

## Acyclic Schiff base salts derived from 1,3-diaminopropane and 1,3-diamino-2-hydroxypropane

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Received 11 August 2007

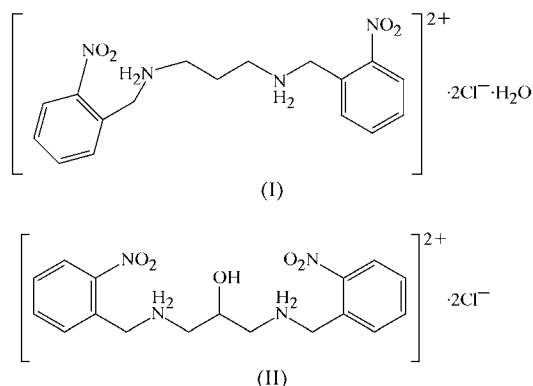
Accepted 23 August 2007

Online 22 September 2007

Two salts of acyclic Schiff base cationic ligands, namely *N,N'*-bis(2-nitrobenzyl)propane-1,3-diammonium dichloride monohydrate,  $C_{17}H_{22}N_4O_4^{2+} \cdot 2Cl^- \cdot H_2O$ , (I), and 2-hydroxy-*N,N'*-bis(2-nitrobenzyl)propane-1,3-diammonium dichloride,  $C_{17}H_{22}N_4O_5^{2+} \cdot 2Cl^-$ , (II), were synthesized as precursors in order to obtain new acyclic and macrocyclic multidentate ligands and complexes. The cation conformations in compounds (I) and (II) are different in the solid state, although the cations are closely related chemically. Similarly, the hydrogen-bonding networks involving ammonium cations, hydroxyl groups and chloride anions are also different. In the cation of compound (II), the hydroxyl group is disordered over two sets of sites, with occupancies of 0.785 (8) and 0.215 (8).

### Comment

The Schiff base acyclic cations in the title salts, (I) and (II), are chemical precursors for a variety of acyclic and macrocyclic multidentate ligands and their metal complexes. The cations in compounds (I) and (II) are closely related, compound (II) formally resulting from (I) after substitution of an H atom by

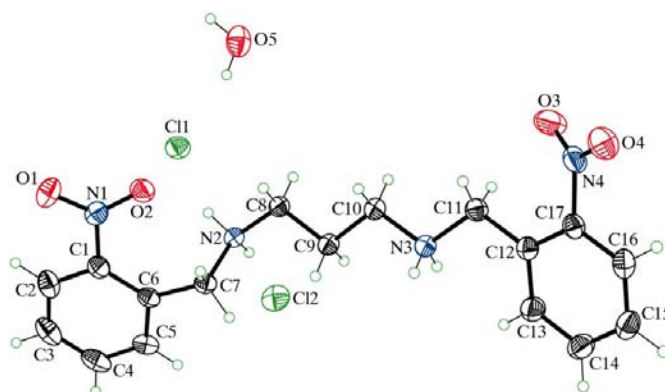


an OH functionality. The hydroxyl group is known to be an efficient donor and acceptor group for hydrogen bonding, and

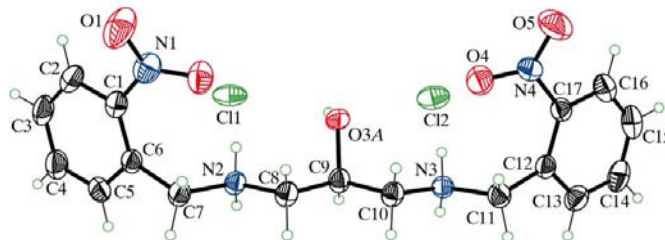
the introduction of this functional group is thus expected to induce significant changes in the crystal structure. However, an unexpected conformational modification was also observed for the cations. Moreover, compound (I) crystallizes as a hydrate, while compound (II) is unsolvated.

The cation in compound (II) approximates to  $C_s$  point group symmetry (Fig. 2), while in compound (I) the cation is clearly asymmetric (Fig. 1). The aryl rings make significantly different dihedral angles in each cation,  $35.2 (1)^\circ$  for compound (I) and  $63.8 (2)^\circ$  for compound (II). The nitro groups are twisted out of the planes of the adjacent aryl rings, with  $NO_2$ /arene dihedral angles of  $12.0 (2)$  and  $27.3 (2)^\circ$  for the nitro groups containing atoms N1 and N4 in compound (I), and  $31.7 (3)$  and  $24.2 (5)^\circ$  for the corresponding groups in compound (II). This twisted arrangement for nitro groups is a common feature in molecules including a nitrobenzene fragment [*e.g.*  $40.5^\circ$  (Peseke *et al.*, 1999),  $34.4^\circ$  (Qiu *et al.*, 2006), and  $23.3$  and  $17.6^\circ$  (Obregón-Solís *et al.*, 2001)].

