



عنوان مقاله

ساختار کریستالی کمپلکس رودیم (III) پیریدین:



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چکیده

کمپلکس رودیم (III)، (py= pyridine)، $[\text{Rh}(\text{py})_2(\text{CH}_3\text{CN})\text{Cl}_2]$ سنتز و شناسایی شد. ساختار کمپلکس بوسیله پراش اشعه ایکس مشخص گردید. این کمپلکس دارای سیستم کریستالی مونوکلینیک ($Z=4$) و گروه فضایی $P2_1/c$ با پارامتری بلوری: $\alpha = 90^\circ$ ، $c = 7.7125(15) \text{ \AA}$ ، $b = 27.525(6) \text{ \AA}$ ، $a = 7.6268(15) \text{ \AA}$ و $V = 1478.3(6) \text{ \AA}^3$ می باشد.

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

Crystal Structure of Rhodium (III) pyridine Complex: $[\text{Rh}(\text{py})_2(\text{CH}_3\text{CN})\text{Cl}_3]$

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Abstract

The complex of Rh(III), $[\text{Rh}(\text{py})_2(\text{CH}_3\text{CN})\text{Cl}_3]$, (py= pyridine) has been synthesized and characterized. The structure of the complex has been determined by X-ray diffraction (monoclinic, $P2_1/c$, $Z = 4$), $a = 7.6268(15) \text{ \AA}$, $b = 27.525(6) \text{ \AA}$, $c = 7.7125(15) \text{ \AA}$, $\alpha = 90^\circ$, $V = 1478.3(6) \text{ \AA}^3$ 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. ¹H 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(CH₃CN)Cl₃]

The py ligand (2 mmol) was mixed with RhCl₃ (1mmol) in CH₃CN (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(CH₃CN)Cl₃] complex suitable for X-ray diffraction analyses were collected.

3. X-ray crystallography study of [Rh(py)₂(CH₃CN)Cl₃]

Orange crystals of [Rh(py)₂(CH₃CN)Cl₃] were grown by slow diffusion of diethyl ether into a solution of the complex in CH₂Cl₂ at room temperature. Single-crystal X-ray diffraction measurements were carried out with a Bruker Apex II diffractometer equipped with a graphite monochromator for data collection at 293(2)K. The determination of unit cell dimensions and data collection was performed with (Mo $\kappa\alpha$) radiation ($\lambda = 0.71073 \text{ \AA}$).

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(CH₃CN)Cl₃] complex was synthesized by reaction of RhCl₃ with pyridine and in CH₃CN. The [Rh(py)₂(CH₃CN)Cl₃] complex is air-stable and can be readily recrystallized. The elemental analysis of the complex is consistent with C₁₂H₁₃Cl₃N₃Rh 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(CH₃CN)Cl₃], respectively. The Rh^{III} ion is situated in the center of the complex with three Cl atoms and nitrogen atom belonging to molecule of CH₃CN



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 $N_1-Rh(1)-N_2$ ($177.63(7)^\circ$), $N(3)-Rh(1)-Cl(2)$ ($179.35(15)^\circ$) and $Cl(1)-Rh(1)-Cl(3)$ ($178.22(2)^\circ$), 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 $Rh(1)-Cl$ ($2.3355(7)-2.3425(7) \text{ \AA}$) distances slightly longer than $Rh(1)-N$ ($2.0037(19)-2.0555(19) \text{ \AA}$) distances.

