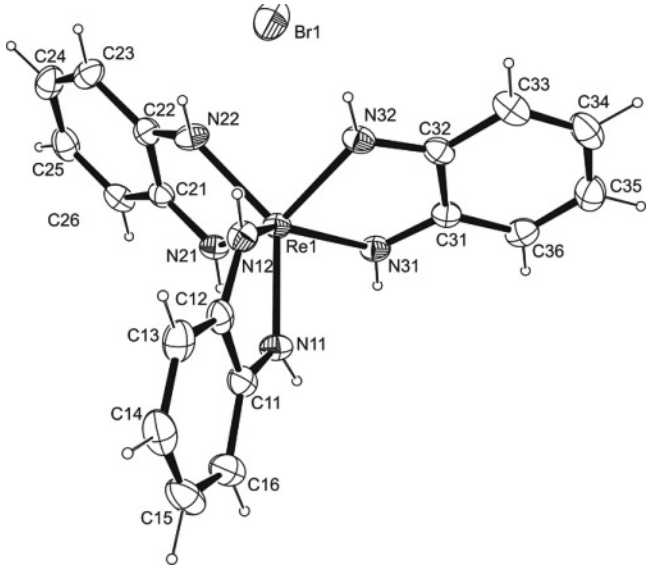
Crystal structure of tris(*ortho*-phenylenediamide-*N,N'*)-rhenium(VII) bromide, $C_{18}H_{18}BrN_6Re$

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 September 22, 2014, accepted February 03, 2015, available online March 11, 2015, CCDC no. 1267/4246



Abstract

$C_{18}H_{18}BrN_6Re$, monoclinic, $P2_1/n$ (no. 14), a = 11.0894(3) Å, b = 12.8030(3) Å, c = 13.1540(3) Å, β = 96.957(1)°, V = 1853.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.0171, $wR_{ref}(F^2)$ = 0.0324, T = 200 K.

Table 1. Data collection and handling.

Crystal:	violet blocks, size 0.086×0.088×0.136 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	87.25 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.64°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17539, 4617
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3931
$N(param)_{refined}$:	259
Programs:	SHELX, WinGX, MERCURY, PLATON [10–13]

Source of material

The title compound was prepared upon reacting $ReBr_3(dab)(PPh_3)_2$ (dab = 1,2-diaminobenzene) with the symmetric two-fold Schiff-base derived from 1,3-diamino-propan-2-ol and 2-hydroxy-benzaldehyde in ethanol. Crystals suitable for the diffraction study were obtained upon free evaporation of the solvent at ambient conditions.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). All nitrogen-bound H atoms were located on a difference Fourier map and refined freely using DFIX instructions, the N–H distances set to 0.88 Å.

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 ndesired 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 addition, the spatial requirements of pharmaceuticals are of importance as this factor influences on their interaction with enzymatic systems and, as a consequence, the pathway and rate of conjugation, functionalization and secretion from the body. In continuation of our ongoing research on the field of rhenium coordination compounds, the coordination of a multidentate ligand towards a rhenium(V) starting material was attempted [3]. A structural analysis of the crystalline reaction product showed the formation of an unexpected product. The crystal structures of two other comparable rhenium coordination compounds as found in the current reaction product are apparent in the literature [4]. The compound is a homoleptic rhenium(VII) coordination compound featuring three chelating *ortho*-phenylenediamine ligands that are invariably two-fold deprotonated. The positive charge of the coordination unit is balanced by a bromide anionpresent in the crystal structure. A conformational analysis of the five-membered chelate rings according to Cremer & Pople [5] shows the latter to invariably adopt E_1 conformations on the rhenium atom [6]. Re–N bond lengths cover a narrow range of 1.991(2)–2.0106(19) Å only. The least-squares planes as defined by the respective carbon atoms of each aromatic moiety enclose angles of 45.82(7)°, 65.94(8)° and 68.82(9)°. In the crystal, classical hydrogen bonds of the N–H···Br type are observed next to C–H···N contacts whose range falls below the sum of van-der-Waals radii of the atoms participating in them [7]. The classical hydrogen bonds are only supported by both NH groups each of two of the chelating ligands only while one chelating ligand does not participate in the formation of any intra- or intermolecular

