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Crystal structure of tricarbonyl-chlorido-(2*E*)-2-(6-(*E*-(2-hydroxyphenylimino)methyl)pyridine-2-yl)methyleneaminophenol-rhenium(I), $C_{22}H_{15}ClN_3O_5Re$

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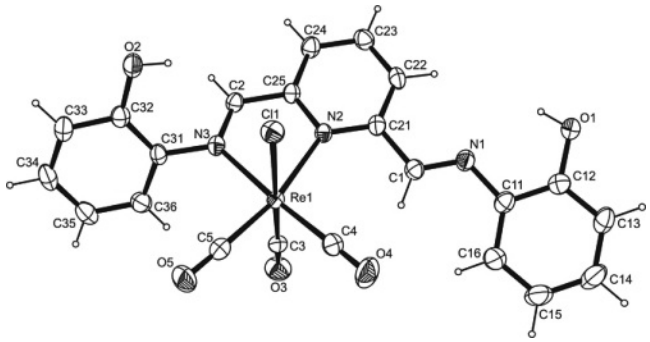

Abstract

$C_{22}H_{15}ClN_3O_5Re$, monoclinic, $P2_1/c$ (no. 14), a = 13.1731(4) Å, b = 10.6615(3) Å, c = 16.7609(5) Å, β = 112.546(1)°, V = 2174.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.0177, $wR_{ref}(F^2)$ = 0.0381, T = 200 K.

Table 1. Data collection and handling.

Crystal:	red platelets, size 0.08×0.181×0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	57.52 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	23177, 4972
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4338
$N(param)_{refined}$:	291
Programs:	SHELX, WinGX, MERCURY, PLATON [14–17]

Source of material

(2*E*)-2-(6-(*E*-(2-hydroxyphenylimino)methyl)pyridine-2-yl)-methyleneaminophenol was reacted with $Re(CO)_5Cl$ in a mixture of toluene and dichloromethane. Crystals suitable for the diffraction study were obtained upon evaporation of the reaction mixture 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). The H atoms of the hydroxyl groups were allowed to rotate with a fixed angle around the C–O bonds to best fit the experimental electron density (HFIX 147 in the SHELX program suite [14]), with U_{iso}(H) set to 1.5U_{eq}(O).

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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, the title compound was synthesized. The molecular and crystal structure of four other rhenium coordination compounds featuring a symmetric double-Schiff base ligand have been reported earlier [3–6] as has one rhenium(I) coordination compound that features half the title compound's Schiff base ligand in its coordination sphere [7]. The title compound is a hexacoordinate rhenium(I) coordination compound. The octahedral coordination sphere is constructed by three carbonyl ligands in *fac*-configuration, as well as a chlorido ligand and a symmetric two-fold Schiff-base, the latter coordinating *via* the pyridyl-type nitrogen atom as well as one of the imine-group nitrogen atoms. A puckering analysis of the five-membered chelate ring according to Cremer & Pople [8] shows the latter to adopt a $^{N(2)}T_{Re(1)}$ conformation [9]. The two Re–N bonds differ slightly with values of 2.167(2) Å and 2.2467(19) Å, with the shorter bond being established towards the imine-type nitrogen atom. The Re–Cl bond length of 2.4795(6) Å is in good agreement with other rhenium(I) tricarbonyl coordination compounds featuring a *N,N,Cl* set of ligator atoms whose metrical parameters have been deposited with the Cambridge Structural Database [10]. In the crystal, intra- and intermolecular classical hydrogen bonds of the O–H···N, O–H···O and O–H···Cl type are observed next to C–H···Cl contacts whose range fall below the sum of van-der-Waals radii of the atoms participating in them [11]. The classical hydrogen bonds are supported by the phenolic hydroxyl groups and, invariably, show bifurcation between an intramolecular component as established towards the imine-type nitrogen atoms as acceptors and an intermolecular component as established towards the chlorine atom and the oxygen atom of the

