

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

V. Balamurugan,^[a] Maninder Singh Hundal,^[b] and Rabindranath Mukherjee*^[a]

Abstract: Using a group of six neutral M^{II}Cl₂-containing coordination compounds as building blocks, the first systematic investigation of C–H...Cl hydrogen-bonding interactions was performed. Single-crystal X-ray structural analyses of four new compounds (pseudo-tetrahedral Co^{II} and Zn^{II}; distorted trigonal bipyramidal Zn^{II}) authenticate the metal coordination geometry. To provide a unified view of the presence of noncovalent interactions in this class of compounds, we have re-examined the packing diagram of two previously reported compounds (a distorted square-pyramidal Cu^{II}

complex and a *trans*-octahedral Co^{II} complex). The organic ligands of our choice comprise bidentate/tridentate pyrazolylmethylpyridines and an unsymmetrical tridentate pyridylalkylamine. This systematic investigation has allowed us to demonstrate the existence of versatile C–H...Cl₂M interactions and to report the successful application of such units as inorganic supra-

molecular synthons. Additional noncovalent interactions such as C–H...O and O–H...Cl hydrogen bonding and π – π stacking interactions have also been identified. Formation of novel supramolecular architectures has been revealed: 2D lamellar (*p*-cyclophane) and 3D lamellar, 3D “stitched staircase” (due to additional hydrogen-bonding interactions by water tetramers, with an average O–O bond length in the tetramer unit of 2.926 Å, acting as “molecular clips” between staircases), 3D linked ladder, and single-stranded 1D helix.

Keywords: crystal engineering · hydrogen bonding · π interactions · supramolecular chemistry · water tetramer

Introduction

The field of crystal engineering of supramolecular architectures is currently experiencing enormous growth.^[1–4] A realistic approach to crystal engineering or synthesis is the identification and exploitation of reliable synthons^[1d,e] that can control the dimensionality of the molecular assembly and therefore lead to controlled crystal structures or architectures. Hydrogen bonds often play a dominant role in crystal engineering because they combine, in addition to specificity, strength with directionality, and hence these features, in combination, control the design of various molecular assem-

blies.^[2,3] Such bonds have been extensively used in the field of organic crystal engineering to assemble organic molecular building blocks into well-defined crystalline networks.^[1–3] The central aim of inorganic crystal engineering^[4] is the development of a general protocol for the propagation of organic ligand-bound metal-containing modules in directions dictated by the coordination geometry of the metal center. This can be achieved by using covalent or noncovalent interactions, leading to novel supramolecular architectures of varying dimensionality and topology.

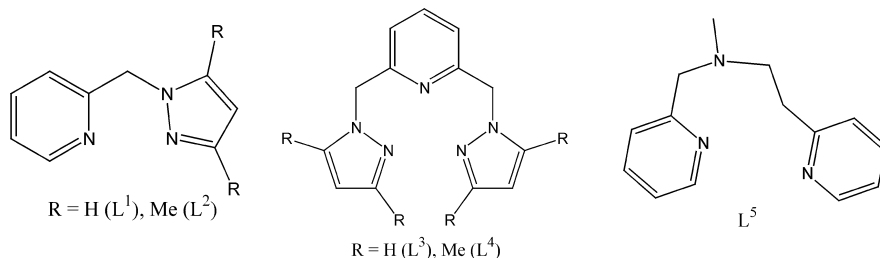
In addition to the commonly occurring C–H...N/O/S hydrogen-bonding interactions,^[2] the existence of C–H...Cl hydrogen bonds,^[5] in general, and charge-assisted (for strengthening noncovalent forces)^[6] terminal M–Cl bonds^[7] of chlorometalate anions,^[7–10] in particular, have been well-appreciated in recent times. Such interactions have been shown to be capable of playing a decisive role in the supramolecular structure of solids. It should be noted here that terminal M–Cl bonds are distinctly directional acceptors of hydrogen bonds (with typical H...Cl–M angles in the range of 90–130°).^[9] The present investigation originated from our search for the possibility of the existence and influence of C–H...Cl hydrogen-bonding interactions in primarily neutral coordination complexes of a selected group of ligands (L¹ –

[a] V. Balamurugan, Prof. Dr. R. Mukherjee
Department of Chemistry
Indian Institute of Technology
Kanpur 208 016 (India)
Fax: (+91) 512-2597437
E-mail: rnm@iitk.ac.in

[b] Prof. Dr. M. S. Hundal
Department of Chemistry
Guru Nanak Dev University
Amritsar 143 005 (India)

Supporting information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author.

L^5) with $M^{II}Cl_2$ moieties.^[11–14] Herein we combine the major features of the approaches of organic and inorganic crystal engineering. Thus, organic ligands are coordinated to metal



ions in well-defined geometries, as in the strategy for designing inorganic coordination polymers. However, the chosen ligands do not have a second site suitable for coordination to another metal center, but rather carry sites suitable for linking molecules through noncovalent interactions. As a first step towards this goal we have selected six complexes— $[(L^2)CoCl_2]$ (**1**),^[12] $[(L^1)_2CoCl_2] \cdot 4H_2O$ (**2**),^[11c] $[(L^4)CuCl_2]$ (**3**),^[15] $[(L^1)ZnCl_2]$ (**4**), $[(L^3)ZnCl_2]$ (**5**), and $[(L^5)ZnCl_2]$ (**6**)—to explore the potential of these coordination building blocks for systematically studying the formation of periodic *supramolecules*. The complexes **1**, **4**, **5**, and **6** were synthesized^[12] and structurally characterized, while the structures of complexes **2** and **3** were re-analyzed. Our aim was to investigate how systematic change in 1) the nature of the metal ion, 2) the nature and denticity of ligands, 3) the ori-

entation of metal-bound chloride ions, and 4) ligands' ring substituents would influence network topology. In this contribution we provide examples of the presence of a wide variety of noncovalent interactions such as C–H...Cl (intra- and intermolecular), C–H...O and O–H...Cl (intermolecular) hydrogen bonding and π – π stacking in a selected group of simple coordination complexes. Such secondary interactions led to the formation of novel supramolecular networks. The primary concern of this work is the demonstration of the gener-

ality and versatility of the existence of C–H...Cl₂M^{II} hydrogen-bonding interactions in simple coordination compounds (metal–ligand units), which eventually act as inorganic supramolecular synthons.

