

even the β -O-Si interaction proposed by Brook and co-workers.² The latter effect, however, is probably small compared to the C-Si π -bonding considered above. For reasonable values of bond distances and angles in silyl carbonyl compounds, overlap of 3d silicon orbitals is expected to be larger with the carbon π -orbital than with the oxygen lone pairs.⁶

Extension of the approach given above to other chromophoric groups can easily be carried out. For example, class 2 substituents on C=C chromophores should produce a spectral shift of the same type as found for class 1 substituents, decreasing the energy of the π - π^* transitions. A further prediction from our theory is that compounds with a boron atom attached

(6) Such β -interactions may, of course, be important in lowering the energies of transition states, *i.e.*, for rearrangement reactions.^{3,7}

(7) A. G. Brook, *J. Org. Chem.*, **25**, 1072 (1960); *J. Am. Chem. Soc.*, **80**, 1886 (1958); A. G. Brook, C. M. Warner, and M. McGriskin, *ibid.*, **81**, 981 (1959); A. G. Brook and W. W. Limburg, *ibid.*, **85**, 832 (1963).

directly to a carbonyl group (such as $R_2BCOC_6H_5$), when they are synthesized, will show transitions above 400 $m\mu$ and so will appear visibly colored.^{8,9}

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(8) Observations on α -boryl ketones should provide a good test of theory, for β π -bonding of the type suggested by Brook² should be negligible to the p -orbital on boron.

(9) NOTE ADDED IN PROOF.—A similar, though less detailed, explanation for the spectral properties of α -silyl ketones has recently been advanced independently by L. E. Orgel, quoted in "Volatile Silicon Compounds," E. B. Ebsworth, Pergamon Press, Ltd., Oxford, 1963, p. 81.

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Book Reviews

Absorption Spectra and Chemical Bonding. By C. K. JØRGENSEN. Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962. 347 pp. 14 × 22 cm. Price, \$10.00.

Probably the largest amount and certainly the dullest¹ prose being written today is the scientific, so-called "literature." As a notable exception, one might cite the works of Christian Klíxbüll Jørgensen. Former astronomer and sometime symbolic logician, he writes in a style unmistakably his own and often refreshing in its dissimilarity to the usual run of insipid syntax. Of course, roses (excepting Zephirine Drouhin and a few others) come equipped with thorns; that is, one seldom finds unadulterated virtue, with no catches, in this world. Some of Jørgensen's prose seems inspired by the stream of consciousness school. Both in his style of writing and in his scientific thinking he is *durchaus eigentümlich*, with all the good and bad consequences this may have. In the volume under review, his *Eigentümlichkeit* is much in evidence.

I cannot but applaud Jørgensen's stated purpose of trying "to win over some of the mental inertia which has caused most chemists to think of chemical bonds in terms of a valency-bond and hybridization description." I am afraid, though, that the preaching which follows will be mainly to the already converted, because of the pell-mell attack on the subject matter. The presentation has indeed some logic of its own, but not, I fear, the sort which is appropriate for instructing the uninitiated.

Having offered these animadversions, I hasten to say also that this book has its attractions for the serious (but not entirely naive) student of coordination chemistry. It contains a great deal of interesting factual information and many stimulating and unusual observations. It is also noteworthy for its eclectic approach; probably no element in the periodic table goes unmentioned, and all aspects of the subject, as summarized in the title, are discussed to some extent.

(1) Not, however, the most abominable, for which due acknowledgment may be given to the social "sciences" and "communications sciences."

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Progress in Inorganic Chemistry. Volume 4. Edited by F. A. COTTON. Interscience Publishers, Division of John Wiley and Sons, Inc., New York, N. Y., 1962. 540 pp. 15 × 23 cm. Price, \$15.00.

