Title	Crystal Structure of Ruthenium Phthalocyanine with Diaxial Monoatomic Ligand: Bis(Triphenylphosphine) Iminium Dichloro(Phthalocyaninato(2-)) Ruthenium(III)
Author(s)	Yu, Derrick Ethelbhert; Kikuchi, Akira; Taketsugu, Tetsuya; Inabe, Tamotsu
Citation	Journal of Chemistry, 2013, 486318 https://doi.org/10.1155/2013/486318
Issue Date	2013
Doc URL	http://hdl.handle.net/2115/51038
Rights(URL)	http://creativecommons.org/licenses/by/3.0/
Туре	article
File Information	JoC2013_486318.pdf



Hindawi Publishing Corporation Journal of Chemistry Volume 2013, Article ID 486318, 6 pages http://dx.doi.org/10.1155/2013/486318

Research Article

Crystal Structure of Ruthenium Phthalocyanine with Diaxial Monoatomic Ligand: Bis(Triphenylphosphine)Iminium Dichloro(Phthalocyaninato(2-))Ruthenium(III)

Derrick Ethelbhert Yu, Akira Kikuchi, Tetsuya Taketsugu, and Tamotsu Inabe

Correspondence should be addressed to Derrick Ethelbhert Yu; derrick.yu@dlsu.edu.ph

Received 27 June 2012; Accepted 6 September 2012

Academic Editor: Mitsushiro Nomura

Copyright © 2013 Derrick Ethelbhert Yu et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Axially-ligated iron phthalocyanines have been found to be good molecular conductors with giant negative magnetoresistance (GNMR) which originates from a strong intramolecular π -d interaction between the metal and phthalocyanine. Ab initio theoretical calculations showed that substitution of ruthenium into the phthalocyanine complex would result in a significant increase in the π -d interaction of the system, potentially intensifying GNMR. This paper presents the crystal preparation and X-ray structural characterization of bis(triphenylphosphine)iminium dichloro(phthalocyaninato(2-))ruthenium(III), PNP [Ru^{III}(Pc²⁻)Cl₂]. It is observed that [Ru^{III}(Pc²⁻)Cl₂] system has a symmetric planar RuPc unit with perpendicular axial ligands which results in a unidirectional and uniform solid-state arrangement, suitable for π -d interaction-based molecular conductors with potentially exceptional GNMR.

1. Introduction

Metallophthalocyanine complexes with mono- or diatomic linear diaxial ligands (Scheme 1) are suitable molecular conductors due to their ability to form a slip-stacked solid-state arrangement that permits intermolecular π - π overlap for electron conduction [1, 2]. Moreover, the existence of strong intramolecular π -d interaction in axially ligated iron(III) phthalocyanine (Fe^{III}(Pc)L₂; where L = CN, Cl, Br) molecular conductors has resulted in anisotropic giant negative magnetoresistance (GNMR) of up to 95% decrease in electrical resistance at 15 Tesla [3].

Ab initio theoretical calculations using MOLPRO software package [4] performed on the D_{4h} Fe^{III}(Pc)L₂ system corroborated experimental observation that the strength of GNMR is directly related to the strength of π -d interaction in the order of L = CN > Cl > Br. On the electronic structure representation of [Fe^{III}(Pc)L₂] species, the Fe³⁺d⁵ configuration gives two-fold degenerate $(d_{xy})^2(d_{xz})^2(d_{yz})^1 = (d_{xy})^2(d_{xz})^1(d_{yz})^2$ while the HOMO is a singly occupied

molecular orbital of the delocalized π -system of the Pc. Electronic structure calculations using two state-averaged complete active space multiconfigurational SCF method (active space orbitals: Pc- π , Fe- d_{xz} and d_{yz} ; Stuttgart-Köln ECP + DZ basis) resulted in ΔE (orbital energy difference between d_{yz}/d_{xz} and HOMO; intensity of the π -d interaction) of 8.5450 eV, 8.3839 eV, and 7.8655 eV for L = Br, Cl, and CN, respectively. Using the same theoretical calculation framework to Ru^{III}(Pc)L₂, which is electronically isostructural with the Fe^{III}(Pc)L₂ species, the d^5 homologue system resulted in a remarkable increase of around two-fold in the π -d interactions across all Ru^{III} (Pc)L₂ species (L: CN = 3.7518 eV, Cl = 3.8419 eV, Br = 3.9411 eV). Given that the intensity of the unique intramolecular π -d interaction as the origin of the varying anisotropic GNMR in M^{III}(Pc)L₂, thus the importance of the synthesis of ruthenium(III) phthalocyanine with linear axial ligands.

The synthesis of crystalline ruthenium phthalocyanine Ru(Pc) complexes has long been a challenge in phthalocyanine chemistry. Even upon the report of pure Ru(Pc)

¹ Department of Chemistry, College of Science, De La Salle University, 2401 Taft Avenue, Manila 1004, Philippines

² Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Table 1: Crystallographic data collection parameters of $PNP[Ru^{III}(Pc)Cl_2]$ at 123 K.

$C_{68}H_{46}N_9Cl_2P_2Ru_1$
1223.10
Triclinic
a = 10.4425(11)Å
b = 12.2391(11)Å
c = 13.159 (11)Å
$\alpha = 75.523(3)^{\circ}$
$\beta = 64.686(3)^{\circ}$
$\gamma = 65.883(3)^{\circ}$
$V = 1381.9(2)\text{Å}^3$
$P\overline{1}$ (#2)
1
1.470g/cm^3
4.92 cm^{-1}
49.0°
10394/4588
[R(int) = 0.1173]
0.0803
0.2345
1.105

synthesis more than three decades ago, the ambiguities of its solid-state/materials science still remain as only very few crystal structures of 6-coordinated axially ligated Ru(Pc) complexes have been reported [5, 6]. However, these Ru(Pc) complexes have bulky and/or unsymmetrical axial ligands unsuitable for structure-property correlation studies. To date, only one axially-ligated magnetic Ru $^{3+}(d^5)$ -centered Pc crystal has been reported. Yet, this reported Ru $^{III}(Pc)L_2$ crystal has unsymmetrical mixed axial cyano and pyridine ligands from an attempted identical di-axial ligation synthesis [7]. Herein, we report the crystal structure of ruthenium(III) phthalocyanine with identical di-axial linear ligands which can form symmetrical octahedral architecture that could be a potential component for magnetotransport material application.

2. Methodology

2.1. Crystallization. Dichloro(phthalocyaninato(1-)) ruthenium(III), $Ru^{III}(Pc^{1-})Cl_2$, was prepared via the method reported by Myers et al. in preparing various $M^{III}(Pc^{1-})Cl_2$ through the reaction of $M^{II}(Pc)$ with thionyl chloride oxidizing agent [8]. $Ru^{II}Pc$ (500 mg; 0.81 mmol) synthesized using the procedure of Farrell et al. [9], was suspended in nitrobenzene (10 mL). Thionyl chloride (2 mL; 28 mmol) was subsequently added to the reaction vessel and refluxed at $70^{\circ}C$ for 3 hours. A 1:10 mole ratio of $Ru^{III}(Pc^{1-})Cl_2$ and bis(triphenylphosphine) iminium chloride (PNPCl) was dissolved in a 1:1:1:1 (volume) dimethylformamide: acetone: ethanol: hexane solvent system. The resulting solution

Table 2: Intramolecular bond lengths (Å) of PNP[Ru^{III}(Pc)Cl₂].