The conformation of the central chain linking the nitrophenyl groups for both ligands is described by the C—C—N—C and N—C—C—C torsion angles (Tables 1 and 3). As can be seen, the conformation stabilized for compound (II) is the expected all-*trans* chain commonly found in aliphatic systems, while compound (I) presents a synclinal conformation for the



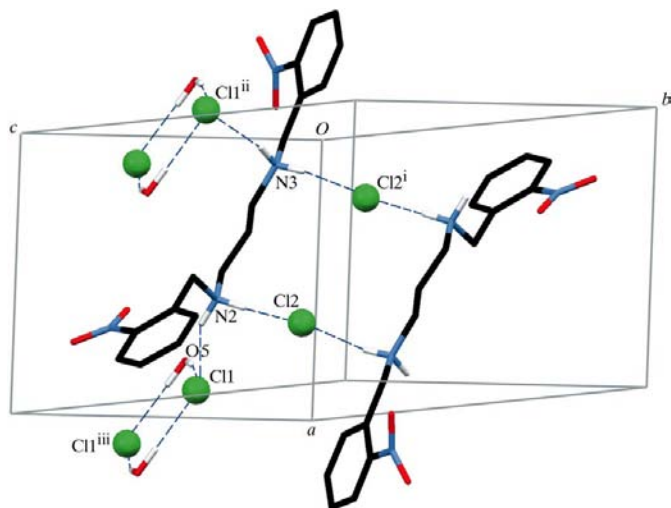
**Figure 1**  
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.



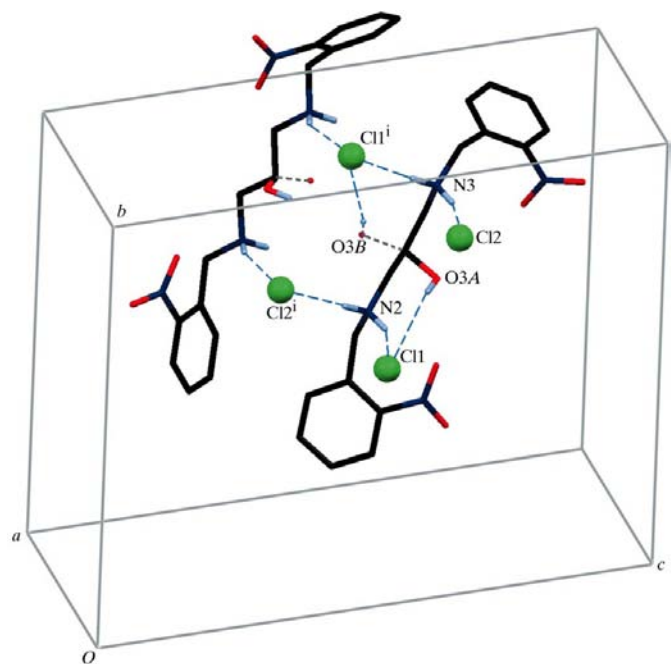
**Figure 2**  
The molecular structure of compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Only the major disorder component of the OH group is shown.

C7/N2/C8/C9 section, defining a *trans-gauche-trans-trans-trans* conformation for the complete C6–C12 chain. These observations suggest that compounds (I) and (II) are highly flexible cations, with quite free rotation about all  $\sigma$  bonds, assuming that no hindrance occurs with peripheral nitrobenzene groups. This flexible behaviour, probably retained or even increased in solution, makes compounds (I) and (II) good candidates for coordinating transition metals.

In both compounds, the cations and anions are engaged in hydrogen-bond networks, two-dimensional in compound (I)



**Figure 3** Part of the crystal structure of compound (I), showing the hydrogen-bonded (dashed lines) network. [Symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $x - 1, y, z$ ; (iii)  $2 - x, -y, 1 - z$ .]



