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PLATINUM(II) AND PALLADIUM(II) COMPLEXES OF ETHYLENEDIMORPHOLINE

by

William Eventoff

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Chemistry)
in The University of Michigan
1972

Doctoral Committee:

Professor P. G. Rasmussen, Chairman
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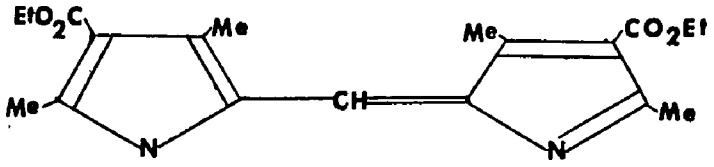
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CHAPTER 1

INTRODUCTION

Although five and six coordinate compounds of platinum(II) and palladium(II) are known, the coordination chemistry of these two elements deals almost exclusively with four-coordinate square planar complexes. Whereas, nickel(II) can be forced into tetrahedral geometry by the use of sterically forcing ligands, the same is not true for the second and third row d^8 elements.

Porter[1] in trying to isolate non-planar complexes of palladium(II), used the ligand ethyl 3,3',5,5'-tetramethylpyrromethene-4,4'-dicarboxylate, (I).



(I)

Due to steric interactions between the methyl groups in the 5 and 5' positions on adjacent chelate groups, the bis(ethyl 3,3',5,5'-tetramethylpyrromethene-4,4'-dicarboxylate)-palladium-(II) complex was assumed to have a non-planar structure.

Indeed, the complex bis(3,3',5,5'-tetramethyldipyrromethenido) nickel(II) does in fact have a distorted tetrahedral structure.[2] However, a recent crystal structure determination[3] has shown that rather than a non-planar coordination geometry, the ligand has been deformed in order to allow square planar coordination. A small amount or the coordination sphere is shown in figure I, in order to illustrate the type of deformation. The deformation consists of a folding

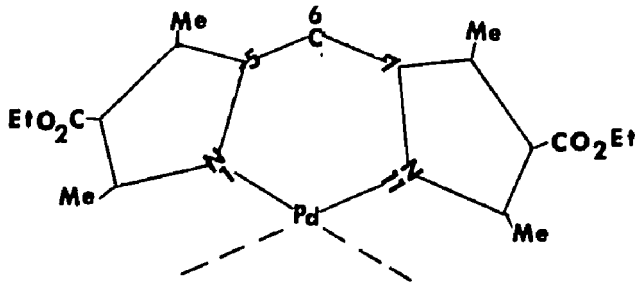


Figure I

Part of the Molecular Structure of bis(ethyl 3,3',5,5'-tetramethylpyrromethene-4,4'-dicarboxylate.

of the ligand out or the PdN_4 plane by bending around the N(1)——N(11) vector. Further, the pyrrole rings are folded away from the plane of the chelate ring by folding along the N(1)——C(5) and N(11)——C(7) vectors. Similar deformations

have been found in bis-N-t-butylsalicylaldiminatopalladium(II)[4] and bis(2,2'-bipyridyliminatopalladium)(II).[5]

In the complex bis(1,10-phenanthroline)palladium(II), the hydrogen atoms in the 2 and 9 positions ot one chelate group should crowd the hydrogen atoms in the corresponding positions on the other chelate group. Thus the compound would not be expected to be planar. However, preliminary crystallographic data,[6] indicate that the phenanthroline ligand is not planar, but is folded along its 2-fold axis, and that the coordination geometry is essentially square planar.

In the compound (2,9-dimethyl-1,10-phenanthroline)palladium(II)nitrite, the steric interactions are minimized by many small deformations, which all taken together allow the palladium atom to maintain a square planar coordination sphere.[7]

While structural data are lacking for platinum(II) complexes, the same type of results would be expected.

Lott has recently synthesized metal complexes of ethylenedimorpholine (EDM), or the type $MEDMX_2$ (where M = Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+} and X = Cl^-, Br^- or I^-).[8] All of the first row complexes are monomeric. Their infrared spectra show no shift in the C-O-C stretching bands at 1065 and 920 cm^{-1}, which indicates that the etheral oxygen is uncoordinated. These complexes have been assigned a

tetrahedral structure. This has been verified for the cobalt chloride derivative, and also for the isomorphous nickel, copper and zinc chlorides, by a crystal structure determination.[9] The Co-O distance of 4.14 Å, verifies the lack of oxygen coordination. Apparently the energy gained by tetradentate coordination is not surficient to stabilize both morpholine rings in a boat configuration which is required for simultaneous nitrogen and oxygen coordination. Ethylenedimorpholine behaves in a manner similar to a substituted ethylenediamine, its steric erfects forcing tetrahedral coordination with the first row metals.

The palladium(II) complexes behave in a quite different manner,[8] although here again the etheral oxygens are uncoordinated. The bromo and chloro derivatives appear to be square planar polymeric compounds, while the iodo derivative is a monomer which exhibits quite complex behavior. In acetone solution, it dimerizes to an iodo bridged species. In the presence of excess EDM, both the monomer and dimer form a bis chelate complex. These changes are summarized in Figure II. The bis chelate is paramagnetic, and due to the steric effects of EDM has been assigned a tetrahedral structure. It has not, however, been isolated in the solid state.

In this work, the synthesis of stable, isolatable platinum(II) complexes of EDM was undertaken, in order to investigate their stereochemistry and reactivity. A further

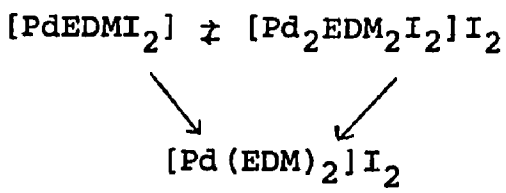


Figure II

Reactions of $PdEDMI_2$ in Acetone

study of the palladium(II) complexes of this ligand and its substituted derivatives, consisting of the isolation of the paramagnetic $(PdEDM_2)^{2+}$ cation and the synthesis of palladium(II) complexes of 2,2',6,6'-tetramethylethylenedimorpholine, was also undertaken.

CHAPTER 2

EXPERIMENTAL

A. Physical Measurements

Infrared spectra were recorded on a Beckman I.R. 10 or Perkin Elmer 457 spectrometer. The compounds were examined as nujol mulls between KBr plates or in solution, if possible, using 1 mm matched KBr cells.

A Cary 14 spectrometer was used for recording spectra in the region 20,000 to 2500 Å. The samples were all examined as either acetone or methylene chloride solutions, using 1 cm matched quartz cells.

Conductivity measurements were made using an apparatus which is described elsewhere.[10] The samples were examined as either acetone or methylene chloride solutions.

X-Ray powder photographs were obtained using Ni filtered Cu K_α radiation. The samples were prepared as duco mounts, or packed in glass capillaries, they were then mounted in a 114.59 mm camera. The d values were obtained by measuring 20 values with a film reader and converting using the appropriate tables.[11]

Magnetic susceptibilities were measured by the Faraday method. The magnetic field was provided by a Varian model

V-3400 series 9 inch electromagnetic. Weights were recorded with a Cahn electrobalance. Hg $[Co(SCN)_4]$ was used as a calibrant. All susceptibilities were corrected for the diamagnetism of the metal and ligands.

Elemental analyses were determined by Spang Microanalytical Laboratories, Ann Arbor, Michigan or Galbraith Laboratories Inc., Knoxville, Tennessee.

B. Preparations

B.1. Preparation of ethylenedimorpholine:

Ethylenedimorpholine was prepared by a modified version of the literature preparation.[12] Morpholine, 14.4 ml (.165 mole), 20 ml of dry benzene and 3.46 ml of 1,2-dibromoethane (.04 mole) were added in the above order to a 100 ml flask fitted with a reflux condenser. The reaction mixture was heated slightly to initiate precipitation, after which it was allowed to cool and stand overnight. The reaction mixture was then refluxed for four hours, allowed to cool, and the morpholine hydrobromide filtered off. The benzene was removed by distillation and the residue extracted with anhydrous ether. The ether was removed under reduced pressure and the yellow white solid purified by vacuum sublimation at 90 to 110°C. The white crystals had a melting point equal to 73-75°C (reported 73-74°C).

B.2. Preparation of dichloroethylenedimorpholine-platinum(II):

Dichlorobisbenzonitrileplatinum(II), 0.0471 g (.1m-mole) was dissolved in 20 ml of acetone, and to the resulting solution 1 g of ethylenedimorpholine was added. The reaction mixture was stirred overnight, and then filtered. The tan precipitate was washed with 3 x 15-ml portions of anhydrous ether, and dried under vacuum for 2 hours.

Anal. Calcd. for $Pt(C_{10}H_{20}N_2O_2)Cl_2$: C, 25.76; H, 4.29 N, 6.01

Found: C, 25.90; H, 4.15; N, 5.79.

B.3. Preparation of dibromoethylenedimorpholine-platinum(II):[13]

This compound was prepared in a manner identical to the chloro derivative, except the reaction mixture had to be stirred for 24 hours.

Anal. Calcd. for $Pt(C_{10}H_{20}N_2O_2)Br_2$: C, 21.64; H, 3.61 N, 5.05

Found: C, 23.57; H, 4.01; N, 5.09.

B.4. Preparation of diiodoethylenedimorpholineplatinum(II):

Potassium tetrachloroplatinate, 0.2065 g (.5 mmole) and .332 g (2 mmole) of potassium iodide were dissolved in 20 ml of water. To the resulting mixture, 1 ml of benzonitrile was added. The mixture was heated to between 60

and 70°C and kept there for 3 1/2 hours. The mixture was filtered and the product washed with 3 x 15-ml portions of water followed by 3 x 15 ml portions of methanol. The orange brown crystals were dried under vacuum for two hours.

The above product, 0.0665 g, was dissolved in 20 ml of acetone and 1 g of ethylenedimorpholine was added. The reaction mixture was stirred for 48 hours. The solution was filtered and the precipitate washed with 3 x 15-ml portions or anhydrous ether, and dried under vacuum for two hours.

Anal. Calcd. for $Pt(C_{10}H_{20}N_2O_2)I_2$: C, 18.50; H, 3.09; N, 4.35

Found: C, 18.71; H, 3.26; N, 4.37.

B.5. Attempted preparation of dihydridoethylenedimorpholineplatinum(II):

Diiodoethylenedimorpholineplatinum(II), 0.03 g (0.046 mmole) was suspended in 25 ml of refluxing ethanol. To the refluxing suspension, 2 ml of 1 M sodium hydroxide were added. The reaction mixture blackened at once. The reaction mixture was refluxed for five minutes and then distilled (5 ml collected) into a few milliliters of 2,4-dinitrophenylhydrazine sulfate (.45 g of 2,4-dinitrophenylhydrazine, .4 g of sulfuric acid, 50 ml or methanol and 3 ml of water). The remainder of the refluxing solution was

filtered hot and the black solid saved. A little water was added to the 2,4-dinitrophenylhydrazine sulfate solution, and the orange solid collected.

Anal. Calcd. for the 2,4-dinitrophenylhydrazine derivative of acetaldehyde ($C_8H_8N_4O_4$):

C, 42.85; H, 3.57; N, 25.00

Found: C, 42.72; H, 3.62; N, 24.68

B.6. Attempted preparation of diphenylethylenedimorpholineplatinum(II):

A 25 ml flask equipped with a reflux condenser and dropping funnel was charged with 0.24 g (10 mmoles) of magnesium metal and a small crystal of iodine. The dropping funnel was filled with a solution containing 1 ml of bromobenzene in 10 ml of anhydrous ether; 2 ml were added rapidly to the magnesium turnings. The mixture warmed to initiate the reaction. The heat was removed and the remainder of the bromobenzene solution added at a rate which kept the mixture refluxing. The reaction mixture was refluxed for 1/2 hour after all of the bromobenzene solution had been added. To the cool solution of phenylmagnesiumbromide, 0.0175 g (.027 mmole) of diiodoethylenedimorpholineplatinum(II) was added and the reaction mixture refluxed for one hour during which time a black solid formed. The reaction mixture was poured slowly into a mixture of 10 ml of 10% sulfuric acid and ice. The solution was filtered to yield a black solid.

