research communications

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

Kseniia Piletska,[a]* Konstantin V. Domasevitch[b] and Alexander V. Shtemenko[a]

[a]Department of Inorganic Chemistry, Ukrainian State University of Chemical Technology, Gagarin Ave. 8, Dnipropetrovsk 49005, Ukraine, and [b]Inorganic Chemistry Department, National Taras Shevchenko University of Kyiv, Volodymyrska Street 64/13, Kyiv 01601, Ukraine. *Correspondence e-mail: ksenijapiletska@gmail.com

In the title compound, [ReBr($C_{13}H_{10}N_4$)$(CO)_3$], the Re^I atom has a distorted octahedral coordination environment. Two N atoms of the 5-phenyl-3-(pyridin-2-yl)-1*H*-1,2,4-triazole ligand and two of the three carbonyl groups occupy the equatorial plane of the complex, with the third carbonyl ligand and the bromide ligand in the axial positions. The three carbonyl ligands are arranged in a *fac* configuration around the Re^I atom. Mutual N—H$\cdots$Br hydrogen bonds arrange molecules into centrosymmetric dimers. Additional stabilization within the crystal structure is provided by C—H$\cdots$O and C—H$\cdots$Br hydrogen bonds, as well as by slipped π–π stacking interactions [centroid-to-centroid distance = 3.785 (5) Å], defining a three-dimensional network.

1. Chemical context

The coordination chemistry of rhenium and technetium has been well studied over the last half century, particularly in view of the potential applications of their [186/188]Re and ^{99m}Tc isotopes in therapeutic and diagnostic agents in nuclear medicine (Volkert & Hoffman, 1999; Alberto *et al.*, 1999). Complexes of the type [$M(CO)_3(NN)X$] (*M* = Tc, Re; *NN* = bidentate nitrogen donor; *X* = anionic ligand) have been shown to possess interesting photophysical, photochemical and excited-state redox properties (Striplin & Crosby, 2001; Stufkens & Vlcěk, 1998), making this class of complexes applicable as fluorescent probes, in addition to their potential usage as radio-imaging and therapeutic agents. Moreover, metal carbonyls display intense infrared absorptions in the range 1800 to 2200 cm^{-1}, which is the IR transparency window for biological media (Hildebrandt, 2010). In addition to their luminescent properties, the vibrational signature of *fac*-[Re$(CO)_3(NN)$] is appropriate for IR imaging (Policar *et al.*, 2011; Clède *et al.*, 2012). They are thus valuable as small molecular units enabling multimodal imaging involving vibrational-based detections (IR, Raman) and fluorescence (Clède *et al.*, 2012). In [Re$(CO)_3(NN)X$] compounds, the photophysical properties of the complexes are closely dependent on the ligand. When *NN* is a ligand with low π^* orbitals, the corresponding [Re$(CO)_3(NN)$] unit is luminescent (Wrighton & Morse, 1974) and this property has often been used in subcellular bio-imaging (Lo *et al.*, 2012; Baggaley *et al.*, 2012; Xiang *et al.*, 2013; Coogan & Fernandez-Moreira, 2014).

