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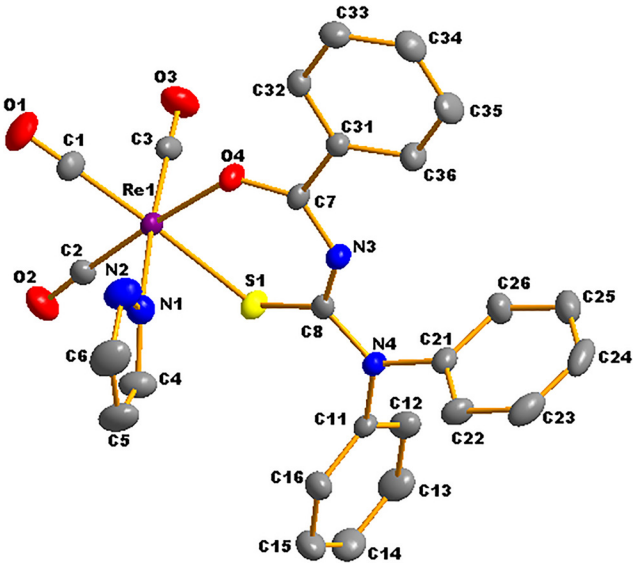
The crystal structure of *fac*-tricarbonyl (*N′*-benzoyl-*N*,*N*-diphenylcarbamimidothioato-κ²*S*,*O*)-(pyrazole-κ*N*)rhenium(I) — methanol (1/1) $C_{26}H_{23}O_4N_4SRe$



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Abstract

$C_{26}H_{23}O_4N_4SRe$, triclinic, $P\bar{1}$ (no. 2), a = 9.919(2) Å, b = 11.752(3) Å, c = 12.717(3) Å, α = 111.098(7)°, β = 94.467(7)°, γ = 98.295(7)°, V = 1354.9(5) Å^3, Z = 2, $R_{gt}(F)$ = 0.0342, $wR_{ref}(F^2)$ = 0.0843, T = 102.0(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.

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Table 1: Data collection and handling.

Crystal:	Yellow cuboid
Size:	0.32 × 0.17 × 0.06 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	4.61 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	28,629, 6727, 0.067
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 6176
$N(param)_{refined}$:	352
Programs:	Bruker [1], SIR97 [2], Olex2 [3], SHELX [4], Diamond [5]

Source of material

Fac-[Re(*S*,*O*)(CO)$_3$(H$_2$O)] (*S*,*O* = *N′*-benzoyl-*N*,*N*-diphenylcarbamimidothioate 20 mg, 0.029 mmol) was dissolved in methanol (3 ml) and pyrazole (3.29 mg, 0.00571 mmol) dissolved in (2 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}) ν(CO): 2015, 1889.

Experimental details

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

Comment

The chemistry of *fac*-[Re(CO)$_3$]$^+$ precursor has recently drawn attention of several research groups because of its

