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Crystal structure of *fac*-tricarbonyl-(nitrate- $\kappa^1\text{O}$)-bis(pyridine- κN)-rhenium, $\text{C}_{13}\text{H}_{10}\text{O}_6\text{N}_3\text{Re}$

Table 1: Data collection and handling.

Crystal:	Yellow cuboid
Size:	0.12 × 0.10 × 0.09 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	8.29 mm ⁻¹
Diffraction, scan mode:	Bruker D8 Quest Photon II, φ and ω
θ_{max} , completeness:	28.0°, >99%
$N(hkl)_{\text{measured}}$:	22423, 3551, 0.059
$N(hkl)_{\text{unique}}$, R_{int} :	
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3221
$N(\text{param})_{\text{refined}}$:	208
Programs:	Bruker [1], Mercury [2], Olex2 [3], SHELX [4, 5]

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Abstract

$\text{C}_{13}\text{H}_{10}\text{O}_6\text{N}_3\text{Re}$, monoclinic, $P2_1/c$ (no. 14), $a = 7.9325(9)$ Å, $b = 13.811(2)$ Å, $c = 13.458(2)$ Å, $\beta = 92.637(4)^\circ$, $V = 1472.83(4)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0249$, $wR_{\text{ref}}(F^2) = 0.0568$, $T = 100(2)$ 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 the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was crystallised from the intermediate *fac*-[Re^I(CO)₃(HOCH₃)₃]NO₃ in the presence of excess pyridine during the reaction indicated in literature [6]. The title compound was crystallized from the methanol filtrate in high purity. IR (ATR, cm⁻¹): $\nu(\text{CO})$ 2018, 1897, 1882.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Re1	0.82346 (2)	0.60717 (2)	0.23467 (2)	0.01993 (6)
O1	0.9999 (4)	0.7809 (2)	0.3355 (3)	0.0446 (8)
O2	0.8813 (4)	0.7187 (3)	0.0431 (2)	0.0434 (8)
O3	1.1633 (4)	0.5106 (2)	0.2097 (3)	0.0400 (8)
O4	0.5694 (3)	0.65047 (19)	0.2630 (2)	0.0259 (6)
O5	0.5590 (4)	0.7776 (2)	0.1658 (2)	0.0408 (8)
O6	0.3334 (4)	0.7254 (3)	0.2329 (3)	0.0407 (8)
N1	0.6918 (4)	0.4887 (2)	0.1523 (2)	0.0203 (6)
N2	0.7788 (4)	0.5261 (2)	0.3727 (2)	0.0204 (6)
N3	0.4848 (4)	0.7193 (2)	0.2186 (3)	0.0266 (7)
C1	0.9329 (5)	0.7147 (3)	0.3013 (3)	0.0279 (9)
C2	0.8561 (5)	0.6769 (3)	0.1148 (3)	0.0297 (9)
C3	1.0357 (5)	0.5481 (3)	0.2198 (3)	0.0249 (8)
C4	0.7270 (6)	0.5722 (3)	0.4530 (3)	0.0285 (9)
H4	0.703536	0.639508	0.448206	0.034*
C5	0.7061 (6)	0.5265 (3)	0.5426 (3)	0.0349 (10)
H5	0.669290	0.562043	0.598025	0.042*
C6	0.7389 (6)	0.4287 (3)	0.5512 (3)	0.0315 (9)
H6	0.725332	0.395332	0.612100	0.038*
C7	0.7924 (6)	0.3809 (3)	0.4680 (4)	0.0353 (10)
H7	0.816355	0.313577	0.471064	0.042*
C8	0.8107 (5)	0.4309 (3)	0.3811 (3)	0.0285 (9)
H8	0.847268	0.396869	0.324635	0.034*
C9	0.5407 (5)	0.4549 (3)	0.1772 (3)	0.0275 (8)
H9	0.491407	0.480334	0.234745	0.033*
C10	0.4537 (6)	0.3844 (3)	0.1223 (3)	0.0310 (9)
H10	0.347529	0.361627	0.142356	0.037*
C11	0.5234 (6)	0.3479 (3)	0.0381 (3)	0.0325 (10)
H11	0.466412	0.299450	−0.000679	0.039*
C12	0.6782 (6)	0.3833 (3)	0.0111 (3)	0.0330 (10)

Table 2: (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H12	0.728798	0.359978	−0.046907	0.040*
C13	0.7571 (5)	0.4526 (3)	0.0697 (3)	0.0280 (9)
H13	0.863475	0.476323	0.050879	0.034*

Experimental details

In the structure, all H atoms were positioned geometrically and refined using a riding model, $C-H_{aromatic} = 0.95 \text{ \AA}$. The H atom isotropic displacement parameters were fixed; $U_{iso}(H) = 1.2 U_{eq}(C)$.

