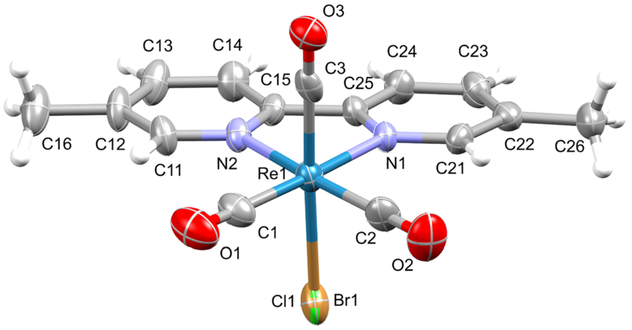
DE GRUYTER
Z. Kristallogr. - N. Cryst. Struct. 2023; 238(5): 969–971

Lehlohonolo Moherane, Marcus Makhatshwa, Frederick P. Malan, Hendrik G. Visser and Amanda-Lee E. Manicum*

The crystal structure of (bromido, chlorido)-tricarbonyl-(5,5′-dimethyl-2,2′-bipyridine)-rhenium(I), $C_{15}H_{12}Br_{0.2}Cl_{0.8}N_2O_3Re_1$



https://doi.org/10.1515/ncrs-2023-0303
Received June 28, 2023; accepted July 19, 2023;

Abstract

$C_{15}H_{12}Br_{0.2}Cl_{0.8}N_2O_3Re_1$, monoclinic, $P2_1/c$ (no. 14), $a = 14.6713(4)$ Å, $b = 11.4724(3)$ Å, $c = 9.6206(3)$ Å, $\beta = 106.592(3)$, $V = 1551.87(8)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0452$, $wR_{ref}(F^2) = 0.1110$, $T = 149.99(10)$ K.

CCDC no.: 2282749

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 block
Size:	$0.22 \times 0.17 \times 0.07$ mm
Wavelength:	MoKα radiation (0.71073 Å)
μ:	8.46 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy R, ω
θ_{max}, completeness:	26.4°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	23,005, 3168, 0.078
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2897
$N(param)_{refined}$:	202
Programs:	CrysAlis^{Pro} [1], Olex2 [2], WinGX [3], Shelx [4, 5]

1 Source of materials

The synthesis of the starting synthon, *fac*-$[NEt_4]_2[Re(CO)_3(Br)_3]$, was strictly performed under Schlenk conditions. The reported complex was synthesized according to published procedures [6, 7]. To *fac*-$[NEt_4]_2[Re(CO)_3(Br)_3]$ (251 mg, 0.325 mmol) in methanol 5,5′-dimethyl- 2,2′-bipyridyl (bid; 119 mg, 0.648 mmol) was added and refluxed for 6 h at room temperature. The light-yellow precipitate was filtered off, dried, and weighed to yield the title complex. Crystals were obtained by recrystallization using warm methanol and dilute HCl solution and allowing the resultant solution to crystallize at room temperature. The molecular structure of *fac*-$[Re(CO)_3$(5,5′-DiMBpy)(Cl0.82Br0.18)] was confirmed with SCXRD. Yield: 289 mg, **IR** (ATR, cm^{-1}): νCO = 2024.8, 1900.8.

2 Experimental details

The aromatic and methyl H atoms were place in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.93 (aromatic) and 0.96 Ang (methyl) and their U_{iso} values were set to $1.2U_{eq}$ (aromatic) and $1.5U_{eq}$ (methyl). The highest peak is 2.82 eAng^{-3} and deepest hole is –1.04 eAng^{-3}. The graphics were generated using the Mercury program with 50 % probability ellipsoids.

***Corresponding author: Amanda-Lee E. Manicum**, Department of Chemistry, Tshwane University of Technology, Pretoria 0001, South Africa, E-mail: manicumae@tut.ac.za. https://orcid.org/0000-0003-4064-1307
Lehlohonolo Moherane and Marcus Makhatshwa, Department of Chemistry, Tshwane University of Technology, Pretoria 0001, South Africa, E-mail: lehlohonolomoherane@gmail.com (L. Moherane). https://orcid.org/0000-0001-6927-7575 (L. Moherane). https://orcid.org/0000-0002-7403-6730 (M. Makhatshwa)
Frederick P. Malan, Department of Chemistry, University of Pretoria, 02 Lynnwood Road, Hatfield, Pretoria 0002, South Africa. https://orcid.org/0000-0003-2446-2165
Hendrik G. Visser, Department of Chemistry, University of the Free State, PO Box 339, Bloemfontein 9300, South Africa

