# trans-Bis(N,N-diethylethylenediamine-N,N')dioxorhenium(V) chloride trihydrate

Hendrik P. Engelbrecht, Stefanus Otto and Andreas Roodt*

*Department of Chemistry, University of the Orange Free State, Bloemfontein 9300, South Africa. E-mail: roodta@cem. nw.uovs.ac.za*

## Abstract

The Re atom of the title complex, [ReO$_2$(C$_6$H$_{16}$N$_2$)$_2$]-Cl·3H$_2$O, lies on an inversion centre and exhibits a distorted octahedral geometry, with the two oxo ligands in the apical positions and the four N atoms of the two functionalized ethylenediamine ligands in the equatorial plane. The most important bond lengths and angles are Re—O 1.769 (2), Re—N 2.242 (3) and 2.172 (3) Å, and N—Re—N 80.25 (11)°. The functionalized N atoms exhibit an unexpected *trans* orientation.

## Comment

An important factor in the mechanism of *in vivo* radiopharmaceutical behaviour (*i.e.* uptake, retention and washout from biological systems) is the reactivity and substitution behaviour introduced by the ligands which direct the complex to/from the specific site. In this context, the [ReO$_2$(deten)$_2$]$^+$ (deten is N,N-diethylethylenediamine) complex reported here was used as a simplified model for the [$^{99m}$TcO(D,L-HMPAO)] complex (D,L-HMPAO is 3,6,6,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime; Asenbaum *et al.*, 1998; Jurisson *et al.*, 1993), widely utilized as a brain-imaging agent, to investigate the steric influence of bulky equatorial nitrogen-donor chelating ligands on the reactivity observed (Roodt, Abou-Hamdan *et al.*, 1999) in complex-formation reactions.

The title complex, (I), displays a distorted octahedral geometry, with the two *trans* oxo ligands in the apical positions and the four N atoms of the two deten ligands in the equatorial plane. Interestingly, the two functionalized deten N atoms are in a *trans* orientation with respect to one another. This is surprising since it is expected from an electronic point of view that these two atoms would be *cis* to each other to ensure the minimum *trans* labilization. This geometry is retained in solution since $^1$H NMR showed no evidence of the *cis* isomer being formed. It is therefore concluded that the two ethyl groups exert quite a large steric effect, resulting in the unexpected *trans* orientation.



(I)
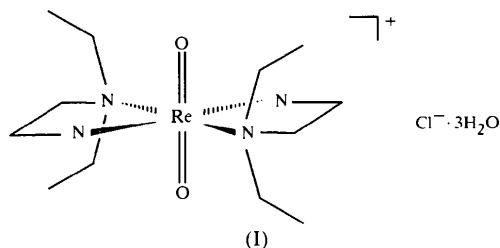
Two disordered solvent water molecules (OW1 and OW2) sharing almost similar positions in the unit cell, were encountered together with another (OW3) sharing a position with the 50% disordered chloride anion. Volhard analysis confirmed the presence of only one chloride anion per Re atom. In the final stages of the refinement, residual electron density was encountered at the chloride position. Subsequent placement of the third water solvent molecule led to a substantial decrease in the final *R* value (*ca* 0.6%). Hydrogen bonding between the O=Re=O core, the chloride ion and the solvent molecules is illustrated by closest contacts (see Table 1).

All bond angles and distances within the functionalized ethylenediamine ligands are within normal ranges and those around the two donor N atoms are close to expected values for an ideal tetrahedron. The significant difference of 0.072 (3) Å in the bond distances of the functionalized [Re—N1$_f$ = 2.242 (3)Å] *versus* the unfunctionalized [Re—N2$_u$ = 2.172 (3) Å] N atoms stems from both the strong electronic *trans* labilization and the increased steric crowding at the metal centre.

A comparison of the title compound with related complexes found in the literature is shown in Table 2. The Re—N2$_u$ bond distance in the title compound of 2.172 (3) Å is in the same range as the average Re—N bond distance of the closely related [ReO$_2$(en)$_2$]$^+$ and [ReO(OH)(en)$_2$]$^{2+}$ complexes of 2.16 (1) and 2.17 (1) Å, respectively. The corresponding average Re—N bond distance in the [ReO$_2$(cyclam)]$^+$ compound (cyclam is 1,4,8,11-tetraazacyclotetradecane) is slightly shorter at 2.138 (11) Å. The Re—N1$_f$ bond distance, however, is significantly longer, as mentioned above.

