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The crystal structure of *fac*-tricarbonyl((pyridin-2-yl)methanamino- κ^2N,N')-(pyridin-2-yl)methanamino- κN)rhenium(I) nitrate, $C_{15}H_{16}O_3N_4Re$

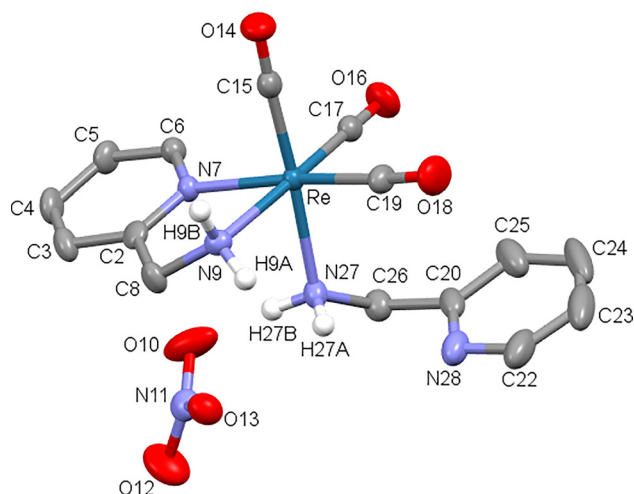


Figure 1: Shows the molecular structure of $C_{15}H_{16}O_3N_4Re$. Hydrogen atoms were omitted for clarity.

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Abstract

$C_{15}H_{16}O_3N_4Re$, triclinic, $P\bar{1}$ (no. 2), $a = 7.4939(2)$ Å, $b = 10.1316(2)$ Å, $c = 13.8351(3)$ Å, $\alpha = 103.453(2)^\circ$, $\beta = 101.992(2)^\circ$, $\gamma = 107.880(2)^\circ$, $V = 926.98(4)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0341$, $wR_{ref}(F^2) = 0.0861$, $T = 150$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.51 × 0.26 × 0.25 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	6.60 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy R, ω
θ_{max} , completeness:	30.9°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	33,002, 5109, 0.093
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 4684
$N(param)_{refined}$:	244
Programs:	Olex2 [1], Shelx [2–4]

1 Source of material

Fac-[Re(N,N) (CO)₃(H₂O)] ($N,N = (2\text{-picolylamine-}\kappa^2N,N')$) (20 mg, 0.051 mmol) was dissolved in methanol (5 mL) and 2-picolyamine (5.36 mL, 0.051 mmol) dissolved in (10 mL) methanol was added. The solution was then stirred for 30 min and then refluxed for 24 h at room temperature and the light yellow solution was left to crystallize (Yield = 15.25 mg, 84 %; FTIR (cm⁻¹) Vco: 2024, 1909).

2 Experimental details

All hydrogen atoms were positioned geometrically using a riding model, with fixed C–H_{Aromatic} = 0.97 Å. The H atoms isotropic displacement parameters were fixed; U_{iso} (H) = 1.2 U_{eq} (C) for aromatic, allowing them to ride on the parent atom. The graphics were obtained using the mercury program with 50 % probability ellipsoids. All the H-atoms on the title structure were omitted for clarity.

3 Comment

Since the inception of the [2 + 1] mixed ligand model by Mundwiler and co-workers [5], rhenium(I) tricarbonyl complexes of *fac*-[Re(CO)₃]⁺ synthon have been exploited for various applications [6–8]. The stable organometallic

