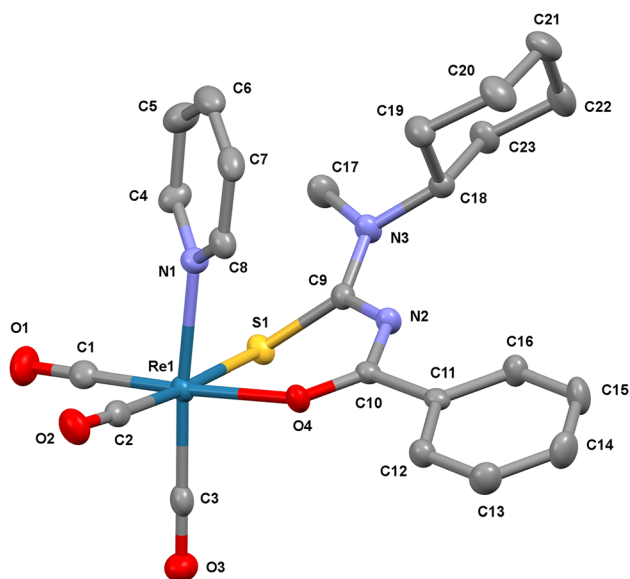


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# The crystal structure of *fac*-tricarbonyl(*N*-benzoyl-*N,N*-cyclohexylmethylcarbamimidothioato- $\kappa^2$ S,O)-(*pyridine*- $\kappa$ N)rhenium(I), C<sub>23</sub>H<sub>24</sub>N<sub>3</sub>O<sub>4</sub>ReS



**Table 1:** Data collection and handling.

Crystal:	Yellow block
Size:	0.14 × 0.13 × 0.10 mm
Wavelength:	Mo K $\alpha$ radiation (0.71073 Å)
$\mu$ :	5.40 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy R, $\omega$
$\theta_{\max}$ , completeness:	31.1°, >99 %
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	73,180, 6553, 0.072
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 5438
$N(\text{param})_{\text{refined}}$ :	290
Programs:	CrysAlis <sup>PRO</sup> [1], Olex2 [2], WinGX [3], SHELX [4, 5]

## 1 Source of materials

The title complex was synthesized using the starting precursor, *fac*-[NEt<sub>4</sub>]<sub>2</sub> [Re(CO)<sub>3</sub>Br<sub>3</sub>], as explained by Albert *et al.* [6], Manicum *et al.* [7, 8]. *fac*-[NEt<sub>4</sub>]<sub>2</sub> [Re(CO)<sub>3</sub>Br<sub>3</sub>], (201.1 mg, 0.336 mmol) was dissolved in 5 mL of acidic water (pH = 2.2) and stirred at room temperature for 10 min. AgNO<sub>3</sub> (134.4 mg, 0.7912 mmol) was added to the solution and stirred for 24 h at room temperature. The precipitate, AgBr, was separated and weighed. *N*-(cyclohexyl(methyl)carbamothioyl) benzamide (*N*-CyHMCB) bidentate ligand (72.11 mg, 0.336 mmol) was added to the filtrate and the reaction mixture was stirred at room temperature for 24 h. The light-yellow precipitate (*fac*-[Re(*N*-CyHMCB)(CO)<sub>3</sub>(OH<sub>2</sub>)]) was filtered off and dried. *fac*-[Re(*N*-CyHMCB)(CO)<sub>3</sub>(OH<sub>2</sub>)], (74.5 mg, 0.132 mmol) was dissolved in methanol (5 mL), and pyridine (0.07 mL) was added. The solution was first stirred for 24 h at room temperature. The light-yellow solid (product) was obtained by evaporation of the solvent and the precipitate was recrystallized from ethylacetate:hexane (8:2). Yield = 71.52 mg, 86 %, IR (KBr, cm<sup>-1</sup>):  $\nu_{\text{CO}}$  2103, 2007, 1879.