Results and Discussion

Synthesis and properties of the investigated compounds:

Mixing equimolar quantities of an EtOH/MeCN solution of $MCl_2 \cdot xH_2O$ ($M = Co^{II}$, $x = 6$; $M = Zn^{II}$, $x = 0$) and appropriate ligand (L^1 – L^5) at room temperature, resulted in the formation of desired new compounds $[(L^2)CoCl_2]$ (**1**), $[(L^1)ZnCl_2]$ (**4**), $[(L^3)ZnCl_2]$ (**5**), and $[(L^5)ZnCl_2]$ (**6**). In each case, X-ray-quality crystals were readily obtained (Table 1). Each

Table 1. Crystallographic data for $[(L^2)CoCl_2]$ (**1**), $[(L^3)ZnCl_2]$ (**4**), $[(L^1)ZnCl_2]$ (**5**), and $[(L^5)ZnCl_2]$ (**6**).

	1	4	5	6
empirical formula	C ₁₁ H ₁₃ N ₃ Cl ₂ Co	C ₉ H ₉ N ₃ Cl ₂ Zn	C ₁₃ H ₁₃ N ₃ Cl ₂ Zn	C ₁₄ H ₁₇ N ₃ Cl ₂ Zn
formula weight	317.07	295.46	375.55	363.58
crystal system	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
<i>a</i> [Å]	8.113(3)	12.241(2)	8.519(5)	8.662(3)
<i>b</i> [Å]	8.228(1)	7.487(5)	8.833(5)	11.497(2)
<i>c</i> [Å]	10.727(5)	14.001(3)	11.580(5)	15.478(4)
α [°]	76.35(4)		79.460(5)	
β [°]	76.90(4)	113.35(6)	69.940(5)	95.99(3)
γ [°]	75.99(3)		70.940(5)	
volume [Å ³]	664.1(4)	1178.1(8)	771.2(7)	1533.0(7)
<i>Z</i>	2	4	2	4
ρ_{calcd} [g cm ⁻³]	1.586	1.666	1.617	1.575
μ [mm ⁻¹]	1.674	2.507	1.938	1.943
<i>F</i> (000)	322	592	380	744
crystal size [mm]	0.5 × 0.2 × 0.1	0.2 × 0.3 × 0.2	0.3 × 0.3 × 0.2	0.4 × 0.3 × 0.3
diffractometer	Enraf Nonius MACH2	Siemens P4	Siemens P4	Siemens P4
θ range for data collect.	1.99–24.99°	1.81–27.50°	1.88–24.99°	2.21–24.98°
reflections collected	2520	2833	2899	2431
independent reflect. (R_{int})	2338 (0.0162)	2709 (0.0610)	2702 (0.0289)	2242 (0.0362)
absorption correction	analytical	not measured	not measured	not measured
reflections with $I > 2\sigma(I)$	2000	1409	2290	1750
no. of param.	162	136	202	179
GOF on F^2	1.120	0.983	1.064	1.066
final $R1^{[a]}$ ($I > 2\sigma(I)$)/ $wR2^{[b]}$	0.0300/0.0811	0.0842/0.2102	0.0440/0.1099	0.0730/0.1930
$R1^{[a]}$ / $wR2^{[b]}$ (all data)	0.0380/0.0848	0.1651/0.2457	0.0541/0.1161	0.0927/0.2102
max./min. peak [$e \text{ \AA}^{-3}$]	0.43/–0.28	1.70/–0.99	1.00/–0.65	1.63/–0.52

[a] $R1 = \sum(|F_o| - |F_c|) / \sum |F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)]\}^{1/2}$.

new complex gave satisfactory microanalytical results. The characterization data of dark blue $[(L^2)CoCl_2]$ (**1**), which is soluble in most common organic solvents, have already been described.^[12] The Zn^{II} compounds are soluble in *N,N*-dimethylformamide/dimethyl sulfoxide (Me_2SO) and in aqueous $MeOH$. The bulk properties of each isolated complex was further examined by its 1H NMR spectral behavior (see Figures S1–S4 in the Supporting Information).^[11d,e,12,13,16] The only paramagnetic compound $[(L^2)CoCl_2]$ (**1**) gives rise to paramagnetically shifted resonances^[11d,12] ranging from $\delta \sim +60$ to -20 ppm relative to Me_4Si . The peaks have been assigned in comparison with available data on complexes of this class of ligands. Each diamagnetic compound $[(L^1)ZnCl_2]$ (**4**), $[(L^3)ZnCl_2]$ (**5**), and $[(L^5)ZnCl_2]$ (**6**) displayed clean spectra. Thus, 1H NMR spectral results convincingly demonstrated that the compound present in solution corresponds to that of the observed crystal structure (see below), excluding the possibility of having other polymorphs in the product of the compound in question.

Structural analysis of compounds: X-ray analysis of complex $[(L^2)CoCl_2]$ (**1**) indicates that the coordination environment around Co^{II} is pseudo-tetrahedral, with coordination from the bidentate ligand L^2 and two chloride ions (see Figure S5 in the Supporting Information). The angle between the pyridyl ring and that of the pyrazole ring is $\approx 49.6^\circ$, confirming its nonplanarity.^[11,14] From a study of the crystal packing diagram we identify a discrete dimeric unit, as exemplified by others in various systems with other noncovalent interactions^[1c,10b,17] involving intermolecular C–H...Cl contacts (the Co–Co distance = 6.405 \AA). In the dimer the Co–Cl bond (of two only one is involved) of one molecule is linked with the pyridyl C–H of the other in the adjacent layer (Figure 1,

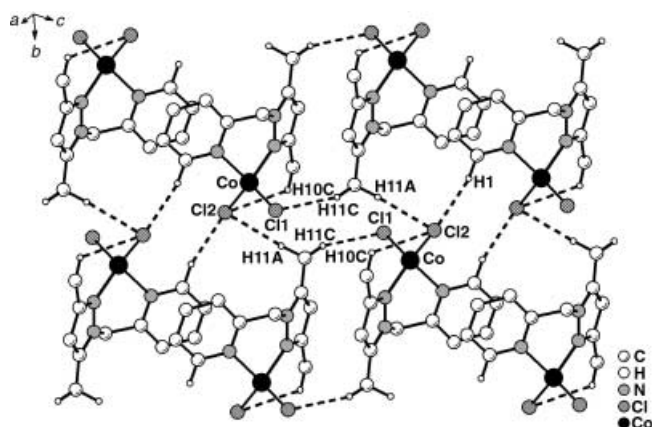


Figure 1. View of the dimerization of $[(L^2)CoCl_2]$ (**1**) unit, the pyridyl–pyridyl/ π – π stacking (projection down *b* axis), the pyrazole–pyrazole/ π – π stacking (projection down *c* axis), and formation of a lamellar structure (projection down *b* axis). All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity.

