Fall 1974

PART ONE: THE THERMAL DECOMPOSITION OF NICKEL-FLUORIDE AND ZINC-FLUORIDE TETRAHYDRATES
PART TWO: THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(ORTHO-AMINOBENZOATO)COPPER(II)

BRUCE A. LANGE

Follow this and additional works at: https://scholars.unh.edu/dissertation

Recommended Citation
https://scholars.unh.edu/dissertation/1065

This Dissertation is brought to you for free and open access by the Student Scholarship at University of New Hampshire Scholars' Repository. It has been accepted for inclusion in Doctoral Dissertations by an authorized administrator of University of New Hampshire Scholars' Repository. For more information, please contact nicole.hentz@unh.edu.
INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms
300 North Zeeb Road
Ann Arbor, Michigan 48106
LANGE, Bruce A., 1948-
PART ONE: THE THERMAL DECOMPOSITION OF NICKEL
AND ZINC FLUORIDE TETRAHYDRATES. PART TWO: THE
CRYSTAL AND MOLECULAR STRUCTURE OF
BIS(ORTHO-AMINOBENZOATO)COPPER(II),
Cu(H$_2$N$_2$C$_6$H$_4$COO)$_2$.

University of New Hampshire, Ph.D., 1974
Chemistry, inorganic

Xerox University Microfilms, Ann Arbor, Michigan 48106

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED.
PART ONE
THE THERMAL DECOMPOSITION OF NICKEL AND ZINC FLUORIDE TETRAHYDRATES

PART TWO
THE CRYSTAL AND MOLECULAR STRUCTURE OF
BIS(ORTHO-AMINOBENZOATO)COPPER(II), Cu(H₂NC₆H₄COO)₂

by

BRUCE A. LANGE
B.S., Lowell Technological Institute
Lowell, Massachusetts, 1970

A THESIS

Submitted to the University of New Hampshire
In Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Graduate School
Department of Chemistry
September, 1974
TO MY PARENTS
ACKNOWLEDGEMENTS

This work was carried out in the chemistry laboratories of Parsons Hall under the direction of Dr. Helmut M. Haendler.

The author wishes to sincerely express his gratitude to Dr. Hanedler whose knowledge, patience, helpful counsel and, most importantly, friendship created a research and academic atmosphere in which the author felt that Dr. Haendler was a colleague rather than an overseer.

In addition, thanks is extended to the author's parents whose confidence, love and help was always available when it was sorely needed.

The author is grateful for the financial assistance of a U.N.H. fellowship, Dissertation Year Fellowship, Tuition Fellowship and teaching assistantship. Gratitude is also due the Atomic Energy Commission for partial support of this research.
TABLE OF CONTENTS

LIST OF TABLES ......................................................... vii
LIST OF FIGURES ....................................................... viii
ABSTRACT ................................................................. ix

PART ONE

THE THERMAL DECOMPOSITION OF NICKEL AND ZINC FLUORIDE
TETRAHYDRATES. .............................................................. 1

I. INTRODUCTION .................................................... 2

II. EXPERIMENTAL .................................................... 4

A. Starting Materials .................................................. 4
B. Preparation of NiCO₃ ................................................ 4
C. Preparation of NiF₂·4H₂O ........................................... 4
D. Preparation of ZnF₂·4H₂O ........................................... 5
E. Analytical Procedures .............................................. 5
   1. Determination of Nickel and Zinc .............................. 5
   2. Determination of Fluoride ...................................... 5
F. Differential Thermal Analyses ..................................... 6
G. Dynamic Thermogravimetric Analyses ............................. 7
H. Isothermal Thermogravimetric Analyses ........................ 8
I. X-Ray Powder Diffraction Photographs ............................ 8
J. Infrared Spectra ................................................... 12

III. RESULTS AND DISCUSSION ........................................ 13

A. Differential Thermal Analysis of NiF₂·4H₂O ................ 13
B. Thermogravimetric Analysis of NiF₂·4H₂O
   in Dry Air and in Dry Helium or Argon. ....................... 13
C. Thermogravimetric Analysis of NiF$_2$•4H$_2$O in the Presence of Water Vapor ................. 18

D. Infrared Analysis of NiF$_2$•4H$_2$O and Its Decomposition Products ............................ 19

E. Thermogravimetric Analysis of ZnF$_2$•4H$_2$O in Dry Atmospheres ........................... 26

PART TWO

THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(ORTHO-AMINOBENZOATO) COPPER(II), Cu(H$_2$NC$_6$H$_4$COO)$_2$ ................................................ 27

I. INTRODUCTION .................................................. 28

II. THE METHOD OF CRYSTAL STRUCTURE ANALYSIS .................................................. 30

III. EXPERIMENTAL .................................................. 41

A. Starting Materials ............................................. 41

B. Preparation of Sodium Ortho-aminobenzoate Reagent ........................................... 41

C. Preparation of Single Crystals of Bis(ortho-aminobenzoato)copper(II) .................... 41

D. Determination of the Space Group, Unit Cell Dimensions and Density of Cu(H$_2$NC$_6$H$_4$COO)$_2$ .............................. 42

E. Intensity Measurements ........................................ 42

IV. SOLUTION AND REFINEMENT OF THE STRUCTURE .................................................. 47

V. RESULTS AND DISCUSSION ......................................... 56

APPENDIX ..................................................................... 71

A. Attempted Structure Analysis of Bis(para-aminobenzoato)diaquocopper(II), Cu(H$_2$NC$_6$H$_4$COO)$_2$•2H$_2$O .............................................. 72

B. Computer Programs ................................................ 84

BIBLIOGRAPHY ........................................................ 97
LIST OF TABLES

I. Differential Thermal Analysis of NiF$_2$·4H$_2$O ............. 7
II. Isothermal Thermogravimetric Analyses ................... 9
III. X-Ray Powder Diffraction Data for NiOHF·3NiF$_2$ ... 16
IV. Infrared Absorption Spectra ............................... 20
V. Crystal Data for Cu(H$_2$NC$_6$H$_4$COO)$_2$ ................... 43
VI. Final Positional and Thermal Parameters ................. 51
VII. Summary of Refinement Stages ............................ 53
VIII. Calculated and Observed Structure Factors
      for Cu(H$_2$NC$_6$H$_4$COO)$_2$ ............... 54
IX. Bond Distances and Angles in Cu(H$_2$NC$_6$H$_4$COO)$_2$ ... 63
X. Crystal Data for Cu(H$_2$NC$_6$H$_4$COO)$_2$·2H$_2$O .......... 75
XI. Instrumental Settings and Measurement
    Parameters ........................................... 77
LIST OF FIGURES

1. TGA Curve for NiF$_2$·4H$_2$O and ZnF$_2$·4H$_2$O in Dry Atmospheres ................. 10
2. TGA Curve for NiF$_2$·4H$_2$O in Atmospheres Containing Water Vapor .................. 11
3. Powder Diffraction Patterns (Debyeograms) .................................................. 15
4. 3300 and 1665 cm$^{-1}$ Infrared Peaks Found in NiF$_2$·4H$_2$O .......................... 22
5. 3430 and 1645 cm$^{-1}$ Infrared Peaks Found in NiF$_2$·H$_2$O ............................ 24
6. Flow Diagram of the Structure Determination Procedure for a Compound Containing a Heavy Atom ................................................................. 31
7. Crystal Morphology of Cu(H$_2$NC$_6$H$_4$COO)$_2$ ........................................... 45
8. Contents of One Unit Cell for Cu(H$_2$NC$_6$H$_4$COO)$_2$ ................................... 57
9. Coordination Around Copper in Cu(H$_2$NC$_6$H$_4$COO)$_2$ .................................. 59
10. Polymeric Structure in Cu(H$_2$NC$_6$H$_4$COO)$_2$ ............................................ 61
11. Thermal Ellipsoid Drawing of Cu(H$_2$NC$_6$H$_4$COO)$_2$ .................................... 67
ABSTRACT

PART ONE
THE THERMAL DECOMPOSITION OF NICKEL AND ZINC FLUORIDE TETRAHYDRATES

by

BRUCE A. LANGE

Nickel(II) fluoride tetrahydrate, NiF₂·4H₂O, decomposes in three steps when heated, the products depending upon the atmosphere in which the decomposition occurs. In dry air or in dry argon there is an initial loss of three moles of water at about 125° and the monohydrate, NiF₂·H₂O, is formed. At approximately 225° the monohydrate loses water and hydrogen fluoride and NiOHF·3NiF₂ is formed. This compound loses an additional mole of hydrogen fluoride at about 430° and the final product is a mixture of nickel fluoride and nickel oxide in a 3:1 mole ratio. In the presence of water vapor the final decomposition product is solely nickel oxide; the other steps are the same. Zinc fluoride tetrahydrate, ZnF₂·4H₂O, loses four moles of water at temperatures above about 75°, forming anhydrous zinc fluoride. The decomposition schemes of both NiF₂·4H₂O and ZnF₂·4H₂O were deduced using differential thermal analysis, thermogravimetric analysis, chemical analysis, X-ray diffraction and infrared spectroscopy.
PART TWO

THE CRYSTAL AND MOLECULAR STRUCTURE OF

BIS(ORTHO-AMINOBENZOATO)COPPER(II), Cu(H₂NC₆H₄COO)₂

by

BRUCE A. LANGE

Bis(ortho-aminobenzoato)copper(II), Cu(H₂NC₆H₄COO)₂, crystallizes in the monoclinic space group P2₁/c with cell dimensions a = 12.95(1), b = 5.25(1), c = 9.39(1) Å, and β = 93.31(1)°. The structure was determined using three-dimensional X-ray diffraction data gathered on multiple-film, equi-inclination, integrated Weissenberg photographs taken about two crystal axes. The intensities were read using a Welch Densichron. Initial refinement was carried out with block diagonal least squares methods. Subsequent refinement with full matrix least squares calculations led to a final conventional R-factor of 0.031. Coordination about the copper is that of a distorted octahedron. Four equatorial positions are occupied by two amino nitrogens and two carboxylate oxygens with both the nitrogens and oxygens in trans positions. The octahedral coordination is completed in the axial positions by two carbonyl oxygens which do not originate from the same ligands that occupy the equatorial sites. This bonding configuration generates a structure in which each copper in the (100) plane is attached to four other coppers via carboxylate bridges to give a two-dimensional network coincident with the (100) plane. The Cu-O and Cu-N distances
in the equatorial plane are 1.973(5) and 2.024(7) Å, while the Cu-O axial bond length is 2.415(5) Å. Significant hydrogen bonding is found in this structure and it serves to strengthen the two-dimensional network. It is suggested that the two-dimensional polymeric character of Cu(H$_2$NC$_6$H$_4$COO)$_2$ accounts for its extreme insolubility and high stability.
PART ONE

THE THERMAL DECOMPOSITION OF NICKEL AND ZINC FLUORIDE TETRAHYDRATES
PART ONE

I. INTRODUCTION

Directly and indirectly, several studies have been made on the thermal decomposition of nickel(II) fluoride tetrahydrate but they have produced conflicting results. Kurtenacker, Finger and Hey\(^1\) noted that nickel oxide is formed when \(\text{NiF}_2\cdot4\text{H}_2\text{O}\) is heated above 200\(^\circ\) for a prolonged period of time. Van My, Perinet and Bianco\(^2\) reported that \(\text{NiF}_2\cdot4\text{H}_2\text{O}\) decomposes to nickel(II) fluoride monohydrate when heated at 78\(^\circ\) and that the monohydrate decomposes exclusively to nickel fluoride when heated to 220\(^\circ\) in either vacuum or air. In preparing samples of nickel fluoride for heat capacity studies, Catalano and Stout\(^3\) found that \(\text{NiF}_2\cdot4\text{H}_2\text{O}\) loses three moles of water (at ca. 120\(^\circ\)) to form \(\text{NiF}_2\cdot\text{H}_2\text{O}\) and that, when the monohydrate is heated to 400\(^\circ\) in a stream of hydrogen fluoride, the final mole of water is lost with the resulting formation of pure anhydrous nickel fluoride. Recently, Patil and Secco\(^4\) examined the thermal decomposition of \(\text{NiF}_2\cdot\text{H}_2\text{O}\) and concluded that between 110\(^\circ\) and 220\(^\circ\) all four molecules of water of hydration are lost with the subsequent formation of anhydrous nickel fluoride. It appears that this conclusion was based solely on thermogravimetric and differential thermal analyses and no X-ray diffraction, infrared or chemical studies were reported to confirm the
identity of the final product, which was reported as nickel fluoride. In this same paper, Patil and Secco examined the thermal decomposition of ZnF$_2$·4H$_2$O and found that between 60° and 200° it decomposed to zinc fluoride. These latter results are in general agreement with those found in this study.

The purpose of this work was to reexamine the thermal decompositions of nickel(II) fluoride tetrahydrate and zinc fluoride tetrahydrate in different atmospheres. The various intermediates and products encountered in these reactions were isolated and characterized through the use of X-ray diffraction and infrared techniques in conjunction with thermogravimetric, differential thermal and elemental analyses.
II. EXPERIMENTAL

A. Starting Materials

Analytical grade 48% hydrofluoric acid (Baker), reagent grade \( \text{NiSO}_4 \cdot 6\text{H}_2\text{O} \) (Fisher), reagent grade \( \text{NaHCO}_3 \) (Fisher) and certified grade \( \text{ZnCO}_3 \) (Baker and Adamson) were used without further purification.

B. Preparation of \( \text{NiCO}_3 \)

Powdered \( \text{NaHCO}_3 \) (25 g, 0.39 mol) and powdered \( \text{NiSO}_4 \cdot 6\text{H}_2\text{O} \) (78.93 g, 0.30 mol) were each dissolved in 200 ml of distilled water. The two solutions were mixed and a light green precipitate formed accompanied by the evolution of gas. The precipitate was removed by filtration, washed with distilled water, dried in air at room temperature and ground to a fine powder.

C. Preparation of \( \text{NiF}_2 \cdot 4\text{H}_2\text{O} \)

\( \text{NiF}_2 \cdot 4\text{H}_2\text{O} \) was prepared by the method of Kurtenacker, Finger and Hey\(^1\). Freshly precipitated \( \text{NiCO}_3 \) (13.01 g, 0.109 mol) was slowly added to 48% hydrofluoric acid (18 ml, 0.45 mol) with a resulting violent evolution of gas. The resulting green solution was left to stand overnight in air at room temperature, after which an additional 8 ml of 48% HF was added. Over a period of nine days the solution was evaporated to dryness in air at room temperature. The remaining light green, crusty solid was ground to a fine powder.
The reaction was carried out in a Teflon container and the product was stored in polyethylene to prevent the formation of fluorosilicate.

**Anal.** Calcd for NiF$_2$·4H$_2$O: F, 22.52; Ni, 34.79.
Found: F, 22.37, 22.00; Ni, 35.19, 35.19.

D. Preparation of ZnF$_2$·4H$_2$O

ZnF$_2$·4H$_2$O was prepared by the general method of Kurtenacker, Finger and Hey\(^1\). Anhydrous ZnCO$_3$ was added in small amounts to approximately 30 ml of 48% hydrofluoric acid. The reaction mixture was stirred in a polyethylene container and left to stand overnight. The following day additional HF was added and the mixture was allowed to evaporate to dryness. The salt was ground and washed first with 95% ethanol and then with diethyl ether. The product was dried in air at room temperature and stored in a polyethylene container.

