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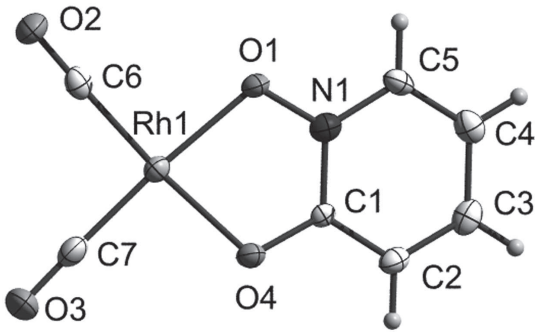
Crystal structure of dicarbonyl(pyridin-2-olate-1-oxido-κ^2*O*,*O*′)rhodium(I), $C_7H_4NO_4Rh$



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Abstract

$C_7H_4NO_4Rh$, monoclinic, $P2_1/c$ (no. 14), $a = 3.5780(12)$ Å, $b = 10.932(4)$ Å, $c = 20.866(7)$ Å, $\beta = 94.792(11)°$, $V = 813.3(12)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0345$, $wR_{ref}(F^2) = 0.0712$, $T = 100$ K.

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The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

$RhCl_3 \cdot H_2O$ (0.1 g, 0.48 mmol) was dissolved in 6 cm^3 of DMF and refluxed for 30 min. The solution was cooled to room temperature. [Rh(hpno)(CO)$_2$] was synthesized by addition of 1-hydroxypyridine *N*-oxide (0.053 g, 0.48 mmol) in 3 cm^3 of DMF. A yellow precipitate was formed after the addition of ice water. The precipitate was filtered off and dried. Yellow needle-shaped crystals formed in acetone and methanol. IR: ν(CO) 2067, 2005 cm^{-1}. **^{1}H-NMR** (300 MHz, Acetone-d6) δ = 8.18 (d, J = 6.6 Hz, 1H), 7.62 (t, J = 7.1 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.87 (t, J = 6.1 Hz, 1H). **^{13} C-NMR** (151 MHz, Acetone-d6) δ = 185.42 (d, J1Rh = 70.1 Hz), 184.81 (d, J1Rh = 71.6 Hz), 161.92 (*s*), 135.78 (*s*), 135.24 (*s*), 115.73 (*s*), 112.25 (*s*).

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Table 1: Data collection and handling.

Crystal:	Yellow, needle, size 0.085×0.175×0.815 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	20.77 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
$2\theta_{max}$:	56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10720, 1951
$N(param)_{refined}$:	118
Programs:	Bruker software [19], SHELX [20], Diamond [21], WinGX [22]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	4*e*	1.1607	0.2148	0.4035	0.028
H(2)	4*e*	0.9493	0.3189	0.3120	0.025
H(5)	4*e*	0.8527	−0.1019	0.3175	0.026
H(4)	4*e*	1.1154	0.0021	0.4062	0.029

Experimental details

The H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}(C)$, respectively. The highest peak is located 1.75 Å from C5 and the deepest hole is situated 1.72 Å from H3.

The dispacement parameters of C1 and N1 indicate that these positions may suffer a N/C disorder, which doesn't affect the coordination of the Rh(I).

Discussion

2-hydroxypyridine *N*-oxide (hpno) is a heterocyclic, hard bidentate ligand with a hydroxyl and ketone group which can coordinate with hard metal ions by the two oxygen atoms to form a five-membered ring chelate [1, 2]. This study forms part of research in our group on the relationships of structure and

