

#2612 THE INSTITUTE OF PAPER CHEMISTRY

(Metal-Carbohydrates)

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PROJECT REPORT FORM

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SIGNED Frank A. Lemke

STRUCTURE STUDIES OF METAL-CARBOHYDRATE COMPLEXES

SUMMARY

During the summer of 1966, known preparations and purifications of $\text{CaCl}_2 \cdot \text{xylose} \cdot 3\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot \text{mannose} \cdot 4\text{H}_2\text{O}$ were successfully performed. Through the use of diffraction data, density data, and chemical analyses, these two compounds were identified and exact molecular formulas were calculated. Weissenberg techniques were employed and a complete set of intensity data was obtained for the $\text{CaCl}_2 \cdot \text{xylose} \cdot 3\text{H}_2\text{O}$ complex.

A new compound, $\text{ZnCl}_2 \cdot \text{xylose}$, was prepared and preliminary x-ray diffraction data were obtained.

EXPERIMENTAL AND DISCUSSION

KNOWN CRYSTALLIZATIONS OF CaCl_2 -SUGAR COMPLEXES

Five grams of D(+) xylose and eight grams of calcium chloride were partially dissolved in 7 cc. of distilled water, then brought to a boil and complete solution on a hot-water bath. The solution did not crystallize on standing, but when an equal volume of absolute ethanol was added and the solution evaporated in a bath, it soon crystallized to a rather solid mass. This was thinned with a small amount of absolute ethanol and the solid mass was broken up with a spatula. The crystals were drained by filtration with a Büchner funnel and then washed with absolute ethanol. The partially dried crystals were dried thoroughly in a vacuum desiccator. Six grams of the first fraction were dissolved in 9 cc. of absolute ethanol and 1.5 cc. of distilled water and filtered through a Büchner funnel. The solution was evaporated to one half of its original volume in a hot-water bath, and then 9 cc. of absolute ethanol was added. On further evaporation in a vacuum desiccator, the solution crystallized two days later. The complex was washed with absolute ethanol and the crystals were drained and partially dried on a Büchner funnel. The crystals were extremely long and slender and rather difficult to wash. The final hygroscopic product was placed in a vacuum desiccator to prevent solution in the humid atmosphere.

Five grams of assumed β -D-mannose and eight grams of crystallized calcium chloride dihydrate were dissolved in a boiling-water bath in 7 ml. of distilled water. On standing in a vacuum desiccator for five days at room temperature, the solution crystallized to a solid mass. This was thinned out with absolute ethanol, filtered on a Büchner funnel, and washed thoroughly with absolute ethanol. The crystals were broken up with a pick and partially dried on the funnel. They were transferred to a vacuum desiccator for complete drying. A solution of 9.96 gm. of the complex in 10 ml. of distilled water was filtered through a Büchner funnel followed by 4 ml. of distilled water. The solution was then allowed to stand out on a watchglass for two days until nearly complete recrystallization occurred. The crystals were washed with absolute ethanol, transferred to a Büchner funnel, and washed with more absolute ethanol. The final crystal complex was thoroughly dried in a vacuum desiccator--an illustrative sketch of $\text{CaCl}_2 \cdot \text{mannose} \cdot 4\text{H}_2\text{O}$ appears on p. 96 of Research Notebook 1849.

ATTEMPTED CRYSTALLIZATION OF NEW SALT-SUGAR COMPLEXES

Attempts were made at crystallizing such new and interesting salt-sugar complexes as CuCl_2 -xylose, CoCl_2 -xylose, AlCl_3 -xylose, FeCl_3 -xylose, β -D-Glucose Pentaacetate- ZnCl_2 , SrCl_2 -xylose, and ZnCl_2 -pentose sugars. Unfortunately, no immediate results were obtained since the solutions either evaporated down to viscous syrups or various salts and sugars crystallized separately in given solvents. Research Notebook 1849, p. 95+ may be consulted for preparation procedures.

TRIAL PREPARATIONS AND FINAL CRYSTALLIZATION PROCEDURE FOR ZnCl_2 -XYLOSE

The trial preparations leading up to the successful crystallization of ZnCl_2 -xylose will not be presented in this report, but may be referred to on pp. 115-138 of Research Notebook 1849.

The desired ZnCl_2 -xylose complex was finally arrived at by dissolving 1.5 gm. of ZnCl_2 and 0.5 gm. of xylose in 30 ml. of diglyme at 100°C . on a hot-water bath. An illustration of the apparatus employed appears on p. 136. A test tube of the supersaturated solution was placed in an Erlenmeyer flask of cold water and cooled slowly in a refrigerator. An illustration of this apparatus also appears on p. 136. Crystals gradually precipitated out of the solution near the bottom of the test tube where the temperature gradient was at a minimum. The crystals were transparent and hexagonally shaped. An illustrative sketch appears on page 137.

DEBYE-SCHERRER IDENTIFICATION OF ZnCl_2 -XYLOSE

A control Debye-Scherrer powder pattern was taken of xylose crystals alone. The newly isolated ZnCl_2 -xylose were then photographed with the Debye-Scherrer powder camera, and the resulting pattern was distinctly different from that of xylose. There was no need to compare the ZnCl_2 -xylose pattern with a control pattern of ZnCl_2 crystals because a simple flame test charred the complex crystals thus indicating that xylose was present and that a combination of ZnCl_2 and xylose must have produced the new and distinct Debye-Scherrer powder pattern.

EMPIRICAL AND CALCULATED UNIT CELL DIMENSIONS AND DENSITIES

CaCl_2 -xylose- $3\text{H}_2\text{O}$ - Measured Cell Dimensions--pp. 120-23

Calculated Unit Cell Density--p. 123

Empirical Unit Cell Density--p. 113

ZnCl_2 -xylose - - - Measured Cell Dimensions--pp. 130-131

Proposed Unit Cell Density--p. 137

Due to lack of time, empirical unit cell density data was not collected on the ZnCl_2 -xylose complex. Since most time and effort was concentrated on collecting data on the CaCl_2 -xylose- $3\text{H}_2\text{O}$ and ZnCl_2 -xylose complexes, only an experimental unit cell density determination was run on the CaCl_2 -mannose- $4\text{H}_2\text{O}$ crystals. See p. 117 in Research Notebook 1849 for data.

CHLORINE ANALYSES

In order to determine molecular formulas for the CaCl_2 -xylose- $3\text{H}_2\text{O}$ and ZnCl_2 -xylose complexes, chlorine analyses were conducted by the Analytical Chemistry Department. Data for CaCl_2 -xylose- $3\text{H}_2\text{O}$ appears on p. 112, and that for ZnCl_2 -xylose appears on p. 134.

ASH TEST DETERMINATION OF PER CENT $ZnCl_2$ IN SALT-SUGAR COMPLEXES

Data obtained from the ashing tests appear on pages 116 and 126. The ash test data, however, was concluded to be insignificant in determining the per cent $ZnCl_2$ present since neither test produced the required per cent of $ZnCl_2$ based on the molecular formulas derived from the chlorine analyses data. The fact that a residue remained after ashing was used as a simple check for the presence of $ZnCl_2$.

WEISSENBERG LINE-UPS AND LAYER PHOTOGRAPHS OF $CaCl_2$ -XYLOSE- $3H_2O$

After an annoying light leak was remedied by taping over the metal rings of the ends of the Weissenberg camera with black tape, a series of line-up shots and photographs of seven layers in the $CaCl_2$ -xylose- $3H_2O$ crystal were taken and developed. These photographs are presently stored in brown envelopes in the x-ray diffraction laboratory.

