

Crystal Structure of an Acetylene Sorption Complex of Dehydrated Fully Mn(II)-Exchanged Zeolite X

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The crystal structure of an acetylene sorption complex of dehydrated fully Mn(II)-exchanged zeolite X, $Mn_{46}Si_{100}Al_{92}O_{384} \cdot 30C_2H_2$ ($a=24.705(3)$ Å) has been determined by single-crystal X-ray diffraction techniques. The structure was solved and refined in the cubic space group $Fd\bar{3}$ at 21(1) °C. The complex was prepared by dehydration at 380 °C and 2×10^{-6} Torr for 2 days, followed by exposure to 300 Torr of acetylene gas for 2 h at 24 °C. The structure was refined to the final error indices, $R_1=0.060$ and $R_2=0.054$ with 383 reflections for which $I > 3\sigma(I)$. In the structure, Mn^{2+} ions are located at two different crystallographic sites; sixteen Mn^{2+} ions at site I are located at the centers of the double six rings and thirty Mn^{2+} ions are found at site II in the supercage, respectively. Each of these latter Mn^{2+} ions is recessed *ca.* 0.385(2) Å into the supercage from its three-oxygen plane. Thirty acetylene molecules are sorbed per unit cell. Each Mn^{2+} ion at site II lies on a threefold axis in the supercage of the unit cell, close to three equivalent trigonally arranged zeolite framework oxygen atoms ($Mn(II)\text{-O}=2.135(9)$ Å) and symmetrically to both carbon atoms of a C_2H_2 molecules. At these latter distances, the Mn(II)-C interactions are weak ($Mn(II)\text{-C}=2.70(5)$ Å), probably resulting from electrostatic attractions between the divalent cations and the polarizable π -electron density of the acetylene molecules.

Introduction

Considerable effects has been made by determining the nature of aluminosilicate sorptive and catalytic sites in order to postulate reaction mechanisms, perhaps to observe reaction intermediates, and ultimately, to devise highly specific catalytic system. Structural characterization of the crystalline zeolites can be most useful in pursuing these objectives.

Zeolites have extensive commercial application as catalysts for hydrocarbon cracking or for specific high yield rearrangement reactions involving hydrocarbons and other organic molecules.¹ Especially, because unsaturated hydrocarbons are sorbed more tenaciously than saturated ones, and because the carbon atoms in acetylene were likely to be equivalent in the cation-acetylene complex inside the cavity of zeolite, C_2H_2 was selected as the sorbate material.

Several hydrocarbon sorption complexes of transition metal ion exchanged zeolite A and X have been studied. Upon treating dehydrated $CoNa_4\text{-A}$ and $Mn_4Na_4\text{-A}$ with ethylene and acetylene molecules,²⁻⁴ respectively, four ethylene and/or acetylene molecules are sorbed per unit cell. In the structure of ethylene sorption complex of dehydrated $Mn_{46}\text{-X}$,⁵ thirty ethylene molecules are sorbed per unit cell. Each of transition metal ions lies on threefold axes in the large cavity (or supercage) of unit cell, close to three equivalent trigonally arranged zeolite oxygen atoms and symmetrically close to both carbon atoms of C_2H_4 molecule.

Carter *et al.*⁶ have studied the adsorption of ethylene at room temperature on a series of ion-exchanged synthetic near-faujasites by infrared spectroscopy and by microcalorimetry. It has been found that the nature of the adsorption of the ethylene is dependent on the nature of the exchangeable cations. It has also been found that in all cases except that of Cd-X and Ag-X the ethylene is relatively weakly held. Furthermore, all of the adsorbed ethylene molecules except for Ag-X, have been shown to

be freely rotating. In addition, the symmetry of the ethylene-cation complex is most probably that described by the point group C_2 . Hence, the interaction between C_2H_4 and these zeolites can be described as weak chemisorption.⁶

As part of a continuing study to ascertain more precisely the effects and properties of sorption structure upon transition metal exchanged zeolites system, the acetylene sorption complex of the dehydrated fully $Mn_{46}\text{-X}$ has been determined.

