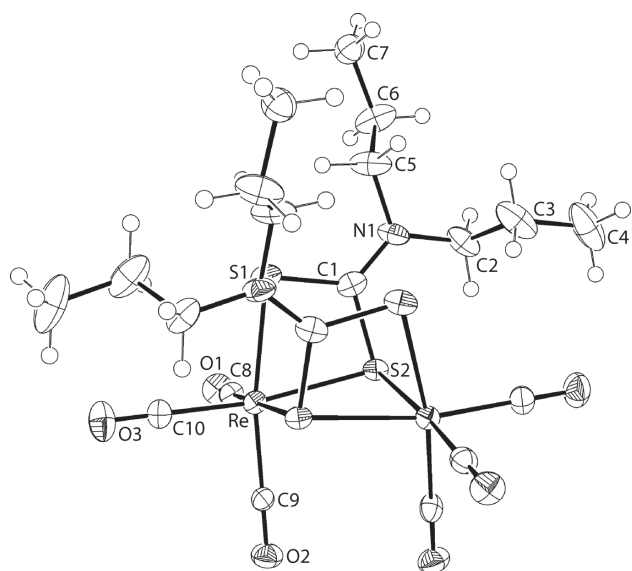




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Crystal structure of hexacarbonyl-bis(μ_2 -di-*n*-propyldithiocarbamate- $\kappa^3S,S':S$; $\kappa^3S:S:S'$)-di-rhenium(I), $C_{20}H_{28}N_2O_6Re_2S_4$



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Abstract

$C_{20}H_{28}N_2O_6Re_2S_4$, monoclinic, $C2/c$ (no. 15), $a = 17.9296(4)$ Å, $b = 9.60120(10)$ Å, $c = 16.1859(3)$ Å, $\beta = 103.934(2)^\circ$, $V = 2704.34(9)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0336$, $wR_{ref}(F^2) = 0.0902$, $T = 100$ 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:	Brown prism
Size:	0.09 × 0.07 × 0.04 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	20.5 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	31700, 2420, 0.046
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2402
$N(param)_{refined}$:	156
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

All chemicals and solvents were used as purchased without purification. The melting point was determined using a Melt-temp II digital melting point apparatus and was uncorrected. The solid-state IR spectrum was obtained on a Bruker Vertex 70v FTIR Spectrometer from 4000 to 400 cm⁻¹. The ¹H and ¹³C{¹H} NMR spectra were recorded at room temperature in DMSO-*d*₆ solution on a Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

Bromopentacarbonylrhenium was prepared from the reaction of a 1:1 molar ratio of Re₂(CO)₁₀ (Merck) and Br₂ (Panreac) in dichloromethane at 273 K. White solids were obtained from the slow evaporation of the solvent. The solids were recrystallised in acetone prior to use. The dithiocarbamate ligand was prepared *in situ* (acetone) from the reaction of CS₂ (Panreac 0.25 mmol) with di-*n*-propylamine (Merck, 0.25 mmol) and NaOH (0.02 mL; 50% w/v); CS₂ was added dropwise to the acetone solution (15 mL). The resulting mixture solution was kept at 273 K for 0.5 h. Bromopentacarbonylrhenium(I) (0.25 mmol, 0.102 g) in acetone (10 mL) was added to the solution containing the prepared sodium di-*n*-propyldithiocarbamate salt. The resulting mixture was stirred under reflux for 2 h. The filtrate was evaporated slowly until a light-brown precipitate was obtained. The precipitate was recrystallised from acetone-dichloromethane by slow evaporation to yield light-brown crystals. Yield: 0.15 g, 67.2%; **M.pt.**: 425–427 K. **IR** (cm⁻¹): 2006 (s) ν (CO), 1879(vs, br) ν (CO),