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

contacts whatsoever. The C–H···N contact involves one CH group in *ortho* position to the functional groups of one of the two ligands whose NH groups give rise to N–H···Br hydrogen bonds already. The latter contact could also be considered to be the result of the orientation of the molecules in the crystal as fostered by the N–H···Br contacts. In terms of graph-set analysis [8, 9], the descriptor for the classical hydrogen bonds is *DDDD* on the unary level while the C–H···N contacts necessitate a $C^1_1(6)$ descriptor on the same level. In total, the entities of the title compound are connected to undulated chains along the crystallographic *b* axis. Furthermore, three C–H···π contacts could be discussed also involving hydrogen atoms of the chelating ligand whose NH groups were not part of the system of classical hydrogen bonds. The shortest intercentroid distance between two centers of gravity in neighbouring molecules was measured at 3.5271(13) Å.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(13)	4*e*	–0.1225	0.1416	0.6432	0.035
H(14)	4*e*	–0.2800	0.2361	0.7006	0.042
H(15)	4*e*	–0.2412	0.3649	0.8270	0.044
H(16)	4*e*	–0.0450	0.4019	0.8982	0.036
H(23)	4*e*	0.3250	–0.1732	0.8680	0.033
H(24)	4*e*	0.3796	–0.2350	1.0318	0.039
H(25)	4*e*	0.4144	–0.1194	1.1714	0.037
H(26)	4*e*	0.3911	0.0594	1.1480	0.032
H(33)	4*e*	0.4576	0.2443	0.5216	0.038
H(34)	4*e*	0.5697	0.3953	0.5114	0.041
H(35)	4*e*	0.6111	0.5062	0.6534	0.039
H(36)	4*e*	0.5386	0.4677	0.8071	0.031
H(11)	4*e*	0.177(2)	0.345(2)	0.896(2)	0.030(8)
H(12)	4*e*	0.110(2)	0.121(2)	0.670(1)	0.019(7)
H(21)	4*e*	0.314(2)	0.197(2)	1.014(2)	0.030(8)
H(22)	4*e*	0.263(2)	–0.009(2)	0.769(2)	0.031(8)
H(31)	4*e*	0.403(3)	0.341(2)	0.890(2)	0.034(8)
H(32)	4*e*	0.342(3)	0.135(2)	0.642(2)	0.043(9)

