

# Functionalised azetidines as ligands: some basic coordination chemistry

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**Abstract** Crystal structure determinations on Cu(II) and Zn(II) complexes of tridentate and quadridentate azetidine derivatives show the ligands to be facultative for square-pyramidal and trigonal bipyramidal coordination geometries. While various contributions to the chirality of the complexes are possible, single diastereoisomeric forms (as enantiomer mixtures) have been isolated in all cases in the solid state. Analysis of lattice interactions indicates that H-bonding and aromatic stacking interactions are generally important.

**Keywords** Azetidines · Metal complexes ·  
Crystal structures · Lattice interactions

We dedicate this manuscript to Prof. Jack Harrowfield and Dr. Jacques Vicens in celebration of their 65th birthdays.

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## Introduction

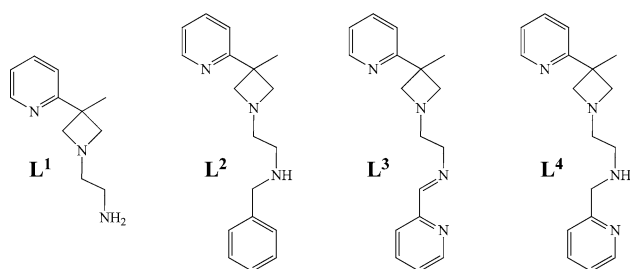
While the coordination chemistry of azetidine derivatives is relatively unexplored [1], we have recently shown that such ligands may be of utility in the formation of water-soluble catalysts for important reactions such as Suzuki-Miyaura and Sonogashira couplings [2, 3]. In these instances, both tridentate and quadridentate azetidine derivatives proved to give rise to efficient catalysts and, to define in greater detail the coordination chemistry of such ligands, we report herein some structural studies of complexes of Cu(II) and Zn(II), metal ions which frequently display quite different coordination preferences. The azetidine derivatives employed are shown in Fig. 1. An aspect of interest in the structural studies was that of the intermolecular interactions of the complexes as possible indicators of the mechanisms for substrate and catalyst association in reactions.

## Experimental

### Synthesis and characterisation

The complexes  $\text{Cu}(\mathbf{L}^1)\text{Cl}_2 \cdot \text{H}_2\text{O}$  and  $\text{Cu}(\mathbf{L}^4)\text{Cl}_2$ , and the ligands  $\mathbf{L}^2$  and  $\mathbf{L}^3$  were available from our earlier work [2, 4, 5]. All other chemicals were commercial products and were used as received. Cation exchange chromatography for complex purification was performed using SP Sephadex C25  $\text{Na}^+$  form resin in glass columns under gravity flow. Elemental analyses were performed using a Chemtronics TEA-3000 instrument.

$[\text{Zn}(\mathbf{L}^1)\text{Cl}_2] - \text{Cu}(\mathbf{L}^1)\text{Cl}_2 \cdot \text{H}_2\text{O}$  (2.0 g) was dissolved in water (30 mL), zinc powder (2.0 g) added and the mixture stirred at room temperature for 12 h. The colourless solution produced was filtered and reduced to a volume



**Fig. 1** Tri- and quadridentate azetidine derivatives used in the present work

~3 mL under vacuum. Vapour diffusion of ethanol into this solution produced colorless crystals suitable for a structure determination. The bulk material was collected by filtration, washed with cold ethanol and dried under vacuum. Yield, 1.5 g. Anal. calcd. for  $[\text{Zn}(\text{L}^1)\text{Cl}_2] = \text{C}_{11}\text{H}_{17}\text{Cl}_2\text{N}_3\text{Zn}$ : C 40.33, H 5.23, N 12.83. Found: C 40.7, H 5.4, N 12.8%.

