Synthesis, spectroscopic analysis and crystal structure of (N-{2-[(2-aminoethyl)amino]ethyl}-4′-methyl-[1,1′-biphenyl]-4-sulfonamidato)tricarbonylrhenium(I)

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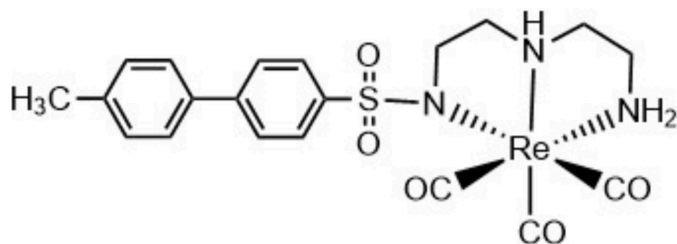
The title compound, $[Re(C_{17}H_{22}N_3O_2S)(CO)_3]$ is a net neutral *fac*-Re(I)(CO)$_3$ complex of the 4-methylbiphenyl sulfonamide derivatized diethylenetriamine ligand. The NNN-donor monoanionic ligand coordinates with the Re core in tridentate fashion, establishing an inner coordination sphere resulting in a net neutral complex. The complex possesses pseudo-octahedral geometry where one face of the octahedron is occupied by three carbonyl ligands and the other faces are occupied by one sp^2 nitrogen atom of the sulfonamide group and two sp^3 nitrogen atoms of the dien backbone. The Re—Nsp^2 bond distance, 2.173 (4) Å, is shorter than the Re—Nsp^3 bond distances, 2.217 (5) and 2.228 (6) Å, and is similar to the range reported for typical Re—Nsp^2 bond lengths (2.14 to 2.18 Å).

1. Chemical context

Organometallic compounds have garnered significant interest due to their notable properties in cell imaging and anticancer applications. Particularly, Re complexes are noted for their kinetic inertness and large Stokes shift (Stephenson *et al.*, 2004; Guo *et al.*, 1997). Research has shown that tridentate ligand systems are more robust and possess better pharmacokinetics than those bearing bidentate ligands, leading to reduced side effects (Schibli *et al.*, 2000). Our focus involves a sulfonamide ligand, which has a diethylenetriamine (dien) backbone and 4-methylbiphenyl (4-Mebip) as the pendant group. The N(SO$_2$)(4-Mebip)dienH ligand, along with its bidentate Pt^{II} complex have both been reported to exhibit remarkable anticancer properties against non-small lung cancer (Kaluthanthiri *et al.*, 2023). Motivated by its potential as a cytotoxic drug lead, here we have focused on rhenium, in its lowest oxidation state because it exhibits less reactivity toward species in the cellular environment (Schibli & Schubiger, 2002). Given rhenium's soft metal center characteristics, a preference for soft donors, particularly nitrogen, is observed and tridentate metal complexes featuring nitrogen donors are commonly employed (Christoforou *et al.*, 2007; Kaushalya *et al.*, 2022; Darshani *et al.*, 2020). In this study, the Re(CO)$_3$[N(SO$_2$)(4-Mebip)dien] complex was successfully synthesized and its molecular structure was confirmed by single-crystal X-ray diffraction analysis and ^{1}H NMR spectroscopy. Furthermore, comprehensive characterization was conducted using FTIR, UV–vis, and fluorescence spectroscopic techniques.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H11N···O3^{i}	0.89	2.27	3.053 (7)	146
N1—H12N···O2^{ii}	0.89	2.59	3.028 (7)	111
N2—H2N···O4^{iii}	0.98	1.98	2.941 (5)	167

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

hydrogen bonding. Interleaved between the double-stranded hydrogen-bonded chains are hydrophobic layers of stacked
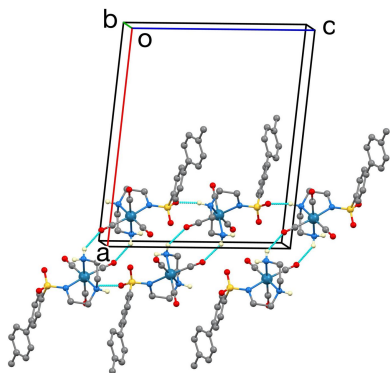
2. Structural commentary

