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# Three overcrowded zinc(II) complexes with potentially hexadentate polypyridyl ligands

**Alan Hazell,[a]* Ole Mønsted,[b] Jens Christian Rasmussen[b] and Hans Toftlund[c]**

[a]Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Århus C, Denmark, [b]Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark, and [c]Department of Chemistry, University of Southern Denmark, Odense Campus, Campusvej 55 M, DK-5230 Odense, Denmark
Correspondence e-mail: ach@chem.au.dk

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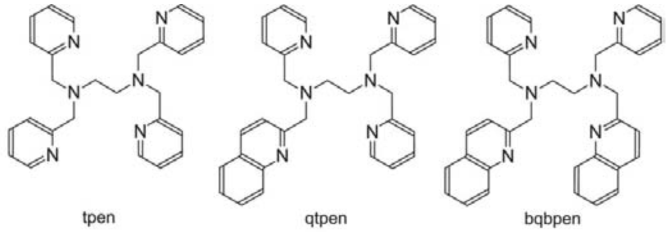
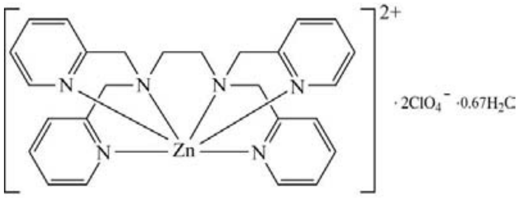
In each of [*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethane-1,2-diamine-$\kappa^6N$]zinc(II) bis(perchlorate) 0.67-hydrate, $[Zn(C_{26}H_{28}N_6)](ClO_4)_2\cdot0.67H_2O$, (I), [*N*,*N*,*N*′-tris(2-pyridylmethyl)-*N*′-(2-quinolylmethyl)ethane-1,2-diamine-$\kappa^6N$]zinc(II) bis(perchlorate), $[Zn(C_{30}H_{30}N_6)](ClO_4)_2$, (II), and [*N*,*N*′-bis(2-pyridylmethyl)-*N*,*N*′-bis(2-quinolylmethyl)ethane-1,2-diamine-$\kappa^6N$]zinc(II) bis(perchlorate) monohydrate, $[Zn(C_{34}H_{32}N_6)](ClO_4)_2\cdot H_2O$, (III), the Zn atom is coordinated to all six N atoms of the ligand. Compound (I) has one complex cation in a general position and one on a twofold axis. The coordination environments are intermediate between a regular octahedron and a pentagonal bipyramid which lacks one equatorial bond; complexes (II) and (III) are shown to be closer to the latter description. The quinolyl groups are in equatorial positions and the deviation from octahedral geometry increases with the number of these groups. This study demonstrates the systematic changes in the geometry at the central Zn atom as the overlap between the ligands increases.

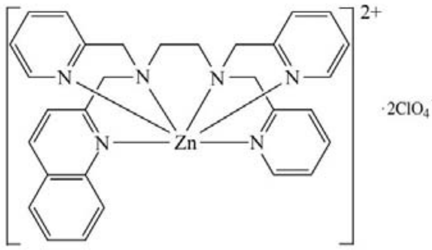
## Comment

Ligands based on *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethane-1,2-diamine (tpen) are potentially hexadentate, but some metal atoms such as chromium(III) also form complexes in which only five or four N atoms are coordinated (Eriksen *et al.*, 1999). Recently, this type of hexadentate ligand with all four of the pyridyl groups replaced by quinolyl groups has attracted interest as a fluorescent sensor for zinc(II) (Mikata *et al.*, 2005). This work reports the structures of three zinc(II) complexes with the tpen ligand and with ligands in which an intermediate number of pyridyl groups have been replaced by quinolyl groups (see scheme); the complexes with tpen, (I), *N*,*N*,*N*′-tris(2-pyridylmethyl)-*N*′-(2-quinolylmethyl)ethane-1,2-diamine (qtpen), (II), and *N*,*N*′-bis(2-pyridylmethyl)-*N*,*N*′-bis(2-quinolylmethyl)ethane-1,2-diamine (bqpben), (III), have all been isolated as the perchlorate salts. In each of the three cations, all six N atoms are coordinated to the Zn$^{II}$ atom.