$[\text{Cu}(\text{L}^2)\text{Cl}_2] \cdot \text{H}_2\text{O} - \text{L}^2$  (1.0 g) was dissolved in methanol (100 mL),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.61 g in 50 mL methanol) added, and the mixture stirred for 0.5 h at room temperature. The resulting deep-blue solution was evaporated to dryness under reduced pressure, the residue dissolved in water (100 mL) and the solution absorbed onto SP Sephadex C-25 ( $\text{Na}^+$  form). The one major blue band was collected by elution with  $0.3 \text{ mol L}^{-1}$  NaCl, evaporated to dryness under reduced pressure and the residue extracted with ethanol to leave NaCl behind. The extract was evaporated to dryness under reduced pressure. Yield, 0.92 g. Slow evaporation of an ethanolic solution gave blue crystals suitable for a crystal structure determination. Anal. calcd. for  $[\text{Cu}(\text{L}^2)\text{Cl}_2] \cdot \text{H}_2\text{O} = \text{C}_{18}\text{H}_{25}\text{Cl}_2\text{CuN}_3\text{O}$ : C 49.83, H 5.81, N 9.69. Found: C 50.1, H 5.6, N 9.8%.

$[\text{Cu}(\text{L}^3)(\text{OCIO}_3)_2] \cdot \text{H}_2\text{O} - \text{L}^3$  (1.0 g) and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.64 g) were dissolved in methanol (100 mL) and the solution was evaporated to dryness under reduced pressure after stirring for 1 h. The residue was dissolved in water (200 mL), absorbed onto SP Sephadex C-25 ( $\text{Na}^+$  form) and washed with water (300 mL). Elution with  $0.3 \text{ mol L}^{-1}$  NaCl gave one major blue band. The eluate was evaporated to dryness under reduced pressure, the residue was extracted with ethanol to leave NaCl behind, and the extract taken to dryness under reduced pressure. Yield, 0.80 g. Slow evaporation of an ethanolic solution containing excess  $\text{LiClO}_4$  produced blue crystals suitable for a crystal structure determination. Anal. calcd. for  $[\text{Cu}(\text{L}^3)(\text{OCIO}_3)_2] \cdot \text{H}_2\text{O} = \text{C}_{17}\text{H}_{22}\text{Cl}_2\text{CuN}_4\text{O}_9$ : C 36.41, H 3.95, N, 9.99. Found: C 36.8, H 4.2, N 9.8%.

$[\text{Zn}(\text{L}^4)\text{Cl}]\text{ClO}_4 - [\text{Cu}(\text{L}^4)\text{Cl}_2]$  (0.5 g) was dissolved in water (50 mL), Zn powder (2.0 g) added and the mixture stirred for 12 h at room temperature. The colourless solution was filtered and its volume reduced to 3 mL under

reduced pressure. Addition of excess  $\text{LiClO}_4$  resulted in slow deposition of crystals suitable for a structure determination. The bulk was collected by filtration, washed with cold ethanol and dried under vacuum. Yield, 0.24 g. Anal. Calcd. for  $[\text{Zn}(\text{L}^4)\text{Cl}]\text{ClO}_4 = \text{C}_{17}\text{H}_{22}\text{Cl}_2\text{N}_4\text{O}_4\text{Zn}$ : C 42.30, H 4.59, N 11.61. Found: C 42.2, H 4.7, N 11.8%.

### Crystal structure determinations

The data for compounds  $[\text{Zn}(\text{L}^1)\text{Cl}_2]$ ,  $[\text{Cu}(\text{L}^2)\text{Cl}_2] \cdot \text{H}_2\text{O}$  and  $[\text{Zn}(\text{L}^4)\text{Cl}]\text{ClO}_4$  were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer [6] using graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda$  0.71073 Å). The crystals were introduced in glass capillaries with a protecting “Paratone-N” oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of ( $\varphi$ - and  $\omega$ -scans giving complete data sets up to  $\theta = 25.7^\circ$  and a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000 [7]. The structures were solved by direct methods or Patterson map interpretation with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on  $F^2$  with SHELXL-97 [8]. Absorption effects were corrected empirically with the program SCALEPACK [7]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to nitrogen and oxygen atoms were found on Fourier-difference maps and all the others were introduced at calculated positions; all were treated as riding atoms with a displacement parameter equal to 1.2 (NH,  $\text{NH}_2$ ,  $\text{OH}_2$ , CH,  $\text{CH}_2$ ) or 1.5 ( $\text{CH}_3$ ) times that of the parent atom.