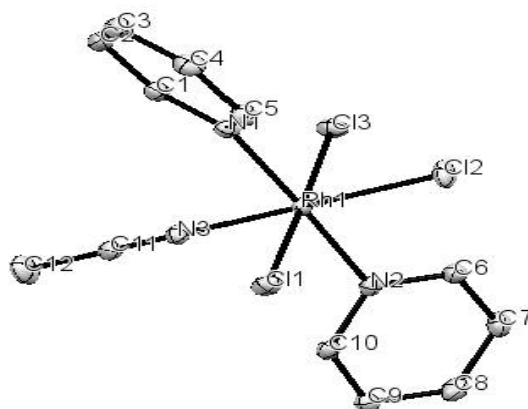


Fig.1. ORTEP of $[Rh(py)_2(CH_3CN)Cl_3]$

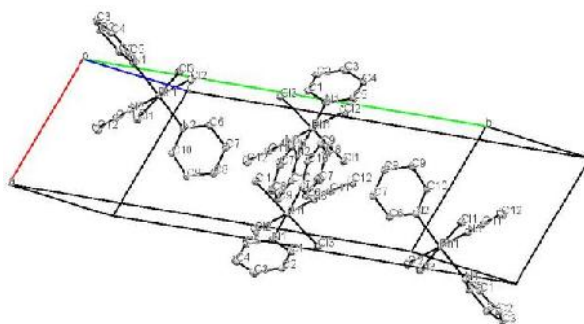


Fig. 2. Unit cell of $[Rh(py)_2(CH_3CN)Cl_3]$



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Table 1 Summary of crystal data and data collection parameters for [Rh(py)₂(CH₃CN)Cl₃]

Empirical formula	C ₁₂ H ₁₃ Cl ₃ N ₃ Rh
Formula weight	408.51
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	7.6268(15)
<i>b</i> (Å)	27.525(6)
<i>c</i> (Å)	7.7125(15)
β (°)	90
Volume (Å ³)	1478.3(6)
<i>Z</i>	4
<i>D</i> (g/cm ³)	1.836
Absorption Coefficient(mm ⁻¹)	1.685
<i>T</i> (K)	120(2)
Crystal size (mm)	0.50 × 0.48 × 0.47
<i>R</i> ₁ , <i>wR</i> ₂	0.0279, 0.0663
<i>R</i> indices (all data)	<i>R</i> ₂ = 0.0331, <i>wR</i> ₂ = 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(CH₃CN)Cl₃]

<i>Bond lengths</i> (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)
<i>Bond angles</i> (°)			
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)

References:

- Rogan, J., Poleti, D., Karanovic´ L., Bogdanovic´, G., Bire´, A. S-d., Petrovic´, D. M. 2000. Mixed ligand Co(II), Ni(II) and Cu(II) complexes containing terephthalato ligands. Crystal structures of diaqua(2,2'-dipyridylamine)(terephthalato)metal(II) trihydrates (metal=cobalt or nickel). *Polyhedron*, 19, pp.1415–1421.
- Olenyuk, B., Leininger, S., Plenyuk, , and Stang, P.J.,2000. Self-assembly of Discrete Cyclic Nanostructures Mediated by Transition Metals *Chem. Rev.* 100, pp. 853-858.



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- Jung-Sook, K., Uk, Lee., Bon-Kweon, Koo., 2010. Synthesis and ¹D Chain Crystal Structure of Zinc(II) Terephthalate Complex: [Zn(tp)(py)(H₂O)]_n *Bull. Korean Chem. Soc.* 31(6), 1743-1746.
- Koizumi, T-A, Tomon, T., and Tanaka, K., 2005. Synthesis and electrochemical properties of bis(bipyridine)ruthenium(II) complexes bearing pyridinyl- and pyridinylidene ligands induced by cyclometalation of *N*'-methylated bipyridinium analogs *J. Organomet. Chem.* 690, pp. 1258-1264.
- Patel, R.N., Singh, N., Shukla, K.K., Gundla, V.L.N., and Chauhan, U.K., 2006. Synthesis, characterization and biological activity of ternary copper(II) complexes containing polypyridyl ligands. *Spect. Chim. Acta, A.*, 63, pp. 21-26.
- Mohamed, A. A., 2010. Advances in the coordination chemistry of nitrogen ligand complexes of coinage metals. *Coord. Chem. Rev.*, 254, 1918-1947.