

Europium(III) Catalyzed Recyclization of 2-(5-Isoxazolyl)phenol: Synthesis and Structure of Benzopyran Derivative

Yunghee Oh,^{*} Chul Ho Lee, Jae Soo Choi,[†] and Sung Kwon Kang^{*,*}

Department of Chemistry, Donggeui University, Pusan 614-714, Korea

[†]Department of Chemistry, Chungnam National University, Daejeon 305-764, Korea. *E-mail: skkang@cmu.ac.kr

Received October 9, 2007

Key Words : Benzopyran, Recyclization, Europium, Isoxazolylphenol, X-ray structure

Europium complexes exhibit sharp red emission bands due to its 4f electrons. Especially those coordinated by chelating oxygen ligands such as β -diketones show good stability in the air and can be used as red emitting materials.¹ To improve the emitting color or luminescence efficiency, neutral nitrogen donating ligand such as phenanthroline or 2,2'-bipyridine was added to the Eu compound coordinated by oxygen donating ligands.^{1c} However, Eu compounds only with nitrogen donating ligands especially with aromatic nitrogens^{2,3} are not much compared to the oxygen ligated Eu compounds due to weaker metal-nitrogen interaction.^{3,4} We had reported that Eu(III) complex obtained from the reaction of EuCl₃ and 2,2'-dipyridylamine was decomposed to 2,2'-dipyridinium chloride and Eu compound in methanol solution.⁵

Herein, we investigate new Eu(III) complexes coordinated by both of nitrogen and oxygen by using 2-(5-isoxazolyl)phenol ligand in the same condition as corresponding 2,2'-dipyridylamine reaction.

Experimental Section

When EuX₃ (X = NO₃, Cl) reacted with 2-(5-isoxazolyl)phenol in the ethanol solution, a recyclized product, benzopyran derivative (**I**), was produced.

2 M NaOH solution (3 mL, 6 mmols) was added to 2-(5-isoxazolyl)phenol (0.484 mg, 3 mmols) and ethanol (20 mL). The mixture was stirred for about 30 min. until the color changed to yellow. Ethanol (20 mL) solution of EuX₃·nH₂O (1 mmol) was added to the yellowish ligand solution followed by stirring another 1 hour at room temperature. Filtered off the salts, the filtrate was stood for 1 week in the air. White crystals were filtered, washed with cold ethanol and dried in vacuum; Yield 89%, mp 270 °C, ¹H

NMR (300 MHz, CD₃OD, 25 °C) 7.2-8.2 ppm. At the first stage of the reaction, Eu complex was produced. It was evidenced by red light emission of the product, which is the typical property of Eu(III) complex.⁶ When the reaction mixture was kept for one week, new organic compound, **I**, was produced, not containing Eu metal.

The data for X-ray structure determination was collected on a CAD-4 diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 295 K. The unit cell dimensions were determined on the basis of 22 reflections in the range of $8.03^\circ < \theta < 13.14^\circ$. The data was collected by the $\omega/2\theta$ scan mode. The standard direct method was used to position the heavy atoms. The remaining non-hydrogen atoms were located from the subsequent difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms ($B_{H} = 1.2B_{eq}$). The structure was refined in a full matrix least-squares calculation on F^2 . Program used to solve structure and to refine structure; SHELXS97 and SHELXL97.⁷ Molecular graphics; Ortep-3 for windows.⁸

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-660511). The data can be obtained free of charge via www.ccdc.cam.ac.uk/deposit (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-01223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

The compound **I** emits green light when it is excited by uv light. It is clear that Eu(III) catalyzes the formation of **I**.⁹ When 2-(5-isoxazolyl)phenol was reacted with base without Eu(III), **I** was not produced. The Eu(III) catalytic reaction can be used to synthesize organic compounds containing nitrogen atom especially benzopyrans, which are now interestingly investigated because of its biological activities.¹⁰ Although, at this stage, we have not thoroughly figured out the reaction mechanism, we are still investigating the reaction mechanism including recyclization. We propose an Eu complex ligated by nitrogen as well as oxygen before nitrogen-oxygen cleavage as an intermediate as shown in Figure 2. As the intermediate of Eu complex coordinated by nitrogen donating ligand is unstable in the

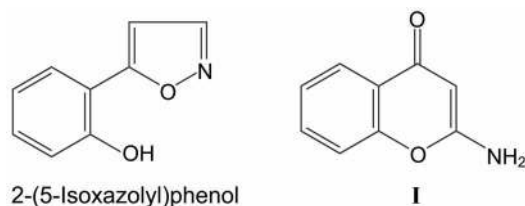
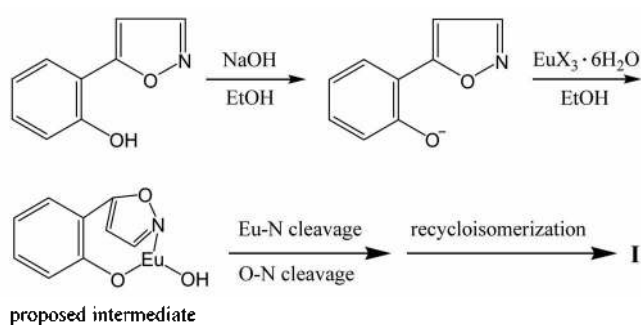