TABLE 2: Intramolecular bond lengths (A) of PNP[Ru	(PC)Cl ₂].
Atom	Distance
Ru1-N3	1.982(9)
Ru1-N1	1.993(8)
P1-N5	1.552(3)
P1-C23	1.796(10)
N2-C8	1.335(12)
N3-C16	1.395(12)
N5-P1	1.552(3)
C2-C3	1.380(13)
C3-H3	0.9300
C5-C6	1.396(14)
C6-H6	0.9300
C10-C11	1.383(14)
C11-H11	0.9300
C13-C14	1.384(15)
C14-H14	0.9300
C17-C18	1.402(16)
C19-C20	1.353(19)
C20-H20	0.9300
C22-H22	0.9300
C24-C25	1.371(15)
C25-H25	0.9300
C27-C28	1.359(15)
C29-C30	1.375(13)
C30-H30	0.9300
C32-C33	1.354(14)
C33-H33	0.9300
Ru1-N3	1.982(9)
Ru1-Cl1	2.355(3)
P1-C17	1.767(12)
N1-C1	1.363(12)
N2-C9	1.349(12)
N4-C1	1.329(12)
C1-N4	1.329(12)
C2-C7	1.424(13)
C4-C5	1.373(15)
C5-H5	0.9300
C7-C8	1.463(13)
C10-C15	1.417(14)
C12-C13	1.406(15)
C13-H13	0.9300
C15-C16	1.449(14)
C18-C19	1.421(18)
C19-H19	0.9300
C21-C22	1.389(18)
C23-C28	1.382(13)
C24-H24	0.9300
C26-C27	1.391(16)
C27-H27	0.9300
C29-C34	1.403(14)
C31-C32	1.390(16)
C32-H32	0.9300

Table 2: Continued.

TABLE 3: Intramolecular bond angles (°) of PNP[Ru^{III}(Pc)Cl₂].

TABLE 2. C	Johnnaca.
Atom	Distance
C34-H34	0.9300
Ru1-N1	1.993(8)
Ru1-Cl1	2.355(3)
P1-C29	1.789(10)
N1-C8	1.392(12)
N3-C9	1.365(13)
N4-C16	1.337(12)
C1-C2	1.463(13)
C3-C4	1.379(14)
C4-H4	0.9300
C6-C7	1.373(13)
C9-C10	1.481(13)
C11-C12	1.376(14)
C12-H12	0.9300
C14-C15	1.362(13)
C17-C22	1.384(16)
C18-H18	0.9300
C20-C21	1.34(2)
C21-H21	0.9300
C23-C24	1.386(14)
C25-C26	1.404(16)
C26-H26	0.9300
C28-H28	0.9300
C30-C31	1.398(15)
C31-H31	0.9300
C33-C34	1.361(15)

was then left in an evacuated dessicator compartment at 25°C. Bis(triphenylphosphine)iminium dichloro(phthalocyaninato(2-)) ruthenium(III), PNP[Ru^{III}(Pc²⁻)Cl₂], crystallized into dark blue crystals after 8 weeks.

2.2. X-Ray Crystal Structure Determination. A blue block crystal of PNP [Ru^{III}(Pc²⁻)Cl₂] (Formula: C₆₈H₄₆N₉Cl₂ RuP_2) having approximate dimensions of 0.15 \times 0.10 \times 0.05 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation. Indexing was performed from 3 oscillations that were exposed for 90 seconds. The crystal-to-detector distance was 127.40 mm. The data were collected at a temperature of 123 K to a maximum 2θ value of 49.0° . A total of 44 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° step, at $\chi = 45.0^{\circ}$ and $\phi = 0.0^{\circ}$. The exposure rate was 150.0 [sec/ $^{\circ}$]. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° step, at $\chi = 45.0^{\circ}$ and $\phi = 180.0^{\circ}$. The exposure rate was 150.0 [sec/°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. All post measurement data processing was performed using the CrystalStructure crystallographic software package [10].

