

## Syntheses of Metallic Monoazo Complexes\*

by

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(Received April 18, 1968)

### Monoazo 金屬錯鹽의 合成

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韓治善 · 朴大詰 · 南宮河一 · 姜龍翊

(1968, 4, 18. 受理)

#### 要 約

몇가지 ortho-hydroxy monoazo 化合物들을 合成하여 이것들을 遷移元素로 金屬化시켰다. 三酸化크롬, 酢酸銅 및 酢酸코발트를 이 金屬錯鹽生成反應에 使用하였다. 이 研究에서 다음과 같은 事實들을 알 수 있었다. (1) 이 金屬錯鹽生成反應에서의 溶媒는 다른 여러가지 有機溶媒보다는 물이 가장 좋고, (2) 金屬錯鹽生成反應 混合液의 가장 適當한 液性온 pH=4.5~5.5 程度이었으며, (3) 이들 monoazo 金屬錯鹽의 물에 대한 溶解性은 주로 그 錯鹽의 組成에 달렸으나 어느 程度는 分子內의 黃酸基의 存在에 의하여서도 影響을 받는다. 그리고 (4) 分子當 두개의 ortho-hydroxy 基를 가진 金屬錯鹽이 더 강한 結合能을 가지고 있다.

#### ABSTRACT

Some ortho-hydroxy monoazo-compounds have been synthesized and these were metallized with transition elements. Chromium trioxide, cupric acetate and cobalt acetate were used for the metallization. The following facts have been found in this investigation: (1) water is the best solvent, when compared to various organic solvents, for the metallization, (2) the optimum pH for the metallizing mixture ranges from 4.5 to 5.5, (3) the solubility of these metallic monoazo-compounds in water depends mainly on the composition of the complexes and to some extent on the presence of sulfonic acid groups in the molecules, and (4) metallized compounds having two ortho-hydroxy groups per molecule have stronger binding characteristics.

Extensive studies of the metallization of azobenzene derivatives were reported after the fact that the azo-

group could be metallized became known.<sup>(1-10)</sup> However, the experimental detail on the metallization of azo-com-

\* (a) Abstracted from a report submitted to the Ministry of Science and Technology(MOST) by C. S. Hahn, 1967; (b) Supported by a grant(E67-PO9R-28) from MOST; (c) This paper comprises a portion of the dissertation submitted by D. C. Park in partial fulfillment of the requirements for the M. S. degree in The Graduate School of Yonsei University, Seoul, Korea, 1968.

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pounds has not been precisely reported in the literature. Thus, the authors have synthesized some azo-compounds for metallization with the intent of disclosing the reaction conditions for metallization. The metals chosen were transition elements: chromium, copper and cobalt. In addition, the relation between the solubility and the composition of these complexes as well as other properties were also studied.

### Results and Discussion

In order to investigate the dependence of the bond between the azo-group and transition metals on the presence of functional groups in the molecules, the following preliminary experiments were performed. Azo-compounds having a hydroxyl group at the *ortho* position with respect to the azo-group and those without the hydroxyl group were synthesized by coupling diazonium salts with the corresponding coupling components.

Each of the diazonium salts obtained by the usual method possesses a sulfamyl group at the *para* instead of the *ortho* position. *p*-Sulfamyl substituted diazonium components were used primarily to increase the water-solubility of the resulting azo-compounds.

These azo-compounds thus synthesized were treated with cupric acetate in methyl alcohol by refluxing for about three hours. The composition ratio of the reactants was one to one and the reaction mixture was kept weakly basic with ammonium hydroxide. The results of the metallization under the above conditions are shown in Table 1. Whether or not compounds 1-6 were metallized was readily confirmed by the difference of water solubilities, the variation of colours and the change of melting points. Since all the original azo-compounds prior to metallization had a sulfamyl group in their molecules, they were soluble either in various organoprotic solvents or water to some extent. However, those which were suspected to be metallized were found to be insoluble in both organic solvents and water, and they were sparingly soluble in boiling aprotic solvents. The colour of the metallized azo-compounds was without exception deepened and the variation of the colours was easily discerned by the human eye. Also, the melting points of the metallized compounds were too high to be measured by a common oil bath, whereas those of the original compounds were, in general, low enough to be measured. These facts made clear the variation of the original com-