In conjunction with this crystallographic study, a kinetic investigation revealed a significant decrease
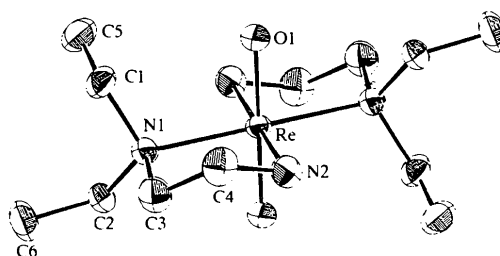


Fig. 1. The structure of (I) showing the numbering scheme and displacement ellipsoids (30% probability). H atoms, solvent water molecules and the chloride anion have been omitted for clarity.

in reaction rate (2–3 orders of magnitude) for the substitution of the deten ligand in the title complex compared with the ethylenediamine substitution in the analogous $[ReO_2(en)_2]^+$ complex. This was primarily attributed to the steric effect (Roodt, Engelbrecht *et al.*, 1999) induced by the deten ligand.

## Experimental

[ReOCl$_3$(PPh$_3$)$_2$] (860 mg, 1.04 mmol) was dissolved in a mixture of acetone (35 ml) and water (3.5 ml), and *N,N*-diethylethylenediamine (3.9 ml, 27.8 mmol) was added. The reaction mixture was refluxed for 90 min and allowed to cool to room temperature, followed by filtration to collect the crude product. The precipitate was washed with toluene (2 × 5 ml) and ether (2 × 5 ml) and dried overnight in a vacuum desiccator over $P_2O_5$. The complex was recrystallized by dissolving the crude product in the minimum amount of water, yielding orange–brown crystals suitable for X-ray analysis after 4 d of slow evaporation of the solvent at room temperature (yield 335 mg, 60%). Spectral data: IR (KBr): $\nu$(ReO) = 810 cm$^{-1}$; $^1$H NMR (D$_2$O, 300 MHz, H$_2$O = 4.60 p.p.m.): 0.95 (triplet, 6H, C12 and C14), 2.7–2.8 (multiplet, 4H), 2.95–3.1 (multiplet, 4H).

### Crystal data

[ReO$_2$(C$_6$H$_{16}$N$_2$)$_2$]Cl·3H$_2$O
$M_r$ = 540.11
Triclinic
$P\bar{1}$
$a$ = 8.1819 (6) Å
$b$ = 8.3833 (6) Å
$c$ = 8.4079 (6) Å
$\alpha$ = 106.244 (1)°
$\beta$ = 94.879 (1)°
$\gamma$ = 109.663 (1)°
$V$ = 511.06 (6) Å$^3$
$Z$ = 1
$D_x$ = 1.755 Mg m$^{-3}$
$D_m$ = 1.77 Mg m$^{-3}$
$D_m$ measured by flotation in benzene/iodomethane

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 40 reflections
$\theta$ = 2.57–28.28°
$\mu$ = 6.101 mm$^{-1}$
$T$ = 296 (2) K
Cube
0.36 × 0.33 × 0.22 mm
Brown

### Data collection

Siemens SMART diffractometer
CCD detection scans
Absorption correction: empirical (spherical harmonious functions using *SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.164, $T_{max}$ = 0.261
3182 measured reflections

2185 independent reflections
2185 reflections with
$I > 2\sigma(I)$
$R_{int}$ = 0.014
$\theta_{max}$ = 28.28°
$h$ = −10 → 10
$k$ = −9 → 11
$l$ = −8 → 10
Intensity decay: none

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.049
$S$ = 1.058

$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.971 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.319 e Å$^{-3}$
Extinction correction: none

