

values of  $\alpha_c$  and  $\alpha_h$  are generally of a few tens of  $\mu\text{V/K}$  and proportional to  $T$  when Fermi level is situated in a band.<sup>12</sup> Therefore, the sign-change of  $\alpha$  from + to - with temperature should be primarily attributed to the augmentation of  $\sigma_e/\sigma_{tot}$  as  $T$  increases. Such a tendency is apparently strengthened for the nonmetallic phases, in which carriers are considered to move *via* hopping process by the aid of lattice vibration. The mobility of electron seems to be more easily activated than hole, since the electrons are associated with  $\text{Ni}^{2+}$  ions and can move from sites to sites, keeping the local symmetry as octahedral for both  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$ . But hopping of holes associated with  $\text{Ag}^{2+}$  ions would require a large change of local symmetry, from 4-fold rectangular ( $\text{Ag}^{2+}$ ) to 2-fold linear ( $\text{Ag}^+$ ).

In conclusion,  $\text{AgNi}_{1-x}\text{Fe}_x\text{O}_2$  undergoes a metal-insulator transition through the Anderson localization process with relatively a small substitution ratio  $x_c=0.1$  with respect to  $\text{AgNi}_{1-x}\text{Co}_x\text{O}_2$ , due to the large random potential introduced by  $\text{Fe}^{3+}$  ions and partly the reduced covalency of Ni-O bond.

**Acknowledgment.** This work was supported by the grant of (961-0306-057-2) from Korea Science and Engineering Foundation.

### References

1. Pabst, A. *Amer. Mineral.* **1946**, 31, 539.
2. Doumerc, J. P.; Ammar, A.; Wichainchai, A.; Pouchard, M.; Hagenmuller, P. *J. Phys. Chem. Solids* **1987**, 48, 37.
3. Rogers, D. B.; Shannon, R. D.; Prewitt, C. T.; Gillson, J. L. *Inorg. Chem.* **1971**, 10, 723.
4. Wichainchai, A.; Dordor, P.; Doumerc, J. P.; Marquestqut, E.; Pouchard, M.; Hagenmuller, P. *J. Solid State Chem.* **1988**, 74, 126.
5. Shin, Y. J.; Doumerc, J. P.; Dordor, P.; Pouchard, M.; Hagenmuller, P. *J. Solid State Chem.* **1993**, 107, 194.
6. Shin, Y. J.; Doumerc, J. P.; Dordor, P.; Delmas, C.; Pouchard, M.; Hagenmuller, P. *J. Solid State Chem.* **1993**, 107, 303.
7. Shannon, R. D.; Rogers, D. B.; Prewitt, C. T. *Inorg. Chem.* **1971**, 10, 713.
8. Shin, Y. J.; Kwak, J. H.; Yoon, S. *Bull. Kor. Chem. Soc.* **1997**, 18(7), 775.
9. Marcy, H. O.; Marks, T. J.; Kannewurf, C. R. *IEEE Trans. Instru. Meas.* **1990**, 39, 756.
10. Kim, D.; Honig, J. M. *Phys. Rev. B* **1994**, 49, 4438.
11. Shannon, R. D. *Acta Crystallogr.* **1976**, A32, 751.
12. Mott, N. F. *Metal-Insulator Transitions*; Taylor and Francis: London, 1991.
13. for example, Mott, N. F.; Kaveh, M. *Adv. Phys.* **1985**, 34, 329.
14. Bowser, J. R. *Inorganic Chemistry*; Brooks/Cole: Belmont, 1993.

