Brief Communication

Synthesis of Highly Soluble Axially-Ligated Ruthenium(III) Phthalocyanine Salt: Potassium Dithiocyanato(phthalocyaninato)ruthenium(III)

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ABSTRACT

Partially-oxidized di-axially ligated ruthenium(III) phthalocyanine crystalline salts are deemed to be highly conducting molecular solids with giant negative magnetoresistance. Solubility as a prerequisite for crystallization has always been a challenge especially in ruthenium complexes. This paper presents the synthesis of highly soluble potassium dithiocyanato(phthalocyaninato(-2))ruthenium(III) salt from the poorly soluble dibromo(phthalocyaninato(-1))ruthenium(III) radical complex. The synthesis involves the reduction of the Phthalocyanine ligand and substitution of axial ligands utilizing potassium thiocyanide to afford the product.

Keyword: Axially-ligated Ruthenium(III) phthalocyanine, Molecular conductor.

INTRODUCTION

Axially-ligated Iron(III) phthalocyanines $(Fe^{III}(Pc)L_2$; where L = CN, Cl, Br; Scheme 1a) were reported to be highly conducting molecular systems with anisotropic giant negative magnetoresistance (GNMR) which are considered to be suitable functional materials that are significant in information technology advancement[1]. $Fe^{III}(Pc)L_2$ is a product of molecular engineering wherein its structural parts are designed for functional purposes. Pc is a flat π-conjugated molecular system in which electrons are delocalized, while octahedral coordinating central metals allow the attachment of di-axial ligands, generating slip-stacked solid-state arrangement that results in intermolecular Pc π-π orbital (HOMO) overlaps which create electronic conduction band[2], and thereby allowing electron transport in varying degrees depending on the effectiveness of the overlap[3,4]. Consequently, the unique single molecule/intramolecular π-d interaction between the Pc-π and the magnetic Fe-d (d^5; s = 1/2) orbitals generate GNMR, which can be further enhanced correspondingly by axial ligand field energy which raises the orbital energy of the Fe-d nearer to the Pc-π, thereby intensifying the π-d interaction, hence increasing GNMR[1]. Moreover, the electronic structure of the axial ligands can also affect the π-d orbital interactions that alter the magnetic property of the $Fe^{III}(Pc)L_2$ system[5,6].
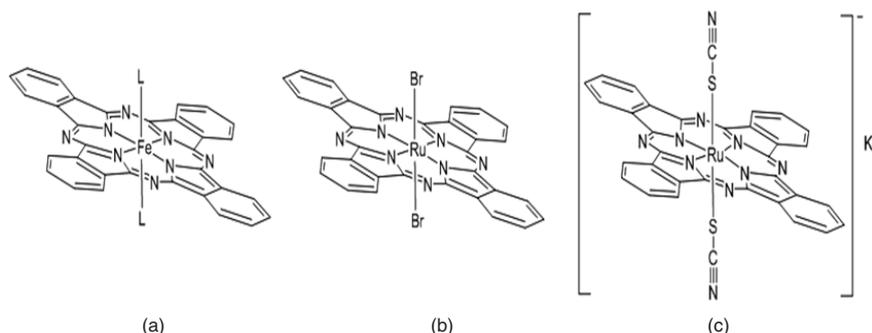
Scheme 1. Structures of (a) Fe^{III}(Pc)L$_2$ (where L = CN, Cl, Br); (b) Ru^{III}(Pc)Br$_2$; (c) K[Ru^{III}(Pc)(SCN)$_2$]