Table 2). This is an example of self-complementary hydrogen-bonding interactions.^[1c] Notably, using pyridyl groups, such dimers stack^[18–20] with a distance of $\approx 3.650 \text{ \AA}$ (strong π – π interactions are accepted to have values around 3.3 \AA ,

Table 2. Hydrogen-bonding (C–H...Cl) parameters for $[(L^2)CoCl_2]$ (**1**).

<i>D</i> –H... <i>A</i>	H... <i>A</i> , \AA	<i>D</i> ... <i>A</i> , \AA	<i>D</i> –H... <i>A</i>
C1–H1...Cl2	2.543 ^[ii]	3.575 ^[ii]	159.64° ^[ii]
C10–H10C...Cl2	2.886	3.632	126.33°
C11–H11A...Cl2	2.678 ^[iii]	3.756 ^[iii]	177.19° ^[iii]
C11–H11C...Cl1	2.734 ^[iv]	3.740 ^[iv]	154.84° ^[iv]

Symmetry codes: [i] $1-x, 2-y, 1-z$; [ii] $x, 1+y, z$; [iii] $x, -1+y, z$; [iv] $-x, 1-y, 2-z$.

and weaker interactions above 3.6 \AA)^[18] along the *b* axis in a staggered fashion (the Co–Co distance = 7.571 \AA). This stacking, with additional intermolecular C–H...Cl secondary interactions between dimers (pyrazole C–H), eventually leads to the formation of a 2D network. When viewed down the *b* axis a channel ($5.53 \times 2.97 \text{ \AA}^2$) is clearly seen (Figure 1). Each Cl2 atom of a coordination module (pyrazole C–H) is involved in an intramolecular C–H...Cl interaction^[21] as well. Furthermore, intermolecular C–H...Cl interactions between the pyrazole methyl substituent and Cl1, and π – π stacking interactions^[18–20] involving pyrazole–pyrazole rings ($\approx 3.678 \text{ \AA}$) in a staggered manner (Co–Co distance = 7.854 \AA ; a channel of $\approx 9.00 \times 6.52 \text{ \AA}^2$ is formed) lead to the formation of a novel 3D network array of two alternate channels (see Figure S6 in the Supporting Information). Interestingly, in each modular unit of **1**, one of the chloride ions acts as hydrogen acceptor to three molecules (trifurcated)^[9] through C–H...Cl interactions (Figure 1).

Careful study of the extended structure of previously reported^[11c] *trans*-octahedral $[(L^1)_2CoCl_2] \cdot 4H_2O$ (**2**) reveals two intramolecular C–H...Cl contacts (CH_2 spacer) and two intermolecular contacts (pyridyl C–H) to two molecules in two different layers. These secondary interactions lead to the formation of a molecular “staircase” (Figure 2, Table 3, the neighboring Co–Co distance is 8.854 \AA). We believe the

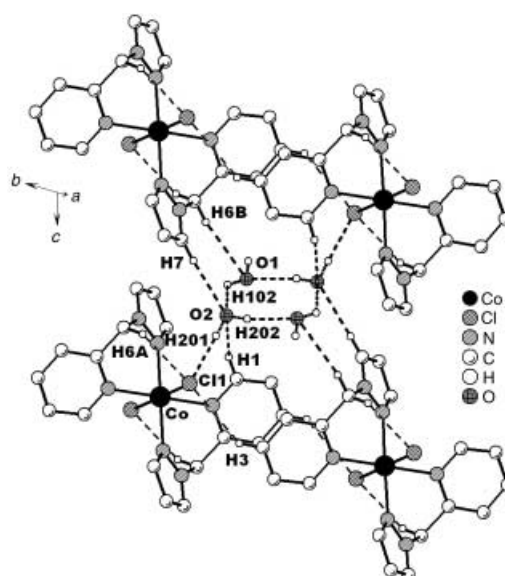


Figure 2. Water tetramer connecting four inorganic supramolecular synthons, *trans*- $[(L^1)_2CoCl_2]$ in $[(L^1)_2CoCl_2] \cdot 4H_2O$ (**2**) through C–H...O and O–H...Cl hydrogen-bonding interactions. All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity.

Table 3. Hydrogen-bonding parameters for $[(L^1)_2CoCl_2] \cdot 4H_2O$ (**2**).

$D-H \cdots A$	$H \cdots A$ [Å]	$D \cdots A$ [Å]	$D-H \cdots A$ [°]
C-H \cdots Cl			
C3-H3 \cdots Cl1	2.822 ^[i]	3.651 ^[ii]	133.49 ^[i]
C6-H6A \cdots Cl1	2.483 ^[iii]	3.326 ^[iii]	134.08 ^[iii]
C-H \cdots O			
C1-H1 \cdots O2	2.565 ^[iii]	3.474 ^[iii]	141.29 ^[iii]
C6-H6B \cdots O1	2.599	3.664	168.53
C7-H7 \cdots O2	2.278	3.343	168.73
O-H \cdots Cl			
O2-H201 \cdots Cl1	2.174 ^[iv]	2.987 ^[iv]	151.02 ^[iv]

Symmetry codes: [i] $1-x, -1-y, -z$; [ii] $1-x, -y, -z$; [iii] $x, y, -1+z$; [iv] $x, y, 1+z$.

formation of such a novel molecular “staircase” is due to the presence of the *trans*-octahedral structure of the inorganic supramolecular synthon $[(L^1)_2CoCl_2]$. Most interestingly, the crystal-packing diagram of **2** reveals the existence of water tetramers (Table 4),^[22] which was not appreciated

Table 4. Hydrogen-bonding (O \cdots O) parameters for $[(L^1)_2CoCl_2] \cdot 4H_2O$ (**2**).

$O1-O2$	2.916 Å	$O1-O2-O1$	97.92°
$O1-O2^{[i]}$	2.936 Å	$O2-O1-O2^{[ii]}$	82.08°

Symmetry codes: [i] $1-x, -1-y, 1-z$.

earlier.^[11c] Furthermore, these water tetramers provide sites for additional hydrogen-bonding interactions, C-H \cdots O (pyridyl C-H; CH₂ spacer; pyrazole C-H) and O-H \cdots Cl. Thereby they act as “molecular clips”^[23] to stitch two adjacent molecular staircases, affording novel 3D supramolecular networks resembling “stitched staircases” (Figure 3). Notably, in each modular unit of **2** both the chloride ions act as hydrogen acceptors to three molecules (trifurcated)^[9] through C-H \cdots Cl and O-H \cdots Cl interactions.