N3 Ru1 N3 N3 Ru1 N1 N3 Ru1 Cl1 N3 Ru1 Cl1 N1 Ru1 Cl1 N1 Ru1 Cl1 N5 P1 C17 N1 Ru3 Cl N1 C8 C8 N2 C9 122.7(8) C3 C2 C7 120.0(9) C4 C3 C2 117.9(10) C6 C5 C7 C6 C5 117.3(10) C6 C7 C2 N2 C2 N1 C1 C1 C1 C11 C12 C13 C11 C12 C13 C11 C10 C15 C14 C13 C1 C15 C10 N1 C2 C15 C14 C13 C17 C18 C17 C18 C19 C19 C19 C19 C19 C19 C10 C11 C10	Atom	Angle
N3 Ru1 N1 90.3(3) N3 Ru1 Cl1 90.4(2) N1 Ru1 Cl1 91.6(2) N1 Ru1 Cl1 91.6(2) N5 P1 C17 110.3(4) N5 P1 C23 111.2(3) Cl N1 C8 109.8(8) C8 N2 C9 122.7(8) Cl6 N3 Ru1 125.7(6) N4 Cl N1 128.8(9) C3 C2 C7 120.0(9) C4 C3 C2 117.9(10) C5 C4 C3 122.2(10) C7 C6 C5 121.2(10) C7 C6 C5 121.2(10) C7 C6 C5 121.2(10) C8 C7 C2 121.4(9) N2 C8 N1 127.7(9) N2 C8 N1 127.7(9) N2 C8 N1 127.7(9) C12 C11 C10 117.3(10) C11 C12 C13 122.0(10) C14 C13 C12 120.0(10) C15 C14 C13 122.0(10) C14 C15 C10 121.1(10) C15 C14 C13 122.0(10) C15 C14 C15 C10 121.1(10) C17 C18 C19 129.0(10) C19 C19 C18 118.3(12) C10 C10 C15 120.0(10) C20 C19 C18 119.0(13) C22 C17 C18 119.0(14) C21 C22 C21 121.6(11) C22 C21 C22 119.0(14) C25 C24 C23 121.6(11) C26 C27 C26 C25 119.0(14) C27 C26 C25 119.0(14) C27 C26 C25 119.0(14) C27 C26 C25 119.0(11) C28 C27 C26 C25 119.2(11) C29 C30 C31 118.8(11) C32 C31 C30 120.4(10) C33 C34 C29 119.7(10) N3 Ru1 N1 89.7(3) N3 Ru1 C1 89.6(2) N3 Ru1 C1 89.6(2) N1 Ru1 C1 N1 89.6(2) N1 Ru1 C1 N1 Ru1 C1 Ru1 Ru	N3 Ru1 N3	
N3 Ru1 Cl1 N1 SP 1 C17 N1 Ru1 Cl3 Cl N1 C8 N5 P1 C23 N1 Ru1 Cl N1 C8 N6 N2 C9 N6 N3 Ru1 N6 C8 N2 C9 N6 C16 N3 Ru1 N6 C3 C2 N6 C7 C2 N6 C6 C5 N6 C7 C2 N7 C8 N1 N7 C9 N3 N8 C9 N2 C9 N8 C9 N2 C9 N9 C10 C15 N1 C17 N1 C18 N4 C1 N1 N1 C28 N2 C9 N2 C8 N1 N2 C9 N2 C8 N1 N2 C9 N3 N3 N3 N1 N3 Ru1 N3 Ru1 N1 N3 Ru1 N1 N1 N3 Ru1 N1 N1 N9 N6(2) N1 Ru1 C11 N9 N6(2) N1 Ru1 Cl1 N9 N6(2	N3 Ru1 N1	
N1 Ru1 Cl1 N5 P1 C23 111.2(3) C1 N1 C8 109.8(8) C68 N2 C9 122.7(8) C16 N3 Ru1 125.7(6) N4 C1 N1 128.8(9) C3 C2 C7 120.0(9) C4 C3 C2 117.9(10) C5 C4 C3 C3 C7 C6 C5 117.3(10) C6 C7 C6 C7 C6 C5 121.2(10) C7 C6 C5 121.4(9) N2 C9 N3 128.3(9) C11 C10 C15 120.9(9) C12 C11 C10 C11 C12 C13 C14 C13 C12 120.0(10) C14 C15 C10 C17 C18 C17 C2 C19 C19 C20 C21 C22 119.0(14) C20 C20 C21 C22 119.0(14) C20 C20 C21 C22 119.0(14) C22 C27 C26 C25 119.0(14) C23 C33 C34 118.8(10) C24 C25 C26 118.8(11) C25 C26 C25 119.9(11) C32 C33 C34 119.9(10) C33 C32 C31 C30 C39 C34 119.9(10) C33 C31 C31 C33 C31 C34 C29 119.7(10) N3 Ru1 N1 N3 Ru1 N1 N3 Ru1 Cl1 N3 Ru1 Cl1 N5 P1 C29 110.5(3)	N3 Ru1 Cl1	
N1 Ru1 Cl1 N5 P1 C17 N1 10.3(4) N5 P1 C23 111.2(3) C1 N1 C8 109.8(8) C8 N2 C9 122.7(8) C16 N3 Ru1 125.7(6) N4 Cl N1 128.8(9) C3 C2 C7 120.0(9) C4 C3 C2 117.9(10) C5 C4 C3 122.2(10) C7 C6 C5 117.3(10) C7 C6 C5 117.3(10) C7 C6 C5 117.3(10) C10 C15 C12 C11 C10 C11 C12 C13 C14 C13 C12 C15 C14 C13 C14 C15 C10 C15 C14 C13 C14 C15 C10 C15 C16 C19 C17 C18 C17 C18 C17 C18 C17 C18 C17 C18 C19 C19 C19 C20 C21 C22 C17 C18 C17 C20 C20 C21 C22 C17 C18 C17 C20 C20 C21 C22 C17 C18 C17 C20 C19 C20 C21 C22 C17 C18 C17 C20 C19 C20 C21 C22 C17 C18 C18 C19 C20 C21 C22 C19 C20 C20 C20 C20 C21 C22 C19 C20 C20 C20 C20 C21 C22 C19 C10 C20 C21 C22 C20	N1 Ru1 Cl1	
N5 P1 C17 N5 P1 C23 111.2(3) C1 N1 C8 109.8(8) C8 N2 C9 122.7(8) C16 N3 Ru1 125.7(6) N4 C1 N1 128.8(9) C3 C2 C7 120.0(9) C4 C3 C2 C5 C4 C3 C6 C5 C7 C6 C5 117.3(10) C6 C7 C2 121.4(9) N2 C8 N1 127.7(9) N2 C8 N1 127.7(9) C11 C10 C15 C12 C11 C10 C11 C12 C13 C14 C13 C12 C15 C14 C13 C14 C15 C10 N4 C16 N3 122.0(10) C17 C2 C2 C1 C17 C18 C17 C18 C19 C19 C19 C18 C17 C22 C21 C17 C22 C19 C19 C22 C17 C22 C19 C22 C17 C22 C19 C22 C19 C23 C20 C21 C22 C19 C21 C21 C21 C22 C21 C22 C21 C23 C22 C23 C24 C24 C25 C26 C25 C24 C25 C26 C27 C26 C25 C27 C26 C25 C28 C27 C26 C29 C30 C31 C33 C31 C34 C19 C32 C31 C30 C33 C32 C31 C34 C19 C35 C34 C29 C35 C34 C36 C39 C34 C47 C37 C38 C37 C38 C31 C39 C30 C31 C39 C31 C30 C39 C34 C29 C30 C31 C30 C30 C30 C30 C39 C34 C40 C30 C30 C30 C30 C31 C30 C31 C30 C31 C31 C31 C32 C31 C30 C33 C32 C31 C34 C29 C35 C34 C37 C38 C37 C38 C37 C39 C30 C39 C30 C31 C30	N1 Ru1 Cl1	
111.2(3) C1 N1 C8 C1 N1 C8 C8 N2 C9 122.7(8) C16 N3 Ru1 125.7(6) N4 C1 N1 128.8(9) C3 C2 C7 120.0(9) C4 C3 C2 117.9(10) C5 C4 C3 122.2(10) C7 C6 C5 117.3(10) C7 C6 C5 117.3(10) C7 C9 N3 128.3(9) C11 C10 C15 120.9(9) C12 C11 C10 C11 C12 C13 C14 C13 C12 C14 C13 C12 C14 C13 C12 C15 C14 C13 C14 C15 C10 C15 C14 C13 C12 C17 C18 C19 C19 C18 C19 C19 C18 C19 C20 C21 C20 C2	N5 P1 C17	
C1 N1 C8 C8 N2 C9 122.7(8) C16 N3 Ru1 125.7(6) N4 C1 N1 128.8(9) C3 C2 C7 120.0(9) C4 C3 C2 117.9(10) C5 C4 C3 122.2(10) C6 C5 C4 C3 121.2(10) C7 C6 C5 117.3(10) C6 C7 C2 121.4(9) N2 C8 N1 127.7(9) N2 C9 N3 128.3(9) C11 C10 C15 120.9(9) C12 C11 C10 C11 C12 C13 C14 C13 C12 C15 C14 C13 C14 C15 C10 N4 C16 N3 C22 C17 C18 C19 C19 C18 C19 C19 C18 C19 C20 C19 C20 C21 C22 119.0(14) C20 C21 C22 119.0(14) C21 C22 C21 C22 C27 C26 C23 C24 C23 C24 C25 C24 C23 C25 C24 C23 C25 C24 C23 C27 C26 C25 119.2(11) C28 C27 C26 C29 C30 C31 C30 C30 C31 C30 C30 C31 C30 C31 C31 C31 C31 C32 C33 C34 C29 C31 C31 C33 C34 C29 119.7(10) N3 Ru1 N1 S9.7(3) N3 Ru1 C11 S9.6(2) N3 Ru1 C11 S9.6(2) N1 Ru1 C11 N1 Ru1 C11 S9.6(2) N1	N5 P1 C23	
