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عنوان مقاله

ساختار کریستالی کمپلکس رودیم (III) پیریدین: $[Rh(py)_2(CH_3CN)Cl_2]$

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چکیده

کمپلکس رودیم (III)، $[Rh(py)_2(CH_3CN)Cl_2]$, (py= pyridine) سنتز و شناسایی شد. ساختار کمپلکس بوسیله پراش اشعه ایکس مشخص گردید. این کمپلکس دارای سیستم کریستالی مونوکلینیک (Z=4) و گروه فضایی $P\ 2_1/c$ با پارامتری بلوری: a = 7.6268(15) Å, b= 27.525(6) Å, c = 7.7125(15) Å, α = 90°, V= 1478.3(6) (4)Å^3 و می باشد.

واژه‌های کلیدی: کمپلکس رودیم (III)، پیریدین، ساختار کریستالی.

Crystal Structure of Rhodium (III) pyridine Complex:$[Rh(py)_2(CH_3CN)Cl_3]$

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Abstract

The complex of Rh(III), $[Rh(py)_2(CH_3CN)Cl_3]$, (py= pyridine) has been synthesized and characterized. The structure of the complex has been determined by X-ray diffraction (monoclinic, $P2_1/c$, Z = 4), a = 7.6268(15) Å, b= 27.525(6) Å, c = 7.7125(15) Å, α = 90°, V= 1478.3(6) Å3 and reveals that the complex is a distorted octahedron with two py rings are roughly perpendicular to each other. The bond lengths of Rh(1)-N are in the range of 2.0037(19)- 2.0555(19)Å and the bond length of Rh(1)–Cl are (2.3355(7)- 2.3425(7) Å.

Keywords: Rh(III) complex, pyridine, Crystal structure.

1. Introduction

The coordination chemistry of pyridine-based nitrogen ligands has seen a revival in recent years. Aromatic nitrogen heterocycles such as pyridine(py), 2,2´ -bipyridine (bpy), and di-2-pyridylamine (dpa) are classical but evergreen ligands in transition metal chemistry [Rogan, et al, Olenyuk, et al Jung-Sook, et al, Koizumi, et al, Patel]. They have in common the neutral character, the aromatic rings which are relevant when thinking of the π–π stacking interactions and the coordination mode in their metal complexes. Several metal complexes with nitrogen ligands are biologically important species which are related to wide aspects of life processes including oxygen transport, digestion and gene transcription [Mohamed]. In this paper, we report the structural determination of Rh complex with pyridine.

2. Experimental

2.1. Materials

All solvents and chemicals were reagent grade or better and used as received.

2.2. Physical Measurements

UV-vis spectra were taken on a JASCO 7850 spectrophotometer. The IR spectra (KBr disks) were obtained on a Shimadzu 470 spectrophotometer. ^{1}H NMR data from DMSO-d6 solutions were obtained by using a Bruker DRX-500 MHz AVANCE spectrometer. Heraeus CHN-O-Rapid elemental analyzer performed the elemental analysis.

2.3. Preparation of $[Rh(py)_2(CH_3CN)Cl_3]$

The py ligand (2 mmol) was mixed with $RhCl_3$ (1mmol) in CH_3CN (25 ml). The resulting solution were refluxed for 1 h and then filtered. The filtrates were left for about 2 weeks at room temperature, and then the orange crystals of $[Rh(py)_2(CH_3CN)Cl_3]$ complex suitable for X-ray diffraction analyses were collected.

3. X-ray crystallography study of $[Rh(py)_2(CH_3CN)Cl_3]$

Orange crystals of $[Rh(py)_2(CH_3CN)Cl_3]$ were grown by slow diffusion of diethyl ether into a solution of the complex in CH_2Cl_2 at room temperature. Single-crystal X-ray diffraction measurements were carried out with a Bruker Apex II diffractometer equipped with a graphite monochoromator for data collection at 293(2)K. The determination of unit cell dimensions and data collection was performed with (Mo kα) radiation (λ= 0.71073Å).

Data reduction processing was carried out by the use of the program SAINT, which applied Lorentz and polarization correction to three-dimensionally integrated diffraction spots. The space group was confirmed by XPREP routine in SHELXTL97 program. The structure was solved by direct method using SHELEXS97. All non-hydrogen atoms were anisotropic and hydrogen atoms were isotropic. Further details of the structural analyses are given in Table **1**. Selected bond lengths and angles are listed in Table **2** .

