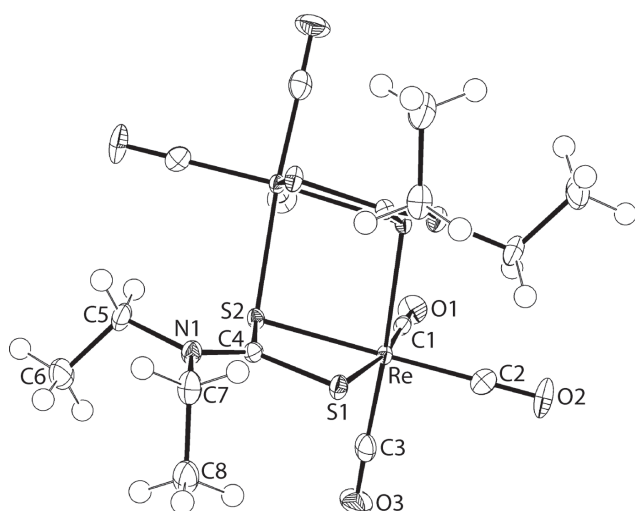


See Mun Lee, Kong Mun Lo, Peter J. Heard and Edward R.T. Tiekink\*

# Redetermination of the crystal structure of bis( $\mu_2$ -di-ethyldithiocarbamato- $\kappa^3 S, S': S; \kappa^3 S: S: S'$ )-hexacarbonyl-di-rhenium(I), $C_{16}H_{20}N_2O_6Re_2S_4$



<https://doi.org/10.1515/ncrs-2019-0070>

Received January 23, 2019; accepted February 14, 2019; available online March 11, 2019

## Abstract

$C_{16}H_{20}N_2O_6Re_2S_4$ , monoclinic,  $C2/c$  (no. 15),  $a = 15.3490(2)$  Å,  $b = 11.79920(10)$  Å,  $c = 13.33770(10)$  Å,  $\beta = 103.9980(10)^\circ$ ,  $V = 2343.80(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{gt}(F) = 0.0166$ ,  $wR_{ref}(F^2) = 0.0445$ ,  $T = 100(2)$  K.

CCDC no.: 1897176

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

\*Corresponding author: Edward R.T. Tiekink, Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my

See Mun Lee and Kong Mun Lo: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Peter J. Heard: Office of the Provost, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.07 \times 0.07 \times 0.04$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
$\mu$ :	$23.5 \text{ mm}^{-1}$
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$
$\theta_{\text{max}}$ , completeness:	$67.1^\circ$ , >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	14197, 2104, 0.026
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 2067
$N(\text{param})_{\text{refined}}$ :	141
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Re	0.47350(2)	0.76325(2)	0.60383(2)	0.00765(7)
S1	0.43243(4)	0.55949(6)	0.61125(5)	0.01035(14)
S2	0.39126(5)	0.73591(6)	0.74333(6)	0.00872(15)
O1	0.51144(14)	1.01967(19)	0.62497(16)	0.0184(4)
O2	0.58218(19)	0.75068(19)	0.4380(2)	0.0222(6)
O3	0.30706(14)	0.8176(2)	0.43129(16)	0.0255(5)
N1	0.34025(14)	0.5172(2)	0.75464(17)	0.0107(5)
C1	0.49772(18)	0.9238(3)	0.6177(2)	0.0114(6)
C2	0.5414(2)	0.7549(2)	0.5003(3)	0.0137(7)
C3	0.3685(2)	0.7961(3)	0.4966(2)	0.0155(6)
C4	0.38259(17)	0.5904(3)	0.7099(2)	0.0092(5)
C5	0.30327(18)	0.5474(3)	0.8441(2)	0.0137(6)
H5A	0.324167	0.624212	0.868469	0.016*
H5B	0.326616	0.493557	0.901227	0.016*
C6	0.2019(2)	0.5449(3)	0.8178(2)	0.0216(7)
H6A	0.178385	0.593927	0.758031	0.032*
H6B	0.180515	0.572200	0.877036	0.032*
H6C	0.180936	0.467142	0.801268	0.032*
C7	0.33083(19)	0.3978(3)	0.7196(2)	0.0145(6)
H7A	0.316292	0.350005	0.774337	0.017*
H7B	0.388636	0.371085	0.707616	0.017*
C8	0.2574(2)	0.3845(3)	0.6203(2)	0.0191(6)
H8A	0.273254	0.428466	0.564965	0.031(10)*
H8B	0.200309	0.412214	0.631581	0.029(10)*
H8C	0.251381	0.304351	0.600641	0.036(11)*