C8 N2 C9 122.7(8) C16 N3 Ru1 125.7(6) N4 C1 N1 128.8(9) C3 C2 C7 120.0(9) C4 C3 C2 117.9(10) C5 C4 C3 122.2(10) C4 C5 C6 121.2(11) C7 C6 C5 117.3(10) C6 C7 C2 121.4(9) N2 C8 N1 127.7(9) N2 C9 N3 128.3(9) C11 C10 C15 120.9(9) C12 C11 C10 117.3(10) C11 C12 C13 122.0(10) C14 C13 C12 120.2(10) C15 C14 C13 118.5(10) C14 C15 C10 121.1(10) N4 C16 N3 126.1(9) C22 C17 C18 118.3(12) C17 C18 C19 119.0(13) C20 C19 C18 119.0(14) C21 C20 C19 122.7(16) C22 C21 C22 119.0(14) C17 C22 C21 121.6(13) C28 C23 C24 118.8(10) C25 C24 C23 121.6(11) C27 C26 C25 119.2(11) C28 C27 C26 120.7(11) C29 C30 C31 118.9(10) <t< td=""><td>C1 N1 C8</td><td></td></t<>	C1 N1 C8	
C16 N3 Ru1 N4 C1 N1 128.8(9) C3 C2 C7 120.0(9) C4 C3 C2 117.9(10) C5 C4 C3 122.2(10) C4 C5 C6 121.2(10) C7 C6 C5 117.3(10) C6 C7 C2 121.4(9) N2 C8 N1 127.7(9) N2 C9 N3 128.3(9) C11 C10 C15 120.9(9) C12 C11 C10 117.3(10) C11 C12 C13 122.0(10) C14 C13 C12 120.2(10) C15 C14 C13 118.5(10) C14 C15 C10 N4 C16 N3 126.1(9) C22 C17 C18 118.3(12) C17 C18 C19 C19 C18 C19 C19 C18 C19 C19 C18 C19 C20 C21 C22 119.0(14) C17 C22 C21 121.6(13) C28 C23 C24 118.8(10) C25 C24 C23 121.6(11) C26 C27 C26 118.8(11) C27 C26 C25 119.0(14) C29 C30 C31 118.9(11) C32 C33 C34 119.9(10) C33 C34 C29 119.0(10) C33 C31 C30 C34 C29 C34 119.9(10) C35 C31 C30 C30 C32 C31 119.4(10) C32 C33 C34 119.9(10) C33 C34 C29 119.7(10) N3 Ru1 N1 89.7(3) N3 Ru1 C11 89.6(2) N1 Ru1 C11 88.4(2) N5 P1 C29 110.5(3)	C8 N2 C9	
N4 C1 N1 C3 C2 C7 120.0(9) C4 C3 C2 117.9(10) C5 C4 C3 122.2(10) C4 C5 C6 121.2(10) C7 C6 C5 117.3(10) C6 C7 C2 121.4(9) N2 C8 N1 127.7(9) N2 C9 N3 128.3(9) C11 C10 C15 120.9(9) C12 C11 C10 C11 C12 C13 C11 C12 C13 C14 C13 C12 C15 C14 C13 C14 C15 C10 N4 C16 N3 C22 C17 C18 118.3(12) C17 C18 C19 C19 C19 C18 C19 C20 C21 C22 119.0(14) C17 C22 C21 121.6(13) C28 C23 C24 118.8(10) C25 C24 C23 121.6(11) C26 C25 119.2(11) C27 C26 C25 119.2(11) C28 C27 C26 C29 C30 C31 C33 C34 C29 N3 Ru1 N1 89.7(3) N3 Ru1 N1 89.7(3) N3 Ru1 C11 88.4(2) N5 P1 C29 110.5(3)	C16 N3 Ru1	
C3 C2 C7 C4 C3 C2 C4 C3 C2 C5 C4 C3 C5 C4 C3 C6 C5 C7 C6 C5 C7 C6 C5 C8 N1 C9 C9 N3 C11 C10 C15 C12 C11 C10 C11 C12 C13 C14 C13 C12 C15 C14 C13 C14 C15 C10 C15 C14 C13 C12 C10 C15 C14 C13 C12 C10 C15 C14 C13 C14 C15 C10 C15 C14 C13 C16 C15 C17 C18 C19 C17 C18 C19 C19 C19 C18 C19 C20 C21 C22 C19 C18 C19 C20 C21 C22 C19 C18 C20 C20 C21 C22 C20 C21 C22 C20 C21 C22 C20 C20 C21 C21 C22 C20 C20 C21 C22 C21 C23 C24 C25 C26 C26 C25 C27 C26 C27 C26 C29 C30 C31 C32 C33 C34 C32 C37 C36 C33 C32 C31 C32 C33 C34 C33 C34 C29 C33 C34 C39 C30 C31 C30 C30 C30 C30 C30 C31 C30 C30 C30 C	N4 C1 N1	
C5 C4 C3 122.2(10) C4 C5 C6 121.2(10) C7 C6 C5 117.3(10) C6 C7 C2 121.4(9) N2 C8 N1 127.7(9) N2 C9 N3 128.3(9) C11 C10 C15 120.9(9) C12 C11 C10 117.3(10) C11 C12 C13 122.0(10) C14 C13 C12 120.2(10) C15 C14 C13 118.5(10) C14 C15 C10 121.1(10) N4 C16 N3 126.1(9) C22 C17 C18 118.3(12) C17 C18 C19 119.0(13) C20 C19 C18 119.4(14) C21 C2 C2 C1 122.7(16) C20 C2 C2 C2 119.0(14) C17 C2 C2 C2 119.0(14) C17 C2 C2 C2 119.0(14) C17 C2 C2 C2 119.0(14) C25 C24 C23 121.6(11) C25 C24 C23 121.6(11) C25 C24 C23 120.7(11) C25 C26 C25 119.2(11) C27 C26 C25 120.7(11) C29 C30 C31 118.9(11) C32 C33 C34 121.6(11) C33 C34 C29 119.7(10) <	C3 C2 C7	
C5 C4 C3 122.2(10) C4 C5 C6 121.2(10) C7 C6 C5 117.3(10) C6 C7 C2 121.4(9) N2 C8 N1 127.7(9) N2 C9 N3 128.3(9) C11 C10 C15 120.9(9) C12 C11 C10 117.3(10) C11 C12 C13 122.0(10) C14 C13 C12 120.2(10) C15 C14 C13 118.5(10) C14 C15 C10 121.1(10) N4 C16 N3 126.1(9) C22 C17 C18 118.3(12) C17 C18 C19 119.0(13) C20 C19 C18 119.4(14) C21 C2 C2 C1 122.7(16) C20 C2 C2 C2 119.0(14) C17 C2 C2 C2 119.0(14) C17 C2 C2 C2 119.0(14) C17 C2 C2 C2 119.0(14) C25 C24 C23 121.6(11) C25 C24 C23 121.6(11) C25 C24 C23 120.7(11) C25 C26 C25 119.2(11) C27 C26 C25 120.7(11) C29 C30 C31 118.9(11) C32 C33 C34 121.6(11) C33 C34 C29 119.7(10) <	C4 C3 C2	
C4 C5 C6 121.2(10) C7 C6 C5 117.3(10) C6 C7 C2 121.4(9) N2 C8 N1 127.7(9) N2 C9 N3 128.3(9) C11 C10 C15 120.9(9) C12 C11 C10 117.3(10) C11 C12 C13 122.0(10) C14 C13 C12 120.2(10) C15 C14 C13 118.5(10) C14 C15 C10 121.1(10) N4 C16 N3 126.1(9) C22 C17 C18 118.3(12) C17 C18 C19 119.0(13) C20 C19 C18 119.4(14) C21 C20 C19 122.7(16) C20 C21 C22 119.0(14) C17 C22 C21 121.6(13) C28 C23 C24 118.8(10) C25 C24 C23 121.6(11) C25 C24 C23 121.6(11) C27 C26 C25 119.2(11) C28 C27 C26 120.7(11) C29 C30 C31 118.9(11) C32 C31 C30 120.4(10) C33 C34 C29 119.7(10) N3 Ru1 N1 89.7(3) N3 Ru1 C1 89.6(2) N1 Ru1 C1 88.4(2)	C5 C4 C3	
C7 C6 C5 C6 C7 C2 C6 C7 C2 C8 N1 C6 C7 C2 C8 N1 C7 C9 N3 C8 N1 C8 C9 N3 C8 C9 N3 C8 C11 C10 C15 C9 C9 C12 C11 C10 C11 C12 C13 C14 C13 C12 C15 C14 C13 C14 C15 C10 C15 C14 C15 C16 C17 C18 C17 C18 C19 C19 C19 C18 C19 C20 C21 C20 C21 C20 C21 C20 C21 C20 C21 C20 C20 C21 C22 C15 C24 C23 C24 C23 C24 C25 C26 C25 C26 C27 C26 C27 C26 C27 C28 C27 C28 C23 C29 C30 C31 C30 C30 C30 C31 C30 C30 C31 C30	C4 C5 C6	
N2 C8 N1 N2 C9 N3 C11 C10 C15 C12 C11 C10 C11 C12 C13 C14 C13 C12 C15 C14 C13 C14 C15 C10 N4 C16 N3 C22 C17 C18 C17 C18 C19 C20 C19 C18 C19 C20 C21 C20 C21 C20 C21 C20 C21 C20 C22 C11 C10 C20 C21 C22 C20 C20 C20 C20	C7 C6 C5	
