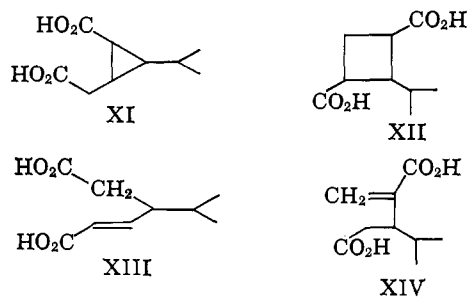


Aside from the transformations already discussed, permanganate-periodate degradation¹³ of X, followed by hypobromite oxidation of the resultant methyl ketone, gave the crystalline acid XI, m.p. 131–132° (previously described as XII). Esterification followed by a base-catalyzed reverse Michael addition and hydrolysis gave XIII (rather than the reported isomeric acid, XIV). It should be noted that XIII (as well as



XIV) would be expected to give isopropylsuccinic acid upon oxidative ozonolysis, as has been observed.² However, hydrogenation of XIII gave 3-isopropyladipic acid¹⁴ (m.p. and m.m.p. 79–80°, infrared spectrum superimposable on that of an authentic sample). Infrared spectra and gas chromatographic retention times of the corresponding dimethyl esters were also identical. These results confirm the structure of XIII and exclude the original structural assignment.

Ultraviolet and n.m.r. absorption spectra lend further support to these conclusions. Thus, X shows $\lambda_{\text{max}}^{\text{cyclohexane}}$ 205 m μ (ϵ 5070), characteristic of many vinylcyclopropanes,¹⁵ and a single broad proton absorption, attributable to the cyclopropyl hydrogen at C-6, at τ 10.08.

Although it may be concluded that a synthesis of the first bicyclo[2.1.1]hexene remains to be realized,¹² it is interesting to note that the original clue to this circumstance (absence of a resolved isopropyl doublet) was, in fact, irrelevant.¹⁶

We plan to prepare the full details of both this synthetic and degradative work for publication in the near future.

(12) These results were presented in part by Prof. W. G. Dauben at the 19th National Symposium on Organic Chemistry in Tempe, Arizona, June 14–17, 1965.

(13) R. Lemieux and R. von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).

(14) C. G. Overberger, A. Fischman, C. W. Roberts, L. N. Arond, and J. Lal, *J. Am. Chem. Soc.*, **73**, 2540 (1951).

(15) We are indebted to Professor W. G. Dauben for measuring this ultraviolet absorption spectrum, as well as for comparison of the result with those obtained from many similar chromophores.

(16) This spectral feature is evidently not an infallible diagnostic tool. For an ominous comment on this type of error, see T. S. Eliot, "Murder in the Cathedral," Harcourt, Brace and Company, New York, 1935, p. 44.

(17) Public Health Service Postdoctoral Fellow, 1964–1965.

Jerrold Meinwald, Albrecht Eckell, Karen L. Erickson¹⁷

Department of Chemistry, Cornell University
Ithaca, New York 14850

Received June 28, 1965

A Stable Paramagnetic Complex of Gold¹

Sir:

No paramagnetic compound of gold in the formal oxidation state II hitherto has been isolated in pure

(1) Support from the National Science Foundation is gratefully acknowledged.

form and fully characterized.^{2–4} Known compounds having the appropriate stoichiometry are diamagnetic, and in two cases have been shown by X-ray diffraction studies to consist of distinguishable Au(I) and Au(III) units.^{5,6} An electron spin resonance spectrum which almost certainly corresponds to the gold(II) diethyldithiocarbamate complex in solution has been reported,⁷ but the compound could not be isolated. Rich and Taube have presented⁸ convincing kinetic evidence for the transient existence of a complex of Au(II) in aqueous solution as a result of one-electron reduction of AuCl₄[−]. Very recently MacCragh and Koski have reported⁹ the e.s.r. and optical spectra of gold(II) phthalocyanine. Although the compound was not obtained completely free of unspecified organic components and no magnetic moment data were given, there is little doubt that the reported sample contained Au(II). We now report the isolation and full characterization of a monomeric, paramagnetic Au(II) complex.

The complex [(n-C₄H₉)₄N][Au(mnt)₂]¹⁰ shows a reversible one-electron polarographic reduction wave in DMF at −0.961 v.¹¹ The reduction of this complex with [(n-C₄H₉)₄N]BH₄ in carefully degassed THF solution at low temperature gives in small yield the light green, microcrystalline complex [(n-C₄H₉)₄N]₂[Au(mnt)₂].¹² The poor yield is presumed to be due in part to further reduction of the Au(II) complex by the boron hydride by-products of the initial reaction; the reaction was carried out under the lowest possible pressure in order to remove as much as possible of the boron hydride.