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

Atom	x	y	z	U _{iso} [*] /U _{eq}
Re	0.50575(2)	0.18792(3)	0.13502(2)	0.02114(13)
S1	0.54197(9)	0.43843(17)	0.15283(11)	0.0274(3)
S2	0.59562(8)	0.22353(16)	0.27875(10)	0.0211(3)
O1	0.6337(3)	0.1362(6)	0.0427(3)	0.0338(11)
O2	0.4825(3)	−0.1287(5)	0.1425(3)	0.0353(11)
O3	0.3869(3)	0.1967(6)	−0.0367(3)	0.0417(14)
N1	0.6350(3)	0.4966(6)	0.3056(4)	0.0308(13)
C1	0.5970(4)	0.4037(7)	0.2538(4)	0.0268(14)
C2	0.6847(4)	0.4637(8)	0.3886(5)	0.0337(16)
H2A	0.737041	0.498279	0.390171	0.040*
H2B	0.687814	0.361175	0.394820	0.040*
C3	0.6596(5)	0.5234(11)	0.4635(6)	0.053(2)
H3A	0.654213	0.625675	0.456992	0.063*
H3B	0.608815	0.484558	0.465054	0.063*
C4	0.7171(5)	0.4901(14)	0.5462(6)	0.066(3)
H4A	0.767752	0.525795	0.544055	0.099*
H4B	0.719949	0.388918	0.554583	0.099*
H4C	0.700686	0.533870	0.593645	0.099*
C5	0.6282(4)	0.6459(8)	0.2820(6)	0.0392(19)
H5A	0.590901	0.654918	0.226209	0.047*
H5B	0.606751	0.696256	0.324433	0.047*
C6	0.7005(5)	0.7149(8)	0.2765(6)	0.044(2)
H6A	0.722902	0.665525	0.234553	0.052*
H6B	0.737793	0.710208	0.332566	0.052*
C7	0.6861(5)	0.8661(8)	0.2501(5)	0.0375(17)
H7A	0.654287	0.870488	0.191693	0.056*
H7B	0.735312	0.912592	0.252843	0.056*
H7C	0.659484	0.912759	0.288556	0.056*
C8	0.5850(4)	0.1559(7)	0.0780(4)	0.0266(14)
C9	0.4904(4)	−0.0111(7)	0.1402(4)	0.0249(13)
C10	0.4312(4)	0.1938(7)	0.0269(4)	0.0272(15)

1615(s) v(CN), 1087 (m) v(CS), 898 (m) v(CS). ¹H NMR (DMSO-d₆): δ 0.87–0.93 (m, 3H, CH₃), 1.68–1.70 (m, 2H, CH₂), 3.56–3.60 (m, 2H, NCH₂). ¹³C{¹H} NMR (DMSO-d₆): δ 11.5 (CH₃), 20.5 (CH₂), 50.9 (CH₂N), 195.9 (CS₂), 196.1, 200.8, 213.3 (CO).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.98–0.99 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(C). The maximum and minimum residual electron density peaks of 1.97 and 2.04 e Å^{−3}, respectively, were located 0.91 and 0.86 Å from the Re atom, respectively.

Comment

Full characterisation by X-ray crystallography of binuclear molecules of the general formula {(CO)₃Re[S₂CNR₂]₂ is available for R = Et [5], n-Bu [6] and CH₂C(=O)OH [7]. The interesting feature of these structures is the observed syn-disposition of the dithiocarbamate groups, a feature quite distinct from that generally found in the far more numerous zinc-triad

structures of general formula {M[S₂CNR₂]₂ where by anti-dispositions are the norm [8]. The syn-dispositions in the rhenium(I) complexes raise the possibility of stabilising intramolecular π(chelate)···π(chelate) interactions [9, 10]. The X-ray crystallographic analysis of the title complex, {(CO)₃Re[S₂CN(n-Pr)₂]₂, was undertaken as part of on-going structural studies in this area.