The filtrate was extracted with anhydrous ether and the yellow ether layer dried overnight over anhydrous sodium sulfate. The ether was allowed to evaporate and the white solid sublimed to yield a small amount of white crystals. The melting point of the crystals was 67-70°C (reported for biphenyl 69-71°C).

B.7. Attempted preparation of bis(benzyl)ethylene-dimorpholineplatinum(II):

This reaction was identical to the reaction with phenylmagnesium bromide, except benzylchloride was used to prepare the Grignard reagent. Once again a black solid formed. A white solid, with a melting point equal to 48-51°C, was isolated from the organic layer (melting point reported for bisbenzyl is 52°C).

B.8. Preparation of 2,2',6,6'-tetramethylethylene-dimorpholine:

In a 100 ml flask equipped with a reflux condenser, 20.4 ml (.165 mole) of 2,6-dimethylmorpholine, 35 ml of dry benzene and 3.46 ml (.04 mole) of 1,2-dibromoethane were combined in the above order. The mixture was warmed to reflux, cooled to room temperature and allowed to stand overnight. The reaction mixture was then refluxed for 7 hours. The benzene was removed by distillation, and the gummy orange mass extracted with 200 ml of anhydrous ether.

The ether was removed under vacuum, and the oily residue was transfered to a semimicro distillation apparatus. The oil was vacuum distilled using an air cooled condenser. The product is a yellow oil.

Anal. Calcd. ror $C_{14}H_{28}N_2O_2$: C, 65.62; H, 10.93; N, 10.93

Found: C, 66.63; H, 10.92; N, 10.28

B.9. Preparation of dichloro-2,2',6,6'-tetramethyl-ethylenedimorpholinepalladium(II):

Palladium(II) chloride, 0.0880 g (0.5 mmole) was suspended in 20 ml of acetone, and to the suspension 5 ml of a solution containing 2.5 g of 2,2',6,6'-tetramethyl-ethylenedimorpholine in 25 ml or acetone were added. The reaction mixture was stirred for 48 hours. The reaction mixture was filtered to yield a tannish precipitate and yellow solution. The acetone was removed under vacuum to yield a yellow powder which was shaken with anhydrous ether, filtered off and washed with 3 x 15-ml portions of anhydrous ether. The product was then dried for 3 hours under vacuum. An additional amount of product can be obtained by Soxhlet extraction of the tan precipitate with acetone.

Anal. Calcd. for $Pd(C_{14}H_{28}N_2O_2)Cl_2$: C, 38.70; H, 6.46; N, 6.46

Found: C, 36.9; H, 6.20; N, 6.08.

B.10. Preparation of dibromo-2,2',6,6'-tetramethylethylenedimorpholinepalladium(II):

Palladium(II) chloride, 0.088 g (0.5 mmole), was suspended in 25 ml of acetone, and 0.238 g (2 mmoles) of potassium bromide (powdered) was added. The mixture was stirred for six hours. The reaction mixture was filtered to remove the potassium chloride that forms. To the resulting red solution containing potassium tetrabromopalladate, 5 ml of a solution containing 2.5 g of 2,2',6,6'-tetramethylethylenedimorpholine in 25 ml of acetone were added. An orange precipitate forms immediately. The reaction mixture was allowed to stir overnight. It was then filtered and the product washed with 3 x 15-ml portions of anhydrous ether. The product was dried under vacuum for 3 hours. The product was purified by Soxhlet extraction with acetone.

Anal. Calcd. for $Pd(C_{14}H_{28}N_2O_2)Br_2$: C, 32.15; H, 5.35; N, 5.35.

Found: C, 31.91; H, 5.41; N, 5.14

B.11. Attempted preparation of diiodo-2,2',6,6'-tetramethylethylenedimorpholinepalladium(II):

Potassium tetraiodopalladate, 0.1320 g (.2 mmole), was dissolved in 25 ml of acetone, stirred for three hours and filtered. To the resulting solution, 5 ml of a solution containing 2.5 g of 2,2',6,6'-tetramethylethylenedimorpholine in 25 ml of acetone were added. The reaction mixture was

refluxed for 48 hours. The reaction mixture was cooled to room temperature, and the acetone removed under reduced pressure. The solid was shaken with anhydrous ether, and filtered off. The product was washed with 3 x 15-ml portions of anhydrous ether, and dried under vacuum for 3 hours. Attempted purification of the brown solid by Soxhlet extraction with methylene chloride failed.

B.12. Attempted preparation of bis(ethylenedimorpholine)palladium(II)tetrafluoroboron:

Diiodoethylenedimorpholinepalladium(II), 0.0140 g (0.025 mmole),was dissolved in 15 ml of acetone, and the solution was allowed to equilibrate for two hours. To the resulting dark red solution, a 50 fold excess of ethylenedimorpholine and 0.0063 g (.05 mmole) of potassium tetrafluoroborate was added. The reaction mixture was allowed to stir overnight. There was no noticable color change. The red solution was allowed to evaporate, and the solid was washed with 50 ml of anhydrous ether. Nothing was isolated but starting material.

B.13. Attempted preparation of bis(ethylenedimorpholine) palladium(II)nitrate:

Diiodoethylenedimorpholinepalladium(II), 0.056 g(0.1 mmole) was dissolved in 25 ml of acetone, and the solution was allowed to equilibrate for two hours; 1 g of ethylenedimorpholine was added. The usual lightening of color

took place. To the resulting light red solution,0.034 g (0.2 mmoles) of silver nitrate was added (a positive nitrogen pressure over the reaction mixture was maintained throughout the reaction). The solution turned yellow. The reaction mixture was allowed to stir overnight. The reaction mixture was filtered, and the yellow solution evaporated under reduced pressure. The tannish residue was washed with 50 ml of anhydrous ether. All attempts to purify the product were unsuccessful.

B.14. Attempted preparation of bis(ethylenedimorpholine) palladium(II)perchlorate:

An anion exchange column was prepared using Dowex 3 containing ionic hydroxyl functions; 3 M sodium perchlorate was passed slowly through the column, until the effluent was neutral (initial pH=12). The column was washed with water and then acetone.

15 ml of acetone containing 0.056 g(0.1 mmole) of diiodo-ethylenedimorpholinepalladium(II) and 1 g of ethylenedi-morpholine was passed through the column. The effluent was yellow. The column was washed with 25 ml of acetone, and the washings were combined with the original effluent. Evaporation of this solution yielded a small amount of dark yellow oil, which could not be solidified by a variety of methods.

B.15. Attempted preparation of bis(ethylenedimorpholine)palladium(II)iodotrichloroaluminum:

Diiodoethylenedimorpholinepalladium(II), 0.056 g(0.1 mmole) was dissolved in 25 ml of acetone, and the solution was allowed to equilibrate for two hours; 1 g of ethylenedimorpholine was added followed by 0.0273 g(0.2 mmole) of aluminum trichloride. The reaction mixture was stirred for 19 hours. 15 ml of methanol were added, and stirring was continued for five hours. The solution was evaporated under reduced pressure. The residue was washed with anhydrous ether. The semi-solid residue could not be solidified.

B.16. Preparation of 1,10-phenanthrolineethylenedimorpholinepalladium(II) Iodide:

A nitrogen atmosphere was maintained in the reaction vessel throughout the reaction; 0.056 g(0.1 mmole) of diiodoethylenedimorpholinepalladium(II) was dissolved in 25 ml of acetone, and the solution allowed to equilibrate for two hours; 1 g of excess ethylenedimorpholine was added. To the resulting light red solution, a solution of 0.0198 g(0.1 mmole) of 1,10-phenanthroline heminydrate in 10 ml of dimethoxypropane (the solution had been stirred for one hour prior to the addition to insure the removal of the water) was added. The reaction mixture was stirred overnight. The orange solution was evaporated under reduced

pressure, and the orange solid washed with 50 ml of anhydrous ether. The product was dried under nitrogen for two hours. The molar conductivity of the compound in acetone is equal to 210.

Anal. Calcd. for $Pd(C_{22}H_{28}N_4O_2)I_2$: C, 35.80; H, 3.78; N, 7.55

Found: C, 35.49; H, 4.15; N, 7.55.

CHAPTER 3

PLATINUM COMPLEXES

A. Results

The dihaloethylenedimorpholineplatinum(II) complexes can be prepared by stirring an acetone solution of the corresponding dihalobis(benzonitrile)platinum(II) complex in the presence of excess ethylenedimorpholine for from 12 to 48 hours. The complexes are all crystalline solids, however they are not isomorphous. Their infrared spectra show no shift in the C-O-C stretching bands at 1065 and 920 cm^{-1}, indicating a lack of oxygen coordination.

Dichloroethylenedimorpholineplatinum(II) is a tan diamagnetic powder, which is insoluble in all common solvents.

Dibromoethylenedimorpholineplatinum(II) is a yellow powder, which is paramagnetic having a magnetic moment equal to 2.97 $\pm$ .3 B.M. It is also insoluble in all common solvents.

The iodo derivative is a yellow powder. It is soluble in acetone and methylene chloride, and is a non-electrolyte in both. It is paramagnetic, having a magnetic moment of 2.76 $\pm$ .2 B.M. at 297°K. The magnetic moment decreases with temperature, having values of 2.22 $\pm$ .2 and 1.38 $\pm$ .2 B.M. at 195 and 77°K respectively. The spectrum of the

complex between 16000 and 3300 Å consists of two absorption bands centered at 25,800 (1200) and 31,020 (650) cm^{-1} (molar extinction coefficients are given in parentheses). The complex is not soluble enough for a molecular weight determination in solution, and is not volatile enough for study by mass spectral techniques.

The reaction of diiodoethylenedimorpholineplatinum(II) with sodium hydroxide in refluxing ethanol leads to the isolation of two products. The organic product was identified as acetaldehyde by its 2,4-dinitrophenylhydrazine derivative. The black inorganic solid was identified as platinum metal by its powder pattern, observed and reported d values and intensities are given in Table I.

The reaction of diiodoethylenedimorpholineplatinum(II) with both phenylmagnesium bromide and benzylmagnesium bromide led to the isolation of two products. The inorganic black solid produced in both cases was identified through its powder pattern as platinum metal. The organic products in both cases were dimerized starting material. Biphenyl was identified by its melting point and powder pattern, observed and reported values and intensities are given in Table II. Bibenzyl was identified by its melting point.

