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Protonation products of pentaaminopentane as novel building blocks for hydrogen-bonded networks[1]

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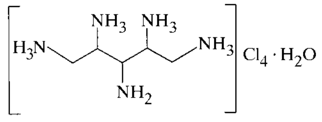
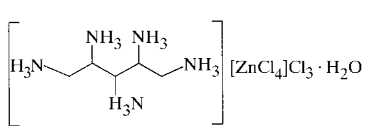
The structures of 3-amino-1,2*R*,4*S*,5-tetraammoniopentane tetrachloride monohydrate, $C_5H_{21}N_5^{4+}\cdot 4Cl^-\cdot H_2O$, and 1,2*R*,3,4*S*,5-pentaammoniopentane tetrachlorozincate trichloride monohydrate, $(C_5H_{22}N_5)[ZnCl_4]Cl_3\cdot H_2O$, have been determined from single-crystal X-ray diffraction data. Both compounds show a complex network of N—H···O, O—H···Cl and N—H···Cl hydrogen bonds. There are a total of 14 H atoms of the tetra-cation and 15 H atoms of the penta-cation available for hydrogen bonding. However, due to the particular shape of the primary linear polyammonium cations, only a certain number of H atoms can be involved in hydrogen-bond formation. It is further shown that hydrogen bonding has an influence on the conformation of such alkylammonium cations.

Comment

Polyamines such as spermidine, spermine or caldopentamine are widespread in nature (Geneste & Hesse, 1998) and are of importance in a variety of physiological processes. Their presence is essential for the growth and division of cells and it is believed that hydrogen bonding between the positively charged ammonium groups and the phosphate moieties of DNA is of particular importance. It has therefore been suggested that these compounds could have a considerable potential as antitumour drugs (Labarre, 1985). All these compounds have the general composition NH_2–$(CH_2)_m$–{[NH–$(CH_2)_n$]$_q$–NH}$_r$–$(CH_2)_p$–NH_2 ($3 \leq m$, n, $p \leq 5$; $0 \leq q \leq 2$; $r = 0, 1$), *i.e.* they carry both primary and secondary amino groups within their structure. A related class of polymeric compounds are the linear polyethyleneimines [NH_2–CH_2–CH_2–(NH–CH_2–CH_2)$_n$–NH_2] which have been intensively investigated as polyelectrolytes and as metal complexing agents (Zelewsky *et al.*, 1993). However, besides the simple 1,2-diaminoethane, linear primary polyamines of composition NH_2–CH_2–(CH–NH_2)$_n$–CH_2–NH_2 which contain solely primary amino groups have received scant attention. This is particularly remarkable since the corresponding polyalcohols (sugar alcohols) have been well known for many years. A structural report of the protonated triamine ($n = 1$) appeared some years ago (Cini *et al.*, 1991) and the structure of a fully protonated tetraamine ($n = 2$) has been elucidated very recently in our own laboratory (Zimmer *et al.*, 1998). Linear primary polyamines with $n > 1$ could be of particular interest with regard to metal complex formation. As a result of steric constraints, it is not possible for the entire donor set to be coordinated to the same metal cation and consequently the formation of polynuclear species is to be expected. The protonated forms of these ligands are of further interest because the charge to molecular weight ratio of these cations is rather high. It should be kept in mind that the N:C ratio of the primary polyamines is double that of the above-mentioned linear polyethyleneimines, and consequently, linear primary polyamines have an exceptionally high charge density. This can be seen by the dramatic increase of acidity which is observed for the increasing number of amino groups. The first pK_a values for the fully protonated forms have been found to be 7.1, 3.6, 1.4, and < 1 for the di-, tri-, tetra- and pentaamine, respectively (Zimmer *et al.*, 1998). The combination of the high acidity, the high charge density and the high number of N—H protons means that these compounds could also serve as novel hydrogen-donating building blocks in a hydrogen-bonding network. Consequently, they represent an interesting class of compounds in the context of supramolecular chemistry and crystal engineering. In this contribution, we report the structure and the hydrogen-bonding scheme of the chloride hydrate and the chloride–tetrachlorozincate hydrate salt of the tetra- and pentaprotonated 1,2*R*,3,4*S*,5-pentaamine, respectively [compounds (I) and (II), respectively].