CONSTRUCTION AND USE OF WEISSENBERG LATTICE ROW TEMPLATES

From an original lattice row template, 39 individual patterns were traced and cut out of durable plastic, and then carefully filed down to pencil width accuracy. These templates were then used to trace lattice rows on .005-inch matte acetate placed over each x-ray photograph. The sheets of matte acetate were sprayed with approximately ten coats of Blair low odor matte fixative. The mattes then became transparent and, when replaced over the respective x-ray photographs, they made dot intensity indexing much easier.

CONSTRUCTION OF A WEISSENBERG DOT INTENSITY SCALE

A dot intensity scale was photographed by exposing x-ray film to Cu radiation for time intervals corresponding to a square progression appearing on page 125. Each dot on the intensity scale was then labeled with its respective exposure time in seconds.

DOT INTENSITY INDICES FOR $\text{CaCl}_2\text{-XYLOSE-}3\text{H}_2\text{O}$

The dot intensity scale was then used to visually index the dots on each of the three film layers for each of the seven crystal layers photographed.

A program for the 1620 Computer must now be written to determine an average scale factor for intensity data between each of the three film sets for each of the seven crystal layers photographed. In addition, the dot intensity indices must be suitably corrected to arrive at the respective structure factors which will serve as coefficients in subsequent Fourier synthesis.

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John W. Swanson
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Gerald F. Richards

STRUCTURE STUDIES OF METAL-CARBOHYDRATE COMPLEXES

SUMMARY

Many of the simple carbohydrate compounds react with metal salts to form metal-carbohydrate complexes (30). Most of these complexes have been studied in solution, and only a few of them have been isolated as solid crystalline materials. This project is concerned with the structure of these solid materials and in particular with the crystal structure of calcium chloride-carbohydrate complexes.

In order to execute the research proposed, some new equipment was purchased or constructed, techniques and procedures were developed for the handling of films and data, and provisions were made for making the calculations. These can be summarized:

1. A low temperature gas-flow crystal for cooling crystals to a constant temperature near that of liquid nitrogen has been developed and placed into routine operation. Four sets of intensity data have been obtained using this apparatus.
2. Dark room facilities of the fiber microscopy laboratory and photography laboratory have been used to process the necessary films. Materials have been obtained and techniques established for the processing and indexing of intensity films.
3. A library of computer programs written for the I.B.M. 1620 has been developed. These programs have been used in the solution of three crystal structures. Many of these programs, with slight modification, will be usable on the I.B.M. 360 machine.

The crystal structure of D-xylose·CaCl₂·3H₂O has been worked out in detail. Each calcium atom is bonded to four hydroxyl groups and to three oxygens from the water molecules. The calcium atoms are bridged by means of the xylose ring with one calcium bonded to the hydroxyl pair O₁, O₂ and the other to O₃, O₄. This forms a chainlike structure throughout the crystal. The oxygen atoms are distributed about the calcium in a distorted pentagonal bipyramid arrangement. Average Ca-O distances are around 2.40 Å. The chlorine atoms are not in the coordination sphere of the calcium. They are held in the cell by means of hydrogen bonds to the hydroxyl groups and to the water molecules. The xylose ring complexed as the α-anomer in the normal chair conformation. All the bond lengths and bond angles appear normal within the level of accuracy of the structure.

Compounds D-mannose·CaCl₂·4H₂O and α-D-gulose·CaCl₂·H₂O have been prepared. These compounds are reasonably stable. Preliminary diffraction data indicates that their structures can probably be solved by x-ray methods.

An effort has been made to prepare some new metal carbohydrate compounds, particularly compounds which contain the metals, zinc and aluminum. This effort has resulted in the preparation of a new compound, a 1:1 complex between ZnCl₂ and the ether, diglyme.

Project 2612 seems to have stimulated some interest in structural chemistry among other staff members. It has contributed directly or indirectly to the work of other Institute personnel, and it has been closely associated with the thesis subjects of several students.

INTRODUCTION

Project 2612 is concerned with the study of compounds which are formed by the reaction of sugar molecules with compounds containing a metal ion. In particular, it was proposed that the crystal and molecular structure be determined for D-xylose·CaCl₂·3H₂O, D-mannose·CaCl₂·4H₂O, and α-D-gulose·CaCl₂·H₂O (1-8). It was also proposed that an attempt be made to prepare and study the structure of a complex between CaCl₂ and xylobiose. Some of the reasons for undertaking this research are as follows.

1. The execution of a research program of this nature helps introduce a new research tool to the research program of The Institute of Paper Chemistry. It requires the purchasing and building of equipment, development of laboratory and dark room facilities, establishment of procedures and techniques, and the acquiring and writing of computer programs to carry out the laborious calculations. With large computing facilities available, this technique is practical and it should be made a part of the research tools of the students and faculty.
2. Reactions between metal complexing agents and polyhydroxy compounds have been studied in solution. Reeves (9) conjectures that the metal attaches itself to two suitably oriented hydroxyl groups forming a complex. Cupramonium-glycol reactions have been used extensively to study the conformation of carbohydrates (10-17). The exact nature of these complexes is unknown. It is desirable to know the atoms

which form the coordination sphere of the metal. It is possible that the ring oxygen participates in the bonding between sugar and the metal.

3. The crystal structures of only a few of the simple sugars are known. These have been reviewed by Jeffrey and Rosenstein (18) and more recently by John Ham (19). The molecular structure of the sugar involved in the complex should be known when the crystal structure of the complex is completed.
4. The conformation of the ring in α -D-gulose has been the subject of considerable debate (20-29). In its pure form α -D-gulose does not crystallize. A satisfactory solution of the structure of α -D-gulose \cdot $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ may provide information on the conformation of α -D-gulose.
5. Metal salts are used extensively in the pulp and paper industry, although their role is not clearly understood. In particular, the aluminum ion is used in size systems and the zinc ion is active in vulcanizing systems. A knowledge of these structures may provide a better insight into these systems.
6. Metal-carbohydrate complexes are important in other areas which are related to the paper industry. The government forestry laboratories are experimenting with metal salts as fire retardants.
7. The metal carbohydrate complexes are biologically important. Metal ions may be transferred through the bloodstream as complexes with simple sugars (30).

8. This research is closely related to other research being carried out at The Institute of Paper Chemistry, particularly the work of Thompson, Morak (31), and Gaillard, and the student thesis research of Bayer (32), Hintz (33), Hanby (34), and Richards (35).

EXPERIMENTAL

THE X-RAY DIFFRACTION TECHNIQUE

A crystalline material (one single crystal of this material) can be developed from a small grouping of atoms which comprise a unit cell. The edges of this cell form a natural coordinate system which are used to define the positions of the atoms in the cell. Three coordinates define each atom in the cell. These coordinates are normally expressed as fractions of a cell edge length. Usually, groups of atoms in the cell are related to other groups by some simple relationship (i.e., one group is the mirror image of the other through a certain plane). This relationship is known as a space group. A crystal visible to the eye can be thought of as this small unit cell constantly repeating itself along all three of its axes.

The only unambiguous means for determining the structure of a crystalline material is by some diffraction technique (x-rays, neutrons) When a structure is correctly solved the coordinates of each atom are known in the unit cell. All the bond angles and bond lengths can be calculated. The complete stereochemistry is known.

The following is a brief attempt to describe the methods used in this structure research. When a single crystal is placed in a columnated beam of X-rays and simultaneously the crystal is subjected to the rotation of a Weissenberg camera, a diffraction pattern arises which can be recorded on a film. This film is illustrated in Figure 1. Several of these films are obtained for each crystal analysis.

Each reflection spot shown in Figure 1 can be assigned a set of three integers called Miller indexes (h,k,l) which uniquely define the reflection spot. This assignment is called indexing.

The unit cell dimensions can be calculated from the spacing of the spots on the photograph. The crystal class is determined by the symmetry of the spots on the photograph, and the space group is obtained by observing systematic absences of reflections (i.e., all reflections whose h index are even are absent from the photograph).