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C2	0.5542 (6)	0.2674 (4)	0.6564 (3)	0.0263 (8)
C3	0.4152 (6)	0.1228 (5)	0.6221 (4)	0.0321 (10)
H3	0.389983	0.059977	0.553967	0.039*
C4	0.3175 (7)	0.0738 (5)	0.6870 (4)	0.0346 (10)
H4	0.223945	-0.023494	0.664628	0.041*
C5	0.3553 (6)	0.1673 (4)	0.7868 (4)	0.0318 (9)
H5	0.289052	0.134969	0.833464	0.038*
C6	0.4910 (6)	0.3076 (4)	0.8158 (3)	0.0256 (8)
H6	0.516936	0.371776	0.883543	0.031*
C8	0.6604 (6)	0.3271 (4)	0.5870 (3)	0.0285 (9)
H8A	0.700671	0.252123	0.547751	0.034*
H8B	0.571018	0.350405	0.536040	0.034*
C15	1.0148 (7)	0.5430 (5)	0.8787 (3)	0.0279 (9)
C17	0.7459 (6)	0.6605 (4)	0.9177 (3)	0.0261 (8)
C19	1.0016 (7)	0.7673 (5)	0.8176 (4)	0.0298 (9)
C20	0.6238 (7)	0.8696 (5)	0.7543 (4)	0.0356 (11)
C22	0.8244 (9)	1.0328 (6)	0.6952 (6)	0.0547 (17)
H22	0.877147	1.052670	0.641082	0.066*
C23	0.8821 (9)	1.1427 (6)	0.7859 (7)	0.064 (2)
H23	0.973456	1.236760	0.794702	0.077*
C24	0.8070 (11)	1.1166 (7)	0.8654 (7)	0.073 (3)
H24	0.844003	1.192570	0.929305	0.088*
C25	0.6751 (9)	0.9761 (6)	0.8503 (5)	0.0545 (16)
H25	0.622018	0.954013	0.903831	0.065*
C26	0.4813 (7)	0.7148 (5)	0.7283 (4)	0.0323 (9)
H26A	0.449452	0.698987	0.791693	0.039*
H26B	0.357827	0.697795	0.675714	0.039*
N7	0.5891 (5)	0.3581 (4)	0.7521 (3)	0.0213 (7)
N9	0.8374 (5)	0.4613 (4)	0.6476 (3)	0.0243 (7)
H9A	0.857639	0.521934	0.608376	0.029*
H9B	0.944281	0.436088	0.661486	0.029*
N11	0.1137 (5)	0.3339 (4)	0.5232 (3)	0.0317 (8)
N27	0.5714 (5)	0.6110 (4)	0.6869 (3)	0.0272 (7)
H27A	0.620875	0.640185	0.637285	0.033*
H27B	0.472664	0.521922	0.653867	0.033*
N28	0.6960 (6)	0.8964 (4)	0.6774 (4)	0.0409 (9)
O10	0.1276 (6)	0.3314 (5)	0.6135 (3)	0.0590 (11)
O12	-0.0461 (5)	0.2904 (5)	0.4542 (3)	0.0582 (11)
O13	0.2672 (5)	0.3935 (4)	0.5026 (3)	0.0351 (7)
O14	1.1457 (5)	0.5279 (4)	0.9301 (3)	0.0408 (8)
O16	0.7029 (5)	0.7072 (4)	0.9890 (3)	0.0423 (8)
O18	1.1243 (5)	0.8797 (4)	0.8349 (3)	0.0497 (10)
Re1	0.80884 (2)	0.57883 (2)	0.79542 (2)	0.01999 (7)

precursor has three tightly coordinated CO ligands and three water molecules, the latter of which can be readily substituted by suitable ligand systems to produce relatively stable octahedral tricarbonyl complexes [9–11]. Furthermore, the nuclear properties of the two radionuclides of rhenium, ^{186}Re ($t_{1/2} = 90$ h; $E_{\text{max}} = 1.07$ MeV) and ^{188}Re ($t_{1/2} = 17$ h; $E_{\text{max}} = 2.12$ MeV) which are high-energy beta emitters, ideal for radiotherapy related research, intrigued

many research groups across the world [11–13]. Subsequently, there has been a reasonable pursuit of technetium tricarbonyl chemistry since this radionuclide work in tandem with the above-discussed rhenium tricarbonyl system [14–16].

In this work, three labile aqua ligands in the *fac*- $[\text{Re}(\text{CO})_3(\text{OH}_2)_3]^+$ synthon are first bidentately substituted in the equatorial position by 2-picolyamine, and then monodentately in the axial position by the same ligand, by incorporating the [2 + 1] mixed ligand model. The title compound (see the Figure 1) is balanced by a nitrate (NO_3^-) counter ion, revealing that the overall charge of the complex bears a +1 charge. The structure exhibits an octahedral distortion as seen in the Re1–N7–C2–C8–N9 five-membered ring bite angle of $75.81(13)^\circ$. The bond distances between rhenium and the bonded carbonyl ligands range from 1.908(5) to 1.921(5) \AA , and the rhenium to nitrogen bond distances range from 2.186(3) \AA to 2.236(4) \AA . The reported bond distances and bite angles correlate well with the bond distances and bite angles of other structures reported in the literature [5, 6, 9].