**Anal.** Calcd for ZnF$_2$·4H$_2$O: F, 21.66; Zn, 37.27.
Found: F, 22.49, 22.50; Zn, 37.77, 37.84.

E. Analytical Procedures

1. **Determination of Nickel and Zinc**

   Nickel and zinc were determined gravimetrically by precipitation with anthranilic acid\(^5\).

2. **Determination of Fluoride**

   Fluoride was determined by the gravimetric lead chlorofluoride method\(^6\).
F. Differential Thermal Analyses

All differential thermal analyses (dta) were performed on a DuPont Differential Thermal Analyzer, model 900, using a Differential Scanning Calorimeter cell. Runs were made under both air and helium atmospheres, in the latter case a flow rate of 2 CFH was used. A temperature (T) scale of 2 mv/in. and a differential thermal (ΔT) scale of either 0.02, 0.04 or 0.08 mv/in. was used. In all runs a heating rate of 15⁰/min was used and temperature measurements were made with a chromel-alumel thermocouple with the reference junction immersed in an ice-water bath.

The results of the differential thermal analyses performed on NiF₂·4H₂O in a helium atmosphere and in the presence of water vapor are given in Table I. The temperatures given are those of the onset of the thermal processes as determined by the intersection of a line drawn along the base line with a line drawn along that portion of the peak having a constant slope. All peaks were endothermic. The magnitudes of the peaks are given in terms of ΔT; however, comparisons between peak magnitudes are only valid in the same thermogram since this property is a function of sample size.
Table I

Differential Thermal Analysis of NiF$_2$·4H$_2$O in He Atmosphere

<table>
<thead>
<tr>
<th>Temperature</th>
<th>AT</th>
</tr>
</thead>
<tbody>
<tr>
<td>129°</td>
<td>3°</td>
</tr>
</tbody>
</table>

Differential Thermal Analysis of NiF$_2$·4H$_2$O In Air (Water Vapor Present)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>AT</th>
</tr>
</thead>
<tbody>
<tr>
<td>132°</td>
<td>6°</td>
</tr>
<tr>
<td>506°</td>
<td>0.15°</td>
</tr>
</tbody>
</table>

G. Dynamic Thermogravimetric Analyses

Dynamic thermogravimetric analyses were carried out with a DuPont Thermogravimetric Analyzer, model 950. Analyses were performed under both air and helium atmospheres. In the latter case a flow rate of 2 CFH was used with the gas flow directed parallel to the surface of the sample. The heating rate in all cases was 15°/min. A chromel-alumel thermocouple with the reference junction placed in ice water was employed for temperature measurement. Sample sizes of approximately 22 mg were used and the instrument was set so that the per cent weight loss could be read directly.

The thermograms of ZnF$_2$·4H$_2$O (dotted line) and
NiF\textsubscript{2}\textperiodcentered\textperiodcentered\textsubscript{4}H\textsubscript{2}O (solid line) taken in helium atmospheres are shown in Figure 1. The thermogram of the decomposition of NiF\textsubscript{2}\textperiodcentered\textperiodcentered\textsubscript{4}H\textsubscript{2}O as carried out in air with water vapor present is shown in Figure 2. The solid line represents the behavior when the only water vapor present is that resulting from the decomposition and the dotted line represents the results of supplying water vapor externally.

H. Isothermal Thermogravimetric Analyses

Isothermal thermogravimetric analyses were carried out on a recording thermobalance similar to one described by Wendlandt\textsuperscript{7} and modified by Kingston\textsuperscript{8}. Runs were performed under both air and argon atmospheres. With the argon atmosphere a flow rate of 4 CFH was used with the gas flow directed perpendicular to the surface of the sample. In those analyses requiring dry atmospheres the air or argon was first passed through a Drierite column. A chromel-alumel thermocouple was used for temperature measurement. Sample sizes of approximately 40 mg were used and all analyses were performed in platinum vessels. The results of the isothermal thermogravimetric analyses are given in Table II.

I. X-Ray Powder Diffraction Photographs

The X-ray powder diffraction photographs were made with nickel filtered copper radiation (\(\lambda = 1.54178\ \text{\AA}\)) in 57.3 mm Philips cameras. The samples were placed in 0.3 mm glass capillaries and, in cases where the samples were air- or water-sensitive, these capillaries were filled and sealed
Table II

Isothermal Thermogravimetric Analyses

<table>
<thead>
<tr>
<th>Compound Formed</th>
<th>Found in Dry Air or Argon</th>
<th>Found in Wet Atmospheres</th>
<th>Calcd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NiF}_2 \cdot \text{H}_2\text{O} )(^d)</td>
<td>c</td>
<td>31.7</td>
<td>32.01</td>
</tr>
<tr>
<td>( \text{NiOHF} \cdot 3\text{NiF}_2 )(^e)</td>
<td>42.69</td>
<td>42.75</td>
<td>42.98</td>
</tr>
<tr>
<td>( 3\text{NiF}_2 + \text{NiO} )(^f)</td>
<td>45.96</td>
<td>-</td>
<td>45.94</td>
</tr>
<tr>
<td>( \text{NiO} )(^g)</td>
<td>-</td>
<td>54.67</td>
<td>55.72</td>
</tr>
</tbody>
</table>

\(^a\) As per cent weight loss from \( \text{NiF}_2 \cdot 4\text{H}_2\text{O} \)

\(^b\) Average of 3 determinations

\(^c\) \( \text{NiF}_2 \cdot \text{H}_2\text{O} \) unstable to prolonged heating at 125°

\(^d\) \( \text{NiF}_2 \cdot 4\text{H}_2\text{O} \) heated at 125°

\(^e\) \( \text{NiF}_2 \cdot \text{H}_2\text{O} \) heated at 250°

\(^f\) \( \text{NiOHF} \cdot 3\text{NiF}_2 \) heated at 430°

\(^g\) \( \text{NiOHF} \cdot 3\text{NiF}_2 \) heated at 430° with water vapor
Figure 1

TGA Curve for NiF$_2$·4H$_2$O and ZnF$_2$·4H$_2$O in Dry Atmospheres

NiF$_2$·4H$_2$O
ZnF$_2$·4H$_2$O
Figure 2

TGA Curve for NiF$_2$·4H$_2$O in Atmospheres Containing Water Vapor
in glove bags under an atmosphere of dry nitrogen. All powder films were corrected for shrinkage and the values for the interplanar spacings were calculated using the computer program UNH-28. The intensities of the diffraction lines were estimated visually for qualitative identification or read with a Welch Densichron when greater precision was required.

J. Infrared Spectra

Infrared spectra in the 4000 - 200 cm\(^{-1}\) range were obtained using a Beckman IR-12 Spectrophotometer. In all cases the spectra were run using cesium iodide pellets.
III. RESULTS AND DISCUSSION

A. Differential Thermal Analysis of NiF$_2$$\cdot$4H$_2$O

The Differential thermal analysis curve resulting from the thermal decomposition of NiF$_2$$\cdot$4H$_2$O in a dry atmosphere is very similar to that found for the decomposition which takes place in the presence of water vapor (see Table I). Both curves show a large endothermic peak at approximately 130° which undoubtedly marks the point at which the first three waters of hydration are lost$^{2,3}$. After this initial peak both curves are nearly featureless except that the dta curve for the reaction taking place in an atmosphere containing water vapor does show the suggestion of a long endothermic process beginning at about 500°.

B. Thermogravimetric Analysis of NiF$_2$$\cdot$4H$_2$O in Dry Air and in Dry Helium or Argon

Dynamic thermogravimetric analyses performed on NiF$_2$$\cdot$4H$_2$O show a rapid, major weight loss of approximately 35% starting at about 130° and continuing through 180° after which there is a more gradual weight loss of an additional 8% up to approximately 650°. Above 650° there is no further weight change. The results of isothermal thermogravimetric analyses are given in Table II and indicate that by heating NiF$_2$$\cdot$4H$_2$O at 125°, 250° and 430° it is possible to isolate
three separate compounds. Chemical analysis of these compounds in conjunction with X-ray diffraction and infrared studies indicate that in the absence of water NiF$_2$·4H$_2$O decomposes in the following way:

\[
\begin{align*}
niF_2 \cdot 4H_2O & \overset{123^\circ}{\longrightarrow} niF_2 \cdot H_2O + 3H_2O \\
niF_2 \cdot H_2O & \overset{240^\circ}{\longrightarrow} niOHF \cdot 3niF_2 + HF \\
niOHF \cdot 3niF_2 & \overset{430^\circ}{\longrightarrow} 3niF_2 + niO + HF
\end{align*}
\]

Nickel(II) fluoride monohydrate, NiF$_2$·H$_2$O, is a greenish-yellow compound that rapidly picks up atmospheric water to quantitatively reform the tetrahydrate. Nickel(II) fluoride monohydrate is not stable to prolonged heating at 123° and can only be isolated in pure form if it is removed from the oven immediately upon its formation (as indicated by weight loss). X-Ray powder diffraction photographs show that NiF$_2$·H$_2$O is amorphous. The infrared spectra is listed in Table IV and clearly shows the presence of water.

*Anal.* Calcd for NiF$_2$·H$_2$O: F, 33.10; Ni, 51.83. Found: F, 33.56, 32.83; Ni, 51.04, 50.84.

NiOHF·3NiF$_2$ is formed when NiF$_2$·H$_2$O is heated at 250° and is completely stable at this temperature. This bright yellow compound is extremely hygroscopic and has a very distinct powder pattern shown in Figure 3 and tabulated in Table III.
Figure 3

Powder Diffraction Patterns (Debyeograms)

ZnF$_2$.4H$_2$O

ZnF$_2$

NiF$_2$.4H$_2$O

NiOHF.3NiF$_2$

NiF$_2$ + NiO

NiF$_2$

NiO
Table III

X-Ray Powder Diffraction Data for NiOHF·3NiF₂

<table>
<thead>
<tr>
<th>dhkl, Å</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.56</td>
<td>100</td>
</tr>
<tr>
<td>2.23</td>
<td>70</td>
</tr>
<tr>
<td>1.70</td>
<td>80</td>
</tr>
<tr>
<td>1.49</td>
<td>45</td>
</tr>
<tr>
<td>1.28</td>
<td>10</td>
</tr>
<tr>
<td>1.11</td>
<td>10</td>
</tr>
<tr>
<td>0.90</td>
<td>20</td>
</tr>
</tbody>
</table>

The bands at 3500 cm⁻¹ and 1055 cm⁻¹ in the infrared spectra of this compound are indicative of the hydroxo group, and thereby help to confirm its proposed identity. It seems likely that Patil and Secco mistook this material for nickel fluoride since the weight loss to this compound (42.98%) is very close to that expected for nickel fluoride (42.67%).

Heating NiOHF·3NiF₂ at 450°C results in the formation of nickel fluoride and nickel oxide in exactly a 3:1 mole ratio which further confirms the identity of NiOHF·3NiF₂. Although powder diffraction studies show that each component is independently present, this mixture exhibits properties which suggest that the mixing is very intimate. For example, it should be possible to separate the fluoride from the oxide by dissolving the former in hot water (the solubility of nickel fluoride is about 4 g/100 ml of water at 25°C), but such a separation was not possible with this final decomposition product.


In analyzing this compound the lead chlorofluoride method was not used, rather the compound was ignited to NiO in the presence of water vapor.
C. Thermogravimetric Analysis of NiF$_2$·4H$_2$O in the Presence of Water Vapor

The decomposition of nickel(II) fluoride tetrahydrate in contact with water vapor is identical, in all but two respects, to the decomposition which takes place in dry atmospheres (see Figure 2). Nickel(II) fluoride monohydrate is stable to prolonged heating at 125° when there is water vapor present and at 430° decomposes solely to nickel oxide rather than to a mixture of the fluoride and the oxide.

Two different methods were used in exposing NiF$_2$·4H$_2$O to water vapor during its decomposition. In the first method the only water in the reaction vessel was that which was initially present as the four waters of hydration, i.e., the water was self-generated by the nickel(II) fluoride tetrahydrate. In the second method water vapor was introduced externally by bubbling argon through hot water and into the reaction chamber. With both methods the final product was nickel oxide, but the oxide was found to form more rapidly when the water vapor was supplied externally. As NiOHF·3NiF$_2$ decomposes to nickel fluoride and nickel oxide, the nickel fluoride reacts with water to form nickel oxide and hydrogen fluoride. The reaction between nickel fluoride and water vapor to form nickel oxide has been previously studied.\textsuperscript{12,13}

Presumably, the sweeping action of the dry air or argon used in the first part of this study removed all of the water vapor prior to the decomposition of NiOHF·3NiF$_2$.
thereby preventing the reaction between nickel fluoride and water vapor. This appears even more likely when it is noted that there is no water formed when NiOHF·3NiF₂ decomposes to nickel fluoride and nickel oxide, and that the time interval between 240° and 430° (ca. 15 minutes) is of sufficient length to ensure that the dry gases have flushed out any water vapor remaining from the first two decomposition steps. The presence of water vapor apparently represses the decomposition of the monohydrate, making it stable at higher temperatures.

D. Infrared Analysis of NiF₂·4H₂O and its Decomposition

Products

The results of the infrared analyses are given in Table IV. Bands at approximately 230, 300 and 400 cm⁻¹ are found in the spectra of all compounds studied and these peaks probably arise from the various Ni-F stretching and bending modes. Patil and Secco⁴ also assign the band at 500 cm⁻¹ as a Ni-F mode, but the fact that this band appears to shift to 570 cm⁻¹ in the monohydrate could be an indication that it is resulting from a Ni-O mode. The band found at 700 cm⁻¹ with NiF₂·4H₂O probably results from a wagging mode of water.¹⁴ Weak bands at 780, 800 and 810 cm⁻¹, given by NiF₂·4H₂O, NiF₂·H₂O and NiOHF·3NiF₂ respectively, are believed to be overtones of the strong bands found at 392, 380 and 405 cm⁻¹.

The sharp, strong band exhibited by NiF₂·4H₂O at
Table IV

Infrared Absorption Spectra

<table>
<thead>
<tr>
<th>Compound</th>
<th>3300 br</th>
<th>2360</th>
<th>1665 s</th>
<th>-</th>
<th>895</th>
<th>780</th>
<th>700</th>
<th>500</th>
<th>-</th>
<th>392</th>
<th>303</th>
<th>225</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni\textsubscript{2}F\textsubscript{4}H\textsubscript{2}O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>895</td>
<td>780</td>
<td>700</td>
<td>500</td>
<td>392</td>
<td>303</td>
<td>225</td>
<td></td>
</tr>
<tr>
<td>Ni\textsubscript{2}F\textsubscript{4}H\textsubscript{2}O</td>
<td>3430 br</td>
<td>-</td>
<td>1645 s</td>
<td>1035 vw</td>
<td>800</td>
<td>570</td>
<td>380</td>
<td>300</td>
<td>230</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiOHF\textsubscript{3}NiF\textsubscript{2}</td>
<td>3500 s</td>
<td>-</td>
<td>1635 vw</td>
<td>1055 s</td>
<td>810</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>405</td>
<td>295</td>
<td>240</td>
<td></td>
</tr>
<tr>
<td>NiF\textsubscript{2}</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>445</td>
<td>375</td>
<td>285</td>
</tr>
</tbody>
</table>

\(^a\) Cesium iodide pellets used; vw, very weak; w, weak; s, strong; br, broad
895 cm\(^{-1}\) is not found with any of the other compounds. It is likely that this band is due to a rocking mode of coordinated water.\(^{14}\)

The identity of NiOHF\(\cdot\)3NiF\(_2\) is well substantiated by its infrared spectrum. The 1055 cm\(^{-1}\) band is indicative of hydroxo compounds and results from the Ni-O-H bend.\(^{11}\) The 3500 cm\(^{-1}\) band is sharper and higher in frequency than the O-H stretching band found with water—a result that is again indicative of an hydroxo compound.\(^{11}\) The absence of a peak in the 1600 cm\(^{-1}\) region strongly points to the fact that the bands at 3500 and 1055 cm\(^{-1}\) are indeed not due to molecular water.

