Redetermination of the crystal structure of tetrakis(tricarbonyl-μ_3-methane thiolato-rhenium(I) – Localization of hydrogen atoms, $C_{16}H_{12}O_{12}Re_4S_4$

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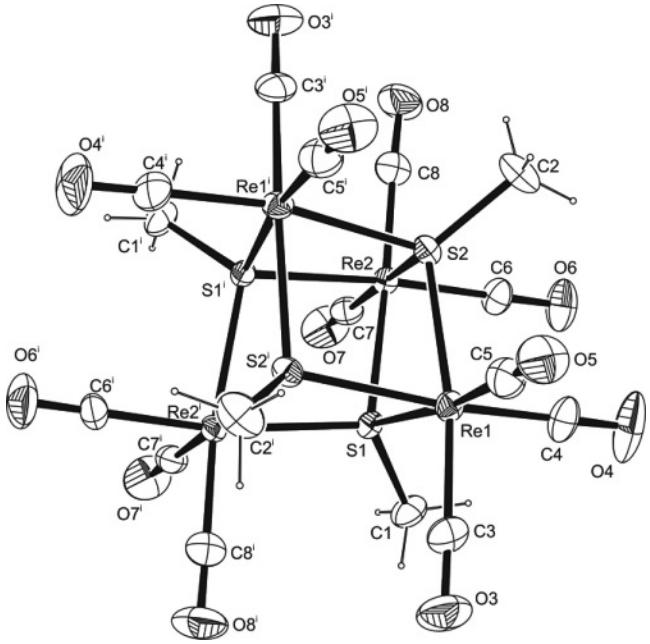
Received July 24, 2014, accepted March 13, 2015, available online March 24, 2015, CCDC no. 1267/4277



Abstract

$C_{16}H_{12}O_{12}Re_4S_4$, trigonal, $P3_121$ (no. 152), a = 10.0250(4) Å, c = 25.809(1) Å, V = 2246.4 Å^3, Z = 3, $R_{gt}(F)$ = 0.0192, $wR_{ref}(F^2)$ = 0.0320, T = 200 K.

Table 1. Data collection and handling.

Crystal:	colourless platelets, size 0.078×0.138×0.139 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	164.42 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14836, 3707
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3271
$N(param)_{refined}$:	166
Programs:	SHELX, WinGX, MERCURY, PLATON [8–11]

Source of material

The compound was obtained upon reacting $Re(CO)_5Cl$ with the Schiff-base derived from dimethylsulfoxide and 2-aminobenzothiazole in ethanol. Crystals suitable for the diffraction study were obtained upon free evaporation of the solvent at room temperature.

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Experimental details

The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [8], with U_{iso}(H) set to 1.5U_{eq}(C). The measured crystal was refined as an inversion twin (0.338(8) / 0.662(8)).

Discussion

Next to cardiovascular diseases, cancer has become one of the main fatal diseases in industrialized countries. Apart from classical surgery, chemo- and radiotherapeutic treatments have entered the arsenal of possible cures for certain types of cancer. All methods, however, suffer from their own set of problematic side-effects and, as a consequence, the development of radiopharmaceuticals – combining the advantages of chemotherapy as well as radiation methods while at the same time avoiding their unique respective undesired side-effects – has been a topic of research [1, 2]. Tailoring and fine-tuning of the envisioned radiopharmaceuticals' properties such as lipophilicity and, in particular, inertness is of paramount importance with respect to possible future *in vivo* applications in contemporary medicine and requires sound knowledge about structural parameters of the ligands applied if a more heuristic approach in the synthesis is to triumph over pure trial-and-error as it is encountered in this specific field of coordination chemistry up to the present day. In continuation of our interest in rhenium-based coordination compounds that might serve as radiopharmaceuticals, a rhenium(I) starting material was reacted with a Schiff-base derived from dimethylsulfoxide and 2-aminobenzothiazole. A structural analysis of the crystalline reaction product showed the formation of an unexpected compound whose crystal structure has been reported earlier [3], however, at room temperature only and without the localization of hydrogen atoms. As inter- and intramolecular forces play a vital role in the dissociation behaviour of compounds and can influence on the ratios of uptake and metabolic transformation, the current study is intended to close this gap for the title compound. The title compound is a tetranuclear rhenium(I)–sulfur cluster. The asymmetric unit consists of half a molecule. The octahedral coordination sphere around each rhenium atom is comprised of three carbonyl ligands as well as three methanethiolato anionic ligands, the latter acting as μ_3 bridging ligands. The four rhenium and four sulfur atoms occupy the corners of a distorted cube. The intracyclic angles between the sulfur and rhenium atoms are measured at 75.64(4)–77.85(4)° and 100.60(4)–103.40(4)° with the range for the narrower angles found on the rhenium atoms. Both ranges are in good agreement with the values reported for the determination of the structure at room temperature without localized hydrogen atoms in the refinement process [3]. The Re–S bond lengths cover