It can be observed in Figure 1 that some reflection spots are darker or more intense than others. It is this intensity for each reflection $I_{h,k,l}$ which is related to the positions of the atoms in the unit cell. The intensities are the primary set of data, and they are usually obtained by visually estimating the intensity of the spot relative to a standard. The number of these measurements can range from a few hundred to several thousand, depending on the magnitude of the unit cell being studied.

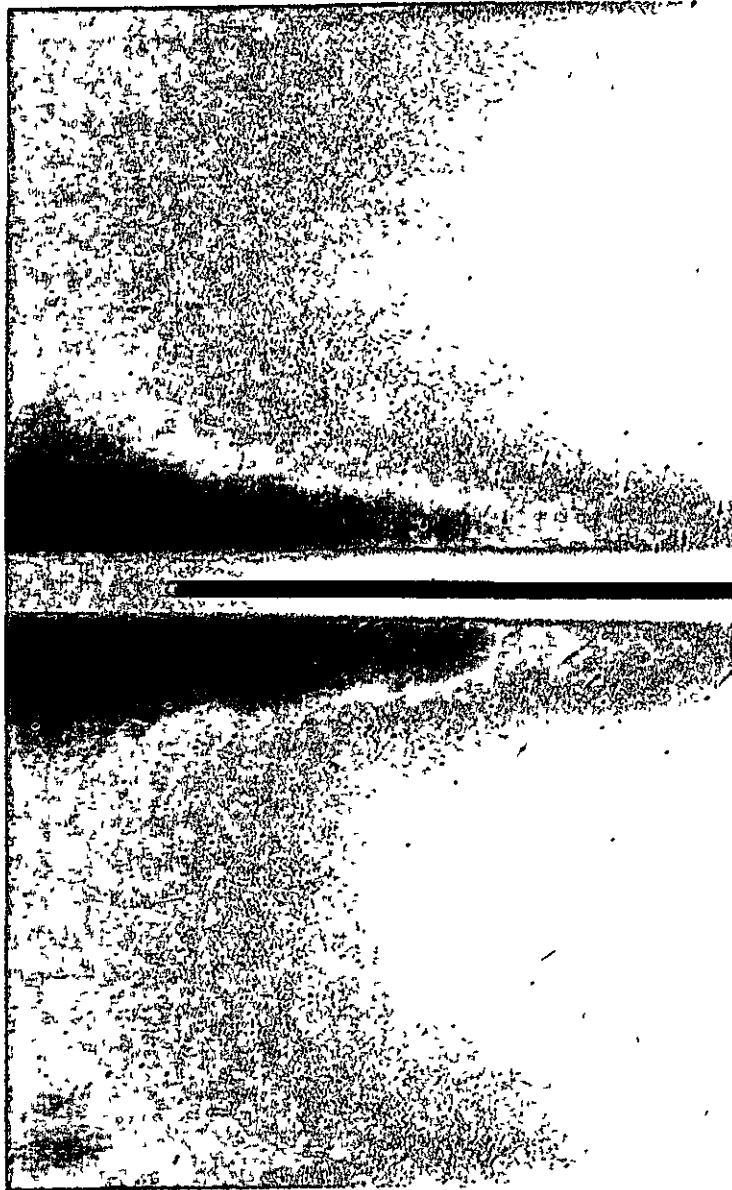


Figure 1. Weissenberg Photograph

The intensity data $I_{h,k,l}$ are related to a quantity called the structure factor, $F_{h,k,l}$ by the following formula:

$$I_{h,k,l} = KALP |F_{h,k,l}^o|^2$$

The observed intensities $I_{h,k,l}$ are reduced to the observed structure factors $|F_{h,k,l}^o|$ on a computer by correcting for the constant, K; absorption, A; Lorentz, L; and polarization, P, terms. A set of observed structure factors are thus obtained from the experimental intensity data. Note that only the absolute value of the structure factor is obtainable. Assuming a set of coordinates for each atom in the unit cell a set of structure factors $F_{h,k,l}^c$ can be calculated from the following formula:

$$F_{h,k,l}^c = \sum_j f_j \exp(hx_j + ky_j + lz_j) \quad (1)$$

where x_j, y_j, z_j 's are the coordinates of the j atom in the cell. f_j is a quantity proportional to the number of electrons in the j th atom. If the assumed x_j, y_j, z_j 's are nearly correct then $|F_{h,k,l}^o|$ will be nearly the same as $|F_{h,k,l}^c|$ for all h,k,l . This is one criteria for correctness and it is usually expressed by a factor R where:

$$R = \frac{\sum (|F_{h,k,l}^o| - |F_{h,k,l}^c|)}{\sum |F_{h,k,l}^o|}$$

The problem is to find the set of x, y, z , coordinates for each atom in the cell which will make the above R small (i.e. $R = .10$).

If the correct signs (+ or -) for the $|F_{h,k,l}^O|$'s are known (in a centrosymmetric crystal), and the electron density expression is calculated using these $|F_{h,k,l}^O|$'s, then peaks will be produced in the calculation which correspond to the positions of atoms in the unit cell. At the outset these signs are not known. The electron density expression has the general form:

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{h,k,l} \exp - 2\pi i(hx + ky + lz) \quad (2)$$

Here, V is the volume of the unit cell.

The procedure used in this research was to first locate the coordinates of the heavier atoms in the cell. This was done by summing an expression similar in form to Equation (2) but replacing $F_{h,k,l}$ with $|F_{h,k,l}^O|^2$. (These are obtained directly from the intensity data.) This is called the Patterson function. The coordinates of peaks derived from this expression correspond to the ends of vectors which can be formed between atoms in the cell. The height of the peak is proportional to the product of the number of electrons in the atoms from which the vector is derived. Peaks due to vectors between heavy atoms have the highest magnitude. From the coordinates of these vector peaks the positional coordinates of the heavy atoms in the unit cell were derived. The coordinates obtained from the heavier atoms were used in Equation (1) to calculate the $F_{h,k,l}^C$'s. The calculated $F_{h,k,l}^C$'s which agreed well in magnitude with the observed $|F_{h,k,l}^O|$'s were used in Equation (2) to calculate ρ . Although this calculation is approximate (since only the

the signs of a fraction of the $F_{h,k,l}^c$'s are correct) peaks corresponding to other atoms appeared in the cell. Coordinates of these peaks, along with the coordinates of the heavy atoms, were now used in Equation (1). This procedure was repeated until the phases (signs) associated with the $F_{h,k,l}^c$'s were accurate enough such that when they were used in Equation (2) only 16 peaks (corresponding to 16 atoms) appeared in the calculation.

LOW TEMPERATURE EQUIPMENT

The atoms in the unit cell can be pictured as being in a constant state of motion, oscillating about their mean coordinates in the unit cell. This motion may depend on a number of vibrational and rotational modes which are operating within the molecule and crystal. The motion is temperature dependent, and it decreases the scattering contribution (f_j in Equation 1 decreases) that each atom makes to a reflection. This effect is accounted for in the calculation of $F_{h,k,l}^c$ by introducing another parameter for each atom called a temperature factor. One way to reduce the atomic motion and to minimize the possible errors in the temperature factor is to cool the crystal. For the above reasons a low temperature cryostat was constructed and placed in routine operation in the X-ray laboratory.

The crystal is cooled by means of a nitrogen gas stream which is delivered from a reservoir of liquid nitrogen contained in the cryostat. The design of the cryostat is such that the nitrogen gas stream is jacketed by liquid nitrogen until it is about 1 cm. from the crystal. The temperature at

the crystal is constant and near that of liquid nitrogen. A several-fold increase in intensity is observed for many reflections as a result of this temperature change. This gives rise to excellent films with very good reflection to background contrast.