Table 1. The results of metallization of substituted 4-azobenzenesulfonamides

No.	Substituent(X)	Mp, °C	Upon metallization
1. 4-N, N-Dimethylaminophenylazo-4'-benzenesulfonamide	$(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4-\text{SO}_2\text{NH}_2$	260-1.5	Recovered
2. 4-Hydroxyphenylazo-4'-benzenesulfonamide	$\text{HO}-\text{C}_6\text{H}_4-\text{SO}_2\text{NH}_2$	254-6	Recovered
3. 4-Naphtholazo-4'-benzenesulfonamide	$\text{HO}-\text{C}_{10}\text{H}_7-\text{SO}_2\text{NH}_2$	262-3	Recovered
4. 2-Hydroxy-4-aminophenylazo-4'-benzenesulfonamide	$\text{H}_2\text{N}-\text{C}_6\text{H}_3(\text{OH})-\text{SO}_2\text{NH}_2$	222-5	Metallized
5. 2-Naphtholazo-4'-benzenesulfonamide	$\text{C}_{10}\text{H}_7(\text{OH})-\text{SO}_2\text{NH}_2$	254-5	Metallized
6. 2-Hydroxy-5-bromophenylazo-4'-benzenesulfonamide	$\text{Br}-\text{C}_6\text{H}_3(\text{OH})-\text{SO}_2\text{NH}_2$	225-7	Metallized

Table 2. Intermediates selected for the coupling reaction

No.	Diazonium component	No.	Coupling component
7.	1-Diazo-2-naphthol-4-sulfonic acid	14.	1-Phenyl-3-methyl-5-pyrazolone
8.	2-Diazophenol-4-sulfonic acid	15.	2-Naphthol-6-sulfonic acid
9.	Metanilic acid	16.	$\beta$ -Naphthol
10.	2-Amino-4-nitrophenol	17.	2-Naphthol -3,6-disulfonic acid
11.	1-Diazo-2-naphthol-4-sulfonic acid, 6-nitro	18.	2-Naphthol-6-sulfonic acid
12.	1-Diazo-2-naphthol-4-sulfonic acid	19.	$\beta$ -Naphthol
13.	1-Diazo-2-naphthol-4-sulfonic acid, 6-nitro	20.	$\beta$ -Naphthol

pounds upon metallization.

Based on the above criteria, it was found, as shown in Table 1, that compounds 4-6 were metallized while compounds 1-3 were not. The original compounds 1-3 and 4-6 differ only in respect to the presence of a hydroxyl group in their molecules. The latter have a hydroxyl group at the *ortho* position with respect to the azo-group, and the former have no hydroxyl group. Even when the former has a hydroxyl group, it is at the *para*, not *ortho*, position. These facts clearly show that azo-compounds which are intended for metallization with transition elements should possess at least a hydroxyl group at the *ortho* position. Therefore, it can readily be recognized that the metallic complex of azo-compounds is a sort of chelate type coordinate compound.

In order to simplify the metallization, the feasibility of an one-pot reaction, in which the metallization and the coupling reaction are supposed to proceed at the same time, has been studied. However, it was not successful, and it has been found that a stepwise metallization must be undertaken. That is, each metallizing agent should be treated with its respective azo-compound which is obtained separately.

Since the presence of a hydroxyl group is the basic requirement for the metallization of monoazo-compounds, the intermediates were also selected in accordance with this requirement, as shown in Table 2. All the intermediates were synthesized except  $\beta$ -naphthol which was Japanese reagent grade and used without further purification.

The diazonium and coupling components on the same row in Table 2 were coupled by the usual method, and the monoazo-compounds so obtained are listed in Table 3. Elemental analyses were not performed on the intermediates and the monoazo-compounds, but

only on the final metallized products. The estimates of yields in Table 3 are based on the crude products.