Experimental Section

Large colorless single crystals of Na-zeolite X with the stoichiometry $Na_{92}Al_{92}Si_{100}O_{384}$ were prepared in St. Petersburg, Russia.⁷ The crystal, an octahedron about 0.2 mm in cross-section, was lodged in a fine Pyrex capillary.

To prepare fully Mn(II)-exchanged zeolite X, an exchange solution of $Mn(NO_3)_2$ with the concentration of 0.05 M was used. Ion exchange was accomplished by flow methods. The solution was allowed to flow past the crystal at a velocity of approximately 1.0 cm/s for three days. The crystal was dehydrated at 380 °C and 2×10^{-6} Torr for two days. To prepare the acetylene sorption complex, the crystal was treated with 300 Torr of zeolitically dried acetylene for two h at 24(1) °C. Under these conditions, the crystal was removed from the vacuum system by torch. Microscopic examination showed that the crystal had become black.

X-Ray Data Collection

The cubic space group $Fd\bar{3}$ was used throughout this work. Diffraction data were collected with an automated Enraf-Nonius four-circle computer controlled CAD-4 diffractometer equipped with a pulse-height analyzer and a graphite monochromator, using Mo $K\alpha$ radiation ($K\alpha_1$, $\lambda=0.70930$ Å, $K\alpha_2$, $\lambda=0.71359$ Å). The unit cell constant at

21(1) °C, determined by least-squares refinement of 25-intense reflections for which $14^\circ < 2\theta < 24^\circ$ is $a=24.705(3)$ Å.

The ω - 2θ scan technique was used. The data were collected using variable scan speeds, ranging between 0.26 and 0.34 deg min⁻¹ in ω . The intensities of three reflections in diverse regions of reciprocal space were recorded after every three h to monitor crystal and X-ray source stability. Only small random fluctuations of these check reflections were noted during the course of data collection. The intensities of all lattice points for which $2\theta < 60^\circ$ were recorded. Of the 1770 reflections examined, only the 383 whose net counts exceeded three times their corresponding estimated standard deviations were used in structure solution and refinement. The intensities were corrected for Lorentz and polarization effects. An absorption correction ($\mu R=0.134$ and $\rho_{\text{calc}}=1.506$ g/cm³)⁸ was made empirically using a ψ scan. The calculated transmission coefficient ranged from 0.992 to 0.999. This correction had little effect on the final R indices.

Structure Determination

Full-matrix least-squares refinement was initiated by using the atomic thermal parameters of the framework atoms [Si, Al, O(1), O(2), O(3) and O(4)] in the structure of a carbon monoxide sorption complex of dehydrated Mn(II)-exchanged zeolite X, Mn₄₆X·30CO.⁹ Isotropic refinement of the framework atoms converged to an R_1 index, $(\sum |F_o - F_c|)/\sum F_o$ of 0.332 and a weighted R_2 index, $(\sum w(F_o - F_c)^2/\sum wF_o^2)^{1/2}$ of 0.375.

The initial difference Fourier function revealed two large peaks at (0.0, 0.0, 0.0) and (0.224, 0.224, 0.224) with heights of 15.6 and 11.4 eÅ⁻³, respectively. The first peak is Mn(1) position at site I in the hexagonal prism (D6R). The second peak is Mn(2) position at site II in the supercage. These positions were stable in least-squares refinement. Isotropic refinement of framework and cations converged to $R_1=0.078$ and $R_2=0.088$ with occupancies of 16.6(2) and 31.3(5), respectively (see Table 1).

A successive difference Fourier function showed that the carbon atoms of the acetylene molecules appeared at the 96-

fold position (0.300, 0.273, 0.279) with a peak height of 1.47 eÅ⁻³. This peak corresponds closely to the final result, that approximately 60.4(27) carbon atoms are found very near to this position. It was assumed that one C₂H₂ molecule is associated with each Mn²⁺ ion at Mn(2) recessed approximately 0.385(2) Å into the supercage at a near-tetrahedral 4-coordinate position. Refinement of about sixty carbon atoms per unit cell at this position, constrained to be no more than twice the number of Mn²⁺ ions at Mn(2). Simultaneous positional, occupancy and isotropical thermal parameter refinement for all atoms converged to $R_1=0.065$ and $R_2=0.060$.

