



Structure and bonding of transition metal complexes  
by Donald Leslie Ward

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry  
Montana State University  
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Abstract:

The crystal and molecular structures of two transition metal complexes were solved by the X-ray diffraction method; a comparison of the first structure with an independent, duplicate determination of the structure has yielded information about the precision of the X-ray method and a study of the second structure has yielded information about the relationship between the geometry of the molecule in the crystal and the geometry when free of the intermolecular forces in the crystal.

Ethylenebisbiguanidenickel(II) chloride monohydrate crystallizes in space group P21/c with  $a = 6.905(5)\text{Å}$ ,  $b = 11.680(4)\text{Å}$ ,  $c = 18.038(22)\text{Å}$ ,  $\beta = 101.41(10)^\circ$ , and  $Z = 4$ . The nickel(II) ion is in square-planar configuration and the complex ion is essentially planar except for the ethylene bridge. Extensive hydrogen bonding, involving the water of hydration and the two chloride ions, joins the complex ions into infinite sheets parallel to the (100) plane with additional hydrogen bonds acting between the sheets. The final R is 3.1% for 1714 observed intensities.

The comparison of the atomic parameters and standard deviations of the two independent determinations of the structure has indicated general good agreement between the two determinations. However, the comparison also indicates that there are significant differences between certain classes of parameters and that the estimated standard deviations of the two determinations have been underestimated, on the average, by a factor of about 1.7,

Dicarbonylnitrosyltriphenylphosphinecobalt(0) crystallizes in space group P1 with  $a = 11.055(2)\text{Å}$ ,  $b = 11.024(4)\text{Å}$ ,  $c = 10.260(2)\text{Å}$ ,  $\alpha = 121.07(2)^\circ$ ,  $\beta = 101.01(2)^\circ$ ,  $\gamma = 105.14(2)^\circ$ , and  $Z = 2$ . The cobalt and phosphorus atoms are in approximately tetrahedral configurations and the nitrosyl and carbonyl groups are disordered. There is no indication of hydrogen bonding. The final R is 3.2% for 2006 observed intensities.

Non-bonded repulsion energies were calculated for the molecule with respect to rotation about the Co-P bond and about the three P-C (phenyl) bonds for the molecule in the crystal and for the free molecule. It was found that the configuration in the crystal minimizes the energy in the crystal but that the free molecule rotates approximately  $20^\circ$  about the Co-P bond to minimize the energy.

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## TABLE OF CONTENTS

	Page
LIST OF TABLES . . . . .	vi
LIST OF FIGURES . . . . .	viii
ABSTRACT . . . . .	ix
INTRODUCTION . . . . .	1
PART I	
Ethylenebisbiguanidenickel(II)chloride monohydrate	
INTRODUCTION . . . . .	3
I. The Crystal and Molecular Structure . . . . .	6
Preparation of the crystals . . . . .	6
Density determination . . . . .	6
Determination of space group and cell parameters . . . . .	7
Collection of the data . . . . .	7
Determination of the structure . . . . .	10
The structure . . . . .	11
Hydrogen bonding . . . . .	18
Bonding within the complex ion . . . . .	26
II. The Comparison of the Two Determinations . . . . .	28
Experimental differences . . . . .	28
Refinement differences . . . . .	28
Comparison of parameter differences . . . . .	29
The CHI-square test . . . . .	30
The half-normal probability plot analysis . . . . .	32
SUMMARY AND CONCLUSIONS . . . . .	40

## PART II

## Dicarbonylnitrosyltriphenylphosphinecobalt(0)

INTRODUCTION . . . . .	43
I. The Crystal and Molecular Structure . . . . .	45
Preparation of the crystals . . . . .	45
Density determination . . . . .	45
Determination of space group and cell parameters .	46
Collection of the data . . . . .	46
Determination of the structure . . . . .	48
The structure . . . . .	58
Bonding to the cobalt(0) atom . . . . .	62
II. The Study of the Angular Configuration . . . . .	69
Introduction . . . . .	69
The molecule in the crystal . . . . .	69
The free molecule . . . . .	71
SUMMARY AND CONCLUSIONS . . . . .	76
APPENDIX I. Normal Probability Plot Analysis . . . . .	79
APPENDIX II. Determining the External Geometry and	
Dimensions of a Single Crystal . . . . .	82
LITERATURE CITED . . . . .	87

