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STRUCTURAL STUDIES
OF
METAL-RIBONUCLEOTIDE
COMPLEXES

A thesis presented to the
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by

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ABSTRACT

The crystal and molecular structures of five binary complexes between transition-metal ions and 5'-ribonucleotides have been determined by X-ray crystallographic means. All data were collected by diffractometry and the structures refined by the full-matrix least-squares method.

The complex \( \text{Ni}(\text{C}_{10}\text{H}_{11}\text{N}_{4}\text{O}_{8}\text{P})(\text{H}_{2}\text{O})_{5}.2\text{H}_{2}\text{O} \) crystallizes in the orthorhombic space group \( \text{P2}_1\text{2}_1\text{2}_1 \) with four molecules in a unit cell of dimensions \( a = 6.853(1) \), \( b = 10.812(2) \), \( c = 25.925(3) \) \( \text{Å} \). Refinement converged with \( \text{R} \) and \( \text{R}_w \) values of 0.054 and 0.059 respectively.

The structure is monomeric with nickel octahedrally co-ordinated to \( \text{N}(7) \) of the base and to five water molecules. The monomer is stabilized by three intramolecular hydrogen bonds involving co-ordinated water molecules, phosphate oxygens, and the exocyclic \( \text{O}(6) \) atom of the base.

The complex of empirical formula \( \text{Co}(\text{C}_{9}\text{H}_{12}\text{N}_{3}\text{O}_{8}\text{P})(\text{H}_{2}\text{O}) \) crystallizes in the monoclinic space group \( \text{P2}_1 \) with two formula units in a unit cell of dimensions \( a = 10.002(1) \), \( b = 7.459(2) \), \( c = 9.429(1) \) \( \text{Å} \), \( \beta = 96.58(1) \) \( ^\circ \). The final \( \text{R} \) and \( \text{R}_w \) values were 0.073 and 0.063 respectively.

The structure is polymeric in two dimensions. The cobalt is in a distorted tetrahedral environment, being co-ordinated to \( \text{N}(3) \) of the base, two oxygens of two
different phosphate groups, and a water molecule. There is a weak interaction between the metal ion and the exocyclic O(2) atom of the base.

The complex of empirical formula Cd(C_9H_{12}N_3O_8P)(H_2O).H_2O crystallizes in the orthorhombic space group P2_12_1_2_1 with four formula units in a unit cell of dimensions a = 5.294(1), b = 17.070(1), c = 16.371(1) Å. Final R and R_w values of 0.038 and 0.045 respectively were obtained.

The structure is polymeric in three dimensions. The cadmium is in a distorted square-pyramidal environment, being co-ordinated to N(3) of the base, three oxygen atoms of three phosphate groups, and a water molecule. There is a weak interaction between the metal ion and the O(2) atom of the base.

The complex of empirical formula Cu(C_{10}H_{11}N_4O_8P).H_2O crystallizes in the orthorhombic space group P2_12_1_2_1 with four formula units in a unit cell of dimensions a = 17.412(3), b = 15.772(3), c = 5.077(1) Å. Refinement returned R and R_w values of 0.083 and 0.061 respectively.

The structure is polymeric in one dimension. The copper is co-ordinated to N(7) of the base and three oxygens of three phosphate groups. Weak axial bonds to a further phosphate oxygen and the exocyclic O(6) atom of the base complete the pseudo octahedral co-ordination geometry (4 + 1 + 1).
The complex of empirical formula \( \text{Cu}_3\left(\text{C}_{10}\text{H}_{12}\text{N}_{5}\text{O}_{8}\text{P}\right)_3\text{(H}_2\text{O})_8\cdot 4\text{H}_2\text{O} \) crystallizes in the orthorhombic space group \( \text{P2}_1\text{2}_1\text{2} \) with four formula units in a unit cell of dimensions \( a = 20.813(4), b = 23.356(3), c = 11.392(1) \ \text{Å} \). The final \( R \) and \( R_w \) values were 0.11 and 0.09 respectively.