As shown in Figure 4, the shapes of the 1665 and 3300 cm\(^{-1}\) peaks found for NiF\(_2\)\(\cdot\)4H\(_2\)O (H-O-H bend and H-O-H stretch\(^{15}\) ) indicate that there are two types of water in this compound, i.e., the two waters are not equivalent. In examining the 1665 cm\(^{-1}\) peak, a strong, sharp peak can be seen superimposed upon a broad, somewhat weaker peak. Likewise, the broad band at 3300 cm\(^{-1}\) is actually composed of two peaks, one at 3200 cm\(^{-1}\) and the other at 3450 cm\(^{-1}\). However, with NiF\(_2\)\(\cdot\)H\(_2\)O these characteristics disappear and the broad peak at 1645 cm\(^{-1}\) and the single peak at 3430 cm\(^{-1}\) indicate the presence of only one type of water (see Figure 5).

The band at 2360 cm\(^{-1}\) found in the spectrum of NiF\(_2\)\(\cdot\)4H\(_2\)O is believed to be a combination band and this assignment is in accordance with that made by Patil and Secco.\(^4\)
Figure 4

3300 and 1665 cm\(^{-1}\) Infrared Peaks

Found in NiF\(_2\)·4H\(_2\)O
Figure 5

3430 and 1645 cm$^{-1}$ Infrared Peaks

Found in NiF$_2$·H$_2$O
E. Thermogravimetric Analysis of ZnF$_2$·4H$_2$O in Dry Atmospheres

In comparison to the manner in which NiF$_2$·4H$_2$O decomposes, the decomposition of ZnF$_2$·4H$_2$O is quite straightforward. Above 75°, ZnF$_2$·4H$_2$O loses all four waters with the resulting formation of pure, anhydrous zinc fluoride. This result poses a very interesting question. If nickel(II) fluoride tetrahydrate and zinc fluoride tetrahydrate are isostructural, as maintained by Nierlich et al., why are the thermal decompositions so markedly different? It is suggested that there is a difference in the structures of these two compounds—a difference which is undetectable in the powder diffraction patterns, but which does manifest itself in the nature of the thermal decompositions.
PART TWO

THE CRYSTAL AND MOLECULAR STRUCTURE OF

BIS(ORTHO-AMINOBENZOATO) COPPER(II), Cu(H$_2$NC$_6$H$_4$COO)$_2$
PART TWO

I. INTRODUCTION

Ortho-aminobenzoic acid (anthranilic acid) is an important precursor to tryptophan, one of the twenty biologically important α-amino acids. In addition, it forms stable, highly insoluble compounds with numerous divalent and trivalent metals and may be used as a reagent for quantitative determinations of these metals.\textsuperscript{17,18}

Several spectroscopic studies have been performed on the divalent metal ortho-aminobenzoates in an effort to elucidate their structures, but the results of these studies are at variance. Sandhu \textit{et al.}\textsuperscript{19} propose a structure in which the ortho-aminobenzoate acts as a tridentate ligand, giving rise to a distorted octahedral coordination about the central metal. Khakimov \textit{et al.}\textsuperscript{20} also conclude that the compounds have a distorted octahedral structure. Hill and Curran\textsuperscript{21} and Decker and Frye\textsuperscript{22} advocate a square planar structure in which the ortho-aminobenzoate is bidentate.

Thus the determination of this structure was undertaken with two objectives in mind: (1) to ascertain unequivocally the structure of bis(ortho-aminobenzoato)copper(II); and (2) to use this determination as a starting point for a series of structural studies on the compounds
formed between ortho-, meta- and para-aminobenzoic acids and a variety of metal ions. The ultimate goal of this study is to relate structural and bonding properties of these acids to their biological activities.
II. THE METHOD OF CRYSTAL STRUCTURE ANALYSIS

The process of a crystal structure determination consists of a series of successive steps with each step depending upon the accuracy and proper interpretation of the preceding step. Thus, every stage of a structure determination must be approached with meticulous care in order to ensure a successful analysis. A brief flow diagram of the steps in a typical structure analysis is shown in Figure 6.

The crystal selected for a structure determination must meet certain requirements. Of primary importance is that it be a true single crystal, i.e., one devoid of any twinning or fractures. The crystal should be small enough to ensure that it is bathed in X-rays at all orientations and, if the material is air sensitive or prone to decomposition, it must be sealed in a capillary under a suitable atmosphere.

Having mounted the crystal on a glass fiber or in a capillary, one of the real crystal axes must be aligned to within 5' of arc, parallel to the rotation axis of a goniometer—a device which allows orientation of a crystal without necessitating its removal or remounting. The properly aligned crystal is then ready for analysis by any of a number of diffraction techniques.

One of the most powerful tools for structure
Figure 6

Flow Diagram of the Structure Determination Procedure for a Compound Containing a Heavy Atom

<table>
<thead>
<tr>
<th>Step</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. SELECTION OF A SINGLE CRYSTAL</td>
<td>Determine crystal class, space group and unit cell constants</td>
</tr>
<tr>
<td>2. PRELIMINARY PHOTOGRAPHS</td>
<td>For use in determining Z, the number of molecules per unit cell</td>
</tr>
<tr>
<td>3. DETERMINE CRYSTAL DENSITY</td>
<td>Determine the positions of heavy atoms in the unit cell</td>
</tr>
<tr>
<td>4. COLLECT INTENSITY DATA</td>
<td>For use in calculating preliminary phase angles</td>
</tr>
<tr>
<td>5. CALCULATE PATTERSON MAP</td>
<td>Determine other areas of high electron density</td>
</tr>
<tr>
<td>6. POSTULATE TRIAL STRUCTURE</td>
<td>Refinement of the positional and thermal parameters of the atoms</td>
</tr>
<tr>
<td>7. CALCULATE FOURIER MAP</td>
<td>Location of hydrogen atoms</td>
</tr>
<tr>
<td>8. REFINEMENT PROCEDURE USING ANOMALOUS DISPERSION, ANISOTROPIC TEMPERATURE FACTORS AND WEIGHING SCHEMES</td>
<td></td>
</tr>
<tr>
<td>9. REFINED STRUCTURE WITH ALL NON-H ATOMS LOCATED</td>
<td></td>
</tr>
<tr>
<td>10. CALCULATE DIFFERENCE MAP</td>
<td></td>
</tr>
</tbody>
</table>
12. FINAL REFINED STRUCTURE WITH ALL ATOMS LOCATED

13. FINAL DIFFERENCE MAP Check for areas of high electron density that have not been accounted for

14. CALCULATION OF BOND DISTANCES AND ANGLES

15. THERMAL ELLIPSOID DRAWING OF STRUCTURE
analysis is the Weissenberg camera. This camera coordinates the rotation of a crystal into the diffraction condition \( \lambda = 2d_{hk\ell}\sin \theta \) with a movement of the recording film parallel to the axis of rotation. As a result, two types of measurements may be performed. The positions of the diffraction spots can be used for the determination of lattice constants, space group and crystal class. In addition, the spot positions can be used for indexing, a process of determining which crystal planes are giving rise to which diffraction spots. On the other hand, it is the intensities of the diffraction spots that provide the key to ascertaining the arrangement of atoms in the crystal.

Basically, two techniques are available for the measurement of diffraction intensities. The first involves measuring the actual amount of diffracted radiation directly with a scintillation or proportional counter. The second takes advantage of the fact that the amount of darkening on a photographic film due to the impingement of X-rays is linearly proportional to the strength of those X-rays. It is the latter technique that was employed in this determination. Two modifications have been made on the Weissenberg camera to increase the accuracy of intensity measurements. The first is an integrating mechanism which spreads the spot over an area of adjustable size to create a plateau of uniform absorbance. The second modification involves the use of multiple films to record the diffraction spots. The reasoning behind this modification is as follows. A
particularly strong reflection will saturate a film, i.e., expose all of the silver in the emulsion with the result that all reflections above a certain intensity will give the same value of absorbance. However, the acetate base of a film acts as a filter, reducing the X-ray intensity by a factor of about 4. Thus, after a strong reflection passes through the first, second or third film (up to seven), it is no longer strong enough to saturate a film and its intensity can be recorded. Then, by multiplying the unsaturated intensity by the product of the film absorption factors of the intervening films, the true intensity value can be ascertained. The structure solution may be initiated after the intensities have been corrected for: (1) absorption by the crystal, (2) factors resulting from the partial polarization of the X-rays and (3) for differences in the amount of time each crystal spends in the diffraction condition (Lorentz factor).

X-rays are waves and, as a result, the secondary X-rays generated by the various atoms in a crystal may be represented by vectors. The magnitude of the vector reflects the scattering power of the atom (as determined by the number of electrons), and the direction of the vector represents the phase difference between the secondary wave and a wave scattered by hypothetical electrons at the origin of the cell. The resultant diffracted wave for any set of planes (hkl) is merely the vector sum of the wavelets scattered by the individual atoms. The phase of each wavelet
can be expressed in terms of the position of the scattering atom \((x,y,z)\) and in terms of the \(h,k,l\) values of the diffracting plane via the following relation:

\[
\delta = 2n(hx+ky+lz)
\]

Using this formula it is then possible to calculate the magnitude and phase of the resultant vector from a given set of \(hkl\) planes due to \(j\) atoms at positions \(x_j, y_j,\) and \(z_j:\)

\[
|F_{hkl}| = \left\{ \sum_j f_j \cos^2 n (hx_j + ky_j + lz_j) + (\sum_j f_j \sin^2 n (hx_j + ky_j + lz_j)) \right\}^{\frac{1}{2}}
\]

\[
\alpha_{hkl} = \tan^{-1} \frac{\sum_j f_j \sin n (hx_j + ky_j + lz_j)}{\sum_j f_j \cos n (hx_j + ky_j + lz_j)}
\]

where \(|F_{hkl}|\) is the amplitude of the structure factor, \(f_j\) is the scattering factor of the \(j^{th}\) atom, and \(\alpha_{hkl}\) is the phase angle of the resultant vector. This resultant vector is referred to in crystallography as the structure factor. The quantity \(|F_{hkl}|^2\) is directly proportional to the intensity of the radiation being scattered by the \(hkl\) plane. Thus, with the above equation it is possible to calculate the intensities of the diffraction spots arising from any given arrangement of atoms. It is important to note that \(|F_{hkl}|\) is only the amplitude of the structure factor. The actual structure factor, \(F_{hkl}\), is a vector, the resultant of \(j\) waves scattered in the direction of the \(hkl\) reflection by the \(j\) atoms in the unit cell. It is convenient to
express $F_{hkl}$ in algebraic form by using complex notation:

$$F_{hkl} = \sum \cos^2 n(hx_j + ky_j + lz_j) + i \sum \sin^2 n(hx_j + ky_j + lz_j)$$

which may also be cast in the following exponential form:

$$F_{hkl} = \sum f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

Again, it must be remembered that $F_{hkl}$ is a vector and has a phase angle associated with it.

The ability to calculate intensities from a given arrangement of atoms is necessary, but it is also mandatory to work in the opposite direction, i.e., to calculate atomic positions from observed intensities. The diffracted wave is a periodic function, therefore with Fourier analysis it is possible to find a series of sine and cosine terms which, when combined, will duplicate the resultant wave. To perform this analysis a Fourier transform is carried out on the structure factor equation with the following result:

$$\rho(x,y,z) = \frac{1}{V} \sum \sum \sum |F_{hkl}| \cos 2\pi (hx + ky + lz - \alpha_{hkl})$$

where $\rho(x,y,z)$ is the electron density at the point $x,y,z$, and $V$ is the volume of the unit cell. Thus, by knowing the structure factor amplitude ($|F_{hkl}|$) and the structure factor phase angle ($\alpha_{hkl}$), a three-dimensional electron density map (Fourier map) of the crystal can be generated.

At this point difficulty is encountered. It is simple enough to calculate $|F_{hkl}|$ since it is merely proportional to the square root of the measured intensity, $I_{hkl}$,
but there is no way to measure the phase angle experimentally. This is the "phase problem." Thus, intensity measurements yield only half the required amount of data.

To overcome this problem it is necessary to postulate a trial structure and to use the phases calculated from the trial system as input to the electron density equation. In this work the heavy atom method was used to develop a trial structure. This method works on the assumption that, if one atom has a much larger atomic scattering factor than the others, the phase angle for the whole structure will be very close to that of the heavy atom alone. In some cases, the position of a heavy atom may be deduced from an inspection of the space group symmetry, but in the majority of structure analyses the heavy atom is located from a Patterson map. To generate this map \( |F_{hkl}|^2 \) is used as the coefficient in the electron density equation and, because \( |F_{hkl}|^2 \) is dimensionless, the phase angle is not needed.

\[
P(x,y,z) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l} |F_{hkl}|^2 \cos 2\pi(nhx + khy + lhz)
\]

The peaks of a Patterson map represent interatomic vectors, e.g., if there are two atoms in a unit cell at \( x_1, y_1, z_1 \) and \( x_2, y_2, z_2 \), there will be a peak found on the Patterson map at \( u, v, w \), where:

\[
\begin{align*}
u &= x_2 - x_1 \\
v &= y_2 - y_1 \\
w &= z_2 - z_1.
\end{align*}
\]

The magnitude of a peak is proportional to the product of
the atomic numbers of the two atoms defining the vector and, for this reason, the vector between two heavy atoms is readily identifiable. Because heavy atoms are generally related by symmetry elements, the actual atomic coordinates can usually be deduced from the vector. For example, if the two atoms are related by a center of symmetry, then \( x_1 = -x_2 \), \( y_1 = -y_2 \) and \( z_1 = -z_2 \). Therefore,

\[
\begin{align*}
    u &= 2x_1 \quad x_1 = u/2 \\
    v &= 2y_1 \quad y_1 = v/2 \\
    w &= 2z_1 \quad z_1 = w/2
\end{align*}
\]

Having located a heavy atom, the phase angles calculated from the trial structure can be incorporated with the observed structure factor amplitudes to generate the Fourier map. If the trial structure is reasonably correct, the density map should reveal the positions of other areas of high electron density (atoms). These new atoms are then added to the trial structure to generate better phases which, in turn, allow the calculation of better Fourier maps. Finally, the trial structure becomes the actual structure.