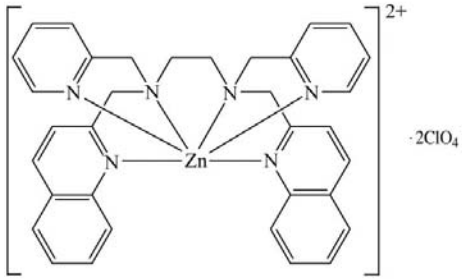




(I)



(II)



(III)

$[Zn(tpen)](ClO_4)_2\cdot0.67H_2O$, (I) (Fig. 1), crystallizes with one complex cation in a general position and with one on a twofold rotation axis. The perchlorate ions and the water molecule are all in general positions. The structure is very similar to that of $[Zn(tpen)](ClO_4)_2\cdot0.67CH_3OH$, (IV) (Mikata *et al.*, 2005), which differs from (I) only in the solvent molecule being methanol. For $[Zn(qtpen)](ClO_4)_2$, (II) (Fig. 2), and $[Zn(bqbpen)](ClO_4)_2\cdot H_2O$, (III) (Fig. 3), the coordination around the Zn$^{II}$ atom is very similar to that in $[Zn(tpen)]^{2+}$, with the quinolyl groups in equatorial positions. Both N$sp^3$ atoms have the *S* configuration for the crystal studied. There is an intramolecular C—H$\cdots\pi$ bond involving atom H3 of an axial pyridine group and the benzene ring of the equatorial quinolyl group in (II).

The coordination polyhedron around the Zn$^{II}$ centres is irregular (Tables 1 and 2) and is closer to being a pentagonal bipyramid, with N3—Zn1—N6 as the axis and with one

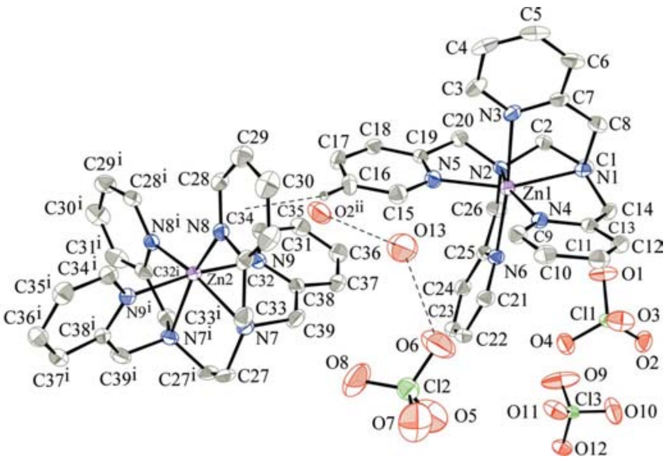


**Figure 1**
A view of (I), showing the atom-labelling scheme. Perchlorate atom Cl3 is drawn at $(-x + 1, y + 1, -z + \frac{3}{2})$ to avoid overlap. Displacement ellipsoids are drawn at the 50% probability level. Most H atoms have been omitted for clarity. Intramolecular C—H$\cdots\pi$ and O—H$\cdots$O hydrogen bonds are represented by dashed lines. [Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $x, 1 - y, -\frac{1}{2} + z$.]