Further refinement employing anisotropic thermal parameters for all species except carbon atom at acetylene molecule converged with $R_1=0.058$ and $R_2=0.050$. All shifts in the final cycle of least-squares refinement were less than 0.01% of their corresponding standard deviations. The occupancy numbers of Mn(1), Mn(2), and acetylene molecules were fixed at the values shown in Table 1. Hydrogen atoms were calculated and added to this model. It was unsuccessful to attempt to refine the positional parameters of hydrogen atoms. The final error indices converged to $R_1=0.060$ and $R_2=0.054$.

All crystallographic calculations were done using MolEN¹⁰ supplied by Enraf-Nonius. The full-matrix least-squares program used minimized $\sum w(F_o - F_c)^2$; the weight of observation was the reciprocal square of $\sigma(F)$, its standard deviation. Atomic scattering factors^{11,12} for Si, Al, O⁻¹, C, and Mn²⁺ were used. All scattering factors were modified to account for the anomalous dispersion.¹³ The final structural parameters and selected interatomic distances and angles are presented in Table 1 and 2, respectively.

Discussion

Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite. The 14-hedron with 24 vertices known as the sodalite cavity or β cage may be viewed as the principal building block of the aluminosilicate framework of the zeolite (see Figure 1).¹⁴ These β -cages are connected tetrahedrally at six-rings by bridging oxygens to

Table 1. Positional, Thermal^a, and Occupancy Parameters

Atom	Wyc. Pos.	site	x	y	z	U_{11}^b or U_{iso}^d	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Occupancy ^c	
												varied	fixed
Si	96(g)		-522(2)	1223(2)	338(2)	106(17)	95(18)	81(17)	-15(21)	-1(18)	-4(23)		96
Al	96(g)		-541(2)	380(2)	1206(2)	83(19)	72(20)	62(20)	1(19)	6(22)	-28(22)		96
O(1)	96(g)		-1108(4)	23(5)	1044(4)	101(63)	267(63)	216(60)	-8(54)	-66(43)	-27(57)		96
O(2)	96(g)		-17(4)	-11(4)	1473(4)	156(49)	87(46)	179(51)	-80(48)	21(50)	-41(50)		96
O(3)	96(g)		-312(4)	643(4)	591(4)	208(53)	57(49)	11(46)	28(49)	14(48)	-34(41)		96
O(4)	96(g)		-634(4)	839(4)	1703(4)	325(62)	106(53)	123(54)	-76(56)	140(57)	-74(46)		96
Mn(1)	16(c)	I	0	0	0	127(13)	127(13)	127(13)	42(17)	42(17)	42(17)	16.2(2)	16
Mn(2)	32(e)	II	2257(1)	2257(1)	2257(1)	344(13)	344(13)	344(13)	119(17)	119(17)	119(17)	31.3(5)	30
C	96(g)		3091(18)	2726(22)	2789(25)	1520(253) ^d						60.4(27)	60
H(1)	96(g)		3368	2390	2847 ^e								30
H(2)	96(g)		2511	3426	2668 ^e								30

^a Positional and 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. ^b The anisotropic temperature factor: $\exp[-2\pi^2 a^2 (U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2hkhU_{12} + 2hhlU_{13} + 2khlU_{23})]$. ^c Occupancy factors are given as the number of atoms or ions per unit cell. ^d $U_{\text{iso}} = (B_{\text{iso}}/8\pi^2)$. ^e These hydrogen coordinates were calculated by the computer system MolEN using C-H=1.085 Å.

