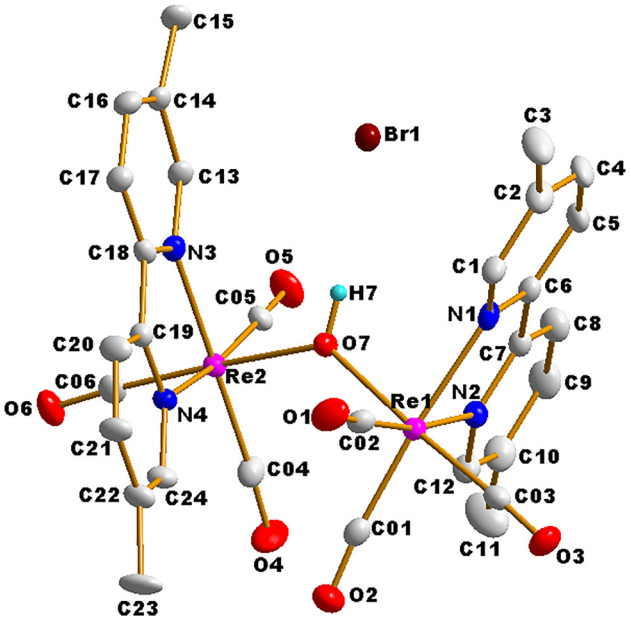
Lehlohonolo Moherane*, Orbett T. Alexander, Hendrik G. Visser and Amanda-Lee E. Manicum

The crystal structure of [μ-hydroxido-bis [(5,5′-dimethyl-2,2′-bipyridine-κ²*N*,*N*′)-tricarbonylrhenium(I)] bromide hemihydrate, $C_{30}H_{26}N_4O_9Re_2Br$



https://doi.org/10.1515/ncrs-2021-0210
Received May 26, 2021; accepted June 14, 2021;
published online June 30, 2021

Abstract

$C_{30}H_{26}N_4O_9Re_2Br$, triclinic, $P\bar{1}$ (no. 2), a = 9.407(6) Å, b = 11.769(8) Å, c = 15.055(11) Å, α = 82.70(2)°, β = 76.68(3)°, γ = 77.364(2)°, V = 1577.5(19) Å^3, Z = 2, $R_{gt}(F)$ = 0.0291, $wR_{ref}(F^2)$ = 0.0868, T = 100 K.

CCDC no.: 2084390

The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.37 × 0.13 × 0.04 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	8.99 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	66,539, 7825, 0.075
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 7101
$N(param)_{refined}$:	417
Programs:	Bruker [1], SIR97 [2], WinGX [3], Shelx [4], Diamond [5]

Source of material

fac-$[NEt_4]_2[Re(CO)_3(Br)_3]$ (100 mg, 0.1298 mmol) was dissolved in water (20 mL) and added to 5,5′-dimethyl-2,2′-bipyridine (DMbpy) (47.92 mg, 0.2601 mmol) dissolved in ethanol (3 mL). The solution was stirred for 48 h and the solvent was filtered off. The yellow solid was washed with water, cold ethanol and petroleum ether and the product eluted in the filtrate. The product was evaporated, and recrystallized using DCM:hexane, 1:1. Crystals suitable for single crystal X-ray diffraction were obtained.

Yield: 68.8 mg, **IR** (ATR, cm^{-1}): ν_{CO} = 2005.70, 1898.55, 1864.07.

Experimental details

The aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.95 and 0.98 Å and U_{iso}(H) = 1.5 U_{eq}(C) and 1.2 U_{eq}(C), respectively. The placement of the H atoms on the methyl groups was that of an idealised methyl group according to the electron-density map (HFIX 137). The highest peak is 1.8 e. Å^{-3} and deepest hole is –1.7 e. Å^{-3}.