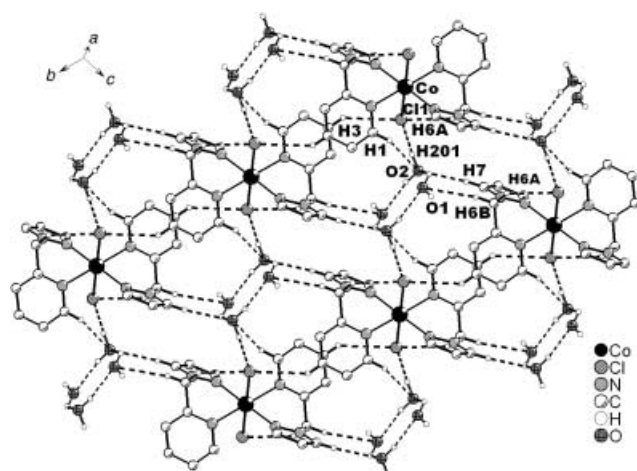


Figure 3. The water tetramer linked through four *trans*-octahedral $[(L^1)_2CoCl_2]$ units (projection down c axis) in $[(L^1)_2CoCl_2] \cdot 4H_2O$ (**2**) by O-H \cdots Cl and C-H \cdots O hydrogen bonds (projection down a axis). All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity.

Re-examination the structure (see Figure S7 in the Supporting Information) of distorted square-pyramidal ($\tau = 0.16$)^[24] $[(L^4)CuCl_2]$ (**3**) reveals the existence of intramolecular^[21] C-H \cdots Cl contacts (each chloride ion, present in the equatorial plane, interacts with a CH₂ spacer), which did not attract the attention of Manoharan et al.^[15]

The structure analysis of $[(L^1)ZnCl_2]$ (**4**) shows that the geometry at the Zn^{II} center is pseudo-tetrahedral, with coordination from the bidentate ligand L^1 and two chloride ions (see Figure S8 in the Supporting Information). Here the angle between the pyridyl ring and the pyrazole ring is about 59.5°, confirming its nonplanarity.^[11,14] Careful study of the crystal packing diagram again reveals a discrete dimeric unit (the Zn-Zn distance: 7.044 Å) involving intermolecular C-H \cdots Cl contacts, linking a Zn-Cl bond (out of two only one is involved, the other remains as a silent “spectator”) of one molecule with a pyridyl C-H of the other in the same plane (Figure 4, Table 5; see also Figure 1). We be-

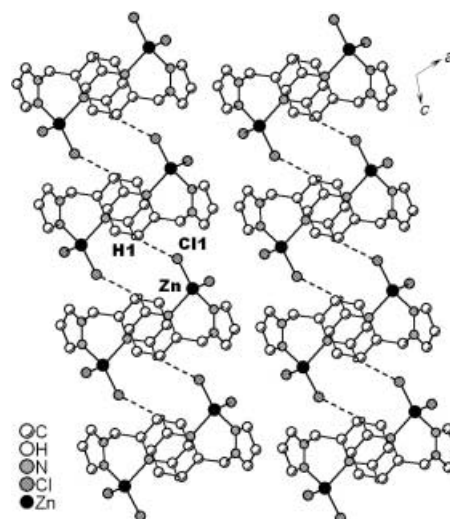


Figure 4. View of the dimerization of $[(L^1)ZnCl_2]$ (**4**) unit and the pyridyl-pyridyl/ π - π stacking (projection down b axis). All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity.

Table 5. Hydrogen-bonding (C-H \cdots Cl) parameters for $[(L^4)CuCl_2]$ (**3**), $[(L^1)ZnCl_2]$ (**4**), $[(L^3)ZnCl_2]$ (**5**), and $[(L^5)ZnCl_2]$ (**6**).

$D-H \cdots A$	$H \cdots A$ [Å]	$D \cdots A$ [Å]	$D-H \cdots A$ [°]
(3) C6-H6A \cdots Cl	2.666	3.380	130.80
(4) C1-H1 \cdots Cl1	2.870	3.595	135.72
(5) C7-H7 \cdots Cl2	2.743 ^[i]	3.633 ^[ii]	139.52 ^[i]
C11-H11 \cdots Cl1	2.591 ^[iii]	3.472 ^[iii]	138.24 ^[iii]
(6) C7-H7B \cdots Cl2	2.785	3.615	133.43 ^[iii]

Symmetry codes: [i] $1-x, 1-y, 2-z$; [ii] $1+x, y, z$; [iii] $1/2-x, 1/2+y, 1/2-z$.

lieve that reduced steric congestion in $[(L^1)ZnCl_2]$ (**4**) compared to $[(L^2)CoCl_2]$ (**1**) (that is, L^1 vs L^2) is the reason behind the availability of two mononuclear units in the same plane. It is notable that using pyridyl groups in a stag-

gered manner, such dimers stack along the *b* axis (π – π stacking distance ≈ 3.858 Å)^[18–20], leading to a 2D network resembling a molecular ladder^[25] (Figure 4). Furthermore, the formation of multiple ladders, leading to a 3D network, is also observed due to π – π stacking interactions^[18–20] between pyrazole rings (≈ 3.476 Å)^[18–20] of adjacent ladders in a staggered fashion along the *c* axis (Figure 5).

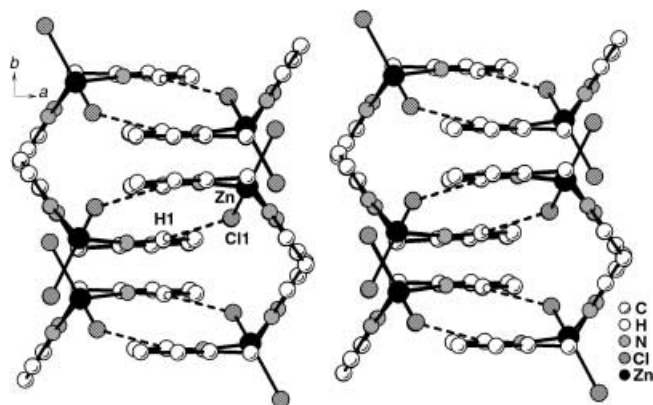


Figure 5. View of the linked ladder, the pyridyl–pyridyl/ π – π stacking (projection down *c* axis), and the pyrazole–pyrazole/ π – π stacking interaction in $[(L^1)ZnCl_2]$ (**4**) (see also Figure 4). All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity.