The structure consists of irregular helical chains. Each of the three independent coppers is in a square-pyramidal environment, with \( \text{N}(7) \) of the bases occupying the axial positions. Whereas the square-planes of two of the coppers each consists of one phosphate oxygen and three water molecules, that of the third consists of two oxygens from two phosphates, and two water molecules. The structure is stabilized by intramolecular hydrogen bonds involving co-ordinated water molecules, phosphate oxygens, and the exocyclic \( \text{O}(6) \) atoms of the bases.

A system has been devised for classifying the structures of binary metal/ribonucleotide complexes.
# TABLE OF CONTENTS

## CHAPTER 1: INTRODUCTION

1.1 The Interaction of Metal Ions with Nucleic Acids and their Constituents ................................................. 1

1.2 The Nucleotide Ligand ................................................................................................................................. 3

1.3 Nucleotide Conformation
   - The Orientation of the Base Moiety Relative to the Sugar Ring .............................................................. 13
   - The Orientation of the Phosphate Moiety Relative to the Sugar Ring ....................................................... 18
   - The Conformation of the Sugar Ring ........................................................................................................... 18
   - The Configuration about the Phosphoester Linkage .................................................................................. 20
   - The Overall Nucleotide Conformation ...................................................................................................... 24

1.4 Base Stacking ............................................................................................................................................. 24

1.5 Intercalation .................................................................................................................................................. 27

1.6 Current Research into the Interaction of Metal Ions with Nucleic Acids and their Constituents
   - Non-crystallographic Investigations ........................................................................................................... 28
   - Crystallographic Investigations ................................................................................................................ 31
   - The Advantages of Crystallographic Investigations .................................................................................. 33

## CHAPTER 2: PREPARATIONS OF METAL-NUCLEOTIDE COMPLEXES

2.1 The Method of Ogawa and Sakaguchi ............................................................................................................. 54

2.2 The Degree of Hydration in Transition-Metal/Nucleotide Complexes ......................................................... 55

2.3 Isomers of Transition-Metal/Nucleotide Complexes .................................................................................... 59

2.4 Variations on the Method of Ogawa and Sakaguchi
   - General Considerations .............................................................................................................................. 60
   - The Variation of Bau and Shiba .................................................................................................................. 62
   - Other Methods .......................................................................................................................................... 63
2.5 The Preparation and Crystal Growth of Six Complexes Between Metal Species and 5'-Ribonucleotides

(i) The Preparation of a 1:1 Complex between Nickel(II) Ions and Inosine 5'-Monophosphate

(ii) The Preparation of a 1:1 Complex between Cobalt(II) Ions and Cytosine 5'-Monophosphate

(iii) The Preparation of a 1:1 Complex between Cadmium(II) Ions and Cytosine 5'-Monophosphate

(iv) The Preparation of a 1:1 Complex between Copper(II) Ions and Inosine 5'-Monophosphate

(v) The Preparation of a 1:1 Complex between Copper(II) Ions and Guanosine 5'-Monophosphate

(vi) The Preparation of a 1:6 Complex between Mercuric Chloride and Uracil 5'-Monophosphate

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CHAPTER 3: THE CRYSTAL AND MOLECULAR STRUCTURE OF A MONOMERIC 1:1 COMPLEX BETWEEN NICKEL(II) AND INOSINE 5'-MONOPHOSPHATE, [C_{10}H_{11}N_{4}O_{8}P]Ni(H_{2}O)_{5}·2H_{2}O

3.1 Preliminary Investigations and Data Collection

3.2 Structure Determination and Refinement

3.3 Description of the Structure
   The Nickel Ion Co-ordination
   The Geometry of the Nucleotide
   The Extended Crystal Structure

Tables for Chapter 3

Figures for Chapter 3

---

CHAPTER 4: THE CRYSTAL AND MOLECULAR STRUCTURE OF A POLYMERIC 1:1 COMPLEX BETWEEN COBALT(II) AND CYTIDINE 5'-MONOPHOSPHATE, [(C_{9}H_{12}N_{3}O_{8}P)Co(H_{2}O)]_{n}

