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# THE CRYSTAL AND MOLECULAR STRUCTURES OF COBALT COMPLEX WITH GLYCYLGLYCINE AND CIS-1,2-CYCLOBUTANE DICARBOXYLIC ACID

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# THE CRYSTAL AND MOLECULAR STRUCTURES OF COBALT COMPLEX WITH GLYCYLGLYCINE AND CIS-1,2-CYCLOBUTANE DICARBOXYLIC ACID

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## TABLE OF CONTENTS

Page

LIST OF TABLES .......... vi

LIST OF FIGURES .......... ix

PART I. THE CRYSTAL AND MOLECULAR STRUCTURE OF HEXAQUO-COBALT(II) DI(BISGLYCYLGLYCINATOCOBALTATE(III)) HEXAHYDRATE .......... 1

Chapter

1. INTRODUCTION .......... 1
2. EXPERIMENTAL .......... 10
3. STRUCTURE DETERMINATION AND REFINEMENT .......... 16
4. DISCUSSION OF THE STRUCTURE .......... 35
5. SUMMARY AND CONCLUSION .......... 74

PART II. THE REFINEMENT OF CIS-1,2-CYCLOBUTANE DICARBOXYLIC ACID .......... 76

Chapter

1. INTRODUCTION .......... 76
2. EXPERIMENTAL .......... 80
3. STRUCTURE REFINEMENT .......... 83
4. DISCUSSION OF THE STRUCTURE .......... 89
5. SUMMARY .......... 124

REFERENCES .......... 125

## LIST OF TABLES

Table Page

PART I.

1a. Single Crystal Data for Some Cobalt Complexes with Glycylglycines........................................ 8

1b. Crystal Data of $[Co^{II}(H_2O)_6][Co^{III}(GG)_2]_2 \cdot 6H_2O$......... 14

2. Co(1)-Co(2) Vectors for Space Group Cc in Patterson Map 20

3. Fractional Coordinates of Atoms Obtained from Patterson Synthesis.............................................. 24

4. Positions of Hydrogen Atoms........................... 28

5. Atomic Parameters of $[Co^{II}(H_2O)_6][Co^{III}(GG)_2]_2 \cdot 6H_2O$.... 30

6. Anisotropic Temperature Factors ( $x10^4$ )............... 32

7. Structure Factors x 2................................. 34

8. Hydrogen Bonds........................................ 41

9. Van der Waals Contacts Less Than 3.50 Å............... 44

10. Bond Lengths.......................................... 46

11a. Bond Angles Around Cobalt Atoms....................... 49

11b. Bond Angles of Peptide Ligands........................ 51

12. Comparison of Bond Lengths in Co(III)-Glycylglycine Complexes............................................. 58

13. Comparison of Bond Angles Around Deprotonated Peptide Nitrogen.............................................. 59

14. Least-Squares Planes.................................. 62

## LIST OF TABLES

(Continued)

Table Page

15. Principle Axes and Direction Cosines of Anisotropic Ellipsoids.......... 66

16. Conformation Angles of Peptide Ligands.......... 71

PART II.

1. Crystal Data of cis-1,2-Cyclobutanedicarboxylic Acid.. 81

2. Observed ($F_o$) and Calculated ($F_c$) Structure Factors x10.......... 86

3. Positional and Isotropic Thermal Parameters.......... 87

4. Anisotropic Thermal Parameters $x10^4$.......... 88

5. Hydrogen-Bond Distances and Angles.......... 91

6. Intermolecular Contacts.......... 93

7. Bond Lengths.......... 95

8. Bond Angles.......... 107

9. Geometry of Carboxyl Groups in Cyclobutanedicarboxylic Acids.......... 108

10. A Comparison of Four-Membered Rings in Cyclobutanedicarboxylic Acids.......... 110

11. Right-Handed Conformational Angles.......... 111

12. Least-Squares Planes.......... 113

13. Absolute Planes.......... 114

14. Angles Between Least-Squares Planes.......... 119

## LIST OF TABLES

(Continued)

Table Page

15. Principal Axes and Direction Cosines with Respect to the Real Axes of Anisotropic Ellipsoids.............. 120
16. Angles Formed between Orientations of Thermal Ellipsoids and the Normals of Mean Planes............ 121
17. Summary of Magnitudes and Orientations of the Thermal Ellipsoids of Carboxyl Oxygens in Cyclobutanedicarboxylic Acids.................................... 122

## LIST OF FIGURES

Figure Page

PART I.

1. Patterson Section w=.30. Arbitrary Scale.............. 22
2. ac Projection of the Structure......................... 36
3. Configuration of $[Co^{II}(H_2O)_6]^{++}$........................ 52
4. Coordination Sphere of Co(III)......................... 54
5. Bond Distances of $[Co^{III}(GG)_2]^-$........................ 55
6. Bond Angles of $[Co^{III}(GG)_2]^-$........................... 56
7. A Stereoscopic View of $[Co^{III}(GG)_2]^-$.................. 70
8. Labeling of Conformation Angles........................ 72

PART II.

1. Projection of the Structure onto ac Plane.............. 90
2. A Stereoscopic View of the Molecule.................... 94
3. Bond Lengths of cis-1,2-Cyclobutanedicarboxylic Acid... 96

4a. Bond Lengths and Angles in trans-1,2-Diacid............ 97

4b. Bond Lengths and Angles in cis-1,3-Diacid.............. 98

4c. Bond Lengths and Angles in trans-1,3-Diacid............ 99

4d. Bond Lengths and Angles in trans-1,3-Diacid............ 100

4e. Bond Lengths and Angles in trans-1,3-Dianion........... 101

4f. Bond Lengths and Angles in trans-1,3-Diacid (puckered). 102

5. Bond Angles of cis-1,2-Cyclobutanedicarboxylic Acid.... 106
6. The Deviations of Atoms from Planes of Carboxyl Groups. 115
7. Deviations from Planes of Rings Formed by Hydrogen Bonded Acid Groups.................................... 117

# PART I

# THE CRYSTAL AND MOLECULAR STRUCTURE OF HEXAQUOCOBALT(II) DI(BISGLYCYLGLYCINATOCOBALTATE(III)) HEXAHYDRATE

## CHAPTER 1

## INTRODUCTION

Proteins which contain amino acids, peptides and enzymes etc. are found in the cells of all animals and plants. They occupy a central position in the architecture and functioning of living matter. They are intimately connected with all phases of chemical and physical activity that constitute the life of the cell. There is hardly an important physiological function in which proteins do not participate. In essence, the objective of protein chemistry is to explain the special physiological functions of these large complex molecules in terms of their structure. The experimental approach consists largely in examination of the parts of the molecules, the probable arrangement of these parts in individual proteins, and the chemical and physical behavior of the intact proteins. These tasks are formidable and present considerable technical difficulties because of the great diversity and complexity of proteins.

As we know, many metal ions play an important role as cofactors in a number of biological reactions. In this connection, the determination of the structures of amino acids and peptides complexed with metal ions may bring a better understanding about the structures and functions of proteins and may help towards clarifying the reaction mechanisms involved in the biological roles of these molecules.

There are many methods for determining a molecular structure; infrared, ultraviolet, e.s.r. and n.m.r. spectra are all capable of yielding precise information about individual atoms, individual bonds or other specific details of a structure, but only diffraction methods are at present unique in being able to reveal complete, three-dimensional pictures of complicated molecules.

Crystallographers are, by definition, limited to dealing with substances in solid state. At first sight this imposes a severe handicap on those biochemically oriented crystallographers because the strictly crystalline solids in living matter are limited to a very few examples. Biological reactions characteristically take place in the liquid phase. There is therefore a logical need to define the extent to which any crystal-structure analysis is relevant to anything which goes on in solution. However, one could certainly assume that if a proposed model of configuration violates the geometrical requirement established for molecules in solid state, then such a model would unlikely be a valid representation for molecules existing in the solution from which the crystals grow. Most of the crystal-structure analyses of metal-amino acid and metal-peptide complexes have been carried out on the assumption that such complexes act as models for the metal-binding sites on proteins.

The study of a cobalt complex with glycylglycine is one of the peptide complexes investigated in a series of studies in this research laboratory.

The role of metal ions in the activation of enzymatic activity has been suggested as that of forming a bridge between enzyme and substrate. This idea has been advanced by Hellerman et al.[1,2] on the basis of careful studies of the metal content of arginase, the metal ion activation of this enzyme, as well as of metal ion coordination with arginine.

In 1948 Smith[3] extended this idea to the metal activation of dipeptidase and showed that the hydrolysis splitting of glycylglycine ($GGH_2$) is strongly activated by $Co^{++}$ and to a lesser degree by $Mn^{++}$. $Mg^{++}$ does not accelerate this hydrolysis, and $Zn^{++}$ acts as an inhibitor. Hydrolysis does not occur for compounds in which the free amino group is suppressed as in benzoyl glycylglycine, or in which the carboxyl group is substituted as in glycylglycinamide or in which both amino and carboxyl group are replaced as in carbobenzoxyglycylglycinamide. Smith has cited the formation of a red color in solution of $GGH_2$ and $Co^{++}$ as evidence for complex formation. The specific combination of glycylglycine and Co(II) ions leads to the idea that the function of the metal is to act as a bridge in forming the enzyme-substrate compound. Using the visible absorption in the region of 520 mμ as a measure of the strength of coordination between substrate and $Co^{++}$, he suggests that a strong coordination is necessary for the activation of the specific glycylglycine dipeptidase by $Co^{++}$. The specificity of the enzyme would depend, therefore, not only on the protein, but also on the ability of the metal ion to combine with the substrate.

Hemoglobin is an example of oxygen carriers in metallo-proteins for the biological reactions. A reaction site in the coordination sphere of the iron(II) is left open for combination with an oxygen molecule in the lungs. The oxygenated hemoglobin is transported by the blood from the lungs to other parts of the body. Oxygen is then released for oxidation-reduction process.

Cobalt has been found to be one of those metals which are essential to life and present in the form of complex. In Australia, "sheep-sick"[76] has been known for many years by sheep raisers to be a result of cobalt deficiency.

Vitamin B-12, a cobalt-containing molecule, sometimes known as coenzyme B-12, is an essential vitamin structurally related to the homoproteins. In this compound, there is a direct cobalt-carbon bond. Vitamin B-12 brings about molecular rearrangement, such as the conversion of methylmalonic acid to succinic acid.[77]

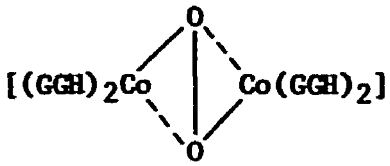
It is interesting to note that replacement[76] of the zinc in carboxypeptidase by cobalt gives a much more efficient enzyme than the naturally occurring one. Just why Nature did not use cobalt in the first place is a mystery.

Model compounds for oxygen carriers[78] have also been studied. A revisible oxygen-carrying compound in the solid state has been reported by Wang[79] in the structure of Bis(3-fluorosalicylaldehyde) ethylenediiminecobalt (II).

An interesting study was made[78] of the use of the bis-salicylaldehydeethylenediiminecobalt (II) oxygen carriers as a means of separating $O^{18}$ and $O^{16}$ isotopes.

In addition to cobalt complexes, Ibers and his colleagues[80] have also reported the oxygen adduct of a synthetic, reversible molecular carrier in the structure of iridium complexes.

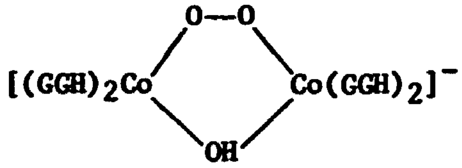
In 1951 Gilbert and co-workers,[4] following the earlier work by Smith, reported a study of the oxygenation of cobalt(II) complexes with glycylglycine ligand among several other peptides in alkaline solution. These authors also observed that oxygen was taken up in the formation of the complex, and that it could not be formed in the absence of oxygen. From such a reaction they isolated red crystals of what they called an 'irreversibly oxygenated' cobalt(II) species. The product was assumed to contain the molecular oxygen grouping $O_2$, Co and GGH in the ratio of 1:2:4, and the formula of the type



was postulated for it.

The formulation is similar to one suggested for the cobalt-histidine-oxygen complex by Hearon, Burk and co-workers.[5,6] Later kinetic studies[7] showed that an unstable intermediate brown species also was formed at high pH. This slowly is converted into the red species, at a rate which increases markedly at lower pH.

The above 'peroxo' formulation of the red species has been accepted, especially in the kinetic studies of Tanford et al.[7] and in the studies of other dipeptide complexes by Miller and Li.[8] Then in 1964 n.m.r., anion-exchange, and polarographic measurements were interpreted by Tang and Li[9] as evidence for the following structure.



However, in contradiction, Cagliotti and his co-workers[10] had previously interpreted the polarographic data as indicating that the product of the 'irreversible oxygenation' was a cobalt(III) compound without the peroxo-group. They assigned a formula $[Co(GGH)_2OH]$ to the red species. Further, Beck[11] had prepared what was apparently the same species in solution by reaction of the ligand with 'cobalt(III) hydroxide'; and Beck and Gorog[12] later prepared it from the ligand and hexa-amminecobalt(III) chloride. From the latter reaction, a solid compound was isolated, and this was assigned the structure $NH_4(Co(GGH)_2(OH)_2)$. In both cases, the identity of the product with that of the red species from the 'irreversible oxygenation' was demonstrated by the identity of their absorption spectra in solution.

Gillard,[13] in attempting to prepare the red 'irreversible oxygen carrying' complex of Gilbert,[4] isolated a number of cobalt complexes with the unsubstituted glycylglycine and with its monoanion and dianion. A single crystal, X-ray diffraction analysis of the structure of $NH_4(Co(GG)_2)\cdot 2H_2O$ has been carried out, the stereochemistry of the complex anion being reported. The complex anion contains two terdentate glycylglycinate ligands arranged so that the co-ordination of the Co(III) ion is a distorted octahedron which has precise $C_2$ symmetry as a requirement of the crystallographic space group. Again, there is no peroxo-group observed in this structure. Freeman and his co-workers[14] also found no evidence at all for a molecular oxygen carrier in their structures of red complexes of cobalt with glycylglycine. A summary of single crystal data for some cobalt complexes with glycylglycine ligands is given in Table 1a. In the light of a variety of different species of cobalt complexes with glycylglycine obtained by the method of Gilbert,[4] it appears likely that the reaction conditions as well as the reagents used are very critical for preparing the complex. However, all of the cobalt complexes with glycylglycine fall into

## TABLE 1a

### Single Crystal Data for Some Cobalt Complexes with Glycylglycines

| Compound | Space group | a | b | c | β | $\rho_c$(g/c.c.) | $\rho_o$(g/c.c.) | Ref. |
|---|---|---|---|---|---|---|---|---|
| $[Co^{II}(H_2O)_6][Co^{III}(GG)_2]_2 \cdot 6H_2O$ | C2/c | 24.100 | 11.062 | 13.670 | 104.35 | 1.718 | 1.72 | This work |
| $[Co^{II}(H_2O)_6][Co^{III}(GG)_2]_2 \cdot 12H_2O$ | $P2_1/a$ | 9.418 | 31.262 | 7.445 | 108.08 | 1.628 | 1.624 | 81 |
| $Ba[Co^{III}(GG)_2]_2 \cdot nH_2O$ | Pbcn | 24.72 | 12.52 | 12.72 | — | 1.78 | 1.78 | 81 |
| $Co(GGH)_2ClO_4$ | $P4_12_12$ | 7.600 | — | 24.68 | — | 1.95 | 1.92 | 81 |
| $NH_4[Co(GG)_2] \cdot 2H_2O$ | Iba2 | 10.90 | 15.23 | 8.47 | — | 1.76 | 1.75 | 24 |
| $Na[Co(GG)_2] \cdot 4H_2O$ | $P2_1/c$ | 13.0 | 23.0 | 6.0 | 107.6 | 1.73 | 1.74 | 24 |
| $K[Co(GG)_2] \cdot 5H_2O$ | Pnna | 6.25 | 11.4 | 24.75 | — | 1.68 | 1.68 | 24 |
| $NEt_4[Co(GG)_2] \cdot 5H_2O$ | $P2_1/c$ | 10.5 | 12.15 | 20.0 | 92.2 | 1.41 | 1.41 | 24 |
| $Ca[Co(GG)_2]_2 \cdot 15H_2O$ | $P2_1/c$ | 25.3 | 11.0 | 13.9 | 103.8 | 1.67 | 1.68 | 24 |
| $Ca[Co(GG)_2]_2 \cdot 8H_2O$ | Ortho-rhombic | 11.0 | 14.0 | 20.3 | — | 1.74 | 1.73 | 24 |
| $Ca[Co(GG)_2]_2 \cdot 6H_2O$ | $P2_1/c$ | 8.2 | 11.3 | 16.3 | 100.5 | 1.77 | 1.77 | 24 |

one of the two types of complex ions: $[Co(GG)_2]^-$ anion and $[Co(GGH)_2]^+$ cation. The occurrence of molecular oxygen has been a controversy for many years. The space group and cell dimensions for crystals, prepared in our laboratory under similar conditions as those reported by Gilbert,[4] are different from those observed for other red cobalt-glycylglycine complexes.[14,24] We therefore expected to find a novel type of structure for which the configurations and interactions in the complex could be studied. The prelimilary result of the present structure has been published.[81]

# CHAPTER 2

## EXPERIMENTAL

The cobalt complex with glycylglycine was prepared under the similar conditions as reported by Gilbert, Otey and Price;[4] one gram of glycylglycine and 2.5 grams of $CoSO_4 \cdot 7H_2O$ were dissolved together in 15 ml $H_2O$. About 60 ml saturated $Ba(OH)_2$ solution was added to raise the pH value to 10, as checked with a pH meter. Oxygen($O_2$) was bubbled through the mixture for 12 hours, using a fritted glass tube for bubbling. After the oxygenation, 1.3 grams additional $CoSO_4 \cdot 7H_2O$ was added and 14 ml of $Ba(OH)_2$(sat'd) was used to adjust the pH back to about 10. Oxygen was then bubbled for 15 hours more. After this final oxygenation, the pH was adjusted to 10.5, requiring 3 ml of the saturated $Ba(OH)_2$ solution. The mixture was filtered to remove precipitated metal hydroxides, and the residue was discarded. The filtrate was acidified with chilled 2 N $H_2SO_4$ until the supernatant tested positive on $SO_4^{=}$ with a $BaCl_2$ solution. About 3 to 4 ml of $H_2SO_4$ was required. $BaSO_4$ was filtered off. Then 250 ml of cold absolute ethanol was added. The solution was chilled in an ice bath and filtered after one hour to remove a white powdery precipitate which had formed. The filtrate was placed in an ice bath overnight. Deep purple, easily filterable, thin plate crystals precipitated out. These were filtered by suction, washed with absolute ethanol(25 ml) and ether(25 ml) and air dried. The yield was about 0.4 gram.

Some attempts were made to reproduce the crystals. However, the reproducibility is critical and multi-crystal forms were obtained. A variety of crystal forms were reported by other investigators.[24,81] Some of the crystals are different only in the number of water molecules of hydration as can be seen in Table 1a.

The crystals were much too thin for X-ray diffraction work. Recrystallization of the complex is necessary in order to obtain suitable crystals for measuring intensities. The compound is very soluble in water, and thus the excessive water added makes it difficult to effect recrystallization. Only about an equal volume of ethanol was added to the solution to force precipitation. However, excellent large red crystals were obtained by layering 1-2 ml of an approximately 0.1M aqueous solution with equal volume of alcohol at room temperature on standing over night. The crystals are reddish, thin square plates, elongated along the c-axis and the plate face proved to be (100) plane. Working in the open air a slow decomposition was observed, which did not deteriorate the crystal, but changed the unit cell dimensions slightly. Shadow peaks occurred which grew in intensity. This is probably caused by the loss of water of hydration. The crystals with their mother liquid were therefore sealed in thinwalled capillaries. Under these conditions the decomposition was not observed.

A capillary containing a beautiful red prism was firmly fixed in a goniometer head with clay. The goniometer was then mounted on a General Electric XRD-5 X-ray diffraction unit equipped with a scintillation counter and single crystal orienter. The crystal was determined to be monoclinic and the c-axis was vertical. The conditions for possible reflections are: hkl for h + k = 2n, h0l for l = 2n (h = 2n). Based on these extinctions the space group is either C2/c or Cc. However, the reasonable centrosymmetric space group C2/c was assumed since glycylglycine has no asymmetric carbon, and this was verified later by the full structure analysis. The cell dimensions were calculated with a least-squares method from the two-theta values of 45 randomly collected strong reflections which were measured at room temperature with a one degree take-off angle of the tube using CuKα radiation ($\lambda$=1.5418 Å). The density of the crystal was determined as 1.72 g/ml by means of the floatation method using a liquid mixture of $CCl_4$ and $CH_3I$. Assuming 4 molecules in a unit cell, the molecular weight of the cobalt complex was calculated as 914.4 and this corresponds to two cobalt atoms, four glycylglycine molecules and one molecular oxygen $O_2$ as reported in the literature[4] in addition to 12-14 water molecules of hydration. It happened in this case that the complete structure was quite different from what we expected. The molecular formula obtained from the solution of the structure of this complex was

$$[Co^{II}(H_2O)_6][Co^{III}(GG)_2]_2\cdot 6H_2O$$

while one cell contained four of these molecules. The crystal data are presented in Table 1b.

A red crystal of the size 0.10 x 0.78 x 1.24 mm was chosen for intensity measurements and mounted with c* parallel to the polar axis. Integrated intensities were collected with θ-2θ scan mode using Zr-filtered MoKα radiation (λ=0.7107 Å), pulse height analysis to reduce unwanted background and a scintillation counter. The take-off angle of the tube was 2 degrees. A total of 2468 independent reflections within a 2θ range of 46 degrees were collected. Among these intensities, 292 were below the threshold of measurement. A monitor reflection was checked once an hour; the intensity showed a steady slight decrease. At the end of all intensity measurements, 20 reflections were randomly picked and checked. All the intensities declined almost evenly by about 40%. This phenomenon most likely was due to the dissolution of the crystal into its mother liquid. Some small crystals appeared at the bottom of the capillary, which were too far away from the X-ray beam to have any interference.

The thin plate crystal and the high absorptivity of the heavy atom in the complex made it necessary to correct absorption on the intensity data using the 3-dimensional numerical integration[17]

$$I = I_o \int^{v} e^{-ut}\, dv$$

where I = intensity with absorption,

$I_o$ = intensity without absorption,

u = linear absorption coefficient,

t = total path length traversed by X-ray beams in the crystal,

dv = the diffracting element of volume.

## TABLE 1b

## Crystal Data of $[Co^{II}(H_2O)_6][Co^{III}(GG)_2]_2 \cdot 6H_2O$

| | |
|---|---|
| Space Group | C2/c |
| Cell Dimensions | $a = 24.100(8)$ Å |
| | $b = 11.062(3)$ Å |
| | $c = 13.670(7)$ Å |
| | $\alpha = \gamma = 90°$ |
| | $\beta = 104.35°(5)$ |
| | $a^* = 0.04283(1)$ |
| | $b^* = 0.09040(3)$ |
| | $c^* = 0.07551(3)$ |
| | $\alpha^* = \gamma^* = 90°$ |
| | $\beta^* = 75.65°(5)$ |
| Density | $\rho_o = 1.72$ g/c.c. |
| | $\rho_c = 1.718$ g/c.c. |
| Unit Cell Volume | $V_c = 3530.6$ Å$^3$ |
| Molecular Weight | M.W. = 913.045 |
| Molecular Formula | $[Co^{II}(H_2O)_6][Co^{III}(GG)_2]_2 \cdot 6H_2O$ |
| No. of Molecules | Z = 4 |
| | F(000) = 1860 |

Lorentz-Polarization corrections were also made on the intensities by multiplying them by the factor[17]

$$Lp = \frac{2 \sin 2\theta}{1 + \cos^2 2\theta}$$

In order to get well resolved peaks in the Patterson map the intensity data were modified by the following sharpening function[15,16]

$$M(s) = \left( \frac{\Sigma Z_i}{\Sigma f_i} \right)^2 \exp\left( \frac{p \sin^2\theta}{\lambda^2} \right)$$

where $p$ = sharpening parameter ( = 0 )

$\Sigma Z_i$ = sum of the atomic numbers

$\Sigma f_i$ = sum of the scattering factors at $\sin \theta/\lambda$ of the amplitude which is modified.

# CHAPTER 3

## STRUCTURE DETERMINATION AND REFINEMENT

A three-dimensional Patterson map was calculated for 1/8 the unit cell on a grid of approximately 0.23 Å for each grid point using the Patterson function at the vector point P(u,v,w)

$$P(u,v,w) = \frac{1}{V_c} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} |F(hkl)|^2 \cos 2\pi(hu + kv + lw)$$

which can be reduced for a monoclinic crystal to

$$P(u,v,w) = \frac{4}{V_c} \sum_{0}^{\infty}\sum_{0}^{\infty}\sum_{0}^{\infty} \{[F^2(hkl)+F^2(\bar{h}kl)]\cos 2\pi hu \cos 2\pi kv \cos 2\pi lw$$
$$+ [-F^2(hkl)+F^2(\bar{h}kl)]\sin 2\pi hu \cos 2\pi kv \sin 2\pi lw\}$$

Thirty sections parallel to C plane up to $w=0.50$ were drawn. Each section was computed from $u=0$ to 0.50 and $v=0$ to 0.50. The Patterson synthesis has the symmetry C2/m. Ignoring the overlapping, the peak heights in the Patterson map represent vectors, the relative numbers of which are proportional to the product

$$( Z_1 \times Z_2 )$$

where Z's are atomic numbers of atom 1 and atom 2 on either side of the vector. The proportionality constant is usually obtained from the origin peak height divided by $\Sigma Z_i^2$.

The cobalt atoms (27 electrons) are the heaviest scatterers the complex relative to the other atoms: oxygen, nitrogen, carbons, and consequently the Co-Co peaks will stand out strongly against the Co-O, Co-N, Co-C heavy-light peaks by a factor of approximately $(Z_H Z_H)/(Z_H Z_L)$ = about 4. It is therefore in general possible to recognize the Co-Co vectors, and to determine the Co-atom locations from these vectors.

A peak at the vector point ( u,v,w ) in a Patterson map indicates that there exist in the crystal, atoms at $(x_1, y_1, z_1)$ and $(x_2, y_2, z_2)$ such that

$$u = x_2 - x_1$$
$$v = y_2 - y_1$$
$$w = z_2 - z_1$$

The vectors $(\bar{u}, v, \bar{w})$, $(u, \bar{v}, w)$, $(\bar{u}, \bar{v}, \bar{w})$ are derived from it by the 2/m symmetry of the Patterson function for a monoclinic crystal. Consequently, only one vector out of these four vectors in the Patterson map is of importance.

The space group as observed from reciprocal lattice symmetry and systematic extinctions is either Cc or C2/c. The Patterson solution has to be pursued in both space groups till such time that one of the space groups can be excluded.