Table 3: Fractional coordinates and atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh(1)	4*e*	0.47530(9)	0.10733(3)	0.13681(1)	0.0187(2)	0.0173(2)	0.0177(2)	0.0010(1)	0.0024(1)	−0.0015(1)
O(4)	4*e*	0.6511(8)	0.2284(2)	0.2067(1)	0.024(2)	0.015(1)	0.022(1)	0.001(1)	−0.001(1)	−0.001(1)
O(1)	4*e*	0.5978(8)	−0.0111(2)	0.2101(1)	0.026(2)	0.014(1)	0.020(1)	−0.001(1)	−0.001(1)	−0.002(1)
O(2)	4*e*	0.237(1)	−0.0898(3)	0.0437(2)	0.040(2)	0.024(2)	0.025(2)	−0.004(1)	0.000(1)	−0.006(1)
O(3)	4*e*	0.307(1)	0.2985(3)	0.0365(2)	0.067(3)	0.025(2)	0.028(2)	0.005(2)	−0.004(2)	0.004(1)
C(3)	4*e*	1.057(1)	0.1724(4)	0.3677(2)	0.016(2)	0.031(2)	0.023(2)	−0.002(2)	0.001(2)	−0.006(2)
C(1)	4*e*	0.776(1)	0.1710(3)	0.2604(2)	0.010(2)	0.014(2)	0.015(2)	0.002(1)	0.003(1)	−0.002(1)
N(1)	4*e*	0.749(1)	0.0472(3)	0.2623(2)	0.019(2)	0.021(2)	0.026(2)	−0.000(1)	0.004(1)	−0.002(1)
C(2)	4*e*	0.931(1)	0.2341(4)	0.3134(2)	0.022(2)	0.017(2)	0.024(2)	−0.003(2)	0.005(2)	−0.004(2)
C(6)	4*e*	0.322(1)	−0.0134(4)	0.0785(2)	0.019(2)	0.026(2)	0.020(2)	0.003(2)	0.005(2)	0.004(2)
C(5)	4*e*	0.874(1)	−0.0172(4)	0.3166(2)	0.024(2)	0.017(2)	0.025(2)	0.002(2)	0.004(2)	0.004(2)
C(4)	4*e*	1.029(1)	0.0447(4)	0.3694(2)	0.020(2)	0.028(2)	0.024(2)	0.004(2)	0.002(2)	0.003(2)
C(7)	4*e*	0.371(1)	0.2238(4)	0.0742(2)	0.031(3)	0.024(2)	0.024(2)	0.003(2)	0.001(2)	−0.009(2)

reactivity of metal complexes having different *O*,*O*′-, *O*,*N*-, *O*,*S*- and *P*,*P*′-bidentate ligands [3–5]. Metal complexes with hpno have been less studied hpno is a versatile ligand and the complexes that formed by this ligand with different metals have various uses in chemical, biological and pharmaceutical fields [6–11]. Crystal structures of dicarbonyl rhodium(I) complexes with different bidentate ligands have been less studied [12–15]. A precursor [Rh(BID)$(CO)_2$] where (BID) represents different monocharged bidentate ligands have been studied as a catalyst [16]. In the title structure, a slightly distorted square planar geometry is observed. The small O—Rh—O angle of 80.75(11)° confirms the distortion, while the C—Rh—C angle is 89.70(18)°. When this structure is compared with rhodium cupferrate complexes (cupferrate also coordinates as a five-membered ring) which was synthesized in our laboratory, the coordination with regard to *O*,*O*′ single charge, five membered ring is the same, with a slightly smaller bite angle of 78° [17, 18].