In order to use the cryostat effectively a few additions were made to the diffraction laboratory. These include a supporting structure for the cryostat, facilities for controlling the moisture content of the air near the crystal, and an air conditioning unit to help control the humidity in the room. A detailed description of the design of the apparatus, discussions on the many advantages of low temperature data, and the detailed procedures used in acquiring low temperature data can be found in other sources (36, 37, 38, 19).

At the present time four sets of intensity data (three by students) have been acquired with this apparatus.

COMPUTING AND PROGRAMING

It can be seen from Equations (1) and (2) that the computing required in this research is great. With approximately 1300 reflections the computing time required for one electron density map was approximately six hours on the I.B.M. 1620 machine.

The data reduction computer programs (converting $I_{h,k,l}$ to $|F_{h,k,l}^o|$), the programs for calculating structure factors (Equation 1); and the summation

program for the electron density calculations (Equation 2) were obtained from the crystallographic laboratory of the University of Pittsburgh (39). These programs were written for a machine with 20K core storage, card input, and typewriter or card output. When the high speed printer and the disc storage become available, the summation program was modified by Bill Scott to permit continuous running without any operator attention. All the electron density calculations for this research were started near midnight and taken off the computer early in the morning. Thus computing time was utilized that would normally have been lost.

When the structure is nearly correct, that is the parameters are nearly correct for each atom in the unit cell, then the parameters are adjusted by means of a least squares procedure to give the best fit between the $|F^O_{h,k,l}|$'s and the $|F^C_{h,k,l}|$'s. The function minimized is normally $\sum (|F^O_{h,k,l}| - |F^C_{h,k,l}|)^2$. This calculation was made with a program written for a 1620-40K computer by Mair (40). On the average, one hour's computing time was required per calculation.

There were a number of programs used which altered the formats of the data cards for convenient usage of the above programs. These were written by John Ham.

These computer programs are cataloged and stored in the computer room along with their instructions. The programs have been used in the solution of three structures (two by students).

When the I.B.M. 1620 computer is replaced by the I.B.M. 360 many of these programs will still be applicable; however, some new programs will be obtained which are written especially for the new computing system.

DARK ROOM FACILITIES AND PROCEDURES

It has been convenient to use the dark room in the fiber microscopy laboratory for most of the routine film processing. However the intensity films were developed in the photography laboratory. Tanks, film holders, and safety lights have been purchased. Kodak no-screen medical X-ray film and Kodak high speed X-ray developer were used in processing the films. The techniques for handling the films and details on the film processing can be found elsewhere (19,37).

THE CRYSTAL STRUCTURE OF D-XYLOSE·CaCl₂·3H₂O

PREPARATION OF CRYSTALS

D-xylose·CaCl₂·3H₂O crystallized easily from a mixture of D-xylose and CaCl₂·2H₂O in water (6). They were recrystallized from a water, ethanol mixture to give clear, white needle-like crystals. The crystals were hygroscopic and difficult to handle during summer humidity. In the winter they were handled more easily, but the crystals would decompose when exposed to the air for several days.

CRYSTAL DATA AND INTENSITY DATA

The crystal data are tabulated in Table I. The only reflection absences that occurred were for Ok0 data when $k = 2n + 1$. This placed the

TABLE I

Crystal Data

D-xylose \cdot CaCl₂ \cdot 3H₂O

C₅ O₈ H₁₆ CaCl₂

Crystal Class--Monoclinic

Space Group--P2₁

2 Molecules per unit cell

Cell Dimensions, Å

Room Temperature

Low Temperature

a = 8.47 ± .02

a = 8.375 ± .002

b = 12.78 ± .02

b = 12.599 ± .02

c = 7.23 ± .02

c = 7.194 ± .002

= 115°

= 114.40°

density calculated 1.46 g/cm³

density measured 1.50 g/cm³

Crystal size in m.m.

crystal 1 .14 x .10 x .24

crystal 2 .17 x .14 x .34

linear absorption coefficient μ = 75.1/cm.

crystal in space group $P2_1$. Room temperature cell dimensions were determined from the average of several measurements made on films containing h0l data and rotation photographs. Low temperature cell dimensions were determined from back-reflection Weissenberg films with the use of an analytical least-squares extrapolation method to minimize systematic errors. Notice the considerable shrinkage of the cell dimensions on going from room temperature to 80°K . The density was measured by flotation.

At the outset of this study, before the low temperature apparatus had been placed in operation, it was decided to obtain some intensity data at room temperature in order to test the computer programs (none of the programs had been used) and to attempt to solve the structure. This proved to be poor judgment, as the data did not lead to a correct structure. The data were too few in number and too poor in quality. A small needlelike crystal, 0.1 mm in diameter, was sealed in a glass capillary and photographs containing data h0l - h6l were recorded. The intensities were estimated by comparing the intensity of the spots on the films with a calibration strip prepared from the same crystal. After averaging, scaling, and correcting the data there were 350 independent reflections. These data were used to calculate a three dimensional Patterson function. The heavier atoms were not located from this calculation. However, all the programs were operated effectively.

When the low temperature equipment became available a complete set of intensity data was obtained. Two crystals were used (Table I). Each

crystal was glued into a 0.3 mm glass capillary with Epoxy 907, and the capillary was sealed. Multiple films, four films packed into the film holder at the same time, were used for each exposure. Exposure times ranged from twelve to fourteen hours. Both crystals were small enough (Table I) so that absorption was not a serious factor. Films containing data h0l - h7l were taken from crystal 1, 0kl - 4kl from crystal 2. Calibrated intensity strips were made with a range of intensity from approximately 20 - 1400. These strips were used to visually estimate the intensities of the reflections after the photographs had been developed and processed.

The data were scaled and averaged. Data from both crystals were placed on a common scale by the method of Hamilton, Rollett, and Sparks (41). The Lorentz and Polarization corrections were made on the 1272 observable $I_{h,k,l}$'s to give the $|F_{h,k,l}^0|$'s. No absorption correction was applied.

All the intensity data are recorded in the notebooks and the films are marked and stored in the X-ray room.

STRUCTURE SOLUTION

The solution of this structure was carried out in a straight forward manner for a problem of this type. Table II summarizes how the solution progressed. First, the Patterson function was calculated using all 1272 $|F_{h,k,l}^0|^2$ as coefficients in the summation. Since Ca^{++} and Cl^- are isoelectric, the peaks on the maps corresponding to these atoms were essentially the same height. The coordinates of the Calcium and one chlorine

TABLE II
 Progress of Structure Determination
 D-xylose · CaCl₂ · 3H₂O

<u>Calculation Type</u>	<u>New atoms located in the unit cell</u>	<u>R Index All located atoms in calculation</u>
Patterson function	Ca, Cl ₁	0.41
electron density No. 1	Cl ₂	0.35
electron density No. 2	O ₆ , O ₃ , O ₄ , O ₁ , O ₇ , O ₈	0.30
electron density No. 3	O ₂ , C ₁ , O ₅	0.26
electron density No. 4	C ₂ , C ₄	0.25
electron density No. 5	C ₃ , C ₅	0.24
Least Squares Refinement Isotropic temperature factors		
Cycle 1		.174
Cycle 2		.137
Cycle 3		.126
Cycle 4		.123
Least Squares Refinement Anisotropic temperature factors		
Cycle 1		.114
Cycle 2		.107

atoms were determined and the structure factor calculation corresponding to these coordinates gave an R index of 0.41. All atoms were given the same isotropic temperature factor, $B = 1 \text{ \AA}^2$. All the 1272 pieces of data were used in every calculation. These structure factors were used to calculate an electron density map from which the coordinates of the second Chlorine atom were obtained. Inspection of the Patterson showed the peak corresponding to this atom to have a smaller peak height than that due to the other chlorine. This was probably due to the resolution of the Patterson calculation. Coordinates from all three atoms were now used to calculate structure factors which gave an $R = 0.35$. These structure factors were used to calculate another electron density map from which coordinates of six oxygen atoms were determined. This iterative process continued (Table II) until all 16 atoms were located in the unit cell. The R index was around 0.24 at this time.