The equivalent positions for space group C2/c are

| | | | |
|---|---|---|---|
| $x$ | $y$ | $z$ | (1) |
| $\bar{x}$ | $\bar{y}$ | $\bar{z}$ | (2) |
| $x$ | $\bar{y}$ | $\frac{1}{2} + z$ | (3) |
| $\bar{x}$ | $y$ | $\frac{1}{2} - z$ | (4) |

and 4 additional positions by C centering symmetry ($\frac{1}{2}$ + x, $\frac{1}{2}$ + y, z). The locations give rise to three Harker peaks in the Patterson map for each cobalt atom. The positions of these peaks are

| u | v | w | |
|---|---|---|---|
| 2x | 2y | 2z | (5) |
| 0 | 2y | $\frac{1}{2}$ | (6) |
| 2x | 0 | $\frac{1}{2} + 2z$ | (7) |

In a C-centered cell there is always a very high peak (equal to the origin peak) at u=1/2, v=1/2, and w=0 in the Patterson synthesis. There are two H-H peaks observed on the Harker line (6) (0, 2y, 1/2) in the Patterson synthesis, their positions are

| Atom | u | v | w | Peak height |
|---|---|---|---|---|
| Co(1) | 0 | 0 | $\frac{1}{2}$ | 1382 |
| Co(2) | 0 | 0.152 | $\frac{1}{2}$ | 1337 |

The next step is to search the Harker sections (7) for H-H peaks. A problem arose from the fact that only one H-H peak existed on the map (peak height, P.H.=1252) instead of two H-H vectors for two cobalt atoms as expected from the two peaks on the Harker line. Similarly, only one H-H peak (P.H.=576) was observed satisfying formula (5) (i.e. at v=0.152), although some other high peaks were present. Actually these observations could have been explained by placing one Co atom at the origin and one in a general location, but the resulting structure was not the expected one. The lower symmetry Cc was therefore used for the initial solution.

The equivalent positions for space group Cc are

| | | | |
|---|---|---|---|
| $x$ | $y$ | $z$ | (8) |
| $x$ | $\bar{y}$ | $\frac{1}{2} + z$ | (9) |

plus two translation positions due to C-centering symmetry $(\frac{1}{2}+x,\ \frac{1}{2}+y,\ z)$, which yield one Harker peak for each Co-atom at

| u | v | w | |
|---|---|---|---|
| 0 | $2y$ | $\frac{1}{2}$ | (10) |

the positions of the vectors obtained on the Harker line in the Patterson map are the same as those observed for C2/c, namely, $v_1=0$ and $v_2=0.152$. Two additional positions of the vectors generated by non-symmetry related Co(1) and Co(2) atoms are

| u | v | w | |
|---|---|---|---|
| $x_2 - x_1$ | $y_2 - y_1$ | $z_2 - z_1$ | (11) |
| $x_2 - x_1$ | $y_2 + y_1$ | $\frac{1}{2} + z_2 - z_1$ | (12) |

In the crystal, for the space group Cc, only relative x and z coordinates of Co(1) and Co(2) atoms can be obtained. The position of Co(1) atom $(x_1,y_1,z_1)$ was then assigned to the origin (0, 0, 0). Therefore, the coordinates $(x_2,\ y_2,\ z_2)$ of Co(2) have to be chosen with respect to this origin. In other words, the coordinates for Co(2) must not only satisfy the vectors on the Harker sections but also the general vectors of formulas (11) and (12) with respect to the coordinates of Co(1). The coordinates of Co(2) was determined as

| $x_2$ | $y_2$ | $z_2$ |
|---|---|---|
| 0.277 | 0.076 | 0.310 |

The Harker and the general vectors due to Co(1) and Co(2) atoms for space group Cc are listed in the Table 2.

TABLE 2

Co(1) - Co(2) Vectors for Space Group Cc in Patterson Map

| Peak No. | Peak type | (u | v | w) | (u | v | w) | Peak Height |
|---|---|---|---|---|---|---|---|---|
| 1 | Harker | 0 | $2y_1$ | 1/2 | 0 | 0 | 1/2 | 1382 |
| 2 | Harker | 0 | $2y_2$ | 1/2 | 0 | 0.152 | 1/2 | 1337 |
| 3 | General | $x_2-x_1$ | $y_2-y_1$ | $z_2-z_1$ | 0.277 | 0.076 | 0.310 | 1149 |
| 4 | General | $x_2-x_1$ | $y_2+y_1$ | $\frac{1}{2}+z_2-z_1$ | 0.221 | 0.423 | 0.188 | 1197 |

In the Patterson map there was one more unidentified large peak with height=1252 at P(0.057,1/2,0.122) which may be due to the symmetry related atoms (actually this peak could have been interpreted at this point). But we decided to leave it alone until a Fourier map was calculated. At this point we have lost the expected structure (two cobalts bridged by oxygen) because Co(1) and Co(2) atoms are separated by a length of about 7 Å which is too far to allow for a peroxo-group to bond these two metal atoms. It was decided as a next step to search for the peptide ligands arround the cobalt atoms.

In this structure one expects to have the relative peak height (P.H.) for heavy-heavy (H-H), heavy-light (H-L) and light-light (L-L) vectors as follows

| | Co - Co | Co - O<br>Co - N<br>Co - C | O - O<br>N - N<br>C - C | O - N<br>O - C<br>N - C | Co - H |
|---|---|---|---|---|---|
| rel. P.H. | 27 | 8 | 2.5 | | 1 |

The vectors caused by the Co-atoms and their coordinated light atoms (O atoms or N atoms) were expected to be located in the Patterson map around the origin with the distances about 2 Å. One general H-L peak with height about 440 at P(0.027, 0.129, 0.103) was observed. The positions of four coordinated light atoms, which lie almost at the apexes of a square plane with Co(2) as the center, were deduced from this vector together with other vectors associated with these positions and all equivalent positions of Co-atoms. If the coordination of the cobalt atom is octahedral one expects to find two light atoms located at the other two apexes of the octahedron around Co(2). The coordinates of these two atoms were first estimated intuitively from the model and then all vectors were checked with the coordinates of the cobalt atoms. In fact, there is an elegant way of searching light atoms; it is clear that in the Patterson map there exists an image of the structure resulting from each of the heavy atoms in the structure. Figure 1 which shows one Patterson section at $w=0.30$, illustrates a part of the glycylglycine molecule forming a five-membered ring with cobalt atom. With the aid of the image of the ligands in the map and the conformations and bond distances established for peptide molecules, the other atoms of two molecules of glycylglycine complexed with the Co(2) were found from the Patterson synthesis. Owing to the overlap of vectors, it was not possible

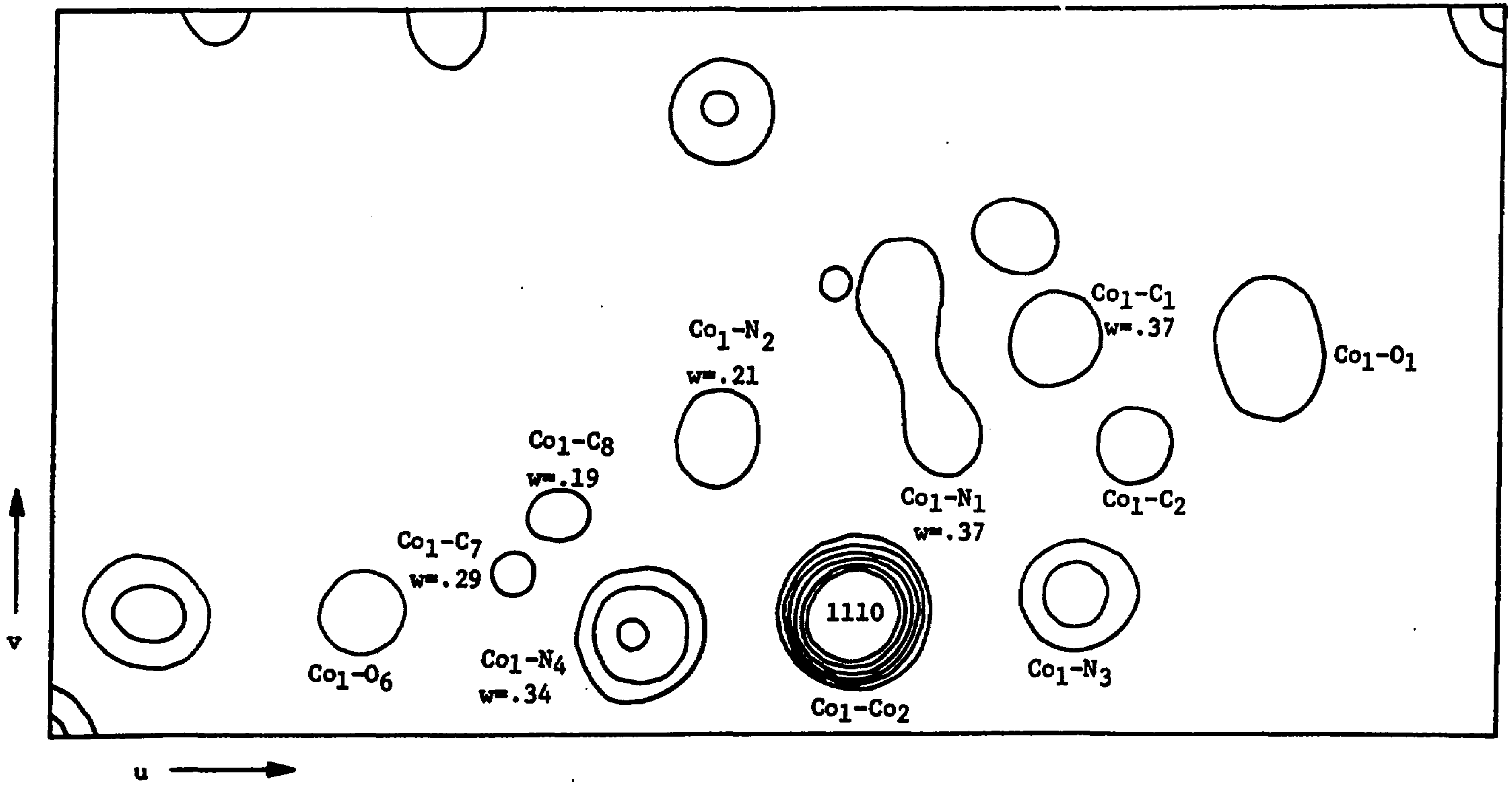


**Figure 1.** Patterson Section w=.30. Arbitrary Scale

to solve , with confidence, for the ligands of the Co(1), from the Patterson map.

The positions of the twenty atoms solved from the Patterson synthesis are presented in the Table 3 (still in space group Cc).

After locating the twenty atoms, all further attempts were futile in the search for additional chemically sensible atoms from the Patterson map. Taking Cc as the space group, structure factors were then calculated using the parameters of these twenty atoms from Table 3 by the following equation.

$$F(hkl) = \Sigma_j f_j \exp 2\pi i(hx_j + ky_j + lz_j)\cdot T_j$$

where $T_j$ = temperature factor = $\exp[-B_j(\sin\theta/\lambda)^2]$, $B = 8\pi^2\overline{u^2}$,

$\overline{u^2}$ is the mean-square amplitude of vibration.

$f_j$ = scattering factor of jth atom at $(\sin\theta)/\lambda$,

The isotropic temperature factor (Biso) for all atoms was initially assigned as 3.5 Å$^2$. The parameters of all atoms but Co-atoms were omitted from the refinement until the latter cycles. After 4 cycles of refinement, the R value was 0.499 and the first electron-density map was made by the following equation

$$\rho(x,y,z) = \frac{1}{V_c} \sum_{hkl}\sum\sum |F_{hkl}| \exp[-2\pi i(hx + ky + lz - \alpha_{hkl})]$$

Assuming that Friedel's Law holds, the above expression for space group Cc can be written as

## TABLE 3

### Fractional Coordinates of Atoms Obtained from Patterson Synthesis

| Atom | x | y | z |
|---|---|---|---|
| Co(1) | 0.000 | 0.000 | 0.000 |
| Co(2) | 0.277 | 0.076 | 0.310 |
| O(1) | 0.422 | 0.236 | 0.285 |
| O(2) | 0.316 | 0.846 | 0.113 |
| O(3) | 0.272 | 0.935 | 0.207 |
| O(4) | 0.307 | 0.947 | 0.408 |
| O(5) | 0.283 | 0.865 | 0.538 |
| O(6) | 0.109 | 0.076 | 0.310 |
| N(1) | 0.307 | 0.204 | 0.408 |
| N(2) | 0.235 | 0.180 | 0.217 |
| N(3) | 0.357 | 0.093 | 0.280 |
| N(4) | 0.207 | 0.076 | 0.340 |
| C(1) | 0.349 | 0.290 | 0.379 |
| C(2) | 0.380 | 0.198 | 0.310 |
| C(3) | 0.364 | 0.000 | 0.208 |
| C(4) | 0.316 | 0.932 | 0.177 |
| C(5) | 0.275 | 0.924 | 0.474 |
| C(6) | 0.217 | 0.000 | 0.438 |
| C(7) | 0.160 | 0.096 | 0.283 |
| C(8) | 0.169 | 0.152 | 0.192 |

$$\begin{aligned}\rho(x,y,z) = \frac{4}{V_c}\Big[ \sum_{hkl}^{l=2n}\sum\sum & \{[|F(hkl)|\cos\alpha + |F(\bar{h}kl)|\cos\bar{\alpha}]\cos2\pi hx\cos2\pi ky\cos2\pi lz \\ & + [-|F(hkl)|\cos\alpha + |F(\bar{h}kl)|\cos\bar{\alpha}]\sin2\pi hx\cos2\pi ky\sin2\pi lz \\ & + [|F(hkl)|\sin\alpha - |F(\bar{h}kl)|\sin\bar{\alpha}]\sin2\pi hx\cos2\pi ky\cos2\pi lz \\ & + [|F(hkl)|\sin\alpha + |F(\bar{h}kl)|\sin\bar{\alpha}]\cos2\pi hx\cos2\pi ky\sin2\pi lz\} \\ + \sum_{hkl}^{l=2n+1}\sum\sum & \{[-|F(hkl)|\cos\alpha + |F(\bar{h}kl)|\cos\bar{\alpha}]\sin2\pi hx\sin2\pi ky\cos2\pi lz \\ & + [-|F(hkl)|\cos\alpha - |F(\bar{h}kl)|\cos\bar{\alpha}]\cos2\pi hx\sin2\pi ky\sin2\pi lz \\ & + [|F(hkl)|\sin\alpha + |F(\bar{h}kl)|\sin\bar{\alpha}]\cos2\pi hx\sin2\pi ky\cos2\pi lz \\ & + [-|F(hkl)|\sin\alpha + |F(\bar{h}kl)|\sin\bar{\alpha}]\sin2\pi hx\sin2\pi ky\sin2\pi lz\}\Big]\end{aligned}$$

In this Fourier map another cobalt atom was located, related to the Co(2) by a 2-fold rotation. The space group was therefore C2/c rather than Cc, and all further computations were performed in the C2/c space group. In this Fourier also six atoms surrounding Co(1) were located. Therefore, one cobalt atoms is located at a center of symmetry and coordinated with six water molecules, while another cobalt atom is in a general position surrounded by two glycylglycine (GG) molecules. This means that the structure has a ratio of Co to GG of 3:4 rather than 1:2 as expected.

The refinement proceeded with two cobalt atoms, two glycylglycine molecules and three water molecules of coordination in several cycles of structure factor least-squares calculations. Another difference Fourier synthesis revealed one water molecule but also 4 fractional molecules of water (occupancy 1/4 to 1/2) in the interstitial sites between the complexed cobalt ions. The approximate positions along with the peak-heights on absolute electron density scale in the map for these 4 peaks were

| Peak No. | x | y | z | P.H.(e/Å$^3$) |
|---|---|---|---|---|
| 1($O_{11}$) | -0.047 | 0.283 | 0.164 | 2.88 |
| 2($O_{12}$) | 0.067 | 0.413 | 0.057 | 1.70 |
| 3($O_{13}$) | -0.078 | 0.460 | 0.007 | 1.29 |
| 4($O_{14}$) | 0.002 | 0.461 | -0.138 | 1.27 |

The observed density indeed indicated three additional molecules of water of hydration (in agreement with one full and four half molecules of water). It should be realized, however, that the observed density is somewhat unreliable, because the crystals are not stable outside the mother liquor. Peaks 2 and 3 are separated by 1.6 Å while peaks 3 and 4 are separated by 2.3 Å. It is therefore obvious that position 3 can not exist simultaneously with both positions 2 and 4, because the interatomic distances are too short. Peak 1 was elongated towards peak 3, this may indicate that peak 1 is hydrogen-bonded to peak 3 in a part of the crystal. In light of the facts observed above, it appears that position 1 might correspond to one water molecule with some disorder due to different hydrogen bonding in different cells which results in a decrease of its peak height. Positions 2 and 4 which from proper hydrogen bonds, may exist in one unit cell while position 3 exists in another unit cell. This model has one molecule of water too many in comparison with the observed density. However, there was another possible designation for these four peaks, which is that positions 1 and 3 exist in one unit cell while positions 2 and 4 exist in another one.

This explanation is simple and straightforward The former one seems more reasonable for the structure, however, because it explains most of the observations while it has better hydrogen bonds by which the complex ions are held together.

Assigning initially the isotropic temperature factor of 5.0 along with occupancy number of 1/2 for the four disordered water molecules, further refinements were executed and the second difference synthesis was then calculated. From the map 20 hydrogen atoms were located with the aid of a model. The positions of these hydrogen atoms are listed in Table 4. They are all the hydrogens attached to the glycylglycine residues, the hydrogens bonded to the three coordinated $H_2O$ molecules, and the two bonded to the full occupancy $H_2O$ molecule. The average peak heights for the hydrogen was 0.43 e/$Å^3$. The positions were determined from the difference Fourier and used in further refinements without change.

The structure was further refined with the inclusion of hydrogen atoms, three disordered water molecules given isotropic temperature factors and all other atoms given anisotropic temperature factors. All refinements were done by block-diagonal least-squares minimizing the quantity $\Sigma w(|KF_o|-|F_c|)^2$. The weighting scheme for the refinement was

$$\sqrt{w} = |F_o|/P_1 \quad \text{if} \quad |F_o| \leq P_1$$

$$\text{or} \quad \sqrt{w} = P_1/|F_o| \quad \text{if} \quad |F_o| > P_1$$

where $P_1$ was given the value of 45.0. For all reflection data, up to $2\theta$ value of 46 degree, the final reliability index R was 0.060 and all

## TABLE 4

### Positions of Hydrogen Atoms

| Atom | x | y | z | Biso |
|---|---|---|---|---|
| H(1) | 0.265 | 0.264 | 0.400 | 3.70 |
| H(2) | 0.313 | 0.182 | 0.464 | 3.70 |
| H(3) | 0.234 | 0.265 | 0.220 | 3.70 |
| H(4) | 0.245 | 0.177 | 0.141 | 3.70 |
| H(5) | 0.336 | 0.350 | 0.336 | 3.70 |
| H(6) | 0.380 | 0.300 | 0.441 | 3.70 |
| H(7) | 0.376 | 0.046 | 0.155 | 3.70 |
| H(8) | 0.390 | -0.056 | 0.269 | 3.70 |
| H(9) | 0.184 | -0.083 | 0.417 | 3.70 |
| H(10) | 0.203 | 0.029 | 0.490 | 3.70 |
| H(11) | 0.149 | 0.231 | 0.185 | 3.70 |
| H(12) | 0.155 | 0.096 | 0.136 | 3.70 |
| H(13) | 0.000 | 0.210 | 0.093 | 5.30 |
| H(14) | 0.052 | 0.262 | 0.030 | 5.30 |
| H(15) | 0.084 | 0.102 | -0.040 | 5.30 |
| H(16) | 0.094 | -0.042 | -0.088 | 5.30 |
| H(17) | 0.048 | -0.144 | 0.177 | 5.30 |
| H(18) | 0.056 | 0.012 | 0.207 | 5.30 |
| H(19) | 0.138 | 0.279 | -0.060 | 5.30 |
| H(20) | 0.085 | 0.233 | -0.157 | 5.30 |

of the positional and temperature parameter shifts were less than 1/8 their estimated standard deviations in the last cycle.

All of the final parameters of atoms along with their estimated standard deviations are presented in Table 5 and 6.

The final values for the observed and calculated structure factors for all of the reflections are given in Table 7. All of the atomic scattering factors used in the structure factor calculations were taken from the International Tables for X-ray Crystallography[18] except the one for hydrogen which was reported by Stewart, Davidson and Simpson.[19]

The final difference Fourier map was computed with all atoms including 20 hydrogen atoms in the structure factor calculation, which showed about 10 spurious peaks with heights between 0.30 and 0.69 $e/Å^3$. More than half of these peaks were located around the positions of the disordered water molecules. This indicates that the errors may be due to the inaccuracies of the model used for the disordered water molecules. The lowest negative electron density is $-0.34$ $e/Å^3$. The high background counts of the intensity data and the absorptions of the crystal in its mother liquid may also contribute to the error. In this structure, the disorder of the water molecules is a handicap, however, we are mainly interested in the configurations and the interactions of the cobalt complex with glycylglycine, and the final R value indicates that such a discussion is possible.

## TABLE 5

Atomic Parameters of $[Co^{II}(H_2O)_6][Co^{III}(GG)_2]_2 \cdot 6H_2O$

| Atom | x | y | z | Biso |
|---|---|---|---|---|
| $Co^{II}$ | 0.0 | 0.0 | 0.0 | |
| $Co^{III}$ | 0.2785(1) | 0.0763(1) | 0.3093(1) | |
| O(1) | 0.4236(2) | 0.2292(4) | 0.2834(4) | |
| O(2) | 0.3108(2) | -0.1536(4) | 0.1124(3) | |
| O(3) | 0.2681(2) | -0.0546(4) | 0.2136(3) | |
| O(4) | 0.3103(2) | -0.0356(4) | 0.4161(3) | |
| O(5) | 0.2886(2) | -0.1436(4) | 0.5378(3) | |
| O(6) | 0.1123(2) | 0.0787(5) | 0.3002(3) | |
| N(1) | 0.3028(2) | 0.2133(5) | 0.3995(3) | |
| N(2) | 0.2325(2) | 0.1816(4) | 0.2056(3) | |
| N(3) | 0.3483(2) | 0.0992(4) | 0.2753(4) | |
| N(4) | 0.2096(2) | 0.0496(5) | 0.3448(3) | |
| C(1) | 0.3510(3) | 0.2782(6) | 0.3716(5) | |
| C(2) | 0.3779(3) | 0.1981(6) | 0.3052(4) | |
| C(3) | 0.3638(3) | 0.0052(6) | 0.2132(4) | |
| C(4) | 0.3110(3) | -0.0739(5) | 0.1756(4) | |
| C(5) | 0.2744(2) | -0.0728(5) | 0.4662(4) | |
| C(6) | 0.2142(3) | -0.0245(6) | 0.4339(4) | |
| C(7) | 0.1624(3) | 0.0908(6) | 0.2871(4) | |
| C(8) | 0.1714(3) | 0.1547(6) | 0.1936(4) | |

TABLE 5 - Continued

| Atom | x | y | z | Biso |
|---|---|---|---|---|
| O(7) | 0.0111(3) | 0.1826(5) | 0.0408(4) | |
| O(8) | 0.0813(2) | 0.0101(4) | -0.0321(3) | |
| O(9) | 0.0364(2) | -0.0482(4) | 0.1482(3) | |
| O(10) | 0.1013(3) | 0.2439(6) | -0.0706(5) | |
| O(11)* | -0.0464(5) | 0.2809(10) | 0.1639(11) | |
| O(12)* | 0.0679(9) | 0.4119(18) | 0.0552(15) | 10.22 |
| O(13)* | -0.0737(11) | 0.4667(25) | 0.0077(19) | 13.42 |
| O(14)* | 0.0015(11) | 0.4605(24) | -0.1371(19) | 13.29 |

* Occupancy number = 1/2

## TABLE 6

Anisotropic Temperature Factors ( $\times 10^4$ )

$\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})]$

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{23}$ | $B_{13}$ | $B_{12}$ |
|---|---|---|---|---|---|---|
| Co(1) | 11(1) | 53(1) | 29(1) | 10(1) | 6(1) | 4(1) |
| Co(2) | 10(1) | 41(1) | 20(1) | - 4(1) | 5(1) | - 3(1) |
| O(1) | 15(1) | 82(5) | 70(3) | -38(7) | 25(3) | -23(4) |
| O(2) | 25(1) | 54(4) | 36(3) | -21(5) | 24(3) | - 7(3) |
| O(3) | 13(1) | 46(4) | 32(2) | - 5(5) | 9(2) | - 6(3) |
| O(4) | 13(1) | 60(4) | 27(2) | 9(5) | 6(2) | 3(3) |
| O(5) | 19(1) | 64(4) | 29(2) | 22(5) | 10(2) | 2(3) |
| O(6) | 12(1) | 110(5) | 45(3) | 17(6) | 9(2) | 2(4) |
| N(1) | 14(1) | 64(5) | 26(3) | -10(6) | 9(3) | - 4(4) |
| N(2) | 14(1) | 46(4) | 28(3) | 0(6) | 10(3) | 5(3) |
| N(3) | 15(1) | 45(4) | 30(3) | -15(5) | 13(3) | - 7(3) |
| N(4) | 12(1) | 56(5) | 27(3) | 0(6) | 3(3) | 1(3) |
| C(1) | 18(1) | 54(6) | 47(4) | -20(8) | 18(4) | -14(5) |
| C(2) | 14(1) | 59(6) | 33(4) | 3(7) | 12(3) | - 4(4) |
| C(3) | 14(1) | 52(5) | 37(4) | -13(7) | 17(3) | 2(4) |
| C(4) | 14(1) | 49(5) | 25(3) | 8(7) | 4(3) | 5(4) |
| C(5) | 12(1) | 47(5) | 26(3) | - 5(6) | 5(3) | - 7(4) |
| C(6) | 14(1) | 79(7) | 27(3) | 8(8) | 8(3) | -10(5) |

## TABLE 6 - Continued

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{23}$ | $B_{13}$ | $B_{12}$ |
|---|---|---|---|---|---|---|
| C(7) | 13(1) | 59(6) | 30(3) | - 18(7) | 9(3) | 2(4) |
| C(8) | 14(1) | 64(6) | 31(3) | 5(7) | 3(3) | 7(5) |
| O(7) | 34(2) | 68(5) | 71(4) | - 30(7) | 42(4) | -10(4) |
| O(8) | 14(1) | 93(5) | 42(3) | - 2(6) | 15(2) | 1(3) |
| O(9) | 18(1) | 81(5) | 35(3) | 13(6) | 5(3) | 11(3) |
| O(10) | 29(1) | 113(6) | 83(4) | 16(9) | 21(4) | -36(5) |
| O(11) | 29(3) | 82(11) | 179(14) | -130(20) | 122(11) | -23(9)* |

* Occupancy number = 1/2

## TABLE 7

### Structure Factors x 2

[illegible]

