

A two-dimensional layer in *N,N'*-bis[2-(hydroxymethyl)benzyl]ethylenediamine and a three-dimensional network in *N,N'*-bis[2-(hydroxymethyl)benzyl]ethylenediammonium bis(perchlorate)

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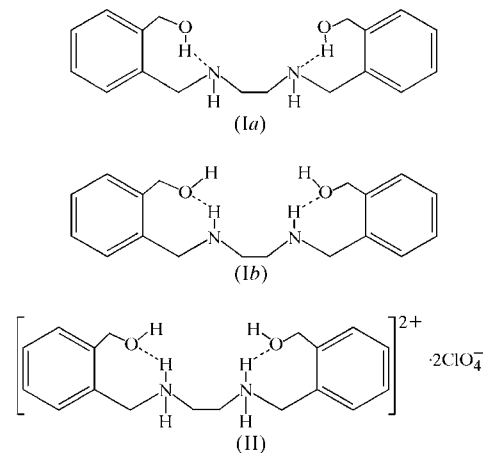
In both title compounds, $C_{18}H_{24}N_2O_2$, (Ia), and $C_{18}H_{26}N_2O_2 \cdot 2ClO_4^-$, (II), respectively, the two aryl rings are strictly parallel, with an inversion centre lying at the mid-point of each central CH_2-CH_2 bond. Molecules in (Ia) are linked into two-dimensional layers by $N-H \cdots O$ hydrogen bonds. The component ions in (II) are joined together by a combination of $N/O/C-H \cdots O$ hydrogen bonds and $C-H \cdots \pi$ and anion $\cdots \pi$ interactions, forming a three-dimensional network. A structural understanding of (Ia) and (II) may provide some useful information about how and why their metal-organic complexes display various biological activities and function in catalytic processes.

Comment

In recent decades, tetradentate Schiff bases known generally as $salenH_2$ (Kahwa *et al.*, 1986) have been studied extensively owing to their potential biological activities, *e.g.* antibacterial, antitumour (Santos *et al.*, 2001; Viswanathan *et al.*, 1998; García-Zarracino *et al.*, 2002) and catalytic (Mohebbi *et al.*, 2005). They not only offer greater flexibility than the corresponding Schiff bases, but also adopt two additional sites capable of σ -bonding which should be helpful in designing new useful inorganic complexes (Atwood & Rutherford, 1995; Xu *et al.*, 2004; Tinoco *et al.*, 2007). In order to gain more insight into these analogues, we have synthesized a new tetradentate ligand, (Ia), containing an N_2O_2 donor set, and its diammonium bis(perchlorate), (II), and we report here the molecular and supramolecular structures.

Both title compounds crystallize in the space group $P2_1/c$, with one-half of the molecule representing the asymmetric unit (Fig. 1). The conformation of the central chain in (Ia)

is described by the torsion angles $C3-C2-N1-C1 = -72.6(1)^\circ$, $C2-N1-C1-C1^i = 175.5(1)^\circ$ and $N1-C1-C1^i-N1^i$ constrained by symmetry to be 180° [symmetry code:



(i) $-x, 1-y, -z$], resulting in the less common *gauche-trans-trans* conformation (Xia *et al.*, 2006). The corresponding angles in (II) are $-178.9(3)$, $-168.1(3)$ and 180° , respectively, forming the general *trans-trans-trans* conformation (Palladino *et al.*, 2006; Matiková-Málarová *et al.*, 2007; Yang, Wang *et al.*, 2007; Yang, Han *et al.*, 2007; Liu *et al.*, 2007). Both N atoms in the tetradentate ligand can be potentially coordinated to a metal ion, according to previously reported analogues (Panda *et al.*, 2004; Ghosh *et al.*, 1994), giving rise to many other conformations. This indicates that these highly flexible molecules can rotate freely about all the σ bonds. However, when (II) is coordinated to a metal ion, it should first be deprotonated using a moderately basic medium.