The fourth volume of the series "Progress in Inorganic Chemistry" contains these seven articles: (1) The Polymorphic Modifications of Arsenic Trioxide, by K. A. Becker, K. Plieth, and I. N. Stanski; (2) The Nephelauxetic Series, by C. K. Jørgensen; (3) Peroxides, Superoxides, and Ozonides of the Metals of Groups Ia, IIa, and IIb, by N. Vannerberg; (4) Isopolytungstates, by D. L. Kepert; (5) Phosphonitrile Polymers, by C. D. Schmulbach; (6) The *trans* Effect in Metal Complexes, by F. Basolo and R. G. Pearson; and (7) The Coupling of Vibrational and Electronic Motions in Degenerate Electronic States of Inorganic Complexes. Part II. States of Triple Degeneracy and Systems of Lower Symmetry, by A. D. Liehr.

This reviewer cannot imagine the inorganic chemist capable of digesting the entire seven-course meal. Articles 1, 3, 4, and 5 are mainly descriptive. They are well written and usefully referenced.

Articles 2, 6, and 7 are more theoretical in the order Basolo and Pearson (mildly theoretical), Jørgensen (highly theoretical), and Liehr (whew!). The account of the *trans* effect is very readable and complete in every detail. The article on the nephelauxetic series is well worth reading, although it will be rough going for most inorganic chemists. It is by far the most complete treatment of the subject yet presented. I think it is fair to say that the article overemphasizes many of the author's own prejudices concerning the electronic structures of transition metal complexes. This is not unexpected since he and C. Schäfer gave us the nephelauxetic fever in the first place.

The Liehr article is wasted in this series, being too theoretical for inorganic chemists. It should have been published in one of the volumes read mainly by chemical physicists.

Finally, I should mention that a very useful cumulative index (covering volumes 1-4) appears on p. 577.

In summary, "Progress in Inorganic Chemistry" continues to provide excellent critical reviews of interest to inorganic

chemists. The price of volume 4 is \$15.00, which means that the series will continue to be localized in libraries.

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Reactions of Coordinated Ligands and Homogeneous Catalysis. Advances in Chemistry Series, No. 37. Edited by DARYLE H. BUSCH. Preface by JOHN C. BAILAR, JR. The American Chemical Society, Washington, D. C., 1963. 15.5 × 23.5 cm. vii + 255 pp. Price, \$7.00 paperback.

"Reactions of Coordinated Ligands and Homogeneous Catalysis" is a collection of eighteen papers, seventeen of which were selected from a symposium which was held at the 141st National Meeting of the American Chemical Society in Washington, D. C., from March 20 to March 29, 1962. Professor Busch's opening lecture on the same topic is included as an introductory paper. Several very interesting papers from the symposium are missing in this record and several are greatly expanded and much more complete than they were at the time of the original presentation.

A wide range of subject matter is included in this book, as it was in the symposium. On the one hand we have the excellent papers of Myron L. Bender and Gunther L. Eichhorn on metal ion catalysis in nucleophilic organic reactions and in biological systems, and on the other, the more traditionally inorganic papers such as "Oxidation of Oxalato Complexes of Chromium(III) by Cerium(IV) in Aqueous Sulfuric Acid," by Teggin, *et al.* It seems to this reviewer that this variety is one of the attractive features of the book as it was in the case of the symposium. Thus, persons working in various fields, but interested in reactions of coordinated ligands, were brought together at the meetings and surveys of a wide spectrum of efforts are included in the publication.

The introductory survey by Daryle H. Busch defined the symposium and gives the reader a brief resume of work in each of the areas to be covered in the papers which follow.

Some of the papers are of the review type and give a general description of recent advances in a given field of interest. The paper on metal-cyclopentadienyls and metal-arenes by Marvin D. Rausch is an example. It provides an excellent survey, which is very useful to persons not currently active in metal-cyclopentadienyl or arene chemistry. Other papers are specific and are devoted to reporting some recent experiments and new results in a specialized area. The paper by McCarley, *et al.*, on the reaction between pyridine and pentavalent niobium (which it reduces) and tantalum (which it does not) represents a report of new information and experimental results, although most of this work has now appeared in the literature (*Inorg. Chem.*, 2, 540, 547 (1963)).

