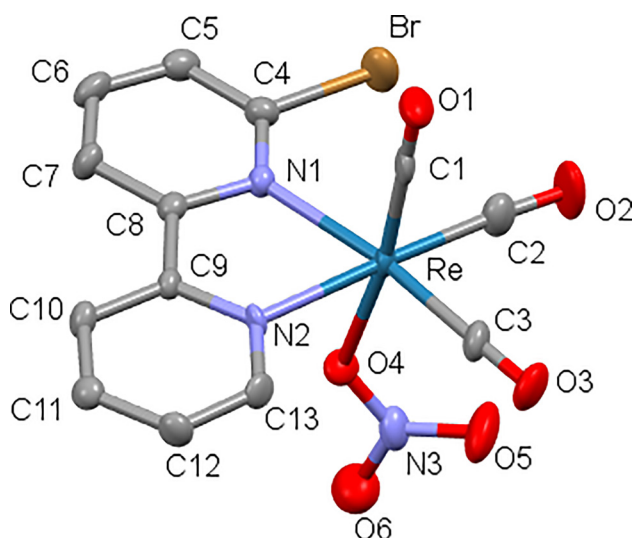


Marcus Mkhathshwa\*, Frederick P. Malan, Katlego Makgopa and Amanda-Lee E. Manicum

# The crystal structure of *fac*-tricarbonyl(6-bromo-2,2-bipyridine- $\kappa^2N,N$ )-(nitrate- $\kappa O$ )rhenium(I), $C_{13}H_7BrN_3O_6Re$



Shows the molecular structure of  $C_{13}H_7BrN_3O_6Re$ . Hydrogen atoms were omitted for clarity.

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## Abstract

$C_{13}H_7BrN_3O_6Re$ , monoclinic,  $P2_1/n$  (no. 14),  $a = 7.2645(1) \text{ \AA}$ ,  $b = 10.0607(1) \text{ \AA}$ ,  $c = 20.7717(2) \text{ \AA}$ ,  $\beta = 97.1800(10)^\circ$ ,  $V = 1506.22(3) \text{ \AA}^3$ ,  $Z = 4$ ,  $R_{gt}(F) = 0.0359$ ,  $wR_{ref}(F^2) = 0.0810$ ,  $T = 150 \text{ K}$ .

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of

\*Corresponding author: Marcus Mkhathshwa, Department of Chemistry, Tshwane University of Technology, Pretoria 0001, South Africa, E-mail: marcusmkhathshwa43@gmail.com. <https://orcid.org/0000-0002-7403-6730>

Frederick P. Malan, Department of Chemistry, University of Pretoria, Pretoria 0001, South Africa. <https://orcid.org/0000-0003-2446-2165>

Katlego Makgopa and Amanda-Lee E. Manicum, Department of Chemistry, Tshwane University of Technology, Pretoria 0001, South Africa. <https://orcid.org/0000-0003-2750-9790> (K. Makgopa). <https://orcid.org/0000-0003-4064-1307> (A.E. Manicum)

Table 1: Data collection and handling.

Crystal:	Yellow cuboid
Size:	0.35 × 0.18 × 0.16 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
$\mu$ :	19.3 mm <sup>-1</sup>
Diffractometer, scan mode:	XtALAB Synergy R, $\omega$
$\theta_{max}$ , completeness:	79.0°, >99 %
$N(hkl)_{measured}$ , $N(hkl)_{unique}$ , $R_{int}$ :	31772, 3207, 0.054
Criterion for $I_{obs}$ , $N(hkl)_{gt}$ :	$I_{obs} > 2\sigma(I_{obs})$ , 3171
$N(param)_{refined}$ :	217
Programs:	CRYSTALS <sup>PRO</sup> [1], Olex2 [2], WinGX [3], SHELX [4, 5]

the atoms including atomic coordinates and displacement parameters.

