heating progressed, the pressure in the system rose, thereby indicating formation of hydrogen by decomposition of hydride. When the pressure in the system reached 20 mm., the stopcock to the pump was opened and the system was quickly pumped down to less than 1 mm. This was repeated as necessary. The pumping time was purposely made short in order to minimize loss of silane, which has an appreciable vapor pressure at -196°. When hydrogen evolution ceased, the product was measured to be 6.3 cc. (STP) of gas (0.3 mmole) and was identified as silane by its infrared spectrum. A trace ($<1\%$) of ether contaminant was readily removed by fractionation at -155°. The calculated yield of silane based upon hydride was 7.1%.

Similar yields of silane were obtained by heating a mixture of silica and lithium aluminum hydride in a stream of helium gas at atmospheric pressure. The helium was passed through a heated U-tube reactor and a trap at -196° and was then vented to the atmosphere through a mercury bubbler. Ether removal was effected by first heating the reactants at 155° for 5 min. in the helium gas stream. Heating to 200° gave the desired product, silane. It is possible that higher yields could be obtained by agitating the reaction mixture.

Heating the reaction mixture above 200° liberated more hydrogen, indicating unreacted hydride, but no further yield of silane was obtained. We did not observe silane formation from heated mixtures of lithium hydride and silica or from the lithium hydride–aluminum metal–silica system. These facts suggest that the reactive species is an aluminum hydride, which is in agreement with the proposed[1] aluminum chlorohydride intermediate reported for the Al–$AlCl_3$-catalyzed hydrogenation of silica.

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Characterization of the Brown Molybdenyl Bisacetylacetonate

Sir:

We wish to correct our earlier report[1] of the constitution and valency of the brown molybdenyl bisacetylacetonate. Recent data have shown that this has been erroneously described as an isomer of the known yellow molybdenum(VI) compound, $MoO_2(C_5H_7O_2)_2$. It is now proposed that this is actually a molybdenum(V) complex, μ-oxo-dioxotetrakis-(2,4-pentanedionato)-dimolybdenum(V), with the simplest formula of $[(C_5H_7O_2)_2Mo{=}O]_2O$.

The differences between the elemental analysis for these molybdenum(VI) and molybdenum(V) complexes were so slight that it was difficult to derive an accurate formula. The molybdenum(VI) valency and the molybdenyl structure was supported by its diamagnetism and the presence of the strong Mo=O absorption (961 cm.$^{-1}$) in the infrared (NaCl region). There was no indication of hydroxy absorption in the infrared spectrum, thus discounting the possibility of $MoO(OH)(C_5H_7O_2)_2$ or its hydroxo-bridged dimer. Unfortunately, the molecular weight and dipole moment could not be determined in solution because of rapid dissociation and apparent oxidation.

Although the visible absorption spectra of the yellow and brown molybdenyl bisacetylacetonates were found to be distinctly different, their significance was not realized until the recent publication of papers dealing with the visible absorption and magnetic susceptibility of oxopentachloromolybdate(V), $[MoOCl_5]^{2-}$, in the crystalline state and in various concentrations of HCl. In particular, the report of Haight[2] revealed that this green molybdenum(V) species underwent dimerization by hydrolysis in 5–6 *M* HCl solution to give a species which was postulated to be $[OCl_4Mo\text{–}O\text{–}MoCl_4O]^{4-}$. The electron paramagnetic resonance study of Gray and associates[3] indicates that this species may be paramagnetic. Further dilution of the HCl solution causes disappearance of paramagnetism, and Haight[2] proposes the formation of new dimeric species. This effect of hydrolysis led to the suspicion that the diamagnetic, brown molybdenyl bisacetylacetonate was actually a similar molybdenum(V) complex. An investigation of the oxidation state, independent syntheses from hydrolyzed $[MoOCl_5]^{2-}$, and the absorption spectra confirmed this suspicion.