# CHAPTER 4

## DISCUSSION OF THE STRUCTURE

Figure 2 shows the complex, indicating the numbering system, projected onto the ac plane. The structure is quite different from what we expected. No molecular oxygen was found in the structure but cobalt atoms in two oxidation states were observed instead. It seems safe to assume that the cobalt atom on the special position, the center of symmetry (0,0,0) is Co(II) and that the cobalt atom in the general position is Co(III) thus satisfing the condition of charge neutrality of the complex molecule. The Co(II) atom is octahedrally coordinated by six water molecules: $H_2O(7)$, $H_2O(8)$, $H_2O(9)$, $H_2O(7')$, $H_2O(8')$, $H_2O(9')$ ("'" means center of inversion symmetry). The Co-O distance in the $Co(H_2O)_6$ ion are 2.1 Å in agreement with Co(II)-O distances in the literature[23] of 2.1 Å but significantly longer than literature values for Co(III)-O distances of 1.9 Å, thus indicating that the $Co(H_2O)_6$ ion is indeed $[Co(II)(H_2O)_6]^{++}$. Similarly the distances (vide infra) in the $Co(GG)_2$ complex leave little doubt that this is a Co(III) complex, i.e. $[Co(III)(GG)_2]^-$. The formula of the complex in this structure is therefore:

$$[Co(II)(H_2O)_6]^{++}[Co(III)(GG)_2]_2^-[H_2O]_6$$

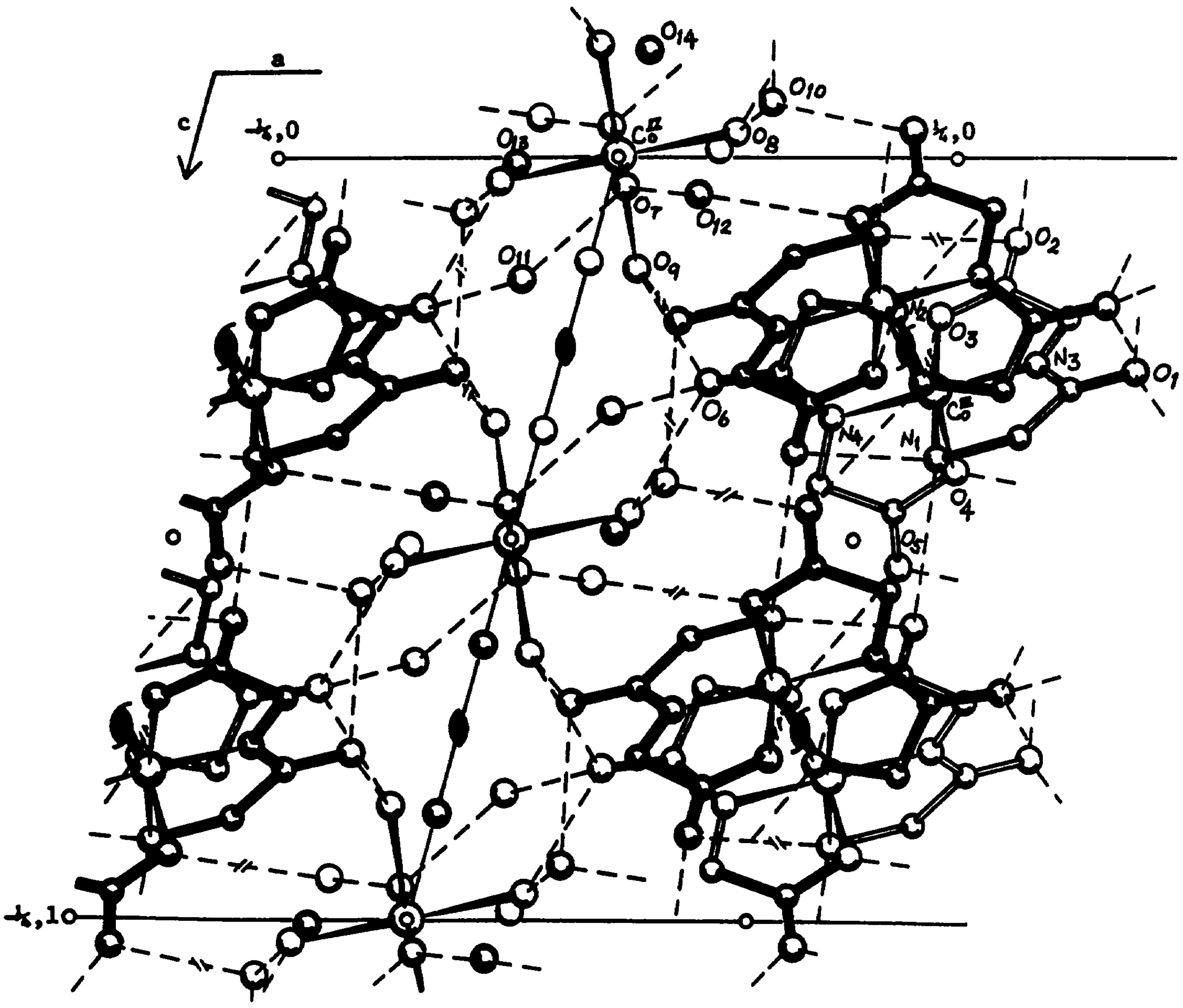


Figure 2. ac Projection of the Structure

The Co(III) atom is surrounded by two independent terdentate glycylglycine molecules that lie almost in plane at right angle(89.48°) to each other. The largest deviation of any atom from the least-squares plane through each of the glycylglycine ligands is on the order of 0.24 Å. The coordination of the Co(III) ion is a distorted octahedron. The ligands are bonded to the Co(III) via the N (amino), deprotonated N (peptide) and O (carboxyl) atoms forming two 5-membered chelate rings for each glycylglycine molecule. The peptide oxygens are not involved in the chelation to the metal probably due to the high pH value of the solution from which the complex was made. The peptide units remain planar and the deprotonated peptide nitrogens [N(3), N(4)] stay trigonal as they are in the corresponding free peptide molecules despite the change in coordination, perhaps in order to preserve the resonance energy of the amide groups.[23] This Co(III) complex cation is similar to that found in $NH_4[Co(GG)_2]\cdot 2H_2O$ by Gillard et al.[13] and in $[Co^{II}(H_2O)_6][Co^{III}(GG)_2]_2\cdot 12H_2O$ by Freeman.[20] The latter structure incidentally is identical to the present structure except for the water contents while also the space group and the cell dimension are different. The observation of the cobalt atoms in two different oxidation states is not unusual, a structure with octahedral coordination of the central cobalt(II) through face-sharing of oxygens with the cobalt(III) octahedra has been reported by Bertrand and his coworkers.[22] In a bisglycylglycine-metal complex, the ligands may be either bi- or terdentate or both. The bidentate can have a number of probable combinations of bonding atoms: amine--peptide oxygen, amine--peptide nitrogen, carboxylate--peptide nitrogen, carboxylate--peptide oxygen. On the other hand in the terdentate peptide ligand only one bonding mode has been observed: amine--peptide nitrogen--carboxylate (the amine, peptide oxygen, carboxylate bonding mode would lead one 5-membered and 7-membered ring; the later is unusual in chelates). It is also possible that the ligand bridges two or more metal in various polymeric structures.[22,23] Apparently a wide variety of complexes are possible with glycylglycine.[24]

A significant aspect of the complex is the loss of the protons from the peptide nitrogens of the two independent terdentate glycylglycine ligands. This loss of the amide hydrogen atom when coordinated to a metal ion was first illustrated in the copper(II) complexes of picolinylamide[25] and biuret.[26]

In the structure the complex molecules extend more or less along the diagonal of the ac projection, and there are well defined layers of $Co(H_2O)_6^{2+}$ and $Co(GG)_2^-$ ion parallel to the (100) plane. The cation layers are hydrophilic and in contrast the anion layers are hydrophobic. $H_2O(10)$, $H_2O(11)$, $H_2O(12)$, $H_2O(13)$ and $H_2O(14)$ are uncoordinated water molecules which fill in the interstitial sites between complex ions to aid the crystal packing, however, $H_2O(11)$, $H_2O(12)$, $H_2O(13)$ and $H_2O(14)$ are fractional as previously discussed in Chapter 3.

Within the $Co(GG)_2^-$ anion layers each complex is linked to its neighbours by four pairs of N (amino)····O (carboxyl) hydrogen bonds:

| | | |
|---|---|---|
| (1) | $N(1)\cdots\cdots\cdots O(2)(\,x,\ \bar{y},\ z+\frac{1}{2}\,)$ | 2.944 Å |
| (2) | $N(1)\cdots\cdots\cdots O(2)(\,\frac{1}{2}-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z\,)$ | 3.078 Å |
| (3) | $N(2)\cdots\cdots\cdots O(3)(\,\frac{1}{2}-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z\,)$ | 3.121 Å |
| (4) | $N(2)\cdots\cdots\cdots O(5)(\,x,\ \bar{y},\ z-\frac{1}{2}\,)$ | 2.967 Å |

Hydrogen bonds (1) and (4) join the complex anions related by a glide plane along c direction while (2) and (3) unite the complexes related by a 2-fold screw axis along b direction. The packing of the crystal on bc plane is the result of these four hydrogen bonds.

On the other hand the complex $Co(H_2O)_6^{2+}$, in the cation layer is related to its immediate neighbours by a 2-fold axis parallel to b axis. The $Co(H_2O)_6^{++}$ is extensively hydrogen bonded, although no direct bonds exist between cations. For each asymmetric unit, there are three $H_2O$ molecules coordinated to a Co(II) atom and each of those $H_2O$ molecule forms two hydrogen bonds. The complex cation $Co(H_2O)_6^{2+}$ and complex anion $Co(GG)_2^-$ are united by some direct hydrogen bonds and by hydrogen bonds formed by the uncoordinated water molecules which fill in the gaps between the complex ions. The skeletal hydrogen bonds are as following:

Cation layer                                        Anion layer

$H_2O(7)\cdots 2.664$ Å $\cdots H_2O(11)\cdots 2.855$ Å $\cdots O(6)(\bar{x},\ y,\ \frac{1}{2}-z)$

$H_2O(7)\cdots 2.866$ Å $\cdots H_2O(12)\cdots 2.924$ Å $\cdots O(4)(\frac{1}{2}-x,\ y-\frac{1}{2},\ \frac{1}{2}-z)$

$H_2O(8)\cdots 2.707$ Å $\cdots$ $H_2O(10)\cdots 2.864$ Å $\cdots O(5)(\frac{1}{2}-x,\ y+\frac{1}{2},\ \frac{1}{2}-z)$
                                        $H_2O(10)\cdots 2.836$ Å $\cdots O(1)(\frac{1}{2}-x,\ \frac{1}{2}-y,\ \bar{z})$

$H_2O(8)\cdots\cdots\cdots 2.761$ Å $\cdots\cdots\cdots O(6)(x,\ \bar{y},\ z-\frac{1}{2})$

$H_2O(9)\cdots\cdots\cdots 2.784$ Å $\cdots\cdots\cdots O(6)(x,\ y,\ z)$

$H_2O(9)\cdots\cdots\cdots 2.725$ Å $\cdots\cdots\cdots O(1)(\frac{1}{2}-x,\ y-\frac{1}{2},\ \frac{1}{2}-z)$

The hydrogen bonds between $H_2O(12)$ and $H_2O(14)$ of length 2.770 Å, $H_2O(12)$ and $H_2O(14)$ of length 2.639 Å and their symmetry related hydrogen bonds also form a net and help to knit the layers of the complex anions together. The disordered $H_2O(13)$ likewise forms hydrogen bonds with $H_2O(11)$ of length 2.919 Å and with $O(4)(x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2})$ of 2.869 Å. The hydrogen bonds involving $H_2O(12)$, $H_2O(13)$ and $H_2O(14)$ are probably inaccurate to a larger extent than the other hydrogen bonds due to the disorder of water molecules. All of the hydrogen bonds are summarized in Table 8 and are also presented as dotted lines in Figure 2 except those of the disordered water molecules.

There seems a short van der Waals distance between O(10) and O(12) of length 2.783 Å which is unlikely to be a hydrogen bond due to an improbable angle O(7)-O(12)-O(10) of 64.72° for tetrahedral configuration. Another short van der Waals distance exists between O(11) and a 2-fold related O(11) of length 2.817 Å. There is a number of moderate short van der Waals distances within the $Co(GG)_2^-$ complex anions, especially in the vicinity of the carboxyl groups of the glycylglycine molecules. They are the contacts between O(2) and $C(5)(x, \bar{y}, z-\frac{1}{2})$ of length 3.190 Å, O(2) and $C(7)(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ of length 3.139 Å, C(3) and $O(5)(x, \bar{y}, z-\frac{1}{2})$ of length 3.037 Å, C(4) and O(5) of length 3.021 Å, O(5) and $O(5)(\frac{1}{2}-x, -\frac{1}{2}-y, 1-z)$ of length 3.018 Å. However, these van der Waals contacts of the atoms may be the consequence of the hydrogen bondings which occurred at the adjacent atoms. Within the water region, there are three moderate van der Waals interactions: $H_2O(7)$ and $H_2O(10)$ of length 3.024 Å;

## TABLE 8

### Hydrogen Bonds

A. H-Bonds in Anion Layer; Co(GG)$_2^-$

| Atom 1 | Atom 2 | Distance (Å) |
|---|---|---|
| N(1) | O(2)$(x, \bar{y}, z+\frac{1}{2})$ | 2.944 |
| N(1) | O(2)$(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$ | 3.078 |
| N(2) | O(3)$(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$ | 3.121 |
| N(2) | O(5)$(x, \bar{y}, z-\frac{1}{2})$ | 2.967 |
| **B. H-Bonds in Cation Layer; Co(H$_2$O)$_6^{2+}$/H$_2$O** | | |
| O(8) | O(10)$(x, y, z)$ | 2.707 |
| O(7) | O(11)$(x, y, z)$ | 2.664 |
| O(7) | O(12)$(x, y, z)$ | 2.866 |
| O(11) | O(13)$(x, y, z)$ | 2.919 |
| O(12) | O(14)$(x, y, z)$ | 2.770 |
| O(12) | O(14)$(\bar{x}, 1-y, \bar{z})$ | 2.639 |
| **C. Interlayer H-Bonds** | | |
| O(8) | O(6)$(x, \bar{y}, z-\frac{1}{2})$ | 2.761 |
| O(9) | O(6)$(x, y, z)$ | 2.784 |
| O(9) | O(1)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 2.725 |
| O(5) | O(10)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 2.864 |

TABLE 8 - Continued

| Atom 1 | Atom 2 | Distance (Å) |
|---|---|---|
| O(1) | O(10)$(\frac{1}{2}-x, \frac{1}{2}-y, \bar{z})$ | 2.836 |
| O(6) | O(11)$(\bar{x}, y, \frac{1}{2}-z)$ | 2.855 |
| O(4) | O(12)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 2.924 |
| O(13) | O(4)$(x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2})$ | 2.869 |
| O(14) | O(1)$(x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2})$ | 2.845 |

$H_2O(14)(\bar{x}, 1-y, \bar{z})$ of 3.113 Å and $H_2O(14)$ and $H_2O(14)(\bar{x}, y, -\frac{1}{2}-z)$ of 3.070 Å. All of the van der Waals contacts less than 3.50 Å are listed in Table 9. The shortest contacts between $Co(H_2O)_6^{2+}$ complexes is of length 3.639 Å at $H_2O(9)$ with $H_2O(9)(\bar{x}, y, \frac{1}{2}-z)$.

Intramolecular bond distances and bond angles of the structure are listed in Table 10 and 11, respectively. Figure 3 gives the configuration of the centrosymmetrical complex cation $Co(H_2O)_6^{2+}$. The water molecules are arranged about the Co(II) atoms--the center of symmetry--in an almost regular octahedron, the average edge length of the octahedron being 2.959 Å. The shortest edge is between $H_2O(7)$ and $H_2O(8)$ which also make the smallest bond angle of 86.6° with Co(II) atom. The $Co(II)-OH_2$ bonds have a mean length of 2.093 Å, in good agreement with the mean value found in the $Co(H_2O)_6^{2+}$ ion of a Tutton's salt(2.094 Å)[27]. The length of a $Co(III)-OH_2$ bond is about 1.98 Å[28], giving a difference of 0.11 Å between Co-O bond-lengths for cobalt in oxidation states II and III. This proves quite conclusively that the cobalt on center of symmetry is a $Co^{++}$ ion.

There are three absolute planes for each $Co(H_2O)_6^{2+}$ ion since the ion is symmetrical with respect to Co(II) atom. The equations for these planes are as following:

Plane 1. O(7)O(7')O(8)O(8'), ("'" means center of inversion)

$$5.005x - 2.934y + 11.765z = 0$$

Plane 2. O(7)O(7')O(9)O(9')

$$23.655x - 0.134y - 5.853z = 0$$

## TABLE 9

### Van der Waals Contacts Less Than 3.50 Å

| Atom 1 | Atom 2 | Distance (Å) |
|---|---|---|
| O(2) | O(4)$(x, \bar{y}, z-\frac{1}{2})$ | 3.401 |
| O(2) | O(5)$(x, \bar{y}, z-\frac{1}{2})$ | 3.445 |
| O(2) | C(5)$(x, \bar{y}, z-\frac{1}{2})$ | 3.190 |
| O(2) | N(2)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 3.448 |
| O(2) | N(4)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 3.391 |
| O(2) | C(7)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 3.139 |
| O(2) | C(8)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 3.338 |
| O(3) | O(5)$(x, \bar{y}, z-\frac{1}{2})$ | 3.378 |
| O(3) | N(1)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 3.254 |
| O(3) | C(1)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 3.370 |
| N(3) | O(5)$(x, \bar{y}, z-\frac{1}{2})$ | 3.246 |
| N(3) | O(12)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 3.380 |
| C(2) | O(10)$(\frac{1}{2}-x, \frac{1}{2}-y, \bar{z})$ | 3.427 |
| C(3) | O(5)$(x, \bar{y}, z-\frac{1}{2})$ | 3.037 |
| C(3) | O(12)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 3.350 |
| C(4) | O(5)$(x, \bar{y}, z-\frac{1}{2})$ | 3.021 |
| C(4) | C(5)$(x, \bar{y}, z-\frac{1}{2})$ | 3.218 |
| C(4) | N(2)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 3.449 |
| C(4) | C(8)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 3.465 |

TABLE 9 - Continued

| Atom 1 | Atom 2 | Distance (Å) |
|---|---|---|
| O(7) | O(10)$(x, y, z)$ | 3.024 |
| O(8) | C(6)$(x, \bar{y}, z-\frac{1}{2})$ | 3.353 |
| O(9) | C(1)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 3.390 |
| O(9) | C(2)$(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ | 3.450 |
| O(10) | O(12)$(x, y, z)$ | 2.783 |
| O(10) | O(14)$(x, y, z)$ | 3.358 |
| O(11) | O(11)$(\bar{x}, y, \frac{1}{2}-z)$ | 2.817 |
| O(13) | N(3)$(x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2})$ | 3.347 |
| O(13) | C(2)$(x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2})$ | 3.279 |
| O(14) | O(10)$(x, y, z)$ | 3.358 |
| O(14) | C(2)$(x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2})$ | 3.378 |
| O(14) | C(3)$(x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2})$ | 3.461 |
| O(5) | O(5)$(\frac{1}{2}-x, -\frac{1}{2}-y, 1-z)$ | 3.018 |
| O(5) | C(5)$(\frac{1}{2}-x, -\frac{1}{2}-y, 1-z)$ | 3.479 |
| O(10) | O(13)$(\bar{x}, 1-y, \bar{z})$ | 3.422 |
| O(11) | O(14)$(\bar{x}, 1-y, \bar{z})$ | 3.113 |
| O(11) | O(2)$(x-\frac{1}{2}, y+\frac{1}{2}, z)$ | 3.414 |
| O(11) | C(3)$(x-\frac{1}{2}, y+\frac{1}{2}, z)$ | 3.467 |
| O(14) | O(14)$(\bar{x}, y, -\frac{1}{2}-z)$ | 3.070 |

## TABLE 10

### Bond Lengths

| Bond | Length (Å) |
|---|---|
| **Coordination of Co(II)** | |
| Co(II) - O(7) | 2.095(5) |
| Co(II) - O(8) | 2.114(5) |
| Co(II) - O(9) | 2.068(4) |
| **Coordination of Co(III)** | |
| Co(III) - O(3) | 1.926(4) |
| Co(III) - O(4) | 1.922(4) |
| Co(III) - N(1) | 1.949(5) |
| Co(III) - N(2) | 1.955(5) |
| Co(III) - N(3) | 1.870(5) |
| Co(III) - N(4) | 1.865(5) |
| **Peptide Backbone** | |
| O(1) - C(2) | 1.259(8) |
| O(2) - C(4) | 1.233(7) |
| O(3) - C(4) | 1.285(7) |
| O(4) - C(5) | 1.295(7) |
| O(5) - C(5) | 1.234(7) |
| O(6) - C(7) | 1.271(8) |

TABLE 10 - Continued

| Bond | Length (Å) |
|---|---|
| N(1) - C(1) | 1.494(9) |
| N(2) - C(8) | 1.471(8) |
| N(3) - C(2) | 1.314(8) |
| N(3) - C(3) | 1.448(8) |
| N(4) - C(6) | 1.449(8) |
| N(4) - C(7) | 1.297(8) |
| C(1) - C(2) | 1.523(9) |
| C(3) - C(4) | 1.524(9) |
| C(5) - C(6) | 1.506(9) |
| C(7) - C(8) | 1.522(9) |
| **Bond Distances Involving Hydrogens** | |
| N(1) - H(1) | 1.07 |
| N(1) - H(2) | 0.92 |
| N(2) - H(3) | 0.94 |
| N(2) - H(4) | 1.00 |
| C(1) - H(5) | 0.95 |
| C(1) - H(6) | 1.06 |
| C(3) - H(7) | 1.02 |
| C(3) - H(8) | 1.10 |
| C(6) - H(9) | 0.96 |

TABLE 10 - Continued

| Bond | Length (Å) |
|---|---|
| C(6) - H(10) | 1.06 |
| C(8) - H(11) | 0.99 |
| C(8) - H(12) | 1.02 |
| O(7) - H(13) | 0.88 |
| O(7) - H(14) | 1.35 |
| O(8) - H(15) | 1.03 |
| O(8) - H(16) | 1.06 |
| O(9) - H(17) | 1.14 |
| O(9) - H(18) | 1.06 |
| O(10) - H(19) | 0.94 |
| O(10) - H(20) | 1.16 |

## TABLE 11(a)

### Bond Angles Around Cobalt Atoms

| Atoms | Angle |
|---|---|
| **Coordination of Co(II)** | |
| O(7)-Co(II)-O(8) | 86.6(2) |
| O(7)-Co(II)-O(9) | 89.6(2) |
| O(8)-Co(II)-O(9) | 91.5(2) |
| **Coordination of Co(III)** | |
| O(3)-Co(III)-O(4) | 89.6(2) |
| O(3)-Co(III)-N(1) | 169.2(2) |
| O(3)-Co(III)-N(2) | 90.0(2) |
| O(3)-Co(III)-N(3) | 84.7(2) |
| O(3)-Co(III)-N(4) | 94.8(2) |
| O(4)-Co(III)-N(1) | 91.1(2) |
| O(4)-Co(III)-N(2) | 169.3(2) |
| O(4)-Co(III)-N(3) | 93.6(2) |
| O(4)-Co(III)-N(4) | 85.0(2) |
| N(1)-Co(III)-N(2) | 91.3(2) |
| N(1)-Co(III)-N(3) | 84.5(2) |
| N(1)-Co(III)-N(4) | 96.0(2) |

TABLE 11(a) - Continued

| Atoms | Angle |
|---|---|
| N(2)-Co(III)-N(3) | 97.0(2) |
| N(2)-Co(III)-N(4) | 84.3(2) |
| N(3)-Co(III)-N(4) | 178.6(2) |

## TABLE 11(b)

## Bond Angles of Peptide Ligands

| Ligand A | Angle | Ligand B | Angle | Average | Freeman[23]* | α-Glycylglycine[30] |
|---|---|---|---|---|---|---|
| Co(III)-N(1)-C(1) | 110.0(4) | Co(III)-N(2)-C(8) | 109.4(4) | 109.7 | 110(0.4) | |
| N(1)-C(1)-C(2) | 110.2(5) | N(2)-C(8)-C(7) | 110.4(5) | 110.3 | 111(0.6) | 110.3 |
| C(1)-C(2)-O(1) | 120.6(6) | C(8)-C(7)-O(6) | 120.4(5) | 120.5 | 119(0.5) | 120.1 |
| C(1)-C(2)-N(3) | 113.1(5) | C(8)-C(7)-N(4) | 112.8(5) | 113.0 | 115(0.5) | 116.8 |
| O(1)-C(2)-N(3) | 126.4(6) | O(6)-C(7)-N(4) | 126.7(6) | 126.6 | 126(0.5) | 123.1 |
| Co(III)-N(3)-C(2) | 119.2(4) | Co(III)-N(4)-C(7) | 119.4(4) | 119.3 | 120(0.9) | |
| Co(III)-N(3)-C(3) | 115.2(4) | Co(III)-N(4)-C(6) | 114.8(4) | 115.0 | 116(0.6) | |
| C(2)-N(3)-C(3) | 125.5(5) | C(6)-N(4)-C(7) | 125.7(5) | 125.6 | 123(0.8) | 121.6 |
| N(3)-C(3)-C(4) | 107.2(5) | N(4)-C(6)-C(5) | 108.4(4) | 107.8 | 111(0.6) | 112.7 |
| C(3)-C(4)-O(2) | 120.3(5) | C(6)-C(5)-O(5) | 121.0(5) | 120.2 | 120(1.2) | 115.6 |
| C(3)-C(4)-O(3) | 117.1(5) | C(6)-C(5)-O(4) | 116.9(5) | 117.0 | 118(1.1) | 117.6 |
| O(2)-C(4)-O(3) | 122.6(6) | O(4)-C(5)-O(5) | 122.1(5) | 122.4 | 123(0.5) | 126.7 |
| Co(III)-O(3)-C(4) | 114.7(4) | Co(III)-O(4)-C(5) | 114.5(4) | 114.6 | 115(0.5) | |

* mean bond angles in peptide ligand molecules

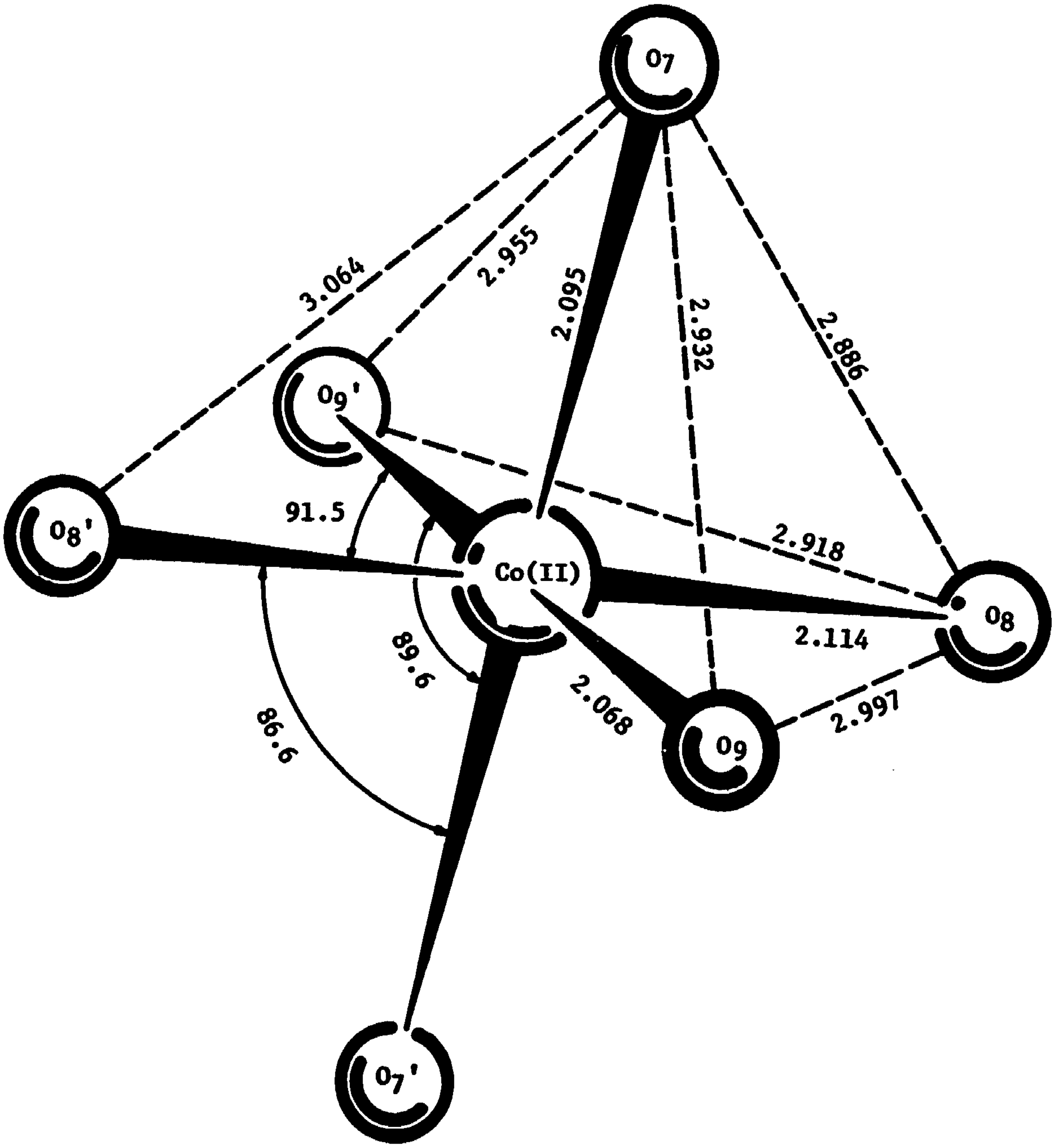


Figure 3. Configuration of $[Co^{II}(H_2O)_6]^{++}$

Plane 3. O(8)O(8')O(9)O(9')

$$0.040x + 10.676y + 3.459z = 0$$

Figure 4 shows the coordination sphere of Co(III). The edge lengths of the octahedron range from 2.56 Å between N(3) and O(3) to 2.87 Å between N(1) and N(4) with a mean value of 2.71 Å. Among the fifteen bond-angles at Co(III) made with six coordinated atoms, angles N(2)-Co(III)-N(4), N(1)-Co(III)-N(3), O(4)-Co(III)-N(4) and O(3)-Co(III)-N(3) are in the neighbourhood of 85°, which result in a distorted octahedral configuration. N(3)-Co(III)-N(4) is almost linear with a magnitude of 176.6° angle.