## Synthesis and X-Ray Crystal Structure of Copper(II) Complex with Chiral Tetradentate $\text{N}_4$ Mono Amide Ligand, 2(S)-2,9-diamino-4,7-diazanonane-3-one(S-aladienH)

Bae-Wook Lee, Dong-Yeub Kim<sup>†</sup>, Bok-Jo Kim, Chang-Eon Oh, Bong-Gon Kim<sup>†</sup>, and Myung-Ki Doh\*

Department of Chemistry, Yeungnam University, Kyongsan 712-749, Korea

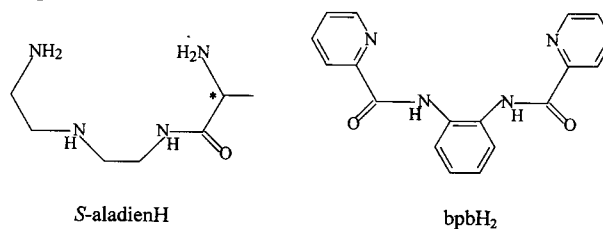
<sup>†</sup>Department of Chemical Industry, Yeungnam Junior College, Taegu 705-037, Korea

\*Department of Chemical Education, Kyeongsang National University, Chinju 660-701, Korea

Received January 20, 1998

Transition metal complexes of chelating ligands containing an amide functional group have received much attention as a result of a marked increase in the lability of amide portion.<sup>1</sup> Many investigations have revealed that the deprotonated nitrogen of organic amides donates to metal ions, stabilizing high oxidation states. Several examples of deprotonated bis-amides with the picolinamide unit as a basic component have been shown to act as tetradentate  $\text{N}_4$  ligands.<sup>2</sup> The bis-picolinamide ligands,  $N,N'$ -bis(2'-pyridinecarboxamide)-*cis*-1,2-cyclohexane(*cis*-bpch),<sup>2a</sup>  $N,N'$ -bis(2'-pyridinecarboxamide)-*trans*-1,2-cyclohexane(*trans*-bpch),<sup>2b</sup>  $N,N'$ -bis(2'-pyridinecarboxamide)-1,2-benzene(*bpbH*)<sup>2c</sup> and  $N,N'$ -bis(6'-methylpyridine-2'-carboxamido)-1,2-benzene(6-me**bpbH**)<sup>2d</sup> have a pronounced tendency for planar  $\text{N}_4$  tetradentate coordination to Cu(II) ion on deprotonation. They have been shown to take stereochemistries of a distorted

square-pyramid. However, few Cu(II) complexes have tetradentate chiral mono amide functionality. On the other hand, edda(ethylenediaminediacetato) type ligands seem to have a certain characteristic of hardly coordinating with metal ions in a plane.<sup>3</sup>



Thus, in this study we described the synthesis, spectral properties and X-ray crystal structure of  $[\text{Cu}(\text{S-aladien})\text{H}_2\text{O}]^+$  with chiral tetradentate mono amide ligand, 2(S)-2,9-

diamino-4,7-diazanonane-3-one(*S*-aladienH).

### Experimental

**Preparation of *S*-aladienH ligand.** *S*-phthaloyl-lalanyl was prepared from *S*-alanine (0.2 mol, 17.8 g) and phthalic anhydride (0.22 mol, 32.6 g) according to the method of Asperger *et al.*<sup>4</sup> and *N*-(*S*-phthaloyl-lalanyl)diethylenetriamine was prepared from the *S*-phthaloyl-lalanyl (0.12 mol, 26.3 g) and dien (0.12 mol, 12.4 g) by using dicyclohexylcarbodiimide (DCC) as a peptide reagent in dichloromethane.<sup>5</sup> The *S*-aladienH was obtained to remove the amine protecting group of *N*-(*S*-phthaloyl-lalanyl)diethylenetriamine by using hydrazine in ethanol. Yield of oil phase was ca. 50%. <sup>13</sup>C NMR (D<sub>2</sub>O), δ=21.04 (CH<sub>3</sub>), 39.27, 39.75, 48.41, 50.71 (CH<sub>2</sub> of dien backbone), 53.12 (chiral carbon of *S*-alanine moiety), 178.13 (C=O).

