Crystal structure of dichloro(*N*,*N*-dimethylpyridin-4-amine)-(η^6-*p*-cymene)ruthenium(II), $RuCl_2(C_7H_{10}N_2)(C_{10}H_{14})$

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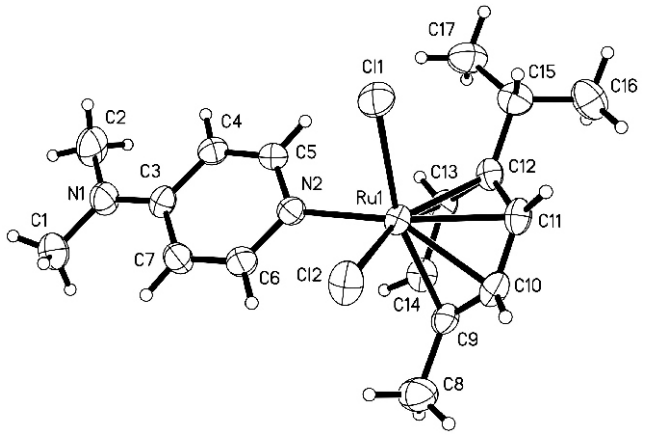

Abstract

$C_{17}H_{24}Cl_2N_2Ru$, monoclinic, $P12_1/c1$ (no. 14), a = 15.010(5) Å, b = 7.825(3) Å, c = 20.903(5) Å, β = 133.20(1)°, V = 1789.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.059, $wR_{ref}(F^2)$ = 0.113, T = 298 K.

Source of material

$[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (0.245 mg, 0.4 mmol) dissolved in dichloromethane (20 mL) was treated with *N*,*N*-dimethylpyridin-4-amine (DMAP, 0.098 mg, 0.8 mmol). The orange-red solution was heated under reflux for 1 h, cooled to room temperature, filtered and evaporated to 2 mL under reduced pressure. Then it was layered with petroleum ether and filtered to give orange-red residue. The solid residue was washed several times with petroleum ether. It is soluble in dichloromethane, acetone, and methanol. Orange-red crystals were obtained by crystallization from dichloromethane/petroleum ether (yield 0.21 mg; 61.2 %).

Experimental details

All H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of $d(Csp^2—H_{pyridyl})$ = 0.93 Å and $d(Csp^2—H_{p\text{-}cymene})$ = 0.98 Å with U_{iso} = 1.2 U_{eq}(parent atom) and $d(Csp^3—H)$ = 0.96 Å with U_{iso} = 1.5 U_{eq}(parent atom).

Discussion

Organometallic compounds are generally considered to be toxic and unstable, undergoing decomposition when exposed to air and water [1]. Arene ruthenium compounds as anticancer agents had first been introduced by Tocher et al. in 1992 [2], who had observed a cytotoxicity enhancement by coordinating the anticancer agent metronidazole (1-β-hydroxyethyl-2-methyl-5-nitroimidazole) to a benzene ruthenium dichloro fragment, stimulating the search for organometallic anticancer drugs [3-5]. The accelerating pace of reported applications for DMAP (*N*,*N*-dimethylpyridin-4-amine) and the availability of DMAP in commercial quantities at modest prices has continued to stimulate great interest in its use as a catalyst in the fields of organic, polymer, analytical and biochemistry [6]. It has a relatively high toxicity and is particularly dangerous because of its ability to be absorbed through the skin [7]. In order to develop new synergistic anticancer drugs, we try to coordinate DMAP to the arene-ruthenium half-sandwich "piano-stool" unit which is an excellent scaffold for the coupling of organic segments for targeted chemotherapy [8].

The title complex adopts a typical "three-legged piano-stool" configuration with the tetrahedral arrangement of the *p*-cymene and the other three ligands (DMAP bound via nitrogen atom, and two chlorido ligands) about the metal center ruthenium. The *p*-cymene ring is planar with mean deviation of 0.005(4) Å, the pyridyl ring is also planar with mean deviation of 0.003(4) Å, and the dihedral angle between the two rings is 33.7(2)°. The ruthenium to carbon distances are almost equal, with an average d(Ru—C) = 2.176(4) Å [range 2.153(6)-2.192(5) Å]. The C—C distances in the *p*-cymene ring are equal, as well as there are no alternate short and long bond lengths. It indicates that there is no localization and shows no trends associated with non-planarity of the arene ring. The distances d(Ru—Cl1) and d(Ru—Cl2) are 2.409(2) and 2.414(2) Å, respectively. These bond lengths are similar to the average bond length in other arene-Ru(II) complexes [9-12]. The distance d(Ru—N2) is 2.125(5) Å, similar to the average d(Ru—N) in other arene-Ru(II) pyridine derivatives [9-11].

Table 1. Data collection and handling.