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1[a]	0.65644 (13)	0.53894 (17)	0.9558 (2)	0.0426 (8)
C1	0.7829 (7)	0.7461 (9)	0.8499 (11)	0.042 (2)
C2	0.8801 (7)	0.5910 (9)	1.0348 (10)	0.041 (2)
C3	0.9002 (6)	0.6100 (7)	0.7672 (9)	0.0305 (19)
C11	0.6449 (6)	0.6219 (8)	0.5397 (11)	0.037 (2)
H11	0.652842	0.701428	0.568228	0.044*
C12	0.5804 (7)	0.5943 (9)	0.4041 (11)	0.043 (2)
C13	0.5696 (7)	0.4785 (10)	0.3664 (11)	0.044 (3)
H13	0.526251	0.456159	0.276604	0.053*
C14	0.6222 (7)	0.3930 (9)	0.4599 (11)	0.039 (2)
H14	0.616263	0.313091	0.433163	0.046*
C15	0.6833 (6)	0.4276 (7)	0.5925 (9)	0.0281 (17)
C16	0.5270 (7)	0.6895 (10)	0.3069 (13)	0.054 (3)
H16A	0.505978	0.747948	0.365444	0.082*
H16B	0.471405	0.656210	0.235714	0.082*
H16C	0.568669	0.726326	0.256323	0.082*
C21	0.8566 (6)	0.3210 (8)	0.9190 (9)	0.0329 (19)
H21	0.898313	0.355021	1.003397	0.039*
C22	0.8566 (7)	0.2007 (8)	0.9061 (10)	0.034 (2)
C23	0.7947 (7)	0.1515 (8)	0.7810 (11)	0.037 (2)
H23	0.791943	0.069321	0.767979	0.045*
C24	0.7379 (7)	0.2236 (8)	0.6772 (10)	0.035 (2)
H24	0.696326	0.191307	0.591452	0.041*
C25	0.7417 (6)	0.3438 (8)	0.6981 (9)	0.0282 (17)
C26	0.9212 (8)	0.1282 (10)	1.0244 (11)	0.047 (3)
H26A	0.986241	0.131901	1.016350	0.070*
H26B	0.899333	0.047064	1.014601	0.070*
H26C	0.920093	0.158389	1.119175	0.070*
Cl1[b]	0.65644 (13)	0.53894 (17)	0.9558 (2)	0.0426 (8)
N1	0.8012 (5)	0.3927 (6)	0.8196 (7)	0.0263 (15)
N2	0.6953 (5)	0.5412 (6)	0.6300 (8)	0.0298 (16)
O1	0.7824 (6)	0.8488 (8)	0.8583 (11)	0.067 (2)
O2	0.9306 (6)	0.5973 (7)	1.1505 (8)	0.060 (2)
O3	0.9638 (5)	0.6324 (6)	0.7276 (8)	0.0437 (16)
Re1	0.79487 (2)	0.57988 (3)	0.84168 (4)	0.02986 (14)

[a]Occupancy: 0.184 (8), [b]Occupancy: 0.816 (8).

3 Comment

In the previous five years, the chemistry of the relatively inert and low oxidation state rhenium(I) (Re) and technetium(I) (Tc) was derived from the *fac*-$[M(CO)_3(H_2O)_3]^+$ precursor. This precursor has been studied and employed by numerous research groups, mainly for their significance in the nuclear medicine arena, such as radiopharmacy, photocatalysis, and currently, chemotherapy [7, 8]. Furthermore, the *fac*-$[Re(H_2O)_3(CO)_3]^+$ precursor is very useful for designing molecules with different properties and applying various coordination models such as the “2 + 1” and most recently introduced “2 + 1 + 1” mixed ligand approach [9]. The various coordination models, enables a wide range of rhenium(I) tricarbonyl complexes to be obtained by displacing the three labile water ligands with alternative ligands [8]. Specifically, rhenium(I) tricarbonyl diimine complexes, [(*N,N'*)Re(CO)$_3$(X)] (X = halide), exhibit remarkable photophysical and photochemical properties, which can be altered by either the nature of diimine ligand (*N,N'*) or the L ligand itself (Cl, Br) as indicated by Wrighton and co-workers in the 1970s [10, 11]. These rhenium(I) complexes with their associated properties, are often applied in anti-microbial, anti-inflammatory, anti-viral and anti-tumor studies [12–16].

