

at 490  $m\mu$  ( $\epsilon$  5000) for a monomeric, pentavalent molybdenum acetylacetonate,  $\text{Mo}(\text{OH})_3(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ .<sup>4</sup> Although the absorption intensities of the brown molybdenyl bisacetylacetonate indicate charge transfer, it is proposed that the shoulder at approximately 400  $m\mu$  ( $\nu$ , 25,000  $\text{cm}^{-1}$ ) is due to the  $(d_{xy})^1$  to  $(d_{x^2-y^2})^1$  transition where the observed absorption is artificially high because of the large adjacent charge transfer peaks. In their ligand field molecular orbital analysis of  $[\text{MoOCl}_5]^{2-}$ , Gray and associates<sup>5</sup> state that this  $t_{2g} \rightarrow e_g$  transition ( ${}^2B_2 \rightarrow {}^2B_1$  by their M.O. symbolism) is the only electronic transition localized in the  $x$ - $y$  plane perpendicular to the  $\text{Mo}=\text{O}$  axis. This is the peak which is strongly enhanced by the aqueous dilution of  $[\text{MoOCl}_5]^{2-}$  in hydrochloric acid, and Haight<sup>2</sup> believes that this intensification is due to dimerization by oxygen bridging to form  $[\text{OCl}_4\text{Mo}-\text{O}-\text{MoCl}_4\text{O}]^{4-}$ . He suggests that one of the four equatorial chlorides can be substituted with the bridge oxygen to intensify the absorption without changing the energy of the transition. Assuming the preservation of octahedral coordination, the analogous *cis* configuration for the brown molybdenyl bisacetylacetonate, as an oxygen-bridged dimer,  $[(\text{C}_5\text{H}_7\text{O}_2)_2\text{Mo}=\text{O}]_2\text{O}$ , would have a non-linear  $\text{O}=\text{Mo}-\text{O}$  group. This bent, non-equivalent molybdenum-oxygen bonding increases

(4) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 4570 (1962).

the complexity of the infrared absorption in the molybdenum-oxygen sensitive region ( $<1000 \text{ cm}^{-1}$ ) compared to  $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ . It is difficult to separate ligand absorptions completely from molybdenum-oxygen absorptions, especially in the absence of comparable inorganic, oxygen-bridged molybdenum compounds. By comparison with  $\text{Mo}(\text{C}_5\text{H}_7\text{O}_2)_3$  and  $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ , however, it appears that strong absorption around 435  $\text{cm}^{-1}$  is sufficiently distinct to be attributed to the  $\text{Mo}-\text{O}-\text{Mo}$  group.

The apparent cause of diamagnetism in this new, dimeric molybdenum(V) complex is  $d\pi-p\pi$  interaction along the proposed  $\text{Mo}-\text{O}-\text{Mo}$  bridge. This is believed analogous to the situation in diamagnetic  $(\text{Ru}_2\text{Cl}_{10}\text{O})^{4-}$ , which is known to have a linear  $\text{Ru}-\text{O}-\text{Ru}$  arrangement with  $\text{Ru}-\text{O}$  bond lengths shorter than those expected from single bond radii.<sup>5</sup> Dunitz and Orgel<sup>6</sup> gave an M.O. interpretation of this structure and the diamagnetism to demonstrate the possibility of  $\pi$ -bonding in the  $\text{Ru}-\text{O}-\text{Ru}$  group.

(5) A. M. Mathieson, D. P. Mellor, and N. C. Stephenson, *Acta Cryst.* **5**, 185 (1952).

(6) J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 2594 (1953).

CLIMAX MOLYBDENUM COMPANY  
OF MICHIGAN  
RESEARCH LABORATORY  
DETROIT, MICHIGAN

MELVIN L. LARSON  
FRED W. MOORE

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## Book Reviews

**An Introduction to the Chemistry of Complex Compounds.** By A. A. GRINBERG, Professor of Chemistry, Lensovet Institute of Technology, Leningrad. Second Edition, 1951. Translated by Mrs. J. R. Leach. Edited by D. H. Busch and R. F. Trimble, Jr. Pergamon Press, Ltd., London, 1962. Distributed in the U. S. by Addison-Wesley Publishing Co., Inc., Reading, Mass. xxi + 363 pp. 15.5  $\times$  23.5 cm. Price, \$15.00

The translation of the Second Edition of Grinberg's monograph on coordination compounds marks the first appearance in English of an important Russian work dealing with coordination compounds. Although the author does not say so in his preface, it seems clear that the book is intended as a fairly thorough introductory textbook.