REFINEMENT OF STRUCTURE

With the atoms located in the unit cell in positions which were nearly correct a least squares calculation was applied in order to improve the coordinates. The function minimized was $\sum (|F_{h,k,l}^o| - |F_{h,k,l}^c|)^2$. For the heavy atoms the scattering factors of Cromer and Waber (43) were used while those of Hansen, Herman, Lea, and Skillman (42) were used for carbon and oxygen. At first isotropic temperature factors were applied. The progress of the refinement is shown in Table II. After four cycles the

R index was 0.123. At this time the temperature factors were allowed to vary anisotropically. This takes into account the fact that the atoms may have greater motion in one direction than in another. Two cycles of anisotropic refinement gave an R of 0.107. The parameters corresponding to this refinement are listed in Table III and the anisotropic temperature factors in Table IV. It must be pointed out that the results at this time are good but they can be improved by including in the calculation the position of the hydrogen atoms and by properly weighting the data. This is being done now.

DESCRIPTION OF THE STRUCTURE

Figure II views the structure down the c axis with portions of four unit cells shown in order to best illustrate the features of the complex. Figure III shows the same features but this is viewed down the b axis. The atomic numbering is the conventional numbering for carbohydrates. The two different chlorines are also identified by numbers. Each Ca is linked to seven oxygen atoms, O_1, O_2 from one ring, O_3, O_4 from the second ring, and O_6, O_7, O_8 from the waters of hydration, forming a chainlike structure throughout the crystal. The structure can be viewed as a polymeric type structure with the xylose rings being bridged together by calcium atoms. Chlorine atoms are not involved in the coordination sphere of the calcium. Table V gives the bond lengths and their standard deviations. The bond lengths from calcium to the oxygen atoms in the water molecules are essentially equal, 2.35\AA . The lengths from the hydroxyl oxygens to calcium are

TABLE III

ATOMIC PARAMETERS*

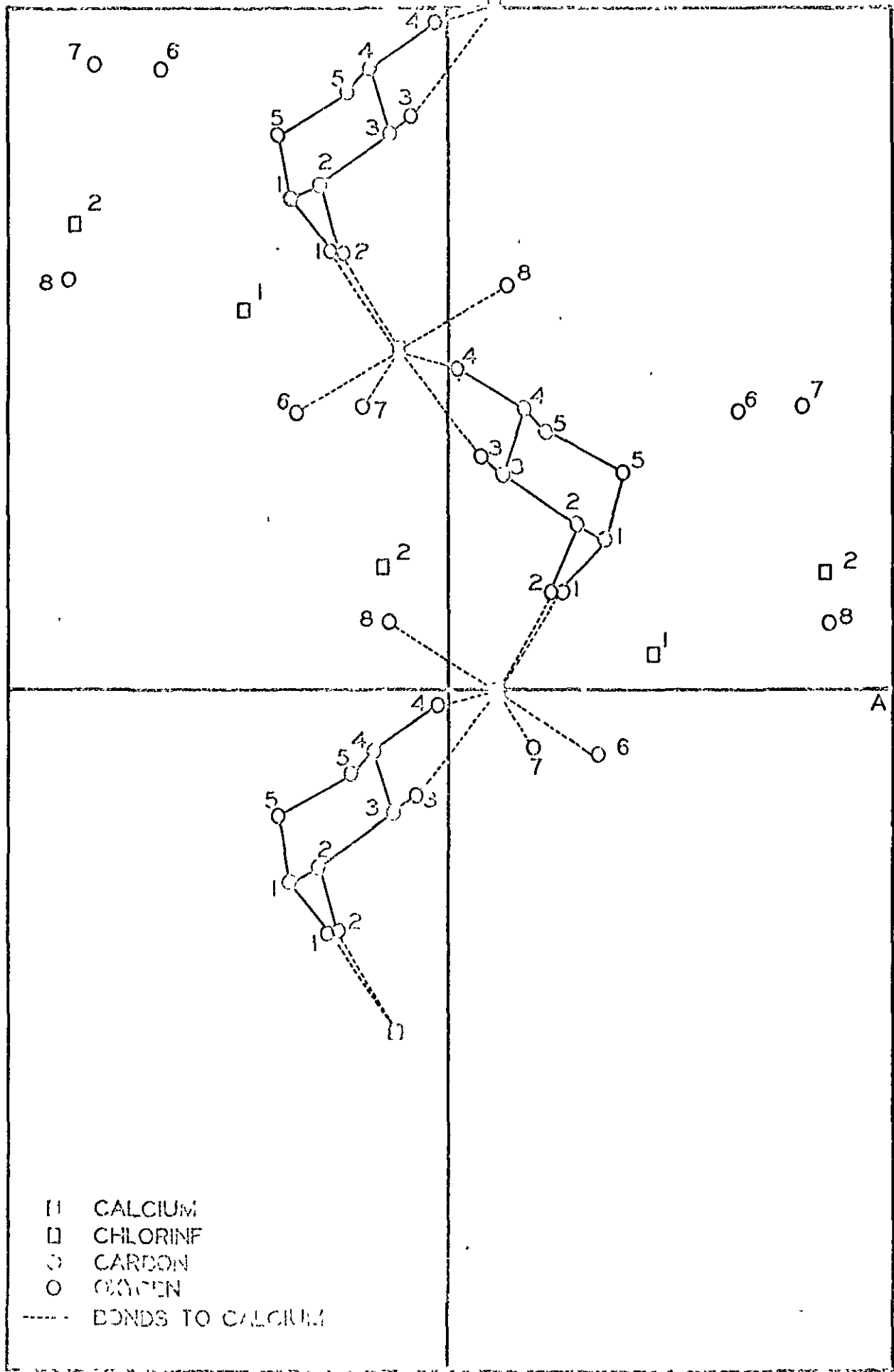
Atom	x	y	z
Ca	0.11255	0.00060	0.10190
C ₁ ₁	0.46530	0.04991	0.87228
C ₁ ₂	0.85032	0.17583	0.56694
O ₁	0.25436	0.14459	0.44243
O ₂	0.23805	0.14335	0.06329
O ₃	0.07064	0.34226	0.89911
O ₄	0.02379	0.47756	0.17362
O ₅	0.88463	0.31148	0.51702
O ₆	0.65751	0.40705	0.83862
O ₇	0.80429	0.41698	0.48923
O ₈	0.86417	0.09745	0.16513
C ₁	0.35929	0.21713	0.39825
C ₂	0.29483	0.24063	0.17441
C ₃	0.12433	0.31114	0.10812
C ₄	0.17425	0.41029	0.24189
C ₅	0.21823	0.37785	0.45228

*These are listed as fractions of a unit cell length with x corresponding to a, y to b, and z to c.

TABLE IV

ANISTROPIC TEMPERATURE FACTORS

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{14}
Ca	0.00126	-0.00028	0.00062	-0.0009	-0.00095	-0.00065
Cl ₁	0.00121	0.00017	0.00095	-0.00033	-0.00091	0.00027
Cl ₂	0.00400	-0.00022	0.00196	-0.00030	-0.00069	-0.00103
O ₁	0.00411	0.00056	0.00204	-0.00043	-0.00293	-0.00048
O ₂	0.00285	0.00000	0.00233	0.00023	0.00060	0.00152
O ₃	0.00677	0.00050	0.00042	0.00194	0.00213	0.00163
O ₄	0.00501	0.00009	0.00357	-0.00230	0.00040	-0.00300
O ₅	0.00493	0.00025	0.00297	-0.00083	-0.00513	-0.00221
O ₆	0.00655	0.00102	0.00436	-0.00247	0.00234	-0.00238
O ₇	0.01107	0.00069	0.00125	0.00083	0.00194	0.00225
O ₈	0.00326	0.00003	0.00313	-0.00199	-0.00069	-0.00172
C ₁	-0.00031	-0.00099	0.00405	-0.00199	-0.00016	-0.00230
C ₂	0.00117	-0.00032	0.00254	-0.00060	-0.00330	-0.00135
C ₃	0.00316	0.00029	0.00258	0.00176	0.00260	0.00469
C ₄	0.00404	-0.00070	0.00438	-0.00142	0.00187	0.00221
C ₅	0.00754	0.00044	0.00338	0.00092	-0.00432	0.00438



- CALCIUM
- CHLORINE
- CARBON
- OXYGEN
- BONDS TO CALCIUM

Figure 2. Structure viewed along the c-axis.