The Re(CO)$_3$[N(SO$_2$)(4-Mebip)dien] complex is shown in Fig. 1. The Re—C distances in Re—CO bonds are in the range of 1.895 (8)–1.914 (6) Å, which is consistent with related data reported (Christoforou *et al.*, 2007; Darshani *et al.*, 2020). The longest Re—C distance is *trans* to the sp^2 nitrogen atom N3. The C11—C14 bond distance between the two phenyl rings of the anionic ligand in the biphenyl group in Re(CO)$_3$ [N(SO$_2$)(4-Mebip)dien] is 1.484 (8) Å. The biphenyl moiety is twisted out of planarity, the dihedral angle between the two planes being 36.5 (3)°. The average Re—N bond length in our Re complex is 2.206 Å, which is consistent with the distances found in related Re(CO)$_3$ complexes containing a dien backbone (Christoforou *et al.*, 2007). The Re—N3 bond (sp^2 nitrogen) distance [2.173 (4) Å] in the complex is significantly shorter than the other Re—N (sp^3 N) bonds [2.217 (5) and 2.228 (6) Å], which explains the anionic nature of the N3 amino nitrogen. The S—N bond length for the deprotonated sulfonamido group is 1.579 (4) Å for the complex and is within the accepted range for S—N bonds available in deprotonated sulfonamides coordinated to Re, Cu and Zn metals (Christoforou *et al.*, 2007; Goodwin *et al.*, 2004; Congreve *et al.*, 2003).

3. Supramolecular features

The unit cell is shown in Fig. 2. The intermolecular interactions are predominantly N—H···O hydrogen bonds as listed in Table 1 and shown in Fig. 3. The N1···O2 separations in these hydrogen bonds are in the range 2.941 (5)–3.053 (7) Å. The graph sets (Etter *et al.*, 1990) are centrosymmetric $R_2^2(10)$ rings and $C_1^1(6)$ chains, forming double-stranded chains in the [001] direction. One of the NH$_2$ H atoms is not involved in the

Figure 2
View of the unit cell. H atoms are not shown.

Figure 3
View of the hydrogen bonding, shown as blue dashed lines, and chain formation along the [001] direction. H atoms on C are omitted and the unit cell axes are shown.
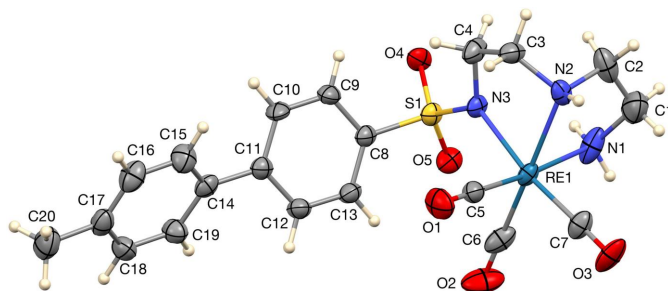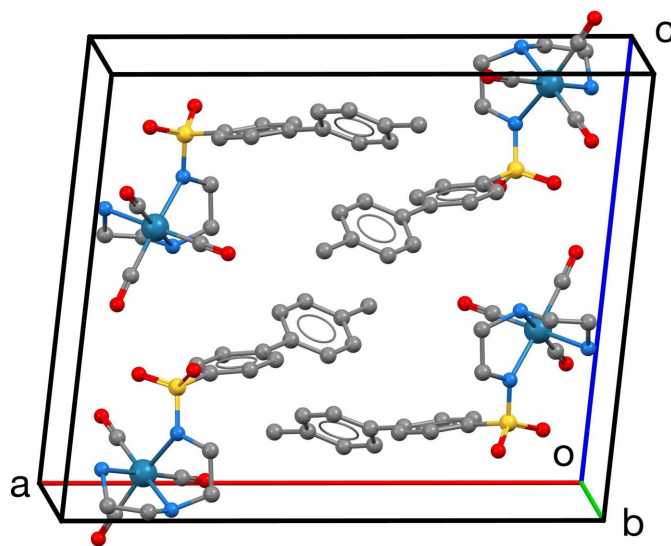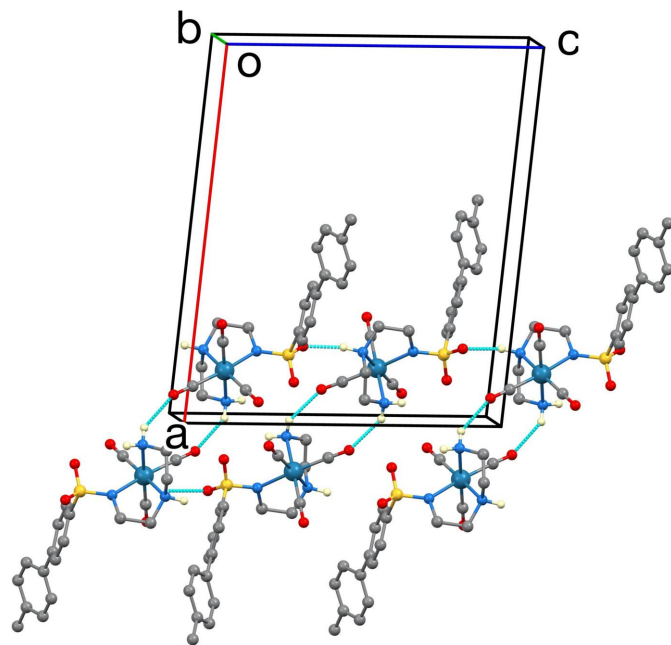