N2 C9 N3 C11 C10 C15 C12 C11 C10 C11 C12 C13 C14 C13 C12 C15 C14 C13 C14 C15 C10 N4 C15 C10 N4 C16 N3 C22 C17 C18 C19 C20 C19 C20 C19 C18 C21 C20 C19 C20 C19 C20 C21 C22 C17 C22 C21 C17 C22 C21 C17 C22 C21 C25 C24 C23 C24 C25 C26 C25 C26 C27 C26 C25 C27 C26 C25 C27 C27 C28 C27 C28 C27 C28 C27 C29 C30 C30 C29 C34 C29 C30 C31 C32 C31 C30 C32 C33 C34 C32 C31 C33 C34 C29 N3 Ru1 N1 N3 Ru1 N1 N3 Ru1 N1 N3 Ru1 N1 N3 Ru1 Cl1 N3 Ru1 Cl1 N5 P1 C29 N10.5(3)	C6 C7 C2	
N2 C9 N3 128.3(9) C11 C10 C15 120.9(9) C12 C11 C10 117.3(10) C11 C12 C13 122.0(10) C14 C13 C12 120.2(10) C15 C14 C13 118.5(10) C14 C15 C10 121.1(10) N4 C16 N3 126.1(9) C22 C17 C18 118.3(12) C17 C18 C19 119.0(13) C20 C19 C18 119.4(14) C21 C20 C19 122.7(16) C20 C21 C22 119.0(14) C17 C22 C21 121.6(13) C28 C23 C24 118.8(10) C25 C24 C23 121.6(11) C24 C25 C26 118.8(11) C27 C26 C25 119.2(11) C28 C27 C26 120.7(11) C29 C30 C31 118.9(11) C32 C31 C30 120.4(10) C33 C32 C31 119.4(10) C32 C33 C34 121.6(11) C32 C33 C34 121.6(11) C32 C33 C34 120.4(10) C33 C34 C29 119.7(10) N3 Ru1 N1 89.7(3) N3 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 88.4(2)	N2 C8 N1	127.7(9)
C12 C11 C10 C11 C12 C13 C14 C13 C12 C15 C14 C13 C15 C14 C13 C14 C15 C10 N4 C16 N3 C22 C17 C18 C17 C18 C19 C19 C19 C18 C20 C19 C18 C21 C20 C19 C20 C21 C22 C19 C21 C20 C21 C22 C19 C21 C25 C24 C23 C24 C25 C26 C25 C26 C27 C26 C25 C27 C26 C25 C27 C26 C25 C27 C28 C23 C29 C30 C31 C30 C29 C34 C29 C30 C31 C30 C32 C31 C32 C33 C34 C29 C30 C31 C33 C34 C29 N3 Rul N1 N3 Rul Cl1 N3 Rul Cl1 N3 Rul Cl1 N5 P1 C29 N5 P1 C29 N5 P1 C29 N10, C(10) S1 10, C(10) S1 11, S(10) S2 C(10) S2 (10) S2 (10) S3 (10) S4 (20) S6 (20) S6 (20) S7 (30) S8 (20) S8 (2	N2 C9 N3	
C11 C12 C13 C14 C13 C12 C15 C14 C13 C14 C15 C10 N4 C15 C10 N4 C16 N3 C22 C17 C18 C17 C18 C19 C19 C19 C18 C20 C19 C18 C21 C20 C19 C20 C21 C22 C17 C22 C11 C28 C23 C24 C25 C24 C23 C27 C26 C27 C26 C25 C27 C26 C27 C26 C27 C28 C27 C28 C27 C26 C27 C28 C28 C27 C29 C29 C30 C31 C29 C30 C31 C30 C32 C31 C32 C31 C30 C33 C32 C31 C33 C34 C29 C30 C31 C33 C34 C29 C33 C34 C33 C34 C34 C35 C35 C37 C36 C37 C37 C38 C37 C38 C37 C39 C31 C39 C30 C31 C30 C30 C30 C30 C30 C31 C30 C30 C30 C30 C30 C30 C30 C30 C31 C30 C30 C31 C30 C30 C30 C30 C30 C31 C30 C30 C30 C30 C30 C31 C30 C30 C31 C30 C30 C30 C	C11 C10 C15	120.9(9)
C14 C13 C12 C15 C14 C13 C14 C15 C10 C14 C15 C10 C14 C16 N3 C22 C17 C18 C17 C18 C19 C19 C19 C19 C20 C19 C18 C19 C20 C21 C20 C20 C21 C20	C12 C11 C10	117.3(10)
C15 C14 C13 C14 C15 C10 C14 C15 C10 C14 C15 C10 C14 C15 C10 C22 C17 C18 C22 C17 C18 C19 C20 C19 C18 C21 C20 C19 C20 C21 C22 C17 C22 C21 C20 C21 C22 C21 C23 C24 C25 C24 C25 C26 C25 C27 C26 C27 C26 C27 C28 C29	C11 C12 C13	122.0(10)
C14 C15 C10 121.1(10) N4 C16 N3 126.1(9) C22 C17 C18 118.3(12) C17 C18 C19 119.0(13) C20 C19 C18 119.4(14) C21 C20 C19 122.7(16) C20 C21 C22 119.0(14) C17 C22 C21 121.6(13) C28 C23 C24 118.8(10) C25 C24 C23 121.6(11) C24 C25 C26 118.8(11) C27 C26 C25 119.2(11) C28 C27 C26 120.7(11) C29 C30 C31 120.8(10) C30 C29 C34 119.9(10) C32 C31 C30 120.4(10) C32 C33 C34 121.6(11) C32 C33 C34 121.6(11) C33 C34 C29 119.7(10) N3 Ru1 N1 89.7(3) N3 Ru1 N1 89.7(3) N3 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 88.4(2) N5 P1 C29 110.5(3)	C14 C13 C12	120.2(10)
N4 C16 N3 126.1(9) C22 C17 C18 118.3(12) C17 C18 C19 119.0(13) C20 C19 C18 119.4(14) C21 C20 C19 122.7(16) C20 C21 C22 119.0(14) C17 C22 C21 121.6(13) C28 C23 C24 118.8(10) C25 C24 C23 121.6(11) C24 C25 C26 118.8(11) C27 C26 C25 119.2(11) C27 C28 C23 120.7(11) C29 C30 C31 119.9(10) C30 C29 C34 119.9(10) C32 C31 C30 120.4(10) C33 C32 C31 119.4(10) C32 C33 C34 121.6(11) C33 C34 C29 119.7(10) N3 Ru1 N1 89.7(3) N3 Ru1 Cl1 89.6(2) N3 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 88.4(2) N5 P1 C29 110.5(3)	C15 C14 C13	118.5(10)
C22 C17 C18 C17 C18 C19 C17 C18 C19 C20 C19 C18 C21 C20 C19 C22 C21 C22 C19 C18 C17 C22 C21 C23 C24 C25 C24 C23 C24 C25 C26 C27 C26 C25 C27 C26 C25 C27 C26 C25 C27 C28 C23 C29 C29 C20 C2	C14 C15 C10	121.1(10)
C17 C18 C19 C20 C19 C18 C20 C19 C18 C21 C20 C19 C20 C21 C22 C21 C22 C21 C28 C23 C24 C25 C24 C23 C24 C25 C26 C27 C26 C25 C27 C28 C25 C28 C27 C26 C29 C21 C29 C21 C29 C21 C29 C21 C29 C21 C29 C20 C20 C21 C20	N4 C16 N3	126.1(9)
C20 C19 C18 119.4(14) C21 C20 C19 122.7(16) C20 C21 C22 119.0(14) C17 C22 C21 121.6(13) C28 C23 C24 118.8(10) C25 C24 C23 121.6(11) C24 C25 C26 118.8(11) C27 C26 C25 119.2(11) C27 C28 C23 120.7(11) C27 C28 C23 120.8(10) C30 C29 C34 119.9(10) C32 C31 C30 120.4(10) C32 C31 C30 120.4(10) C32 C33 C34 121.6(11) C33 C32 C31 119.7(10) N3 Ru1 N1 89.7(3) N3 Ru1 N1 89.7(3) N3 Ru1 Cl1 89.6(2) N3 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 88.4(2) N5 P1 C29 110.5(3)	C22 C17 C18	118.3(12)
C21 C20 C19 C20 C21 C22 C17 C22 C21 C19 C17 C22 C21 C18.8(10) C28 C23 C24 C25 C24 C23 C24 C25 C26 C27 C26 C25 C28 C27 C26 C27 C28 C23 C29 C30 C31 C29 C30 C31 C32 C31 C30 C32 C31 C30 C32 C31 C30 C33 C32 C31 C33 C34 C29 C34 C25 C35 C35 C37 C36 C37 C38 C39 C39 C39 C30 C31 C31 C30 C31 C30 C32 C31 C30 C33 C32 C31 C33 C34 C29 C34 C35 C31 C35 C31 C37 C37 C30 C37 C30 C38 C31 C39 C31 C30 C31 C30 C31 C31 C30 C31 C31 C30 C31 C32 C31 C30 C33 C34 C29 C33 C34 C29 C33 C34 C29 C34 C35 C31 C35 C37 C30 C37 C37 C30 C37	C17 C18 C19	119.0(13)