## 2 Experimental details

All the hydrogen atoms were positioned geometrically and refined using a riding model with fixed C–H<sub>Aromatic</sub> = 0.97 Å; C–H<sub>Methyl</sub> = 0.96 Å. The H atoms isotropic displacement

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### Abstract

C<sub>23</sub>H<sub>24</sub>N<sub>3</sub>O<sub>4</sub>ReS, orthorhombic, *Pbca* (no. 61),  $a = 15.1264(4)$  Å,  $b = 15.1167(5)$  Å,  $c = 20.1500$  Å,  $V = 4607.5(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $T = 150(2)$  K,  $R_{\text{gt}}(F) = 0.0416$ ,  $wR_{\text{ref}}(F^2) = 0.0691$ .

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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 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	U <sub>iso</sub> */U <sub>eq</sub>
C1	0.9576 (3)	0.3976 (3)	0.6787 (2)	0.0231 (8)
C2	0.9621 (3)	0.3719 (3)	0.5492 (2)	0.0229 (8)
C3	1.0041 (3)	0.5338 (3)	0.60326 (19)	0.0233 (8)
C4	0.7412 (3)	0.3490 (3)	0.6613 (2)	0.0260 (9)
H4	0.766036	0.366106	0.702659	0.031*
C5	0.6657 (3)	0.2981 (3)	0.6615 (2)	0.0326 (10)
H5	0.639454	0.280115	0.702166	0.039*
C6	0.6286 (3)	0.2736 (3)	0.6013 (2)	0.0316 (9)
H6	0.576853	0.238062	0.600066	0.038*
C7	0.6678 (3)	0.3015 (3)	0.5436 (2)	0.0281 (9)
H7	0.642954	0.286455	0.501773	0.034*
C8	0.7440 (3)	0.3518 (3)	0.5473 (2)	0.0241 (8)
H8	0.771213	0.370281	0.507138	0.029*
C9	0.7247 (2)	0.5736 (2)	0.64389 (18)	0.0190 (7)
C10	0.7691 (2)	0.5767 (2)	0.53014 (18)	0.0182 (7)
C11	0.7454 (2)	0.6206 (3)	0.46589 (18)	0.0183 (7)
C12	0.7991 (3)	0.6077 (3)	0.41046 (19)	0.0232 (8)
H12	0.849996	0.571062	0.413620	0.028*
C13	0.7784 (3)	0.6480 (3)	0.3511 (2)	0.0295 (9)
H13	0.815535	0.639597	0.313579	0.035*
C14	0.7041 (3)	0.7006 (3)	0.3456 (2)	0.0318 (10)
H14	0.689942	0.727837	0.304476	0.038*
C15	0.6502 (3)	0.7134 (3)	0.4004 (2)	0.0316 (10)
H15	0.598970	0.749429	0.396866	0.038*
C16	0.6712 (3)	0.6735 (3)	0.4604 (2)	0.0250 (8)
H16	0.634333	0.682653	0.497998	0.030*
C17	0.6505 (3)	0.5511 (3)	0.7513 (2)	0.0301 (9)
H17A	0.707889	0.525691	0.763320	0.045*
H17B	0.603777	0.507592	0.759450	0.045*
H17C	0.639552	0.604068	0.778106	0.045*
C18	0.5643 (3)	0.5947 (3)	0.64901 (19)	0.0201 (8)
H18	0.575368	0.639444	0.613448	0.024*
C19	0.5271 (3)	0.5126 (3)	0.6155 (2)	0.0288 (9)
H19A	0.513822	0.466907	0.649289	0.035*
H19B	0.571255	0.488025	0.584254	0.035*
C20	0.4423 (3)	0.5370 (4)	0.5778 (2)	0.0362 (11)
H20A	0.456717	0.578844	0.541521	0.043*
H20B	0.416414	0.483176	0.557647	0.043*
C21	0.3749 (3)	0.5795 (4)	0.6245 (2)	0.0367 (11)
H21A	0.322501	0.598294	0.598734	0.044*
H21B	0.355365	0.535175	0.657608	0.044*
C22	0.4133 (3)	0.6581 (3)	0.6599 (2)	0.0333 (10)
H22A	0.369215	0.681432	0.691708	0.040*
H22B	0.426136	0.705211	0.627159	0.040*
C23	0.4981 (3)	0.6350 (3)	0.6972 (2)	0.0279 (9)
H23A	0.523372	0.688959	0.717515	0.033*
H23B	0.484801	0.592302	0.733145	0.033*
N1	0.7813 (2)	0.3757 (2)	0.60527 (16)	0.0213 (6)
N2	0.7138 (2)	0.5930 (2)	0.57954 (16)	0.0205 (7)
N3	0.6510 (2)	0.5751 (2)	0.68101 (16)	0.0225 (7)
O1	0.9898 (2)	0.3636 (2)	0.72413 (15)	0.0360 (7)
O2	0.99820 (19)	0.3184 (2)	0.51869 (15)	0.0311 (7)
O3	1.0644 (2)	0.5806 (2)	0.60287 (15)	0.0317 (7)
O4	0.83560 (17)	0.52501 (17)	0.52858 (13)	0.0203 (5)