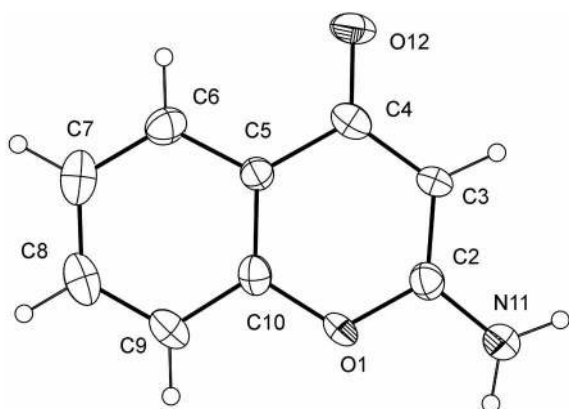
Figure 1. 2-(5-Isoxazolyl)phenol and 4H-1-benzopyran-2-amino-4-one (**I**).

**Figure 2.** Synthetic Route of **I**.**Table 1.** Crystal data and structure refinement for **I**, $C_9H_7NO_2$

Chemical formula	$C_9H_7NO_2$
Formula weight	161.16
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2(1)/c$
Unit cell dimensions	$a = 7.1869(14)$ Å $a = 90^\circ$ $b = 10.156(2)$ Å $\beta = 102.89(3)^\circ$ $c = 10.575(2)$ Å $\gamma = 90^\circ$
Volume	$752.4(3)$ Å ³
Z, Calculated density	4, 1.423 mg/m ³
F(000)	336
Crystal size	$0.23 \times 0.2 \times 0.2$ mm
Reflections collected/unique	1478 / 1399 [$R_{int} = 0.0540$]
Data/restraints/parameters	1399 / 0 / 109
Goodness-of-fit on F^2	0.962
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0790$, $wR2 = 0.1145$
R indices (all data)	$R1 = 0.2444$, $wR2 = 0.1635$
Largest diff. peak and hole	0.207 and -0.289 eÅ ⁻³

reaction condition, it will be decomposed to organic compound **I** and Eu compound.⁵

The crystallographic data and structure refinement parameters of **I**, $C_9H_7NO_2$, are summarized in Table 1. The selected bond distances and bond angles are summarized in Table 2. And an ORTEP view of including the atomic numbering scheme is shown in Figure 3. All atoms in **I** are

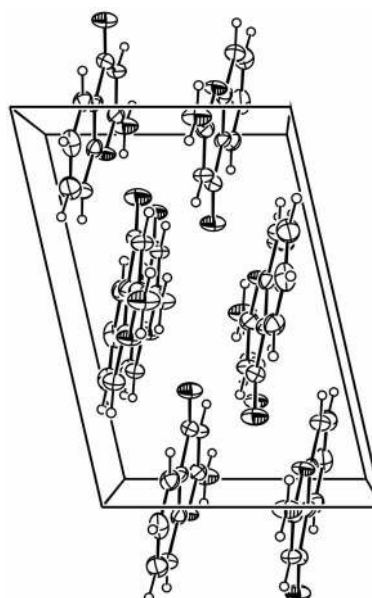
**Figure 3.** ORTEP diagram of $C_9H_7NO_2$, showing the atom numbering scheme.**Table 2.** The selected bond distances (Å) and angles ($^\circ$) of **I**, $C_9H_7NO_2$

O(1)-C(2)	1.355(6)	O(1)-C(10)	1.387(5)
C(2)-N(11)	1.322(6)	C(2)-C(3)	1.359(7)
C(3)-C(4)	1.403(7)	C(4)-O(12)	1.247(6)
C(4)-C(5)	1.465(7)	C(5)-C(10)	1.381(7)
C(2)-O(1)-C(10)	118.4(5)	N(11)-C(2)-O(1)	111.6(5)
N(11)-C(2)-C(3)	125.2(6)	O(12)-C(4)-C(3)	124.8(6)
O(1)-C(2)-C(3)	123.2(6)	C(2)-C(3)-C(4)	121.8(6)

Table 3. Hydrogen bonding geometries (Å, $^\circ$) of **I**, $C_9H_7NO_2$

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(DHA)$
N(11)-H(11A)...O(12)#1	0.86	2.14	2.921(6)	150.4
N(11)-H(11B)...O(12)#2	0.86	2.09	2.876(6)	150.9

