

# Extensive hydrogen-bonding network and an unusual cation conformation in [tris(hydroxymethyl)methyl]ammonium tetraoxidorhenate(VII)

Małgorzata Hołyńska\* and Tadeusz Lis

Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie St, 50-383 Wrocław, Poland

Correspondence e-mail: holynska@wcheto.chem.uni.wroc.pl

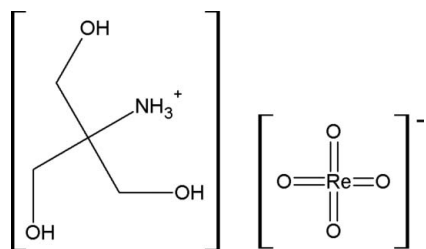
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Key indicators: single-crystal X-ray study;  $T = 110$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.020;  $wR$  factor = 0.034; data-to-parameter ratio = 24.0.

The title compound,  $(\text{C}_4\text{H}_{12}\text{NO}_3)[\text{ReO}_4]$ , contains two cations and two anions in the asymmetric unit, related by a non-crystallographic centre of symmetry. The crystal structure is stabilized by an extensive hydrogen-bonding network with the formation of puckered layers perpendicular to  $[001]$ . In the tris(hydroxymethyl)ammonium cations, intramolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds are present with the formation of an  $S_1^1(6)$  graph-set motif. The crystal structure is further consolidated by  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds.

## Related literature

For related structures, see: Castellari & Ottani (1997); Eilerman & Rudman (1980); Hołyńska & Lis (2004, 2008); Lock & Turner (1975); Marsh *et al.* (1998); Rudman *et al.* (1979, 1983); Shakked *et al.* (1980); Tusvik *et al.* (1999). For the dielectric properties of rhenates(VII) with organic ammonium cations, see: Czarnecki & Małuszyńska (2000). For graph-set notation, see: Etter *et al.* (1990). For the synthesis of rhenic(VII) acid, see: Johnson *et al.* (1967).



## Experimental

### Crystal data

$(\text{C}_4\text{H}_{12}\text{NO}_3)[\text{ReO}_4]$   
 $M_r = 372.35$   
 Orthorhombic,  $Pca2_1$   
 $a = 21.450$  (5) Å  
 $b = 6.867$  (2) Å  
 $c = 12.219$  (4) Å

$V = 1799.8$  (9) Å<sup>3</sup>  
 $Z = 8$   
 Mo  $K\alpha$  radiation  
 $\mu = 13.51$  mm<sup>-1</sup>  
 $T = 110$  K  
 $0.21 \times 0.16 \times 0.14$  mm

### Data collection

Oxford Diffraction KM-4-CCD diffractometer  
 Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)  
 $T_{\min} = 0.104$ ,  $T_{\max} = 0.268$

24604 measured reflections  
 5888 independent reflections  
 5084 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.029$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$   
 $wR(F^2) = 0.034$   
 $S = 1.02$   
 5888 reflections  
 245 parameters

1 restraint  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 2.00$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.27$  e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

|             |           |             |           |
|-------------|-----------|-------------|-----------|
| Re1—O11     | 1.736 (2) | Re2—O12     | 1.728 (4) |
| Re1—O21     | 1.728 (2) | Re2—O22     | 1.730 (3) |
| Re1—O31     | 1.727 (2) | Re2—O32     | 1.736 (3) |
| Re1—O41     | 1.702 (5) | Re2—O42     | 1.726 (2) |
| O41—Re1—O31 | 109.6 (2) | O42—Re2—O12 | 108.4 (2) |
| O41—Re1—O21 | 108.7 (2) | O42—Re2—O22 | 109.4 (2) |
| O31—Re1—O21 | 108.7 (2) | O12—Re2—O22 | 109.6 (2) |
| O41—Re1—O11 | 110.6 (2) | O42—Re2—O32 | 109.3 (2) |
| O31—Re1—O11 | 110.0 (2) | O12—Re2—O32 | 110.8 (2) |
| O21—Re1—O11 | 109.2 (2) | O22—Re2—O32 | 109.3 (2) |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$                         | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------------------|-------|-------------|-------------|---------------|
| N2—H2A $\cdots$ O21                   | 0.91  | 2.03        | 2.858 (4)   | 150           |
| N2—H2B $\cdots$ O11 <sup>i</sup>      | 0.91  | 1.88        | 2.788 (4)   | 173           |
| N2—H2C $\cdots$ O31 <sup>ii</sup>     | 0.91  | 1.98        | 2.879 (4)   | 169           |
| O112—H112 $\cdots$ O212               | 0.84  | 2.12        | 2.773 (4)   | 134           |
| O112—H112 $\cdots$ O41                | 0.84  | 2.49        | 2.942 (4)   | 115           |
| O212—H212 $\cdots$ O32 <sup>ii</sup>  | 0.84  | 1.89        | 2.721 (4)   | 168           |
| O312—H312 $\cdots$ O112 <sup>ii</sup> | 0.84  | 1.92        | 2.704 (4)   | 156           |
| N1—H1A $\cdots$ O312 <sup>iii</sup>   | 0.91  | 1.83        | 2.738 (4)   | 176           |
| N1—H1B $\cdots$ O42 <sup>ii</sup>     | 0.91  | 2.05        | 2.872 (4)   | 150           |
| N1—H1C $\cdots$ O22                   | 0.91  | 1.98        | 2.862 (4)   | 164           |
| O111—H111 $\cdots$ O211 <sup>iv</sup> | 0.84  | 1.89        | 2.681 (3)   | 157           |
| O211—H211 $\cdots$ O311               | 0.84  | 2.13        | 2.774 (4)   | 134           |
| O211—H211 $\cdots$ O12 <sup>ii</sup>  | 0.84  | 2.54        | 2.960 (4)   | 112           |
| O311—H311 $\cdots$ O11                | 0.84  | 1.88        | 2.714 (4)   | 170           |