## 1 Source of materials

The starting complex was synthesized according to a published procedure [6].  $[NEt_4]_2[Re(CO)_3(Br)_3]$  (995 mg; 1.3 mmol) was dissolved in 5 mL of water (pH 2.2) by stirring for 10 min at room temperature. Silver nitrate (661 mg; 3.9 mmol) was added to the solution and stirred for 24 h at room temperature. The dark-grey silver bromide (130 mg; 6.9 mmol) that precipitated was filtered off. 6-Bromo-2,2-bipyridine (308 mg; 1.3 mmol), was added to the filtrate and stirred for 36 h at room temperature. The yellow precipitate was filtered and dried. Although *fac*-[ $Re(CO)_3(Brbpy)(H_2O)$ ] structure was expected from the filtrate, crystals of *fac*-[ $Re(CO)_3(Brbpy)(NO_3)$ ] were obtained, which could be due to the presence of excess nitrate ions from the silver nitrate salt and nitric acid ( $HNO_3$ , used for preparation of pH 2.2 water). Crystals suitable for the collection with X-ray diffraction formed. Yield = 563 mg, 83 %, IR (FTIR  $cm^{-1}$ ):  $\nu_{CO} = 2024, 1921$  [DFM1]  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ):  $\delta$  (ppm)  $\delta$  9.16–9.15 (m, 1H), 8.76 (d,  $J = 1.0$  Hz, 1H), 8.72–8.71 (m, 1H), 8.39 (d, 1H), 7.99 (d,  $J = 1.8$  Hz, 1H), 7.87–7.84 (m, 1H), 7.52–7.49 (m, 1H).  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta$  (ppm) 157.97, 157.09, 156.44, 153.84, 150.02, 143.50, 141.93, 141.20, 138.11, 132.96, 128.87, 125.34, 120.28.

## 2 Experimental details

All hydrogen atoms were geometrically positioned and discernibly refined using a riding model, with fixed

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br	0.43740 (13)	0.42345 (8)	0.23869 (4)	0.0422 (2)
C1	0.9142 (9)	0.2668 (6)	0.3426 (3)	0.0250 (13)
C2	0.5909 (11)	0.1549 (7)	0.2933 (4)	0.0335 (15)
C3	0.7723 (9)	0.0558 (6)	0.3957 (3)	0.0281 (14)
C4	0.5092 (9)	0.5121 (7)	0.3178 (3)	0.0250 (13)
C5	0.4639 (9)	0.6462 (7)	0.3174 (3)	0.0278 (14)
H5	0.397156	0.686662	0.280209	0.033*
C6	0.5191 (10)	0.7184 (7)	0.3726 (4)	0.0302 (15)
H6	0.494111	0.810959	0.373956	0.036*
C7	0.6114 (9)	0.6547 (6)	0.4265 (3)	0.0253 (13)
H7	0.650459	0.703263	0.464980	0.030*
C8	0.6464 (8)	0.5190 (6)	0.4235 (3)	0.0201 (12)
C9	0.7411 (8)	0.4480 (6)	0.4797 (3)	0.0177 (11)
C10	0.7921 (8)	0.5097 (6)	0.5399 (3)	0.0224 (12)
H10	0.766977	0.601191	0.545959	0.027*
C11	0.8796 (8)	0.4341 (6)	0.5901 (3)	0.0228 (12)
H11	0.915376	0.473716	0.631276	0.027*
C12	0.9153 (9)	0.3022 (7)	0.5809 (3)	0.0253 (13)
H12	0.975079	0.249559	0.615314	0.030*
C13	0.8622 (8)	0.2471 (6)	0.5200 (3)	0.0220 (12)
H13	0.887517	0.155860	0.513203	0.026*
N1	0.5976 (7)	0.4461 (5)	0.3681 (2)	0.0201 (10)
N2	0.7766 (7)	0.3182 (5)	0.4707 (2)	0.0175 (10)
N3	0.3340 (8)	0.1199 (6)	0.4218 (3)	0.0287 (12)
O1	1.0532 (7)	0.2873 (5)	0.3235 (3)	0.0363 (12)
O2	0.5439 (9)	0.1010 (6)	0.2457 (3)	0.0506 (16)
O3	0.8263 (7)	-0.0483 (5)	0.4069 (3)	0.0371 (12)
O4	0.4323 (6)	0.2199 (4)	0.4206 (2)	0.0253 (9)
O5	0.3642 (8)	0.0158 (6)	0.3934 (3)	0.0523 (16)
O6	0.1981 (8)	0.1273 (6)	0.4536 (3)	0.0511 (15)
Re	0.68498 (4)	0.23286 (2)	0.37591 (2)	0.01883 (9)

