http://dx.doi.org/10.5012/bkcs.2012.33.5.1447

Revisit of Unusual Ruthenium(III) Dichloro Complex

Won K. Seok,* Na Yeon Kim, and Hoseop Yun†

*Department of Chemistry, Dongguk University, Seoul 100-715, Korea. *E-mail: wonkseok@dongguk.edu*
†Department of Molecular Science and Technology, Ajou University, Suwon 442-749, Korea
Received January 12, 2012, Accepted February 10, 2012

Key Words : $[Ru^{III}(bpy)_2Cl_2][PF_6]$ complex, Bulky hexafluorophosphate anion, CAN

Diverse oxidation chemistry associated with polypyridyl ruthenium complexes emerged.[1] Especially oxo-metal reagents in high oxidation state have been found to be versatile stoichiometric and/or catalytic oxidants toward a variety of organic and inorganic substrates *via* electron transfer, oxygen atom transfer, hydride transfer, and proton-coupled electron transfer pathways.[2] Among multiple ruthenium species appeared in the syntheses and mechanistic studies, Ru(III) complex is quite interesting material to investigate. However, there is a complication since Ru(III), once formed, undergoes disproportionation reaction to give Ru(II) and Ru(IV).

Ammonium cerium nitrate ($[(NH_4)_2][Ce(NO_3)_6]$, CAN) is employed for the preparation of the nitrate complexes in coordination chemistry as well as the ring opening catalysts in organic syntheses.[3] We obtained an unexpected Ru(III) nitrate complex, $[Ru^{III}(dppm)_2(O_2NO)][ClO_4]$ (dppm = 1,1-bis(diphenylphosphino)methane), from the reaction of $[Ru^{II}(dppm)_2Cl_2]$ with CAN in perchloric acid and a blue crystalline *trans*-$[Ru^{III}(depe)_2Cl_2][PF_6]$ (depe = 1,2-bis(diethylphosphino)ethane).[4]

In order to extend our understanding of Ru(III) complexes containing polypyridyl ligands and also examine the validity of oxidation mechanisms previously proposed, we have prepared $[Ru^{III}(bpy)_2Cl_2][PF_6]$ by the reaction of $[Ru(bpy)_2Cl_2]$ (bpy = 2,2'-bipyridine) with CAN as one-electron oxidizing reagent in saturated ammonium hexafluorophosphate solution. It also deserves special emphasis that Ru complexes containing bulky anions are quite useful as precursors in preparing different types of complexes for their good solubility in organic solvents.

In a typical reaction, *cis*-$[Ru^{III}(bpy)_2Cl_2][PF_6]$ was obtained by adding 10 mL of saturated $[NH_4][PF_6]$ solution to the reaction mixture of *cis*-$[Ru^{II}(bpy)_2Cl_2]$ (0.096 g, 0.2 mmol) and CAN (0.164 g, 0.3 mmol) in methanol (37 mL) and water (13 mL).

$$cis\text{-}[Ru^{II}(bpy)_2Cl_2] \xrightarrow[[NH_4][PF_6]]{\text{CAN}} cis\text{-}[Ru^{III}(bpy)_2Cl_2][PF_6]$$

A yellow solid with 54% yield was isolated by suction filtration followed by washing with water and methanol.[5] Broad resonance peaks between −8 and 18 ppm for bipyridyl protons in the ^{1}H NMR spectrum for the product are observed, which suggest the existence of a paramagnetic material. The peak at 145 ppm in the ^{31}P NMR spectrum shown as sharp septet indicates the phosphorous atom in the PF_6 anion salt. In the ESR spectrum of the prepared complex, the *g*-tensor values are well matched with those of other Ru(III) complexes previously studied.[4b,6]

Single crystals were grown from acetonitrile solution added to diethyl ether. A prismatic crystal of the Ru(III) of approximate dimensions of 0.3 × 0.2 × 0.2 mm was mounted and a Rigaku Rapid R-axis diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å) was employed for data collection.[7] A total of 11232 (2715 independent) reflections were collected, which yielded 1244 reflections observed for $I > 2\sigma(I)$. The final agreement factors were $R[F^2 > 2\sigma(F^2)] = 0.0208$ and $wR(F^2) = 0.0474$.

The crystal structure of this salt is composed of mononuclear cationic ruthenium complex in six-coordinate with four nitrogen atoms of the bpy ligands and two chlorine atoms *cis* each other balanced by hexafluorophosphate anion. Figure 1 shows the perspective view of the *cis*-$[Ru^{III}(bpy)_2Cl_2][PF_6]$ compound with atom labeling. The ruthenium atom in this molecule has an imposed two-fold rotational symmetry and there is a unique chloride and a unique bpy ring per molecular unit. Because of the ionic nature of the Ru(III), neither stacking interactions nor close contacts are observed in the lattice.