(I)



(II)

As expected from simple electrostatic considerations, the non-protonated amino group of 3-amino-1,2*R*,4*S*,5-tetraammoniopentane tetrachloride monohydrate, (I), was located in the middle of the molecule at the 3 position. The fourfold protonated cation (Fig. 1) is surrounded by seven chloride anions forming N—H···Cl hydrogen bonds to the ammonium and amino groups. Additionally, one water molecule accepts an N—H···O H atom from one of the ammonium groups (N4). It is well known that the ammonium group is a significantly stronger hydrogen-bond donor than an amino group

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[1] Linear primary polyamines as building blocks for coordination polymers. Part 2. Part 1: Zimmer *et al.* (1998).

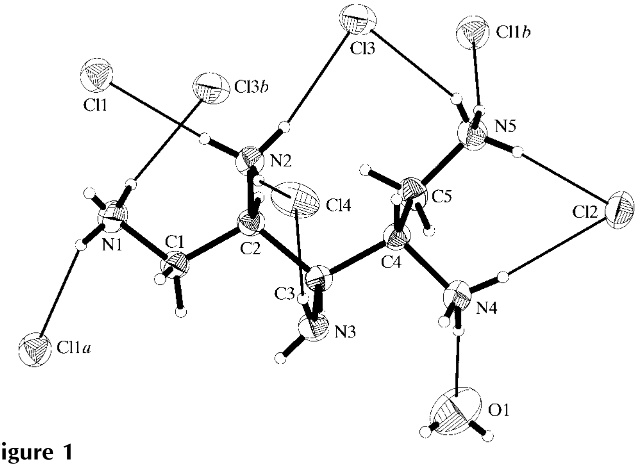

Figure 1
The tetraammonioaminopentane cation of (I) with its hydrogen-bond-accepting environment (seven chloride anions and one water molecule). Displacement ellipsoids are drawn at the 50% probability level, radii of the H atoms are of arbitrary size. [Symmetry codes: (*a*) $x + 1, y, z$; (*b*) $-x, -y, -z + 1$.]

(Reiss *et al.*, 1999) and consequently each ammonium group is capable of binding to two or three hydrogen acceptors while the amino group is involved in only one weak hydrogen bond [H···Cl 2.55 (3)/2.43 (3) Å] to the disordered chloride counter-ion Cl4/Cl4″ (Table 2). It is further noteworthy that in accord with the low basicity of the free amino group, N3 does not act as a hydrogen—bond acceptor in this structure.