a small range of 2.4888(12)–2.5154(12) Å which is slightly narrower than the values reported for the title compound at room temperature [3] and markedly longer than the most common values reported for Re–$(S)_3$ coordination environments in compounds whose metrical parameters have been deposited with the Cambridge Structural Database [4]. The Re–C bond lengths are found in between 1.907(6) Å and 1.924(6) Å which is longer than reported for the compound at room temperature [3]. The Re···Re distances vary from 3.8504(3) Å to 3.9457(3) Å which is slightly shifted to smaller values with regards to the situation found at room temperature [3]. In the crystal, C–H···O contacts are observed whose range falls below the sum of van-der-Waals radii of the atoms participating in them [5]. These are supported by part of the methanethiolato groups as donors and by some of the carbonyl groups as acceptors. In total, the molecules are connected to a three-dimensional network in the crystal. In terms of graph-set analysis [6, 7], the descriptor for these contacts is $C^1_1(6)C^1_1(6)$ on the unary level.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	6*c*	1.1576	0.8867	0.0613	0.047
H(1B)	6*c*	1.1050	0.7096	0.0511	0.047
H(1C)	6*c*	1.0520	0.7584	0.1028	0.047
H(2A)	6*c*	0.3750	0.6759	0.1005	0.056
H(2B)	6*c*	0.4403	0.5816	0.1310	0.056
H(2C)	6*c*	0.3138	0.4990	0.0865	0.056