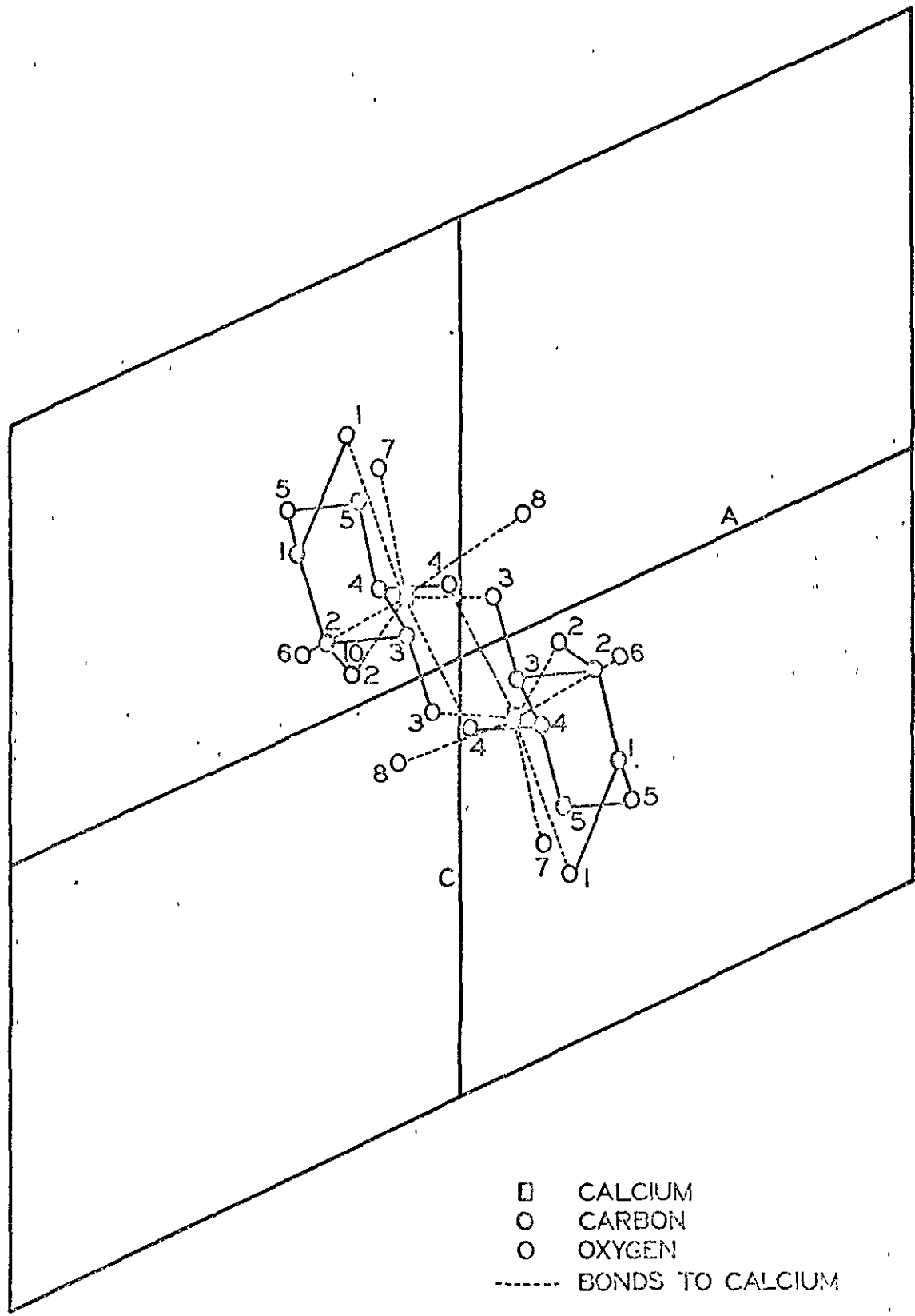


Figure 3 Structure Viewed Down b axis

TABLE V

BOND LENGTHS AND THEIR STANDARD DEVIATIONS
FOR D-XYLOSE \cdot Ca Cl₂ \cdot 3H₂O

Bond	Bond Length, Å	Standard Deviation, Å
C ₁ -O ₁	1.39	0.025
C ₁ -O ₅	1.43	0.025
C ₁ -C ₂	1.50	0.03
C ₂ -O ₂	1.43	0.025
C ₂ -C ₃	1.58	0.03
C ₃ -C ₄	1.53	0.03
C ₃ -O ₃	1.43	0.03
C ₄ -O ₅	1.46	0.03
C ₄ -O ₄	1.43	0.025
C ₅ -O ₅	1.52	0.025
Ca-O ₁	2.49	0.02
Ca-O ₂	2.45	0.02
Ca-O ₃	2.44	0.02
Ca-O ₄	2.41	0.02
Ca-O ₆	2.34	0.02
Ca-O ₆	2.35	0.02
Ca-O ₇	2.35	0.02

slightly longer, 2.45\AA with $\text{Ca} - \text{O}_1$ longer than the average. Errors in the bond lengths are such that this difference is not quite significant, but it may be related to the fact that $\text{C}_1 - \text{O}_1$ is slightly shorter than the other C - O bonds. Again, the errors are still large at this stage of the refinement, but they should end up approximately one-third their present value.

The oxygen atoms appear to be distributed about the calcium as a distorted pentagonal bipyramid with O_6, O_8 at the top and bottom and $\text{O}_1, \text{O}_2, \text{O}_3, \text{O}_4, \text{O}_7$ forming the pentagon. These angles are given in Table VI. A coordination number of seven for calcium is unusual. The calcium atom apparently has a strong affinity for the oxygen atoms, coordinating to all oxygens available in the system with the exception of the xylose ring oxygen.

The chlorine atoms are held in the cell by means of hydrogen bonds to four oxygens. Cl_1 has contacts of around 3\AA with $\text{O}_1, \text{O}_2, \text{O}_7, \text{O}_8, \text{Cl}_2$ with $\text{O}_3, \text{O}_4, \text{O}_7, \text{O}_8$. These chlorines provide electrical neutrality, but do not bond to the calcium.

