



# Crystal structure of bromido-*fac*-tricarbonyl-[5-(3,4,5-trimethoxyphenyl)-3-(pyridin-2-yl)-1*H*-1,2,4-triazole- $\kappa^2 N^2, N^3$ ]rhenium(I) methanol monosolvate

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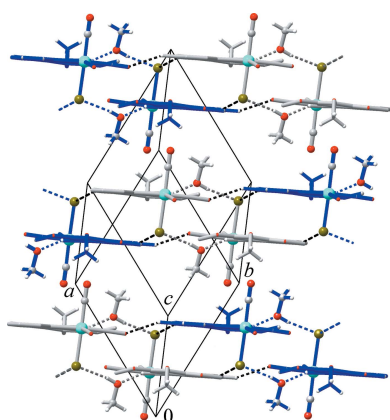
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In the title compound, [ReBr(C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub>)(CO)<sub>3</sub>]·CH<sub>3</sub>OH, the Re<sup>I</sup> atom adopts a distorted octahedral coordination sphere with a facial arrangement of the three carbonyl ligands. Two N atoms of the chelating 5-(3,4,5-trimethoxyphenyl)-3-(pyridin-2-yl)-1*H*-1,2,4-triazole ligand and two carbonyl ligands define the equatorial plane of the complex, with the third carbonyl ligand and the bromide ligand in axial positions. Conventional hydrogen bonds including the methanol solvent molecules assemble the complex molecules through mutual N—H···O—H···Br links [N···O = 2.703 (3) Å and O···Br = 3.255 (2) Å] into centrosymmetric dimers, whereas weaker C—H···O and C—H···Br hydrogen bonds [C···O = 3.215 (3)–3.390 (4) Å and C···Br = 3.927 (3) Å] connect the dimers into double layers parallel to the (111) plane.

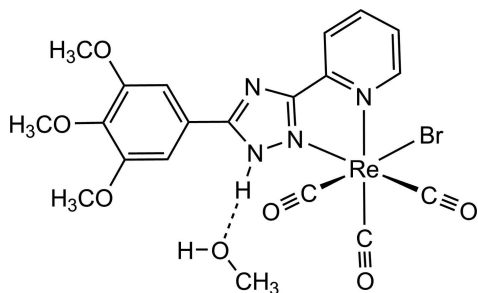
## 1. Chemical context

Rhenium(I) metal complexes have attracted attention because of their chemical characteristics exhibiting increased potentials for biochemical applications (Fernández-Moreira *et al.*, 2010; Lo *et al.*, 2012). Rhenium tricarbonyl complexes with the general formula *fac*-[Re(CO)<sub>3</sub>(N<sup>^</sup>N)] (where N<sup>^</sup>N is an *N,N'*-chelating ligand) are kinetically stable and have luminescence properties with long life times (Kowalski *et al.*, 2015; Guo *et al.*, 1997), high photostability (Lo, 2015) and large Stokes shifts (Lo, 2015; Stephenson *et al.*, 2004), which makes these compounds ideal candidates for either *in vitro* or *in vivo* visualization of biological processes (Shen *et al.*, 2001; Thorp-Greenwood, 2012).

Triazole derivatives are an interesting type of ligand. 1,2,4-Triazoles have biological relevance since they show antiviral (Abdullah *et al.*, 2012), antibacterial (Varvarason *et al.*, 2000; Jassim *et al.*, 2011), antifungal (Luo *et al.*, 2009), anticancer (Sztanke *et al.*, 2008) and antituberculous (Mandal *et al.*, 2010) activities. Moreover, metal complexes containing triazole derivatives have interesting photophysical and photochemical properties (Piletska *et al.*, 2015; Chen *et al.*, 2013), and this class of complexes, apart from their biological activity (Chohan & Hanif, 2010), is used for fluorescent probing in addition to their potential use in radio-imaging. Introduction of substituents in the triazole derivatives affects the  $\sigma$ -donor and  $\pi$ -acceptor properties (Van Diemen *et al.*, 1991), and consequently affects the photophysical properties of an organometallic compounds in which they are incorporated. In

