Crystal structure of *fac*-2-((*E*)-(2-aminoethylimino)methyl)phenolato-κ^3N,N',O) tricarbonyl rhenium(I), $C_{12}H_{11}N_2O_4Re$

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

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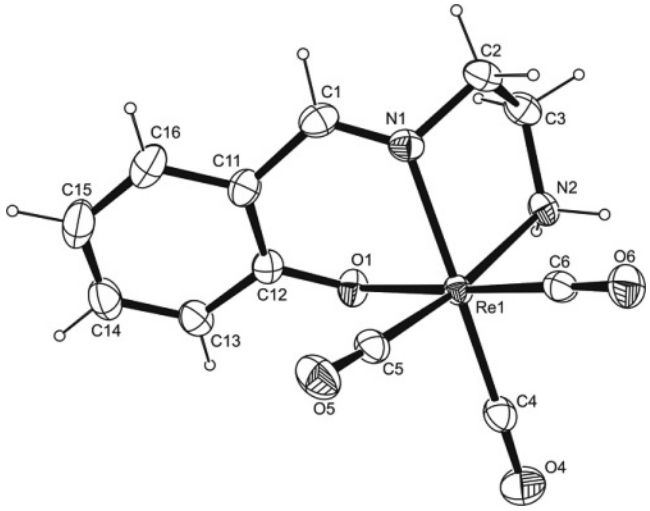

Abstract

$C_{12}H_{11}N_2O_4Re$, triclinic, $P\bar{1}$ (no. 2), a = 7.6865(3) Å, b = 9.8671(4) Å, c = 10.2152(4) Å, α = 99.634(1)°, β = 109.285(1)°, γ = 112.180(1)°, V = 638.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.0138, $wR_{ref}(F^2)$ = 0.0350, T = 200 K.

Table 1. Data collection and handling.

Crystal:	green platelets, size 0.05×0.245×0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	95.30 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.74°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11393, 3166
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3056
$N(param)_{refined}$:	180
Programs:	SHELX, WinGX, MERCURY, PLATON [13–16]

Source of material

The title compound was obtained upon reacting 2-((*E*)-(2-aminoethylimino)methyl)phenol with $Re(CO)_5Cl$ in toluene. Crystals suitable for the diffraction study were obtained upon free evaporation of the solvent at room temperature.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic carbon atoms and the formyl group, C–H 0.99 Å for methylene groups) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). Both nitrogen-bound H atoms were located on a difference Fourier map and refined freely.

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

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 the symmetric double-Schiff base of the organic ligand have been reported earlier [3–6]. 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 2-((*E*)-(2-aminoethylimino)methyl)phenolato moiety. The latter shows a κ^3N,N',O coordination mode as a tridentate ligand with the nitrogen atoms acting as neutral donor atoms and the oxygen atom as anionic bonding partner. A conformational analysis of the two chelate rings according to Cremer & Pople [7] shows the five-membered ring to adopt a $^3T_2$ ($^{C2}T_{N1}$) conformation [8] while the six-membered chelate ring was found to be present in a $^1S_2$ ($^{Re1}S_{O1}$) conformation [9]. The two Re–N bond lengths differ markedly with 2.148(2) Å and 2.2290(19) Å, with the shorter bond established by the imine-type nitrogen atom. A survey of metrical data for compounds with comparable rhenium coordination spheres whose data has been deposited with the Cambridge Structural Database [10] shows that both these values found in the title compound are significantly bigger than the most common ones observed. In the crystal, classical hydrogen bonds of the N–H···O type are apparent. Hydrogen bonds are observed between the amino group as donor and the phenolate-type oxygen atom on the one hand and the oxygen atom of the carbonyl group in *para* position to this phenolate ligand on the other hand. In total, the molecules are connected to chains along the c direction. In terms of graph-set analysis [11, 12], the N–H···O hydrogen bonds require a $R^2_2(8)R^2_2(10)$ descriptor on the first level. The crystal structure is further stabilized by $\pi\cdots\pi$ interactions as the shortest