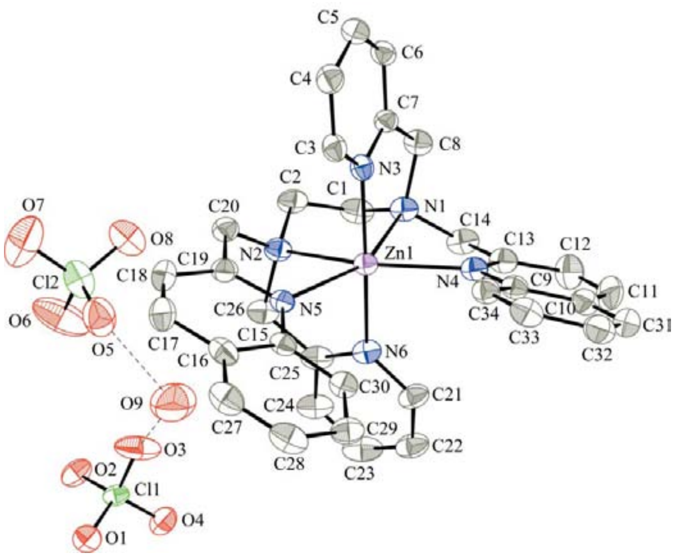


**Figure 3**
A view of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

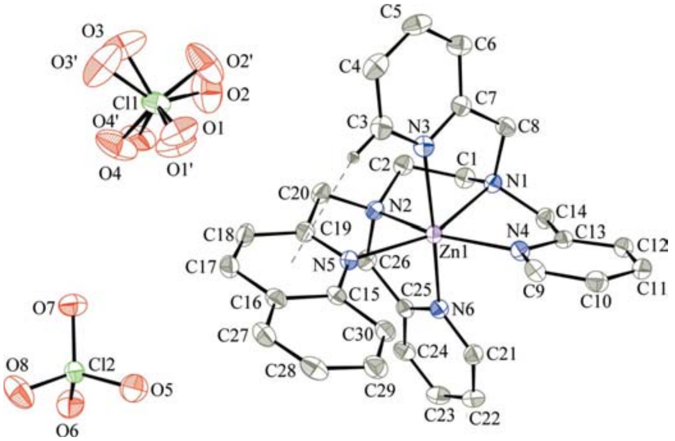


**Figure 2**
A view of (II), showing the atom-labelling scheme; atoms Cl1 and Cl1′ are superimposed. Displacement ellipsoids are drawn at the 50% probability level. Most H atoms have been omitted for clarity. The intramolecular C—H$\cdots\pi$ bond is represented by a dashed line.

equatorial bond lacking, than it is to being a regular octahedron. The two possibilities were compared by constructing an observed polyhedron with unit bond lengths and calculating the r.m.s. values, $\delta_{\rm oct}$, of the deviations of the positions, $\delta$, from those of an ideal octahedron with bond angles all 90° and those, $\delta_{\rm pbp}$, of an ideal pentagonal bipyramid with eight bond angles of 90°, three of 72° and one of 144°. These calculations gave $\delta_{\rm oct} = 0.191$ (38) and 0.185 (18) Å and $\delta_{\rm pbp} = 0.172$ (7) and 0.151 (8) Å for the two $[\rm Zn(tpen)]^{2+}$ cations in (I), $\delta_{\rm oct} = 0.198$ (24) Å and $\delta_{\rm pbp} = 0.133$ (4) Å for the $[\rm Zn(qtpen)]^{2+}$ cation in (II), and $\delta_{\rm oct} = 0.217$ (32) Å and $\delta_{\rm pbp} = 0.102$ (3) Å for the $[\rm Zn(bqbpen)]^{2+}$ cation in (III).

Another aspect of the introduction of quinolyl groups in the equatorial plane is an increase of the N4—Zn—N5 angle from 119.5 (1) and 121.0 (1)° in $[\rm Zn(tpen)]^{2+}$, to 125.04 (1)° in $[\rm Zn(qtpen)]^{2+}$ and 129.8 (1)° in $[\rm Zn(bqbpen)]^{2+}$. This distortion is accompanied by a twisting of the equatorial aromatic groups out of the plane defined by the $\rm Zn^{II}$ atom and the four equatorial N atoms. The twist angle is in the range 8.2 (2)–10.7 (3)° for the pyridine rings in the two $[\rm Zn(tpen)]^{2+}$ cations and is 14.6 (2)° in (II). The quinoline ring systems are twisted even more, by 22.0 (2)° in (II) and by 23.5 (2) and 25.8 (2)° in (III). The Zn—N bond lengths vary between 2.082 (3) and 2.236 (3) Å in the four complex cations. The variation of the Zn—N bond lengths from $\rm Zn^{II}$ to the N atoms of the ethane-1,2-diamine part of the ligands behaves normally, but the bond lengths to the aromatic ligands are much more irregular, particularly when the ligand with four quinolyl groups, (IV) (Mikata *et al.*, 2005), is included in the comparisons. This last complex also exhibits overcrowding of the axial quinolyl groups, resulting in very long bonds to the axial N atoms of the ligands of 2.401 (2) and 2.371 (2) Å compared with an average of 2.138 (1) Å here for (II) and (III). Generally, the bond lengths to the axial N atoms decrease as the number of equatorial quinolyl groups increases. This general observation is more specific when the correlation between the lengths $d_{\rm eq}$ and $d_{\rm ax}$ is considered (Fig. 4): for a given cation in a general position, the longest axial bond is paired with that of the closest equatorial aromatic system. This almost linear correlation, shown in Fig. 4 (gradient = −0.823 and regression coefficient = −0.964 for eight points), may be explained by the interaction between an H atom of the axial pyridyl group and the $\pi$-system of the closest equatorial aromatic system. For the cations in special positions, there are two aromatic systems which are equally close and the points for these lie below the regression line.