As shown in Table 1, the Ru(III)-Cl bond length is 2.337(1) Å, which might otherwise have been expected in a compound of this type.[8,9] Table of all the other bond distances (Å) and angles (°) of *cis*-$[Ru^{III}(bpy)_2Cl_2][PF_6]$ is available as supplementary material. It is noteworthy that there have been few crystal structural studies on mononuclear Ru(III) chloro complexes containing bipyridyl and its analogue ligands.[10] Although it is not particularly surprising, the marked shortening of the Ru(III)-Cl bond distance upon oxidation of the metal is observed by comparison with the Ru(II)-Cl containing structures.[8] A similar decrease in the Ru-Cl bond distance is apparent in the structures of *cis*-$[Ru^{II}(bpy)_2Cl_2]\cdot 3.5H_2O$ (Ru-Cl = 2.426 Å) which individual

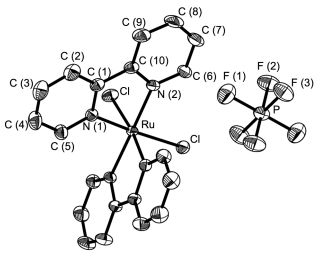

Figure 1. Molecular structure of the *cis*-$[Ru^{III}(bpy)_2Cl_2][PF_6]$ in the crystals. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Selected geometric parameters (Å, °)

Ru-Cl	2.337(1)	Ru-N(1)	2.053(1)	Ru-N(2)	2.073(1)
Cl-Ru-N(1)	172.75(4)	Cl-Ru-N(2)	96.02(4)	Cl-Ru-N(1)*	89.88(4)
Cl-Ru-N(2)*	86.64(4)	N(1)-Ru-N(2)	78.59(6)	N(1)-Ru-N(1)*	86.16(8)
N(1)-Ru-N(2)*	98.51(5)	N(2)-Ru-N(2)*	176.08(8)	Cl-Ru-Cl*	94.67(2)

Table 2. Comparison of bond distances [Å] and angles (°) for related Ru(II) and Ru(III) dichloro complexes containing the bpy ligand (Å, °)

Complex	Avg. Ru-N	Avg. Ru-Cl	Avg. N-Ru-N	Cl-Ru-Cl	Space group	Ref.
$[Ru^{II}(bpy)_2Cl_2]\cdot 3.5H_2O$	2.034(2)	2.426(1)	79.1(9)	89.16(13)	*C*2/*c*	11
$[Ru^{III}(bpy)_2Cl_2][Cl\cdot 2H_2O]$	2.056(2)	2.325(3)	78.7(2)	93.7(1)	$P\bar{1}$	11
$[Ru^{III}(bpy)_2Cl_2][PF_6]$	2.063(1)	2.337(1)	78.6(1)	94.67(2)	*C*2/*c*	This work

water molecule within the crystal involves hydrogen bonding with the coordinated chlorides and *cis*-$[Ru^{III}(bpy)_2Cl_2]$-$[Cl\cdot 2H_2O]$ (Ru-Cl = 2.325 Å) where Δ (Ru^{III}-Ru^{II}) = 0.101 Å.[9]

The geometry of $[Ru^{III}(bpy)_2Cl_2]^+$ cation is, like that of the its Ru(II) counterpart, very close to octahedral. The bpy "bite angle" and *cis*-positioned dichloro angle around the central ruthenium metal in Ru(III) is 78.59(6) and 94.67(2)°. As in the Ru(II) structure the bpy ring ligands are bent back slightly from coordinated chloride with the *trans*-N-Ru-N bond angle being 176.08(8)°. Each six-membered pyridine ring in the bpy ligands is virtually planar with deviations from 0.0006 to 0.0071 Å. The dihedral angle between pair of planar six-membered pyridine in the bpy ligand is 4.42(12)°, quite similar to averaged value 3.55° of $[Ru^{III}(bpy)_2Cl_2]$-$[Cl\cdot 2H_2O]$. A variety of known bpy structures show that their angles range from 0° to 31° with an average value of 8°.[11] There are no significant distortions in the bpy rings induced by change in oxidation state at the metal. The observed inter-planar angle between pair of bpy group in the Ru(III) complex is 84.76(4)°.