**Figure 4** The packing structure of compound (II), showing the hydrogen bonds (long-dashed lines). Both disorder components for the OH functionality are shown, the bonds of the minor component being represented by short-dashed lines. [Symmetry code: (i)  $x + \frac{1}{2}, -y + \frac{3}{2}, 1 - z$ .]

and one-dimensional in compound (II), involving  $\text{NH}_2^+$  or O–H functionalities as donor groups and  $\text{Cl}^-$  or nitro groups as acceptors. In the case of compound (II), the O–H group is disordered over two sites with occupancies of 0.785 (8) and 0.215 (8) for atoms O3A and O3B, respectively (see *Experimental*). The major component of the disordered hydroxyl group forms a hydrogen bond with a  $\text{Cl}^-$  anion in the asymmetric unit, and two  $\text{Cl}^-$  anions are also connected to  $\text{NH}_2^+$  groups, one within the asymmetric unit and the other within a symmetry-related unit. The minor component of the disordered hydroxyl group forms a weaker bond with a symmetry-related  $\text{Cl}^-$  anion. Finally, two strong intermolecular N–H...Cl bonds form a one-dimensional network stabilizing the crystal structure (Table 4 and Fig. 4). For compound (I), as the hydroxyl donor group is no longer present in the cation, a water molecule is inserted in the lattice, which participates in efficient O–H...Cl contacts (Table 2 and Fig. 3).

### Experimental

The title salts of acyclic cationic ligands, (I) and (II), were obtained by a three-step reaction procedure. The condensation between 1,2-diaminoethane, for compound (I), or 1,3-diamino-2-hydroxypropane, for compound (II), with 2-nitrobenzyl chloride produced the corresponding imines. Selective reduction of the imines with sodium borohydride in methanol gave the corresponding amines, which were isolated as oils. They were converted to their chloride salts using HCl dissolved in ethanol [yields: 70% for compound (I) and 47% for compound (II)]. Suitable colourless crystals of compounds (I) and (II) were obtained by slow evaporation of ethanol solutions at 298 K.

### Compound (I)

#### Crystal data

$\text{C}_{17}\text{H}_{22}\text{N}_4\text{O}_4^{2+} \cdot 2\text{Cl}^- \cdot \text{H}_2\text{O}$   
 $M_r = 435.30$   
 Triclinic,  $P\bar{1}$   
 $a = 8.630$  (3) Å  
 $b = 11.449$  (4) Å  
 $c = 11.629$  (4) Å  
 $\alpha = 116.353$  (17)°  
 $\beta = 92.09$  (2)°

$\gamma = 98.82$  (2)°  
 $V = 1010.2$  (6) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.36$  mm<sup>-1</sup>  
 $T = 297$  (2) K  
 $0.5 \times 0.5 \times 0.4$  mm

#### Data collection

Siemens P4 diffractometer  
 Absorption correction:  $\psi$  scan  
 (XSCANS; Siemens, 1999)  
 $T_{\min} = 0.845$ ,  $T_{\max} = 0.867$   
 8783 measured reflections  
 4456 independent reflections

3585 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.072$   
 3 standard reflections  
 every 97 reflections  
 intensity decay: 5.0%

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.113$   
 $S = 1.05$   
 4456 reflections  
 261 parameters  
 2 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.30$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.36$  e Å<sup>-3</sup>

**Table 1**

Selected torsion angles (°) for (I).

C8–N2–C7–C6	158.61 (14)	C8–C9–C10–N3	176.86 (13)
C7–N2–C8–C9	62.25 (18)	C11–N3–C10–C9	174.09 (13)
N2–C8–C9–C10	–179.01 (12)	C10–N3–C11–C12	170.94 (13)

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2 <i>B</i> ...Cl2	0.90	2.11	3.0043 (17)	170
N2—H2 <i>C</i> ...Cl1	0.90	2.27	3.0976 (16)	153
N3—H3 <i>B</i> ...Cl2 <sup>i</sup>	0.90	2.13	2.9890 (17)	159
N3—H3 <i>C</i> ...Cl1 <sup>ii</sup>	0.90	2.25	3.1142 (17)	161
O5—H5 <i>B</i> ...Cl1 <sup>iii</sup>	0.91 (4)	2.24 (2)	3.141 (2)	173 (4)
O5—H5 <i>C</i> ...Cl1	0.89 (3)	2.35 (2)	3.213 (2)	165 (3)

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $x - 1, y, z$ ; (iii)  $-x + 2, -y, -z + 1$ .**Compound (II)***Crystal data*