The closer the trial structure is to the real structure, the closer the calculated structure factor amplitudes, \( |F_C| \), will be to the observed structure factor amplitudes, \( |F_0| \). The value of \( |F_C| \) depends upon either five or ten variables. There are three positional parameters, one or six temperature factors and a scale factor which is merely a constant relating the absolute values.
of $|F_c|$ to the relative values of $|F_o|$. The refinement procedure uses least squares methods to minimize the quantity

$$||F_o| - |F_c||^2$$

by refining the five or ten variables. It should be noted that there are five or ten variables for each atom so that the least squares process may be called upon to refine hundreds of variables.

A measure of the agreement between $|F_c|$ and $|F_o|$, an indication of the correctness of a structure, is afforded by a quantity called the residual index, $R$, where

$$R = \frac{||F_o| - |F_c||}{|F_o|}$$

Most well behaved structures exhibit an $R$-index of less than 0.1.

The temperature factor mentioned above takes into account the effect of thermal motion upon the scattering power of an atom. If an atom is postulated as vibrating an equal distance in all directions (isotropic vibration), the corrected scattering factor is given by the following expression:

$$f = f_o e^{-B\sin^2\theta}/\lambda^2$$

where $B$ is the isotropic temperature factor and $f_o$ is the atomic scattering factor. A more realistic picture of thermal vibration is one in which the motion of the atom is ellipsoidal (anisotropic vibration) and, in this case,
the scattering factor formula assumes the following form:

\[ f = f_0 \exp[-2\pi^2 (U_{11} a^2 + U_{22} b^2 + U_{33} c^2 + 2U_{12} hka b + 2U_{13} hla c + 2U_{23} klb c^2)] \]

where the first three \( U_{ij} \)'s describe the magnitudes of the principal axes of the thermal ellipsoids, and the last three \( U_{ij} \)'s describe the orientation of the thermal ellipsoid relative to the crystal axes. \( U \) is defined as the mean square amplitude of vibration as expressed in angstroms.

The last stage of a structure determination generally involves the calculation of a difference map. To produce this map the coefficient \( |F_0| - |F_c| \) is used in the electron density equation instead of \( F_{hk1} \). Any residual electron density is revealed by this map and thereby serves two important functions. First, it can be used to locate hydrogen atoms since the density due to the single electron is usually insufficient to be visible on the original Fourier map. Secondly, it serves as a check on the final postulated structure, for there should be no peaks on a final difference map with a magnitude greater than that found for hydrogens. If indeed there is a large peak on the difference map, it is likely that an atom has been improperly located or that there is an atom which has not been accounted for. This property of a difference map also makes it useful in the intermediate stages of an analysis.
III. EXPERIMENTAL

A. Starting Materials

Analytical grade CuSO$_4$·5H$_2$O (Mallinckrodt) and ortho-aminobenzoic acid (Eastman) were used without further purification. The purity of the ortho-aminobenzoic acid was confirmed by its excellent melting point (146-147°C).\(^{23}\)

B. Preparation of Sodium Ortho-aminobenzoate Reagent\(^{17}\)

Ortho-aminobenzoic acid (3.0 g, 0.0218 mol) was dissolved in 22 ml of 0.1 N NaOH. The resulting solution was filtered and then diluted to 100 ml with distilled water. Small amounts of the ortho-aminobenzoic acid were added to the solution until it was just acid to litmus. The reagent was stored in a tightly-stoppered, light-proof container under refrigeration.

C. Preparation of Single Crystals of Bis(ortho-aminobenzoato) Copper(II)

Single crystals of Cu(H$_2$NC$_6$H$_4$COO)$_2$ were prepared by a method of diffusion mentioned by Bunn.\(^{24}\) CuSO$_4$·5H$_2$O (0.1 g, 0.0004 mol) was dissolved in 10 ml of distilled water and placed in a 10 ml flask while 10 ml of sodium ortho-aminobenzoate reagent were placed in a second 10 ml flask. Both flasks were placed in a 250 ml beaker and submerged under 250 ml of distilled water, thereby allowing the two reactants to diffuse toward each other through the aqueous
medium. The small, dark green, diamond-shaped crystals formed predominantly in the copper sulfate flask and were removed by filtration.

D. Determination of the Space Group, Unit Cell Dimensions and Density of Cu\(\text{H}_2\text{NC}_6\text{H}_4\text{COO}\)\(_2\)

Preliminary Weissenberg photographs showed the crystals to be monoclinic. Systematic absences of h0l with \(l = 2n + 1\), and 0k0 with \(k = 2n + 1\) indicated the space group \(P2_1/c\). Intensity statistics, resulting from a comparison of the observed intensities with various averaged values, indicate a centrosymmetric structure further confirming \(P2_1/c\).

The unit cell dimensions were determined using zero level Weissenberg photographs and rotation photographs taken about \([100]\), \([010]\), and \([001]\) with nickel filtered Cu-K\(\alpha\) radiation (\(\lambda = 1.54178\ \text{Å}\)). The computer programs WEISS and ROTOSC (see Appendix B) were used in evaluating all cell constants. All measurements were made at 21°. These dimensions along with other pertinent crystal data are given in Table V.

The observed density of Cu\(\text{H}_2\text{NC}_6\text{H}_4\text{COO}\)\(_2\) corresponds to two formula units per unit cell. The density measurements were made by pycnometry using an aqueous soap solution of known density to ensure the wetting of the Cu\(\text{H}_2\text{NC}_6\text{H}_4\text{COO}\)\(_2\) powder.

E. Intensity Measurements

Intensity data for Cu\(\text{H}_2\text{NC}_6\text{H}_4\text{COO}\)\(_2\) were gathered
Table V

Crystal Data for Cu(H$_2$NC$_6$H$_4$COO)$_2$

Monoclinic; P2$_1$/c

\[
\begin{align*}
a &= 12.95(1) \text{ Å} \\
b &= 5.25(1) \\
c &= 13.39(1) \\
\beta &= 93.3(1)^\circ
\end{align*}
\]

\[
\begin{align*}
V &= 637.4 \text{ Å}^3 \\
D_m &= 1.75 \text{ g.cm}^{-3} \\
D_x &= 1.749 \\
Z &= 2
\end{align*}
\]
with nickel filtered Cu-Kα radiation ($\lambda = 1.54178 \, \text{Å}$) using multiple-film, equi-inclination, integrated Weissenberg photographs for layers 0-3 of a crystal mounted on the b-axis, and layers 0-4 of a crystal mounted on the c-axis. The relationship of the crystal axes to the morphology of one of these crystals is depicted in Figure 7. Four Kodak No-Screen medical X-ray films were used for each layer, the average film absorption factor being 3.8(2) as calculated using the program FILMABS (see Appendix B). The dimensions of the crystals were 0.07 x 0.18 x 0.11 mm and 0.06 x 0.15 x 0.07 mm respectively, as referred to [100], [010], and [001]. The intensities of the reflections were measured with a Welch Densichron for which an 0.5 mm aperture was made. The photometer was calibrated with a standard density wedge and the resulting calibration curve was reduced to a fourth order polynomial by means of a polynomial regression treatment.

The following procedure was used in evaluating the net relative intensities of the diffraction spots for each layer. Three measurements were taken for every reflection—two background measurements (one on either side of the spot) and a measurement of the total intensity of the diffraction spot. Each reading was corrected by the calibration polynomial, then the two background intensities were averaged and subtracted from the total intensity to give the net intensity. This procedure was repeated for those reflections with sufficient intensity to be visible on the second, third
Figure 7
Crystal Morphology of Cu(H$_2$NC$_6$H$_4$COO)$_2$

$\phi = 280^\circ$

Rotation Axis = b

$\phi = 13^\circ$

Rotation Axis = b

0.11 r

0.07

0.18 mm
or fourth films of the multiple-film configuration. However, these net intensities were then multiplied by the appropriate film absorption factors. Those intensities found on more than one film were averaged to give a final net intensity. Each level of both crystals was treated in a similar fashion using the program PREDUCE (see Appendix B) and the intensities were corrected for Lorentz and polarization factors. Finally, the two sets of net relative intensities were cross-scaled and correlated using the method of Hamilton.\(^{25}\) The value of the linear absorption coefficient, \(\mu\), with copper radiation for \(\text{Cu(H}_2\text{NC}_6\text{H}_4\text{COO)}_2\) is 26.52 cm\(^{-1}\) and, in view of the small magnitude of \(\mu\), no correction for absorption was made. A scale factor to place the relative intensities on an absolute scale and a value for the overall temperature factor, \(B\), were derived with a Wilson calculation. This Wilson calculation involves plotting \(\ln(I_{rel}/\Sigma f_j^2)\) versus \(\sin^2\theta/\lambda^2\). The slope and intercept of the resulting line gives \(-2B\) and \(\ln C\) respectively, where \(B\) is the aforementioned overall temperature factor and \(C\) is proportional to the scale factor \(k\). 445 non-zero reflections were recorded, a non-zero reflection being defined as a diffraction spot visible on any film.
IV. SOLUTION AND REFINEMENT OF THE STRUCTURE

Symmetry considerations and three-dimensional, sharpened Patterson functions were used in locating the copper atom and two of the oxygen atoms. Due to symmetry constraints inherent in the space group $P2_1/c$ and, because there are two Cu($H_2NC_6H_4COO)_2$ molecules per unit cell ($Z$), it was possible to deduce the locations of the copper atoms in the unit cell. In examining the symmetry of $P2_1/c$, it is found that there is one set of four general positions (4e) and four sets of two special positions (2a, 2b, 2c, 2d). Because there are two copper atoms per unit cell, they must occupy one of the sets of special positions. Further examination shows the four sets of special positions to be equivalent, the only difference being in the selection of the origin. Thus, the copper atoms were placed on the positions 0,0,0 and $0,\frac{1}{2},\frac{1}{2}$ (2a). The largest peak found on the Patterson map was at $0,\frac{1}{2},\frac{1}{2}$, confirming the validity of the above reasoning. The second strongest peaks on the Patterson map arise from Cu-O vectors and, because one copper lies on the origin, the $u,v,w$ coordinates of one Patterson peak are equivalent to the $x,y,z$ coordinates of the oxygen. There will be other Cu-O peaks where this condition does not hold (e.g., between a copper at $0,\frac{1}{2},\frac{1}{2}$ and an oxygen), but often the desired peak can be found.
Using the phase angles calculated with the copper and two oxygens, the remaining non-hydrogen atoms were located on the three-dimensional Fourier maps. The initial refinement of the structure was made using the least squares method with a block diagonal approximation where only limited correlations between parameters for the various atoms are assumed. The refinement on all non-hydrogen atoms and their isotropic temperature factors yielded an R-value of 0.056 after four cycles of refinement. Further refinement, using full matrix least squares calculations with anisotropic temperature factors for all non-hydrogen atoms and copper scattering factors corrected for anomalous dispersion, lowered R to 0.044. Anomalous dispersion describes an effect whereby the wavelet of radiation scattered by a heavy atom undergoes a change in magnitude and a shift in phase due to absorption effects in the scattering atom. To correct for anomalous dispersion the following equation is used:

\[ f_{\text{anom}}^o = f_o + \Delta f' + i \Delta f'' \]

where \( f_o \) is the normal scattering factor, and \( \Delta f' \) and \( \Delta f'' \) are the terms which represent the change in magnitude and change in phase respectively.

At this stage in the structure solution, a difference map was generated and all six hydrogen atoms were readily located. The average amplitude of the hydrogen peaks was 0.4 e/Å². An additional three cycles of refinement (full matrix), including these hydrogen atoms to which constant
isotropic temperature factors of 5.0 were assigned, gave a final R-value of 0.0307. In the final cycle the ratio of the largest shift in any of the positional parameters to its estimated standard deviation was less than 0.3—an indication that further refinement would not yield any significant improvement. A final difference map showed no peaks with an intensity greater than 0.29 e/Å³. During the process of full matrix least squares refinement, a correlation matrix was generated, the coefficients of which indicate the amount of correlation among the various positional and thermal parameters of the atoms. These coefficients can range from 0 to 1, the latter describing cases in which two parameters are completely dependent. A correlation matrix can indicate an improper selection of space group by revealing symmetry elements which were not thought present. For example, if the correlation matrix demonstrates high correlation coefficients between all the parameters of two supposedly unrelated atoms, it is likely that they are actually related by a center of symmetry. In this work the correlation matrix showed no elements greater than 0.39. An error analysis revealed no systematic errors as a function of either \( \sin^2 \theta \) or \( |F_o| \). Systematic errors manifest themselves as systematic shifts in results and may be inherent in the method of observation, the apparatus used or the observer. Random errors, on the other hand, can be treated with statistical methods. The error analysis also indicated that all but six reflections had \( \frac{|F_o| - |F_c|}{F_o} \) less than
twice the final R-value or \(|F_o| - |F_c|\) less than one-half the \(|F_o|\) value of the weakest reflection—again an indication of consistent results.

In both the block diagonal and full matrix least squares procedures the function minimized was \(|F_o| - |F_c|\)^2. The atomic scattering factors for the non-hydrogen atoms were taken from those tabulated by Hanson, while those for hydrogen were taken from the paper of Stewart. Corrections for anomalous dispersion were made only for copper and the values of \(\Delta f'\) and \(\Delta f''\) (-2.15 and 0.75) were those given in a report by Cromer. The values of the refined parameters are given in Table 'I along with their estimated standard deviations (in parentheses). The full matrix least squares refinement was performed with the ORXFLS-3 program of Busing et al. The National Research Council of Canada Crystallographic Programs were used for all of the remaining computational work. The thermal ellipsoid drawing of \(\text{Cu(H}_2\text{NC}_6\text{H}_4\text{COO})_2\) was made using the program ORTEP-II of Johnson. A summary of the stages in the refinement procedure is given in Table VII and a tabulation of the observed structure factors and the final calculated structure factors is given in Table VIII.
Table VI