Figure 1
The asymmetric unit with 50% probability displacement ellipsoids and atom labels. H atoms are represented by spheres of arbitrary radius.

biphenyl moieties, as can be seen in Fig. 2. The closest distance [4.079 (4) Å] between centers of gravity (Cg) of these rings is between the phenyl ring C14–C19 carrying the methyl group and its centrosymmetric equivalent at $1 - x$, $2 - y$, $2 - z$. There are no other $Cg \cdots Cg$ distances closer than 5.5 Å. The phenyl ring C8–C13 has no close intermolecular contacts to other phenyl rings, but has a close contact to carbonyl C5—O1 at x, $\frac{3}{2} - y$, $-\frac{1}{2} + z$, with $Cg \cdots$ O1 3.758 (7) Å.

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.45, update of March 2024; Groom *et al.*, 2016) for the diethylenetriamine $SO_2Re(CO)_3$ fragment yielded four hits, LIMDIV and LIMDOB (Christoforou *et al.*, 2007); SUNFUF and SUNGAM (Darshani *et al.*, 2020). These structures have been mentioned above. A similar search for [*N*-(2-aminoethyl)ethane-1,2-diamine]Re(CO)$_3$ salts yielded seven hits: BUPXAO, BUPXES, BUPYIX, and BUPYOD (Abhaya-wardhana *et al.*, 2020), IWENAZ (Mundwiler *et al.*, 2004), TIYVIH and TIYVON (Christoforou *et al.*, 2007). In these structures, the Re—N distances are in the range 2.203 (7)–2.244 (3) Å, with a mean value 2.219 Å for 21 individual measurements. The Re—C distances are in the range 1.878 (12)–1.956 (15) Å with a mean value 1.917 Å. There is no indication that the Re—N or Re—C distances to the central ligand atoms differ from those to the terminal atoms.

5. Synthesis, crystallization and spectroscopic data

The ligand N(SO$_2$)(4-Mebip)dienH was synthesized by following a reported procedure (Fig. 4; Kaluthanthiri *et al.*, 2023). A solution of the ligand N(SO$_2$)(4-Mebip)dienH (0.0272 g, 0.0816 mmol) in 2 ml of methanol was added to a solution of [Re(CO)$_3$(H$_2$O)$_3$]Br (0.033 g, 0.0816 mmol) in 3 ml of water. The solution was then adjusted to pH 7–8 with aqueous NaOH and refluxed for 16 h (Fig. 4). The complex formed was collected by filtration as a white powder (0.025 g, 51% yield). Crystals suitable for X-ray crystallography were grown by slow evaporation of an acetonitrile/ methanol solution. UV–vis (MeOH) [λ_{max} (nm)]: 203, 266; FT–IR (ATR) (cm^{-1}): 969 ([(S—N)], 1342, 1128 [ν(S=O)], 2008, 1865 [ν(CO)]. ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm): 7.81 (*m*, 2H, Ha/a′), 7.74 (*m*, 2H, Hb/b′), 7.62 (*m*, 2H, Hc/c′) 7.29 (*m*, 2H, Hd/d′), 6.69 (*b*, 1H, N2H), 5.15 (*m*, 1H, *endo* N1H),
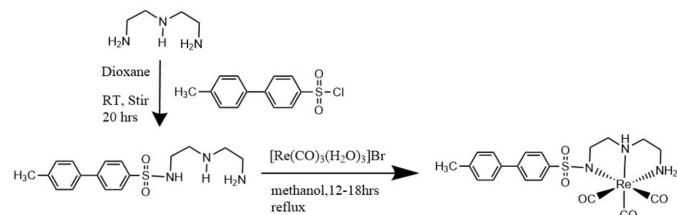
3.47 (*m*, 1H, *exo* N1H), 3.34–3.38 (*m*, 1H, CH), 2.64–2.90 (*m*, 7H, CH$_2$), 2.35 (*s*, 3H, CH$_3$). Although the ligand shows excellent fluorescence properties even at low concentrations, its Re complex offers quenched fluorescence properties attributed to the direct binding of sulfonamide nitrogen to Re center in the complex (Fig. 5). Furthermore, a slight blue shift (about 9 nm) was observed in the complex.

