

+1.03 V vs. Ag|AgClO₄) in acetonitrile to an iron(IV) complex [FeCl₂(diphos)₂]²⁺, which can be isolated as an unstable, highly oxidizing, deep purple-brown perchlorate salt ($\mu_{\text{eff}} = 3.65$ BM) by nitric acid oxidation of [FeCl₂(diphos)₂]⁺. The room temperature magnetic moment is close to the theoretical value of 3.6 BM for spin-paired iron(IV).⁸ The lower values of 3.17 and 2.76 BM reported⁹ for [FeBr₂(diars)₂](BF₄)₂ and [FeCl₂(diars)₂](BF₄)₂, respectively, are probably due to iron(III) impurity, not tetragonal distortion as originally suggested,⁹ since we find a value of 3.35 BM for [FeCl₂(diars)₂](ReO₄)₂.

The first major difference in coordinating properties of diphos and diars occurs with manganese. Diphos reacts with anhydrous manganese(II) chloride in isopropyl alcohol to give yellow crystalline high-spin MnCl₂(diphos)₂ ($\mu_{\text{eff}} = 6.04$ BM), whereas under the same conditions diars fails to react, and only the adduct MnCl₂·2*i*-C₃H₇OH can be recovered.¹⁰ Oxidation of MnCl₂(diphos)₂ with (C₆H₅)₃C⁺PF₆⁻ in dichloromethane generates the orange high-spin d⁴ manganese(III) salt [MnCl₂(diphos)₂]PF₆ ($\mu_{\text{eff}} = 5.09$ BM), which undergoes reversible, one-electron electrochemical oxidation ($E = 0.72$ V vs. Ag|AgClO₄) in acetonitrile. The resulting high-spin manganese(IV) d³-complex [MnCl₂(diphos)₂]²⁺ can be isolated as its crystalline orange-brown perchlorate ($\mu_{\text{eff}} = 3.99$ BM) from nitric acid oxidation of the manganese(III) complex. These compounds are to our knowledge the first reported tertiary phosphine complexes of manganese in its higher oxidation states. Chromium(III) chloride reacts with diphos to form the reddish d³ cation, [CrCl₂(diphos)₂]⁺ ($\mu_{\text{eff}} = 3.89$ BM). Electrochemical reduction of this species demonstrates the presence of a strongly reducing chromium(II) species, [CrCl₂(diphos)₂]⁰; there is no chemical or electrochemical indication of a chromium(IV) complex.

The six-coordinate [Mⁿ⁺Cl₂(diphos)₂]ⁿ⁻² complexes appear to represent one of the most extensive series of isostructural complexes presently known for the first-row transition metals. Like their diars analogs, they appear to adopt a configuration in which the chlorine atoms are mutually trans. The electronic spectra of corresponding diphos and diars complexes are virtually identical in the visible spectral region except for band shifts to higher energies in the phosphine derivatives. For example, in methanol solution the d-d transition for the green d⁶ *trans*-[CoCl₂(diars)₂]⁺ ion at 16,390 cm⁻¹

(ϵ 85) is shifted in the purple *trans*-[CoCl₂(diphos)₂]⁺ ion to 17,790 cm⁻¹ (ϵ 78). This feature reflects the expected¹¹ stronger ligand field of the diphosphine compared with the diarsine. In general, the diphos complexes are chemically more robust in solution than their diars analogs, a feature which is most apparent in the manganese system.

The marked similarity in the coordinating abilities of diphos and diars is further demonstrated electrochemically by the observation that the six-coordinate species, [Mⁿ⁺Cl₂L₂]ⁿ⁻² (L = diphos, diars), undergo reversible one-electron redox reactions in acetonitrile solution by cyclic voltammetry. Electrochemically irreversible redox reactions are observed whenever there is a change in the coordination environment of the metal, e.g., in the reduction of a six-coordinate d⁷ species to a five-coordinate d⁸ species. The basic trend of the redox potentials appears to reflect the high relative stability of the low spin d⁶ (Fe^{II}, Co^{III}, Ni^{IV}) electron configuration and suggests that the electrons are added to or removed from orbitals which do not reside predominantly on the ligands but which have considerable metal character.¹² Interestingly, the redox potentials for corresponding diphos and diars complexes are generally very similar.¹³ Details will be reported in a subsequent communication.

Our results suggest that *o*-phenylenebis(dimethylphosphine) forms complexes in a wider range of formal oxidation states than either its arsenic analog or the more flexible bidentate ligand 1,2-bis(dimethylphosphino)ethane,¹⁴ presumably as a consequence of the combined effects of the strong σ -donor dimethylphosphino groups and the rigid *o*-phenylene backbone. We are investigating these aspects and extending to other transition metals the chemistry of this most versatile di(tertiary phosphine).

