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Z. Kristallogr. NCS 2018; 233(3): 485–487

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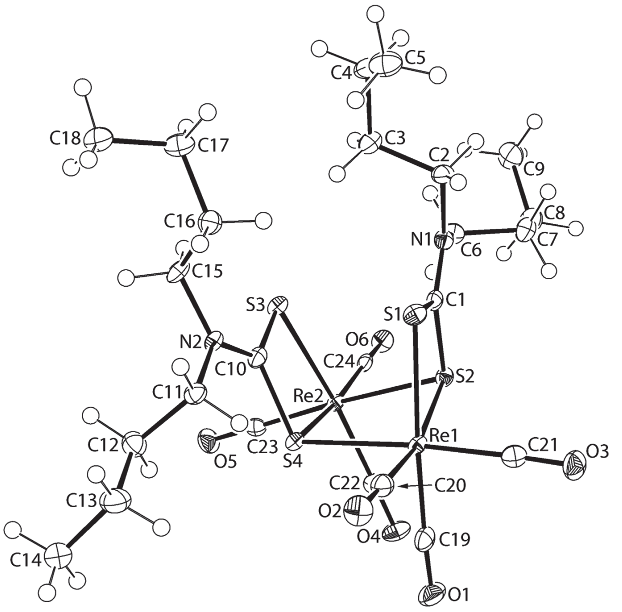
Crystal structure of bis(μ$_2$-di-*n*-butyldithiocarbamato-κ^3*S*,*S*′:*S*;κ^3*S*:*S*:*S*′)-hexacarbonyldirhenium(I), $C_{24}H_{36}N_2O_6Re_2$



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, $\alpha = 72.540(2)°$, $\beta = 73.074(2)°$, $\gamma = 85.369(2)°$, $V = 1557.05(6)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0214$, $wR_{ref}(F^2) = 0.0466$, $T = 100(2)$ 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.

Table 1: Data collection and handling.

Crystal:	Cube, colourless
Size:	0.08 × 0.06 × 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%)
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	30121, 7111, 0.026
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6456
$N(param)_{refined}$:	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). ^{1}**H 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 $U_{iso}(H) = 1.2$–$1.5U_{eq}(C)$. Owing to poor agreement, the (6 3 3) reflection was

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{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*
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 ($^{-}S_2CNRR'$) 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 $\{Re[S_2CN(n\text{-}Bu)_2](CO)_3\}_2$ is shown in the figure (50% displacement ellipsoids) and features two μ_2-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 Re_2S_2 core approximates a rectangle. Each rhenium atom is also coordinated by three terminally bound carbonyl groups which occupy facial positions in the approximately octahedral C_3S_3 donor set. Globally, the dithiocarbamate ligands are *syn*, lying to the same side of the central Re_2S_2 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.

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