Table 2
Experimental details.

Crystal data	
Chemical formula	[Re(C$_{17}$H$_{22}$N$_3$O$_2$S)(CO)$_3$]
M_r	602.66
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	18.5651 (9), 7.6604 (4), 15.4897 (11)
β (°)	95.472 (2)
V (Å^3)	2192.8 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.67
Crystal size (mm)	0.22 × 0.13 × 0.05
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.572, 0.765
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	119413, 4849, 3513
R_{int}	0.102
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.643
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.071, 1.08
No. of reflections	4849
No. of parameters	273
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.00, −1.80

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/1* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

Figure 4
Synthetic route for preparation of N(SO$_2$)(4-Mebip)dienH and Re(CO)$_3$[N(SO$_2$)(4-Mebip)dien].

Figure 5
Fluorescence emission spectra of N(SO$_2$)(4-Mebip)dienH and Re(CO)$_3$[N(SO$_2$)(4-Mebip)dien] in methanol at 298 K.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were located in difference maps and treated as riding in geometrically idealized positions with C—H distances of 0.94 Å and with U_{iso}(H) = $1.2U_{eq}$ for the attached C atom (0.97 Å and $1.5U_{eq}$ for the methyl group). The H atoms on nitrogen had N—H distances of 0.89 Å for NH$_2$ and 0.98 Å for NH, and U_{iso} values were assigned as $1.2U_{eq}$ for the N atom.

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Synthesis, spectroscopic analysis and crystal structure of (*N*-{2-[(2-aminoethyl)-amino]ethyl}-4′-methyl-[1,1′-biphenyl]-4-sulfonamidato)tricarbonylrhenium(I)

Dinithi Kaluthanthiri, Theshini Perera and Frank R. Fronczek

Computing details

(*N*-{2-[(2-Aminoethyl)amino]ethyl}-4′-methyl-[1,1′-biphenyl]-4-sulfonamidato)tricarbonylrhenium(I)