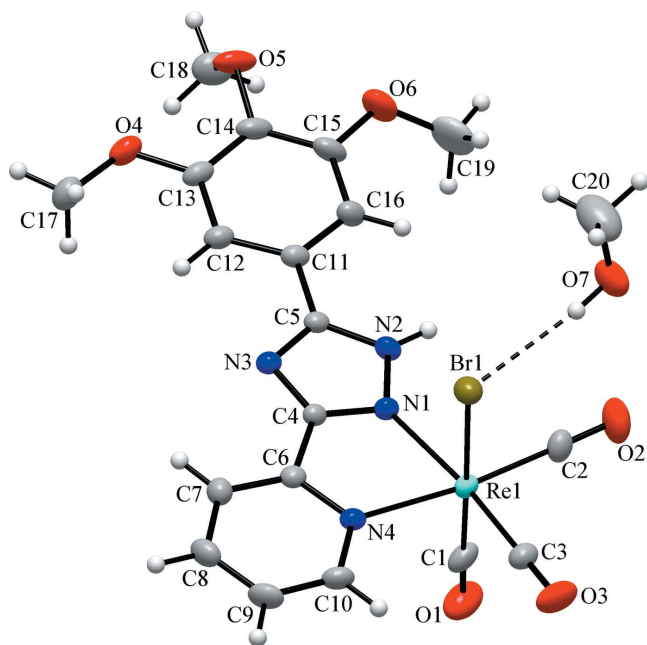


this context, we report here the synthesis and crystal structure analysis of a novel  $\text{Re}^{\text{I}}$  complex, *i.e.*  $[\text{ReBr}(\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_3)(\text{CO})_3]\cdot\text{CH}_3\text{OH}$  (Fig. 1), which contains the triazole ligand 5-(3,4,5-trimethoxyphenyl)-3-(pyridin-2-yl)-1*H*-1,2,4-triazole.



## 2. Structural commentary

The three carbonyl ligands bonded to the  $\text{Re}^{\text{I}}$  atom are arranged in a *fac* configuration. The distances of atoms C1, C2 and C3 to the  $\text{Re}^{\text{I}}$  atom are 1.902 (4), 1.910 (2) and 1.907 (2) Å, respectively, and the  $\text{Re}-\text{N}$  bond lengths involving the chelating organic ligand are 2.151 (2) and 2.205 (2) Å. The two N atoms and two carbonyl C atoms define the equatorial plane, while the octahedral coordination sphere is completed by the third carbonyl C atom and the Br atom [ $\text{Re}-\text{Br} = 2.6222$  (3) Å] in axial positions. The CO ligands are almost linearly coordinated, with  $\text{O}-\text{C}-\text{Re}$  bond angles of 178.2 (3), 177.8 (3) and 177.8 (3)°. The  $\text{C}-\text{Re}-\text{C}$  bond angles between carbonyl C atoms are 90.6 (1), 90.2 (1) and 88.7 (1)°,



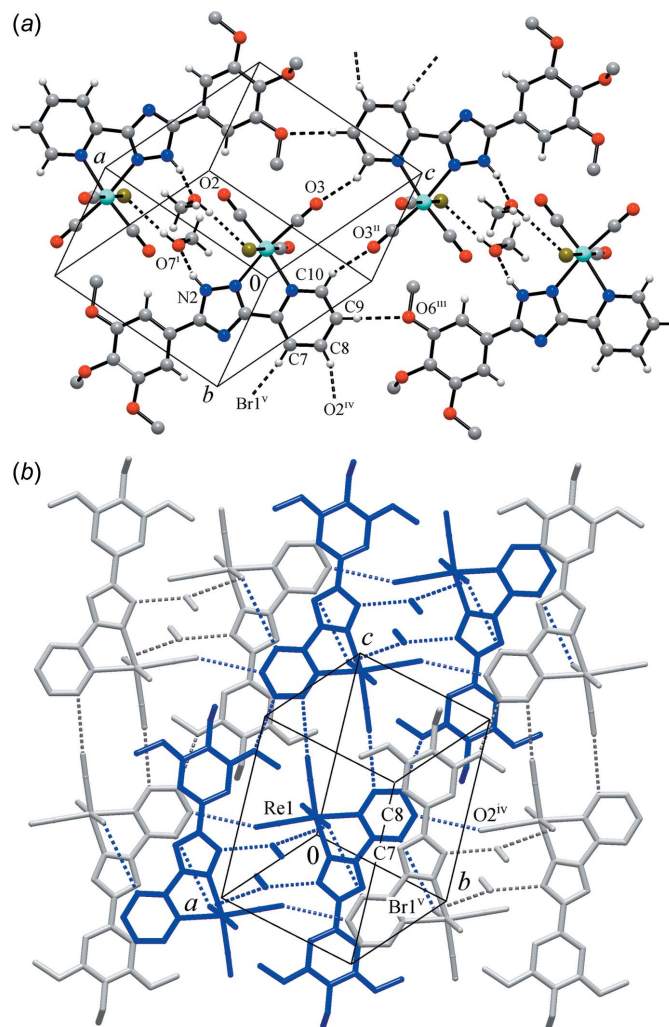
**Figure 1**

The structures of the molecular entities in the solvated title complex. Displacement ellipsoids are drawn at the 40% probability level and the dashed line indicates hydrogen bonding involving the methanol solvent molecule.

close to ideal values, whereas the *cis* equatorial bite angle of the chelating ligand ( $\text{N1}-\text{Re1}-\text{N4}$ ) is 73.42 (8)°.