In this communication, we report the synthesis and crystal structure analysis of a novel Re^I complex which contains the
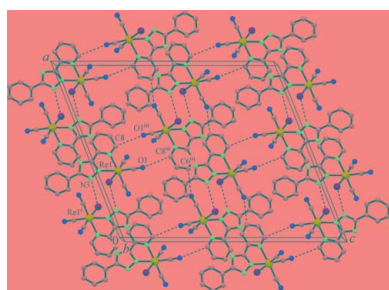
triazole ligand 5-phenyl-3-(pyridin-2-yl)-1H-1,2,4-triazole, [Re(CO)$_3$(C$_{13}$H$_{10}$N$_4$)Br]. Its luminescent properties will be reported in a forthcoming article.
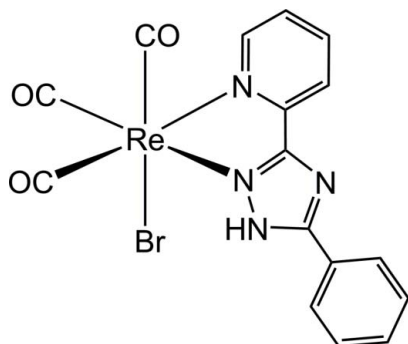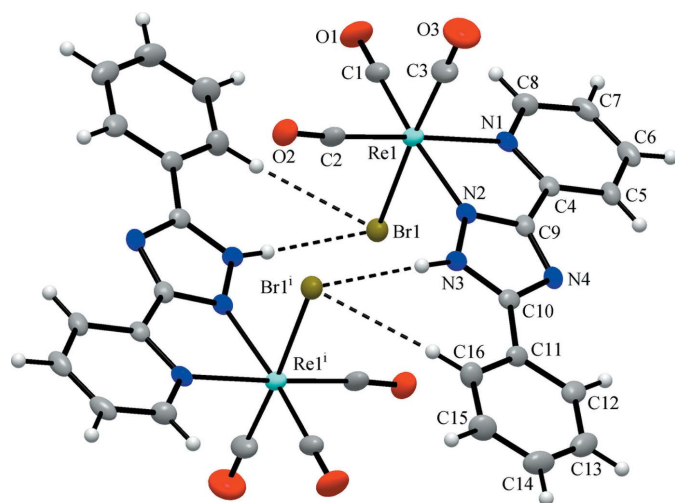

2. Structural commentary

In the title compound, the Re^{I} atom is in a slightly distorted octahedral coordination environment (Fig. 1). The three carbonyl ligands bonded to the Re^{I} atom are arranged in a *fac*-configuration. The distances of C1, C2, and C3 to the Re^{I} atom are 1.905 (4), 1.915 (4), and 1.922 (6) Å, respectively, and the Re—N bonds lengths are 2.201 (3) and 2.164 (3) Å. The CO ligands are almost linearly coordinated with O—C—Re bond angles of 178.4 (4), 175.6 (3) and 179.0 (4)°. The C—Re—C bond angles between CO carbon atoms are 87.78 (17), 90.4 (2) and 89.18 (19)°, close to ideal values, whereas the *cis* equatorial bite angle [N1—Re1—N2] is 74.33 (11)°. All other bond lengths and angles are comparable to those found for related Re^{I} complexes (Rajendran *et al.*, 2000).

3. Supramolecular features

The title compound adopts a typical molecular structure. There is only one relatively strong donor (N—H) and one

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$\cdots$Br1^{i}	0.87	2.51	3.360 (3)	168
C16—H16$\cdots$Br1^{i}	0.94	2.87	3.784 (4)	165
C6—H6$\cdots$O2^{ii}	0.94	2.38	3.194 (5)	145
C8—H8$\cdots$O1^{iii}	0.94	2.56	3.285 (5)	134

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

acceptor (Br) site for hydrogen-bonding interactions, which arrange molecules into dimers (Table 1, Fig. 1). Weak hydrogen bonds of the type C—H$\cdots$O with carbonyl O atoms as acceptor groups play a supporting role in the crystal packing. Nevertheless, these interactions demonstrate a clear discrimination of the C—H binding sites that follow a common pattern. The C—H$\cdots$O hydrogen bonds present are provided by the 2- and 4-C—H protons of the pyridine ring, which are the most polarized and acidic. Besides C—H$\cdots$Br interactions, weak slipped π–π stacking interactions between pyridine and phenyl rings (symmetry code: $1 - x, -y, -z$) [with a shortest separation of C6$\cdots$C11($1 - x, -y, -z$) = 3.265 (6) Å, a centroid-to-centroid distance of 3.785 (5) Å and an interplanar angle of 7.1 (3)°] also appear to be involved in the stabilization of the crystal structure (Fig. 2).

