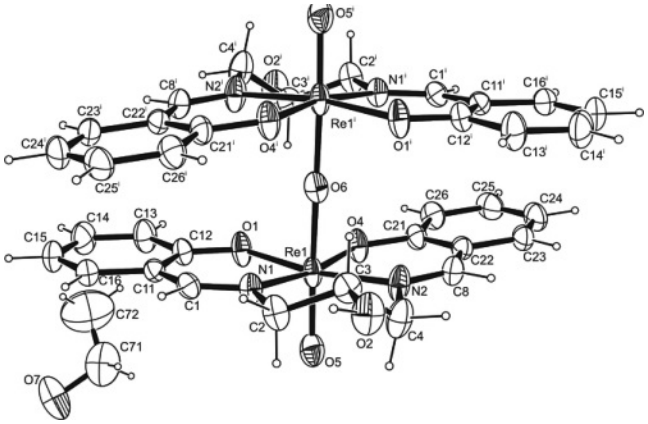
Z. Kristallogr. NCS **230** (2015) 153-155 / **DOI** 10.1515/ncrs-2014-0245 **153**

Crystal structure of (μ_2-oxo)-dioxo-bis(*N,N'*-2- hydroxypropylene-bis(salicylideneimine)-κ^4*N,N',O,O'*)-di-rhenium(V) ethanol solvate, $C_{38}H_{44}N_4O_{11}Re_2$

Gratien Habarurema, Thomas I. A. Gerber, Eric C. Hosten and Richard Betz*

Nelson Mandela Metropolitan University, Summerstrand Campus, Department of Chemistry, University Way, Summerstrand, PO Box 77000, Port Elizabeth 6031, South Africa

Received July 08, 2014, accepted March 09, 2015, available online March 11, 2015, CCDC no. 1267/4266



Abstract

$C_{38}H_{44}N_4O_{11}Re_2$, triclinic, $P\bar{1}$ (no. 2), a = 10.2062(7) Å, b = 10.3724(7) Å, c = 10.4524(7) Å, α = 93.597(2)°, β = 118.678(2)°, γ = 97.337(2)°, V = 953.0 Å^3, Z = 1, $R_{gt}(F)$ = 0.0181, $wR_{ref}(F^2)$ = 0.0414, T = 200 K.

Table 1. Data collection and handling.

Crystal:	green platelets, size 0.138×0.146×0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	64.11 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14706, 4693
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4299
$N(param)_{refined}$:	291
Programs:	SHELX, WinGX, MERCURY, PLATON [13–16]

Source of material

The title compound was obtained upon reacting the free ligand (*N,N'*-2-hydroxypropylene-bis(salicylideneimine)) with $ReOBr_3(PPh_3)_2$ in ethanol. Crystals suitable for the diffraction study were obtained upon free evaporation of the solvent.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic carbon atoms, C–H 0.99 Å for methylene groups and C–H 1.00 Å for methine groups) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). The H atoms of the methyl group 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 [13]), with U_{iso}(H) set to 1.5U_{eq}(C). The H atoms of the hydroxyl groups were allowed to rotate with a fixed angle around the C–O bond to best fit the experimental electron density (HFIX 147 in the SHELX program suite [13]), with U_{iso}(H) set to 1.5U_{eq}(O).

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(V) starting material was reacted with a twofold Schiff-base derived from salicylaldehyde and 1,3-diaminopropan-2-ol. The structural analysis of the compound showed the formation of a dinuclear rhenium coordination compound. Similar compounds with reduced versions of Schiff-base ligand systems have been reported earlier in the literature [3–6]. The structural analysis shows the presence of a μ_2-oxo-bridged centrosymmetric dinuclear rhenium(V) coordination compound. The asymmetric unit contains half a molecule. The octahedral coordination sphere of each rhenium atom is completed by a twofold Schiff-base derived from salicylaldehyde and 1,3-diaminopropan-2-ol acting as an equatorial tetradentate *O,O',N,N'* ligand as well as an oxido ligand. The atoms of each chelating ring as well as the accompanying phenyl group are nearly co-planar in both cases (r.m.s. of all fitted non-hydrogen atoms = 0.0198 Å and 0.0270 Å), the angle enclosed by the respective least-squares planes measuring 7.04(14)°. A conformational analysis of the two chelate rings involving the phenolic oxygen atoms according to Cremer & Pople [7] is precluded in one case by the small puckering amplitude (τ = 3.0°) but shows the adoption of a ^{Re1}E conformation in the second case [8]. The C_3 moiety connecting the two Schiff-base moieties shows orientational disorder with the major component being present with slightly more than 71%. A conformational analysis of the pertain-