It should be noted from Tables 2 and 3 that either one or both of the intermediates, diazonium and

Table 3. Monoazo-compounds synthesized for the metallization

No.	Compounds	Yield, %
21.	1-Phenyl-3-methyl-4-(2'-naphtholazo-4'-sulfonic acid)-5-pyrazol	99
22.	1-(1'-Azo-2'-hydroxy-5'-benzenesulfonic acid)-2-naphthol-6-sulfonic acid	97
23.	1-(1'-Azo-3'-benzene-sulfonic acid)-2-naphthol	88
24.	1-(2'-Azo-4'-nitrophenol)-2-naphthol-3, 6-disulfonic acid.	92
25.	1-(2'-Naphtholazo-6'-sulfonic acid)-2-naphthol-4-sulfonic acid, 6-nitro	92
26.	1-(2'-Naphtholazo)-2-naphthol-4-sulfonic acid	96
27.	1-(2'-Naphtholazo)-2-naphthol-4-sulfonic acid, 6-nitro	98

coupling components, in the same row have sulfonic acid groups and all the resulting monoazo-compounds are mono- or dibasic sulfonic acids. This was simply because of an attempt to increase the water-solubility. It was initially expected that the azo-compounds having a sulfamyl group in Table 1 would be easily soluble in water. However, the azo-compounds possessing the sulfamyl group and no sulfonic acid groups were not as soluble in water as had originally been expected, although it is true that the sulfamyl group contributed to the solubility. Furthermore, the water-solubility of the metallized complexes having no sulfonic acid groups was less. Therefore, sulfonic acid groups were substituted into the original monoazo-compounds prior to the coupling reaction in an attempt to increase the water-solubility.

Table 4. 1:2 Metallized mono-azo compounds

No.	Yield, %	Formula	Calcd., %			Found*, %		
			C	H	N	C	H	N
21—Cr	85	C <sub>40</sub> H <sub>27</sub> O <sub>10</sub> N <sub>8</sub> S <sub>2</sub> Na <sub>2</sub> Cr	51.01	2.89	11.90	51.25	2.80	11.78
21—Cu	99	C <sub>40</sub> H <sub>28</sub> O <sub>10</sub> N <sub>8</sub> S <sub>2</sub> Na <sub>2</sub> Cu	50.34	2.96	11.74	50.46	2.82	12.02
21—Co	80	C <sub>40</sub> H <sub>28</sub> O <sub>10</sub> N <sub>8</sub> S <sub>2</sub> Na <sub>2</sub> Co	50.59	2.97	11.80	51.33	2.75	11.64
22—Cr	93	C <sub>32</sub> H <sub>17</sub> O <sub>10</sub> N <sub>4</sub> S <sub>4</sub> Na <sub>4</sub> Cr	39.00	1.74	5.69	38.54	1.63	5.77
22—Cu	88	C <sub>32</sub> H <sub>18</sub> O <sub>10</sub> N <sub>4</sub> S <sub>4</sub> Na <sub>4</sub> Cu	38.52	1.82	5.61	37.73	1.75	5.74
22—Co	80	C <sub>32</sub> H <sub>18</sub> O <sub>10</sub> N <sub>4</sub> S <sub>4</sub> Na <sub>4</sub> Co	38.68	1.83	5.64	38.31	1.76	5.73
23—Cr	82	C <sub>32</sub> H <sub>20</sub> O <sub>8</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub> Cr	51.20	2.69	7.46	50.33	2.51	7.40
23—Cu	88	C <sub>32</sub> H <sub>20</sub> O <sub>8</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub> Cu	50.43	2.65	7.35	50.70	2.68	7.31
23—Co	85	C <sub>32</sub> H <sub>20</sub> O <sub>8</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub> Co	50.73	2.66	7.40	50.78	2.61	7.39
24—Cr	91	C <sub>32</sub> H <sub>17</sub> O <sub>14</sub> N <sub>6</sub> S <sub>2</sub> N <sub>2</sub> Cr	44.10	1.97	9.64	44.15	1.88	9.59
24—Cu	86	C <sub>32</sub> H <sub>18</sub> O <sub>14</sub> N <sub>6</sub> S <sub>2</sub> Na <sub>2</sub> Cu	43.47	2.05	9.51	43.51	2.11	9.58
24—Co	88	C <sub>32</sub> H <sub>18</sub> O <sub>14</sub> N <sub>6</sub> S <sub>2</sub> Na <sub>2</sub> Co	43.70	2.06	9.55	43.60	2.12	9.50
25—Cr	90	C <sub>40</sub> H <sub>10</sub> O <sub>20</sub> N <sub>6</sub> S <sub>4</sub> Na <sub>4</sub> Cr	40.86	1.63	7.15	40.01	1.66	5.38
25—Cu	83	C <sub>40</sub> H <sub>20</sub> O <sub>20</sub> N <sub>6</sub> S <sub>4</sub> Na <sub>4</sub> Cu	40.43	1.70	7.07	40.35	1.61	7.18
25—Co	90	C <sub>40</sub> H <sub>20</sub> O <sub>20</sub> N <sub>6</sub> S <sub>4</sub> Na <sub>4</sub> Co	40.59	1.70	7.10	40.50	1.61	7.18
26—Cr	91	C <sub>40</sub> H <sub>23</sub> O <sub>10</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub> Cr	54.49	2.63	6.36	54.63	2.69	6.30
26—Cu	91	C <sub>40</sub> H <sub>24</sub> O <sub>10</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub> Cu	53.72	2.71	6.26	53.64	2.80	6.33
26—Co	96	C <sub>40</sub> H <sub>24</sub> O <sub>10</sub> N <sub>4</sub> S <sub>2</sub> Na <sub>2</sub> Co	54.00	2.72	6.30	54.05	2.78	6.38
27—Cr	93	C <sub>40</sub> H <sub>21</sub> O <sub>14</sub> N <sub>6</sub> S <sub>2</sub> Na <sub>2</sub> Cr	49.44	2.18	8.65	49.51	2.11	8.60
27—Cu	94	C <sub>40</sub> H <sub>22</sub> O <sub>14</sub> N <sub>6</sub> S <sub>2</sub> Na <sub>2</sub> Cu	48.81	2.25	8.54	48.89	2.34	8.49
27—Co	82	C <sub>40</sub> H <sub>22</sub> O <sub>14</sub> N <sub>6</sub> S <sub>2</sub> Na <sub>2</sub> Co	49.04	2.26	8.58	49.15	2.32	8.48