The title structure is a rhenium(I) tricarbonyl complex with a bid ligand and a mixed halogen (Cl0.82Br0.12) ligand. The rhenium metal center is fulfilled by a bid bidentate ligand coordinated equatorially, three facially coordinated carbonyl ligands, and a halogen (Cl/Br) ligand on the axial position producing a distorted octahedral geometry. The complex has associated bond angles of 101.3(4)° (C1–Re1–N2), 97.3(3)° (C2–Re1–N1), 94.9(3)° (C3–Re1–N2), and 75.1(3)° (N1–Re1–N2), and are comparable to the same angles of similar structures previously reported [17]. The Re–C bond distances (Re1–C1, Re1–C2, and Re1–C3) are 1.919(10), 1.925(10), and 1.911(10) Å, respectively, and they are comparable to similar reported structures in literature [18–21]. Furthermore, the rhenium to nitrogen bond distances is 2.163(7) Å (Re1–N1) and 2.186(7) Å (Re1–N2), respectively, again comparable to reported structures [22–26]. The rhenium to halogen bond distance of 2.612 Å(Re1–Cl1/Br1) is longer compared to Re–Cl bond distances in literature [27], while comparable to Re–Br bond distances which appear in the range of 2.59–2.64 Å of similar structures in literature [28]. Thus, the two atoms (Cl and Br) at the axial position appear as a substitutional disorder and has been treated as such to refine using a free variable (final occupancy: Cl1 = 0.816(8); Br1 = 0.184(8)) where Cl1/Br1 have been constrained to occupy the same position.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work was funded by National Research Foundation of South Africa (Grant No. 129468), Tshwane University of Technology, the University of Pretoria and the University of the Free State.

Conflict of interest statement: The authors declare no conflicts of interest.