Final Positional and Thermal Parameters$^a$, $^b$

for Cu(H$_2$NC$_6$H$_4$COO)$_2$

I

Positional and Isotropic Thermal Parameters

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.000000(0)</td>
<td>0.000000(0)</td>
<td>0.000000(0)</td>
<td></td>
</tr>
<tr>
<td>O(1)</td>
<td>0.0340(4)</td>
<td>0.1858(10)</td>
<td>0.1792(5)</td>
<td></td>
</tr>
<tr>
<td>O(2)</td>
<td>0.1273(4)</td>
<td>0.2556(10)</td>
<td>0.3806(5)</td>
<td></td>
</tr>
<tr>
<td>N(1)</td>
<td>0.1032(5)</td>
<td>0.7331(13)</td>
<td>0.0714(6)</td>
<td></td>
</tr>
<tr>
<td>C(1)</td>
<td>0.1179(6)</td>
<td>0.1708(14)</td>
<td>0.2568(7)</td>
<td></td>
</tr>
<tr>
<td>C(2)</td>
<td>0.2112(6)</td>
<td>0.0536(14)</td>
<td>0.1975(8)</td>
<td></td>
</tr>
<tr>
<td>C(3)</td>
<td>0.2037(6)</td>
<td>0.8404(15)</td>
<td>0.1070(7)</td>
<td></td>
</tr>
<tr>
<td>C(4)</td>
<td>0.2905(7)</td>
<td>0.7388(17)</td>
<td>0.0499(9)</td>
<td></td>
</tr>
<tr>
<td>C(5)</td>
<td>0.3871(7)</td>
<td>0.8480(19)</td>
<td>0.0819(10)</td>
<td></td>
</tr>
<tr>
<td>C(6)</td>
<td>0.3957(7)</td>
<td>0.0524(21)</td>
<td>0.1727(10)</td>
<td></td>
</tr>
<tr>
<td>C(7)</td>
<td>0.3094(6)</td>
<td>0.1543(18)</td>
<td>0.23.2(8)</td>
<td></td>
</tr>
<tr>
<td>H(1)</td>
<td>0.119(7)</td>
<td>0.621(18)</td>
<td>0.010(10)</td>
<td>5.0</td>
</tr>
<tr>
<td>H(2)</td>
<td>0.074(8)</td>
<td>0.691(19)</td>
<td>0.146(10)</td>
<td>5.0</td>
</tr>
<tr>
<td>H(4)</td>
<td>0.287(7)</td>
<td>0.601(18)</td>
<td>0.987(9)</td>
<td>5.0</td>
</tr>
<tr>
<td>H(5)</td>
<td>0.449(7)</td>
<td>0.787(19)</td>
<td>0.033(9)</td>
<td>5.0</td>
</tr>
<tr>
<td>H(6)</td>
<td>0.462(7)</td>
<td>0.134(18)</td>
<td>0.202(9)</td>
<td>5.0</td>
</tr>
<tr>
<td>H(7)</td>
<td>0.313(8)</td>
<td>0.275(19)</td>
<td>0.299(10)</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Table VI—Continued

II
Anisotropic Thermal Parameters (x10^4 Å²)

<table>
<thead>
<tr>
<th>Atom</th>
<th>U_{11}</th>
<th>U_{22}</th>
<th>U_{33}</th>
<th>U_{12}</th>
<th>U_{13}</th>
<th>U_{23}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>226.0(8.5)</td>
<td>159.1(8.7)</td>
<td>153.3(7.6)</td>
<td>16.7(7.4)</td>
<td>-15.4(2.8)</td>
<td>-3.0(6.1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>209.9(29.6)</td>
<td>223.4(33.5)</td>
<td>164.0(27.2)</td>
<td>-0.7(13.4)</td>
<td>-4.9(11.4)</td>
<td>0.7(12.7)</td>
</tr>
<tr>
<td>O(2)</td>
<td>342.8(33.9)</td>
<td>277.7(33.6)</td>
<td>180.0(27.6)</td>
<td>6.4(14.1)</td>
<td>-8.9(12.3)</td>
<td>-56.2(13.2)</td>
</tr>
<tr>
<td>N(1)</td>
<td>200.6(38.1)</td>
<td>215.5(45.1)</td>
<td>202.7(42.8)</td>
<td>10.1(15.8)</td>
<td>17.5(16.3)</td>
<td>-5.6(15.0)</td>
</tr>
<tr>
<td>C(1)</td>
<td>232.8(45.7)</td>
<td>81.9(51.4)</td>
<td>221.4(41.4)</td>
<td>16.5(19.6)</td>
<td>8.6(17.8)</td>
<td>19.2(19.1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>221.8(41.5)</td>
<td>96.0(67.3)</td>
<td>160.0(38.8)</td>
<td>2.1(18.0)</td>
<td>9.2(15.0)</td>
<td>26.1(17.8)</td>
</tr>
<tr>
<td>C(3)</td>
<td>220.9(46.6)</td>
<td>173.3(51.4)</td>
<td>137.2(40.1)</td>
<td>-7.2(20.6)</td>
<td>-7.7(16.6)</td>
<td>42.0(19.0)</td>
</tr>
<tr>
<td>C(4)</td>
<td>345.4(54.2)</td>
<td>258.9(55.7)</td>
<td>310.6(50.3)</td>
<td>62.7(22.5)</td>
<td>19.3(21.5)</td>
<td>8.1(20.3)</td>
</tr>
<tr>
<td>C(5)</td>
<td>235.3(55.0)</td>
<td>487.0(66.8)</td>
<td>402.8(58.4)</td>
<td>24.6(25.8)</td>
<td>19.3(22.1)</td>
<td>-22.6(27.3)</td>
</tr>
<tr>
<td>C(6)</td>
<td>265.8(51.6)</td>
<td>517.6(100.7)</td>
<td>428.2(53.9)</td>
<td>-12.0(27.2)</td>
<td>14.1(20.9)</td>
<td>0.6(27.4)</td>
</tr>
<tr>
<td>C(7)</td>
<td>258.2(49.9)</td>
<td>339.1(58.1)</td>
<td>245.5(47.2)</td>
<td>-25.4(24.1)</td>
<td>-7.7(19.3)</td>
<td>-8.9(21.7)</td>
</tr>
</tbody>
</table>

The anisotropic thermal parameter is defined as:

\[ f = f_0 \exp[-2 \sum_{ij} \{ U_{ij} \exp^2(a^2h^2a+b^2k^2b+c^2l^2c)\}] \]

Estimated standard deviations are given in parentheses, x, y, and z are fractional coordinates.
### Table VII

**Summary of Refinement Stages**

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Method of Atom Location</th>
<th>Method of Refinement</th>
<th>Temperature Factors</th>
<th>Cycles of Refinement</th>
<th>R-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Patterson</td>
<td>-</td>
<td>Isotropic</td>
<td>0</td>
<td>0.5360</td>
</tr>
<tr>
<td>Cu,O(1),O(2)</td>
<td>Patterson</td>
<td>Blk. Diag.</td>
<td>Isotropic</td>
<td>1</td>
<td>0.2939</td>
</tr>
<tr>
<td>Cu,O(1),O(2),C(1),C(2),C(3),N(1)</td>
<td>Fourier</td>
<td>Blk. Diag.</td>
<td>Isotropic</td>
<td>2</td>
<td>0.2225</td>
</tr>
<tr>
<td>All non-H-atoms</td>
<td>Fourier</td>
<td>Blk. Diag.</td>
<td>Isotropic</td>
<td>5</td>
<td>0.0565</td>
</tr>
<tr>
<td>All non-H-atoms</td>
<td>Fourier</td>
<td>Blk. Diag.</td>
<td>Anisotropic</td>
<td>4</td>
<td>0.0475</td>
</tr>
<tr>
<td>Cu(anom. disp.), All non-H-atoms</td>
<td>Fourier</td>
<td>Full Matrix</td>
<td>Anisotropic</td>
<td>3</td>
<td>0.0436</td>
</tr>
<tr>
<td>Cu(anom. disp.), All atoms</td>
<td>Difference</td>
<td>Full Matrix</td>
<td>Isotropic for H-atoms, Anisotropic for non-H-atoms</td>
<td>3</td>
<td>0.0307</td>
</tr>
</tbody>
</table>
Table VIII

Calculated and Observed Structure Factors

for Cu(H$_2$NC$_6$H$_4$COO)$_2$
V. RESULTS AND DISCUSSION

The contents of one unit cell for Cu\((H_2NC_6H_4COO)_2\) are shown in Figure 8 and the coordination around copper is shown in Figure 9. Each copper atom has distorted octahedral coordination. Each ortho-aminobenzoate group functions as a tridentate ligand but the three sites of attachment on the ligand are not associated with the same copper atom. The amino nitrogen, N(1), and the carboxylate oxygen, O(1), coordinate the copper equatorially and are cis to each other. The axial positions of the distorted octahedron are occupied by two carbonyl oxygens, O(2), each of which belongs to a different ortho-aminobenzoate ligand, the ligands being related by the center of symmetry at the copper atom. Thus, four ortho-aminobenzoate residues are associated with each copper. The result of this mode of coordination is that each copper in the (100) plane is attached to four other coppers via carboxylate bridges to give a two-dimensional polymeric sheet structure coincident with (100). This two-dimensional network is illustrated in Figure 10. This arrangement is similar to one found in copper gamma-amino-butyrurate dihydrate where the entire molecule serves as a bridge. The aromatic rings of the ortho-aminobenzoate extend in a nearly perpendicular manner on either side of the sheets and may provide lateral stability. The polymeric structure may be the source of the extreme insolubility of
Figure 8

Contents of One Unit Cell for Cu(H$_2$NC$_6$H$_4$COO)$_2$
Figure 9

Coordination Around Copper in Cu(H$_2$NC$_6$H$_4$COO)$_2$
Figure 10

Polymeric Structure in $\text{Cu(H}_2\text{NCC}_6\text{H}_4\text{COO})_2$
the compound.

In this structure hydrogen bonding is found between the amino nitrogen, N(1), and a carbonyl oxygen, O(2), in an adjacent molecule and is represented by the dotted lines shown in Figure 10. The N(1)-O(2) distance is 3.155(8) Å and the N(1)-H(1)•••O(2) angle is 162(8)°. This length is well within the range found for hydrogen bonds formed between amine groups and oxygen (2.57-3.22 Å). The angle being within 30° of a straight line further confirms that it is a satisfactory hydrogen bond. Thus, the hydrogen bonding provides additional cross-linking in the polymeric network and, in conjunction with the bridging configuration, determines the packing of the structures. It is interesting to note the importance of hydrogen bonding in crystal structures because, if hydrogen bonds are present, they usually determine the actual structure. Therefore, it is important that trial structures conform to reasonable hydrogen bonding schemes, as is the case with the structure of Cu(H₂NC₆H₄COO)₂.

In Table IX are listed the bond distances and angles found in bis(ortho-aminobenzoato)copper(II). The axial bond length of Cu-O(2) (2.415 Å) is noticeably longer than the equatorial bond lengths of Cu-O(1) (1.973 Å) and Cu-N(1) (2.024 Å), as would be expected with the Jahn-Teller effect in operation. The C-O distances in the carbonyl group are significantly different (C(1)-O(1)=1.276 Å, C(1)-O(2)=1.244 Å), an indication that the π delocalization between these two bonds is not equal—undoubtedly a consequence of
Table IX

Bond Distances and Angles in Cu(H$_2$NC$_6$H$_4$COO)$_2$ \textsuperscript{a}

<table>
<thead>
<tr>
<th>Distances (Å)</th>
<th>\textsuperscript{a}Cu — O(1)</th>
<th>C(5) — C(6)</th>
<th>C(5) — C(6)</th>
<th>1.371(14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu — O(2)\textsuperscript{b}</td>
<td>2.415(5)</td>
<td>C(6) — C(7)</td>
<td>1.381(12)</td>
<td></td>
</tr>
<tr>
<td>Cu — N(1)</td>
<td>2.024(7)</td>
<td>C(7) — C(2)</td>
<td>1.396(11)</td>
<td></td>
</tr>
<tr>
<td>C(1) — O(1)</td>
<td>1.276(8)</td>
<td>N(1) — H(1)</td>
<td>0.86(9)</td>
<td></td>
</tr>
<tr>
<td>C(1) — O(2)</td>
<td>1.244(8)</td>
<td>N(1) — H(2)</td>
<td>0.85(10)</td>
<td></td>
</tr>
<tr>
<td>C(1) — C(2)</td>
<td>1.492(10)</td>
<td>C(4) — H(4)</td>
<td>0.93(9)</td>
<td></td>
</tr>
<tr>
<td>C(2) — C(3)</td>
<td>1.405(10)</td>
<td>C(5) — H(5)</td>
<td>1.00(9)</td>
<td></td>
</tr>
<tr>
<td>C(3) — N(1)</td>
<td>1.439(10)</td>
<td>C(6) — H(6)</td>
<td>0.98(9)</td>
<td></td>
</tr>
<tr>
<td>C(3) — C(4)</td>
<td>1.380(11)</td>
<td>C(7) — H(7)</td>
<td>0.90(10)</td>
<td></td>
</tr>
<tr>
<td>C(4) — C(5)</td>
<td>1.393(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table IX--Continued

Bond Distances and Angles in Cu(H$_2$NC$_6$H$_4$COO)$_2^a$

<table>
<thead>
<tr>
<th></th>
<th>Bond Distances (Å)</th>
<th>Angles (deg.)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1) → Cu → N(1)</td>
<td>87.1(2)</td>
<td>C(3) → C(4) → C(5)</td>
<td>119.9(7)</td>
</tr>
<tr>
<td>O(1) → Cu → O(2)</td>
<td>89.4(2)</td>
<td>C(4) → C(5) → C(6)</td>
<td>119.7(8)</td>
</tr>
<tr>
<td>O(2) → Cu → N(1)</td>
<td>93.8(2)</td>
<td>C(5) → C(6) → C(7)</td>
<td>120.8(9)</td>
</tr>
<tr>
<td>Cu → O(1) → C(1)</td>
<td>126.7(4)</td>
<td>C(6) → C(7) → C(2)</td>
<td>120.7(8)</td>
</tr>
<tr>
<td>O(1) → C(1) → O(2)</td>
<td>123.1(7)</td>
<td>H(1) → N(1) → H(2)</td>
<td>121(9)</td>
</tr>
<tr>
<td>O(1) → C(1) → C(2)</td>
<td>119.6(6)</td>
<td>C(3) → C(4) → H(4)</td>
<td>123(6)</td>
</tr>
<tr>
<td>O(2) → C(1) → C(2)</td>
<td>117.4(6)</td>
<td>C(5) → C(4) → H(4)</td>
<td>117(6)</td>
</tr>
<tr>
<td>C(1) → C(2) → C(3)</td>
<td>121.7(6)</td>
<td>C(4) → C(5) → H(5)</td>
<td>120(5)</td>
</tr>
<tr>
<td>C(1) → C(2) → C(7)</td>
<td>120.4(7)</td>
<td>C(6) → C(5) → H(5)</td>
<td>120(5)</td>
</tr>
<tr>
<td>C(3) → C(2) → C(7)</td>
<td>118.0(7)</td>
<td>C(5) → C(6) → H(6)</td>
<td>124(5)</td>
</tr>
<tr>
<td>C(2) → C(3) → N(1)</td>
<td>118.8(6)</td>
<td>C(7) → C(6) → H(6)</td>
<td>115(5)</td>
</tr>
<tr>
<td>C(4) → C(3) → N(1)</td>
<td>120.3(7)</td>
<td>C(6) → C(7) → H(7)</td>
<td>123(6)</td>
</tr>
<tr>
<td>C(2) → C(3) → C(4)</td>
<td>120.9(7)</td>
<td>C(2) → C(7) → H(7)</td>
<td>116(6)</td>
</tr>
</tbody>
</table>

---

$^a$Estimated standard deviations are given in parentheses and are calculated from those derived for the positional parameters.