## LIST OF TABLES

		Page
PART I		
Ethylenebisbiguanidenickel(II)chloride monohydrate		
TABLE 1	Crystal Data . . . . .	8
TABLE 2	Observed and Calculated Structure Factors . .	12
TABLE 3	Positional Parameters of Non-hydrogen Atoms .	14
TABLE 4	Thermal Parameters of Non-hydrogen Atoms . .	15
TABLE 5	Hydrogen Atom Parameters . . . . .	16
TABLE 6	Least-squares Planes . . . . .	17
TABLE 7	Bond Distances . . . . .	19
TABLE 8	Bond Angles . . . . .	20
TABLE 9	Hydrogen Bonding . . . . .	22
TABLE 10	CHI-square Test . . . . .	31
TABLE 11	$\delta_{p_i}$ for Nickel and Chlorine $\beta_{ij}$ 's . . . . .	34
PART II		
Dicarbonylnitrosyltriphenylphosphinecobalt(0)		
TABLE 12	Crystal Data . . . . .	47
TABLE 13	Observed and Calculated Structure Factors . .	51
TABLE 14	Positional Parameters of Non-hydrogen Atoms .	55
TABLE 15	Thermal Parameters of Non-hydrogen Atoms . .	56
TABLE 16	Hydrogen Atom Parameters . . . . .	57
TABLE 17	Least-squares Planes . . . . .	61
TABLE 18	Bond Distances . . . . .	63

TABLE 19	Bond Angles . . . . .	64
TABLE 20	Comparison of Nitrosyl and Carbonyl Bond Distances . . . . .	66
TABLE 21	Non-bonded Repulsion Energies . . . . .	74

## LIST OF FIGURES

		Page
PART I		
Ethylenebisbiguanidenickel(II)chloride monohydrate		
FIGURE 1	Bond Distances and Angles . . . . .	21
FIGURE 2	Crystal Structure Projected onto (100) Plane	24
FIGURE 3	Crystal Structure Projected onto (010) Plane	25
FIGURE 4	Half-normal Probability Plot for all Parameters . . . . .	33
FIGURE 5	Half-normal Probability Plot for Nickel and Chlorine $\beta_{ij}$ 's . . . . .	35
FIGURE 6	Half-normal Probability Plot for Nickel and Chlorine $\beta_{ii}$ 's . . . . .	36
FIGURE 7	Half-normal Probability Plot for Nickel and Chlorine $\beta_{ij}$ 's ( $i \neq j$ ) . . . . .	37
PART II		
Dicarbonylnitrosyltriphenylphosphinecobalt(0)		
FIGURE 8	Molecular Structure . . . . .	59
FIGURE 9	Stereographic Packing Diagram . . . . .	65
FIGURE 10	Non-bonded Repulsion Energies as a Function of Rotation about the Co-P Bond . . . . .	72
APPENDIX II		
FIGURE 11	Graphical Illustration of View Through the Alignment Microscope of the Diffractometer	84



## ABSTRACT

The crystal and molecular structures of two transition metal complexes were solved by the X-ray diffraction method; a comparison of the first structure with an independent, duplicate determination of the structure has yielded information about the precision of the X-ray method and a study of the second structure has yielded information about the relationship between the geometry of the molecule in the crystal and the geometry when free of the intermolecular forces in the crystal.

Ethylenebisbiguanidenickel(II)chloride monohydrate crystallizes in space group  $P2_1/c$  with  $a = 6.905(5)\text{\AA}$ ,  $b = 11.680(4)\text{\AA}$ ,  $c = 18.038(22)\text{\AA}$ ,  $\beta = 101.41(10)^\circ$ , and  $Z = 4$ . The nickel(II) ion is in square-planar configuration and the complex ion is essentially planar except for the ethylene bridge. Extensive hydrogen bonding, involving the water of hydration and the two chloride ions, joins the complex ions into infinite sheets parallel to the (100) plane with additional hydrogen bonds acting between the sheets. The final R is 3.1% for 1714 observed intensities.