Crystal data

[Re(C$_{17}$H$_{22}$N$_3$O$_2$S)(CO)$_3$]	$F(000) = 1176$
$M_r = 602.66$	$D_x = 1.825$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 18.5651$ (9) Å	Cell parameters from 2346 reflections
$b = 7.6604$ (4) Å	$\theta = 2.6$–24.1°
$c = 15.4897$ (11) Å	$\mu = 5.67$ mm^{-1}
$\beta = 95.472$ (2)°	$T = 296$ K
$V = 2192.8$ (2) Å^3	Needle, colorless
$Z = 4$	$0.22 \times 0.13 \times 0.05$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer	119413 measured reflections
Radiation source: fine-focus sealed tube	4849 independent reflections
TRIUMPH curved graphite monochromator	3513 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.102$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$\theta_{max} = 27.2°$, $\theta_{min} = 1.1°$
$T_{min} = 0.572$, $T_{max} = 0.765$	$h = -23 \rightarrow 23$
	$k = -9 \rightarrow 9$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2 + 6.5423P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.035$	
$wR(F^2) = 0.071$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.08$	$\Delta\rho_{max} = 2.00$ e Å^{-3}
4849 reflections	$\Delta\rho_{min} = -1.80$ e Å^{-3}
273 parameters	Extinction correction: *SHELXL2017/1* (Sheldrick 2015b), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
0 restraints	
Hydrogen site location: inferred from neighbouring sites	Extinction coefficient: 0.00017 (5)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Re1	0.86146 (2)	0.45261 (3)	0.61070 (2)	0.04344 (9)
S1	0.82122 (8)	0.3572 (2)	0.81148 (8)	0.0456 (4)
O1	0.7335 (3)	0.7018 (7)	0.5732 (4)	0.0875 (16)
O2	0.9354 (3)	0.7562 (8)	0.7131 (3)	0.104 (2)
O3	0.9230 (3)	0.6052 (8)	0.4508 (3)	0.0879 (17)
O4	0.8016 (2)	0.2083 (5)	0.8619 (2)	0.0563 (11)
O5	0.8906 (2)	0.4354 (6)	0.8338 (2)	0.0568 (11)
N1	0.9482 (3)	0.2530 (9)	0.6360 (3)	0.0769 (19)
H11N	0.991541	0.302049	0.634639	0.092*
H12N	0.945892	0.205082	0.688023	0.092*
N2	0.8135 (3)	0.2133 (6)	0.5486 (3)	0.0487 (12)
H2N	0.801808	0.237533	0.486680	0.058*
N3	0.8132 (2)	0.3099 (6)	0.7118 (2)	0.0440 (12)
C1	0.9364 (5)	0.1159 (12)	0.5660 (6)	0.099 (3)
H1C	0.949062	0.163356	0.511455	0.119*
H1D	0.967551	0.016551	0.580794	0.119*
C2	0.8629 (5)	0.0603 (10)	0.5568 (4)	0.080 (2)
H2A	0.852992	−0.008484	0.606844	0.096*
H2B	0.854413	−0.012739	0.505655	0.096*
C3	0.7445 (4)	0.1752 (9)	0.5872 (4)	0.0598 (18)
H3A	0.727485	0.059835	0.569374	0.072*
H3B	0.707984	0.259311	0.565914	0.072*
C4	0.7553 (4)	0.1838 (10)	0.6838 (4)	0.0655 (19)
H4A	0.710554	0.219162	0.706318	0.079*
H4B	0.768274	0.069138	0.706919	0.079*
C5	0.7818 (4)	0.6059 (8)	0.5873 (4)	0.0525 (16)
C6	0.9077 (4)	0.6386 (11)	0.6748 (4)	0.069 (2)
C7	0.9009 (3)	0.5469 (10)	0.5110 (4)	0.0607 (17)
C8	0.7558 (3)	0.5190 (8)	0.8291 (3)	0.0457 (14)
C9	0.6854 (3)	0.4687 (8)	0.8401 (4)	0.0550 (16)
H9	0.672952	0.351064	0.838917	0.066*
C10	0.6339 (3)	0.5938 (8)	0.8529 (4)	0.0561 (17)
H10	0.586941	0.558250	0.860192	0.067*
C11	0.6498 (3)	0.7698 (8)	0.8553 (3)	0.0492 (15)
C12	0.7211 (3)	0.8167 (8)	0.8449 (4)	0.0534 (16)
H12	0.733858	0.934122	0.846868	0.064*
C13	0.7730 (3)	0.6936 (8)	0.8319 (4)	0.0506 (15)
H13	0.820003	0.728879	0.824931	0.061*
C14	0.5948 (3)	0.9040 (8)	0.8704 (4)	0.0517 (16)