**Preparation of [Cu(*S*-aladien)H<sub>2</sub>O] BPh<sub>4</sub>·H<sub>2</sub>O.** *S*-aladienH (10 mmol, 3.2 g) and CuCl<sub>2</sub>·2H<sub>2</sub>O (8 mmol, 1.4 g) was dissolved in 50 mL water and pH was maintained at 8.0, and then the mixture was stirred for 4h. at 60 °C. The solution was diluted to 500 mL and then loaded onto a cation exchange resin (SP Sephadex C25) column. After the column was washed thoroughly with water, the adsorption band separated with 0.1 M NaClO<sub>4</sub>. The solution was evaporated to dryness and crystallized from an ethanol-ni-

tromethane mixture (1:1 by volume) added to sodium tetraphenylborate (NaBPh<sub>4</sub>). A blue-violet precipitate (1.4 g) was collected by filtration. Yield: 30%. Calc. for Cu<sub>1</sub>C<sub>31</sub>H<sub>39</sub>O<sub>3</sub>N<sub>4</sub>B<sub>1</sub>: C, 63.02; H, 6.83; N, 9.49. Found: C, 63.68; H, 6.77; N, 9.19.

**X-ray data collection.** The preliminary experiments as well as unit cell parameters and intensity data collection were performed on an Enraf Nonius CAD4 TURBO diffractometer with a graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda=0.71069$  Å). The intensity data were collected by the  $\omega$ -2 $\theta$  scan technique. A total of 6518 reflections up to  $2\theta_{\max}=52.64^\circ$  was collected, of which 1704 independent reflections with  $I>3\sigma(I)$  were used for the structure analysis. Crystallographic data and additional details of data collection and structure determination are summarized in Table 1. The structure was solved by MULTAN and refined by a full matrix least-squares refinement, using structure solution package MolEN.<sup>6</sup> The neutral atomic scattering factors for all the non-hydrogen atoms were taken from the literature.<sup>7</sup> The final error indices were  $R=0.073$  and  $R_w=0.079$ , respectively. The selected bond lengths and angles with their estimated standard deviations in the complex are summarized in Table 2.

### Results and Discussion

**Absorption and CD spectrum.** The absorption and CD spectrum of [Cu(*S*-aladien)H<sub>2</sub>O]<sup>+</sup> shows an absorption band at 548 nm and a weak negative CD band at 538 nm (Figure 1). In general, Cu(II) complexes with an amide functional group were arranged approximately in a plane around the central metal ion. A stronger ligand to axial position in the Cu(II) ion would cause the d-d absorption band to shift to a lower energy.<sup>8</sup> In many cases, a shoulder band appears at about 900 nm as a result of such a ligation.<sup>9</sup> For example, edda (ethylenediaminediacetate) type ligands seem to have a certain characteristic of hardly coordinating with a metal ion in a plane. In particular, H<sub>2</sub>epro[(*S,S*)-1,1'-ethylenedipyrrolidine-2,2'-dicarboxylic acid] hardly coordinates with Cu(II) in plane because of the rigid pyrrolidinyl groups.<sup>10</sup> But, [Cu(bpb)H<sub>2</sub>O] and [Cu(6-mebpb)H<sub>2</sub>O] with bis-picolinamide tetradentate ligands, bpbH<sub>2</sub> and 6-mebpbH<sub>2</sub> have been reported to coordinate in a plane to Cu(II) ion.<sup>2c,d</sup> In [Cu(*S*-aladien)H<sub>2</sub>O]<sup>+</sup> with a chiral mono amide ligand, the

**Table 1.** Summary of Crystallographic Data and Intensity Collection for [Cu(*S*-aladien)H<sub>2</sub>O] BPh<sub>4</sub>·H<sub>2</sub>O