The data for  $[\text{Cu}(\text{L}^3)(\text{OCIO}_3)_2] \cdot \text{H}_2\text{O}$  were collected at 100(2) K using an ADSC Quantum 210 detector on beamline 4A MXW of the Pohang Light Source (Synchrotron). Crystal evaluation and data collection were done using  $\lambda = 0.76999$  Å radiation with a detector-to-crystal distance of 6.0 cm. Preliminary cell constants and an orientation matrix were determined from 36 sets of frames collected at scan intervals of  $5^\circ$  with an exposure time of 1 s per frame. The basic scale file was prepared using the program HKL2000 [7]. The reflections were successfully indexed by the automated indexing routine of the DENZO program [7]. The 4002 reflections were harvested by collecting 72 sets of frames with  $5^\circ$  scans and an exposure time of 1 s per frame. This highly redundant data set was corrected for Lorentz and polarization effects; and negligible corrections for crystal decay were also applied. The space group  $P-1$  was determined by the program XPREP [9]. The structure was solved by direct methods [10] and refined on  $F^2$  by full-matrix least-squares procedures [8]. The hydrogen atoms were placed geometrically, with N–H

distances of 0.91 Å and C–H distances of 0.97 Å, and these atoms were refined using a riding model.

Crystal data and structure refinement parameters are given in Table 1 and selected bond lengths and angles in Table 2. The molecular plots were drawn with Crystal-Maker<sup>TM</sup> [11]. CCDC reference numbers 737334–737337.

## Results and discussion

Unlike its Cu(II) analogue, which displays rather complicated solid state structural chemistry [4], the complex [Zn(L<sup>1</sup>)Cl<sub>2</sub>] crystallises in a simple molecular form. The coordination geometry around Zn is approximately trigonal bipyramidal (Fig. 2a), with the central N(2) of the azetidone ligand and the two chloro ligands comprising the trigonal plane (N(2)–Zn–Cl 122.71(4) and 116.17(4), Cl–Zn–Cl 120.88(2)°), and the N(1)–Zn–N(3) axis being rather bent (162.83(5)°). The bound ligand is conformationally chiral and both enantiomers are present. While, at first sight, a view of the lattice down *b* (Fig. 2b) gives the impression that chloro-bridged dimers like those present in the Cu(II)

analogue [4] may be involved, this is purely a consequence of the projection taken and the entities for which chloro-ligands superimpose appear in fact to be linked only by various CH···Cl contacts. Reciprocal NH···Cl interactions (Fig. 2c), similar to those between some units in the Cu(II) complex lattices [4], are apparent between enantiomer pairs lying parallel to the *c* axis. There is no evidence for stacking of the pyridine units seen in the form of significant overlap in projection of parallel rings, although edge pairs of C atoms in separate parallel rings lie just slightly >3.5 Å apart and there do appear to be significant aromatic-CH···Cl contacts (to add generally to those involving aliphatic methylene groups) (Figs. 3, 4, 5).

In its bound form, the *N*-benzyl derivative of L<sup>1</sup>, L<sup>2</sup>, also tridentate, provides two contributors to the chirality of the complex, the conformation of the five-membered chelate ring and the configuration of the asymmetric terminal N. As in the Pd(II) complex [2], these do not appear to be independent (at least in the solid state), so that a given ring conformation is associated with but one configuration at N, but the Cu(II) complex [Cu(L<sup>2</sup>)Cl<sub>2</sub>]·H<sub>2</sub>O differs from its Pd(II) analogue in that the orientation of the benzyl