$C-H_{\text{Aromatic}} = 0.95 \text{ \AA}$ . The isotropic displacement parameters of the H atoms were fixed;  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic, allowing them to ride on the parent atom. The images were created using the MERCURY program with 50 % probability ellipsoids. For clarity, all of the H-atoms on the title structure were removed.

### 3 Comment

For many years, organometallic complexes have been the focus of significant research as non-invasive imaging contrast agents [7–10]. Rhenium(I) complexes with a *fac*-[M(CO)<sub>3</sub>(*N,N'*)(L)]<sup>*n*</sup> (where M = Re, *N,N'* = *N,N'*-bidentate or  $\alpha$ -diimine ligand, L = monodentate ligand, and *n* = 0 charge) moiety have received widespread attention in the scientific community since their initial investigation by Wrighton and Morse (1974) [11]. Interestingly, luminous Re(I) tricarbonyl complexes coupled with  $\alpha$ -diimine ligands have

received continued interest due to their photophysical and photochemical features, which are applicable for cancer cell bioimaging [7, 8, 12]. Due to their biological stability, low toxicity, high Stokes shifts, and extended luminescence lifetimes, the octahedral  $d^6$  and low-spin Re(I) tricarbonyl complexes have found use in many aspects *in vivo* [6, 13–18]. This work focuses on the crystallographic study of the coordination chemistry of the molecular structure of *N,N'*-bidentate ligand [6-bromo-2,2'-bipyridine (Brbpy)] in the equatorial plane, which is *trans* to two carbonyls (CO) ligands and an *O*-coordinated monodentate ligand [nitrate (NO<sub>3</sub>)] in the axial position. This was achieved by utilizing the [2 + 1] approach in the interest of the chemistry of Re(I) and its analogue, Tc(I), tricarbonyl complexes, aimed at the continuous application of cancer theranostics. The technique entails the replacement of two labile water molecules in the equatorial plane, followed by the axial coordination of the monodentate aqua ligand.

In this investigation, the title complex shows a slightly distorted octahedron, which comprises three facially arranged carbonyl ligands, one bidentate bpy-based ligand, as well as a monodentate nitrate ligand. Its molecular structure is shown in the Figure, in which the hydrogen atoms were removed for clarity. The distortion from ideal octahedral geometry is most noticeable in the bond angles C1–Re–C3 at 87.9(3)°, C1–Re–C2 at 88.8(3)°, and N2–Re–C1 at 94.3(2)°. The bond lengths between rhenium and the three carbons of the carbonyl ligands ranging between 1.912(7) and 1.932(6) Å, whereas the bond distances between Re–O4, Re–N1, and Re–N2 are 2.162(4), 2.237(5), and 2.175(4) Å, respectively. The acquired results are consistent with other structures previously published by Domínguez *et al.* [9], Ramoba *et al.* [19], and Moremi *et al.* [20]. The small bite angle of the title structure was determined to be 74.87(17)° for N1–Re–N2, which is just the same as that reported by Domínguez *et al.* (74.67(19)°) of a comparable structure [9]. Moreover, the crystal structure is at least stabilized by six intermolecular (six C–H...O) hydrogen bonding interactions. Complexes pack in a head-to-head fashion and are held together by intra- and intermolecular hydrogen bonds [21–23].

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