## 3. Supramolecular features

In the crystal, the packing of the molecules is influenced by a set of weak interactions, including conventional hydrogen bonding with common NH and OH donor groups and weaker hydrogen bonds formed by CH groups (Table 1). Two pairs of relatively short hydrogen bonds ( $\text{O7}-\text{H}\cdots\text{Br1}$  and  $\text{N2}-\text{H}\cdots\text{O7}$ ), both involving the methanol solvent molecules, assemble the complex molecules into centrosymmetric dimers (Fig. 2). As may be compared with the closely related complex  $[\text{ReBr}(\text{L})(\text{CO})_3]$  [ $\text{L} = 5$ -phenyl-3-(pyridin-2-yl)-1*H*-1,2,4-triazole; Piletska *et al.*, 2014], a key prerequisite for the formation of dimers is the presence of acidic NH functions and sterically



**Figure 2**

(a) Part of the crystal structure of the title complex, showing dimers formed by conventional hydrogen bonding involving the methanol solvent molecules and weak  $\text{C}-\text{H}\cdots\text{O}$  interactions providing interconnection of the dimers into chains. (b) A partial view of the double layer in a projection approximately on the (111) plane; individual chains are marked in blue and grey and the dotted lines indicate hydrogen bonding within a layer. [Symmetry codes: (i)  $1-x, -y, -z$ ; (ii)  $-x, -y, 1-z$ ; (iii)  $-1+x, y, 1+z$ ; (iv)  $-1+x, 1+y, z$ ; (v)  $-x, 1-y, -z$ .]

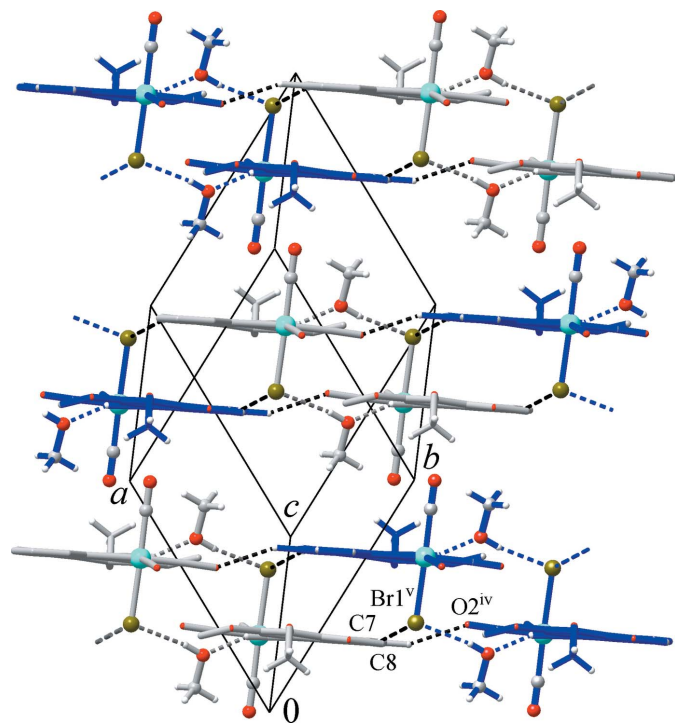
**Table 1**  
Hydrogen-bond geometry (Å, °).

<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>
O7—H1O···Br1	0.85	2.41	3.255 (2)	172
N2—H1N···O7 <sup>i</sup>	0.87	1.89	2.703 (3)	154
C7—H7···Br1 <sup>ii</sup>	0.94	3.01	3.927 (3)	165
C8—H8···O2 <sup>iii</sup>	0.94	2.52	3.390 (4)	153
C9—H9···O6 <sup>iv</sup>	0.94	2.49	3.278 (3)	142
C10—H10···O3 <sup>v</sup>	0.94	2.39	3.215 (3)	146

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

accessible Br sites. In the latter, they afford two mutual N—H···Br hydrogen bonds, whereas in the present case, these links appear to be extended by the inclusion of methanol, resulting in an N—H···O(Me)—H···Br motif.

Each of the four pyridine CH groups functions as a donor of weak hydrogen bonds (Fig. 2). These groups establish hydrogen bonds to two carbonyl O atoms (C8···O2<sup>iv</sup> and C10···O3<sup>ii</sup>), a methoxy O atom (C9···O6<sup>iii</sup>) and a very weak bond with bromine as acceptor (C7···Br<sup>v</sup>) (for symmetry codes, see Table 1). These distal yet directional interactions (the hydrogen-bonding angles are in the range 142–165°; Table 1) unite the above dimers into flat double layers, which extend parallel to the (111) plane. Within a layer, the pyridine and triazole moieties of adjacent molecules are actually parallel, with shortest contacts of C7···N3<sup>v</sup> = 3.430 (4) Å [symmetry code: (v)  $-x, 1 - y, -z$ ]. However, this situation is unlikely to be a consequence of slipped  $\pi$ – $\pi$  interactions, since



**Figure 3**  
Packing of successive double layers, which are turned towards one another by the methyl and carbonyl groups (the view is along the direction of the hydrogen-bonded chains indicated with blue and grey bonds). [Symmetry codes: (iv)  $-1 + x, 1 + y, z$ ; (v)  $-x, 1 - y, -z$ .]

