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*Research Article*

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

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Axially-ligated iron phthalocyanines have been found to be good molecular conductors with giant negative magnetoresistance (GNMR) which originates from a strong intramolecular $\pi$-$d$ 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 $\pi$-$d$ 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 [$Ru^{III}(Pc^{2-})Cl_2$]. It is observed that [$Ru^{III}(Pc^{2-})Cl_2$] system has a symmetric planar RuPc unit with perpendicular axial ligands which results in a unidirectional and uniform solid-state arrangement, suitable for $\pi$–$d$ 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 $\pi$-$\pi$ overlap for electron conduction [1, 2]. Moreover, the existence of strong intramolecular $\pi$-$d$ interaction in axially ligated iron(III) phthalocyanine ($Fe^{III}(Pc)L_2$; 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 $D_{4h}$ $Fe^{III}(Pc)L_2$ system corroborated experimental observation that the strength of GNMR is directly related to the strength of $\pi$-$d$ interaction in the order of L = CN > Cl > Br. On the electronic structure representation of [$Fe^{III}(Pc)L_2$] species, the $Fe^{3+}d^5$ 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 $\pi$-system of the Pc. Electronic structure calculations using two state-averaged complete active space multiconfigurational SCF method (active space orbitals: Pc-$\pi$, Fe-$d_{xz}$ and $d_{yz}$; Stuttgart-Köln ECP + DZ basis) resulted in $\Delta E$ (orbital energy difference between $d_{yz}/d_{xz}$ and HOMO; intensity of the $\pi$-$d$ 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 $Ru^{III}(Pc)L_2$, which is electronically isostructural with the $Fe^{III}(Pc)L_2$ species, the $d^5$ homologue system resulted in a remarkable increase of around two-fold in the $\pi$-$d$ interactions across all $Ru^{III}$ $(Pc)L_2$ species (L: CN = 3.7518 eV, Cl = 3.8419 eV, Br = 3.9411 eV). Given that the intensity of the unique intramolecular $\pi$-$d$ interaction as the origin of the varying anisotropic GNMR in $M^{III}(Pc)L_2$, 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)

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

| | |
|---|---|
| Empirical formula | $C_{68}H_{46}N_9Cl_2P_2Ru_1$ |
| Formula weight | 1223.10 |
| Crystal system | Triclinic |
| Lattice parameters | $a$ = 10.4425(11)Å |
| | $b$ = 12.2391(11)Å |
| | $c$ = 13.159 (11)Å |
| | $\alpha$ = 75.523(3)° |
| | $\beta$ = 64.686(3)° |
| | $\gamma$ = 65.883(3)° |
| | $V$ = 1381.9(2)Å$^3$ |
| Space group | $P\bar{1}$ (#2) |
| $Z$ value | 1 |
| Calculated density | 1.470 g/cm$^3$ |
| $\mu$(MoK$\alpha$) | 4.92 cm$^{-1}$ |
| $2\theta_{max}$ | 49.0° |
| Reflections collected/unique | 10394/4588 |
| | [$R$(int) = 0.1173] |
| $R1$ [$I > 2.00\sigma(I)$] | 0.0803 |
| $wR2$ (all data) | 0.2345 |
| Goodness-of-fit indicator | 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°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)$Cl_2$].

| 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.

| 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[$Ru^{III}(Pc^{2-})Cl_2$], crystallized into dark blue crystals after 8 weeks.

*2.2. X-Ray Crystal Structure Determination.* A blue block crystal of PNP [$Ru^{III}(Pc^{2-})Cl_2$] (Formula: $C_{68}H_{46}N_9Cl_2RuP_2$) having approximate dimensions of 0.15 × 0.10 × 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-K$\alpha$ 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 $2\theta$ value of 49.0°. A total of 44 oscillation images were collected. A sweep of data was done using $\omega$ scans from 130.0 to 190.0° in 5.0° step, at $\chi = 45.0°$ and $\phi = 0.0°$. The exposure rate was 150.0 [sec/°]. A second sweep was performed using $\omega$ scans from 0.0 to 160.0° in 5.0° step, at $\chi = 45.0°$ and $\phi = 180.0°$. 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].