B. Discussion

The diamagnetism of the chloro derivative would indicate a normal square planar coordination geometry around the

Table 1

Observed and Reported d Values and Intensities for Platinum(o)

$I_{obs.}$	$I_{rep.}$	$d_{obs.}$	$d_{rep.}$
100	100	2.26	2.26
50	53	1.95	1.96
50	31	1.38	1.38
30	33	1.17	1.18

Table 2

Observed and Reported d Values and Intensities for Biphenyl

$I_{obs.}$	$I_{rep.}$	$d_{obs.}$	$d_{rep.}$
50	30	9.42	9.49
10	20	4.76	4.74
100	100	4.63	4.63
70	50	4.20	4.25
1	7	4.10	4.08
70	45	3.85	3.84
20	3	3.35	3.40
40	30	3.15	3.18

platinum. Although insolubility alone, does not require the compound to be polymeric, a polymeric structure with bridging ethylenedimorpholine groups, as shown in Figure III cannot be ruled out. This type of coordination is known to

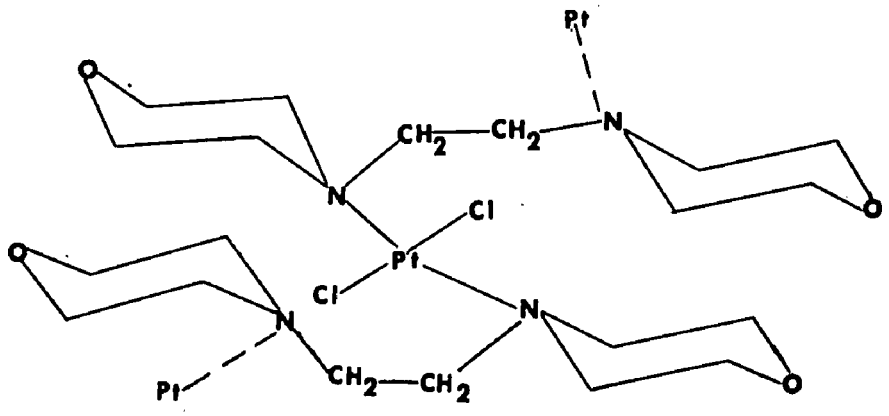


Figure III

Proposed Structure of $PtEDMCl_2$

occur with ethylenediamine.[14,15] Furthermore, molecular models indicate that steric interactions which prevent square planar coordination in monomeric ethylenedimorpholine complexes are greatly reduced when a bridging mode of coordination is used. A square planar monomeric compound can be formed if the ligand is in the configuration in which the ethylene bridge is axial to the rings. This

alleviates the steric interactions between the chlorides and the morpholine rings. Since the molecular weight could not be determined, the exact method used to maintain square planar coordination cannot be determined.

Both the bromo and iodo derivatives are paramagnetic. The paramagnetism itself, while indicative of a tetrahedral or distorted tetrahedral geometry, does not rule out a square planar structure.

There is a number of possible structures which may be assigned to the bromo derivative, due to its incomplete characterization. Here again, the insolubility of the complex could indicate a polymeric structure. However, a polymeric structure based on a structure similar to that postulated for the chloro derivative, would be expected to be diamagnetic. This plus the fact that steric interactions are minimized in a bridging structure, making tetrahedral distortion unnecessary tends to rule out this possibility. A monomeric structure based on either a tetrahedral or square planar geometry, depending on the in-plane ligand field, is a possibility. The final possibility is a Magnus type salt, bis(ethylenedimorpholine)platinum(II) tetrabromoplatinate(II), in which case the cation due to the steric effects of ethylenedimorpholine, is most likely tetrahedral. However, this possibility seems unlikely due to the distinctive colors of tetrahalometalate salts, (ML_4)

($M'X_4$), in general. Usually these compounds have a distinctive green color when both M and M' are platinum(II), although a pink color is also possible.[16] On this basis, a monomeric structure which is either square planar or tetrahedral seems more probable.

The iodo derivative is soluble in acetone and methylene chloride. The solubility and non-electrolytic behavior suggests a monomeric formulation. Once again there are two possibilities, either a tetrahedral or square planar stereochemistry.

The large molar extinction coefficients of the two bands found in the U.V. region makes classification of these bands as d-d transitions highly speculative, and no real information can be gained from the spectrum.

The halogen atoms in the paramagnetic complexes should be readily replacable. Substitution reactions using either a hydrido or organo group as the incoming group were attempted. It was hoped that the complex, if formed, would be stable, but would readily give up the hydrido or organo ligand and function as either a hydrogenating or alkylating agent.

In attempting to form the hydrido complex, the method of Chatt and Shaw was used.[17] By analogy to the mechanism Chatt and Shaw propose for the formation of $PtHCl(PEt_3)_2$ by the same reaction, shown in Figure IV, a hydrido complex is initially formed, explaining the acetaldehyde formed.

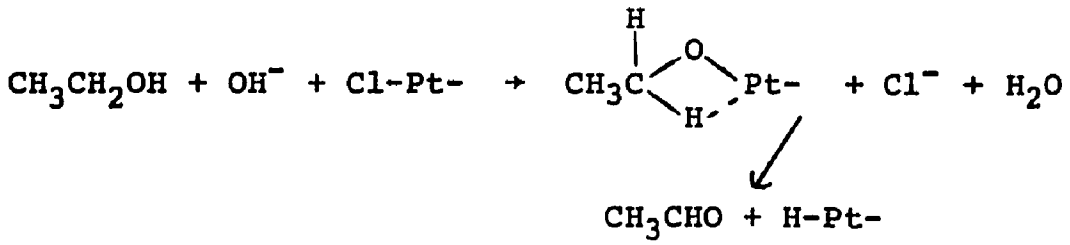


Figure IV
Mechanism for the Formation of $PtHCl(Pet_3)_2$

This complex then undergoes a rapid internal oxidation-reduction reaction to yield platinum metal.

This same type of behavior was noted with the aryl derivatives. The results suggest that the aryl complex is formed. However it decomposes by an oxidation-reduction reaction to yield the coupled organic product and the platinum metal.

Chatt and Shaw have suggested that the main influence on the stability of transition metal aryl(alkyl) and hydrido complexes is the energy separation between the highest filled molecular orbital and the lowest unfilled molecular orbital, a anti-bonding sigma orbital, for d^8 configuration.[18] The stability of the complex can be increased if this energy separation is made larger, and this can be affected by the use of π-acid type ligands.

Since ethylenedimorpholine is not a π-acid type ligand, its inability to stabilize the organo and hydrido complexes is not surprising. There is also the possibility that on

forming the organo or hydrido derivatives the complex still is in a $^3A_2$ configuration. Therefore the $d_{x^2-y^2}$ σ^* orbital is populated, and the carbon to metal or hydride to metal bond would be weakened.

CHAPTER 4

THE CRYSTAL STRUCTURE OF DIIODOETHYLENEDIMORPHOLINEPLATINUM(II)

A. Introduction

As shown in Chapter 3, chemical and physical characterization of the paramagnetic dihaloethylenedimorpholineplatinum(II) complexes, did not allow an unambiguous assignment of the coordination geometry around the platinum atom to be made. In order to determine unambiguously the coordination geometry, a crystal structure determination of the iodo derivative was undertaken.

The iodo derivative was chosen because of its solubility, which made easier the growth of crystals suitable for a crystallographic investigation. The iodo and bromo derivatives are not isomorphous. However, through an examination of the steric interactions present in the iodo derivative, some insight into the coordination geometry of the bromo derivative can be gained.

B. Experimental

Crystals were grown by the slow evaporation of an acetone solution at a constant temperature of 27°C. Preliminary precession and Weissenberg data indicated that the crystals were monoclinic, with a = 17.56(2) Å, b = 10.60(2) Å,

$c = 16.73(2)$ Å and $\beta = 96.40(15)°$ (estimated standard deviations in the last decimal place are given in parentheses). The data showed systematic absences: $h + k = 2n + 1$ for hk0 reflections, $k = 2n + 1$ for 0kℓ reflections, $\ell = 2n + 1$ for 00ℓ reflections, $h = 2n + 1$ for h0l reflections and $\ell = 2n + 1$ for h0ℓ reflections. These data indicate a c centered cell with a c glide plane, and thus the possible space groups are C_c or $C_{2/c}$. The density of 2.80 g/cc determined by floatation in a bromoform-carbon tetrachloride mixture is in good agreement with the density of 2.87 g/cc calculated for eight molecules per unit cell.

A crystal .25 x .05 x .05 mm was used for the collection of intensity data. The intensity data were collected using a Syntex $P\bar{1}$ four circle automated diffractometer, Mo K_α radiation, a graphite single crystal monochromator and a scintillation counter. The data were collected using a θ-2θ scan technique, with background counted on each side of the peak. The time spent counting background was variable, being a function of peak height. Two standard reflections were measured after every fiftieth reflection, and showed no decrease in intensity throughout the collection process. The intensity data were corrected for Lorenz and polarization effects. No absorption correction was applied ($\mu_l = 139$ cm^{-1}). The data set consisted of 2303 non-zero structure amplitudes.

C. Determination of the Structure

The programs of the X-Ray 70 system were used for the computations, and the program ORTEP was used in drawing the figures.[19,20] The data were placed on an absolute scale, and a set of normalized structure factors was calculated. A statistical analysis of the normalized structure factors indicated a centrosymmetric structure.

A three-dimensional sharpened origin removed Patterson function was calculated. An examination of the Harker line Ov1/2 and Harker plane u1/2w led to the location of the platinum atom. With eight molecules per unit cell, two different types of platinum would be expected if the structure were acentric. The fact that only one peak, assignable to platinum, which was not unreasonably broad, was found on the Harker line Ov1/2 indicated that the structure was centrosymmetric. These data, plus the statistical results led to the selection of the centrosymmetric space group $C_{2/c}$ for all subsequent calculations.

A Fourier synthesis phased by the platinum atom led to the location of the two unique iodide ions. Successive Fourier synthesis revealed the positions of the remaining non-hydrogen atoms. Block-diagonal least-squares refinement of scale factor, positional parameters and isotropic temperature factors for all atoms, led to convergence at an

R factor of .168. A difference Fourier synthesis was calculated, and was featureless except for indicating anisotropic motion of the platinum and iodide ions. The platinum atom was assigned anisotropic temperature factors, and two cycles of block-diagonal least-squares refinement of scale factor, positional parameters and temperature factors for all atoms decreased the R factor to .145. An additional two cycles of block-diagonal least-squares refinement of scale factor, positional parameters and temperature factors for all atoms, in which the iodide ions were also assigned anisotropic temperature factors, converged to an R factor of .129. Allowing all of the atoms to vibrate anisotropically reduced the R factor to .126. However this decrease is not significant according to the statistical methods of Hamilton.[21]

Scattering factors for Pt(II) and I^- were taken from Cromer and Weber.[22] Scattering factors for neutral C, N, O were taken from The International Tables for X-Ray Crystallography.[23]

The final positional and thermal parameters are given in Tables 3 and 4 respectively. A complete list of the final observed and calculated structure factors is given in Table 5.

Table 3[a]

Final Positional Parameters for Diiodoethylenedimorpholineplatinum(II)

Atom	x	y	z
Pt	1353(1)	988(1)	9956(1)
I1	2196(2)	464(3)	4151(2)
I2	621(2)	1678(3)	8577(2)
N1	1930(19)	442(33)	1088(21)
N2	671(23)	2085(38)	626(24)
O1	3040(21)	1204(37)	7025(23)
O2	5308(23)	9248(40)	4188(25)
C1	2791(31)	559(53)	1112(33)
C2	1788(29)	5126(51)	3075(32)
C3	2707(29)	3607(49)	2955(31)
C4	3207(26)	4073(46)	3738(28)
C5	3360(28)	6257(47)	3299(30)
C6	4200(32)	6549(56)	3533(35)
C7	4068(26)	8447(45)	4354(28)
C8	4569(31)	9363(53)	3940(33)
C9	5506(51)	7899(89)	4015(56)
C10	5153(24)	7056(40)	4621(25)

[a]All values are x 10^4. Standard errors are given in parenthesis.

