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Preparation and X-Ray Crystallographic Studies of Copper N-Methylimidazole Complexes with Substituted N-Phthaloylalaninato Ligands

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PREPARATION AND X-RAY CRYSTALLOGRAPHIC STUDIES OF COPPER *N*-METHYLIMIDAZOLE COMPLEXES WITH SUBSTITUTED *N*-PHTHALOYLALANINE LIGANDS

by

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ABSTRACT

Quasiracemates contain two molecules (or ions) of opposite handedness, in which one enantiomer has a substitution of a chemically different, but similarly shaped group. Metal based complexes that are enantiomeric, racemic and quasiracemic were synthesized. Racemic metal compounds are synthesized from equimolar concenteration of chemically identical ligands having both handedness (R and S). Quasiracemic metal complexes were synthesized from two stercially similar, but chemically different ligands, and these complexes tend to mimic the centrosymmetric pattern in racemic metal complexes. This project was begun by previous master's student, Hiral Patel, to study the crystal packing of metal based quasiracemic complexes, and the goal of this study was to extend this approach. Substituted *N*-phthaloylalanines were synthesized and characterized by ^{1}H-NMR. Anions of these compounds and *N*-methylimdiazole are used as ligands to prepare metal complexes with a square planar geometry about copper. Two new crystal structures and one improved structure previously done determined. The new structures are (1) a new quasiracemate, bis(*N*-methylimidazole)((D)-3-chloro-*N*-pthaloyl-aninato)((L)-3-nitro-phthaloylalaninato)copper(II), Cu(**7**,D)(**9**,L)(*N*-MeIm)$_2$, (2) a racemate, bis(*N*-methylimidazole)bis((D,L)-3-methyl-*N*-pthaloylalaninato)-copper(II), Cu(**2**,D,L)$_2$(*N*-MeIm)$_2$, and (3) an improved structure of quasiracemate, bis(*N*-methylimidazole)((D)-3-chloro-*N*-phthaloyalaninato)((L)-3-methyl-phthaloylalaninato)-copper(II) Cu(**7**,D)(**2**,L)(*N*-MeIm)$_2$,. The chloro and nitro groups are disordered in both the quaisracemic complexes and the methyl phthaloyl ring is disordered over three and two positions in the quaisracemic and the racemic complexes, respectively. Analysis of

the structures showed that crystal packing of quaisracemic and racemic complexes is similar, whereas the enantiomeric complex has a different packing pattern.

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INTRODUCTION

Molecules aggregate to form crystals and there are topological features that contribute to the determination of the arrangement of molecules in crystals also known as crystal packing. Crystals often have centers of symmetry. Molecular shape has been considered as one of the main features responsible for crystal packing.[1-5] Crystals contains millions of atoms, the simplest translational repeat of the three-dimensional pattern is called the unit cell. A unit cell is a rectangular box that repeats in the three directions of space. Symmetry operations may be present in the structure reducing the minimum repeat unit of the structure to a fraction of the unit cell called the assymetric unit.[6] The symmetry operations can generate the unit cell from the asymmetric unit, and with translations in (±) x, (±) y and (±)z, the entire crystal structure is generated. The order of importance of symmetry operators in the packing of crystals has been studied and was found to be inversion center > twofold screw > glide > translation [2,4-5]. Thus, a wide variety of chemical frameworks studied indicates that there is a large tendency toward centrosymmetry in crystals.

Chiral structures cannot be superimposed on their mirror images, and they cannot contain a center of symmetry. Enantiomers are of one handedness (R or S) and do not contain a center of inversion in their crystals. Racemate structures contain equimolar concentration of two enantiomers with opposite handedness (R and S).[1] Racemates often crystallize in structures with a center of symmetry between the two-enantiomer molecules. Figure 1a shows the results of cocrystallisation of R and S molecules to form a racemic crystal, with center of inversion. Any dipole moments cancel out because the molecules

are related by the center of inversion and this tendency towards centrosymmteric was estimated to occur in more that 90% of the cases studied.[1,2-7] Cancellation of the dipole moment prevents many physical properties from occurring such as second harmonic generation of light, which requires a permanent dipole moment.

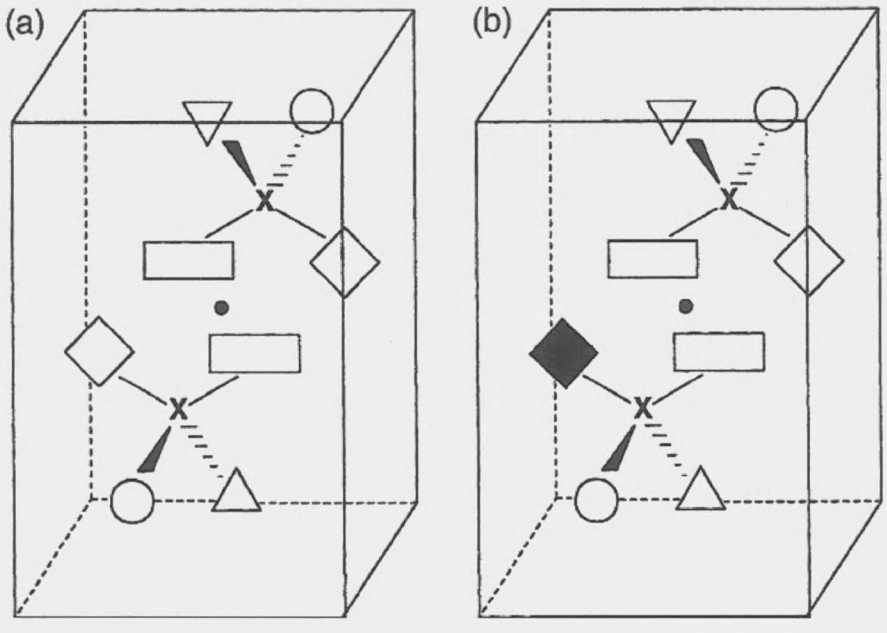
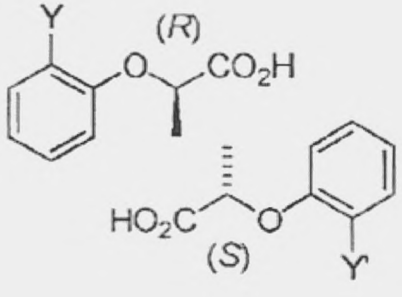


Figure 1. The centrosymmetric pattern of a racemate (a) and a quasiracemate (b). The filled diamond and open diamond represent chemically different, but similarly shaped groups. [1]

Consider a slight change in the racemic structure, Figure 1(a). One group on an enantiomeric molecules is changed to a chemically different but similarly shaped group. This is symbolized by substitution of a filled diamond for an open diamond in Figure 1(b). If this structural change is small, the overall shape of the molecule is similar to the original molecule. These two molecules should pack in a fashion similar to the racemate about a "pseudo"inversion center. Because the two molecules of differing handedness are chemically different, this structure is not a true racemate. It is known as a quasiracemate.

A. Fredga did a detailed study on quasiracemates by studying melting phase diagrams and demonstrated that two compounds in a quasiracemate should have an isosteric relationship and opposite molecular chirality to form quasiracemates.[1,2-4] These studies did provide insight to quasiracemate behavior, but the exact factors that influence quasiracemate formation were not known. A recent study by Davis *et al.* [3] has shown that structures of quasiracemates have pseudoinversion centers in contrast to true, crystallographic inversion centers found in 'true racemates'. The two different compounds that make up a quasiracemate are isosterically similar, and their crystal structures tend to have isostructural relationships with 'true racemates' with the same pattern of crystal packing and nearly identical unit cell dimensions. This was observed for the synthesis of quasiracemate compounds of 2-phenoxypropionic acids with the phenyl ring substituted by Cl, Br and CH_3 groups. The compounds studied are shown in Figure 2. Quasiracemates, are formed from the components that are of opposite chirality and are sterically similar to each other, **D-F**. These sets of structures have pseudoinversion centers similar to true inversion centers found in racemic structures, **A-C**.



	Y	Y'
A	Cl	Cl
B	Br	Br
C	CH_3	CH_3
D	Br	Cl
E	Cl	CH_3
F	Br	CH_3

Figure 2. Substituted 2-Phenoxypropionic acids that form racemic (**A-C**) and quaisracemic (**D-F**) crystals.[3]

In another example of a structural study of quasiracemates, Wheeler *et al.* [2] synthesized five crystals from 2-(2,4-dichlorophenoxy)propanoic acid (Figure 3a) and 2-(2-chloro-4-nitrophenoxy)propanoic acid (Figure 3b). The five crystals were the two racemates of each compound R(a)/S(a), R(b)/S(b), an enantiomer of each compound R(a), S(b), and a quasiracemate of the two compounds R(a)/ S(b) (Figure 3c). In this example, centrosymmetry and molecular shape play the dominant role in packing of the crystal.

Symbiolic diagrams representative of these five crystals are shown in Figure 4. The top row shows enantiomers of two different compounds. The group with a slightly different chemical composition is represented by a filled circle. The second row shows racemates of these two compounds (right) and (left) and a quasiracemate (center). In most cases the quasiracemate mimics the centrosymmetric pattern of the racemates of (a) and (b) but there is usually a difference between the packing motif of the racemate and the enantiomers. The goal of any study of quasiracemates is to prepare this set of five structures and compare the packing. It is not always possible to obtain all five of the set.

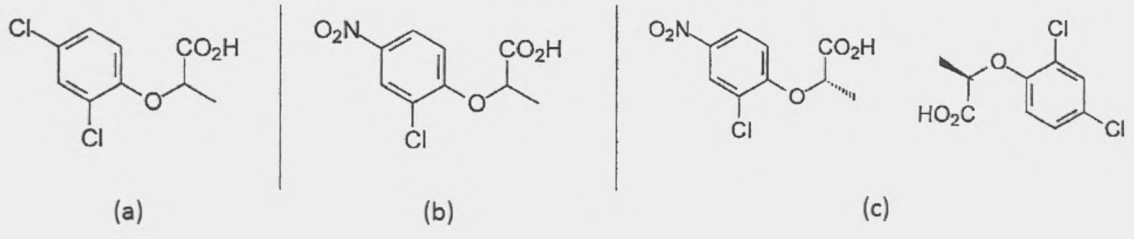


Figure 3. 2-(2,4-dichlorophenyl)propanoic acid (a), 2-(2-chloro-4-nitrophenyl)propanoic acid (b). Quasiracemate formed by these two compounds (c).[2]

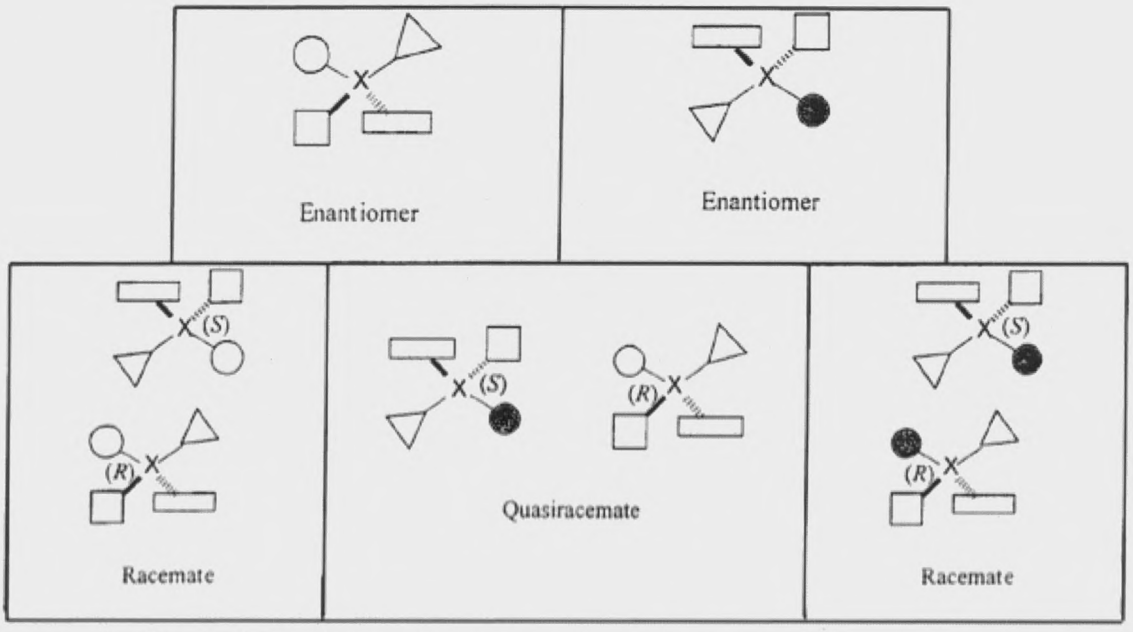


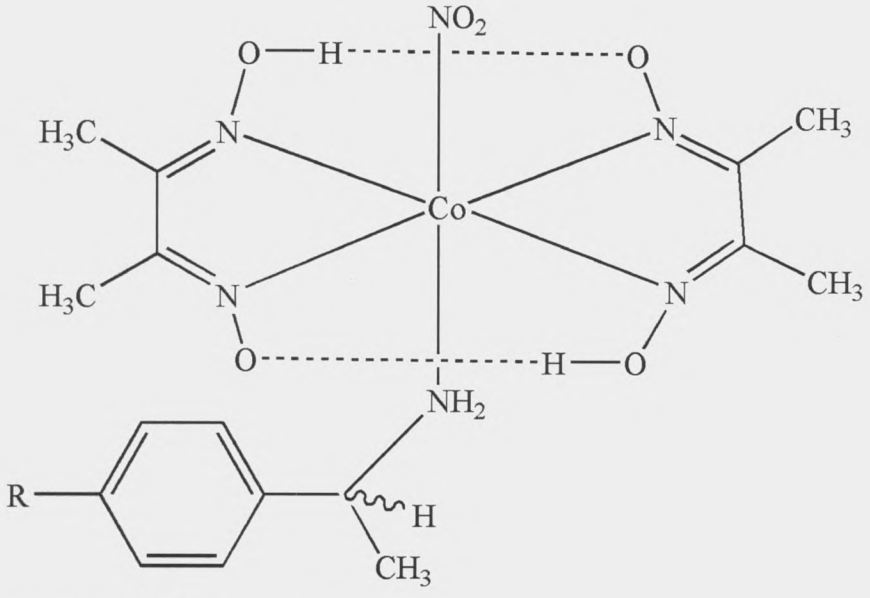
Figure 4. Illustration of the five types of compounds of interest in the study of quasiracemates. The top row shows two enantiomers, which differ by one functional group (shaded circle). The bottom row shows true racemates (right and left) and a quasiracemate (center) formed by two enantiomers.[5]

There has been very little use of metals to form quasiracemates. Certain metals have geometries (octahedral and square planar) that tend to arrange ligands about a center of symmetry. Metal centers such as these should be good candidates for bringing together components of a quasiracemate.

Copper(II) is usually found to form square planar complexes,[8-9] while cobalt(II) has been found to adopt octahedral complex geometry. To form a complex, ligands assemble or bind with metal ions and the geometry of the complex depends on coordination number and coordination geometry preferences of the metal, such as copper with coordination number 4, and square planar geometry. Packing in the crystal is also in part directed by non-covalent forces originating from the structural features of ligands of choice.

Two examples of metal-based quasiracemates from the literature are described here. The first uses cobalt, which tends to form octahedral complexes. Figure 5 shows

quasiracemate systems studied by Reemers *et al.* [10-11] Both **A** and **B** are homochiral but they are not chemically equivalent, the cocrystallisation of **A** and **B** forms the solid **C**, which is a heterochiral quaisracemate. This solid has two components of opposite chirality (R and S) and forms a quasiracemate. These structures were compared through analysis of crystal packing and observation of lattice parameters.



A: R = OCH_3, *R* config. ligand

B: R = Cl, *S* config. ligand

C: cocrystal formed by A and B

Figure 5. Example of a metal base quasiracemate (**C**) formed from cobalt complexes with two different homochiral ligands (**A** and **B**).[10]

In another example, a non-centrosymmetric quasiracemate was formed by using bisoxazoline ligands with a substituted phenyl ring, Figure 6.[12] The ligand on the left has two chiral centers both of R configuration. The ligand on the right has two chiral centers as well, both S. The donor group, D, is-NEt_2 and the acceptor group, A, is CN. Note the zinc is tetrahedral so there is no pseudoinversion center possible in this structure.

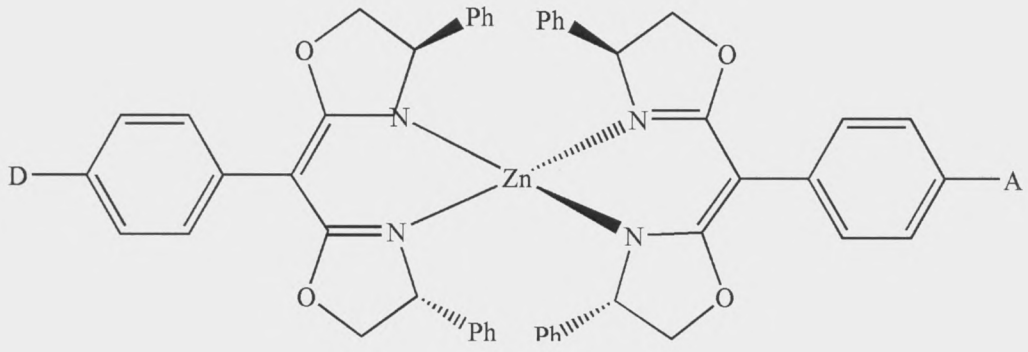
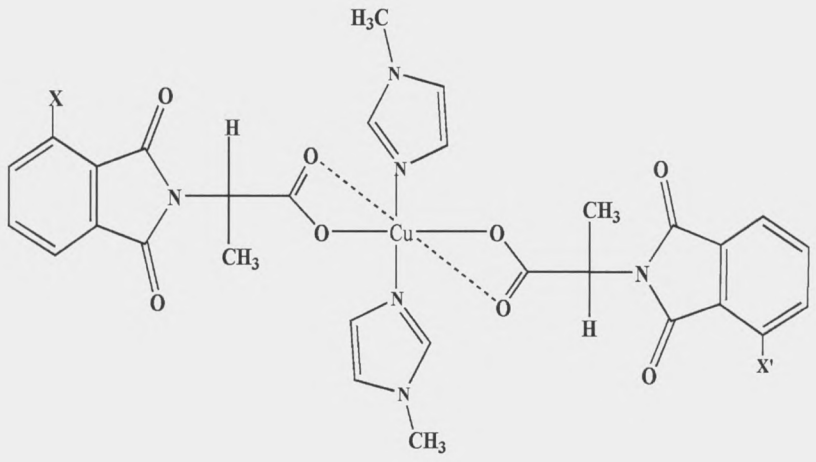


Figure 6. Example of a zinc based quasiracemate containing two bisoxazoline ligands of configuration (R,R), (left ligand) and (S,S), (right ligand)[12]

A previous student on this project, Hiral Patel, synthesized three crystal structures of copper complexes of substituted *N*-phthaloylalanines, Figure 7, Page 8. [13] In one structure, the X, X′=H and the two carboxylates were S configuration, this is an enantiomeric complex that was not disordered. In one structure X, X′= 3-Cl and one ligand was of R and one ligand was of S configuration, this is a racemic complex. In one structure one ligand was X = Cl, R and the other was X′= CH_3, S, this is a quasiracemic complex.

From the detailed study of these structures, it was found that the racemic complex and the quasiracemic complex of similarly shaped ligands have similar packing patterns, and the complex of pure enantiomer ligands have different packing pattern. The racemic and quasiracemic complexes have a true center of symmetry and pseudocenter of symmetry, respectively. The enantiomeric complex cannot contain a center of symmetry. The racemate and quasiracemate complexes were found to be disordered as chlorine atoms were found on both sides of the aromatic ring of the *N*-phthaloylalanine ligand in the ratio of approximately 80:20. The entire methyl phthaloyl ligand was also disordered over 3 positions. However, the enantiomeric complex was not disordered.



X	Configuration	X′	Configuration	Types of Complex
H	S	H	S	Enantiomeric
Cl	R	Cl	S	Racemic
Cl	R	CH_3	S	Quasiracemic

Figure 7. Structure of copper complexes with chiral *N*-phthaloylalanine and nonchiral *N*-methylimidazole ligands

The research described here is an extension of the approach taken previously by Patel with some modification in the synthesis of *N*-phthaloylalanine and the copper complexes. The main goals were 1) to synthesize *N*-phthaloylalanines from phthalic anhydrides and alanine, 2) to synthesize of copper complexes; enantiomic, racemic and quasiracemic using *N*-phthaloylalanine and *N*-methylimidazole as ligands and 3) to study and compare the crystals of these compounds. Copper(II) complexes have square planar geometry and with the ligands used here form a center of symmetry by binding to two oxygen atoms of a carboxylate from an *N*-phthaloylalanine and two nitrogen atoms of *N*-methyl imidazole. None of the copper complexes synthesized by Hiral Patel and in this thesis have hydrogen bonding groups on the aromatic ring, so it has been assumed that molecular

shape and van der Waals forces are the most important factors for the crystal packing. The basic plan of the synthesis is shown in Figure 8.