The binuclear molecule of two-fold symmetric {Re[S₂CN(n-Pr)](CO)₃]₂ is shown in the figure (50% displacement ellipsoids; unlabelled atoms are related by the symmetry operation (i): 1 − x, y, 1/2 − z). The independent μ₂-bridging dithiocarbamate ligand chelates one rhenium(I) atom with similar Re–S bond lengths, i.e. Re–S1 = 2.4898(16) Å and Re–S2 = 2.5140(15) Å, while simultaneously bonding to the symmetry-related rhenium atom via one sulphur atom at a somewhat longer Re–S² bond length of 2.5671(15) Å. The participation of the S2 atom in two bonds with the rhenium(I) atom accounts for the disparity in the C–S bond lengths, with C1–S2 of 1.778(7) Å being considerably longer than C1–S1 of 1.725(7) Å. The molecule is disposed about a central Re₂S₂ core which approximates a rectangle. The dithiocarbamate ligands lie to the same side of the core and the separation between the ring centroids is 2.875(3) Å. The observed “syn” conformation of the dithiocarbamate ligands in the title complex matches literature precedents [5–7], with the comparable separations in the R = [5] and n-Bu [6] compounds being 2.8813(10) and 2.9177(13) Å, respectively. Such π···π interactions between chelate rings are well-known in the structural chemistry of metal complexes [9, 10]. The independent rhenium atom is also coordinated by three terminally bound carbonyl ligands to complete a C₃S₃ donor set. The carbonyl ligands occupy facial positions in the approximately octahedral geometry. The major distortion from a regular octahedral geometry results from the acute chelate angle, S1–Re–S2 of 70.75(5)°, with the major deviation of a trans angle from the ideal 180° seen in the C10–Re–S2 angle of 169.9(2)°.

The molecular packing features methylene- and methyl-C–H···O(carbonyl) interactions [C5–H5b···O2ⁱⁱ: H5b···O2ⁱⁱ = 2.47 Å, C5···O2ⁱⁱ = 3.359(9) Å with angle at H5b = 150° and C7–H7a···O3ⁱⁱⁱ: H7a···O3ⁱⁱⁱ = 2.52 Å, C7···O3ⁱⁱⁱ = 3.440(9) Å with angle at H7a = 156° for symmetry operations (ii) 1 − x, 1 + y, 1/2 − z and (iii) 1 − x, 1 − y, −z]. These combine to generate supramolecular layers in the bc-plane. The organic substituents project to either side of the layer, and these stack along the a-axis direction without directional interactions between them.

There are now three {(CO)₃Re[S₂CNR₂]₂ derivatives with all-alkyl dithiocarbamate ligands, i.e. R = Et [5], n-Pr and n-Bu [6], which adopt the same structural motif. All three structures were subjected to an analysis of the Hirshfeld surfaces

and two-dimensional fingerprint plots (full and delineated) in order to delineate any trends in the molecular packing, at least in terms of prominent contributions to the surface contacts. For this purpose Crystal Explorer 17 [11] was utilised following established procedures [12]. The common feature of the Hirshfeld surface are the significant contributions by $H \cdots H$ and $H \cdots O/O \cdots H$ contacts. A trend appears in the series for $H \cdots H$ contacts which increase from the smallest to largest R substituent, i.e. 20.2, 30.3 and 35.0%, respectively. This correlates with the greater H content across the series. The greatest contributions to the Hirshfeld surfaces come from $H \cdots O/O \cdots H$ contacts. While the percentages are around 40%, no definitive trends are noted in the respective values of 42.5, 37.5 and 40.9%. The next most prominent surface contacts are $H \cdots S/S \cdots H$ [10.5, 11.0 and 5.8%] and $H \cdots C/C \cdots H$ [9.8, 8.9 and 5.6%]. The percentage contributions in the $R = Et$ and $n-Pr$ crystals are about the same but, a notable drop is evident in the $R = n-Bu$ crystal. A similar trend is noted for $O \cdots O$ contacts [5.3, 5.5 and 1.8%]. The only other contacts of note are of the type $C \cdots O/O \cdots C$ which show a systematic downward trend [7.7, 3.6 and 1.8]. As a general comment, as the contribution of the two main surface contacts, i.e. $H \cdots O/O \cdots H$ and $H \cdots H$, systematically increase [62.7, 67.8 and 75.9%, respectively], there is a fall-off in some of the less significant contributors to the Hirshfeld surface.

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