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005) and *SHELXTL-NT* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZ2176).

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## supporting information

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## Extensive hydrogen-bonding network and an unusual cation conformation in [tris(hydroxymethyl)methyl]ammonium tetraoxidorhenate(VII)

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### S1. Comment

The title compound was obtained as starting material for other syntheses (*e.g.* reaction with acetyl chloride - Hołyńska & Lis, 2008). It was chosen as the tris(hydroxymethyl)methylammonium cation gives rise to an extensive hydrogen bonding network, which allows for selective crystallization of products containing Re, reducing the risk of cocrystallization of impurities and crystal structure disorder. Moreover, rhenates(VII) with organic ammonium cations crystallizing in non-centrosymmetric space groups are promising materials with respect to their dielectric properties. For example, the previously discovered ferroelectric with a Curie temperature above room temperature is pyridinium rhenate(VII) (Czarnecki & Małuszyńska, 2000).

The title compound (1) is a product of the reaction of rhenic(VII) acid with tris(hydroxymethyl)methylamine (TRIS) in aqueous solution, comprising discrete tris(hydroxymethyl)methylammonium cations (protonated TRIS here denoted as TRISH<sup>+</sup>) and rhenate(VII) anions (Fig. 1, Scheme 1).

There are two symmetry-independent rhenate(VII) anions (containing atoms Re1 and Re2, respectively) with the expected (see *e.g.* Hołyńska & Lis, 2004 for example of rhenate(VII) anions in low symmetry environment) slightly distorted tetrahedral geometry. The Re—O bond lengths are listed in Table 1. Their values are consistent with those for other rhenates(VII), *e.g.* 1.723 (4) Å for potassium rhenate(VII) reported by Lock & Turner (1975). These bond lengths are not much affected by the presence of hydrogen bonds, as all rhenate(VII) O atoms participate in these interactions as acceptors (Table 2).

It is interesting to note that both symmetry-independent TRISH<sup>+</sup> cations are of unusual conformation. Usually the cation symmetry is close to C<sub>3</sub> (*e.g.* Rudman *et al.*, 1983) or even exactly threefold (as in [TRISH]Cl appearing in a preliminary report by Rudman *et al.*, 1979) with no intramolecular hydrogen bonds. In (1) both cations exhibit the presence of such intramolecular hydrogen bond (Table 2) with the formation of a S<sub>1</sub><sup>1</sup>(6) graph-set motif (Etter *et al.*, 1990). The relevant N—C—C—O torsion angles are given in Table 1. Bond lengths characterizing the cations, among them the C—N bond length (which is longer than in the TRIS molecule - 1.477 (3) Å as reported for the neutral TRIS molecule by Eilerman & Rudman, 1980) are in accordance with the values reported for other structures (*e.g.* Castellari & Ottani, 1997). TRIS is a constituent of buffers used in biochemical studies in the pH range of 7–9 (Castellari & Ottani, 1997). Upon protonation it forms salts with biologically relevant anions (*e.g.* tris(hydroxymethyl)methylammonium deoxycholate reported by Tusvik *et al.*, 1999), also a report on its interaction with nucleotides in the crystalline state is available (Shakked *et al.*, 1980).