* Correspondence author (e-mail: Richard.Betz@nmmu.ac.za)

ing six-membered chelate rings according to Cremer & Pople [7] in this case shows the adoption of a $^5H_4$ conformation on C(4) and C(3) as well as the presence of a ^4E conformation on C(6) [8]. The Re–O bond lengths differ markedly with values of 1.703(2) Å, 1.91548(16) Å, 2.0106(18) Å and 2.0154(18) Å, the longest two being realized to the phenolate-type oxygen atoms and the shortest one for the terminal oxido ligand. In comparison to the other examples mentioned in the literature [3–6] whose metrical parameters have been deposited with the Cambridge Structural Database [9], the Re–O distance involving the bridging oxido ligand is among the shortest ever observed. Apart from the coordination compound, the crystal structure also contains one molecule of ethanol. In the crystal, classical hydrogen bonds of the O–H···O type are observed next to C–H···O contacts whose range falls below the sum of van-der-Waals radii of the atoms participating in them [10]. The classical hydrogen bonds are apparent in between the solvens molecule as donor and the phenolic oxygen atom as acceptor. The ethanol molecule also serves as acceptor for the hydroxyl group of the 2-propanol moiety. The C–H···O contacts are apparent in between the vinylic hydrogen atom of one Schiff-base group and the oxygen atom of the 2-propanol moiety on the one hand as well as the methylene group of the solvens molecule and one of the phenolic coordinating oxygen atoms. Another C–H···O contact is established by one of the hydrogen atoms in *para* position to a phenolic oxygen atom as donor and a terminal oxido ligand as acceptor. In terms of graph-set analysis [11, 12], the descriptor for the classical hydrogen bonds is *DD* on the unary level while the C–H···O contacts necessitate a $DR^2_2(12)R^2_2(16)$ descriptor on the same level. In total, the entities of the title compound are connected to layers perpendicular to the crystallographic *b* axis. The crystal structure is further characterized by strong $\pi\cdots\pi$ stacking as the shortest intercentroid distance between two centers of gravity was measured at 3.5557(14) Å and is apparent in between the two different *N,O* chelate rings in neighbouring molecules.

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(7)	2*i*		0.3576	0.8320	0.5438	0.103
H(1)	2*i*		0.4619	0.3462	–0.1909	0.032
H(8)	2*i*		0.9414	–0.0629	0.1920	0.038
H(13)	2*i*		0.2566	0.2820	0.1851	0.049
H(14)	2*i*		0.0916	0.4185	0.0549	0.054
H(15)	2*i*		0.1035	0.5089	–0.1391	0.049
H(16)	2*i*		0.2805	0.4586	–0.2036	0.038
H(23)	2*i*		0.9956	–0.1981	0.3650	0.040
H(24)	2*i*		0.9660	–0.2941	0.5464	0.050
H(25)	2*i*		0.7933	–0.2309	0.6125	0.049
H(26)	2*i*		0.6524	–0.0711	0.5015	0.042
H(71A)	2*i*		0.4295	0.6306	0.4338	0.100
H(71B)	2*i*		0.4558	0.6584	0.5983	0.100
H(72A)	2*i*		0.1948	0.6289	0.4970	0.196
H(72B)	2*i*		0.2551	0.4993	0.4734	0.196
H(72C)	2*i*		0.1799	0.5829	0.3408	0.196
H(2)	2*i*	0.713	0.7606	0.1458	–0.2868	0.063
H(2A)	2*i*	0.713	0.7525	0.3119	–0.0864	0.039
H(2B)	2*i*	0.713	0.6045	0.2422	–0.2352	0.039
H(3)	2*i*	0.713	0.6596	0.0316	–0.1595	0.037
H(4A)	2*i*	0.713	0.9319	0.0463	0.0271	0.051
H(4B)	2*i*	0.713	0.9279	0.1938	0.0786	0.051
H(3A)	2*i*	0.287	0.8001	0.1118	–0.2523	0.069
H(5A)	2*i*	0.287	0.5687	0.1222	–0.2361	0.056
H(5B)	2*i*	0.287	0.6359	0.2741	–0.2220	0.056
H(6)	2*i*	0.287	0.8564	0.2467	–0.0009	0.041
H(7A)	2*i*	0.287	0.9121	0.0237	–0.0015	0.042
H(7B)	2*i*	0.287	0.7319	–0.0264	–0.0951	0.042