In compound (I), the Zn and Cl atoms and the water molecules pack in layers perpendicular to the $b$ axis at $y = \pm\frac{1}{4}$. Within the layers, the cations form zigzag chains parallel to the (101) direction (Fig. 5). The two independent cations are

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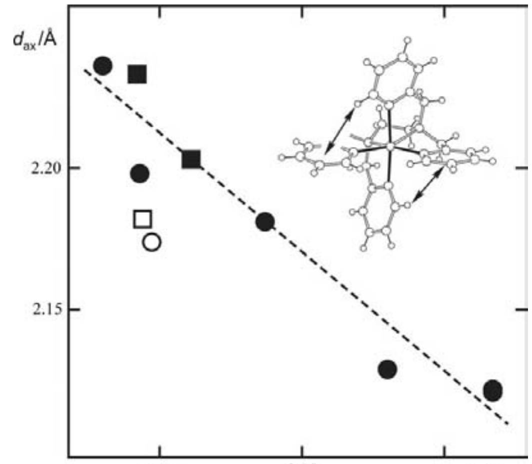

**Figure 4**
The correlation between equatorial and axial Zn—N bond lengths for which the distance between an H atom of an axial pyridyl group and the closest equatorial aromatic $\pi$-system is lowest. Filled circles: this work; filled squares: compound (IV), $[Zn(tpen)]^{2+}$ (Mikata *et al.*, 2005). Points for the cations in special positions are shown as open circles for (I) and as squares for (IV).

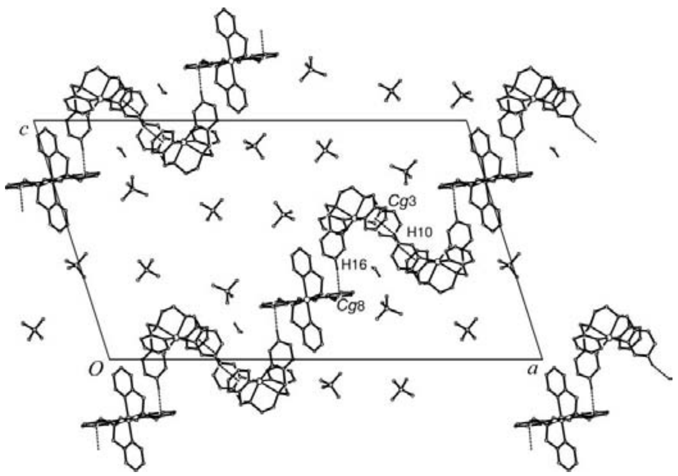

**Figure 5**
A packing diagram for (I), showing the slice ($y$ = 0 to $\frac{1}{2}$) perpendicular to the *b* axis. Intermolecular C—H$\cdots\pi$ bonds are shown as dashed lines. H atoms have been omitted, except for those of the water molecules and those involved in C—H$\cdots\pi$ bonds.

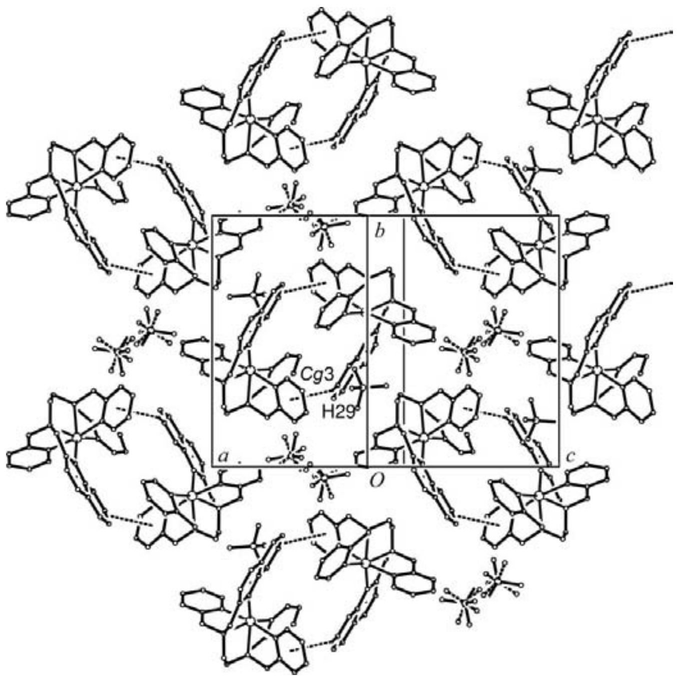

**Figure 6**
Packing diagram for (II), showing the slice (0, $y$, 0) to ($\frac{1}{2}$, $y$, $\frac{1}{2}$) parallel to [101]. Intermolecular C—H$\cdots\pi$ bonds are shown as dashed lines. H atoms have been omitted except for those involved in C—H$\cdots\pi$ bonds.