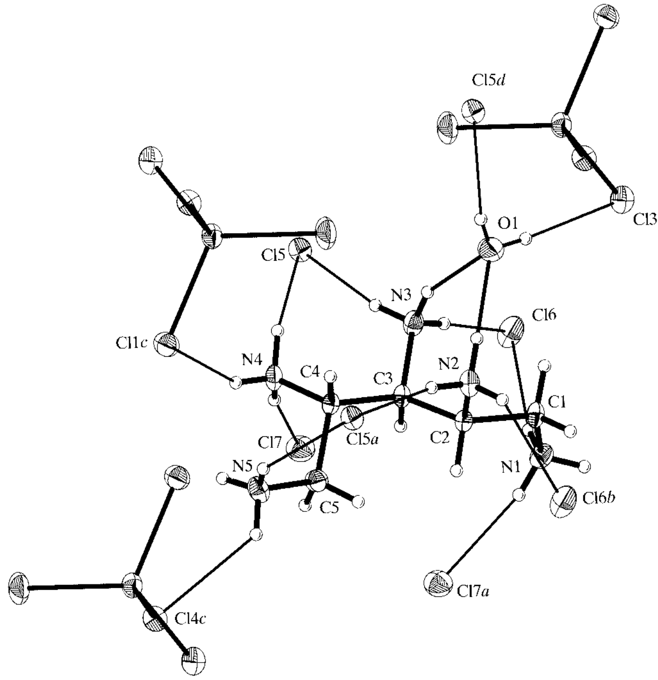

Figure 3
The pentaammoniopentane cation of (II) with its hydrogen-bond-accepting environment (six chloride anions, one water molecule and three tetrachlorozincates). Displacement ellipsoids are drawn at the 50% probability level, radius of the H atoms are of arbitrary size. [Symmetry codes: (*a*) $1 - x, 1 - y, -1 - z$; (*b*) $1 + x, y, z$; (*c*) $2 - x, 1 - y, -z$; (*d*) $1 - x, 2 - y, -z$.]

It has been pointed out previously for a variety of solid-state structures that the conformation of aliphatic diammonium cations is arranged in a way that maximizes the number of hydrogen bonds to the counter-ions or water molecules, and, if conformational flexibility is possible, the observed conformation in the solid state does not necessarily correspond to the lowest energy structure of an isolated molecule (Frank & Reiss, 1997). This is also true for the tetracation of (I), where the observed conformation proceeds from an all-*trans* arrangement of the carbon chain C1–C4 with additional rotation around the C3—C4 bond of 120°. Comparison with the structure of xylitol (Kim & Jeffrey, 1969) shows similar behaviour; the first four C atoms of both molecules form an approximately planar zigzag chain, whereas the C5 atom is turned out of this plane. The angle between the mean plane defined by C1–C4 and the C4—C5 vector is 56° for xylitol and 60° for the cation of (I). The N4 atom is also located within this plane. Clearly, this conformation results in an optimal distribution of the ammonium groups and the amino group over the molecular surface with regard to hydrogen-bond formation (Fig. 1). All C—C bond lengths are in the normal range [1.520 (2)–1.548 (2) Å], the C—N bond

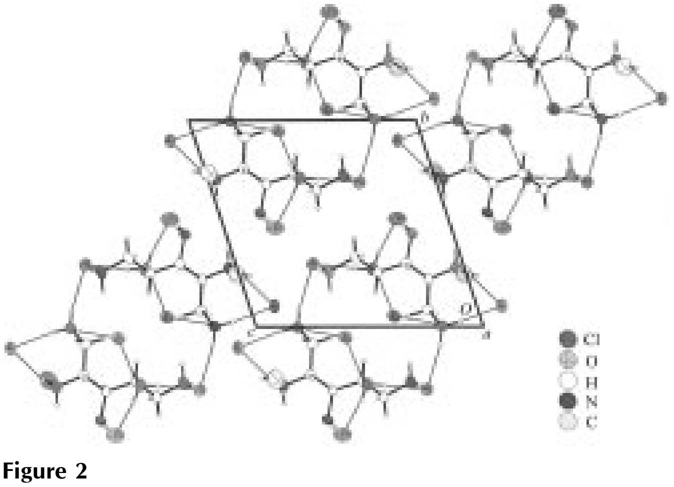

Figure 2
The packing of compound (I) viewed along the *a* axis.

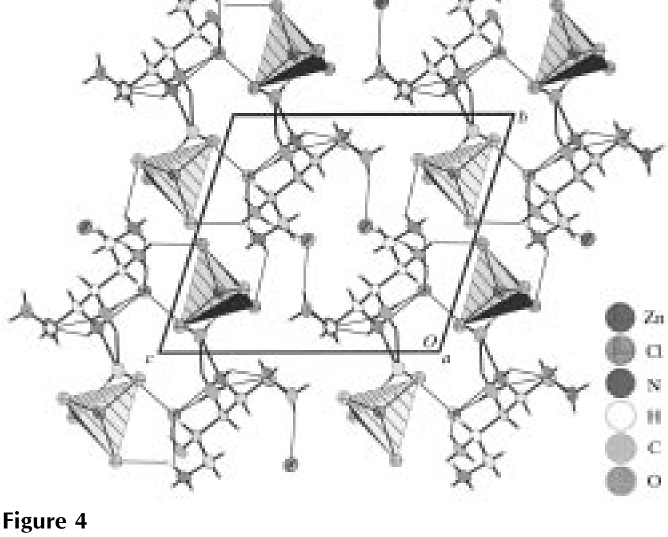

Figure 4
The packing of compound (II) viewed along the *a* axis.

lengths of the ammonium groups vary between 1.481 (2) and 1.499 (2) Å, while the C—N distance of the amino group is somewhat shorter [1.459 (2) Å].

