

# 완전히 카드뮴 이온으로 교환된 제올라이트 A를 진공 탈수한 후 아세틸렌 기체로 흡착한 결정구조

고 광 락 · 한 영 옥\* · 김 양

부산대학교 화학과

\*부산교육대학 과학교육과

## Crystal Structure of an Acetylene Sorption Complex of Vacuum Dehydrated Fully Cadmium(II)-Exchanged Zeolite A

Kwang Nak Koh, Young Wook Han,\* and Yang Kim

Department of Chemistry, Pusan National University, Pusan 609-735

\* Department of Science Education, Pusan Teachers College, Pusan 607-071

### 요 약

Cd<sup>2+</sup> 이온으로 이온 교환된 제올라이트 A를 탈수한 후 C<sub>2</sub>H<sub>2</sub> 기체를 흡착한 결정구조를 단결정 X-선 회절법으로 입방공간군 *Pm3m*을 사용하여 해석하였다. (*a*=12.202(3) Å 이고 *Z*=1 임).

이 결정은 723 K에서 2.67×10<sup>-4</sup> Pa의 진공하에서 2일간 탈수시킨 뒤 1.60×10<sup>4</sup> Pa의 C<sub>2</sub>H<sub>2</sub> 기체를 298 K에서 흡착시켜 만들었다.

단위 세포당 6개의 Cd<sup>2+</sup> 이온은 모두 골조의 결정학적으로 서로 다른 2개의 3회 회전축상 6-산소고리 위치에 위치한다. 즉 이들 Cd<sup>2+</sup> 이온중 2개는 3개의 O(3) 산소로 이루어진 (111) 평면에서 0.694 Å 만큼 sodalite 동공내로 들어간 위치에 위치하였고 나머지 4개의 Cd<sup>2+</sup> 이온은 O(3)의 (111) 평면에서 큰 동공으로 0.586 Å 들어가 있었다. 이 4개의 Cd<sup>2+</sup> 이온은 거의 정사면체형으로서, 3개의 골조 산소로부터 2.220(9) Å 그리고 C<sub>2</sub>H<sub>2</sub> 분자(여기서는 한자리 배위자로 간주)의 탄소로부터는 2.74(7) Å 떨어진 위치에 있다.

I>3σ(I)인 292개의 회절점으로 R<sub>1</sub>=0.093, R<sub>2</sub>=0.105까지 정밀화시켰다.

### Abstract

The crystal structure of an acetylene sorption complex of vacuum dehydrated fully Cd<sup>2+</sup>-exchanged zeolite A has been determined from three-dimensional X-ray diffraction data gathered by counter method. The structure was solved and refined in the cubic space group *Pm3m* at 294(1) K ; *a*=12.202(3) Å and *Z*=1. The crystal was prepared by dehydration at 723 K and 2.67×10<sup>-4</sup> Pa for 2 days, followed by exposure to 1.60×10<sup>4</sup> Pa of acetylene gas at 298(1) K. All six Cd<sup>2+</sup> ions per unit cell are associated with 6-oxygen rings of the aluminosilicate framework. They are distributed over two distinguished threefold axes of unit cell ; two of these Cd<sup>2+</sup> ions are recessed 0.694 Å into the sodalite unit from (111) plane of three O(3)'s and each approaches three framework oxides ; the other four Cd<sup>2+</sup> ions extend approximately 0.586 Å into the large cavity. These four Cd<sup>2+</sup> ions are in a near tetrahedral environment, 2.220(9) Å from three framework oxide ions and 2.74(7) Å from each carbon atom of an acetylene molecule(which is here counted as a monodentate ligand). Full - matrix least - squares re-

finement converged to the final error indices  $R_1 = 0.093$  and  $R_2 = 0.105$  using the 292 independent reflections for which  $I > 3\sigma(I)$ .

## INTRODUCTION

Successful exploitation of the selective sorptive properties of aluminosilicates, zeolites, rely upon an appreciation of the structural features of these molecular sieves; i.e., the dimensions of zeolites channels and cages, the nature of active sites, and the zeolitic framework oxygens and the sorbed guest molecules. To this purpose, a variety of the sorption structures of transition metal exchanged zeolite have been studied using single crystal X-ray diffraction technique.

