Crystal structure of bis(4,5-diaza-fluoren-9-one-κ^2N,N) dioxo-μ_2-oxodirhenium(V)- acetonitrile (1:2), $C_{26}H_{18}Cl_4N_6O_5Re_2$

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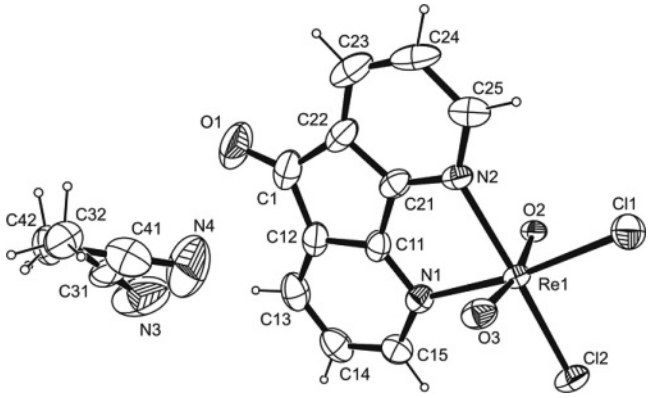
Received May 13, 2014, accepted September 11, 2014, available online October 06, 2014, CCDC no. 1267/4164



Abstract

$C_{26}H_{18}Cl_4N_6O_5Re_2$, monoclinic, $P2_1/c$ (no. 14), a = 10.0110(4) Å, b = 14.1829(6) Å, c = 10.7113(4) Å, β = 96.265(2)°, V = 1511.8 Å^3, Z = 2, $R(F)$ = 0.0230, $wR_{ref}(F^2)$ = 0.0542, T = 200 K.

Table 1. Data collection and handling.

Crystal:	green blocks, size 0.23×0.24×0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	84.01 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.7°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14255, 3768
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2691
$N(param)_{refined}$:	226
Programs:	SHELX [6], WinGX [7], MERCURY [8], PLATON [9]

Source of material

The compound was obtained upon reacting $ReCl_3(MeCN)(PPh_3)_2$ with the chelating ligand in acetonitrile.

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). 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 [6]), with U_{iso}(H) set to 1.5U_{eq}(C).

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]. 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, the title compound was synthesized. A similar compound featuring bromido instead of chlorido ligands has recently been described in the literature [2]. The compound is a centrosymmetric dinuclear rhenium(V) coordination compound. The asymmetric unit contains half of the coordination compound as well as a molecule of acetonitrile. The latter is disordered over two positions at a ratio of nearly 0.5:0.5. The two rhenium atoms are connected by means of an oxido bridge. The central Re atoms are hexacoordinate. The respective octahedral coordination sphere is completed by means of a chelating molecule of 4,5-diaza-fluoren-9-one as well as an oxido and two chlorido ligands in *cis* configuration. The two Re–O bond lengths of 1.699(3) Å and 1.9019(2) Å for the double as well as the single bond, respectively, are in good agreement with values found for other compounds containing the O=Re–O–Re moiety whose structural data has been deposited with the Cambridge Structural Database [3]. The two Re–N bonds are nearly identical with respect to their length, a finding that also holds true for the two Re–Cl bonds. The Re–O–Re angle is measured at 180°. The least-squares planes as defined by the non-hydrogen atoms of the the two individual pyridine subunits present on the 4,5-diaza-fluoren-9-one ligand intersect at an angle of 0.6(3)° only. In the crystal, a multitude of C–H···O, C–H···N and C–H···Cl contacts is observed whose range invariably falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them. These are supported by all the hydrogen atoms on the 4,5-diaza-fluoren-9-one ligand as donors and involve both chlorine atoms as acceptors. Only the nitrogen of the disordered acetonitrile molecule acts as acceptor. In terms of graph-set analysis [4, 5], the descriptor for the C–H···O contacts is $C^1_1(6)$ on the unary level while the C–H···N contacts necessitate a *DD* descriptor on the same level. The description of the C–H···Cl contacts can be achieved by means of a $DC^1_1(5)C^1_1(6)$ descriptor. In total, the entities of the crystal structure are connected to a three-dimensional network. A series of potential Re–Cl···π interactions can be ruled

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out on grounds of unfavourable angles of interaction. π-Stacking is a prominent feature in the crystal structure as the shortest intercentroid distance between two centers of gravity is measured at 3.610(3) Å only.

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(13)	4*e*		0.7759	0.3770	0.5703	0.055
H(14)	4*e*		0.9180	0.3718	0.4116	0.055
H(15)	4*e*		0.9668	0.2316	0.3176	0.043
H(23)	4*e*		0.5178	0.0379	0.7688	0.062
H(24)	4*e*		0.5436	–0.1149	0.6943	0.062
H(25)	4*e*		0.6815	–0.1457	0.5359	0.052
H(32A)	4*e*	0.506	0.2311	0.3400	0.5784	0.074
H(32B)	4*e*	0.506	0.2173	0.3316	0.4286	0.074
H(32C)	4*e*	0.506	0.1867	0.4298	0.4934	0.074
H(42A)	4*e*	0.494	0.1763	0.4028	0.4414	0.072
H(42B)	4*e*	0.494	0.2776	0.4677	0.5298	0.072
H(42C)	4*e*	0.494	0.2097	0.3777	0.5871	0.072

