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Crystal structure of dicarbonyl(pyridin-2-olate-1-oxido-κ²O,O')rhodium(I), C₇H₄NO₄Rh

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Abstract

C₇H₄NO₄Rh, monoclinic, P2₁/c (no. 14), a = 3.5780(12) Å, b = 10.932(4) Å, c = 20.866(7) Å, β = 94.792(11)°, V = 813.3(12) Å³, Z = 4, R_{w}(F) = 0.0345, wR_{ref}(F²) = 0.0712, T = 100 K.

CCDC no.: 1453966

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

RhCl₃·H₂O (0.1 g, 0.48 mmol) was dissolved in 6 cm³ 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 cm³ 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 addition of 1-hydroxypyridine 4·methanol. IR: ν(Rh(CO) 2067, 2005 cm⁻¹, 1H-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), 13C-NMR (151 MHz, Acetone-d₆) δ = 185.42 (d, JRh = 70.1 Hz), 184.81 (d, JRh = 71.6 Hz), 161.92 (s), 135.78 (s), 135.24 (s), 115.73 (s), 112.25 (s).

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 displacement parameters of C1 and N1 indicate that these positions may suffer an 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...
reactivity of metal complexes having different $O,O'$-, $O,N'$, $O,S$- and $P,P'$-bidentate ligands [3–5]. Metal complexes with hpon have been less studied hpon is a versatile ligand and the complexes 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 $[\text{Rh(BID)}(\text{CO})_3]$ 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 $\text{O}^\text{-Rh}^\text{-O}$ angle of 80.75(11)$^\circ$ confirms the distortion, while the $\text{C}^\text{-Rh}^\text{-C}$ angle is 89.70(18)$^\circ$. 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$^\circ$ [17, 18].

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References