Symmetry transformations used to generate equivalent atoms: #1 $x, -y + 1/2, z + 1/2$ #2 $-x + 1, y + 1/2, -z + 1/2$

**Figure 4.** A molecular packing diagram of $C_9H_7NO_2$, viewing normal to b -axis.

placed at the same plane, which means this molecule is a conjugated system. The bond distances of O1-C2 (1.355(6) Å) and O1-C10 (1.387(5) Å) are much shorter than the normal C-O single bond of 1.416 Å. The C2-N11 distance of 1.322(6) Å is also shorter than the typical C-N single bond distance of 1.474 Å.¹¹ These bond distances and angles are also supporting the conjugated system in the heterocyclic ring. Figure 4 shows a molecular packing diagram for **I** in solid. The molecules are weakly held together by N-H...O hydrogen bonds in the unit cell. The hydrogen bond distances and angles are summarized in Table 3.

In conclusion, benzopyran derivative, 4H-1-benzopyran 2-amino-4-one (**I**), was prepared from the reaction of 2-(5-isoxazolyl)phenol and EuX_3 ($X = NO_3, Cl$). The compound **I** emits green light when irradiated by UV light. Structure of **I** was characterized by single crystal X-ray and ¹H NMR

methods. A proposed intermediate, Eu(III) complex coordinated by nitrogen donating ligands might be unstable and decomposed to organic and metal compounds. The mechanistic study is in progress.

Acknowledgement. This work was supported by Dong-eui University Foundation Grant (2005AA096). X-ray data were collected at the Center for Research Facilities in Chungnam National University.

References

1. (a) Paw, W.; Cummings, S. D.; Mansour, M. A.; Geiger, D. K.; Eisenberg, R. *Coord. Chem. Rev.* **1998**, *171*, 125. (b) Wu, F. B.; Zhang, C. *Analyt. Biochem.* **2002**, *311*, 57. (c) Liu, H.-G.; Jang, K.; Feng, X.-S.; Kim, C.; Yoo, Y.-J.; Lee, Y.-J. *Bull. Kor. Chem. Soc.* **2005**, *26*, 1969. (d) Kang, J.-G.; Kim, T.-J. *Bull. Kor. Chem. Soc.* **2005**, *26*, 1057. (e) Kido, J.; Okamoto, Y. *Chem. Rev.* **2002**, *102*(6), 2357.
2. Mazzanti, M.; Wietzke, R.; Pecaut, J.; Latour, J.-M.; Remy, M. *Inorg. Chem.* **2002**, *41*, 2389.
3. Wietzke, R.; Mazzanti, M.; Latour, J.-M. *Inorg. Chem.* **1998**, *37*, 6690.
4. Melby, L. R.; Rose, N. J.; Abramson, E.; Caris, J. C. *J. Am. Chem. Soc.* **1964**, *86*, 5117.
5. Oh, Y.; Lee, C.; Lee, B.; Shin, B. *Key Engineering Mater.* **2005**, *277-279*, 966.
6. When we evaporated all the solvent, the residual white solid shows red light emission by uv light. We could not characterize the structure as it turned to the Compound I during the recrystallization process.
7. Sheldrick, G. M. *SHELXS97* and *SHELXL97*, Program for the Refinement of Crystal Structures; University of Göttingen: Germany, 1997.
8. Farrugia, L. J. *J. Appl. Cryst.* **1997**, *30*, 565.
9. For example of metal-catalyzed cyclization, see (a) Seregin, I. V.; Gevorgyan, V. *J. Am. Chem. Soc.* **2006**, *128*, 12050. (b) Dubé, P.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 12062. (c) Anniyappan, M.; Muralidharan, D.; Perumal, P. T. *Tetrahedron* **2002**, *58*, 10301.
10. (a) Roma, G.; Cinone, N.; Braccio, M. D.; Grossi, G.; Leoncini, G.; Signorello, M. G.; Carotti, A. *Bioorg. Medicin. Chem.* **2000**, *8*, 751. (b) Kim, N.; Lee, S.; Yi, K. Y.; Yoo, S.; Lee, C. O.; Park, S. H.; Lee, B. H. *Bioorg. Medicin. Chem. Lett.* **2003**, *13*, 1661. (c) Salim, A. A.; Pawlus, A. D.; Chai, H. B.; Farnsworth, N. R.; Kinghorn, A. D.; Carcache-Blanco, E. J. *Bioorg. Medicin. Chem. Lett.* **2007**, *17*(1), 109. (d) Koufaki, M.; Kiziridi, C.; Papazafiri, P.; Vassilopoulos, A.; Varr, A.; Nagy, Z.; Farkas, A.; Makriyannis, A. *Bioorg. Medicin. Chem. Lett.* **2006**, *14*, 6666.
11. Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: 1984.