Figure 5 and 6 show the configuration of complex anion $Co(GG)_2^-$ with the indications of bond distances and angles respectively. All bond distances and angles of the ligands appear fairly consistent with those reviewed by Freeman[23] for peptide ligand molecules. As in similar complexes,[23] the dimensions of the complexed glycylglycine ligands are not significantly different from those of free peptides, with the exception of the C'=O and C'-N bonds in peptide groups at whose N (peptide) atoms Co(III) is bound. The C'-N bonds [ C(2)-N(3) and C(7)-N(4) ] have greater, and C'-O bonds [ C(2)-O(1) and C(7)-O(6) ] smaller, double-bond character than those in free peptides,[21] as can be seen in Table 12. The mean length of C-O (coordinated) bond is longer by 0.03 Å than those observed in α-glycylglycine. The mean Co(III)-N (amino) and Co(III)-O bond distances are compatible with value in similar complexes,[23,29] and Co(III)-N(amino) bonds (1.952 Å)

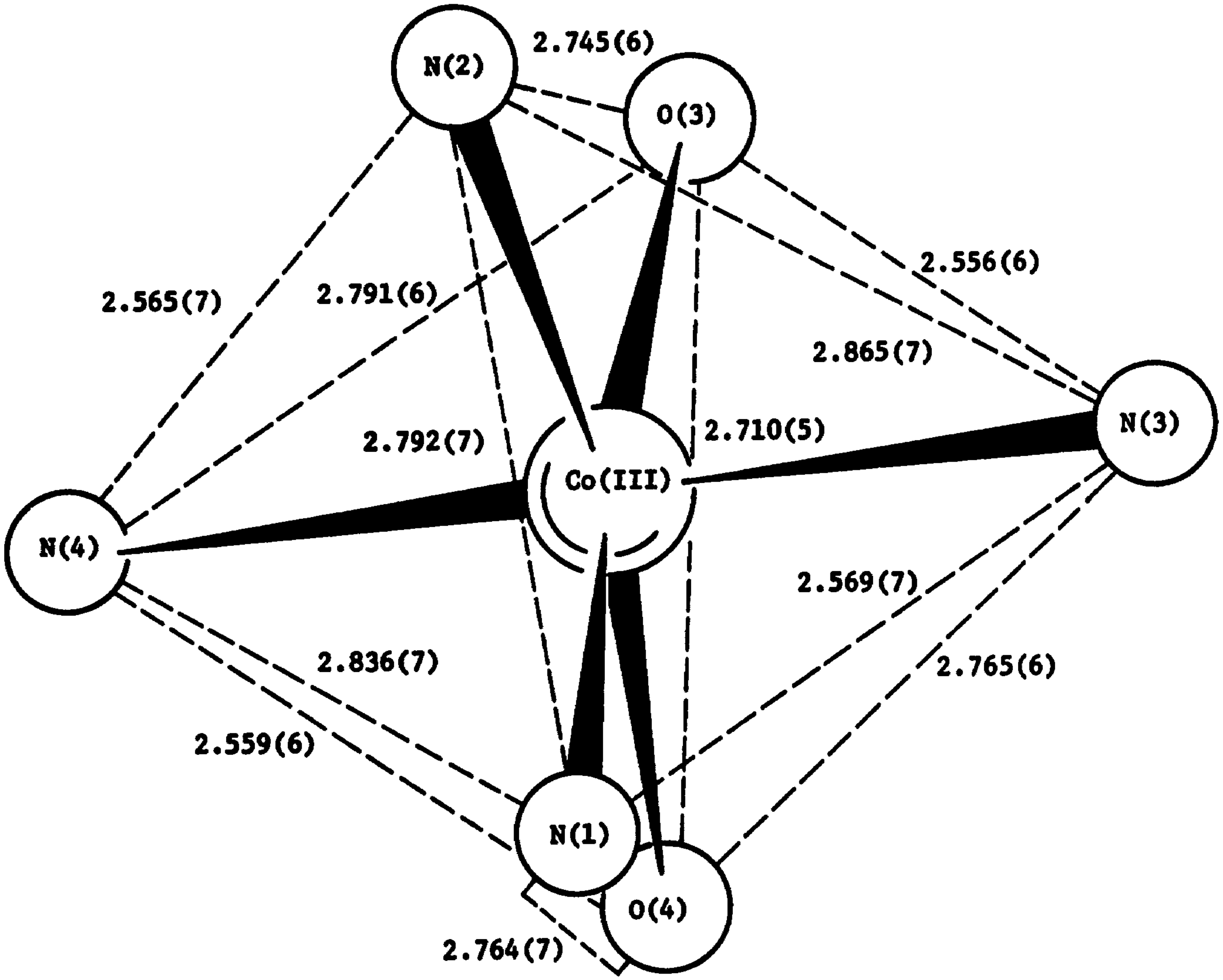


Figure 4. Coordination Sphere of Co(III)

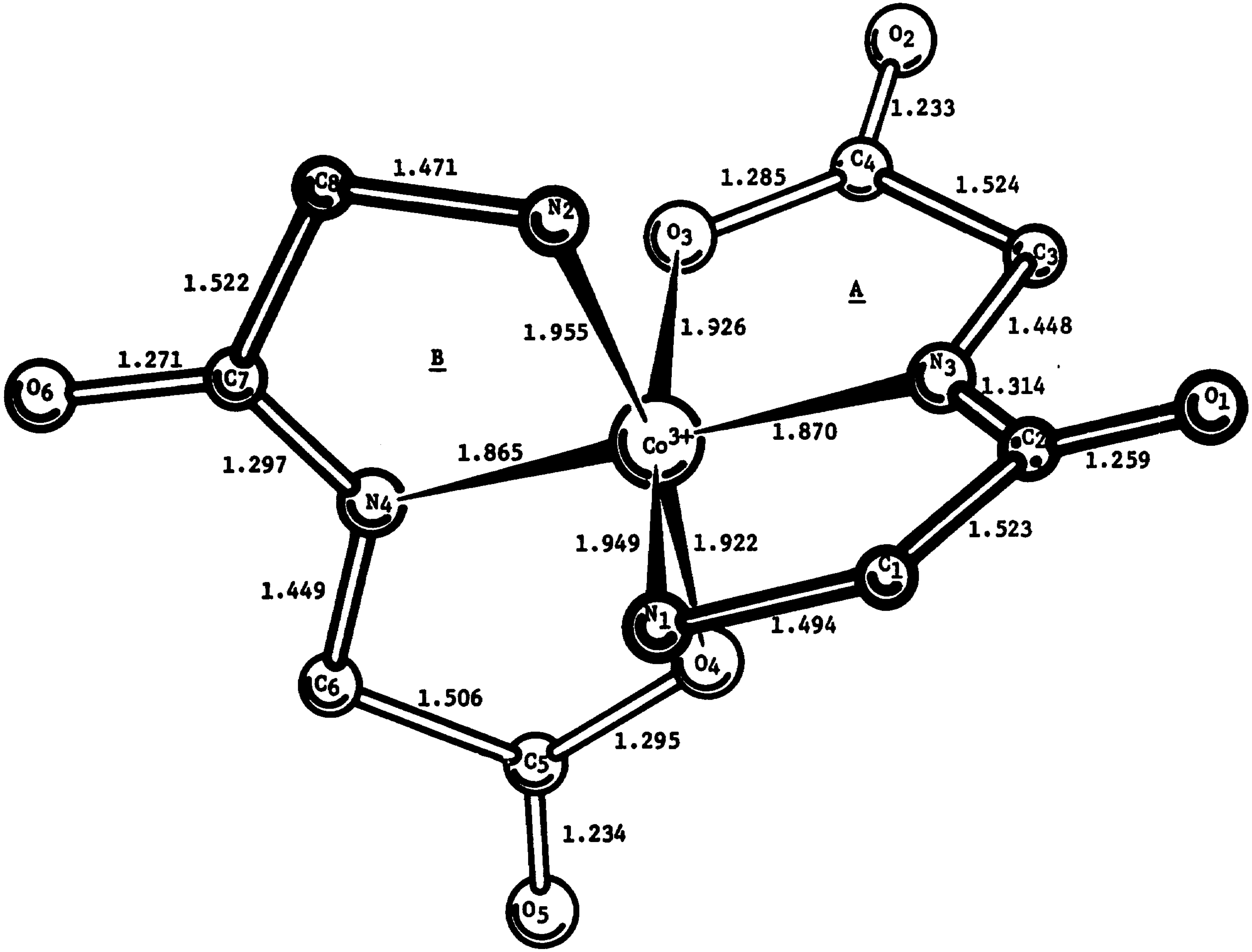


Figure 5. Bond Distances of $[Co^{III}(GG)_2]^-$

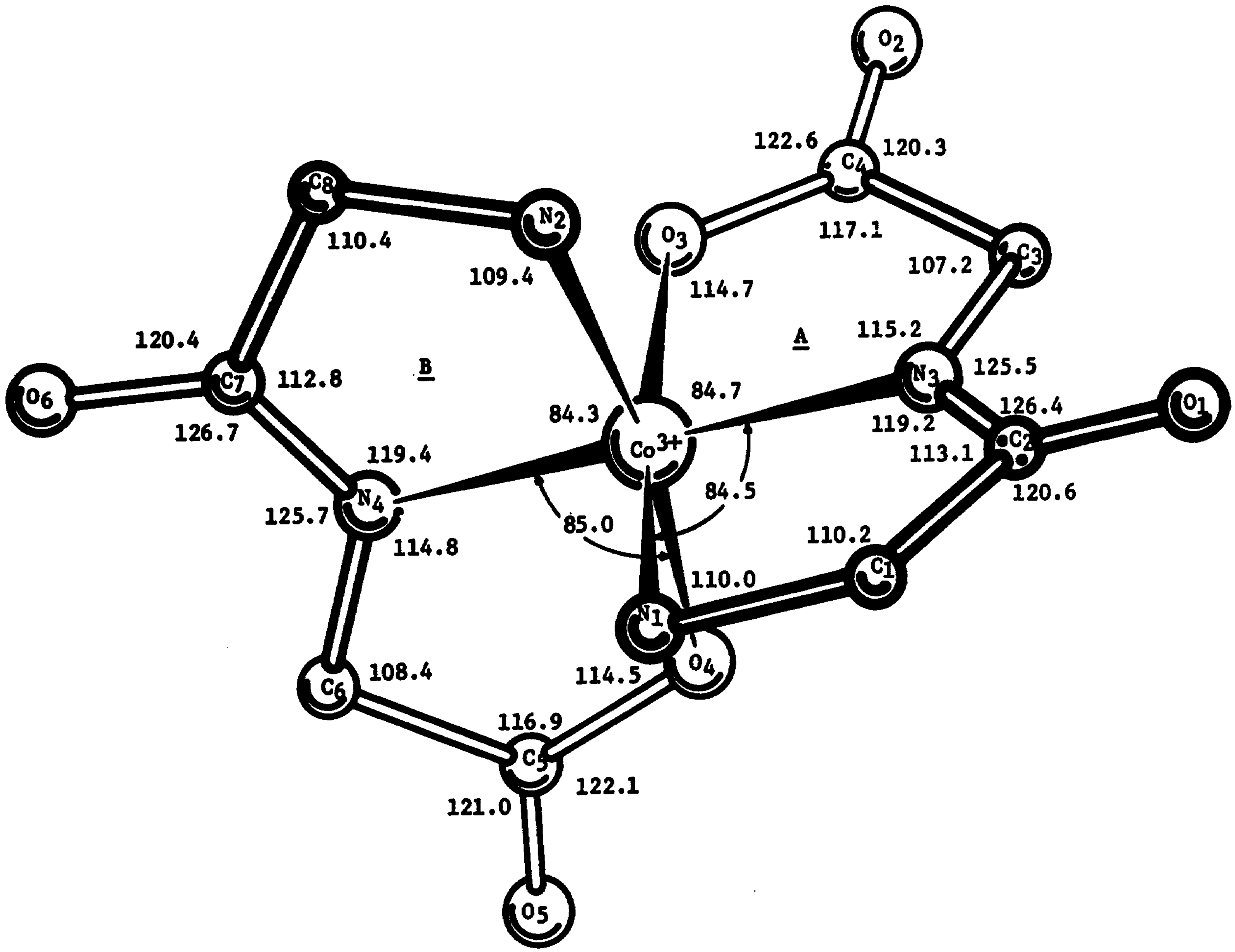


Figure 6. Bond Angles of $[Co^{III}(GG)_2]^-$

show the expected longer lengths in comparison with Co(III)-N(peptide) bonds (1.868 Å). As most of the cases, in the carboxyl group the C-O bond (1.290 Å) joining the metal ion is longer than another C-O bond (1.233 Å) by about 0.06 Å. The $C^{\alpha}$-C' and $C^{\alpha}$-C(carboxyl) bond lengths (1.522 and 1.515 Å respectively) also indicate the expected shortening in comparison with the average aliphatic C-C distance of 1.54 Å since the former cases are of the $sp^2$-$sp^3$ type while the latter the $sp^3$-$sp^3$ type of bond. The average standard deviation of bond length between heavy and light atoms is on the order of 0.005 Å and that between light and light atoms 0.008 Å. Table 12 summarizes some bond lengths in Co(III)-glycylglycine complexes, in which the mean bond lengths in complexed peptide ligands[23] and the bond lengths in free peptides[21,30] are also included in column E, F and G.

Probably the most interesting bond-angles to discuss are those around the deprotonated peptide nitrogens N(3) and N(4). Both atoms have a set of three coplanar bonds with the sum of the bond angles 360.0 and 359.9 for N(3) and N(4) respectively. Table 13 demonstrates the differences between these bond angles and others observed in structures of copper chelates of peptides where the peptide nitrogen is deprotonated. The small differences of angles between column I (the present structure) and column II might be attributed to differences in strength of the cobalt and copper coordination bonds. The values given in column II are average angles of structures made in the solution with the pH values of neutral to alkaline range. The characteristic bond

## TABLE 12

### Comparison of Bond Lengths in Co(III)-Glycylglycine Complexes[29]

| Bond | Bond - Lengths (Å) | | | | | | |
|---|---|---|---|---|---|---|---|
| | A. | B. | C. | D. | E. | F. | G. |
| Co(II)-O(water) | 2.093 | $2.09_5$ | | | | | |
| Co(III)-N(amino) | 1.952 | 1.96 | 1.96 | 1.91 | | | |
| Co(III)-N(peptide) | 1.868 | 1.87 | 1.86 | 1.94 | | | |
| Co(III)-O(carboxyl) | 1.924 | 1.94 | 1.93 | 1.98 | | | |
| $H_2N-CH_2$ | 1.483 | 1.50 | 1.50 | 1.48 | 1.49 | 1.497 | 1.487 |
| $H_2C-C$(peptide) | 1.522 | 1.52 | 1.49 | 1.52 | 1.53 | 1.528 | 1.51 |
| C=O(peptide) | 1.265 | $1.26_5$ | $1.26_5$ | 1.36 | 1.26 | 1.249 | 1.24 |
| C-N(peptide) | 1.305 | 1.30 | 1.31 | 1.25 | 1.30 | 1.328 | 1.325 |
| $-N-CH_2$ | 1.449 | 1.46 | 1.46 | 1.41 | 1.46 | 1.462 | 1.445 |
| $H_2C-C$(carboxyl) | 1.515 | 1.53 | 1.52 | 1.54 | 1.52 | 1.516 | 1.527 |
| C=O(carboxyl) | 1.233 | 1.24 | 1.24 | 1.29 | 1.24 | 1.239 | 1.253 |
| C-O(carboxyl) | 1.290 | $1.28_5$ | $1.28_5$ | 1.21 | 1.28 | 1.262 | 1.252 |

A: Present structure
B: $[Co(II)(H_2O)_6][Co(III)(GG)_2]_2 \cdot 12H_2O$
C: $Ba[Co(III)(GG)_2]_2 \cdot nH_2O$(n = 12-17)
D: $Co(GGH)_2ClO_4$
E: mean bond lengths in peptide ligand molecules.[23]
F: α-Glycylglycine.[30]
G: weighted mean values in free peptides.[21]
Estimated s.d.'s = 0.007 Å for metal--light-atom bond lengths, 0.01 Å for light-atom--light-atoms in B, C, E; 0.01 Å and 0.015 Å, respectively, in D; 0.005 Å and 0.01 Å, respectively, in A. E.s.d.'s = 0.007 Å in F.

## TABLE 13

### Comparison of Bond Angles Around Deprotonated Peptide Nitrogen

| | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| M N C' | 119.3 | 120 | 115 | 116 | 136 | |
| M N $C_\alpha$ | 115.0 | 116 | 127 | 127 | 109 | |
| C' N $C_\alpha$ | 125.6 | 123 | 117 | 116 | 115 | 122 |

M: Metal ion

I: Present structure

II: Adjacent carboxyl group is bonded to the same metal ion (Freeman[23])

III: Adjacent carboxyl group is not bonded to the same metal ion (Freeman[23])

IV: Dipotassium bis (glycylglycinato) cuprate (II) hexahydrate[31]

V: $Cu_2$ (gly-l-leu-l-tyr)[32]

VI: Free Peptide[30,33]

angles, however, depend on whether or not the N(peptide) atom is shared by two neighboring 5-membered chelate rings. If the carboxyl group adjacent to N(peptide) is not bonded to the same metal to form the second ring the bond angles about N(peptide) change significantly as seen in column III and IV. But it should be realized that those results are from structures prepared at high pH values. An entirely different type of chelation is encounted in $Cu_2$ (gly-l-leu-l-tyr)$_2$, the bond angles change drastically as indicated in column V. The latter type of chelation, however, was observed in crystals prepared from the solution with neutral pH value. The configurations about the peptide C atoms [ C(2) and C(7) ] and carboxyl C atoms [ C(4) and C(5) ] are also trigonal in nature with the sum of the bond angles about 360° in accordance with those observed in free peptides.[23,30] The last two colums in Table 11(b) are bond angles of complexed peptides given by Freeman[23] and that of α-glycylglycine reported by Biswas et al.,[30] respectively.

The chelate ring angles are listed as follows:

| (1) | | (2) | |
|---|---|---|---|
| N(1)-Co(III)-N(3) | 84.5 | N(3)-Co(III)-O(3) | 84.7 |
| Co(III)-N(1)-C(1) | 110.0 | Co(III)-N(3)-C(3) | 115.2 |
| N(1)-C(1)-C(2) | 110.2 | N(3)-C(3)-C(4) | 107.2 |
| C(1)-C(2)-N(3) | 113.1 | C(3)-C(4)-O(3) | 117.1 |
| C(2)-N(3)-Co(III) | 119.2 | C(4)-O(3)-Co(III) | 114.7 |
| Sum | 537.0 | | 538.9 |

| (3) | | (4) | |
|---|---|---|---|
| N(2)-Co(III)-N(4) | 84.3 | N(4)-Co(III)-O(4) | 85.0 |
| Co(III)-N(2)-C(8) | 109.4 | Co(III)-N(4)-C(6) | 114.8 |
| N(2)-C(8)-C(7) | 110.4 | N(4)-C(6)-C(5) | 108.4 |
| C(8)-C(7)-N(4) | 112.8 | C(6)-C(5)-O(4) | 116.9 |
| C(7)-N(4)-Co(III) | 119.4 | C(5)-O(4)-Co(III) | 114.5 |
| Sum | 536.3 | | 539.6 |

The extent of deviation from the planarity of the 5-membered rings can be seen from the sums of the inner angles of the chelate rings. This non-planarity can also be understood from the least-squares plane calculation (vide infra). The buckling of the rings falls in the following order:

Ring (3) > Ring (1) > Ring (2) > Ring (4)

It can be seen from Table 11(b) some significant differences in bond angles do exist between complexed glycylglycine and free glycylglycine molecules probably in order to accomodate the chelate ring formation for the former case.

Table 14 presents some least-squares planes pertinent to the structure. It is an interesting aspect of the complex anion that three coordination bonds of Co(III) with each glycylglycine--Co(III)-N(amino), Co(III)-N(peptide) and Co(III)-O(carboxyl)--are essentially coplanar within experimental error. Plane 1 was calculated with Co(III), N(1), N(3) and O(3) atoms of the peptide molecule A the average deviation of atoms from the least-squares plane 1 is 0.0001 Å.

## TABLE 14

## Least-Squares Planes

### A. Coordination of Co(III)

Plane (1): $6.550x - 6.925y + 8.758z = 4.005$

| Atom | Co(III) | N(1) | N(3) | O(3) | N(4)* |
|---|---|---|---|---|---|
| Dev.(Å) | 0.0002 | -0.0001 | 0.0000 | -0.0001 | (0.0442) |

Plane (2): $1.200x + 8.482y + 8.307z = 3.535$

| Atom | Co(III) | N(2) | N(4) | O(4) | N(3)* |
|---|---|---|---|---|---|
| Dev.(Å) | 0.015 | -0.008 | 0.002 | -0.008 | (0.011) |

### B. Peptide Groups

Plane (3): $8.106x - 5.228y + 9.648z = 4.971$

| Atom | C(1) | C(2) | O(1) | N(3) | C(3) | Co(III)* | N(1)* |
|---|---|---|---|---|---|---|---|
| Dev.(Å) | 0.005 | 0.000 | -0.002 | -0.011 | 0.007 | -0.128 | 0.222 |

Plane (4): $0.045x + 9.396y + 6.982z = 2.842$

| Atom | C(8) | C(7) | O(6) | N(4) | C(6) | Co(III)* | N(2)* |
|---|---|---|---|---|---|---|---|
| Dev.(Å) | -0.029 | 0.023 | -0.002 | 0.041 | -0.033 | (0.046) | (0.310) |

### C. Carboxyl Groups

Plane (5): $4.572x - 7.256y + 9.033z = 3.549$

| Atom | C(3) | C(4) | O(2) | O(3) | Co(III)* | N(3)* |
|---|---|---|---|---|---|---|
| Dev.(Å) | 0.001 | -0.005 | 0.002 | 0.002 | -0.035 | -0.191 |

Plane (6): $2.471x + 8.514y + 7.998z = 3.790$

| Atom | C(6) | C(5) | O(4) | O(5) | Co(III)* | N(4)* |
|---|---|---|---|---|---|---|
| Dev.(Å) | 0.001 | -0.004 | 0.001 | 0.001 | 0.021 | -0.092 |

TABLE 14-Continued

**D. Peptide Ligand Molecules**

Plane (7): $7.674x - 6.267y + 8.986z = 4.437$

| Atom | N(1) | C(1) | C(2) | O(1) | N(3) |
|---|---|---|---|---|---|
| Dev.(Å) | 0.140 | -0.148 | -0.036 | -0.076 | 0.088 |
| Atom | C(3) | C(4) | O(2) | O(3) | Co(III)* |
| Dev.(Å) | 0.238 | -0.009 | -0.078 | -0.118 | (0.002) |

Plane (8): $0.145x + 8.818y + 7.975z = 3.128$

| Atom | N(2) | C(8) | C(7) | O(6) | N(4) |
|---|---|---|---|---|---|
| Dev.(Å) | 0.147 | -0.194 | -0.014 | -0.023 | 0.090 |
| Atom | C(6) | C(5) | O(5) | O(4) | Co(III)* |
| Dev.(Å) | 0.148 | -0.013 | -0.063 | -0.078 | (0.052) |

**E. Five-Membered Rings**

Plane (9): $8.572x - 5.889y + 8.967z = 4.803$

| Atom | Co(III) | N(1) | C(1) | C(2) | N(3) | O(1)* |
|---|---|---|---|---|---|---|
| Dev.(Å) | -0.091 | 0.119 | -0.100 | 0.006 | 0.067 | 0.019 |

Plane (10): $5.155x - 6.776y + 9.353z = 3.768$

| Atom | Co(III) | N(3) | C(3) | C(4) | O(3) | O(2)* |
|---|---|---|---|---|---|---|
| Dev.(Å) | 0.044 | -0.070 | 0.066 | -0.022 | -0.018 | -0.073 |

Plane (11): $1.380x - 9.057y - 7.760z = -2.791$

| Atom | Co(III) | N(2) | C(8) | C(7) | N(4) | O(6)* |
|---|---|---|---|---|---|---|
| Dev.(Å) | 0.085 | -0.128 | 0.124 | -0.035 | -0.045 | -0.097 |

Plane (12): $1.888x + 8.605y + 7.991z = 3.623$

| Atom | Co(III) | N(4) | C(6) | C(5) | O(4) | O(5)* |
|---|---|---|---|---|---|---|
| Dev.(Å) | 0.031 | -0.044 | 0.038 | -0.006 | -0.018 | -0.016 |

* atom not included the L.S. plane calculation.

N(4) is out of plane 1 by about 0.044 Å. Plane 2 is likewise calculated with Co(III), N(2), N(4) and O(4) atoms of the peptide molecule B. The average deviation of atoms from the least-squares plane 2 is 0.008 Å. The distance of N(3) to the plane 2 is about 0.011 Å. Plane 1 intersects plane 2 at an angles of 89.9°. Co(III)-N(1), Co(III)-N(2), Co(III)-O(3) and Co(III)-O(4) bonds are not coplanor. As a result, the coordination at Co(III) is a distorted octahedron. The mean deviation of atoms from the least-squares plane calculated with N(1), N(2), O(3) and O(4) is 0.181 Å.

The extent of deviations from planarity for the peptide groups, $C^{\alpha}C'ON$ which are "invariably planar[33]" in free peptides, are shown in Table 14 (plane 3 and 4). Peptide group C(1)C(2)O(1)N(3)C(3) is planar, however, peptide group C(8)C(7)O(6)N(4)C(6) definitely is not planar. The cobalt (III) atom lies out of the peptide unit plane 3 and 4 by -0.128 Å and 0.046 Å. The terminal N(1) and N(2) stay at the distances of 0.222 Å and 0.310 Å from the plane 3 and 4 respectively.

