the formation of 2D network (*ab* plane) in $[(HL^2)_2MnCl_2]$ **2** via C–H⋯Cl and N–H⋯Cl hydrogen bonding. All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity.

are termed 'short').[14] The strength of N–H⋯Cl interactions is reasonable[19b,28] and in **1** the N–H⋯Cl interaction is quite strong.

4. Conclusions

Using two bidentate pyridine amide ligands, two manganese(II) complexes have been synthesized and structurally characterized. Structural analysis reveals that the complexes have distorted octahedral geometry. Examination of non-covalent interactions of these complexes and also for that already reported in the literature reveal that in these complexes strong intermolecular C–H⋯Cl and reasonable N–H⋯Cl hydrogen bonding interactions are present. The secondary interactions result in the formation of self-complementary dimers, which in turn lead to 2D supramolecular architectures.

Acknowledgements

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