THE JOHN CURTIN SCHOOL OF MEDICAL RESEARCH 620/1963

ANNUAL REPORT TO THE COUNCIL 1962

BIOLOGICAL INORGANIC CHEMISTRY UNIT

Staff

Professor	F. P. Dwyer, D.Sc., F.R.A.C.I. F.A.A. (Deceased 21.6.62).
Fellow	A. M. Sargeson, B.Sc., Ph.D.
Senior Research Fellow	B. Halpern, B.Sc., Ph.D.
Visiting Fellow	K. R. Turnbull, M.Sc., (Resigned 31.7.62).
Senior Technical Officer	I. K. Reid
Technical Officer	L. James

STUDENTS

Three students obtained their degree of Doctor of Philosophy during the year - B. Bosnich, D. A. Buckingham and J. A. Broomhead. T. A. MacDermott completed the requirements for the degree. Two others were engaged in research to obtain the degree, G. H. Searle, M.Sc., (1.9.60, The Preparation, stereochemistry and kinetics of disubstituted triethyl-enetetramine cobalt (III) complexes) and H. Amling (6.11.61, resigned 25.11.62, The kinetics and mechanism of the formation of cobalt (III) carbonato complexes). The Unit also jointly supervised Mr. K. R. Turnbull, M.Sc., a candidate for the degree of Doctor of Philosophy in the Chemistry Department of the School of General Studies. Both students and staff gave two seminars each during the year on their research or related topics.

RESEARCH ACTIVITIES

The work of the Unit is concerned with the synthesis of metal complexes, their fundamental chemistry and their application to biology. A simple general method for resolving racemic amino acids with optically active coordination compounds has been discovered and patented (Dwyer, Halpern and Turnbull). Both optical antipodes are equally accessible and the method should reduce the existing high cost of the un-natural form of the amino acids.

A number of stereospecific quadridentate complexes have been made for use as resolving agents and as templates to carry out stereospecific reactions which are catalysed by metal ions, (Dwyer, Halpern and Sargeson). In this context a study has been made of a nickel amino acid ester complex, which transesterifies and amidates easily, with a view to a peptide synthesis, (Halpern). An aldol type condensation of aldehydes with active methylene groups in a coordinated ligand and the relative rates of reaction with different metal ions and change in charge on the complex have also been investigated, (Gill ø Halpern, Sargeson and Turnbull). A study of metal catalysed reactions with pyridoxal and amino acids and similar Schiffs' base models has been commences, (Sargeson). It is hoped that the stereospecific multidentates mentioned previously may be used to carry out the foregoing reactions in a stereospecific manner so that only one optical isomer is produced.

A study of the kinetics and mechanism of the addition of carbonate ion to coordinated water in cobalt (III) complexes is partly completed, (Amling and Sargeson). The reaction is extremely rapid below pH7 ($T^1/_2 < 1$ sec.) and it probably takes place by the addition of carbon dioxide to the coordinated water and not by addition of carbonate or bicarbonate ion as formerly supposed.

ø Chemistry Department, School of General Studies.

/The kinetics of aquation

The kinetics of aquation of all the isomers of the dichloro triethylenetetramine cobalt (III) ion has been carried out and the sterochemical course of the reactions through the chloroaquo ions to the diaquo ions has been determined. This study has given information not only on the reactivity of isomers but has also given some insight into the fundamental mechanisms of aquation of cobalt (III) complexes, (Sargeson and Searle).

The study of the fundamental chemistry and preparative procedures for cobalt (III) and chromium (III) complexes has been continued with the preparation of sodium tetraoxalato-diol-dicobalt (III), the resolution of potassium diaquo-dioxalato chromate (III) and the preparation of sodium bis-oxalato acetylacetone cobalt (III) and bis-acetylacetone oxalato cobalt (III), (Reid).

The stereospecificity and conformational investigations on cobalt (III) tris(propylenediame) complexes has also been continued and the D and L isomers of cobalt complexes containing both d and l propylenediamine molecules in the same ion have been isolated, (Dwyer, Sargeson and James).

OTHER ACTIVITIES

Shortly before his tragic death, Professor Dwyer and two members of the Unit (Buckingham and Sargeson) completed four chapters for a book entitled "Metal Chelates and Chelating Agents", edited by Professors F. P. Dwyer and D. P. Mellor. This book is now at the printers and should appear in 1963. Professor Dwyer also gave a series of lectures in May in the United States at the invitation of the American Chemical Society. Both staff and students attended the Pre-A.N.Z.A.A.S. Symposium on Co-ordination Chemistry and also the A.N.Z.A.A.S Meeting in August and Mr. Searle presented a paper at the Symposium.

Joint research projects have also been initiated with Professor G. B. Kauffman at Fresno State College, California, with Professor S. T. Spees at the University of Minnesota and with Dr. J. Garnett at the University of New South Wales.

PUBLICATIONS

Dwyer, F. P., Halpern, B.

"Co-ordination Compounds as Resolving Agents", NATURE, 196, 270 (1962).

Broomhead, J. A., McKenzie, H.A., Mellor, D. P. ∅

"Complexes of Copper (II) with Pyrrolidine", AUST.J.CHEM., 14, 649.

Dwyer, F. P., Broomhead, J. A.

"The Preparation and Resolution of the Bis-(2,2'-Bipyridine)-1,10-Phenanthrolinenickel (II) and the Bis-(1,10-Phenanthroline)-2,2'-Bipyridinenickel (II) Ions, AUST.J.CHEM., 15, 453.

PAPERS ACCEPTED FOR PUBLICATION

1. Dwyer, F. P., Reid, I. K., Sargeson, A. M.

"Mechanism of the Inversion Reaction Between d, Cis-Dichlorobis-(Ethylenediamine) Cobalt (III) Ion and Silver Carbonate", J.AMER. CHEM.SOC.

2. Dwyer, F. P., MacDermott, T.E., Sargeson, A. M.

"Stereospecific Influences in Metal Complexes Containing Optically Active Ligands. Part VI. Oxalato-Levo Propylenediamine Cobalt (III) Complexes." J.AMER.CHEM.SOC.

∅ Not a member of the Australian National University.

/3. Dwyer, F.P.,

3. Dwyer, F. P., Halpern, B., Turnbull, K. R.

"Resolution of Racemic-α-Acids. I. Neutral-α-Amino Acids", AUST.J.CHEM.

4. MacDermott, T. E., Sargeson, A. M.

"Rotatory Dispersion and Configuration of Cobalt (III) Complexes", AUST.J.CHEM.

5. Sargeson, A. M.

"The Rate of Racemisation and Isomerisation of the Cis Chloroaquo Bis (Ethylenediamine) Cobalt (III) Ion", AUST.J.CHEM.

6. Reid, I. K., Sargeson, A. M.

"Potassium Diol Tetraoxalato Cobaltate (III) Trihydrate (Durrants' Salt)", INORGANIC SYNTHESES, VOL.VIII.