The carboxyl groups are certainly planar within the limits of experimental accuracy. The largest deviation is on the order of 0.005 Å at the carboxyl carbon. The cobalt (III) atom is at a distance from the planes composed of the carboxyl groups by a mean value of 0.028 Å and the peptide N atoms swing out of the respective carboxyl planes with a mean value of 0.142 Å.

Planes 9 to 12 were calculated for the five-membered chelate rings. The deviations of atoms from the planes illustrate that the chelate rings are not planar as described previouly. N(2) deviates the most from the plane by 0.128 Å. Finally, the distances of the peptide atoms from the least-squares planes 7 and 8 also demonstrate the extent of the deviation from planarity for the complexed peptide molecules. The average deviation is about 0.095 Å. Plane 7 and plane 8 intersect at an angle of 89.5 Å.

The magnitude of the principal axes of the vibration ellipsoids of atoms are present in Table 15 along with the direction cosines with respect to the cell edges. For computational and interpretational convenience it has become customary to assign six "temperature" parameters[62,63] to each atom, these six parameters defining an ellipsoid whose three (mutually perpendicular) principal axes may have varing lengths (amplitudes of atomic motion) and orientation. Ignoring systematic errors in the experimental data, which can give rise to spurious temperature factors, the orientation of the vibration ellipsoids have been found to be closely related to the geometry of the molecule. In the present structure the vibration ellipsoids implied by the temperature-factor parameters are generally in agreement with those to be expected on the basis of the geometry of the complex molecule and the intermolecular packing. The unbonded water molecules have large anisotropic thermal motion; particularly, for $H_2O(11)$, a very long ellipsoidal axis was observed probably due to disorder. The location of $H_2O(11)$ is most likely not precisely the same in the two hydrogen bonding schemes. Each coordinated water molecule is involved in two hydrogen bonds, and has moderate thermal motion with the exception of $H_2O(7)$ which is hydrogen-bonded to the disordered $H_2O(12)$

## TABLE 15

## Principle Axes and Direction Cosines of Anisotropic Ellipsoids

| Atom | B | $l_1$ | $l_2$ | $l_3$ |
|---|---|---|---|---|
| Co(II) | 2.74 | 0.329 | 0.886 | 0.235 |
| | 2.52 | 0.911 | -0.207 | -0.570 |
| | 1.87 | 0.247 | -0.414 | 0.787 |
| Co(III) | 2.35 | 0.947 | -0.319 | -0.216 |
| | 2.01 | 0.318 | 0.933 | -0.245 |
| | 1.37 | 0.037 | 0.169 | 0.945 |
| O(1) | 5.88 | 0.282 | -0.593 | 0.661 |
| | 3.59 | -0.485 | 0.590 | 0.745 |
| | 2.33 | 0.828 | 0.548 | -0.088 |
| O(2) | 5.47 | 0.937 | -0.143 | 0.075 |
| | 2.97 | -0.297 | -0.804 | 0.573 |
| | 1.89 | -0.181 | 0.577 | 0.816 |
| O(3) | 2.97 | 0.922 | -0.379 | -0.154 |
| | 2.31 | 0.291 | 0.548 | -0.832 |
| | 2.03 | 0.256 | 0.745 | 0.533 |
| O(4) | 3.03 | 0.450 | 0.878 | 0.046 |
| | 2.83 | 0.884 | -0.411 | -0.435 |
| | 1.84 | 0.129 | -0.244 | 0.899 |
| O(5) | 4.25 | 0.998 | -0.040 | -0.206 |
| | 3.43 | 0.019 | 0.906 | 0.404 |
| | 1.75 | -0.055 | -0.420 | 0.891 |
| O(6) | 5.51 | -0.026 | 0.978 | 0.208 |
| | 3.19 | -0.391 | -0.201 | 0.967 |
| | 2.51 | 0.920 | -0.058 | 0.147 |
| N(1) | 3.34 | -0.637 | 0.747 | -0.025 |
| | 2.98 | 0.769 | 0.633 | -0.276 |
| | 1.77 | -0.053 | 0.201 | 0.961 |
| N(2) | 3.13 | 0.955 | 0.284 | -0.151 |
| | 2.20 | -0.272 | 0.953 | -0.060 |
| | 1.97 | -0.121 | 0.102 | 0.987 |

TABLE 15 - Continued

| Atom | B | $l_1$ | $l_2$ | $l_3$ |
|---|---|---|---|---|
| N(3) | 3.33 | 0.904 | -0.304 | 0.067 |
| | 2.43 | 0.427 | 0.678 | -0.686 |
| | 1.71 | -0.021 | 0.670 | 0.725 |
| N(4) | 2.92 | 0.902 | 0.348 | -0.472 |
| | 2.74 | -0.325 | 0.937 | 0.204 |
| | 1.81 | 0.284 | -0.032 | 0.858 |
| C(1) | 4.34 | 0.789 | -0.422 | 0.236 |
| | 3.23 | -0.569 | -0.230 | 0.906 |
| | 2.23 | 0.231 | 0.877 | 0.351 |
| C(2) | 3.23 | 0.837 | -0.540 | -0.118 |
| | 2.80 | 0.494 | 0.817 | 0.166 |
| | 2.28 | -0.236 | -0.204 | 0.979 |
| C(3) | 3.20 | 0.771 | -0.102 | 0.418 |
| | 2.88 | -0.451 | -0.785 | 0.524 |
| | 1.96 | -0.450 | 0.612 | 0.742 |
| C(4) | 3.35 | 0.975 | 0.202 | -0.334 |
| | 2.46 | -0.159 | 0.927 | 0.368 |
| | 1.65 | 0.157 | -0.316 | 0.868 |
| C(5) | 2.92 | 0.895 | -0.444 | -0.268 |
| | 2.22 | 0.389 | 0.827 | -0.490 |
| | 1.75 | 0.220 | 0.344 | 0.830 |
| C(6) | 4.20 | -0.440 | 0.894 | 0.188 |
| | 2.71 | 0.890 | 0.423 | -0.058 |
| | 1.86 | -0.115 | -0.147 | 0.980 |
| C(7) | 3.27 | 0.511 | 0.784 | -0.468 |
| | 2.85 | 0.854 | -0.418 | 0.087 |
| | 1.85 | -0.094 | 0.458 | 0.880 |
| C(8) | 3.64 | 0.855 | 0.486 | -0.388 |
| | 3.05 | -0.411 | 0.848 | 0.425 |
| | 2.02 | 0.316 | -0.211 | 0.818 |

TABLE 15 - Continued

| Atom | B | $l_1$ | $l_2$ | $l_3$ |
|---|---|---|---|---|
| O(7) | 7.63 | 0.849 | -0.166 | 0.275 |
| | 4.45 | -0.521 | -0.416 | 0.851 |
| | 2.92 | -0.085 | 0.894 | 0.447 |
| O(8) | 4.57 | 0.046 | 0.999 | -0.039 |
| | 3.15 | 0.624 | -0.006 | 0.602 |
| | 2.70 | 0.780 | -0.054 | -0.797 |
| O(9) | 4.53 | 0.756 | 0.655 | -0.181 |
| | 3.75 | -0.612 | 0.703 | 0.503 |
| | 2.25 | 0.233 | -0.277 | 0.845 |
| O(10) | 8.08 | 0.752 | -0.633 | -0.367 |
| | 5.76 | 0.229 | -0.014 | 0.886 |
| | 3.80 | 0.618 | 0.774 | -0.284 |
| O(11) | 15.60 | 0.344 | -0.300 | 0.777 |
| | 3.62 | 0.587 | 0.808 | -0.101 |
| | 0.96 | 0.733 | -0.506 | -0.622 |

and as a result shows relatively high anisotropy of atomic vibration. In the peptide backbone, the atoms that form bonds to two or three neighboring atoms generally have smaller amplitudes of vibration than do terminal atoms, such as carbonyl oxygen O(1), O(2), O(5) and O(6). The largest components of vibration for O(1) and O(6) are more or less perpendicular to the related planes of the peptide units (81.5° and 60.0° respectively) while the ones for O(2) and O(5) are close to the planes of the carboxyl groups (30.5° and 5.6°) as can be seen in Figure 7.

The conformation angles for the glycylglycine ligands are presented in Table 16 and the labeling of these angles is also indicated in Figure 8. The sense of rotation is such that the angles are positive for a right-handed rotation; when looking along any bond, the far end rotates clockwise relative to the near end as proposed for polypeptide conformation by various authors[34] in the 1965 Gordon Conference on Proteins. The standard conformation represents the fully stretched polypeptide chain which corresponds to $\phi=\psi=\omega=0$. The conformation angles $\phi$, $\psi$ and $\omega$ defined here for the complexed peptides are similar to those proposed for free polypeptides considering that the hydrogen bound to the peptide nitrogen is replaced by the metal ion. This conformation can be described by the following relationship: $C^{\alpha}$-C' bond cis to N-Co(III) bond with respect to rotation around the N-$C^{\alpha}$ bond ($\phi$); N-$C^{\alpha}$ bond cis to C'-O bond with respect to rotation around the $C^{\alpha}$-C' bond ($\psi$); and C'-O bond trans to N-Co(III) bond with respect to rotation around the N-C' bond ($\omega$).

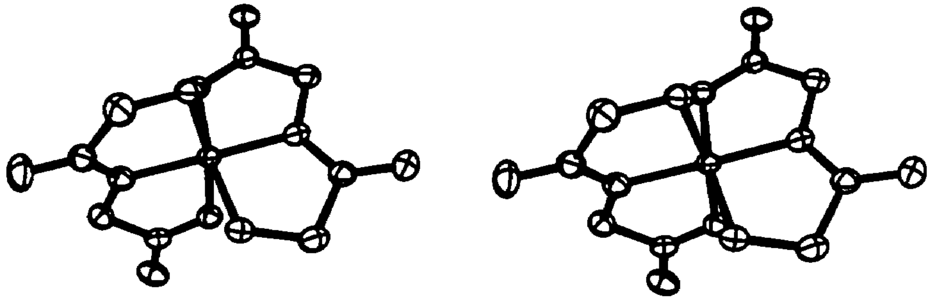


**Figure 7. A Stereoscopic View of $[\mathrm{Co}^{III}(\mathrm{GG})_2]^-$**

## TABLE 16

### Conformation Angles of Peptide Ligands*

| Angle | Atoms | Angle | Atoms | Angle | Configuration | β-GG[35,37] |
|---|---|---|---|---|---|---|
| | **Peptide Ligand A** | | **Peptide Ligand B** | | | |
| | Co(III)N(1)-C(1)C(2) | 342.8 | C(7)C(8)-N(2)Co(III) | 20.5 | cis | |
| $\psi_1$ | N(1)C(1)-C(2)O(1) | 188.8 | O(6)C(7)-C(8)N(2) | 167.5 | cis | 330.8 |
| | N(1)C(1)-C(2)N(3) | 9.3 | N(4)C(7)-C(8)N(2) | 345.1 | cis | |
| $\omega$ | Co(III)N(3)-C(2)O(1) | 4.3 | O(6)C(7)-N(4)Co(III) | 359.0 | trans | 1.3 |
| $\upsilon^{\circ}$ | C(3)N(3)-C(2)O(1) | 1.7 | O(6)C(7)-N(4)C(6) | 3.4 | cis | 355.6 |
| | C(1)C(2)-N(3)C(3) | 1.2 | C(8)C(7)-N(4)C(6) | 6.0 | trans | |
| | C(1)C(2)-N(3)Co(III) | 3.8 | C(8)C(7)-N(4)Co(III) | 1.5 | cis | |
| $\phi_2$ | Co(III)N(3)-C(3)C(4) | 11.6 | C(5)C(6)-N(4)Co(III) | 353.0 | cis | 357.7 |
| | C(2)N(3)-C(3)C(4) | 194.1 | C(5)C(6)-N(4)C(7) | 168.8 | cis | |
| $\psi_2$ | N(3)C(3)-C(4)O(2) | 172.5 | O(5)C(5)-C(6)N(4) | 183.5 | cis | 184.7 |
| | N(3)C(3)-C(4)O(3) | 351.5 | O(4)C(5)-C(6)N(4) | 4.3 | cis | 0.2 |
| | Co(III)O(3)-C(4)O(2) | 180.8 | O(5)C(5)-O(4)Co(III) | 181.0 | cis | |
| | Co(III)O(3)-C(4)C(3) | 1.8 | C(6)C(5)-O(4)Co(III) | 0.21 | cis | |

* trans-Configuration = 180°

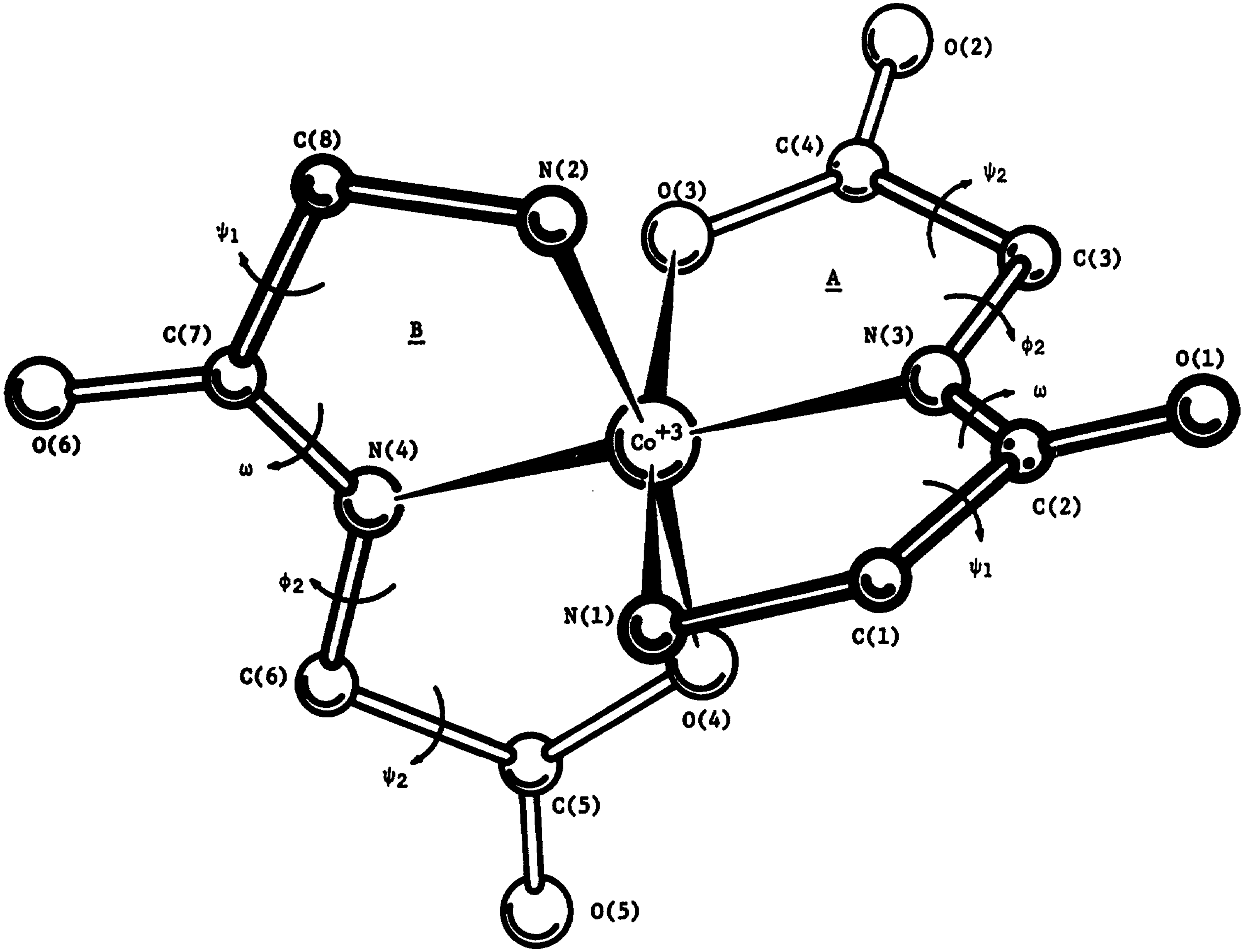


Figure 8. Labeling of Conformational Angles

The $\phi$ angle for the terminal nitrogen residue is usually not defined. Thus there is only one $\psi$ angle for the first residue of each glycylglycine ligand. At the last residue of glycylglycine there are one $\phi$ and two $\psi$ angles; however, the $\psi$ angle related to C=O was chosen for the examination of the conformation map predicted with theoretical values. The conformation angles $\phi$ and $\psi$ for both glycylglycine ligands in the cobalt complex lie in the "disallowed" region as indicated in the conformation map for glycyl residues reported by Ramachandran et al.[35,36] for angle $N-C^{\alpha}-C'(\tau)=110°$. This can be expected for a chelate ring, such as Co(III)O(3)C(4)C(3)N(3) or Co(III) O(4)C(5)C(6)N(4), formed at high pH value in a solution. If the $\tau$ angle is decreased at the $\alpha$-carbon atom, so is the allowed conformation for the peptides.

In the present structure, the C'-O (peptide) bonds are trans to Co(III)-N (peptide) bonds as the trans conformation of the peptide units in the free peptide molecules. The values of $\phi$ are approximately within $\pm 15°$ and the values of $\psi$ are in the vicinity of 170° compatible with those compiled for glycine and glycyl residue by Ramachandran.[35] The conformation angles of $\beta$-glycylglycine[37] are also included in Table 16. The aspect of nonplanarity of a peptide unit may be seen from the dihedral angle $\omega$. C(2)-O(1) bond rotates 4.3° out of the plane composed of Co(III), N(3) and C(2) atoms, likewise C(7)-O(6) bond 1° away from the plane through Co(III), N(4) and C(7) atoms. These conformation angles also illustrate that the peptide groups in the cobalt complex are not quite planar.

# CHAPTER 5

## SUMMARY AND CONCLUSION

The crystal and molecular structure of cobalt with glycylglycine was determined by X-ray diffraction using the heavy-atom method and Fourier syntheses and refined by three-dimensional least-squares techniques. The final reliability index for all reflections is 0.060. No molecular oxygen was found in the structure but cobalt atoms in two oxidation states with various ligands were observed. The structure contains two Co(III) and one Co(II) atoms. The former, each chelated with two independent terdentate glycylglycines, lie at the general positions, whereas the latter, coordinated with six water molecules, occupy the special positions---the origin and the equivalent positions. The cobalt coordinations are octahedral. In the crystal, there are well defined layers of $Co(H_2O)_6^{2+}/H_2O$ and $Co(GG)_2^-$ complex ions; the former layers are hydrophilic regions and the latter layers are hydrophobic regions. Each complex ions is joined to its neighbors by hydrogen bonds. All bond-lengths and bond-angles appear normal. The peptide units remain planar and the deprotonated peptide nitrogens remain trigonal as they are in the free peptides despite the change in coordination, apparently in order to preserve the resonance energy of the amide groups.[23] Bisglycylglycine ligands almost lie in plane at right angle to each other, the largest deviation of atom from the least-squares plane of glycylglycine is on the order of 0.24 Å. The $Co(GG)_2^-$ complex anion in the present structure differs from that observed in $NH_4[Co(GG)_2]\cdot 2H_2O$ by Gillard,[13] in that the Co(III) atom lie in general not in special positions, so that the two glycylglycine ligands are not related by strict $C_2$ symmetry as required by the space group for the latter structure. Some fractional molecules of water were observed in the interstitial sites of the crystal. In conclusion the end product of the oxygenation of glycylglycine-Co(II) mixture in alkaline solution is a Co(III) complex in lieu of an irreversible oxygen adduct as previously reported.[4] The present evidence suggests that the purple-red crystal types so far characterized contain no molecular oxygen, and that the real oxygen carrier may be a brown intermediate complex reported by Tanford et al.[7]

# PART II

# THE REFINEMENT OF CIS-1,2-CYCLOBUTANE DICARBOXYLIC ACID

## CHAPTER 1

## INTRODUCTION

The studies of the structures of cyclobutane derivatives have given rise to some interesting problems: the conformations of the four-membered ring, the lengthened C-C bonds and the thermal vibrations of the ring atoms as well as the atoms in the side chains.

Cyclobutane ring exists in both planar and puckered conformations. In accordance with a number of investigations, the puckered conformation seems more favorable than the planar one. However, planar rings have been found in compounds such as tetraphenylcyclobutane,[38,39] octahydroxycyclobutane,[40] trans-1,3-cyclobutanedicarboxylic acid,[41,72] cis, trans, cis-1,2,3,4-tetracynocyclobutane,[42] and cis, trans, cis-1,2,3,4-cyclobutanetetracarboxylic acid.[43] It is interesting to note that all of these molecules have a center of symmetry which is retained as a crystallographic element of symmetry. On the other hand, X-ray structures of perchlorocyclobutane,[39,44] cis-and trans-1,2-dibromo-1,2-dimethoxy-carbonyl-cyclobutane,[45] cis-1,3-cyclobutanedicarboxylic acid,[46] trans-1,2-cyclobutanedicarboxylic acid,[47] and cyclobutane-1,1-dicarboxylic acid[48] provide examples of the puckered form. A surprising case has been reported by Adman and Margulis[74] for the disodium salt of trans-1,3-cyclobutanedicarboxylic acid. The neutral acid, previously reported as planar conformer,[41] now is found to be puckered while the dianion has a planar cyclobutane ring. The dihedral angles of the puckered form are in the vicinity of 150 degrees. In the solid state, probably a combination of the intermolecular forces and the characteristics of a molecule determine the ring conformation.

Cyclobutane structures were also studied by other techniques such as electron diffraction,[49-53] nmr splitting patterns,[54,55] microwave,[56,57,68] and infrared-Raman spectroscopy.[58-60,70] However, the conclusions drawn depend to a great extent on the interpretation of the spectral data.

The conformation of cyclobutane itself was originally described as planar by Wilson[61] until Dunitz and Schomaker[49] described it as puckered as a result of an electron diffraction study. This controversy was resolved by an infrared-Raman experiment of Rathjens and his coworkers.[58] A barrier height of about 400 $cm^{-1}$ to the planar configuration was calculated for cyclobutane. Those molecules in vibrational states having an energy below this value will posses $D_{2d}$ symmetry (puckered form); the molecules with a higher energy than the barrier will have $D_{4h}$ symmetry (planar form). The average ring conformation of cyclobutane itself in the gas phase at any given time is therefore non-planar. It appears that in the solid state the puckered form of the ring is permanently bent. Edgell[59] and Claassen[60] concluded from infrared-Raman studies that gaseous octafluorocyclobutane is planar. Electron diffraction data, however, again required a molecule of lower symmetry of $D_{2d}$. The extent of deviations from planarity might be a sensitive function of the nature of any ring substitution due to the repulsions of nonbonded atoms[49,54] at the expense of the ring strain.

The evidence of lengthened C-C bonds in cyclobutane rings have been reported in a number of structures. Values as exceptionally high as 1.60 ± 0.04 and 1.63 ± 0.02 Å were given in the case of perfluorocyclobutane by electron diffraction method.[51,52] However, the standard deviations are rather high. Chang and his coworkers[53] have redetermined the structure and given a C-C distance of 1.566 ± 0.008 Å, which is within the experimental error of the earlier values. The C-C bond length of cyclobutane itself of the earlier work[49] was reported as 1.568 Å ± 0.02 Å, which was revised to 1.548 ± 0.03 Å by a sectored electron diffraction reinvestigation.[50] In perchlorocyclobutane and in the tetraphenyl compound least squares refinements[39] of the early X-ray diffraction data showed that C-C separations were shorter than those given in the original report by 0.02 Å and 0.013 Å, respectively, for the longest C-C bond in each compound. However the differences in length are on the order of the standard deviation(0.015 Å).

It is worth noting that the oxygen atoms of the carboxyl group or groups on the cyclobutane ring typically show a large anisotropy, with the major axis oriented perpendicular to the plane of the carboxylic acid group. In view of the consistency of this pattern of temperature anisotropies, it must be concluded that they seem to represent librations[75] around the C-C bond of the carboxylic acid group, as opposed, say to lattice vibration (which would have parallel effects on all the atoms) or to unknown experimental errors.

To gain more information on the cyclobutane system we have determined the crystal structure of cis-1,2-cyclobutane-dicarboxylic acid.

# CHAPTER 2

## EXPERIMENTAL

A sample of cis-1,2-cyclobutanedicarboxylic acid, m.p. 139-140°, was kindly furnished by Dr. J. J. Bloomfield. Because there was uncertainty about the accuracy of the old data, the intensities were remeasured. A prismatic crystal of the size 0.17 x 0.35 x 0.27 mm with a mozaic spread of about 0.5° was mounted on a glass fiber along the b-axis. All X-ray diffraction data were collected on this crystal. The crystals are monoclinic and belong to the space group $P2_1/c$ (extinction of h0l reflections for l=2n and 0k0 reflections for k=2n). Cell dimensions were calculated by the least-squares method from the high $2\theta$ values of 48 reflections measured at room temperature. The crystal density was determined as 1.423 g/c.c. by flotation method using a mixture of $CH_2Cl_2$ and $CCl_4$. The new crystal data are summarized in Table 1. Integrated intensities were measured on a G.E. XRD-5 diffractometer with the $\theta$-$2\theta$ scan mode using Ni-filtered Cu Kα radiation ($\lambda$=1.54178 Å). The take off angle of the tube was 3°. A total of 1256 reflections with $2\theta$ value less than 140° were measured of which 81 reflections were too weak to be observed. The lowest observable intensity for the reflection is 20 counts. Therefore the intensity of the unobserved reflections was

## TABLE 1

### Crystal Data of cis-1,2-Cyclobutanedicarboxylic Acid

| | |
|---|---|
| Formula | $C_6H_8O_4$ |
| Molecular Weight | M.W. = 144.13 |
| Space group | $P2_1/c$ |
| Cell dimensions | a = 10.710(3) Å |
| | b = 8.559(2) Å |
| | c = 7.343(2) Å |
| | β = 95.03°(1) |
| | a* = 0.09373(2) |
| | b* = 0.11683(2) |
| | c* = 0.13671(2) |
| | β* = 84.97°(1) |
| Cell volume | Vc = 670.54 $Å^3$ |
| Density | $\rho_c$ = 1.428 $g/cm^3$ |
| | $\rho_o$ = 1.423 $g/cm^3$ |
| No. of molecule | Z = 4 |
| | F(000) = 304 |

given as 10 count. The intensity data were corrected as usual for the Lorentz and polarization factors and for absorption ($\mu$=10.59 cm$^{-1}$).

# CHAPTER 3

## STRUCTURE REFINEMENT

The trial structure was determined by the symbolic addition method[64] from the old data. The signs of the three reflections: 553, 630 and 281 were chosen as positive to define the origin. A total of 86 signed reflections with E values above 1.5 were used to calculate the E-map. The oxygen and carbon peaks were identified from the map with the aid of a model. These atomic positions were refined initially with isotropic temperature factors and in the latter cycles with anisotropic ones by block-diagonal least-squares calculations until the R value $(=\Sigma||kF_o|-|F_c||/\Sigma|kF_o|)$ was 9.5%.