The solid is not noticeably affected by standing for short periods in contact with air. Solutions are quickly oxidized by air to regenerate the red color of the monoanionic complex. In the absence of air, solutions retain their green color indefinitely; the complex shows no tendency to disproportionate to Au(I) and Au(III).

In solution the complex shows an e.s.r. spectrum consisting of four equally spaced, equally intense lines. Four lines are expected from electron-metal-nucleus interaction since gold in natural abundance is 100% ¹⁹⁷Au with $I = 3/2$. The g value in 2:1 DMF–diglyme is 2.009, and the hyperfine constant $A_{\text{av}}(^{197}\text{Au})$ is 41.7 gauss; for the gold(II) diethyldithiocarbamate complex⁷ in benzene solution, $g = 2.040$, $A_{\text{av}}(^{197}\text{Au}) = 29.4$ gauss. The conductance of the [(n-C₄H₉)₄N]₂[Au(mnt)₂] com-

(2) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Division, John Wiley and Sons, Inc., New York, N.Y., 1962, p. 862.

(3) A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford University Press, London, 1962, p. 857.

(4) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 210 (1964).

(5) N. Elliott and L. Pauling, *J. Am. Chem. Soc.*, **60**, 1846 (1938).

(6) F. H. Brain, C. S. Gibson, J. A. J. Jarvis, R. F. Phillips, H. M. Powell, and A. Tyabji, *J. Chem. Soc.*, 3686 (1952).

(7) T. Vännegard and S. Åkerström, *Nature*, **184**, 183 (1959).

(8) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 6 (1954).

(9) A. MacCragh and W. S. Koski, *J. Am. Chem. Soc.*, **87**, 2496 (1965).

(10) The abbreviation mnt refers to the ligand maleonitriledithiolate; see H. B. Gray, *Prog. Transition Metal Chem.*, **1**, in press, and references therein.

(11) Relative to Ag/AgClO₄ electrode; we thank Mr. R. Williams for assistance.

(12) *Anal. Calcd.* for C₄₀H₇₈N₆S₄Au: C, 49.91; H, 7.54; N, 8.73; S, 13.33. *Found:* C, 50.57, 49.80; H, 7.77, 7.55; N, 8.43, 8.48; S, 13.62, 12.95.

(13) Alfred P. Sloan Research Fellow, 1964–1966.

plex is $132 \text{ cm}^2 \text{ mole}^{-1} \text{ ohm}^{-1}$ in DMF at 25° , in the range expected for a 2:1 electrolyte.

Since all the dianionic bis(mnt) complexes investigated by X-ray diffraction methods have been found to be square planar,¹⁰ we expect a square-planar structure for $\text{Au}(\text{mnt})_2^{2-}$. In acetone, the lowest electronic band in $\text{Au}(\text{mnt})_2^{2-}$ occurs at $13,750 \text{ cm}^{-1}$ (ϵ 368), as compared with $13,300 \text{ cm}^{-1}$ (ϵ 40) for the $\text{Au}(\text{mnt})_2^-$ complex, 8300 cm^{-1} (ϵ 100) for $\text{Cu}(\text{mnt})_2^{2-}$, and 6400 cm^{-1} (ϵ 337) for $\text{Cu}(\text{mnt})_2^-$. Magnetic susceptibility measurements on samples of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Au}(\text{mnt})_2]$

give $\mu_{\text{eff}} = 1.85 \pm 0.05 \text{ B.M.}$, in the range expected for a complex with one unpaired electron and in reasonable agreement with the g value. Considering the magnetic results, it is highly probable that no significant intermolecular interaction between $\text{Au}(\text{mnt})_2^{2-}$ groups occurs in $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Au}(\text{mnt})_2]$.

James H. Waters, Harry B. Gray¹⁸

Department of Chemistry, Columbia University
New York, New York 10027

Received June 17, 1965

Book Reviews

Organoboron Chemistry. Volume 1. Boron-Oxygen and Boron-Sulfur Compounds. By HOWARD STEINBERG, Vice President and Director of Research, U. S. Borax Research Corp. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1964. xxxii + 950 pp. $17 \times 23.5 \text{ cm}$. \$33.00.