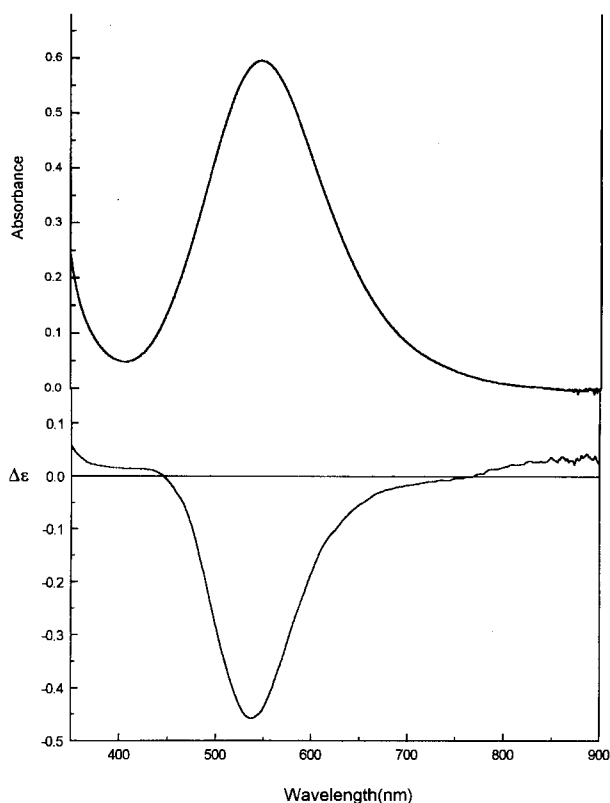
Empirical formula	Cu <sub>1</sub> C <sub>31</sub> H <sub>40</sub> N <sub>4</sub> O <sub>3</sub> B <sub>1</sub>
Formula weight	591.04
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>a</i> (#14)
Z	4
Cell parameters	
a (Å)	16.117(6)
b (Å)	10.889(4)
c (Å)	17.103(6)
$\beta$ (°)	101.20(3)
V (Å <sup>3</sup> )	2944(2)
D <sub>calc.</sub> (gcm <sup>-3</sup> )	1.295
$\mu$ (cm <sup>-1</sup> with Mo-K $\alpha$ )	13.7
Transmission factor	84.9323-99.9093
Scan type	$\omega$ -2 $\theta$
Scan width ( $\omega$ )(deg)	1.46+0.75tan( $\theta$ )
2 $\theta_{\max}$ (deg)	52.64
No. of reflections measured	6518
No. of reflections observed ( $I>3\sigma(I)$ )	1704
<i>F</i> (000)	1248
No. of variable	361
Discrepancy indices	
<i>R</i> <sup>a</sup>	0.073
<i>R</i> <sub>w</sub> <sup>b</sup>	0.079
Goodness of fit indicator <sup>c</sup>	1.74
Max. shift in final cycles	less than 0.01

<sup>a</sup>  $R = \sum |F_o - F_c| / \sum F_o$ . <sup>b</sup>  $R_w = [(\sum w(F_o - F_c)^2) / \sum w(F_o^2)]^{1/2}$ , where,  $w = [(\sigma(F^2))^{-1}]$ . <sup>c</sup> Estimated standard deviation of an observation of unit weight:  $[\sum w(F_o - F_c)^2 / (N_o - N_v)]^{1/2}$ , where  $N_o$ =Number of observations and  $N_v$ =Number of variables.

**Table 2.** The selected bond distances (Å) and angles (°) for [Cu(*S*-aladien)H<sub>2</sub>O] BPh<sub>4</sub>·H<sub>2</sub>O

bond distances (Å)		bond angles (°)	
Cu1-N1	2.04(1)	N1-Cu1-N2	106.0(4)
Cu1-N2	2.03(1)	N1-Cu1-N3	164.2(4)
Cu1-N3	1.89(1)	N1-Cu1-N4	86.4(5)
Cu1-N4	2.02(1)	N2-Cu1-N3	85.0(4)
Cu1-O1	2.38(2)	N2-Cu1-N4	167.5(5)
O2-C1	1.28(2)	N3-Cu1-N4	82.7(5)
N3-C1	1.29(2)	O1-Cu1-N1	89.6(5)
N4-C6	1.14(2)	O1-Cu1-N2	90.4(4)
		O1-Cu1-N3	101.9(6)
		O1-Cu1-N4	90.4(8)

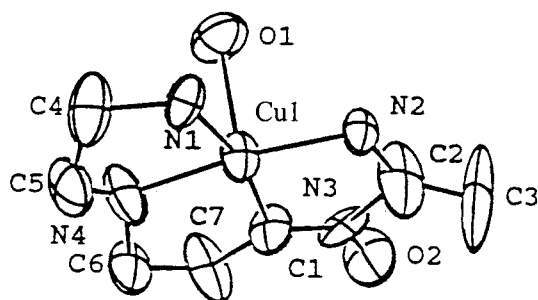
Numbers in parentheses are estimated standard deviations in the least significant digits.