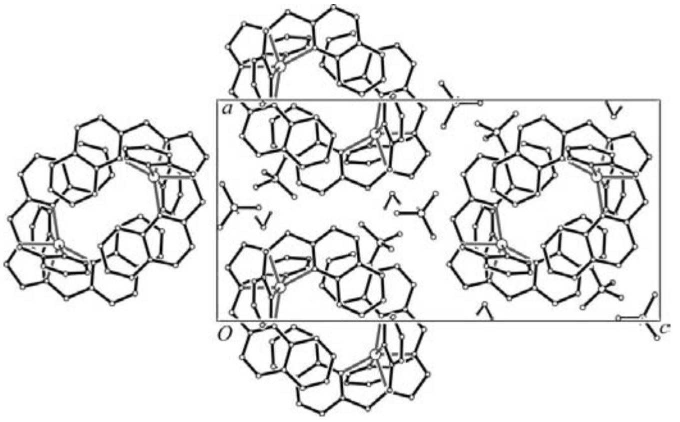

**Figure 7**
Unit-cell contents of (III), viewed down the *b* axis. H atoms have been omitted for clarity except for those of the water molecules.

linked by C—H$\cdots\pi$ hydrogen bonds and the cation which is in a general position is hydrogen bonded to a symmetry-related cation. These hydrogen bonds link the cations into infinite chains, and these chains are separated by perchlorate ions and water molecules. In the layer at $y = \pm\frac{3}{4}$, the chains are displaced by *c*/2 so that they are above the perchlorate ions of the neighbouring layer. The packing interactions are hydrogen bonds of the O—H$\cdots$O(perchlorate) and C—H$\cdots\pi$ types (Table 3).

In (II), the cations lie in layers parallel to the (101) plane; intermolecular C—H$\cdots\pi$ hydrogen bonds link pairs of cations (Fig. 6). The dimers are close-packed within these layers and are almost superimposed on those of the neighbouring layer. The perchlorate ions are located between the layers so that the packing utilizes C—H$\cdots$O and C—H$\cdots\pi$ interactions (Table 4).

In (III), the cations pack alternately up the $2_1$ screw axes parallel to *b* at (0, $y$, $\frac{1}{4}$) and ($\frac{1}{2}$, $y$, $\frac{3}{4}$), giving close-packed columns with the perchlorate ions and water molecules in the spaces between these columns (Fig. 7). The axial Zn—N bonds are parallel to *b*, resulting in open channels parallel to the *b* axis. C—H$\cdots\pi$ bonds link the cation columns along the $2_1$ axis. The C—H$\cdots\pi$, O—H$\cdots$O(perchlorate) and C—H$\cdots$O interactions are listed in Table 5.

In a large proportion of their salts, perchlorate anions tend to be disordered, which results in large apparent displacement parameters. Here, in compounds (I) and (III), which are both hydrates, the water molecules are hydrogen bonded to two perchlorate ions, ensuring the anions are ordered. In the anhydrous compound, (II), one of the perchlorate ions (Cl1) was so disordered that it was modelled as two interpenetrating regular tetrahedra, but even then the $U_3/U_1$ value was unrealistically high.

## Experimental

**Caution:** Perchlorate salts and ethanolic solutions of perchlorate salts are potentially explosive and should be handled accordingly.

For the preparation of [Zn(tpen)]($ClO_4$)$_2$·0.67$H_2O$, (I), a solution of zinc perchlorate hexahydrate (0.896 g, 2.4 mmol) in absolute ethanol (15 ml) was added slowly to a solution of tpen (1 g, 2.4 mmol) in absolute ethanol (10 ml). The mixture was stirred for 30 min at 333 K and then cooled to room temperature. The white crystals which formed were filtered off and washed with ethanol (5 ml) (yield 1.49 g, 92%). The crystals were recrystallized from a mixture of water and ethanol (1:1 *v*/*v*). Analysis found: C 45.36, H 3.94, N 12.09, Cl 9.51%; calculated for [Zn($C_{26}H_{28}N_6$)]($ClO_4$)$_2$·0.67$H_2O$: C 44.56, H 4.22, N 11.99, Cl 10.18%. For the preparation of [Zn(qtpen)]($ClO_4$)$_2$, (II), a solution of zinc perchlorate hexahydrate (0.785 g, 2.11 mmol) in absolute ethanol (12 ml) was added slowly to a solution of qtpen (1 g, 2.11 mmol) in absolute ethanol (12 ml), which was heated to 323 K. The mixture was cooled to room temperature and the white crystals which formed were filtered off and washed with ice-cold ethanol (4 ml) (yield 1.4 g, 94%). The crystals were dissolved in boiling water, filtered and cooled to room temperature (yield 1.3 g, 85%). Analysis found: C 48.83, H 3.79, N 11.37, Cl 9.43%; calculated for [Zn($C_{30}H_{30}N_6$)]($ClO_4$)$_2$: C 44.77, H 4.09, N 11.37, Cl 9.60%.For the preparation of [Zn(bqbpen)]($ClO_4$)$_2$·$H_2O$, (III), a solution of zinc perchlorate hexahydrate (0.524 g, 1.4 mmol) in absolute ethanol (10 ml) was added slowly to a solution of bqbpen (0.74 g, 1.4 mmol) in absolute ethanol (12 ml), which was heated to 333 K. The mixture was cooled to room temperature and the white crystals which formed were filtered off and washed with ethanol (5 ml) (yield 1 g, 90%). The crystals were dissolved in boiling water, filtered and cooled to room temperature. Analysis found: C 51.17, H 4.03, N 10.47, Cl 8.73%; calculated for [Zn($C_{34}H_{32}N_6$)]($ClO_4$)$_2$·$H_2O$: C 50.60, H 4.25, N 10.41, Cl 8.79%.