$C_{17}H_{22}N_4O_5 \cdot 2Cl^-$	$V = 2079.8 (14) \text{ \AA}^3$
$M_r = 433.29$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 7.075 (2) \text{ \AA}$	$\mu = 0.35 \text{ mm}^{-1}$
$b = 15.844 (8) \text{ \AA}$	$T = 298 (2) \text{ K}$
$c = 18.554 (6) \text{ \AA}$	$0.4 \times 0.2 \times 0.2 \text{ mm}$

*Data collection*

Siemens P4 diffractometer	2729 reflections with $I > 2\sigma(I)$
Absorption correction: $\psi$ scan ( <i>XSCANS</i> ; Siemens, 1999)	$R_{int} = 0.089$
$T_{min} = 0.739, T_{max} = 0.934$	3 standard reflections
6209 measured reflections	every 97 reflections
3692 independent reflections	intensity decay: 10.2%

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.055$	H-atom parameters constrained
$wR(F^2) = 0.145$	$\Delta\rho_{max} = 0.36 \text{ e \AA}^{-3}$
$S = 1.04$	$\Delta\rho_{min} = -0.30 \text{ e \AA}^{-3}$
3692 reflections	Absolute structure: Flack (1983),
259 parameters	with 1557 Friedel pairs
8 restraints	Flack parameter: $-0.03 (11)$

**Table 3**  
Selected torsion angles (°) for (II).

C8—N2—C7—C6	156.9 (4)	C8—C9—C10—N3	174.4 (3)
C7—N2—C8—C9	−177.5 (3)	C11—N3—C10—C9	175.2 (3)
N2—C8—C9—C10	−178.0 (3)	C10—N3—C11—C12	−158.2 (3)

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2 <i>D</i> ...Cl2 <sup>i</sup>	0.90	2.19	3.060 (4)	163
N2—H2 <i>E</i> ...Cl1	0.90	2.34	3.109 (3)	143
N3—H3 <i>C</i> ...Cl2	0.90	2.30	3.120 (3)	151
N3—H3 <i>D</i> ...Cl1 <sup>i</sup>	0.90	2.15	3.037 (3)	167
O3 <i>A</i> —H3 <i>A</i> <i>A</i> ...Cl1	0.85	2.80	3.422 (4)	132
O3 <i>B</i> —H3 <i>B</i> <i>A</i> ...Cl1 <sup>i</sup>	0.85	2.24	2.95 (2)	140

Symmetry code: (i)  $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$ .

The geometry of the water molecule in compound (I) was regularized using two restraints; O—H = 0.85 (2) Å. Other H atoms were

placed in idealized positions and refined using a riding approximation, with C—H bond lengths set at 0.93 (aromatic CH) or 0.97 Å (methylene CH<sub>2</sub>), and with  $U_{iso}(H) = 1.2U_{eq}(C)$ . For compound (II), the hydroxyl O atom was found to be disordered over two positions and the corresponding site-occupation factors were refined, with their sum constrained to unity; the occupancies converged to 0.785 (8) (atom O3*A*) and 0.215 (8) (atom O3*B*). In order to obtain a sensible geometry, C—O bond lengths were restrained to 1.45 (1) Å. Site O3*A* was refined anisotropically, with restrictions on its  $U^{ij}$  parameters approximating isotropic behaviour. Site O3*B* was refined isotropically due to its limited occupancy. Hydroxyl atom H3*A**A* bonded to O3*A* was included in a calculated position and refined using a riding model (O—H constrained to 0.85 Å), but allowing free rotation about the C—O axis. The other hydroxyl H atom, H3*A**B*, was included in a calculated position and refined as riding on O3*B*. Other H atoms were placed in idealized positions and all were refined as riding on their carrier atoms, with bond lengths fixed at 0.90 (ammonium NH), 0.93 (aromatic CH), 0.97 (methylene CH<sub>2</sub>) or 0.98 Å (methine CH). In compound (II), all H atoms were refined with fixed isotropic displacement parameters calculated as  $U_{iso}(H) = xU_{eq}(\text{carrier atom})$ , where  $x = 1.5$  for hydroxyl groups and  $x = 1.2$  otherwise. For compound (II), 1557 measured Friedel pairs were used for the refinement of the Flack (1983) parameter, using this parameter only for crystal chirality determination.

For both compounds, data collection: *XSCANS* (Siemens, 1999); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus* and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL-Plus*.

The authors acknowledge the Facultad de Ciencias Químicas, UANL, and PAICYT for financial support (project No. CA1260-06).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3137). Services for accessing these data are described at the back of the journal.

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