**Table 1** Crystal data and structure refinement details

	[Zn(L <sup>1</sup> )Cl <sub>2</sub> ]	[Cu(L <sup>2</sup> )Cl <sub>2</sub> ]·H <sub>2</sub> O	[Cu(L <sup>3</sup> )(OCIO <sub>3</sub> ) <sub>2</sub> ]·H <sub>2</sub> O	[Zn(L <sup>4</sup> )Cl]ClO <sub>4</sub>
Chemical formula	C <sub>11</sub> H <sub>17</sub> Cl <sub>2</sub> N <sub>3</sub> Zn	C <sub>18</sub> H <sub>25</sub> Cl <sub>2</sub> CuN <sub>3</sub> O	C <sub>34</sub> H <sub>44</sub> Cl <sub>4</sub> Cu <sub>2</sub> N <sub>8</sub> O <sub>18</sub>	C <sub>17</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> Zn
<i>M</i> (g mol <sup>-1</sup> )	327.55	433.85	1121.65	482.66
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1
<i>a</i> (Å)	9.8673(4)	10.8054(5)	8.6300(17)	8.0683(5)
<i>b</i> (Å)	10.0616(4)	11.2074(8)	9.0030(18)	9.1816(4)
<i>c</i> (Å)	14.0955(6)	17.1139(13)	14.357(3)	13.1485(8)
$\alpha$ (°)	90	92.708(3)	82.32(3)	86.000(4)
$\beta$ (°)	99.622(3)	102.405(4)	72.65(3)	87.038(3)
$\gamma$ (°)	90	105.948(4)	83.92(3)	85.990(4)
<i>V</i> (Å <sup>3</sup> )	1379.73(10)	1933.7(2)	1052.6(4)	968.22(9)
<i>Z</i>	4	4	1	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.577	1.490	1.770	1.656
$\mu$ (mm <sup>-1</sup> )	2.149	1.417	1.352	1.577
<i>F</i> (000)	672	900	574	496
Reflections collected	39241	91737	30487	46935
Independent reflections	2612	7332	4002	3664
Observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	2352	6044	3735	3320
<i>R</i> <sub>int</sub>	0.017	0.034	0.019	0.027
Parameters refined	155	453	300	254
<i>R</i> 1	0.021	0.035	0.049	0.026
<i>wR</i> 2	0.055	0.098	0.171	0.069
<i>S</i>	1.043	1.029	1.103	1.069
$\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	-0.30	-0.57	-1.32	-0.40
$\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	0.31	1.07	0.88	0.35

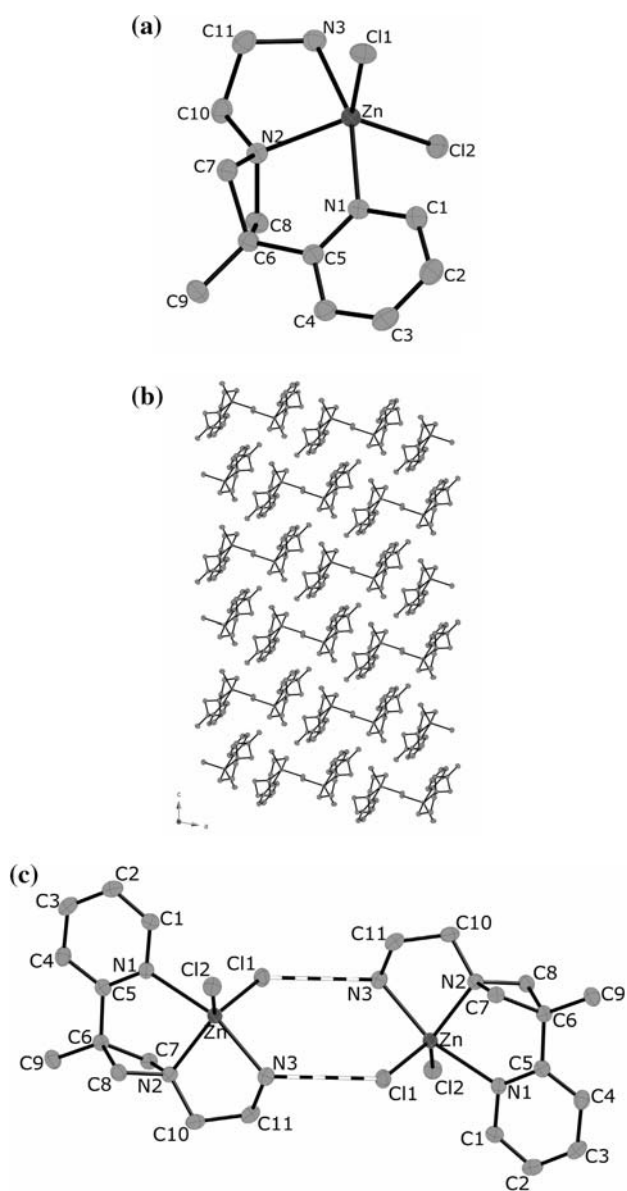
**Table 2** Selected bond lengths (Å) and angles (°)