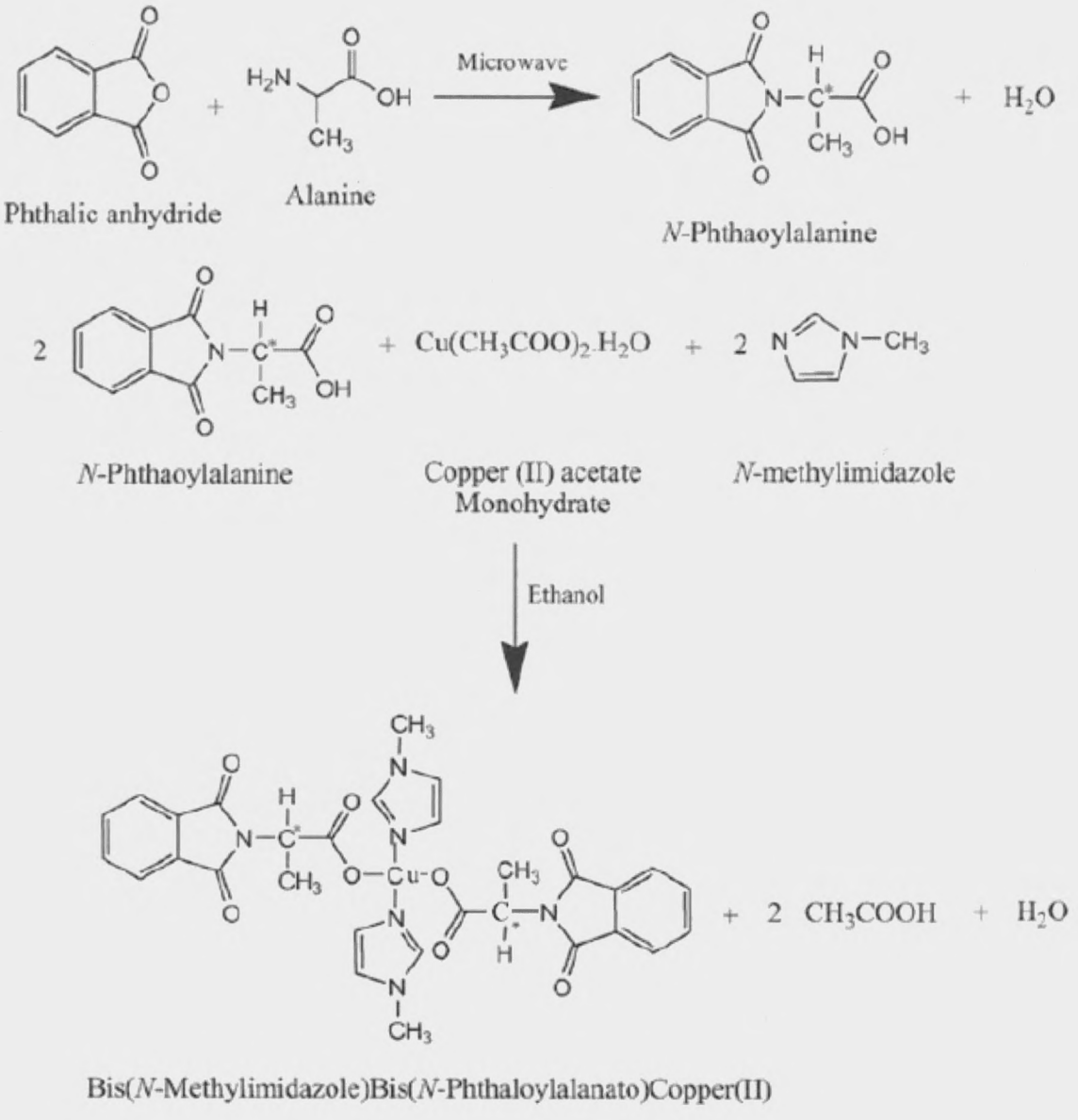


Figure 8. Synthetic strategy for preparation of *N*-phthaloylalanines and subsequent formation of copper complexes. [13]

N-phthaloylalanines are synthesized from phthalic anhydride and alanine by a microwave technique. Phthalic anhydrides are available with several substitutions on the six membered ring, so a variety of compounds can be tested. Alanine provides a source of

molecular chirality. Phthalic anhydrides are readily condensed with amino acids through several methods including microwave irradiation.[14,15] Alanine was used as either the racemic mixture (D,L) or an enantiomer (D) or (L).

Hiral Patel used several nitrogen based ligands including pyridine, imidazole, and bipyridine in her studies. [13] *N*-methylimidazole formed the highest quality crystals, so it was also used in this study. In this work, simplification of the previously used synthetic procedures was accomlished. An improved crystal of one of the quasiracemates previously prepared was grown in a different solvent resulting in an improved crystal structure. Two new crystal structures of copper complexes have also been solved. One is a new quasiracemate (using the same notation as in Figure 7, Page 8 X = Cl, R and X′= CH_3,S) and the other is a true racemate (referring to the structure in Figure 7, Page 8 X = Cl, R and X′ = Cl, S). The three structures solved and the two copper complexes previously prepared by[13] are all compared.

MATERIALS USED

Various substituted phthalic anhydrides and different optical configurations of alanine were used to form *N*-phthaloylalanines. These compounds were then used to form complexes using copper and an additional nitrogen containing ligand, *N*-methyl imidazole. These copper complexes were enantiomeric, racemic or quasiracemic based on the chirality of the *N*-phthaloylalanine used. The list of starting material phthalic anhydrides, alanines and nitrogen-based ligand are shown in Tables 1, 2 and 3 respectively. The structures of these compounds are shown in Figure 9.

Table 1. Phthalic Anhydrides Used in this Research

Number	Chemical Name	Supplier	Molecular Weight (g/mol)	Chemical Formula
1	Phthalic anhydride	J.T.Baker Chemical & Co. (Baker analyzed Reagent)	148.12	$C_6H_4(CO)_2O$
2	3-Methylphthalic anhydride	Acros Organics	162.14	$C_9H_6O_3$
3	4-Methylphthalic anhydride	Acros Organics	162.14	$C_9H_6O_3$
4	3-Fluorophthalic anhydride	Acros Organics	166.11	$C_8H_3FO_3$
5	4-Fluorophthalic anhydride	Acros Organics	166.11	$C_8H_3FO_3$
6	3-Chlorophthalic anhydride	Acros Organics	182.56	$C_8H_3ClO_3$
7	3-Nitrophthalic anhydride	Acros Organics	193.12	$C_8H_3NO_5$
8	4-Nitrophthalic anhydride	Acros Organics	193.12	$C_8H_3NO_5$
9	4-Bromophthalic anhydride	Acros Organics	227.01	$C_8H_3BrO_3$

Table 2. Alanines Used in this Research

Number	Name	Supplier	Molecular Weight (g/mol)	Chemical Formula
10	D,L-Alanine	Sigma Chemical Company	89.1	$CH_3CH(NH_2)(COOH)$
11	D-Alanine	Sigma Chemical company	89.09	$CH_3CH(NH_2)(COOH)$
12	L-Alanine	Eastman Company	89.09	$CH_3CH(NH_2)(COOH)$

Table 3. Nitrogen Based Ligand Used in this Research

Number	Name	Supplier	Molecular Weight (g/mol)	Chemical Formula
13	*N*-Methyl Imidazole	Acros Organics	82.11	$C_4H_6N_2$

Chemical structures of organic compounds used

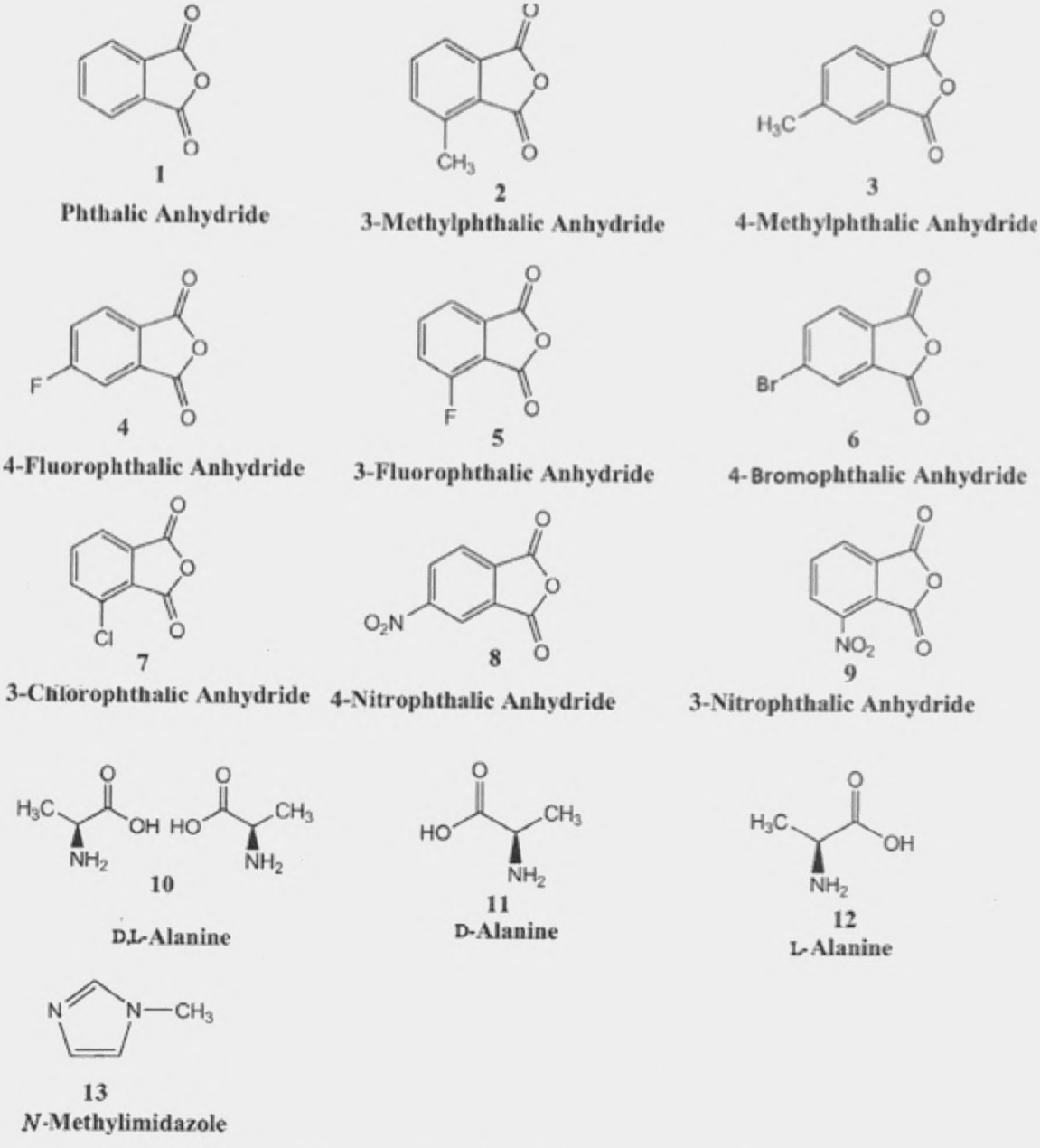


Figure 9. Chemical structures of materials that were used in our research.

EXPERIMENTAL METHODS

Purification of phthalic anhydride

Purification of phthalic anhydride is necessary as it is usually contaminated by the presence of hydrolysis product, phthalic acid. The purification is done by dissolving 5.0 g of phthalic anhydride in 100 mL of ethyl acetate. This solution is washed with 25 mL of 5% sodium bicarbonate twice using a separatory funnel. The solvent is allowed to evaporate overnight to give pure phthalic anhydride. This gave 30 % recovery, 1.50 g of pure phthalic anhydride that could be used for the *N*-phthaloylalanine syntheses.

Naming convention for *N*-phthaloylalanines

Different phthaloylalanine are named throughout with reference to the number of the starting anhydrides, Figure 9. For example, 3-nitrophthalic anhydride has been assigned as **9**, so, (D,L)-3-nitro-*N*-phthaloylalanine will be identified as (**9,**D,L) where D, L indicates the racemate of alanine was used. Enantiomeric *N*-phthaloylalanines will have only one letter. For example, (**9,**D) is the condensation product of **9** and D-alanine.

Synthesis of *N*-Pthaloylalanines

Preparation of (D, L) –*N*-phthaloylalanine (1,D,L)

This compound has been made by several methods. [14,15] In previous work DMF was used as the solvent, better results were obtained in this work using ethyl acetate.[15] Hiral Patel used DMF as the solvent, but it is difficult to remove the solvent completely. Better results were obtained by switching to ethyl acetate. The preparation of *N*-phthaloylalanines is represented by the full description of synthesis of (D,L)-*N*-phthaloylalanine, (**1**,D,L). In a 125 ml Erlenmeyer flask, phthalic anhydride (2.000 mmol, 0.2962 g) and D,L-alanine (2.200 mmol, 0.1960 g, 10% excess) were mixed together in 5

mL of glacial acetic acid. A watch glass was placed on top of the flask. The mixture was shaken using tongs after every 30 s while being heated in microwave (Hotpoint Counter Saver 3, Model REM4G 001, 800 W) for 2 min at 50 % power. After heating, the mixture was kept at room temperature for approximately 10 min with the watch glass on top of flask. To the cooled mixture, ethyl acetate (20.0 mL) was added. Using a separatory funnel, the solution was washed twice with 20 mL of de-ionized water and further washed once with 20 mL of brine solution. The top layer of ethyl acetate solution was transferred to a watch glass for a slow evaporation. It took overnight to form crystals of *N*-phthaloylalanine (**1**,D,L) (0.35184g, 80% yield), which were scraped off the watch glass and examined under microscope. The product was white needle shape crystals. Similarly, other *N*-phthaloylalanines were synthesised by using different combination of substituted phthalic anhydride and different alanines. Table 4 summarizes the results of synthesis of the *N*-phthaloylalanines. Some of the products were oily upon initial evaporation. By grinding with water and then allowing the solvent to evaporate yielded crystals were obtained.

Table 4. Summary of *N*-Phthaloylalanines Synthesised

N-Phthaloylalanine	Molecular Weight (g/mol)	Color	Yield (g)
2,D,L[a]	233.22	Off white	0.380 (81.4%)
2,D[a]	233.22	Off white	0.224 (48.2%)
2,L[a]	233.22	Off white	0.265 (56.8%)
3,D	233.22	Yellow	0.224 (48.0%)
3,L	233.22	Yellow	0.210 (45.1%)
4,D,L	237.18	White	0.400 (84.3%)
4,L	237.18	White	0.369 (77.8%)
5,D	237.18	White	0.418 (88.2%)
6,L	298.14	White	0.310 (52.0%)
7,D	253.64	White	0.411 (81.0%)
8,D	265.19	Yellow	0.345 (65.0%)
8,L	265.19	Yellow	0.318 (60.0%)
9,D,L	265.19	White	0.494 (93.2%)
9,L	265.19	White	0.222 (42%)
9,D	265.19	White	0.424 (80.0%)
a- All reaction except those with 2 were done of 2 min. 2 was reacted for 3 min.			

These products were characterized by ^{1}H-NMR to confirm the formation of products, and to assure these compounds are suitable for further use in the synthesis of copper complexes.

Using d-chloroform as a solvent, ^{1}H-NMR spectra of above mentioned *N*-phthaloylalanines from Table 4 were recorded. The ^{1}H-NMR spectrum showed the formation of correct product with 50% microwave power and 2 min of reaction time for all compounds with two exceptions. For (D,L)-3-methyl-*N*-phthaloylalanine **(2,**D,L**)** the spectrum showed the presence of starting material (Described further in the results and discussion section). Longer reaction time at 50% power, 3 min brought the reaction to completion. The ^{1}H-NMR spectrum of the attempt to prepare 3-hydroxyl phthaloylalanine showed a large amount of an unidentified impurity, and this compound was not used further for copper complex formation reactions. The ^{1}H-NMR spectra with peak assignments for *N*-phthaloylalanines from Table 4 are compiled in Appendix A. For the two products containing fluorine, the proton coupled ^{19}F also in Appendix A.

Preparation of copper complexes

Preparation of *N*-methylimidazole stock solution

Because a small amount of *N*-methylimidazole is used, it was convenient to use a stock solution. This stock solution was prepared by mixing 1.0 mL of *N*-methylimidazole (12.54 mmol, density = 1.03g/1mL) with ethanol to produce a final volume of 50 mL. A 1.0 mL portion of this stock solution of *N*-methylimidazole contains 0.0206 g (0.2509 mmol) of *N*-Methyl Imidazole. This is in excess of the 0.2000 mmol required for the preparation of the copper compounds described below.

Synthesis of bis(*N*-Methylimidazole)bis((D,L)-3-nitropthaloylalaninato)copper(II) (Cu(9, D,L)$_2$(*N*-MeIm)$_2$

The preparation of racemic and enantiomeric complexes is illustrated by the full description of synthesis of Cu(**9**,D,L)$_2$(*N*-MeIm)$_2$. The preparation of quasiracemic complexes is described in a separate section. (D,L)-3-nitrophthaloylalanine (**9**,D,L) (0.02652 g, 0.100 mmol) and copper acetate (0.0099g, 0.0500 mmol) were added to a beaker with 20 mL of ethanol. The solution was heated with watch glass on top of the beaker until all reactants dissolved. At this point, *N*-methylimidazole (1 mL, 0.2509 mmol, approximately 20% excess) stock solution was added dropwise and the color of solution was changed to sky blue from dark blue. The solution was heated further for 10 minutes near the boiling point of ethanol keeping the watch glass on top of the beaker. Crystals were grown by slow evaporation in the beaker covered with the watch glass. This usually took 2-4 days in most cases and crystals were isolated before all the solvent evaporated. If the solvent was completely evaporated, about 10 mL of ethanol was added

to aid in isolation of the crystals. The quality of the crystals for X-ray diffraction was evaluated under microscope. Similarly, other copper complexes were made by reacting different substituted (Table 4) *N*-phthaloylalanines with copper acetate and *N*-methylimidazole. Using the abbreviated naming system described above for *N*-phthaloylalanines, the copper compound will be named using the format Cu(**9**,D,L)$_2$(*N*-MeIm)$_2$ where (**9**,D,L) in this case means the carboxylate anion of (**9**,D,L), and *N*-MeIm is *N*-methylimidazole.

Some of the mixtures did not form crystals and instead formed a glassy layer after slow evaporation. Attempts to recrystallized these products with ethanol were not successful. Results of attempts to form racemic and enantiomeric copper complexes, which have single type of *N*-phthaloylalanine are shown in Table 5. To form quasiracemates, two different but sterically similar *N*-phthaloylalanines were used and two equivalents of *N*-methylimidazole were used with copper acetate, (Described in next section).

Table 5. Summary of Preparation of Racemic and Enantiomeric Copper Complexes

Number	Complex	Molecular Weight (g/mol)	Yield (g)	Notes
Racemates				a) Crystals formed and were sent for X ray diffraction analysis. b) Successful crystal structure obtained. c) Glassy product formed, no crystals could be isolated.
1	(Cu(**7**,D,L)$_2$(*N*-MeIm)$_2$	733.01	c	
2	(Cu(**2**,D,L)$_2$(*N*-MeIm)$_2$	692.17	0.4567 (33%) [a,b]	
3	(Cu(**4**,D,L)$_2$(*N*-MeIm)$_2$	700.11	c	
4	(Cu(**1**,D,L)$_2$(*N*-MeIm)$_2$	664.13	0.3718 (28%)[a]	
5	(Cu(**9**,D,L)$_2$(*N*-MeIm)$_2$	754.13	c	
Enantiomers				
1	(Cu(**7**,D)$_2$(*N*-MeIm)$_2$	733.01	0.3811 (26%) [a]	
2	(Cu(**2**,L)$_2$(*N*-MeIm)$_2$	692.17	0.4845 (35%) [a]	
3	(Cu(**4**,D)$_2$(*N*-MeIm)$_2$	700.11	0.4480 (32%)[a]	
4	(Cu(**9**,L)$_2$(*N*-MeIm)$_2$	754.13	0.5278 (35%) [a]	

Preparation of quasiracemates

Preparation of bis(*N*-methylimidazole)((D)-3-chloro-*N*-methylphthaloylalaninato)(-(L)-3-methyl-*N*-phthaloylalaninato)copper(II), Cu(7,D)(2,L)(*N*-MeIm)$_2$

Quasiracemates contain different chemical substances but the molecules are sterically similar. In this work, they are formed by reaction of two different *N*-phthaloylalanines with copper acetate and *N*-methylimidazole. Preparation of quasiracemic complexes is similar to preparation of the racemic or enantiomeric complexes. It was found that

methanol was a better solvent for the quasiracemates than ethanol. Two different acids for example, (D)-3-chloro-*N*-phthaloylalanine (**7**,D) (0.0253g, 0.100 mmol) and (L)-3-methyl-*N*-phthaloylalanine (**2**,L) (0.0233g, 0.100 mmol), are reacted with copper acetate (0.01997g, 0.100 mmol) in a beaker. The compounds were dissolved in 20 mL methanol by heating on a hot plate with watch glass on top of the beaker. After the reactants dissolved, 1 mL *N*-methylimidazole of stock solution was added and the solution was heated for an additional 10 min. The color changed from sky blue to dark blue. The crystals were formed by a slow evaporation process that took 3-4 days. The crystals were isolated in the presence of solvent and evaluated under the microscope. If the solvent was completely evaporated, 10 mL of methanol was used as an aid in isolating the crystals. Similarly, other quasiracemate copper complexes were synthesized using the above procedure. The results of these syntheses are shown in Table 6. In this example, according to abbreviated naming system described above, this compound is named Cu(**7**,D)(**2**,L)(*N*-MeIm)$_2$.

Table 6. Summary of Synthesis of Copper Based Quasiracemates

Number	Complex	Molecular Weight (g/mol)	Yield	Notes
1	Cu(**7**,D)(**2**,L)(*N*-MeIm)$_2$	712.59	0.4988 (35%) [a,b]	a) Crystals formed and were sent for X-ray analysis.
2	Cu(**4**,D)(**1**,L)(*N*-MeIm)$_2$	682.12	0.2592 (19%) [a]	
3	Cu(**7**,D)(**9**,L)(*N*-MeIm)$_2$	743.57	0.5353 (36%) [a,b]	b) Successful crysal structures obtained.

X-Ray Crystallography

The copper complexes that were synthesized were examined under a 7-30x optical microscope. Crystals that were judged suitable for X-ray analysis (single crystals of size between 0.1 and 1.0 nm) were sent to Dr. Kraig A. Wheeler at Eastern Illinois University for collection of X-ray data. Nine sets of crystals were sent (those indicated by [a] in Tables 4 and 5). Of these a crystals, three have produced successful structures so far. Two are quasiracemic complexes, and one is a racemic complex. These three crystals along with an enantiomeric complex and a racemic complex prepared by Hiral Patel will be compared in the results and discussion section. Crystallographic data is compiled in Appenidx B.

RESULTS AND DISCUSSION

Synthesis and ^{1}H-NMR characterization of *N*-phthaloylalanines

Quasiracemic crystals are synthesized from two non-identical molecules of different optical configuration that are of similar shape. These crystals usually have a centrosymmtery pattern. Work of Dr. Raymond Davis and coworkers, [3] as described in the introduction, have confirmed that organic quasiracemates usually mimic the centrosymmetry pattern of 'true racemates' that they are derived from. Molecular shape has been considered one of the most important topological features for the formation of these crystals. The research in this thesis extends these ideas to the preparation of metal-based quasiracemates.

A previous research student, Hiral Patel, developed a synthesis of *N*-phthaloylalanines, and this has been modified in this thesis. The solvent was switched from DMF to acetic acid. Her previous preparation of 3-methyl-*N*-phthaloylalanine produced an impure product containing starting material, 3-methylphthalic anhydride. Longer reaction time used here completed this reaction. The overall synthesis scheme was shown on Figure 8 on page 9. These products were characterized by ^{1}H-NMR and spectra have been compiled in see Appendix A.

Chemical shift assignments of *N*-phthaloylalanines are listed in Appendix A in Table A1 and Table A2. The spectra of compounds 2-9 are shown in Figures A2-A9. Integration of the spectra and splitting patterns are consistent with the proposed structures. In the case of two fluorine containing compounds, proton decoupled ^{19}F-NMR are consistent with proposed structures. The ^{1}H-NMR spectrum of (D,L)-3-nitro-*N*-phthaloylalanine, (**9**,D,L)

shown in Figure 10 is a representative of a typical *N*-phthaloylalanine ^{1}H-NMR. As expected the single proton derived from alanine, $H_{(ala)}$ shows a quartet at 5.08 ppm, the methyl group from alanine is doublet at 1.76 ppm, $CH_{3(ala)}$, the aromatic protons consist doublet from two protons (H_A, H_C) at 8.15 ppm and triplet from one proton H_B at 7.95 ppm. Two separate doublets may be expected for H_A and H_C but they appear to be overlapping. The carboxylate –OH shows up as a broad peak at 3.0 ppm.