In the structures of dehydrated  $\text{Co}_4\text{Na}_4\text{-A}$ <sup>1)</sup> and  $\text{Mn}_4\text{Na}_4\text{-A}$ ,<sup>2)</sup> the transition metal ions adopt positions close to the anionic zeolite framework where they achieve trigonal near-planar coordination. Upon treating dehydrated  $\text{Co}_4\text{Na}_4\text{-A}$  and  $\text{Mn}_4\text{Na}_4\text{-A}$  with acetylene molecules<sup>3),4)</sup>, each transition metal ion lies on threefold axes in the large cavity of unit cell, close to three equivalent trigonally arranged zeolite framework oxygen atoms and symmetrically to both carbon atoms of a  $\text{C}_2\text{H}_2$  molecule. However, the interaction of acetylene molecule with transition ion are weak, probably resulting from electrostatic attraction between bivalent cations and the polarizable  $\pi$ -electron density of the acetylene molecule.<sup>3),4)</sup>

The crystal structure of an ethylene sorption complex of fully  $\text{Ag}^+$ -exchanged zeolite A has been determined.<sup>5)</sup> In this structure, about 3.8  $\text{Ag}^+$  ions per unit cell are recessed ca. 1.2 Å into the large zeolite cavity where each forms lateral  $\pi$ -complex with an ethylene molecule.

Carter et. al. have studied the sorption of ethylene at room temperature onto a series of ion-exchanged synthetic near faujasites by infrared spectroscopy and by microcalorimetry.<sup>6)</sup> Of the transition metal ion examined,  $\text{Ag}^+$  and  $\text{Cd}^{2+}$  were found to hold  $\text{C}_2\text{H}_4$  most strongly. Furthermore, the adsorbed ethylene molecule is reported to be freely rotating in all cases,

except for their  $\text{Ag}^+$  and  $\text{Cd}^{2+}$  complexes.

As a part of continuing study to ascertain more precisely the effect of sorption upon transition metal exchanged zeolite system (i.e., to determine shifts in cation position, to observe cation-sorbate interactions, and perhaps to detect resultant changes in sorbed molecule geometry), crystal structure of an acetylene sorption complex of vacuum dehydrated  $\text{Cd}^{2+}$ -exchanged zeolite A has been determined by single crystal X-ray diffraction techniques.

## EXPERIMENTAL SECTION

Single crystals of the synthetic molecular sieve sodium zeolite 4A, stoichiometry  $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$ , were prepared by Charnell's method.<sup>7)</sup> A single crystal about 85  $\mu\text{m}$  on an edge was selected and lodged in a fine capillary. To prepare fully  $\text{Cd}^{2+}$ -exchanged zeolite A, an exchange solution of  $\text{Cd}(\text{NO}_3)_2$  and  $\text{Cd}(\text{OOCCH}_3)_2$  in the mole fraction of 1:1, with total concentration of 0.05 M, was used. Ion exchange was accomplished by allowing the solution to flow past each crystal at a velocity of approximately 0.5 cm/s for 3 days at 298 K. The crystal was washed for 1 hr with distilled water at 353 K. The clear, colorless, hydrated  $\text{Cd}^{2+}$ -exchanged crystals was dehydrated for 2 days at 723 K and  $2.67 \times 10^{-4}$  Pa. To prepare the acetylene complex, the crystal was treated with  $1.60 \times 10^4$  Pa of zeolitically dried acetylene for 1 hr at 298(1) K. The resulting reddish yellow crystal, still in acetylene atmosphere, was sealed in its capillary by a torch.

Diffraction intensities were subsequently collected at 294(1) K. The space group  $Pm\bar{3}m$  (no systematic absences) was used throughout this work for reasons discussed previously.<sup>8-9)</sup> Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Enraf Nonius CAD 4 diffractometer equipped with graphite monochromator and PDP micro 11/73 computer.  $\text{Mo K}\alpha$  radiation was used for all experiment. The unit cell constant, as determined by a least-squares

refinements of 25 intense reflections for which  $19^\circ < 2\theta < 24^\circ$  are 12.202(3) Å for acetylene sorption complex of Cd<sub>6</sub>-A.