It is quite interesting to compare the crystal structure of *cis*-$[Ru^{III}(bpy)_2Cl_2][PF_6]$ with that of *cis*-$[Ru^{III}(bpy)_2Cl_2]$-$[Cl\cdot 2H_2O]$.[9] As shown in Table 2, the difference in crystallographic system is Cl^- complex crystallizes in the triclinic space group of *P*1, whereas monoclinic *C*2/*c* for the complex containing PF_6^-. Effects of ligand electronic asymmetry observed in the crystal structure are, once again, evident in the Ru(III)-N(bpy) distances for both complexes. The Ru(III)-N(bpy) bond distance of 2.053(5) Å *trans* to the coordinated chlorides in the complex containing PF_6^- is comparable with the pair of Ru(III)-N(bpy) bonds (2.054(5) and 2.045(5); average 2.050(5) Å) in the complex containing Cl^-, but longer than that in the parent Ru(II) (2.013(2) Å) containing the shortest Ru-N(bpy) bond length. The Ru(III)-N(bpy) bond distance of 2.073 Å *trans* to another bpy nitrogen atom is longer than that in Ru(II) structure (2.054 Å). This observation points to the importance of Ru(III)-bpy back-bonding. The bpy ligand is a relatively weak π-acid whose σ-donor capacity is expected to be significantly greater than that of chloride ion at Ru(II). For a bipyridyl nitrogen atom *trans* to a second bipyridyl nitrogen atom, competition exists for electron density involving the same filled d π orbitals.[12]

The "bite angle" of the bpy ligand in the Cl^- salt is quite similar to that in the PF_6^- salt, however the angle is more or less narrower than for the parent Ru(II) molecule. The *cis*-positioned dichloro angle of 94.67(2)° for the hexafluorophosphate containing salt is 1° wider than that for chloride one (93.7(1)°), which Ru(III) complexes generally possess much larger angles than corresponding Ru(II) by an average of 5°. The widening of the angle is probably a consequence of increased Cl-Cl repulsion due to the shortening of the Ru(III)-Cl bond in Ru(III) compared to Ru(II). All of these observations point that the bulky phosphate anion gives some influence on the geometry of the molecular cation in the complex.

In the present study, we prepared and characterized $[Ru^{III}(bpy)_2Cl_2][PF_6]$. The Ru(III)-Cl bond length is 2.337(1) Å and the marked shortening of the Ru-Cl bond distance upon oxidation of the metal. The *cis*-positioned dichloride angle of 94.87(2)° is 5° wider than that in the corresponding Ru(II) molecule.

References

1. Hu, Z.; Du, H.; Man, W.-L.; Leung, C.-F.; Liang, H.; Lau, T.-C. *Chem. Commun.* **2012**, *48*, 1102 and references therein
2. Chen, Z.; Concepcion, J. J.; Hu, X.; Yang, W.; Hoertz, P. G.; Meyer, T. J. *Proc. Nat. Acad. Sci.* **2010**, *107*, 7225.
3. Wu, A. Dehestani, A.; Saganic, E.; Crevier, T. J.; Kaminsky, W.; Cohen, D. E.; Mayer, J. M. *Inorg. Chim. Acta* **2006**, *68*, 2842 and references therein.
4. (a) Seok, W. K. *Bull. Korean Chem. Soc.* **2007**, *28*, 173. (b) Seok, W. K.; Zhang, L. J. *Bull. Korean Chem. Soc.* **2009**, *30*, 2401.
5. $[Ru^{III}(bpy)_2Cl_2][PF_6]$, Anal. Calc. for $C_{20}H_{16}N_4Cl_2PF_6Ru$: C, 38.17; H, 2.56; N, 8.9-. Found: C, 37.87; H, 2.35; N, 8.80. ESR (acetone): g_1 = 3.10, g_2 = 1.90, g_3 = 1.58. ^{1}H NMR (200 MHz, CD_3CN) δ -8.0, -2.2, 13.4, 16.2, 18.0. ^{31}P NMR (200 MHz, benzene-d_6) δ 145.
6. Winter, R. F.; Brunner, B. M.; Scheiring, T. *Inorg. Chim. Acta* **2000**, *310*, 21.
7. *Crystal data*: $C_{40}H_{32}N_8Cl_2PF_6Ru$, monoclinic, space group *C*2/*c*, 629.31 amu, *a* = 15.1713(3), *b* = 13.2604(3), *c* = 12.5217(3) Å, *β* = 109.1907 (7)°, *V* = 2379.10(9) Å^3, Z = 4, *T* = 293(2) K, d_{calc} = 1.757 Mg m^{-3}, μ = 1.014 mm^{-1}. Crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 705543.
8. Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 3060 and references therein.
9. Eggleston, D. S.; Goldsby, K. A.; Hodgson, D. J.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 4573.
10. Toupet, L.; Dixneuf, P. H.; Akkurt, M.; Daoudi, M.; Sam, N.; Kerbal, A,; Chohan, Z. H.; Ben Hadda, T. *J. Chem. Crystal.* **2009**, *39*, 423 and references therein.
11. Scaringe, R. P.; Singh, P.; Eckberg, R. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1975**, *14*, 1127 and references therein.
12. Taube, H. *Survey of Progress in Chemistry*; Academic Press: New York, 1973.