The quest to further intensify π-d interaction to enhance GNMR has led to the possibility of replacing Fe^{3+} with its higher d^5 homologue, Ru^{3+}, in the Fe^{III}(Pc)L$_2$ complex due to fact that the Ru-d orbitals occupy higher energy level than the Fe-d orbitals, hence, the Ru-d orbitals will be nearer to the Pc-π orbital and would result into greater π-d interaction. *Ab initio* calculations derived the degree of π-d orbital interactions in Ru^{III}(Pc)L$_2$ by the orbital energy difference/proximity of Pc-π (HOMO) and Fe-d$_{xz}$/d$_{yz}$ as L = CN: 3.7518 eV, L = Cl: 3.8419 eV, and L = Br: 3.9411 eV, as compared with L = CN: 7.8655 eV, L = Cl: 8.3839 eV, and L = Br: 8.5450 eV for the Fe^{III}(Pc)L$_2$ series[7]. As thus, it is expected that Ru^{III}(Pc)L$_2$ will generate around 2-fold more π-d interaction than Fe^{III}(Pc)L$_2$ species.

The synthesis of Ru^{3+} compounds are rarely reported due to their labile and complex nature. For Pc chemistry, a perennial challenge is the solid-state synthesis of Ru^{III}(Pc)L$_2$ with identical di-axial structurally-linear ligands that are highly pure and soluble[8]. The recent synthesis of the highly-insoluble di-axially ligated Ru^{III}(Pc^{-1})Br$_2$ radical complex paved the way for the generation of the Ru^{III}(Pc)L$_2$ system[9]. However, good solubility is an essential prerequisite for crystallization and eventual creation of new functional materials. Thus, in this study, we present the synthesis of highly-soluble K[Ru^{III}(Pc^{-2})(SCN)$_2$] salt from the poorly soluble Ru^{III}(Pc^{-})Br$_2$ radical complex. The conversion into the soluble K[Ru^{III}(Pc^{-2})(SCN)$_2$] salt makes it possible for its eventual electro-oxidation/crystallization to produce partially-oxidized [Ru^{III}(Pc)L$_2$]$^{-0.5}$ species which are deemed to be highly-conducting molecular systems with anticipated stronger GNMR than its Fe^{III}(Pc)L$_2$ counterpart.

Methodology

Ru^{II}(Pc) is synthesized from RuCl$_3$·nH$_2$O and 2-cyanobenzamide, while Ru^{III}(Pc^{-})Br$_2$ was derived from the reaction of Ru^{II}(Pc^{-2}) and Thionyl bromide, based on previously reported procedures[9,10].

The title compound, K[Ru^{III}(Pc)(SCN)$_2$], was synthesized by reacting Ru^{III}(Pc)Br$_2$ (200 mg; $\approx$0.3 mmol) and KSCN (600 mg; $\approx$6 mmol)) in a 50 mL acetone suspension for 5 days at room temperature. The resulting suspension was filtered to remove excess KSCN and evaporated in vacuo. The solid product was rinsed with water and dried in vacuo. Further purification was done by vapor diffusion of diethyl ether into a saturated ethanol solution of the crude product, which afforded violet solids at 75% yield.

K[Ru^{III}(Pc)(SCN)$_2$] was characterized by negative-mode electrospray ionization mass spectrometer (Jeol JMST100LP) in 1:5 DMF:EtOH solvent system; UV-Vis spectrophotometer (Hitachi U-2900) in DMF solvent; IR spectrophotometer (Thermo-Nicolet Magna 5000) in pelletized KBr; and SEM-EDX (Phenom XL 2015 LR1) in Au coating.

RESULTS AND DISCUSSION

The conversion of Ru^{III}(Pc^{-})Br$_2$ to K[Ru^{III}(Pc^{-2})(SCN)$_2$] involve nucleophilic substitution of axial Br by SCN ligands. The Br^{-} leaving group is in turn oxidized by the Pc^{-} radical, hence the formation of reduced Pc^{-2} and Br radical to eventually produce K[Ru^{III}(Pc^{-2})(SCN)$_2$] and Br$_2$.

