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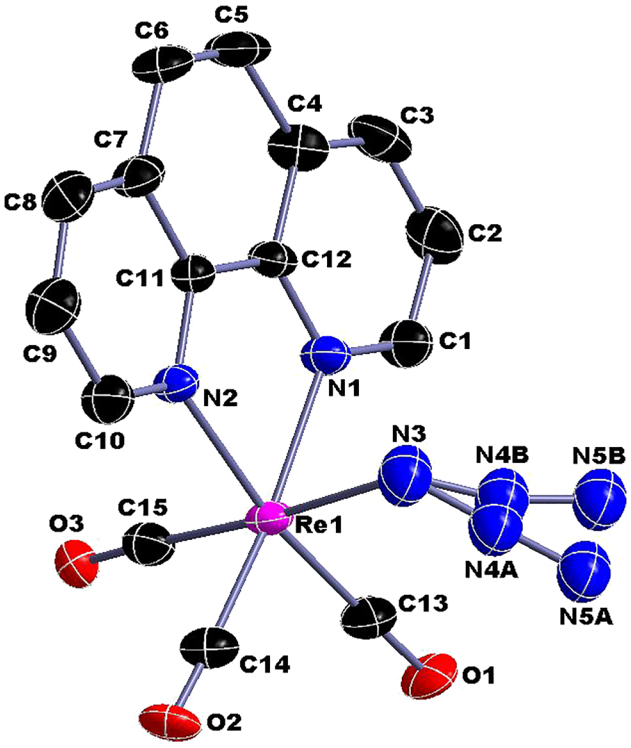
The crystal structure of *fac*-tricarbonyl(1,10-phenanthroline-κ^2N,N')-(azido-κ^1N)rhenium(I), $C_{15}H_8N_5O_3Re$



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Abstract

$C_{15}H_8N_5O_3Re$, monoclinic, *C*2/*c* (no. 15), a = 18.7508(8) Å, b = 12.2267(6) Å, c = 15.8442(11) Å, β = 123.6160(10)°, V = 3025.0(3) Å^3, Z = 8, $R_{gt}(F)$ = 0.0377, $wR_{ref}(F^2)$ = 0.0902, T = 292 K.

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The molecular structure of $C_{15}H_8N_5O_3Re$ is shown in figure. All the H-atoms and the water molecules were omitted for clarity. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

Table 1: Data collection and handling.

Crystal:	Orange cuboid
Size:	0.26 × 0.26 × 0.21 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	8.06 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
θ_{max}, completeness:	28.3°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	48093, 3765, 0.058
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma\ (I_{obs})$, 3,607
$N(param)_{refined}$:	212
Programs:	Bruker,[1] SHELX,[2–4] Olex2,[5] Diamond[6]

1 Source of materials

The title compound was synthesized by first reacting $AgNO_3$ (22 mg, 0.1298 mmol) with *fac*-$[NEt_4]_2[Re(CO)_3(Br)_3]$ (100 mg, 0.1298 mmol) in methanol and left stirring for 24 h at room temperature. The resulting mixture was filtered to remove the AgBr, and to the resulting filtrate, 1,10-phenanthroline (23 mg, 0.1298 mmol) was added and refluxed for a further 8 h. The azide salt (9 mg, 0.1428 mmol) was then introduced into the stirring mixture and the solution was left to reflux for 24 h. The light-orange precipitate was filtered off, dried *in vacuo*, and weighed to yield the title complex. Suitable crystals for X-ray diffraction were obtained from the vapour diffusion method using a mixture of methanol and toluene. Yield: 60 % yield, 22 mg, IR (ATR, cm^{-1}): ν(CO) = 2057, 2000, ν(N_3) = 1893, 1865. ^{1}H NMR (DMSOd_6): δ = 9.39 (dd, J = 1.2, 5.1 Hz, 2H), 8.95 (dd, J = 1.3, 8.3 Hz, 2H), 8.29 (s, 2H), 8.08 (q, J = 4.5 Hz, 2H) (Table 1).

2 Experimental details

All hydrogen atoms were positioned geometrically using a riding model, with fixed C–H aromatic = 0.97 Å and the O–H atoms = 0.82 Å. The H atom isotropic displacement parameters were fixed; U_{iso}(H) = 1.2U_{eq} (C) for aromatic and U_{iso}(H) = 1.5U_{eq} (O), allowing them to ride on the parent atom. The graphics

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were obtained using the DIAMOND program[6] with 50 % probability ellipsoids.

3 Comment

There is currently an ongoing and growing interest in rhenium(I) tricarbonyl complexes for potential use in diagnostic and therapeutic radiopharmacy. The reasons for the attraction of these complexes stem from several advantageous properties: their d^6 low-spin configuration, their compact size resulting from their low positive charge, their versatile coordination behaviour, their high chemical and kinetic stability, and their tuneable unique photophysical and luminescent properties.[7–14] These attributes provide a compelling rationale for this study, which seeks to explore the relatively underexplored area of azide-labeled rhenium (I) tricarbonyl chemistry for biological purposes.

We herein have the title structure which is constructed by three facial carbonyl ligands, the 1,10-phenanthroline bidentate ligand in the equatorial position, in trans position to the two carbonyl ligands, and lastly an *N*-coordinated azido monodentate ligand in the axial position. The synthesized complex was obtained utilizing the [2 + 1] mixed ligand coordination strategy from the *fac*-$[Re(MeOH)_3(CO)_3]^+$ metal precursor. The Re–C bond distances (Re1–C13, Re1–C14, and Re1–C15 are 1.916(7), 1.920(6), and 1.911(7) Å, respectively, and they are comparable to similar reported structures in literature.[15–18] It is worth noting that there is a 63:37 positional disorder observed on the azido moiety. The typical linear resonance conformation is observed in both terminal azido modelled disorders, with an average N–N bond distance of 1.15 Å. The observed rhenium to nitrogen bond distances are 2.182(5) Å (Re1–N1), 2.176(4) Å (Re1–N2) and 2.175(6) Å (Re1–N3), respectively, which are also comparable to literature reported structures.[16–19]

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