4. Synthesis and crystallization

Pentacarbonylrhenium(I) bromide (0.1 g, 0.246 mmol) was reacted with 5-phenyl-3-(pyridin-2-yl)-1H-1,2,4-triazole (0.1 g, 0.492 mmol) in benzene at 353 K, with stirring, under a steady stream of argon for five h. The dark-yellow solution was removed from the heat and allowed to cool overnight. The yellow product was collected by suction filtration, washed with a 50 ml portion of petroleum ether and dried. Yield = 0.107g,

Figure 1
The structure of the title complex, showing the association of molecules into a centrosymmetric dimer by means of mutual hydrogen bonds of the N—H$\cdots$Br and C—H$\cdots$Br types. Displacement ellipsoids are drawn at the 40% probability level. [Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.]
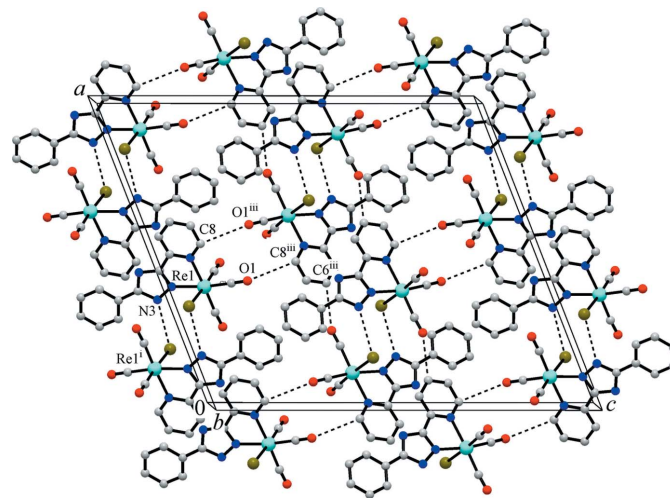

Figure 2
The crystal structure of the title complex, showing weak hydrogen-bonding interactions (indicated by dotted lines) of the type C—H$\cdots$O between carbonyl O atoms and pyridyl C—H groups of the organic ligands. [Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iii) $-x + 1, y, -z + \frac{1}{2}$.]

Table 2
Experimental details.

Crystal data	
Chemical formula	$[ReBr(C_{13}H_{10}N_4)(CO)_3]$
M_r	572.39
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	213
a, b, c (Å)	20.8082 (15), 7.2521 (4), 24.386 (2)
β (°)	111.599 (7)
V (Å^3)	3421.5 (4)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	9.46
Crystal size (mm)	$0.14 \times 0.12 \times 0.11$
Data collection	
Diffractometer	Stoe Imaging plate diffraction system
Absorption correction	Numerical (*X-RED* and *X-SHAPE*; Stoe & Cie, 2001)
T_{min}, T_{max}	0.319, 0.385
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	14578, 4092, 2844
R_{int}	0.057
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.661
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.023, 0.050, 0.84
No. of reflections	4092
No. of parameters	226
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.03, −1.14

Computer programs: *IPDS* (Stoe & Cie, 2001), *SHELXS97* and *SHELXL2014* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 1999) and *WinGX* (Farrugia, 2012).

(76.4%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a methanol solution of the complex. IR (KBr, cm^{-1}): ν_{as}(CO) 2028 (*s*), ν_s(CO) 1912 (*s*).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned with idealized geometry and were refined with C—H = 0.94, N—H = 0.87 Å and U_{iso}(H) = 1.2U_{eq}(C,N).

References

Alberto, R., Schibli, R., Waibel, R., Abram, U. & Schubiger, A. P. (1999). *Coord. Chem. Rev.* **901**, 190–192.

Baggaley, E., Weinstein, J. A. & Williams, J. A. G. (2012). *Coord. Chem. Rev.* **256**, 1762–1785.

Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Clède, S., Lambert, F., Sandt, C., Gueroui, Z., Réfrégiers, M., Plamont, M.-A., Dumas, P., Vessières, A. & Policar, C. (2012). *Chem. Commun.* **48**, 7729–7731.

Coogan, M. P. & Fernandez-Moreira, V. (2014). *Chem. Commun.* **50**, 384–399.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Hildebrandt, P. (2010). *Angew. Chem. Int. Ed.* **49**, 4540–4541.

Lo, K. K.-W., Choi, A. W.-T. & Law, W. H.-T. (2012). *Dalton Trans.* **41**, 6021–6047.