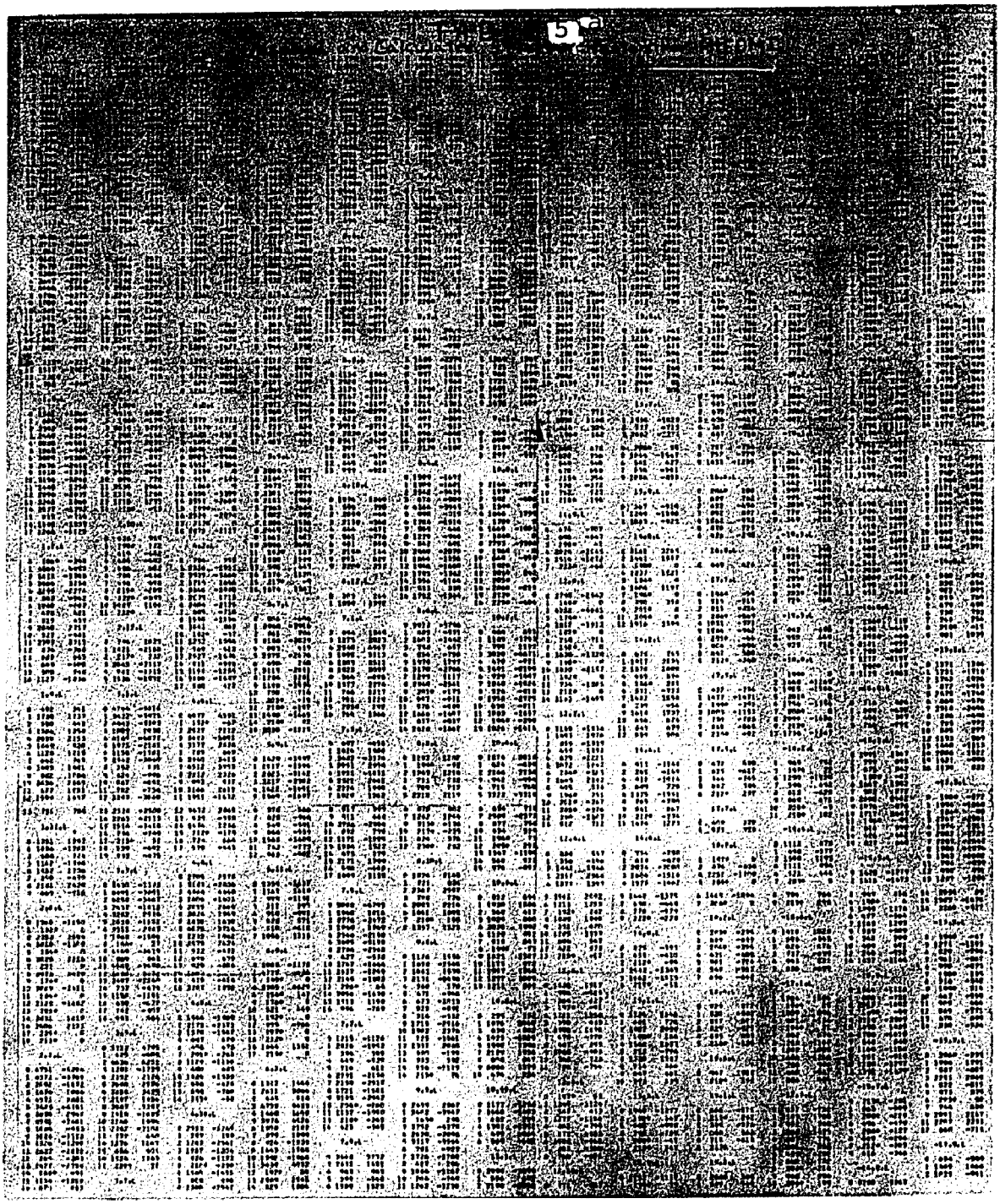
Table 4[a,b]

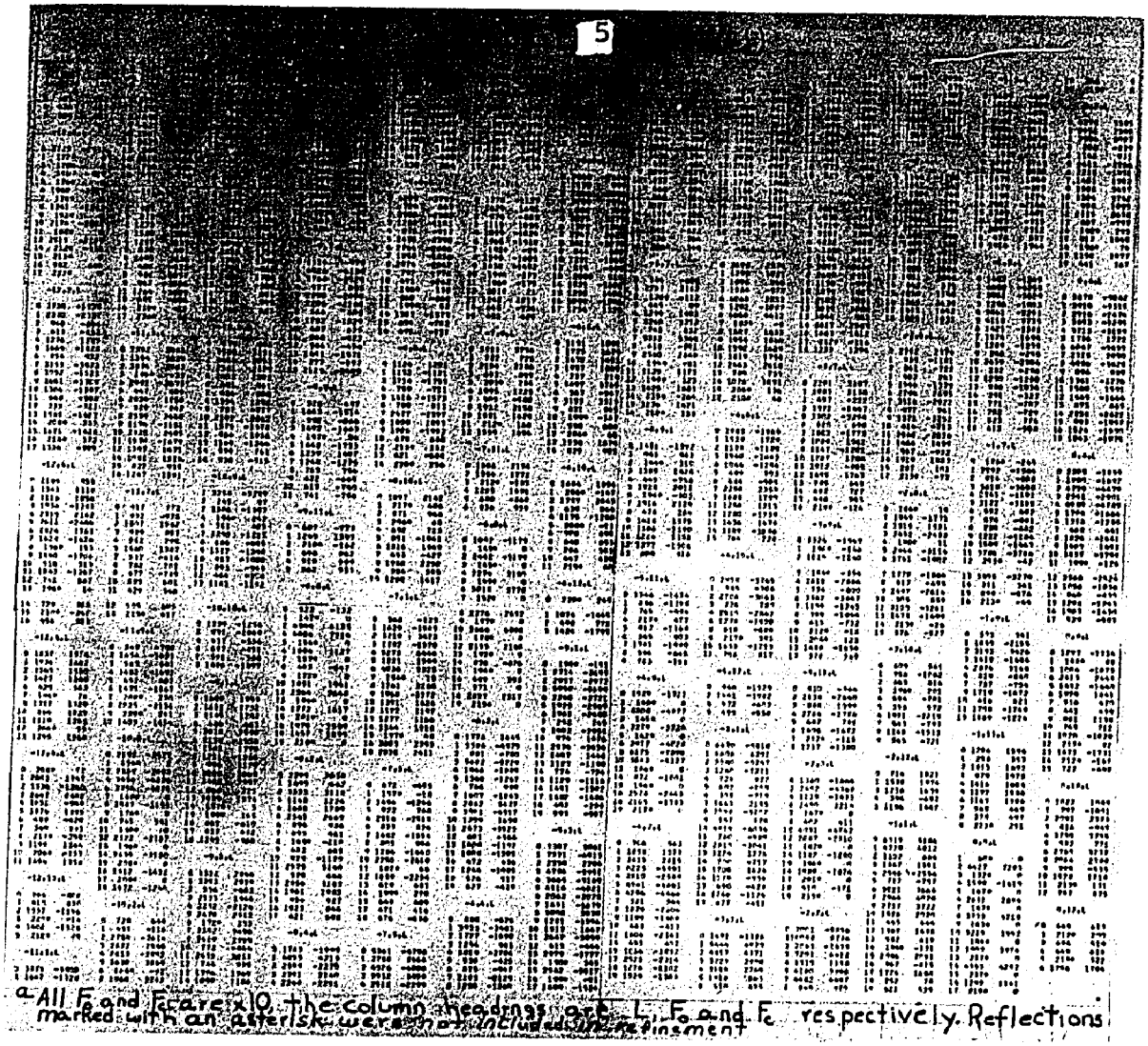
Final Thermal Parameters for Diiodoethylenedimorpholineplatinum(II)

Atom	U_{11}(U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	504(10)	180(7)	324(8)	-68(7)	57(7)	0(7)
I1	688(21)	376(16)	399(17)	44(15)	134(15)	88(14)
I2	695(23)	445(19)	451(19)	-86(17)	4(17)	85(16)
N1	312(79)					
N2	383(96)					
O1	540(98)					
O2	642(112)					
C1	469(135)					
C2	468(125)					
C3	455(123)					
C4	387(104)					
C5	412(117)					
C6	549(143)					
C7	418(108)					
C8	514(138)					
C9	303(94)					
C10	1090(281)					

[a] All values are x 10^4. The standard errors are given in parenthesis.

[b] The form of the temperature factor expression is: $\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*\cos\gamma^* + 2U_{13}hla^*c^*\cos\beta^* + 2U_{23}klb^*c^*\cos\alpha^*)$; or, if isotropic, $\exp(-2\pi U(2\sin\theta_{hkl})^2/\lambda)$.





[a] All F_o and F_c are x10. The column headings are L, F_o and F_c respectively. Reflections marked with an asterisk were not included in the refinement

D. Description of the Structure

The structure consists of discrete monomeric units of diiodoethylenedimorpholineplatinum(II). The molecular geometry and atom numbering scheme is given in Figure V and a list of bond lengths and angles is given in Table 6. The platinum atom is four coordinate, the coordination sphere being composed of the two ethylenedimorpholine nitrogens and the two iodide ions, arranged in a slightly distorted square planar fashion. The equation of the least-squares plane defined by the platinum, nitrogen and iodide ions is given in Table 7 along with the standard deviations of the atoms from the plane. The Pt-N1 and Pt-N2 bond lengths of 2.12(3) and 2.08(4) Å, respectively, are normal.[24-28] The Pt-I1 and Pt-I2 bond lengths of 2.614(4) and 2.615(4) Å, respectively, are also reasonable.[29] The N1PtN2 angle of 85.3(1.4)° is in the range normally found for chelated ethylenediamine type ligands.[30] The I1PtI2 angle of 87.74 (12)° is smaller than the normal value of 90° expected for LPtL' angle in a regular square planar geometry. This deviation is caused by the steric effects of the ethylene-dimorpholine ligand. Decreasing the I1PtI2 angle increases the distance, and thus decreases the interaction, between the iodides and the morpholine rings.

Figure V

The Molecular Geometry of $PtEDMI_2$

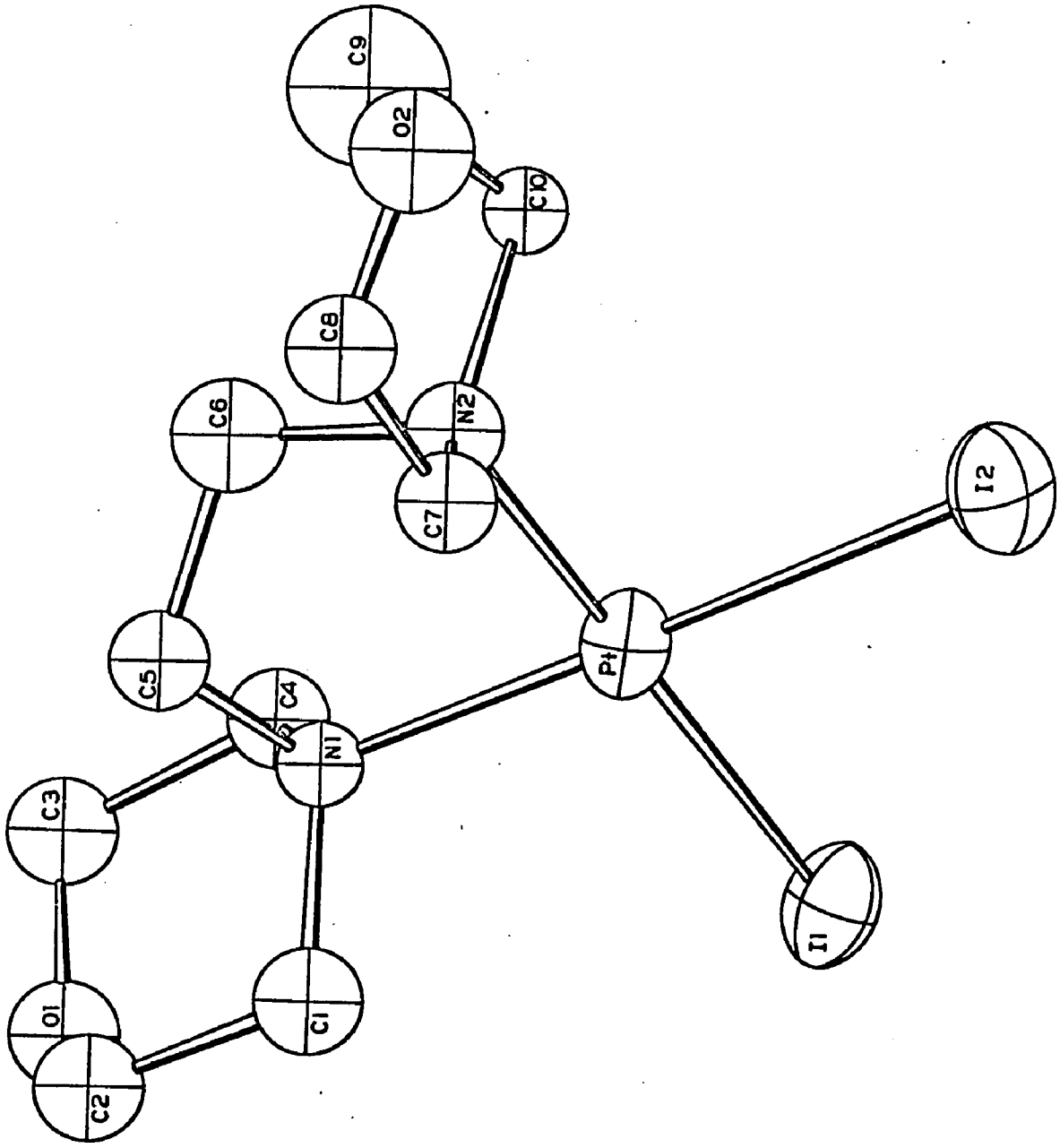


Table 6

Intramolecular Bond Lengths and Angles
For Diiodoethylenedimorpholineplatinum(II)