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)	4*e*		0.86549(1)	0.00052(1)	0.36014(1)	0.02360(8)	0.02867(9)	0.02000(8)	–0.00220(7)	0.00466(5)	0.00025(7)
Cl(1)	4*e*		0.8839(1)	–0.16418(9)	0.3358(1)	0.0538(7)	0.0332(6)	0.0401(6)	–0.0033(5)	0.0059(5)	–0.0052(5)
Cl(2)	4*e*		1.0290(1)	0.03049(9)	0.2220(1)	0.0366(6)	0.0512(7)	0.0297(6)	–0.0021(5)	0.0141(4)	0.0016(5)
O(1)	4*e*		0.5975(5)	0.2531(3)	0.7372(4)	0.077(3)	0.091(4)	0.059(3)	0.029(3)	0.019(2)	–0.021(3)
O(2)	2*c*		1	0	½	0.035(2)	0.023(2)	0.023(2)	–0.001(2)	0.008(2)	0.003(2)
O(3)	4*e*		0.7271(3)	0.0181(2)	0.2562(3)	0.028(2)	0.049(2)	0.030(2)	–0.002(1)	0.003(1)	0.003(1)
N(1)	4*e*		0.8544(4)	0.1487(3)	0.4156(3)	0.029(2)	0.034(2)	0.027(2)	–0.000(2)	0.002(1)	–0.003(2)
N(2)	4*e*		0.7323(3)	–0.0125(3)	0.5087(3)	0.025(2)	0.038(2)	0.024(2)	–0.002(2)	0.004(1)	0.005(2)
C(1)	4*e*		0.6495(5)	0.2046(4)	0.6645(5)	0.042(3)	0.063(4)	0.038(3)	0.018(3)	0.000(2)	–0.012(3)
C(11)	4*e*		0.7765(4)	0.1548(3)	0.5071(4)	0.027(2)	0.037(3)	0.032(2)	0.007(2)	0.001(2)	–0.004(2)
C(12)	4*e*		0.7420(5)	0.2354(4)	0.5692(4)	0.037(2)	0.044(3)	0.034(3)	0.012(2)	–0.001(2)	–0.007(2)
C(13)	4*e*		0.7957(5)	0.3189(4)	0.5323(5)	0.050(3)	0.038(3)	0.048(3)	0.009(2)	–0.008(2)	–0.011(2)
C(14)	4*e*		0.8793(6)	0.3151(4)	0.4381(5)	0.054(3)	0.032(3)	0.049(3)	–0.002(2)	–0.006(2)	0.001(2)
C(15)	4*e*		0.9082(5)	0.2314(3)	0.3816(4)	0.034(2)	0.034(3)	0.039(3)	–0.006(2)	0.002(2)	0.002(2)
C(21)	4*e*		0.7142(4)	0.0730(3)	0.5547(4)	0.025(2)	0.047(3)	0.028(2)	–0.001(2)	0.003(2)	–0.001(2)
C(22)	4*e*		0.6373(5)	0.0982(4)	0.6497(4)	0.031(2)	0.069(4)	0.027(2)	0.009(2)	0.006(2)	–0.003(2)
C(23)	4*e*		0.5723(5)	0.0261(5)	0.7033(5)	0.030(2)	0.094(5)	0.033(3)	–0.003(3)	0.009(2)	0.001(3)
C(24)	4*e*		0.5885(5)	–0.0641(5)	0.6591(5)	0.039(3)	0.079(4)	0.036(3)	–0.024(3)	0.006(2)	0.017(3)
C(25)	4*e*		0.6703(5)	–0.0826(4)	0.5628(5)	0.043(3)	0.049(3)	0.036(3)	–0.010(2)	0.002(2)	0.009(2)
N(3)	4*e*	0.506	0.491(1)	0.420(1)	0.499(1)	0.060(8)	0.19(2)	0.058(8)	–0.01(1)	0.001(6)	0.030(9)
C(31)	4*e*	0.506	0.384(1)	0.400(1)	0.501(1)	0.053(8)	0.08(1)	0.022(5)	0.010(7)	0.010(5)	0.005(6)
C(32)	4*e*	0.506	0.243(2)	0.373(2)	0.500(3)	0.06(1)	0.03(1)	0.06(1)	–0.007(7)	0.021(7)	–0.01(1)
N(4)	4*e*	0.494	0.452(1)	0.303(1)	0.466(2)	0.042(7)	0.14(2)	0.13(1)	0.018(8)	0.013(7)	–0.01(1)
C(41)	4*e*	0.494	0.360(1)	0.344(1)	0.483(1)	0.054(9)	0.053(9)	0.062(9)	–0.019(8)	–0.008(6)	0.008(7)
C(42)	4*e*	0.494	0.246(2)	0.403(2)	0.513(3)	0.053(9)	0.03(1)	0.06(1)	0.007(7)	0.012(8)	–0.00(1)

Acknowledgments. The authors thank Mr Jacques van Ree for helpful discussions.

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