"Organoboron Chemistry" is the first of a series of three volumes intended to give complete coverage of this vast field. In the present volume, attention is focused on compounds containing organic groups bonded to boron through boron-oxygen or boron-sulfur bonds. Even with this restriction of scope, the extent of the area is such that the reader will pick up a book purporting to be comprehensive with a feeling of skepticism; he will put it down with a feeling of awe.

The volume is indeed comprehensive and covers all pertinent literature (including patents and unclassified government reports where available) from the early nineteenth century through the end of 1961. Mere collection of this information and logical organization of it is a worthwhile venture that has been successfully completed, but the author has attempted far more and has succeeded in a satisfying way. He has presented his own analysis of the data and explanations of others and also advanced plausible mechanistic interpretations of his own in many instances throughout the book. This extends to a critical examination of mechanisms suggested by others and a substitution of more likely ones where necessary. It is this aspect which will reward the reader with greater insight into the area of his own interest and will also no doubt serve to stimulate much new research. Perhaps the greatest testimony that can be offered to this contribution is the fact that many of Steinberg's novel proposals have already begun to appear in current literature in nearly verbatim form.

Chapters 1, 2, and 3 deal with introductory material and a brief but lucid and useful treatment of nomenclature. Chapter 4 covers in 173 pages the symmetrical orthoborates of monohydric alcohols and phenols. Despite the length of the chapter, the reader will find it simple to find what he seeks, since the Table of Contents is unusually complete and useful.

Chapters 5 through 20 continue the systematic examination of more complex compounds. Chapter 21 treats the related compounds containing sulfur in place of part or all of the oxygen.

The book concludes with a brief but critical chapter on the hydrolytic stability of the boron-oxygen system with emphasis on those quantitative studies that have thus far been carried out. Finally, a series of three appendixes collects useful information on infrared assignments, bond distances and energies, and heat of formation for a few compounds. The active worker in this field will find these most helpful.

Dr. Steinberg has been an active worker in organoboron chemistry for a decade, and the book he has produced reflects this fact. It is the product of a man who knows his field and shows it on every page.

This work will remain the standard work in its field for at least a generation. As such, it will be essential on the shelves of any adequate chemical library. Despite its price (really only four

cents per page), it will be less often found in one's personal library unless one actively works in this field.

Riley Schaeffer

Department of Chemistry, Indiana University
Bloomington, Indiana

Boron, Metallo-Boron Compounds and Boranes. Edited by ROY M. ADAMS, Geneva College, Beaver Falls, Pa. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1964. xxiii + 765 pp. $16 \times 24 \text{ cm}$. \$27.50.

"Boron, Metallo-Boron Compounds and Boranes" contains eight chapters on a number of aspects of the chemistry of boron. The eight chapters are essentially eight discontinuous views of relatively unconnected subjects and vary considerably in their quality. Chapter 1 by W. A. Gale is a short review of the borax industry from a historical viewpoint. The chapter is a mine of obscure information (did you know that in ancient times borax was collected in the mountainous desert regions of Tibet and transported to Lahsa to barter for Cowrie shells and other commodities?) which is in fact good entertainment. Chapter 2 by the same author collects considerable equilibria data for aqueous borate systems. Chapter 3 by N. P. Nies and G. W. Campbell treats the over-all field of inorganic boron-oxygen compounds in 143 pages and covers nearly 800 references. In many respects this is the most useful chapter in the book since it collects and organizes a vast body of information. Nearly five pages of the index is devoted to this material and as a result information is readily available. Individual sections contain most of the structural and physical data available for the multitude of compounds known. Chapter 4 by A. E. Newkirk presents a summary of methods for preparing pure elemental boron, a detailed treatment of the complex structural chemistry of the element, and a concise review of the physical and chemical properties of the substance. A similar summary of the refractory binary borides is supplied in Chapter 5 by Professor Post. Useful tables of crystallographic and other data are included together with clear diagrams illustrating the structure of some of the more important forms. Chapter 6 by R. M. Adams and A. R. Siedele treats the rapidly expanding class of ionic boron hydrides. Again a collection of a very large amount of data is presented in the chapter with its nearly 600 references and is useful from this point of view alone. In Chapter 7 Adams has reviewed the chemistry of the boranes and the very extent of the information collected from nearly 800 references is in itself a contribution. The concluding chapter by A. J. Levinskass on toxicology of boron compounds is one of the most welcome in the book. The advances that have been made within the last 15 years have brought boron compounds into a much more common use, and relatively little publicity has been given to the potential hazard owing to toxicity. Any active worker in this field would do well to give the chapter a thorough reading.

In some respects the strengths of the book lead to its deficiencies as well. So much information has been collected that one would