$^b$The dotted line represents a bond between a copper atom and the carbonyl oxygen of a ligand attached to a different copper atom.
the bonding configuration. The C(1)-O(2)-Cu and C(3)-N(1)-Cu bond angles (126.30° and 112.1°) support sp² and sp³ hybridization of O(2) and N(1) respectively. However, the 126.7° magnitude of the C(1)-O(1)-Cu angle is somewhat larger than that expected for sp³ hybridization and may result from the rigidity of the organic ligand or partial π delocalization. The Cu-N(1) and Cu-O(1) distances and the N(1)-Cu-O(1) angle are comparable with the corresponding average values, 2.00(8), 1.96(6) and 84°, obtained from a large number of reported copper(II) complexes with amino acids and peptides. The planarity of the two amino nitrogens and the two carboxylate oxygens is required by symmetry, i.e., the center of symmetry located at the copper atom. This plane is defined by the normal equation: 0.7452X + 0.4897Y + 0.4374Z = 0.0, where X, Y and Z are the orthogonalized atomic coordinates in angstroms and the coefficients are the direction cosines of the normal to the plane. The distance of any point from the plane is given by the relation:

$$P_i = 0.7452X + 0.4897Y + 0.4374Z.$$ 

Thus, the distance of the carbonyl oxygen from this plane is 2.410 Å.

A thermal ellipsoid drawing of one molecule of Cu(H₂NCO₂HCOO)₂ is depicted in Figure 11, the axial oxygens, O(2), having been omitted since strictly speaking they are not part of the molecule. In this drawing each atom is represented as an ellipsoid, the dimensions of which show the
Figure 11

Thermal Ellipsoid Drawing of Cu(H₂N₅C₆H₄COO)₂
extent of anisotropic vibration for the atom. A number of interesting features are revealed in this drawing. Those atoms on the outskirts of the molecule, i.e., C(4), C(5), C(6), exhibit large thermal displacements, generally with the largest dimension of the ellipsoid oriented parallel to a bond. As the number of bonds to an atom increases (bonds to hydrogen not included), the magnitude of the thermal vibration decreases and the ellipsoid becomes more spherical in shape. This effect is particularly pronounced for C(3) and C(7), each of which is attached to three other atoms. On the other hand, O(2) exhibits extensive thermal motion in what appears to be a wagging mode. This large thermal displacement of the O(2) would seem to indicate that it is not that strongly bonded to copper or, at any rate, not as strongly as are N(1) and O(1) whose thermal ellipsoids are markedly smaller. The thermal motion of the copper is clearly related to the nature of its coordination. The long axis of the thermal ellipsoid is directed towards the axially coordinated O(2) atoms—again a probable indication that the axial bonds are weaker than the equatorial bonds. The other two principal axes are much shorter and nearly equal in length and they lie in the plane defined by the four equatorially coordinated atoms. However, unlike the case with the long axis, the shorter axes are directed between rather than along the bonds.

\[ \text{Cu(H}_2\text{NCO}_2\text{HCOO)} \] is one of a rare group of copper-amino acid complexes where both oxygens of the carboxylate
group are active in bonding. Other examples include copper(II) glutamate dihydrate, glycylglycylglycinato-copper(II) chloride sesquihydrate, diammine(ortho-phthalato)copper(II), copper gamma-aminobutyrate and the dihydrate. However, bis(ortho-aminobenzoato)copper(II) is unique in that each carbonyl oxygen, O(2), comes from a different ligand.

The powder diffraction pattern of bis(ortho-aminobenzoato)zinc(II) is extremely similar to, but not identical with that of the copper complex. The same also holds true for the nickel and cobalt complexes with ortho-aminobenzoic acid. Intuitively, one would surmise that the Zn-O(2) distance is shorter than the Cu-O(2) distance and that the Zn-O(2) distance has a magnitude of ca. 2.0 Å, giving rise to undistorted octahedral coordination. This supposition is borne out in part by studies made of copper and nickel beta-alanine hexahydrates where the axial Cu-O and Ni-O distances were 2.53 and 2.17 Å respectively. Preliminary investigations have shown that bis(ortho-aminobenzoato)zinc(II) also belongs to the space group P2_1/c and that it has lattice constants very similar to those of the copper compound. Further studies have been hampered by the tendency of the zinc complex to form twin crystals.
A. Attempted Structure Analysis of Bis(para-aminobenzoato)diaquocopper(II),

\[ \text{Cu(H}_2\text{N}_6\text{H}_4\text{COO)}_2 \cdot 2\text{H}_2\text{O} \]
A. Experimental

1. Starting Materials

Analytical grade CuSO₄·5H₂O (Mallinckrodt) was used without further purification. Certified grade para-aminobenzoic acid (Fisher) was recrystallized twice from hot ethanol and air dried at room temperature.

2. Preparation of Sodium Para-aminobenzoate Reagent

Para-aminobenzoic acid (3.0 g, 0.0218 mol) was dissolved in 22 ml of 0.1 N NaOH. The resulting solution was filtered and then diluted to 100 ml with distilled water. Small amounts of the para-aminobenzoic acid were added to the solution until it was just acid to litmus. The reagent was stored in a tightly-stoppered, light-proof container under refrigeration.

3. Preparation of Single Crystals of Bis(para-aminobenzoato)diaquocopper(II)

Single crystals of Cu(H₂NC₆H₄COO)₂·2H₂O were prepared by the method of diffusion mentioned by Bunn. CuSO₄·5H₂O (0.084 g, 0.00034 mol) was dissolved in 10 ml of distilled water and placed in a 10 ml flask while 10 ml of sodium para-aminobenzoate reagent were placed in a second 10 ml flask. Both flasks were placed in a 250 ml beaker and submerged under 200 ml of distilled water, thereby allowing the two reactants to diffuse toward each other through the aqueous medium. The large, dark green, needle-shaped crystals formed predominantly in the copper sulfate flask and
were removed by filtration. The long needles were cut per-
pendicular to the long axis to form small sections which
could then be mounted for the crystal structure analysis.
The dimensions of the crystals were 0.15 x 0.15 x 0.09 mm
and 0.10 x 0.14 x 0.14 mm, as referred to [100], [010] and
[001].

Anal. Calcd for Cu(H$_2$NC$_6$H$_4$COO)$_2$·2H$_2$O: C, 45.21;
H, 4.30; N, 7.53.
Found: C, 45.18, 45.18; H, 4.15, 4.15; N, 7.54, 7.62.

4. Determination of Unit Cell Dimensions, Density
and Extinction Conditions for Cu(H$_2$NC$_6$H$_4$COO)$_2$·2H$_2$O

The unit cell dimensions were determined using
zero-level Weissenberg photographs and rotation photographs
taken about [100], [010] and [001] with nickel filtered
CuK$_\alpha$ radiation (\(\lambda = 1.54178\ \text{\AA}\)). The computer programs
WEISS and ROTOSC (see Appendix B) were used in evaluating
all cell constants. All measurements were made at 21°. The
unit cell dimensions along with other pertinent data are
given in Table X. It should be noted that although the unit
cell angles are given as 90°, the cell may not be orthogonal.
This will be discussed further under the possibilities of
pseudo-symmetry.

The observed density of Cu(H$_2$NC$_6$H$_4$COO)$_2$·2H$_2$O cor-
responds to two formula units per unit cell. The density
measurements were made by the use of pycnometry using an
aqueous soap solution of known density to ensure the wetting
of the Cu(H$_2$NC$_6$H$_4$COO)$_2$·2H$_2$O powder.
Table X

Crystal Data for Cu(H$_2$NC$_6$H$_4$COO)$_2$·2H$_2$O

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>17.139 Å</td>
</tr>
<tr>
<td>b</td>
<td>6.904</td>
</tr>
<tr>
<td>c</td>
<td>6.195</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>90°</td>
</tr>
<tr>
<td>$\beta$</td>
<td>90°</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>90°</td>
</tr>
<tr>
<td>V</td>
<td>733.040 Å$^3$</td>
</tr>
<tr>
<td>$D_m$</td>
<td>1.660 g·cm$^{-3}$</td>
</tr>
<tr>
<td>$D_x$</td>
<td>1.683</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
</tbody>
</table>

Systematic Absences:

- hko: $h = 2n + 1$
- h0o: $(h = 2n + 1)$
The following space group systematic absence was observed on Weissenberg and precession films: \( hko, h = 2n + 1 \).

Intensity statistics indicated a centrosymmetric space group. Axial assignments were made on the assumption that the space group was \( \text{Pmna} \). \(^{43}\)

5. **Intensity Measurements**

Intensity data for \( \text{Cu(H}_2\text{NC}_6\text{H}_4\text{COO)}_2 \cdot 2\text{H}_2\text{O} \) were gathered with nickel filtered \( \text{CuK}_{\alpha} \) radiation (\( \lambda = 1.54178 \, \text{Å} \)) using a Charles Supper equi-inclination single crystal diffractometer, which was outfitted with a type 85010100 Norelco scintillation tube connected to a Norelco electronic circuit panel model 12206/7. The integrated intensities of the reflections were measured by scanning each peak with a Pace-Supper control unit mounted on the diffractometer. Stationary counts were taken on either side of the peak to determine the background level. Pertinent instrumental settings and measurement parameters are given in Table XI. Prior to the intensity measurement procedure a series of check reflections were recorded. During the course of intensity measurement, these reflections were remeasured after every 25 reflections to check for possible instrument malfunction.

Two crystals were used in collecting the intensity data. Layers 0-6 were recorded for a crystal mounted on the \( c \)-axis and layers 0-8 for a crystal mounted on the \( a \)-axis. To determine the net relative intensity of a peak, the two background counts were first averaged, then multiplied by 2 to correct for the difference in background and
Table XI

Instrumental Settings and Measurement Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation</td>
<td>CuKα</td>
</tr>
<tr>
<td>Filter</td>
<td>Ni</td>
</tr>
<tr>
<td>Background Counting Time:</td>
<td>50 sec</td>
</tr>
<tr>
<td>Peak Scanning Time:</td>
<td>100 sec</td>
</tr>
<tr>
<td>Background Counting Position:</td>
<td>1.67° on either side of calculated peak position</td>
</tr>
<tr>
<td>Scan Rate:</td>
<td>2°/min (8000 position on control)</td>
</tr>
<tr>
<td>Detector Voltage:</td>
<td>880 volts</td>
</tr>
<tr>
<td>P.H.A. Baseline:</td>
<td>5 volts</td>
</tr>
<tr>
<td>P.H.A. Window:</td>
<td>13 volts</td>
</tr>
<tr>
<td>Time Constant:</td>
<td>2.0</td>
</tr>
<tr>
<td>Chart Speed:</td>
<td>30&quot;/hour</td>
</tr>
<tr>
<td>X-Ray Voltage:</td>
<td>35 kV</td>
</tr>
<tr>
<td>X-Ray Amperage:</td>
<td>15 mA</td>
</tr>
</tbody>
</table>
peak counting times. The average background was then subtracted from the overall peak intensity to give the net relative peak intensity. After being corrected for Lorentz and polarization factors, the two sets of data were cross-scaled and correlated using the method of Hamilton. A two sigma test was used to ascertain which reflections were to be considered observed. In this test any reflection with a net intensity not greater than two times the square root (sigma) of the total background count is classified as an unobserved reflection. Of the 742 reflections recorded, 451 were treated as observed.

6. Attempted Solution and Discussion

The attempt to solve the crystal structure of \( \text{Cu(H}_2\text{NC}_6\text{H}_4\text{COO)}_2\cdot\text{2H}_2\text{O} \) has thus far proved unsuccessful. According to the extinction conditions, this compound should belong to one of three possible orthorhombic space groups, i.e., Pmma, Pma2 or Pmc2\(_1\). An analysis of intensity statistics—a process whereby the observed intensities are compared to various averaged values—clearly indicated that the structure was centrosymmetric, i.e., had a center of symmetry. Of the three possible space groups only Pmma is centrosymmetric, so this seemed the likely choice. However, from this point on a series of irreconcilable anomalies were encountered.

In a survey conducted by Nowacki, it was found that nearly 60% of the surveyed crystals were distributed among only 8 of the possible 230 space groups, and Pmma is not among these 8 common groups. More importantly, this
space group seems to place too many symmetry restrictions on
the atom positions in $\text{Cu(H}_2\text{NC}_6\text{H}_4\text{COO)}_2\cdot2\text{H}_2\text{O}$. For this com-
pound $Z = 2$, thus there are two coppers, four \underline{para}-amino-
benzoate ligands and four water molecules per unit cell.
However, in order for the atoms of the organic ligand and
of water to lie on general positions, \textit{i.e.}, positions which
do not lie on symmetry elements, there would have to be
eight ligands and eight waters per unit cell, and this re-
quires that $Z = 4$, not 2. With $Z = 2$ every atom must lie
on a special position; one consequence of such a situation
is that the entire organic ligand must be perfectly planar.

In spite of the seemingly unrealistic symmetry re-
quirements, the assumption was made that \text{Pmma} was the correct
space group and a Patterson map was generated. At this
point a third problem was encountered. The strongest peak
on the Patterson was located at $u = 0$, $v = \frac{1}{2}$, $w = 0$, a po-
sition not reconcilable with the symmetry inherent in \text{Pmma}.
A second peak with an intensity approximately one-third that
of the $0,\frac{1}{2},0$ peak was found which did agree with the sym-
metry and, in spite of its low intensity, it was assigned
as arising from a Cu-Cu vector. Using the phases calculated
from the postulated copper positions, a Fourier map was pro-
duced but again problems were met. First, peaks were found
on the map which did not lie on the symmetry elements as
required by the assumptions made. Secondly, the majority
of the peaks on the Fourier made no chemical sense, \textit{i.e.},
no semblance of any recognizable chemical entities could be
found. This was in marked contrast to the case with bis(ortho-
aminobenzoato)copper(II) where fragments of the ring system
and likely Cu-O and Cu-N distances were readily located. At-
ttempts at refining and solving the structure with those few
atoms that did meet symmetry and chemical requirements proved
futile, no significant reduction in the R-factor was ever
accomplished. In addition, during the course of refinement,
large temperature factors were generated for the atoms. Be-
cause an increase in a temperature factor decreases the value
of the scattering factor, such behavior often represents an
attempt by the refinement method to remove an atom from its
assigned position by spreading the electron density over a
large volume.

Realizing that no progress was being made with Pmma,
it seemed plausible that the intensity statistics had given
false indications and that the space group was actually
non-centrosymmetric. Both non-centrosymmetric space groups
allow the placement of the ligand and water atoms on general
positions but Pmc2₁₄₆ could not be justified in terms of
either of the strong peaks on the Patterson map and so was
rejected. The second strongest peak could be justified on
the basis of the symmetry in Pma2₄₇ if the assumption was
made that the z coordinate of the 2c set of special positions
is very close to 0.0. A Fourier map was calculated but, as
with Pmma, the resulting atom positions made no chemical
sense and no reduction in the R-factor was ever achieved.
The Fourier maps also exhibited symmetry elements which
should not have been present for Pma2. Again, the refinement
process generated suspiciously high temperature factors.

Rigorous remeasurement of films confirmed all cell constants and the crystal density was redetermined using the floatation method rather than pycnometry, but all results checked with those previously calculated. Thus, it seems highly probable that the fault lies in the assignment of the space group or even more basically in the identification of the crystal class.

The crystal class of a compound can be incorrectly identified if there is the presence of pseudo-symmetry. For example, a monoclinic lattice with the non-orthogonal angle being very close to 90° may lead to the false conclusion that the system is orthorhombic. On the possibility that this might be the case with Cu(H₂N₆H₄COO)₂·2H₂O, solution and refinement was attempted using the space group, P2/c, a monoclinic space group with the same symmetry extinctions as Pmma. However, as before the results were characterized by uninterpretable Patterson maps and the inability to lower the R-factor.