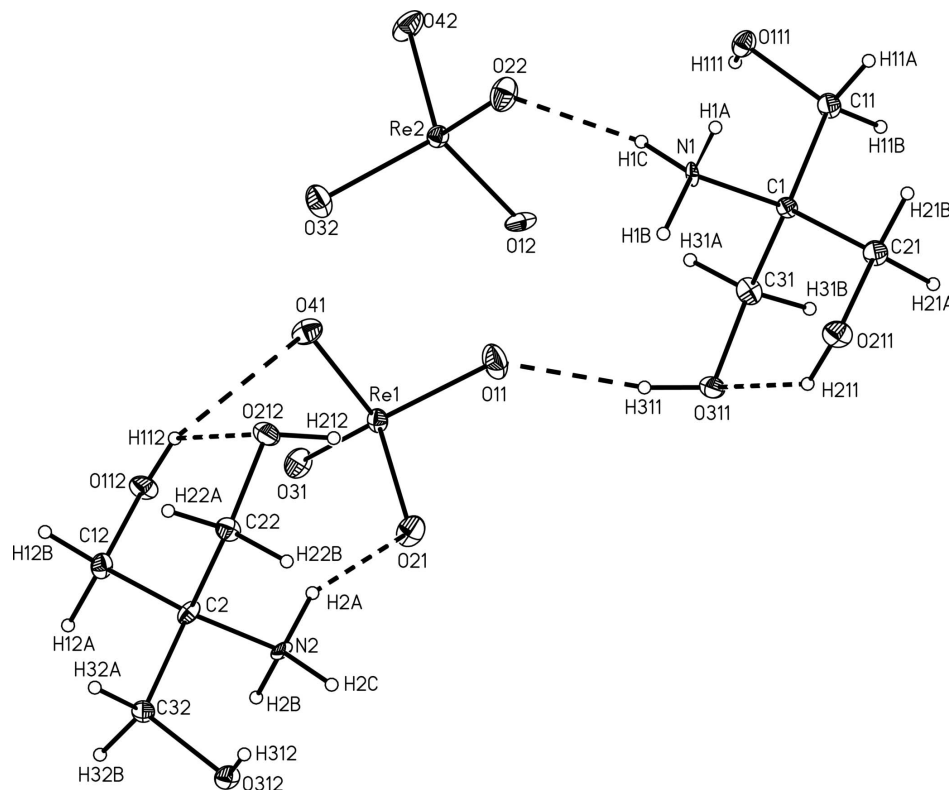
All cation ammonium and hydroxyl groups are donors in N—H···O or O—H···O hydrogen bonds, both to other TRISH<sup>+</sup> cations or to rhenate(VII) anions. The shortest Re···Re distance is 4.210 (2) Å. Thus, puckered hydrogen-bonded layers perpendicular to [001] are formed (Fig. 2). The hydrogen bonding scheme stabilizing an individual layer is illustrated in Fig. 3.

## S2. Experimental

The title compound was obtained in the reaction of 0.19 g of tris(hydroxymethyl)methylamine (TRIS) with an excess of rhenic(VII) acid in aqueous solution, with slow evaporation leading to colourless crystals. The reaction was carried out in a quartz beaker. Rhenic(VII) acid was obtained according to the literature procedure (Johnson *et al.*, 1967) in reaction of 0.3 g of metallic Re with an excess of a 30% aqueous hydrogen peroxide solution.