For this crystal, reflections from two intensity-equivalent regions of reciprocal space ( $hkl$ ,  $h \leq k \leq l$  and  $lkh$ ,  $l \leq k \leq h$ ) were examined using  $\omega$ - $2\theta$  scan technique. The data were collected using variable scan speed, ranging between 0.250° and 0.317° in  $\omega$ /min. The intensities of three reflections in diverse regions of reciprocal space were recorded after every three hours to monitor crystal and X-ray source stability. Only small, random fluctuations of these check reflections were noted during the course of data collections. For each region of reciprocal space, the intensities of all lattice points for which  $2\theta < 70^\circ$  were recorded. The raw data from each region were corrected for Lorentz and polarization effects, including that due to incident beam monochromatization: the reduced intensities were assigned to each average reflection by the computer programs, PAINT and WEIGHT.<sup>10)</sup>

An absorption correction ( $\mu = 2.14 \text{ mm}^{-1}$ ,  $\rho_{\text{calc}} = 2.018 \text{ gr cm}^{-3}$ ,  $Z = 1$  and  $F(000) = 1046$  for acetylene sorption complex of Cd<sub>6</sub>-A) was judged to be unnecessary and was not applied.<sup>11)</sup> Of the 868 pairs of reflections for the crystal of acetylene sorption complex of Cd<sub>6</sub>-A, only 292 pairs, for which  $I > 3\sigma(I)$ , were used in subsequent structure determinations.

The initial structural parameters used in the least-squares refinement<sup>10)</sup> were the atomic parameters

of the framework atoms (Si,Al), O(1), O(2), O(3), and Cd<sup>2+</sup> ions at Cd(1) and Cd(2) in dehydrated Cd<sup>2+</sup> exchanged zeolite A treated with ethylene molecules.<sup>12)</sup> Anisotropic refinement of this structural model converged to an R<sub>1</sub> index,  $(\sum(|F_o| - |F_c|) / \sum F_o)$ , of 0.105 and a weighted R<sub>2</sub> index,  $(\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2}$ , of 0.110.

A successive difference Fourier map indicated that the carbon atoms of the acetylene molecules appeared at the 24 fold position (0.3047, 0.3047, 0.3320) with a peak height of 1.1(2) e Å<sup>-3</sup>. This corresponds closely to the final result, that approximately 8.0 carbon atoms are found very near this position. It was assumed that one C<sub>2</sub>H<sub>2</sub> molecule is associated with each Cd<sup>2+</sup> ion at Cd(1), such coordination is reasoned that Cd<sup>2+</sup> ion at Cd(1) recessed approximately 0.586(2) Å into the large cavity at a near tetrahedral 4-coordinate position. Refinement of a model, with all atoms treated anisotropically except carbon which was refined isotropically, converged to R<sub>1</sub> = 0.093 and R<sub>2</sub> = 0.105 (see Table 1). The relatively high R values are probably due to the some loss of crystallinity through the processes of ion exchange, dehydration and gas absorption.

The quantity minimized in the least-squares treatment was  $(\sum w(F_o - F_c)^2)$  and the weights (w) were the reciprocal squares of  $\sigma(F_o)$ , the standard deviation of each observation. Atomic scattering factors for O<sup>-</sup> and (Si,Al)<sup>1.75+</sup> for the zeolite framework,

Table 1. Positional, Thermal, and Occupancy Parameters for Acetylene Sorption Complexes of Ca<sub>6</sub>-A

Atom	Wyc Pos	x	y	z	<sup>b</sup> $\beta_{11}$ <sup>b</sup> $\beta_{\text{iso}}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	Occupancy	
											varied	fixed
(Si,Al)	24(k)	0	1817(4)	3681(4)	30(3)	18(2)	11(2)	0	0	3(5)		1.0
O(1)	12(h)	0	2000(10)	5000	80(20)	50(10)	30(10)	0	0	0		1.0
O(2)	12(i)	0	2990(10)	2990(10)	40(10)	43(7)	43(7)	0	0	100(20)		1.0
O(3)	24(m)	1117(7)	1117(7)	3270(10)	32(5)	32(5)	49(9)	10(10)	-10(10)	-10(10)		1.0
Cd(1)	8(g)	2111(3)	2111(3)	2111(3)	55(2)	55(2)	55(2)	37(5)	37(5)	37(5)	0.48(1)	1/2
Cd(2)	8(g)	1505(7)	1505(7)	1505(7)	75(3)	75(3)	75(3)	123(7)	123(7)	123(7)	0.26(1)	1/4
C(1)	24(m)	3130(50)	3130(50)	3830(70)	9(3) <sup>d</sup>						0.34(2)	1/3

<sup>a</sup> Positional and anisotropic thermal parameters are given  $\times 10^4$ . Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. <sup>b</sup> The anisotropic temperature factor =  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ . Rms displacements can be calculated from  $\beta_{ii}$  values by using the formula  $u_i = 0.225(\beta_{ii})^{1/2}$ , where  $a = 12.202(2)$  Å for acetylene sorption structure of Cd<sub>6</sub>-A. <sup>c</sup> Occupancy for (Si) = 1/2; Occupancy for (Al) = 1/2. <sup>d</sup> Isotropic thermal parameter is in units of Å<sup>2</sup>.