Table 3: Intramolecular bond angles (°) of PNP[$Ru^{III}(Pc)Cl_2$].

| Atom | Angle |
|---|---|
| N3 Ru1 N3 | 179.999(1) |
| 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) |
| 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 | 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 | 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) |
| 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 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 P1 C23 | 107.7(5) |

Table 3: Continued.

| Atom | Angle |
|---|---|
| C1 N1 Ru1 | 124.6(6) |
| C9 N3 C16 | 108.0(8) |
| C1 N4 C16 | 124.3(8) |
| N4 C1 C2 | 122.3(9) |
| C3 C2 C1 | 133.3(9) |
| C4 C3 H3 | 121.1 |
| C5 C4 H4 | 118.9 |
| C4 C5 H5 | 119.4 |
| C7 C6 H6 | 121.4 |
| C6 C7 C8 | 132.2(9) |
| N2 C8 C7 | 124.0(9) |
| N2 C9 C10 | 122.0(9) |
| C11 C10 C9 | 133.3(10) |
| C12 C11 H11 | 121.3 |
| C11 C12 H12 | 119.0 |
| C14 C13 H13 | 119.9 |
| C15 C14 H14 | 120.7 |
| C14 C15 C16 | 132.3(10) |
| N4 C16 C15 | 123.9(9) |
| C22 C17 P1 | 119.1(9) |
| C17 C18 H18 | 120.5 |
| C20 C19 H19 | 120.3 |
| C21 C20 H20 | 118.7 |
| C20 C21 H21 | 120.5 |
| C17 C22 H22 | 119.2 |
| C28 C23 P1 | 122.3(8) |
| C25 C24 H24 | 119.2 |
| C24 C25 H25 | 120.6 |
| C27 C26 H26 | 120.4 |
| C28 C27 H27 | 119.6 |
| C27 C28 H28 | 119.6 |
| C30 C29 P1 | 122.1(8) |
| C29 C30 H30 | 120.5 |
| C32 C31 H31 | 119.8 |
| C33 C32 H32 | 120.3 |
| C32 C33 H33 | 119.2 |
| C33 C34 H34 | 120.2 |
| N3 Ru1 N1 | 90.3(3) |
| N1 Ru1 N1 | 179.999(1) |
| N1 Ru1 Cl1 | 88.4(2) |
| N3 Ru1 Cl1 | 90.4(2) |
| Cl1 Ru1 Cl1 | 179.999(1) |
| C17 P1 C29 | 108.2(5) |
| C29 P1 C23 | 108.8(5) |
| C8 N1 Ru1 | 125.4(6) |
| C9 N3 Ru1 | 126.1(7) |
| P1 N5 P1 | 179.999(1) |
| N1 C1 C2 | 108.9(8) |
| C7 C2 C1 | 106.6(8) |
| C2 C3 H3 | 121.1 |
| C3 C4 H4 | 118.9 |

Table 3: Continued.

| Atom | Angle |
|---|---|
| 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 |

## 3. Results and Discussion

The low solubility of $Ru^{III}(Pc)Cl_2$ can be a cause of deterrent for the compound to be used as a precursor in synthesizing $PNP[Ru^{III}(Pc)Cl_2]$ salt crystal. However, the difficulty can be overcome by a delicate mixture of 1 : 1 : 1 : 1 dimethylformamide : acetone : ethanol : hexane crystallization solvent which produced the title compound.

In Figure 1, it can be observed that $PNP[Ru^{III}(Pc)Cl_2]$ units form ordered solid-state arrangement. Particularly, the anion component of the title compound, $[Ru^{III}(Pc)Cl_2]^-$, affords unidirectional orientation. The crystallographic parameters of $PNP[Ru(Pc)Cl_2]$ are listed in Table 1. The crystal structure of $PNP[Ru(Pc)Cl_2]$ is seen to be isostructural with its Fe homologue, $PNP[Fe^{III}(Pc)Cl_2]$, which also has a triclinic ($Z = 1$) crystal system [3].

At the molecular level (Figure 2), the regularity is brought about by the planarity of the RuPc and the linearity of the diaxial chloro ligands which give it a uniform octahedral architecture, that is, the central $Ru^{3+}$ is aligned with the planarity of the Pc moiety which is manifested by the bond lengths, as well