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	[ReBr(C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> O <sub>3</sub> )(CO) <sub>3</sub> ].CH <sub>4</sub> O
<i>M<sub>r</sub></i>	694.51
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	213
<i>a, b, c</i> (Å)	10.9569 (6), 11.0012 (6), 11.9738 (7)
$\alpha, \beta, \gamma$ (°)	69.073 (6), 75.593 (7), 61.409 (6)
<i>V</i> (Å <sup>3</sup> )	1178.37 (14)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	6.90
Crystal size (mm)	0.21 × 0.18 × 0.15
Data collection	
Diffractometer	Stoe IPDS
Absorption correction	Numerical ( <i>X-RED</i> and <i>X-SHAPE</i> ; Stoe & Cie, 1999)
<i>T<sub>min</sub>, T<sub>max</sub></i>	0.325, 0.424
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	22150, 5649, 4658
<i>R<sub>int</sub></i>	0.054
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.660
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.019, 0.034, 0.84
No. of reflections	5649
No. of parameters	302
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.77, -0.98

Computer programs: *IPDS* (Stoe & Cie, 2000), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 1999) and *WinGX* (Farrugia, 2012).

the corresponding slippage angle exceeds 56° and the inter-centroid distance is as long as Cg(C6–C10/N4)···Cg(C4/C5/N1–N3)<sup>v</sup> = 4.090 (3) Å [for the lack of an overlap between heteroaromatic planes, see Fig. 2, part (B)]. At the same time, successive double layers are turned towards one another by methyl groups of the trimethoxyphenyl and methanol entities (Fig. 3). Thus, the interlayer interactions are very weak and the only remarkable contact is found between two inversion-related carbonyl groups [O1···C1<sup>vi</sup> = 3.295 (3) Å and O1···Cg(C1=O1)<sup>vi</sup> = 3.226 (3) Å; symmetry code (vi)  $-x, -y, -z$ ]. Although such weak interactions are characteristic of related metal–carbonyl structures (Sparkes *et al.*, 2006), in the present case, their significance is relatively minor.

#### 4. Synthesis and crystallization

Pentacarbonylrhenium(I) bromide (0.15 g, 0.369 mmol) was mixed with 5-(3,4,5-trimethoxyphenyl)-3-(pyridin-2-yl)-1*H*-1,2,4-triazole (0.138 g, 0.442 mmol) in benzene (30 ml). The mixture was refluxed for 4 h under a stream of argon and then allowed to cool to room temperature. The yellow product was collected by suction filtration, washed with hexane and dried (yield 0.138 g, 77%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a methanol–dichloromethane solution of the complex. IR (KBr, cm<sup>-1</sup>):  $\nu_{as}(\text{CO})$  2028 (*s*),  $\nu_s(\text{CO})$  1894 (*s*). <sup>1</sup>H NMR (400 MHz, *d*<sup>6</sup>-DMSO):  $\delta$  9.02 (*d*, 1H, CH=N, Py), 8.39 (*d*, 1H, CH=C, Py),

8.35 (*dd*, 1H, CH, Py), 7.75 (*dd*, 1H, CH, Py), 7.44 [*s*, 2H, 2 CH, Ph(OCH<sub>3</sub>)<sub>3</sub>], 3.93 [*s*, 9H, 3 O-CH<sub>3</sub>, Ph(OCH<sub>3</sub>)<sub>3</sub>].

## 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C- and N-bound H atoms were positioned with idealized geometry and were refined with aryl C—H = 0.94 Å, methyl C—H = 0.97 Å and N—H = 0.87 Å, and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and  $1.2U_{\text{eq}}(\text{C,N})$  otherwise. The O-bound H atom of the methanol solvent molecule was found from a difference map and was refined with O—H = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

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## supporting information

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## Crystal structure of bromido-*fac*-tricarbonyl[5-(3,4,5-trimethoxyphenyl)-3-(pyridin-2-yl)-1*H*-1,2,4-triazole- $\kappa^2N^2,N^3$ ]rhenium(I) methanol monosolvate

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### Computing details

Data collection: *IPDS* (Stoe & Cie, 2000); cell refinement: *IPDS* (Stoe & Cie, 2000); data reduction: *IPDS* (Stoe & Cie, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

### Bromido-*fac*-tricarbonyl[5-(3,4,5-trimethoxyphenyl)-3-(pyridin-2-yl)-1*H*-1,2,4-triazole- $\kappa^2N^2,N^3$ ]rhenium(I) methanol monosolvate

#### Crystal data

[ReBr(C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub>)(CO)<sub>3</sub>]·CH<sub>4</sub>O

$M_r = 694.51$

Triclinic,  $P\bar{1}$

$a = 10.9569$  (6) Å

$b = 11.0012$  (6) Å

$c = 11.9738$  (7) Å

$\alpha = 69.073$  (6)°

$\beta = 75.593$  (7)°

$\gamma = 61.409$  (6)°

$V = 1178.37$  (14) Å<sup>3</sup>

$Z = 2$

$F(000) = 668$

$D_x = 1.957$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 8000 reflections

$\theta = 2.4$ – $28.0$ °

$\mu = 6.90$  mm<sup>-1</sup>

$T = 213$  K

Prism, yellow

$0.21 \times 0.18 \times 0.15$  mm

#### Data collection

Stoe IPDS

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  oscillation scans

Absorption correction: numerical

(*X-RED* and *X-SHAPE*; Stoe & Cie, 1999)