[Zn(L <sup>1</sup> )Cl <sub>2</sub> ]	Zn–N1	2.2988(14)	N1–Zn–N2	81.91(5)
	Zn–N2	2.1209(14)	N2–Zn–N3	80.94(5)
	Zn–N3	2.1765(14)	Cl1–Zn–Cl2	120.883(18)
	Zn–Cl1	2.2952(4)		
	Zn–Cl2	2.2729(5)		
[Cu(L <sup>2</sup> )Cl <sub>2</sub> ] $\cdot$ H <sub>2</sub> O	Cu1–N1A	2.060(2)	N1A–Cu1–N2A	88.00(9)
	Cu1–N2A	2.047(2)	N2A–Cu1–N3A	83.71(9)
	Cu1–N3A	2.035(2)	Cl1A–Cu1–Cl2A	111.79(3)
	Cu1–Cl1A	2.5335(7)		
	Cu1–Cl2A	2.3043(7)		
	Cu2–N1B	2.062(2)	N1B–Cu2–N2B	88.31(9)
	Cu2–N2B	2.040(2)	N2B–Cu2–N3B	83.51(9)
	Cu2–N3B	2.032(2)	Cl1B–Cu2–Cl2B	106.54(3)
	Cu2–Cl1B	2.4887(7)		
	Cu2–Cl2B	2.3197(7)		
[Cu(L <sup>3</sup> )(OCIO <sub>3</sub> ) <sub>2</sub> ] $\cdot$ H <sub>2</sub> O	Cu–N1	2.009(3)	N1–Cu–N2	90.50(11)
	Cu–N2	2.004(3)	N2–Cu–N3	82.56(11)
	Cu–N3	1.955(3)	N3–Cu–N4	80.41(11)
	Cu–N4	2.075(3)	N4–Cu–N1	108.66(11)
	Cu–O3	2.757(3)	O3–Cu–O5	166.32(4)
[Zn(L <sup>4</sup> )Cl]ClO <sub>4</sub>	Zn–N1	2.2065(16)	N1–Zn–N2	84.70(6)
	Zn–N2	2.0891(18)	N2–Zn–N3	81.60(6)
	Zn–N3	2.1990(16)	N3–Zn–N4	79.43(6)
	Zn–N4	2.0770(17)	N4–Zn–N1	100.00(6)
	Zn–Cl1	2.2727(5)		

substituent on the ring is equatorial rather than axial. This is presumably a consequence of five-coordination at Cu (rather than the strict square-planar coordination at Pd) rendering the axial site more congested. The coordination geometry at Cu is possibly best described as square-pyramidal and it is certainly much further from trigonal-bipyramidal than that of Zn in [Zn(L<sup>1</sup>)Cl<sub>2</sub>]. Again the complex can be described as molecular, although the two Cu–Cl bond lengths in both inequivalent complex units of the lattice do differ significantly (Cu–Cl(basal) 2.3043(7) or 2.3197(7); Cu–Cl(axial) 2.5335(7) or 2.4887(7) Å, respectively). These inequivalent complex units lie in sheets, of exclusively one or the other (though as racemates, i.e. as enantiomer mixtures), which lie in alternation parallel to the *ab* plane. Closely similar enantiomer (heterochiral) pairs linked by reciprocal NH $\cdots$ Cl(basal) interactions can be found in both sheets but the presence of lattice water adds to the complexity of the overall H-bonding network, two inequivalent water molecules serving to link homochiral pairs in different sheets through either Cl(axial) $\cdots$ O $\cdots$ Cl(axial) or Cl(axial) $\cdots$ O $\cdots$ Cl(basal) contacts. In addition, there now appears to be evidence for stacking of the bound pyridine units, slightly different overlaps in projection applying for heterochiral pairs in the

