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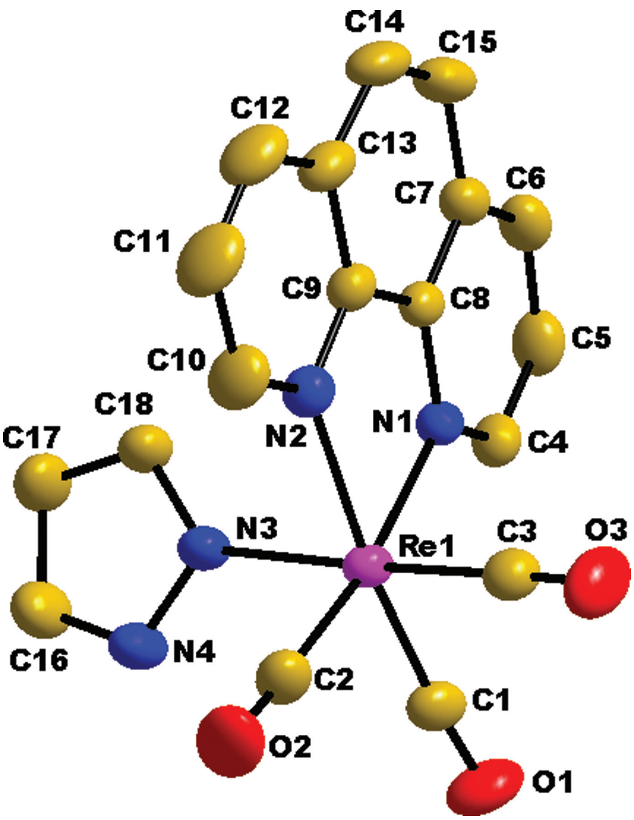
The crystal structure of *fac*-tricarbonyl(1,10-phenanthroline-κ^2*N*,*N′*)-(pyrazole-κ*N*)rhenium(I) nitrate, $C_{18}H_{12}O_3N_4Re$



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Abstract

$C_{18}H_{12}O_3N_4Re$, triclinic, $P\bar{1}$ (no. 2), $a = 8.3476(15)$ Å, $b = 9.5742(17)$ Å, $c = 12.435(2)$ Å, $\alpha = 87.606(5)°$, $\beta = 74.502(5)°$, $\gamma = 88.028(5)°$, $V = 956.6(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0213$, $wR_{ref}(F^2) = 0.0523$, $T = 100(2)$ 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.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	$0.51 \times 0.26 \times 0.25$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	6.40 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14935, 4594, 0.031
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4333
$N(param)_{refined}$:	269
Programs:	Bruker [1], SIR97 [2], Olex2 [3], SHELX [4], Diamond [5]

Source of material

The starting complex *fac*-[Re(CO)$_3$(Phen)(H$_2$O)] was prepared according to a published procedure [6]. To [Re(CO)$_3$(Phen)(H$_2$O)] (300 mg, 0.640 mmol) dissolved in methanol (10 mL), pyrazole (44 mg, 0.640 mmol) was added dropwise and the solution was refluxed for 24 h. The bright yellow solid (product) was obtained by evaporation of the solvent and recrystallized in cold methanol. Yellow cuboid crystals, were obtained (Yield = 217 mg, 65%).