other hydroxyl group, respectively. The C–H···Cl contacts exclusively stem from hydrogen atoms on the central pyridyl moiety as well as the vinylic hydrogen atom of the Schiff-base functionality whose nitrogen atom acts as donor towards the rhenium atom. In total, the molecules are connected to planes perpendicular to the crystallographic *a* axis. In terms of graph-set analysis [12, 13], the descriptor for the classical hydrogen bonds is $S(5)S(5)R^2_2(20)R^2_2(26)$ on the unary level while the C–H···Cl contacts necessitate a $C^1_1(5)C^1_1(6)R^2_2(12)$ descriptor on the same level. The shortest intercentroid distance between two centers of gravity was measured at 4.2404(16) Å and is found in between the central pyridyl moiety and the phenolate moiety of the Schiff-base subunit whose nitrogen atom coordinates to the central atom.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	4*e*	0.0474	0.0415	0.722	0.048
H(2A)	4*e*	0.0276	0.0283	0.1705	0.052
H(1)	4*e*	0.2641	0.0643	0.5996	0.029
H(2)	4*e*	0.0495	0.2183	0.2395	0.027
H(13)	4*e*	0.2119	–0.0614	0.9179	0.041
H(14)	4*e*	0.4019	–0.0812	0.9622	0.052
H(15)	4*e*	0.4881	–0.0273	0.8689	0.055
H(16)	4*e*	0.3847	0.0348	0.7278	0.047
H(22)	4*e*	–0.0064	0.1758	0.5565	0.032
H(23)	4*e*	–0.1314	0.2601	0.4284	0.034
H(24)	4*e*	–0.0830	0.2677	0.3072	0.032
H(33)	4*e*	0.1321	0.0425	0.0203	0.036
H(34)	4*e*	0.3048	0.1190	0.0392	0.041
H(35)	4*e*	0.4212	0.1992	0.1723	0.041

