Peter J. Heard, Nathan R. Halcovitch, Lee See Mun and Edward R.T. Tiekink*

Crystal structure of bis(μ_2 -di-*n*-butyldithiocarbamato- $\kappa^3 S, S':S; \kappa^3 S:S:S'$)-hexacarbonyl-dirhenium(I), $C_{24}H_{36}N_2O_6Re_2$

<https://doi.org/10.1515/ncrs-2017-0370>

Received November 27, 2017; accepted February 24, 2018; available online March 16, 2018

Abstract

$C_{24}H_{36}N_2O_6Re_2$, triclinic, $P\bar{1}$ (no. 2), $a = 10.3013(2)$ Å, $b = 11.3471(2)$ Å, $c = 14.5967(3)$ Å, $\alpha = 72.540(2)^\circ$, $\beta = 73.074(2)^\circ$, $\gamma = 85.369(2)^\circ$, $V = 1557.05(6)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0214$, $wR_{ref}(F^2) = 0.0466$, $T = 100(2)$ K.

CCDC no.: 1825597

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

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

Nathan R. Halcovitch: Department of Chemistry, Lancaster University, Lancaster LA1 4YB, United Kingdom

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

Table 1: Data collection and handling.

Crystal:	Cube, colourless
Size:	$0.08 \times 0.06 \times 0.06$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	8.07 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
θ_{max} , completeness:	28.7° , > 88% (up to 25.2° , > 99%)
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	30121, 7111, 0.026
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6456
$N(\text{param})_{\text{refined}}$:	347
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX and ORTEP [4]

Source of materials

Bromopentacarbonylrhenium was prepared from a 1:1 molar ratio of $Re_2(CO)_{10}$ (Alfa Aesar) and Br_2 (Panreac) in dichloromethane at 0° . White solids were obtained from the slow evaporation of the solvent. The solids were recrystallized in acetone before use. The dithiocarbamate ligand was prepared *in situ* (acetone) from the reaction of CS_2 (Panreac 0.25 mmol) with di-*n*-butylamine (Merck, 0.25 mmol) and NaOH (0.02 mL; 50% w/v); CS_2 was added dropwise into the acetone solution (15 mL). The resulting mixture solution was kept at 273 K for 0.5 h. Bromopentacarbonylrhenium(I) (0.25 mmol) in acetone (10 mL) was added into the solution and the resulting mixture was stirred for 2.5 h. The filtrate was evaporated until a precipitate was obtained. The precipitate was washed with *n*-hexane and recrystallised from its dichloromethane solution. Colourless blocks were obtained from the slow evaporation of the solvent. Yield: 61%. **M.p.**: 450 K. **IR** (KBr, cm^{-1}): 2031 (s), 2012 (s), 1888 (vs). **1H NMR** ($CDCl_3$): 0.96–1.04 (m, 6H, CH_3), 1.33–1.49 (m, 4H, CH_2-CH_3), 1.66–1.89 (m, 4H, $-CH_2-CH_2N$), 3.68–3.82 (m, 4H, NCH_2-).

Experimental details

The C-bound H atoms were geometrically placed ($C-H = 0.98-0.99$ Å) and refined as riding with $U_{\text{iso}}(H) = 1.2-1.5U_{\text{eq}}(C)$. Owing to poor agreement, the (6 3 3) reflection was