Policar, C., Waern, J. B., Plamont, M. A., Clède, S., Mayet, C., Prazeres, R., Ortega, J.-M., Vessières, A. & Dazzi, A. (2011). *Angew. Chem. Int. Ed.* **50**, 860–864.

Rajendran, T., Manimaran, B., Lee, F.-Y., Lee, G.-H., Peng, S.-M., Wang, C.-C. & Lu, K.-L. (2000). *Inorg. Chem.* **39**, 2016–2017.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Stoe & Cie (2001). *X-SHAPE, X-RED* and *IPDS*. Stoe & Cie GmbH, Darmstadt, Germany.

Striplin, D. R. & Crosby, G. A. (2001). *Coord. Chem. Rev.* **211**, 163–175.

Stufkens, D. J. & Vlček, A. Jr (1998). *Coord. Chem. Rev.* **177**, 127–179.

Volkert, W. A. & Hoffman, T. J. (1999). *Chem. Rev.* **99**, 2269–2292.

Wrighton, M. & Morse, D. L. (1974). *J. Am. Chem. Soc.* **96**, 998–1003.

Xiang, H., Cheng, J., Ma, X., Zhou, X. & Chruma, J. J. (2013). *Chem. Soc. Rev.* **42**, 6128–6185.

supporting information

Crystal structure of bromido-*fac*-tricarbonyl[5-phenyl-3-(pyridin-2-yl)-1*H*-1,2,4-triazole-*κ²N,N′*]rhenium(I)

Kseniia Piletska, Konstantin V. Domasevitch and Alexander V. Shtemenko

Computing details

Data collection: *IPDS* (Stoe & Cie, 2001); cell refinement: *IPDS* (Stoe & Cie, 2001); data reduction: *IPDS* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Bromido-*fac*-tricarbonyl[5-phenyl-3-(pyridin-2-yl)-1*H*-1,2,4-triazole-*κ²N,N′*]rhenium(I)

Crystal data

[ReBr(C$_{13}$H$_{10}$N$_4$)(CO)$_3$]	$F(000) = 2144$
$M_r = 572.39$	$D_x = 2.222$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 20.8082\ (15)$ Å	Cell parameters from 8000 reflections
$b = 7.2521\ (4)$ Å	$\theta = 3.0–28.0°$
$c = 24.386\ (2)$ Å	$\mu = 9.46$ mm^{-1}
$\beta = 111.599\ (7)°$	$T = 213$ K
$V = 3421.5\ (4)$ Å^3	Prism, yellow
$Z = 8$	$0.14 \times 0.12 \times 0.11$ mm