C15	0.5233 (4)	0.8895 (10)	0.8371 (4)	0.070 (2)
H15	0.508519	0.791583	0.804678	0.084*
C16	0.4733 (4)	1.0176 (11)	0.8511 (5)	0.075 (2)
H16	0.425596	1.003962	0.827930	0.090*
C17	0.4927 (4)	1.1647 (10)	0.8984 (5)	0.0662 (19)
C18	0.5630 (4)	1.1776 (9)	0.9336 (5)	0.0654 (18)
H18	0.577106	1.273921	0.967606	0.079*
C19	0.6130 (4)	1.0513 (9)	0.9197 (4)	0.0613 (16)
H19	0.660456	1.064908	0.944103	0.074*
C20	0.4383 (4)	1.3088 (11)	0.9120 (5)	0.092 (3)
H20A	0.461891	1.420204	0.911398	0.138*
H20B	0.419068	1.292329	0.966780	0.138*
H20C	0.399557	1.304649	0.866244	0.138*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Re1	0.04118 (13)	0.06022 (16)	0.02905 (11)	−0.00246 (13)	0.00405 (8)	0.00870 (12)
S1	0.0592 (9)	0.0527 (9)	0.0250 (6)	−0.0062 (8)	0.0056 (6)	0.0006 (6)
O1	0.070 (3)	0.073 (4)	0.118 (4)	0.023 (3)	0.002 (3)	−0.001 (3)
O2	0.113 (5)	0.112 (5)	0.079 (4)	−0.062 (4)	−0.029 (3)	0.013 (3)
O3	0.071 (3)	0.134 (5)	0.062 (3)	−0.002 (3)	0.023 (2)	0.050 (3)
O4	0.090 (3)	0.052 (3)	0.0283 (19)	−0.006 (2)	0.012 (2)	0.0072 (18)
O5	0.056 (2)	0.074 (3)	0.039 (2)	−0.009 (2)	−0.0056 (18)	−0.002 (2)
N1	0.044 (3)	0.138 (6)	0.049 (3)	0.022 (3)	0.008 (3)	0.029 (4)
N2	0.071 (3)	0.047 (3)	0.028 (2)	0.012 (3)	0.006 (2)	0.004 (2)
N3	0.055 (3)	0.055 (3)	0.023 (2)	−0.009 (2)	0.0078 (19)	−0.002 (2)
C1	0.085 (6)	0.093 (7)	0.126 (8)	0.017 (5)	0.041 (6)	0.006 (6)
C2	0.112 (7)	0.076 (5)	0.052 (4)	0.042 (5)	0.008 (4)	−0.002 (4)
C3	0.080 (5)	0.056 (4)	0.044 (3)	−0.025 (4)	0.010 (3)	−0.003 (3)
C4	0.070 (4)	0.087 (5)	0.041 (3)	−0.027 (4)	0.016 (3)	−0.015 (3)
C5	0.059 (4)	0.049 (4)	0.051 (4)	−0.009 (3)	0.013 (3)	−0.004 (3)
C6	0.056 (4)	0.100 (6)	0.050 (4)	−0.017 (4)	−0.004 (3)	0.027 (4)
C7	0.053 (4)	0.084 (5)	0.045 (3)	0.005 (4)	0.006 (3)	0.016 (4)
C8	0.057 (4)	0.050 (4)	0.031 (3)	−0.012 (3)	0.010 (2)	−0.005 (2)
C9	0.070 (4)	0.043 (3)	0.053 (3)	−0.019 (4)	0.016 (3)	−0.011 (3)
C10	0.050 (4)	0.055 (4)	0.065 (4)	−0.028 (3)	0.014 (3)	−0.015 (3)
C11	0.060 (4)	0.052 (4)	0.036 (3)	−0.007 (3)	0.008 (3)	−0.001 (3)
C12	0.064 (4)	0.044 (4)	0.053 (4)	−0.012 (3)	0.011 (3)	0.001 (3)
C13	0.053 (4)	0.054 (4)	0.047 (3)	−0.015 (3)	0.012 (3)	−0.001 (3)
C14	0.053 (4)	0.062 (4)	0.040 (3)	−0.006 (3)	0.008 (3)	0.009 (3)
C15	0.065 (5)	0.087 (6)	0.057 (4)	−0.003 (4)	0.001 (3)	−0.011 (4)
C16	0.053 (4)	0.109 (7)	0.063 (4)	0.001 (4)	0.002 (3)	0.005 (4)
C17	0.069 (5)	0.069 (5)	0.065 (4)	0.011 (4)	0.025 (4)	0.016 (4)
C18	0.068 (5)	0.046 (4)	0.083 (5)	0.002 (4)	0.013 (4)	−0.002 (4)
C19	0.056 (4)	0.055 (4)	0.072 (4)	−0.001 (4)	0.002 (3)	−0.003 (4)
C20	0.075 (5)	0.100 (7)	0.106 (6)	0.019 (5)	0.030 (5)	0.012 (5)

Geometric parameters (Å, º)