(11) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 1047 (1959); M. A. Bennett, R. J. H. Clark, and A. D. J. Goodwin, *Inorg. Chem.*, **6**, 1625 (1967).

(12) This is in agreement with the most recent conclusions based on esr studies of nickel(III)-diars complexes: P. T. Manoharan and M. T. Rogers, *J. Chem. Phys.*, **53**, 1682 (1970); P. K. Bernstein and H. B. Gray, *Inorg. Chem.*, **11**, 3035 (1972). For a contrary conclusion, see P. Kreisman, R. Marsh, J. R. Preer, and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 1067 (1968).

(13) A similar effect was observed with corresponding metal complexes of the 1,2-dithiolene and -diselenolene ligands, (CF₃)₂C₂S₂ and (CF₃)₂C₂Se₂, respectively: A. Davison and E. T. Shawl, *Inorg. Chem.*, **9**, 1920 (1970).

(14) G. Booth and J. Chatt, *J. Chem. Soc.*, 3238 (1965).

L. F. Warren, M. A. Bennett*

Research School of Chemistry, Australian National University
Canberra, A.C.T., Australia 2600

Received December 11, 1973

Book Reviews

Cannabis and Its Derivatives. Edited by W. D. M. PATON (University of Oxford) and J. CROWN (Institute for Study of Drug Dependence). Oxford University Press, London. 1973. xii + 198 pp. £4.00.

Marijuana. Edited by R. MECHOULAM (Hebrew University). Academic Press, New York, N. Y. 1973. xiv + 409 pp. \$24.50.

It is most timely that these two books on *Cannabis sativa* and

its active ingredients are available. After years of neglect, scientific research in this area has finally again become fashionable—no doubt because of the impact cannabis abuse has had, especially in Western societies. The lay person or politician will find no easy answers to the questions of long term harm vs. benefit or legalization vs. severe restriction of pot. However, much new data are summarized in somewhat different formats in these two books.

The first, edited by Paton and Crown, represents the proceedings of a symposium held in London in May 1972. Some 26 well-known scientists and administrators participated to review the pharmacology and experimental psychology of cannabis, especially the cannabinoids. A total of 13 major chapters and one for brief presentations covers each specialist's work plus descriptions of the NIMH program and UN reference samples. Hence, this book is more of a status report of research completed or in progress in relation to the literature.

The second book is appropriately edited by Mechoulam, who with Gaoni in 1964 first isolated in pure form the putative active ingredient of marijuana, Δ^1 -THC. This book represents a more thorough review of the chemistry, pharmacology, metabolism, and clinical effects of marijuana by seven scientists, five of whom also contributed to the first book. However, the overlap is complementary and not redundant. In such a rapidly advancing field it is almost impossible to keep up. Many of the writers in the second book had to add addendums to make their contributions more timely. While it is easy to point out that both volumes have some areas of research inadequately reviewed (such as the section on biogenic amines has an insufficient review of the interaction of Δ^1 -THC with acetylcholine), it would be a gross injustice not to compliment the contributors and editors on jobs well done. I personally am most appreciative for I learned much that I did not know, in spite of being active in this field.

The Mechoulam book uses only the terminology of *Chemical Abstracts* for Δ^1 -THC based on the monoterpene numbering system. On the other hand, the Paton and Crown book allowed both that and the formal system for numbering pyrans to be used; hence, Δ^1 -THC = Δ^8 -THC and Δ^6 -THC = Δ^8 -THC, etc. Hopefully, some of our chemist friends will pressure most other scientists to adopt *Chemical Abstracts* terminology in due time.

When two superb scientists—Mechoulam on the chemical side and Paton on the pharmacological side—invite equally competent colleagues and investigators to join them in reviewing the literature, the result is obviously at a high level and almost free of bias in discussing an emotionally loaded topic. Both books are recommended to all chemistry, pharmacy, and medical libraries and to those interested in the scientific aspects of marijuana. It is too bad that the price of these books is so high, for I would expect a rather large printing, especially of the second book.

E. F. Domino, *University of Michigan*

Vinyl and Diene Monomers. Part Three. Edited by EDWARD C. LEONARD (Kraftco Corp., Glenview, Ill.). Wiley-Interscience, New York, N. Y. 1971. xi + 498 pp. \$26.75.

In fact, all three parts of Leonard's "Vinyl and Diene Monomers" constitute Volume 24 of "High Polymers," edited by H. Mark, C. S. Marvel, H. W. Melville, and P. J. Flory.