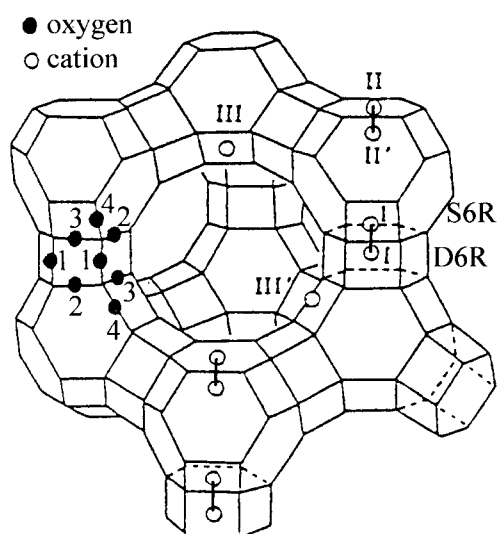


Figure 1. A stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1 to 4. Silicon and aluminum atoms alternate at the tetrahedral intersections. Si substitutes for about 4% of the Al's. Extraframework cation positions are labeled with Roman numerals.

give double six-rings (D6R's, hexagonal prisms), and concomitantly, to give an interconnected set of even larger cavities (supercages) accessible in three dimensions through 12-ring (24-membered) windows. The Si and Al atoms occupy the vertices of these polyhedra. The oxygen atoms lie approximately half-way between each pair of Si and Al atoms but are displaced from those points to give near tetrahedral angles about Si and Al.

Table 2. Selected Interatomic Distances (Å) and Angles (deg)^a for $Mn_{46}\text{-X} \cdot 30C_2H_2$

Si-O(1)	1.592(11)	O(1)-Si-O(2)	112.8(6)
Si-O(2)	1.657(11)	O(1)-Si-O(3)	108.3(5)
Si-O(3)	1.648(10)	O(1)-Si-O(4)	112.2(6)
Si-O(4)	1.592(11)	O(2)-Si-O(3)	106.6(5)
Mean Si-O	1.622	O(2)-Si-O(4)	104.8(6)
Al-O(1)	1.704(11)	O(3)-Si-O(4)	112.1(5)
Al-O(2)	1.745(11)		
Al-O(3)	1.747(10)		
Al-O(4)	1.686(11)	O(1)-Al-O(2)	114.3(6)
Mean Al-O	1.721	O(1)-Al-O(3)	104.7(5)
Mn(1)-O(3)	2.290(9)	O(1)-Al-O(4)	114.1(5)
Mn(2)-O(2)	2.135(9)	O(2)-Al-O(3)	107.1(5)
Mn(2)-C	2.70(5)	O(2)-Al-O(4)	101.5(5)
C-C	1.18(7)	O(3)-Al-O(4)	115.4(5)
H(1)-O(2)	3.21		
H(2)-O(4)	3.40		
O(3)-Mn(1)-O(3)	90.0(3)	Si-O(1)-Al	128.8(6)
O(2)-Mn(2)-O(2)	116.8(4)	Si-O(2)-Al	132.4(6)
O(2)-Mn(2)-C	94.9(13)	Si-O(3)-Al	123.4(6)
Mn(2)-C-C	77.4(34)	Si-O(4)-Al	162.1(7)

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

The exchangeable cations, which compensate for the negative charge of the framework, occupy the various positions. They are usually found at the following as shown in Figure 1: site I at the center of a D6R (hexagonal prism), site I' in the sodalite (β) cavity on the opposite side of one of the D6R's 6-rings from site I, site II' inside the sodalite cavity near the S6R entrance to the supercage, site II in the supercage opposite the S6R from site II', site III in the supercage on a twofold axis opposite a 4-ring between two 12-rings, and site III' somewhat off two-fold axis of site III.¹⁵

In the structure of acetylene sorption complex of dehydrated $Mn_{46}\text{-X}$, the mean values of the Si-O and Al-O bond lengths are 1.622 Å and 1.721 Å, respectively. The individual bond lengths show marked variations: Si-O from 1.592(11) Å to 1.657(11) Å and Al-O from 1.686(11) Å and 1.745(11) Å. Mn^{2+} ions coordinate only to O(2) and O(3) in this structure and as a consequence of substantially covalent interactions, the Al-O(2), Si-O(2), Al-O(3) and Si-O(3) bonds are lengthened (see Table 2). The Si-O-Al bond angles range from 128.8(6)° to 162.1(7)°. No significant change in framework of structure has resulted from acetylene sorption.