Re1—C6	1.895 (8)	C4—H4A	0.9700
Re1—C5	1.896 (7)	C4—H4B	0.9700
Re1—C7	1.914 (6)	C8—C13	1.375 (8)
Re1—N3	2.173 (4)	C8—C9	1.389 (8)
Re1—N2	2.217 (5)	C9—C10	1.381 (9)
Re1—N1	2.228 (6)	C9—H9	0.9300
S1—O5	1.433 (4)	C10—C11	1.381 (8)
S1—O4	1.448 (4)	C10—H10	0.9300
S1—N3	1.579 (4)	C11—C12	1.394 (8)
S1—C8	1.775 (6)	C11—C14	1.484 (8)
O1—C5	1.163 (7)	C12—C13	1.376 (8)
O2—C6	1.170 (9)	C12—H12	0.9300
O3—C7	1.143 (7)	C13—H13	0.9300
N1—C1	1.510 (10)	C14—C15	1.381 (9)
N1—H11N	0.8900	C14—C19	1.387 (9)
N1—H12N	0.8900	C15—C16	1.381 (10)
N2—C2	1.486 (8)	C15—H15	0.9300
N2—C3	1.493 (7)	C16—C17	1.372 (10)
N2—H2N	0.9800	C16—H16	0.9300
N3—C4	1.479 (7)	C17—C18	1.370 (9)
C1—C2	1.423 (10)	C17—C20	1.524 (9)
C1—H1C	0.9700	C18—C19	1.372 (9)
C1—H1D	0.9700	C18—H18	0.9300
C2—H2A	0.9700	C19—H19	0.9300
C2—H2B	0.9700	C20—H20A	0.9600
C3—C4	1.493 (8)	C20—H20B	0.9600
C3—H3A	0.9700	C20—H20C	0.9600
C3—H3B	0.9700		
C6—Re1—C5	86.6 (3)	H3A—C3—H3B	108.1
C6—Re1—C7	87.1 (3)	N3—C4—C3	110.3 (5)
C5—Re1—C7	87.9 (3)	N3—C4—H4A	109.6
C6—Re1—N3	101.4 (2)	C3—C4—H4A	109.6
C5—Re1—N3	94.7 (2)	N3—C4—H4B	109.6
C7—Re1—N3	171.2 (2)	C3—C4—H4B	109.6
C6—Re1—N2	172.9 (2)	H4A—C4—H4B	108.1
C5—Re1—N2	99.0 (2)	O1—C5—Re1	179.1 (6)
C7—Re1—N2	97.5 (2)	O2—C6—Re1	178.4 (7)
N3—Re1—N2	73.78 (16)	O3—C7—Re1	178.4 (6)
C6—Re1—N1	98.1 (3)	C13—C8—C9	119.0 (6)
C5—Re1—N1	174.9 (3)	C13—C8—S1	121.6 (5)
C7—Re1—N1	94.3 (2)	C9—C8—S1	119.4 (5)
N3—Re1—N1	82.45 (18)	C10—C9—C8	119.9 (6)
N2—Re1—N1	76.3 (2)	C10—C9—H9	120.1
O5—S1—O4	117.7 (3)	C8—C9—H9	120.1
O5—S1—N3	109.4 (2)	C11—C10—C9	122.1 (6)