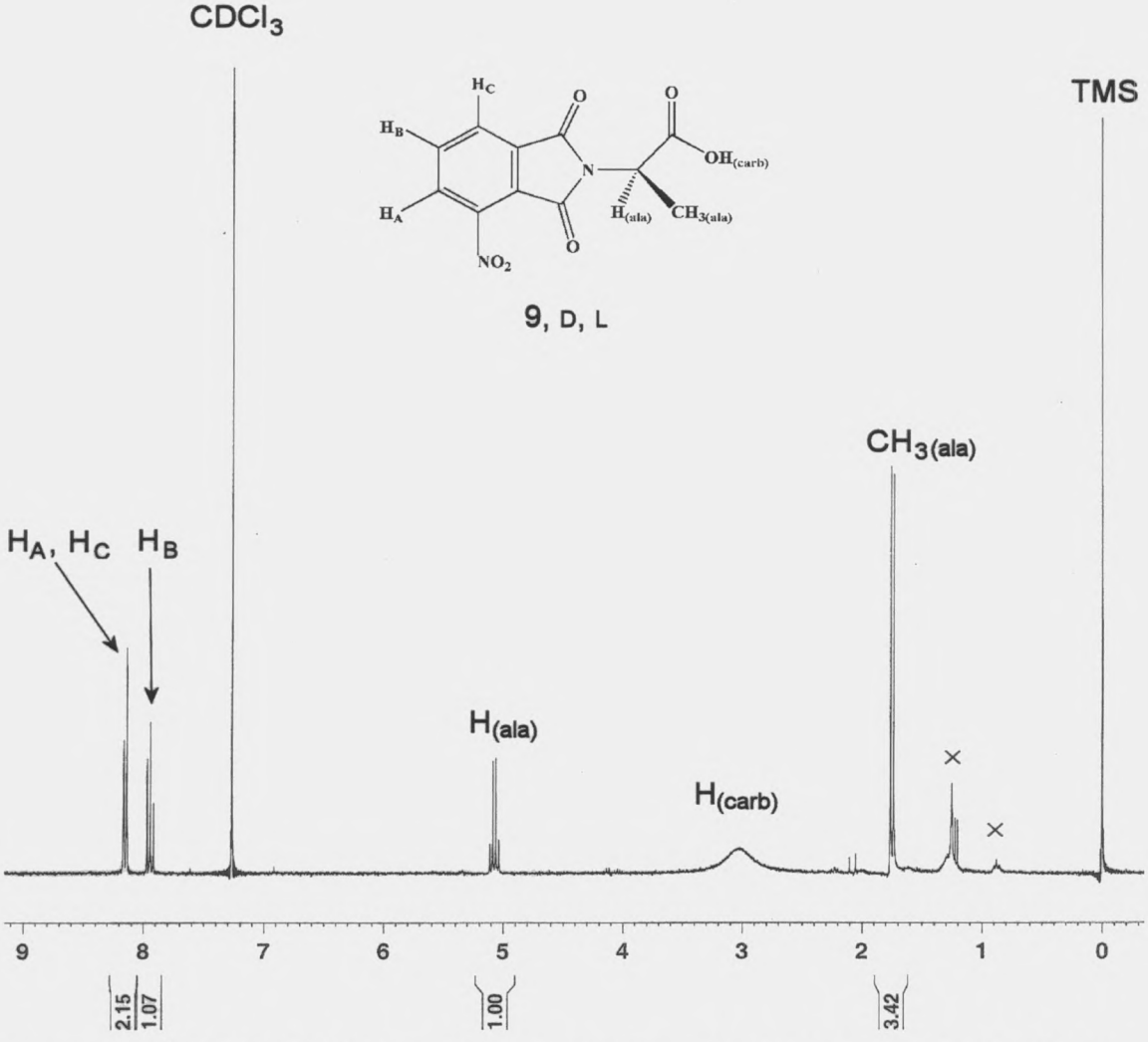


Figure 10. ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of (D,L)-3-nitro-*N*-phthaloylalanine, (**9**,D,L).

The power level of 50% was used in the *N*-phthaloylalanines synthesis because Hiral Patel had found that 100% microwave power caused racemization. It was found that 2 min reaction time at 50% power was sufficient to complete the reaction with the exception of (**2**,D,L) or (**2**,D) or (**2**,L) as shown in the partial ^{1}H-NMR spectrum of the product after 2 min (Figure 11a). The peaks at 2.69 and 2.74 ppm are the CH_3 group on the phthaloyl rings. In the desired product, there expected to be a singlet in this region. The two peaks indicate an approximately 50:50 mixture of starting material (3-methylphthalic anhydride) and the desired product (3-methyl-*N*-phthaloylalanine). The aromatic protons are expected to be a triplet and two doublets, but Figure 11(a) is more complicated than that. In fact, it is a combination of the aromatic region for the starting material, **2**, and the desired product (**2**,D,L). The peaks were identified by comparison of the spectra of pure **2** (Appendix A, Figure A6) and (**2**,D,L) (Appendix A, Figure A2). Increasing reaction time to 3 min completes the reaction as seen by the singlet at 2.69 (Figure 11(b)) indicating all the starting material has reacted. The ^{1}H-NMR spectra showed that these products were pure enough to use as ligands for copper complex synthesis.

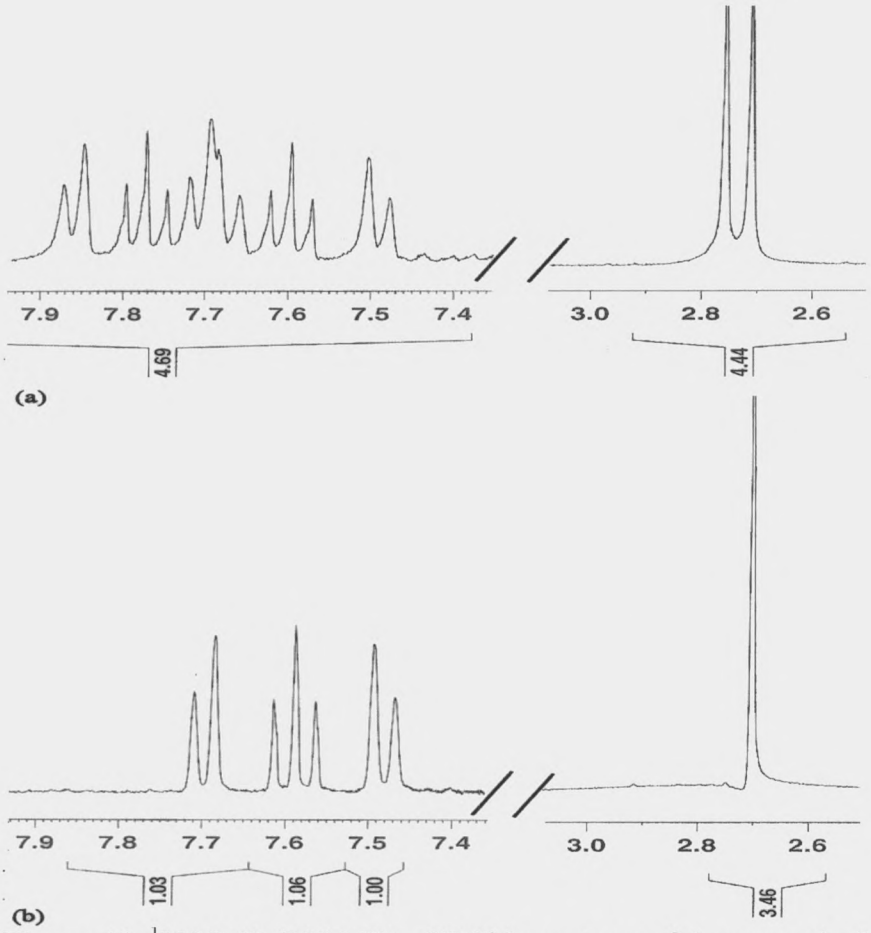


Figure 11. ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of the aromatic (left) and methyl group on the *N*-phthaloyl ring (right) regions of the product of reaction of 3-methyl-*N*-phthalic anhydride with D,L alanine (a) 2 min reaction shows an approximately 50:50 mixture of starting anhydride and desired product (b) 3 min reaction shows only the final product. (Full spectrum is in Figure A2, Appendix A)

Synthesis of metal complexes

We chose copper(II) to form our complexes because of the reliable square planar geometry and the centrosymmetric arrangement of ligands. The copper forms a center of symmetry and drives the crystal packing. In this and previous research, [13] copper formed better crystals than octahedral metals such as Co(II) or Ni(II). In the case of enantiomeric and racemic copper complexes, *N*-phthaloylalanines, *N*-methylimidazole and copper acetate were reacted in the ratio of 2:2:1, respectively; whereas in the case of a quasiracemic complexes, two different *N*-phthaloylalanines, *N*-methylimidazole and

copper acetate are reacted in the ratio of 1:1:2:1. The complexes that have been characterized by X-Ray crystallography all have the expected square planar geometry.

The synthesis of quasiracemic copper complexes has been modified. Previously, the two different *N*-phthaloylalanines of opposite handedness were reacted in ethanol separately along the *N*-methylimidazole and copper acetate. These separate complexes were dissolved together in ethanol to give a mixed ligand copper complex. The new modified method, as described in experimental section, eliminates separate preparation and gives better crystals by using methanol as the solvent.

Crystals were usually isolated before all the solvent was evaporated, and if the crystals were fully dry, solvent was added for isolation. Crystals were examined under microscope and well-shaped crystals of size 0.1-1.0 mm were sent to Dr. Kraig A. Wheeler at Eastern Illinois University for collection of single crystal X-ray data.

Crystallographic database search

A database search was done to determine if there were comparable structures done by other researchers. This will allow comparison of the packing patterns of the same ligand in different metal complex. A previous search of database for the anion of *N*-phthaloylamino acids bound to any metal by Hiral Patel found 21 structures but none of the structures contained square planar geometry and none contained *N*-phthaloylalaninato as a ligand.[13] In a new search of the Cambridge Crystallographic Database version of May 2011 for *N*-phthaloylamino acids, 24 structures (3 new ones) were found of which one structure (Ref code XUQCES)[16] was found similar to our expected copper complex structures. This structure from the literature contains two *N*-phthaloylglycinato ligands

instead of *N*-phthaloylalaninato as ligand. It is square planar and contains two water molecules as additional ligands. Structure will be compared to the copper complexes prepared for this research. The bonding environment around copper is shown for the two compounds in Figure 12.

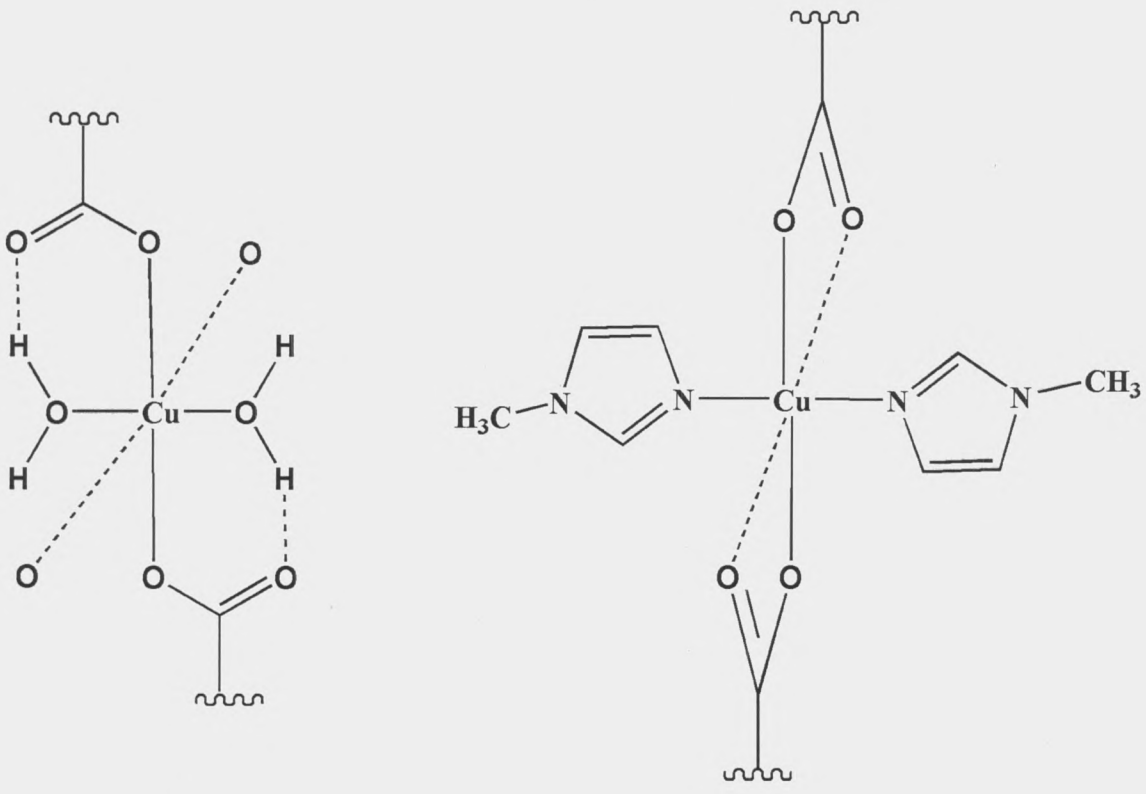


Figure 12. Comparison of the square planar ligand environment of bis(aqua)bis(*N*-phthaloylglycine)Cu(II) from the literature[16] and Cu(II) *N*-phthaloylalanine complexes prepared for this thesis

Both structures contain square planar copper with bonds of approximately 2 Å to the directly bound atoms. Conformations of the *N*-phthaloylalaninato ligands are the same in each structure with benzene ring approximately perpendicular to the plane of the carboxylate group. In the structure from the literature, the water ligand allows a hydrogen

bond to the carboxylate group of the *N*-phthaloylalaninato ligand. In order to form this hydrogen bond, the plane of carboxylate lies nearly coplanar with the square planar arrangement of atoms bound to copper (Figure 12a). There is a long weak interaction to carboxylate oxygen above and below the plane of the square planar geometry about copper. These oxygen atoms are carboxylate atoms of adjacent complexes.

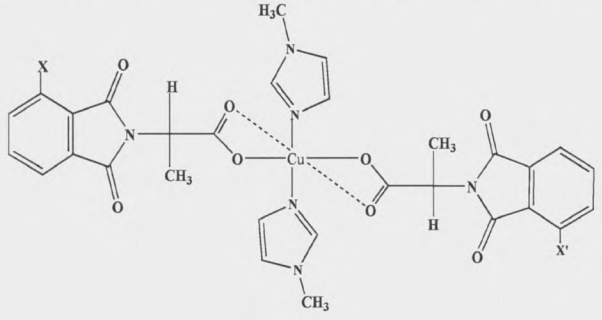
In structure Cu(**7**,D,L)$_2$(*N*-MeIm)$_2$, the *N*-methylimidazole ligand does not provide a hydrogen for hydrogen bonding so the carboxyl oxygen instead forms the weak interaction with copper at about 2.7 Å. In order to do this, the plane of carboxylate is approximately perpendicular to plane of square planar arrangement of atoms bound to copper. Thus, the carboxylate group of the *N*-phthaloylalaninato ligand in the complexes studied in this thesis has a conformation rotated about 90^0 from that of the carboxylate in the structure from the literature. So while the acid ligands are similar, the possibility of hydrogen bonding changes the orientation of the carboxylate group bound to copper. To conclude: while both structures are square planar about copper with two longer weaker interactions. The method that the carboxylate binds to copper is quite different in the two structures.

X-Ray crystallography

In one study of molecular shape and crystal packing, Dr. Wheeler and his co-workers synthesized a series of five crystals; two enantiomers, two racemates and a quasiracemate (see Figure 4, page 5).[2] As described in the introduction, enantiomers have different crystal packing from quasiracemates and racemates. Racemates and quasiracemate have similar crystal packing. The racemates have a true center of inversion and quasiracemate have pseudocenter of inversion. Quasiracemates are formed from the molecules that are chemically different, but sterically similar to each other.

The approach was extended to metal compounds in the master's thesis of Hiral Patel[13], completed in 2010. She synthesized three copper complexes that were studied by single crystal X-ray diffraction. She was not able to prepare the entire five compound series but did prepare a quasiracemic, a true racemic complex, and an enantiomeric complex of similar structure. Her research confirmed that racemates and quasiracemates of similar compounds are isostructural. The enantiomer is different from the others because an inversion center or pseudoinversion center is not possible. All three structures have shown the square planar geometry about the copper(II) ion.

Table7. List of Complexes that were Studied by Single Crystal X-Ray Diffraction



Compound	X	X′	Type of Complex	Reference
Cu(**7**,D)(**9**,L)(*N*-MeIm)$_2$	NO_2	Cl	Quasiracemic	This work
Cu(**7**,D)(**2**,L)(*N*-MeIm)$_2$	CH_3	Cl	Quasiracemic	This work, [13]
Cu(**2**,D,L)$_2$(*N*-MeIm)$_2$	CH_3	CH_3	Racemic	This work
Cu(**7**,D,L)$_2$(*N*-MeIm)$_2$	Cl	Cl	Racemic	[13]
Cu(**1**,L)$_2$(*N*-MeIm)$_2$	H	H	Enantiomeric	[13]

New crystal structures

Synthesis of pure *N*-phthaloylalanines and use of methanol as a solvent yielded crystals of new copper based complexes. Two new complexes and one improvement of a previous crystal study have come out of work for this thesis so far. These three crystals are the first three entries in Table 7, (above). A short description of each of the structures and an atomic displacement plot of the three new structures is described in the next few paragraphs. Bond lengths, bond angles, and interplanar dihedral angles will be listed and compared in a later section. Notice all three structures have square planar geometry about copper consisting of two *N*-phthaloylalaninato ligands and two *N*-methylimidazole

ligands. Each structure also has two weaker long Cu···O interactions to the carboxylate oxygen not directly bound to the copper.

bis(*N*-methylimidazole)((D)-3-chloro-*N*-pthaloyalaninato)((L)-3-nitro-*N*-phthaloylalaninato)copper(II) Cu(7,D)(9,L)(*N*-MeIm)$_2$

The atomic displacement diagram of the structure is shown in Figure 13. This is a new quasiracemate structure that is interesting because one group has three atoms -(NO_2) and other group is one atom -(Cl). A cross section of the nitro and the chloro group superimposed upon one another was constructed using the van der Waals radii from the literature[17] (O = 1.52 Å, N = 1.55 Å and Cl = 1.75 Å) and the bond distances from the crystal structure (C-Cl = 1.703 Å, C-N = 1.377 Å, N-O(average of two) = 1.227 Å) (C-N-O = 120°). This cross section is shown in Figure 14 below the atomic displacement plot. The nitro group is shown with solid lines and the chloro group is shown with dotted lines. The diagram clearly shows that the volume occupied by these groups is similar. The crystal structure showed a disorder in the Cl atom and nitro group, which were each found on the two sides of the phthaloyl aromatic ring in a ratio of approximately 82:18. The other atoms in the structure are well ordered.

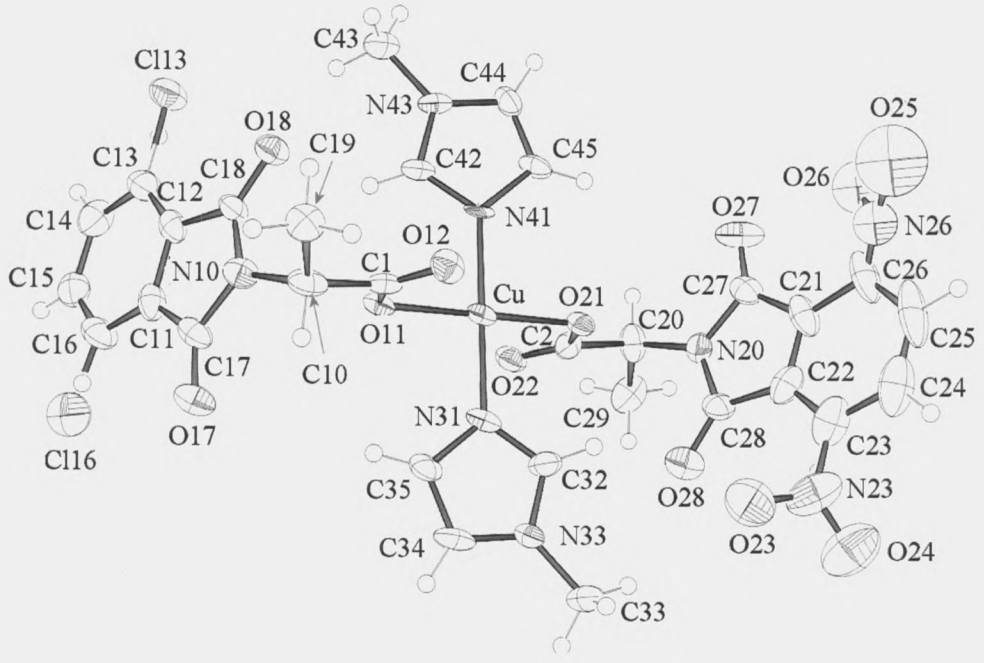


Figure 13. Shows an ORTEP diagram (50% probability ellipsoids) of the quasiracemate, bis(*N*-methylimidazole)((D)-3-chloro-*N*-phthaloylalaninato)((L)-3-nitro-*N*-phthaloylalaninato)copper(II) Cu(**7,**D)(**9,**L)(*N*-MeIm)$_2$ the two chlorine atoms and nitro groups are shown indicating the disorder on two sides of the aromatic ring (82:18).