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Re1	0.40511(2)	0.27796(2)	0.19086(2)	0.01285(4)
Re2	0.39780(2)	0.24905(2)	0.45674(2)	0.01121(4)
S1	0.48696(9)	0.49522(8)	0.14289(6)	0.01645(17)
S2	0.28273(8)	0.37480(8)	0.32572(6)	0.01362(16)
S3	0.59125(9)	0.39904(8)	0.38438(6)	0.01580(17)
S4	0.55783(8)	0.19842(8)	0.30727(6)	0.01288(16)
O1	0.2678(3)	0.0216(3)	0.2747(2)	0.0311(7)
O2	0.6050(3)	0.1905(3)	0.02274(19)	0.0258(6)
O3	0.1977(3)	0.3460(3)	0.0705(2)	0.0265(6)
O4	0.1866(3)	0.0414(3)	0.5203(2)	0.0265(6)
O5	0.5463(3)	0.0839(2)	0.60121(19)	0.0242(6)
O6	0.2157(3)	0.3495(2)	0.62371(18)	0.0203(5)
N1	0.3637(3)	0.6121(3)	0.2807(2)	0.0149(6)
N2	0.7855(3)	0.3384(3)	0.2362(2)	0.0138(6)
C1	0.3792(3)	0.5105(3)	0.2529(2)	0.0142(7)
C2	0.4341(4)	0.7281(3)	0.2146(3)	0.0180(7)
H2A	0.3755	0.7991	0.2253	0.022*
H2B	0.4513	0.7296	0.1439	0.022*
C3	0.5676(4)	0.7403(3)	0.2353(3)	0.0201(8)
H3A	0.6290	0.6735	0.2184	0.024*
H3B	0.5509	0.7299	0.3076	0.024*
C4	0.6373(4)	0.8657(4)	0.1751(3)	0.0244(8)
H4A	0.5752	0.9322	0.1919	0.029*
H4B	0.7196	0.8711	0.1957	0.029*
C5	0.6775(4)	0.8877(4)	0.0623(3)	0.0284(9)
H5A	0.7293	0.8169	0.0457	0.043*
H5B	0.7335	0.9627	0.0292	0.043*
H5C	0.5957	0.8977	0.0395	0.043*
C6	0.2783(4)	0.6156(3)	0.3802(3)	0.0177(7)
H6A	0.3219	0.6702	0.4044	0.021*
H6B	0.2727	0.5315	0.4274	0.021*
C7	0.1358(4)	0.6614(4)	0.3803(3)	0.0213(8)
H7A	0.0900	0.6048	0.3593	0.026*
H7B	0.1408	0.7442	0.3314	0.026*
C8	0.0520(4)	0.6689(4)	0.4840(3)	0.0251(8)
H8A	−0.0444	0.6805	0.4846	0.030*
H8B	0.0591	0.5891	0.5340	0.030*
C9	0.0947(4)	0.7720(4)	0.5159(3)	0.0291(9)
H9A	0.1858	0.7554	0.5247	0.044*
H9B	0.0305	0.7764	0.5792	0.044*
H9C	0.0953	0.8508	0.4642	0.044*
C10	0.6625(4)	0.3201(3)	0.2991(2)	0.0157(7)
C11	0.8397(4)	0.2618(3)	0.1682(3)	0.0171(7)
H11A	0.9088	0.3102	0.1086	0.021*
H11B	0.7653	0.2413	0.1452	0.021*
C12	0.9036(4)	0.1423(4)	0.2168(3)	0.0230(8)
H12A	0.8350	0.0929	0.2761	0.028*
H12B	0.9788	0.1619	0.2394	0.028*
C13	0.9577(4)	0.0672(4)	0.1425(3)	0.0296(9)
H13A	0.8835	0.0538	0.1162	0.036*
H13B	1.0301	0.1154	0.0854	0.036*
C14	1.0137(5)	−0.0562(4)	0.1881(4)	0.0402(12)
H14A	1.0891	−0.0436	0.2125	0.060*
H14B	1.0463	−0.1003	0.1374	0.060*
H14C	0.9422	−0.1050	0.2440	0.060*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C15	0.8773(4)	0.4344(3)	0.2320(3)	0.0190(8)
H15A	0.9681	0.3986	0.2324	0.023*
H15B	0.8419	0.4640	0.2919	0.023*
C16	0.8899(4)	0.5430(3)	0.1379(3)	0.0203(8)
H16A	0.9337	0.5144	0.0784	0.024*
H16B	0.7979	0.5723	0.1341	0.024*
C17	0.9720(4)	0.6503(4)	0.1355(3)	0.0239(8)
H17A	0.9651	0.7219	0.0783	0.029*
H17B	0.9319	0.6745	0.1976	0.029*
C18	1.1196(4)	0.6209(4)	0.1263(3)	0.0282(9)
H18A	1.1279	0.5554	0.1858	0.042*
H18B	1.1677	0.6950	0.1204	0.042*
H18C	1.1593	0.5931	0.0667	0.042*
C19	0.3210(4)	0.1160(4)	0.2455(3)	0.0206(8)
C20	0.5285(4)	0.2235(3)	0.0854(3)	0.0193(8)
C21	0.2773(4)	0.3225(3)	0.1153(3)	0.0195(8)
C22	0.2655(4)	0.1196(3)	0.4947(3)	0.0179(7)
C23	0.4894(4)	0.1455(3)	0.5475(2)	0.0152(7)
C24	0.2852(3)	0.3126(3)	0.5615(2)	0.0143(7)

omitted from the final cycles of refinement. The maximum and minimum residual electron density peaks of 1.57 and 1.06 e Å^{−3}, respectively, were located 0.97 and 0.67 Å from the S3 and Re1 atoms.