\* The elemental analysis were primarily made at the University of Tokyo, Japan, but some were made at Sung-Kyun-Kwan University, Seoul, Korea.

Each of the fundamental monoazo-compounds in Table 3 thus synthesized was bonded with chromium, copper and cobalt by treating with chromium trioxide, cupric acetate and cobalt acetate, respectively. Sodium or potassium bichromate instead of chromium trioxide was also effective for the metallization and resulted in equivalent yields. The purity of the final products was confirmed by paper chromatography<sup>(11a)</sup> and elemental analysis. The results of the analyses are summarized in Table 4. Since all the products have sulfonic acid groups within the molecules, the complexes were isolated by salting out using a saturated sodium chloride solution. Many solvents such as water, aqueous alcohol and various other organic solvents were examined for use in metallization, and it was found that water was the best one among them all. The reaction mixture, in general, was refluxed for four to five hours, keeping the pH between 4.5 and 5.5. However, the metallizing mixture of compounds 4—6 in Table 1 was kept weakly basic when these were treated with cupric acetate. This was based on the expectation that the metallizing mixture would reach equilibrium in this range of

basicity due to the presence of a sulfamyl group. The reliability of this anticipation was proved by examining the reaction conditions. Also, since the monoazo-compounds in Table 3 have two substituted hydroxyl groups and since sulfonic acid is formed during the metallization, the metallizing media for compounds 21—27 were kept in the weakly acidic range. In fact, the acidity of some metallized azo-compounds which are similar to those in this investigation have been reported<sup>(12)</sup>. Therefore, it is concluded from the present study that the optimum pH for the metallizing mixture is the pH of the metallizing azo-compound.

It has been previously noted that the solubility in water of the fundamental azo-compounds substituted with sulfonic acid groups instead of sulfamyl groups was significantly increased. However, the water-solubility of the metallized complexes composed of the metals and the fundamental azo-compounds in a ratio of one to one was not satisfactory for practical purpose, and it was found that solubility is not substantially dependent on the presence of water soluble functional groups. Therefore, the composition ratio of the resulting

metallic complexes was varied. An excess amount of the fundamental azo-compound was added to the metallizing mixture in order to obtain a one to two complex. The results of elemental analyses in Table 4 clearly prove that the composition ratio of the metals to the fundamental azo-compounds is one to two. These one to two complexes are apparently different from the one to one complexes in respect to solubility. The former are very soluble in water compared to the latter. The dependence of water-solubility on the variation of composition ratio seems likely to be due to differences in the structures of the complexes.