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

	x	y	z	U_{iso}*/U_{eq}
Re1	0.15615 (2)	0.26486 (2)	0.61077 (2)	0.02059 (6)
S1	0.13423 (10)	0.46874 (10)	0.74707 (10)	0.0256 (2)
O4	0.3664 (3)	0.3055 (3)	0.6821 (3)	0.0266 (6)
O2	−0.1446 (3)	0.2264 (3)	0.5100 (3)	0.0363 (8)
O1	0.1892 (4)	0.0175 (3)	0.4294 (3)	0.0473 (10)
N3	0.4193 (3)	0.5187 (3)	0.7938 (3)	0.0232 (7)
O3	0.0642 (4)	0.1328 (4)	0.7692 (3)	0.0426 (9)
N1	0.2368 (4)	0.3666 (4)	0.5072 (3)	0.0263 (8)
N4	0.3080 (3)	0.6801 (3)	0.8412 (3)	0.0214 (7)
O9	0.5471 (4)	0.1927 (4)	0.4341 (4)	0.0519 (10)
N2	0.3377 (4)	0.3371 (4)	0.4425 (4)	0.0357 (9)
C2	−0.0301 (4)	0.2388 (4)	0.5471 (4)	0.0243 (8)
C32	0.6289 (4)	0.2788 (4)	0.7371 (4)	0.0238 (8)
H32	0.566938	0.210060	0.682115	0.029*
C3	0.0987 (5)	0.1825 (4)	0.7086 (4)	0.0287 (9)
C33	0.7604 (5)	0.2659 (4)	0.7690 (4)	0.0285 (9)
H33	0.788788	0.188586	0.735104	0.034*
C7	0.4436 (4)	0.4044 (4)	0.7505 (3)	0.0212 (8)
C31	0.5870 (4)	0.3918 (4)	0.7851 (3)	0.0207 (8)
C11	0.1889 (4)	0.7385 (4)	0.8419 (3)	0.0204 (8)
C34	0.8517 (5)	0.3657 (5)	0.8506 (4)	0.0325 (10)
H34	0.941648	0.356410	0.873265	0.039*
C16	0.1444 (5)	0.7616 (4)	0.7470 (4)	0.0279 (9)
H16	0.190542	0.738956	0.681836	0.034*
C8	0.2972 (4)	0.5551 (4)	0.7921 (3)	0.0202 (8)
C1	0.1771 (4)	0.1104 (4)	0.4981 (4)	0.0295 (9)
C12	0.1242 (5)	0.7729 (4)	0.9379 (4)	0.0296 (9)
H12	0.157561	0.758404	1.003213	0.036*
C35	0.8098 (5)	0.4785 (5)	0.8982 (5)	0.0376 (11)
H35	0.872351	0.547556	0.952203	0.045*
C36	0.6770 (5)	0.4915 (4)	0.8675 (4)	0.0311 (10)
H36	0.647750	0.568217	0.902636	0.037*
C4	0.1875 (5)	0.4534 (5)	0.4804 (5)	0.0365 (11)
H00Q	0.114482	0.491746	0.512520	0.044*
C15	0.0303 (5)	0.8188 (5)	0.7490 (4)	0.0378 (12)
H15	−0.001597	0.835238	0.684432	0.045*
C5	0.2571 (6)	0.4808 (5)	0.3988 (5)	0.0424 (12)
H00S	0.241245	0.538965	0.365348	0.051*
C21	0.4346 (4)	0.7584 (4)	0.9072 (4)	0.0243 (9)
C14	−0.0360 (5)	0.8513 (5)	0.8423 (5)	0.0400 (12)
H14	−0.114006	0.889657	0.842126	0.048*
C26	0.4815 (5)	0.7536 (4)	1.0109 (4)	0.0305 (10)
H26	0.431680	0.696680	1.037661	0.037*
C22	0.5071 (4)	0.8416 (4)	0.8684 (4)	0.0287 (9)
H22	0.475438	0.845396	0.797456	0.034*
C13	0.0100 (5)	0.8288 (5)	0.9381 (5)	0.0365 (11)
H13	−0.036551	0.851448	1.003008	0.044*
C6	0.3530 (6)	0.4059 (5)	0.3774 (5)	0.0458 (13)
H00Y	0.418534	0.402692	0.326200	0.055*
C25	0.6010 (5)	0.8318 (5)	1.0752 (4)	0.0356 (11)
H25	0.633182	0.828552	1.146242	0.043*
C9	0.5515 (7)	0.0657 (6)	0.3820 (6)	0.0563 (16)
H93	0.627847	0.055567	0.336982	0.084*
H91	0.464686	0.022111	0.332147	0.084*
H92	0.565101	0.031071	0.440745	0.084*
C23	0.6269 (5)	0.9196 (5)	0.9345 (5)	0.0393 (12)
H23	0.676935	0.977127	0.908576	0.047*
C24	0.6735 (5)	0.9144 (5)	1.0366 (5)	0.0393 (12)
H24	0.755806	0.967739	1.080758	0.047*
H00B	0.394 (6)	0.287 (6)	0.457 (5)	0.049 (17)*
H94	0.624 (12)	0.254 (12)	0.494 (10)	0.16 (5)*

potential use as a therapeutic radiopharmaceutical. This has led to an increased investigation of rhenium metal complexes for their potential use as therapeutic and diagnostic agents [6–9]. Our research group is focusing on the synthesis of rhenium(I) tri- and dicarbonyl complexes for both diagnostic (depending on the type of the bidentate ligand used) and therapeutic applications [10–14]. This is done by coordinating a series of bi- and monodentate ligand systems to a rhenium metal center using a [2+1] mixed ligand approach. These coordinating ligands for the structure reported comprises of donor atoms such as sulfur and oxygen.

The molecular structure of the title complex comprises of three facial tricarbonyl ligands, a thiourea bidentate ligand in the equatorial plane which is *trans* to two of the carbonyl ligands and an *N*-coordinated pyrazole monodentate ligand in the axial position. The molecular structure has a guest molecule (methanol solvent) which is omitted for clarity. The bond distances between rhenium and the three carbons of the carbonyl ligands range between 1.894(4) and 1.917(5) Å, whereas Re1–O4, Re1–N1 and Re1–S1 were arranged in an increasing order as follows: 2.123(3), 2.196(4) and 2.452(12) Å, respectively. The results obtained correlate well with other structures already reported in literature by our research group [10, 11] and Warsink [15]. The polyhedron geometry of the complex reveals an octahedral distortion around the rhenium metal center. This distortion is more evident in the bond angles C3–Re1–N1 and C2–Re1–O4 which were reported as 175.64(16)° and 176.38(14)° respectively. The bite angle of the title structure was found to be 87.67(8)° and deviated slightly from the bite angle of a similar bidentate ligand coordinated to rhodium reported by Warsink (91.1(1)°) [15].

The molecules are arranged in a head-to-head manner and are stabilized by couple of intra- and intermolecular hydrogen bonds.

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