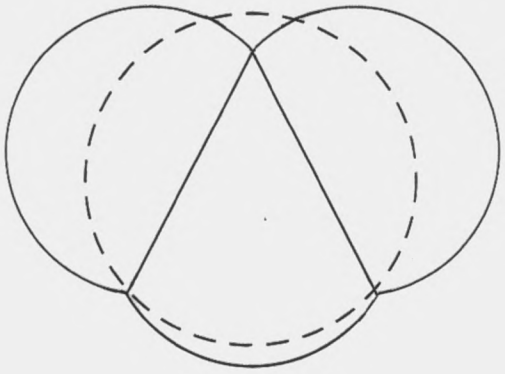


Figure 14. Cross-section of a space-filling model of a nitro group (solid lines) and a chloro group (dotted lines). The figure was drawn using van der walls radii from the literature[17] (Cl = 1.75 Å, N= 1.5 Å, O = 1.5 Å) and bond distances and angles from the crystal structure (C-Cl = 1.703 Å, C-N = 1.377 Å, N-O(average of two) = 1.227 Å). (C-N-O =120°)

bis(*N*-Methylimidazole)((D)-3-Chloro-*N*-phthaloyalaninato)((L)-3-Methyl-phthaloylalaninato)copper(II) Cu(7,D)(2,L)(*N*-MeIm)$_2$

The atomic displacement diagram of the structure is shown in Figure 15. This is a structure previously solved.[13] By crystallizing in methanol, higher quality crystals were obtained. A more precise structure of this quasiracemate was obtained as measured was indicated by the lower R value obtained from refinement. The CH_3 and Cl groups are of similar size (van der Waals radii[17], CH_3 = 2.0 Å, Cl = 1.75 Å). The 3-methylphthaloyl group shows disorder over three positions in ratio of approximately 60:20:20. The Cl atom is also disordered over both sides of the aromatic ring in a ratio of approximately 71:29 as was seen in the racemic complex shown in Figure 13. The *N*-methylimidazole ligands and atoms derived from alanine are well ordered.

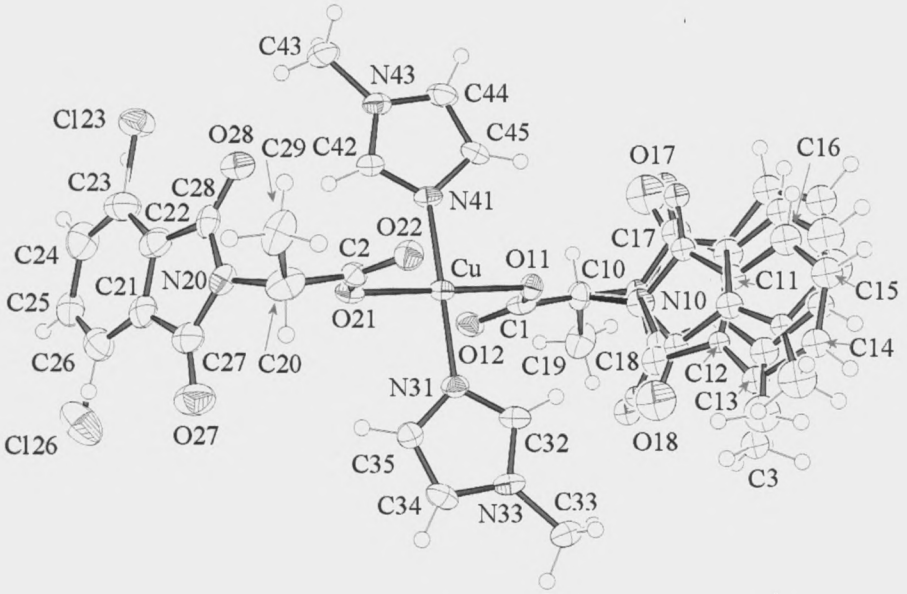


Figure 15. An ORTEP diagram (50% probability ellipsoids) of the structure of the quasiracemate, bis(*N*-methylimidazole)((D)-3-chloro-*N*-phthaloylalaninato)((L)-3-methyl-*N*-phthaloylalaninato)copper(II) Cu(**7,D**)(**2,L**)(*N*-MeIm)$_2$. Chlorine atoms disorder on two sides of the aromatic ring (71:29). The *N*-phthaloyl group is disordered over three positions (44:34:22)

bis(*N*-Methylimidazole)bis((D,L)-3-methyl-*N*-pthaoylalaninato)copper(II),

Cu(2,D,L)$_2$(*N*-MeIm)$_2$

The atomic displacement diagram of the structure is shown in Figure 16. This structure is a racemate. This structure has a crystallographic inversion center at the copper, so only one half of the complex is unique. The structure shows a similar packing pattern to above-mentioned quasiracemate, which will be described in the structure comparison section. The structure shows disorder of the 3-methyl-*N*-phthaloyl group over two positions in a ratio of 60:40. The *N*-methylimidazole ligands and the atoms derived from alanine are well ordered.

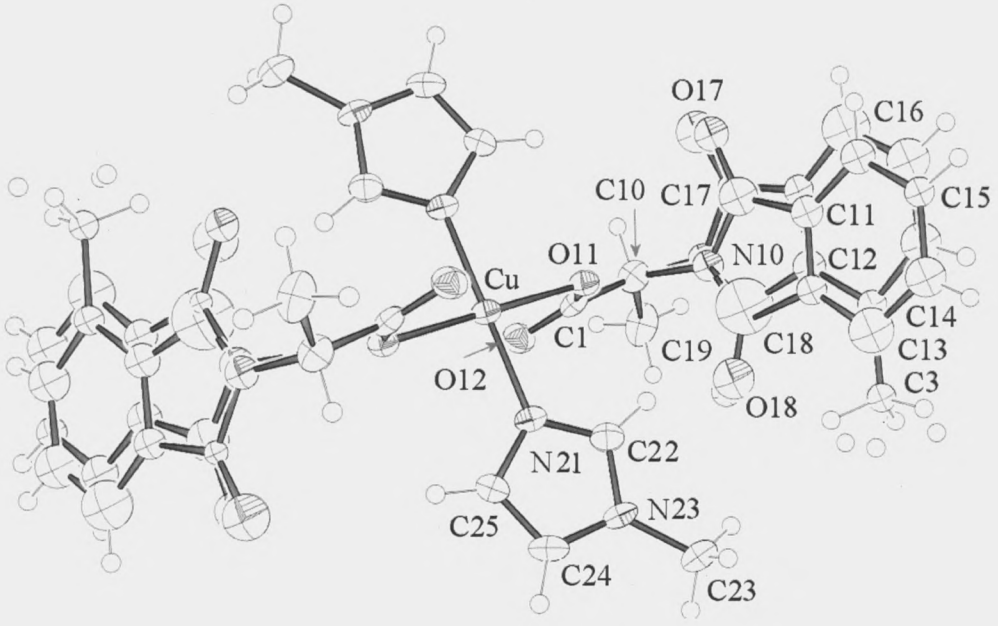


Figure 16. An ORTEP diagram (50% probability ellipsoids) of the racemate, bis(*N*-methylimidazole)bis((D,L)-3-methyl-*N*-phthaloylalaninato)copper(II) Cu**(2,**D,L)$_2$(*N*-MeIm)$_2$. The 3-methyl-*N*-phthaloyl group is disordered over two positions (60:40)

Summary and comparisons of crystal structures

All the quasiracemic and racemic complexes using *N*-methylimidazole are isostructural having crystallography inversion centers (racemate) or pseudoinversion centers (quasi-racemate). In all structures, copper has a square planar geometry. The two ligands, *N*-methylimidazole and *N*-phthaloylalaninato are trans in all structures.

With the previous work of Hiral Patel[13] and work carried out for this thesis, crystal structures of five copper complexes have been obtained. These compounds are shown in the table below. In subsequent tables the structures will be identified by the groups X and X′(see the Figure on Table 7, page 31).

All of the copper complexes prepared for this thesis and those previously prepared contain disorder in the substituted phthaloyl group. In order to make the diagrams easier to view, only the major component of a disordered group will be shown in subsequent diagrams. For the 3-chloro-*N*-phthaloyl group, only one of the two positions occupied by chlorine will be shown. For the 3-methyl-*N*-phthaloyl group, only the major component of the two or three positions of the disorder this group will be shown. Also note that the disorder does not effect the atoms bound directly to copper, and thus does not effect bond distances and angles about copper.

The structures will be compared in several ways including *N*-phthaloylalaninato ligand conformations, geometry about the copper, selected dihedral interplanar angles and crystal packing. Each of these properties will be discussed in turn.

Conformation of *N*-phthaloylaninato ligands and *N*-phthaloylalanines

The *N*-phthaloylalaninato ligand (see Figure 17, page 38) has two primary degrees of freedom: Rotation about the $N_{(phthaloyal)}$-C_{α} (N-C2) and C_{α}-$C_{(carboxylate)}$ (C2-C4) single bonds, where C is the α carbon of the original alanine group. Connected to these single bonds are two planar portions of the molecule, the carboxylate group and the *N*-phthaloyl group. Even with these two degrees of freedom, the overall conformation of the ligand is consistent for one structure to another. Table 8 shows the dihedral angles of *N*-phthaloylalaninato from the crystal structures of five copper complexes with phthaloylalaninato as a ligand. The organic compound *N*-phthaloylalanine, **1**, has been studied by singe crystal X-ray diffraction three times, twice as an enantiomer (two polymorphs) and once as racemates.[18-20]

Similar values for the dihedral angle and two selected torsion angles show that the ligand has a fairly fixed conformation due to steric interaction between CH_3 group and carboxyl oxygens on the phthaloyl group. For the two racemic structures there are half as many distance and angles due to the inversion center. The conformation does not change significantly from the free acid to the carboxylate form that binds to copper. Note that there is about a 20° change in one torsion angle (C1-N-C2-C3) in the enantiomeric complex. This will certainly change the overall shape of the complex, and create a different packing pattern.

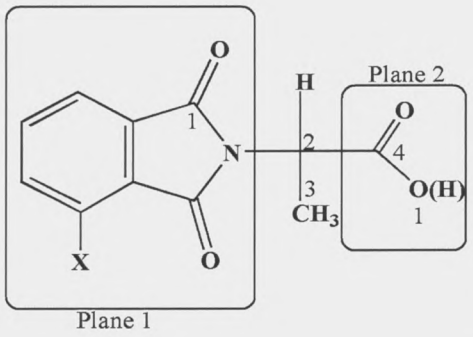
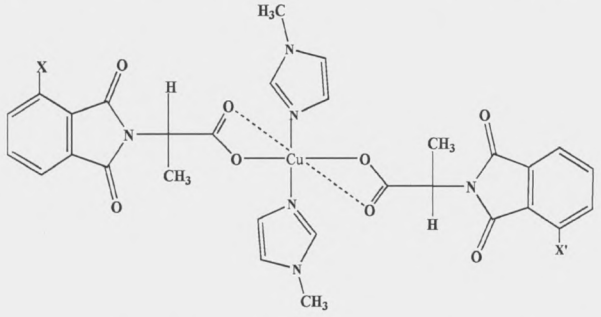


Figure 17. Definition of planes within *N*-phthaloylalanines and *N*-phthaloylaninato ligands

Table 8. Dihederal Angles between Selected Planes in *N*-phthaloylalanines



Compound X	X′	Plane1-Plane2 angle (°)	C1-N-C2-C3 torsion angle(°)	C3-C2-C4-O1 (°)
Cl,D	NO_2, L	74.26 80.57	124.98 131.05	150.93 154.59
Cl,D	CH_3,L	80.34 80.35	124.78 125.46	151.90 153.84
CH_3,D	CH_3,L	79.30	125.75	153.25
H,L	H,L	85.95 87.47	141.05 143.30	135.24 135.58
Cl,D	Cl,L	79.05	128.23	153.77
(**1**,L)-polymorph 1		88.26	111.31	176.70
(**1**,L)-polymorph 2		68.20	114.47	146.19
(**1**,D,L)		81.14	123.01	163.76

Geometric parameters about copper

The geometry of all copper complexes is square planar with two additional longer interactions between second oxygen of carboxylate and copper, Cu···O. The structure of the copper complexes can be seen in Figure 18. Selected bond distances and angles about copper are shown in Table 9. The Cu-O and Cu-N bond distances fall into a narrow range all slightly less than 2.0 Å. The angles about the copper in the square planar portion are all close to 90° or 180° as expected. The two weak O···Cu interactions are also consistent at about 2.7 Å. The conclusion drawn from the values in Table 9 is that the substituents on the phthaloyl ring at least for those studied here do not significantly affect the geometry about the Cu(II) ion.

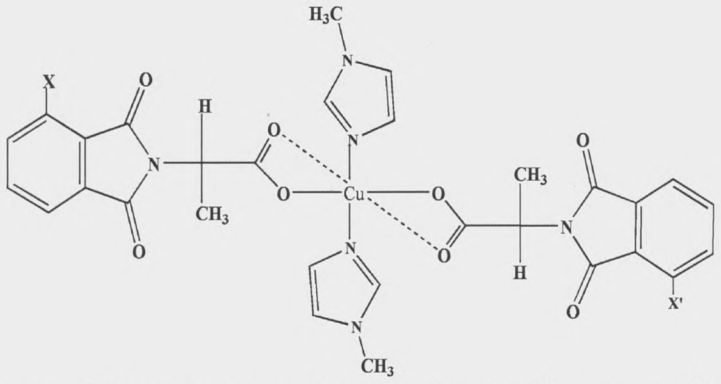


Figure 18. Structure of the copper complexes studied by X-ray crystallography showing the interactions of the *N*-methylimidazole and *N*-phthaloylalaninato ligands. The four solid bonds to copper are the four atoms that define the square planar geometry, the dotted line is a longer non-bonded interaction to the carboxylate

Table 9- Bond distances and Angles between the Atoms of Ligands Bound to Copper

Compound X	X′	Cu-O (Å)	Cu-N (Å)	Cu···O(Å)	O-Cu-N (°)	O-Cu-O (°)	N-Cu-N (°)
Cl,D	NO_2,L	1.983(6) 1.980(5)	1.963(6) 1.971(6)	2.707(8) 2.711(8)	88.9(3) 91.1(2) 89.3(2) 90.7(2)	179.7(3)	179.4(4)
Cl,D	CH_3,L	1.973(2) 1.984(2)	1.975(3) 1.977(3)	2.710(3) 2.722(3)	88.9(1) 89.1(1) 90.7(1) 91.3(1)	179.3(1)	179.0(2)
CH_3,D	CH_3,L	1.987(3)	1.976(5)	2.711(5)	88.9(2) 91.1(2)	a	a
H,L	H,L	1.961(4) 1.970(4)	1.968(5) 1.981(5)	2.680(6) 2.809(6)	89.0(2) 89.3(2) 90.9(2) 90.9(2)	178.1(2)	179.1(2)
Cl,D	Cl,L	1.982(2)	1.971(2)	2.724(3)	89.15(7) 90.85(7)	a	a
a-These angles are 180° by symmetry.							

Dihedral angles between ligand planes and the square planar arrangement about copper

The previous section showed the bond distance and angles are relatively constant. To show the orientation of the ligands bond to copper is also relatively fixed, the dihedral angles of selected planes of the ligands bound to copper were determined. The planes in question are the planes of the *N*-methylimidazole ligands and the planes defined by the three atoms of the carboxylate group. These planes are illustrated in Figure 19 and the dihedral angles are listed in Table 10.

The *N*-methylimidazole ligands are nearly coplanar with the square plane about copper (range of dihedral angle 7-14°). The carboxylate groups are perpendicular to this square plane (range approximately 88.0-90°). The values from the five structures also agree closely with one another.

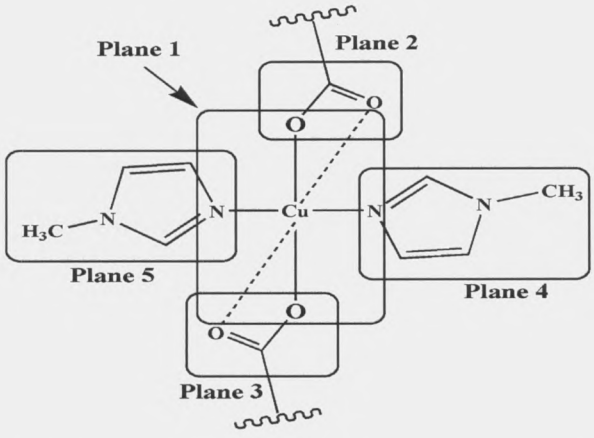
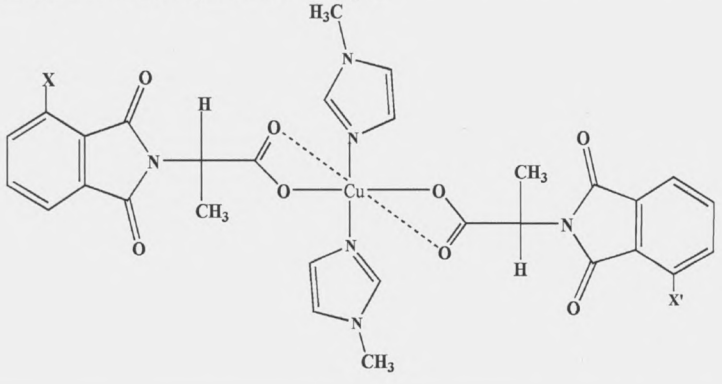


Figure 19. The definition of selected planes in the complex. Plane 1 is the plane of the four atoms that make up the square planar geometry about copper. Plane 2 and 3 are planes through the carboxylate group of the phthaloylalaninato ligand. Planes 4 and 5 are the planes of *N*-methylimidazole.

Table 10. Dihederal Angles between Selected Planes in Ligands and the Plane Defined by the Square Planar Geometry about Copper



Compound X	X′	Plane 2 (°)	Plane 3 (°)	Plane 4 (°)	Plane 5 (°)
Cl,D	NO_2,L	87.9	88.5	7.22	12.91
Cl,D	CH_3,L	88.4	89.8	12.60	11.79
CH_3,D	CH_3,L	89.0	88.8	12.41	12.67
H,L	H,L	89.5	89.8	9.76	7.07
Cl,D	Cl,L	88.1	88.1	13.92	13.77

Overall shape of metal complexes

Although there are two space groups, ($P2_1$ and $P2_1/c$), different substituents (-Cl, $-NO_2$, and CH_3), and varying degree of disorder, the overall configuration of the complexes is quite similar. This is made clear by the numerical values presented in the last two sections. This means the overall shapes of the complexes are very similar. This similarity has been further illustrated on next page by ball and stick diagrams of the complexes all in the same orientation, Figure 20. The quasiracemates and racemates are almost identical. Only the enantiomer is slightly different with both ligands being of the same handedness.

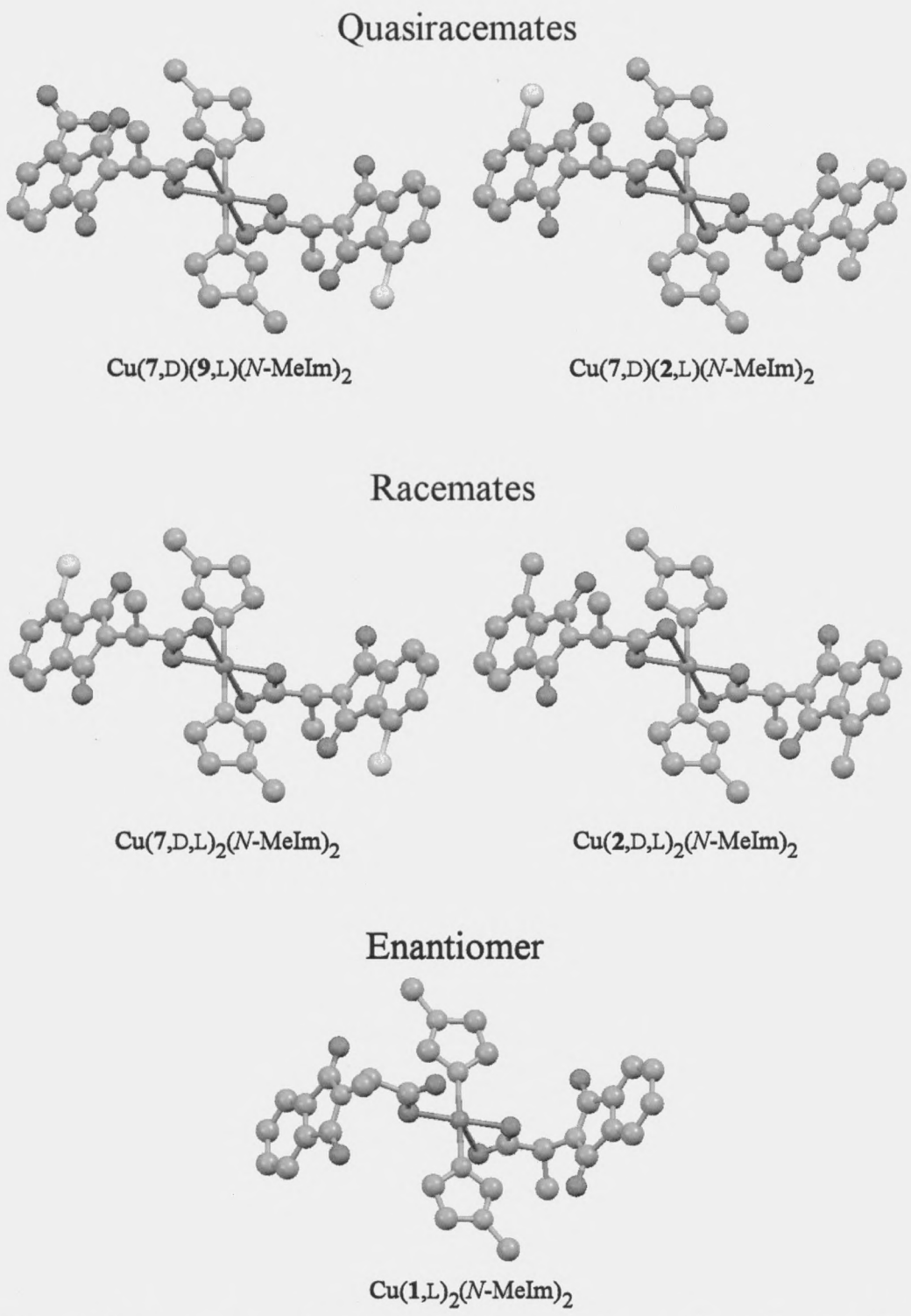


Figure 20. Comparison of the crystal structures of the complexes drawn with the same orientation with respect to the square planar geometry about copper. Note the quasiracemates and racemates are in nearly identical configurations. Hydrogen atoms have been omitted for clarity.

Comparison of crystal packing

The quasiracemic and racemic complexes have either an inversion center or pseudo-inversion center. All these structures pack in the crystal in a similar fashion. The enantiomer has an approximate 2 fold rotation axis, running through the copper, and it packs in a different way.

We can further show the similarities of the quasiracemic and racemic complexes through finding a transformation of the atomic coordinates that bring the structures into approximate coincidence for corresponding atoms. If we take the racemic Cl-Cl compound as the base structure, the transformations that bring the two quasiracemic structures into coincidence with the Cl-Cl compound are shown in Table 11.