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References

- 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. Cryst.* 2009, *42*, 339–341.
- Sheldrick G. M. A short history of SHELX. *Acta Cryst.* 2008, *A64*, 112–122.
- Sheldrick G. M. SHELXTL – integrated space-group and crystal-structure determination. *Acta Cryst.* 2015, *A71*, 3–8.
- Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* 2015, *C71*, 3–8.
- Mundwiler S., Kündig M., Ortner K., Alberto R. A new [2 + 1] mixed ligand concept based on $[\text{Re}^{99(m)}(\text{OH}_2)_3(\text{CO})_3]^+$: a basic study. *Dalton Trans* 2004, *9*, 1320–1328.
- Ramoba L. V., Alexander O. T., Visser H. G., Manicum A. The crystal structure of fac-tricarbonyl (1,10-phenanthroline- κ^2N,N')-(pyrazole- κN) rhenium(I)nitrate, $\text{C}_{18}\text{H}_{16}\text{O}_3\text{N}_4\text{Re}$. *Z. Kristallogr. N. Cryst. Struct.* 2020, *235*, 1203–1205.

7. Probst B., Rodenberg A., Guttentag M., Hamm P., Alberto R. A highly stable rhenium-cobalt system for photocatalytic H₂ production: unravelling the performance-limiting steps. *Inorg. Chem.* 2010, 49, 6453–6460.
8. Mukherjee J., Siewert I. Manganese and rhenium tricarbonyl complexes equipped with proton relays in the electrochemical CO₂ reduction reaction. *Eur. J. Inorg. Chem.* 2020, 46, 4319–4333.
9. Moremi J. M., Vatsha B., Alexander O. T., Makgopa K., Manicum A. The crystal structure of fac-tricarbonyl(4,4-dimethyl-2,2-dipyridyl-κ²-N,N') (pyrazole-κN)rhenium(I)nitrate, C₁₈H₁₂O₃N₄Re. *Z. Kristallogr. N. Cryst. Struct.* 2020, 236, 33–35.
10. Manicum A., Alexander O. T., 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.
11. Triantis C., Shegani A., Kiritsis C., Ischyropoulou M., Roupa I., Psycharis V., Raptopoulou C., Kyprinidou P., Pelecanou M., Pirmettis I., Papadopoulos M. S. Dicarboxylate-[M(CO)₃(N,O)(C)(P)] (M = Re, ^{99m}Tc) complexes with a new [2 + 1 + 1] donor atom combination. *Inorg. Chem.* 2018, 57, 8354–8363.
12. Karges J., Cohen S. M. Rhenium (V) complexes as cysteine-targeting coordinate covalent warheads. *J. Med. Chem.* 2023, 66, 3088–3105.
13. Yu S. H., Patra M., Ferrari S., Garcia P. R., Veldhuis N. A., Kaminskas L. M., Graham B., Quinn J. F., Whittaker M. R., Gasser G., Davis T. P. Linker chemistry dictates the delivery of a phototoxic organometallic rhenium (I) complex to human cervical cancer cells from core crosslinked star polymer nanoparticles. *J. Mat. Chem.* 2018, 6, 7805–7810.
14. Manicum A., Schutte-Smith M., Visser H. G., Pretorius C., Roodt A. Crystal structure of tetraethylammonium fac-tricarbonyl(hexafluoroacetylacetonato-κ₂O,O')-(nitrito-κ-O) rhenium(I), C₁₆H₂₁O₈N₂F₆Re. *Z. Kristallogr. N. Cryst. Struct.* 2016, 231, 263–266.
15. Dilworth J. R., Pasco S. I. The radiopharmaceutical chemistry of technetium and rhenium. In *The Chemistry of Molecular Imaging*; Long N., Wong W.-T., Eds., 1st ed.; John Wiley & Sons, Inc.: Cambridge, MA, 2015.
16. Kama D. V., Brink A., Alberto R., Roodt A. Exploring structural implications of diphosphinamine ligands in medicine and catalysis. *Acta Cryst* 2021, 77, C1015.