Although a similar $C(7)$ motif (Bernstein *et al.*, 1995) exists in both compounds, in (Ia) it is formed by intramolecular $O1-H1E \cdots N1$ hydrogen bonds and in (II) by $N1-H1C \cdots O1$ hydrogen bonds. In order to investigate further the reason for this, the hydrogen-bonding energy and total molecular energy of the two practical and one posulated conformation were calculated according to our earlier method (Hu *et al.*, 1999; Hu, 1998) using the program *GAUSSIAN03W* (Frisch *et al.*, 2004) at the RB3LYP/6-31G(d) level. It can be seen from

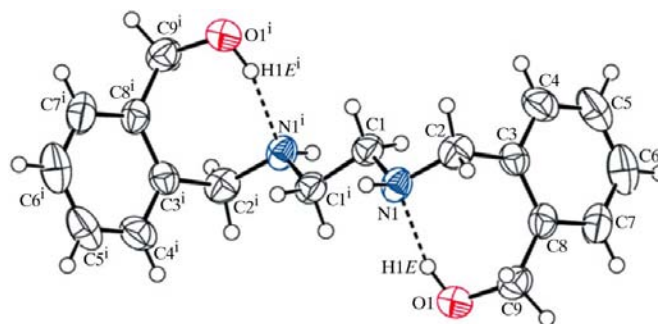


Figure 1

The molecular structure of (Ia), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Some hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x, 1-y, -z$.]

Table 1 that the dication has the lowest total molecular energy and the postulated form (Ib) has the highest. The Mulliken charges on the N atoms in (Ia) and (Ib) are -0.594 and -0.569 , respectively. This indicates that the neutral N atoms in (Ia) may be more easily protonated than those in (Ib). We also have found that when Lewis acids are absent, the neutral molecules preferentially adopt conformation (Ia). Some contrast experiments have been carried out by displacing the solvent with ethanol, acetone and water. However, no crystals adopting conformation (Ib) were obtained.

In the crystal structure of (Ia), the molecules are linked by means of $N-H \cdots O$ hydrogen bonds into two-dimensional layers. Amino atom N1 in the molecule at (x, y, z) acts as a

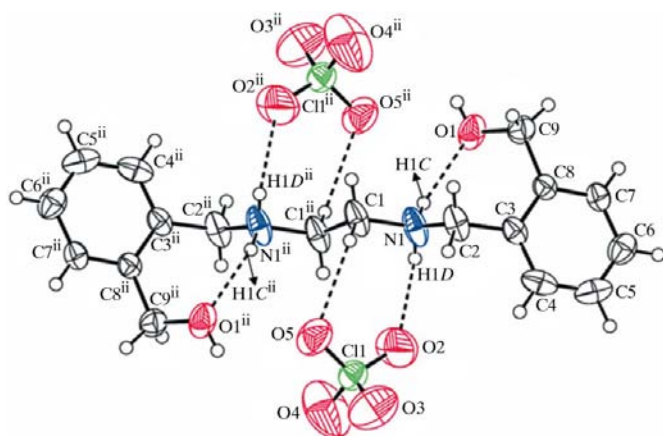


Figure 2
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Some hydrogen bonds are shown as dashed lines. [Symmetry codes: (ii) $1 - x, 1 - y, 1 - z$.]

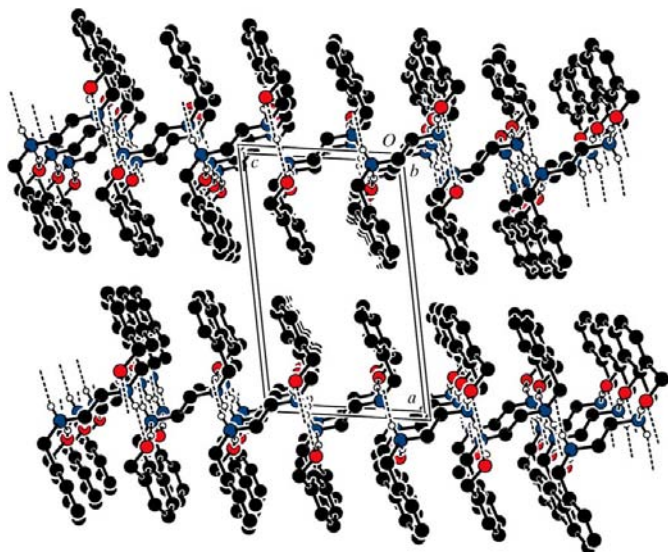


Figure 3
Part of the crystal structure of (Ia), showing the formation of the two-dimensional network running parallel to the (100) plane. Hydrogen bonds are shown as dashed lines.

hydrogen-bond donor *via* atom H1C to hydroxyl atom O1 in the molecule at $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$, forming a one-dimensional $C(7)$ chain running parallel to the [010] direction, which is generated by the 2_1 screw axis at $(0, y, \frac{1}{4})$. Adjacent $C(7)$ chains related by the inversion centre at the mid-point of the CH_2-CH_2 unit thus link the molecules into two-dimensional layers (Fig. 2) running parallel to the (100) plane. There are two halves of such a layer passing through the unit cell, with the reference layer in the domain $-0.474 < x < 0.474$ and the other in the domain $0.526 < x < 1.474$. No $C-H \cdots \pi$ or $\pi-\pi$ stacking interactions are observed between adjacent layers.