Table 11. Coordinate Transformations of Quasiracemates that Bring Atoms into Coincidence with Cu(**7**,D,L)$_2$(*N*-MeIm)$_2$

Compound	Space Group	Transformation to x	Transformation to y	Transformation to z
Cu(**7**,D)(**9**,L)(*N*-MeIm)$_2$	$P2_1$	x	y + 0.009	z - 0.75
Cu(**7**,D)(**2**,L)(*N*-MeIm)$_2$	$P2_1$	x -. 0.5	y - 0.814	z - 0.750

In case of the CH_3/CH_3 racemic complex and the Cl/Cl racemic complex, both structures are in $P2_1/c$, and the complexes are in the exact corresponding location in cell. The copper is on a crystallographic inversion center at (0,0,0) so no transformation is necessary. In the case of quasiracemate, the 2_1 symmetry operator is in a different position in the space group. Also the z coordinate is not fixed in $P2_1$ as it is in $P2_1/c$. The

transformation in these two cases involves shift of the origin and a translation along the z to place the pseudo-inversion center in $P2_1$ the same relative position as the true inversion center is in $P2_1/c$. These transformations are shown in Table 11.

Figure 21 is a packing diagram of Cu(**7**,D)(**9**,L)(*N*-MeIm)$_2$ showing the contents of one unit cell (two whole complexes). The view is down the b-axis of the unit cell with a-axis runs horizontally and the c-axis running approximately vertically. The origin of the unit cell is in the lower left corner of the figure at the back. This view is down the 2_1 screw axis which is common to the two space groups $P2_1/c$ for the racemic complex and $P2_1$ for the quasiracemic complexes. The complex to the left in Figure 21 is related to the complex to the right by a 2_1 screw axis symmetry operation. All other molecules in the crystal are generated by translation of the two complexes.

Because of the transformations shown in Table 11, Page 42, which showed that the four crystal structures of racemic and quasiracemic complexes have similar orientations in the crystal, and Figure 20 showed that the shapes in these four crystal structures were nearly identical except for the different substituents, this means that the packing diagrams for other quasiracemic complexes and racemic complexes would be nearly identical to Figure 21 except the substituents on the aromatic ring will differ from one structure to another. If the sizes of substituents are comparable (in the cases shown here $-NO_2$, $-CH_3$ or -Cl) the overall shapes of the complexes are similar, and the packing of the molecules will be isostructural. These results fit with our hypothesis that overall molecular shape is an important factor in determining crystal packing.

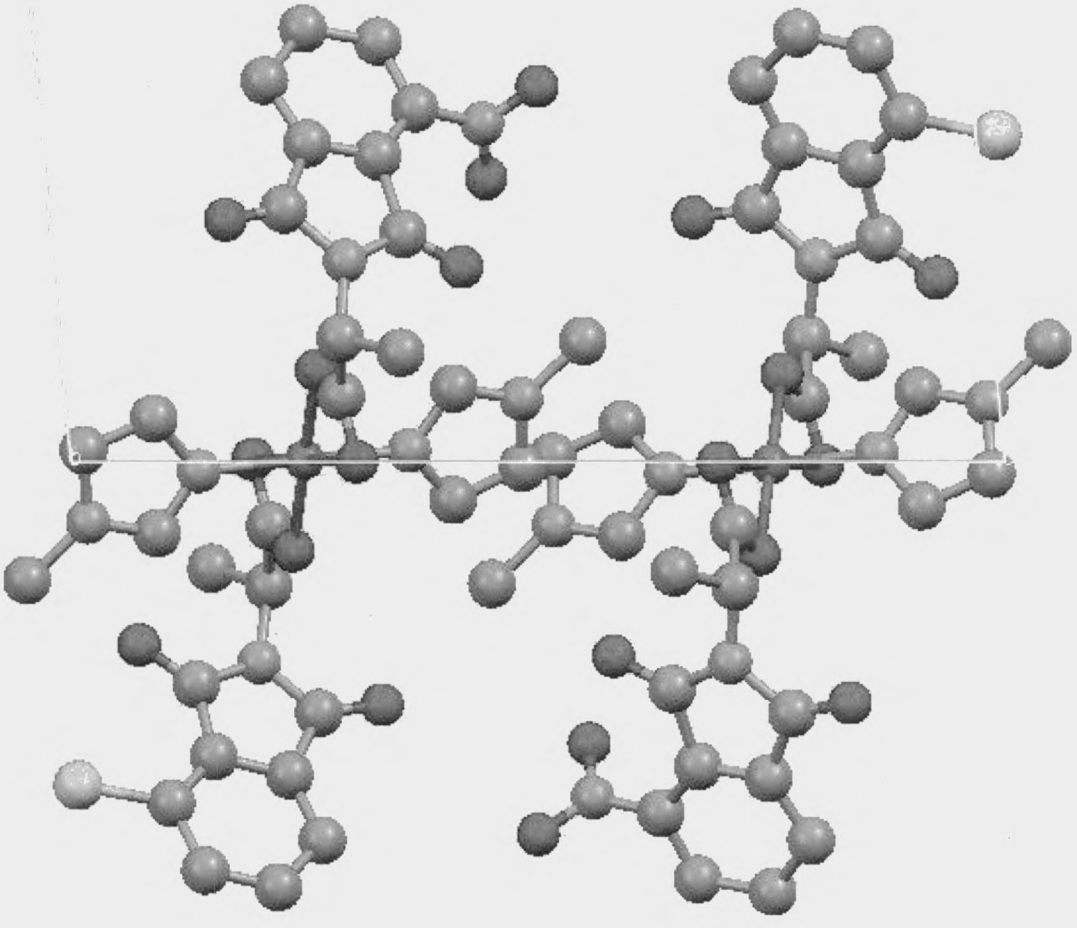


Figure 21. Packing diagram of quasiracemate, Cu(**7**,D)(**9**,L)(*N*-MeIm)$_2$. The view is shown looking down the b-axis. The origin of the cell is in the lower left corner. The a axis is horizontal and the c-axis is approximately vertical. Hydrogen atoms have been omitted for clarity

In contrast, the enantiomeric complex packs in a different way. The packing is shown in Figure 22. The view shown in the Figure is down the b-axis. The a-axis is horizontal and the c-axis is approximately vertical. The origin is in the lower left of the cell at the back. This view is down the 2_1 screw axis of the space group. The left complex in the figure is related to the right complex by the 2_1 screw axis. If the packing was the same as the quasiracemic complex or racemic complexes, the orientation of the complex should be similar to that of Figure 21 because both views are down the common symmetry operation in both space groups. The orientations of the complexes are clearly different in Figures 21 and Figures 22 showing the packing is also different.

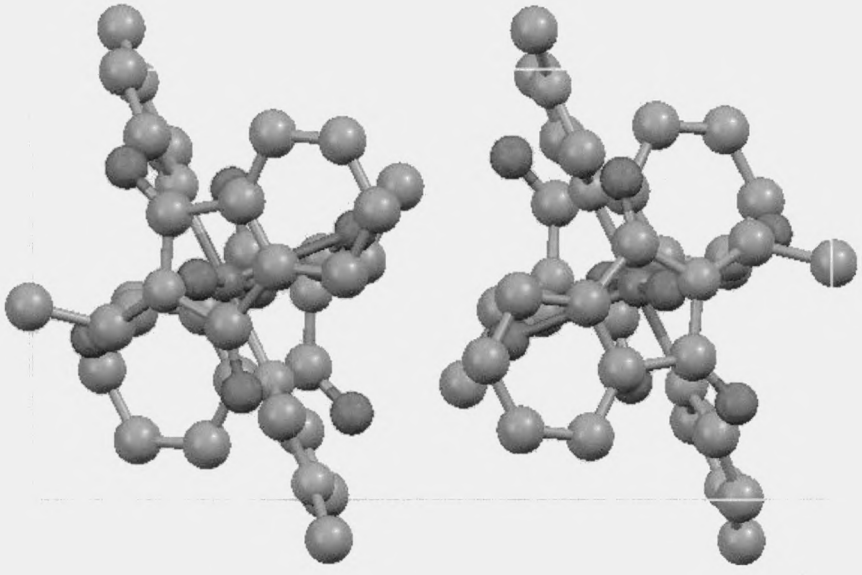


Figure 22. Packing diagram of enantiomer, Cu(**1**,L)$_2$(*N*-MeIm)$_2$. The view is shown looking down the b-axis. The origin of the cell is in the lower left corner. The a-axis is horizontal and the c-axis is approximately vertical. Hydrogen atoms have been omitted for clarity

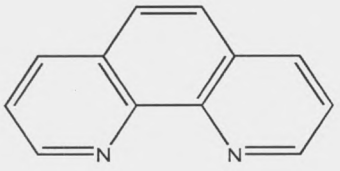
Apparently, the arrangement of two methyl groups on the alanine of the same optical configuration changes the shape of the complex to create a different packing pattern.

CONCLUSIONS AND FUTURE WORK

Metal based enantiomeric, quasiracemic and racemic copper complexes were synthesized using copper(II) acetate monohydrate, substituted *N*-phthaloylalanines and *N*-methylimidazole. The synthetic methods are described in the experimental section and have been modified and improved from previous work. These modified methods have fewer steps and can be carried out with a variety of substituted *N*-phthaloylalanines. The complexes that formed crystals were evaluated under microscope, and crystals that were judged to be suitable were sent out for possible X-ray diffraction analysis.

Two new crystal structures were successfully obtained; a racemic complex bis(*N*-methyl imidazole)bis((D,L)-3-methyl-*N*-pthaoylalaninato)copper(II), and a quasiracemic complex bis(*N*-methylimidazole)((D)-3-chloro-*N*-pthaloyalaninato)((L)-3-nitro-phthaloylalanato)-copper(II). An improved crystal structure determination of a quasiracemic complex previously studied by Hiral Patel, bis(*N*-methylimidazole)((D)-3-chloro-*N*-phthaloyalaninato)((L)-3-methyl-*N*-phthaloylalaninato)copper(II), was also obtained. The study of these structures and the previously prepared compounds has shown that quasiracemic and racemic complexes of similar structure are isostructural. Substituents chloro, nitro and methyl do not change the overall structure to a large degree, so packing in crystals are very similar among complexes with these substituents on the *N*-phthaloyl group. This shows that molecular shape plays an important role in crystal packing.

There are several possibilities for future work in these systems. Different nitrogen ligands could replace the two *N*-methylimidazoles. One interesting possibility is the bidentate ligand 1,10-phenanthroline.



This ligand forces the *N*-phthaloylalaninato ligands to be cis and thus will not have an inversion or pseudoinversion center. Some preliminary crystals using this ligand have been obtained, but have not been studied by X-ray analysis in time to be included in this thesis. Other transition metals that bind well to carboxylates may be used. Also, there are other substituted phthalic anhydrides that may be used as starting materials For example, all crystal structures described here are substituted in the 3-position. There are several commercial available phthalic anhydrides with groups in the 4-position, but suitable crystals using ligands derived from these anhydrides have not been obtained. Attempts to prepare crystals using different solvents or ligands other than *N*-methylimidazole may yield crystals of these compounds. Finally, alanine may be replaced by other amino acids.

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APPENDIX A - ^{1}H-NMR DATA

All *N*-phthaloylalanines that were prepared for this thesis were characterized by ^{1}H-NMR. Two compounds containing fluorine were characterized by ^{19}F-NMR. All spectra were obtained on a Brüker spectrometer operating at 300 MHz. The solvent for all experiments was $CDCl_3$. Figure A1 shows the spectra of the solvent and illustrates two impurities in the solvent. These are indicated by (×) in this and following spectra. Chemical shifts are reported in ppm vs TMS for ^{1}H-NMR and trifluoro acetic acid for ^{19}F-NMR. Coupling constants are reported in Hz. *N*-Phthaloylalanines had substitution at either the 3 or 4 position on the aromatic ring. Chemical shift assignments are reported in separate tables for these two classes of compounds. Spectra of the enantiomer (X,D) or (X,L) and racemates (X,D,L) are identical, where X is a number from 2-9 of the phthalic anhydride from Figure 9, Page 13. The actual compound used for each of the following spectra is identified

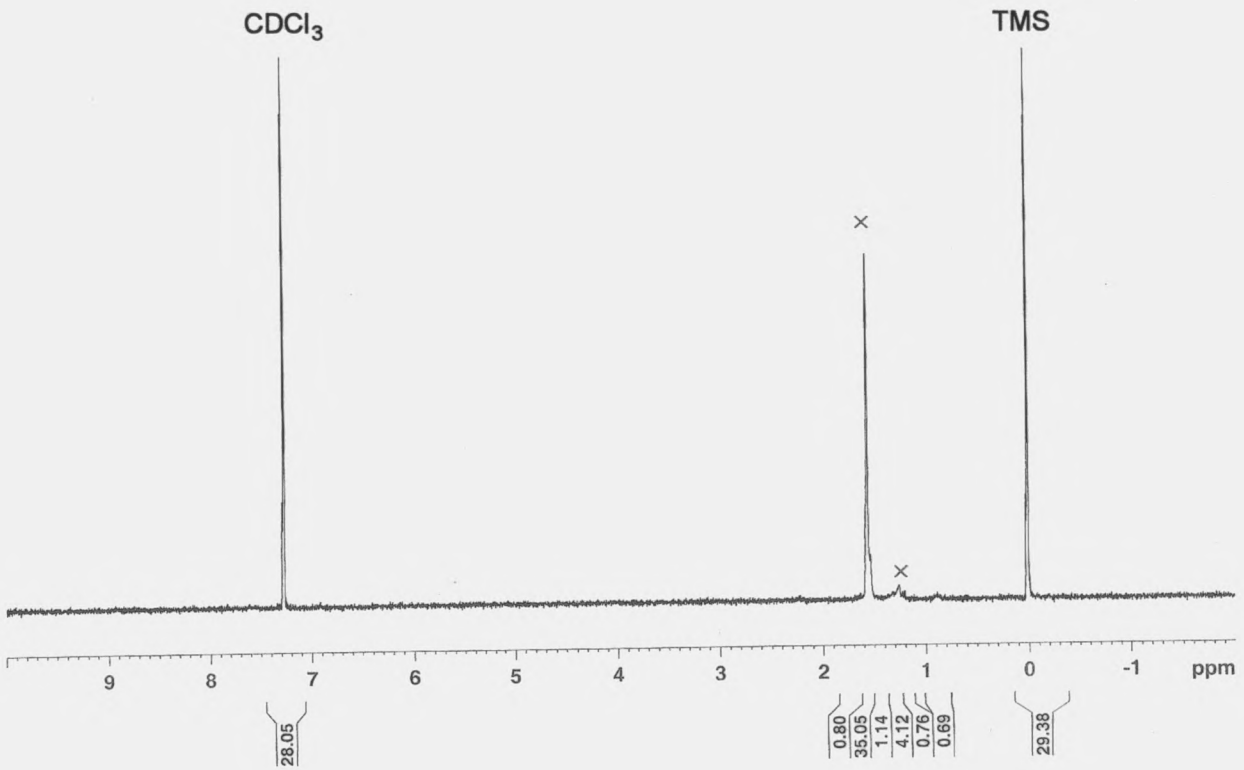
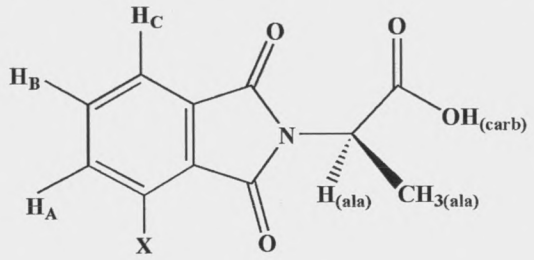


Figure A1. The ^{1}H-NMR (300 MHz) spectrum of solvent, d-chloroform illustrating two impurities in the solvent. These impurities are indicated by (×) in this and the following spectra

N-phthaloylalanines substituted at the 3-position on aromatic ring

Table A1 shows the chemical shift assignments for *N*-phthaloylalanines that are substituted at the 3 position illustrated in the chemical structure. Compounds substituted at position 3 on the aromatic ring of *N*-phthaloylalanine show a common splitting pattern of aromatic protons; two doublets (H_A and H_C) and triplet (H_B). This is the case for (**2**,D,L), Figure A2 and assignment of H_A and H_C is ambiguous, and may be the reverse of the listing in the table. In the case of the compound with a 3-F group, Figure A3, the spectra is complicated by coupling to the F atom. These protons have been assigned using the splitting pattern and integration. In the case of (**7**,L), Figure A4, and (**9**,D,L), Figure A5, the two doublets were coincident. The protons identified as $H_{(ala)}$ and $CH_{3(ala)}$ split each other to appear as a quartet and a doublet, respectively. The OH proton appears as a broad resonance with variable chemical shift. The spectra of 3-methylphthalic anhydride (**2**) is included in the table to support the discussion of the reaction conditions in the results and discussion section (Page 24). The ^{1}H-NMR spectra of the compounds with substitution in the 3-position are collected after Table A1.

Table A1- ^{1}H-NMR Data of *N*-phthaloylalanines Substituted at the at 3-Position of the Aromatic Ring, (Chemical Shifts are in ppm (300 MHz), Coupling Constants are in Hz)



Compound	$CH_{3\ (ala)}$	$H_{(ala)}$	$H_{(carb)}$	H_A or H_C	H_B	H_C or H_A	Ring CH_3
2 D,L X= CH_3	1.72 d, J = 7.3, 3H	5.03 q,J =7.3, 1H	2.72 br, 1H	7.70 d, J=7.3, 1H	7.59 t, J =7.5, 1H	7.49 d, J =7.6, 1H	2.69 s, 3H
5,D X= F	1.74 d, J =7.3, 3H	5.03 q,J =7.3, 1H	2.55 br, 1H	7.40 td, JHF-JHH=7.7, 1H	H_B and H_c M 7.70-7.78, 2H		-
7, L X =Cl	1.74 d, J = 7.3, 3H	5.06 q,J =7.3, 1H	2.45 br, 1H	7.80 d, J =4.1,1H	7.78 t, J =4.23, 1H	7.67 d,J =4.1,1H	-
9,D,L X = NO_2	1.76 d,J = 7.4, 3H	5.08 q,J = 7.4, 1H	3.02 br, 1H	8.15 d,J =7.7, 2H	7.95 t, J =7.8, 1H		-
2				7.86 d,J =7.4, 1H	7.77 t, J = 7.5, 1H	7.67 d, J =7.5, 1H	2.74 s, 3H

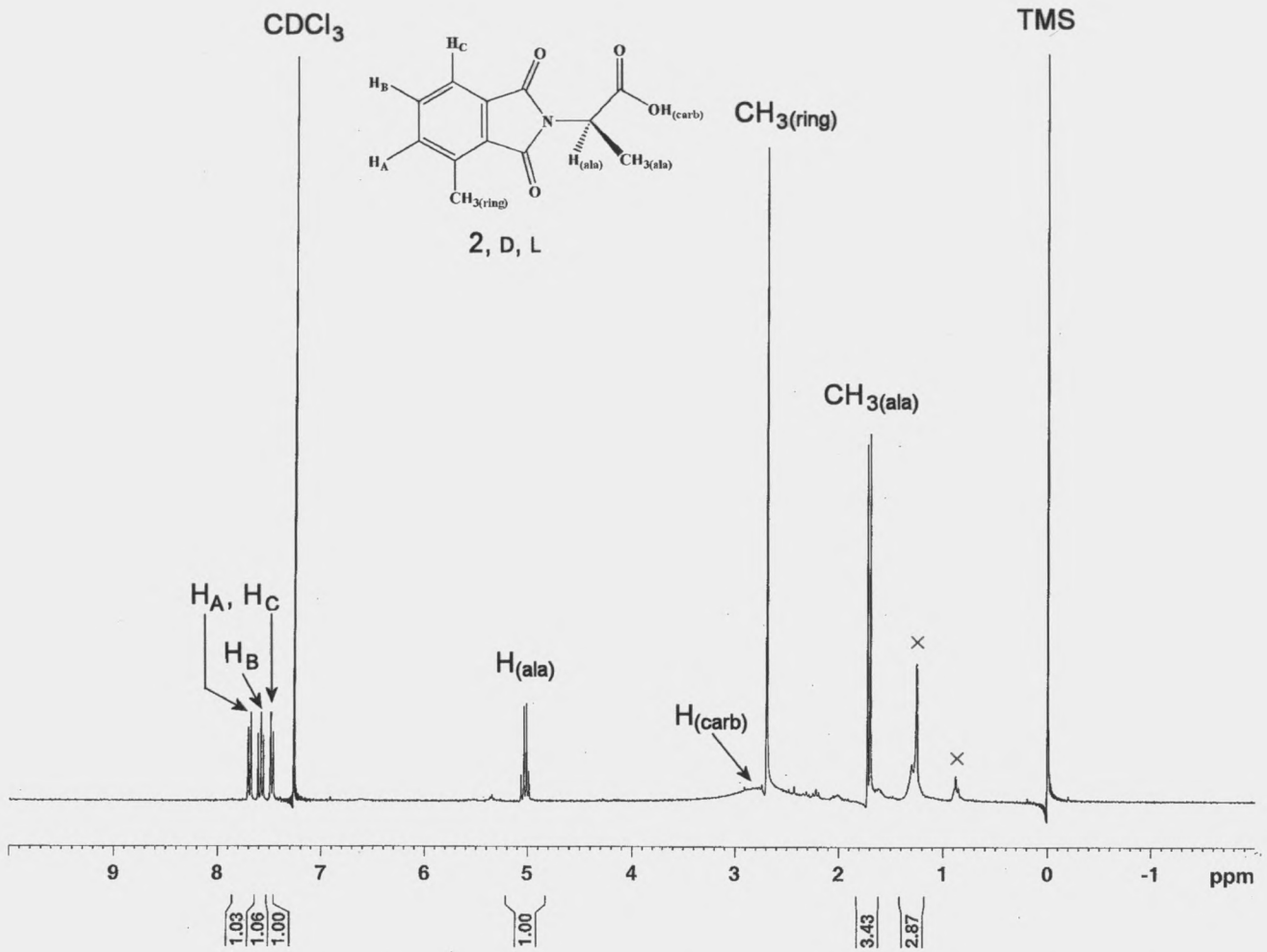
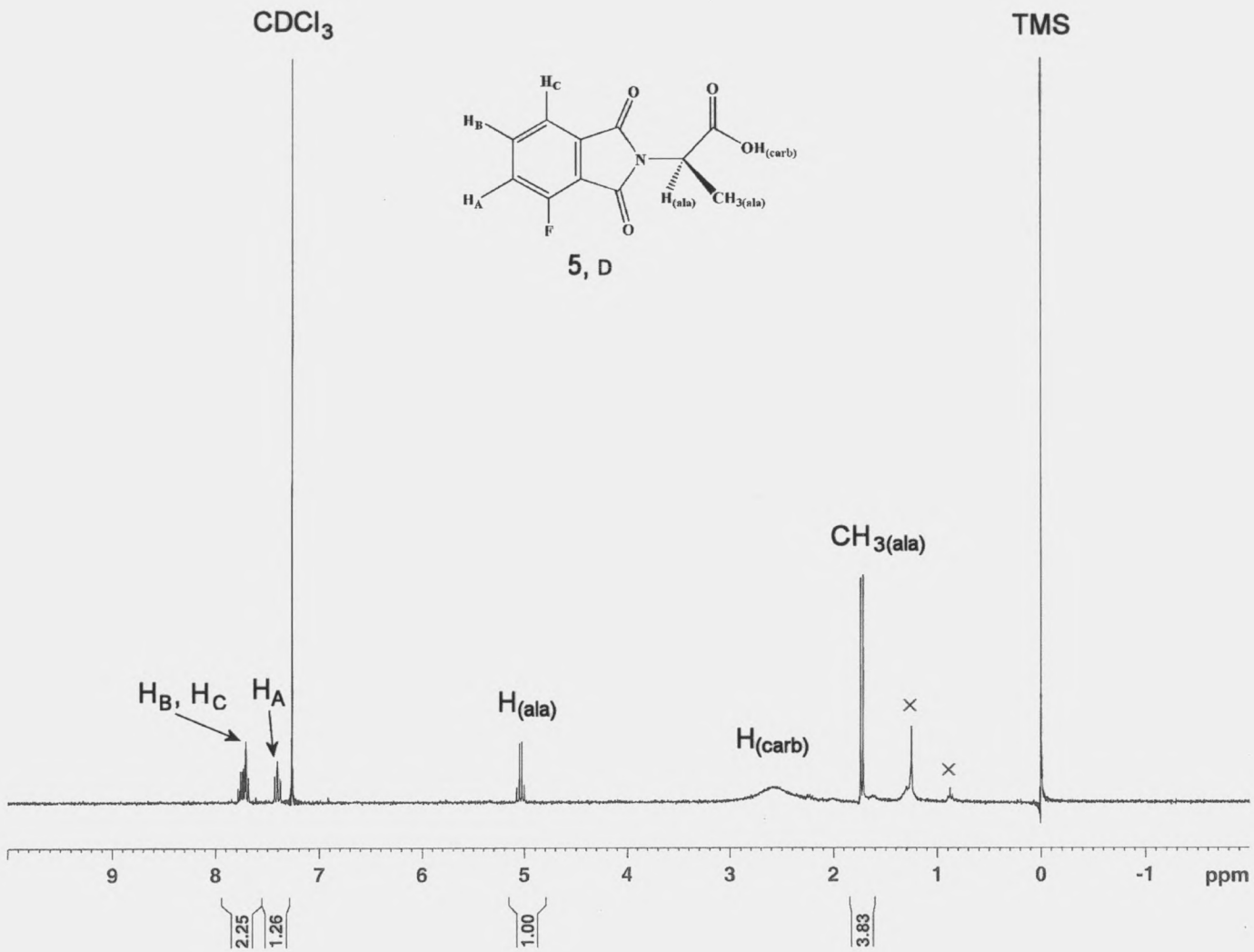