$\text{Cd}^{2+}$  for the exchangeable cations, and C(valence) for the  $\text{C}_2\text{H}_2$  molecule were used.<sup>13),14)</sup> The function describing  $(\text{Si,Al})^{1.75+}$  is the mean of the  $\text{Si}^0$ ,  $\text{Si}^{4+}$ ,  $\text{Al}^0$ , and  $\text{Al}^{3+}$  functions. The scattering factors for  $\text{Cd}^{2+}$  and  $(\text{Si,Al})^{1.75+}$  were modified to account for the anomalous dispersion correction.<sup>15),16)</sup> Final positional, thermal, and occupancy parameters are presented in Table 1; bond length and angles are given in Table 2.

**Table 2.** Selected Interatomic Distances(Å) and Angles(deg)

(Si,Al)—O(1)	1.624(6)
(Si,Al)—O(2)	1.664(9)
(Si,Al)—O(3)	1.686(8)
Cd(1)—O(3)	2.220(9)
Cd(2)—O(3)	2.26(1)
Cd(1)—C(1)	2.74(7)
C(1)—C(1)	1.20(9)
O(1)—(Si,Al)—O(2)	112.5(8)
O(1)—(Si,Al)—O(3)	111.6(5)
O(2)—(Si,Al)—O(3)	106.6(3)
O(3)—(Si,Al)—O(3)	107.9(4)
(Si,Al)—O(1)—(Si,Al)	164(1)
(Si,Al)—O(2)—(Si,Al)	150.7(6)
(Si,Al)—O(3)—(Si,Al)	136.7(7)
O(3)—Cd(1)—O(3)	113.3(2)
O(3)—Cd(2)—O(3)	110.9(3)
O(3)—Cd(1)—C(1)	91(1)
Cd(1)—C(1)—C(1)	77(4)

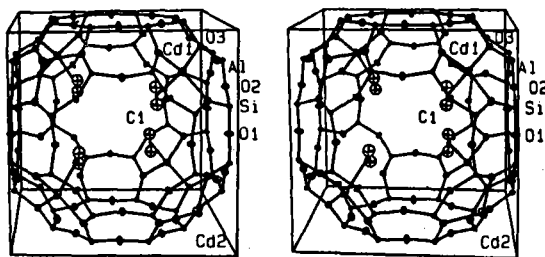
Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding value.

## DISCUSSION

In the crystal structure of an acetylene sorption complex of dehydrated  $\text{Cd}_6\text{-A}$ , all six  $\text{Cd}^{2+}$  ions are found on two distinguished threefold axes of unit cell (see Table 1). About 4.0  $\text{Cd}^{2+}$  ions at Cd(1) extended 0.586(2) Å into the large cavity from the (111) plane at O(3). Each  $\text{Cd}^{2+}$  ion at Cd(1) is a near tetrahedral environment, 2.220(9) Å from three O(3) framework oxygen atoms and 2.74(7) Å from each carbon atoms of an acetylene molecule (which is here counted as a monodentate ligand). To balance electrostatic charge, the 2.0  $\text{Cd}^{2+}$  ions at Cd(2) per unit cell are recessed 0.694(5) Å into the sodalite unit from the O(3) plane of the 6-ring. Each of these  $\text{Cd}^{2+}$  ions

at Cd(2) is coordinated to three O(3) framework oxygens at 2.26(1) Å.

It should be noted that the cation to O(3) distances presented here have not taken into account the probable but unobserved (due to disorder) conformational difference between the two sets of O(3) atoms; one set is associated with the  $\text{Cd}^{2+}$  ions at Cd(1) and the other with the  $\text{Cd}^{2+}$  ions at Cd(2). Only the average 12-membered ring of framework atoms (see Fig 1) is determined.