Figure 1 displays the ESI-MS spectra of K[Ru^{III}(Pc^{-2})(SCN)$_2$] with the predominant peak at m/z = 729.9 which corresponds to [Ru^{III}(Pc^{-2})(SCN)$_2$]$^{-}$ (calculated m/z = 729.9). In Fig. 2, SEM-EDX elemental analysis confirms the presence of Ru and K.
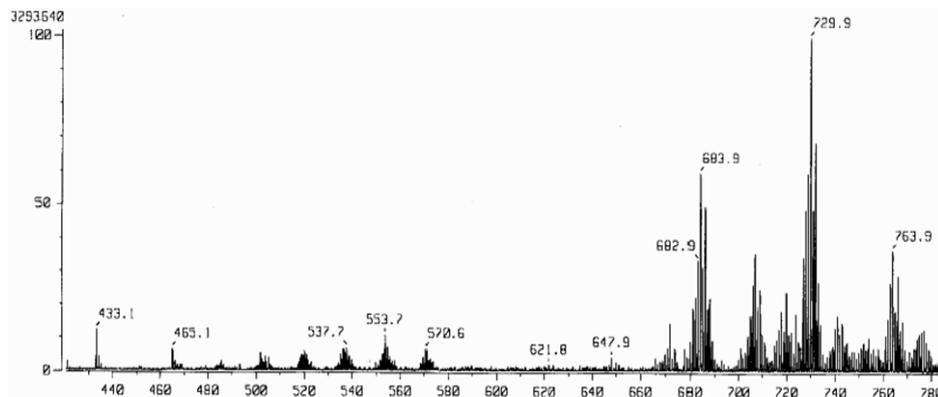
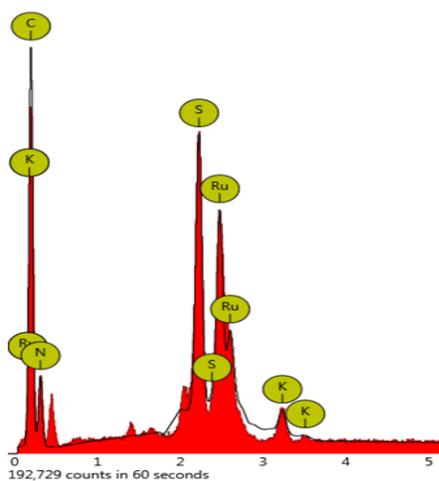**Fig. 1. Mass spectra of K[Ru^{III}(Pc^{-2})(SCN)$_2$]**

Fig. 2. SEM-EDX spectra of K[Ru^{III}(Pc^{-2})(SCN)$_2$]

The UV-Vis spectra Fig. 3 confirms the integrity of the Pc ring with the characteristic Q and Soret bands at 630 nm and 340 nm, respectively. Moreover, in reference to the UV-Vis spectra of Ru^{III}(Pc-)Br$_2$, the absence of absorption peak at around 500 nm which is due to the additional e$_g$ (π) $\rightarrow$ a$_{1u}$ (π) transitions observed in Pc^{-1} radical[11,12] confirmed the Pc ring reduction to Pc^{-2}.
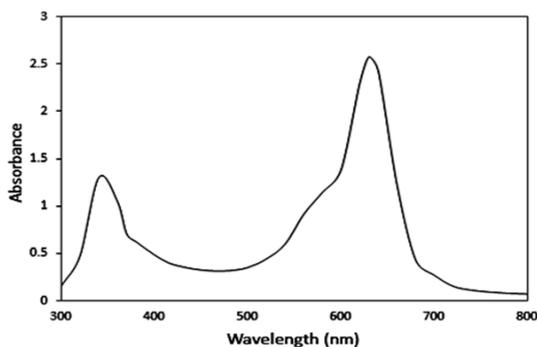

Fig. 3. UV-Vis spectra of K[Ru^{III}(Pc^{-2})(SCN)$_2$]

