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Citation	Journal of Chemistry, 2013, 486318 https://doi.org/10.1155/2013/486318
Issue Date	2013
Doc URL	https://hdl.handle.net/2115/51038
Rights(URL)	https://creativecommons.org/licenses/by/3.0/
Type	journal 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)

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Received 27 June 2012; Accepted 6 September 2012

Academic Editor: Mitsushiro Nomura

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 [$\mathrm{Ru^{III}(Pc^{2-})Cl_2}$]. It is observed that [$\mathrm{Ru^{III}(Pc^{2-})Cl_2}$] system has a symmetric planar RuPc unit with perpendicular axial ligands which results in a unidirectional and uniform solid-state arrangement, suitable for 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 ($\mathrm{Fe^{III}(Pc)L_2}$; 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} $\mathrm{Fe^{III}(Pc)L_2}$ 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 [$\mathrm{Fe^{III}(Pc)L_2}$] species, the $\mathrm{Fe}^{3+}d^5$ 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 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 $\mathrm{Ru^{III}(Pc)L_2}$, which is electronically isostructural with the $\mathrm{Fe^{III}(Pc)L_2}$ species, the d^5 homologue system resulted in a remarkable increase of around two-fold in the π-d interactions across all $\mathrm{Ru^{III}}$ $\mathrm{(Pc)L_2}$ species (L: CN = 3.7518 eV, Cl = 3.8419 eV, Br = 3.9411 eV). Given that the intensity of the unique intramolecular π-d interaction as the origin of the varying anisotropic GNMR in $\mathrm{M^{III}(Pc)L_2}$, 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
	$\alpha = 75.523(3)^\circ$
	$\beta = 64.686(3)^\circ$
	$\gamma = 65.883(3)^\circ$
	$V = 1381.9(2)$Å^3
Space group	$P\bar{1}$ (#2)
Z value	1
Calculated density	1.470 g/cm^3
μ(MoKα)	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-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 $\chi = 45.0°$ and $\phi = 0.0°$. The exposure rate was 150.0 [sec/°]. A second sweep was performed using ω 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
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

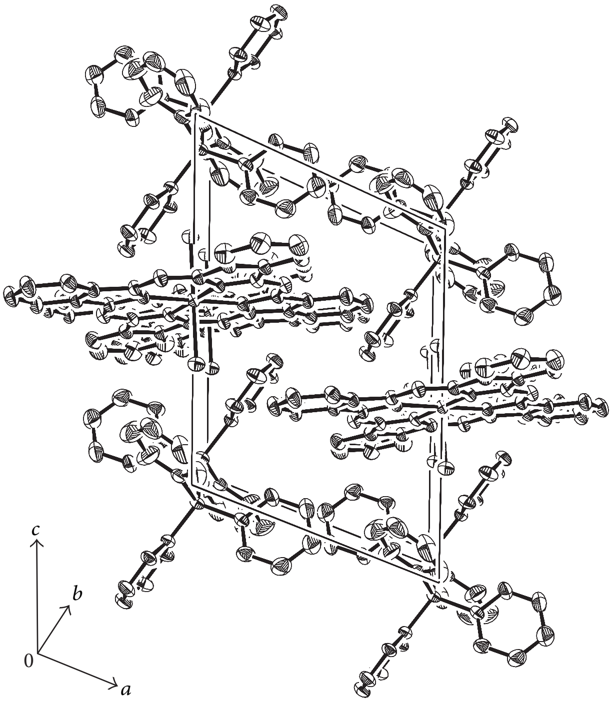


Figure 1: Crystal structure of PNP[$\text{Ru}^{\text{III}}(\text{Pc})\text{Cl}_2$] (crystal system = triclinic; $Z = 1$).

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 [$\text{Ru}^{\text{III}}(\text{Pc})\text{Cl}_2]^-$ 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 [$\text{Ru}^{\text{III}}(\text{Pc})\text{Cl}_2]^-$ 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.

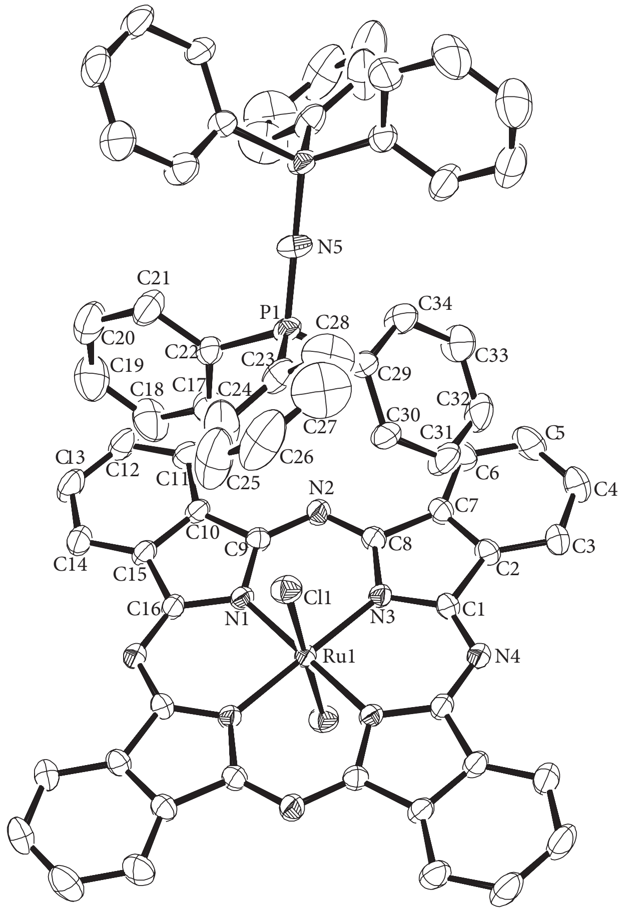
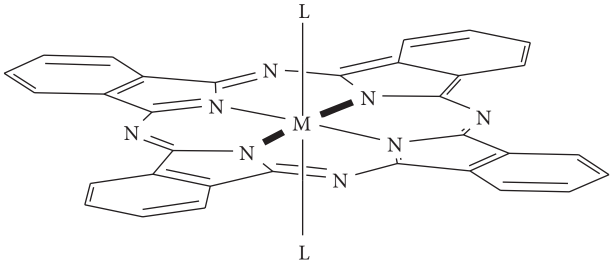


Figure 2: ORTEP molecular structure representation of PNP[$\text{Ru}^{\text{III}}(\text{Pc})\text{Cl}_2$] (hydrogens are omitted for clarity).



Scheme 1: Structure of $\text{M}^{\text{III}}(\text{Pc})\text{L}_2$ (where M = central metal and L = axial ligands).

4. Conclusion

The synthesis of the crystalline PNP[$\text{Ru}^{\text{III}}(\text{Pc})\text{Cl}_2$] revealed an ordered octahedral structural architecture of the $\text{Ru}(\text{Pc})\text{Cl}_2$ 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 π-π orbital overlap for electron conduction. Furthermore, PNP[$\text{Ru}^{\text{III}}(\text{Pc})\text{Cl}_2$] is found to be isomorphous with its Fe homologue, thus opening prospects for the solid-state synthesis of other possible $\text{Fe}(\text{Pc})\text{L}_2$ homologue species of ruthenium. The resulting $\text{Ru}(\text{Pc})\text{L}_2$ is expected to have stronger π-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.

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)L_2]$_2$ 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 magnetotransport properties in the TPP[Fe(Pc)L_2]$_2$ 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.