

12/10/76

CHELATE CONFORMATION IN METAL COMPLEXES

A thesis submitted for the degree of
Doctor of Philosophy

by RODNEY JAMES GEUE, B.Sc. (Hons.)

Department of Physical and Inorganic Chemistry
The University of Adelaide

September 1975

<u>CONTENTS</u>	Page
SYNOPSIS	v
DECLARATION	vii
ACKNOWLEDGEMENTS	viii
INTRODUCTION	1
LIGAND TERMINOLOGY	9
<u>CHAPTER 1.</u> THE CRYSTAL STRUCTURE OF $(-)$ ₅₈₉ - <i>S,S</i> -6,9-DIAZA-2,13-DITHIATETRADECANE-5,10-DICARBOXYLATO-COBALT(III) PERCHLORATE	13
1.1 ABSTRACT	13
1.2 PREAMBLE	13
1.3 EXPERIMENTAL AND DATA REDUCTION	17
1.4 REFINEMENT TERMINOLOGY	20
1.5 STRUCTURE SOLUTION AND REFINEMENT	23
1.6 TABLES AND PERSPECTIVE PROJECTIONS	25
1.7 STRUCTURAL FEATURES AND DISCUSSION	26
<u>CHAPTER 2.</u> THE CRYSTAL STRUCTURE OF BIS-(DIHYDRO-1 <i>H</i> ,3 <i>H</i> ,5 <i>H</i> -OXAZOLO[3,4- <i>c</i>]OXAZOLE-7 <i>a</i> -CARBOXYLATO)COPPER(II)	40
2.1 ABSTRACT	40
2.2 PREAMBLE	40
2.3 EXPERIMENTAL AND DATA REDUCTION	43
2.4 STRUCTURE SOLUTION AND REFINEMENT	45
2.5 TABLES AND PERSPECTIVE PROJECTIONS	48

	Page
2.6 STRUCTURAL FEATURES AND DISCUSSION	48
<u>CHAPTER 3.</u> THE CRYSTAL STRUCTURE OF (+) ₅₈₉ -BIS-(1,1,1-TRIS(AMINO-METHYL)ETHANE)COBALT(III) CHLORIDE (+) ₅₈₉ -R,R-TARTRATE PENTAHYDRATE	72
3.1 ABSTRACT	72
3.2 EXPERIMENTAL AND DATA REDUCTION	73
3.3 STRUCTURE SOLUTION AND REFINEMENT	82
3.4 TABLES AND PERSPECTIVE PROJECTIONS	87
3.5 STRUCTURAL FEATURES AND DISCUSSION	88
<u>CHAPTER 4.</u> CORRELATION OF ABSOLUTE CONFIGURATION AND SIGNED ROTATORY STRENGTH IN DISSYMMETRIC Co(III) COMPLEXES	117
4.1 INTRODUCTION	117
4.2 OPTICAL ACTIVITY AND ROTATORY POWER	125
4.3 THE PIPER-KARIPÉDES THEORY FOR D_3 Co(III)L ₆ CHROMOPHORES	129
4.3.1 The Crystal Field Model	132
4.3.2 Application to $\lambda\lambda$ -[Co(tame) ₂] ³⁺	137
4.4 THE RICHARDSON THEORY FOR DISSYMMETRIC Co(III) COMPLEXES	148
4.4.1 The Crystal Field Model for D_3 Complexes	150
4.4.2 Application to $\lambda\lambda$ -[Co(tame) ₂] ³⁺	155
<u>CHAPTER 5.</u> CONFORMATIONAL ANALYSIS OF METAL COMPLEXES	169
5.1 INTRODUCTION	169
5.2 ENERGY REPRESENTATION AND FORCE FIELD	173

	Page
5.3 THE MOLECULAR ENERGY MINIMIZATION PROCEDURE	182
5.4 THE REFINEMENT OF SYMMETRIC MOLECULES	189
5.4.1 Energy Minima and Saddle-points of Symmetric Configurations	190
5.4.2 Symmetry-dependent Refinement	193
5.4.3 Evasion of Saddle-point Convergence	197
5.5 ENERGY MINIMIZATION RESULTS AND DISCUSSION	200
5.5.1 Conformers of $[\text{Co}(\text{tame})_2]^{3+}$	201
5.5.2 Symmetric Conformers of $[\text{Co}(\text{tn})_3]^{3+}$	217
5.5.3 Chair Conformers of $[\text{Co}(\text{tn})_2\text{CO}_3]^+$	234
5.5.4 Discussion of the Geometric Isomers of $[\text{Co}(\text{dien})_2]^{3+}$	251
<u>CHAPTER 6.</u> ENERGY MINIMIZED CONFIGURATIONS AND THEIR SIGNED ROTATORY STRENGTHS	258
6.1 INTRODUCTION	258
6.2 COMPARISON OF OBSERVED AND CALCULATED DATA	262
6.3 CONCLUDING DISCUSSION	274
<u>APPENDICES</u>	280
I CATALOGUE OF COMPUTER PROGRAMS	280
II MODIFICATIONS TO BOYD'S ENERGY MINIMIZATION PROGRAM	283
III SUPPLEMENTARY INFORMATION ON THE STRUCTURE ANALYSES	288
<u>BIBLIOGRAPHY</u>	290