$T_{\min} = 0.325$ ,  $T_{\max} = 0.424$

22150 measured reflections

5649 independent reflections

4658 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.054$

$\theta_{\max} = 28.0$ °,  $\theta_{\min} = 2.4$ °

$h = -14 \rightarrow 14$

$k = -14 \rightarrow 14$

$l = -15 \rightarrow 15$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.019$   
 $wR(F^2) = 0.034$   
 $S = 0.84$   
 5649 reflections  
 302 parameters  
 0 restraints  
 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  
 $w = 1/[\sigma^2(F_o^2) + (0.007P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.77 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.98 \text{ e } \text{\AA}^{-3}$

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional R-factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and R-factors based on ALL data will be even larger.

*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	0.154206 (13)	0.050031 (12)	0.169575 (9)	0.02510 (3)
Br1	0.25284 (3)	0.20300 (3)	0.21180 (2)	0.03551 (7)
O1	0.0338 (3)	-0.1259 (3)	0.1269 (2)	0.0619 (7)
O2	0.4513 (3)	-0.1785 (3)	0.1342 (2)	0.0647 (7)
O3	0.1502 (3)	-0.1065 (3)	0.43714 (17)	0.0564 (6)
O4	0.0599 (2)	0.6925 (2)	-0.58379 (15)	0.0424 (5)
O5	0.3238 (2)	0.5465 (3)	-0.66521 (15)	0.0496 (6)
O6	0.4851 (2)	0.2842 (3)	-0.53647 (19)	0.0588 (7)
O7	0.5906 (2)	0.0402 (3)	0.1603 (2)	0.0607 (6)
H1O	0.5022	0.0743	0.1740	0.091*
N1	0.1308 (2)	0.1987 (2)	-0.00751 (16)	0.0251 (5)
N2	0.2059 (2)	0.2076 (2)	-0.11623 (17)	0.0277 (5)
H1N	0.2870	0.1422	-0.1341	0.042*
N3	0.0134 (2)	0.4101 (2)	-0.13551 (17)	0.0276 (5)
N4	-0.0517 (2)	0.2340 (2)	0.17886 (16)	0.0261 (5)
C1	0.0776 (3)	-0.0582 (3)	0.1415 (2)	0.0372 (7)
C2	0.3389 (3)	-0.0940 (3)	0.1465 (2)	0.0374 (7)
C3	0.1518 (3)	-0.0502 (3)	0.3364 (2)	0.0337 (6)
C4	0.0180 (3)	0.3209 (3)	-0.02390 (19)	0.0236 (5)
C5	0.1328 (3)	0.3353 (3)	-0.1915 (2)	0.0258 (5)
C6	-0.0881 (3)	0.3444 (3)	0.0779 (2)	0.0256 (5)
C7	-0.2134 (3)	0.4647 (3)	0.0716 (2)	0.0330 (6)
H7	-0.2349	0.5395	-0.0004	0.040*
C8	-0.3074 (3)	0.4739 (3)	0.1731 (3)	0.0393 (7)
H8	-0.3944	0.5547	0.1712	0.047*

