

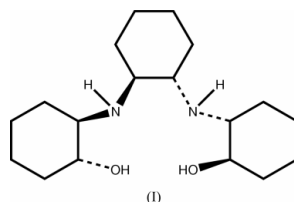
# *N,N'*-Bis(2-hydroxycyclohexyl)-*trans*-cyclohexane-1,2-diamine: a structure reanalysed at low temperature

Alvaro S. de Sousa\* and  
Manuel A. FernandesSchool of Chemistry, Molecular Sciences  
Institute, University of the Witwatersrand,  
Private Bag 3, Wits 2050, Johannesburg,  
South AfricaCorrespondence e-mail:  
alvaro@aurum.wits.ac.za**Key indicators**Single-crystal X-ray study  
 $T = 123\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$   
 $R$  factor = 0.044  
 $wR$  factor = 0.131  
Data-to-parameter ratio = 17.1For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $\text{C}_{18}\text{H}_{34}\text{N}_2\text{O}_2$ , has been prepared and its solid-state structure redetermined at low temperature. The crystalline structure contains only *RSSR* and *SRRS* diastereomeric pairs occurring in alternating layers within the crystal, reinforcing the idea that a high degree of diastereoselectivity is attained in the reaction of polyamines and cyclohexene oxide. The compound crystallizes in space group *C2/c* and the molecule sits on a crystallographic twofold axis.

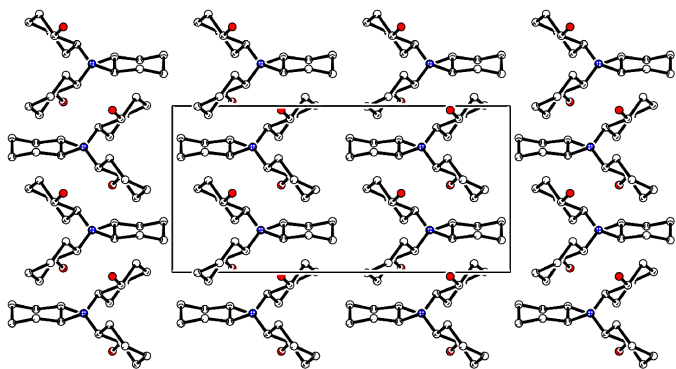
Received 22 October 2003  
Accepted 29 October 2003  
Online 8 November 2003**Comment**

The title compound, (I), has been prepared and good crystal quality permits a clear elucidation of the solid-state structure. A previous study (de Sousa *et al.*, 1997) of the solid-state structure of (I) was not reported in any detail due to the collection of an inadequate data set as a result of poor crystal quality. The design of new ligands to optimize both the observed selectivity patterns towards metal ions and the coordination sphere hydration of metal complexes for diagnostic techniques in medicine requires careful investigation of novel structural features (Hancock, 1992*a,b*; de Sousa *et al.*, 1991) in ligand architecture.

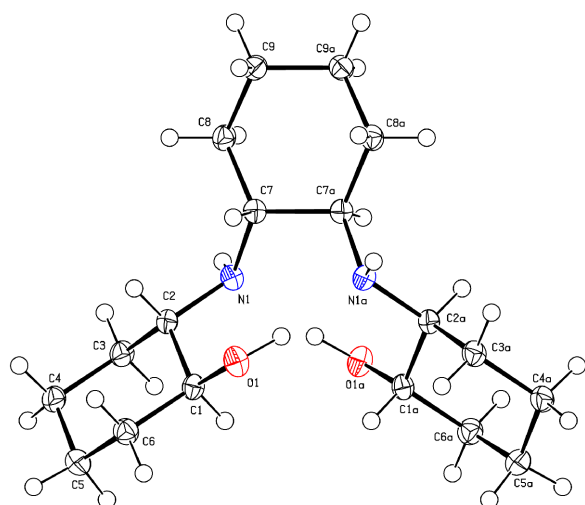


Compound (I) has four donor atoms, two O and two N, and represents an example in which donor atoms are linked *via* cyclohexanediyl bridges that are more rigid than the flexible ethylene bridge counterparts. The structure consists of a single *RSSR* and *SRRS* diastereomeric pair. The (*R,R*)-*trans*-1,2-diaminocyclohexane moiety has both *trans*-2-hydroxycyclohexyl substituents exhibiting *S,S* chirality, whereas the (*S,S*)-*trans*-1,2-diaminocyclohexane moiety has both *trans*-2-hydroxycyclohexyl substituents exhibiting *R,R* chirality. These occur as alternating *RSSR* and *SRRS* enantiomeric layers within the crystal. This is in line with the observation that cyclohexene oxide is a useful synthetic reagent for producing rigid highly preorganized pendent donor groups with remarkable diastereomeric selectivity (de Sousa *et al.*, 1997), in which hydrogen bonding during the reaction is believed to assist in the stereochemical control (Cobb & Marson, 2001).