***Corresponding author: Lehlohonolo Moherane,** Department of Chemistry, Tshwane University of Technology, 0001 Pretoria, South Africa, E-mail: LehlohonoloMoherane@gmail.com. https://orcid.org/0000-0001-6927-7575
Orbett T. Alexander and Hendrik G. Visser, Department of Chemistry, University of the Free State, 9301 Bloemfontein, South Africa. https://orcid.org/0000-0003-4926-8342 (O.T. Alexander)
Amanda-Lee E. Manicum, Department of Chemistry, Tshwane University of Technology, 0001 Pretoria, South Africa. https://orcid.org/0000-0003-4064-1307

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

Atom	x	y	z	U_{iso}*/U_{eq}
Re1	0.47912 (2)	0.76356 (2)	0.65205 (2)	0.01447 (6)
Re2	0.78173 (2)	0.78395 (2)	0.78668 (2)	0.01459 (6)
O1	0.2263 (4)	0.7703 (3)	0.8212 (2)	0.0303 (7)
O2	0.4463 (4)	1.0289 (3)	0.6515 (2)	0.0300 (7)
O3	0.2410 (4)	0.8437 (3)	0.5372 (2)	0.0290 (7)
O4	0.7785 (4)	0.9886 (3)	0.6391 (2)	0.0355 (8)
O5	1.0724 (3)	0.6629 (3)	0.6680 (2)	0.0306 (7)
O6	0.9493 (4)	0.9241 (3)	0.8701 (2)	0.0288 (7)
O7	0.6434 (3)	0.6990 (2)	0.73385 (18)	0.0170 (5)
H7	0.662 (6)	0.625 (5)	0.744 (4)	0.036 (15)*
N1	0.5052 (4)	0.5799 (3)	0.6341 (2)	0.0186 (6)
N2	0.6716 (4)	0.7262 (3)	0.5400 (2)	0.0173 (6)
N3	0.7681 (4)	0.6445 (3)	0.8959 (2)	0.0170 (6)
N4	0.5725 (4)	0.8418 (3)	0.8819 (2)	0.0150 (6)
C1	0.4138 (5)	0.5110 (4)	0.6834 (3)	0.0198 (7)
H1	0.331116	0.544999	0.727713	0.024*
C01	0.4641 (4)	0.9275 (4)	0.6549 (3)	0.0208 (8)
C02	0.3205 (5)	0.7703 (3)	0.7576 (3)	0.0205(8)
C2	0.4339 (5)	0.3931 (4)	0.6731 (3)	0.0269 (9)
C03	0.3329 (5)	0.8111(3)	0.5792(3)	0.0201(7)
C3	0.3305 (6)	0.3204 (4)	0.7355 (3)	0.0361 (11)
H3A	0.329946	0.251642	0.705180	0.054*
H3B	0.229437	0.367336	0.749008	0.054*
H3C	0.365355	0.295167	0.792773	0.054*
C04	0.7781 (5)	0.9101 (4)	0.6933 (3)	0.0220 (8)
C4	0.5537 (6)	0.3460 (4)	0.6081 (3)	0.0289 (10)
H4	0.570375	0.265460	0.598535	0.035*
C05	0.9633 (5)	0.7092 (3)	0.7113 (3)	0.0190 (7)
C5	0.6495 (5)	0.4142 (4)	0.5567 (3)	0.0247 (8)
H5	0.732036	0.381483	0.511741	0.030*
C06	0.8893 (4)	0.8678 (4)	0.8393 (3)	0.0204 (8)
C6	0.6236 (4)	0.5321 (3)	0.5718 (2)	0.0181 (7)
C7	0.7195 (4)	0.6126 (3)	0.5213 (3)	0.0186 (7)
C8	0.8483 (5)	0.5789 (4)	0.4570 (3)	0.0267 (9)
H8	0.880988	0.499117	0.444656	0.032*
C9	0.9301 (5)	0.6610 (4)	0.4106 (3)	0.0297 (10)
H9	1.019059	0.637777	0.366753	0.036*
C10	0.8806 (5)	0.7781 (4)	0.4289 (3)	0.0274 (9)
C11	0.9639 (6)	0.8710 (5)	0.3812 (4)	0.0438 (14)
H11A	0.930569	0.901075	0.324137	0.066*
H11B	1.070837	0.837913	0.367379	0.066*
H11C	0.944671	0.934801	0.421003	0.066*
C12	0.7496 (5)	0.8066 (4)	0.4942 (3)	0.0229 (8)
H12	0.713937	0.886049	0.506986	0.028*
C13	0.8713 (4)	0.5463 (3)	0.8985 (3)	0.0187 (7)
H13	0.959595	0.538994	0.852059	0.022*
C14	0.8560 (5)	0.4544 (3)	0.9656 (3)	0.0193 (7)
C15	0.9699 (5)	0.3434 (4)	0.9583 (3)	0.0253 (9)
H15A	0.954763	0.298232	0.912087	0.038*
H15B	0.959838	0.297465	1.017689	0.038*
H15C	1.069893	0.361719	0.940420	0.038*
C16	0.7285 (5)	0.4683 (4)	1.0339 (3)	0.0228 (8)
H16	0.715074	0.408295	1.081824	0.027*
C17	0.6204 (5)	0.5688 (3)	1.0332 (3)	0.0203 (7)
H17	0.533050	0.578544	1.080271	0.024*
C18	0.6418 (4)	0.6554 (3)	0.9622 (3)	0.0169 (7)
C19	0.5329 (4)	0.7638 (3)	0.9531 (3)	0.0164 (7)
C20	0.3960 (5)	0.7873 (4)	1.0133 (3)	0.0234 (8)
H20	0.370097	0.732986	1.063578	0.028*
C21	0.2976 (5)	0.8908 (4)	0.9992 (3)	0.0235 (8)
H21	0.202621	0.906772	1.039174	0.028*
C22	0.3374 (5)	0.9714 (4)	0.9268 (3)	0.0227 (8)
C23	0.2345 (5)	1.0840 (4)	0.9088 (3)	0.0315 (10)
H23A	0.133003	1.079571	0.942045	0.047*
H23B	0.236537	1.098086	0.842989	0.047*
H23C	0.266645	1.148048	0.929531	0.047*
C24	0.4779 (4)	0.9428 (3)	0.8710 (3)	0.0199 (7)
H24	0.508390	0.998041	0.822531	0.024*
Br1	0.73677 (5)	0.40622 (3)	0.77872 (3)	0.02126 (9)
O8[a]	0.6439 (14)	1.1597 (9)	0.7718 (7)	0.071 (3)
H8A[a]	0.663878	1.128466	0.719848	0.106*
H8B[a]	0.669734	1.227376	0.757639	0.106*