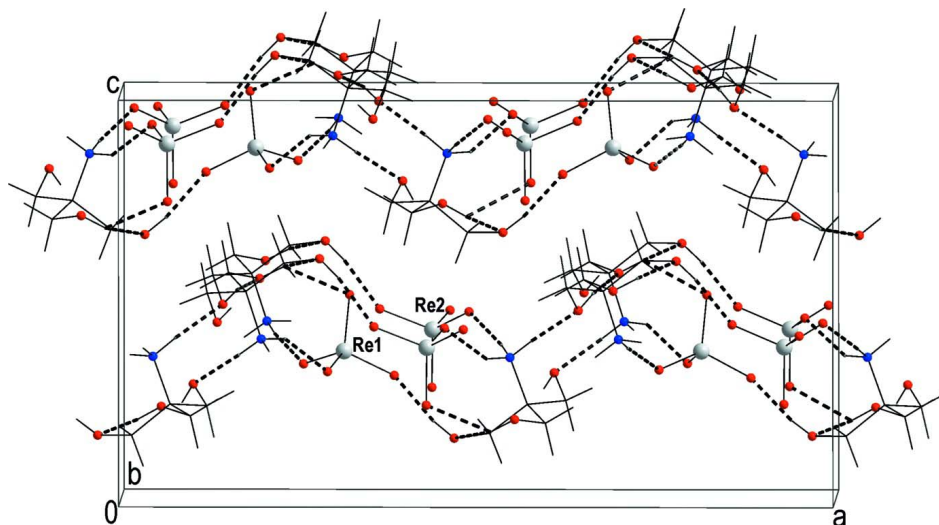
## S3. Refinement

The structure was solved by direct methods in the space group  $P1$ , and the present solution was obtained by switching to a higher symmetry. It was possible to end up in a false minimum in the  $Pca2_1$  space group (*e.g.* with the following approximate coordinates for the Re atoms: 0.57, 0.024, 0.97 for Re1; 0.69, 0.51, 1.01 for Re2; see Marsh *et al.*, 1998, for a review of some pitfalls connected with the  $Pca2_1$  space group). All H atoms were generated geometrically and refined with  $U_{eq}=nU_{eq}(\text{parent atom})$ , where  $n = 1.5$  for hydroxyl H atoms, and  $n = 1.2$  for the remaining H atoms. During the refinement, extinction was also taken into account. Furthermore, it was found that the structure is a racemic twin (with a refined BASF parameter value of 0.375 (6)). On the final difference Fourier map the highest peak of  $2.00 \text{ e}/\text{\AA}^3$  was found at  $0.62 \text{ \AA}$  from atom Re2. The crystal structure contains a pseudosymmetry centre at approximately (0.37, 0.73, 0.38).

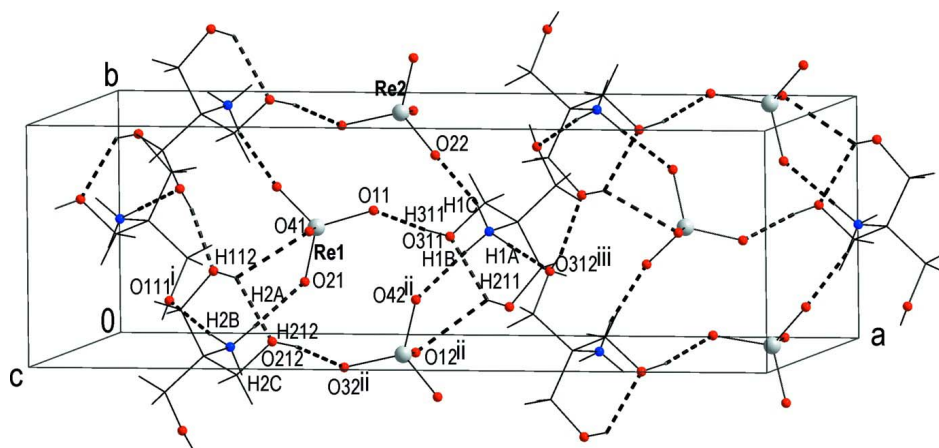


**Figure 1**

The symmetry-independent part of (1). Thermal ellipsoids are drawn at 30% probability level. Hydrogen bonds are denoted with dashed lines.

**Figure 2**

Puckered hydrogen-bonded layers perpendicular to [001]. Hydrogen bonds are denoted with dashed lines.

**Figure 3**

One of the layers with hydrogen bonding scheme. Hydrogen bonds are denoted with dashed lines. Symmetry codes as in Table 2.

### [tris(hydroxymethyl)methyl]ammonium tetraoxidorhenate(VII)

#### Crystal data

(C<sub>4</sub>H<sub>12</sub>NO<sub>3</sub>)[ReO<sub>4</sub>]

*M<sub>r</sub>* = 372.35

Orthorhombic, *Pca*2<sub>1</sub>

Hall symbol: P 2c -2ac

*a* = 21.450 (5) Å

*b* = 6.867 (2) Å

*c* = 12.219 (4) Å

*V* = 1799.8 (9) Å<sup>3</sup>

*Z* = 8

*F*(000) = 1392

*D<sub>x</sub>* = 2.748 Mg m<sup>-3</sup>

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 20472 reflections

θ = 4.2–35.0°

μ = 13.51 mm<sup>-1</sup>

*T* = 110 K

Needle, colourless

0.21 × 0.16 × 0.14 mm

*Data collection*

Oxford Diffraction KM-4-CCD  
diffractometer  
Radiation source: fine-focus sealed tube  
Graphite monochromator  
 $\omega$  scans  
Absorption correction: analytical  
(*CrysAlis RED*; Oxford Diffraction, 2006)  
 $T_{\min} = 0.104$ ,  $T_{\max} = 0.268$

24604 measured reflections  
5888 independent reflections  
5084 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.029$   
 $\theta_{\max} = 35.0^\circ$ ,  $\theta_{\min} = 4.2^\circ$   
 $h = -33 \rightarrow 28$   
 $k = -9 \rightarrow 11$   
 $l = -14 \rightarrow 19$