C9	-0.2715 (3)	0.3632 (3)	0.2763 (2)	0.0402 (7)
H9	-0.3335	0.3675	0.3465	0.048*
C10	-0.1442 (3)	0.2460 (3)	0.2766 (2)	0.0346 (6)
H10	-0.1209	0.1709	0.3482	0.042*
C11	0.1808 (3)	0.3865 (3)	-0.3176 (2)	0.0292 (6)
C12	0.0921 (3)	0.5169 (3)	-0.3878 (2)	0.0311 (6)
H12	0.0019	0.5697	-0.3557	0.037*
C13	0.1380 (3)	0.5683 (3)	-0.5059 (2)	0.0335 (6)
C14	0.2732 (3)	0.4897 (3)	-0.5527 (2)	0.0374 (7)
C15	0.3585 (3)	0.3574 (3)	-0.4825 (2)	0.0392 (7)
C16	0.3131 (3)	0.3051 (3)	-0.3641 (2)	0.0363 (7)
H16	0.3713	0.2156	-0.3160	0.044*
C17	-0.0765 (4)	0.7778 (3)	-0.5387 (3)	0.0465 (8)
H17A	-0.1313	0.7229	-0.5112	0.070*
H17B	-0.1212	0.8642	-0.6019	0.070*
H17C	-0.0701	0.8046	-0.4721	0.070*
C18	0.2920 (4)	0.5205 (4)	-0.7592 (3)	0.0544 (9)
H18A	0.3399	0.4181	-0.7525	0.082*
H18B	0.3221	0.5733	-0.8358	0.082*
H18C	0.1920	0.5521	-0.7538	0.082*
C19	0.5582 (4)	0.1362 (5)	-0.4788 (4)	0.0857 (14)
H19A	0.5877	0.1254	-0.4045	0.128*
H19B	0.6395	0.0928	-0.5309	0.128*
H19C	0.4977	0.0888	-0.4613	0.128*
C20	0.6343 (5)	0.1423 (5)	0.1534 (5)	0.0861 (14)
H20A	0.6044	0.1685	0.2282	0.129*
H20B	0.5936	0.2272	0.0878	0.129*
H20C	0.7353	0.1024	0.1395	0.129*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Re1	0.02840 (6)	0.02390 (6)	0.02089 (5)	-0.01144 (4)	-0.00314 (3)	-0.00318 (3)
Br1	0.03337 (16)	0.03401 (17)	0.04178 (14)	-0.01567 (13)	-0.00360 (12)	-0.01181 (12)
O1	0.088 (2)	0.0571 (16)	0.0582 (14)	-0.0442 (15)	-0.0299 (13)	-0.0010 (12)
O2	0.0457 (15)	0.0503 (16)	0.0727 (16)	0.0050 (13)	-0.0118 (12)	-0.0217 (12)
O3	0.0822 (18)	0.0659 (16)	0.0272 (10)	-0.0472 (15)	-0.0099 (10)	0.0052 (10)
O4	0.0561 (14)	0.0372 (12)	0.0284 (9)	-0.0229 (11)	-0.0026 (9)	-0.0001 (8)
O5	0.0627 (15)	0.0786 (16)	0.0239 (9)	-0.0539 (14)	0.0066 (9)	-0.0060 (9)
O6	0.0325 (12)	0.0807 (19)	0.0418 (11)	-0.0187 (13)	0.0098 (9)	-0.0108 (11)
O7	0.0342 (13)	0.0493 (15)	0.0909 (17)	-0.0084 (12)	0.0067 (12)	-0.0335 (13)
N1	0.0260 (12)	0.0283 (12)	0.0190 (9)	-0.0126 (10)	0.0005 (8)	-0.0049 (8)
N2	0.0231 (11)	0.0347 (13)	0.0223 (10)	-0.0118 (10)	0.0026 (8)	-0.0090 (9)
N3	0.0268 (12)	0.0283 (12)	0.0256 (10)	-0.0136 (10)	0.0001 (9)	-0.0045 (9)
N4	0.0261 (12)	0.0302 (12)	0.0223 (9)	-0.0149 (10)	0.0005 (8)	-0.0057 (8)
C1	0.055 (2)	0.0295 (16)	0.0275 (13)	-0.0215 (15)	-0.0095 (12)	0.0000 (11)
C2	0.0396 (18)	0.0311 (17)	0.0327 (14)	-0.0084 (15)	-0.0097 (12)	-0.0050 (12)
C3	0.0403 (17)	0.0340 (16)	0.0288 (13)	-0.0204 (14)	-0.0052 (11)	-0.0036 (11)

C4	0.0228 (13)	0.0272 (14)	0.0210 (10)	-0.0123 (11)	-0.0026 (9)	-0.0042 (9)
C5	0.0245 (13)	0.0302 (15)	0.0245 (11)	-0.0156 (12)	-0.0021 (10)	-0.0042 (10)
C6	0.0267 (14)	0.0281 (14)	0.0252 (11)	-0.0151 (12)	-0.0013 (10)	-0.0071 (10)
C7	0.0294 (15)	0.0302 (16)	0.0363 (13)	-0.0111 (13)	-0.0043 (11)	-0.0075 (11)
C8	0.0273 (15)	0.0377 (18)	0.0515 (16)	-0.0126 (14)	0.0053 (13)	-0.0190 (14)
C9	0.0362 (17)	0.049 (2)	0.0382 (14)	-0.0234 (16)	0.0148 (12)	-0.0212 (14)
C10	0.0394 (17)	0.0419 (18)	0.0258 (12)	-0.0254 (15)	0.0047 (11)	-0.0070 (11)
C11	0.0306 (15)	0.0369 (16)	0.0239 (11)	-0.0202 (13)	-0.0006 (10)	-0.0062 (10)
C12	0.0366 (16)	0.0359 (16)	0.0246 (11)	-0.0220 (13)	-0.0003 (11)	-0.0054 (11)
C13	0.0464 (18)	0.0344 (16)	0.0251 (12)	-0.0260 (15)	-0.0045 (12)	-0.0012 (11)
C14	0.0446 (18)	0.056 (2)	0.0238 (12)	-0.0368 (16)	0.0029 (12)	-0.0070 (12)
C15	0.0284 (15)	0.062 (2)	0.0294 (13)	-0.0249 (15)	0.0052 (11)	-0.0125 (13)
C16	0.0296 (15)	0.0466 (18)	0.0267 (12)	-0.0179 (14)	-0.0026 (11)	-0.0015 (12)
C17	0.053 (2)	0.0380 (19)	0.0382 (15)	-0.0163 (16)	-0.0077 (14)	-0.0012 (13)
C18	0.064 (2)	0.075 (3)	0.0333 (15)	-0.039 (2)	0.0008 (15)	-0.0156 (16)
C19	0.045 (2)	0.098 (4)	0.087 (3)	-0.021 (2)	0.031 (2)	-0.036 (3)
C20	0.060 (3)	0.086 (3)	0.134 (4)	-0.029 (3)	-0.005 (3)	-0.062 (3)