Three of the total of seven counter-ions that are hydrogen bonded to the cation of (I) are involved in a chelate ring of the type N—H···Cl···H—N. According to Etter's nomenclature (Etter, 1990) this can be described as $R^1_2(7)$ (N5, C5, C4, N4, Cl2), $R^1_2(7)$ (N2, C2, C3, N3, Cl4) and $R^1_2(9)$ (N2, C2, C3, C4, C5, N5, Cl3). N2 and N5 both exhibit the maximum of three N—H···Cl interactions. N1 binds two chloride ions, whereas N3 and N4 are involved in only one hydrogen bond to a chloride anion. In addition, N4 exhibits a hydrogen bond [N···O 2.792 (3) Å] with a water molecule (O1). Cl4 is disordered with a site-occupancy ratio of 0.12:0.88. This is plausible if it is considered that the ammonium groups N2 and N3 interact with both possible positions Cl4 and Cl4″ in such a way that the anion forms either a shorter contact to H23 (Cl4) or a shorter contact to H32 (Cl4″) (Table 2).

The pentaammonium cation of 1,2*R*,3,4*S*,5-pentaammoniopentane tetrachlorozincate trichloride monohydrate, (II), the completely protonated form of the tetra-cation of (I), also exhibits a partially planar zigzag (all *trans*) structure (C1–C4). The torsion angle C1—C2—C3—C4 is 179.8°. Again, the C5—N5 vector is rotated out of the plane spanned by the first four C atoms by an angle of 61.3° into a synclinal conformation. Also, the C1—N1 vector is rotated out-of-plane by an angle of 59.5°. All C—C bond lengths within the cation [1.539 (2)–1.559 (2) Å] fall in the expected range. The cation is surrounded by six chloride ions, three tetrachlorozincate anions and one water molecule (Table 4). N—H···O distances of 1.84 (3) and 1.87 (3) Å indicate strong hydrogen bonding. Neglecting some weak N—H···Cl interactions, classification according to Etter's rules (Etter, 1990) yields one large ring structure [$R^4_2(18)$], a water-containing ring [$R^4_4(10)$] and three rings in which the water molecule and the two Cl anions Cl6 and Cl5 are chelated [$R^1_2(7)$, $R^1_2(8)$, $R^1_2(9)$] (Fig. 3). The tetrachlorozincate anion shows some trigonal distortion (C_{3v}) with an elongated Zn—Cl3 bond [Zn—Cl 2.3197 (13) Å, other Zn—Cl distances: 2.2587 (11)–2.2721 (14) Å]. This deformation of the complex anion can be explained by the fact that only Cl3 shows a significant interaction with the protons of the cation (Table 4). The packing of (II) (Fig. 4) can be described in terms of wavy layers of $ZnCl_4^{2-}$ anions perpendicular to the *a* axis, which form only weak hydrogen-bonding interactions. The $ZnCl_4^{2-}$ anions form channels along [100] accommodating stacks of cations and chloride anions which are connected by hydrogen bonds (Table 4).

The present investigations established that protonated linear primary polyamines can serve as novel and interesting building blocks for extended hydrogen-bonded structures. In contrast to the neutral amino group, the positively charged ammonium groups exhibit a high tendency to be involved in multiple N—H···Cl and N—H···O interactions. This type of hydrogen bonding is probably one of the major driving forces for the solid-state structure. It is, however, noteworthy that in the structures of (I) and (II), not all of the N—H protons are involved in hydrogen bonding. The compact structure of the cations and the steric crowding do not allow for all the potential hydrogen-bonding interactions to take place.