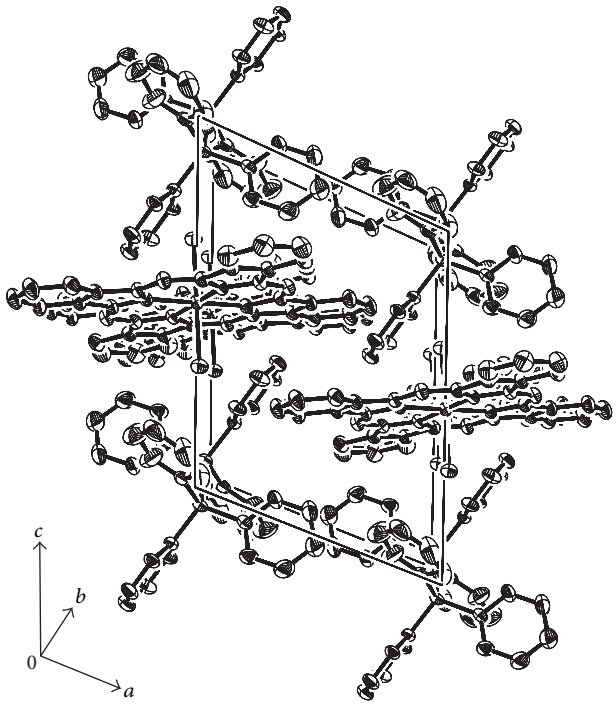



Figure 1: Crystal structure of PNP[$Ru^{III}$(Pc)$Cl_2$] (crystal system = triclinic; $Z = 1$).

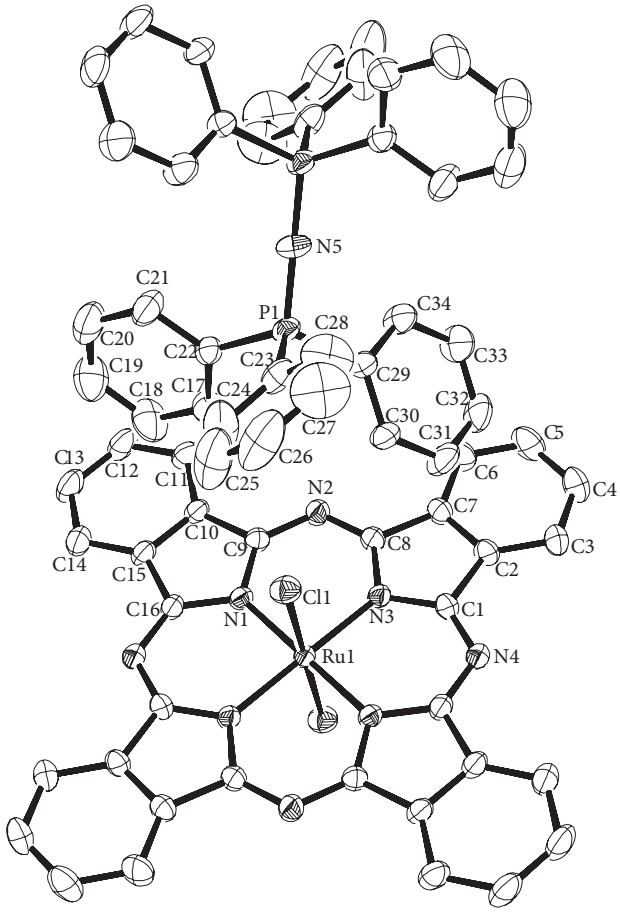
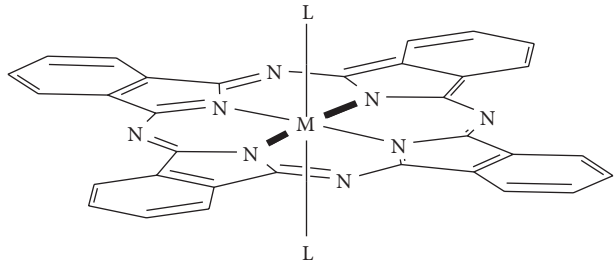



Figure 2: ORTEP molecular structure representation of PNP[$Ru^{III}$(Pc)$Cl_2$] (hydrogens are omitted for clarity).




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

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 [$Ru^{III}$(Pc)$Cl_2$]$^-$ 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 $\pi$-$\pi$ 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)$Cl_2$] revealed an ordered octahedral structural architecture of the Ru(Pc)$Cl_2$ 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 $\pi$-$\pi$ orbital overlap for electron conduction. Furthermore, PNP[$Ru^{III}$(Pc)$Cl_2$] is found to be isomorphous with its Fe homologue, thus opening prospects for the solid-state synthesis of other possible Fe(Pc)$L_2$ homologue species of ruthenium. The resulting Ru(Pc)$L_2$ is expected to have stronger $\pi$-$d$ interactions than its Fe counterparts 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.

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