Discussion

The biological efficacy of metal dithiocarbamates ([−]S₂CNRR') is well known and has been the subject of a review [5]. The heavy element, rhenium, continues to attract interest as both putative therapeutic agents as well as radiopharmaceuticals and dithiocarbamates feature in these investigations [6–8]. In continuation of studies into the biological efficacy of heavy metal dithiocarbamate compounds as anti-cancer, e.g. bismuth [9], and anti-microbial, e.g. gold [10], agents, attention has been directed towards rhenium and it was in this context that the title complex was studied.

The binuclear complex of {Re[S₂CN(n-Bu)₂](CO)₃]₂ is shown in the figure (50% displacement ellipsoids) and features two μ₂-bridging dithiocarbamate ligands, each chelating one rhenium(I) atom and simultaneously bonding to the other *via* one sulphur atom. The Re–S bond lengths formed by the chelating ligands span the narrow range 2.4953(9) to 2.5125(8) Å and the bridging Re–S bond lengths are considerably longer at 2.5659(8) Å (Re1–S4) and 2.5511(8) Å (Re2–S2). This disparity in Re–S bond lengths implies the central Re₂S₂ core approximates a rectangle. Each rhenium atom is also coordinated by three terminally bound carbonyl groups which occupy facial positions in the approximately octahedral C₃S₃ donor set. Globally, the dithiocarbamate ligands are *syn*, lying to the same side of the central Re₂S₂ core.

The structure resembles closely that reported for the diethyldithiocarbamate analogue [11], i.e. with a *syn*-disposition of dithiocarbamate ligands and *fac*- C_3S_3 coordination geometries. The main difference relates to the latter conforming to crystallographic 2-fold symmetry; the Re—S (chelating) bond lengths are 2.4813(15) and 2.5050(15) Å and the bridging distance is 2.5475(15) Å.

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

References

1. Rigaku/Oxford Diffraction: CrysAlis^{PRO}. Rigaku Corporation, The Woodlands, TX, USA (2015).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallog.* **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.* **45** (2012) 849–854.
5. Hogarth, G.: Metal-dithiocarbamate complexes: chemistry and biological activity. *Mini Rev. Med. Chem.* **12** (2012) 1202–1215.
6. Lo, K. K.-W.: Luminescent rhenium(I) and iridium(III) polypyridine complexes as biological probes, imaging reagents, and photocytotoxic agents. *Acc. Chem. Res.* **48** (2015) 2985–2995.
7. Berry, D. J.; Torres Martin de Rosales, R.; Charoenphun, P.; Blower, P. J.: Dithiocarbamate complexes as radiopharmaceuticals for medical imaging. *Mini Rev. Med. Chem.* **12** (2012) 1174–1183.
8. Medici, S.; Peana, M.; Nurchi, V. M.; Lachowicz, J. I.; Crisponi, G.; Zoroddu, M. A.: Noble metals in medicine: latest advances. *Coord. Chem. Rev.* **284** (2015) 329–350.
9. Ishak, D. H. A.; Ooi, K. K.; Ang, K. P.; Akim, A. Md.; Cheah, Y. K.; Nordin, N.; Halim, S. N. B. A.; Seng, H.-L.; Tiekink, E. R. T.: A bismuth diethyldithiocarbamate compound promotes apoptosis in HepG2 carcinoma, cell cycle arrest and inhibits cell invasion through modulation of the NF- κ B activation pathway. *J. Inorg. Biochem.* **130** (2014) 38–51.
10. Chen, B.-J.; Jamaludin, N. S.; Khoo, C.-H.; See, T.-H.; Sim, J.-H.; Cheah, Y.-K.; Halim, S. N. A.; Seng, H.-L.; Tiekink, E. R. T.: In vitro antibacterial and time kill evaluation of mononuclear phosphane-gold(I) dithiocarbamates. *J. Inorg. Biochem.* **163** (2016) 68–80.
11. Flörke, U.: Private communication to the Cambridge Structural Database. Refcode, KOGRIJ (2014).