References

1. System C. S. *CrysAlis^{Pro} Software System*; Rigaku Oxford Diffraction: Yarnton, UK, 2021.

2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
3. Farrugia L. J. WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* 1999, *32*, 837–883.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
5. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
6. Manicum A., Schutte-Smith M., Visser H. G. The synthesis and structural comparison of fac-$[Re(CO)_3]^+$ containing complexes with altered β-diketone and phosphine ligands. *Polyhedron* 2018, *145*, 80–87.
7. Manicum A., Alexander O., Schutte-Smith M., Visser H. G. Synthesis, characterization and substitution reactions of fac-[Re(*O,O*-bid)$(CO)_3$(P)] complexes, using the “2 + 1” mixed ligand model. *J. Mol. Struct.* 2020, *1209*, 127953–127964.
8. Schutte-Smith M., Marker S. C., Wilson J. J., Visser H. G. Aquation and anation kinetics of rhenium(I) dicarbonyl complexes: relation to cell toxicity and bioavailability. *Inorg. Chem.* 2020, *59*, 15888–15897.
9. Manicum A., Schutte-Smith M., Malan F. P., Visser H. G. Steric and electronic influence of Re(I) tricarbonyl complexes with various coordinated β-diketones. *J. Mol. Struct.* 2022, *1264*, 133278–133291.
10. Gallardo H., Cepeda-Plaza M., Nonell S., Günther G., Chamorro E., Pizarro N., Vega A. Structural and photophysical properties of $[(CO)_3(phen)Re(l{-}Br)Re(phen)(CO)_3] + [(CO)_3Re(l{-}Br)_3Re(CO)_3]^-$: where does its luminescence come from? *Polyhedron* 2015, *97*, 227–233.
11. Kumar A., Sun S.-S., Lees A. J. Photophysics and photochemistry of organometallic rhenium diimine complexes. *Top. Organomet. Chem.* 2010, *29*, 1–35.
12. Kapp L. E., Schutte-Smith M., Twigge L., Visser H. G. Synthesis, characterization, and DNA binding of four imidazo[4,5-*f*] 1,10-phenanthroline derivatives. *J. Mol. Struct.* 2022, *1247*, 131235–131245.
13. Mkhatshwa M., Moremi J. M., Makgopa K., Manicum A. Nanoparticle functionalized with Re(I) tricarbonyl complexes for cancer theranostics. *Int. J. Mol. Sci.* 2021, *22*, 6546–6563.
14. Matlou M. L., Louis H., Charlie D. E., Agwamba E. C., Amodu I. O., Tembu V. J., Manicum A. Anticancer activities of Re(I) tricarbonyl and its imidazole-based ligands: insight from a theoretical approach. *ACS Omega* 2023, *8*, 10242–10252.
15. Moherane L., Louis H., Ekereke E. E., Agwamba E. C., Visser H. G., Benjamin I., Uwem O., Edet U. O., Manicum A. Polypyridyl coordinated Re(I) complexes for human tenascin-C (TNC) as an antibreast cancer agent: an intuition from molecular modeling and simulations. *Polycyclic Aromat. Compd.* 2023, 1–18; https://doi.org/10.1080/10406638.2023.2189737.
16. Manicum A., Louis H., Agwamba E. C., Chima C. M., Nzondomyo W. J., Sithole S. A. Acetylacetone and imidazole coordinated Re(I) tricarbonyl complexes: experimental, DFT studies, and molecular docking approach. *Chem. Phys. Impact* 2023, *6*, 100165–100178.
17. Moherane L., Alexander O. T., Schutte-Smith M., Kroon R. E., Mokolokolo P. P., Biswas S., Prince S., Visser H. G., Manicum A. E. Polypyridyl coordinated rhenium(I) tricarbonyl complexes as model devices for cancer diagnosis and treatment. *Polyhedron* 2022, *228*, 116178–116188.
18. Manicum A. E., Schutte-Smith M., Alexander O. T., Twigge L., Roodt A., Visser H. G. First kinetic data of the CO substitution in fac-[Re(L,L′-Bid)$(CO)_3$(X)] complexes (L,L′-Bid = acacetylacetonate or tropolonate) by tertiary phosphines PTA and PPh3: synthesis and crystal structures of water-soluble rhenium(I) tri- and dicarbonyl complexes with 1,3,5-triaza-7- phosphaadamantane (PTA). *Inorg. Chem. Commun.* 2019, *101*, 93–98.
19. Moherane L., Alexander O. T., Visser H. G., Manicum A. E. The crystal structure of [μ-hydroxido-bis[(5,5′-dimethyl-2,2′-bipyridine-κ^2*N,N′*)-tricarbonylrhenium(I)] bromide hemihydrate, $C_{30}H_{26}N_4O_9Re_2Br$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 1027–1029.
20. Makhakhayi L., Malan F. P., Tembu V. J., Nkambule C. M., Manicum A. E. The crystal structure of *fac*-tricarbonyl(*N*-benzoyl-*N,N*-cyclohexylmethylcarbamimidothioato-κ^2*S,O*)-(pyridine-κ*N*)rhenium(I), $C_{23}H_{24}N_3O_4ReS$. *Z. Kristallogr. N. Cryst. Struct.* 2023, *238*, 697–699.
21. Schutte-Smith M., Visser H. G. Crystal and molecular structures of *fac*-[Re(Bid)- $(PPh_3)(CO)_3$] [Bid is tropolone (TropH) and tribromotropolone ($TropBr_3H$)]. *Acta Crystallogr.* 2022, *C78*, 351–359.
22. Schutte-Smith M., Roodt A., Alberto R., Twigge L., Visser H. G., Kirstena L., Koen R. Structures of rhenium(I) complexes with 3-hydroxyflavone and benzhydroxamic acid as *O,O′*- bidentate ligands and confirmation of p-stacking by solid-state NMR spectroscopy. *Acta Crystallogr.* 2019, *C75*, 378–387.
23. Matlou M. L., Malan F. P., Nkadimeng S., Mcgaw L., Tembu V. J., Manicum A. E. Exploring the in vitro anticancer activities of Re(I) picolinic acid and its fluorinated complex derivatives on lung cancer cells: a structural study. *J. Biol. Inorg. Chem.* 2023, *28*, 29–41.
24. Sithole S. A., Malan F. P., Katerere D. R., Manicum A. E. The crystal structure of *fac*-tricarbonyl(2-pyridin-2-yl-quinoline-κ^2*N,N′*)- (pyrazole-κ*N*)rhenium(I)nitrate, $C_{20}H_{14}N_4O_3ReNO_3$. *Z. Kristallogr. N. Cryst. Struct.* 2023, *238*, 685–687.
25. Mkhatshwa M., Malan F. P., Makgopa K., Manicum A. E. The crystal structure of *fac*-tricarbonyl(6-bromo-2,2-bipyridine-κ^2*N,N*)- (nitrato-κ*O*) rhenium(I), $C_{13}H_7BrN_3O_6Re$. *Z. Kristallogr. N. Cryst. Struct.* 2023, *238*, 667–669.
26. Moremi M. J., Alexander O. T., Vatsha B., Makgopa K., Manicum A. E. The crystal structure of *fac*-tricarbonyl(4,4-dimethyl-2,2-dipyridyl-κ^2*N,N′*)- (pyrazole-κ*N*)rhenium(I) nitrate, $C_{18}H_{16}O_3N_4Re$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 33–35.
27. Chabolla S. A., Dellamary E. A., Machan C. W., Tezcan F. A., Kubiak C. P. Combined steric and electronic effects of positional substitution on dimethyl-bipyridine rhenium(I)tricarbonyl electrocatalysts for the reduction of CO_2. *Inorg. Chim. Acta* 2014, *422*, 109–113.
28. Heard P. J., Sroisuwan P., Tocher D. A. Synthesis and reactivity of *N,N,N′,N′*-tetramethyldiaminomethane complexes of tricarbonylrhenium(I). X-ray molecular structures of $[ReBr(CO)_3(TMDM)]$ and $[\{Re(bipy)(CO)_3\}_2(\mu{-}OH)]$ $[SbF_6]$. *Polyhedron* 2003, *22*, 1321–1327.