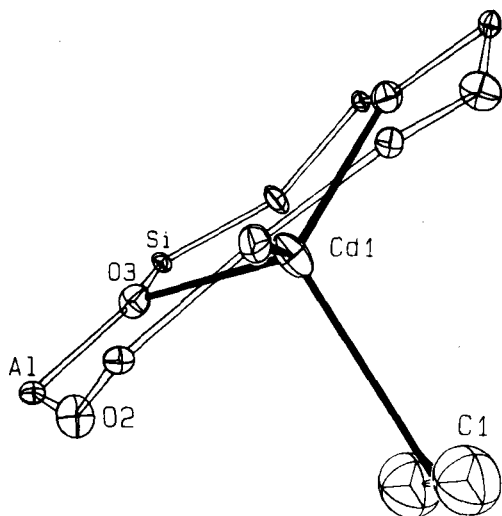
**Fig. 1.** The stereoview of large cavity of vacuum dehydrated  $\text{Cd}_6\text{-A}$  treated with  $\text{C}_2\text{H}_2$ . The hydrogen atoms, whose positions were not determined, are not shown. Four acetylene molecules are coordinated to each  $\text{Cd}^{2+}$  ion at Cd(1). Ellipsoids of 20% probability are used.

To bind one molecule of  $\text{C}_2\text{H}_2$ , each  $\text{Cd}^{2+}$  ion moves a small distance (0.354 Å, see Table 3 and reference 12) from its triad of O(3) atoms, further into the large cage. Accordingly the  $\text{Cd}^{2+}\text{-O(3)}$  bonds lengthen slightly, from 2.162(7) Å in the three-coordinate dehydrated structure to 2.220(9) Å (see Table 2) in the four-coordinate acetylene complex—this distance a little bit longer than the distance observed in four-coordinate ethylene (2.210(6) Å) complexes. The three equivalent O(3)— $\text{Cd}^{2+}$ —O(3) angles have decreased respectively from the nearly trigonal planar values of 118.9(2)° in the dehydrated complex to more tetrahedral value of 113.3(3)° in the acetylene complex (see Fig. 2).

**Table 3.** Deviations of atoms(Å) from the (111) plane at O(3)

O(2)	0.342(7)
Cd(1)	0.586(2)
Cd(2)	-0.694(5)

A negative deviation indicates that the atom lies on the same side of the plane as the origin.



**Fig. 2.**  $\text{Cd}(\text{C}_2\text{H}_2)_2^{2+}$  complex in one corner of the large cavity. The approximately tetrahedral coordination about  $\text{Cd}^{2+}$  can be seen. The hydrogen atoms, whose positions were not determined, are not shown. Ellipsoids of 40% probability are used.

From our crystallographic study of the ethylene complex and this acetylene complex, two conclusions may be reached ;

- (1) The sorbed gaseous molecules interact preferentially with the  $\text{Cd}^{2+}$  ions and
- (2) These interactions are weak, for the resultant bonds from  $\text{Cd}^{2+}$  ions to sorbed molecules may be long, and concomitant changes in  $\text{Cd}^{2+}$ -framework geometries are small. That is, the long  $\text{Cd}^{2+}$ -framework interactions are maintained.

Certainly the most interesting feature of this structure is the binding of  $\text{C}_2\text{H}_2$  molecules by  $\text{Cd}^{2+}$  ions. With all eight carbon atoms (four molecules of  $\text{C}_2\text{H}_2$ ) distributed about one equipoint (Wyckoff position 24m), the  $\text{Cd}^{2+}$ - $\text{C}_2\text{H}_2$  interaction is symmetric, that is, each  $\text{C}\equiv\text{C}$  bond is normal to and bisected by a plane of symmetry which contains a threefold axis (and hence a  $\text{Cd}^{2+}$  ion), so that both carbons are equidistant from  $\text{Cd}^{2+}$  ( $\text{Cd}^{2+}$ - $\text{C}\equiv\text{C}$  = 2.74(7) Å). With this particular equivalent carbon atom arrangement, a  $\text{C}\equiv\text{C}$  bond does not intersect a unit cell threefold axis. We can conclude that the binding in this complex is weak

and probably results from the electrostatic interaction between the dipositive  $\text{Cd}^{2+}$  ions and the polarizable  $\pi$ -electron density of the  $\text{C}_2\text{H}_2$  molecules.

The high charge of the  $\text{Cd}^{2+}$  ions severely inhibits the synergic bonding<sup>17)</sup> usually ascribed to symmetric metal-alkyne complexes, i.e., donation of  $\pi$ -electron density of acetylene into an empty  $\sigma$ -acceptor orbital of the metal and "back-donation" of accumulated charge from metal d or dp hybrid orbitals into  $\pi$ -acceptor orbitals of acetylene. Acetylene apparently functions solely as an electron donor, perhaps as it does in  $\pi$ - $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{C}_2(\text{CF}_3)_2$ .<sup>18)</sup> Infrared studies of this compound have shown that the acetylenic stretching frequency is only slightly effected by complexation, indicating that its triple-bond character is retained. In contrast, the C-C triple bond of most monoacetylene complexes of platinum<sup>19)</sup> is so altered that it closely resembles a C-C double bond.