Figure A2. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of (D,L)-3-methyl-*N*-phthaloylalanine, (**2**,D,L)



FigureA3. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of (D)-3-fluoro-*N*-phthaloylalanine (**5,**D)

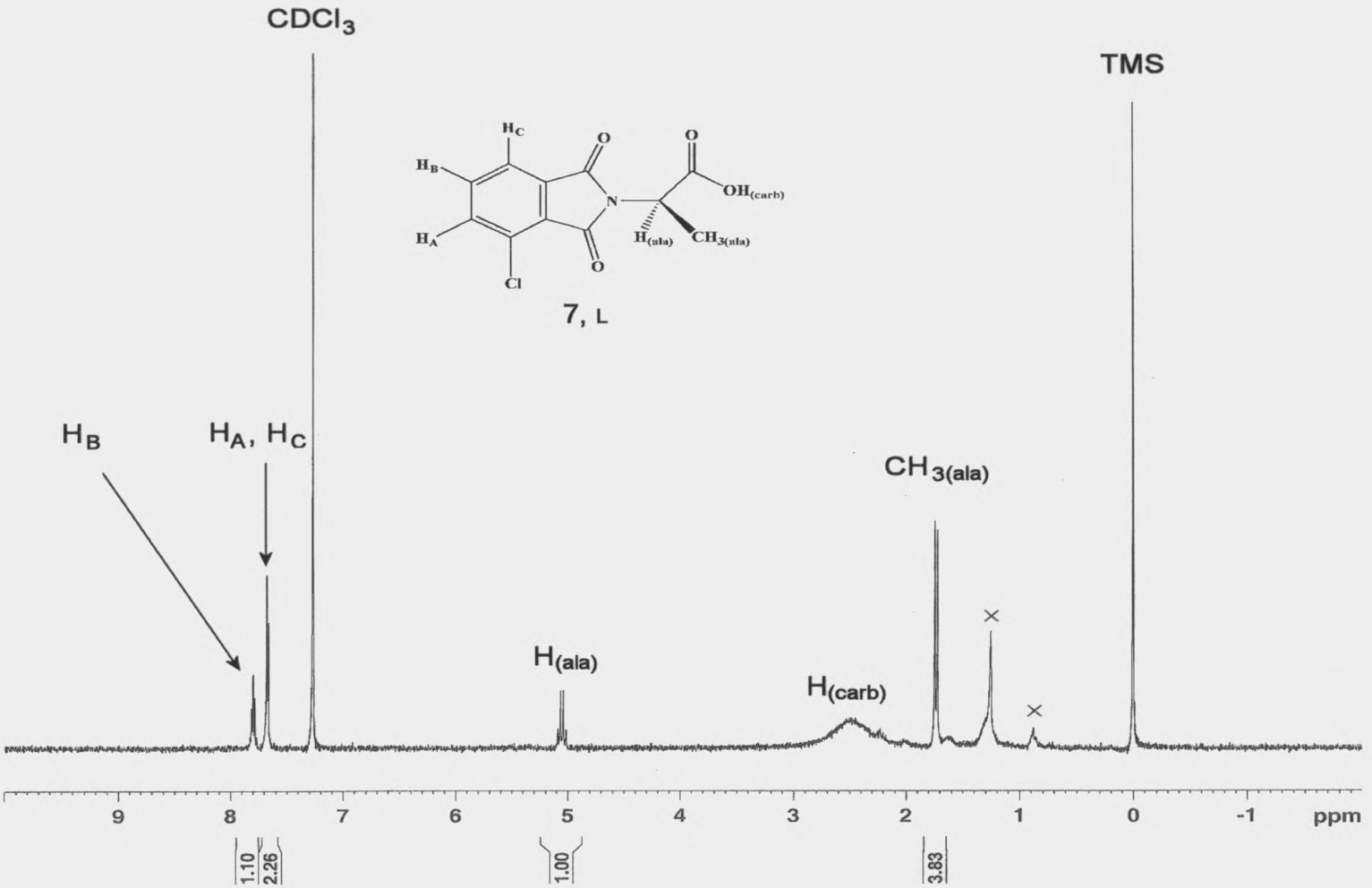


Figure A4. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of (L)-3-chloro-*N*-phthaloylalanine, (**7,**L)

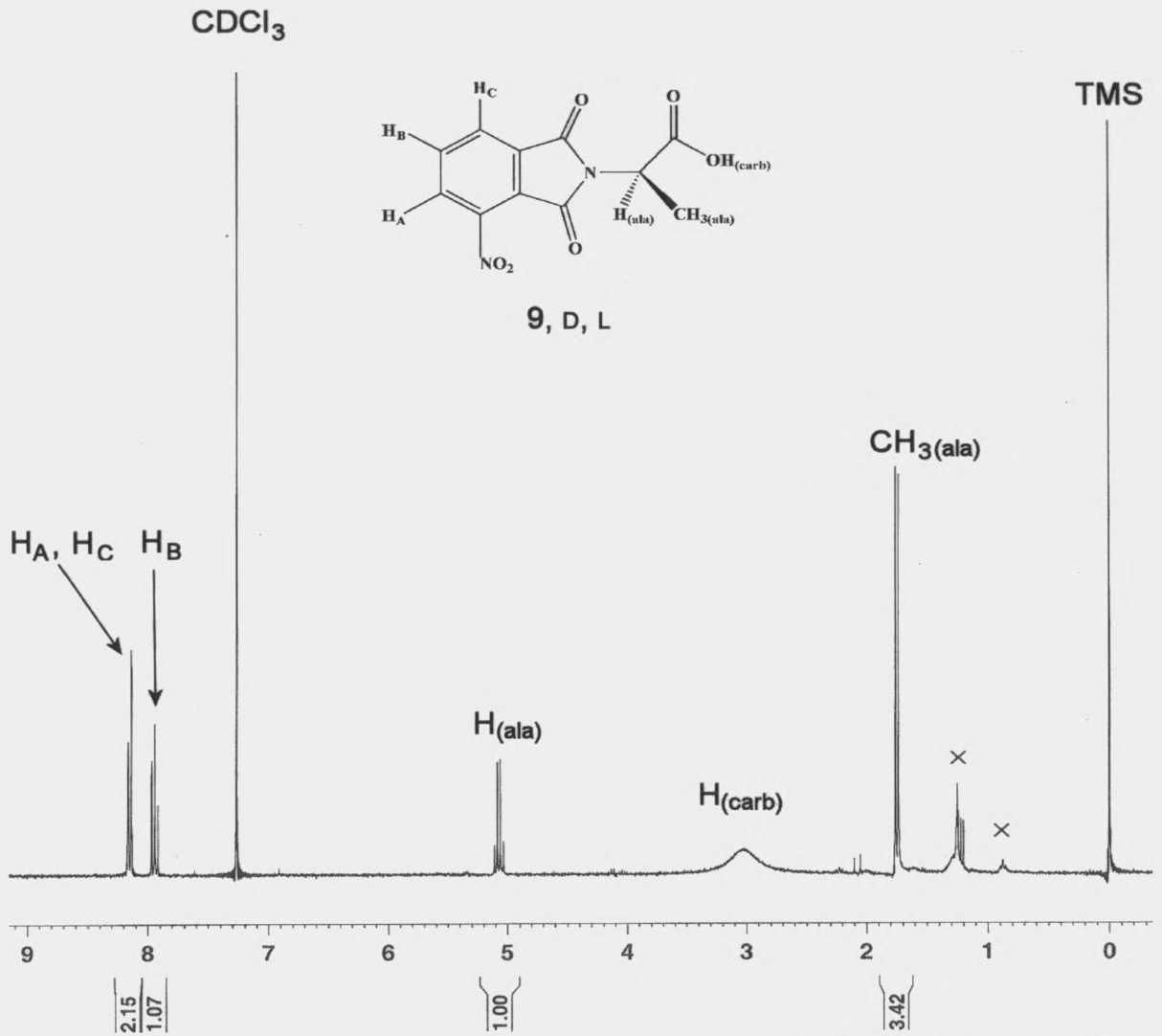


Figure A5. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of (D,L)-3-nitro-*N*-phthaloylalanine (**9,**D,L)

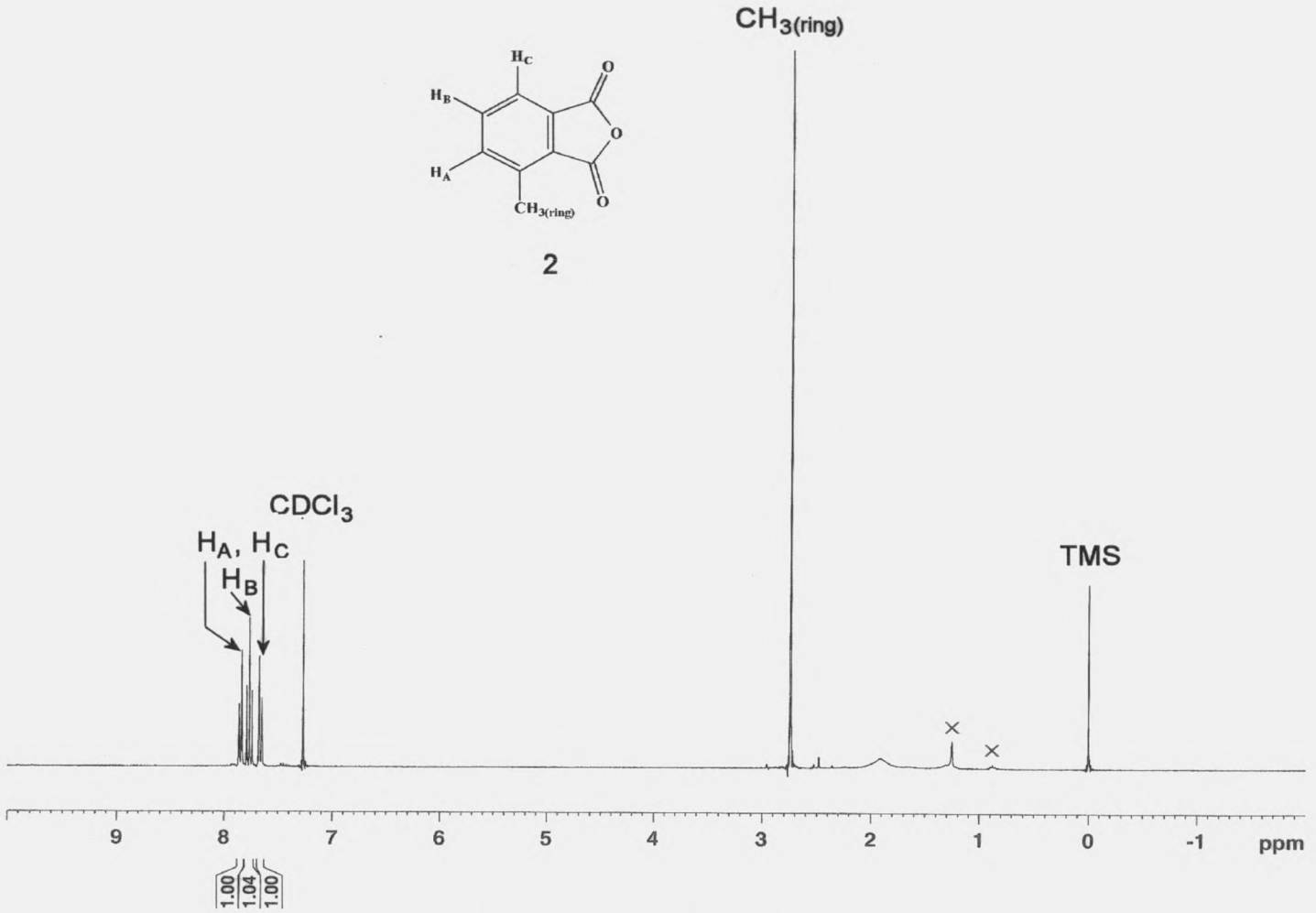
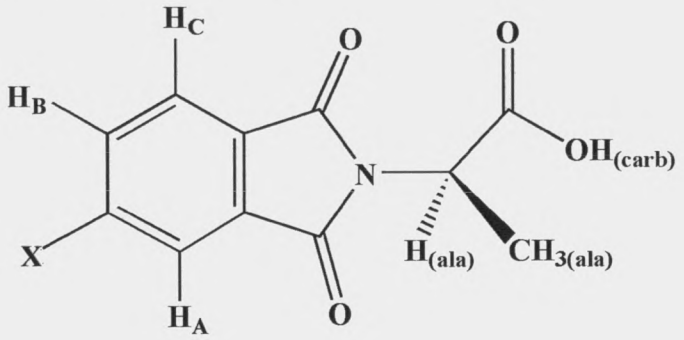


Figure A6. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of 3-methylphthalic anhydride, (**2**)

N-phthaloylalanines substituted at the 4-position

Table A2 shows the chemical shift assignments for *N*-phthaloylalanines that are substituted at the 4 position illustrated in the chemical structure. Compounds substituted at position 4 on the benzene ring of *N*-phthaloylalanine are expected to show a common splitting pattern of aromatic protons; a singlet (H_A) and two separate doublets (H_B or H_C). All compounds except the compound with a 4-F group showed this pattern. For these three compounds, the identity of which doublet was from H_B and which was from H_C could not be assigned so there are two arrows from the labels for H_B and H_C indicating this ambiguity. In the case of the compound containing fluorine, the coupling to fluorine and the difference in the magnitude $J_{F\text{-}H(1\text{-}2)}$ vs $J_{F\text{-}H(1\text{-}3)}$ coupling constants allowed assignment of the doublets. The OH proton from the carboxylate acid group appears as a broad resonance with variable chemical shift. The ^{1}H-NMR spectra of the compounds are collected after Table A2.

Table A2- ^{1}H-NMR Data of *N*-Phthaloylalanines Substituted at the at 4-Position of the Aromatic Ring, (Chemical Shifts are in ppm (300 MHz), Coupling Constants are in Hz)



Compound	$CH_{3\ (ala)}$	$H_{(ala)}$	$H_{(carb)}$	H_A	H_B or H_c	H_C or H_B	Ring CH_3
3, L X= CH_3	1.72 d, J = 7.3, 3H	5.03 q, J =7.3, 1H	Not detected br, 1H	7.66 s, 1H	7.75 d, J, 7.6, 1H	7.53 d, J = 7.5, 1H	2.53 s, 3H
4,D X= F	1.74 d, J =7.4, 3H	5.02 q, J =7.3, 1H	2.60 br, 1H	7.60 dd, J_{HF12}=6.9, J_{HH13}=2.2, 1H	7.40 td, J_{HH} = J_{HF} =6.5, 1H	7.87 dd, J_{HH}=6.1, J_{HF13}=4.5, 1H	-
6, L X=Br	1.73 d, J =7.3, 3H	5.03 q, J =7.3, 1H	3.77 br, 1H	8.00 d, J =1.3, 1H	7.89, dd, J_{12} =7.9, J_{13} =1.7, 1H	7.74, d, J =7.9, 1H	-
8,D X = NO_2	1.79 d, J = 7.4, 3H	5.10 q, J = 7.6, 1H	2.38 br, 1H	8.70 d, J = 1.8, 1H	8.65 dd, J_{12} = 8.1, J_{13} 2.18, 1H	8.10 d, J =8.1, 1H	-

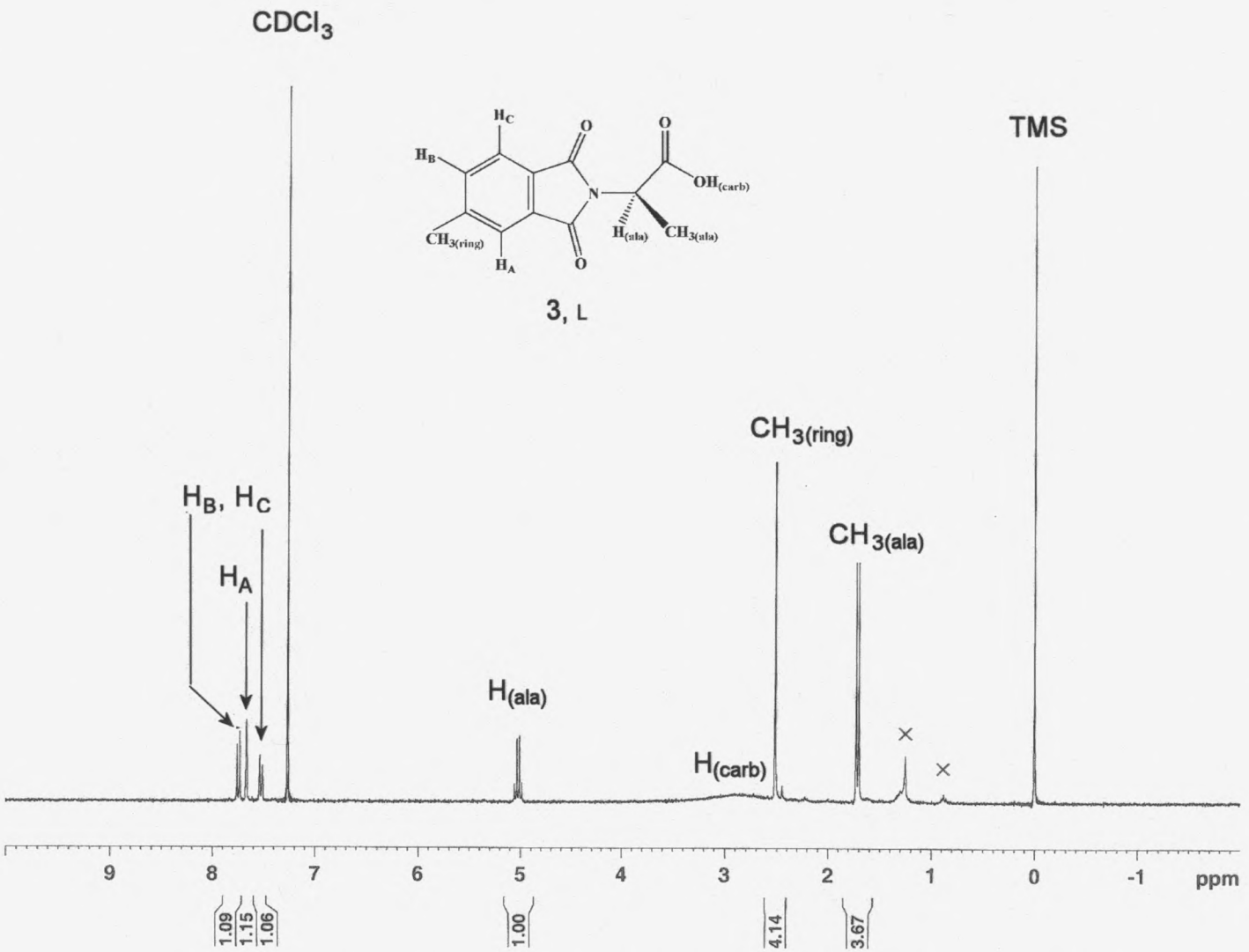


Figure A7. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of (L)-4-methyl-*N*-phthaloylalanine, (**3,**L)