## Source of material

All chemicals and solvents were used as purchased without purification. The melting point was determined using

an Electrothermal digital melting point apparatus and was uncorrected. The solid-state IR spectrum was obtained on a Perkin Elmer Spectrum 400 FT Mid-IR/Far-IR spectrophotometer from 4000 to 400 cm<sup>-1</sup> (abbreviations: vs, very strong; s, strong). The <sup>1</sup>H NMR spectrum was recorded at room temperature in CDCl<sub>3</sub> solution on a Bruker AVANCE-400 MHz instrument.

Bromopentacarbonylrhenium was prepared from a 1:1 molar ratio of Re<sub>2</sub>(CO)<sub>10</sub> (Alfa Aesar) and Br<sub>2</sub> (Panreac) in dichloromethane at 0 °C. White solids were obtained from the slow evaporation of the solvent. The solids were recrystallized in acetone before use. Bromopentacarbonylrhenium(I) (0.25 mmol, 0.102 g) in acetone (10 mL) was added to sodium diethyldithiocarbamate hydrate (BDH; 0.25 mmol, 0.036 g) in acetone (10 mL). The resulting mixture was stirred and refluxed for 2 h. The filtrate was evaporated until a precipitate was obtained. The precipitate was recrystallized from dichloromethane by slow evaporation to yield colourless blocks. Yield: 0.15 g, 71.6%; M.p: 519–521 K. Solid-state IR (cm<sup>-1</sup>): 2010 (s) ν(CO), 1941(s) ν(CO), 1895 (vs) ν(CO), 1520(s) ν(CN), 1004 (m) ν(CS), 984 ν(CS). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.36 (t, 3H, CH<sub>3</sub>, J = 7 Hz), 1.45 (t, 3H, CH<sub>3</sub>, J = 7 Hz), 3.60–3.69 (m, 1H, CH<sub>2</sub>), 3.74–3.81 (m, 1H, CH<sub>2</sub>), 3.83–3.90 (m, 2H, CH<sub>2</sub>).

### Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.98–0.99 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$ . The maximum and minimum residual electron density peaks of 0.43 and 1.28 e Å<sup>-3</sup>, respectively, were located 1.01 and 0.76 Å from the C2 and Re atoms.

### Comment

Molecules of the general formula {Re[S<sub>2</sub>CNR<sub>2</sub>](CO)<sub>3</sub>}<sub>2</sub> are well known [5–10] and crystal structure determinations are known for the R = Et [8], R = nBu [10] and R = CH<sub>2</sub>C(=O)OH [7] compounds. No details are available for the R = Et species as this is available only as a private communication to the Cambridge Structural Database [8, 9]. As a continuation of studies in rhenium dithiocarbamates [10], herein the crystal and molecular structures of the R = Et complex are described.

The binuclear molecule of {Re[S<sub>2</sub>CNEt<sub>2</sub>](CO)<sub>3</sub>}<sub>2</sub> is shown in the figure (70% displacement ellipsoids with unlabelled atoms related by the symmetry operation  $i: 1 - x, y, 3/2 - z$ ) and is disposed about a 2-fold axis of symmetry. The molecule features two μ<sub>2</sub>-bridging dithiocarbamate ligands, simultaneously chelating one rhenium(I) atom and binding to the other *via* one sulphur atom. The Re–S1, S2 and S2<sup>i</sup> bond lengths of 2.4935(7), 2.5091(7) and 2.5538(7) Å, respectively indicate a symmetric mode of coordination of the chelate. The values lie within the ranges for the equivalent bonds reported for