**Figure 1.** Absorption and CD spectrum of  $[\text{Cu}(\text{S-aladien})\text{H}_2\text{O}]^+$  ( $1.5 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ ) in aqueous solution.

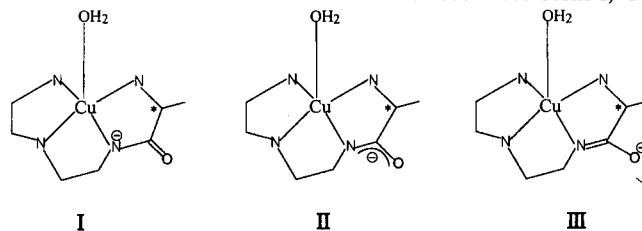
weak shoulder band could not be observed. Therefore, we suggested that *S*-aladienH ligand coordinates with a plane of Cu(II) ion because of the planar preference of the amide group within the *S*-aladienH ligand. On the other hand, this complex exhibits weak negative Cotton effect in the d-d region. It was indicated that the optical activity in the planar form complex was not derived from contributions of configuration or conformation but the vicinal effect of the asymmetric carbon of *S*-aladien.

**The X-ray Crystal Structure.** Figure 2 shows a perspective drawing of the cation  $[\text{Cu}(\text{S-aladien})\text{H}_2\text{O}]^+$  together with the atomic labeling scheme. In this figure, the Cu(II) ion has a distorted square-pyramidal geometry in which four sites of plane are occupied by the nitrogen of the *S*-ala-



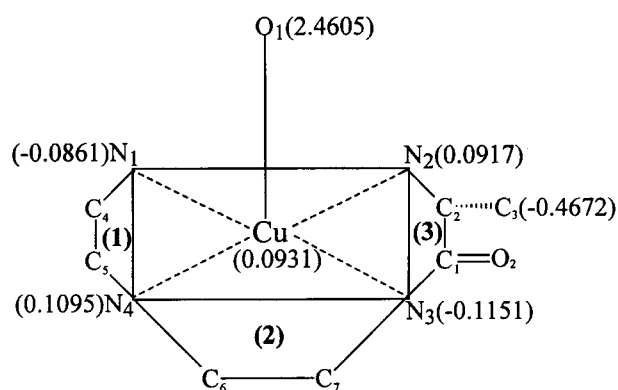
**Figure 2.** A perspective drawing of the  $[\text{Cu}(\text{S-aladien})\text{H}_2\text{O}]^+$  with the labeling of the atoms. Thermal ellipsoids are drawn to include 50% probability. A hydrate and  $\text{BPh}_4$  ion are omitted for clarity.

dien ligand and an aqua ligand coordinates to an apical position of the pyramid. The bond lengths are given in Table 2. The Cu-N(3) amide bond length (1.89 Å) is significantly shorter than those of the others Cu-N(1): 2.04 Å, Cu-N(2): 2.03 Å and Cu-N(4): 2.02 Å. This indicates that basicity of deprotonated nitrogen in amide moiety of a ligand is increased. Also, the Cu-O(1) bond length (2.38 Å) is significantly longer than coordinated nitrogen atoms in a plane. The C(1)-N(3) and C(1)-O(2) bond lengths within amide moiety of a ligand are 1.29 and 1.28 Å, respectively. For an N-coordinated in deprotonated amide moiety, it was reported that the negative charge would be delocalized along the amide C-N and C-O bonds.<sup>11</sup> In the resonance form I, C-