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*	0.274690(8)	0.026048(9)	0.417372(6)	0.01929(5)	0.02262(6)	0.01740(5)	0.00108(4)	0.00627(4)	–0.00002(4)
Cl(1)	4*e*	0.13493(5)	–0.14072(6)	0.35683(4)	0.0275(3)	0.0261(3)	0.0293(3)	–0.0023(3)	0.0105(3)	–0.0041(3)
O(1)	4*e*	0.0752(2)	0.0153(2)	0.7731(1)	0.028(1)	0.045(1)	0.023(1)	–0.0016(9)	0.0096(8)	0.0049(9)
O(2)	4*e*	0.0395(2)	0.0330(2)	0.1248(1)	0.035(1)	0.049(1)	0.024(1)	–0.0109(9)	0.0144(9)	–0.0061(9)
O(3)	4*e*	0.4384(2)	0.2405(2)	0.4875(1)	0.035(1)	0.040(1)	0.047(1)	–0.011(1)	0.014(1)	–0.009(1)
O(4)	4*e*	0.3831(2)	–0.1328(2)	0.5813(1)	0.061(2)	0.056(2)	0.032(1)	0.024(1)	0.019(1)	0.018(1)
O(5)	4*e*	0.4314(2)	–0.0993(2)	0.3461(1)	0.043(1)	0.056(2)	0.042(1)	0.020(1)	0.025(1)	0.002(1)
N(1)	4*e*	0.1612(2)	0.0670(2)	0.6563(1)	0.028(1)	0.028(1)	0.021(1)	–0.0030(9)	0.009(1)	–0.0008(9)
N(2)	4*e*	0.1372(2)	0.1249(2)	0.4396(1)	0.023(1)	0.019(1)	0.019(1)	–0.0005(8)	0.0087(9)	–0.0013(8)
N(3)	4*e*	0.1842(2)	0.1235(2)	0.2975(1)	0.025(1)	0.020(1)	0.019(1)	–0.0024(8)	0.0097(9)	–0.0008(8)
C(1)	4*e*	0.1907(2)	0.0821(2)	0.5931(2)	0.026(1)	0.024(1)	0.024(1)	0.001(1)	0.011(1)	–0.002(1)
C(2)	4*e*	0.0948(2)	0.1784(2)	0.2917(2)	0.025(1)	0.021(1)	0.020(1)	0.002(1)	0.009(1)	0.002(1)
C(3)	4*e*	0.3773(2)	0.1599(3)	0.4622(2)	0.021(1)	0.036(2)	0.022(1)	0.005(1)	0.007(1)	0.001(1)
C(4)	4*e*	0.3425(2)	–0.0712(3)	0.5212(2)	0.029(1)	0.037(2)	0.026(1)	0.004(1)	0.012(1)	–0.003(1)
C(5)	4*e*	0.3735(2)	–0.0535(3)	0.3739(2)	0.028(1)	0.034(2)	0.023(1)	0.003(1)	0.007(1)	0.003(1)
C(11)	4*e*	0.2354(2)	0.0274(3)	0.7385(2)	0.030(1)	0.027(1)	0.022(1)	0.002(1)	0.008(1)	–0.002(1)
C(12)	4*e*	0.1862(2)	0.0006(2)	0.7969(2)	0.026(1)	0.025(2)	0.026(1)	0.000(1)	0.008(1)	–0.004(1)
C(13)	4*e*	0.2471(3)	–0.0409(3)	0.8795(2)	0.044(2)	0.037(2)	0.022(1)	0.006(1)	0.013(1)	0.001(1)
C(14)	4*e*	0.3592(3)	–0.0523(3)	0.9056(2)	0.045(2)	0.054(2)	0.024(2)	0.021(2)	0.005(1)	0.003(1)
C(15)	4*e*	0.4104(3)	–0.0219(3)	0.8496(2)	0.031(2)	0.069(2)	0.033(2)	0.019(2)	0.006(1)	–0.004(2)
C(16)	4*e*	0.3493(2)	0.0162(3)	0.7663(2)	0.032(2)	0.056(2)	0.030(2)	0.007(1)	0.013(1)	–0.002(1)
C(21)	4*e*	0.1105(2)	0.1273(2)	0.5098(2)	0.027(1)	0.021(1)	0.020(1)	–0.005(1)	0.011(1)	–0.003(1)
C(22)	4*e*	0.0106(2)	0.1771(3)	0.5063(2)	0.031(2)	0.030(2)	0.024(1)	–0.002(1)	0.017(1)	–0.003(1)
C(23)	4*e*	–0.0630(2)	0.2278(3)	0.4312(2)	0.028(1)	0.030(2)	0.032(2)	0.004(1)	0.015(1)	–0.002(1)
C(24)	4*e*	–0.0351(2)	0.2306(2)	0.3597(2)	0.031(2)	0.025(1)	0.024(1)	0.006(1)	0.011(1)	0.003(1)
C(25)	4*e*	0.0639(2)	0.1785(2)	0.3661(2)	0.026(1)	0.019(1)	0.021(1)	0.000(1)	0.011(1)	–0.000(1)
C(31)	4*e*	0.2137(2)	0.1221(2)	0.2232(2)	0.028(1)	0.022(1)	0.021(1)	0.005(1)	0.013(1)	0.004(1)
C(32)	4*e*	0.1432(2)	0.0767(2)	0.1434(2)	0.028(1)	0.023(1)	0.024(1)	0.002(1)	0.011(1)	0.001(1)
C(33)	4*e*	0.1788(2)	0.0749(3)	0.0749(2)	0.039(2)	0.030(2)	0.023(1)	0.004(1)	0.015(1)	0.001(1)
C(34)	4*e*	0.2815(2)	0.1199(3)	0.0863(2)	0.043(2)	0.036(2)	0.034(2)	0.007(1)	0.027(1)	0.003(1)
C(35)	4*e*	0.3512(2)	0.1665(3)	0.1655(2)	0.032(2)	0.037(2)	0.041(2)	0.002(1)	0.022(1)	0.004(1)
C(36)	4*e*	0.3183(2)	0.1652(3)	0.2344(2)	0.027(1)	0.031(2)	0.030(2)	0.001(1)	0.012(1)	0.002(1)

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