In the present structure, all Mn^{2+} ions are located at two different sites of high occupancy. Sixteen Mn^{2+} ions at Mn(1) are at the centers of hexagonal prisms (site I), one in each of the sixteen D6R's in a unit cell. The Mn(1)-O(3) distance, 2.290(9) Å, is longer than the sum of the ionic radii of Mn^{2+} and O^{2-} , $0.80+1.32=2.12$ Å.¹⁶

Thirty acetylene molecules were adsorbed per unit cell. Although each Mn(II) remains tightly bound to its three nearest oxygen atoms, the binding to acetylene does weaken the interaction with the framework: in the fully dehydrated structure of $Mn_{46}\text{-X}$, Mn-O(2)=2.09(2) Å;⁵ in the ethylene sorption complex, $Mn_{46}\text{-X} \cdot 30C_2H_4$, Mn-O(2)=2.12(2) Å;⁵ and in the acetylene sorption complex, $Mn_{46}\text{-X} \cdot 30C_2H_2$, Mn-O=2.135(9) Å, respectively (see Table 3). The O(2)-Mn(II)-O(2) bond angles have decreased from a nearly trigonal planar value of 119.6(4)° in dehydrated $Mn_{46}\text{-X}^5$ to 116.9(5)° in ethylene complex⁵ and to 116.8(4)° in acetylene sorption complex (see Table 3). The Mn(II)-C distance, 2.70(5) Å is longer than the sum of the ionic radius of Mn^{2+} and the van der Waals radius of carbon as found in graphite ($0.80+1.70=2.50$ Å).¹⁷ This indicates that Mn(II)- C_2H_2 interaction is relatively weak.

The deviation of cations from 6-ring plane in dehydrated and sorption complex of $Mn_{46}\text{-X}$ has increased from 0.14(1) Å to 0.385(2) Å, which lie into the supercage (see Table 4). To interact with acetylene the Mn(II) ions at Mn(2) have

Table 3. Interatomic Distances (Å) and Angles (deg)^a

	Mn-O	Mn-C	C-C or C-O	O-Mn-O
$Mn_{4.5}\text{-A}(\text{dehydrated})$	2.11(1)			119.6(1)
$Mn_{4.5}\text{-A} \cdot 4.5C_2H_2$	2.177(10)	2.67(17)	0.9(3)	114.9(7)
$Mn_{46}\text{-X}(\text{dehydrated})$	2.09(2)			119.4(9)
$Mn_{46}\text{-X} \cdot 30C_2H_4$	2.12(2)	2.74(2)	1.38(7)	117(1)
$Mn_{46}\text{-X} \cdot 30C_2H_2$	2.135(9)	2.70(5)	1.18(7)	116.8(4)
$Mn_{46}\text{-X} \cdot 30CO$	2.108(11)	2.464(2)	0.98(7)	118.1(6)

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

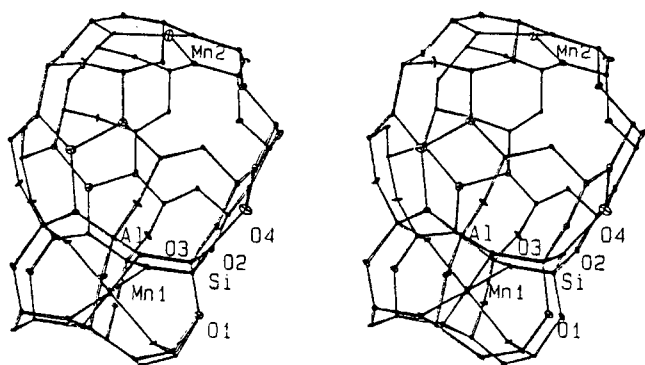


Figure 2. A stereoview of a sodalite cavity with an attached double six-ring in $\text{Mn}_{46}\text{-X}\cdot 30\text{C}_2\text{H}_2$. One Mn^{2+} ion at Mn(1) lies at site I and four Mn^{2+} ions at Mn(2) lie at site II. All double six-rings have this arrangement. About 75% of the sodalite cavities may have this arrangement. The remaining 25% may have only three Mn^{2+} ions at Mn(2). Ellipsoids of 20% probability are shown.