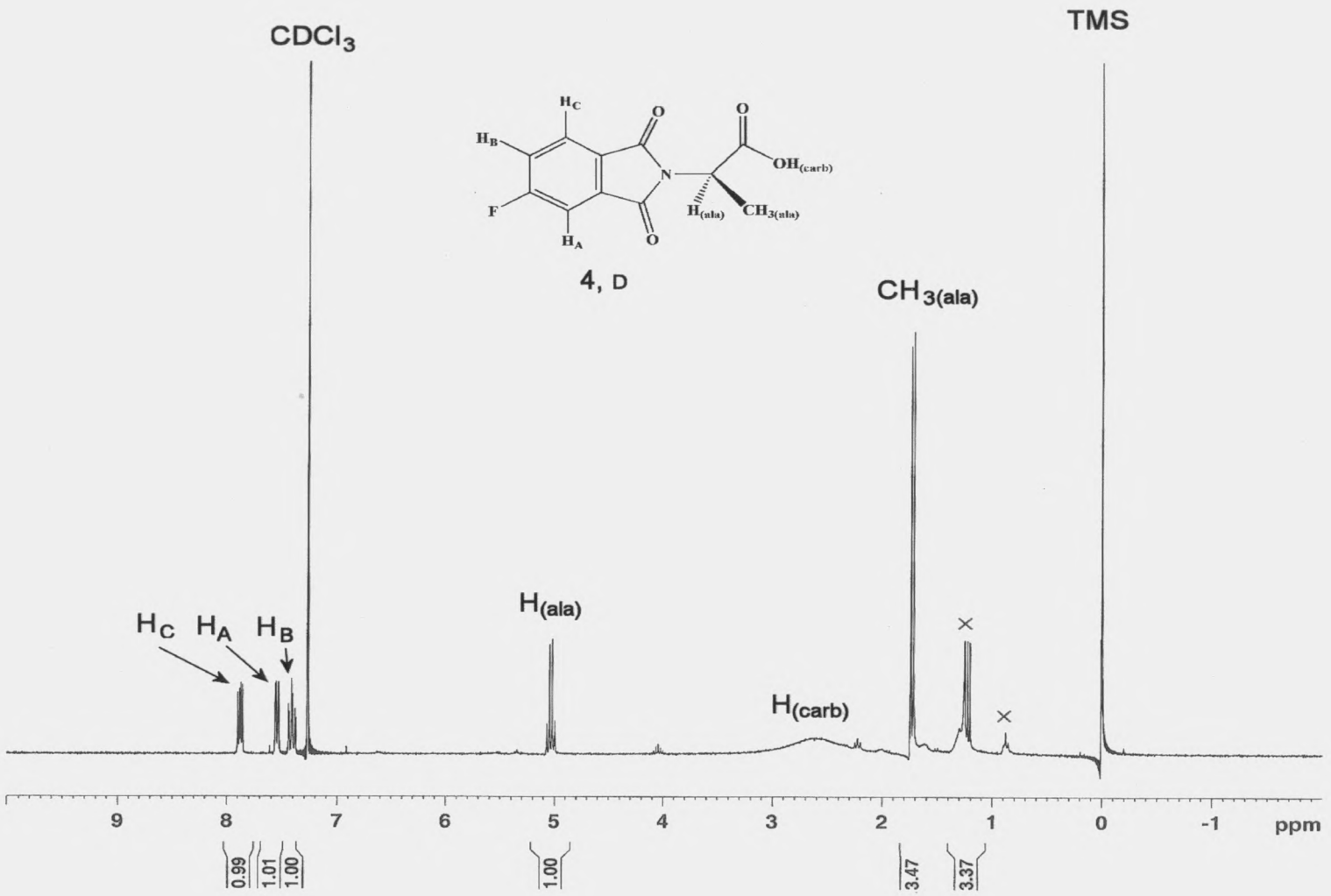


Figure A8. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of (D)-4-fluoro-*N*-phthaloylalanine, (**4,**D)

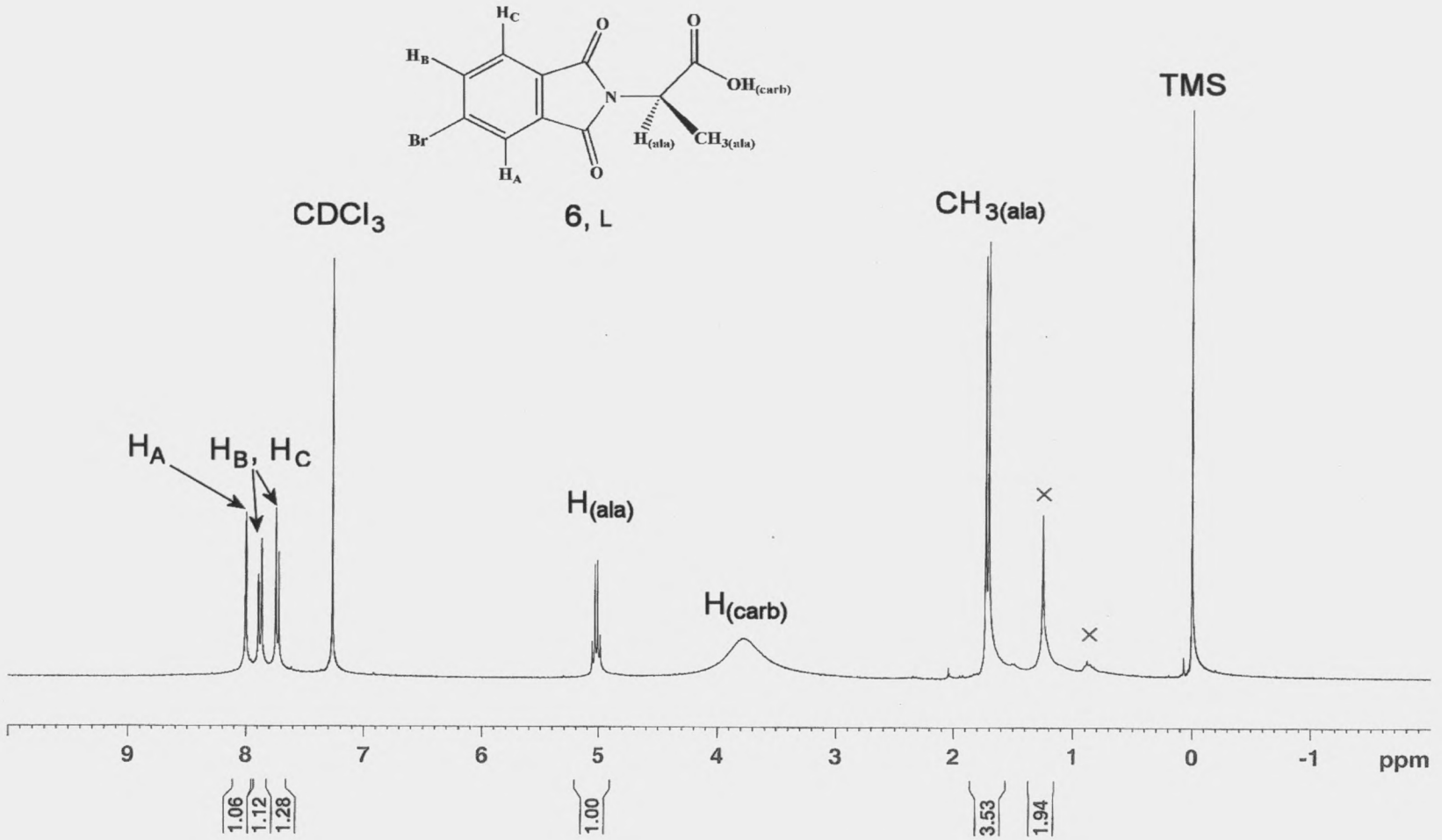


Figure A9. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of (L)-4-bromo-*N*-phthaloylalanine, (**6,**L)

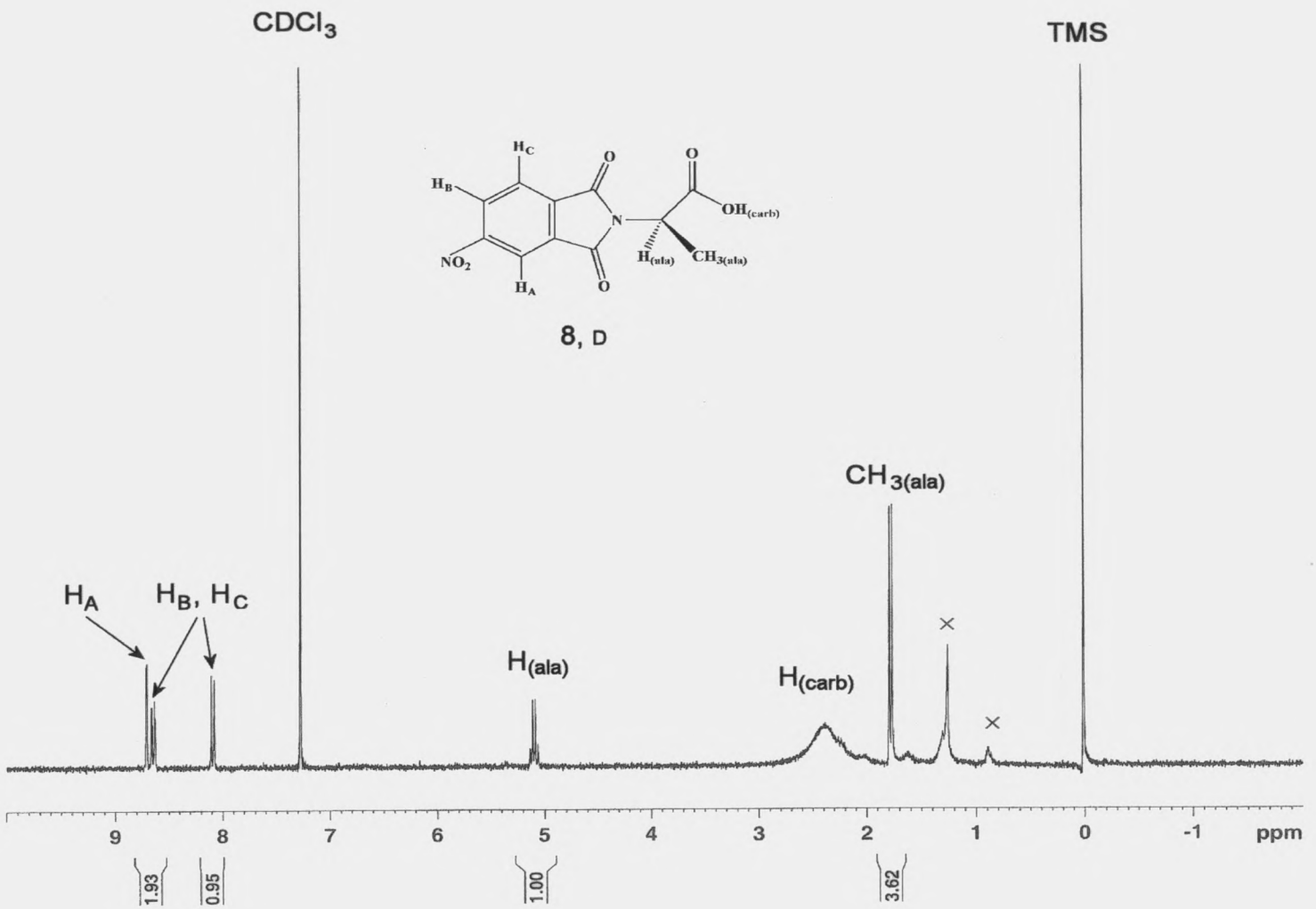
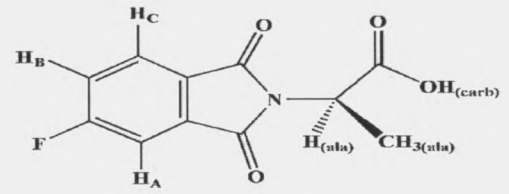


Figure A10. The ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of (D)-4-nitro-*N*-phthaloylalanine, (**8,**D)

^{19}F-NMR Spectra

Two compounds studied here contain fluorine. Dr. David Konas ran ^{19}F-NMR spectra for these two compounds (**4**,D), Figure A11 and (**5**,D), Figure A12. The splitting patterns were consistent with the structures in (**4**,D) the fluorine atom is split by H_A and H_B by two different coupling constants leading to a doublet of doublets. The proton H_C also couples to fluorine with a smaller coupling constant resulting in a total of 8 peaks. In (**5**, D) the fluorine is split by three decreasing coupling constants that decrease in the order $J_{F\text{-}HA}$, $J_{F\text{-}HB}$ and $J_{F\text{-}HC}$. This leads to a larger splitting into a doublet, followed by a splitting to a doublet of doublets and finally each of these four peaks is split by a small $J_{F\text{-}HC}$ coupling.



4, D

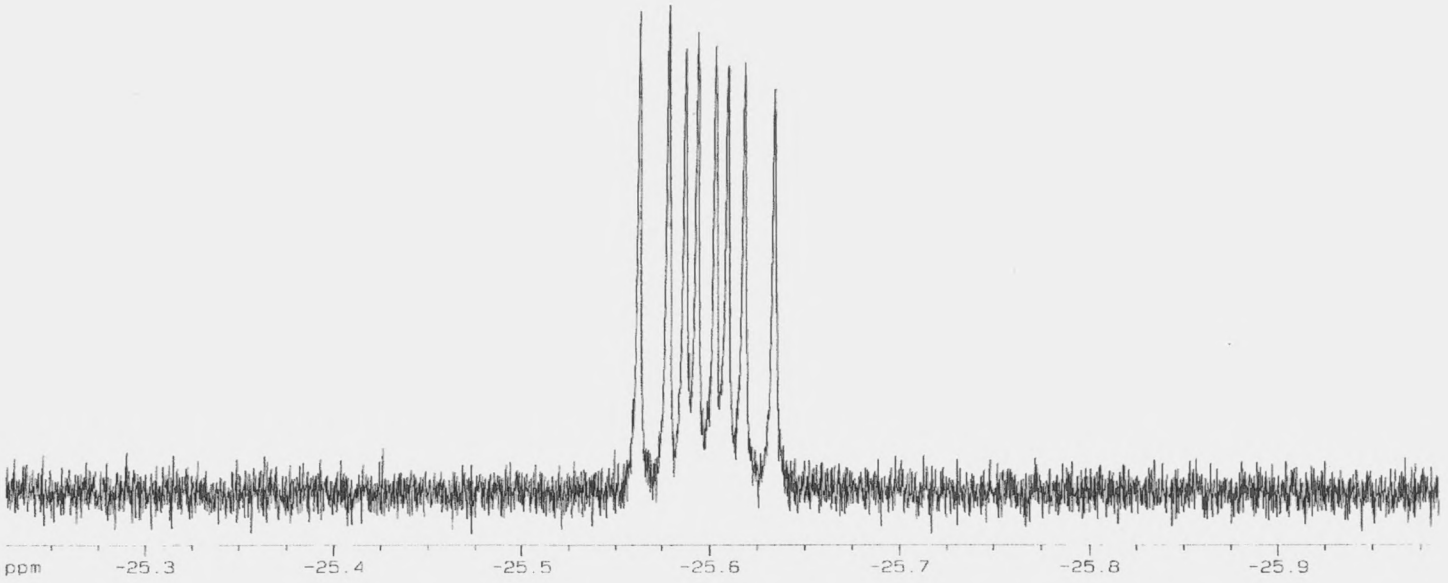
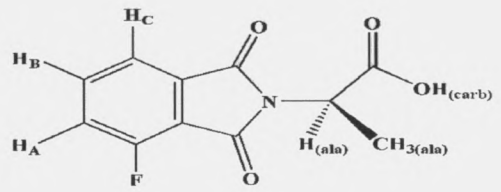


Figure A11. The ^{19}F -NMR (300 MHz, $CDCl_3$) spectrum of (D)-3-fluoro-*N*-phthaloylalanine (**4,**D)



5, D

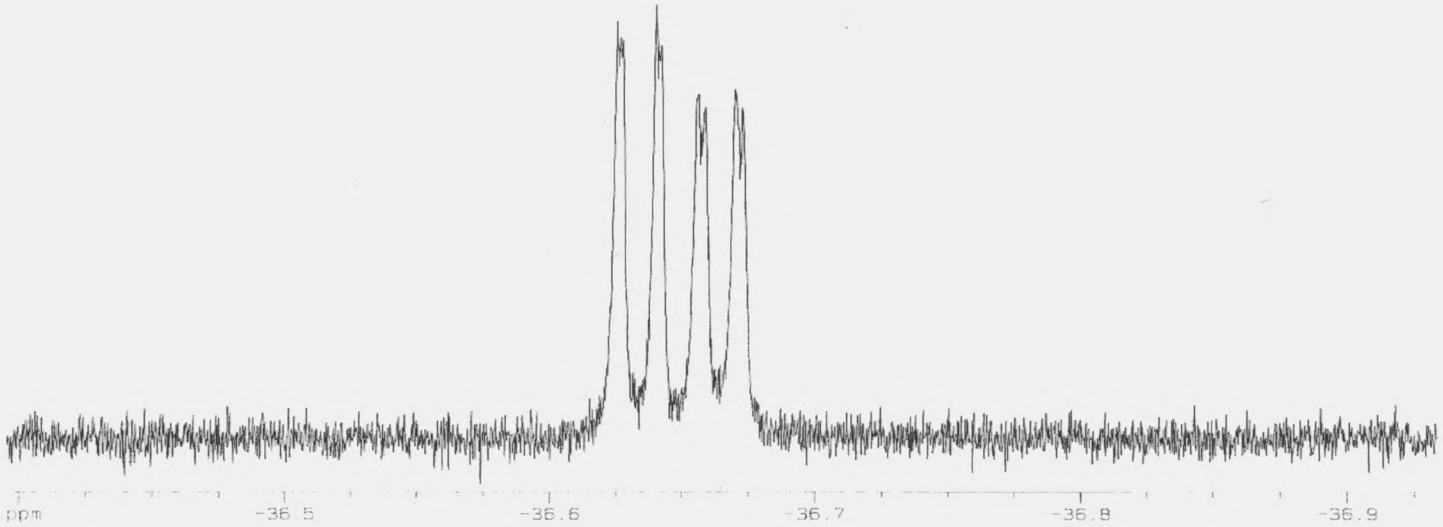


Figure A12. The ^{19}F -NMR (300MHz, $CDCl_3$) spectrum of (D)-4-fluoro-*N*-phthaloylalanine (**5,**D)

APPENDIX B – CRYSTALLOGRAPHIC TABLES

Table B1. Crystal Data and Structure Refinement Parameters for bis(*N*-methyl-imidazole)bis((D,L)-3-methyl-*N*-phthaloylalanato)Copper(II), Cu(**2**,D,L)$_2$(*N*-MeIm)$_2$

Empirical formula (as refined)*	$C_{31.01}\ H_{28.74}\ Cl\ Cu\ N_6\ O_{8.01}$
Empirical formula (undisordered)	$C_{32}\ H_{32}\ Cu\ N_6\ O_8$
Formula weight	692.17
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.4988(2) Å
	b = 8.2483(2) Å
	c = 16.4634(3) Å
	β = 95.1910(10) °
Volume, Z	1555.08(5) Å^3, 2
Density (calculated)	1.522 Mg/m^3
Absorption coefficient	2.313 mm^{-1}
F (000)	734
θ range for data collection	3.86 to 67.58
Limiting indices	-11 < h < 13,
	-9 < k < 9,
	-19 < l < 19
Reflections collected	12317
Independent reflections	2704 (R_{int} = 0.0344)
Completeness to	θ = 67.58 ° 96.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2704 / 32 / 209
Goodness-of-fit on F	1.105
Final R indices [I>2σ(I)]	R_1 = 0.1097 wR_2 = 0.2715
R indices (all data)	R_1 = 0.1129, wR_2 = 0.2732
Largest diff. peak and hole	2.683 and -0.782 e/Å^{-3}

Table B2: Atomic Coordinates [x 10^4 Å] and Equivalent Isotropic Displacement Parameters [x 10^3 Å] for bis(*N*-methylimidazole)bis((D,L)-3-methyl-*N*-phthaloyl-alanato)Copper(II), Cu(**2**,D,L)$_2$(*N*-MeIm)$_2$. U(eq) is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor.

	x	y	z	U(eq)
Cu	0	0	0	22(1)
O(11)	1381(4)	-1438(6)	211(3)	25(1)
O(12)	-20(4)	-3095(6)	553(3)	32(1)
O(18)	2785(12)	-2443(17)	1957(7)	29(4)
O(17)	3818(11)	-3836(17)	-568(6)	38(3)
N(10)	3110(14)	-3460(30)	691(10)	28(8)
N(21)	163(5)	768(7)	1142(3)	25(1)
N(23)	953(5)	1149(8)	2386(3)	30(1)
C(1)	1002(6)	-2797(9)	439(4)	27(2)
C(10)	1912(7)	-4184(9)	506(5)	33(2)
C(19)	1667(8)	-5483(10)	1111(5)	44(2)
C(17)	3921(15)	-3230(30)	141(11)	49(7)
C(11)	4862(11)	-2200(20)	541(11)	32(4)
C(12)	4552(11)	-1827(19)	1292(11)	29(4)
C(18)	3425(9)	-2589(15)	1365(8)	12(3)
C(13)	5217(18)	-710(30)	1867(13)	73(8)
C(14)	6244(14)	-190(20)	1538(13)	48(4)
C(15)	6558(10)	-618(17)	744(9)	25(3)
C(16)	5864(11)	-1693(19)	204(10)	35(4)
C(3)	4958(6)	-551(9)	2775(5)	-15(2)
C(22)	1099(7)	510(9)	1654(4)	29(2)
C(25)	-605(6)	1626(9)	1566(4)	28(2)
C(24)	-108(7)	1874(10)	2335(4)	34(2)
C(23)	1829(8)	1066(13)	3108(5)	46(2)
C(17A)	3820(14)	-3510(30)	10(11)	16(5)
C(11A)	4843(13)	-2550(30)	313(13)	30(5)
C(12A)	4630(15)	-2000(30)	1069(14)	35(7)
C(18A)	3470(30)	-2600(60)	1210(20)	100(20)
C(13A)	5350(14)	-940(20)	1645(12)	23(5)
C(14A)	6334(18)	-510(30)	1229(17)	52(7)
C(15A)	6551(19)	-1090(30)	430(16)	59(7)
C(16A)	5830(20)	-2180(40)	-89(17)	78(9)
C(3A)	5038(15)	-390(20)	2535(13)	21(4)
N(10A)	3070(20)	-3590(40)	607(14)	34(12)
O(18A)	2960(20)	-2320(30)	1854(13)	55(9)
O(17A)	3598(18)	-4320(30)	-637(10)	59(6)

Table B3. Anisotropic Displacement Parameters [$Å^2 \times 10^3$] for bis(*N*-methylimidazole)bis((D,L)-3-methyl-*N*-phthaloylalanato)Copper(II), Cu(**2**,D,L)$_2$(*N*-MeIm)$_2$. The anisotropic displacement factor exponent takes the form:

$\exp\{-2\pi^2[(ha^*)^2U_{11} + (kb^*)^2U_{22} + (lc^*)^2U_{33} + 2(hka^*b^*)U_{12} + 2(hla^*c^*)U_{13} + 2(klb^*c^*)U_{23}]\}$

	U11	U22	U33	U23	U13	U12
Cu	28(1)	21(1)	19(1)	1(1)	3(1)	-1(1)
O(11)	29(2)	25(3)	21(2)	2(2)	4(2)	0(2)
O(12)	32(3)	34(3)	32(3)	0(2)	7(2)	-4(2)
N(21)	31(3)	25(3)	18(3)	-1(2)	3(2)	-2(2)
N(23)	40(4)	33(3)	16(3)	-4(2)	1(2)	-1(3)
C(1)	33(4)	31(4)	17(3)	-2(3)	-5(3)	0(3)
C(10)	37(4)	28(4)	33(4)	3(3)	1(3)	-1(3)
C(19)	47(5)	27(4)	54(5)	9(4)	-11(4)	-4(4)
C(22)	35(4)	26(4)	27(4)	-2(3)	6(3)	1(3)
C(25)	29(4)	29(4)	28(4)	-2(3)	9(3)	1(3)
C(24)	46(5)	33(4)	25(4)	-3(3)	13(3)	1(3)
C(23)	45(5)	66(6)	24(4)	-8(4)	-3(3)	-1(4)

Table B4. Crystal Data and Structure Refinement Parameters for bis(*N*-methylimidazole)((D)-3-chloro-*N*-Phthaloylalanato)((L)-3-nitro-*N*-phthaloyl-alanto)Copper(II), Cu(**7**,D)(**9**,L)(*N*-MeIm)$_2$.