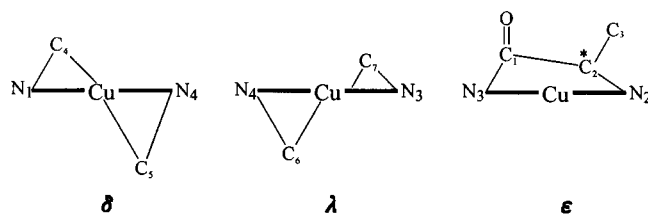


N has a single bond character, and C-O a double bond character. Conversely, in resonance form III, C-N has a double bond character, and C-O a single bond character.<sup>12</sup> These bonds of amide portion can also be intermediate(II) between double and single bonds. In a  $[\text{Co}(\text{S-aladien})\text{H}_2\text{O}]^+$ , the amide C-N and C-O bond lengths are consistent with the intermediate of these resonance forms. This represents that the negative charge would be completely delocalized along the amide C-N and C-O bonds.

The N(1)-Cu-N(3) and N(2)-Cu-N(4) bond angles are  $164.2^\circ$  and  $167.5^\circ$ , respectively. The deviations of the atoms from the least-squares plane comprising the four nitrogen



**Scheme 1.** The numbers in parentheses are the deviations of the atoms from the least-squares plane comprising the four nitrogen donors.



**Scheme 2.** The chelate ring conformations calculated from the least-squares plane.

donors are shown in Scheme 1. From these data, it is confirmed that two nitrogens N(2), N(4) are slightly raised with respect to the other two nitrogens N(1), N(3) atoms. Also, dihedral angles between relevant planes from the least-squares plane are as follows: plane(1)-(2); 5.95°, plane(1)-(3); 9.94°, plane(2)-(3); 6.65°. The plane (1), (2) and (3) indicate the planes which are composed of N(1)-C(4)-C(5)-N(4), N(2)-C(2)-C(1)-N(3) and N(4)-C(6)-C(7)-N(3), respectively. Thus, we identified the fact that the four nitrogen atoms of the ligand are mostly coordinated coplanarly, and the Cu(II) ion is raised slightly (0.0931 Å) out of the plane of the four nitrogen atoms towards O(1) coordinated in the apical position. The methyl group and amide oxygen are oriented slightly down from the least-squares plane.

Furthermore, the five membered chelate rings conformation are shown in Scheme 2. From the least-squares plane data, carbons were distant C(1); 0.1628 Å, C(2); 0.0281 Å, C(4); 0.2332 Å, C(5); -0.3752 Å, C(6); -0.4034 Å and C(7); 0.1282 Å, respectively. The distances of C(1), C(2) within peptide portion are all positive values; therefore, the conformation is envelope ( $\epsilon$ ). But, two chelate ring conformations of the dien backbone are considerably deviated from the envelope. They have a  $\delta$  and  $\lambda$  conformation, respectively. The ring conformation of N(1)-C(4)-C(5)-N(4) [ $\delta$ ] is more puckered than N(4)-C(6)-C(7)-N(3) [ $\lambda$ ]. From this result, we suggest that the fixed orientation of chiral carbon in the ligand and the planar preference of amide portion affect the pucker of neighboring dien moiety.

**Acknowledgment.** This research was supported by the Basic Science Research Institute Program (BSRI-97-3403), Ministry of Education, Korea and we thank Professor Heo, N. H. of Kyungbuk University of Korea, for the collection of X-ray intensity data.