C20 C21 C22 C17 C22 C21 C17 C22 C21 C18.8(10) C28 C23 C24 C25 C24 C23 C24 C25 C26 C27 C26 C25 C28 C27 C26 C29 C27 C26 C29 C20 C29 C30 C31 C29 C30 C31 C32 C31 C30 C32 C31 C30 C32 C31 C30 C32 C31 C30 C33 C34 C29 C33 C34 C33 C34 C29 C35 C37 C30 C37 C30 C30 C38 C39 C30 C39 C30 C30 C39 C30	C20 C19 C18	119.4(14)
C17 C22 C21 C28 C23 C24 C25 C24 C23 C24 C25 C26 C27 C26 C25 C28 C27 C26 C27 C28 C23 C29 C34 C30 C29 C34 C30 C29 C34 C30 C31 C32 C31 C30 C32 C31 C30 C32 C31 C30 C33 C32 C31 C33 C34 C29 C33 C34 C29 C33 C34 C29 C34 C29 C35 C37 C36 C37 C38 C37 C38 C38 C38 C38 C39 C39 C39 C30 C30 C30	C21 C20 C19	122.7(16)
C28 C23 C24 118.8(10) C25 C24 C23 121.6(11) C24 C25 C26 118.8(11) C27 C26 C25 119.2(11) C28 C27 C26 120.7(11) C27 C28 C23 120.8(10) C30 C29 C34 119.9(10) C29 C30 C31 118.9(11) C32 C31 C30 120.4(10) C33 C32 C31 119.4(10) C32 C33 C34 121.6(11) C33 C34 C29 119.7(10) N3 Ru1 N1 89.7(3) N3 Ru1 Cl1 89.6(2) N3 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 88.4(2) N5 P1 C29 110.5(3)	C20 C21 C22	119.0(14)
C25 C24 C23 121.6(11) C24 C25 C26 118.8(11) C27 C26 C25 119.2(11) C28 C27 C26 120.7(11) C27 C28 C23 120.8(10) C30 C29 C34 119.9(10) C29 C30 C31 118.9(11) C32 C31 C30 120.4(10) C33 C32 C31 119.4(10) C32 C33 C34 121.6(11) C33 C34 C29 119.7(10) N3 Ru1 N1 89.7(3) N3 Ru1 Cl1 89.6(2) N3 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 88.4(2) N5 P1 C29 110.5(3)	C17 C22 C21	121.6(13)
C24 C25 C26 C27 C26 C25 C28 C27 C26 C28 C27 C26 C29 C30 C30 C29 C34 C29 C30 C31 C32 C31 C30 C33 C32 C31 C32 C33 C34 C33 C34 C29 C34 C29 C35 C31 C37 C30 C37 C30 C38 C31 C39 C31 C30 C31 C31 C31 C31 C31 C32 C33 C34 C33 C34 C29 C33 C34 C29 C34 C29 C35 C31 C37 C30 C37 C30 C38 C31 C37 C30 C38 C31 C38 C31 C39 C30 C30 C31 C30 C30 C31 C3	C28 C23 C24	118.8(10)
C27 C26 C25 C28 C27 C26 C28 C27 C26 C27 C28 C23 C30 C29 C34 C29 C30 C31 C32 C31 C30 C33 C32 C31 C32 C33 C34 C33 C34 C29 C34 C29 C35 C31 C37 C30 C37 C30 C38 C31 C39 C31 C30 C31 C31 C31 C31 C31 C31 C31 C32 C31 C33 C34 C29 C33 C34 C29 C34 C29 C35 C31 C37 C30 C37 C30 C38 C31 C38 C31 C39 C30 C30 C31 C30 C31 C31 C30 C31 C30 C31 C30 C32 C31 C33 C34 C33 C34 C33 C34 C33 C34 C33 C34 C34 C29 C35 C31 C37 C30 C	C25 C24 C23	121.6(11)
C28 C27 C26 C27 C28 C23 C30 C29 C34 C29 C30 C31 C32 C31 C30 C32 C31 C32 C31 C33 C32 C31 C33 C34 C33 C34 C33 C34 C33 C34 C39 C31 C30 C31 C30 C31 C30 C32 C31 C32 C31 C32 C31 C33 C34 C29 C33 C34 C30 C31 C31 C31 C32 C31 C32 C31 C33 C34 C29 C33 C34 C29 C40 C51 C51 C51 C52 C51 C51 C51 C51 C51 C51 C52 C51	C24 C25 C26	118.8(11)
C27 C28 C23 C30 C29 C34 C19.9(10) C29 C30 C31 C32 C31 C30 C33 C32 C31 C32 C33 C34 C33 C34 C29 C33 C31 C34 C29 C35 C31 C37 C30 C37 C30 C38 C31 C39 C31 C31 C30 C31 C30 C31 C30 C32 C33 C34 C33 C34 C29 C33 C34 C29 C33 C34 C29 C34 C29 C35 C30 C37 C30 C37 C30 C38 C31 C39 C30 C30 C31 C30 C31 C31 C31 C31 C31 C31 C31 C32 C33 C34 C33 C34 C29 C33 C34 C29 C34 C20 C35 C31 C37 C30 C	C27 C26 C25	119.2(11)
C30 C29 C34 C29 C30 C31 C29 C30 C31 C32 C31 C30 C33 C32 C31 C32 C33 C34 C33 C34 C29 C33 C31 C31 C30 C31 C30 C32 C31 C33 C34 C29 C33 C34 C29 C33 C34 C29 C34 C29 C35 C31 C37 C30 C37 C30 C38 C31 C39 C30 C30 C31 C31 C31 C31 C31 C32 C31 C33 C34 C29 C33 C34 C29 C34 C20 C35 C31 C37 C30 C3	C28 C27 C26	120.7(11)
C29 C30 C31 C32 C31 C30 C33 C32 C31 C33 C32 C31 C32 C33 C34 C33 C34 C29 C33 C34 C29 C33 C34 C29 C33 C34 C29 C33 C31 C34 C29 C35 C31 C37 C30 C37 C30 C38 C34 C29 C38 C34 C29 C39 C30 C39 C30 C31 C31 C31 C31 C31 C31 C32 C31 C33 C34 C29 C33 C34 C29 C34 C29 C35 C31 C37 C30 C3	C27 C28 C23	120.8(10)
C32 C31 C30	C30 C29 C34	119.9(10)
C33 C32 C31 119.4(10) C32 C33 C34 121.6(11) C33 C34 C29 119.7(10) N3 Ru1 N1 89.7(3) N3 Ru1 N1 89.7(3) N3 Ru1 Cl1 89.6(2) N3 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 88.4(2) N5 P1 C29 110.5(3)	C29 C30 C31	118.9(11)
C32 C33 C34 121.6(11) C33 C34 C29 119.7(10) N3 Ru1 N1 89.7(3) N3 Ru1 Cl1 89.6(2) N3 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 88.4(2) N5 P1 C29 110.5(3)	C32 C31 C30	120.4(10)
C33 C34 C29 119.7(10) N3 Ru1 N1 89.7(3) N3 Ru1 N1 89.7(3) N3 Ru1 Cl1 89.6(2) N3 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 88.4(2) N5 P1 C29 110.5(3)	C33 C32 C31	119.4(10)
N3 Ru1 N1 89.7(3) N3 Ru1 N1 89.7(3) N3 Ru1 Cl1 89.6(2) N3 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 88.4(2) N5 P1 C29 110.5(3)	C32 C33 C34	121.6(11)
N3 Ru1 N1 89.7(3) N3 Ru1 Cl1 89.6(2) N3 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 88.4(2) N5 P1 C29 110.5(3)	C33 C34 C29	119.7(10)
N3 Ru1 Cl1 89.6(2) N3 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 88.4(2) N5 P1 C29 110.5(3)	N3 Ru1 N1	89.7(3)
N3 Ru1 Cl1 89.6(2) N1 Ru1 Cl1 88.4(2) N5 P1 C29 110.5(3)	N3 Ru1 N1	89.7(3)
N1 Ru1 Cl1 88.4(2) N5 P1 C29 110.5(3)	N3 Ru1 Cl1	89.6(2)
N5 P1 C29 110.5(3)	N3 Ru1 Cl1	89.6(2)
. ,	N1 Ru1 Cl1	88.4(2)
C17 P1 C23 107.7(5)	N5 P1 C29	110.5(3)
	C17 P1 C23	107.7(5)