### Compound (I)

*Crystal data*

[Zn($C_{26}H_{28}N_6$)]($ClO_4$)$_2$·0.67$H_2O$
$M_r$ = 700.86
Monoclinic, $C2/c$
$a$ = 41.064 (3) Å
$b$ = 9.3590 (7) Å
$c$ = 23.785 (2) Å
$\beta$ = 107.625 (2)°
$V$ = 8711.9 (12) Å$^3$
$Z$ = 12
Mo $K\alpha$ radiation
$\mu$ = 1.09 mm$^{-1}$
$T$ = 120 K
0.41 × 0.26 × 0.08 mm

*Data collection*

Siemens SMART CCD area-detector diffractometer
Absorption correction: integration (*XPREP*; Siemens, 1995)
$T_{min}$ = 0.681, $T_{max}$ = 0.919
41218 measured reflections
10019 independent reflections
6179 reflections with $I > 2.5\sigma(I)$
$R_{int}$ = 0.063

*Refinement*

$R[F > 2\sigma(F)]$ = 0.037
$wR(F)$ = 0.038
$S$ = 0.99
6179 reflections
591 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 (4) e Å$^{-3}$
$\Delta\rho_{min}$ = −0.35 (4) e Å$^{-3}$

**Table 1**
Comparison of Zn—N bond lengths (Å) for complexes with tpen, (I), qtpen, (II), and bqbpen, (III).

| | (I) Molecule 1 | (I) Molecule 2 | (II) | (III) |
|---|---|---|---|---|
| Zn—N1 | 2.188 (3) | 2.208 (3) | 2.189 (2) | 2.205 (2) |
| Zn—N2 | 2.173 (3) | 2.208 (3) | 2.229 (2) | 2.208 (2) |
| Zn—N3 | 2.236 (3) | 2.175 (3) | 2.181 (2) | 2.122 (2) |
| Zn—N4 | 2.092 (3) | 2.097 (3) | 2.180 (2) | 2.217 (3) |
| Zn—N5 | 2.082 (3) | 2.097 (3) | 2.137 (2) | 2.217 (2) |
| Zn—N6 | 2.199 (3) | 2.175 (3) | 2.129 (2) | 2.121 (2) |

**Table 2**
Comparison of N—Zn—N angles (°) for complexes with tpen, (I), qtpen, (II), and bqbpen, (III).

| | (I) Molecule 1 | (I) Molecule 2 | (II) | (III) |
|---|---|---|---|---|
| N1—Zn—N2 | 82.7 (1) | 81.9 (2) | 81.96 (7) | 79.6 (1) |
| N1—Zn—N3 | 78.5 (1) | 78.8 (1) | 79.37 (7) | 81.57 (9) |
| N1—Zn—N4 | 79.8 (1) | 79.5 (1) | 77.09 (7) | 76.18 (9) |
| N1—Zn—N5 | 157.3 (1) | 157.5 (1) | 156.00 (7) | 153.5 (1) |
| N1—Zn—N6 | 106.1 (1) | 96.0 (1) | 95.72 (7) | 93.57 (9) |
| N2—Zn—N3 | 100.0 (1) | 96.0 (1) | 91.55 (7) | 94.32 (9) |
| N2—Zn—N4 | 157.1 (1) | 157.5 (1) | 157.42 (7) | 154.04 (9) |
| N2—Zn—N5 | 81.1 (1) | 79.5 (1) | 77.14 (7) | 75.40 (9) |
| N2—Zn—N6 | 79.0 (1) | 78.7 (1) | 80.03 (7) | 81.3 (1) |
| N3—Zn—N4 | 90.9 (1) | 92.8 (1) | 92.76 (7) | 91.81 (8) |
| N3—Zn—N5 | 88.7 (1) | 90.6 (1) | 89.48 (7) | 91.16 (9) |
| N3—Zn—N6 | 185.0 (1)† | 173.1 (1) | 170.82 (7) | 174.03 (9) |
| N4—Zn—N5 | 119.5 (1) | 121.2 (1) | 125.04 (7) | 129.82 (8) |
| N4—Zn—N6 | 91.7 (1) | 90.6 (1) | 93.68 (7) | 91.04 (9) |
| N5—Zn—N6 | 86.3 (1) | 92.8 (1) | 92.16 (7) | 91.04 (9) |

† Angle defined as <180° for bonds bent toward the ethanediamine group.