*Geometric parameters (Å, °)*

Re1—C1	1.902 (3)	C7—C8	1.383 (4)
Re1—C3	1.907 (3)	C7—H7	0.9400
Re1—C2	1.910 (3)	C8—C9	1.369 (4)
Re1—N1	2.1515 (18)	C8—H8	0.9400
Re1—N4	2.205 (2)	C9—C10	1.373 (4)
Re1—Br1	2.6222 (3)	C9—H9	0.9400
O1—C1	1.137 (3)	C10—H10	0.9400
O2—C2	1.146 (4)	C11—C12	1.385 (4)
O3—C3	1.142 (3)	C11—C16	1.388 (4)
O4—C13	1.355 (3)	C12—C13	1.386 (3)
O4—C17	1.423 (4)	C12—H12	0.9400
O5—C14	1.368 (3)	C13—C14	1.401 (4)
O5—C18	1.410 (4)	C14—C15	1.383 (4)
O6—C15	1.359 (4)	C15—C16	1.389 (4)
O6—C19	1.412 (5)	C16—H16	0.9400
O7—C20	1.388 (5)	C17—H17A	0.9700
O7—H1O	0.8500	C17—H17B	0.9700
N1—C4	1.310 (3)	C17—H17C	0.9700
N1—N2	1.354 (3)	C18—H18A	0.9700
N2—C5	1.344 (3)	C18—H18B	0.9700
N2—H1N	0.8700	C18—H18C	0.9700
N3—C5	1.329 (3)	C19—H19A	0.9700
N3—C4	1.342 (3)	C19—H19B	0.9700
N4—C10	1.344 (3)	C19—H19C	0.9700
N4—C6	1.350 (3)	C20—H20A	0.9700
C4—C6	1.462 (3)	C20—H20B	0.9700
C5—C11	1.468 (3)	C20—H20C	0.9700
C6—C7	1.372 (4)		



C1—Re1—C3	90.15 (11)	C8—C9—H9	120.2
C1—Re1—C2	90.62 (13)	C10—C9—H9	120.2
C3—Re1—C2	88.74 (12)	N4—C10—C9	122.8 (2)
C1—Re1—N1	95.06 (9)	N4—C10—H10	118.6
C3—Re1—N1	169.20 (10)	C9—C10—H10	118.6
C2—Re1—N1	100.64 (10)	C12—C11—C16	121.3 (2)
C1—Re1—N4	92.83 (11)	C12—C11—C5	118.7 (2)
C3—Re1—N4	96.92 (10)	C16—C11—C5	120.0 (2)
C2—Re1—N4	173.36 (10)	C11—C12—C13	119.2 (3)
N1—Re1—N4	73.41 (7)	C11—C12—H12	120.4
C1—Re1—Br1	178.32 (9)	C13—C12—H12	120.4
C3—Re1—Br1	89.23 (8)	O4—C13—C12	124.5 (3)
C2—Re1—Br1	90.92 (9)	O4—C13—C14	115.4 (2)
N1—Re1—Br1	85.31 (6)	C12—C13—C14	120.1 (3)
N4—Re1—Br1	85.70 (6)	O5—C14—C15	119.8 (3)
C13—O4—C17	117.1 (2)	O5—C14—C13	120.3 (3)
C14—O5—C18	114.9 (2)	C15—C14—C13	119.9 (2)
C15—O6—C19	117.1 (2)	O6—C15—C14	116.3 (2)
C20—O7—H10	109.6	O6—C15—C16	123.4 (3)
C4—N1—N2	104.04 (18)	C14—C15—C16	120.3 (3)
C4—N1—Re1	118.20 (15)	C11—C16—C15	119.2 (3)
N2—N1—Re1	137.71 (17)	C11—C16—H16	120.4
C5—N2—N1	107.9 (2)	C15—C16—H16	120.4
C5—N2—H1N	126.1	O4—C17—H17A	109.5
N1—N2—H1N	126.1	O4—C17—H17B	109.5
C5—N3—C4	102.6 (2)	H17A—C17—H17B	109.5
C10—N4—C6	117.0 (2)	O4—C17—H17C	109.5
C10—N4—Re1	125.62 (18)	H17A—C17—H17C	109.5
C6—N4—Re1	117.35 (15)	H17B—C17—H17C	109.5
O1—C1—Re1	178.2 (3)	O5—C18—H18A	109.5
O2—C2—Re1	177.9 (3)	O5—C18—H18B	109.5
O3—C3—Re1	177.7 (3)	H18A—C18—H18B	109.5
N1—C4—N3	114.7 (2)	O5—C18—H18C	109.5
N1—C4—C6	117.8 (2)	H18A—C18—H18C	109.5
N3—C4—C6	127.5 (2)	H18B—C18—H18C	109.5
N3—C5—N2	110.8 (2)	O6—C19—H19A	109.5
N3—C5—C11	124.8 (2)	O6—C19—H19B	109.5
N2—C5—C11	124.4 (2)	H19A—C19—H19B	109.5
N4—C6—C7	123.1 (2)	O6—C19—H19C	109.5
N4—C6—C4	113.1 (2)	H19A—C19—H19C	109.5
C7—C6—C4	123.8 (2)	H19B—C19—H19C	109.5
C6—C7—C8	118.8 (3)	O7—C20—H20A	109.5
C6—C7—H7	120.6	O7—C20—H20B	109.5
C8—C7—H7	120.6	H20A—C20—H20B	109.5
C9—C8—C7	118.7 (3)	O7—C20—H20C	109.5
C9—C8—H8	120.6	H20A—C20—H20C	109.5
C7—C8—H8	120.6	H20B—C20—H20C	109.5