Experimental

1,2*R*,3,4*S*,5-Pentaammoniopentane pentachloride (*meso* form) was prepared according to the literature method of Zimmer *et al.* (1998). For the preparation of 3-amino-1,2*R*,4*S*,5-tetraammoniopentane tetrachloride monohydrate, (I), 1,2*R*,3,4*S*,5-pentaammoniopentane pentachloride (50 mg, 0.15 mmol) was dissolved in water (1 ml) and a few mls of ethanol were then added. The resulting microcrystalline precipitate was redissolved carefully by refluxing the suspension and adding small portions of 0.1 *M* HCl. Colourless needle-shaped crystals grew from this solution at 277 K after a few days. For the preparation of 1,2*R*,3,4*S*,5-pentaammoniopentane tetrachlorozincate trichloride monohydrate, (II), 1,2*R*,3,4*S*,5-pentaammoniopentane pentachloride (30 mg, 0.09 mmol) was dissolved in a minimum amount of water and a solution of $ZnCl_2$ (1.5 g) in 6 *M* HCl (8 ml) was added. After cooling to about 277 K, a voluminous precipitate was formed. The liquid phase was decanted and the precipitate was redissolved in 3 *M* HCl (3 ml) with heating. Colourless isometric crystals were formed during cooling of this solution to room temperature.

Compound (I)

Crystal data

$C_5H_{21}N_5^{4+}\cdot 4Cl^-\cdot H_2O$
$M_r = 311.08$
Triclinic, $P\overline{1}$
$a = 6.3740$ (10) Å
$b = 10.588$ (2) Å
$c = 11.303$ (2) Å
$\alpha = 71.35$ (3)°
$\beta = 78.45$ (3)°
$\gamma = 85.97$ (3)°
$V = 708.1$ (2) Å^3
$Z = 2$

$D_x = 1.459$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5000 quasi-centred reflections automatically selected from the whole data set and used in least-squares refinement calculation
$\mu = 0.823$ mm^{-1}
$T = 293$ (2) K
Isometric, colourless
0.40 × 0.34 × 0.30 mm

Data collection

Stoe IPDS diffractometer
φ scans
9244 measured reflections
2870 independent reflections
2361 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 27°$

$h = -7 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
Standard reflections: a maximum of 50 reflections [$I > 6\sigma(I)$] per image
intensity decay: none

Table 1
Selected geometric parameters (Å, °) for (I).

N1—C1	1.496 (2)	C1—C2	1.520 (2)
N2—C2	1.489 (2)	C2—C3	1.545 (2)
N3—C3	1.459 (2)	C3—C4	1.548 (2)
N4—C4	1.499 (2)	C4—C5	1.528 (2)
N5—C5	1.481 (2)		
N1—C1—C2	111.76 (12)	C2—C3—C4	111.48 (11)
N2—C2—C1	111.09 (13)	N4—C4—C5	110.61 (13)
N2—C2—C3	111.22 (12)	N4—C4—C3	106.48 (12)
C1—C2—C3	111.08 (12)	C5—C4—C3	112.50 (11)
N3—C3—C2	115.61 (12)	N5—C5—C4	112.76 (13)
N3—C3—C4	108.50 (11)		
N1—C1—C2—N2	72.60 (16)	N3—C3—C4—N4	50.31 (16)
N1—C1—C2—C3	−163.04 (13)	C2—C3—C4—N4	178.74 (12)
N2—C2—C3—N3	67.57 (16)	N3—C3—C4—C5	171.63 (13)
C1—C2—C3—N3	−56.71 (17)	C2—C3—C4—C5	−59.94 (16)
N2—C2—C3—C4	−56.96 (15)	N4—C4—C5—N5	−79.66 (17)
C1—C2—C3—C4	178.75 (12)	C3—C4—C5—N5	161.40 (13)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.075$
$S = 1.020$
2870 reflections
196 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.1127P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H12···Cl1^{i}	0.85 (3)	2.42 (3)	3.2229 (18)	158 (2)
N1—H13···Cl3^{ii}	0.91 (3)	2.51 (3)	3.3860 (18)	163 (2)
N2—H21···Cl1	0.89 (2)	2.23 (2)	3.1104 (17)	172 (2)
N2—H22···Cl3	0.86 (2)	2.27 (2)	3.1205 (17)	168 (2)
N2—H23···Cl4	0.92 (2)	2.22 (2)	3.120 (2)	165.7 (19)
N2—H23···Cl4′′	0.92 (2)	2.36 (2)	3.210 (5)	153.5 (18)
N3—H32···Cl4	0.87 (3)	2.55 (3)	3.3995 (19)	168 (2)
N3—H32···Cl4′′	0.87 (3)	2.43 (3)	3.230 (5)	152 (2)
N4—H41···Cl2	0.87 (2)	2.38 (2)	3.2254 (17)	163.7 (19)
N4—H42···O1	0.87 (3)	1.93 (3)	2.792 (3)	175 (2)
N5—H51···Cl3	0.87 (2)	2.38 (2)	3.179 (2)	152 (2)
N5—H52···Cl1^{ii}	0.87 (2)	2.33 (2)	3.1830 (18)	167.1 (19)
N5—H53···Cl2	0.89 (2)	2.20 (2)	3.0774 (17)	171.8 (19)