Single-crystal X-ray analysis of the complex $[(L^3)ZnCl_2]$ (**5**) shows that the geometry at the Zn^{II} center is distorted trigonal bipyramidal ($\tau = 0.737$),^[24] with coordination from the tridentate ligand L^3 and two chloride ions (see Figure S9 in the Supporting Information). While the angles between a pyridyl ring and pyrazole rings are between about 59.3 and about 60.8°, the angle between two pyrazole rings is about 77.2°. These data confirm its nonplanarity.^[11,14] Within the present class of compounds, the crystal packing diagram for **5** reveals a noteworthy effect. The most attractive feature of this structure is again the dimerization of the basic coordination module $[Zn(L^3)Cl_2]$ by means of a C–H⋯Cl hydrogen bond involving the pyridine C–H and Cl atom of two adjacent molecules. The packing also revealed extensive pyridine–pyridine/ π – π stacking interactions (distance = 3.616 Å)^[18–20] between adjacent layers, which ultimately resulted in novel closed inorganic *p*-cyclophanes^[26] (Figure 6, Table 5), due to C–H⋯Cl hydrogen bonding. Such dimers propagate in the *ab* plane (due to additional C–H⋯Cl interactions involving pyrazole C–H moieties) to form a channel (5.74×8.70 Å²) when viewed down the *a* axis. It is worth mentioning here that the formation of closed inorganic *p*-cyclophanes due to noncovalent interactions is not a common phenomenon.

As seen in Figure S9 in the Supporting Information, in the X-ray structure of $[(L^5)ZnCl_2]$ (**6**), each Zn^{II} ion adopts a distorted trigonal bipyramidal geometry ($\tau = 0.642$).^[24] The Zn^{II} ions are coordinated to three N atoms (two pyridyl nitrogen atoms and an aliphatic amine) from the unsymmetrical ligand L^4 , which adopts a meridional coordination mode, and two chloride ions. Very interestingly, the packing dia-

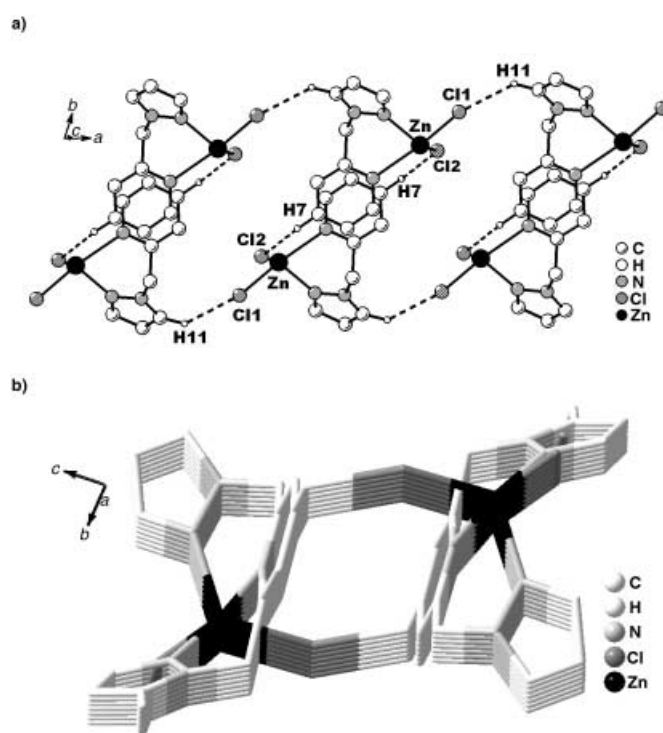


Figure 6. a) View of the dimerization of $[(L^3)ZnCl_2]$ (**5**) unit forming an inorganic cyclophane ring, the pyridyl–pyridyl/ π – π stacking (projection down *b* axis), and b) the formation of a lamellar structure (projection down *b* axis). All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity.

gram of compound **5** reveals that, in each $[(L^5)ZnCl_2]$ module, only one of two chloride ions is involved in an intermolecular C–H⋯Cl hydrogen-bonding interaction with the CH_2 spacer of the ethylpyridyl arm of the next molecule in the layer (see Figure 4). This leads to a 1D single helical architecture along the *c* axis (Figure 7, Table 5). The neigh-

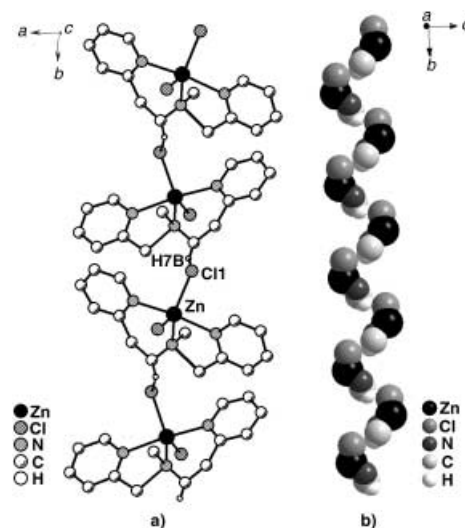


Figure 7. a) A perspective view of the formation of a single helix through C–H⋯Cl hydrogen bonding in $[(L^5)ZnCl_2]$ (**6**). All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity. b) Space-filling view of the inner channel running parallel to the helical axis.

boring Zn–Zn distance is 7.732 Å. In this system an inner channel running parallel to the helical axis exists. The design and synthesis of materials with helical structures are challenging topics of current interest.^[27] It must be remarked that the assembly of a single helical structure as observed here is due to a unique supramolecular event: the perfect periodic self-assembly of a [(L⁵)ZnCl₂] coordination motif, held together by C–H⋯Cl hydrogen bonding interactions. We believe that the distorted trigonal bipyramidal geometry of the metal site, with the novel secondary interaction provided by C–H⋯Cl hydrogen bonding capable of imparting directionality, has provided the required turn to generate a helical structure. To the best of our knowledge, this is the first example of a 1D network of a single helix fully assembled by C–H⋯Cl hydrogen-bonding interactions. It must be noted that, recently, other 1D networks based on helical structures have been reported.^[28]