In the crystal structure of (II), the component ions are linked into a three-dimensional network by a combination of $N/O/C-H \cdots O$ hydrogen bonds and $C-H \cdots \pi$ and anion $\cdots \pi$ interactions, which can be readily analyzed in terms of two simple substructures. First, the combined actions of five inter-ion hydrogen bonds (Table 2) and their respective equivalents result in two-dimensional layers running parallel to the (100) plane. The reference two-dimensional layer lies within the domain $-0.065 < x < 1.065$ and there is only one such layer passing through the unit cell (Fig. 3). Analysis by *PLATON*

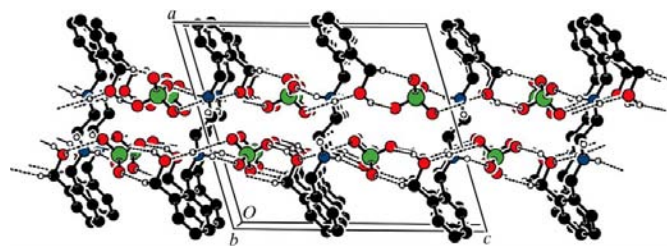


Figure 4
Part of the crystal structure of (II), showing the formation of the two-dimensional network running parallel to the (100) plane. Hydrogen bonds are shown as dashed lines.

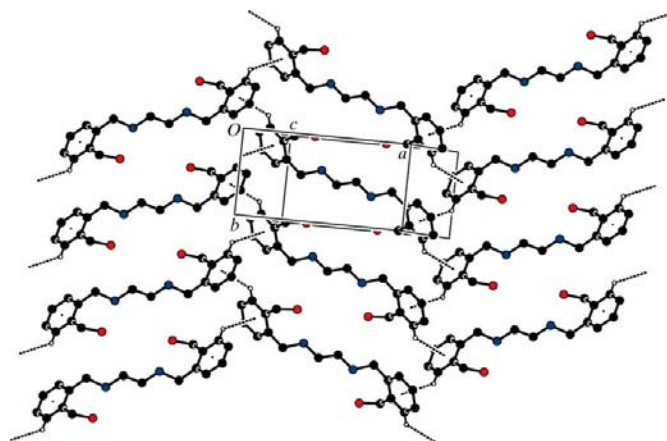


Figure 5
Part of the crystal structure of (II), showing the formation of the two-dimensional network running parallel to the (102) plane built up from $C-H \cdots \pi$ interactions. Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms and perchlorate anions not involved in the motif have been omitted.

(Spek, 2003) indicates that a rather weak anion $\cdots\pi$ interaction exists within the two-dimensional layer formed between the perchlorate anion at (x, y, z) and the C3–C8 benzene ring at $(x, y - 1, z)$ [$O3\cdots Cg1 = 3.849$ (6) Å and $C11 - O3\cdots Cg1 = 117.5$ (3) $^\circ$; $Cg1$ denotes the centroid of the C3–C8 ring]. Secondly, neighbouring layers are interlinked by weak C–H $\cdots\pi$ interactions (Table 2) into a three-dimensional network. In more detail, aromatic atom C7 in the molecule at (x, y, z) acts as donor to the benzene ring at $(2 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, so producing a two-dimensional layer parallel to the $(10\bar{2})$ plane generated by co-operative action between the 2_1 screw axis and the inversion centre (Fig. 4). These two types of (100) and $(10\bar{2})$ layers are joined together to form a three-dimensional network in (II).

In summary, the crystal structures of a ligand with an N_2O_2 donor set and its ammonium perchlorate have been reported. In (Ia), the neutral molecules are linked into a two-dimensional layer. The component ions in (II) are joined together, forming a three-dimensional network. Further research on the synthesis of metal–organic complexes containing the ligand and their potential application is underway in our laboratory.

Experimental

All reagents and solvents were used as obtained without further purification. A mixture of ethylenediamine (2 g, 0.03 mol) and 2-(hydroxymethyl)benzaldehyde (8 g, 0.06 mol) was stirred at 348 K for 10 h, and the resulting white precipitate was removed by filtration and dried in a vacuum. The white precipitate (4 g, 0.013 mol), $LiAlH_4$ (1 g, 0.026 mol) and THF (50 ml) were stirred at 333 K for 6 h. The solvent was removed by rotary evaporation to yield 6.7 g of a powder. Plate-shaped colourless crystals of (Ia) suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of a methanol solution (10 ml) at room temperature. To prepare compound (II), the powder of (Ia) (2 g) was dissolved in methanol (15 ml, adjusted to pH 5 using $HClO_4$). Block-shaped colourless crystals of (II) were obtained by slow evaporation of the solvent over a period of several days.