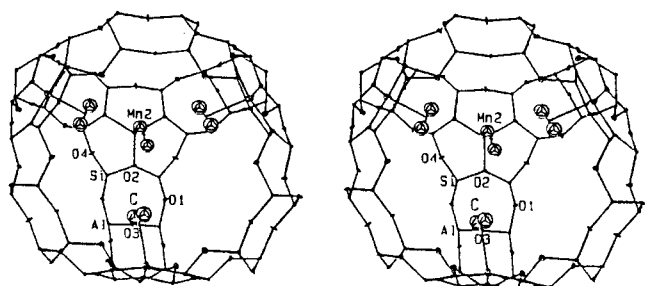


Figure 3. A stereoview of the supercage of an acetylene sorption complex of dehydrated $\text{Mn}_{46}\text{-X}$. Each of thirty acetylene molecules is coordinated to one Mn^{2+} ion at Mn(2). About 75% of the supercages may have this arrangement. Ellipsoids of 20% probability are shown.

moved 0.245 Å further into the supercage from its 6-ring oxygen planes compared with the structure of dehydrated $\text{Mn}_{46}\text{-X}$ (see Table 4).⁵

In the present structure, the Mn(2)-C distance (2.70(5) Å) is somewhat long. Therefore, the interaction is weak and apparently due to an electrostatic interaction between the dipositive Mn(II) ions and the polarizable π -electron density of the acetylene molecules. Since the manganese ions are dipositive, their d orbitals are contracted, and the synergic bonding¹⁸ between the metal and a weak-donor-strong-acceptor such as acetylene is appreciably inhibited.

The value determined for the carbon-carbon triple bond for this equivalent carbon atom description is 1.18(7) Å,

Table 4. Deviations (Å) of Cations from 6-ring Planes

	Mn	C	Remarks
$\text{Mn}_{4.5}\text{-A}(\text{dehydrated})$	-0.11(4)		ref 24
$\text{Mn}_{4.5}\text{-A}\cdot 4.5\text{C}_2\text{H}_2$	0.50(2)	3.1(2)	ref 4
$\text{Mn}_{46}\text{-X}(\text{dehydrated})$	0.14(1)		ref 5
$\text{Mn}_{46}\text{-X}\cdot 30\text{C}_2\text{H}_4$	0.38(1)	3.06(6)	ref 5
$\text{Mn}_{46}\text{-X}\cdot 30\text{C}_2\text{H}_2$	0.385(2)	3.00(5)	this work
$\text{Mn}_{46}\text{-X}\cdot 30\text{CO}$	0.30(2)	2.86(9)	ref 9

A positive deviation indicates that the atom lies in the supercages.

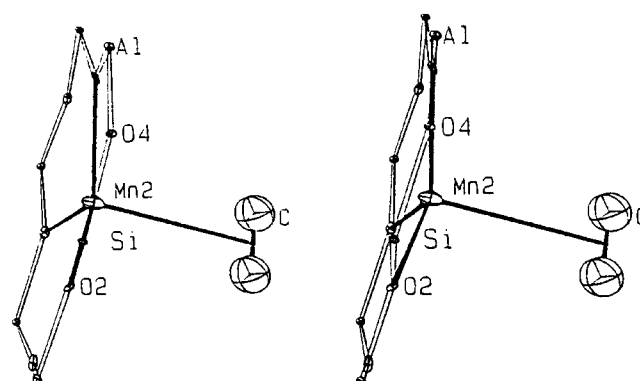


Figure 4. A $\text{Mn}(\text{C}_2\text{H}_2)_2^{2+}$ complex in the supercage. The approximately tetrahedral coordination about Mn^{2+} can be seen. Ellipsoids of 20% probability are used.

somewhat short but understandable as an aberration resulting from large thermal motion foreshortening and from unresolved disorder. In gaseous acetylene the C-C distance is 1.201(5) Å,¹⁹ and in an acetylene complex of zeolite 4A,²⁰ the bonds are imprecisely determined to be 1.03(15) Å.