Table 3: Continued.

Angle

Table 3: Con	ntinued.	
Atom	Angle	Atom
C1 N1 Ru1	124.6(6)	C6 C5 I
C9 N3 C16	108.0(8)	C5 C6 I
C1 N4 C16	124.3(8)	C2 C7 C
N4 C1 C2	122.3(9)	N1 C8 C
C3 C2 C1	133.3(9)	N3 C9 (
C4 C3 H3	121.1	C15 C1
C5 C4 H4	118.9	C10 C1
C4 C5 H5	119.4	C13 C12
C7 C6 H6	121.4	C12 C1:
C6 C7 C8	132.2(9)	C13 C14
N2 C8 C7	124.0(9)	C10 C1:
N2 C9 C10	122.0(9)	N3 C16
C11 C10 C9	133.3(10)	C18 C1
C12 C11 H11	121.3	C19 C1
C11 C12 H12	119.0	C18 C1
C14 C13 H13	119.9	C19 C2
C15 C14 H14	120.7	C22 C2
C14 C15 C16	132.3(10)	C21 C2
N4 C16 C15	123.9(9)	C24 C2:
C22 C17 P1	119.1(9)	C23 C2
C17 C18 H18	120.5	C26 C2
C20 C19 H19	120.3	C25 C2
C21 C20 H20	118.7	C26 C2
C20 C21 H21	120.5	C23 C2
C17 C22 H22	119.2	C34 C2
C28 C23 P1	122.3(8)	C31 C3
C25 C24 H24	119.2	C30 C3
C24 C25 H25	120.6	C31 C3
C27 C26 H26	120.4	C34 C3:
C28 C27 H27	119.6	C29 C3
C27 C28 H28	119.6	027 03
C30 C29 P1	122.1(8)	
C29 C30 H30	120.5	3. Res
C32 C31 H31	119.8	5.10 5
C33 C32 H32	120.3	The low
C32 C33 H33	119.2	for the
C32 C33 1133 C33 C34 H34	120.2	PNP[R
N3 Ru1 N1	90.3(3)	be over
N1 Ru1 N1	179.999(1)	forman
N1 Ru1 N1 N1 Ru1 Cl1	88.4(2)	which p
N3 Ru1 Cl1	90.4(2)	In I
Cl1 Ru1 Cl1		units fo
C17 P1 C29	179.999(1) 108.2(5)	anion o
C29 P1 C23		affords
	108.8(5)	parame The cr
C8 N1 Ru1	125.4(6)	The cr
C9 N3 Ru1	126.1(7)	isostruc
P1 N5 P1	179.999(1)	which a
N1 C1 C2	108.9(8)	about b
C7 C2 C1	106.6(8)	axial ch
C2 C3 H3	121.1	tecture

C3 C4 H4

118.9

	8
C6 C5 H5	119.4
C5 C6 H6	121.4
C2 C7 C8	106.3(8)
N1 C8 C7	108.3(8)
N3 C9 C10	109.7(9)
C15 C10 C9	105.8(9)
C10 C11 H11	121.3
C13 C12 H12	119.0
C12 C13 H13	119.9
C13 C14 H14	120.7
C10 C15 C16	106.5(8)
N3 C16 C15	109.9(9)
C18 C17 P1	122.6(9)
C19 C18 H18	120.5
C18 C19 H19	120.3
C19 C20 H20	118.7
C22 C21 H21	120.5
C21 C22 H22	119.2
C24 C23 P1	119.0(8)
C23 C24 H24	119.2
C26 C25 H25	120.6
C25 C26 H26	120.4
C26 C27 H27	119.6
C23 C28 H28	119.6
C34 C29 P1	118.0(7)
C31 C30 H30	120.5
C30 C31 H31	119.8
C31 C32 H32	120.3
C34 C33 H33	119.2
C29 C34 H34	120.2

sults and Discussion

w solubility of $Ru^{III}(Pc)Cl_2$ can be a cause of deterrent e compound to be used as a precursor in synthesizing Ru^{III}(Pc)Cl₂] salt crystal. However, the difficulty can ercome by a delicate mixture of 1:1:1:1 dimethylmide: acetone: ethanol: hexane crystallization solvent produced the title compound.