The comparison of the atomic parameters and standard deviations of the two independent determinations of the structure has indicated general good agreement between the two determinations. However, the comparison also indicates that there are significant differences between certain classes of parameters and that the estimated standard deviations of the two determinations have been underestimated, on the average, by a factor of about 1.7.

Dicarbonylnitrosyltriphenylphosphinecobalt(0) crystallizes in space group  $P\bar{1}$  with  $a = 11.055(2)\text{\AA}$ ,  $b = 11.024(4)\text{\AA}$ ,  $c = 10.260(2)\text{\AA}$ ,  $\alpha = 121.07(2)^\circ$ ,  $\beta = 101.01(2)^\circ$ ,  $\gamma = 105.14(2)^\circ$ , and  $Z = 2$ . The cobalt and phosphorus atoms are in approximately tetrahedral configurations and the nitrosyl and carbonyl groups are disordered. There is no indication of hydrogen bonding. The final R is 3.2% for 2006 observed intensities.

Non-bonded repulsion energies were calculated for the molecule with respect to rotation about the Co-P bond and about the three P-C (phenyl) bonds for the molecule in the crystal and for the free molecule. It was found that the configuration in the crystal minimizes the energy in the crystal but that the free molecule rotates approximately  $20^\circ$  about the Co-P bond to minimize the energy.

## INTRODUCTION

This dissertation is divided into two parts, each presenting a different crystal structure which makes significant contributions to the literature. The first, that of ethylenebisbiguanidenickel(II)chloride monohydrate (31), represents a duplicate, independent, accurate, diffractometer, X-ray determination of the structure. Significant information concerning the precision of the X-ray method has been learned from a comparison of the two determinations of the structure of this compound.

The second, that of dicarbonylnitrosyltriphenylphosphinecobalt(0) (33), was investigated to assist in understanding its role in the catalysis of the dimerization of norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) (21). A study of the structure has yielded information concerning the relationship between the geometry of the molecule in the crystal and the geometry of the molecule when free of the intermolecular forces in the crystal.

PART I

Ethylenebisbiguanidenickel(II)chloride monohydrate

## INTRODUCTION

The original purpose of this study was the determination of the structure of ethylenabisbiguanide-nickel(II)chloride monohydrate and the study of the nature of the tetradentate ligand along with its effect on the nickel coordination. When the structure determination was completed, prepublication notice was received from Professor Richard Marsh of the California Institute of Technology indicating an independent determination of the structure there (18). The consideration of the precision of the two determinations, the different methods of data collection and solution of the structure suggested that these duplicate structure determinations present an ideal case to study the accuracy and precision of X-ray crystal structure determinations. Such a study is presented along with the structural details of the crystal.

The precision of an experimentally-determined parameter is indicated by the estimated standard deviation. The estimated standard deviations for the atomic parameters determined in X-ray crystal structure studies have been the subject of questions concerning their accuracy. Several statistical methods are available for the comparison of two sets of parameters with respect to their standard

deviations. A simple method is to compare the differences between corresponding parameters to the standard deviations; this can be done for individual parameters, for groups of parameters, or for all parameters at once. The information obtained from this method would indicate agreement or lack of agreement between the two sets of parameters with respect to the standard deviations but does not indicate the correctness of the estimate of the standard deviations.

Another method is the CHI-square test which has been applied to the comparison of parameter sets by Hamilton (15). In this method, parameter differences are weighted by the standard deviations and the sum of the squares of these weighted differences (for  $j$  parameters) is tested as CHI-squared with  $j$  degrees of freedom. One may reject the postulate that the weighted differences are from a normal distribution with zero mean at the  $\alpha\%$  level if the tabulated value of CHI-squared ( $j, \alpha$ ) is less than the sum of the squares of the weighted differences. One would expect the postulate to be true only if there are no systematic errors in the weighted differences; standard deviations that are too small may result from systematic errors and would cause the postulate to be rejected. The CHI-square test can indicate the presence of differences from the normal.

distribution but can not determine the cause of the differences.