The closest C-O(2) distance is 3.48(5) Å. The positions of the two hydrogen atoms of each acetylene molecule were calculated using the computer program HYDRO.¹⁰ This structure is very similar to those found for $\text{Mn}_{4.5}\text{-A}\cdot 4.5\text{C}_2\text{H}_2$ ⁴ and $\text{Cd}_{46}\text{-X}\cdot 28\text{C}_2\text{H}_2$.²¹ The hydrogen atoms lie in the plane of the carbon positions. This plane is parallel to that of the nearest framework oxygens, O(2)'s. Each hydrogen atom is about 3.21 Å from the nearest framework oxygen; the sum of the van der Waals radii of oxygen and hydrogen atom is 1.4+1.2=2.6 Å.²² Therefore, acetylene molecules make no significant approaches to the zeolite framework and the hydrogen atoms of acetylene molecules would be too far to form C-H...O interactions.²³

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Supporting Information Available. Tables of observed and calculated structure factors with esd's (5 pages). Ordering information is given on any current masthead page.

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Synthesis of (Diamine)platinum(II) and (Diamine)platinum(IV) Complexes of Isopropylidenmalonate Ligand and Their Interaction with Guanosine-5'-Monophosphate

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A series of (diamine)isopropylidenmalonatoplatinum(II) complexes and the oxidation products, (diamine)Pt(OOC)₂C=C(CH₃)₂(X)₂, (diamine=ethylenediamine(en), 1,2-diaminopropan(dap), N-methylethylenediamine(men); X=OH, OCOCH₃, OCOCF₃), have been prepared, and their interaction with guanosine-5'-monophosphate (5'-GMP) have been examined by means of ¹H NMR spectroscopy. The present platinum(II) complexes have shown to interact with 5'-GMP through N7 coordination in two consecutive steps in a similar way as with cisplatin, but no interaction between the present platinum(IV) complexes and 5'-GMP was observed. However, in the presence of ascorbic acid, the platinum(IV) complexes have been found to interact with 5'-GMP with the reaction rate depending on their reduction rate.

Introduction

cis-Diamminedichloroplatinum(II) (cisplatin) is one of the most widely used anticancer drugs, but its disadvantages are severe toxicities and acquired resistance. Efforts to overcome such disadvantages over the past two decades have resulted in clinical trials of a few second-generation drugs, such as diammine(1,1-cyclobutanedicarboxylato)platinum(II) and (1,2-diaminocyclohexane)-oxalatoplatinum(II).¹⁻⁵ Converting platinum(II) complexes to their platinum(IV) analogues is another approach to search for new platinum drugs. The antineoplastic activity of several platinum complexes has prompted intensive research on their working mechanism.⁶⁻⁹ However, no systematic research for the platinum(IV) complexes of alkylidenmalonate ligand has been carried out. Nowadays, it is generally accepted that the interaction of these drugs with the nucleobases of the

cellular DNA, and, in particular, with the kinetically preferred guanine, plays an important role in this process. Although we cannot exclude the fact that the active platinum(IV) drugs might exhibit a different mechanism compared to the corresponding platinum(II) complexes, it has been suggested that the former complexes might act as a type of "prodrug" which need activation by in vivo reduction before exerting their antitumor activity.¹⁰⁻¹³ For reduction of the octahedral platinum(IV) complexes to the square planar platinum(II) complexes, several biomolecules, such as ascorbic acid and cysteine-containing peptide, are presented to be utilized.

In order to gain more insight into the mode of the platinum(IV) complex-DNA interaction, we have prepared a series of platinum(IV) complexes, (diamine)Pt(OOC)₂C=C(CH₃)₂(X)₂ complexes (diamine=ethylenediamine(en), 1,2-diaminopropane(dap), N-methylethylenediamine(men); X=OH, OCOCH₃, OCOCF₃) by oxidation of the precursor platinum(II) complexes, (diamine)-Pt(OOC)₂C=C(CH₃)₂.

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