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)	4*e*	0.270752(9)	0.186802(7)	0.815591(7)	0.01732(5)	0.01977(5)	0.01812(5)	0.00101(4)	0.00112(3)	–0.00229(4)
Br(1)	4*e*	0.20701(3)	0.00667(2)	0.52471(2)	0.0470(2)	0.0271(1)	0.0251(1)	–0.0054(1)	0.0004(1)	0.0005(1)
N(11)	4*e*	0.1554(2)	0.2931(2)	0.8576(2)	0.026(1)	0.024(1)	0.021(1)	0.0043(9)	0.0029(9)	–0.0038(8)
N(12)	4*e*	0.1171(2)	0.1624(2)	0.7220(2)	0.024(1)	0.022(1)	0.021(1)	–0.0018(9)	–0.0002(9)	–0.0019(8)
N(21)	4*e*	0.3122(2)	0.1517(2)	0.9647(2)	0.024(1)	0.023(1)	0.019(1)	0.0020(9)	0.0038(9)	–0.0040(8)
N(22)	4*e*	0.2805(2)	0.0306(2)	0.8196(2)	0.026(1)	0.023(1)	0.022(1)	0.0025(9)	–0.0021(9)	–0.0070(9)
N(31)	4*e*	0.3938(2)	0.3014(2)	0.8373(2)	0.021(1)	0.022(1)	0.021(1)	0.0000(9)	0.0005(8)	–0.0054(8)
N(32)	4*e*	0.3554(2)	0.1825(2)	0.6901(2)	0.021(1)	0.027(1)	0.020(1)	0.0000(9)	0.0015(8)	–0.0063(9)
C(11)	4*e*	0.0365(2)	0.2870(2)	0.8202(2)	0.024(1)	0.027(1)	0.020(1)	0.004(1)	0.004(1)	0.0062(9)
C(12)	4*e*	0.0140(2)	0.2098(2)	0.7430(2)	0.021(1)	0.025(1)	0.024(1)	0.001(1)	0.002(1)	0.0095(9)
C(13)	4*e*	–0.1062(2)	0.1918(2)	0.6962(2)	0.027(1)	0.030(1)	0.030(1)	–0.001(1)	–0.003(1)	0.011(1)
C(14)	4*e*	–0.1986(3)	0.2490(2)	0.7294(2)	0.021(2)	0.045(2)	0.040(2)	0.002(1)	0.001(1)	0.019(1)
C(15)	4*e*	–0.1753(3)	0.3267(2)	0.8057(2)	0.026(2)	0.051(2)	0.034(2)	0.015(1)	0.010(1)	0.016(1)
C(16)	4*e*	–0.0601(2)	0.3475(2)	0.8492(2)	0.031(2)	0.036(2)	0.024(1)	0.010(1)	0.006(1)	0.007(1)
C(21)	4*e*	0.3395(2)	0.0525(2)	0.9917(2)	0.016(1)	0.024(1)	0.024(1)	0.001(1)	0.004(1)	0.001(1)
C(22)	4*e*	0.3202(2)	–0.0177(2)	0.9078(2)	0.015(1)	0.023(1)	0.028(1)	–0.002(1)	0.002(1)	–0.001(1)
C(23)	4*e*	0.3369(2)	–0.1260(2)	0.9240(2)	0.020(1)	0.021(1)	0.039(2)	–0.001(1)	–0.001(1)	–0.004(1)
C(24)	4*e*	0.3700(2)	–0.1621(2)	1.0205(2)	0.023(2)	0.024(1)	0.050(2)	0.002(1)	0.003(1)	0.008(1)
C(25)	4*e*	0.3905(2)	–0.0924(2)	1.1047(2)	0.022(2)	0.037(2)	0.033(1)	0.002(1)	0.005(1)	0.012(1)
C(26)	4*e*	0.3764(2)	0.0132(2)	1.0913(2)	0.024(1)	0.035(1)	0.022(1)	0.003(1)	0.006(1)	–0.000(1)
C(31)	4*e*	0.4482(2)	0.3334(2)	0.7563(2)	0.016(1)	0.023(1)	0.022(1)	0.0036(9)	–0.0003(9)	0.0002(9)
C(32)	4*e*	0.4255(2)	0.2648(2)	0.6711(2)	0.018(1)	0.028(1)	0.022(1)	0.005(1)	0.002(1)	0.000(1)
C(33)	4*e*	0.4724(2)	0.2892(2)	0.5793(2)	0.027(2)	0.044(2)	0.026(1)	0.002(1)	0.006(1)	–0.002(1)
C(34)	4*e*	0.5392(2)	0.3781(2)	0.5738(2)	0.024(2)	0.048(2)	0.032(1)	0.005(1)	0.010(1)	0.008(1)
C(35)	4*e*	0.5638(2)	0.4451(2)	0.6590(2)	0.022(2)	0.033(2)	0.045(2)	–0.000(1)	0.005(1)	0.008(1)
C(36)	4*e*	0.5204(2)	0.4232(2)	0.7496(2)	0.020(1)	0.025(1)	0.032(1)	0.002(1)	–0.001(1)	–0.003(1)

Acknowledgments. The authors thank Mr Christopher Swatts 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. Mukiza, J.; Gerber,T. I. A.; Hosten, E. C.; Betz R.: Crystal structure of bis(4,5-diaza-fluoren-9-one-κ^2N,N) dioxo-μ_2-oxodirhenium(V)acetonitrile (1:2), $C_{26}H_{18}C_{l4}N_6O_5Re_2$. Z. Kristallogr. NCS **229** (2014) 341–342.
4. Danopoulos, A. A.; Wong, A. C. C.; Wilkinson, G.; Hursthouse, M. B.; Hussain, B.: Complexes of rhenium and osmium with *o*-phenylenediamine and *o*-aminobenzenethiol. *X*-Ray crystal structures of [Re{*o*-$(HN)_2C_6H_4\}_3$][ReO_4], Re[*o*-$(HN)_2C_6H_4]_3$, Re[o-$(HN)_2C_6H_4]_2$[*o*-$(HN)NC_6H_4$], K[Re{*o*-$(HN)_2C_6H_4\}${*o*-$(HN)_2C_6H_4\}_2$] and M[*o*-$(HN)SC_6H_4$] (M = Re or Os). J. Chem. Soc. Dalton Trans. (1990) 315–331.
5. Cremer, D.; Pople, J. A.: General definition of ring puckering coordinates. J. Am. Chem. Soc. **97** (1975) 1354–1358.
6. Siri, D.; Gaudel-Siri, A.; Tordo, P.: Conformational analysis of five-membered rings by molecular mechanics: application to nitroxides. J. Molec. Struct. (Theochem) **582** (2002) 171–185.
7. Bondi, A.: van der Waals Volumes and Radii. J. Phys. Chem. **68** (1964) 441–451.
8. 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.
9. 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.