C8—C9—C10	119.5 (2)		
C1—Re1—N1—C4	94.2 (2)	N1—C4—C6—C7	-177.2 (3)
C3—Re1—N1—C4	-24.3 (7)	N3—C4—C6—C7	1.7 (4)
C2—Re1—N1—C4	-174.2 (2)	N4—C6—C7—C8	-0.1 (4)
N4—Re1—N1—C4	2.79 (18)	C4—C6—C7—C8	178.5 (2)
Br1—Re1—N1—C4	-84.12 (18)	C6—C7—C8—C9	0.6 (4)
C1—Re1—N1—N2	-88.8 (3)	C7—C8—C9—C10	-0.4 (4)
C3—Re1—N1—N2	152.7 (5)	C6—N4—C10—C9	0.6 (4)
C2—Re1—N1—N2	2.8 (3)	Re1—N4—C10—C9	-179.5 (2)
N4—Re1—N1—N2	179.8 (3)	C8—C9—C10—N4	-0.2 (5)
Br1—Re1—N1—N2	92.9 (2)	N3—C5—C11—C12	-5.7 (4)
C4—N1—N2—C5	-0.1 (3)	N2—C5—C11—C12	176.3 (2)
Re1—N1—N2—C5	-177.32 (19)	N3—C5—C11—C16	174.0 (3)
C1—Re1—N4—C10	83.7 (2)	N2—C5—C11—C16	-4.0 (4)
C3—Re1—N4—C10	-6.7 (2)	C16—C11—C12—C13	-1.6 (4)
N1—Re1—N4—C10	178.2 (2)	C5—C11—C12—C13	178.1 (2)
Br1—Re1—N4—C10	-95.4 (2)	C17—O4—C13—C12	2.6 (4)
C1—Re1—N4—C6	-96.34 (19)	C17—O4—C13—C14	-178.0 (3)
C3—Re1—N4—C6	173.17 (19)	C11—C12—C13—O4	178.6 (3)
N1—Re1—N4—C6	-1.90 (18)	C11—C12—C13—C14	-0.8 (4)
Br1—Re1—N4—C6	84.47 (18)	C18—O5—C14—C15	96.3 (3)
N2—N1—C4—N3	-0.3 (3)	C18—O5—C14—C13	-87.1 (4)
Re1—N1—C4—N3	177.60 (16)	O4—C13—C14—O5	7.0 (4)
N2—N1—C4—C6	178.8 (2)	C12—C13—C14—O5	-173.6 (2)
Re1—N1—C4—C6	-3.3 (3)	O4—C13—C14—C15	-176.4 (3)
C5—N3—C4—N1	0.5 (3)	C12—C13—C14—C15	3.0 (4)
C5—N3—C4—C6	-178.4 (2)	C19—O6—C15—C14	-164.1 (3)
C4—N3—C5—N2	-0.6 (3)	C19—O6—C15—C16	15.2 (5)
C4—N3—C5—C11	-178.8 (2)	O5—C14—C15—O6	-6.9 (4)
N1—N2—C5—N3	0.4 (3)	C13—C14—C15—O6	176.4 (3)
N1—N2—C5—C11	178.7 (2)	O5—C14—C15—C16	173.7 (3)
C10—N4—C6—C7	-0.4 (4)	C13—C14—C15—C16	-2.9 (4)
Re1—N4—C6—C7	179.7 (2)	C12—C11—C16—C15	1.7 (4)
C10—N4—C6—C4	-179.2 (2)	C5—C11—C16—C15	-178.0 (3)
Re1—N4—C6—C4	0.9 (3)	O6—C15—C16—C11	-178.7 (3)
N1—C4—C6—N4	1.6 (3)	C14—C15—C16—C11	0.6 (4)
N3—C4—C6—N4	-179.5 (2)		

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

<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>
O7—H1O $\cdots$ Br1	0.85	2.41	3.255 (2)	172
N2—H1N $\cdots$ O7 <sup>i</sup>	0.87	1.89	2.703 (3)	154
C7—H7 $\cdots$ Br1 <sup>ii</sup>	0.94	3.01	3.927 (3)	165
C8—H8 $\cdots$ O2 <sup>iii</sup>	0.94	2.52	3.390 (4)	153

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C9—H9···O6 <sup>iv</sup>	0.94	2.49	3.278 (3)	142
C10—H10···O3 <sup>v</sup>	0.94	2.39	3.215 (3)	146

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