It was found possible to dissolve this compound readily and completely in 12 *N* hydrochloric acid without heating to obtain the green color characteristic of molybdenum(V). The visible absorption spectrum of this solution was identical with that reported by Haight.[2] Furthermore, the cerimetric titration of this solution, after chloroform extraction of liberated acetylacetone, confirmed the Mo^{+5} oxidation state.

Two independent syntheses of the brown bisacetylacetonate from molybdenum(V) in aqueous solution and acetylacetone were achieved. One was from the reaction of the unneutralized aqueous solution of ammonium oxopentachloromolybdate(V), $(NH_4)_2[MoOCl_5]$. The other synthesis was from a neutralized solution of molybdic oxide in concentrated hydrochloric acid, which had been reduced by molybdenum metal powder. Although the yellow molybdenyl bisacetylacetonate, $MoO_2(C_5H_7O_2)_2$, is transparent in the 350–800 mμ region, the brown molybdenyl bisacetylacetonate had definite and strong absorption. Because of solvolytic decomposition, the absorption spectrum had to be determined immediately after preparation of the solution. The methylene chloride solution gave the following peaks: 485 mμ (ε 6236); approximately 400 mμ (broad shoulder, ε 2068); 327 mμ (ε 9672). The charge transfer peak at 485 mμ closely corresponds to that reported to occur

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(1) M. L. Larson and F. W. Moore, *Inorg. Chem.*, **1**, 856 (1962).

(2) G. P. Haight, Jr., *J. Inorg. Nucl. Chem.*, **24**, 663 (1962).

(3) C. R. Hare, I. Bernal, and H. B. Gray, *Inorg. Chem.*, **1**, 831 (1962).

at 490 $m\mu$ (ϵ 5000) for a monomeric, pentavalent molybdenum acetylacetonate, $Mo(OH)_3(C_5H_7O_2)_2 \cdot 3H_2O$.[4] Although the absorption intensities of the brown molybdenyl bisacetylacetonate indicate charge transfer, it is proposed that the shoulder at approximately 400 $m\mu$ (ν, 25,000 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 $[MoOCl_5]^{2-}$, Gray and associates[3] 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 Mo=O axis. This is the peak which is strongly enhanced by the aqueous dilution of $[MoOCl_5]^{2-}$ in hydrochloric acid, and Haight[2] believes that this intensification is due to dimerization by oxygen bridging to form $[OCl_4Mo{-}O{-}MoCl_4O]^{4-}$. 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 coördination, the analogous *cis* configuration for the brown molybdenyl bisacetylacetonate, as an oxygen-bridged dimer, $[(C_5H_7O_2)_2Mo{=}O]_2O$, would have a non-linear O=Mo–O group. This bent, nonequivalent molybdenum–oxygen bonding increases the complexity of the infrared absorption in the molybdenum–oxygen sensitive region (<1000 cm.$^{-1}$) compared to $MoO_2(C_5H_7O_2)_2$. 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 $Mo(C_5H_7O_2)_3$ and $MoO_2(C_5H_7O_2)_2$, however, it appears that strong absorption around 435 cm.$^{-1}$ is sufficiently distinct to be attributed to the Mo–O–Mo group.

The apparent cause of diamagnetism in this new, dimeric molybdenum(V) complex is $d\pi$–$p\pi$ interaction along the proposed Mo–O–Mo bridge. This is believed analogous to the situation in diamagnetic $(Ru_2Cl_{10}O)^{4-}$, which is known to have a linear Ru–O–Ru arrangement with Ru–O bond lengths shorter than those expected from single bond radii.[5] Dunitz and Orgel[6] gave an M.O. interpretation of this structure and the diamagnetism to demonstrate the possibility of π-bonding in the Ru–O–Ru group.

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

[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).

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 × 23.5 cm. Price, $15.00

The translation of the Second Edition of Grinberg's monograph on coördination compounds marks the first appearance in English of an important Russian work dealing with coördination 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 coördination chemistry through a discussion of complex compounds of which $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and $[Co(NH_3)_4Cl_2]Cl$ 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 coördination. 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 coördination number six, while Chapter V deals with compounds with coördination 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 coördination 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