2185 reflections
127 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 0.3108P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from
*International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Re1—O1 | 1.769 (2) | C3—C4 | 1.513 (6) |
| Re1—N2 | 2.172 (3) | C11···OW2$^i$ | 2.572 (14) |
| Re1—N1 | 2.242 (3) | C11···OW1$^{ii}$ | 2.767 (15) |
| N1—C3 | 1.506 (4) | O1···OW1 | 2.763 (8) |
| N1—C2 | 1.507 (4) | O1···OW2 | 2.779 (9) |
| N1—C1 | 1.512 (4) | OW1···OW2 | 0.699 (8) |
| N2—C4 | 1.485 (5) | OW1···OW3$^{iii}$ | 2.79 (3) |
| C1—C5 | 1.519 (5) | OW2···OW3$^{iv}$ | 2.80 (3) |
| C2—C6 | 1.535 (5) | | |
| O1—Re1—N2 | 90.99 (12) | C2—N1—C1 | 110.2 (3) |
| O1—Re1—N1 | 89.46 (10) | C3—N1—Re1 | 106.1 (2) |
| N2—Re1—N1 | 80.25 (11) | C2—N1—Re1 | 111.48 (19) |
| N2—Re1—N1$^v$ | 99.75 (10) | C1—N1—Re1 | 113.1 (2) |
| C3—N1—C2 | 108.1 (3) | C4—N2—Re1 | 108.7 (2) |
| C3—N1—C1 | 107.6 (3) | | |

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

Table 2. *Comparative crystallographic data for $[ReO(X)(L)_2]^{n+}$ complexes (X = O or OH, and L is a chelating N-donor ligand)*

| Complex | Re—O1 | Re—O2 | Re—N1 | Re—N2 |
|---|---|---|---|---|
| [ReO$_2$(cyclam)]$^+$ $^a$ | 1.775 (9) | | 2.136 (11) | 2.141 (9) |
| [ReO$_2$(en)$_2$]$^+$ $^b$ | 1.769 (7) | 1.761 (7) | 2.152 (9) | 2.171 (8) |
| [ReO$_2$(deten)$_2$]$^+$ $^c$ | 1.769 (2) | | 2.242 (3) | 2.172 (3) |
| [ReO(OH)(en)$_2$]$^{2+}$ $^d$ | 1.666 (4) | 1.947 (6) | 2.170 (10) | 2.160 (10) |
| [ReO(OH)(cyclam)]$^{2+}$ $^e$ | 1.766 (5) | | 2.091 (9) | 2.091 (9) |

Notes: (*a*) Wang *et al.* (1993); (*b*) Lock & Turner (1978), average of Re—N bonds for separate en ligands; (*c*) the present study; (*d*) Roodt, Engelbrecht *et al.* (1999); (*e*) Tsang *et al.* (1993), 50% statistical disorder in Re atom not solved.

The C11 atom and the three water O atoms (OW1–OW3) had occupancies of 0.50.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXL97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL97*.

## References

Asenbaum, S., Brücke, T., Pirker, W., Pietrzyk, U. & Podreka, I. (1998). *J. Nucl. Med.* **39**, 613–618.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Jurisson, S., Berning, D., Jia, W. & Ma, D. (1993). *Chem. Rev.* **93**, 1137–1156.

Lock, C. J. L. & Turner, G. (1978). *Acta Cryst.* B**34**, 923–927.

Roodt, A., Abou-Hamdan, A., Engelbrecht, H. P. & Merbach, A. E. (1999). *Advances in Inorganic Chemistry*, Vol. 48, edited by A. G. Sykes, ch. 2, pp. 69–135. San Diego: Academic Press.

Roodt, A., Engelbrecht, H. P., Botha, J. M. & Otto, S. (1999). *Technetium, Rhenium and Other Metals in Chemistry and Nuclear Medicine*, Vol. 5, edited by M. Nicolini & U. Mazzi, pp. 161–166. Padova: Servizi Grafici Editoriali.

Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data.* University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1995). *SMART* and *SAINT. Area Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Tsang, B. W., Reibenspies, J. & Martell, A. E. (1993). *Inorg. Chem.* **32**, 988–994.

Wang, Y.-P., Che, C.-M., Wong, K.-Y. & Peng, S.-M. (1993). *Inorg. Chem.* **32**, 5827–5832.