Some of the authors have provided extensive and useful bibliographies, others cite only a few salient articles. Those giving specifics and new results, of course, have the shorter lists.

The inevitably few typographical errors appear, but by and large they are obvious and the correct meanings are clear. For example, in the second paper by Busch A_{∞} comes out as A_{∞} and the abbreviation for liter is L. In the paper by Leussing and Tischer m_{μ} appears as M_{μ} and in McCarley, *et al.*, M and X, meaning metal and halogen, are italicized in Table I. An incorrect name is used repeatedly in the paper "Catalytic Hydrogenation by Pentacyanocobaltate(II)," wherein $\text{Co}(\text{OH})\text{CN}_5^{3-}$ is called hydroxypentacyanocobaltate(III): hydroxo is the correct name for ligand OH^- (*J. Am. Chem. Soc.*, 82, 5539 (1960)). The paper by Leussing and Tischer is marred by missing and misplaced parentheses in many of the formulas.

This reviewer finds that most of the papers are clear and well written and particularly would like to applaud the writing of Bender, Eichhorn, and Rausch. On the whole this is an interesting, if incomplete, record of a very successful symposium and it should be useful as supplementary reading in a course in coordination chemistry and as an instructive evening's reading to the

Mass Spectrometry: Organic Chemical Applications. By KLAUS BIEMAN, Massachusetts Institute of Technology. McGraw-Hill Book Co., Inc., 330 West 42nd Street, New York 36, N. Y. 1962. xii + 370 pp. 15 × 22.5 cm. Price, \$13.75.

This very well written book is, as stated by the author, clearly written by an organic chemist with the aim of acquainting other organic chemists with the usefulness of mass spectrometry in solving simple and complex problems in organic chemistry. A book specifically designed to do the same thing for inorganic chemists has not yet appeared. However, the principle of applying mass spectrometric techniques as presented here, with or without the use of isotopically substituted molecules, should be of interest to inorganic chemists. Those particularly concerned with problems of structural analysis can read that portion of the book with considerable profit.

In general, the book fulfills the author's aim in an admirable fashion. The major portion includes the chapters on empirical observations and conclusions concerning the nature and characteristics of mass spectra of organic molecules, the methods for simplifying complex mass spectral data and identifying components of structure, the effects and usefulness of isotopically labeled molecules, and the several chapters describing spectra and structural identification of fatty acids and related substances, amino acids and peptides, alkaloids, steroids and related substances, and a few miscellaneous classes. The author is one of the leading experts in the application of mass spectrometry to these areas and presents interesting graphical examples with explanatory text to illustrate the usefulness (and difficulties) of the method. A commendable effort is made to include previously unpublished results (at time of printing), particularly from the author's laboratory.

The author elects to treat the two chapters on instrumentation and operating techniques in a brief and sometimes superficial fashion, giving the impression that the purchase of a reliable instrument is all that is required for the successful pursuit of projects such as he describes. It is natural for the author to minimize his considerable skill and that of his colleagues. However, the reader should be cautioned.

A more specific but equally significant lapse is the general reference to relative nuclidic masses of C^{12} , O^{16} , N^{14} , etc., as "atomic weights." This leads to statements, such as on p. 3 of the Introduction, "... the seemingly straightforward interpretation of the nature of a peak by simply adding atomic weights..." The "atomic weights" table given on the back cover actually refers to the 1961 *Nuclidic Mass Table* by Konig, Mattach, and Wapstra. As inorganic chemists will appreciate, the mass spectrometer separates the various nuclidic masses (except for anisotopic elements) and permits the measurement of their relative abundances so that atomic weights of the element can be calculated, if desired.

This reviewer saw no typographical errors except possibly for the use of "J" as the symbol for iodine in the above table. The many complicated structural formulas could not be examined expertly, but errors if any must be few. There are fewer literature references than one might expect in such a work. This is due in part to the specific and very modern nature of the subject and in part to the author's efforts to include much of the up-to-date, previously unpublished work. The general arrangement of the book is good and except for the above criticisms makes very pleasant and instructive reading.

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