In this complex, xylose is found as the α -anomer. A water solution of xylose would contain both anomers in equilibrium, but it is the α -anomer which complexes. The xylose molecule is in the conventional C 1 conformation. All the bond lengths and bond angles appear to be normal at the level of accuracy of this refinement. The bond length $\text{C}_1 - \text{O}_1$ is on the borderline of being significantly shorter than the other C-O bonds. Based on previous work

TABLE VI

BOND ANGLES FOR D-XYLOSE • Ca Cl₂ • 3H₂O*

Angle	Bond Angle, °
O ₁ -C ₁ -O ₅	111.2
C ₂ -C ₁ -O ₅	112.1
O ₁ -C ₁ -C ₂	113.1
O ₂ -C ₂ -C ₁	108.6
C ₁ -C ₂ -C ₁	108.3
C ₃ -C ₂ -O ₂	105.2
O ₃ -C ₃ -C ₂	108.9
C ₂ -C ₃ -C ₄	107.0
O ₃ -C ₃ -C ₄	108.8
O ₄ -C ₄ -C ₃	107.2
C ₅ -C ₄ -C ₃	108.1
O ₄ -C ₄ -C ₅	109.4
C ₄ -C ₅ -O ₅	106.0
C ₁ -O ₅ -C ₅	112.5
O ₆ -Ca-O ₁	105.7
O ₆ -Ca-O ₂	80.6
O ₆ -Ca-O ₃	90.8
O ₆ -Ca-O ₄	82.8
O ₆ -Ca-O ₇	86.7
O ₆ -Ca-O ₈	170.8
O ₈ -Ca-O ₁	79.8
O ₈ -Ca-O ₂	95.2
O ₈ -Ca-O ₃	88.0
O ₈ -Ca-O ₄	88.2
O ₈ -Ca-O ₇	102.0
O ₁ -Ca-O ₂	65.6
O ₁ -Ca-O ₇	76.1
O ₇ -Ca-O ₃	78.2
O ₃ -Ca-O ₄	69.3
O ₁ -Ca-O ₃	76.1

(44, 19) this may be expected. Further refinement will resolve this question.

Figure IV shows the distribution of the atoms in one complete cell viewing down the c axis. Figure V gives a complete cell viewed down the b axis. Here the monoclinic angle, β , is obvious.

When the refinement is complete another report will be written discussing the bonding, the relationship of this structure to other carbohydrate structures, and possible relationships with other similar coordination chemistry.

OTHER METAL CARBOHYDRATE COMPLEXES

PREPARATION OF D-MANNOSE \cdot CaCl₂ \cdot 4H₂O

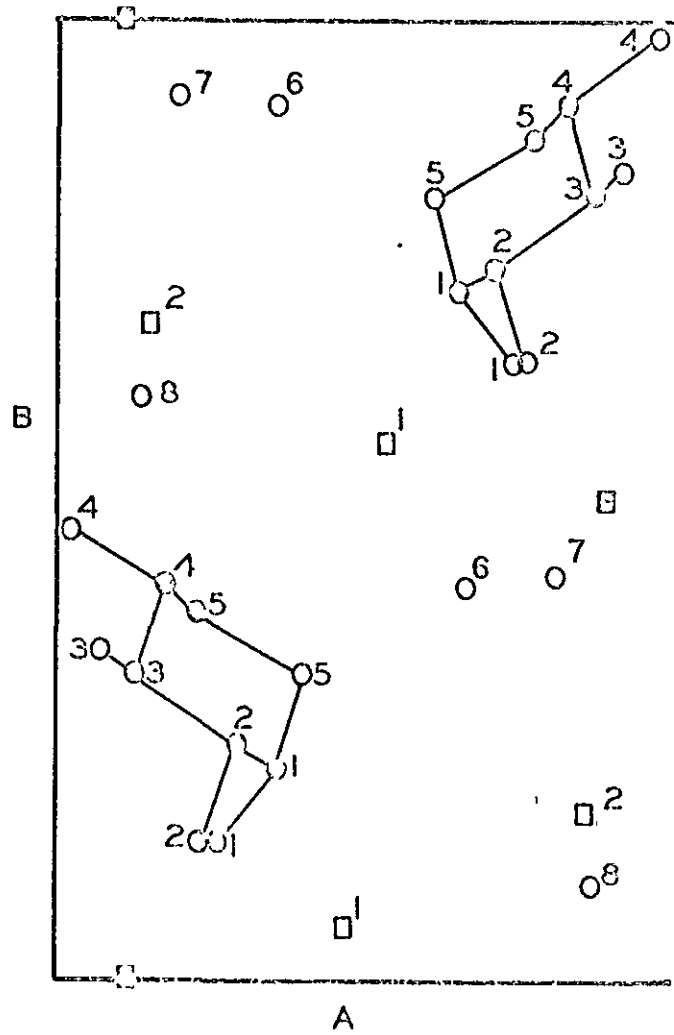
D-mannose \cdot CaCl₂ \cdot 4H₂O crystallized from a mixture of D-mannose and CaCl₂ \cdot 2H₂O in water (1) and it was recrystallized from water. The crystals are white, transparent, somewhat cubelike in shape, and less stable in air than the xylose compound.

CRYSTAL DATA ON D-MANNOSE \cdot CaCl₂ \cdot 4H₂O

The unit cell is monoclinic with probable cell dimensions, $a = 9.7$, $b = 12.2$, $c = 9.5$ Å.

PREPARATION OF α -D-GULOSE \cdot CaCl₂ \cdot H₂O

The compound α -D-gulose is not available commercially. It is prepared by the reduction of gulono- γ -lactone by sodium amalgam (3). This reaction was carried out and the resulting syrup was complexed with CaCl₂ \cdot 2H₂O. About one-half gram of α -D-gulose \cdot CaCl₂ \cdot H₂O .. (next page)



- ¹ CALCIUM
- ² CHLORINE
- CARBON
- OXYGEN

Figure 4 One Unit Cell Viewed Down c Axis

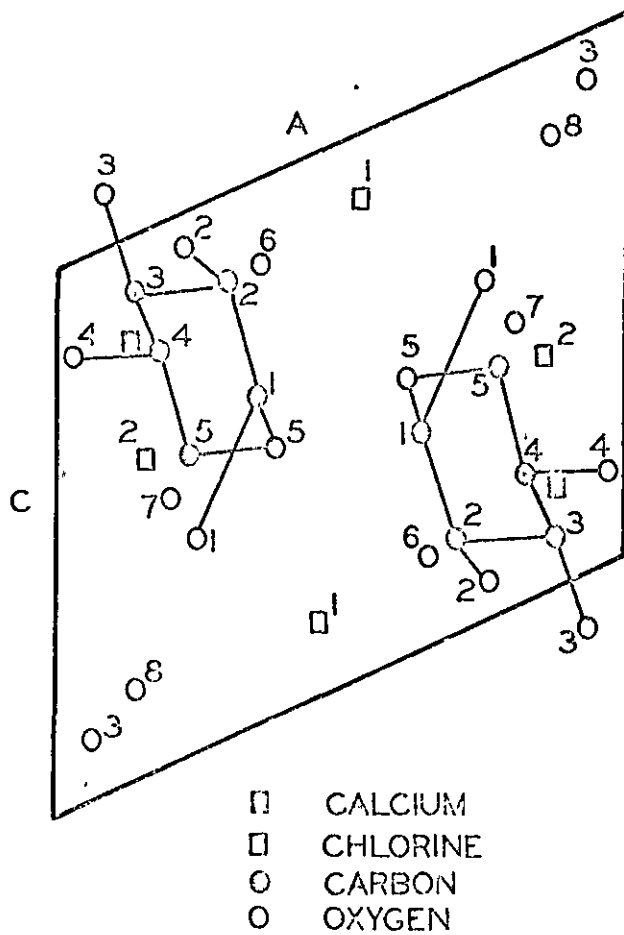


Figure 5 One Unit Cell Viewed Down b Axis

was obtained. This is a difficult preparation in comparison to other CaCl_2 complexes prepared. Paul Seib was primarily responsible for doing the amalgam reduction.

CRYSTAL DATA ON α -D-GULOSE $\cdot \text{CaCl}_2 \cdot \text{H}_2\text{O}$

A few X-ray patterns of this compound have been taken but in each case the crystal was too poorly aligned to give much information. It appears that the crystal is orthorhombic. The diffraction spot shape was excellent. The crystals were so large that they required cutting which made it difficult to find a crystallographic axis. Again, these crystals are quite hygroscopic, and they are difficult to handle in humid weather.