the R = nBu derivative [10]. There is a disparity in the C4–S1, S2 bond lengths owing to the additional bridging interaction of the S2 atom so that the C4–S2 bond [1.770(3) Å] is considerably longer than the C4–S1 bond [1.714(3) Å]. The central Re<sub>2</sub>S<sub>2</sub> core approximates a rectangle owing to the disparity (ca. 0.04 Å) in Re–S2, S2<sup>i</sup> bond lengths. Three terminally bound carbonyl groups complete the coordination geometry of the rhenium atom and occupy facial positions in the approximately octahedral C<sub>3</sub>S<sub>3</sub> donor set. The dithiocarbamate ligands lie on the same side of the central Re<sub>2</sub>S<sub>2</sub> core and may be described as being *syn* [the separation between the mid-points of the chelate rings is 2.8813(10) Å]. This conformation is as found crystallographically for related species [7, 8, 10] and our preliminary <sup>1</sup>H NMR data indicate the same structure is retained in CDCl<sub>3</sub> solution.

In the crystal, molecules are held in place by weak contacts; the two most readily identifiable ones are described in more detail here. The presence of methylene-C7–H···O2(carbonyl) interactions [C7–H7b···O2<sup>ii</sup>: C7–H7b···O2<sup>ii</sup> = 2.54 Å, C7···O2<sup>ii</sup> = 3.260(4) Å with angle at H7b = 129° for  $ii: 1 - x, 1 - y, 1 - z$ ] lead to supramolecular tapes along the *c*-axis. Connections between the tapes leading to a three-dimensional architecture are of the type carbonyl-C≡O3···π(chelate), where the chelate comprises the Re, S1, S2 and C4 atoms [C3≡O3···Cg(RuS<sub>2</sub>C)<sup>iii</sup> = 3.422(2) Å with angle at O3 = 151.7(2)° for  $iii: 1/2 - x, 3/2 - y, 1 - z$ ]. Such chelate interactions [11], including those involving carbonyl ligands [12], are well documented.

**Acknowledgements:** Sunway University is thanked for support of biological and crystal engineering studies of metal dithiocarbamates.

### References

- Agilent Technologies: CrysAlis<sup>PRO</sup>. Agilent Technologies, Santa Clara, CA, USA (2017).
- Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
- Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **71** (2015) 3–8.
- Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.
- Rowbottom, J. F.; Wilkinson, G.: Dithiocarbamate- and carbonyldithiocarbamate-complexes of rhenium(-I), -(III), -(IV), and (V). *J. Chem. Soc. Dalton Trans.* (1974) 684–689.
- Nakamoto, M.; Tanaka, K.; Tanaka, T.: Thermolysis of some carbamatotetracarbonyl- and carbamatopentacarbonylrhenium(I) complexes in the solid state and in solution. *J. Chem. Soc. Dalton Trans.* **10** (1979) 87–91.
- Gorshkov, N. I.; Lumpov, A. A.; Miroslavov, A. E.; Suglovov, D. N.; Katzenellenbogen, J. A.; Luyt, L. G.: Scorpion-like dithiocarbamate-carboxylate ligands for linking M(CO)<sub>3</sub><sup>+</sup> (M = Tc, Re). *Czech. J. Phys.* **53** (2003) A543–A548.

8. Flörke, U.: Private communication to the Cambridge Structural Database. Refcode: KOGRIJ (2014).
9. Groom, C. R.; Allen, F. H.: The Cambridge Structural Database in retrospect and prospect. *Angew. Chem. Int. Ed.* **53** (2014) 662–671.
10. Heard, P. J.; Halcovitch, N. R.; Lee, S. M.; Tiekink, E. R. T.: Crystal structure of bis( $\mu_2$ -di-*n*-butyldithiocarbamato- $\kappa^3S,S';\kappa^3S:S:S'$ )-hexacarbonyl-di-rhenium(I),  $C_{24}H_{36}N_2O_6Re_2$ . *Z. Kristallogr. NCS* **233** (2018) 485–487.
11. Tiekink, E. R. T.: Supramolecular assembly based on emerging intermolecular interactions of particular interest to coordination chemists. *Coord. Chem. Rev.* **345** (2017) 209–228.
12. Zukerman-Schpector, J.; Haiduc, I.; Tiekink, E. R. T.: The metacarbonyl  $\cdot\cdot\pi$ (aryl) interaction as a supramolecular synthon for the stabilisation of transition metal carbonyl crystal structures. *Chem. Commun.* **47** (2011) 12682–12684.