*Refinement*

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.020$   
 $wR(F^2) = 0.034$   
 $S = 1.02$   
5888 reflections  
245 parameters  
1 restraint  
Primary atom site location: structure-invariant  
direct methods  
Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites  
H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0119P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 2.00 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -1.27 \text{ e } \text{\AA}^{-3}$   
Extinction correction: *SHELXL97* (Sheldrick,  
2008),  $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$   
Extinction coefficient: 0.00101 (3)

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

|      | <i>x</i>     | <i>y</i>      | <i>z</i>      | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|---------------|---------------|----------------------------------|
| Re1  | 0.311748 (6) | 0.494021 (19) | 0.362409 (13) | 0.01257 (4)                      |
| O11  | 0.38162 (12) | 0.5562 (4)    | 0.2998 (2)    | 0.0266 (6)                       |
| O21  | 0.29045 (12) | 0.2623 (3)    | 0.3220 (2)    | 0.0217 (6)                       |
| O31  | 0.25389 (12) | 0.6547 (3)    | 0.3237 (2)    | 0.0204 (6)                       |
| O41  | 0.31950 (13) | 0.4971 (3)    | 0.5010 (4)    | 0.0192 (7)                       |
| Re2  | 0.431704 (6) | 0.975939 (17) | 0.393938 (10) | 0.01252 (4)                      |
| O12  | 0.43101 (13) | 0.9629 (4)    | 0.2527 (4)    | 0.0201 (7)                       |
| O22  | 0.48425 (12) | 0.8084 (4)    | 0.4456 (2)    | 0.0239 (6)                       |
| O32  | 0.35819 (12) | 0.9281 (4)    | 0.4468 (2)    | 0.0236 (6)                       |
| O42  | 0.45440 (14) | 1.2076 (3)    | 0.4316 (2)    | 0.0256 (6)                       |
| N1   | 0.54415 (13) | 0.4794 (3)    | 0.3475 (3)    | 0.0087 (7)                       |
| H1A  | 0.5752       | 0.4330        | 0.3909        | 0.010*                           |
| H1B  | 0.5116       | 0.3943        | 0.3478        | 0.010*                           |
| H1C  | 0.5312       | 0.5969        | 0.3733        | 0.010*                           |
| C1   | 0.56824 (16) | 0.5031 (4)    | 0.2313 (5)    | 0.0108 (9)                       |
| C11  | 0.62070 (17) | 0.6555 (5)    | 0.2341 (3)    | 0.0158 (8)                       |
| H11A | 0.6583       | 0.5969        | 0.2674        | 0.019*                           |
| H11B | 0.6313       | 0.6942        | 0.1582        | 0.019*                           |
| O111 | 0.60331 (12) | 0.8244 (3)    | 0.2949 (2)    | 0.0161 (5)                       |
| H111 | 0.5882       | 0.9079        | 0.2523        | 0.024*                           |
| C21  | 0.59498 (17) | 0.3079 (5)    | 0.1935 (3)    | 0.0161 (8)                       |
| H21A | 0.6055       | 0.3169        | 0.1148        | 0.019*                           |
| H21B | 0.6341       | 0.2820        | 0.2340        | 0.019*                           |
| O211 | 0.55315 (12) | 0.1482 (3)    | 0.2097 (2)    | 0.0190 (6)                       |

|      |              |             |            |            |
|------|--------------|-------------|------------|------------|
| H211 | 0.5192       | 0.1715      | 0.1780     | 0.029*     |
| C31  | 0.51492 (18) | 0.5698 (6)  | 0.1573 (3) | 0.0171 (8) |
| H31A | 0.4977       | 0.6936      | 0.1858     | 0.020*     |
| H31B | 0.5313       | 0.5947      | 0.0829     | 0.020*     |
| O311 | 0.46638 (12) | 0.4291 (4)  | 0.1512 (2) | 0.0194 (6) |
| H311 | 0.4369       | 0.4628      | 0.1922     | 0.029*     |
| N2   | 0.19985 (14) | 0.0038 (3)  | 0.4133 (3) | 0.0106 (7) |
| H2A  | 0.2325       | 0.0881      | 0.4100     | 0.013*     |
| H2B  | 0.1679       | 0.0501      | 0.3718     | 0.013*     |
| H2C  | 0.2120       | −0.1145     | 0.3873     | 0.013*     |
| C2   | 0.17844 (17) | −0.0169 (5) | 0.5312 (5) | 0.0126 (9) |
| C12  | 0.15266 (17) | 0.1803 (5)  | 0.5682 (3) | 0.0141 (7) |
| H12A | 0.1130       | 0.2060      | 0.5295     | 0.017*     |
| H12B | 0.1436       | 0.1749      | 0.6476     | 0.017*     |
| O112 | 0.19500 (12) | 0.3372 (3)  | 0.5474 (2) | 0.0174 (6) |
| H112 | 0.2293       | 0.3138      | 0.5778     | 0.026*     |
| C22  | 0.23218 (16) | −0.0833 (5) | 0.6035 (3) | 0.0150 (7) |
| H22A | 0.2164       | −0.1076     | 0.6784     | 0.018*     |
| H22B | 0.2489       | −0.2075     | 0.5748     | 0.018*     |
| O212 | 0.28111 (11) | 0.0562 (4)  | 0.6084 (2) | 0.0205 (6) |
| H212 | 0.3083       | 0.0288      | 0.5614     | 0.031*     |
| C32  | 0.12571 (16) | −0.1669 (5) | 0.5331 (3) | 0.0139 (7) |
| H32A | 0.1175       | −0.2067     | 0.6096     | 0.017*     |
| H32B | 0.0872       | −0.1067     | 0.5038     | 0.017*     |
| O312 | 0.14087 (12) | −0.3355 (3) | 0.4693 (2) | 0.0149 (5) |
| H312 | 0.1612       | −0.4143     | 0.5080     | 0.022*     |