The cyclohexanediyl bridges adopt the expected chair conformation and puckering of the bridge between the two N atoms accommodates the  $\text{N1}-\text{C7}-\text{C7}^i-\text{N1}^i$  torsion angle of  $-67.27(17)^\circ$  [symmetry code: (i)  $2-x, y, \frac{1}{2}-z$ ]. The puck-



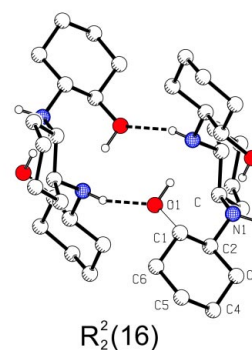
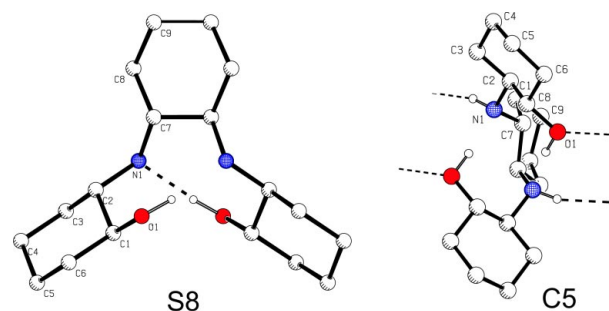
**Figure 1**  
Alternating enantiomeric layers in the structure of (I), viewed along [100]. H atoms have been omitted for clarity.



**Figure 2**  
The molecular structure of (I), showing the atom-labelling scheme and 50% probability displacement ellipsoids. Atoms labelled with the suffix *a* are at the symmetry position  $(2 - x, y, \frac{1}{2} - z)$ .

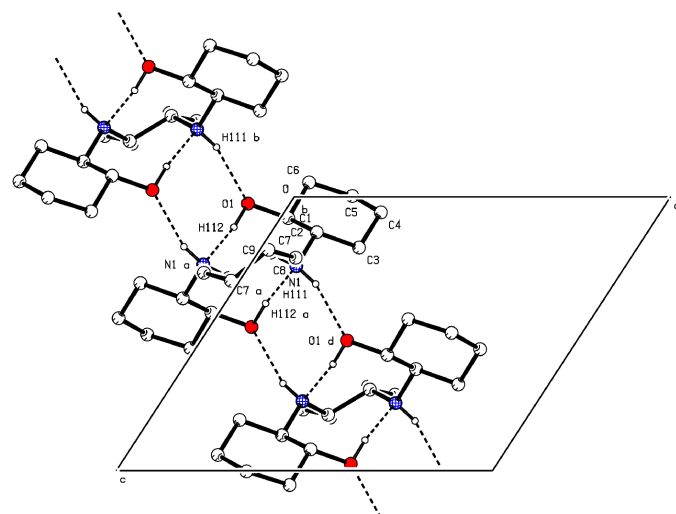
ering observed for the cyclohexanediyl bridge between the two N atoms results in a slight flattening of the chair conformation which rationalizes the marked deviation from ideal strain-free values for the torsion angles  $C8-C7-C7^i-C8^i$  and  $C7^i-C7-C8-C9$  that are  $45.3(2)$  and  $-50.19(16)^\circ$ , respectively. This observed flattening of the chair conformation allows for the possible consideration of a weaker intermolecular  $C-H \cdots O$  interaction between atom H8A on the cyclohexanediyl bridge between the two N atoms and atom O1 of the hydroxycyclohexyl moiety in the adjacent layer at a  $C \cdots O$  distance of  $3.3800(16)$  Å. Bond angles involving the N atoms show significant deviation from what is expected for an  $sp^3$ -hybridized state. Although the bonds involving atom H111,  $C7-N1-H111$  and  $C2-N1-H111$ , have values of  $108$  and  $109^\circ$ , respectively, conforming with tetrahedral geometry, the value of  $116.61(9)^\circ$  for  $C2-N1-C7$  reflects the rotation of the 2-hydroxycyclohexyl moieties towards the molecular cavity as defined by the donor N and O atoms on metal complexation.

Rotation of the 2-hydroxycyclohexyl moieties facilitates hydrogen bonding, as supported by previous *MM2* calcula-



**Figure 3**  
Motifs, viewed along the [101] direction, describing the hydrogen-bonding network.

tions (de Sousa *et al.*, 1997). The rotation of the 2-hydroxycyclohexyl groups that serves to maximize hydrogen bonding within the cavity has the added benefit of simultaneously decreasing  $H \cdots H$  repulsions occurring between adjacent cyclohexenyl bridges. Atoms H2 and H8B are separated by  $2.82$  Å. The distance between equivalent H atoms in the copper complex of compound (I) decreases to a value short of



