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The crystal structure of fac-tricarbonyl(bis(3,5-dimethyl-4H-pyrazole)- κ 1 N)-((nitrate)- κ 1 O)- rhenium(I) — 3,5-dimethyl-4H-pyrazole(1/1), C₁₈H₂₃N₇O₆R

Item Type	Article
Authors	Ramoba, Lesetja V.;Alexander, Orbett T.;Malan, Fredericks P.;Manicum, Amanda-Lee E.
DOI	https://doi.org/10.1515/ncrs-2024-0165
Publisher	De Gruyter
Download date	2026-05-09 17:35:32
Link to Item	https://hdl.handle.net/20.500.14519/799

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The crystal structure of *fac*-tricarbonyl(bis(3,5-dimethyl-4*H*-pyrazole)- κ^1N)-((nitrate)- κ^1O)-rhenium(I)—3,5-dimethyl-4*H*-pyrazole(1/1), $C_{18}H_{23}N_7O_6Re$

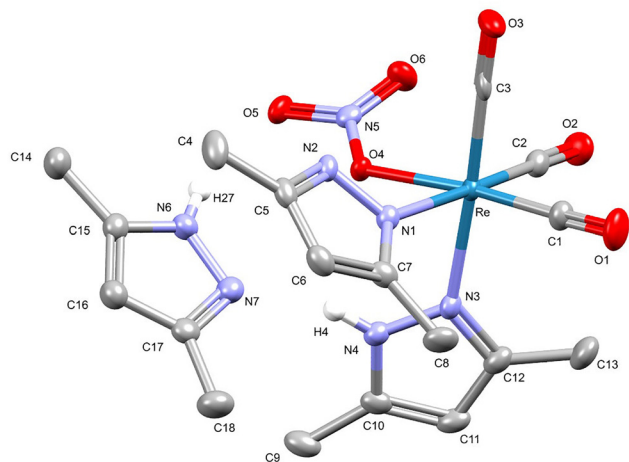


Table 1: Data collection and handling.

Crystal:	Colorless needles
Size:	0.29 × 0.25 × 0.19 mm
Wavelength:	MoK α radiation (0.71073 Å)
μ :	5.35 mm ⁻¹
Diffractometer, scan mode:	Rigaku XtaLAB Synergy R, ω
θ_{\max} , completeness:	26.4°, >99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	37,457, 4680, 0.088
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 4447
$N(\text{param})_{\text{refined}}$:	295
Programs:	OLEX2 ¹ , SHELX ^{2–4}

of the atoms including atomic coordinates and displacement parameters.

<https://doi.org/10.1515/ncrs-2024-0165>

Received April 10, 2024; accepted May 12, 2024;

published online June 19, 2024

Abstract

$C_{18}H_{23}N_7O_6Re$, triclinic, $P\bar{1}$ (no. 2), $a = 10.527(2)$ Å, $b = 10.849(2)$ Å, $c = 11.215(2)$ Å, $\alpha = 72.798(2)^\circ$, $\beta = 69.767(2)^\circ$, $\gamma = 87.496(10)^\circ$, $V = 1145.52(4)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0273$, $wR_{\text{ref}}(F^2) = 0.0727$, $T = 150(2)$ K.

CCDC no.: 2354778

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

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1 Source of material

The title compound was crystallized from the intermediate *fac*-[Re^I(CO)₃(OCH₃)₃]NO₃ in the presence of excess pyrazole ligand during the reaction indicated in the literature.⁵ The title compound was crystallized from the methanol filtrate in high purity. IR (ATR, cm⁻¹): $\nu_{\text{(CO)}}$ 2020, 1892, 1879.

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; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ 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

The radionuclide ^{99m}Tc is the most significant radioisotope in radiopharmaceuticals mainly for imaging purposes.⁵ This isotope has first to be stabilized by chelator ligands