4. Results and discussions

The $[Rh(py)_2(CH_3CN)Cl_3]$ complex was synthesized by reaction of $RhCl_3$ with pyridine and in CH_3CN. The $[Rh(py)_2(CH_3CN)Cl_3]$ complex is air-stable and can be readily recrystallized. The elemental analysis of the complex is consistent with $C_{12}H_{13}Cl_3N_3Rh$ formula, as are the following X-ray structure and spectroscopic characterizations. Fig. 1 and Fig. 2 show the coordination geometry of the ligands about the Rh^{III} and unit cell of $[Rh(py)_2(CH_3CN)Cl_3]$, respectively. The Rh^{III} ion is situated in the center of the complex with three Cl atoms and nitrogen atom belonging to molecule of CH_3CN

occupying each vertex in the equatorial sites, while two nitrogen atoms deriving from molecules of py are located in the apical position. The two rings of py are roughly (but not exactly) perpendicular to each other. There are little deviation from linearity for the trans atoms with angles N_1- Rh(1)-N_2 (177.63(7) °), N(3)-Rh(1)-Cl(2) (179.35(15)°) and Cl(1)-Rh(1)-Cl(3) (178.22(2)°), Therefore the geometry about the Rh^{III} ion is distorted-octahedral. The angle Cl(2)– Rh(1)-N(3) is slightly wider at than the Cl(1)-Rh(1)-Cl(3)or N_1- Rh(1)-N_2. The Rh(1)–Cl (2.3355(7)- 2.3425(7) Å) distances slightly longer than Rh(1)-N (2.0037(19)- 2.0555(19)Å) distances.

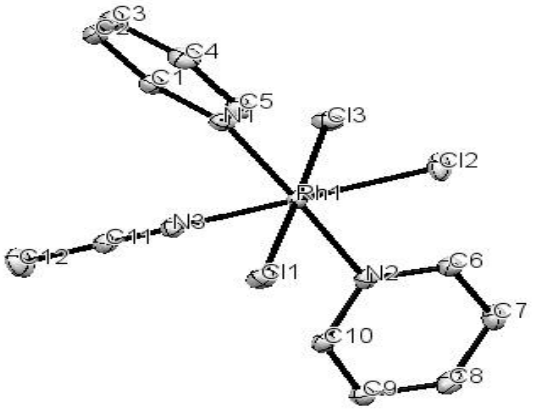

Fig.1. ORTEP of $[Rh(py)_2(CH_3CN)Cl_3]$

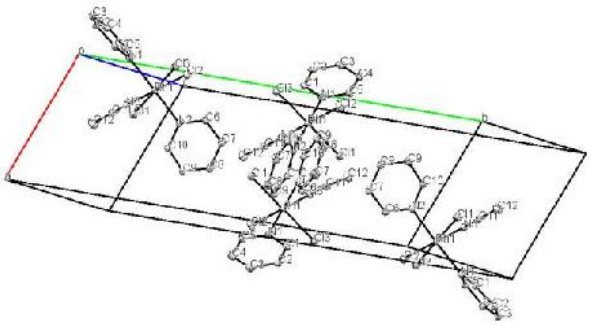

Fig. 2. Unit cell of $[Rh(py)_2(CH_3CN)Cl_3]$

Table 1 Summary of crystal data and data collection parameters for $[Rh(py)_2(CH_3CN)Cl_3]$

Empirical formula	$C_{12}H_{13}Cl_3N_3Rh$
Formula weight	408.51
Crystal system	Monoclinic
Space group	$P\ 2_1/c$
a (Å)	7.6268(15)
b (Å)	27.525(6)
c (Å)	7.7125(15)
β (°)	90
Volume (Å^3)	1478.3(6)
Z	4
D (g/cm^3)	1.836
Absorption Cofficient(mm^{-1})	1.685
T (K)	120(2)
Crystal size (mm)	0.50 × 0.48 × 0.47
R_1, wR_2	0.0279, 0.0663
R indices (all data)	*R*2 =0.0331, wR2 = 0.0685
Largest diff. peak and hole(e.Å^3)	0.712 and -0.582

Table 2. Selected bond lengths (Å) and bond angles (°) for $[Rh(py)_2(CH_3CN)Cl_3]$

Bond lengths(Å)			
Rh(1)-N(1)	2.0491(18)	C(5)-N(1)	1.350(3)
Rh(1)-N(2)	2.0555(19)	C(1)-N(1)	1.352(3)
Rh(1)-N(3)	2.0037(19)	C(11)-N(3)	1.139(3)
Rh(1)-Cl(1)	2.3355(7)	C(10)-N(2)	1.347(3)
Rh(1)-Cl(2)	2.3425(7)	C(6)-N(2)	1.348(3)
Bond angles(°)			
N(3)-Rh(1)-N(1)	89.14(7)	N(2)-Rh(1)-Cl(1)	90.78(6)
N(3)-Rh(1)-N(2)	88.50(7)	Cl(2)-Rh(1)-Cl(1)	90.90(6)
N(1)-Rh(1)-N(2)	177.63(7)	N(3)-Rh(1)-Cl(3)	88.71(6)
N(3)-Rh(1)-Cl(2)	179.35(7)	N(1)-Rh(1)-Cl(3)	90.38(6)
N(1)-Rh(1)-Cl(2)	91.36(6)	N(2)-Rh(1)-Cl(3)	89.39(6)
N(2)-Rh(1)-Cl(2)	91.00(6)	Cl(2)-Rh(1)-Cl(3)	90.87(2)
N(3)-Rh(1)-Cl(1)	89.52(6)	Cl(1)-Rh(1)-Cl(3)	178.22(2)
N(1)-Rh(1)-Cl(1)	89.38(6)	C(5)-N(1)-Rh(1)	121.42(14)

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