After the new intensity data were taken the refinement was resumed. The function minimized in the L.S. calculations was $\Sigma w(|kF_o|-|F_c|)^2$. The weighting scheme for the refinement was

$$\sqrt{w} = |F_o|/P_1 \qquad \text{if} \qquad |F_o| \leq P_1$$

$$\text{and } \sqrt{w} = P_1/|F_o| \qquad \text{if} \qquad |F_o| > P_1$$

with $P_1$ equal to 5.0 electrons on absolute scale. As can be seen from the above equations, the maximum weight is 1 when $|F_o|=P_1$ for data which is most reliable. After several cycles of refinements, the R value was reduced to 8.2%. A difference Fourier map was then computed with axes $x = 0$ to $0.5$, $y = 0$ to $1.0$ and $z = 0$ to $0.5$. The interval between points was about 0.22 Å. The function used for the electron density calculation was

$$\begin{aligned}\rho(xyz) = \frac{4}{V}\Big(\sum^{k+l=2n} & [F(hkl)+F(\bar{h}kl)]\cos 2\pi hx\cdot\cos 2\pi ky\cdot\cos 2\pi lz \\ & + [-F(hkl)+F(\bar{h}kl)]\sin 2\pi hx\cdot\cos 2\pi ky\cdot\sin 2\pi lz \\ + \sum^{k+l=2n+1} & [-F(hkl)+F(\bar{h}kl)]\sin 2\pi hx\cdot\sin 2\pi ky\cdot\cos 2\pi lz \\ & + [-F(hkl)-F(\bar{h}kl)]\cos 2\pi hx\cdot\sin 2\pi ky\cdot\sin 2\pi lz\end{aligned}$$

All hydrogen atoms were located from this difference map. The acid hydrogens apeared to be disordered in such a manner that each carboxyl oxygen is statistically bonded to one-half hydrogen atom. The acid hydrogens were located at:

| | x | y | z | Peak Ht. | Occupancy |
|---|---|---|---|---|---|
| (1) | -.021 | .607 | .400 | .30 | 1/2 |
| (2) | .073 | .387 | .515 | .25 | 1/2 |
| (3) | .398 | .600 | .467 | .19 | 1/2 |
| (4) | .523 | .372 | .450 | .22 | 1/2 |

When the resolution was decreased from the 2θ=140° (d=0.82 Å) to 2θ=60° (d=1.54 Å), the disordered hydrogen peaks (1) and (2) became one peak and located at the middle of these two peaks. Similarly, peaks (3) and (4) also gave this feature. Apparently the latter resolution with d=1.54 Å was not good enough to see the disordered hydrogens.

The structure was further refined by least-squares calculations in which only the hydrogens attached to cyclobutane ring were included.

The hydrogen atoms were refined with the isotropic temperature factors. After several more cycles of refinement, the second difference Fourier map was computed. The disordered acid hydrogens persistently appeared on the map. Thus the acid hydrogens of both carboxyl groups were included in the refinement with the occupancy factor of 1/2. Atomic scattering factors for hydrogen were those of Stewart and coauthors,[65] while all others were those given in the "International Table for X-ray Crystallography".[66] The refinement was terminated when all the shifts of the parameters were less than 1/6 of the corresponding standard deviations. The final R value for all reflections is 0.056. The last difference Fourier map showed no unusual features. The largest positive and negative spurious peaks were 0.15 and -0.24 $e/A^3$ respectively. This may be attributed to experimental error. The positive peaks are not high enough to be significant. The largest negative peak with a height which is possibly not significant is located between two acid groups.

The observed and calculated structure factors are listed in Table 2. Positional and thermal parameters are presented in Table 3 and 4.

## TABLE 2

### Observed ($F_o$) and Calculated ($F_c$) Structure Factors x 10

[illegible]

## TABLE 3

## Positional and Isotropic Thermal Parameters[a]

| Atom | x | y | z | B(Å$^2$) |
|---|---|---|---|---|
| O(1) | 0.0132(2) | 0.5897(2) | 0.2923(2) | |
| O(2) | 0.1233(1) | 0.3956(2) | 0.4261(2) | |
| C(3) | 0.0977(2) | 0.4851(3) | 0.2940(3) | |
| C(4) | 0.1631(2) | 0.4700(3) | 0.1250(3) | |
| C(5) | 0.2009(2) | 0.6140(3) | 0.0204(3) | |
| C(6) | 0.3185(2) | 0.5249(4) | -0.0237(3) | |
| C(7) | 0.2985(2) | 0.4063(3) | 0.1317(3) | |
| C(8) | 0.3809(2) | 0.4453(3) | 0.2999(3) | |
| O(9) | 0.3678(2) | 0.5696(2) | 0.3812(3) | |
| O(10) | 0.4667(1) | 0.3467(2) | 0.3467(3) | |
| H(11)[b] | -0.013 (4) | 0.600 (5) | 0.390 (6) | 4.1(10) |
| H(21)[b] | 0.076 (4) | 0.395 (5) | 0.500 (6) | 3.7(9) |
| H(41) | 0.108 (2) | 0.402 (3) | 0.038 (3) | 4.2(5) |
| H(51) | 0.227 (2) | 0.702 (3) | 0.094 (3) | 5.2(5) |
| H(52) | 0.137 (2) | 0.645 (3) | -0.082 (3) | 5.3(5) |
| H(61) | 0.406 (3) | 0.584 (4) | -0.004 (5) | 7.5(7) |
| H(62) | 0.317 (3) | 0.474 (4) | -0.135 (5) | 8.5(8) |
| H(71) | 0.303 (2) | 0.296 (3) | 0.103 (3) | 3.5(4) |
| H(91)[b] | 0.422 (6) | 0.584 (8) | 0.431 (9) | 8.0(16) |
| H(101)[b] | 0.521 (6) | 0.398 (7) | 0.452 (9) | 7.7(15) |

[a] Standard deviations in the last digits are given in parentheses and hydrogen atoms are numbered according to the atoms to which they are attached.

[b] Occupancy factor = 1/2.

## TABLE 4

Anisotropic Thermal Parameters x$10^4$ in the Form

$\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{23}kl+B_{13}hl+B_{12}hk)]$

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{23}$ | $B_{13}$ | $B_{12}$ |
|---|---|---|---|---|---|---|
| O(1) | 94(2) | 188(3) | 218(4) | 71(5) | 42(4) | 78(3) |
| O(2) | 90(1) | 185(3) | 229(4) | 119(5) | 61(4) | 60(3) |
| C(3) | 58(2) | 124(3) | 182(4) | - 2(6) | -16(4) | -11(4) |
| C(4) | 66(2) | 144(4) | 177(4) | - 7(6) | - 9(4) | - 5(4) |
| C(5) | 97(2) | 173(4) | 221(5) | 55(7) | 36(5) | 5(5) |
| C(6) | 105(2) | 222(5) | 198(5) | 36(8) | 82(5) | 17(6) |
| C(7) | 77(2) | 138(4) | 198(5) | -42(6) | 13(5) | 13(4) |
| C(8) | 63(2) | 132(3) | 205(4) | 2(6) | 42(4) | - 1(4) |
| O(9) | 90(2) | 183(3) | 312(4) | -157(6) | -67(4) | 41(3) |
| O(10) | 92(2) | 169(3) | 289(4) | - 26(6) | -46(4) | 53(4) |

Standard deviations in the last digits are given in parentheses.

# CHAPTER 4

# DISCUSSION OF THE STRUCTURE

In order to facilitate the discussion of structure, the following operations applied to the coordinates given in Table 3 as:

(a): -x, 1-y, 1-z

(b): 1-x, 1-y, 1-z

(c): -x, -1/2+y, 1/2-z

(d): x, 1/2-y, -1/2+z

(e): x, 3/2-y, 1/2+z

(f): -x, 1-y, -z

(g): 1-x, 1-y, -z

(h): 1-x, 1/2+y, 1/2-z

The (xyz) asymmetric unit is not subscripted.

Figure 1 is a projection of the structure onto ac plane. It shows the crystal packing of cis-1,2-cyclobutanedicarboxylic acid. The labeling of the atoms for the compound are indicated in the figure. The molecules form zig-zag chains running along the a-direction with the molecules connected by pairs of centrosymmetrically related hydrogen-bonds between carboxyl groups. Each molecule has two independent hydrogen bonds which occur from O(1) to O(2a) and from O(9) to O(10b) with O···O cistances of 2.637 and 2.651 Å, respectively. The hydrogen bond angles (C-O···O) are in the vicinity of 120° as listed in the Table 5.

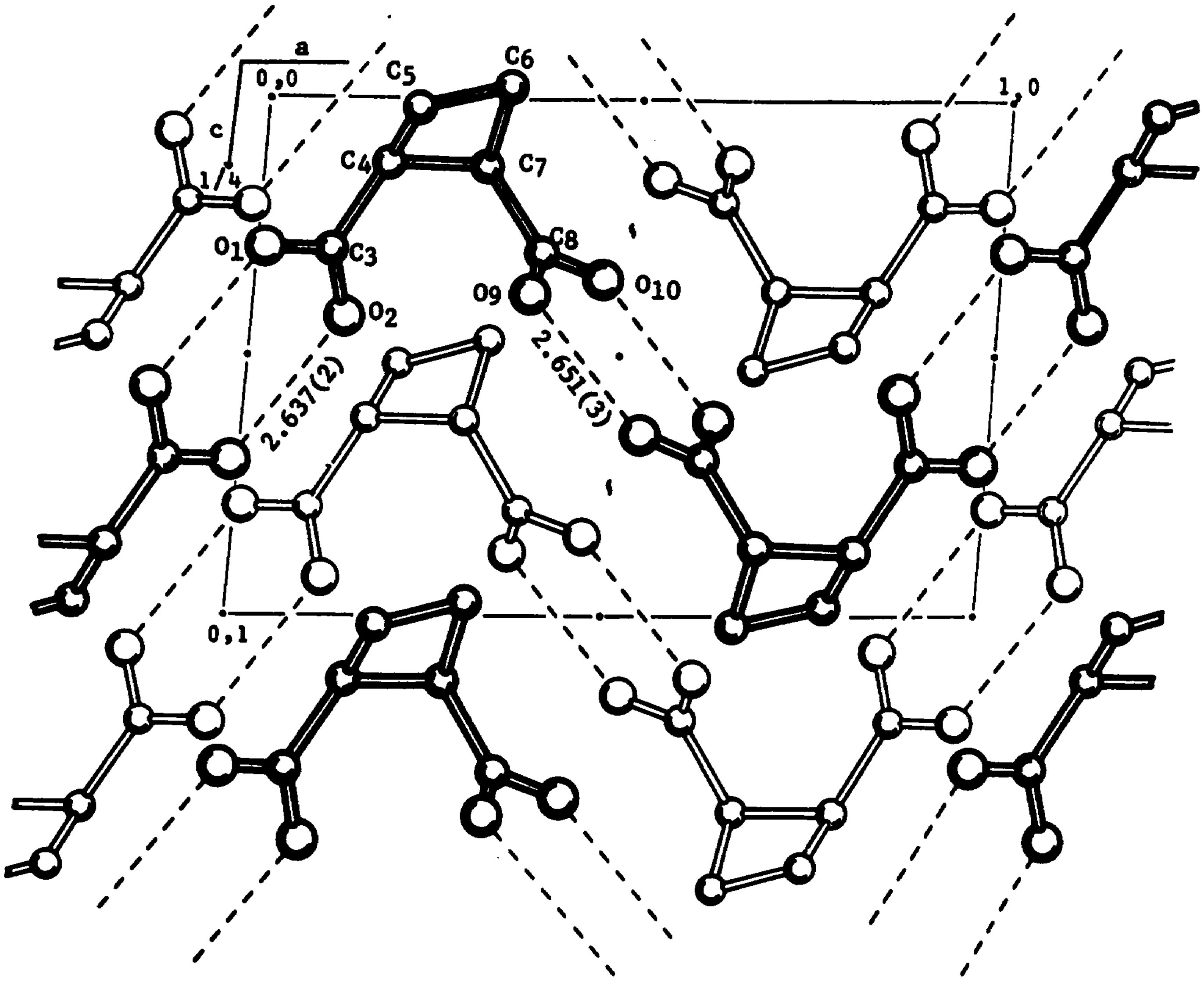


Figure 1. Projection of the Structure onto ac Plane

## TABLE 5

## Hydrogen-Bond Distances and Angles

| Atoms | Distance(Å) | Atoms | Angle |
|---|---|---|---|
| O(1)·····O(2a) | 2.637(2) | C(3)O(1)O(2a) | 117.9(1) |
| O(9)·····O(10b) | 2.651(3) | C(3)O(2)O(1a) | 118.8(1) |
| | | C(8)O(9)O(10b) | 120.1(1) |
| | | C(8)O(10)O(9b) | 116.3(1) |

(a): -x, 1-y, 1-z

(b): 1-x, 1-y, 1-z

All intermolecular contacts for which O···O, C···O distances less than 3.5 Å and C···C distances less than 4.0 Å are tabulated in Table 6. The shortest contacts between atoms of molecular chains for O···O, C···O and C···C are 3.339 (O(2)-O(1c)), 3.449 (O(9)-C(5e)), and 3.836 Å (C(4)-C(4f)), respectively. No unusual distances are observed.

The cyclobutane ring of the present structure is puckered. The dihedral angle between plane through C(4)C(5)C(6) and plane through C(4)C(6)C(7) is 156.4°. This value is consistent with values reported in other compounds which range from 145° in cyclobutane[69] to 161° in perchlorocyclobutane.[39] A stereoscopic view of the molecule with thermal ellipsoids is shown in Figure 2 from which the conformation of the structure can be better comprehended.

The bond distances with their standard deviations ($\sigma$) of the molecule are given in Table 7 and Figure 3 . For the sake of comparison, all bond lengths and angles for some isomers of diacids are also includedhere from Figure 4a to 4f. In the cyclobutane ring, the C(6)-C(7) bond length of 1.556(4) Å is longer and the C(4)-C(5) distance of 1.526(3) Å is shorter than the average value of 1.537(5) given by Sutton[67] for simple aliphatic compounds. The difference of 0.03 Å ($8\sigma$) between the longest and the shortest C-C bond lengths is significant. No good explanation could be given to this observation. However, the near tetrahedral angle of 110.6° made by C(7)-C(6) and C(7)-C(8) bonds may have contributed to the influence on the

## TABLE 6

### Intermolecular Contacts*

| Atoms | Distance, Å | Atoms | Distance, Å |
|---|---|---|---|
| O(1)-O(1a) | 3.448 | O(2)-C(3a) | 3.424 |
| O(2)-O(2a) | 3.442 | O(9)-C(5e) | 3.449 |
| O(9)-O(9b) | 3.407 | O(1)-C(4f) | 3.493 |
| O(10)-O(10b) | 3.491 | C(8)-C(8b) | 3.836 |
| O(2)-O(1c) | 3.339 | C(3)-C(3a) | 3.835 |
| O(9)-O(10h) | 3.477 | C(3)-C(5e) | 3.929 |
| C(4)-O(2d) | 3.464 | C(3)-C(4f) | 3.989 |
| C(7)-O(2d) | 3.461 | C(3)-C(5f) | 3.871 |
| C(8)-O(9b) | 3.411 | C(4)-C(4f) | 3.836 |
| C(8)-O(10b) | 3.440 | C(6)-C(6g) | 3.897 |
| O(1)-C(3a) | 3.417 | C(6)-C(8g) | 3.961 |

* All contacts are listed for which O···O≤3.5 Å, C···O≤3.5 Å and C···C≤4.0 Å. The letters a, b, etc. in parentheses refer to the following operations.

(a) -x, 1-y, 1-z
(b) 1-x, 1-y, 1-z
(c) -x, -1/2+y, 1/2-z
(d) x, 1/2-y, -1/2+z
(e) x, 3/2-y, 1/2+z
(f) -x, 1-y, -z
(g) 1-x, 1-y, -z
(h) 1-x, 1/2+y, 1/2-z

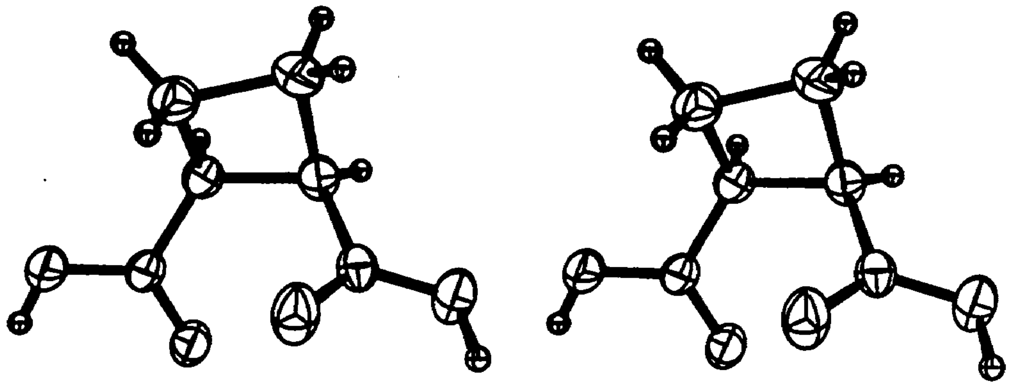


Figure 2. A Stereoscopic View of the Molecule

## TABLE 7

## Bond Lengths

| Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|
| O(1)-C(3) | 1.273(3) | O(1)-H(11) | 0.80(4) |
| O(2)-C(3) | 1.247(3) | O(2)-H(21) | 0.77(4) |
| C(3)-C(4) | 1.483(3) | C(4)-H(41) | 1.01(2) |
| C(4)-C(5) | 1.526(3) | C(5)-H(51) | 0.96(3) |
| C(4)-C(7) | 1.546(3) | C(5)-H(52) | 1.01(2) |
| C(5)-C(6) | 1.531(4) | C(6)-H(61) | 1.07(3) |
| C(6)-C(7) | 1.556(4) | C(6)-H(62) | 0.92(3) |
| C(7)-C(8) | 1.491(3) | C(7)-H(71) | 0.97(2) |
| C(8)-O(9) | 1.234(3) | O(9)-H(91) | 0.67(7) |
| C(8)-O(10) | 1.273(3) | O(10)-H(101) | 1.03(6) |

Standard deviations in the last digits are given in parentheses.

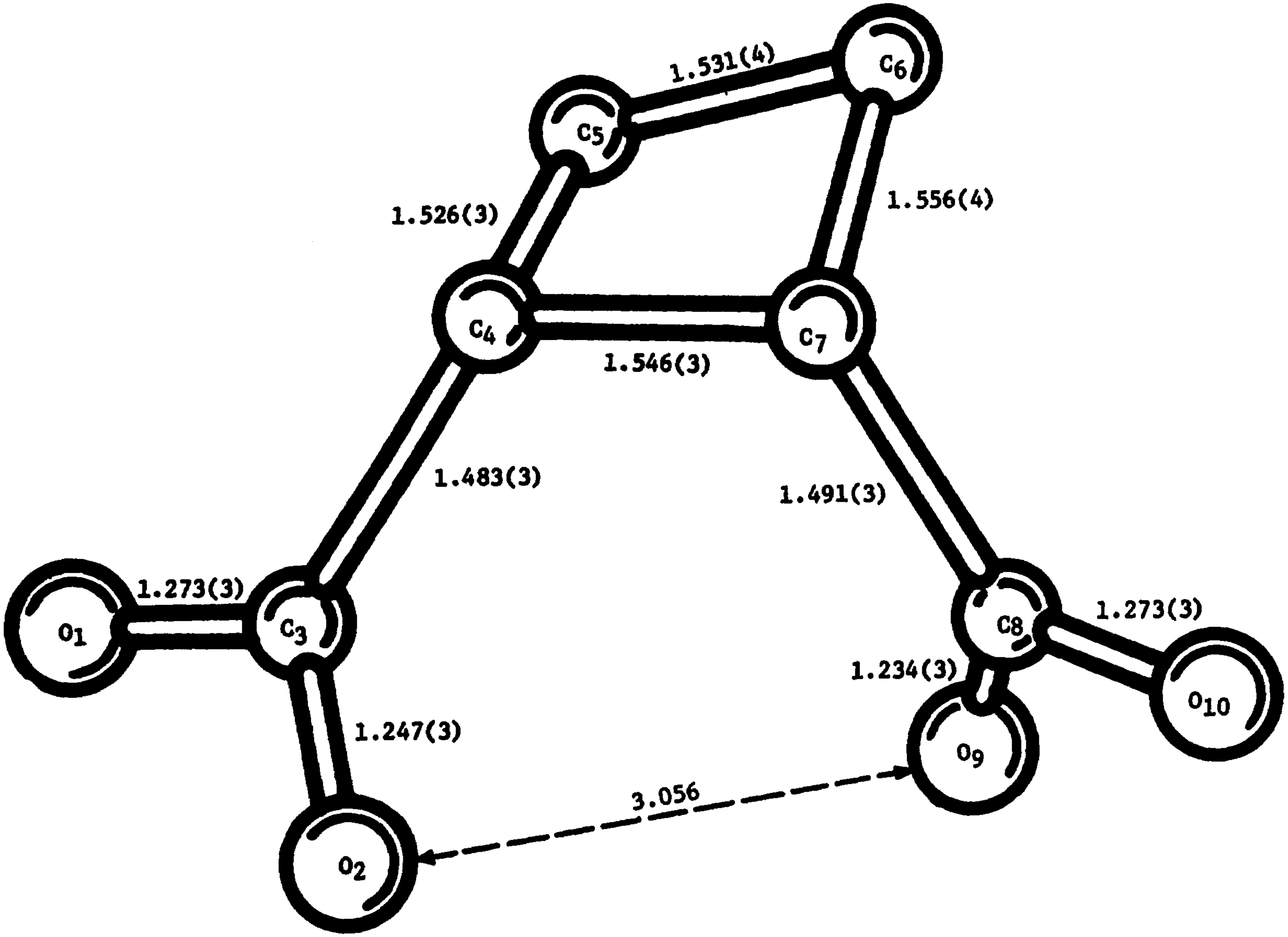


Figure 3. Bond lengths of cis-1,2-Cyclobutanedicarboxylic Acid

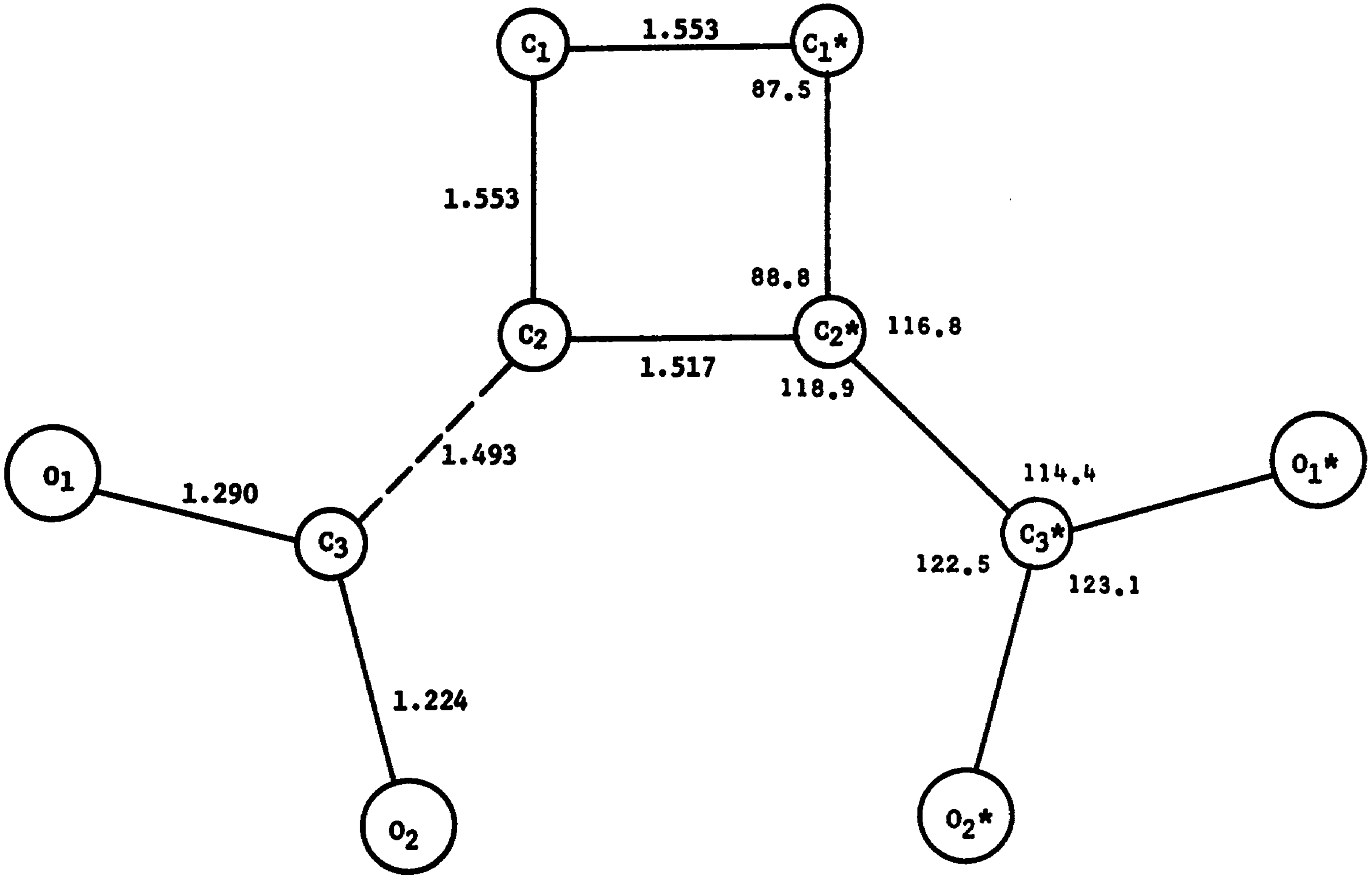


Figure 4a. Bond Lengths and Angles in trans-1,2-Diacid[47]

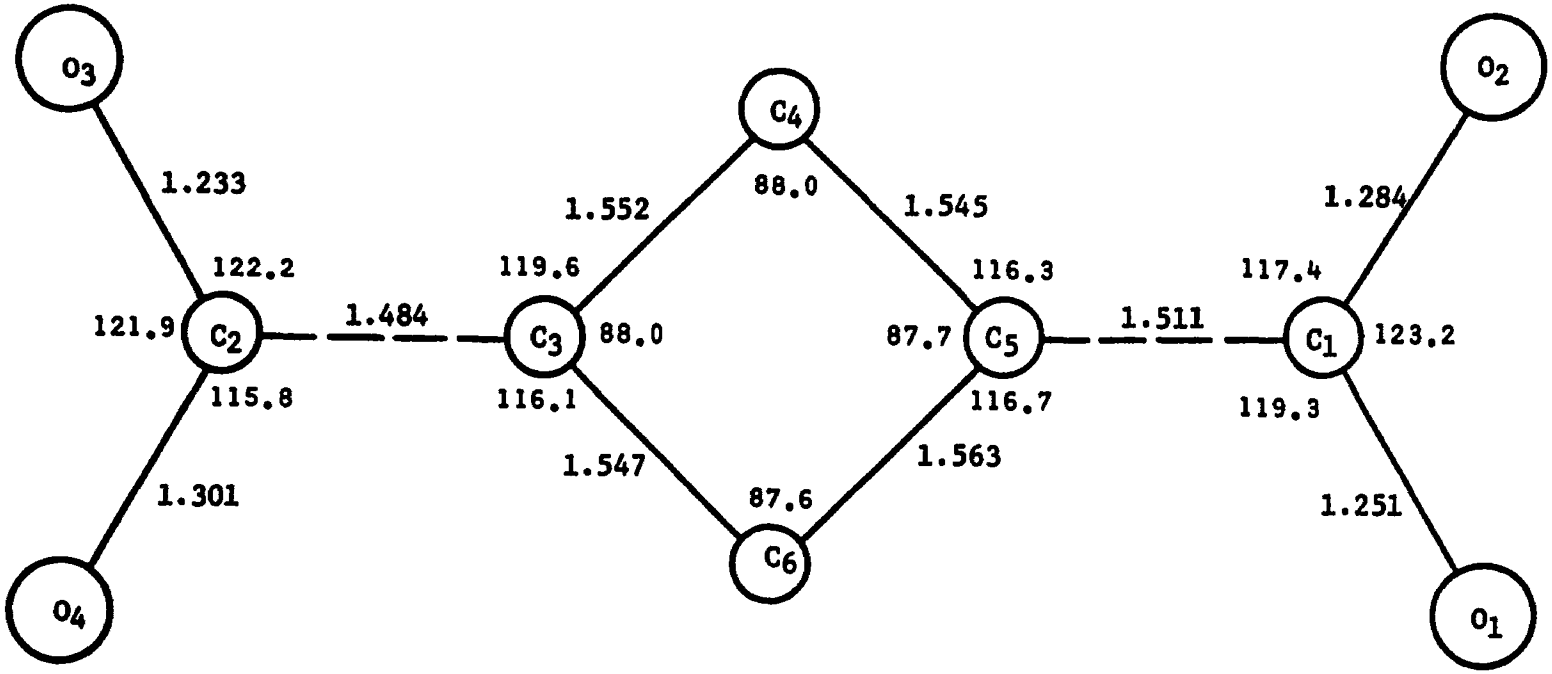


Figure 4b. Bond Lengths and Angles in cis-1,3-Diacid[46]