Data collection

Stoe Imaging plate diffraction system diffractometer	4092 independent reflections
	2844 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.057$
φ oscillation scans	$\theta_{max} = 28.0°$, $\theta_{min} = 3.0°$
Absorption correction: numerical (*X-RED* and *X-SHAPE*; Stoe & Cie, 2001)	$h = -27 \rightarrow 27$
	$k = -9 \rightarrow 8$
$T_{min} = 0.319$, $T_{max} = 0.385$	$l = -32 \rightarrow 32$
14578 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.023$	
$wR(F^2) = 0.050$	H-atom parameters constrained
$S = 0.84$	$w = 1/[\sigma^2(F_o^2) + (0.0225P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
4092 reflections	
226 parameters	$(\Delta/\sigma)_{max} = 0.001$
0 restraints	$\Delta\rho_{max} = 1.03$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -1.14$ e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Re1	0.38382 (2)	0.25265 (3)	0.10559 (2)	0.02798 (5)
Br1	0.32731 (2)	0.54427 (7)	0.04146 (2)	0.03557 (11)
O1	0.40827 (17)	0.4654 (6)	0.21974 (13)	0.0594 (10)
O2	0.24980 (15)	0.1146 (5)	0.11477 (13)	0.0516 (10)
O3	0.4540 (2)	−0.0838 (7)	0.17525 (18)	0.0796 (14)
N1	0.48045 (14)	0.3439 (5)	0.09681 (13)	0.0264 (7)
N2	0.38108 (14)	0.1420 (5)	0.02237 (12)	0.0244 (7)
N3	0.33622 (14)	0.0546 (5)	−0.02600 (12)	0.0258 (7)
H3	0.2960	0.0108	−0.0295	0.031*
N4	0.42685 (15)	0.1255 (5)	−0.04749 (13)	0.0255 (7)
C1	0.3988 (2)	0.3830 (7)	0.17704 (17)	0.0372 (12)
C2	0.2983 (2)	0.1674 (7)	0.10904 (15)	0.0361 (11)
C3	0.4289 (2)	0.0391 (9)	0.14970 (19)	0.0463 (13)
C4	0.49040 (18)	0.2879 (5)	0.04763 (16)	0.0246 (9)
C5	0.54965 (18)	0.3314 (7)	0.03688 (17)	0.0297 (9)
H5	0.5554	0.2910	0.0024	0.036*
C6	0.59958 (19)	0.4352 (7)	0.07811 (18)	0.0341 (10)
H6	0.6407	0.4653	0.0725	0.041*
C7	0.58898 (19)	0.4942 (6)	0.12745 (18)	0.0347 (10)
H7	0.6225	0.5668	0.1557	0.042*
C8	0.5289 (2)	0.4467 (7)	0.13551 (17)	0.0340 (10)
H8	0.5220	0.4883	0.1694	0.041*
C9	0.43441 (18)	0.1817 (6)	0.00714 (16)	0.0258 (8)
C10	0.36475 (18)	0.0474 (6)	−0.06765 (15)	0.0246 (8)
C11	0.33235 (18)	−0.0329 (6)	−0.12595 (15)	0.0268 (9)
C12	0.3677 (2)	−0.0228 (7)	−0.16469 (17)	0.0337 (10)
H12	0.4104	0.0389	−0.1534	0.040*