[a]Occupancy: 0.5.

Comment

A variety of research groups are intensively focused on the organometallic synthon *fac*-$[M(CO)_3]^+$ (M = $^{188/186}$Re, ^{99m}Tc), predominantly on functionalized Re(I) compounds, which are used in the design of therapeutic and diagnostic radiopharmaceutical models [6]. These results propose the possibility of utilizing ^{99m}Tc- and Re-based complexes not only as radiotherapeutic agents but also as chemotherapeutic agents [7]. Recently, studies of alkoxo or amido complexes of low valent fragments of the group 8–10 transition metals have attracted interest [8]. Additionally, studies included a hydroxyl group, 2,2′-bipyridine and rhenium metal centers containing bridged complexes showing that these complexes possess incredible spectroscopic properties [9–15].

The title structure is comprised of two rhenium complexes bridged by one hydroxido ligand (O1, in the sixth axial position). The distorted octahedral geometry of the respective rhenium metal centers is completed by a 5,5′-dimethyl-2,2′-bipyridine bidentate ligand, and the three facially coordinated carbonyls. There is one bromide (Br1) ion balancing the charge of the complex and one half of a water (O5) molecule in the asymmetric unit cell. The placement of the H atom on the hydroxo bridge oxygen (O1) atom was achieved from an electron density map and its presence is corroborated by two long Re–O bonds [2.139(3) and 2.146(3) Å]. The two independent rhenium complexes bridged by a hydroxido

ligand show the following Re-C bond lengths of Re1–C12, Re2–C11, Re1–C21, Re2–C22 and Re1–C32, Re2–C31 recording 1.909(40), 1.911(43), 1.909(48), 1.919(43), 1.900(49) and 1.905(51) Å, respectively. Amongst other hydrogen interactions, there is a classical OH···Br (O–H–X, 2.55(6) Å) hydrogen interaction between the hydrogen (H1) atom of the hydroxyl bridging group and the bromide (Br1) ion in the asymmetric unit cell.

Acknowledgements: The authors would like to acknowledge Tshwane University of Technology (TUT) and the University of the Free State (UFS) for Institutional support.
Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: AEM received financial assistance from the National Research Foundation (NRF) Thuthuka grant specific number 113629. OTA was supported by the South African National Research Foundation (NRF) and the Research Fund of the University of the Free State.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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