Judging from the general readability of the book, the translator and editor have done an excellent job. Editorial comment is inserted in the text in a number of places in the form of footnotes. The device is employed with discretion and is used to good advantage. There are few errors of any note.

Chapter I provides an introduction to coordination chemistry through a discussion of complex compounds of which  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , and  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  are prototypes. The experimental observations relating both to methods of preparation and the properties of the compounds are presented in a clear and interesting manner. In Chapter II an account is given of the development of a theory of coordination. The stereochemical consequences of Werner's spatial models are explored in Chapter III in a discussion of geometrical and optical isomerism, resolution of optically active complex compounds, and anomalous rotatory dispersion. Some attention is given also to the transformations of optically active complex substances in

solution. Chapter IV is a continuation of the treatment of compounds with coordination number six, while Chapter V deals with compounds with coordination number four.

The various types of isomerism (other than geometrical and optical) observed in complex compounds are discussed in Chapter VI. Chapter VII contains an excellent descriptive summary of the *trans* effect. Acid-base properties, oxidation-reduction behavior, and stability constants are dealt with in Chapter IX. Polynuclear complexes and so-called inner complexes (acetylacetonates, dioxanates, etc.) are described in Chapter X along with a few other special topics. The book concludes with a survey of the complex-forming properties of elements in relation to the periodic table. A single chapter (VII) is devoted to theoretical aspects of complex formation.

Grinberg is at his best in relating, in a nice historical context, the experimental facts about the preparations and properties of complexes. The story which unfolds is both interesting and instructive. One cannot but be impressed with the contributions of the early workers in this area of chemistry, particularly with Werner's uncanny insights. In the treatment of the literature since perhaps 1936 the work of the Russian chemists is rather over-emphasized at the expense of English and American work. The imbalance has, however, been partially corrected by a supplementary bibliography provided by the editors.

The book is seriously deficient in its treatment of the more theoretical aspects of coordination chemistry. A reference to the Second Edition of Pauling's "Nature of the Chemical Bond" is the sole reference in the author's bibliography to a work which deals specifically in valence bond terms with the nature of bonding in complexes. Pauling's treatment is presented in the text, but very inadequately. There is, of course, no mention made of

ligand field theory. The editors in their preface state their belief that Grinberg's book might well serve to fill the need for an intermediate level textbook dealing with coordination compounds. This is a good deal to look for in a book which, in addition to being twelve years old, possesses the shortcomings alluded to above. On the other hand, it could be supplemented in practice by a suitable choice of additional readings. The book has very evident merits, and provides a stimulating introduction to an important area of chemistry.

NOYES CHEMICAL LABORATORY  
UNIVERSITY OF ILLINOIS  
URBANA, ILLINOIS

T. L. BROWN

**The Mössbauer Effect.** A Review—with a Collection of Reprints. By HANS FRAUENFELDER, University of Illinois, Urbana, Ill. W. A. Benjamin, Inc., 2465 Broadway, New York, N. Y., 1962. xiv + 336 pp. 15 × 23 cm. Price, \$3.95.

Despite the earnest protestations of the discoverer, the recoilless resonance absorption of  $\gamma$ -radiation has become known as the Mössbauer effect. The present volume by Frauenfelder is devoted to this effect, which promises to be a tool of unusual precision and sensitivity in investigations of solid state and nuclear physics, magnetism, chemical bonding, molecular structure, and a variety of related subjects. As part of the Frontiers in Physics Series, this book is somewhat unusual, since it provides both a review of the field to the fall of 1961 and a collection of 39 reprints of papers, most of which appear in their original format.

Following a Foreword and Preface, six chapters provide the reader with an introduction to the general aspects of resonance in  $\gamma$ -ray emission and absorption and are organized in a manner appropriate to the "Lecture Note" character of the first half of this volume. Chapter 1 is a brief introduction to resonance fluorescence and furnishes a modest historical framework into which Mössbauer's 1957 studies can be fitted. Chapter 2 provides a simple theoretical treatment of lattice vibrations and is followed by a brief discussion of experimental procedures (and pitfalls) in Chapter 3. The next three chapters are devoted, respectively, to applications of the Mössbauer effect to nuclear physics, general physics (the gravitational red shift experiments, uncertainty relationship, polarization, etc.), and solid state physics. Chapter 7 is a bibliography of papers on the Mössbauer effect and provides a bridge to the remainder of the book, which consists of reprints and one original paper. The value of the individual reprints depends, of course, on the interests and orientation of the reader, but they range from such fundamental contributions as the original paper by Mössbauer on work with  $\text{Ir}^{191}$  and the first discussion of the isomer shift by Kistner and Sunyar to much more esoteric treatments of theoretical topics which will be of lesser interest except to the specialist. Except for the magnetism paper by Wertheim and a few paragraphs scattered among various other papers, very little in the way of experimental details can be extracted from this collection. In this area, the reader is left very much on his own. Concerning the preparation of narrow-line sources, for example, the best a physicist can suggest is "find yourself a good chemist."