PREPARATION OF NEW METAL CARBOHYDRATE COMPOUNDS

COMPOUND PREPARATIONS

A review of the literature (30) shows that many carbohydrate metal compounds are known in solution, however, few compounds have been isolated in a crystalline form. It was considered worthwhile to attempt to isolate some new solid compounds particularly those which contain Zn or Al as the metal. This also provided continuity of effort during the summer when some extra help was available. The general procedures followed were to bring the metal salts and the carbohydrates together in mutually suitable solvents at various concentrations and conditions. The greatest difficulty was trying to find solvents compatible with both salt and sugar. Most of the metal chlorides were too acidic in water, so with a little heat the sugar was de-

composed. A considerable variety of crystallizing conditions, solvents, component ratios, and desolving conditions were tried. The exact procedures used are contained in Notebook 1849, however, the general results are tabulated in Table VII.

It can be seen from Table VII that no new carbohydrate metal compounds were prepared. However, in the process of using diglyme (2-Methoxyethyl ether) as a solvent it was noticed that a crystalline material always formed when $ZnCl_2$ was the salt. This was suspected at first to be a $ZnCl_2$ carbohydrate complex. However, upon analysis it was found that no sugar was present. Zinc and chlorine analyzed within a couple percent of the theoretical values predicted from a one-to-one complex of $ZnCl_2$ and diglyme. This analysis was considered good because of the very hygroscopic nature of the crystals. While no new carbohydrate complexes were prepared, the $ZnCl_2$ diglyme complex is new and interesting because the ether oxygens must be involved in the complex. A literature review of area has not been conducted but it should be, as this may be of considerable value.

CRYSTAL DATA, $ZnCl_2 \cdot DIGLYME$

Crystal class - Orthorhombic

Cell dimensions \AA

$$a = 8.62$$

$$b = 9.95$$

$$c = 13.40$$

four molecules per unit cell
calculated density 1.56 g/cm^3
measured density 1.55 g/cm^3

TABLE VII
PREPARATION OF METAL CARBOHYDRATE COMPLEXES

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Salt	Sugar	Solvent	Ratio Salt:Sugar, g.	Heat Source ^c	Technique Used ^d	Results
AlCl ₃	None	Diglyme ^a	5:0	C	4(d)	AlCl ₃ insoluble
"	Xylose	H ₂ O	8:5	A	4(c)	Clear syrup
CaCl ₂	Xylose	H ₂ O	8:5	A	1	CaCl ₂ ·Xylose·3H ₂ O Crystals
"	Mannose	Absolute ethanol	8:5	A	4(b)	CaCl ₂ ·Mannose complex
"	"	H ₂ O	8:5	A	1	CaCl ₂ ·Mannose complex
"	None	Diglyme	5:0	C	1	CaCl ₂ insoluble
CoCl ₂	Xylose	H ₂ O	8:5	A	4(c)	CoCl ₂ crystals
CuCl ₂	Xylose	H ₂ O	8:5	A	1	CuCl ₂ crystals
"	None	Diglyme	5:0	C	4(d)	CuCl ₂ partially soluble
FeCl ₃	Xylose	H ₂ O	8:5	A	1 & 4(c)	Clear syrup
"	"	Methyl cellosolve ^b	8:5	A	4(d)	FeCl ₃ insoluble
Fused ZnCl ₂ (99% pure) ²	Xylose	Diglyme	3:1	A	4(d)	ZnCl ₂ -diglyme crystals
"	None	Ether	5:0	D	4(d)	ZnCl ₂ soluble
"	None	Diglyme	1:0	C	4(d)	ZnCl ₂ crystals
"	Me 2,3,4,6 tetra O-Me-Glucoside	None	2:2	C	4(d)	Sugar decomposed
"	"	H ₂ O	2:2	C	4(d)	Sugar decomposed
"	"	H ₂ O	2:2	D	4(d)	Clear solution; no crystals
"	"	H ₂ O	5:5		4(b)	Clear syrup
ZnCl ₂ (95% pure)	Xylose	H ₂ O	3:1	C	1	Xylose decomposed
"	"	H ₂ O	2:2	A	1 & 4(c)	Black syrup
"	"	H ₂ O + methyl cello- solve	8:5	A	4(c)	Xylose and ZnCl ₂ crystallized separately
"	"	Methyl cellosolve	2:2	A	4(c)	Brown syrup
"	"	"	3:2	A	4(a)	Brown syrup
"	"	H ₂ O + diglyme	3:2	A	2(a)	ZnCl ₂ --diglyme crystals
"	"	Diglyme	(1:1 1:5	A	2(a)	ZnCl ₂ - diglyme crystals
"	"	"	1.5: .5	A	4(c)	ZnCl ₂ - diglyme crystals
"	"	Absolute methanol	3:1	A	4(b)	Black syrup
"	"	Diglyme	(2:1 3:1	A	4(d)	ZnCl ₂ - diglyme crystals
"	"	Benzene	5: .5	D	4(d)	Solutes insoluble
"	"	Dimethyl sulfoxide + H ₂ O	3:2	A	4(c)	Brown syrup
"	Mannose	H ₂ O	8:5	A	4(c)	Light brown syrup
"	"	Diglyme	1.5: .5	A	2(a)	Mannose insoluble
"	"	Absolute ethanol	1.5: .5	A	2(a)	Clear solution; no crystals
"	"	Methyl cellosolve	1.5: .5	A	2(a)	Clear solution; no crystals
"	"	Diglyme	1.5: .5	A	4(d)	Mannose insoluble
ZnCl ₂ (95% pure)	Arabinose	Diglyme	(2:1 2:1	A	4(d)	ZnCl ₂ - diglyme crystals

SUMMARY OF THE RESULTS

The results from project 2612 can be summarized as follows:

1. The method of X-ray diffraction as a tool for studying the detailed structure of solids has been established here at The Institute of Paper Chemistry. In order to do this the following were completed:
 - a. A low temperature cryostat for cooling crystals to a temperature near that of liquid nitrogen has been developed and operated effectively. Few laboratories have this facility. Four sets of intensity data have been taken (by staff and students) using this apparatus.
 - b. A library of computer programs for the I.B.M. 1620 has been developed. These programs have been used in the solution of three crystal structures (staff and students).
 - c. All the necessary materials have been obtained, and the procedures have been worked out for the handling, processing, and indexing of the intensity films.
2. The crystal structure of D-xylose $\cdot \text{CaCl}_2 \cdot 3\text{H}_2\text{O}$ has been completed. Calcium atoms are bonded to the hydroxyl groups of the xylose ring forming a chainlike structure with the xylose rings bridging the calcium atoms. The calcium atom is bonded to all the oxygens in the system except the

ring oxygen. Oxygen atoms are distributed about the Ca in a distorted pentagonal bipyramid arrangement. The xylose ring is in the 4C_1 conformation. All the bond angles and bond lengths appear to be normal in the ring.

3. Compounds D-mannose $\cdot CaCl_2 \cdot 4H_2O$ and α -D-gulose $\cdot CaCl_2 \cdot H_2O$ have been prepared. Some crystal data has been obtained for these compounds.
4. Attempts have been made to prepare some new metal carbohydrate complexes. This has resulted in the preparation of a new compound, a 1:1 complex between $ZnCl_2$ and the ether, diglyme.
5. Project 2612 appears to have stimulated the interest of other chemists on the staff, perhaps providing them with another way to think about chemistry. Project 2612, either directly or indirectly, has helped two students who have completed research in this area. Another student is attempting to solve a large carbohydrate structure.

POSSIBLE FUTURE WORK

The structure of D-xylose $\cdot CaCl_2 \cdot 3H_2O$ is presently being refined in more detail. This should be finished soon, and another report will be submitted.

Crystals of α -D-gulose $\cdot CaCl_2 \cdot H_2O$ are available. This is a six carbon sugar. The conformation of this ring is interesting, and the solution of the structure should be completed.

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Larger carbohydrates such as xylobiose, xylotriose, and other available low molecular weight polysaccharides should be examined as to possible complexing with CaCl_2 .

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