Crystal:	orange-red block, size 0.23 × 0.25 × 0.27 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.72 cm^{-1}
Diffractometer, scan mode:	Bruker APEX, φ/ω
$2\theta_{max}$:	50.4°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8882, 3201
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2968
$N(param)_{refined}$:	204
Programs:	SHELXS-97, SHELXL-97, SHELXTL [13]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.6315	0.6876	1.0121	0.084
H(1B)	4*e*	0.6026	0.8734	0.9743	0.084
H(1C)	4*e*	0.6431	0.7332	0.9450	0.084
H(2A)	4*e*	0.3620	0.7573	0.7619	0.086
H(2B)	4*e*	0.4054	0.5665	0.7855	0.086
H(2C)	4*e*	0.4956	0.7099	0.8072	0.086
H(4)	4*e*	0.2386	0.6178	0.7792	0.044
H(5)	4*e*	0.1180	0.5933	0.8070	0.043
H(6)	4*e*	0.3824	0.7316	1.0497	0.044
H(7)	4*e*	0.5127	0.7566	1.0305	0.045
H(8A)	4*e*	0.2134	1.1124	1.0629	0.080
H(8B)	4*e*	0.2915	0.9446	1.0992	0.080
H(8C)	4*e*	0.2132	0.9874	1.1214	0.080
H(10)	4*e*	0.0748	0.7441	1.0564	0.043
H(11)	4*e*	–0.0862	0.5882	0.9325	0.039
H(13)	4*e*	–0.0291	0.8278	0.7887	0.038
H(14)	4*e*	0.1323	0.9861	0.9150	0.044
H(15)	4*e*	–0.1808	0.4856	0.7869	0.049
H(16A)	4*e*	–0.3236	0.7844	0.7050	0.081
H(16B)	4*e*	–0.3097	0.6812	0.7757	0.081
H(16C)	4*e*	–0.3759	0.5984	0.6844	0.081
H(17A)	4*e*	–0.1097	0.5431	0.7187	0.080
H(17B)	4*e*	–0.1968	0.7017	0.6714	0.080
H(17C)	4*e*	–0.2517	0.5170	0.6481	0.080

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}
Ru(1)	4*e*	0.11105(4)	0.65419(5)	0.94758(3)	0.0309(3)	0.0248(2)	0.0307(3)	0.0041(2)	0.0234(2)	0.0045(2)
Cl(1)	4*e*	0.0712(2)	0.3634(2)	0.8956(1)	0.0516(9)	0.0245(7)	0.063(1)	0.0012(7)	0.0412(9)	–0.0010(7)
Cl(2)	4*e*	0.2782(1)	0.5511(2)	1.0941(1)	0.0423(9)	0.0535(9)	0.0391(9)	0.0140(7)	0.0294(8)	0.0166(7)
N(1)	4*e*	0.4707(5)	0.7068(7)	0.8891(3)	0.038(3)	0.058(3)	0.039(3)	–0.001(3)	0.029(3)	–0.002(3)
N(2)	4*e*	0.2357(4)	0.6604(6)	0.9310(3)	0.031(3)	0.032(2)	0.029(3)	–0.001(2)	0.022(2)	–0.001(2)
C(1)	4*e*	0.5977(6)	0.754(1)	0.9612(5)	0.043(4)	0.069(5)	0.066(5)	–0.010(4)	0.041(4)	–0.012(4)
C(2)	4*e*	0.4300(7)	0.683(1)	0.8037(5)	0.055(4)	0.084(6)	0.053(4)	0.005(4)	0.045(4)	0.002(4)
C(3)	4*e*	0.3937(5)	0.6909(7)	0.9017(4)	0.036(3)	0.037(3)	0.034(3)	0.007(3)	0.027(3)	0.005(3)
C(4)	4*e*	0.2708(5)	0.6413(8)	0.8352(4)	0.038(3)	0.043(3)	0.031(3)	–0.001(3)	0.024(3)	–0.006(3)
C(5)	4*e*	0.1986(5)	0.6277(7)	0.8525(4)	0.034(3)	0.035(3)	0.038(3)	–0.005(3)	0.025(3)	–0.009(3)
C(6)	4*e*	0.3532(5)	0.7079(7)	0.9945(4)	0.036(3)	0.042(3)	0.032(3)	–0.002(3)	0.024(3)	–0.003(3)
C(7)	4*e*	0.4323(5)	0.7237(8)	0.9834(4)	0.031(3)	0.045(3)	0.034(3)	–0.003(3)	0.021(3)	–0.001(3)
C(8)	4*e*	0.2166(6)	0.9947(9)	1.0773(4)	0.049(4)	0.047(4)	0.047(4)	0.006(3)	0.027(4)	–0.006(3)
C(9)	4*e*	0.1099(5)	0.9000(7)	0.9965(4)	0.033(3)	0.030(3)	0.038(3)	0.007(2)	0.025(3)	0.000(2)
C(10)	4*e*	0.0426(5)	0.7801(8)	0.9990(4)	0.038(3)	0.041(3)	0.032(3)	0.013(3)	0.026(3)	0.007(3)
C(11)	4*e*	–0.0536(5)	0.6866(7)	0.9251(4)	0.033(3)	0.030(3)	0.040(3)	0.012(2)	0.027(3)	0.012(3)
C(12)	4*e*	–0.0851(5)	0.7081(7)	0.8438(4)	0.027(3)	0.026(3)	0.034(3)	0.008(2)	0.020(3)	0.009(2)
C(13)	4*e*	–0.0197(5)	0.8270(7)	0.8399(4)	0.037(3)	0.025(3)	0.036(3)	0.011(3)	0.026(3)	0.009(2)
C(14)	4*e*	0.0770(6)	0.9222(7)	0.9159(4)	0.039(3)	0.033(3)	0.039(3)	0.006(3)	0.028(3)	0.009(3)
C(15)	4*e*	–0.1891(6)	0.6016(8)	0.7658(4)	0.043(4)	0.030(3)	0.042(4)	0.004(3)	0.026(3)	0.006(3)
C(16)	4*e*	–0.3109(6)	0.6730(9)	0.7293(5)	0.038(4)	0.064(5)	0.046(4)	–0.001(3)	0.023(3)	0.007(4)
C(17)	4*e*	–0.1866(7)	0.5898(9)	0.6944(4)	0.058(4)	0.055(4)	0.042(4)	–0.009(4)	0.031(4)	–0.011(3)

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