Atomic displacement parameters ( $\text{\AA}^2$ )

|      | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| Re1  | 0.01274 (6) | 0.01028 (5) | 0.01470 (9) | −0.00034 (4) | 0.00299 (6)  | 0.00074 (6)  |
| O11  | 0.0195 (15) | 0.0232 (14) | 0.0373 (17) | −0.0036 (11) | 0.0120 (13)  | −0.0001 (13) |
| O21  | 0.0299 (16) | 0.0150 (12) | 0.0201 (14) | −0.0036 (10) | 0.0061 (12)  | 0.0004 (10)  |
| O31  | 0.0252 (15) | 0.0141 (12) | 0.0218 (14) | 0.0036 (10)  | 0.0011 (12)  | −0.0006 (10) |
| O41  | 0.0268 (17) | 0.0171 (14) | 0.0137 (18) | −0.0031 (10) | −0.0014 (13) | 0.0013 (11)  |
| Re2  | 0.01365 (7) | 0.01088 (5) | 0.01303 (8) | −0.00034 (5) | 0.00093 (6)  | −0.00031 (8) |
| O12  | 0.0235 (16) | 0.0188 (12) | 0.0180 (18) | −0.0037 (11) | −0.0066 (12) | −0.0068 (13) |
| O22  | 0.0284 (16) | 0.0237 (14) | 0.0195 (14) | 0.0086 (11)  | 0.0016 (12)  | 0.0010 (11)  |
| O32  | 0.0176 (14) | 0.0194 (13) | 0.0336 (15) | −0.0005 (10) | 0.0063 (11)  | 0.0011 (12)  |
| O42  | 0.0393 (17) | 0.0163 (12) | 0.0210 (15) | −0.0084 (11) | 0.0083 (12)  | −0.0057 (10) |
| N1   | 0.0087 (13) | 0.0032 (10) | 0.014 (2)   | −0.0006 (9)  | 0.0076 (14)  | 0.0021 (11)  |
| C1   | 0.0109 (18) | 0.0078 (15) | 0.014 (3)   | −0.0007 (13) | 0.0004 (14)  | 0.0006 (11)  |
| C11  | 0.0146 (19) | 0.0104 (16) | 0.022 (2)   | −0.0019 (13) | 0.0032 (15)  | −0.0018 (14) |
| O111 | 0.0204 (14) | 0.0121 (12) | 0.0158 (13) | −0.0001 (10) | 0.0032 (11)  | −0.0008 (9)  |
| C21  | 0.0166 (19) | 0.0093 (16) | 0.022 (2)   | −0.0026 (13) | 0.0030 (16)  | −0.0016 (14) |
| O211 | 0.0208 (15) | 0.0106 (11) | 0.0256 (16) | −0.0020 (10) | −0.0012 (12) | 0.0010 (11)  |
| C31  | 0.016 (2)   | 0.0167 (19) | 0.018 (2)   | 0.0009 (15)  | 0.0001 (15)  | 0.0032 (15)  |
| O311 | 0.0127 (14) | 0.0207 (14) | 0.0250 (16) | −0.0001 (11) | −0.0028 (12) | −0.0077 (12) |