A new method for the comparison of parameter sets has been presented by Abrahams and Keve (2). This method is the normal probability plot analysis and has the features of being able to indicate the correctness of the estimated standard deviations and to give an average factor by which to multiply the estimated standard deviations to obtain a set consistent with the normal distribution. Weighted differences are calculated and ordered in order of increasing magnitude and plotted against the normal distribution for the same number of elements. If the differences themselves follow a normal distribution, the plot will be linear and the slope indicates the average factor by which the estimated standard deviations have been underestimated.

The crystal structure of ethylenebisbiguanidenickel(II)-chloride monohydrate is reported in Section I, a condensed description of the normal probability plot analysis method is given in Appendix I, and a comparison of the parameter sets of the two duplicate determinations is given in Section II.

## SECTION I

### THE CRYSTAL AND MOLECULAR STRUCTURE OF ETHYLENEBISBIGUANIDENICKEL(II)CHLORIDE MONOHYDRATE

#### Preparation of the crystals

Crystals of ethylenebisbiguanidenickel(II)chloride monohydrate were prepared by Dr. David J. MacDonald (24) from nickel(II)chloride hexahydrate, ethylenediamine dihydrochloride and cyanoguanidine using a modification of the method reported by Ray (27) for the preparation of ethylenebisbiguanidecopper(II)sulfate. Using Ray's method one obtains the starting materials in a finely divided condition and mixes them thoroughly; the mixture is melted with constant stirring, cooled, treated with an aqueous solution of  $(\text{NH}_4)_2\text{SO}_4$ , neutralized with ammonia, filtered, and washed with cold water. Dark red-orange crystals are obtained.

#### Density determination

The presence of one molecule of water per formula unit was determined from the weight loss of a finely ground sample heated to  $110^\circ\text{C}$  for 16 hours; a loss of 4.86% was observed compared to a theoretical loss of 4.79%. The density, measured by flotation in a carbontetrachloride-

bromoform mixture is  $1.740 \text{ g.cm}^{-3}$ . For four molecules in the unit cell and one molecule of water per formula unit, the calculated density is  $1.750 \text{ g.cm}^{-3}$ .

#### Determination of space group and cell parameters

Preliminary photographic examination of a single crystal of ethylenebisbiguanidenickel(II)chloride monohydrate showed the conditions for reflection to be  $h0l: l = 2n$ , and  $0k0: k = 2n$ , uniquely determining the space group  $P2_1/c$ . Precise unit cell parameters were determined by least-squares refinement of the  $2\theta$  values of 14 general reflections measured on a General Electric XRD-5 diffractometer using a G. E. single crystal orienter and  $\text{MoK}_\alpha$  ( $\lambda=0.71069\text{\AA}$ ) radiation. The crystal data is listed in Table 1. It was discovered that a  $P2_1/n$  cell could be chosen which would give a  $\beta$  angle nearer to  $90^\circ$  than is the angle for the  $P2_1/c$  cell. This cell was not used so that the results of this structure determination could be easily compared to those of other determinations.

#### Collection of the data

The unique intensity data were collected by  $\theta$ - $2\theta$  scans using zirconium-filtered  $\text{MoK}_\alpha$  ( $\lambda=0.71069\text{\AA}$ ) radiation and a General Electric XRD-5 diffractometer equipped with a



TABLE 1

## Crystal data

Ethylenebisbiguanidenickel(II)chloride monohydrate

 $C_6N_{10}H_{16}NiCl_2 \cdot H_2O$  F.W. 375.91 F(000) = 776Monoclinic, space group  $P2_1/c$ 