Bond Lengths:

Bond	Length (Å)	Bond	Length (Å)
Pt-N1	2.12(3)	O1-C2	1.46(7)
Pt-N2	2.08(4)	O1-C3	1.33(6)
Pt-I1	2.614(4)	O2-C8	1.32(7)
Pt-I2	2.615(4)	O2-C9	1.50(10)
N1-C1	1.51(6)	C1-C2	1.54(7)
N1-C4	1.50(6)	C3-C4	1.57(7)
N1-C5	1.47(6)	C5-C6	1.51(7)
N2-C7	1.51(6)	C7-C8	1.52(8)
N2-C6	1.50(7)	C9-C10	1.53(11)
N2-C10	1.46(6)		

Bond Angles:

Angle	Value (°)	Angle	Value (°)
N1PtN2	85.3(1.4)	O1C3C4	113.3(4.3)
I1PtI2	87.7(1)	C3C4N1	111.9(3.7)
N2PtI1	177.6(1.1)	N1C5C6	110.5(4.0)
N1PtI2	178.9(1.2)	C5C6N2	110.8(4.6)
N1PtI1	93.3(1.0)	C7N2C10	108.2(3.5)
N2PtI2	93.6(1.0)	N2C10C9	105.6(4.5)
C1N1C4	104.9(3.5)	C9O2C8	105.7(4.9)
N1C1C2	111.9(4.3)	O2C8C7	113.3(4.6)
C1C2O1	107.8(4.0)	C8C7N2	115.0(4.2)
C2O1C3	111.0(4.0)	C10C9O2	107.6(6.5)

The average C-C, C-N and C-O bond lengths of 1.53(8), 1.49(6) and 1.40(7) Å, respectively, are all normal.[31] The rings have a normal chair configuration. The ethylene bridge is axial to the rings. The most stable conformer of ethylenedimorpholine, however, is the one in which the ethylene bridge is equatorial to the rings. In a square planar complex, in which ethylenedimorpholine behaves as a bidentate chelate, the steric interactions between the morpholine rings and the two ligands which complete the square plane are minimized if the ethylene bridge is axial to the rings. Thus the presence of the less stable isomer in the present complex is not surprising.

A list of selected intramolecular distances is given in Table 8. The Pt-O1 and Pt-O2 distances of 4.91(4) and 4.81(5) Å respectively show that there is no interaction between the platinum atom and the morpholine oxygen atoms. There is a good deal of steric strain in the molecule, as evidenced by the short I1-C1, I1-C4, I2-C7 and I2-C10 distances of 3.51(6), 3.68(5), 3.47(5) and 3.90(5) Å, respectively. These distances are on the average .5 Å shorter than the sum of the Van der Waals radii.[32] There are no significantly short intermolecular interactions. The unit cell is shown projected on the 010 plane in Figure VI.

Figure VI

The Unit Cell Packing in $PtEdMI_2$ Projected on the 010 Plane

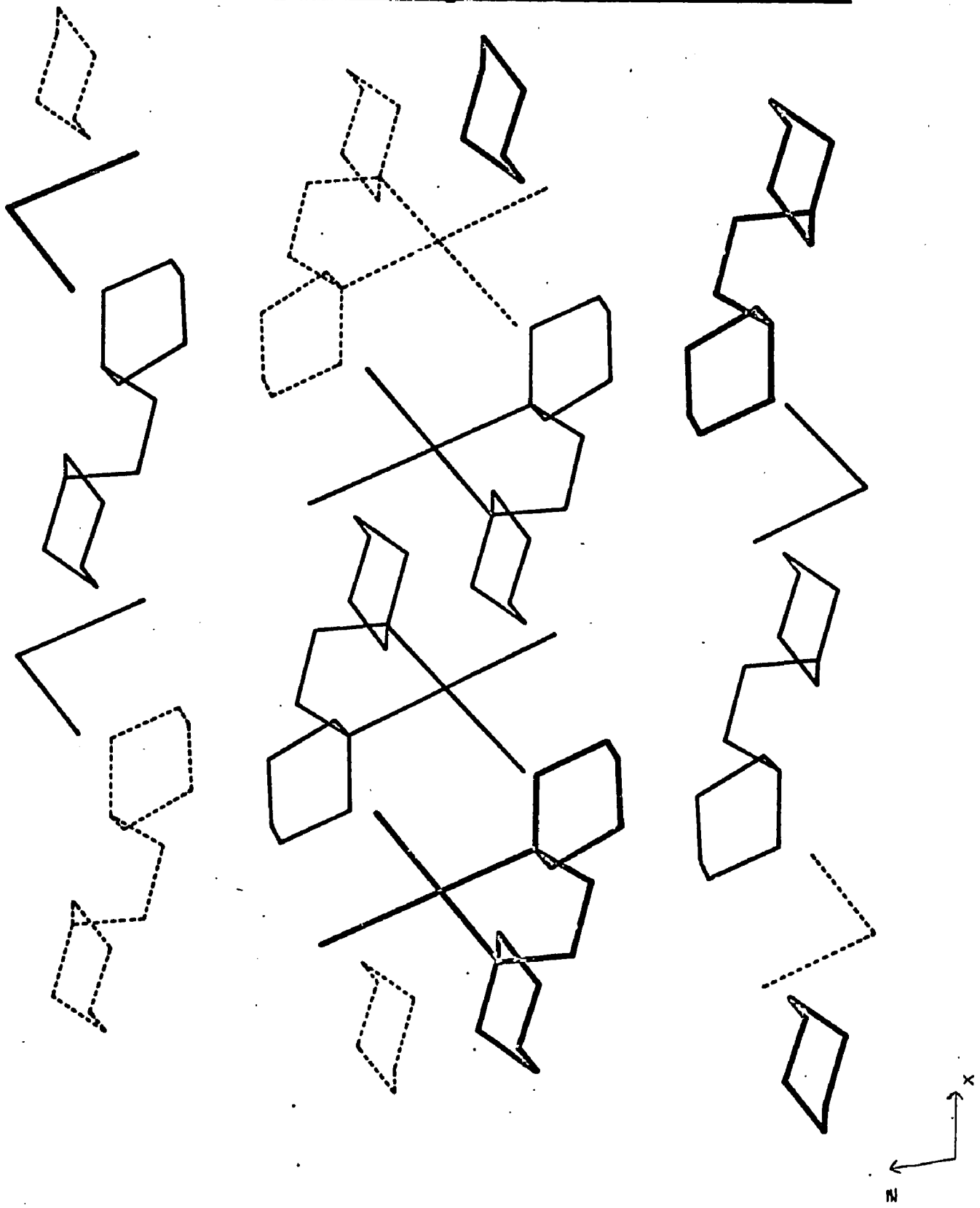


Table 7

The Least-Squares Plane Defined by Platinum, Nitrogen and Iodide and Deviations from the Plane

The equation of the plane in direct space: $11.46x + 8.01y + (-2.03)z = .30$

Atom	Deviation (Å)
Pt	.017
N1	.014
N2	-.023
I1	-.018
I2	.011

E. Discussion

As mentioned in chapter 3, paramagnetism could be consistent with either a square planar or tetrahedral complex. Since the results of the crystallographic investigation have shown that diiodoethylenedimorpholineplatinum(II) is square planar, a discussion of the unusual magnetic properties of the complex with respect to this stereochemistry is in order.

Table 8

Intramolecular Distances for
Diiodoethylenedimorpholineplatinum(II)

Atom 1	Atom 2	Distance (Å)
N1	N2	2.84(6)
I1	I2	3.62(1)
I1	C1	3.51(6)
I1	C4	3.68(5)
I1	C2	4.79(6)
I1	C3	4.94(6)
I2	C7	3.47(5)
I2	C10	3.90(5)
I2	C9	4.88(1)
O1	Pt	4.91(4)
O2	Pt	4.81(5)

There have been many attempts to calculate the relative separation and ordering of the d orbitals of platinum(II) in a ligand field or D_{4h} symmetry, i.e., the compound studied in many cases was potassium tetrachloroplatinate.[33-38] The calculations resulted in the ordering $d_z2 < d_{xz}, d_{yz}$ ($d_{xz}, d_{yz} < d_z2$) $< d_{xy} < d_{x^2-y^2}$. The parenthesis are being used

to indicate that both orders have been suggested. The most recent calculations have all placed the d_z2 orbital lowest in energy. However, Bausch and Grey[35] have pointed out that this may not be universally true for square planar complexes. They have suggested that the relative order of the d_z2 and d_{xz},d_{yz} orbitals are functions of the σ-donor and π-donor/acceptor properties of the ligands. With poor σ-donors and good π-donors, the d_z2 orbital lies lowest, while with good σ donors and good π-acceptors, the d_{xz},d_{yz} set lies lowest. These calculations using D_{4h} symmetry are applicable to the present case, since lowering the symmetry will affect the symmetry properties of the orbitals, and remove the degeneracy of the d_{xz},d_{yz} set but will not change the nature of the problem. The correlation diagram for a d^8 ion in a ligand field of C_{2v} symmetry is given in Figure VII. The figure was drawn assuming an ordering of $d_{xz} < d_{xy} < d_z2 < d_{xy} < d_x2-y2$ for the d orbitals. Due to the uncertainty of the ordering of the three lowest energy orbitals, and the a priori method used in drawing the figure, the order of the high energy terms is uncertain and should not be taken as absolute.