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re(1)	2*i*		0.63677(1)	0.14995(1)	0.13725(1)	0.03378(6)	0.03471(7)	0.02698(6)	0.01982(4)	0.02072(5)	0.01587(4)
O(1)	2*i*		0.4643(2)	0.2090(2)	0.1531(2)	0.046(1)	0.044(1)	0.038(1)	0.030(1)	0.032(1)	0.0223(9)
O(4)	2*i*		0.6540(2)	0.0552(2)	0.3057(2)	0.047(1)	0.044(1)	0.033(1)	0.027(1)	0.028(1)	0.0225(9)
O(5)	2*i*		0.7730(2)	0.2851(2)	0.2346(2)	0.044(1)	0.044(1)	0.031(1)	0.019(1)	0.0135(9)	0.0144(9)
O(6)	1*d*		½	0	0	0.039(2)	0.035(2)	0.039(2)	0.016(1)	0.028(1)	0.016(1)
O(7)	2*i*		0.3636(4)	0.7963(3)	0.4729(3)	0.127(3)	0.060(2)	0.054(2)	0.046(2)	0.064(2)	0.025(1)
N(1)	2*i*		0.5796(3)	0.2375(2)	–0.0564(2)	0.033(1)	0.033(1)	0.026(1)	0.014(1)	0.019(1)	0.0119(9)
N(2)	2*i*		0.8033(3)	0.0567(3)	0.1249(3)	0.037(1)	0.053(2)	0.042(1)	0.027(1)	0.030(1)	0.025(1)
C(1)	2*i*		0.4760(3)	0.3085(3)	–0.1056(3)	0.033(1)	0.025(1)	0.025(1)	0.008(1)	0.015(1)	0.009(1)
C(8)	2*i*		0.8675(3)	–0.0281(3)	0.2072(3)	0.029(1)	0.036(2)	0.035(1)	0.015(1)	0.017(1)	0.010(1)
C(11)	2*i*		0.3784(3)	0.3385(3)	–0.0484(3)	0.026(1)	0.022(1)	0.025(1)	0.006(1)	0.010(1)	0.002(1)
C(12)	2*i*		0.3734(3)	0.2860(3)	0.0709(3)	0.032(1)	0.027(1)	0.033(1)	0.013(1)	0.018(1)	0.008(1)
C(13)	2*i*		0.2632(4)	0.3175(3)	0.1064(4)	0.045(2)	0.047(2)	0.050(2)	0.025(2)	0.033(2)	0.019(2)
C(14)	2*i*		0.1648(4)	0.3988(3)	0.0288(4)	0.041(2)	0.047(2)	0.062(2)	0.023(2)	0.033(2)	0.014(2)
C(15)	2*i*		0.1711(3)	0.4522(3)	–0.0867(4)	0.035(2)	0.037(2)	0.050(2)	0.021(1)	0.017(1)	0.012(1)
C(16)	2*i*		0.2762(3)	0.4221(3)	–0.1243(3)	0.031(1)	0.029(1)	0.033(1)	0.009(1)	0.013(1)	0.008(1)
C(21)	2*i*		0.7387(3)	–0.0365(3)	0.3634(3)	0.033(1)	0.028(1)	0.023(1)	0.011(1)	0.012(1)	0.008(1)
C(22)	2*i*		0.8404(3)	–0.0767(3)	0.3205(3)	0.026(1)	0.025(1)	0.024(1)	0.007(1)	0.008(1)	0.003(1)
C(23)	2*i*		0.9250(3)	–0.1723(3)	0.3919(3)	0.029(1)	0.029(2)	0.032(1)	0.011(1)	0.007(1)	0.004(1)
C(24)	2*i*		0.9082(4)	–0.2294(3)	0.4997(3)	0.043(2)	0.033(2)	0.037(2)	0.015(1)	0.009(1)	0.014(1)
C(25)	2*i*		0.8061(4)	–0.1912(3)	0.5388(3)	0.049(2)	0.035(2)	0.031(2)	0.008(1)	0.014(1)	0.016(1)
C(26)	2*i*		0.7219(3)	–0.0960(3)	0.4727(3)	0.042(2)	0.037(2)	0.028(1)	0.012(1)	0.017(1)	0.012(1)
C(71)	2*i*		0.3857(6)	0.6632(6)	0.4933(5)	0.098(4)	0.107(4)	0.057(3)	0.039(3)	0.042(3)	0.017(3)
C(72)	2*i*		0.2433(8)	0.5880(8)	0.4477(8)	0.122(6)	0.148(7)	0.127(6)	–0.007(5)	0.075(5)	–0.010(5)
O(2)	2*i*	0.713	0.8155(9)	0.1200(8)	–0.2065(9)	0.050(4)	0.060(4)	0.040(3)	0.023(3)	0.036(3)	0.017(3)
C(2)	2*i*	0.713	0.670(1)	0.234(1)	–0.130(1)	0.047(5)	0.038(4)	0.027(5)	0.019(3)	0.026(4)	0.015(3)
C(3)	2*i*	0.713	0.7395(8)	0.1125(7)	–0.1218(7)	0.035(3)	0.034(3)	0.036(3)	0.010(2)	0.028(2)	0.008(2)
C(4)	2*i*	0.713	0.8654(7)	0.105(1)	0.0328(8)	0.038(3)	0.066(5)	0.044(3)	0.026(3)	0.031(3)	0.026(3)