Empirical formula	$C_{30}\ H_{26}\ Cl\ Cu\ N_7\ O_{10}$
Formula weight	743.57
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 11.5518(10) Å
	b = 8.2034(6) Å
	c = 16.5022(11) Å
	β = 95.155(5) °
Volume, Z	1557.5(2) Å^3, 2
Density (calculated)	1.586 Mg/m^3
Absorption coefficient	2.398 mm^{-1}
F (000)	762
θ range for data collection	2.69 to 67.98 °
Limiting indices	-13 < h < 13,
	-8 < k < 9,
	-19 < l < 18
Reflections collected	9229
Independent reflections	4072 (R_{int} = 0.1200)
Completeness to	θ = 67.98 ° 95.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4072 / 1 / 452
Goodness-of-fit on F	1.036
Final R indices [I>2σ(I)]	R_1 = 0.0686, wR_2 = 0.1561
R indices (all data)	R_1 = 0.0999, wR_2 = 0.1744
Absolute structure parameter	0.02(5)
Largest diff. peak and hole	0.924 and -0.853 e/Å^{-3}

Table B5. Atomic Coordinates [x 10^4 Å] and Equivalent Isotropic Displacement parameters [x 10^3 $Å^2$] for bis(*N*-methylimidazole)((D)-3-chloro-*N*-phthaloylalanato)((L)-3-nitro-*N*-phthaloylalanato)Copper(II), Cu(**7**,D)(**9**,L)(*N*-MeIm)$_2$. U (eq) is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor.

	x	y	z	U(eq)
Cu	36(1)	87(2)	7504(1)	25(1)
O(11)	-1338(4)	1519(7)	7294(3)	26(1)
O(12)	42(5)	3196(8)	6959(3)	34(2)
C(1)	-983(8)	2889(12)	7081(4)	29(2)
C(10)	-1876(7)	4249(13)	6996(5)	36(2)
N(10)	-3058(6)	3577(9)	6830(4)	32(2)
C(19)	-1612(7)	5600(13)	6409(5)	39(2)
C(12)	-4547(7)	1963(12)	6251(5)	31(2)
C(13)	-5274(7)	978(13)	5755(5)	40(2)
C(14)	-6259(7)	379(14)	6048(5)	45(2)
Cl(13)	-4960(2)	617(4)	4770(1)	44(1)
C(15)	-6522(8)	782(13)	6823(5)	41(2)
C(16)	-5809(8)	1789(13)	7328(5)	42(2)
C(11)	-4783(7)	2374(13)	7047(6)	35(2)
C(17)	-3834(8)	3377(12)	7411(5)	33(2)
O(17)	-3712(5)	3896(9)	8101(3)	44(2)
C(18)	-3387(7)	2686(12)	6133(5)	30(2)
O(18)	-2801(5)	2555(8)	5558(3)	34(1)
O(21)	1407(4)	-1358(8)	7714(3)	27(1)
O(22)	8(5)	-3006(8)	8060(3)	34(2)
C(2)	1007(7)	-2752(11)	7959(4)	27(2)
C(20)	1899(7)	-4141(12)	8015(6)	38(2)
N(20)	3075(5)	-3476(10)	8125(4)	33(2)
C(29)	1679(8)	-5397(13)	8632(5)	47(3)
C(21)	4854(8)	-2451(13)	7848(6)	42(2)
C(22)	4624(8)	-1881(13)	8583(6)	40(2)
C(23)	5388(5)	-847(6)	8990(3)	57(3)
N(23)	5188(5)	-109(6)	9718(3)	67(3)
O(23)	4304(5)	897(6)	9716(3)	80(3)
O(24)	5725(5)	-415(6)	10362(3)	93(4)
C(24)	6403(5)	-409(6)	8652(3)	67(3)
C(25)	6625(9)	-975(17)	7909(9)	80(4)
C(26)	5839(9)	-2045(15)	7480(8)	60(3)
N(26)	6000(50)	-1930(80)	6900(40)	65(16)
O(26)	5650(50)	-3450(70)	6480(30)	98(17)

Table B5. Atomic Coordinates [x 10^4 Å] and Equivalent Isotropic Displacement parameters [x 10^3 $Å^2$] for bis(*N*-methylimidazole)((D)-3-chloro-*N*-phthaloylalanato)((L)-3-nitro-*N*-phthaloylalanato)Copper(II), Cu(**7**,D)(**9**,L)(*N*-MeIm)$_2$. U (eq) is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor. (cont.)

O(27)	6290(70)	-1210(130)	6260(50)	170(30)
C(27)	3844(8)	-3483(12)	7518(5)	35(2)
O(27)	3670(7)	-4181(11)	6879(3)	63(2)
C(28)	3485(8)	-2548(13)	8782(5)	35(2)
O(28)	2968(6)	-2264(9)	9376(4)	47(2)
N(31)	193(6)	848(9)	8636(3)	29(2)
C(32)	1123(7)	619(13)	9163(4)	33(2)
N(33)	968(6)	1225(10)	9890(4)	32(2)
C(33)	1838(8)	1187(16)	10603(4)	50(3)
C(34)	-81(9)	1950(13)	9832(5)	36(2)
C(35)	-573(8)	1704(13)	9065(4)	33(2)
N(41)	-123(5)	-655(9)	6363(3)	26(2)
C(42)	-1076(7)	-428(11)	5852(4)	28(2)
N(43)	-912(6)	-1089(9)	5122(3)	28(2)
C(43)	-1787(8)	-1014(14)	4421(4)	42(2)
C(44)	172(7)	-1769(13)	5167(5)	32(2)
C(45)	650(8)	-1531(10)	5924(4)	28(2)
Cl(16)	-6189(14)	2250(20)	8179(9)	64(5)

Table B6. Anisotropic Displacement Parameters [$Å^2$ x 10^3] for bis(*N*-methylimidazole)((D)-3-chloro-*N*-phthaloylalanato)((L)-3-nitro-*N*-phthaloyl-alanato)Copper(II), Cu(**7**,D)(**9**,L)(*N*-MeIm)$_2$. The anisotropic displacement factor exponent takes the form:
$\exp\{-2\pi^2[(ha^*)^2U_{11} + (kb^*)^2U_{22} + (lc^*)^2U_{33} + 2(hka^*b^*)U_{12} + 2(hla^*c^*)U_{13} + 2(klb^*c^*)U_{23}]\}$

	U11	U22	U33	U23	U13	U12
Cu	30(1)	27(1)	18(1)	0(1)	9(1)	-3(1)
O(11)	36(3)	25(4)	19(3)	-3(2)	10(2)	2(3)
O(12)	30(3)	36(4)	37(3)	-3(3)	7(3)	-9(3)
C(1)	41(5)	32(6)	14(4)	-6(4)	3(4)	-3(4)
C(10)	42(5)	43(6)	24(4)	1(4)	12(4)	-15(5)
N(10)	39(4)	27(5)	31(4)	4(3)	9(3)	-4(4)
C(19)	42(5)	33(6)	42(4)	5(4)	6(4)	-4(4)
C(12)	32(4)	23(5)	39(5)	2(4)	9(4)	7(4)
C(13)	36(5)	52(6)	34(4)	-4(4)	7(4)	-4(4)
C(14)	38(5)	49(7)	48(5)	11(4)	-1(4)	-10(5)
Cl(13)	41(1)	57(2)	35(1)	-13(1)	10(1)	-11(1)
C(15)	38(5)	44(6)	42(5)	14(4)	6(4)	4(4)
C(16)	44(5)	48(6)	38(5)	7(4)	20(4)	0(5)
C(11)	25(4)	35(5)	47(5)	14(4)	8(4)	2(4)
C(17)	42(5)	25(5)	33(5)	4(4)	18(4)	4(4)
O(17)	52(4)	50(4)	34(3)	0(3)	19(3)	-3(3)
C(18)	30(4)	37(6)	26(4)	3(4)	12(4)	6(4)
O(18)	35(3)	39(4)	30(3)	-1(3)	10(3)	-4(3)
O(21)	27(3)	35(4)	20(3)	2(3)	8(2)	-3(3)
O(22)	37(3)	40(4)	26(3)	3(3)	13(3)	1(3)
C(2)	24(4)	30(6)	27(4)	6(4)	1(4)	-8(4)
C(20)	27(4)	28(5)	59(6)	-2(5)	5(4)	2(4)
N(20)	25(4)	42(5)	32(4)	4(3)	1(3)	-1(3)
C(29)	48(6)	37(6)	56(5)	9(5)	-7(4)	-12(5)
C(21)	35(5)	33(6)	63(6)	15(5)	22(4)	2(4)
C(22)	40(5)	30(5)	49(6)	12(4)	-11(4)	0(4)
C(23)	47(6)	36(6)	84(7)	-1(5)	-12(5)	-3(5)
N(23)	93(8)	46(7)	58(6)	-1(6)	-20(6)	-35(6)
O(23)	83(7)	80(7)	77(6)	-19(5)	13(5)	12(6)
O(24)	112(9)	71(7)	90(7)	-9(5)	-27(6)	-1(7)
C(24)	40(6)	42(7)	117(9)	18(7)	-6(6)	-10(5)
C(25)	29(5)	65(9)	151(11)	53(9)	29(6)	-1(5)
C(26)	35(5)	54(8)	96(9)	33(6)	32(6)	4(5)
C(27)	43(5)	33(6)	31(5)	12(4)	11(4)	8(4)

Table B6. Anisotropic Displacement Parameters [$Å^2 \times 10^3$] for bis(*N*-methylimidazole)((D)-3-chloro-*N*-phthaloylalanato)((L)-3-nitro-*N*-phthaloyl-alanato)Copper(II), Cu(**7**,D)(**9**,L)(*N*-MeIm)$_2$. The anisotropic displacement factor exponent takes the form:
$\exp\{-2\pi^2[(ha^*)^2U_{11} + (kb^*)^2U_{22} + (lc^*)^2U_{33} + 2(hka^*b^*)U_{12} + 2(hla^*c^*)U_{13} + 2(klb^*c^*)U_{23}]\}$ (cont.)

O(27)	90(5)	72(6)	26(3)	1(3)	10(3)	-6(5)
C(28)	41(5)	40(6)	25(4)	10(4)	7(4)	7(4)
O(28)	55(4)	48(5)	39(3)	0(3)	11(3)	-3(3)
N(31)	41(4)	26(4)	21(3)	-4(3)	14(3)	-3(4)
C(32)	38(5)	39(6)	20(4)	-2(4)	0(3)	-1(4)
N(33)	30(4)	47(6)	21(3)	-6(3)	8(3)	-1(4)
C(33)	45(5)	81(10)	23(4)	-11(5)	2(4)	-7(6)
C(34)	54(6)	36(6)	20(4)	-11(4)	12(4)	-11(5)
C(35)	31(4)	46(7)	26(4)	0(4)	14(3)	-9(4)
N(41)	34(4)	36(5)	10(3)	9(3)	12(3)	1(3)
C(42)	38(5)	30(5)	16(3)	-3(3)	6(3)	-10(4)
N(43)	40(4)	28(4)	15(3)	0(3)	3(3)	-9(3)
C(43)	50(5)	51(7)	27(4)	-3(5)	5(4)	3(5)
C(44)	30(5)	32(6)	34(5)	0(4)	12(4)	8(4)
C(45)	43(5)	21(5)	22(4)	-4(3)	13(4)	7(4)

Table B7. Crystal Data and Structure Refinement Parameters for bis(*N*-methyl-imidazole)((D)-3-chloro-*N*-phthaloylalanato)((L)-3-methyl-*N*-phthaloylalanato)Copper(II), Cu(**7**,D)(**2**,L)(*N*-MeIm)$_2$.

Empirical formula (as refined)*	$C_{31.01}\ H_{28.77}\ Cl\ Cu\ N_6\ O_{8.01}$
Empirical formula (undisordered)	$C_{31}\ H_{29}\ Cl\ Cu\ N_6\ O_8$
Formula weight (as refined)	712.56
Formula weight (undisordered)	714.62
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 11.4748(9) Å b = 8.2743 (5) Å c = 16.4696(11) Å β = 95.386 (5) °
Volume, Z	1556.82(19) Å^3, 2
Density (calculated)	1.520 Mg/m^3
Absorption coefficient	2.311 mm^{-1}
F (000)	734
θ range for data collection	2.69 to 67.47 °
Limiting indices	-13 < h < 10, -9 < k < 9, -17 < l < 19
Reflections collected	10561
Independent reflections	4989 (R_{int} = 0.0336)
Completeness to	θ = 67.47 95.3 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4989 / 98 / 481
Goodness-of-fit on F	1.034
Final R indices [I>2σ(I)]	R_1 = 0.0442, wR_2 = 0.1016
R indices (all data)	R_1 = 0.0554, wR_2 = 0.1080
Absolute structure parameter	0.03(3)
Largest diff. peak and hole	0.514 and -0.224 e/Å^{-3}

- Non integer values are due to disorder in the structure

Table B8. Atomic Coordinates [x 10^4 Å] and Equivalent Isotropic Displacement Parameters [$Å^2$ x 10^3] for bis(*N*-methylimidazole))((D)-3-chloro-*N*-phthaloylalanato)((L)-3-methyl-*N*-phthaloylalanato)Copper(II), Cu(**7**,D)(**2**,L)(*N*-MeIm)$_2$. U (eq) is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor.

	x	y	z	U(eq)
Cu	5013(1)	8148(1)	7500(1)	23(1)
Cl(23)	39(1)	8684(2)	4757(1)	45(1)
Cl(26)	-1226(4)	10235(5)	8173(3)	66(1)
O(21)	3645(2)	9580(3)	7281(1)	25(1)
O(22)	5018(2)	11259(3)	6961(2)	32(1)
O(27)	1269(3)	11996(4)	8093(2)	53(1)
O(28)	2173(3)	10601(4)	5550(2)	43(1)
O(11)	6397(2)	6720(3)	7709(1)	25(1)
O(12)	4974(2)	5075(3)	8066(2)	33(1)
O(18)	7929(5)	5782(7)	9325(3)	18(1)
O(17)	8681(6)	3787(8)	6842(3)	32(1)
N(20)	1905(3)	11628(4)	6808(2)	31(1)
N(10)	8045(6)	4531(9)	8067(4)	20(2)
N(31)	5170(3)	8904(4)	8642(2)	27(1)
N(33)	5968(3)	9282(4)	9886(2)	32(1)
N(41)	4832(3)	7368(4)	6361(2)	24(1)
N(43)	4045(3)	6960(4)	5112(2)	29(1)
C(2)	4004(3)	10935(4)	7063(2)	25(1)
C(20)	3101(4)	12308(5)	6991(3)	43(1)
C(29)	3365(4)	13604(5)	6402(3)	46(1)
C(27)	1155(4)	11455(5)	7394(2)	38(1)
C(21)	170(4)	10423(5)	7005(3)	36(1)
C(22)	446(4)	10051(6)	6238(3)	41(1)
C(28)	1574(3)	10749(4)	6117(2)	31(1)
C(23)	-313(4)	9076(6)	5731(3)	47(1)
C(24)	-1283(4)	8438(6)	6038(3)	50(1)
C(25)	-1555(3)	8824(5)	6825(2)	41(1)
C(26)	-842(4)	9854(5)	7300(3)	43(1)
C(1)	6000(4)	5336(5)	7946(2)	31(1)
C(10)	6912(3)	3950(5)	8013(2)	32(1)
C(19)	6693(4)	2670(6)	8634(3)	48(1)
C(17)	8865(8)	4534(13)	7446(5)	37(3)
C(11)	9832(7)	5565(12)	7804(5)	37(3)
C(12)	9632(6)	6124(9)	8553(4)	18(2)
C(18)	8435(7)	5490(11)	8736(5)	27(2)

Table B8. Atomic Coordinates [x 10^4 Å] and Equivalent Isotropic Displacement Parameters [$Å^2$ x 10^3] for bis(*N*-methylimidazole))((D)-3-chloro-*N*-phthaloylalanato)((L)-3-methyl-*N*-phthaloylalanato)Copper(II), Cu(**7**,D)(**2**,L)(*N*-MeIm)$_2$. U (eq) is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor. (cont.)

C(13)	10387(7)	7121(11)	9002(5)	35(2)
C(14)	11454(6)	7558(10)	8562(5)	27(2)
C(15)	11630(9)	6937(13)	7778(6)	54(3)
C(16)	10843(7)	5927(10)	7417(5)	32(2)
C(3)	10284(9)	7845(13)	9694(6)	55(3)
C(32)	6111(3)	8641(5)	9159(2)	30(1)
C(35)	4436(3)	9779(5)	9073(2)	31(1)
C(34)	4910(3)	10044(5)	9835(2)	33(1)
C(33)	6841(4)	9202(6)	10599(2)	45(1)
C(42)	3915(3)	7627(5)	5837(2)	26(1)
C(45)	5631(3)	6498(5)	5948(2)	29(1)
C(44)	5126(4)	6280(6)	5164(2)	36(1)
C(43)	3201(4)	7069(7)	4394(2)	45(1)
C(17A)	8736(10)	4504(18)	7515(7)	11(4)
C(11A)	9811(9)	5481(16)	7684(7)	10(4)
C(12A)	9820(10)	6289(18)	8410(8)	31(5)
C(18A)	8754(11)	5743(18)	8799(7)	24(4)
C(13A)	10742(10)	7193(15)	8730(7)	21(3)
C(14A)	11705(14)	7190(30)	8168(9)	58(8)
C(15A)	11596(12)	6600(20)	7356(9)	38(4)
C(16A)	10655(11)	5710(20)	7128(9)	37(4)
C(3A)	10966(18)	8190(20)	9340(10)	56(5)
N(10A)	8113(13)	4690(20)	8237(8)	38(8)
O(18A)	8346(14)	6250(20)	9397(8)	67(5)
O(17A)	8327(15)	3880(20)	6908(8)	70(6)
C(17B)	8988(8)	4884(14)	7657(6)	25(3)
C(11B)	9902(8)	5901(13)	8094(6)	26(3)
C(12B)	9566(7)	6380(12)	8824(6)	19(2)
C(18B)	8358(9)	5652(16)	8935(7)	35(4)
C(13B)	10207(8)	7412(14)	9310(6)	29(3)
C(14B)	11326(9)	7897(14)	8982(6)	34(3)
C(15B)	11610(11)	7476(18)	8205(8)	40(4)
C(16B)	10915(9)	6479(16)	7756(7)	40(3)
C(3B)	10098(10)	7749(14)	10051(6)	32(3)
N(10B)	8094(10)	4690(17)	8225(6)	35(6)
O(18B)	7755(8)	5772(11)	9494(5)	31(2)
O(17B)	8925(7)	4290(10)	6992(4)	28(2)

Table B9. Anisotropic Displacement Parameters [$Å^2$ x 10^3] for bis(*N*-methylimidazole))((D)-3-chloro-*N*-phthaloylalanato)((L)-3-methyl-*N*-phthaloylalanato)Copper(II), Cu(**7**,D)(**2**,L)(*N*-MeIm)$_2$.

The anisotropic displacement factor exponent takes the form:
$\exp\{-2\pi^2[(ha^*)^2U_{11} + (kb^*)^2U_{22} + (lc^*)^2U_{33} + 2(hka^*b^*)U_{12} + 2(hla^*c^*)U_{13} + 2(klb^*c^*)U_{23}]\}$

	U11	U22	U33	U23	U13	U12
Cu	28(1)	23(1)	18(1)	0(1)	4(1)	-1(1)
Cl(23)	42(1)	56(1)	35(1)	-15(1)	5(1)	-16(1)
Cl(26)	72(3)	45(2)	86(3)	10(2)	38(2)	8(2)
O(21)	33(1)	24(1)	20(1)	1(1)	8(1)	-4(1)
O(22)	32(1)	32(1)	33(1)	4(1)	2(1)	-1(1)
O(27)	71(2)	48(2)	39(2)	-7(1)	3(1)	7(2)
O(28)	46(2)	53(2)	29(1)	2(1)	4(1)	1(1)
O(11)	25(1)	21(1)	28(1)	3(1)	1(1)	4(1)
O(12)	33(2)	39(2)	29(1)	0(1)	9(1)	-7(1)
N(20)	30(2)	28(2)	33(2)	5(1)	-4(1)	-1(1)
N(31)	31(2)	32(2)	20(1)	3(1)	4(1)	-2(1)
N(33)	43(2)	34(2)	19(2)	-4(1)	3(1)	-3(2)
N(41)	36(2)	17(2)	19(1)	-2(1)	3(1)	-1(1)
N(43)	34(2)	34(2)	21(2)	-3(1)	4(1)	-4(2)
C(2)	24(2)	28(2)	24(2)	3(2)	4(1)	-4(2)
C(20)	57(3)	34(2)	38(2)	8(2)	1(2)	-10(2)
C(29)	44(2)	27(2)	64(3)	12(2)	-13(2)	-6(2)
C(27)	52(2)	28(2)	34(2)	8(2)	1(2)	16(2)
C(21)	37(2)	31(2)	40(2)	14(2)	1(2)	6(2)
C(22)	48(2)	39(2)	35(2)	6(2)	-2(2)	4(2)
C(28)	27(2)	25(2)	40(2)	11(2)	-2(2)	5(1)
C(23)	59(3)	50(3)	34(2)	-3(2)	6(2)	2(2)
C(24)	36(2)	53(3)	61(3)	11(2)	2(2)	-13(2)
C(25)	31(2)	46(2)	47(2)	28(2)	10(2)	1(2)
C(26)	42(2)	42(2)	45(2)	11(2)	9(2)	9(2)
C(1)	42(2)	33(2)	17(2)	-5(2)	3(2)	1(2)
C(10)	29(2)	28(2)	39(2)	-1(2)	-1(2)	3(2)
C(19)	46(3)	40(3)	57(3)	20(2)	-4(2)	-9(2)
C(32)	43(2)	26(2)	21(2)	-1(2)	6(1)	1(2)
C(35)	30(2)	35(2)	27(2)	2(2)	4(2)	5(2)
C(34)	38(2)	31(2)	33(2)	-9(2)	13(2)	-6(2)
C(33)	43(2)	63(3)	26(2)	-8(2)	-3(2)	8(2)
C(42)	31(2)	27(2)	22(2)	1(2)	4(1)	-2(2)
C(45)	33(2)	31(2)	26(2)	-4(2)	12(2)	-2(2)
C(44)	47(2)	37(2)	25(2)	-4(2)	10(2)	7(2)
C(43)	44(3)	65(3)	23(2)	-6(2)	-2(2)	-6(2)