SYNOPSIS

The experimental investigation of chelate conformation included the determination of three crystal structures by X-ray analysis. The structures of $(-)_589$ -*S,S*-6,9-diaza-2,13-dithiatetradecane-5,10-dicarboxylato-cobalt(III) perchlorate, $[\text{Co}(\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_4\text{S}_2)]\text{ClO}_4$, bis-(dihydro-1*H*,3*H*,5*H*-oxazolo[3,4-*c*]oxazole-7*a*-carboxylato)copper(II), $\text{Cu}(\text{C}_6\text{H}_8\text{NO}_4)_2$, and $(+)_589$ -bis-(1,1,1-tris(aminomethyl)ethane)cobalt(III) chloride $(+)_589$ -*R,R*-tartrate pentahydrate, $(+)_589$ - $[\text{Co}(\text{C}_5\text{H}_{15}\text{N}_3)_2\text{Cl}-(+)_589$ - $(\text{C}_4\text{H}_4\text{O}_6) \cdot 5.4\text{H}_2\text{O}$ were determined and refined by full matrix least-squares techniques to conventional *R* indices of 0.060, 0.038 and 0.025 respectively. The absolute configuration of the complex cation in the first structure was designated skew chelate pairs, $\Lambda\Delta\Lambda$. In the third structure, the helicity of the complex cation is a function of the ring conformations only and the absolute configuration was designated $\lambda\lambda$.

The $\lambda\lambda$ -bis-(1,1,1-tris(aminomethyl)ethane)cobalt(III) ion was observed to have quasi- D_3 symmetry in the crystal, and parameters indicating the distortion of the mean D_3 chromophore from O_h symmetry were computed from the crystal geometry. The signs of the *net* rotatory strengths of this ion for the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ octahedral transitions were estimated by application of the one-electron static coupling model of Richardson for dissymmetric six-coordinate cobalt(III) complexes with D_3 symmetry. The observed *net* rotatory strength for the complete manifold of *d-d* transitions was large and similar in sign to that predicted, and the model is empirically verified.

The molecular conformational analysis procedure of Boyd, based on the mathematical minimization of potential energy by a Newton-Raphson technique, has been extended to allow the exceptionally fast refinement of molecules possessing one or more symmetry elements in their final configurations. An artifice for evading symmetry saddle-points was also devised. Conformational mechanics was applied to the conformational isomers of bis-(1,1,1-tris(aminomethyl)ethane)cobalt(III), the symmetric conformers of tris-(1,3-diaminopropane)cobalt(III) and the chair configurations of *cis*-carbonatobis-(1,3-diaminopropane)-cobalt(III). Computations on these molecules, supplemented by other examples, verified the symmetry refinement procedure.

Finally, a qualitative assessment of the validity of applying energy minimized molecular configurations of metal complexes to the correlation between absolute configuration and the sign of the observed *d-d* transition rotatory strength, was effected. It is suggested that the agreement between observed and calculated data is generally sufficiently good to permit such applications.

DECLARATION

This thesis is founded on research undertaken by the candidate in the Department of Physical and Inorganic Chemistry at the University of Adelaide unless asserted otherwise.

To the best of the candidate's knowledge the text contains no material written or devised by another person, except where an appropriate reference is made. No work in the thesis has previously been submitted by the candidate for the award of any other degree.

The author accepts full responsibility for any errors present in the treatise, regardless of their nature.

Rodney Geue

September 1975

ACKNOWLEDGEMENTS

I extend genuine gratitude to my supervisor, Dr. M.R. Snow, who through his unflinching interest and patronising attitude, has contributed significantly to the essence of this research.

I sincerely thank Dr. M. Dwyer for his collaboration and encouragement in developments of the mechanics of conformational analysis and for the innumerable stimulating discussions which resulted therefrom. I am also indebted to Dr. G.B. Robertson of the Research School of Chemistry at the Australian National University, Canberra, for the collection of a set of diffractometer data.

Professors D.O. Jordan and D.R. Stranks have my gratitude for their acceptance of myself as a research student in the Department of Physical and Inorganic Chemistry.

I wish to thank the Department of Education and Science for supporting me with a Commonwealth Postgraduate award for the period of this work. My thanks are also due to the staff of the Computing Centre of the University of Adelaide for the continual use of their facilities. I acknowledge the use of computing facilities of the CSIRO Department of Computing Science and thank their staff who assisted in the development of control routines for the manipulation of paper tapes.

My final appreciation is directed to Mrs. Del Hewish who typed the manuscript.