intercentroid distance between two centers of gravity was measured to be only 3.7625(17) Å.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2A)	2*i*	1.141(4)	1.050(3)	0.273(3)	0.023(7)
H(2B)	2*i*	1.128(5)	1.039(4)	0.412(4)	0.038(9)
H(1)	2*i*	0.7041	0.4871	0.1819	0.032
H(2C)	2*i*	0.9712	0.7461	0.0713	0.032
H(2D)	2*i*	0.9920	0.6270	0.1585	0.032
H(3A)	2*i*	1.1490	0.8223	0.3867	0.032
H(3B)	2*i*	1.2717	0.8945	0.2950	0.032
H(13)	2*i*	0.4523	0.7699	0.5010	0.033
H(14)	2*i*	0.1835	0.5289	0.4504	0.043
H(15)	2*i*	0.1268	0.3068	0.2826	0.047
H(16)	2*i*	0.3513	0.3266	0.1726	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)	2*i*	0.73337(1)	0.897855(9)	0.196078(8)	0.01873(5)	0.01898(5)	0.01670(5)	0.00864(4)	0.00938(4)	0.00562(4)
O(1)	2*i*	0.7062(3)	0.8390(2)	0.3829(2)	0.0273(8)	0.0226(8)	0.0164(8)	0.0067(7)	0.0110(7)	0.0042(7)
O(4)	2*i*	0.7236(3)	1.2056(2)	0.2981(2)	0.052(1)	0.030(1)	0.050(1)	0.0226(9)	0.028(1)	0.0086(9)
O(5)	2*i*	0.2624(3)	0.7251(2)	0.0016(2)	0.0223(9)	0.039(1)	0.036(1)	0.0122(8)	0.0099(8)	0.0062(9)
O(6)	2*i*	0.7681(3)	0.9690(2)	–0.0768(2)	0.0352(9)	0.036(1)	0.0264(9)	0.0176(8)	0.0187(8)	0.0162(8)
N(1)	2*i*	0.7733(3)	0.6925(2)	0.1694(2)	0.0260(9)	0.024(1)	0.0180(9)	0.0132(8)	0.0104(8)	0.0054(8)
N(2)	2*i*	1.0756(3)	0.9836(2)	0.3133(2)	0.0209(9)	0.026(1)	0.0169(9)	0.0088(8)	0.0091(8)	0.0052(8)
C(1)	2*i*	0.6761(4)	0.5726(3)	0.1991(3)	0.034(1)	0.023(1)	0.022(1)	0.014(1)	0.011(1)	0.0041(9)
C(2)	2*i*	0.9698(4)	0.7197(3)	0.1604(3)	0.029(1)	0.032(1)	0.027(1)	0.019(1)	0.015(1)	0.009(1)
C(3)	2*i*	1.1355(4)	0.8563(3)	0.2996(3)	0.024(1)	0.035(1)	0.025(1)	0.017(1)	0.0097(9)	0.010(1)
C(4)	2*i*	0.7263(4)	1.0910(3)	0.2573(3)	0.027(1)	0.026(1)	0.025(1)	0.0110(9)	0.015(1)	0.0062(9)
C(5)	2*i*	0.4376(4)	0.7937(3)	0.0794(3)	0.025(1)	0.026(1)	0.023(1)	0.0140(9)	0.0139(9)	0.0095(9)
C(6)	2*i*	0.7589(3)	0.9429(3)	0.0280(3)	0.018(1)	0.022(1)	0.023(1)	0.0103(8)	0.0086(9)	0.0061(9)
C(11)	2*i*	0.5254(4)	0.5625(3)	0.2578(3)	0.028(1)	0.024(1)	0.024(1)	0.011(1)	0.012(1)	0.011(1)
C(12)	2*i*	0.5575(3)	0.6989(3)	0.3560(3)	0.022(1)	0.024(1)	0.020(1)	0.0100(9)	0.0079(9)	0.0095(9)
C(13)	2*i*	0.4295(4)	0.6815(3)	0.4303(3)	0.027(1)	0.035(1)	0.026(1)	0.016(1)	0.013(1)	0.015(1)
C(14)	2*i*	0.2713(4)	0.5375(3)	0.4017(3)	0.029(1)	0.045(2)	0.044(2)	0.018(1)	0.021(1)	0.027(1)
C(15)	2*i*	0.2381(4)	0.4050(3)	0.3030(4)	0.030(1)	0.031(1)	0.049(2)	0.006(1)	0.014(1)	0.021(1)
C(16)	2*i*	0.3682(4)	0.4177(3)	0.2356(3)	0.034(1)	0.022(1)	0.037(2)	0.008(1)	0.011(1)	0.011(1)

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