**Table 3**
Hydrogen-bond geometry (Å, °) for (I).

*Cg*3 is the centroid of the N3/C3–C7 ring and *Cg*8 is the centroid of the N8/C28–C32 ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O13—H131···O6 | 0.86 | 2.06 | 2.907 (5) | 167 |
| O13—H132···O2$^{i}$ | 0.86 | 2.40 | 3.227 (4) | 162 |
| C1—H1*a*···O1 | 0.95 | 2.38 | 3.320 (5) | 169 |
| C9—H9···O13 | 0.95 | 2.40 | 3.250 (5) | 149 |
| C12—H12···O2$^{ii}$ | 0.95 | 2.48 | 3.134 (5) | 126 |
| C14—H14*b*···O3 | 0.95 | 2.46 | 3.321 (4) | 150 |
| C20—H20*a*···O9 | 0.95 | 2.57 | 3.439 (6) | 153 |
| C20—H20*b*···O4$^{iii}$ | 0.95 | 2.44 | 3.355 (5) | 160 |
| C26—H26*b*···O12 | 0.95 | 2.52 | 3.430 (5) | 160 |
| C27—H27*a*···O12$^{i}$ | 0.95 | 2.41 | 3.287 (5) | 154 |
| C33—H33*a*···O8 | 0.95 | 2.53 | 3.440 (6) | 160 |
| C35—H35···O10 | 0.95 | 2.58 | 3.315 (5) | 134 |
| C10—H10···*Cg*3$^{iv}$ | 0.95 | 2.70 | 3.546 (5) | 148 |
| C16—H16···*Cg*8 | 0.95 | 2.52 | 3.454 (5) | 167 |

Symmetry codes: (i) $x, -y+1, z-\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, y-1, z$; (iv) $-x+\frac{3}{2}, -y+\frac{1}{2}, -z+1$.

### Compound (II)

*Crystal data*

[Zn($C_{30}H_{30}N_6$)]($ClO_4$)$_2$
$M_r$ = 738.91
Monoclinic, $P2_1/n$
$a$ = 13.231 (2) Å
$b$ = 15.146 (2) Å
$c$ = 15.167 (2) Å
$\beta$ = 94.634 (3)°
$V$ = 3029.5 (7) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.05 mm$^{-1}$
$T$ = 120 K
0.60 × 0.42 × 0.28 mm

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

*Cg*3 is the centroid of the N3/C3–C7 ring and *Cg*5 is the centroid of the N5/C15–C19 ring.

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| C5—H5$\cdots$O1$'^{\rm i}$ | 0.95 | 2.51 | 3.194 (4) | 129 |
| C17—H17$\cdots$O7 | 0.95 | 2.55 | 3.448 (3) | 157 |
| C18—H18$\cdots$O4$'$ | 0.95 | 2.54 | 3.209 (3) | 128 |
| C20—H20$a\cdots$O7$^{\rm ii}$ | 0.95 | 2.55 | 3.276 (3) | 134 |
| C21—H21$\cdots$O8$^{\rm iii}$ | 0.95 | 2.49 | 3.266 (3) | 139 |
| C27—H27$\cdots$O5 | 0.95 | 2.43 | 3.053 (3) | 123 |
| C3—H3$\cdots$*Cg*5 | 0.95 | 2.85 | 3.639 (3) | 141 |
| C29—H29$\cdots$*Cg*3$^{\rm iv}$ | 0.95 | 2.79 | 3.538 (3) | 136 |

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+1, -y, -z+1$; (iii) $x+\frac{1}{2}, -y-\frac{1}{2}, z+\frac{1}{2}$; (iv) $-x+1, -y, -z+2$.

**Table 5**
Hydrogen-bond geometry (Å, °) for (III).

*Cg*3 is the centroid of the N3/C3–C7 ring and *Cg*9 is the centroid of the C9/C10/C31–C34 ring.