# [N,N'-Bis(5-bromosalicylidene)-1,3-diaminopropane]copper(II)†

Mehmet Kabak,[a] Ayhan Elmalı,[a] Ebru Kavlakoğlu,[a] Yalçın Elerman[a] and T. Nuri Durlu[b]

[a]*Department of Engineering Physics, Faculty of Sciences, University of Ankara, 06100 Beşevler, Ankara, Turkey, and* [b]*Department of Physics, Faculty of Art and Sciences, Kırıkkale University, 71450 Yahşihan, Kırıkkale, Turkey. E-mail: kabak@science.ankara.edu.tr*

## Abstract

The title compound, $[Cu(C_{17}H_{14}Br_2N_2O_2)]$, has a crystallographic twofold axis. The coordination geometry about the $Cu^{II}$ centre is a tetrahedrally distorted square plane formed by the four-coordinate $N_2O_2$ donor set of the Schiff base imine–phenol ligand. The Cu—N and Cu—O distances are 1.967 (5) and 1.914 (4) Å, respectively.

## Comment

Schiff base complexes are considered to be among the most important stereochemical models in main-group and transition metal coordination chemistry due to their preparative accessibility and structural variety (Garnovskii *et al.*, 1993). Transition metal Schiff base complexes are of interest in catalysis (Jacobsen *et al.*, 1991) and in small-molecule binding (Jones *et al.*, 1979; Chen & Martell, 1987). We have reported previously the structures of several dimeric and monomeric Schiff base complexes of copper(II) (Elmali *et al.*, 1993, 1995, 1997; Elerman *et al.*, 1995; Elerman & Geselle, 1997). We report here the results of the reaction of copper(II) with the tetradentate ligand $N,N'$-bis(5-bromo-2-hydroxybenzylidene)-1,3-propanediamine, to form a monomeric Schiff base complex of copper(II), (I).



(I)

The bond lengths and angles around the Cu atom are in good agreement with the values found in other tetracoordinated copper complexes with similar ligands (Baker *et al.*, 1970; Labisbal *et al.*, 1994; Yao *et al.*, 1997; Lo *et al.*, 1997). The Cu atom is coordinated by two imine N atoms and two phenol O atoms from the imine–phenol ligand in a distorted square-planar coordination geometry. The atom with the greatest deviation from the coordination plane [Cu1, N1, O1, N1$^i$ and O1$^i$; symmetry code: (i) $-x, y, -\frac{1}{2} - z$] is O1 at 0.458 (4) Å. The unique half of the Schiff base ligand of the title compound is reasonably planar, with the maximum deviation from the plane defined by atoms O1, N1, C1—C9 and Br1 being 0.168 (4) Å for the O1 atom. However, the entire ligand is not planar, as the two halves are twisted with respect to one another. The least-squares planes through each half of the molecule are inclined at an angle of 35.6 (1)°. In the free ligand, the same interplanar angle is 66.17 (7)° (Elerman *et al.*, 1998); besides, the torsion angle of −41.2 (13)° for N1—C8—C9—C8$^i$ supports the non-planarity of the molecule. It is possible that the Cu atom plays an important role in the planarity of the whole molecule.

The bond distances and angles in the chelating moieties of the molecule are significantly different from those present in the free ligand. In particular, the distances C1—O1 and C6—C7 [1.302 (7) and 1.436 (9) Å, respectively] are shorter than those found in the free ligand [1.342 (7) and 1.448 (8) Å, respectively; Elerman *et al.*, 1998], while the N1—C7 distance [1.288 (8) Å] is longer [1.269 (7) Å for the free ligand]. This trend, which has been observed already in some other complexes (Calligaris *et al.*, 1972; Pahor *et al.*, 1978), shows that an extended conjugation is present in the coordinated ligand.

All bond distances and angles in the title compound are within the ranges found for related derivatives (Riley *et al.*, 1986; Zamian *et al.*, 1995; Schmidt *et al.*, 1996).

† Systematic name: {4,4'-dibromo-2,2'-[1,3-propanediylbis(nitrilomethylidyne)]diphenolato-*O,N,N',O'*}copper(II).