$$a = 6.905(5) \text{ \AA}$$

$$b = 11.680(4)$$

$$c = 18.038(23)$$

$$\beta = 101.41(10)$$

$$V = 1426.0 \text{ \AA}^3$$

$$Z = 4$$

$$D_m = 1.740 \text{ g.cm}^{-3}$$

$$D_x = 1.750 \text{ g.cm}^{-3}$$

scintillation counter, pulse-height discriminator, and a G. E. single crystal orienter. Sixty-second scans ( $2^\circ$  in  $2\theta$ ) were used with stationary backgrounds measured for 30 seconds each at the start and finish of each scan. The crystal was mounted with the a axis parallel to the spindle axis. A chart recording of diffracted intensity vs.  $2\theta$  was monitored during data collection to insure that the reflections were centered in the scan range. The intensities of the standard reflections monitored during data collection showed no systematic variations; there was no evidence of radiation damage to the crystal. Of the 2228 unique reflections which were examined out to  $48^\circ$  in  $2\theta$ , 1714 had an intensity greater than twice the standard deviation of the intensity; the remaining 514 reflections were coded as "unobserved" and were not included in the refinement.

The dimensions of the crystal were measured using a calibrated "Whipple disc" in the alignment microscope of the diffractometer (see Appendix II) (32). The crystal was well-shaped, bound by the planes  $\{10\bar{1}\}$ ,  $\{001\}$ ,  $\{011\}$ , and  $\{01\bar{1}\}$ , and its dimensions in the directions of a, b, and  $c^*$  were approximately .82mm, .28mm, and .13mm, respectively. The linear absorption coefficient for  $\text{MoK}_\alpha$  radiation is

18.21 cm<sup>-1</sup>; absorption corrections, using the method of de Meulenaer and Tompa (25) calculated transmission coefficients ( $I/I_0$ ) ranging from 0.895 to 0.763.

#### Determination of the structure

The positions of the nickel and one chlorine atom were determined from an E-map calculated using 230 reflections whose signs had been determined by the symbolic addition procedure. Several repetitions of Fourier syntheses yielded the positions of the remaining non-hydrogen atoms. Full-matrix least-squares refinement, refining all atoms anisotropically and using unit weights, reduced R to 5.8% and  $R_{\text{wtd}}$  to 8.1% where R and  $R_{\text{wtd}}$  are defined as

$$R = \frac{\sum |F_o - F_c|}{\sum |F_o|} \quad R_{\text{wtd}} = \left\{ \frac{\sum (\sqrt{w} |F_o - F_c|)^2}{\sum (\sqrt{w} |F_o|)^2} \right\}^{\frac{1}{2}}$$

and the function minimized during refinement was

$$\sum w \left( |F_o| - \frac{1}{k} |F_c| \right)^2$$

Absorption corrections were applied reducing R to 4.9% and  $R_{\text{wtd}}$  to 6.1%. The positions of the hydrogen atoms were determined from a difference Fourier. Block-diagonal least-squares refinement, refining hydrogen atoms isotropically and the non-hydrogen atoms anisotropically,

using the weighting scheme described by Stout and Jensen (29), and applying anomalous dispersion corrections (20) for nickel ( $\Delta f' = 0.4$ ,  $\Delta f'' = 1.2$ ) and for chlorine ( $\Delta f' = 0.1$ ,  $\Delta f'' = 0.2$ ), reduced R to 3.12% and  $R_{\text{wtd}}$  to 4.87%. The observed and calculated structure factors are listed in Table 2 for the 1714 "observed" reflections. The positional parameters of the non-hydrogen atoms are listed in Table 3, the thermal parameters for the non-hydrogen atoms are listed in Table 4, and the hydrogen atom parameters are listed in Table 5.

#### The structure

All atoms lie in general positions. The nickel atoms are in square planar configuration and lie nearly along the lines  $x, 0, 0$  and  $x, \frac{1}{2}, \frac{1}{2}$  with distances of 3.621(1) and 3.549(1) Å between the nickel atoms on each of these lines. The tetradentate ethylenbisbiguanide ligand is essentially planar around the nickel. Least-squares planes were calculated using several sets of atoms within the complex ion and using unit weights for each atom; the equations for these planes are given in Table 6. The nickel and the four coordinating nitrogens lie very close to the plane; the deviation for the nickel is .0013 Å and the deviations for the nitrogens are -.0001 Å for N(1) and

















































































































































