Symmetry codes: (i) $1 + x, y, z$; (ii) $-x, -y, 1 - z$.

Compound (II)

Crystal data

$(C_5H_{22}N_5)[ZnCl_4]Cl_3\cdot H_2O$
$M_r = 483.81$
Triclinic, $P\overline{1}$
$a = 7.255$ (4) Å
$b = 10.893$ (6) Å
$c = 12.173$ (6) Å
$\alpha = 107.49$ (4)°
$\beta = 91.52$ (4)°
$\gamma = 96.67$ (4)°
$V = 909.4$ (8) Å^3
$Z = 2$
$D_x = 1.767$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5000 quasi-centred reflections automatically selected from the whole data set and used in least-squares refinement calculation
$\mu = 2.377$ mm^{-1}
$T = 293$ (2) K
Isometric, colourless
0.87 × 0.60 × 0.45 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: numerical using indexed faces and a Gaussian integration method (Stoe & Cie, 1996)
$T_{\min} = 0.232$, $T_{\max} = 0.413$
15 919 measured reflections
4012 independent reflections
3892 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.057$
$\theta_{\max} = 28°$
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$
Standard reflections: a maximum of 50 reflections $[I > 6\sigma(I)]$ per image
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.072$
$S = 1.060$
4012 reflections
238 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 0.4460P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.040$
$\Delta\rho_{\max} = 0.425$ e Å^{-3}
$\Delta\rho_{\min} = -0.611$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.022 (2)

Table 3
Selected geometric parameters (Å, °) for (II).

Zn1—Cl2	2.2587 (11)	N4—C4	1.509 (2)
Zn1—Cl4	2.2668 (14)	N5—C5	1.496 (2)
Zn1—Cl1	2.2721 (14)	C1—C2	1.539 (2)
Zn1—Cl3	2.3197 (13)	C2—C3	1.552 (2)
N1—C1	1.481 (2)	C3—C4	1.559 (2)
N2—C2	1.496 (2)	C4—C5	1.540 (2)
N3—C3	1.504 (2)		
Cl2—Zn1—Cl4	113.25 (4)	C1—C2—C3	115.76 (12)
Cl2—Zn1—Cl1	111.96 (4)	N3—C3—C2	110.10 (13)
Cl4—Zn1—Cl1	107.69 (5)	N3—C3—C4	111.58 (13)
Cl2—Zn1—Cl3	109.74 (4)	C2—C3—C4	113.78 (12)
Cl4—Zn1—Cl3	107.06 (5)	N4—C4—C5	108.50 (14)
Cl1—Zn1—Cl3	106.82 (5)	N4—C4—C3	109.95 (12)
N1—C1—C2	112.85 (15)	C5—C4—C3	110.27 (13)
N2—C2—C1	105.46 (13)	N5—C5—C4	112.57 (14)
N2—C2—C3	113.54 (13)		
N1—C1—C2—N2	174.09 (13)	N3—C3—C4—N4	53.74 (18)
N1—C1—C2—C3	−59.50 (18)	C2—C3—C4—N4	179.06 (13)
N2—C2—C3—N3	68.10 (16)	N3—C3—C4—C5	173.34 (13)
C1—C2—C3—N3	−54.12 (18)	C2—C3—C4—C5	−61.34 (18)
N2—C2—C3—C4	−58.01 (18)	N4—C4—C5—N5	−74.45 (18)
C1—C2—C3—C4	179.78 (14)	C3—C4—C5—N5	165.08 (13)