The IR spectra Fig. 4 indicates Ru–SCN vibration peak at around 2100 cm^{-1} which is a result of the shifting of Ru–S electron density from the S–C bond, thereby making C≡N bond stronger, and thus, shifting the stretching frequency of axial thiocyanate to higher frequency at around 2100 cm^{-1} as compared with unbound thiocyanate stretching vibration that is typically observed at around 2050 cm^{-1}.
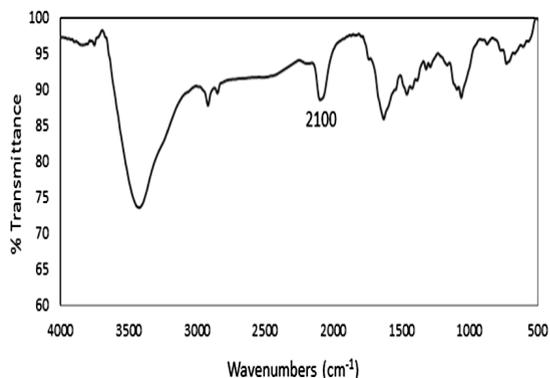

Fig. 4. Infrared spectra of K[Ru^{III}(Pc^{-2})(SCN)$_2$]

CONCLUSION

The conversion of the poorly soluble Ru^{III}(Pc-)Br$_2$ radical complex into the highly soluble K[Ru^{III}(Pc^{-2})(SCN)$_2$] salt has been achieved by the reaction of the former with KSCN which resulted in the axial ligand substitution of Br- to SCN- and the reduction of Pc^{-1} to Pc^{-2}, thereby producing [Ru^{III}(Pc^{-2})(SCN)$_2$]- anion. Thus, the generation of partially-oxidized Ru^{III}(Pc)L$_2$ molecular conductors with exceptional GNMR became possible with the synthesis of the highly soluble K[Ru^{III}(Pc^{-2})(SCN)$_2$] salt precursor.

REFERENCES

1. Yu, D.E.C.; Matsuda, M.; Kikuchi, A.; Taketsugu, T.; Naito, T.; Inabe, T. *J. Mater. Chem.*, **2009**, *19*, 718-723.

2. Inabe, T.; Tajima, H. *Chem. Rev.*, **2004**,

3. Yu, D.E.C.; Imai, H.; Ushio, M.; Takeda, S.; Naito, T.; Inabe, T. *Chem. Lett.*, **2006**, *35*, 602-603.

4. Yu, D.E.C.; Matsuda, M.; Tajima, H.; Naito, T.; Inabe, T. *Dalton Trans.*, **2011**, *40*, 2283-2288.

5. Torizuka, K.; Tajima, H.; Inoue, M.; Hanasaki, N.; Matsuda, M.; Yu, D.E.C.; Naito, T.; Inabe, T. *J. Phys. Soc. Jpn.*, **2013**, *82*, 034719(1-14).

6. Inoue, M.; Torizuka, K.; Tajima, H.; Matsuda, M.; Yu, D.E.C.; Naito, T,; Inabe, T.; Hanasaki, N. *Physica* B., **2010**, *405*, S331-333.

7. Yu, D.E.C.; Kikuchi, A.; Taketsugu, T.; Inabe, T. *J. Chem.*, **2013**, 486318(1-6).

8. Rawling, T.; McDonagh, A. *Coord. Chem. Rev.*, **2007**, *251*, 1128–1157.

9. Gamboa, M.A.V.; Valinton, J.A.A.; Yu, D.E.C. *Curr. Chem. Lett.*, **2015**, *4*, 1-6.

10. Farrell, N.P.; Murray, A.J.; Thornback, J.R.; Dolphin, D.H.; James, B.R. *Inorg. Chim. Acta .,* **1978**, *28*, L144–L146.

11. Minor, P.C.; Gouterman M.; Lever, A.B.P. *Inorg. Chem.*, **1985**, *24*, 1894-1900.

12. Nyokong, T.; Gasyna, Z.; Stillman, M.*J. Inorg. Chem.*, **1987**, *26*, 1087-1095.