4.1 Preliminary Investigations and Data Collection

4.2 Structure Determination and Refinement
4.3 Description of the Structure
The Cobalt Ion Co-ordination
The Geometry of the Nucleotide
The Extended Crystal Structure

Tables for Chapter 4
Figures for Chapter 4

CHAPTER 5: THE CRYSTAL AND MOLECULAR STRUCTURE OF A POLYMERIC 1:1 COMPLEX BETWEEN CADMIUM(II) AND CYTIDINE 5'-MONOPHOSPHATE, [(C₉H₁₂N₃O₈P)Cd(H₂O)₄H₂O]

5.1 Preliminary Investigations and Data Collection
5.2 Structure Determination and Refinement
5.3 Description of the Structure
The Cadmium Ion Co-ordination
The Geometry of the Nucleotide
The Extended Crystal Structure

Tables for Chapter 5
Figures for Chapter 5


6.1 Preliminary Investigations and Data Collection
6.2 Structure Determination and Refinement
6.3 Description of the Structure
The Copper Atom Co-ordination
The Geometry of the Nucleotide
The Extended Crystal Structure

Tables for Chapter 6
Figures for Chapter 6
CHAPTER 7: THE CRYSTAL AND MOLECULAR STRUCTURE OF A POLYMERIC 1:1 COMPLEX BETWEEN COPPER(II) AND GUANOSINE 5'-MONOPHOSPHATE, 
\[ ((C_{10}^0H_{12}^0N_{5}O_{8}P)^3Cu_3(H_2O)^8\cdot4H_2O)_n \]

7.1 Preliminary Investigations and Data Collection 211
7.2 Structure Determination and Refinement 212
7.3 Description of the Structure 214
   The Copper Ion Co-ordination 216
   The Geometry of the Nucleotide 217
   The Extended Crystal Structure 218

Tables for Chapter 7 219
Figures for Chapter 7 263

CHAPTER 8: DISCUSSION

8.1 Classification of Binary Metal/Nucleotide Structures 281
8.2 Monomeric Structures 281
   8.2.1 The MHPu Structural Type 281
   8.2.2 The MHPy Structural Type 292
   8.2.3 The MLPu and MLPy Structural Types 294
   8.2.4 The Role of Water-bridging in the Interaction of Metal Ions with Nucleic Acids and their Constituents 294

8.3 Polymeric Structures 296
   8.3.1 The PLPy Structural Type 296
   8.3.2 The Structure of Cd-CMP(mono) 300
   8.3.3 The Structure of Mn-CMP 302
   8.3.4 General Features of the PLPy Structural Type 303
   8.3.5 The Co-ordinating Properties of the Cytosine Moiety 308
   8.3.6 The "N(3) plus O(2)" Mode of Co-ordination 311
   8.3.7 The PHPy Structural Type 315
8.3.8 The Structure of Co(II)-UMP 316
8.3.9 Conformational Aspects of the PLPy Structures 317
8.3.10 The PLPu Structural Type 322
8.3.11 The Purines as Chelating Ligands 328
8.3.12 Conformational Aspects of the PLPu Structures 329
8.3.13 The gauche-trans and trans-gauche Conformations 330
8.3.14 The PHPu Structural Type 332
8.3.15 The Structure of Cd-IMP(mono) 332
8.3.16 General Features of the PHPu Structural Type 334
8.3.17 Structural Aspects of Cu-GMP 335
8.3.18 Hydrogen Bonding in Cu-GMP 340
8.3.19 A Comparison between the Structures of Cu-GMP and Na₂-ATP 341

8.4 The Ternary Complexes 344

APPENDIX A Comparisons of Bond Lengths and Angles 358
APPENDIX B Computing 387
APPENDIX C Publications 391

REFERENCES 423

ACKNOWLEDGEMENTS 441

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