During the refinement of (I), Cl4 gave significantly higher displacement parameters than the other Cl atoms and a difference electron-density peak near the initially found position. Refinement of the site-occupation factors for both possible positions with $U_{\rm iso}$ values restrained to one common value yielded a ratio of 0.12:0.88. Atomic coordinates of all H atoms were taken from difference Fourier syntheses. Atomic coordinates and individual $U_{\rm iso}$values were refined as well as corresponding $U_{\rm iso}$ values for the NH_2 and the four NH_3 groups. H atoms of the CH and CH_2 groups were included in the refinement using a riding model. Their $U_{\rm iso}$ values were set to 1.2 and $1.3U_{\rm eq}$(C), respectively. The two H atoms of the water molecule were included in the structure model without refining the atomic coordinates and the $U_{\rm iso}$values were set to $1.3U_{\rm eq}$(O). As the water is only

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H12···Cl6	0.88 (3)	2.26 (3)	3.095 (2)	158 (2)
N1—H13···Cl7^{i}	0.86 (3)	2.32 (3)	3.166 (3)	168 (2)
N2—H21···Cl6^{ii}	0.85 (3)	2.40 (3)	3.157 (2)	148 (2)
N2—H22···Cl5^{ii}	0.88 (3)	2.28 (3)	3.131 (2)	165 (2)
N2—H23···O1	0.88 (3)	1.87 (3)	2.734 (3)	166 (3)
N3—H31···Cl5	0.90 (3)	2.24 (3)	3.125 (2)	166 (2)
N3—H32···Cl6	0.83 (3)	2.29 (3)	3.107 (2)	168 (3)
N3—H33···O1	0.99 (3)	1.84 (3)	2.763 (3)	155 (2)
N4—H41···Cl1	0.82 (3)	2.55 (3)	3.228 (2)	141 (3)
N4—H42···Cl7	0.88 (3)	2.24 (3)	3.112 (3)	168 (3)
N4—H43···Cl5	0.92 (3)	2.46 (3)	3.215 (2)	140 (2)
N5—H51···Cl4^{iii}	0.89 (4)	2.57 (4)	3.243 (2)	133 (3)
N5—H53···Cl5^{ii}	0.85 (4)	2.45 (4)	3.166 (3)	141 (3)
O1—H1*W*···Cl3^{iv}	0.76 (2)	2.48 (3)	3.217 (2)	165 (3)
O1—H2*W*···Cl5^{iv}	0.75 (2)	2.36 (3)	3.099 (2)	166 (3)

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

weakly coordinated by its hydrogen accepting and donating environment, a relatively large U_{eq} value of its O atom was found and the H-atom positions could not be refined reliably.

For (II), the atomic coordinates of all H atoms were taken from difference Fourier syntheses. Atomic coordinates and individual U_{iso} values were refined freely for all NH_3 groups. H atoms of the CH and CH_2 groups were included in the refinement using a riding model. Their U_{iso} values were set to 1.2 and $1.3U_{eq}$(C), respectively. The atomic coordinates of the two H atoms of the water molecule are refined with the O—H distance restrained to one common value, while their U_{iso} values have been refined freely.

The distance criterion for the discussion of hydrogen bonds was set to 2.6 and 2.0 Å for the hydrogen–acceptor distance of N—H···Cl and N—H···O, respectively.

For both compounds, data collection: *IPDS Software* (Stoe & Cie, 1998); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1372). Services for accessing these data are described at the back of the journal.

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