This book emphasizes the commercial manufacture, laboratory synthesis, purification, and physical and chemical properties of vinyl and some diene monomers. Since the edition of Schildknecht's "Vinyl and Related Polymers" in 1954, there has been no systematic treatment of these monomers in a single place. It is the task of the present book to provide up-to-date and comprehensive treatise on the subject. However, no reference exceeds the year 1967. For the sake of unity we will include also the contents of the first two parts, as follows.

Part One describes the manufacture, chemical and physical properties, and polymerization behavior of some of the commercially important vinyl monomers, such as acrylonitrile, acrylamides, acrylic and methacrylic acids and the related esters, vinyl acetate, and the higher vinyl esters and vinyl ethers.

Part Two includes styrene, butadiene, ethylene, isobutylene, isoprene, and chloroprene.

Part Three describes the manufacture, physical and chemical properties, storage and handling, and polymerization, polymer characteristics, and polymer applications of vinyl and vinylidene chloride, the fluorovinyl monomers, and certain miscellaneous monomers. This last includes *N*-vinyl compounds, vinylpyridines,

vinylsilanes, acrolein, methacrolein and vinyl ketones, vinyl sulfur compounds, vinyl phosphorus compounds, vinylfuran, and vinylthiophene and certain substituted styrenes, in total 100 different monomers. This last part of the book contains a cumulative subject index of Parts I-III. There are 2720 references cited only in Part Three, but again very few of them are dated later than 1966.

In spite of this criticism, there is no other place where so much information in this field has been gathered together. To this end the editor and the authors of the individual chapters have been successful.

Ioan I. Negulescu, *Polymer Science & Engineering University of Massachusetts*

Essays in Chemistry. Volume 4. Edited by J. N. BRADLEY (University of Essex, U. K.), R. D. GILLARD, and R. F. HUDSON (University Chemical Laboratories, University of Kent at Canterbury, U. K.). Academic Press, London and New York. 1972. x + 147 pp. £2 (paperback).

This fourth volume in the series meets the hoping of the editors, *i.e.*, to provide genuine teaching matter for final year undergraduates, looking at the peculiar topics which in the average review of modern work are presented at a level high above that of the non-specialist. However, the material presented, at least in this volume, is very useful in informing the graduate chemist too in such areas as inorganic chemistry (M. J. Taylor, Variable Valence as a Property of the Main Group Metals—An Account of Low Oxidation States in the Zinc, Aluminum, Tin and Antimony Sub-groups), organic chemistry (T. M. Cresp and M. V. Sargent, Non-benzenoid Monocyclic Conjugated Systems), and analytical chemistry (B. C. Gilbert, Application of Electron Spin Resonance Spectroscopy to the Study of Free Radicals).

In addition to these topics, the present volume contains two other essays signed by A. M. North (The Importance of the Molecular Motion in Polymers) and by G. T. Young (The Chemical Synthesis of Peptides and Proteins).

Each contribution is clearly made in order to accomplish maximum understanding, so that this book is fully recommended to readers interested in one of the above subjects.

Ioan I. Negulescu, *Polymer Science & Engineering University of Massachusetts*

Macromolecular Syntheses. Volume 4. Edited by W. J. BAILEY (University of Maryland). Wiley-Interscience, New York, N. Y. 1972. viii + 199 pp. \$14.95.

Patterned after "Organic Syntheses," this series is a collection of procedures for the preparation of specific polymers that are of general interest or that serve to illustrate useful preparative techniques. The submitted preparations give, where appropriate, detailed experimental directions for monomer synthesis and purification, polymerization, polymer purification, and characterization, and indicate alternative methods of preparation with relevant literature citations. The procedures are checked in the laboratory by independent investigators.

This volume contains forty-one procedures which encompass a variety of initiation methods for the preparation of diverse addition and condensation polymers. The spectrum includes: photo-initiation, cation-radical initiation, ring-opening polymerization, solid-phase polypeptide synthesis; the preparation of "living" polymer, block copolymers, alternating copolymers, metal-containing and stereoregular polymers. Some examples are: copolymers from styrene and ethylene oxide, dimethylketene and acetone, isoprene and maleic anhydride, styrene and methyl methacrylate, vinyl chloride and vinylidene chloride; homopolymers of 1,3-cyclohexadiene, α -phenylethyl isocyanide, phthalaldehyde, 9-vinyladenine, 5-vinylpyridinium salts, ferrocenylmethyl acrylate; and isotactic polymers of 1-butene, epichlorohydrin, phenyl glycidyl ether.

There is a cumulative index for Volumes 1 through 4.

Daniel T. Longone, *University of Michigan*