O4—S1—N3	110.0 (2)	C11—C10—H10	118.9
O5—S1—C8	106.5 (3)	C9—C10—H10	118.9
O4—S1—C8	104.8 (3)	C10—C11—C12	116.9 (6)
N3—S1—C8	108.0 (3)	C10—C11—C14	122.1 (6)
C1—N1—Re1	107.3 (4)	C12—C11—C14	121.0 (6)
C1—N1—H11N	110.2	C13—C12—C11	121.7 (6)
Re1—N1—H11N	110.2	C13—C12—H12	119.2
C1—N1—H12N	110.2	C11—C12—H12	119.2
Re1—N1—H12N	110.2	C8—C13—C12	120.5 (6)
H11N—N1—H12N	108.5	C8—C13—H13	119.8
C2—N2—C3	111.0 (5)	C12—C13—H13	119.8
C2—N2—Re1	113.3 (4)	C15—C14—C19	116.5 (6)
C3—N2—Re1	108.2 (3)	C15—C14—C11	122.5 (6)
C2—N2—H2N	108.1	C19—C14—C11	120.9 (6)
C3—N2—H2N	108.1	C14—C15—C16	121.4 (7)
Re1—N2—H2N	108.1	C14—C15—H15	119.3
C4—N3—S1	115.8 (3)	C16—C15—H15	119.3
C4—N3—Re1	117.1 (3)	C17—C16—C15	121.4 (7)
S1—N3—Re1	125.6 (3)	C17—C16—H16	119.3
C2—C1—N1	110.7 (6)	C15—C16—H16	119.3
C2—C1—H1C	109.5	C18—C17—C16	117.5 (7)
N1—C1—H1C	109.5	C18—C17—C20	120.8 (7)
C2—C1—H1D	109.5	C16—C17—C20	121.7 (7)
N1—C1—H1D	109.5	C17—C18—C19	121.4 (7)
H1C—C1—H1D	108.1	C17—C18—H18	119.3
C1—C2—N2	110.5 (7)	C19—C18—H18	119.3
C1—C2—H2A	109.5	C18—C19—C14	121.7 (6)
N2—C2—H2A	109.5	C18—C19—H19	119.1
C1—C2—H2B	109.5	C14—C19—H19	119.1
N2—C2—H2B	109.5	C17—C20—H20A	109.5
H2A—C2—H2B	108.1	C17—C20—H20B	109.5
N2—C3—C4	110.8 (5)	H20A—C20—H20B	109.5
N2—C3—H3A	109.5	C17—C20—H20C	109.5
C4—C3—H3A	109.5	H20A—C20—H20C	109.5
N2—C3—H3B	109.5	H20B—C20—H20C	109.5
C4—C3—H3B	109.5		
O5—S1—N3—C4	162.7 (5)	C8—C9—C10—C11	0.0 (9)
O4—S1—N3—C4	32.0 (5)	C9—C10—C11—C12	−0.6 (9)
C8—S1—N3—C4	−81.8 (5)	C9—C10—C11—C14	−179.1 (6)
O5—S1—N3—Re1	−31.7 (4)	C10—C11—C12—C13	0.7 (9)
O4—S1—N3—Re1	−162.5 (3)	C14—C11—C12—C13	179.3 (5)
C8—S1—N3—Re1	83.7 (4)	C9—C8—C13—C12	−0.4 (8)
Re1—N1—C1—C2	−48.9 (8)	S1—C8—C13—C12	179.4 (4)
N1—C1—C2—N2	49.9 (9)	C11—C12—C13—C8	−0.3 (9)
C3—N2—C2—C1	−148.2 (6)	C10—C11—C14—C15	−37.0 (9)
Re1—N2—C2—C1	−26.3 (7)	C12—C11—C14—C15	144.5 (6)
C2—N2—C3—C4	76.7 (7)	C10—C11—C14—C19	142.6 (6)

Re1—N2—C3—C4	−48.2 (6)	C12—C11—C14—C19	−35.9 (8)
S1—N3—C4—C3	169.7 (5)	C19—C14—C15—C16	1.4 (10)
Re1—N3—C4—C3	2.9 (7)	C11—C14—C15—C16	−179.1 (6)
N2—C3—C4—N3	29.9 (8)	C14—C15—C16—C17	0.1 (11)
O5—S1—C8—C13	20.8 (5)	C15—C16—C17—C18	−1.9 (10)
O4—S1—C8—C13	146.3 (5)	C15—C16—C17—C20	178.3 (7)
N3—S1—C8—C13	−96.5 (5)	C16—C17—C18—C19	2.2 (10)
O5—S1—C8—C9	−159.4 (4)	C20—C17—C18—C19	−178.0 (6)
O4—S1—C8—C9	−33.9 (5)	C17—C18—C19—C14	−0.7 (11)
N3—S1—C8—C9	83.3 (5)	C15—C14—C19—C18	−1.1 (10)
C13—C8—C9—C10	0.5 (9)	C11—C14—C19—C18	179.3 (6)
S1—C8—C9—C10	−179.3 (5)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11*N*···O3[i]	0.89	2.27	3.053 (7)	146
N1—H12*N*···O2[ii]	0.89	2.59	3.028 (7)	111
N2—H2*N*···O4[iii]	0.98	1.98	2.941 (5)	167

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+2, *y*−1/2, −*z*+3/2; (iii) *x*, −*y*+1/2, *z*−1/2.