The most apparent and important feature of this diagram is the change in ground term from $^3A_2$ to a $^1A_1$ as the strength of the ligand field increases. Thus the magnetic properties

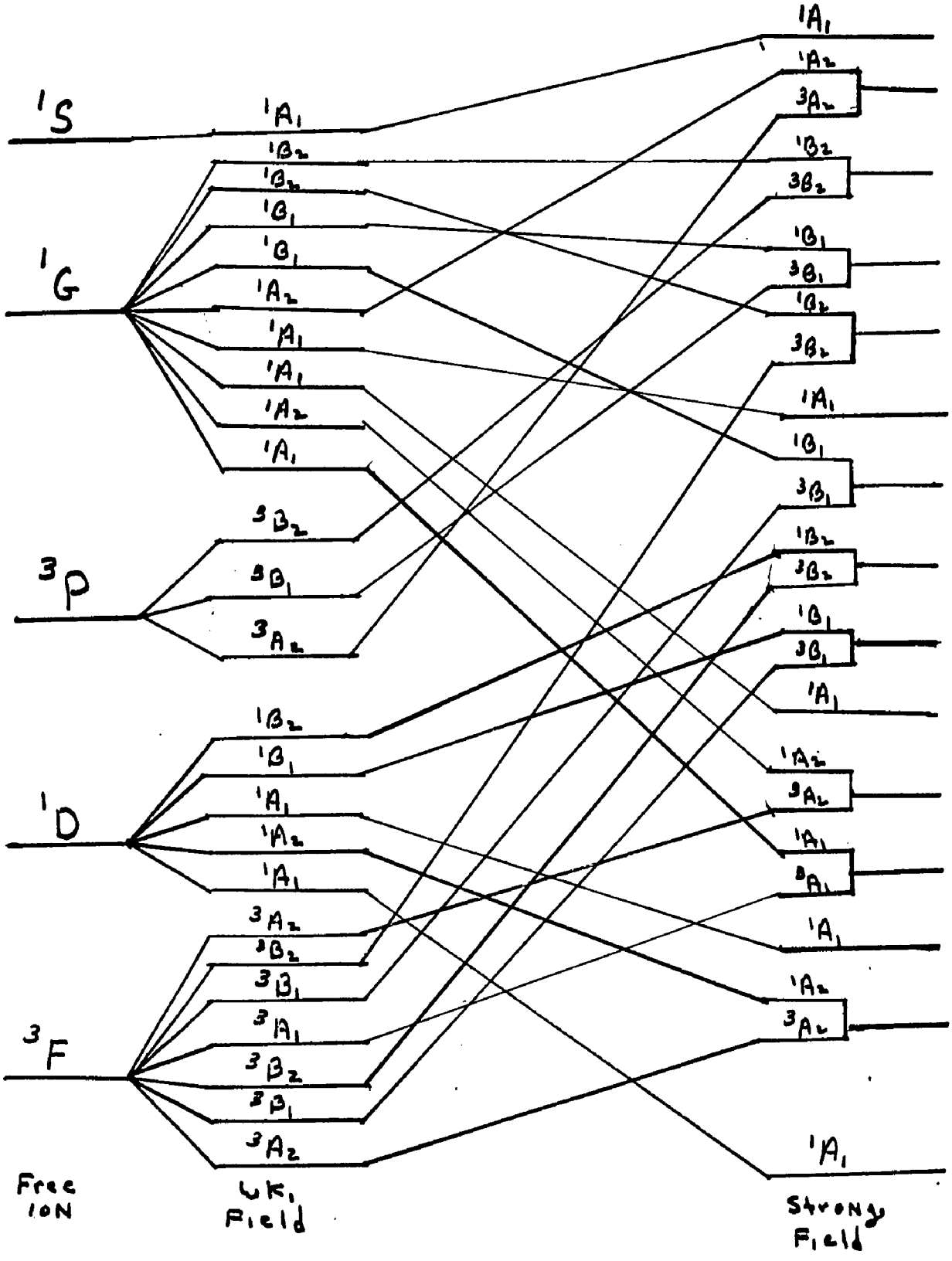
(i.e., diamagnetic or paramagnetic) of a d^8 ion in a square planar ligand field, could be simply a function of the strength of the ligand field. This result has been discussed in detail for nickel(II) by Ballhausen and Liehr[39] and Maki.[40]

Recently Graddon and Mockler have prepared complexes of nickel(II) using o-hydroxycarbonyl compounds as ligands.[41,42] Characterization of the anhydrous bis complexes has shown them to be monomeric, square planar and paramagnetic. Graddon and Mockler have suggested that the paramagnetism is a result of the weak ligand field produced by the four oxygen donor atoms. This result is in accord with the theoretical predictions described in the preceding paragraph.

The paramagnetism of diiodoethylenedimorpholineplatinum(II) must also be due to an in plane ligand field which is not strong enough to force spin pairing. Iodide is a weak ligand, as evidenced by its position in the spectrochemical series.[43] Morpholine is a moderately weak base, having $k_b = 2.44 \times 10^{-6}$.[44] When coupled to form ethylenedimorpholine, the base strength may be expected to increase somewhat due to the fact that it is now a tertiary nitrogen, and etnylenedimorpholine may be expected to be a moderately good ligand. The overall ligand field, however, will be subject to the steric effects within the complex.[45-48] The unfavorable configuration of ethylenedimorpholine and the short C-I contact dis-

Figure VII

Correlation Diagram for a d^8 Ion
In a Ligand Field of C_{2v} Symmetry



tances indicate that there is a good deal of strain in the complex and thus the overall ligand field will be less than that expected by considering the ligands themselves. Thus the suggestion that the in-plane ligand field is not strong enough for the compound to be diamagnetic is reasonable. The magnetic moment of the iodo derivative is smaller than the spin only value expected for two unpaired electrons. This plus the decrease of μ_{eff} with decreasing temperature indicates population of both singlet and triplet states within the complex, with the singlet being the ground state. The separation between singlet and triplet must be on the order of 200 cm^{-1}. In other words, the in-plane ligand field is only slightly stronger then the minimum value required to cause the $^1A_1$ term to become the ground term.

The paramagnetism of the bromo derivative is not as easily explained. As mentioned in Chapter 3, it is probably a monomer. However, since it is not isomorphous with the iodo derivative, the details of the structure are unknown. It is probably safe to say that it is square planar. However, whether the paramagnetism is due to a weak in-plane ligand field or whether there are axial ligands which raise the energy of the d_z2 orbital enough to cause spin unpairing, is unknown. One of these mechanisms, rather than a tetrahedral geometry, probably causes the paramagnetic ground state.

CHAPTER 5

PALLADIUM COMPLEXES

A. Results

A.1. 2,2',6,6'-tetramethylethylenedimorpholine Complexes

While the reaction of palladium chloride or potassium tetrabromopalladate with 2,2',6,6'-tetramethylethylenedimorpholine yields the complexes $PdTMEDMX_2$ (where $X = Cl^-$ or Br^-), the reaction of potassium tetraiodopalladate with 2,2',6,6'-tetramethylethylenedimorpholine in acetone at both room and reflux temperature does not yield any isolatable product. The complexes are crystalline and have very similar powder patterns. They might be isomorphous as evidenced by their d values, which are given in Tables 9 and 10. Their infrared spectra show no shift in the C-O-C stretching bands and therefore the etheral oxygens are uncoordinated.

The chloro derivative is a yellow powder. It is slightly soluble in acetone, in which it is a nonelectrolyte. It is paramagnetic, having a magnetic moment equal to 3.02 $\pm$ .2 B.M. The spectrum of the complex in acetone, between 16000 and 3300 Å consists of one absorption band centered at 25,200 (374) cm^{-1}. The molar extinction coefficient is given in parentheses. The band is slightly asymmetric to higher energy and may well be composed of more than one absorption band.

Table 9

d Values for Dichloro2,2',6,6'-tetramethyl-ethylenedimorpholinepalladium(II)

I	d
100	11.57
50	6.19
90(b)	4.69
10	4.18
30(b)	3.90
60	3.58
5	3.04
15	2.79
25	2.56
5	2.48
2	2.37
2	2.29
30	2.17
10	2.02
10	1.93
10	1.85

Table 10

d Values for Dibromo2,2',6,6'-tetramethyl-ethylenedimorpholinepalladium(II)

I	d
100	11.22
50	6.28
70	5.03
70	4.72
30	4.07
60	3.92
50	3.61
10	3.11
40	2.87
80	2.54
40	2.38
60	2.15
15	2.05
10	2.02
15	1.95
30	1.89

The bromo derivative is an orange powder. It is soluble in acetone, in which it is a nonelectrolyte. It is paramagnetic, having a magnetic moment equal to 1.86 ± .2 B.M. at 297°K. The magnetic moment decreases with temperature having values of 1.42 ± .2 and 0.88 ± .2 B.M. at 195 and 77°K respectively. The compound also undergoes a reversible color change, from orange at 297°K to yellow at 77°K. The spectrum of the complex in acetone, between 16000 and 3300 Å consists of three absorption bands, the one at low energy is a shoulder on the intermediate band, which is a shoulder on the high energy band. The bands are centered at 20,855 (131), 22,050(394) and 24,650(589) cm^{-1} respectively. The molar extinction coefficients are given in parentheses.

A.2. Ethylenedimorpholine Complexes

All of the attempts to isolate the paramagnetic cation $(PdEDM_2)^{2+}$ in the solid state using silver nitrate, sodium tetrafluoroboron, aluminumtrichloride or a perchlorate anion exchange column, resulted in the isolation of eitner starting material, an unpurifiable solid or an oil.

The reaction of bisethylenedimorpholinepalladium(II) iodide with 1,10-phenanthroline in an acetone/dimethoxypropane solution, yielded the compound 1,10-phenanthroline-ethylenedimorpholinepalladium(II) iodide ($(Pd(EDM)(phen))I_2$). The complex is an orange crystalline powder. It is soluble in

acetone, in which it is a 2:1 electrolyte. The infrared spectrum of the compound shows no shift in the C-O-C stretching frequencies, indicating a lack of coordination of the etheral oxygens. The compound is diamagnetic. The spectrum of the compound, consists of one absorption band centered at 20,292(167) cm^{-1}, before the onset of charge transter bands. The molar extinction coefficient is given in parentheses.

B. Discussion

B.1. 2,2',6,6'-tetramethylethylenedimorpholine Complexes

The ligand ethylenedimorpholine has been shown capable of forcing tetrahedral coordination geometry. However, structural studies of the ethylenedimorpholine complexes ethylenedimorpholinecopper(II) nitrite and diiodoethylenedimorpholineplatinum(II), have indicated that either octahedral, which requires four coplanar ligands, or square planar coordination is possible when the ethylene-dimorpholine ligand is in the diaxial bridged configuration. The ligand 2,2',6,6'-tetramethylethylenedimorpholine was synthesized in order to prevent this type of structural isomerism from alleviating the steric strain which is forcing towards a tetrahedral coordination geometry.

The parent 2,6-dimethylmorpholine exists as cis and trans isomers. Each of these isomers when present in the

ethylene bridged dimer tends to prevent square planar coordination. The trans isomer increases the steric effects by preventing the ethylene bridge from being axial to the rings, due to the steric hindrance between the bridging methylene group and the axial methyl group. In the cis isomer, the most stable configuration is the one in which both the methyl groups and the ethylene bridge are equatorial. In this isomer, the bridge is again prevented from being axial due to the steric interactions between the bridging methylene group and the axial methyl groups, and also between the methyl groups themselves.

When 2,6-dimethylmorpholine is coupled to yield the ethylene bridged dimer, three isomers, trans-trans, cis-trans and cis-cis, are possible. All however, as shown, are forcing towards a tetrahedral coordination geometry.

Although the chloro derivative was not soluble enough for a molecular weight determination in solution, its solubility and nonelectrolytic behavior suggest a four coordinate monomeric species. The paramagnetism of the complex does not rule out a square planar geometry, as shown previously. However, the steric requirements of 2,2',6,6'-tetramethylethylenedimorpholine make this possibility unlikely and a square planar coordination sphere with a considerable tetrahedral distortion seems more likely.

The magnetic moment of the complex does not deviate markedly from the spin only value of 2.83 B.M. expected for two unpaired electrons. This result is consistent with a distorted tetrahedral complex, with an orbitally nondegenerate ground state.

As in the case of the chloro derivative, the solubility and nonelectrolytic behavior of the bromo derivative suggests a four coordinate monomeric species. The paramagnetism of the complex and the previously mentioned steric requirements of 2,2',6,6'-tetramethylethylenedimorpholine, make a square planar structure with a significant tetrahedral distortion most likely. The magnetic moment of the complex is below the value of 2.83 B.M. expected for two unpaired electrons, and decreases with decreasing temperature. This combined with the reversible color change from orange to yellow which the complex undergoes on decreasing the temperature, suggests population of both singlet and triplet states within the complex. The separation between singlet and triplet must be on the order of 200 cm^{-1}. Due to the decrease in the magnetic moment with decreasing temperature, it is reasonable to assign the ground term as a spin-singlet.