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References

1. Pearson, R. G.: Hard and soft acids and bases. J. Am. Chem. Soc. **85** (1963) 3533–3539.
2. Santos, M. A.: Hydroxypyridinone complexes with aluminium. In vitro/vivo studies and perspectives. Coord. Chem. Rev. **228** (2002) 187–203.
3. Schutte, M.; Kemp, G.; Visser, H. G.; Roodt, A.: Tuning the reactivity in classic low-spin d_6 rhenium(I) tricarbonyl radiopharmaceutical synthon by selective bidentate ligand variation (*L*,*L*′-Bid; *L*,*L*′ = *N*,*N*′, *N*,*O* and *O*,*O*′ donor atom sets) in *fac*-[Re$(CO)_3$(*L*,*L*′-Bid)(MeOH)]$_n$ complexes. Inorg. Chem. **50** (2011) 12486–12498.
4. Roodt, A.; Visser, H. G.; Brink, A.: Structure/reactivity relationships and mechanism from X-ray data and spectroscopic kinetic analysis. Crystallogr. Rev. **17** (2011) 241–280.
5. Brink, A.; Visser, H. G.; Roodt, A.: Activation of rhenium(I) toward substitution in *fac*-[Re(*N*,*O*-Bid)$(CO)_3(HOCH_3)$] by Schiff-base bidentate ligands (*N*,*O*-Bid). Inorg. Chem. **52** (2013) 8950–8961.
6. Tedeschi, C.; Azema, J.; Gornitzka, H.; Tisnes, P.; Picard, C.: A solid state study of eight coordinate lanthanide(III) complexes (Ln = Eu, Gd, Tb, Dy) with 1-hydroxy-2-pyridinone. Dalton Trans. **9** (2003) 1738–1745.
7. Puerta, D. T.; Cohen, S. M.: Examination of novel zinc binding groups for use in matrix metalloproteinase inhibitors. Inorg. Chem. **42** (2003) 3423–3430.
8. Ma, Z.; Hopson, R.; Cai, C.; Han, S.; Moulton, B.: Modifying lipophilicities of Zn(II) coordination species by introduction of ancillary ligands: a supramolecular chemistry approach. Cryst. Growth Des. **10** (2010) 2376–2381.
9. Jakusch, T.; Dean, A.; Oncsik, T.; Benyei, A. C.; Marco, V. D.; Kiss, T.: Vanadate complexes in serum: speciation modeling study. Dalton Trans. **39** (2010) 212–220.
10. Yraola, F.; Albericio, F.; Corbella, M.; Royo, M.: [Cu(pzph)$(Opo)_2$ (μ-Cl)$_2$]: A new dinuclear copper(II) complex with a chloride bridge and mixed blocking ligands. Inorg. Chim. Acta **361** (2008) 2455–2461.
11. Xu, L.; Li, Y. Z.; Liu, S. H.; Chen, X. T.; Zhou, J. H.: Bis(2-oxopyridinato *N*-oxide-k^2*O*,*O*′)cupper(II). Acta Crystallogr. **E61** (2005) m364–m366.
12. Pretorius, C.; Roodt, A.: (Benzoylacetonato-k^2*O*,*O*′)dicarbonyl rhodium(I). Acta Crystallogr. **E68** (2012) m1451–m1452.
13. Conradie, M. M.; Conradie, J.: Solid state packing of [Rh(β-diketonato)$(CO)_2$] complexes. Crystal structure of [Rh(PhCOCHCOC$_4$H$_3$S)$(CO)_2$]. J. Mol. Struc. **1051** (2013) 137–143.
14. Stuurman, N. F.; Meijboom, R. Conradie, J.: Characterization of [Rh(PhCOCHCOCH$_2$CH$_2$CH$_3$)$(CO)_2$] by X-ray crystallography, a computational and a statistical study. Polyhedron **30** (2011) 660–665.

15. Scarrow, R. C.; Riley, P. E.; Abu-dari, K.; White, D. L.; Raymond, K. N.: Ferric ion sequestering agents. 13. Synthesis, structures, and thermodynamics of complexation of cobalt(III) and iron(III) tris complexes of several chelating hydroxypyridinones. Inorg. Chem. **24** (1985) 954–967.
16. Brink, A.; Roodt, A.; Steyl, G., Visser, H. G.: Steric vs. electronic anomaly observed from iodomethane oxidative addition to tertiary phosphine modified rhodium(I) acetylacetonato complexes following progressive phenyl replacement by cyclohexyl [$PR_3 = PPh_3$, PPh_2Cy, $PPhCy_2$, PCy_3]. Dalton Trans. **39** (2010) 5572–5578.
17. Basson, S. S.; Leipoldt, J. G.; Roodt, A.; Venter, J. A.: Crystal structure of carbonyl(*N*-hydroxy-*N*-nitrosobenzenaminato-*O,O′*)-triphenylphosphinerhodium(I). Inorg. Chim. Acta **118** (1986) L45–L47.
18. Basson, S. S.; Leipoldt, J. G., Venter, J. A.: Structure of pentacoordinated *b*-carbonyl-*cd*-(*N*-hydroxy-*N*-nitrosobenzenaminato-*O,O′*)- *ae*-bis(triphenylphosphine)rhodium(I). Acta Crystallogr. **C41** (1990) 1–4.
19. Bruker:SAINT-Plus (Version 7.12) and SADABS (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA 2004.
20. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
21. Brandenburg, K.: DIAMOND. Visual crystal structure information system. Version 3.0c Crystal Impact, Bonn, Germany 2005.
22. Farrugia, L. J.: WinGX suite for small-molecule single-crystal crystallography. J. Appl. Crystallogr. **45** (2012) 849–854.