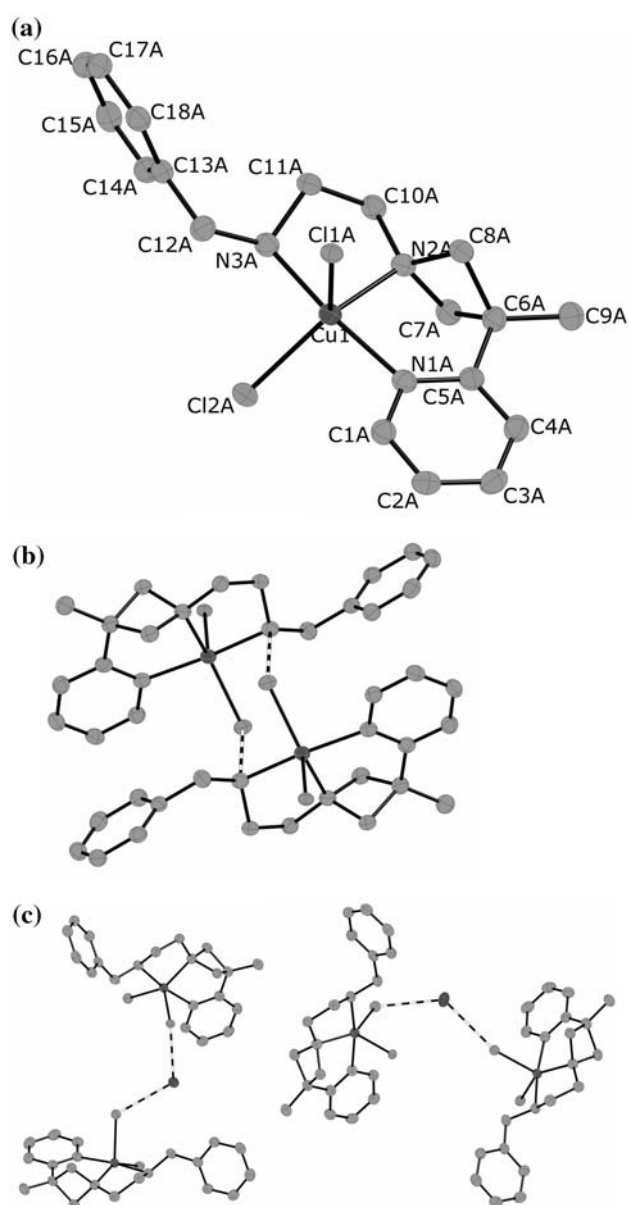
two sheets of complexes but the rings being closely parallel with several C $\cdots$ C separations <3.5 Å in both. The phenyl groups of the benzyl substituents, in contrast, may at most be involved in weak edge-to-face interactions (C $\cdots$ C contacts >3.6 Å).

As is commonly found for complexes of Cu(ClO<sub>4</sub>)<sub>2</sub> with tetramines [12], [Cu(L<sup>3</sup>)(OCIO<sub>3</sub>)<sub>2</sub>] $\cdot$ H<sub>2</sub>O may be described as a molecular octahedral species with a *trans*-CuN<sub>4</sub>O<sub>2</sub> coordination geometry, though the Cu–O separations are long and rather disparate (Cu–O(5) 2.426(2); Cu–O(3) 2.757(3) Å). As is the case with various tetramines involving aromatic donors [13], the ligand L<sup>3</sup> is actually bound in a detectably non-planar, helical form, so that the complex is necessarily chiral, although both enantiomers are found in the present lattice, each helix being associated with a single chiral conformation of the five-membered chelate ring. A view of the lattice down *a* shows, edge-on, sheets of complex units lying parallel to the *ab* plane (other sheets may be identified but this division is convenient). The complexes in each sheet are homochiral and the sheets alternate in chirality along *c*. Hydrogen-bonded pairs of water molecules are sandwiched between every second pair of sheets and each water molecule is H-bonded to otherwise uncoordinated oxygen atoms of two perchlorate in a



**Fig. 2** **a** The molecular species, with atom numbering, found in the lattice of  $[\text{Zn}(\text{L}^1)\text{Cl}_2]$ . As in all figures, displacement ellipsoids are shown at the 50% probability level and hydrogen atoms are omitted for clarity. **b** A partial view down  $b$  of the lattice of  $[\text{Zn}(\text{L}^1)\text{Cl}_2]$ , showing the near superposition of chloro ligands in this projection. **c**  $\text{NH}\cdots\text{Cl}$  bridging, showed as dashed bonds 3.40 Å long, of enantiomeric pairs of complex units in the lattice of  $[\text{Zn}(\text{L}^1)\text{Cl}_2]$ . Note that these interactions involve the equatorial NH protons and that the axial protons also appear to be involved in weaker interactions to chloro ligands of other complex units