Table 3. continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(3)	2*i*	0.287	0.854(2)	0.171(2)	–0.180(2)	0.044(8)	0.07(1)	0.048(8)	0.015(7)	0.037(7)	0.017(8)
C(5)	2*i*	0.287	0.637(3)	0.201(3)	–0.165(3)	0.04(1)	0.10(2)	0.02(1)	0.03(1)	0.023(9)	0.01(1)
C(6)	2*i*	0.287	0.793(2)	0.173(2)	–0.084(2)	0.027(6)	0.05(1)	0.039(7)	0.005(6)	0.025(6)	0.015(6)
C(7)	2*i*	0.287	0.813(2)	0.045(2)	–0.022(2)	0.054(9)	0.030(7)	0.044(8)	0.015(6)	0.041(7)	0.006(6)

Acknowledgments. The authors thank Mr Dane Terrance Leo 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. Abrahams, A.; Gerber, T. I. A.; Mayer, P.: Synthesis and characterization of an oxo-bridged rhenium(V) complex with an amine-phenol tetradentate ligand. Bull. Chem. Soc. Ethiop. **21** (2007) 83–88.
4. Pillai, M. R. A.; Barnes, C. L.; Schlemper, E. O.: Dinuclear complexes of rhenium(V) with amine-phenol ligands: Synthesis, characterization and x-ray crystal structures. Polyhedron **13** (1994) 701–708.
5. Huang, W.-T.; Yao, H.-H.; Chen, B.-H.; Liao, F.-L.; Lo, J.-M.: Structure of μ-oxo-bis{{2,2'-[propane-1,3-diylbis(aminomethyl)]diphenolato}-oxorhenium(V)}. J. Chem. Cryst. **32** (2002) 465–468.
6. Abram, U.; Abram, S.; Macke, H. R.; Koch, P.: μ-Oxoverbrückte, dimere Technetium- und Rheniumkomplexe mit funktionalisierten Aminophenolato-Liganden. Darstellung und Strukturen von $[O{=}TcL^1\text{-}O\text{-}L^1Tc{=}O]\cdot H_2O$ und $[O{=}ReL^1\text{-}O\text{-}L^1Re{=}O]$ (H_2L^1 = N,N'-Bis(2-hydroxybenzyl)-1,3-diamino-2-(4-nitrobenzyl)propan). Z. Anorg. Allg. Chem. **621** (1995) 854–860.
7. Cremer, D.; Pople, J. A.:General definition of ring puckering coordinates.J. Am. Chem. Soc. **97** (1975) 1354–1358.
8. Boeyens, J. C. A.: The conformation of six-membered rings. J. Cryst. Molec. Struct. **8** (1978) 317–320.
9. Allen, F. H.: The Cambridge Structural Database: a quarter of a million crystal structures and rising. Acta Crystallogr. **B58** (2002) 380–388.
10. Bondi, A.: van der Waals Volumes and Radii. J. Phys. Chem. **68** (1964) 441–451.
11. 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.
12. Etter, M. C.; MacDonald, J. C.; Bernstein, J.: Graph-set analysis of hydrogen-bond patterns in organic crystals. Acta Crystallogr. **B46** (1990) 256–262.
13. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
14. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
15. 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.
16. Spek, A. L.: Structure validation in chemical crystallography. Acta Crystallogr. **D65** (2009) 148–155.