C13	0.3397 (3)	−0.1037 (7)	−0.21942 (18)	0.0426 (12)
H13	0.3636	−0.0967	−0.2454	0.051*
C14	0.2775 (3)	−0.1946 (7)	−0.23681 (19)	0.0448 (12)
H14	0.2592	−0.2506	−0.2741	0.054*
C15	0.2425 (2)	−0.2025 (7)	−0.19894 (19)	0.0403 (12)
H15	0.1998	−0.2636	−0.2106	0.048*
C16	0.2693 (2)	−0.1219 (7)	−0.14401 (18)	0.0369 (11)
H16	0.2446	−0.1276	−0.1187	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Re1	0.02700 (7)	0.03224 (11)	0.02386 (7)	−0.00874 (8)	0.00836 (5)	0.00069 (8)
Br1	0.03230 (18)	0.0375 (3)	0.03867 (19)	−0.0024 (2)	0.01516 (15)	0.0035 (2)
O1	0.068 (2)	0.075 (3)	0.0338 (16)	−0.021 (2)	0.0179 (15)	−0.0196 (19)
O2	0.0364 (15)	0.077 (3)	0.0440 (17)	−0.0237 (18)	0.0178 (13)	−0.0038 (18)
O3	0.081 (3)	0.071 (4)	0.079 (3)	0.009 (3)	0.020 (2)	0.034 (3)
N1	0.0216 (14)	0.022 (2)	0.0309 (15)	−0.0032 (15)	0.0036 (12)	0.0023 (15)
N2	0.0224 (14)	0.019 (2)	0.0291 (15)	−0.0061 (14)	0.0071 (12)	0.0002 (14)
N3	0.0250 (14)	0.023 (2)	0.0270 (14)	−0.0053 (15)	0.0074 (11)	−0.0012 (15)
N4	0.0240 (14)	0.018 (2)	0.0350 (16)	−0.0011 (14)	0.0116 (12)	0.0018 (15)
C1	0.032 (2)	0.049 (4)	0.0275 (19)	−0.009 (2)	0.0074 (15)	0.004 (2)
C2	0.036 (2)	0.047 (3)	0.0221 (17)	−0.013 (2)	0.0068 (15)	−0.0053 (19)
C3	0.041 (2)	0.053 (4)	0.043 (2)	−0.007 (3)	0.0144 (19)	0.017 (3)
C4	0.0250 (16)	0.015 (3)	0.0322 (17)	0.0002 (15)	0.0084 (13)	0.0071 (15)
C5	0.0245 (17)	0.023 (3)	0.042 (2)	0.0009 (18)	0.0128 (16)	0.009 (2)
C6	0.0243 (18)	0.021 (3)	0.052 (2)	−0.0034 (19)	0.0086 (17)	0.014 (2)
C7	0.0268 (18)	0.018 (3)	0.047 (2)	−0.0065 (18)	−0.0005 (16)	0.009 (2)
C8	0.038 (2)	0.024 (3)	0.0353 (19)	−0.007 (2)	0.0078 (16)	−0.003 (2)
C9	0.0266 (17)	0.016 (2)	0.0354 (19)	0.0016 (17)	0.0123 (15)	0.0062 (17)
C10	0.0298 (18)	0.013 (2)	0.0293 (17)	0.0031 (17)	0.0089 (14)	0.0020 (17)
C11	0.0324 (19)	0.018 (3)	0.0287 (17)	0.0041 (18)	0.0099 (15)	−0.0024 (17)
C12	0.044 (2)	0.022 (3)	0.037 (2)	0.005 (2)	0.0161 (17)	0.0047 (19)
C13	0.065 (3)	0.030 (3)	0.039 (2)	0.012 (2)	0.025 (2)	0.002 (2)
C14	0.066 (3)	0.030 (3)	0.033 (2)	0.002 (2)	0.012 (2)	−0.008 (2)
C15	0.048 (2)	0.027 (4)	0.041 (2)	−0.006 (2)	0.0107 (19)	−0.013 (2)
C16	0.037 (2)	0.033 (3)	0.042 (2)	0.001 (2)	0.0155 (18)	−0.008 (2)