The visible and U.V. spectrum of the bromo derivative is much more complex then the corresponding spectrum of the chloro derivative. The extinction coefficients of the bands in both spectra are too small for charge transfer transitions, and the bands are most likely ligand field in

origin. The spectrum of the bromo derivative is shifted to lower energy. This shiftis inthe direction expected, by considering the position of bromide with respect to chloride in the spectrochemical series. The increased complexity ot the spectrum of the bromo derivative probably reflects the presence of both types of complexes (i.e., low spin and high spin) in solution.

The failure to synthesize the corresponding iodo derivative, is most likely due to the steric effects of 2,2',6,6'-tetramethylethylenedimorpholine. The steric hindrance in complexes of the type $PdTMEDMX_2$ (where $X = Cl^-$, Br^- or I^-) would be expected to increase as the anions changed from chloride to iodide. The iodide complex would be the least stable, and therefore, the fact that it could not be synthesized is not surprising.

2,2',6,6'-Tetramethylethylenedimorpholine apparently is capable ot forcing palladium(II) into a distorted tetrahedral coordination geometry. However, due to the demonstrated tendency of palladium(II) to maintain a square planar coordination geometry a crystallographic investigation is needed to verify the tetranedral nature of the coordination sphere.

B.2. Ethylenedimorpholine Complexes

As described in Chapter 1, the paramagnetic palladium complex bis(ethylenedimorpholine)palladium(II) iodide

($(PdEDM_2)I_2$) is formed when excess ethylenedimorpholine is added to an acetone solution of diiodoethylenedimorpholinepalladium(II). In attempting to isolate this complex from solution, Lott[49] found that the products isolated from solution are ethylenedimorpholine and diiodoethylenedimorpholinepalladium(II). If the iodide anions in bis(ethylenedimorpholine)palladium(II) iodide are replaced by noncoordinating anions, this reversion should be prevented, and isolation of the paramagnetic species should be possible. However, all attempts to isolate the cation from solution by these methods failed.

Attempts at isolating the cation bis(ethylenedimorpholine)palladium(II) from solution were halted, and an alternate route to paramagnetic tetrahedral complexes of palladium(II) using ethylenedimorpholine was sought. It was felt that the substitution of another sterically hindered chelating ligand for one of the ethylenedimorpholine moieties in the bis complex would yield a complex which was isolatable and tetrahedral. The ligand chosen for this study was 1,10-phenanthroline.

The diamagnetism of the complex 1,10-phenanthroline(ethylenedimorpholine)palladium(II) iodide suggests a regular square planar coordination sphere around the palladium. In other bis chelate complexes of palladium(II), the ligands are deformed in order to allow square planar coordi-

nation. While the actual deformations present in the complex are not known, they may be estimated by analogy to the types of deformations found in other complexes of the two chelates. As mentioned earlier, ethylenedimorpholine can assume a diaxial bridged conformation in order to reduce the steric strain present in a square planar complex, while 1,10-phenanthroline can bend around its 2-fold axis in order to alleviate steric interactions. It is probably a combination of these two effects which allowssquare planar coordination in the present mixed chelate.

APPENDIX I

THE CRYSTAL AND MOLECULAR STRUCTURE OF ETHYLENEDIMORPHOLINECOPPER(II) NITRITE

A. Introduction

Recently, mixed ethylenedimorpholine nitrite complexes, having a general formula MEDM$(NO_2)_2$ (M = Co(II), Ni(II) and Cu(II)) have been reported.[50] Whereas the infrared spectra of the cobalt and nickel complexes indicated that the nitrite groups were bound by oxygen chelation, the spectrum of the copper complex indicated a different mode of coordination.

A determination of the crystal structure of the copper complex was undertaken in order to identify the mode of coordination and the geometry of the complex.

B. Experimental

The preparation of this compound has been described previously.[50] Preliminary Weissenberg and precession data indicated that the blue-green crystals were monoclinic and showed systematic extinctions: h+k = 2n+1 for all hkℓ and ℓ = 2n+1 for hOℓ, indicating either space group $C_{2/c}$ or C_c. The cell parameters determined from precession and Weissenberg data (λ = .7107) are a = 12.01(2), b = 7.29(2), c = 17.72(2) Å and β = 95.40(25)° (estimated standard errors in the least significant digit are given in parentheses).

The calculated density for four molecules per unit cell is 1.52 g/cc, which agrees well with the value 1.51 g/cc determined by floatation in a benzene carbon tetrachloride mixture.

A crystal .3 x .15 x .015 mm mounted along the b axis was used for intensity data collection. The data were collected using a Weissenberg geometry Supper-Pace Automated diffractometer, employing Mo radiation (λ = .7107 Å), a graphite single crystal monochromator and pulse height analysis with a scintillation counter. A stationary counter moving crystal technique was used. Background was counted for 10 seconds on each side of the peak, and a standard reflection monitored before each level of data were collected. Crystal decomposition was noticed after the fourth level and was corrected for by the use of multiple scale factors. All intensities were corrected for Lorenz and polarization effects. No absorption correction was applied (u_ℓ = 14.0 cm^{-1}). The final data set consisted of 888 non-zero structure amplitudes.

C. Determination of the Structure

The programs in the X-Ray 70 system were used for the computations and the program ORTEP was used in drawing the three-dimensional figure.[19,20] Initially the space group C_c was chosen. A three dimensional sharpened origin removed

Patterson function revealed the location of the copper atom. Successive Fourier synthesis led to the location of all non-hydrogen atoms except the two oxygens of one of the nitrite groups. Refinement of scale factors, positional parameters and isotropic temperature factors for all atoms by block-diagonal least-squares led to an R factor of .171. At this point a difference Fourier showed the positions of the remaining two oxygen atoms. Continued refinement of scale factors, positional parameters and isotropic temperature factors for all atoms by full-matrix least-squares led to convergence at an R factor of .146. A set of bond lengths was calculated and were either unreasonably long or short. Each long bond could be paired with a short bond. Within each pair, one member was related to the other by a 2-fold rotation about the C_2 axis in $C_{2/c}$. Therefore, refinement was continued in the centric space group.

The copper atom was placed on the special position 0, y, 1/4 of $C_{2/c}$ and a unique set of atoms was obtained from the set used in C_c. Full-matrix least-squares refinement of scale factors, positional parameters and isotropic temperature factors for all atoms converged to an R factor of .155. Anisotropic temperature factors were given to all atoms, and continued refinement converged to a final R factor of .136. The weighting scheme used was

that suggested by Hughes,[51] $w = 1$ if $F_o < A$, $w = A/F_o$ if $F_o > A$ and $A = F_{min}$.

Scattering factors for Cu(II), neutral N, C and O were used in all calculations.[22] The final positional parameters are given in Table 11 and thermal parameters in Table 12. A list of observed and calculated structure factors is given in Table 13.

D. Description of the Structure

The structure is shown in Figures VIII and IX. Selected bond lengths and angles are given in Table 14. The structure consists of discrete monomeric units of $CuEDM(NO_2)_2$. The copper atom is located on a C_2 axis as required by the space group symmetry. It is coordinated by the two ethylenedimorpholine nitrogens and four nitrite oxygens arranged in a distorted octahedral geometry. The atoms N1, N1', O1, and O1' are the most tightly bound atoms, although they are not strictly planar. The Cu-N1 bond length of 2.01 Å and the Cu-O1 bond length of 1.99 Å are normal.[52-54] Atoms O2 and O2' occupy badly distorted axial positions, above and below the approximate N1, N1', O1, O1' plane, the distortion corresponding to an elongation and bending of the axial bond from its normal position (i.e., Cu-O2 = 2.37(2) Å, O2CuO1 = 55.9(7)°).

Both the ethylenedimorpholine rings are in the chair configuration with the ethylene bridge axial to the rings.

The bond lengths and angles in both ethylenedimorpholine and the nitrite groups are normal within 2.5 σ.

The important non-bonded intramolecular distances are summarized in Table 15. The C2-O6 and C3-O6 distances of

Table 11[a]

Final Positional Parameters for $CuEDM(NO_2)_2$

Atom	X	Y	Z
Cu	0000	9792(3)	25000
N1	5112(12)	6769(26)	3287(8)
C1	6296(23)	8426(42)	4330(14)
C2	6294(16)	7060(42)	3673(12)
C3	4399(16)	6291(33)	3884(10)
C4	4735(16)	8486(24)	2877(9)
C5	4560(26)	7684(4)	4560(12)
O3	5644(22)	7760(36)	4872(9)
N2	6591(14)	2494(34)	3061(15)
O1	5590(12)	2857(23)	3231(8)
O2	6845(13)	3567(31)	2549(11)

[a]all values x 10^4

Table 12[a]

Final Thermal Parameters for $CuEDM(NO_2)_2$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	25(1)	15(5)	31(1)	0	-8(1)	0
N1	37(8)	62(12)	41(9)	-2(7)	0(6)	5(7)
C1	76(16)	80(20)	61(14)	2(14)	23(13)	-5(12)
C2	38(10)	99(20)	63(14)	-4(10)	5(9)	-14(13)
C3	51(11)	76(15)	38(10)	3(9)	-26(9)	1(9)
C4	64(12)	32(11)	32(9)	17(7)	-14(8)	-7(6)
C5	105(20)	78(20)	46(14)	10(18)	-13(13)	-12(12)
O3	147(19)	108(19)	49(9)	-3(14)	10(11)	-15(10)
N2	45(9)	82(17)	120(19)	26(9)	15(11)	-4(15)
O1	58(9)	62(11)	70(10)	4(7)	-9(8)	-20(8)
O2	62(10)	99(17)	95(13)	14(9)	-34(9)	5(12)

[a]all values x 10^3

3.25(3) and 3.15(3) Å, respectively, are slightly shorter than the sum of the Van der Waals radii. However, they are the only short interactions in the structure. The large Cu-O3 distance of 4.71(2) Å indicates that there is no interaction between copper and the morpholine oxygens.