Figure 1, it can be observed that PNP[Ru^{III}(Pc)Cl₂] orm ordered solid-state arrangement. Particularly, the component of the title compound, [Ru^{III}(Pc)Cl₂]⁻, unidirectional orientation. The crystallographic eters of PNP[Ru(Pc)Cl₂] are listed in Table 1. rystal structure of PNP[Ru(Pc)Cl₂] is seen to be actural with its Fe homologue, PNP[Fe^{III}(Pc)Cl₂], also has a triclinic (Z = 1) crystal system [3].

the molecular level (Figure 2), the regularity is brought by the planarity of the RuPc and the linearity of the dihloro ligands which give it a uniform octahedral architecture, that is, the central Ru³⁺ is aligned with the planarity of the Pc moiety which is manifested by the bond lengths, as well

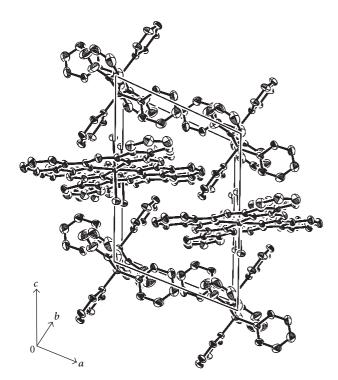


FIGURE 1: Crystal structure of $PNP[Ru^{III}(Pc)Cl_2]$ (crystal system = triclinic; Z = 1).

as the bond angles between the central Ru^{3+} and its adjacent nitrogen atoms being nearly equal (Tables 2 and 3). Furthermore, there is a linear 180° bond angle between the two axial chloro ligands which are perpendicular (90°± 1.6) with respect to the central metal (Table 3), making $[\mathrm{Ru}^{\mathrm{III}}(\mathrm{Pc})\mathrm{Cl}_2]^-$ suitable for slip-stacked intermolecular arrangement, with the cation bis(triphenylphosphine)iminium (PNP) serving as effective space-filler in the crystal system.

The resulting unidirectional and ordered orientation of $[Ru^{III}(Pc)Cl_2]^-$ units is mainly attributed to the steric influence of small and linear axial ligands of the fully conjugated planar Pc from which electrical and magnetic property manifestations can be designed and modulated based on its bulkiness for corresponding intermolecular π - π overlap variations [11], as well as on the chemical properties founded on the ligand field energy [3] of the axial ligands.

4. Conclusion

The synthesis of the crystalline PNP[Ru^{III}(Pc)Cl₂] revealed an ordered octahedral structural architecture of the Ru(Pc)Cl₂ moiety. The regularity of the structure, coupled with the steric influence of the linear axial ligands, could effectively result in a slip-stacked arrangement capable of intermolecular π - π orbital overlap for electron conduction. Furthermore, PNP[Ru^{III}(Pc)Cl₂] is found to be isomorphous with its Fe homologue, thus opening prospects for the solid-state synthesis of other possible Fe(Pc)L₂ homologue species of ruthenium. The resulting Ru(Pc)L₂ is expected to have stronger π -d interactions than its Fe counterparts

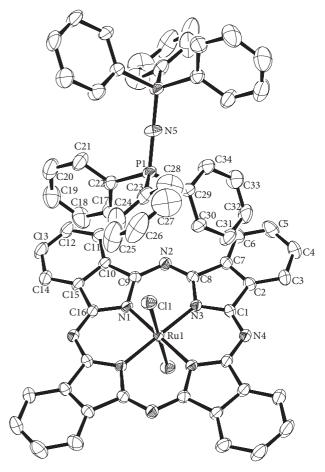
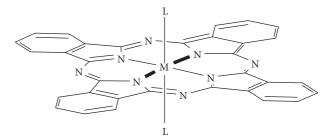


Figure 2: ORTEP molecular structure representation of $PNP[Ru^{III}(Pc)Cl_2]$ (hydrogens are omitted for clarity).



Scheme 1: Structure of $M^{III}(Pc)L_2$ (where M= central metal and L= axial ligands).

that could result in molecular conductors with exceptional GNMR.

Appendix

CCDC 864862 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Hokkaido University Global Center of Excellence (GCOE) Program in chemistry and materials science (2007-2012) funded by the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of the Japan Government.

References

- [1] T. Inabe and H. Tajima, "Phthalocyanines—versatile components of molecular conductors," *Chemical Reviews*, vol. 104, no. 11, pp. 5503–5534, 2004.
- [2] D. E. C. Yu, M. Matsuda, H. Tajima, T. Naito, and T. Inabe, "Stable π-π dependent electron conduction band of TPP[M(Pc)L₂]₂ molecular conductors (TPP = tetraphenylphosphonium; M = Co, Fe; Pc = phthalocyaninato; L = CN, Cl, Br)," *Dalton Transactions*, vol. 40, no. 10, pp. 2283–2288, 2011.
- [3] D. E. C. Yu, M. Matsuda, H. Tajima et al., "Variable magne-totransport properties in the TPP[Fe(Pc)L₂]₂ system (TPP = tetraphenylphosphonium, Pc = phthalocyaninato, L = CN, Cl, and Br)," *Journal of Materials Chemistry*, vol. 19, no. 6, pp. 718–723, 2009.
- [4] H. J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, and M. Schutz, "2006," MOLPRO version 2006.1, a package of ab initio program, http://www.molpro.net/.
- [5] L. R. Subramanian, "Tribute to Professor Dr Michael Hanack," Journal of Porphyrins and Phthalocyanines, vol. 4, no. 3, pp. 300–309, 2000.
- [6] T. Rawling and A. McDonagh, "Ruthenium phthalocyanine and naphthalocyanine complexes: synthesis, properties and applications," *Coordination Chemistry Reviews*, vol. 251, no. 9-10, pp. 1128–1157, 2007.
- [7] M. Weidemann, H. Hueckstaedt, and H. Homborg, "Darstellung und Eigenschaften von (Acido)(pyridin)phthalocyaninato(2–)ruthenaten(II); Kristallstruktur von Tetra(n-butyl)ammonium(cyano)(pyridin)phthalocyaninato(2–)ruthenat(II)," Zeitschrift für Anorganische Und Allgemeine Chemie, vol. 624, no. 5, pp. 846–852, 1998.
- [8] J. F. Myers, G. W. Canham, and A. B. P. Lever, "Higher oxidation level phthalocyanine complexes of chromium, iron, cobalt and zinc. Phthalocyanine radical species," *Inorganic Chemistry*, vol. 14, no. 3, pp. 461–468, 1975.
- [9] N. P. Farrell, A. J. Murray, J. R. Thornback, D. H. Dolphin, and B. R. James, "Phthalocyanine complexes of ruthenium(II)," *Inorganica Chimica Acta*, vol. 28, pp. L144–L146, 1978.
- [10] D. J. Watkin, C. K. Prout, J. R. Carruthers, and P. W. Betteridge, "CrystalStructure 4.0: crystal structure analysis package, Rigaku and Rigaku/MSC (2010)," in CRYSTALS Issue 10, Chemical Crystallography Laboratory, Oxford, UK, 1996.
- [11] D. E. C. Yu, H. Imai, M. Ushio, S. Takeda, T. Naito, and T. Inabe, "One-step synthesis of partially oxidized cobalt(III) phthalocyanine salts with axial ligands," *Chemistry Letters*, vol. 35, no. 6, pp. 602–603, 2006.