Comment

Rhenium and two of its isotopes, ^{186}Re and ^{188}Re , have found use in radiopharmacy as a therapeutic radionuclide. ^{186}Re and ^{188}Re are both beta emitters with half-lives of 90 and 17 h, respectively. ^{186}Re has beta emission energy of 1.08 MeV, and ^{188}Re emits its beta particles with an energy of 2.12 MeV thus allowing for maximum tissue penetration depths of 5 and 11 mm, respectively [7, 8]. These emission properties together with the accessibility achieved from the utilization of the $^{188}W/^{188}Re$ generator, for ^{188}Re , and cyclotron availability, for ^{186}Re , has made rhenium an ideal candidate in clinical oncology [9, 10]. Several classes of rhenium based radiopharmaceuticals exists varying from small molecules, colloids, peptides to antibodies, each of which are coordinated or labelled differently with the rhenium metal centre and are distributed in various ways through the body to the potential disease site, whether it is cancer, arthritis, etc. all of which speaks to the versatility of rhenium-based radiopharmaceuticals [11, 12]. Aside from the direct use of the radioactive isotope, the non-radioactive rhenium can be used as a chemical analogue to the short-lived isotope of technetium namely, ^{99m}Tc , which is widely used in the medicinal world today [13]. When used in conjunction both rhenium and technetium, if the appropriate isotopes are used, can form part of a theranostic treatment regime [14]. Additionally ^{188}Re , when used together with a luminescent probe bound as a ligand system, has been demonstrated to be a potential theranostic agent utilizing the therapeutic nature of the beta particles emitted and diagnostic potential of the luminescent ligand system [15–17].

The crystal structure exhibits the expected distorted octahedral geometry for rhenium-tricarbonyl based systems as indicated by the $N_1-Re_1-N_2$ bond angle of $87.5(1)^\circ$.

The Re_1-C_{1-3} bond lengths are typical for rhenium-tricarbonyl complexes with an average bond distance of $1.905(7) \text{ \AA}$. The nitrate O_4-Re_1 bond distance is $2.153(2) \text{ \AA}$, and the dihedral angle generated by the planes of the two pyridine ligands is $65.4(1)^\circ$. Currently, there are four neutral bis-pyridine based rhenium-tricarbonyl structures known and available in the Cambridge Structural Database (CSD) [18] each varying in what ligand is coordinated in the 6th position on the rhenium metal centre. These are bromido (LODMUN) [19], trifluoromethanesulfonato (PAXLUW) [20], chlorido (PUVHIX) [21] and phenylacetylenyl (VIJWAM) complexes [22]. A pattern of inverse correlation can be observed when comparing the dihedral angle, made by the two planes of the two pyridine ligands, with the $Re-Br/Cl/O/C$ bond distance between the five structures. As the bond distance between the metal and 6th ligand increases for VIJWAM (Re_1-C_4 $2.108(9) \text{ \AA}$), this title compound (Re_1-O_4 $2.153(2) \text{ \AA}$), PAXLUW (Re_1-O_1 $2.194(4) \text{ \AA}$), PUVHIX (Re_1-Cl_1 $2.447(4) \text{ \AA}$) and LODMUN (Re_1-Br_1 $2.560(2) \text{ \AA}$); the dihedral angle decreases ($69.9(3)^\circ$, $65.4(1)^\circ$, $61.8(3)^\circ$, $54.3(1)^\circ$ and $53.5(1)^\circ$). This suggests that the relative position of freely rotating ligands bound equatorially around the metal can be directly affected by changing the 6th axially coordinated ligand (and the bond distance thereof), either by influencing the electron donation ability or the steric influence of the 6th ligand thus providing a means of fine tuning the geometric parameters of a potential radiopharmaceutical.

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