In typographical format, the "Lecture Note" portion of this volume is easy to read; the illustrations are clear and equations are well displayed (and numbered sequentially throughout). Not quite so cheering is the prospect of tackling several of the reprints, which—due to the necessary reduction in size from the usual 8 × 10.5 in. format of, for instance, the *Physical Review* to the 6 × 9 in. dimensions of this book—can only be adequately read under strong illumination and with good eyesight. A final weak point, literally, is the binding, which—as is characteristic of paperbacks—gives way as soon as one has once gone through the book and attempts a re-reading. Repeated reference to this volume undoubtedly will result in a battle-worn copy replete with broken spine, even under the most careful usage.

Any judgment of the value of this paperback volume must be

made in the light of the more recent reviews by Mössbauer, by Boyle and Hall, and by others. Clearly, no monograph which goes through the time-consuming ministrations of the book publisher can compete in timeliness with more rapid channels of communication. Nonetheless this volume deserves the serious attention among chemists of those who teach in the areas of nuclear and radiochemistry, the solid state and chemical bonding, as well as those whose research interests lie in these fields. Among the latter, especially, the Frauenfelder book will provide a welcome introduction into the fundamental theory, practice, and literature of a very rapidly growing technique.

R. G. WRIGHT LABORATORY OF CHEMISTRY  
RUTGERS, THE STATE UNIVERSITY  
NEW BRUNSWICK, NEW JERSEY

ROLFE H. HERBER

**Progress in Stereochemistry.** Vol. 3. Edited by P. B. D. DE LA MARE and W. KLYNE, University of London. Butterworth, Inc., 7235 Wisconsin Avenue, Washington 14, D. C., 1962. viii + 368 pp. 15.5 × 25.0 cm. Price, \$13.50.

This volume, like its predecessors in the series, describes aspects of stereoisomerism in both inorganic and organic systems. Of the eight chapters, four deal exclusively with strictly organic topics. Two, "Nuclear Magnetic Resonance and Stereochemistry" (R. J. Gillespie and R. F. M. White) and "Steric Effects in Acid-Base Reactions" (V. Gold), treat both inorganic and organic topics. Only two, "The Stereochemistry of Some Elements of Group III" (D. C. Bradley) and "Steric Problems in the Hydration of Ions in Solution" (H. Taube), deal with topics that are rigorously inorganic in nature.

The summary on group III covers all of the elements of the boron family in considerable detail and provides an excellent correlation of published data for a variety of compound types. The treatment of lower oxidation states is particularly useful since it brings together otherwise rather widely scattered information. The emphasis is modern, and the documentation up to date. Interpretation of physical data as an indication of structure is extensive and adequate.

The discussion of hydration in solution represents a particularly good compilation and correlation of a very substantial body of information. Both a description of experimental approaches and an interpretation of the data they provide are included. The treatment is not only a summary of published results but also an extensive discussion of the meaning and significance of these results. Again the choice of references is both timely and adequate.

The chapter on nuclear magnetic resonance provides first a general introductory background and then describes specific published applications. The inorganic systems discussed include aluminum trimethyl dimer; boron hydrides and their derivatives; group IV, V, VI, and VII fluorides; and selected phosphorus compounds. In most instances, the data cited are more supportive of structures deduced from other types of data than primarily indicative. However, the importance of n.m.r. measurements in elucidating stereoisomerism is clearly and emphatically delineated. Although the chapter on acids and bases is organically oriented, many of the reactions described involve inorganic acids. To the extent that correlations of the effects of organic structures upon these reactions are emphasized, much of this material will be of interest to the inorganic chemist. Except to mention references to catalysis by inorganic systems in controlling the stereochemistry of certain addition polymers, it does not appear pertinent to discuss the remaining chapters of the book.

The book is recommended to all who are interested in structure and stereochemistry. The chapters are uniformly well written, well documented, and modern. The volume is attractively arranged and printed. Very few errors were noted.

NOYES CHEMICAL LABORATORY  
UNIVERSITY OF ILLINOIS  
URBANA, ILLINOIS

THERALD MOELLER