Space group determination is generally carried out by an examination of extinction conditions, i.e., the systematic absences of reflection spots on a Weissenberg or precession film. Each type of absence is indicative of an element of symmetry, for example, h00 reflections with h = 2n + 1 absent reveals a twofold screw axis parallel to the a-axis. Therefore, any set of extraneous spots, especially ones that occupy positions where there should be
absences, will lead to an improper selection of a space group. These extraneous spots can arise from a number of sources such as satellite crystals, fractured crystals, double crystals or Renninger spots. However, the greatest source of these spots is from twinned crystals. A distinction must be made between a double crystal and a twinned crystal. The former defines two crystals which are attached to each other in a more or less random fashion, while the latter describes the existence of two separate lattices which are symmetry related and often appear to be one crystal. It must be stressed that the orientations of the twinned lattices are not random but often share a common lattice plane or axis which is constant for any example of one species. Twinning always involves the addition of a plane or axis of symmetry and, as a result, the composite crystal may be of a higher symmetry than the individual crystals. Due to the symmetrical arrangement of the two twins, the diffraction spots often interleave thereby masking sets of systematic absences. According to Buerger crystals which belong to space groups with very few or no systematic absences should be regarded with suspicion. Pmma has only one extinction condition, $hk0$, $h = 2n + 1$ ($h00$, $h = 2n + 1$ is a necessary condition of the first) and this may be an indication of twinning in Cu($H_2N$C$_6$H$_4$COO)$_2$·2H$_2$O.

A number of methods are available for the detection of twinning. Examination of a twin crystal with a polarizing microscope will often show optically distinct areas
and double diffraction spots or a set of systematic absences which do not fit any space group also tell of twinning. Although none of these manifestations were found with \( \text{Cu(H}_2\text{NCO}_6\text{H}_4\text{COO})_2\cdot2\text{H}_2\text{O} \), the effects of twinning can be insidious. A number of structures have been supposedly solved, only to have it turn out that the data was gathered on a twin crystal and that the space group, crystal system and atomic arrangement were incorrect. Although the connection is dubious, it is interesting to note that para-aminobenzoic acid is one of those materials that readily forms twin crystals.51,52

Operating on the assumption that twinning is the source of the uninterpretable results, the next obvious step is to prepare new single crystals. It is conceivable that by altering the diffusing medium to a very weak acetic acid solution instead of pure water, or by changing the copper salt anion, it may be possible to avoid the twinning. Likewise, examination of the existing crystals under a more powerful polarizing microscope may reveal the presence of twinning, in which case it might be possible to separate the twins mechanically.

In this work all atomic scattering factors were taken from those tabulated by Hanson,27 and all crystallographic computational work was performed with the National Research Council of Canada Crystallographic Programs.31
B. Computer Programs
Title: Significance Test for Net Peak Intensities (Counter Data)

Object: To determine if the net intensity of a reflection is sufficiently greater than the total background count to warrant classifying it as an observed reflection

Input:  
- TITLE: any information
- BKT: background counting time. This program automatically adjusts the background count to the value it would have if the peak counting time and the background counting time were the same.
- PKT: peak counting time
- S: level of significance constant. If the net peak count is greater than \((S) \cdot (SIGMA)\) where \(SIGMA = (\text{total background})^{1/2}\), then the peak is considered an observed. Values of 1.0, 2.0, or 3.0 are generally used.
- MH,MK,ML: \(h,k,l\) values
- BK1: background count before peak
- PK: total peak count
- BK2: background count after peak
- IEOF: end of file indicator (1 if last, 0 otherwise)

Output: The program prints \(h,k,l\), net intensity and an indicator for each reflection. An indicator of 1 indicates an unobserved, an indicator of 0 indicates an observed.

The program punches cards suitable for input into UNH-26.
Cards: (1) Title Card, any information, all columns
FORMATT(20A4)

(2) Directives Card
Columns 1-7 BKT
 8-14 PKT
15-19 S

(3) Planes Cards
Columns 1-4 MH
 5-8 MK
 9-12 ML
13-21 BK1
22-30 PK
31-39 BK2
40-59 blank
60 IEOF

FORMATT(2F7.2,F5.2)
FORMATT(3I4,3F9.2,20X,I1)

Programmed by Lange
C UNH-37 WRITTEN BY LANGE, JANUARY 1974
C THIS PROGRAM IS FOR USE WITH REFLECTION DATA GATHERED WITH COUNT
C EQUIPMENT. ITS PURPOSE IS TO TEST EACH REFLECTION TO SEE IF IT
C SUFFICIENTLY GREATER THAN THE BACKGROUND COUNT TO BE CONSIDERED
C AN OBSERVED REFLECTION. THE SEVERITY OF THE TEST IS SPECIFIED BY
C THE USER.

DIMENSION TITLE(20)
I=0
II=0
INTEGER READR, PRINTR, PUNCH
READR=5
PRINTR=6
PUNCH=7
READ(READR, 909) TITLE(I), I=1, 20
WRITE(PRINTR, 919) TITLE(I), I=1, 20
WRITE(PRINTR, 906)
100 READ(READR, 900) BKT, PKT, S
102 READ(READR, 901) MH, MK, ML, BK1, PK, BK2, EOF
BK= ((BK1+BK2)*PKT)/(2*BKT)
SIGMA= SQRT(BK)
TEST=S*SIGMA
FIN=C-0.5 BK
500 IF( FIN=TEST) 200, 300, 300
250 FIN=0
200 INDR=1
WRITE(PRINTR, 902) MH, MK, ML, FIN, INDR
WRITE(PUNCH, 903) MH, MK, ML, PK, PKT, BK1, BK2, BKT, INDR
I=I+1
GO TO 350
300 INDR=0
WRITE(PRINTR, 902) MH, MK, ML, FIN, INDR
WRITE(PUNCH, 903) MH, MK, ML, PK, PKT, BK1, BK2, BKT, INDR
II=II+1
350 IF( EOF) 400, 102, 400
400 WRITE(PRINTR, 906) I
WRITE(PRINTR, 907) I
900 FORMAT(2F7.2, F5.2)
901 FORMAT(3l4, 3F9.2, 20X, I1)
902 FORMAT(3l5, F9.2, 10X, I1)
903 FORMAT(3l3, F8.1, 4F7.1, 14X, I1)
906 FORMAT(15H UNOBSEIVEDS= , I7)
907 FORMAT(13H OBSERVEDS= , I7)
908 FORMAT(4IH H K L INTENSITY INDICATOR)
909 FORMAT(20A4)
919 FORMAT(1H120A4)
END
PROGRAM FILMA3S: WRITTEN BY LANGE, APRIL 1973

THIS PROGRAM IS DESIGNED TO CALCULATE THE FILM ABSORPTION FACTOR BETWEEN TWO FILMS IN A MULTI-LAYER INTEGRATED WEISSENBERG PHOTOGRAPH.

THE FOLLOWING INFORMATION MUST BE READ IN:

UPFILM
ALOFLM

THE NUMBER OF THE SPOT BEING USED
THE NET CORRECTED OPTICAL DENSITY OF
THE SPOT ON THE UPPER FILM
THE NET CORRECTED OPTICAL DENSITY OF
THE SAME SPOT ON A LOWER FILM

ENTER UPFILM*ALOFLM

HAVING CALCULATED THE AVERAGE ABSORPTION FACTOR, EACH VALUE OF ALOFLM IS THEN MULTIPLIED BY THIS AVERAGE.

DO YOU WANT INSTRUCTIONS?

WHEN THE END OF THE DATA IS REACHED TYPE 999

% *READ*')

THE PROGRAM FILMA3S: 28:06 FRIDAY AUG 9, 1974

0010 110 FORMAT( 'DO YOU WANT INSTRUCTIONS?')
0015 115 FORMAT( 'WHEN THE END OF THE DATA IS REACHED TYPE 999,
0020 0.990')
0025 120 FORMAT( 'TYPE 0 IF NO, TYPE 1 IF YES')
0030 125 FORMAT( '/ * WHAT ARE THE NUMBERS OF THE FILMS BEING READ?')
0035 126 FORMAT( ' (UPPER FILM,LOWER FILM)')
0040 127 FORMAT( '/ * COMPARISON OF FILM',2X,14,2X,'TO FILM',2X,14)
0045 130 FORMAT( 'PROGRAM FILMA3S: WRITTEN BY LANGE, APRIL 1973')
0050 135 FORMAT( 'THIS PROGRAM IS DESIGNED TO CALCULATE THE FILM')
0055 140 FORMAT( 'ABSORPTION FACTOR BETWEEN TWO FILMS IN A MULTI-
0060 145 FORMAT( 'LAYER INTEGRATED WEISSENBERG PHOTOGRAPH')
0065 150 FORMAT( 'THE FOLLOWING INFORMATION MUST BE READ IN:')
0070 155 FORMAT( 'NSPT THE NUMBER OF THE SPOT BEING USED TO')
0075 160 FORMAT( 'COMPARE TWO FILMS')
0080 165 FORMAT( 'UPFILM THE NET CORRECTED OPTICAL DENSITY OF')
0085 170 FORMAT( 'THE SPOT ON THE UPPER FILM')
0090 175 FORMAT( 'ALOFLM THE NET CORRECTED OPTICAL DENSITY OF')
0095 180 FORMAT( 'THE SAME SPOT ON A LOWER FILM')
0100 185 FORMAT( '/ ENTER NSPT,UPFILM,ALOFLM')
0105 190 FORMAT( 'HAVING CALCULATED THE AVERAGE ABSORPTION FACTOR')
0110 195 FORMAT( 'EACH VALUE OF ALOFLM IS THEN MULTIPLIED BY THIS')
0115 200 FORMAT( 'AVERAGE')
0120 205 FORMAT( '6X,'SPOT',5X,'FILM ABSORPTION FACTOR',5X,'AVE.
0125 210 FORMAT( 'FACTOR X ALOFLM')
0130 215 FORMAT( 'THE AVERAGE VALUE OF THE FILM ABSORPTION FACTOR
0135 220 FORMAT( '6X,F8.4')
0140 225 FORMAT( '5X,14,12X,F8.4,20X,F8.1')
0145 FORMAT( 'DIMENSION NSPT(200),UPFILM(200),ALOFLM(200),ABSFA
0150 240 WRITE(6,110)
0155 WRITE(6,120)
0160 WRITE(5,*CODE)
0165 IF(CODE.EQ.0)GO TO 300
0170 WRITE(6,130)
0175 WRITE(6,140)
0180 WRITE(6,150)
0185 WRITE(6,160)
0190 WRITE(6,170)
0195 WRITE(6,180)
0200 WRITE(6,190)
0205 WRITE(6,200)
0210 WRITE(6,210)
0215 WRITE(6,220)
0220 WRITE(6,230)
0225 WRITE(6,241)
0230 WRITE(6,242)
0235 WRITE(6,115)
0240 WRITE(6,125)
0245 WRITE(6,126)
0250 WRITE(5,*1UPFILM,1.0FILM
0255 WRITE(6,244)
0260 DO 400 I=1,200
0265 READ(5,*NSPT(I),UPFILM(I),ALOFLM(I)
0270 READ(5,*NSPT(I),UPFILM(I),ALOFLM(I)
IF(NSPT(I) .EQ. 999) GO TO 600
ICODE = I
ABSFAC(I) = UPFILM(I) / ALOFLM(I)
CONTINUE
SUM = 0.0
DO 500 1 = 1, ICODE
SUM = SUM + ABSFAC(I)
CONTINUE
AVE = SUM / ICODE
DO 700 1 = 1, ICODE
FIRST(I) = AVE * ALOFLM(I)
CONTINUE
WRITE(6, 127) IUPFLM, LOFLM
WRITE(6, 250)
WRITE(6, 230) (NSPT(I), ABSFAC(I), FIRST(I), I = 1, ICODE)
WRITE(6, 260)
WRITE(6, 270) AVE
END
FRIDAY AUG 9, 1974

DO YOU WANT INSTRUCTIONS?
TyFF0 IF NO, TYPE 1 IF YES.

THE FOLLOWING DATA MUST BE READ IN:

1. TWOYN, THE DISTANCE (IN MM) FROM THE - NTH LEVEL TO THE + NTH LEVEL.
2. RLEVEL, THE VALUE OF N OF THE NTH LEVEL.
3. BLAMB, THE WAVELENGTH OF RADIATION USED.
4. ENTER THE WAVELENGTH.
5. ENTER THE NUMBER OF DATA PAIRS (TWOYN, RLEVEL).

DIMENSION ZETAC20, ZETANC20, NC2S, RLEVEL(20), TWOYN(20)

READ(5,*) CODE
IF (CODE = 1) 500, 510, 510
510 WRITE(6,110)
110 WRITE(6,120)
120 WRITE(6,130)
130 WRITE(6,140)
140 WRITE(6,150)
150 WRITE(6,160)
160 WRITE(6,170)
170 WRITE(6,180)
180 WRITE(6,190)
190 WRITE(6,200)
200 WRITE(6,210)
210 WRITE(6,220)
220 WRITE(6,230)
230 WRITE(6,240)
240 WRITE(6,250)
250 WRITE(6,260)
260 WRITE(6,270)
270 WRITE(6,280)
280 WRITE(6,290)
290 WRITE(6,300)
300 WRITE(6,310)
310 WRITE(6,320)
320 WRITE(6,330)
330 WRITE(6,340)
340 WRITE(6,350)
350 READ(5,*) BLAMB
360 WRITE(6,360)
370 READ(5,*) NN
380 DO 15 I = 1, NN
390 WRITE(6,390)
400 READ(5,*)(TWOYN(I), RLEVEL(I))
410 15 CONTINUE
420 RADIUS = 28.65
430 DO 25 I = 1, NN
440 ZETAN(I) = SIN(ATAN(TWOYN(I)/(RADIUS*2.0))
450 ZETA(I) = ZETAN(I)/RLEVEL(I)
0460 N(I)=I
0510 25 CONTINUE
0515 SUM=0.0
0520 DO 35 I=1,NN
0540 SUM=SUM+ZETA(I)
0545 35 CONTINUE
0550 AVE=SUM/NN
0555 RL=AVE/BLAMB
0580 EDG=BLAMB/AVE
0600 WRITE(6,280)
0610 WRITE(6,290)(N(I),ZETA(I),I=1,NN)
0620 WRITE(6,250)
0630 WRITE(6,300)(ZETA(I),I=1,NN)
0640 WRITE(6,260)
0650 WRITE(6,300)AVE
0655 WRITE(6,305)RL
0660 WRITE(6,270)
0670 WRITE(6,310)EDG
0680 END
This program is designed to calculate reciprocal lattice constants from data obtained from a zero level Weissenberg photograph.