**Figure 4**  
Hydrogen-bonding network, emphasizing the intermolecular interactions along the [101] direction.

the sum of the van der Waals radii of 2.4 Å for two H atoms (de Sousa *et al.*, 1997). This interaction therefore becomes considerably important on complexation of metal ions and especially so with an increase of metal ion radius. Within the molecule of (I), the formation of an *S*(8) motif (Bernstein *et al.*, 1995) is defined by an intramolecular O—H...N hydrogen bond with the amino atom N1 acting as an acceptor, involving H112, and O1 at  $(2-x, y, \frac{1}{2}-z)$  across a crystallographic twofold axis. Atom N1 additionally acts as a hydrogen-bond donor *via* H111 to O1 in the hydroxy moiety of the molecule at  $(x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z)$ , generating, *via* a *c*-glide at  $y = \frac{1}{4}$ , a *C*(5) chain running parallel to the [101] direction. This hydrogen bond is reinforced by an identical hydrogen-bond interaction between the amino atom at  $(x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z)$  and the O atom of the hydroxy moiety at  $(2-x, y, \frac{1}{2}-z)$  that is symmetrically equivalent through a centre of inversion and results in the formation of an  $R_2^2(16)$  motif Bernstein *et al.*, 1995). The [101] motif is, therefore, best represented as a chain of rings *C*(5)[ $R_2^2(16)$ ] with adjacent  $R_2^2(16)$  rings being alternately twisted through an angle of 82.2°. There are two parallel pairs of *C*(5)[ $R_2^2(16)$ ] chains running through the unit cell that are symmetrically related through a twofold screw axis. Chains within each pair are symmetrically related through a twofold axis of rotation. These hydrogen-bonding chains form links between the alternating *SRRS* and *RSSR* enantiomeric layers.

## Experimental

Compound (I) was synthesized as reported in the literature (de Sousa *et al.*, 1997) to obtain the crude compound. This was isolated in a pure form by executing further synthetic procedures, as have been recently reported by Cobb & Marson (2001). *trans*-1,2-Diaminocyclohexane and cyclohexene oxide were both obtained from Merck.

### Crystal data

$C_{18}H_{34}N_2O_2$	$D_x = 1.152 \text{ Mg m}^{-3}$
$M_r = 310.47$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 975 reflections
$a = 11.8682(17) \text{ \AA}$	$\theta = 2.4\text{--}29.3^\circ$
$b = 17.512(3) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$c = 10.2790(15) \text{ \AA}$	$T = 123(2) \text{ K}$
$\beta = 123.074(2)^\circ$	Plate, colourless
$V = 1790.2(5) \text{ \AA}^3$	$0.40 \times 0.34 \times 0.12 \text{ mm}$
$Z = 4$	

### Data collection

Bruker SMART 1K CCD diffractometer	1514 reflections with $I > 2\sigma(I)$
$\omega$ scans	$R_{\text{int}} = 0.024$
Absorption correction: none	$\theta_{\text{max}} = 26.5^\circ$
5446 measured reflections	$h = -8 \rightarrow 14$
1852 independent reflections	$k = -21 \rightarrow 21$
	$l = -12 \rightarrow 10$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0842P)^2 + 0.6514P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.131$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
1852 reflections	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
108 parameters	
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**

Selected geometric parameters (Å, °).

C2—N1—C7	116.61 (9)	C7—N1—H111	108.0 (10)
C2—N1—H111	109.0 (10)		
$C7^i$ —C7—C8—C9	−50.19 (16)	N1—C7—C7 <sup>i</sup> —N1 <sup>i</sup>	−67.27 (17)
C8—C7—C7 <sup>i</sup> —C8 <sup>i</sup>	45.3 (2)		

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

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H111 $\cdots$ O1 <sup>ii</sup>	0.885 (17)	2.172 (17)	3.0273 (14)	162.2 (14)
O1—H112 $\cdots$ N1 <sup>i</sup>	0.99 (2)	1.82 (2)	2.8021 (14)	170.3 (17)
C8—H8A $\cdots$ O1 <sup>ii</sup>	0.99	2.56	3.3800 (16)	140

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

With the exception of H111 and H112, which are involved in hydrogen bonding, all H atoms were located in a difference map then positioned geometrically and allowed to ride on their respective parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N}, \text{O})$ . H111 and H112 were located in a difference map and refined independently of their parent atoms.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXTL* (Bruker, 1999).

The authors are grateful to the University of the Witwatersrand and the H. E. Griffin Trust for their financial support. We also thank the Jan Boeyens Structural Chemistry Laboratory at the University of the Witwatersrand for the use of their computational facilities.

## References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (1998). *SMART-NT*. Version 5.050. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SAINT-Plus* (includes *XPREP* and *SADABS*; Version 6.02) and *SHELXTL* (Version 5.1; includes *XS*, *XL*, *XP* and *XSHELL*). Bruker AXS Inc., Madison, Wisconsin, USA.
- Cobb, A. J. A. & Marson, C. M. (2001). *Tetrahedron: Asymm.* **12**, 1547–1550.
- Hancock, R. D. (1992a). *J. Chem. Educ.* **69**, 615–621.
- Hancock, R. D. (1992b). *Perspectives in Inorganic Chemistry*, edited by A. P. Williams, C. Floriani & A. E. Merbach, pp. 129–151. Weinheim: VCH.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sousa, A. S. de, Croft, G. J. B., Wagner, C. A., Michael, J. P. & Hancock, R. D. (1991). *Inorg. Chem.* **30**, 3525–3529.
- Sousa, A. S. de, Hancock, R. D. & Reibenspies, J. H. (1997). *J. Chem. Soc. Dalton Trans.* pp. 2831–2835.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.