Rationalization of observed noncovalent interactions: The molecular packing in the crystal structures of [(L)M^{II}Cl₂] complexes **1–6** reveals an array of weak C–H⋯Cl hydrogen-bonding interactions, intramolecular as well as intermolecular. However, additional secondary interactions such as C–H⋯O and O–H⋯Cl hydrogen bonding, and π – π stacking have also been observed to be present. In the present group of coordination building blocks, there are four distinct types of C–H⋯Cl interactions between the metal-bound chloride ion (acceptors) and the C–H moieties (donors) on the same or an adjacent molecule. The identified donors are: 1) the H4 or H6 atom of a pyridine ring, 2) the H5 atom of a pyrazole ring, 3) the H atom of the 3- or 5-methyl group of a pyrazole ring, and 4) a H atom from a methylene spacer. There are three distinct types of C–H⋯O(H₂) interactions: with the H6 atom of a pyridine ring, the H atom of a CH₂ spacer, and the H5 atom of a pyrazole ring. There is only one type of O–(H₂)⋯Cl interaction, however. Careful analysis of the supramolecular architectures noticed here (Figure 1–7), along with the above observations, led us to present the following hypotheses. 1) From the point of view of charge distribution in the pyridine ring(s) present in ligands L¹–L⁵, which is tuned by the withdrawal of electrons from the ring carbon atoms towards the nitrogen atom, and donation of electron density to the metal ion, the ring(s) is/are deactivated. This will cause positions 4 and 6 to be electron deficient, and the C–H groups would thereby be ideally suited to take part in C–H⋯Cl hydrogen-bonding interactions. 2) For pyrazole groups present in L¹–L⁴, the electron-deficient sites are the 3 and 5 positions. 3) It is understandable that the H atoms of –CH₂– spacers in L¹–L⁵ are acidic and therefore are expected to participate in C–H⋯Cl hydrogen bonding interactions. 4) We believe that the π – π stacking interactions observed in the structures of compounds **1**, **4**, and **5** are due to the nonplanarity^[11,14] of pyridyl or pyrazole rings in the chosen ligands (L¹–L⁴). This is augmented by the Cl–M–Cl angle, which is dictated by the structural preference of the metal ion. 5) The observation of a single helical structure for **6** must be due to the unsymmetrical nature of the flexible ligand L⁵, allowing a turn/twist necessary to impart helicity.

For six-coordinate “MCl₂” or “MCl₃”-containing coordination complexes, careful analysis of C–H⋯Cl hydrogen-bonding interactions as a function of the Cl–M–Cl angle reveals interesting features. No intermolecular C–H⋯Cl interactions are found with more acute Cl–M–Cl angles; however, intramolecular interactions could be observed. In other words, the coordination unit remains as a mononuclear unit (within the range of H⋯Cl distance considered here: 2.52–2.95 Å), similar to that observed in *cis*-octahedral [(bpc)CoCl₂] (bpc = bis(picolyamino)cyclohexane. The X-ray structure was re-examined and the Cl–Co–Cl angle found to be about 98°). However, intermolecular C–H⋯Cl interactions are seen above ≥ 2.95 Å.^[29] When the Cl–M–Cl angle is more obtuse, such as that in the compound [(trpy)RuCl₃] (trpy = 2,2':6',2''-terpyridine; the Cl–Ru–Cl bond angles are 88.17(9), 93.88(8), and 177.92(9)°), two *trans* chloride ions were utilized to form the “staircase”/“ladder”-type network structure.^[30a] In this compound the other chloride ion does not take part in C–H⋯Cl interactions. The network topology observed for the compound *trans*-octahedral [(L¹)₂CoCl₂]·4H₂O (**2**) is consistent with this hypothesis.

Conclusion

A number of C–H⋯Cl distances observed in this study (2.483–2.886 Å, Tables 2, 3, and 5) are appreciably shorter than the sum of the van der Waals radii for the H and the neutral Cl atoms (2.95 Å).^[7] These can be classified as intermediate contacts (2.52–2.95 Å; distances ≤ 2.52 Å are termed “short”).^[7] These data seem to suggest that a variety of C–H⋯Cl₂M^{II} interactions identified here play a crucial role in the stabilization of the supramolecular assemblies observed. Individually, these intermolecular C–H⋯Cl interactions are clearly weak because of the low acidity of the C–H system. A manifestation of the weakness of these interactions is the ease of deformation, resulting in the wide range of C–H⋯Cl geometries observed. However, the number of potential donors and the fact that a single chloride ion may act as a multi-acceptor system (Figure 1 and 2) may well result in an important collective contribution to cohesion. The arrangements in Figure 1–7 represent by far the most versatile C–H⋯Cl hydrogen bonds known. As far as we are aware, this is the first time that C–H⋯Cl interactions have been explicitly cited as the structure-determining factor in coordination complexes, leading to inorganic crystal engineering. It must be remarked here that, very recently, reports on molecular packing analyses of classical coordination compounds, having M–Cl moieties, have appeared, revealing the existence of C–H⋯ClM interactions.^[30]

In conclusion, we have shown how careful selection of coordination units (organic ligand bound to suitable metal ion; inorganic supramolecular synthons with distorted tetrahedral, distorted square pyramidal/trigonal bipyramidal and *trans*-octahedral geometry) allowed us 1) to exploit predominantly C–H⋯Cl noncovalent interactions, 2) to construct *super*molecules, and 3) to investigate the structure of the final assembled network. The archetypal supramolecular

synthon in some of the structures presented here is the C–H...Cl₂M hydrogen-bonded dimer, formed by self-complementarity of hydrogen-bond interactions. The complementarity can involve both geometric factors and a suitable balance between the number of hydrogen-bond donors and hydrogen-bond acceptors. These complementary supramolecular synthons bring molecules together and also constrain the relative orientation of those components, in much the same way as metal–ligand bonds impart specific stereochemistry to individual “[L(M^{II}Cl₂)]” molecules. The metal–ligand effects and geometry are clear examples of the “inorganic” factors that affect the strength of hydrogen-bonding interactions involving coordination complexes.

The essence of this work is expected to stimulate research interests in the use of coordination complexes as building blocks, in the context of inorganic crystal engineering. The strategy described here is intended to provide a guide for supramolecular synthesis of materials with a specific design or function. Our ongoing efforts are aimed to address such possibilities. However, it should be emphasized that solid-state structures arise from a balance of a large number of intermolecular forces.

Experimental Section

General: Reagent or analytical grade materials were obtained from commercial suppliers and used without further purification. Solvents were dried as described previously.^[11–13] Ligands L¹–L⁵ were prepared as before.^[11–13] Elemental analyses (C, H, N) were performed by the Microanalysis Service Center at the Department of Chemistry, Indian Institute of Technology Kanpur. ¹H NMR spectral measurements were performed on a JEOL-JNM-LA-400 FT (400 MHz) NMR spectrometer.

[(L²)CoCl₂] (1): A solution of ligand L² (0.08 g, 0.43 mmol) in EtOH (5 mL) was added to CoCl₂·6H₂O (0.1 g, 0.42 mmol) dissolved in EtOH (2 mL). After the mixture had been stirred for 2 min, a deep blue microcrystalline solid precipitated. The solid obtained was filtered, washed with ethanol, and dried in vacuo. X-ray quality single crystals were obtained by diffusion of diethyl ether into a solution of the complex in MeCN. Yield: 0.1 g (75%). Elemental analysis calcd (%) for C₁₁H₁₃N₃Cl₂Co: C 41.63, H 4.10, N 13.25; found: C 41.50, H 4.20, N 13.10.