The following information must be read in:

- Enter the number of data pairs (TWOYN, RLEVEL)
- Enter TWOYN, RLEVEL

```
DIMENSION TWOYN(40), RLEVEL(40), QA(40), QB(40), QC(40)
```

```
FORMAT C' DO YOU WANT INSTRUCTIONS?' >
 FORMAT C' TYPE 0 IF NO, TYPE 1 IF YES')
 FORMAT C' HOW MANY DATA SETS ARE TO BE PROCESSED?'>
 FORMAT C' PROGRAM WEISS: WRITTEN BY LAIGE, OCTOBER 1972'>
 FORMAT C' WAVELENGTH OF RADIATION USED'
 FORMAT C' RE Turkish CHARACTERS
```

```
THIS PROGRAM IS DESIGNED TO CALCULATE RECIPROCAL LATTICE CONSTANTS FROM DATA OBTAINED FROM A ZERO LEVEL WEISSBERG PHOTOGRAPH'

THE FOLLOWING INFORMATION MUST BE READ IN:

- Enter the number of data pairs (TWOYN, RLEVEL)
- Enter TWOYN, RLEVEL

```
DIMENSION TWOYN(40), RLEVEL(40), QA(40), QB(40), QC(40)
```

```
WRITE(6,101)
WRITE(6,102)
READ(5,*)CODE
IF(CODE=.EQ.1)500,501,501
501 WRITE(6,110)
WRITE(6,120)
WRITE(6,130)
WRITE(6,140)
WRITE(6,150)
WRITE(6,160)
WRITE(6,170)
WRITE(6,180)
WRITE(6,190)
WRITE(6,200)
WRITE(6,210)
WRITE(6,220)
WRITE(6,230)
WRITE(6,240)
READ(5,*)TWOYN(I), RLEVEL(I))
```
93

0390 25 CONTINUE
0400 DO 50 I=1,N
0410 Q(I)=2.*C*(SIN(TWOYN(I))/(4.*RADIUS)))
0420 QQ(I)=Q(I)/FLEVEL(I)
0425 QA(I)=QQ(I)/BLAMB
0427 QB(I)=QA(I)*FLEVEL(I)
0430 50 CONTINUE
0440 WRITE(6,250)
0450 WRITE(6,260)(Q(I),I=1,N)
0452 WRITE(6,265)(QQ(I),I=1,N)
0455 WRITE(6,270)
0460 WRITE(6,260)(QQ(I),I=1,N)
0465 WRITE(6,265)(QA(I),I=1,N)
0470 SUM=0.*Z
0480 DO 75 I=1,N
0490 SUM=SUM+QQ(I)
0500 75 CONTINUE
0510 AVE=SUM/N
0515 AVER=AVE/BLAMB
0520 WRITE(6,280)
0530 WRITE(6,260)AVE
0535 WRITE(6,265)AVER
0540 WRITE(6,290)
0545 600 CONTINUE
0550 END
PREDUCE 17:31 FRIDAY AUG 9, 1974

0010 110 FORMAT(' DO YOU WANT INSTRUCTIONS?')
0020 120 FORMAT(' TYPE 0 IF NO, TYPE 1 IF YES')
0030 130 FORMAT(' PROGRAM PREDUCE: WRITTEN BY LANGE, MARCH 1973')
0040 140 FORMAT(' THE PURPOSE OF THIS PROGRAM IS TWO-FOLD')
0050 150 FORMAT(' FIRST, IT TAKES THE OPTICAL DENSITY READINGS')
0060 160 FORMAT(' MADE ON AN INTEGRATED VEISSENBERG PHOTOGRAPH BY')
0070 170 FORMAT(' A WELCH DENSICRON AND CONVERTS THEM TO STANDARD')
0080 180 FORMAT(' ASA VALUES VIA A CALIBRATION CURVE. THIS')
0090 190 FORMAT(' CALIBRATION IS ACCOMPLISHED VIA A POLYNOMIAL')
0100 200 FORMAT(' OBTAINED FROM A POLYNOMIAL REGRESSION TREATMENT')
0110 210 FORMAT(' OF AN EXPERIMENTALLY DETERMINED CALIBRATION')
0120 220 FORMAT(' THE PURPOSE OF THIS PROGRAM IS TWO-FOLD')
0130 230 FORMAT(' FIRST, IT TAKES THE OPTICAL DENSITY READINGS')
0140 240 FORMAT(' MADE ON AN INTEGRATED VEISSENBERG PHOTOGRAPH BY')
0150 250 FORMAT(' A WELCH DENSICRON AND CONVERTS THEM TO STANDARD')
0160 260 FORMAT(' ASA VALUES VIA A CALIBRATION CURVE. THIS')
0170 270 FORMAT(' CALIBRATION IS ACCOMPLISHED VIA A POLYNOMIAL')
0180 280 FORMAT(' OBTAINED FROM A POLYNOMIAL REGRESSION TREATMENT')
0190 290 FORMAT(' OF AN EXPERIMENTALLY DETERMINED CALIBRATION')
0200 300 FORMAT(' THE PURPOSE OF THIS PROGRAM IS TWO-FOLD')
0210 310 FORMAT(' FIRST, IT TAKES THE OPTICAL DENSITY READINGS')
0220 320 FORMAT(' MADE ON AN INTEGRATED VEISSENBERG PHOTOGRAPH BY')
0230 330 FORMAT(' A WELCH DENSICRON AND CONVERTS THEM TO STANDARD')
0240 340 FORMAT(' ASA VALUES VIA A CALIBRATION CURVE. THIS')
0250 350 FORMAT(' CALIBRATION IS ACCOMPLISHED VIA A POLYNOMIAL')
0260 360 FORMAT(' OBTAINED FROM A POLYNOMIAL REGRESSION TREATMENT')
0270 370 FORMAT(' THE PURPOSE OF THIS PROGRAM IS TWO-FOLD')
0280 380 FORMAT(' FIRST, IT TAKES THE OPTICAL DENSITY READINGS')
0290 390 FORMAT(' MADE ON AN INTEGRATED VEISSENBERG PHOTOGRAPH BY')
0300 400 FORMAT(' A WELCH DENSICRON AND CONVERTS THEM TO STANDARD')
0310 410 FORMAT(' ASA VALUES VIA A CALIBRATION CURVE. THIS')
0320 420 FORMAT(' CALIBRATION IS ACCOMPLISHED VIA A POLYNOMIAL')
0330 430 FORMAT(' OBTAINED FROM A POLYNOMIAL REGRESSION TREATMENT')
0340 440 FORMAT(' THE PURPOSE OF THIS PROGRAM IS TWO-FOLD')
0350 450 FORMAT(' FIRST, IT TAKES THE OPTICAL DENSITY READINGS')
0360 460 FORMAT(' MADE ON AN INTEGRATED VEISSENBERG PHOTOGRAPH BY')
0370 470 FORMAT(' A WELCH DENSICRON AND CONVERTS THEM TO STANDARD')
0380 480 FORMAT(' ASA VALUES VIA A CALIBRATION CURVE. THIS')
0390 490 FORMAT(' CALIBRATION IS ACCOMPLISHED VIA A POLYNOMIAL')
0400 500 FORMAT(' OBTAINED FROM A POLYNOMIAL REGRESSION TREATMENT')
0410 510 FORMAT(' THE PURPOSE OF THIS PROGRAM IS TWO-FOLD')
0420 520 FORMAT(' FIRST, IT TAKES THE OPTICAL DENSITY READINGS')
0430 530 FORMAT(' MADE ON AN INTEGRATED VEISSENBERG PHOTOGRAPH BY')
0440 540 FORMAT(' A WELCH DENSICRON AND CONVERTS THEM TO STANDARD')
0450 550 FORMAT(' ASA VALUES VIA A CALIBRATION CURVE. THIS')
0460 560 FORMAT(' CALIBRATION IS ACCOMPLISHED VIA A POLYNOMIAL')
0470 570 FORMAT(' OBTAINED FROM A POLYNOMIAL REGRESSION TREATMENT')
0480 580 FORMAT(' THE PURPOSE OF THIS PROGRAM IS TWO-FOLD')
0490 590 FORMAT(' FIRST, IT TAKES THE OPTICAL DENSITY READINGS')
0500 600 FORMAT(' MADE ON AN INTEGRATED VEISSENBERG PHOTOGRAPH BY')
0510 610 FORMAT(' A WELCH DENSICRON AND CONVERTS THEM TO STANDARD')
0520 620 FORMAT(' ASA VALUES VIA A CALIBRATION CURVE. THIS')
0530 630 FORMAT(' CALIBRATION IS ACCOMPLISHED VIA A POLYNOMIAL')
0540 640 FORMAT(' OBTAINED FROM A POLYNOMIAL REGRESSION TREATMENT')
0550 650 FORMAT(' THE PURPOSE OF THIS PROGRAM IS TWO-FOLD')
0560 660 FORMAT(' FIRST, IT TAKES THE OPTICAL DENSITY READINGS')
0570 670 FORMAT(' MADE ON AN INTEGRATED VEISSENBERG PHOTOGRAPH BY')
0580 680 FORMAT(' A WELCH DENSICRON AND CONVERTS THEM TO STANDARD')
0590 690 FORMAT(' ASA VALUES VIA A CALIBRATION CURVE. THIS')
0600 700 FORMAT(' CALIBRATION IS ACCOMPLISHED VIA A POLYNOMIAL')
0610 710 FORMAT(' OBTAINED FROM A POLYNOMIAL REGRESSION TREATMENT')
0620 720 FORMAT(' THE PURPOSE OF THIS PROGRAM IS TWO-FOLD')
0630 730 FORMAT(' FIRST, IT TAKES THE OPTICAL DENSITY READINGS')
0640 740 FORMAT(' MADE ON AN INTEGRATED VEISSENBERG PHOTOGRAPH BY')
0650 750 FORMAT(' A WELCH DENSICRON AND CONVERTS THEM TO STANDARD')
0660 760 FORMAT(' ASA VALUES VIA A CALIBRATION CURVE. THIS')
0670 770 FORMAT(' CALIBRATION IS ACCOMPLISHED VIA A POLYNOMIAL')
0680 780 FORMAT(' OBTAINED FROM A POLYNOMIAL REGRESSION TREATMENT')
0690 790 FORMAT(' THE PURPOSE OF THIS PROGRAM IS TWO-FOLD')
0700 800 FORMAT(' FIRST, IT TAKES THE OPTICAL DENSITY READINGS')
0710 810 FORMAT(' MADE ON AN INTEGRATED VEISSENBERG PHOTOGRAPH BY')
0720 820 FORMAT(' A WELCH DENSICRON AND CONVERTS THEM TO STANDARD')
0730 830 FORMAT(' ASA VALUES VIA A CALIBRATION CURVE. THIS')
0740 840 FORMAT(' CALIBRATION IS ACCOMPLISHED VIA A POLYNOMIAL')
0750 850 FORMAT(' OBTAINED FROM A POLYNOMIAL REGRESSION TREATMENT')
0760 860 FORMAT(' THE PURPOSE OF THIS PROGRAM IS TWO-FOLD')
0770 870 FORMAT(' FIRST, IT TAKES THE OPTICAL DENSITY READINGS')
0780 880 FORMAT(' MADE ON AN INTEGRATED VEISSENBERG PHOTOGRAPH BY')
0790 890 FORMAT(' A WELCH DENSICRON AND CONVERTS THEM TO STANDARD')
0800 900 FORMAT(' ASA VALUES VIA A CALIBRATION CURVE. THIS')
0810 910 FORMAT(' CALIBRATION IS ACCOMPLISHED VIA A POLYNOMIAL')
0820 920 FORMAT(' OBTAINED FROM A POLYNOMIAL REGRESSION TREATMENT')
0830 930 FORMAT(' THE PURPOSE OF THIS PROGRAM IS TWO-FOLD')
0840 940 FORMAT(' FIRST, IT TAKES THE OPTICAL DENSITY READINGS')
0850 950 FORMAT(' MADE ON AN INTEGRATED VEISSENBERG PHOTOGRAPH BY')
0860 960 FORMAT(' A WELCH DENSICRON AND CONVERTS THEM TO STANDARD')
0870 970 FORMAT(' ASA VALUES VIA A CALIBRATION CURVE. THIS')
0880 980 FORMAT(' CALIBRATION IS ACCOMPLISHED VIA A POLYNOMIAL')
0890 990 FORMAT(' OBTAINED FROM A POLYNOMIAL REGRESSION TREATMENT')

DIMENSION BK1(200), BK2(200), FK(200), CBK1(200), CBK2(200)
0500 NSPT(200), CNPK(200), AVEBK(200), CPK(200)
0510 WRITE(6, 110)
0520 WRITE(6, 120)
0530 READ(5, *) CODE
0540 IF(CODE.EQ.0) GO TO 590
0550 WRITE(6, 130)
0560 WRITE(6, 140)
0570 WRITE(6, 150)
0580 WRITE(6, 160)
0590 WRITE(6, 170)
0600 WRITE(6, 180)
0610 WRITE(6, 190)
0620 WRITE(6, 200)
0630 WRITE(6, 210)
0640 WRITE(6, 220)
0650 WRITE(6, 230)
0660 WRITE(6, 240)
0670 WRITE(6, 250)
0680 WRITE(6, 260)
0690 WRITE(6, 270)
0700 WRITE(6, 280)
0710 WRITE(6, 290)
0720 WRITE(6, 300)
0730 WRITE(6, 310)
0740 READ(5, *) JFILM
0750 WRITE(6, 330)
0760 READ(5, *) LEVEL
0770 WRITE(6, 340)
0780 READ(5, *) JFILM
0790 DATA DI, B1, B2, E3, E4/-0.01302, 0.392, 0.0911, -0.0346, 0.00404/
0800 WRITE(6, 350)
0810 READ(5, *) N
0820 WRITE(6, 370)
0830 DO 600 I = 1, N
0840 READ(5, *) NSPT(I), BK1(I), PK(I), BK2(I)
0840 600 CONTINUE
0850 DO 610 I = 1, N
0860 CBK1(I) = DI + B1*5K1(I) + E2*BK1(I)**2 + B3*E3*BK1(I)**3 + B4*PK(I)**4
0870 CPK(I) = DI + B1*PK(I) + B2*PK(I)**2 + B3*PK(I)**3 + B4*PK(I)**4
0890 AVEBK(I) = (CBK1(I) + CBK2(I))/2, 0
0900 CNPK(I) = (CPK(I) - AVEBK(I)) * 1000, 0
0910 610 CONTINUE
0920 LLEVEL = LEVEL + 1
0930 GO TO (620, 630, 640, 650, 660, 670), LLEVEL
0940 620 WRITE(6, 350) JFILM, JFILM
0950 GO TO 630
0960 630 WRITE(6, 370) JFILM, JFILM
1000 GO TO 630
1010 640 WRITE(6, 390) JFILM, JFILM
1020 GO TO 630
1030 650 WRITE(6, 410) JFILM, JFILM
1040 GO TO 680
1050 WRITE(6,430)IFILM,JFILM
1060 GO TO 680
1070 WRITE(6,450)IFILM,JFILM
1080 WRITE(6,460)
1090 WRITE(6,470)
1100 WRITE(6,500)(NSPT(I),CEK1(I),CFK(I),CEK2(I),CMFK(I),I=1,N)
1110 WRITE(6,510)
1120 WRITE(6,520)
1130 WRITE(6,530)
1140 WRITE(6,540)DI,B1,B2,B3,B4
1150 WRITE(6,550)
1160 WRITE(6,560)
1170 END
BIBLIOGRAPHY

15. K. Nakamoto, Ibid., p 166.


27. H.P. Hanson, P. Herman, J.D. Lee, and S. Skillman, Acta Crystallogr., 17, 1040(1964).