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O9—H91$\cdots$O3 | 0.96 | 1.80 | 2.716 (5) | 158 |
| O9—H92$\cdots$O5 | 0.98 | 2.16 | 3.064 (5) | 153 |
| O9—H92$\cdots$O6 | 0.98 | 2.26 | 3.086 (6) | 142 |
| C1—H1$a\cdots$O6$^{\rm i}$ | 0.95 | 2.54 | 3.265 (4) | 134 |
| C2—H2$b\cdots$O4$^{\rm ii}$ | 0.95 | 2.56 | 3.306 (4) | 136 |
| C4—H4$\cdots$O7$^{\rm iii}$ | 0.95 | 2.56 | 3.285 (3) | 133 |
| C5—H5$\cdots$O9$^{\rm ii}$ | 0.95 | 2.37 | 3.162 (5) | 141 |
| C8—H8$b\cdots$O4$^{\rm ii}$ | 0.95 | 2.55 | 3.350 (4) | 141 |
| C20—H20$b\cdots$O5 | 0.95 | 2.59 | 3.403 (4) | 144 |
| C21—H21$\cdots$O7$^{\rm iv}$ | 0.95 | 2.42 | 3.183 (5) | 137 |
| C23—H23$\cdots$O2$^{\rm v}$ | 0.95 | 2.54 | 3.318 (4) | 140 |
| C24—H24$\cdots$O9 | 0.95 | 2.38 | 3.127 (5) | 135 |
| C28—H28$\cdots$O4$^{\rm vi}$ | 0.95 | 2.56 | 3.277 (4) | 132 |
| C29—H29$\cdots$*Cg*3$^{\rm vii}$ | 0.95 | 2.55 | 3.479 (4) | 166 |
| C33—H33$\cdots$*Cg*9$^{\rm viii}$ | 0.95 | 2.63 | 3.544 (3) | 161 |

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (ii) $x, y+1, z$; (iii) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x+1, y, z$; (v) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (vi) $-x+\frac{1}{2}, -y+1, z+\frac{1}{2}$; (vii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (viii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

*Data collection*

Siemens SMART CCD area-detector diffractometer
Absorption correction: integration (*XPREP*; Siemens, 1995
$T_{\rm min}$ = 0.596, $T_{\rm max}$ = 0.778
25310 measured reflections
6946 independent reflections
4838 reflections with $I > 3\sigma(I)$
$R_{\rm int}$ = 0.026

*Refinement*

$R[F > 2\sigma(F)]$ = 0.030
$wR(F)$ = 0.035
$S$ = 1.00
4838 reflections
402 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 1.43 (7) e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −1.18 (7) e Å$^{-3}$

## Compound (III)

*Crystal data*

[Zn(C$_{34}$H$_{32}$N$_6$)](ClO$_4$)$_2$·H$_2$O
$M_r$ = 806.99
Orthorhombic, $P2_12_12_1$
$a$ = 11.891 (3) Å
$b$ = 12.022 (3) Å
$c$ = 23.838 (5) Å
$V$ = 3407.8 (14) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.94 mm$^{-1}$
$T$ = 120 K
0.54 × 0.38 × 0.30 mm

*Data collection*

Siemens SMART CCD area-detector diffractometer
Absorption correction: integration (*XPREP*; Siemens, 1995)
$T_{\rm min}$ = 0.664, $T_{\rm max}$ = 0.774
28487 measured reflections
7803 independent reflections
6872 reflections with $I > 2.5\sigma(I)$
$R_{\rm int}$ = 0.064

*Refinement*

$R[F > 2\sigma(F)]$ = 0.033
$wR(F)$ = 0.038
$S$ = 1.00
6872 reflections
470 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 1.15 (9) e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −0.59 (9) e Å$^{-3}$
Absolute structure: Rogers parameter refined for 2959 Bijvoet pairs where both members have $I > 3\sigma(I)$. For the crystal studied, atoms N1 and N2 have the *S* configuration
Rogers parameter: 0.93 (2)

Water-bound H atoms were kept fixed at positions determined from $\rho_{\rm obs} - \rho_{\rm calc}$ syntheses. Carbon-bound H atoms were fixed in calculated positions, with C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). In (II), one of the perchlorate groups is disordered and was modelled as two interpenetrating regular tetrahedra with a common Cl—O distance and combined occupancy factors of unity for the two tetrahedra. For (III), a Rogers parameter (Rogers, 1981) refined to 0.93 (2), defining the cation as chiral with the Δ configuration in the crystal studied.

For all compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1997) and *KRYSTAL* (Hazell, 1995); program(s) used to refine structure: *ORFLS* (Busing *et al.*, 1962; modified) and *KRYSTAL*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *KRYSTAL* and *PLATON* (Spek, 2003); software used to prepare material for publication: *KRYSTAL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3084). Services for accessing these data are described at the back of the journal.

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