[(L¹)ZnCl₂] (4): A solution of ZnCl₂ (0.086 g, 0.629 mmol) in MeCN (2 mL) was added to a solution of L¹ (0.1 g, 0.629 mmol) in MeCN (2 mL). After the mixture had been stirred for 2 min, a colorless microcrystalline solid precipitated. The solid thus obtained was filtered, washed with MeCN, and dried in vacuo. X-ray quality crystals were obtained by slow evaporation of a MeOH solution of the complex. Yield: 0.15 g (81%). Elemental analysis calcd (%) for C₉H₉N₃Cl₂Zn: C 36.61, H 3.05, N 14.24; found: C 36.30, H 3.20, N 13.92.

[(L³)ZnCl₂] (5): A solution (2 mL) of ZnCl₂ (0.058 g, 0.42 mmol) in MeCN was added to a solution (4 mL) of L³ (0.1 g, 0.42 mmol) in MeCN. After the mixture had been stirred for 2 min, a colorless microcrystalline solid precipitated. The solid thus obtained was filtered, washed with MeCN, and dried in vacuo. Single crystals suitable for structural studies were obtained by slow evaporation of a solution of the complex in a MeOH–H₂O mixture (2:1 v/v). Yield: 0.12 g (77%). Elemental analysis calcd (%) for C₁₃H₁₃N₃Cl₂Zn: C 41.56, H 3.46, N 18.65; found: C 41.50, H 3.50, N 18.70.

[(L⁵)ZnCl₂] (6): A solution of ZnCl₂ (0.060 g, 0.44 mmol) in MeCN (2 mL) was added to a solution of L⁵ (0.1 g, 0.44 mmol) in MeCN (3 mL). After the mixture had been stirred for 30 min the solvent was slowly evaporated. The white solid that formed was filtered, washed with Et₂O, and dried in vacuo. Recrystallization was achieved by slow evaporation of an aqueous solution of the complex. Yield: 0.12 g (75%). Elemental

analysis calcd (%) for C₁₄H₁₇N₃Cl₂Zn: C 46.28, H 4.68, N 11.57; found: C 45.83, H 4.48, N 11.39.

X-ray crystallography: X-ray data were collected at 293(2) K either on an Enraf Nonius MACH2 (Indian Institute of Technology Kanpur; compound **1**) or on a Siemens P4 (Guru Nanak Dev University; compounds **4**, **5**, and **6**) diffractometer, equipped with graphite-monochromated MoK_α radiation (λ = 0.71073 Å). Lorentz and polarization corrections were applied for all compounds. A semiempirical absorption correction was carried out for compound **1**. The structures were solved by direct methods using SIR-92 and refined by full-matrix least-squares methods based on F² using SHELXL-97, incorporated in WINGX 1.64 crystallographic collective package.^[31] All non-hydrogen atoms were refined anisotropically. In most cases hydrogen atoms were located (except for hydrogen atoms of water molecules in the structure of **2** and in **4**, hydrogen atoms were placed geometrically) in difference maps, included in idealized positions, and treated using riding model approximations with displacement parameters derived from those of the atoms to which they were bonded. C–H distances were all normalized to the neutron-derived values (1.08 Å).^[4] Intermolecular contacts of the C–H...Cl type with H...Cl distances ≤ 2.95 Å were accepted and subsequently examined with the DIAMOND package.^[32] CCDC-216153 (**1**), CCDC-216155 (**2**), CCDC-216152 (**4**), CCDC-221353 (**5**) and CCDC-216154 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

We thank Dr. Tapan K. Lal for the synthesis and X-ray analysis of **1** (primary structure). Financial support from the Department of Science & Technology and the Council of Scientific & Industrial Research, Government of India is gratefully acknowledged.

- [1] a) G. R. Desiraju, *Acc. Chem. Res.*, **2002**, *35*, 565–573; b) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658; c) C. B. Aakeröy, A. M. Beatty, *Aust. J. Chem.* **2001**, *54*, 409–421; d) G. R. Desiraju, *Chem. Commun.* **1997**, 1475–1482; e) G. R. Desiraju, *Angew. Chem.* **1995**, *107*, 2541–2558; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311–2327; f) C. B. Aakeröy, K. R. Seddon, *Chem. Soc. Rev.*, **1993**, 397–407.
- [2] G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, **1999**.
- [3] T. Steiner, *Angew. Chem.* **2002**, *114*, 50–80; *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76.
- [4] a) D. Braga, *J. Chem. Soc. Dalton Trans.* **2000**, 3705–3713; b) D. Braga, F. Grepioni, *Acc. Chem. Res.* **2000**, *33*, 601–608.
- [5] a) C. B. Aakeröy, T. A. Evans, K. R. Seddon, I. Pálinkó, *New J. Chem.* **1999**, 145–152; b) P. K. Thallapally, A. Nangia, *Cryst. Eng. Commun.* **2001**, *27*, 1–6.
- [6] a) D. Braga, S. M. Draper, E. Champeil, F. Grepioni, *J. Organomet. Chem.* **1999**, *573*, 73–77; b) D. Braga, F. Grepioni, *New J. Chem.* **1998**, 1159–1161.
- [7] G. Aullón, D. Bellamy, L. Brammer, E. A. Bruton, A. G. Orpen, *Chem. Commun.* **1998**, 653–654.
- [8] a) F. Neve, O. Francescangeli, A. Crispini, *Inorg. Chim. Acta* **2002**, *338*, 51–58; b) W. Li, S.-L. Zheng, C.-R. Zhu, Y.-X. Tong, X.-M. Chen, *Aust. J. Chem.* **2002**, *55*, 561–563; c) A. L. Gillon, G. R. Lewis, A. G. Orpen, S. Rotter, J. Starbuck, X.-M. Wang, Y. Rodríguez-Martín, C. Ruiz-Pérez, *J. Chem. Soc. Dalton Trans.* **2000**, 3897–3905; d) M. Freytag, P. G. Jones, *Chem. Commun.* **2000**, 277–278.
- [9] L. Brammer in *Perspectives in Supramolecular Chemistry - Crystal Design: Structure and Function*, Vol. 7 (Ed.: G. R. Desiraju), Wiley, Chichester, **2003**, pp. 1–75.
- [10] a) L. Brammer, *Dalton Trans.* **2003**, 3145–3157, and references therein; b) L. Brammer, J. K. Swearingen, E. A. Bruton, P. Sherwood, *Proc. Natl. Acad. Sci. (USA)* **2002**, *99*, 4956–4961; c) L.