### References

- (a) Che, C. M.; Leung, W. H.; Li, C. K. *Inorganica Chimica Acta*. **1992**, 196, 43. (b) Ray, M.; Mukherjee, R.; Richardson, J. F.; Buchanan, R. M. *J. Chem. Soc., Dalton trans.* **1993**, 2451. (c) Koikawa, M.; Gotoh, M.; Okawa, H.; Kida, S. *J. Chem. Soc., Dalton trans.* **1989**, 1613. (d) Mak, S. T.; Wong, W. V.; Yam, V. W. W.; Lai, T. F.; Che, C. M. *J. Chem. Soc., Dalton trans.* **1991**, 1915. (e) Ray, M.; Ghosh, D.; Shirin, Z.; Mukherjee, R. *Inorg. Chem.* **1997**, 36, 3568. (f) Lee, B. W.; Oh, C. E.; Doh, M. K. *Bull. Korean Chem. Soc.* **1998**, 19, 457.
- (a) Stephens, F. S.; Vagg, R. S. *Inorganica Chimica Acta*. **1981**, 51, 149. (b) Mulqi, M.; Stephens, F. S.; Vagg, R. S. *Inorganica Chimica Acta*. **1981**, 51, 9. (c) Chapman, R. S.; Stephens, F. S.; Vagg, R. S. *Inorganica Chimica Acta*. **1980**, 43, 29. (d) Chapman, R. S.; Stephens, F. S.; Vagg, R. S. *Inorganica Chimica Acta*. **1981**, 52, 169.
- Brubaker, G. R.; Schaefer, D. P.; Worrell, J. H.; Legg, J. I. *Coord. Chem. Rev.* **1971**, 7, 161.
- Asperger, R. G.; Liu, C. F. *Inorg. Chem.* **1965**, 4, 1395.
- Kim, D. Y.; Lee, D. J.; Heo, N. H.; Jung, M. J.; Lee, B. W.; Oh, C. E.; Doh, M. K. *Inorganica Chimica Acta*. **1998**, 267, 127.
- Molen Structural Analysis Package, Enraf-Nonius, Delft, Netherland, 1990.
- Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Vol IV, The Kynoch Press: Birmingham, England, 1974.
- (a) Tomlinson, A. A. G.; Hathaway, B. J. *J. Chem. Soc. A* **1968**, 1685. (b) Murakami, T.; Nozawa, T.; Hatano, M. *Bull. Chem. Soc. Jpn.* **1973**, 46, 2456.
- (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; 2nd ed.; Interscience Publishers: 1966; p 906. (b) Ojima, H.; Nonoyama, Z. *Anorg. Allgem. Chem.* **1973**, 401, 207.
- Murakami, T.; Hatano, M. *Bull. Chem. Soc. Jpn.* **1976**, 49, 3037.
- (a) Sigel, H.; Martin, B. *Chem. Rev.* **1982**, 82, 385. (b) Barnett, M. T.; Freeman, H. C.; Buckingham, D. A.; Hsu, I. N.; Helm, D. *Chem. Commun.* **1970**, 367.
- McLachlan, G. A.; Brudenell, S. J.; Fallon, G. D.; Martin, R. L.; Spiccia, L.; Edward, R. T. *J. Chem. Soc., Dalton trans.* **1995**, 439.

## Oxidative Decomposition of Di-*tert*-butyl azodicarboxylate and *Ab Initio* Studies on Fragmentation Mechanism

Jin Hoo Chung, Seon-Hee Lim, Chang Kook Sohn\*, and Wang Keun Lee\*

Department of Chemistry Education, Chonnam National University, Kwang-Ju 500-757, Korea

Received February 23, 1998

Oxidative decomposition of 1,1'-azoadamatane<sup>1,2</sup> and *t*-butyl phenyl carbonate<sup>3</sup> upon one-electron oxidation has sparked special interest to us in the nature of azocarboxylate cation radicals, and their fragmentation mechanism. Some azoalkanes, especially tertiary azoalkanes, reacted with cation radical at room temperature lead to rapid evolution of

nitrogen *via* C-N bond cleavages.<sup>4-6</sup> Also, fast decarboxylations of *t*-butyl phenyl carbonate and di-*t*-butyl dicarbonate<sup>7</sup> *via* C-O bond cleavages were observed at the same reaction conditions. Here, we describe a reaction of thianthrene cation radical (Th<sup>+</sup>ClO<sub>4</sub><sup>-</sup>, **1**) with di-*tert*-butyl azodicarboxylate (**2**) and plausible mechanistic postulates and