Geometric parameters (Å, º)

Re1—C1	1.905 (4)	C5—C6	1.374 (6)
Re1—C2	1.915 (4)	C5—H5	0.9400
Re1—C3	1.922 (6)	C6—C7	1.369 (6)
Re1—N2	2.164 (3)	C6—H6	0.9400
Re1—N1	2.201 (3)	C7—C8	1.380 (5)
Re1—Br1	2.6357 (5)	C7—H7	0.9400
O1—C1	1.153 (5)	C8—H8	0.9400
O2—C2	1.135 (4)	C10—C11	1.453 (5)
O3—C3	1.103 (6)	C11—C16	1.380 (6)
N1—C8	1.327 (5)	C11—C12	1.397 (5)
N1—C4	1.352 (5)	C12—C13	1.376 (6)
N2—C9	1.325 (4)	C12—H12	0.9400
N2—N3	1.361 (4)	C13—C14	1.373 (7)
N3—C10	1.353 (4)	C13—H13	0.9400
N3—H3	0.8700	C14—C15	1.371 (6)
N4—C10	1.328 (5)	C14—H14	0.9400
N4—C9	1.346 (5)	C15—C16	1.377 (6)

C4—C5	1.388 (5)	C15—H15	0.9400
C4—C9	1.442 (5)	C16—H16	0.9400
C1—Re1—C2	87.78 (17)	C7—C6—C5	119.4 (3)
C1—Re1—C3	90.4 (2)	C7—C6—H6	120.3
C2—Re1—C3	89.18 (19)	C5—C6—H6	120.3
C1—Re1—N2	168.91 (15)	C6—C7—C8	119.7 (4)
C2—Re1—N2	102.56 (14)	C6—C7—H7	120.2
C3—Re1—N2	93.71 (18)	C8—C7—H7	120.2
C1—Re1—N1	95.31 (14)	N1—C8—C7	122.0 (4)
C2—Re1—N1	176.88 (13)	N1—C8—H8	119.0
C3—Re1—N1	91.22 (15)	C7—C8—H8	119.0
N2—Re1—N1	74.33 (11)	N2—C9—N4	114.0 (3)
C1—Re1—Br1	91.81 (14)	N2—C9—C4	118.2 (3)
C2—Re1—Br1	93.80 (15)	N4—C9—C4	127.6 (3)
C3—Re1—Br1	176.38 (12)	N4—C10—N3	110.0 (3)
N2—Re1—Br1	83.63 (9)	N4—C10—C11	124.8 (3)
N1—Re1—Br1	85.69 (9)	N3—C10—C11	125.2 (3)
C8—N1—C4	118.4 (3)	C16—C11—C12	118.9 (4)
C8—N1—Re1	125.5 (3)	C16—C11—C10	122.9 (3)
C4—N1—Re1	116.1 (2)	C12—C11—C10	118.1 (3)
C9—N2—N3	103.7 (3)	C13—C12—C11	119.6 (4)
C9—N2—Re1	116.5 (3)	C13—C12—H12	120.2
N3—N2—Re1	139.3 (2)	C11—C12—H12	120.2
C10—N3—N2	108.5 (3)	C14—C13—C12	121.3 (4)
C10—N3—H3	125.7	C14—C13—H13	119.4
N2—N3—H3	125.7	C12—C13—H13	119.4
C10—N4—C9	103.8 (3)	C15—C14—C13	119.0 (4)
O1—C1—Re1	178.4 (4)	C15—C14—H14	120.5
O2—C2—Re1	175.6 (3)	C13—C14—H14	120.5
O3—C3—Re1	179.0 (4)	C14—C15—C16	120.8 (4)
N1—C4—C5	122.4 (4)	C14—C15—H15	119.6
N1—C4—C9	114.8 (3)	C16—C15—H15	119.6
C5—C4—C9	122.8 (3)	C15—C16—C11	120.4 (4)
C6—C5—C4	118.1 (4)	C15—C16—H16	119.8
C6—C5—H5	120.9	C11—C16—H16	119.8
C4—C5—H5	120.9		
C9—N2—N3—C10	−0.3 (4)	C5—C4—C9—N2	177.7 (4)
Re1—N2—N3—C10	170.7 (3)	N1—C4—C9—N4	172.3 (4)
C8—N1—C4—C5	1.1 (6)	C5—C4—C9—N4	−7.0 (7)
Re1—N1—C4—C5	−178.5 (3)	C9—N4—C10—N3	−0.7 (5)
C8—N1—C4—C9	−178.2 (4)	C9—N4—C10—C11	179.0 (4)
Re1—N1—C4—C9	2.2 (4)	N2—N3—C10—N4	0.7 (5)
N1—C4—C5—C6	0.0 (6)	N2—N3—C10—C11	−179.1 (4)
C9—C4—C5—C6	179.3 (4)	N4—C10—C11—C16	176.3 (4)
C4—C5—C6—C7	−1.0 (6)	N3—C10—C11—C16	−4.0 (7)
C5—C6—C7—C8	0.9 (7)	N4—C10—C11—C12	−2.2 (6)

C4—N1—C8—C7	−1.3 (6)	N3—C10—C11—C12	177.5 (4)
Re1—N1—C8—C7	178.3 (3)	C16—C11—C12—C13	−1.0 (7)
C6—C7—C8—N1	0.3 (7)	C10—C11—C12—C13	177.5 (4)
N3—N2—C9—N4	−0.1 (5)	C11—C12—C13—C14	0.0 (7)
Re1—N2—C9—N4	−173.6 (3)	C12—C13—C14—C15	0.8 (7)
N3—N2—C9—C4	175.8 (3)	C13—C14—C15—C16	−0.5 (7)
Re1—N2—C9—C4	2.3 (5)	C14—C15—C16—C11	−0.5 (7)
C10—N4—C9—N2	0.5 (5)	C12—C11—C16—C15	1.2 (7)
C10—N4—C9—C4	−174.9 (4)	C10—C11—C16—C15	−177.1 (4)
N1—C4—C9—N2	−3.0 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···Br1[i]	0.87	2.51	3.360 (3)	168
C16—H16···Br1[i]	0.94	2.87	3.784 (4)	165
C6—H6···O2[ii]	0.94	2.38	3.194 (5)	145
C8—H8···O1[iii]	0.94	2.56	3.285 (5)	134

Symmetry codes: (i) −*x*+1/2, −*y*+1/2, −*z*; (ii) *x*+1/2, *y*+1/2, *z*; (iii) −*x*+1, *y*, −*z*+1/2.