|      |             |             |             |              |              |              |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| N2   | 0.0144 (13) | 0.0044 (12) | 0.013 (2)   | 0.0016 (9)   | −0.0018 (13) | −0.0049 (10) |
| C2   | 0.019 (2)   | 0.0092 (17) | 0.010 (2)   | 0.0024 (12)  | 0.0001 (15)  | −0.0013 (13) |
| C12  | 0.0154 (19) | 0.0093 (15) | 0.0176 (19) | 0.0010 (12)  | 0.0031 (14)  | −0.0003 (13) |
| O112 | 0.0152 (14) | 0.0083 (11) | 0.0287 (16) | −0.0024 (10) | −0.0020 (12) | −0.0010 (10) |
| C22  | 0.0139 (19) | 0.0131 (16) | 0.0182 (19) | 0.0004 (12)  | −0.0014 (14) | 0.0007 (14)  |
| O212 | 0.0124 (14) | 0.0215 (13) | 0.0276 (16) | −0.0009 (10) | −0.0023 (11) | −0.0056 (12) |
| C32  | 0.0139 (19) | 0.0098 (16) | 0.018 (2)   | −0.0037 (12) | 0.0023 (15)  | −0.0022 (13) |
| O312 | 0.0173 (14) | 0.0093 (11) | 0.0182 (14) | 0.0009 (9)   | −0.0011 (11) | −0.0013 (9)  |

*Geometric parameters (Å, °)*

|             |           |               |           |
|-------------|-----------|---------------|-----------|
| Re1—O11     | 1.736 (2) | C31—O311      | 1.423 (4) |
| Re1—O21     | 1.728 (2) | C31—H31A      | 0.9900    |
| Re1—O31     | 1.727 (2) | C31—H31B      | 0.9900    |
| Re1—O41     | 1.702 (5) | O311—H311     | 0.8400    |
| Re2—O12     | 1.728 (4) | N2—C2         | 1.519 (7) |
| Re2—O22     | 1.730 (3) | N2—H2A        | 0.9100    |
| Re2—O32     | 1.736 (3) | N2—H2B        | 0.9100    |
| Re2—O42     | 1.726 (2) | N2—H2C        | 0.9100    |
| N1—C1       | 1.520 (7) | C2—C22        | 1.522 (6) |
| N1—H1A      | 0.9100    | C2—C32        | 1.530 (5) |
| N1—H1B      | 0.9100    | C2—C12        | 1.531 (5) |
| N1—H1C      | 0.9100    | C12—O112      | 1.432 (4) |
| C1—C31      | 1.528 (6) | C12—H12A      | 0.9900    |
| C1—C21      | 1.529 (5) | C12—H12B      | 0.9900    |
| C1—C11      | 1.537 (4) | O112—H112     | 0.8400    |
| C11—O111    | 1.427 (4) | C22—O212      | 1.422 (4) |
| C11—H11A    | 0.9900    | C22—H22A      | 0.9900    |
| C11—H11B    | 0.9900    | C22—H22B      | 0.9900    |
| O111—H111   | 0.8400    | O212—H212     | 0.8400    |
| C21—O211    | 1.431 (4) | C32—O312      | 1.433 (4) |
| C21—H21A    | 0.9900    | C32—H32A      | 0.9900    |
| C21—H21B    | 0.9900    | C32—H32B      | 0.9900    |
| O211—H211   | 0.8400    | O312—H312     | 0.8400    |
| O41—Re1—O31 | 109.6 (2) | O311—C31—H31A | 109.2     |
| O41—Re1—O21 | 108.7 (2) | C1—C31—H31A   | 109.2     |
| O31—Re1—O21 | 108.7 (2) | O311—C31—H31B | 109.2     |
| O41—Re1—O11 | 110.6 (2) | C1—C31—H31B   | 109.2     |
| O31—Re1—O11 | 110.0 (2) | H31A—C31—H31B | 107.9     |
| O21—Re1—O11 | 109.2 (2) | C31—O311—H311 | 109.5     |
| O42—Re2—O12 | 108.4 (2) | C2—N2—H2A     | 109.5     |
| O42—Re2—O22 | 109.4 (2) | C2—N2—H2B     | 109.5     |
| O12—Re2—O22 | 109.6 (2) | H2A—N2—H2B    | 109.5     |
| O42—Re2—O32 | 109.3 (2) | C2—N2—H2C     | 109.5     |
| O12—Re2—O32 | 110.8 (2) | H2A—N2—H2C    | 109.5     |
| O22—Re2—O32 | 109.3 (2) | H2B—N2—H2C    | 109.5     |
| C1—N1—H1A   | 109.5     | N2—C2—C22     | 110.5 (3) |