- Brammer, E. A. Bruton, P. Sherwood, *Cryst. Growth Des.* **2001**, *1*, 277–290.
- [11] a) S. Singh, V. Mishra, J. Mukherjee, N. Seethalekshmi, R. Mukherjee, *Dalton Trans.* **2003**, 3392–3397, and references therein; b) R. Mukherjee, *Coord. Chem. Rev.* **2000**, *203*, 151–218; c) T. K. Lal and R. Mukherjee, *Polyhedron* **1997**, *16*, 3577–3583; d) S. Mahapatra, T. K. Lal, R. Mukherjee, *Polyhedron* **1993**, *12*, 1477–1481; e) S. Mahapatra, R. Mukherjee, *J. Chem. Soc. Dalton Trans.* **1992**, 2337.
- [12] T. K. Lal, PhD thesis, Indian Institute of Technology Kanpur (India), **1997**.
- [13] a) T. K. Lal and R. Mukherjee, *Inorg. Chem.* **1998**, *37*, 2373–2382, and references therein; b) N. Gupta, S. Mukerjee, S. Mahapatra, M. Ray, R. Mukherjee, *Inorg. Chem.* **1992**, *31*, 139–141.
- [14] R. Mukherjee in *Comprehensive Coordination Chemistry-II: From Biology to Nanotechnology, Vol. 6* (Eds.: J. A. McCleverty, T. J. Meyer; Volume Ed.: D. E. Fenton), Chapter on Copper, Elsevier, Amsterdam, **2003**, pp. 747–910.
- [15] P. Manikandan, K. R. Justin Thomas, P. T. Manoharan, *J. Chem. Soc. Dalton Trans.* **2000**, 2779–2785.
- [16] a) K. G. Orrell, A. G. Osborne, M. W. da Silva, M. B. Hursthouse, S. J. Coles, *Polyhedron* **1997**, *16*, 3003–3012; b) A. A. Watson, D. A. House, P. J. Steel, *Inorg. Chim. Acta* **1987**, *130*, 167–176; c) D. A. House, P. J. Steel, A. A. Watson, *Aust. J. Chem.* **1986**, *39*, 1525–1536.
- [17] D. Badura, H. Vahrenkamp, *Inorg. Chem.* **2002**, *41*, 6013–6019.
- [18] C. Janiak, *J. Chem. Soc. Dalton Trans.* **2000**, 3885–3896.
- [19] Z. R. Bell, J. A. McCleverty, M. D. Ward, *Aust. J. Chem.* **2003**, *56*, 665–670.
- [20] a) C. Seward, J. Pang, S. Wang, *Eur. J. Inorg. Chem.* **2002**, 1390–1399; b) L. J. Childs, N. W. Alcock, M. J. Hannon, *Angew. Chem.* **2001**, *113*, 1113–1115; *Angew. Chem. Int. Ed.* **2001**, *40*, 1079–1081.
- [21] T. Spaniel, H. Görls, J. Scholz, *Angew. Chem.* **1998**, *110*, 1962–1966; *Angew. Chem. Int. Ed.* **1998**, *37*, 1862–1865.
- [22] a) I. Takahashi, S. Kamimura, M. Hatanaka, H. Kitajima, A. Yamano, T. Ohta, S. Hosoi, *Anal. Sci.* **2003**, *19*, 807–808; b) S. Supriya, S. Manikumari, P. Raghavaiah, S. K. Das, *New J. Chem.* **2003**, *27*, 218–220; c) A. Escuer, F. A. Mautner, E. Penalba, R. Vicente, *Inorg. Chem.* **1998**, *37*, 4190–4196.
- [23] F. Huang, L. N. Zakharov, A. L. Rheingold, J. W. Jones, H. W. Gibson, *Chem. Commun.* **2003**, 2122–2123.
- [24] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* **1984**, 1349–1356 (in a perfect square pyramidal geometry τ equals 0, while it is 1 in a perfect trigonal bipyramidal geometry).
- [25] P. Losier, M. J. Zaworotko, *Angew. Chem.* **1996**, *108*, 2957–2960; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2779–2782.
- [26] F. M. Tabellion, S. R. Seidel, A. M. Arif, P. J. Stang, *Angew. Chem.* **2001**, *113*, 1577–1580; *Angew. Chem. Int. Ed.* **2001**, *40*, 1529–1532, and references therein.
- [27] A. E. Rowan, R. J. M. Nolte, *Angew. Chem.* **1998**, *110*, 65–71; *Angew. Chem. Int. Ed.* **1998**, *37*, 63–68.
- [28] a) P. Vishweshwar, R. Thaimattam, M. Jaskolski, G. R. Desiraju, *Chem. Commun.* **2002**, 1830–1831; b) J. E. Field, D. Venkataraman, *Chem. Commun.* **2002**, 306–307; c) J. Yao, W. Huang, B. Li, S. Gou, Y. Xu, *Inorg. Chem. Commun.* **2002**, *5*, 711–714, and references therein; d) S. J. Geib, C. Vicent, E. Fan, A. D. Hamilton, *Angew. Chem.* **1993**, *105*, 83–85; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 119–121.
- [29] T. M. Kooistra, K. F. W. Hekking, Q. Knijnenburg, B. de Bruin, P. H. M. Budzelaar, R. de Gelder, J. M. M. Smits, A. W. Gal, *Eur. J. Inorg. Chem.* **2003**, 648–655.
- [30] a) F. Laurent, E. Plantalech, B. Donnadiou, A. Jiménez, F. Hernández, M. Martínez-Ripoll, M. Biner and A. Llobet, *Polyhedron* **1999**, *18*, 3321–3331; b) J. C. M. Rivas, R. T. M. de Rosales, S. Parsons, *Dalton Trans.* **2003**, 2156–2163; c) H.-T. Wu, S.-L. Li, T. C. W. Mak, *Dalton Trans.* **2003**, 1666–1668; d) R. Xuan, W. Hu, Z. Yang, R. Xuan, *Acta Crystallogr. Sect. C* **2003**, *59*, m112–m114; e) M. Du, Y.-M. Guo, S.-T. Chen, X.-H. Bu, *J. Mol. Struct.* **2002**, *641*, 29–34; f) Y.-M. Guo, M. Du, S.-T. Chen, X.-H. Bu, *Acta Crystallogr. Sect. E* **2002**, *58*, m454–m456; g) S. M. O. Quintal, H. I. S. Nogueira, V. Félix, M. G. B. Drew, *New J. Chem.* **2000**, *24*, 511–517.
- [31] L. J. Farrugia, WINGX ver 1.64 (**2003**), An Integrated Systems of Windows programs for the Solution, Refinement and Analysis of single-crystal X-ray diffraction data, Department of Chemistry, University of Glasgow.
- [32] DIAMOND ver 2.1c, Crystal Impact GbR, Bonn, Germany, **1999**.

Received: November 6, 2003 [F5701]