Compound (Ia)

Crystal data

$C_{18}H_{24}N_2O_2$ $V = 838.13$ (10) Å³
 $M_r = 300.39$ $Z = 2$
 Monoclinic, $P2_1/c$ Mo $K\alpha$ radiation
 $a = 14.0939$ (2) Å $\mu = 0.08$ mm⁻¹
 $b = 6.9520$ (6) Å $T = 294$ (2) K
 $c = 8.6661$ (7) Å $0.30 \times 0.15 \times 0.04$ mm
 $\beta = 99.226$ (3) $^\circ$

Data collection

Bruker SMART APEX CCD area-detector diffractometer 6213 measured reflections
 1645 independent reflections
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996) 1314 reflections with $I > 2\sigma(I)$
 $T_{min} = 0.947$, $T_{max} = 0.996$ $R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$ H atoms treated by a mixture of independent and constrained refinement
 $wR(F^2) = 0.143$ $\Delta\rho_{max} = 0.21$ e Å⁻³
 $S = 1.11$ $\Delta\rho_{min} = -0.15$ e Å⁻³
 1645 reflections
 106 parameters

Compound (II)

Crystal data

$C_{18}H_{26}N_2O_2 \cdot 2ClO_4^-$ $V = 1090.11$ (19) Å³
 $M_r = 501.31$ $Z = 2$
 Monoclinic, $P2_1/c$ Mo $K\alpha$ radiation
 $a = 12.8926$ (12) Å $\mu = 0.36$ mm⁻¹
 $b = 5.8332$ (6) Å $T = 294$ (2) K
 $c = 15.1397$ (15) Å $0.20 \times 0.10 \times 0.06$ mm
 $\beta = 106.779$ (2) $^\circ$

Data collection

Bruker SMART APEX CCD area-detector diffractometer 8763 measured reflections
 2133 independent reflections
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996) 1806 reflections with $I > 2\sigma(I)$
 $T_{min} = 0.931$, $T_{max} = 0.983$ $R_{int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.060$ H atoms treated by a mixture of independent and constrained refinement
 $wR(F^2) = 0.164$
 $S = 1.05$
 2133 reflections
 151 parameters
 $\Delta\rho_{max} = 0.46$ e Å⁻³
 $\Delta\rho_{min} = -0.36$ e Å⁻³

Table 1

Comparison of intramolecular hydrogen-bond energy and total molecular energy (kJ mol⁻¹).

Compound	Intramolecular hydrogen-bond energy	Total molecular energy
(Ia)	29.71	-92653.84
(Ib)	15.27	-92652.01
(II)	92.74	-92720.10

Table 2

Hydrogen-bond geometry for compounds (Ia) and (II) (Å, $^\circ$).

$Cg1$ is the centroid of the C3–C8 ring of (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
(Ia)				
$O1-H1E\cdots N1$	0.92 (2)	1.86 (2)	2.7461 (16)	161 (2)
$N1-H1C\cdots O1^{iii}$	0.883 (17)	2.366 (17)	3.2042 (15)	159 (1)
(II)				
$O1-H1E\cdots O4^{iv}$	0.81 (4)	2.57 (4)	3.118 (5)	126 (4)
$C9-H9A\cdots O3^{v}$	0.97	2.53	3.487 (5)	168
$N1-H1C\cdots O1$	0.832 (19)	2.09 (3)	2.788 (4)	142 (3)
$N1-H1D\cdots O2$	0.856 (18)	2.39 (4)	3.008 (5)	129 (3)
$C1-H1B\cdots O5$	0.97	2.53	3.302 (4)	137
$C7-H7\cdots Cg1^{vi}$	0.93	2.70	3.434 (3)	136

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

For both compounds, H atoms bonded to C atoms were positioned geometrically, with C–H = 0.93 (aromatic) or 0.97 Å (methylene), and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms bonded to N and O atoms were found in difference Fourier maps, with N–H and O–H distances refined freely [$N-H = 0.83$ (2)– 0.88 (2) Å and $O-H = 0.81$ (4)– 0.92 (2) Å] and with $U_{iso}(H) = 1.2U_{eq}(N)$ or $1.5U_{eq}(O)$.

For both compounds, data collection: SMART (Bruker, 2001); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 2001); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3145). Services for accessing these data are described at the back of the journal.

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