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re(1)	6*c*	0.67685(2)	0.49025(2)	0.042288(8)	0.0237(1)	0.0154(1)	0.0221(1)	0.00931(9)	0.00225(9)	0.00237(9)
Re(2)	6*c*	0.78846(2)	0.91362(2)	0.063800(8)	0.0208(1)	0.0159(1)	0.0172(1)	0.00890(8)	–0.00104(9)	–0.00115(9)
S(1)	6*c*	0.9025(1)	0.7542(1)	0.03283(5)	0.0197(6)	0.0173(6)	0.0173(6)	0.0093(5)	–0.0026(5)	–0.0001(5)
S(2)	6*c*	0.5557(1)	0.6543(1)	0.04965(5)	0.0202(7)	0.0193(6)	0.0193(7)	0.0090(5)	0.0038(5)	0.0001(5)
O(3)	6*c*	0.8740(5)	0.3413(5)	0.0208(2)	0.060(3)	0.045(3)	0.075(4)	0.041(3)	0.003(3)	0.000(3)
O(4)	6*c*	0.7245(6)	0.4773(6)	0.1587(2)	0.116(5)	0.054(3)	0.027(3)	0.032(3)	–0.010(3)	0.013(2)
O(5)	6*c*	0.3772(4)	0.1782(5)	0.0444(2)	0.031(2)	0.033(3)	0.070(4)	0.008(2)	0.006(2)	0.009(2)
O(6)	6*c*	0.8127(6)	0.8639(5)	0.1794(2)	0.071(3)	0.061(3)	0.021(3)	0.029(3)	–0.005(2)	0.004(2)
O(7)	6*c*	1.0909(5)	1.2253(5)	0.0693(2)	0.030(2)	0.029(2)	0.077(4)	0.002(2)	–0.014(2)	–0.003(2)
O(8)	6*c*	0.6038(5)	1.0710(5)	0.0927(2)	0.065(3)	0.053(3)	0.062(3)	0.045(3)	0.020(3)	0.005(3)
C(1)	6*c*	1.0740(6)	0.7802(6)	0.0658(2)	0.025(3)	0.036(3)	0.035(4)	0.016(2)	–0.009(3)	0.001(3)
C(2)	6*c*	0.4037(6)	0.5960(7)	0.0974(2)	0.028(3)	0.040(3)	0.039(4)	0.012(3)	0.014(3)	–0.002(3)
C(3)	6*c*	0.7985(6)	0.3945(6)	0.0294(2)	0.031(3)	0.017(3)	0.044(4)	0.010(3)	–0.002(3)	0.001(3)
C(4)	6*c*	0.7046(7)	0.4794(6)	0.1150(3)	0.047(4)	0.022(3)	0.032(4)	0.013(3)	–0.001(3)	0.008(3)
C(5)	6*c*	0.4897(7)	0.2949(7)	0.0433(3)	0.039(3)	0.034(3)	0.037(4)	0.020(3)	0.006(3)	0.004(3)
C(6)	6*c*	0.8045(7)	0.8828(6)	0.1366(2)	0.038(3)	0.028(3)	0.021(3)	0.016(2)	–0.006(3)	–0.005(3)
C(7)	6*c*	0.9779(6)	1.1075(6)	0.0669(2)	0.027(3)	0.024(3)	0.030(3)	0.015(3)	–0.002(2)	–0.004(2)
C(8)	6*c*	0.6754(6)	1.0147(6)	0.0811(2)	0.023(3)	0.017(3)	0.040(4)	0.005(2)	0.003(3)	0.000(2)

Acknowledgments. The authors thank Mr Saki Marais for helpful discussions.

References

1. Yumata, N. C.; Habarurema, G.; Mukiza, J.; Gerber, T. I. A.; Hosten, E.; Taherkhani, F.; Nahali, M.: Rhenium complexes of di-2-pyridyl ketone, 2-benzoylpyridine and 2-hydroxybenzophenone: A structural and theoretical study. Polyhedron **62** (2013) 89–103.
2. Potgieter, K. C.; Gerber, T. I. A.; Betz, R.; Rhyman, L.; Ramasami, P.:Structural and DFT/TD-DFT investigation of *tris*(bidentate) complexes of rhenium(III) synthesized from the *cis*-$[ReO_2]^+$ core and benzenethiol derivatives. Polyhedron **59** (2013) 91–100.
3. Harrison, W.; Marsh, W. C.; Trotter, J.: Crystal and Molecular Strcuture of Tetrakis(tricarbonyl-μ_3-methane-thiolato-rhenium). J. Chem. Soc. Dalton Trans. (1972) 1009–1011.
4. Allen, F. H.: The Cambridge Structural Database: a quarter of a million crystal structures and rising. Acta Crystallogr. **B58** (2002) 380–388.
5. Bondi, A.: van der Waals Volumes and Radii. J. Phys. Chem. **68** (1964) 441–451.
6. Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N.-L.: Patterns in Hydrogen Bonding: Functionality and Graph Set Analysis in Crystals. Angew. Chem. Int. Ed. Engl. **34** (1995) 1555–1573.
7. Etter, M. C.; MacDonald, J. C.; Bernstein, J.: Graph-set analysis of hydrogen-bond patterns in organic crystals. Acta Crystallogr. **B46** (1990) 256–262.
8. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
9. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
10. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P.A.: Mercury CSD 2.0 - new features for the visualization and investigation of crystal structures. J. Appl. Crystallogr. **41** (2008) 466–470.
11. Spek, A. L.: Structure validation in chemical crystallography. Acta Crystallogr. **D65** (2009) 148–155.