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

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.9673 (4)	0.3612 (4)	0.1614 (4)	0.0252 (9)
C2	0.7182 (4)	0.3702 (4)	0.1489 (4)	0.0225 (8)
C3	0.8150 (4)	0.5433 (4)	0.2343 (4)	0.0217 (8)
C4	0.8166 (5)	0.4617 (4)	0.7352 (4)	0.0323 (10)
H4A	0.7824	0.5451	0.7001	0.048*
H4B	0.8934	0.4761	0.7609	0.048*
H4C	0.7442	0.4082	0.8132	0.048*
C5	0.8617 (4)	0.3944 (4)	0.6306 (4)	0.0221 (8)
C6	0.9584 (4)	0.3072 (4)	0.6053 (4)	0.0250 (8)
H6	1.0179	0.2753	0.6531	0.030*
C7	0.9525 (4)	0.2744 (3)	0.4960 (4)	0.0203 (8)
C8	1.0362 (4)	0.1833 (4)	0.4286 (5)	0.0287 (9)
H8A	0.9773	0.1281	0.4116	0.043*
H8B	1.0823	0.1293	0.4860	0.043*
H8C	1.1038	0.2327	0.3440	0.043*
C9	0.5849 (4)	-0.1320 (4)	0.6416 (5)	0.0292 (9)
H9A	0.5662	-0.0854	0.7079	0.044*
H9B	0.6388	-0.2055	0.6637	0.044*
H9C	0.4991	-0.1634	0.6415	0.044*
C10	0.6619 (4)	-0.0433 (3)	0.5073 (4)	0.0222 (8)
C11	0.7195 (4)	-0.0636 (4)	0.3850 (5)	0.0266 (9)
H11	0.7191	-0.1433	0.3662	0.032*
C12	0.7787 (4)	0.0551 (4)	0.2938 (4)	0.0231 (8)
C13	0.8558 (5)	0.0840 (4)	0.1485 (4)	0.0341 (10)
H13A	0.8092	0.1473	0.0984	0.051*
H13B	0.8613	0.0044	0.1232	0.051*
H13C	0.9475	0.1194	0.1283	0.051*
C14	0.4166 (5)	0.3214 (4)	0.9614 (4)	0.0329 (10)
H14A	0.4558	0.4107	0.9216	0.049*
H14B	0.4050	0.2928	1.0562	0.049*
H14C	0.3282	0.3167	0.9514	0.049*
C15	0.5094 (4)	0.2358 (4)	0.8928 (4)	0.0232 (8)
C16	0.5990 (4)	0.1504 (4)	0.9317 (4)	0.0267 (8)
H16	0.6142	0.1292	1.0140	0.032*
C17	0.6627 (4)	0.1016 (3)	0.8251 (4)	0.0234 (8)
C18	0.7709 (5)	0.0078 (4)	0.8125 (5)	0.0369 (10)
H18A	0.7932	-0.0100	0.7271	0.055*
H18B	0.7386	-0.0728	0.8855	0.055*
H18C	0.8521	0.0447	0.8167	0.055*
N1	0.8568 (3)	0.3384 (3)	0.4551 (3)	0.0175 (6)
N2	0.8019 (3)	0.4128 (3)	0.5382 (3)	0.0185 (6)
N3	0.7573 (3)	0.1460 (3)	0.3575 (3)	0.0187 (7)
N4	0.6869 (3)	0.0833 (3)	0.4878 (3)	0.0191 (6)
H4	0.6609	0.1207	0.5514	0.023*
N5	0.4899 (3)	0.3950 (3)	0.4361 (3)	0.0186 (6)
N6	0.5211 (3)	0.2331 (3)	0.7704 (3)	0.0239 (7)
H6A	0.4730	0.2785	0.7243	0.029*
N7	0.6165 (3)	0.1515 (3)	0.7253 (3)	0.0258 (7)
O1	1.0756 (3)	0.3676 (3)	0.0838 (3)	0.0376 (8)
O2	0.6771 (3)	0.3765 (3)	0.0646 (3)	0.0315 (7)
O3	0.8321 (3)	0.6539 (3)	0.2005 (3)	0.0297 (7)
O4	0.5981 (3)	0.3394 (2)	0.4483 (3)	0.0171 (5)
O5	0.3912 (3)	0.3811 (2)	0.5409 (3)	0.0243 (6)
O6	0.4869 (3)	0.4573 (3)	0.3266 (3)	0.0288 (6)
Re1	0.79120 (2)	0.35760 (2)	0.28640 (2)	0.01497 (7)

with substituents containing dominant physico-chemical properties. However, ligands providing enough stability to this radionuclide core under physiological conditions are limited.⁶ This simply signifies that, tuning the resulting complex properties by introducing various ligands is not favourable.⁶ Therefore, our interest in rhenium chemistry is the ability of this metal ion to form stable octahedral complexes with various suitable chelator ligands.^{7,8} Furthermore, this metal ion has two radioisotopes, ¹⁸⁶Re and ¹⁸⁸Re which exhibit favourable nuclear properties (beta emitters with emission energies of 1.01 and 2.12 MeV, respectively) since it is the analogue of technetium-99m. When used in conjunction, suitable isotopes of both rhenium and technetium can be used in theragnostic medicinal regime.⁸⁻¹³

The ligand employed in this study is a neutral heterocyclic Schiff base pyrazole that can accommodate chelation with a metal ion. The ability of these type of pyrazole ligands to coordinate with one or both nitrogen atoms to form monometallic and bimetallic complexes respectively is what makes these chelator ligands special.

The title complex presented herein consists of three facial carbonyl ligands, a nitrate and one pyrazole ligand coordinated in the equatorial plane, and another pyrazole occupying the axial position, together with a pyrazole guest molecule in the outer coordination sphere. The crystal structure exhibits an octahedral distortion for rheniumtricarbonyl-based complexes as indicated by the N1–Re1–N3 bond angle of 86.45(12)° and O4–Re1–N1 bond angle of 78.15(11)°. The rhenium bond distances for rhenium-carbonyl (Re–C) interactions are typical and within an average of 1.913(4) Å.^{8,12,13} The bond distance between the rhenium (Re1) and the oxygen (O4) of the nitrate moiety is 2.170(3) Å which is in accordance with literature related structures.^{14,15} This title compound is further stabilized by N–H...O, N–H...N, C–H...O, and C–H...N intra- and inter-molecular hydrogen contacts. All bond distances and angles of the presented complex correlate well with other structures already reported in the literature.¹⁴⁻¹⁷

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

Research funding: National Research Foundation of South Africa (Grant No. 129468 and TTK2204193773), Tshwane University of Technology, University of the Western Cape and the University of Pretoria.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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