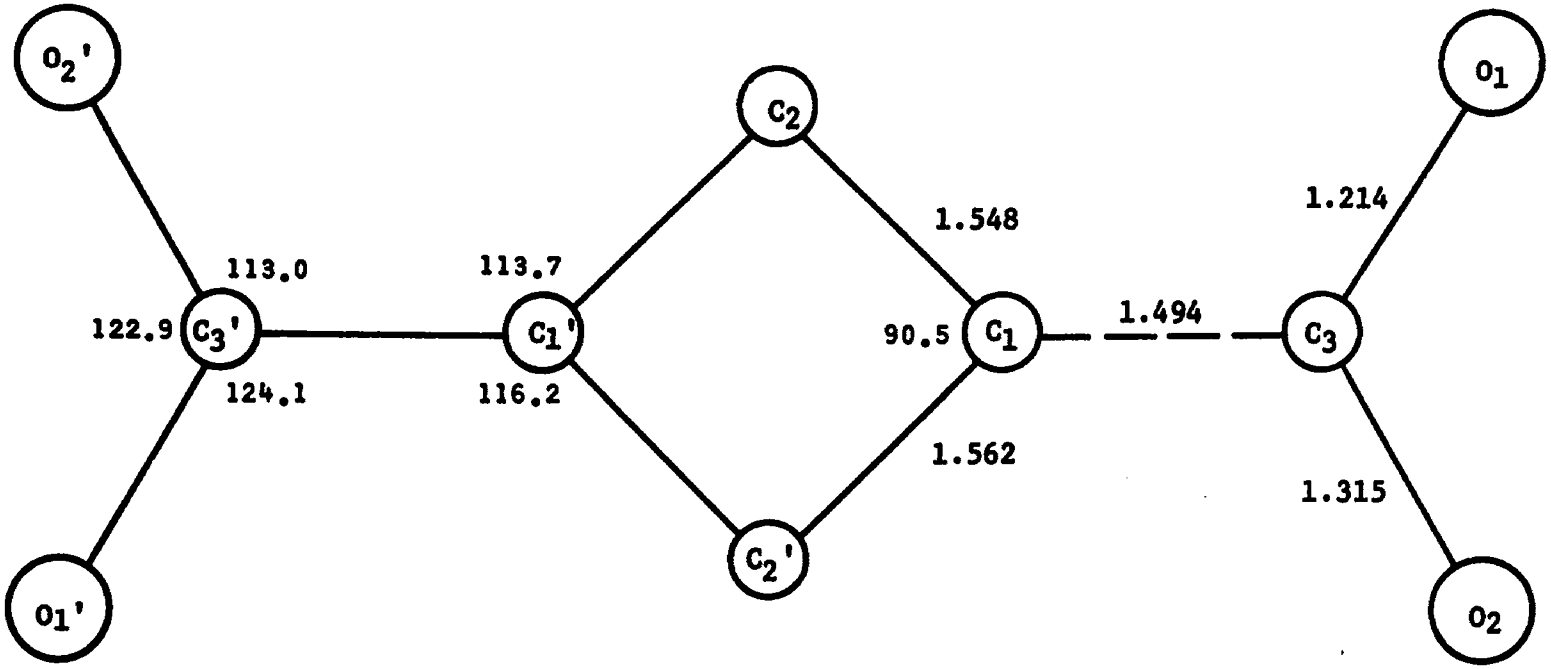


Figure 4c. Bond Lengths and Angles in trans-1,3-Diacid[41]

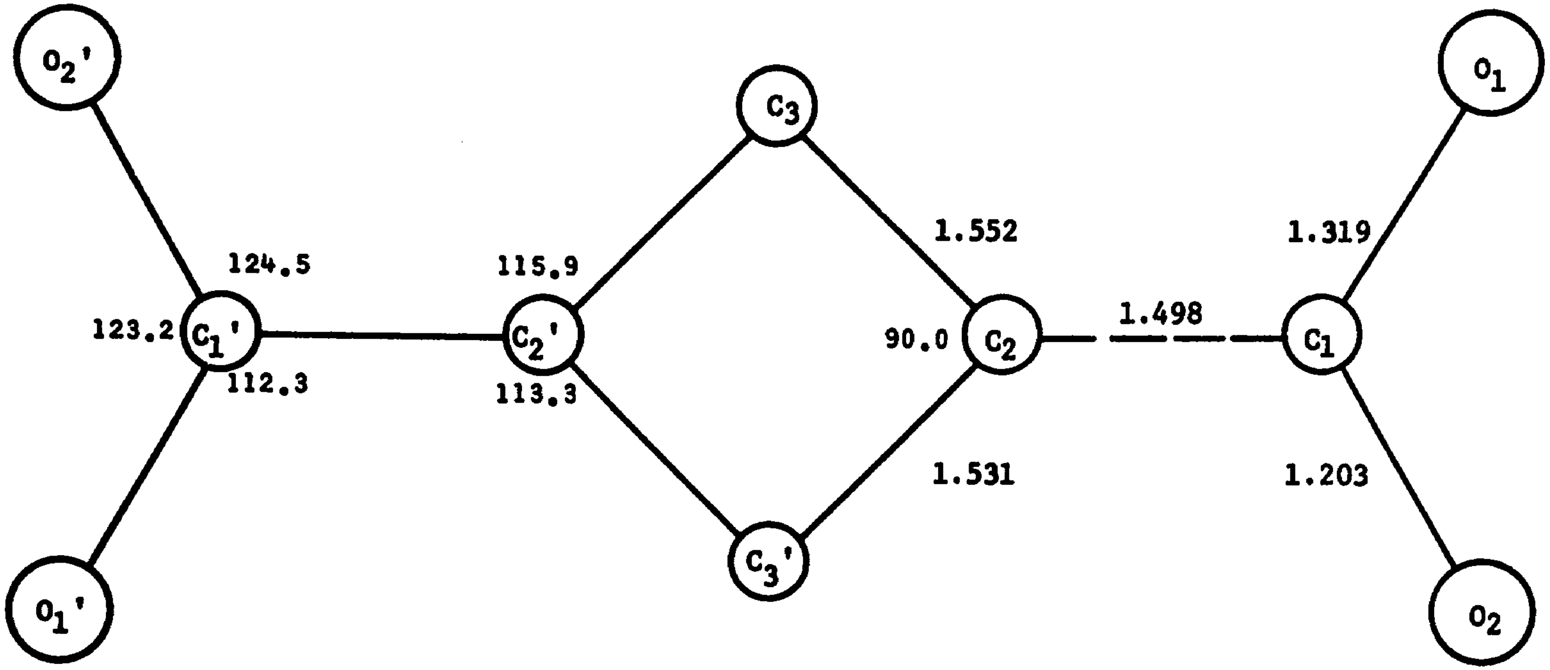


**Figure 4d.** Bond Lengths and Angles in trans-1,3-Diacid[72]

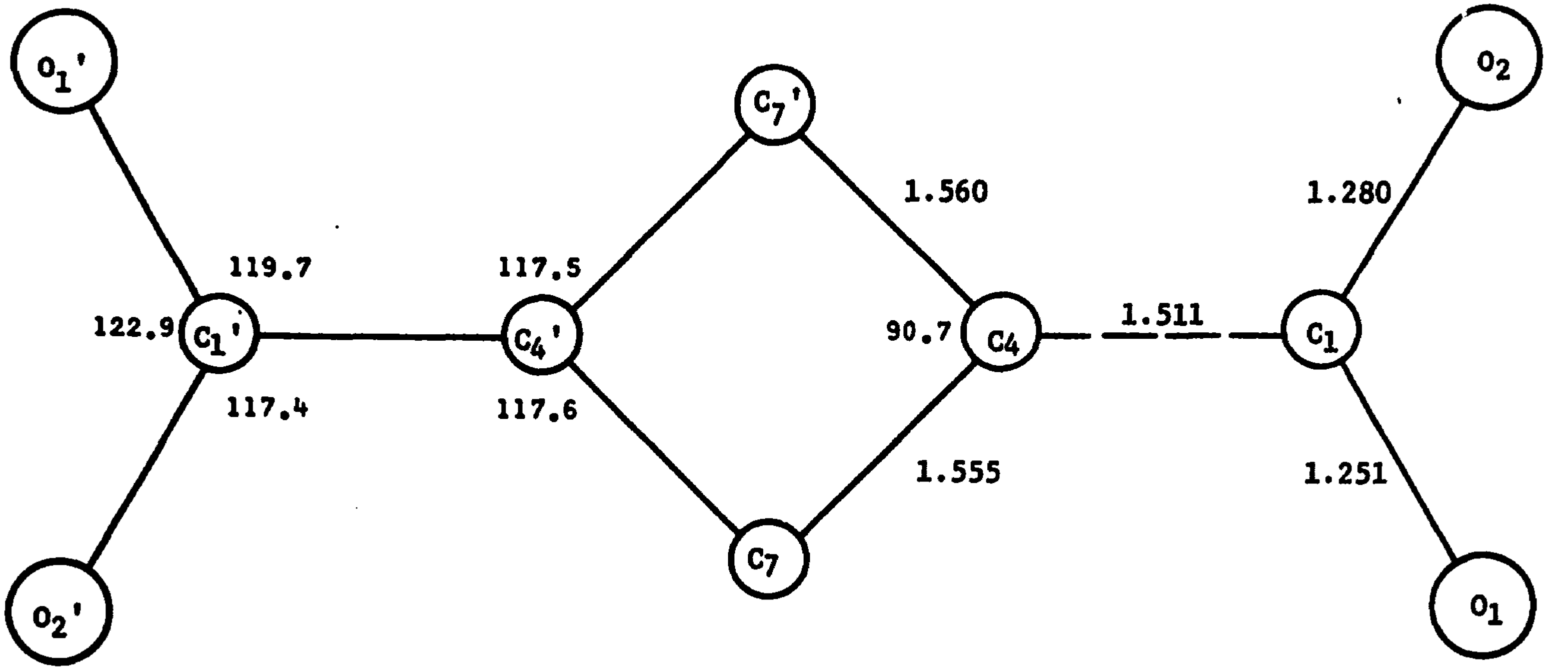


Figure 4e. Bond Lengths and Angles in trans-1,3-Dianion[74]

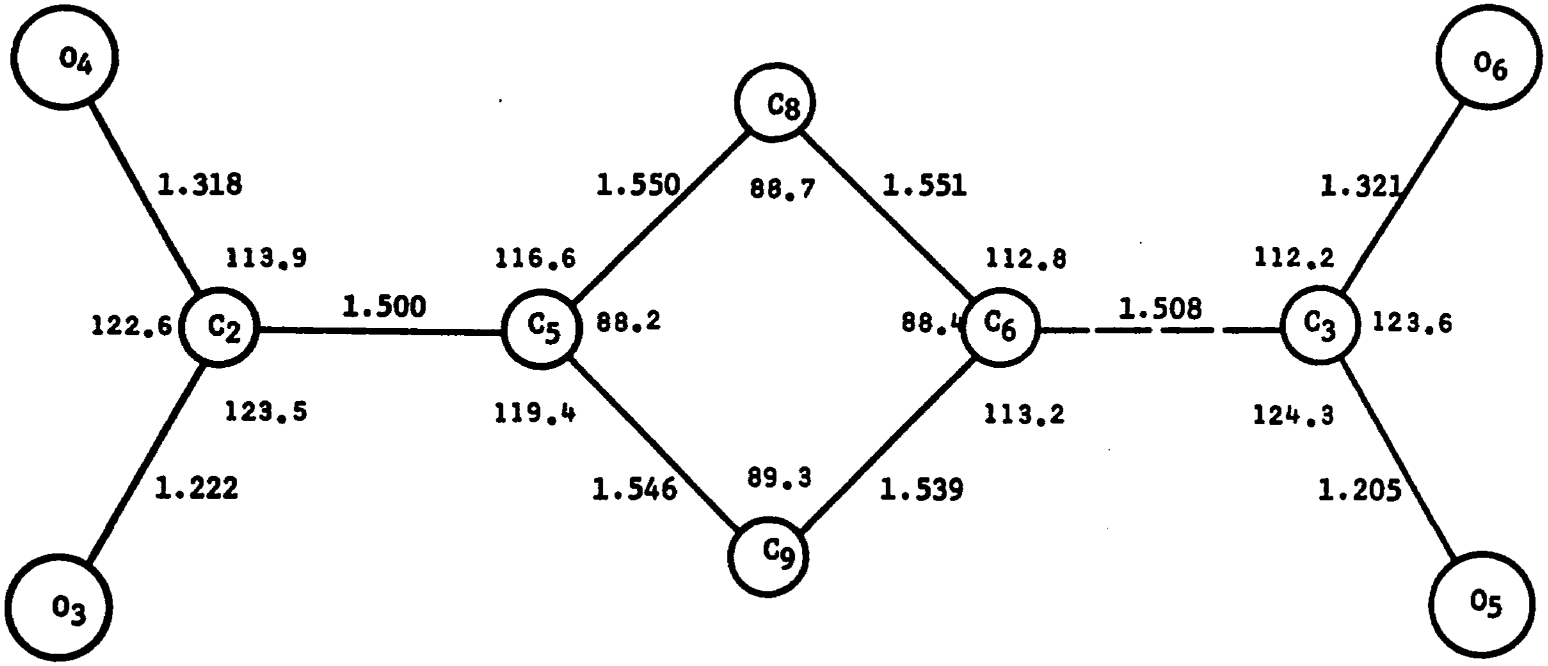


Figure 4f. Bond Lengths and Angles in trans-1,3-Diacid (puckered)[74]

lengthening of C(6)-C(7) bond. This angle is observed to be the smallest exocyclic angle for all isomers of cyclobutanedicarboxylic acid so far reported. The separation of 1.546 Å between C(4) and C(7) is somewhat longer than the normal distance by 0.009 Å which is three times the standard deviation. Long C-C bonds have been reported in a number of cyclobutanes. However, the average C-C length (1.540 Å) of the ring in the present study does not show a significant lengthening. The bond lengths were not corrected for thermal motion. In the trans-1,3-isomer, somewhat lengthened C-C bonds (average 1.555 ± 0.005) were reported by Margulis[41] although the extent of deviation is about three times the estimated standard deviation. Nevertheless, an average value of 1.542(4) Å was observed for the same compound by Seigler.[72] In the case of trans-1,2-isomer,[47] a significant difference in C-C length of the ring was also observed. The longest C-C bond is 1.553(4) Å while the shortest one is 1.517(4) Å. The average C-C length of the ring is 1.544(4) Å. Again, it does not show any significant lengthening. There is no relationship which can be established for C-C bond lengths between flat and puckered cyclobutanes. As expected the bond lengths of C(3)-C(4) (1.483 Å) and C(7)-C(8) (1.491 Å) are shorter than normal C-C bond length since these two bonds are the type of $sp^3$-$sp^2$. These values are compatible with those observed for the other isomers of cyclobutanedicarboxylic acid. Within the carboxyl group the average C-O distance 1.273 Å is apparently shorter than the normal value, 1.312 Å, in carboxylic acids and esters.[67] While the average C=O distance 1.241(5) Å is somewhat longer than the average value of 1.233(5) Å given by Sutton[67] and is also longer than values (1.203 to 1.224 Å) observed for other isomers. These two bond distances indicate that the disorder in carboxyl groups is not in a ratio of 1:1, otherwise, all the C–O bonds should be equal in length. However the magnitudes of electron densities in the difference Fourier map and the thermal factors are approximately the same for each pair of the disordered acid hydrogens. This seems to indicate that the disorder of the acid hydrogens is statistically one to one although the X-ray method cannot determine occupancy of the hydrogen atoms with great precision. The disordered hydrogen bonding was also observed in compounds such as cis-1,3-cyclobutanedicarboxylic acid[46] and trimesic acid.[71]

The repulsion of the two carboxyl oxygens resulted in a separation of 3.056 Å between O(2) and O(9) and the twisting for both carboxyl groups as will be seen later in the torsional angles. The distance of 2.506 Å between C(6) and C(8) is much shorter than the distance of 2.620 Å between C(5) and C(3). This difference is due to the difference of the exocyclic angles at C(4) and C(7). The distances of C(5)···O(1), C(5)···O(2), C(6)···O(9) and C(6)···O(10) are 2.963, 3.674, 2.999 and 3.389 Å, respectively. The shortening in C(4)–C(5) bond and the lengthening in C(6)–C(7) bond appear to minimize the energy of interatomic contacts although the distance between C(6) and O(9) is longer than that between C(5) and O(2).

The C-H bonds average 0.99 Å, somewhat shorter than the spectroscopic value[67] of 1.09 Å, as is often the case in X-ray diffraction determinations Most of the O-H bonds are shorter than the expected value probably due to the disorder of the acid hydrogens. However, the deviations are within experimental error.

The bond angles of the molecule were calculated and are presented in Figure 5 and Table 8. The average inner angle of the four-membered ring is 88.8 degrees. This value is smaller than the inner angle of the planar conformer which is necessarily 90°. The sums of the three angles constituted by C-C bonds at C(4) and C(7) are 332.8° and 312.5° respectively. The difference is significant. The conformation at C(4) is more flat than that at C(7). The exocyclic angle of C(6)C(7)C(8) is smaller than that of C(3)C(4)C(5) by 10.5°, likewise, angle of C(4)C(7)C(8) is smaller than angle of C(3)C(4)C(7) by 5.4°. The carboxyl group at C(4) is equatorial whereas the other carboxyl group at C(7) is axial as a result of puckered conformation.

In the carboxyl groups, the sums of the angles at C(3) and C(8) are 360.1° and 360.0°. In other words the trigonal bonds at C(3) or C(8) are coplanar. The O-C=O angles are larger than the rest of the angles and the C-C=O angles (121°) are greater than the C-C-OH angles (116°). These angles are in good agreement with values compiled by Dunitz and Stricker.[73] Table 9 gives the geometry of carboxyl groups in some isomers of cyclobutanedicarboxylic acid.

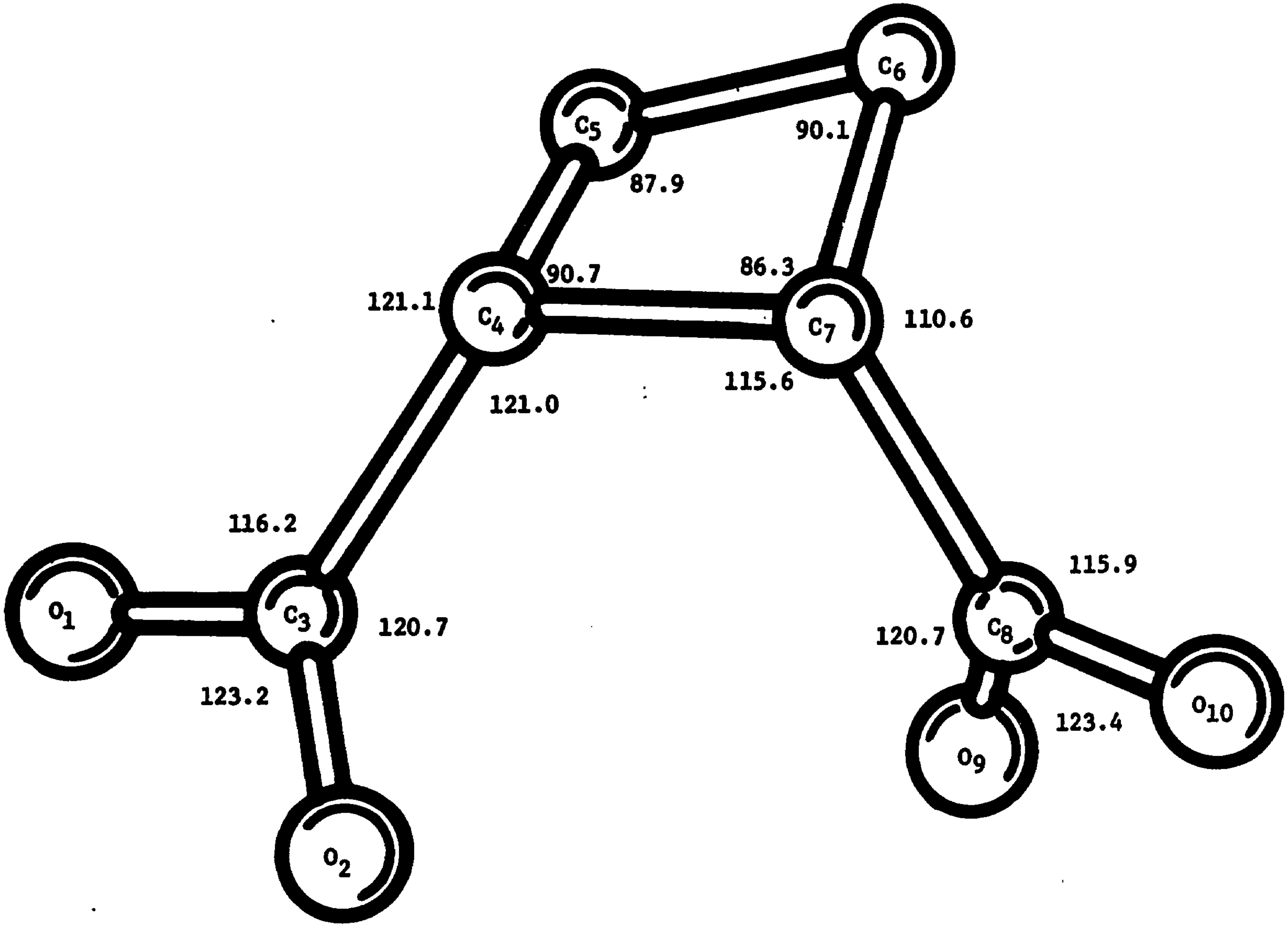


Figure 5. Bond Angles of cis-1,2-Cyclobutanedicarboxylic Acid

## TABLE 8

### Bond Angles

| Atoms | Angle(deg) | Atoms | Angle(deg) |
|---|---|---|---|
| O(1)-C(3)-O(2) | 123.2(2) | C(5)-C(4)-H(41) | 108.2(13) |
| O(1)-C(3)-C(4) | 116.2(2) | C(7)-C(4)-H(41) | 107.9(12) |
| O(2)-C(3)-C(4) | 120.7(2) | C(4)-C(5)-H(51) | 115.3(15) |
| C(3)-C(4)-C(5) | 121.1(2) | C(6)-C(5)-H(51) | 107.9(15) |
| C(3)-C(4)-C(7) | 121.0(2) | H(51)-C(5)-H(52) | 111.3(21) |
| C(5)-C(4)-C(7) | 90.7(2) | C(4)-C(5)-H(52) | 113.6(15) |
| C(4)-C(5)-C(6) | 87.9(2) | C(6)-C(5)-H(52) | 119.2(14) |
| C(5)-C(6)-C(7) | 90.1(2) | C(5)-C(6)-H(61) | 117.9(17) |
| C(6)-C(7)-C(4) | 86.3(2) | C(7)-C(6)-H(61) | 112.7(18) |
| C(6)-C(7)-C(8) | 110.6(2) | H(61)-C(6)-H(62) | 106.8(28) |
| C(4)-C(7)-C(8) | 115.6(2) | C(5)-C(6)-H(62) | 117.9(21) |
| C(7)-C(8)-O(9) | 120.7(2) | C(7)-C(6)-H(62) | 110.6(21) |
| C(7)-C(8)-O(10) | 115.9(2) | C(4)-C(7)-H(71) | 113.9(12) |
| O(9)-C(8)-O(10) | 123.4(2) | C(6)-C(7)-H(71) | 117.4(12) |
| C(3)-O(1)-H(11) | 112 (3) | C(8)-C(7)-H(71) | 111.1(12) |
| C(3)-O(2)-H(21) | 116 (3) | C(8)-O(9)-H(91) | 108 (6) |
| C(3)-C(4)-H(41) | 106.7(13) | C(8)-O(10)-H(101) | 106 (4) |

Standard deviations in last digits are given in parentheses.

## TABLE 9

### Geometry of Carboxyl Groups in Cyclobutanedicarboxylic Acids

| Acid | Bond Lengths | | Bond Angles | | References |
|---|---|---|---|---|---|
| | C=O | C-OH | C-C=O | C-C-OH | |
| cis-1,2- | 1.247(3) | 1.273(3) | 120.7(2) | 116.2(2) | This work |
| | 1.234(3) | 1.273(3) | 120.7(2) | 115.9(2) | |
| trans-1,2- | 1.224(4) | 1.290(4) | 122.5(2) | 114.4(2) | 47 |
| cis-1,3- | 1.251(12) | 1.284(12) | 119.3(6) | 117.4(6) | 46 |
| | 1.233(12) | 1.301(12) | 122.2(6) | 115.8(6) | |
| trans-1,3-(planar) | 1.214(5) | 1.315(5) | 124.1(3) | 113.0(3) | 41 |
| trans-1,3-(planar) | 1.203(4) | 1.319(4) | 124.4 | 112.3 | 72 |
| trans-1,3-(puckered) | 1.222(8) | 1.318(9) | 123.5(6) | 113.9(6) | 74 |
| | 1.205(9) | 1.321(8) | 124.3(8) | 112.2(6) | |

In this table the mean C-C=O angle is above 120° while mean C-C-OH angle is below this value which is consistent with the present study. A summary of mean C-C bond length, mean C-C-C angle and dihedral angle in cyclobutane rings from some published results and the present investigation is presented in Table 10.