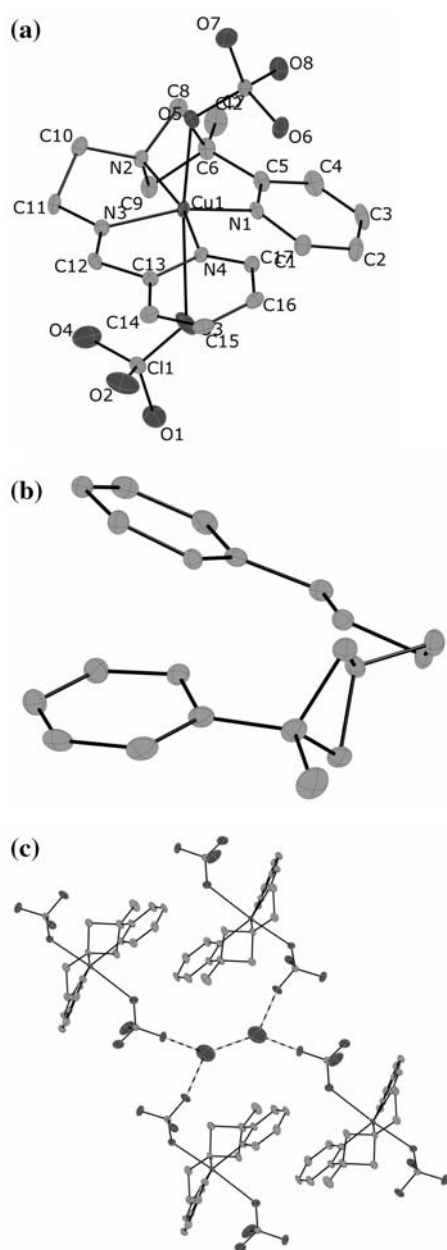
particular sheet, so that the  $(\text{H}_2\text{O})_2$  unit but not one water molecule serves to link sheets of opposite chirality. (Some disorder of the four protons over the five interactions must, of course, be involved.) Directed towards the interior of this “double sheet”, the bound pyridine units of the 2-pyridylazetidine entity lie in parallel pairs with some atomic separations  $<3.5$  Å, though the overlap in



**Fig. 3** **a** The molecular species, with atom numbering, found in the lattice of  $[\text{Cu}(\text{L}^2)\text{Cl}_2]\cdot\text{H}_2\text{O}$  (only one of the two closely similar but strictly inequivalent units of the lattice is shown). **b** One of the two types of heterochiral complex pairs linked by reciprocal  $\text{NH}\cdots\text{Cl}$  interactions found in the lattice of  $[\text{Cu}(\text{L}^2)\text{Cl}_2]\cdot\text{H}_2\text{O}$ . **c** The two modes of linking homochiral pairs of complex units in different sheets via  $\text{Cl}\cdots\text{HOH}\cdots\text{Cl}$  bridging

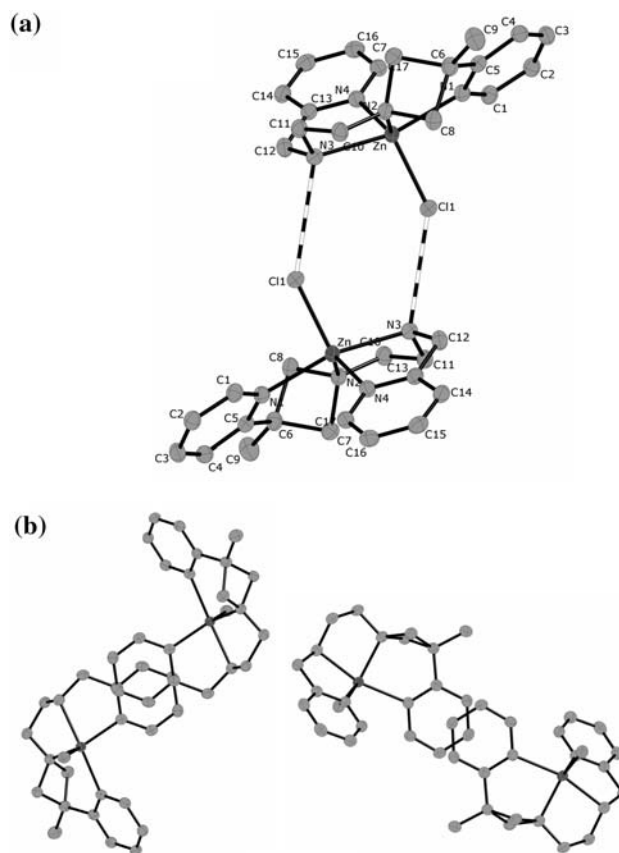
projection is small. The other pyridine units of the bound ligand are oriented towards the outside of the double sheet and appear to be involved in stacking interactions with the similar pyridine units of the adjacent double sheet. Thus, stacking interactions involving bound pyridine units on Cu(II) do appear to be a significant feature of the supramolecular chemistry of these complexes.