**Table 2:** (continued)

Atom	x	y	z	U <sub>iso</sub> */U <sub>eq</sub>
Re1	0.90396 (2)	0.45652 (2)	0.60597 (2)	0.01838 (5)
S1	0.82605 (6)	0.55705 (7)	0.68298 (5)	0.02222 (19)

parameters were fixed;  $U_{iso}(H) = 1.2U_{eq}(C)$  for aromatic and  $U_{iso}(H) = 1.5U_{eq}(C)$  for methyl, allowing them to ride on the parent atom. The graphics were obtained by using the MERCURY program with 50 % probability ellipsoids. All the hydrogen in the structure was omitted for clarity.

### 3 Comment

Organometallic rhenium(I) compounds have shown great promise for the development of new anticancer agents in recent years [8, 9]. A variety of tricarbonyl complexes containing mono- and bidentate ligands with nitrogen, oxygen, selenium, and phosphorus donors were discovered to have significant cytotoxic effects on various cancer cell lines [9–12]. However, the tricarbonyl precursor is particularly appealing not only for its potential use in biological applications but also for its flexibility of  $M(CO)_3$  to accommodate different ligands, which has led to the development of several strategies to saturate the coordination sphere with ligands from a single ligand to a combination of two or more ligands [13–15].

The molecular structure of the title complex comprises three facial tricarbonyl ligands, a thiourea bidentate ligand (*S,O*) in the equatorial plane which is *trans* to the two of the carbonyl ligands and *N*-coordinated pyridine ligand (monodentate) in the axial position as shown in the Figure. The complex was obtained by using the [2 + 1] mixed ligand approach on *fac*- $[M(CO)_3(O_2H)_3]^+$  moiety. In particular, the [2 + 1] approach provides a combination strategy of a bidentate and a monodentate ligand to yield a unique asymmetric tailoring of the complex that affects its (bio) chemical properties such as charge, lipophilicity, and stability [16, 17]. The structure of the titled complex possesses a distorted octahedral geometry around the rhenium metal center as seen with the bond angles C1—Re—O4 and C3—Re—N1, reported as 175.27(14)° and 175.88(14)°, respectively. The bite angle distortion of the structure was 85.96(7)°, which is similar to that of other rhenium metals coordinated with thiourea ligands [18–20]. The bond length between the three carbons from the carbonyl ligands and rhenium metal, Re—C1, Re—C2, and Re—C3 were found as 1.897(4), 1.914(4), and 1.929(4) Å, respectively.

The bond distances Re—S1, Re—N1, and Re—O4 were arranged in decreasing order 2.471(10), 2.220(3), and 2.138(3) Å, respectively. The bond length obtained in this study agrees with the other rhenium and rhodium structures that were reported previously [21–23]. There are three intramolecular hydrogen bonds in the titled complex that stabilizes the complex further from C16—H16...N2 which has the bond length of 2.768(5) Å, C17—H17A...S1 with a bond length of 2.992(5) Å, and C8—H8...O4 with a bond length of 2.986(5) Å.

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