Perhaps what is observed in this zeolite complex is an approximate isolation of the  $\sigma$  portion of what would become a  $\sigma$ - $\pi$  synergic bond, were the metal uncharged and therefore capable of back-donation so as to strengthen the interaction. Angell and Schaffer<sup>20)</sup> have suggested from i.r. studies that this effect alone may account for the binding of carbon monoxide by  $\text{Cd}^{2+}$  in X- and Y- type zeolites.

Because of the combined effects of disorder and moderate thermal motion of the carbon atom, there must be some uncertainty in  $\text{C}\equiv\text{C}$  bond distance ( $\text{C}\equiv\text{C}$  distance in this structure is 1.20(9) Å). For comparison, the  $\text{C}\equiv\text{C}$  distance in gaseous acetylene is 1.201(5) Å. The closest approach distance of carbon atom to framework oxygen, O(3) is 3.5(1) Å. The hydrogen atom of acetylene, although unlocated, should lie in the plane of the carbon position. The hydrogen atoms would therefore also be too far from the nearest oxide ions to interact with them, even if the C-H-O angle were linear. Since the energy of the interaction between acetylene and  $\text{Cd}^{2+}$  ion is not considered great enough to cause an appreciable deviation of the hydrogen atoms from the best acetylene plane, C-H-O should be bent (see Fig 2) and the

hydrogen should be far, more than 2.0 Å from the nearest oxide neighbors.

#### Acknowledgement

The present studies were supported in part by the Basic Science Research Institute Program, Ministry of Education, Korea, 1990, Project NO. BSRI-90-306.

#### REFERENCE

- 1) P. E. Riley and K. Seff, *Inorg. Chem.*, **13**, 1355(1974).
- 2) R. Y. Yanagida, T. B. Vance, and K. Seff, *Inorg. Chem.*, **13**, 723(1974).
- 3) P. E. Riley and K. Seff, *J. Am. Chem. Soc.*, **95**, 8180(1973).
- 4) P. E. Riley and K. Seff, *Inorg. Chem.*, **14**, 714(1975).
- 5) Y. Kim and K. Seff, *J. Am. Chem. Soc.*, **100**, 175(1978).
- 6) T. L. Carter, J. C. Yates, P. J. Lucchesi, J. J. Elliot, and V. Kevorkian, *J. Phys. Chem.*, **70**, 1126(1966).
- 7) J. F. Charnell, *J. Cryst. Growth.*, **8**, 291(1971).
- 8) K. Seff, and M. D. Mellum, *J. Phys. Chem.*, **88**, 3560(1984).
- 9) K. Seff, *Acc. Chem. Res.*, **9**, 121(1976).
- 10) Calculations were performed using the "Structure Determination Package Program" written by B. A. Frenzt, and Y. Okaya. These programs were supplied by Enraf - Nonius, Netherlands, 1987.
- 11) Y. Kim and K. Seff, *J. Phys. Chem.*, **82**, 925(1978).
- 12) K. N. Koh, U. S. Kim, D. S. Kim, and Y. Kim, *Bull. Korean Chem. Soc.*, **12**, 193(1991).
- 13) "International Tables for X-ray Crystallography", Vol. IV. Kynoch Press, Birmingham, England, 1974, pp 73-87.
- 14) P. A. Dole and P. S. Turner, *Acta Crystallogr., Sect. A.*, **24**, 390(1968).
- 15) Reference 13, pp 149-150.
- 16) D. T. Cromer, *Acta Crystallogr.*, **18**, 17(1965).
- 17) A discussion of synergic bonding as related to metal - acetylen complexes is available ; F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 5rd ed Interscience, New York, N. Y., 1988, pp 1157-1162.
- 18) J. L. Boston, S. O. Grim, and G. Wilkinson, *J. Chem. Soc.*, 3468(1963).
- 19) The structure of a Pt(II) complex presented in the following source is an example of symmetric metal - alkyne bonding ; G. R. Davies, W. Hewertson, R. H. B. Mais, P. G. Owston, and C. G. Patel, *J. Chem. Soc.*, **A**, 1873(1970).
- 20) C. L. Angell and P. C. Schaffer, *J. Phys. Chem.*, **70**, 1413(1966).