Finally, it should be noted that all the azo-compounds except No. 23 have two hydroxyl groups at the two *ortho* positions. This is because of an attempt to increase the binding force between the fundamental azo-molecule and the metal. This anticipation is based on the foregoing preliminary experiments, that is, the metallization of azo-compounds is due to the concerted effect of coordinate and chelate bonding. In fact, it has been found that the one to two complexes derived from fundamental azo-compounds having two hydroxyl groups are more strongly bound than either the non-metallized compounds or the one to one metallic complexes. The correctness of these suppositions and the experiments has been proved by determining the sun-light and wash fastness of these one to two complexes. <sup>(11a)</sup>

## Experimental Section

### Preparation of Derivatives of Substituted

#### 4-Azobenzene-sulfonamide (1-6)

Compounds of this series were synthesized by coupling 4-benzenesulfonamide diazonium chloride with the corresponding coupling components. Sulfanilamide was obtained through the following three reaction steps. First, formanilide was made by treating aniline with formic acid. The reaction temperature was maintained between 100 and 110° for 3 hr. Yield, 98%; mp 46-70(bp 148°/7mm Hg); colorless white crystals. Next, treating the above formanilide with chlorosulfonic acid, *p*-formylaminobenzenesulfonyl chloride was obtained. Yield, 98%; during the addition of chlorosulfonic acid the temperature was kept below 50°; reaction temper-

ature, 90°; reaction duration, 1 hr. Finally, into the above *p*-formylaminobenzenesulfonyl chloride was added a 25% aqueous ammonium solution in an ice-bath. The mixture was placed in a sealed system and heated slowly in a boiling water-bath for 1-1.5 hr. White crystalline sulfanilamide was thus synthesized; mp 163-4°; infrared(KBr pellet), 3480 and 3360(NH<sub>2</sub>), 1600-1500 (benzene nuclei) and 1100 cm<sup>-1</sup> (SO<sub>2</sub>). Diazotization of the sulfanilamide was performed by the usual method. N,N-Dimethylaniline to be coupled with the diazonium salt of the above sulfanilamide was used after distillation(bp 52-4°/mm Hg). After the addition of the diazonium salt, the mixture was stirred for 3 hr. The crude product was recrystallized from a mixed solvent of acetone and water(3:1); mp 260-1.5°; leaf-like crystals; Yield, 66%. Coupling components besides the N,N-dimethylaniline in Table 1, *i.e.*,  $\alpha$ - and  $\beta$ -naphthol, phenol, *m*-aminophenol and *m*-bromophenol were Wako(Japanese) reagent grade and used without further purification.

#### 1-Diazo-2-naphthol-4-sulfonic acid (7, 12) and 1-Diazo-2-naphthol-4-sulfonic acid, 6-nitro(11, 13)

Compound 7 was synthesized by the following three steps. 1-Nitroso-2-naphthol was obtained by nitrosating  $\beta$ -naphthol with sodium nitrite, to which were added sodium sulfite and sulfuric acid, and 1-amino-2-naphthol-4-sulfonic acid was obtained. Finally, this was diazotized with sodium nitrite. Yield, 57.2%(from  $\beta$ -naphthol); very stable intermediate; infrared, 1600 (conjugate system), 1500, 1420 and 1050(deformation of substituents on 1-, 2- and *o*-positions), 1200 and 850cm<sup>-1</sup>(SO<sub>3</sub>H). Compound 13 was easily obtained by nitrosating compound 7; yield, almost quantitative (98%).