IR (KBr, cm^{-1}): = 2031, 1906; **^{1}H NMR (DMSO-d$_6$):** = 2.50 (q, $j = 1.9$ Hz, 1H), 6.01 (t, $j = 4.0$ Hz, 1H), 6.83 (dd, $j = 8.0$ Hz, 2H), 7.52 (dd, $j = 12.0$ Hz, 4H), 8.05 (dd, $j = 8.0$ Hz, 2H), 8.84 (dd, $j = 8.0$ Hz, 2H), 9.54 (dd, $j = 8.0$ Hz, 1H); **^{13}C NMR (DMSO-d$_6$):** = 40.2, 103,3, 122.3, 126.8, 130.3, 132.7, 135.1, 137.3, 141.2, 148.7.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Re1	0.62238(2)	0.63841(2)	0.72199(2)	0.02954(5)
O1	0.4660(4)	0.4235(3)	0.9076(2)	0.0559(7)
O2	0.8504(4)	0.4107(3)	0.5891(3)	0.0688(9)
O3	0.3464(4)	0.5565(3)	0.6180(3)	0.0609(8)
N1	0.4932(3)	0.8212(3)	0.8056(2)	0.0288(5)
N2	0.6982(3)	0.8115(3)	0.6006(2)	0.0333(5)
N3	0.8197(3)	0.7025(3)	0.7917(2)	0.0344(6)
N4	0.9101(4)	0.6126(3)	0.8405(3)	0.0452(7)
C1	0.5308(4)	0.5033(3)	0.8395(3)	0.0377(7)
C2	0.7633(4)	0.4946(4)	0.6396(3)	0.0437(8)
C3	0.4491(4)	0.5892(4)	0.6570(3)	0.0382(7)
C4	0.4020(4)	0.8272(3)	0.9113(3)	0.0346(6)
H4A	0.389143	0.744134	0.956964	0.041*
C5	0.3251(4)	0.9496(4)	0.9571(3)	0.0411(7)
H5	0.263207	0.949667	1.033267	0.049*
C6	0.3380(4)	1.0710(4)	0.8927(3)	0.0404(7)
H6	0.282333	1.154553	0.922799	0.048*
C7	0.4347(4)	1.0692(3)	0.7819(3)	0.0348(6)
C8	0.5123(3)	0.9426(3)	0.7420(2)	0.0283(6)
C9	0.6222(4)	0.9368(3)	0.6321(3)	0.0309(6)
C10	0.8058(5)	0.8053(4)	0.4988(3)	0.0460(8)
H10	0.860171	0.718756	0.475041	0.055*
C11	0.8397(5)	0.9231(5)	0.4271(3)	0.0556(10)
H11	0.916752	0.915421	0.355831	0.067*
C12	0.7635(5)	1.0491(4)	0.4580(3)	0.0502(9)
H12	0.786898	1.128666	0.408621	0.060*
C13	0.6501(4)	1.0598(3)	0.5637(3)	0.0387(7)
C14	0.5614(5)	1.1852(4)	0.6046(3)	0.0454(8)
H14	0.575442	1.267240	0.557656	0.055*
C15	0.4578(5)	1.1899(3)	0.7085(3)	0.0433(8)
H15	0.399598	1.274615	0.733155	0.052*
C16	1.0242(5)	0.6786(4)	0.8743(4)	0.0534(10)
H16	1.102169	0.636372	0.909766	0.064*
C17	1.0096(5)	0.8184(4)	0.8490(4)	0.0493(9)
H17	1.073425	0.892119	0.863410	0.059*
C18	0.8813(4)	0.8284(3)	0.7977(3)	0.0388(7)
H18	0.842031	0.913406	0.770383	0.047*
O6	0.8355(4)	1.3339(3)	0.8784(3)	0.0694(7)
N5	0.9652(5)	1.2678(3)	0.8351(3)	0.0703(11)
O4[a]	0.9972(7)	1.1417(5)	0.8339(6)	0.0694(7)
O5A[b]	1.0819(10)	1.3220(8)	0.7666(8)	0.0694(7)
O4A[b]	0.9255(10)	1.1451(8)	0.8123(8)	0.0694(7)
O5[a]	1.0977(7)	1.3399(5)	0.8388(6)	0.0694(7)
H4	0.888(5)	0.513(5)	0.857(4)	0.055(12)*

[a]Occupancy: 0.6, [b]Occupancy: 0.4.

Comment

The organometallic synthon, *fac*-$[Maq_3(CO)_3]^+$ (M = Re, Tc-99m) has significantly intrigued a lot of researchers in the field of nuclear medicine not only due to their potential applications in diagnostic and therapeutic radiopharmacy, but also because of their coordinated water molecules, which are very labile (can easily be replaced or substituted with suitable ligand system) [7–9]. Recently the combination of these two radionuclides (Re, Tc) have been studied and reported on for possible theranostic purposes [10]. ^{99m}Tc is the workhorse for imaging with single photon emission computed tomography (SPECT) and the surrogate rhenium has found an imperative development in the radiotherapy application. The reasons for these are due to the ideal nuclear properties ($t_{1/2}$ = 6.02 h; E_c = 140 keV), widespread availability, and low cost for the former and ($t_{1/2}$ = 90 h; E_{max} = 1.07 MeV) and ($t_{1/2}$ = 17 h; E_{max} = 2.12 MeV) for the latter (^{186}Re and ^{188}Re), respectively. These two radionuclides are working hand in glove with each other for imaging (technetium-99m) and therapy ($^{186/188}$Re) [10–14].

In this study, two of the three coordinated aqua ligands in the starting material *fac*-$[Re(CO)_3(OH_2)_3]^+$ are substituted by a bidentate ligand. The unsubstituted remaining aqua ligand in the axial position is somewhat prone for replacement with a monodentate ligand to form a further stable tricarbonyl complex. These complexes are achieved by the means of the [2+1] mixed ligand approach also known as a two-step kit.

The title compound presented in this study is comprised of three facial carbonyl ligands, the **N**,**N′**-bidentate ligand (1,10-phenanthroline) in the equatorial position, pyrazole in the axial position and nitrate (NO_3^-) as the counter ion. The structure was found to possess an octahedral distortion, as seen in the angles 171.99(11)° for C1—Re1—N2 and 171.66(10)° for C2—Re1—N1, which diverge significantly from 180°. The bite angle distortion obtained on our crystal structure (75.45(9)°) correlates well with the bite angle of a similar structure already reported by Kemp et al. [15]. (75.95(13)°). The bond distances between rhenium and directly bonded neighboring atoms observed ranges from 1.915(3) Å to 2.187(2) Å. There are two molecules observed in the unit cell and they are packed in a head-to-head fashion, stabilized by C—H···O intermolecular hydrogen interactions as illustrated in Figure.

Experimental details

All the hydrogen atoms were positioned geometrically and refined discernibly using a riding model. The H atoms isotropic displacement parameters were fixed; $U_{iso}(H) = 1.2U_{eq}(C)$. All the H-atoms on the title structure were omitted in the figure for clarity.

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