The conformation angles (or torsional angles) are reported in Table 11. The torsional angles around the bonds on the ring average 16.9° and the conformational angle of the two acid groups, C(3)-C(4)-C(7)-C(8), is 326.7°. This twisted angle is a consequence of the ring puckering with an added contribution from the interaction of the substituents, i.e. the two acid groups. In the case of trans-1,2-isomer, a mean torsional angle of the ring was found to be 20° while the conformational angle between the two carboxylic acid groups is observed to be 99.1° which is pretty close to the expected value, 100°, for this puckered ring (substract 20° due to puckering from 120° in the planar form). This indicates that no repulsion existed between these two carboxylic acid groups. The carboxyl groups of the present molecule are found to occur in such a way that the conformations of O(2)-C(3)-C(4)-C(7) and O(9)-C(8)-C(7)-C(4) are twisted with torsional angles of 330.9° and 327.7°, respectively. The reason for this twisting is not difficult to understand; what is present here is the van der Waals repulsion between the two carboxyl oxygens, O(2) and O(9). These torsional angles are therefore considerably

## TABLE 10

## A Comparison of Four-membered Rings in Cyclobutanedicarboxylic Acids

| Acids | Space group | Dihedral angle,(°) | <C-C> (Å) | <C-C-C> (°) | References |
|---|---|---|---|---|---|
| cis-1,2- | $P2_1/c$ | 156 | 1.540(4) | 88.8 | This work |
| trans-1,2- | C2/c | 150 | 1.544(4) | 88.2 | 47 |
| cis-1,3- | $P2_1/n$ | 149 | 1.554(10) | 87.8 | 46 |
| trans-1,3-(planar) | $P2_1/c$ | 180 | 1.555(6) | 90.0 | 41 |
| trans-1,3-(planar) | $P2_1/c$ | 180 | 1.542(4) | 90.0 | 72 |
| trans-1,3-(puckered) | $P\bar{1}$ | 155 | 1.547(10) | 88.7 | 74 |
| trans-1,3-(Na-salt) | $P\bar{1}$ | 180 | 1.558(10) | 90.0 | 74 |
| 1,1- | $P2_1/c$ | puckered | ( not available ) |  | 48 |

## TABLE 11

### Right-Handed Conformational Angles*

| Atoms | Angle(deg.) |
|---|---|
| C(4)C(5)C(7)C(6) | 155.7 |
| C(5)C(4)C(6)C(7) | 156.4 |
| C(4)C(5)C(6)C(7) | 343.1 |
| C(5)C(6)C(7)C(4) | 16.8 |
| C(6)C(7)C(4)C(5) | 343.2 |
| C(7)C(4)C(5)C(6) | 17.1 |
| C(3)C(4)C(7)C(8) | 326.7 |
| C(3)C(4)C(5)C(6) | 144.5 |
| C(3)C(4)C(7)C(6) | 215.7 |
| C(8)C(7)C(6)C(5) | 260.7 |
| C(8)C(7)C(4)C(5) | 94.3 |
| O(1)C(3)C(4)C(7) | 153.1 |
| O(1)C(3)C(4)C(5) | 40.9 |
| O(2)C(3)C(4)C(5) | 218.7 |
| O(2)C(3)C(4)C(7) | 330.9 |
| O(9)C(8)C(7)C(4) | 327.7 |
| O(9)C(8)C(7)C(6) | 63.6 |
| O(10)C(8)C(7)C(4) | 150.6 |
| O(10)C(8)C(7)C(6) | 246.6 |

* cis-Configuration = 0°

greater than the value, 8°, observed for trans-1,2-isomer and values compiled by Dunitz.[73] It appears that the interaction between two acid groups is larger in cis-1,2-diacid than in trans-1,2-diacid.

The equation for planes will be given in the following form:

$$m_1x + m_2y + m_3z = d$$

where m's are components of unit reciprocal vector, $\vec{m}$, normal to the plane, $\vec{m} = m_1\vec{a}^* + m_2\vec{b}^* + m_3\vec{c}^*$, and d is the distance in Angstroms from the origin to the plane and x, y and z are fractional coordinates.

The equations of mean planes for cyclobutane ring and carboxyl groups are listed in Table 12 and 13 and the deviations of atoms from each plane of the carboxyl group are illustrated in Figure 6. In the first carboxyl group, atoms O(1), O(2), C(3) and C(4) lie in plane with the maximum deviation of 0.011 Å at C(3). The mean deviation of atoms from this plane is 0.006 Å. Likewise, in the second carboxyl group, atoms O(10), O(9), C(8) and C(7) are coplanar with the largest deviation of -0.015 Å at C(8). The mean deviation of atoms from this plane is 0.008 Å. The distance between plane O(1)O(2)C(3)C(4) and its centrosymmetric related plane O(1a)O(2a)C(3a)C(4a) is 0.237 Å while that between plane O(10)O(9)C(8)C(7) and its centrosymmetric related plane O(10b)O(9b)C(8b)C(7b) is 0.295 Å. Therefore, each pair of the centrosymmetric related carboxyl groups which is involved in hydrogen bonding is not quite coplanar. This also can be seen from the relatively large deviations of atoms from the corresponding

## TABLE 12

## Least-Squares Planes*

A. Least-squares planes for carboxyl groups

Plane (1). $7.049x + 5.593y + 2.311z = 4.070$

| Atom | O(1) | O(2) | C(3) | C(4) |
|---|---|---|---|---|
| Dev. | -0.004 | -0.004 | 0.011 | -0.003 |

Plane (2). $7.287x + 3.948y - 4.604z = 3.168$

| Atom | O(10) | O(9) | C(8) | C(7) |
|---|---|---|---|---|
| Dev. | 0.005 | 0.006 | -0.015 | 0.004 |

B. Least-squares planes for two carboxyl groups involved in hydrogen bonds

Plane (3). $6.729x + 5.637y + 2.625z = 4.131$

| Atom | O(1) | O(2) | C(3) | C(4) |
|---|---|---|---|---|
| Dev. | 0.049 | 0.047 | 0.033 | -0.056 |
| Atom | O(1a) | O(2a) | C(3a) | C(4a) |
| Dev. | -0.049 | -0.047 | -0.033 | 0.056 |

Plane (4). $6.908x + 3.831y - 4.946z = 2.897$

| Atom | O(10) | O(9) | C(8) | C(7) |
|---|---|---|---|---|
| Dev. | -0.059 | -0.059 | -0.043 | 0.070 |
| Atom | O(10b) | O(9b) | C(8b) | C(7b) |
| Dev. | 0.059 | 0.059 | 0.043 | -0.070 |

C. Least-squares planes for cyclobutane ring

Plane (5). $3.583x + 4.613y + 5.439z = 3.548$

| Atom | C(4) | C(5) | C(6) | C(7) |
|---|---|---|---|---|
| Dev. | -0.115 | 0.116 | -0.114 | 0.113 |

---

* x, y and z are fractional coordinates.

[a] Refer to the operation (-x, 1-y, 1-z).

[b] Refer to the operation (1-x, 1-y, 1-z).

## TABLE 13

### Absolute Planes*

$Ax + By + Cz = D$

| Plane | Atoms | A | B | C | D |
|---|---|---|---|---|---|
| 1 | C(3)C(4)C(5) | 8.969 | 0.159 | 3.456 | 1.970 |
| 2 | C(3)C(4)C(7) | -3.707 | -7.954 | -0.724 | -4.433 |
| 3 | C(3)C(4)C(6) | 4.825 | -6.918 | 2.485 | -2.154 |
| 4 | C(4)C(5)C(7) | 1.621 | 4.098 | 6.228 | 2.969 |
| 5 | C(5)C(6)C(7) | -5.369 | -4.894 | -4.427 | -4.174 |
| 6 | C(6)C(7)C(8) | 8.027 | -4.991 | -2.776 | 0.002 |
| 7 | C(4)C(7)C(8) | 3.541 | 7.167 | -3.398 | 3.521 |
| 8 | C(5)C(7)C(8) | 8.652 | 1.594 | -4.610 | 2.623 |
| 9 | C(4)C(6)C(7) | 2.544 | 5.914 | 4.842 | 3.800 |
| 10 | C(4)C(5)C(6) | -4.502 | -3.055 | -5.831 | -2.899 |

* x, y and z are fractional coordinates.

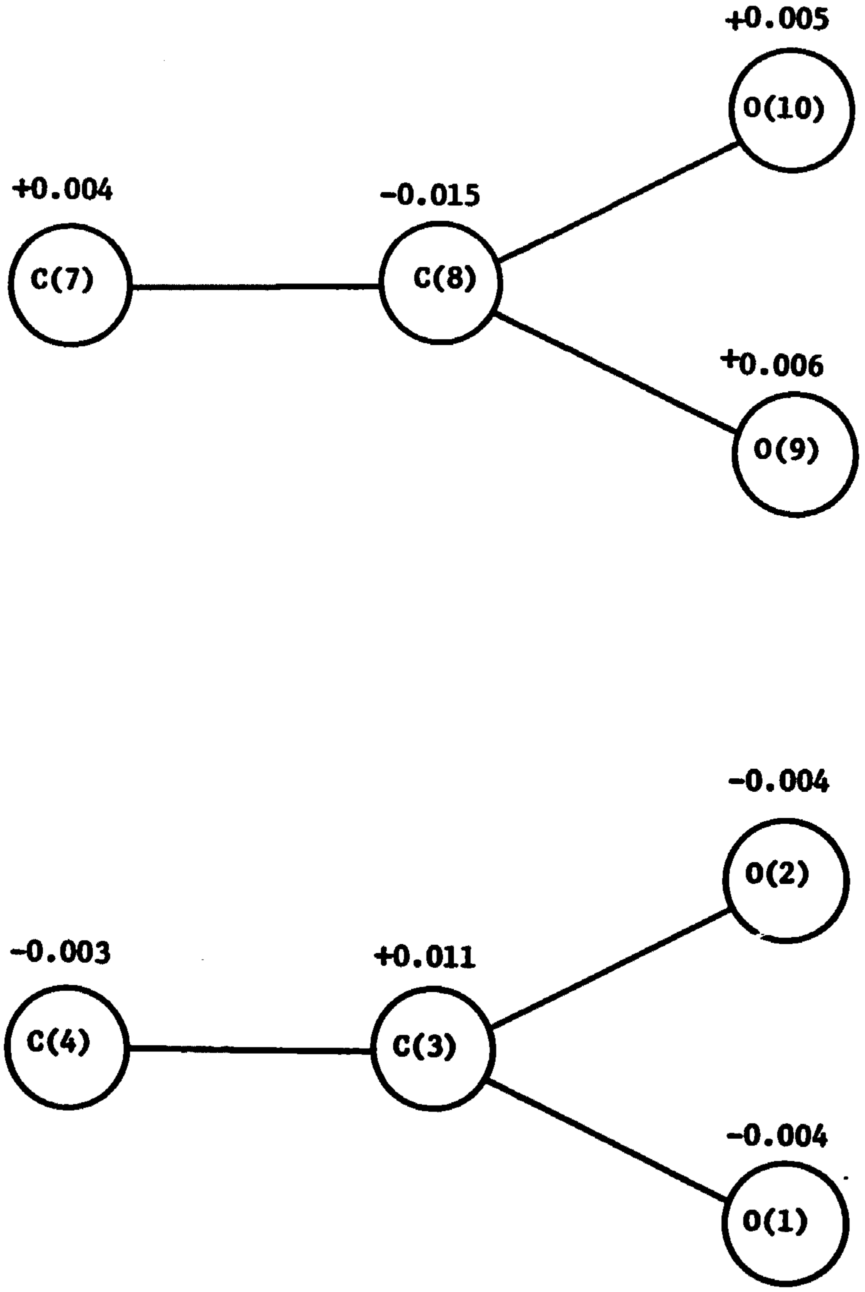
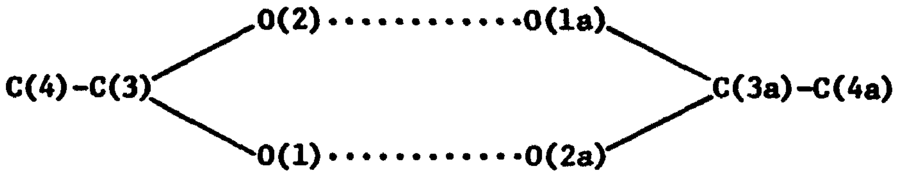
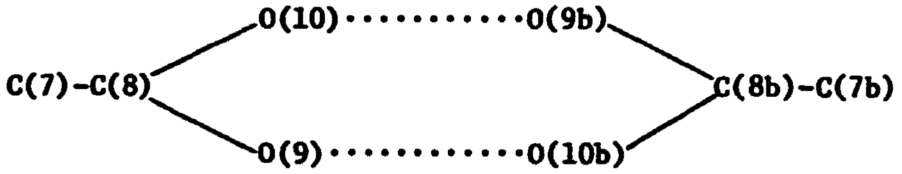


Figure 6. The Deviations of Atoms from Planes of Carboxyl Groups

planes. The mean deviation from the plane passing through:



is 0.046 Å, while that for the plane constituted by:



is 0.058 Å. Values of 0.056 and 0.070 Å are observed to be the largest deviations of atoms for both carboxyl groups as shown in Figure 7. The average deviations of atoms from the least-squares plane of the ring comprised of C(4), C(5), C(6) and C(7) is about 0.115 Å; a result of the non-planarity of the cyclobutane ring.

The angle of intersection between two planes can be expressed by the angle between the two unit normals, say $\vec{m}$ and $\vec{n}$. Then the angle ($\theta$) can be obtained from the dot product of the two unit reciprocal vectors

$$\begin{aligned}\cos\theta &= (m_1\vec{a}^* + m_2\vec{b}^* + m_3\vec{c}^*)\cdot(n_1\vec{a}^* + n_2\vec{b}^* + n_3\vec{c}^*)\\ &= m_1n_1a^{*2} + m_2n_2b^{*2} + m_3n_3c^{*2} + (m_1n_2 + m_2n_1)a^*b^*\cos\gamma^*\\ &\quad +(m_1n_3 + m_3n_1)a^*c^*\cos\beta^* + (m_2n_3 + m_3n_2)b^*c^*\cos\alpha^*\end{aligned}$$

where $a^*$, $b^*$, $c^*$, $\alpha^*$, $\beta^*$ and $\gamma^*$ are reciprocal cell dimensions of the crystal.

The carboxyl groups are arranged in such a way that the plane through O(1), O(2), C(3) and C(4) is approximately "parallel" (30.5°)

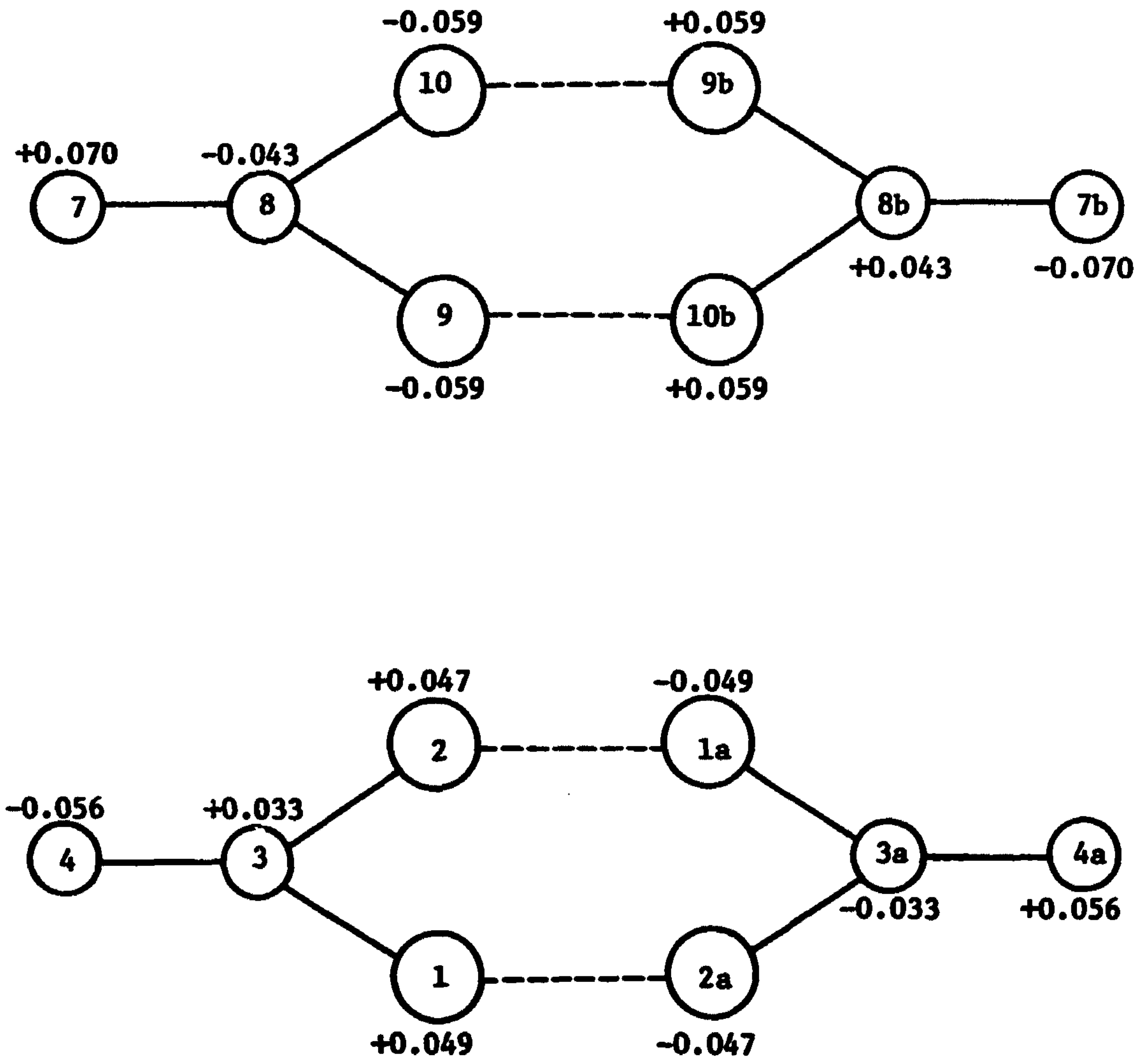


Figure 7. Deviations from Planes of Rings Formed by Hydrogen Bonded Acid Groups

to and the plane through O(10), O(9), C(8) and C(7) is almost "perpendicular" (88.0°) to the mean plane of the cyclobutane ring as a result of twisting due to the repulsion of the carbonyl oxygens as described previously. These two carboxyl groups are tipped 57.5° to each other. In the molecule the angles formed between mean planes are tabulated in Table 14.

The principal axes of vibrational ellipsoids along with their direction cosines are presented in Table 15. Within the ring the anisotropy is small and the largest thermal motion and anisotropy is at atom C(6). This atom, however, has no intermolecular interactions less than 3.50 Å. The anisotropy is also observed to be small for C(3) and C(8) on the side chains. It is worth noting that in the carboxyl groups the main B axis of oxygen atom with double bond character is somewhat greater than that of oxygen atom with single bond character although this is not the case for other cyclobutanedicarboxylic acids. The carboxyl group perpendicular to the cyclobutane ring (C(7)C(8)O(9)O(10)) seems to exert higher thermal movement than the one parallel to the ring.

Table 17 summarizes the magnitudes and orientation of the termal ellipsoids of carboxyl oxygen atoms in some cyclobutanedicarboxylic acids. In the present structure, the main B's for O(1), O(2), O(9) and O(10) are observed to be 6.74, 7.04, 8.86 and 7.12 Å$^2$, respectively. All oxygen atoms have large anisotropy, and the principal axes are more or less perpendicular to the acid groups with angles of 14, 23, 21 and 18° for O(1), O(2), O(9) and O(10). This type of thermal

## TABLE 14

## Angles Between Least-Squares Planes

| Plane I | Plane II | cos θ | θ |
|---|---|---|---|
| O(1)O(2)C(3)C(4) | O(10)O(9)C(8)C(7) | 0.5363 | 57°34' |
| O(1)O(2)C(3)C(4) | C(4)C(5)C(6)C(7) | 0.8613 | 30°32' |
| O(10)O(9)C(8)C(7) | C(4)C(5)C(6)C(7) | 0.0359 | 87°57' |
| O(1)O(2)C(3)C(4) | C(3)C(4)C(5) | 0.7675 | 39°52' |
| O(1)O(2)C(3)C(4) | C(3)C(4)C(7) | -0.8834 | 152°03' |
| O(1)O(2)C(3)C(4) | C(3)C(4)C(6) | -0.0898 | 95°09' |
| O(1)O(2)C(3)C(4) | C(5)C(4)C(7) | 0.7357 | 42°38' |
| O(10)O(9)C(8)C(7) | C(8)C(7)C(6) | 0.4195 | 65°12' |
| O(10)O(9)C(8)C(7) | C(8)C(7)C(4) | 0.8591 | 30°47' |
| O(10)O(9)C(8)C(7) | C(8)C(7)C(5) | 0.9540 | 17°27' |
| O(10)O(9)C(8)C(7) | C(6)C(7)C(4) | 0.0914 | 84°45' |
| C(4)C(5)C(6) | C(4)C(7)C(6) | -0.9160 | 156°21' |
| C(5)C(4)C(7) | C(5)C(6)C(7) | -0.9111 | 155°40' |

## TABLE 15

## Principle Axes and Direction Cosines with Respect to the Real Axes of Anisotropic Ellipsoids

| Atom | B | $l_1$ | $l_2$ | $l_3$ |
|---|---|---|---|---|
| O(1) | 6.74 | 0.466 | 0.791 | 0.355 |
| | 4.35 | -0.414 | -0.202 | 0.921 |
| | 3.32 | 0.782 | -0.578 | 0.164 |
| O(2) | 7.04 | 0.334 | 0.734 | 0.559 |
| | 3.84 | 0.647 | 0.277 | -0.764 |
| | 3.43 | 0.685 | -0.620 | 0.321 |
| C(3) | 4.15 | -0.402 | 0.100 | 0.942 |
| | 3.67 | -0.106 | 0.982 | -0.145 |
| | 2.47 | 0.909 | 0.159 | 0.303 |
| C(4) | 4.23 | 0.026 | 0.973 | -0.231 |
| | 4.01 | -0.452 | 0.216 | 0.901 |
| | 2.84 | 0.891 | 0.082 | 0.366 |
| C(5) | 5.61 | 0.099 | 0.778 | 0.609 |
| | 4.42 | 0.924 | -0.303 | 0.151 |
| | 4.15 | -0.369 | -0.550 | 0.779 |
| C(6) | 6.68 | 0.237 | 0.937 | 0.236 |
| | 5.18 | 0.756 | -0.345 | 0.489 |
| | 3.49 | -0.611 | -0.063 | 0.840 |
| C(7) | 4.76 | -0.255 | -0.642 | 0.743 |
| | 3.66 | 0.434 | 0.592 | 0.638 |
| | 3.39 | 0.864 | -0.487 | -0.203 |
| C(8) | 4.43 | 0.162 | 0.038 | 0.968 |
| | 3.88 | -0.029 | 0.999 | -0.031 |
| | 2.75 | 0.986 | 0.023 | -0.249 |
| O(9) | 8.86 | -0.383 | -0.528 | 0.789 |
| | 4.03 | -0.370 | 0.840 | 0.428 |
| | 3.50 | 0.846 | 0.129 | 0.441 |
| O(10) | 7.12 | -0.498 | -0.348 | 0.835 |
| | 5.06 | 0.251 | 0.819 | 0.492 |
| | 3.38 | 0.830 | -0.457 | 0.246 |

# TABLE 16

## Angles Formed between Orientations of Thermal Ellipsoids and the Normals of Mean Planes

| Plane | Atom | cos θ | θ |
|---|---|---|---|
| O(1)O(2)C(3)C(4) | O(1) | 0.9717 | 13°40' |
| | O(2) | 0.9207 | 22°58' |
| | C(3) | 0.1412 | 81°53' |
| | C(4) | 0.5668 | 55°28' |
| C(7)C(8)O(9)O(10) | C(7) | -0.8814 | 151°48' |
| | C(8) | -0.4335 | 115°41' |
| | O(9) | -0.9357 | 159°20' |
| | O(10) | -0.9517 | 162°07' |
| C(4)C(5)C(6)C(7) | C(4) | 0.3553 | 69°11' |
| | C(5) | 0.9318 | 21°17' |
| | C(6) | 0.7835 | 38°25' |
| | C(7) | 0.1277 | 82°40' |

# TABLE 17

## Summary of Magnitudes and Orientations of the Thermal Ellipsoids of Carboxyl Oxygens in Cyclobutanedicarboxylic Acids

| Acid | Atoms | B(Å$^2$) | θ(°) | H acceptor or donor | O···O(Å) | ν(°) | Ref. |
|---|---|---|---|---|---|---|---|
| cis-1,2- | O(1) | 6.74 | 14 | d | 2.637 | 31 | This work |
| (puckered) | O(2) | 7.04 | 23 | a | 2.637 | 31 | |
| | O(9) | 8.86 | 21 | a | 2.651 | 88 | |
| | O(10) | 7.12 | 18 | d | 2.651 | 88 | |
| trans-1,2- | O(1) | 9.57 | 10 | d | 2.64 | 40 | 47 |
| (puckered) | O(2) | 9.45 | 11 | a | 2.64 | 40 | |
| cis-1,3- | O(1) | 6.76 | 10 | a | 2.616 | 88 | 46 |
| (puckered) | O(2) | 8.58 | 10 | d | 2.616 | 88 | |
| | O(3) | 7.13 | 8 | a | 2.631 | 70 | |
| | O(4) | 8.42 | 17 | d | 2.631 | 70 | |
| trans-1,3- | O(1) | 9.60 | 10 | d | 2.649 | 64 | 72 |
| (planar) | O(2) | 7.56 | 0 | a | 2.649 | 64 | |
| trans-1,3-dianion | O(1)* | 5.48 | 16 | a | 2.623 | 48 | 74 |
| (planar) | O(2)* | 3.77 | 3 | a | 2.552 | 48 | |
| trans-1,3- | O(3)* | 4.66 | 12 | — | ——— | 72 | 74 |
| (puckered) | O(4) | 7.09 | 7 | d | 2.552 | 72 | |
| | O(5)* | 5.61 | 13 | — | ——— | 76 | |
| | O(6) | 6.64 | 14 | d | 2.623 | 76 | |

θ = angle formed between main B axis and normal to plane of carboxyl group.
ν = angle formed between the corresponding carboxyl group and cyclobutane ring.
a = proton acceptor in hydrogen bond.
d = proton donor in hydrogen bond.
* coordinated with sodium ion.

movement was also observed for other diacids (either planar or puckered) as can be seen in Table 17. The librations of oxygen atoms around C-C bond are larger than the expected values. However, in the molecule of disodium salt of trans-1,3-diacid, the oxygen atoms, which are coordinated with sodium ion, show small thermal motion. The anisotropic movement of oxygen atoms in planar terephthalic acid is not as large as that in most of the cyclobutanedicarboxylic acids. The main B axes are: 5.785 and 4.901.

The magnitudes of the movement of the carboxyl group probably depend upon the characteristics of the molecule, and the nature of the environment around it, such as hydrogen bonds, van der Waals interactions and coordinations with other atoms. It appears that in both the planar and the puckered form the carboxyl oxygens have in common a high thermal motion perpendicular to the plane of the acid group and the temperature movement of the ring does not contribute any influence to that of oxygens on the side chains.

# CHAPTER 5

## SUMMARY

Crystals of cis-1,2-cyclobutanedicarboxylic acid $C_4H_6(COOH)_2$ are monoclinic, space group $P2_1/c$, with a = 10.710 ± 0.003, b = 8.559 ± 0.002, c = 7.343 ± 0.002 Å, β = 95.03°, and four molecules per unit cell. The structure was determined by the symbolic addition method. Block diagonal least-squares refinement yields a R-value of 0.056 for 1256 independent reflections.

The cyclobutane ring is puckered with a dihedral angle near 156°. C-C bonds of the ring average 1.540(4) Å which does not show any significant lengthening. One carboxyl group is more or less parallel and the other perpendicular to the mean plane of the ring. C-O bonds are shorter while C=O bonds are longer than the normal values. The acid hydrogens involved in the hydrogen bonding are found to be statistically disordered. In the crystal centrosymmetric hydrogen bonds between carboxyl groups generate infinite zig-zag chains of molecules running in the a-direction.

The thermal movements perpendicular to the planes of carboxyl groups are somewhat larger in the one perpendicular to the ring than that of the other parallel to the ring.

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