#### 2-Aminophenol-4-sulfonic acid(8)<sup>(11d)</sup> and 2-Amino-4-nitrophenol(10)

Compound 8 was synthesized by reducing 2-nitrophenol-4-sulfonic acid obtained by sulfonation and nitration of phenol. The reducing agents were iron powder and hydrochloric acid. Over-all yield, 78%; infrared, 4000-3000 (NH<sub>2</sub>, OH overlapped), 1440 (deformation of OH), 1200-1030(1, 2, 4-substituents) and 1240-1030cm<sup>-1</sup> (SO<sub>3</sub><sup>-</sup>). Compound 10 was synthesized by partial reduction of sodium dinitrophenolate

with sodium sulfide and ammonium chloride. The phenolate was obtained by treating 2,4-dinitrochlorobenzene with sodium hydroxide.

#### 1-Phenyl-3-methyl-5-pyrazolone(14)<sup>(11e)</sup>

This compound was synthesized by treating phenylhydrazine with ethyl acetoacetate. The phenylhydrazine was obtained by reducing benzenediazonium chloride with sodium sulfite. Yield, 80%; bp 135-8°/18mm Hg. Into an alcoholic solution of ethyl acetoacetate was added the above obtained phenylhydrazine and refluxed vigorously for 5 hr. Yield, 98%; infrared, 3400 (C-H), 1600(C=O) and 1400-1300  $\text{cm}^{-1}$  (pyrazoline ring).

#### 2-Naphthol-6-sulfonic acid(15, 18) and 2-Naphthol-3,6-disulfonic acid(17)<sup>(11f)</sup>

These compounds were obtained from the sulfonation mixture of  $\beta$ -naphthol, and isomeric forms of 3,6- and 6,8- disulfonic acids were also obtained from the filtrate of 2-naphthol-6-sulfonic acid, which were separated from each other by fractionation. Yield of the monosulfonic acid was ca 80%; 3,6-isomer of disulfonic acid, ca 10%.

#### Coupling Reaction<sup>(11g)</sup>

Diazotization and coupling reaction were followed by the usual methods. Yields in the formation of these azo-compounds were almost quantitative, higher than 90% in most cases. Azo-compounds thus synthesized were identified by the presence of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  bands in the UV spectra.<sup>(12)</sup>

#### Metallization<sup>(11h)</sup>

Two methods were examined to metallize the fundamental azo-compounds to form 1:2 complexes. The first one was a step-wise metallization, that is, complexes having 1:1 compositions were synthesized in the first place, followed by treating the complexes with an excess amount of the fundamental azo-compounds. The second method was a one-pot metallization, that is, the metallizing agent and the fundamental azo-compound were mixed in the ratio of 1:2 in the initial stage and were refluxed. In the latter case, a slight excess of the fundamental azo-compounds was used. As a typical example, 1-phenyl-3-methyl-4-(2-naphthol-

azo-4'-sulfonic acid)-5-pyrazol was metallized with chromium as follows: chromium trioxide(15g, 0.015 mole) was dissolved in 20 ml of formic acid, added to 50 ml of water, and heated. Care was taken during the addition of the chromium trioxide because of the evolution of gases, and the reaction vessel was cooled since the reaction was exothermic.

The colour of the reaction mixture deepened as the metallization proceeded. Then 1-phenyl-3-methyl-4-(2'-naphtholazo-4'-sulfonic acid)-5-pyrazol(15.1g, 0.034 mole) was dissolved in 500 ml of water and adjusted to pH=4.5-5.5 with dilute hydrochloric acid. To this was added the above chromium trioxide solution at a time, and the whole mixture was refluxed for 20-22 hr. The reaction temperature was maintained at 100°. The residue was filtered off while the mixture was hot. After washing with a small amount of water 2-3 times, the residue was dried. The filtrate was condensed to ca 50 ml, from which more complexes were obtained by cooling. These were combined with the above residue, and washed with dilute hydrochloric acid 2-3 times. Recrystallized from aq. EtOH 3 times, red crystals; obtained 11.7 g (85% yield);  $\lambda_{\text{max}}$  of UV spectrum, 530m  $\mu$ ; single spot on a chromatogram; analysis, No. 21-Cr in Table 4.

#### Acknowledgment

We wish to thank the Ministry of Science and Technology for the financial support, under grant No. E67-PO9R-28. The authors are also grateful to Kook-Jin Bae, Kwi-Ja Lee, Jung-Ja Park, and Kyung-Soon Yang for their valuable assistance. Thanks are extend to Hyuk-Koo Lee, University of Kansas, for the IR spectra measurements.

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