|                |           |                |           |
|----------------|-----------|----------------|-----------|
| C1—N1—H1B      | 109.5     | N2—C2—C32      | 107.5 (4) |
| H1A—N1—H1B     | 109.5     | C22—C2—C32     | 110.5 (3) |
| C1—N1—H1C      | 109.5     | N2—C2—C12      | 107.8 (3) |
| H1A—N1—H1C     | 109.5     | C22—C2—C12     | 111.5 (4) |
| H1B—N1—H1C     | 109.5     | C32—C2—C12     | 108.9 (3) |
| N1—C1—C31      | 109.3 (3) | O112—C12—C2    | 112.6 (3) |
| N1—C1—C21      | 108.4 (3) | O112—C12—H12A  | 109.1     |
| C31—C1—C21     | 111.4 (4) | C2—C12—H12A    | 109.1     |
| N1—C1—C11      | 107.5 (4) | O112—C12—H12B  | 109.1     |
| C31—C1—C11     | 110.9 (3) | C2—C12—H12B    | 109.1     |
| C21—C1—C11     | 109.2 (3) | H12A—C12—H12B  | 107.8     |
| O111—C11—C1    | 111.9 (3) | C12—O112—H112  | 109.5     |
| O111—C11—H11A  | 109.2     | O212—C22—C2    | 112.4 (3) |
| C1—C11—H11A    | 109.2     | O212—C22—H22A  | 109.1     |
| O111—C11—H11B  | 109.2     | C2—C22—H22A    | 109.1     |
| C1—C11—H11B    | 109.2     | O212—C22—H22B  | 109.1     |
| H11A—C11—H11B  | 107.9     | C2—C22—H22B    | 109.1     |
| C11—O111—H111  | 109.5     | H22A—C22—H22B  | 107.8     |
| O211—C21—C1    | 113.3 (3) | C22—O212—H212  | 109.5     |
| O211—C21—H21A  | 108.9     | O312—C32—C2    | 111.6 (3) |
| C1—C21—H21A    | 108.9     | O312—C32—H32A  | 109.3     |
| O211—C21—H21B  | 108.9     | C2—C32—H32A    | 109.3     |
| C1—C21—H21B    | 108.9     | O312—C32—H32B  | 109.3     |
| H21A—C21—H21B  | 107.7     | C2—C32—H32B    | 109.3     |
| C21—O211—H211  | 109.5     | H32A—C32—H32B  | 108.0     |
| O311—C31—C1    | 112.0 (3) | C32—O312—H312  | 109.5     |
| N1—C1—C11—O111 | −47.2 (4) | N2—C2—C12—O112 | −51.4 (4) |
| N1—C1—C21—O211 | 51.0 (4)  | N2—C2—C22—O212 | 64.0 (4)  |
| N1—C1—C31—O311 | −63.1 (4) | N2—C2—C32—O312 | 45.7 (4)  |

*Hydrogen-bond geometry (Å, °)*

| <i>D</i> —H $\cdots$ <i>A</i>         | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|---------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N2—H2A $\cdots$ O21                   | 0.91        | 2.03                | 2.858 (4)                  | 150                           |
| N2—H2B $\cdots$ O111 <sup>i</sup>     | 0.91        | 1.88                | 2.788 (4)                  | 173                           |
| N2—H2C $\cdots$ O31 <sup>ii</sup>     | 0.91        | 1.98                | 2.879 (4)                  | 169                           |
| O112—H112 $\cdots$ O212               | 0.84        | 2.12                | 2.773 (4)                  | 134                           |
| O112—H112 $\cdots$ O41                | 0.84        | 2.49                | 2.942 (4)                  | 115                           |
| O212—H212 $\cdots$ O32 <sup>ii</sup>  | 0.84        | 1.89                | 2.721 (4)                  | 168                           |
| O312—H312 $\cdots$ O112 <sup>ii</sup> | 0.84        | 1.92                | 2.704 (4)                  | 156                           |
| N1—H1A $\cdots$ O312 <sup>iii</sup>   | 0.91        | 1.83                | 2.738 (4)                  | 176                           |
| N1—H1B $\cdots$ O42 <sup>ii</sup>     | 0.91        | 2.05                | 2.872 (4)                  | 150                           |
| N1—H1C $\cdots$ O22                   | 0.91        | 1.98                | 2.862 (4)                  | 164                           |
| O111—H111 $\cdots$ O211 <sup>iv</sup> | 0.84        | 1.89                | 2.681 (3)                  | 157                           |
| O211—H211 $\cdots$ O311               | 0.84        | 2.13                | 2.774 (4)                  | 134                           |

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|                               |      |      |           |     |
|-------------------------------|------|------|-----------|-----|
| O211—H211...O12 <sup>ii</sup> | 0.84 | 2.54 | 2.960 (4) | 112 |
| O311—H311...O11               | 0.84 | 1.88 | 2.714 (4) | 170 |

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Symmetry codes: (i)  $x-1/2, -y+1, z$ ; (ii)  $x, y-1, z$ ; (iii)  $x+1/2, -y, z$ ; (iv)  $x, y+1, z$ .