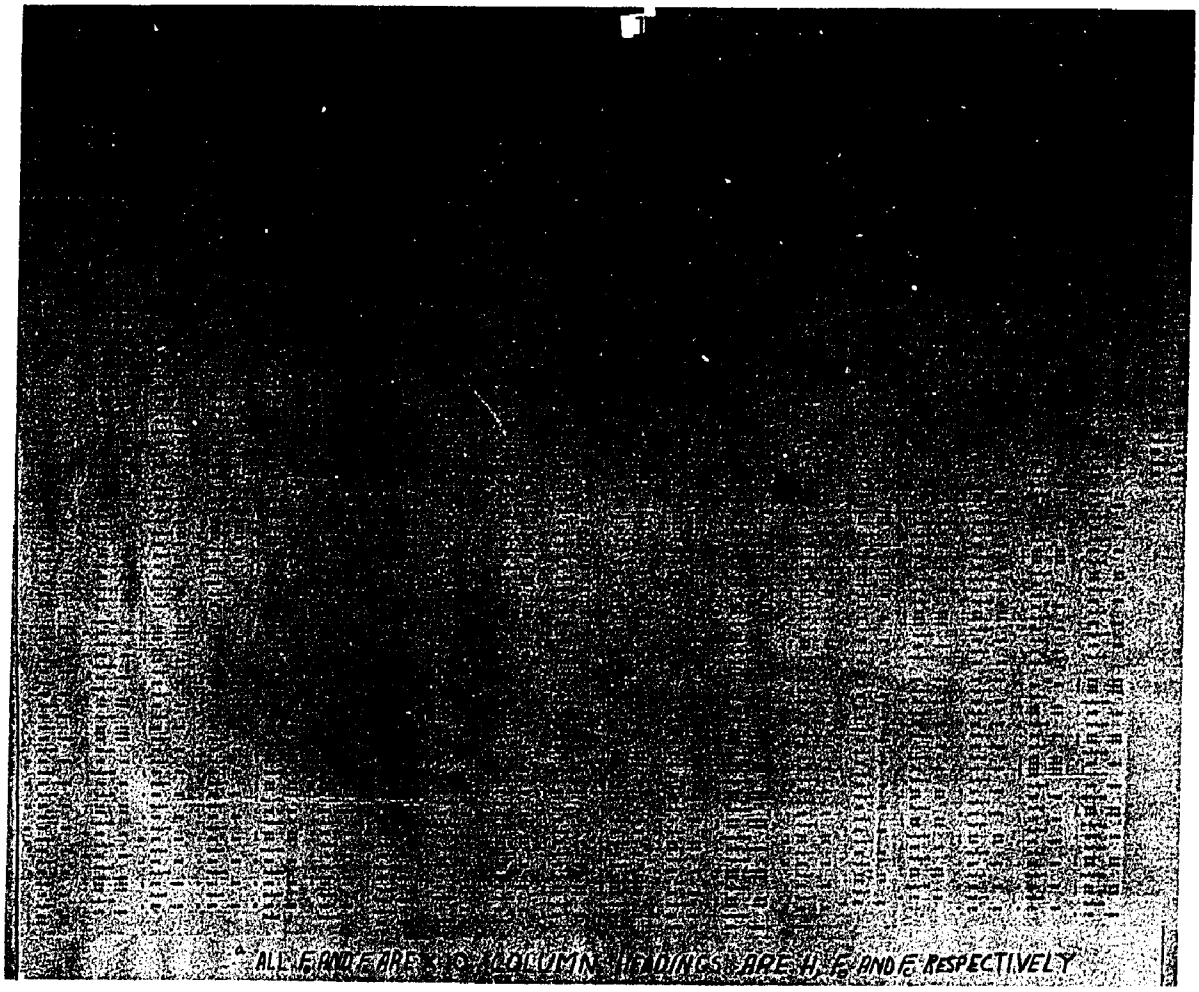

ALL F AND E ARE X-D. A-COLUMN HEADINGS ARE H, F AND E RESPECTIVELY

Table 14

Selected Intramolecular Bond Lengths
And Angles for $CuEDM(NO_2)_2$

Bond Lengths:

Cu-N1	2.01(2)	Å
Cu-O1	1.99(2)	
Cu-O2	2.37(2)	
N1-C2	1.52(3)	
N1-C3	1.46(3)	
N1-C4	1.47(3)	
O3-C1	1.38(4)	
O3-C5	1.36(4)	
C1-C2	1.52(4)	
C3-C5	1.56(3)	
C4-C4'	1.53(3)	
N2-O1	1.29(3)	
N2-O2	1.25(3)	

Bond Angles:

N1CuO1	93.9(7)°
N1CuO1'	163.0(6)
O1CuO1'	90.1(7)
N1CuN1'	86.9(7)
O2CuO1	55.9(7)
C2N1C3	106.8(1.6)
C1C2N1	110.8(2.0)
O3C1C2	109.7(2.5)
C5O3C1	108.1(2.3)
O3C5C3	112.2(2.5)
C5C3N1	110.3(1.9)
N1C4C4'	107.1(1.6)
O2N2O1	109.5(2.2)

With ethylenedimorpholine in the diaxial bridged configuration, coordination of the nitrite anions in a monodentate fashion through nitrogen is not sterically unfavorable. The chelating mode of coordination of the nitrite groups is attributable to the tendency of copper(II) to be six coordinate.[55] Goodgame and Hitchman also report chelating groups in nickel(II) complexes of the type $Ni(L)_n(NO_2)_2$ (where L is a neutral ligand and $n = 2$ if L is monodentate or 1 if L is bidentate).[56] The authors have ascribed the chelation to the tendency of nickel(II) to be six coordinate. As mentioned previously, chelating nitrite groups are also found in complexes of the type $MEDM(NO_2)_2$ (M = Ni(II) or Co(II)), in which, again, the central atom has attained a coordination number of six. Thus, it would appear that the tendency of the metal atom to saturate its coordination sphere is one of the important factors in determining the mode of coordination by the nitrite group in transition metal complexes.

Table 15

Non-Bonded Intramolecular Distances

Cu-O3	4.71(2) Å
Cu-C2	2.97(2)
Cu-C3	2.83(2)
Cu-C4	2.79(2)
N1-N1'	2.77(2)
C2-O2	3.33(3)
C2-O1	3.25(3)
C2-N2	3.52(4)
C3-O2	4.40(3)
C3-O1	3.15(3)
C3-N2	4.16(4)

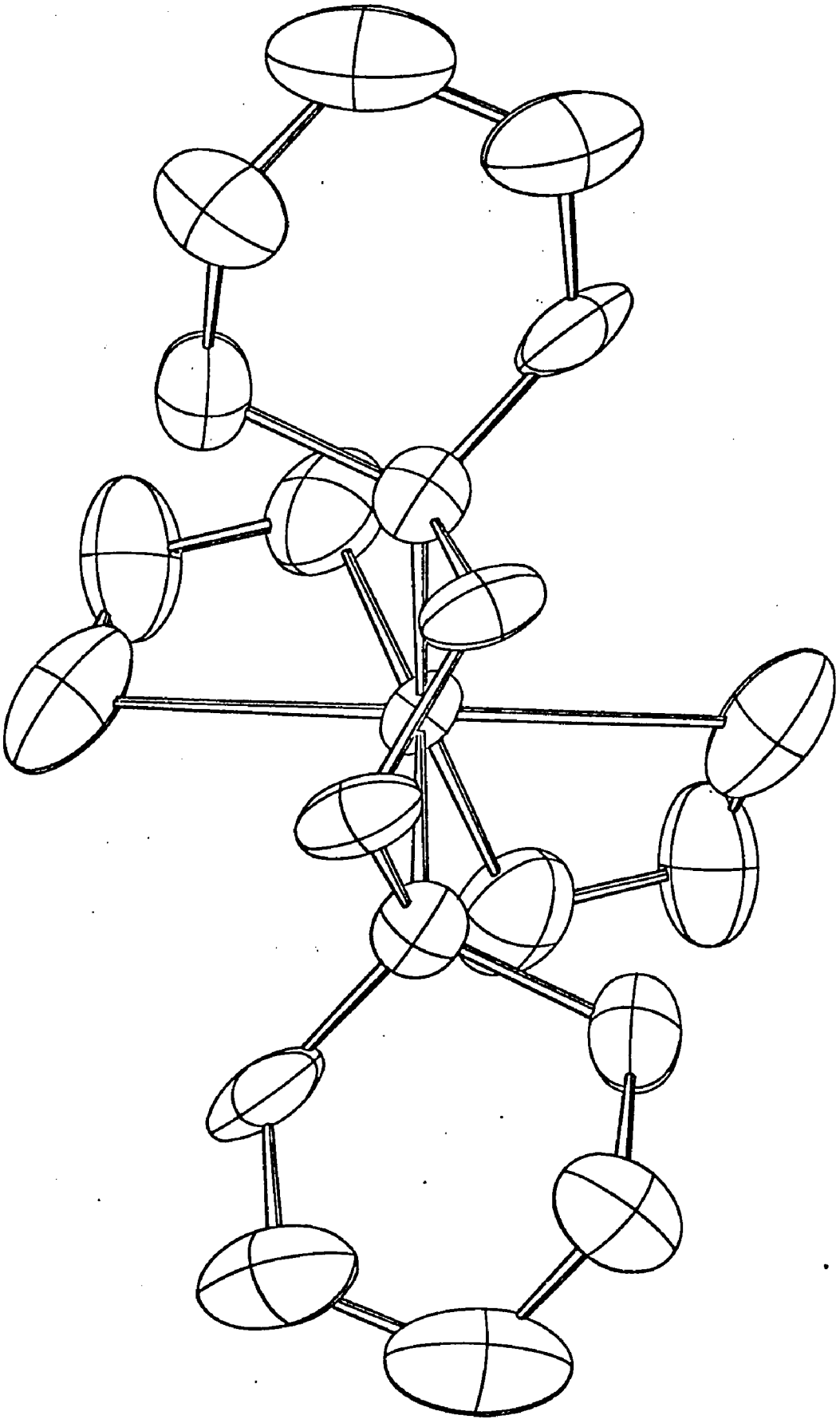


Figure VIII

Molecular Geometry of $CuEDM(NO_2)_2$

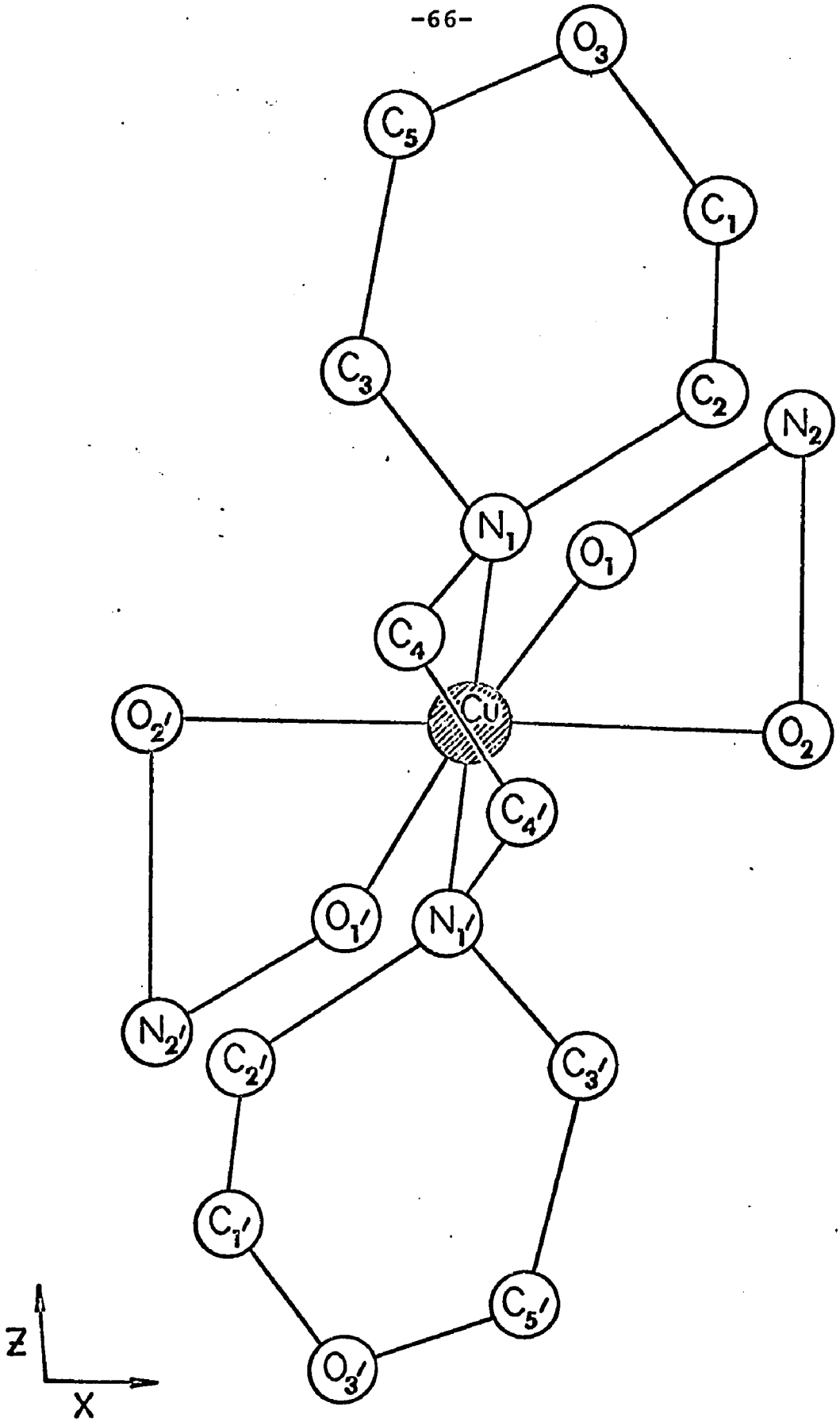


Figure IX

Molecular Geometry of $CuEDM(NO_2)_2$
Projected on the O1O Plane

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