The ligand  $\text{L}^4$ , which is the reduction product of  $\text{L}^3$ , forms in  $[\text{Zn}(\text{L}^4)\text{Cl}]\text{ClO}_4$  a complex which can be



**Fig. 4** **a** The molecular species, shown with atom numbering, present in the lattice of  $[\text{Cu}(\text{L}^3)(\text{OCIO}_3)_2] \cdot \text{H}_2\text{O}$ . **b** The bound form of the ligand  $\text{L}^3$  in  $[\text{Cu}(\text{L}^3)(\text{OCIO}_3)_2] \cdot \text{H}_2\text{O}$ , showing its twisting into a chiral configuration. **c** Interactions of the  $(\text{H}_2\text{O})_2$  unit involved in its bridging of sheets of complex units of opposite chirality in the lattice of  $[\text{Cu}(\text{L}^3)(\text{OCIO}_3)_2] \cdot \text{H}_2\text{O}$

considered ionic in that no perchlorate oxygen atom lies closer than 4 Å from the metal. The coordination geometry, as in  $[\text{Zn}(\text{L}^1)\text{Cl}_2]$ , is close to trigonal bipyramidal and although the presence of an asymmetric N-centre in addition to the chiral five-membered ring might be expected to engender multiple stereoisomers, but a single diastereomer (and its enantiomer) is seen in the lattice. The enantiomers form centrosymmetric pairs as a result of reciprocal



**Fig. 5** **a** A centrosymmetric pair of trigonal bipyramidal complex cations linked by reciprocal  $\text{NH} \cdots \text{Cl}$  interactions (*dashed lines*) found in the lattice of  $[\text{Zn}(\text{L}^4)\text{Cl}]\text{ClO}_4$  (atom numbering shown). **b** Pairwise stacking patterns observed for pyridine units in the lattice of  $[\text{Zn}(\text{L}^4)\text{Cl}]\text{ClO}_4$ . The views are shown perpendicular to the mean ring planes

$\text{NH} \cdots \text{Cl}$  interactions. Pairwise stacking of both types of pyridine unit of the ligand (but not of mixed pairs) involves significant ring overlaps in projection and several  $\text{C} \cdots \text{C}$  contacts  $\sim 3.4$  Å for the pyridyl-substituent rings, though much longer ( $>3.7$  Å) for the pyridine bound directly to the azetidine ring, showing that such interactions may well arise independently of the particular nature of the metal ion. The perchlorate anions also appear to be involved in significant interactions with the bound pyridine units (as seen in simpler complexes [14]), these involving approaches both perpendicular to the ring plane ( $\text{O} \cdots \pi$  interactions?) and essentially within the plane ( $\text{CH} \cdots \text{O}$ ).

## Conclusions

The present results confirm the efficacy of azetidine-N as a donor, albeit supported by adjacent chelation, towards transition metal ions. As an N-donor centre which is susceptible neither to deprotonation nor oxidation (via

deprotonation), it is thus a useful anchoring point for ligands which, as we have shown elsewhere [2, 3], can be used in the formation of catalysts employed under quite vigorous reaction conditions. In the presently-studied systems, it is clear, if unsurprising, that conventional H-bonding plays a significant role in determining the interactions between complex units and thus the crystalline lattice that they form. Interactions involving both aliphatic and aromatic CH groups also are of some importance, as are stacking interactions of bound pyridine groups.

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