tance is not known with a sufficient accuracy because of the complexity of the molecule. (f) The B–O distances observed in BO_3 groups and in B_3O_3 rings are only 0.07 Å. lower than the separations predicted for the single covalent bonds, whereas in comparison with the former radius sum the divergence was of the order of 0.16 Å. The difficulty stressed in the introduction is thus removed. The remaining shortening is probably due to double bond structures (graphite-type resonance in BO_3 and $B_3O_6^{=}$ groups, benzene-type resonance in the B_3O_3 ring of trimethyl triborine trioxane) but these can now be said to contribute to a smaller and hence to a more reasonable extent. Nevertheless, the fact that $>B^{-}{=}\underset{\cdot\cdot}{O}^{+}-$ groups do participate in the representation of the ground state may help to reduce the moment of methyl borate[11] by reducing the O–C moment. (g) The case of BF_3 is analogous to that presented above for the BO_3 group; the percentage shortening below single bond values is approximately the same in both. (h) The B–Cl distance in BCl_3 is seen in Table III to agree with the newly predicted separation. This eliminates the previous necessity of ascribing to the ground state large contributions of configurations such as $>B^{-}{=}\underset{\cdot\cdot}{Cl}:^{+}$. In BBr_3, a slight participation of such structures would account for the small remaining shortening.

It seems evident that in attempting to account for the observed distances in boron compounds the new method of calculating interatomic distances is a definite step forward.

Summary

An electron diffraction investigation of the vapors of methyl borate and of trimethyl triborine trioxane led to the following structures for these compounds.

Methyl borate: Planar BO_3 group, with B—O = 1.38 ± 0.02 Å.; O–C = 1.43 ± 0.03 Å.; and the B–O–C angle equal to 113 ± 3°. Rotation of the methoxy groups about the B–O bonds is indicated.

Trimethyl triborine trioxane: Planar six membered ring, with alternating boron and oxygen atoms. The methyl groups are bonded to the boron atoms, and are in the plane of the ring. B–O = 1.39 ± 0.02 Å.; B–C = 1.57 ± 0.03 Å.; and the B–O–B angle is 112 ± 4°.

The electron configurations of these substances are discussed. The available data on boron compounds are reviewed and it is decided that the method recently suggested by Schomaker and Stevenson for calculating interatomic distances is the most successful method available at present for accounting for the interatomic distances observed in boron compounds.

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[JOINT CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF POMONA COLLEGE, AND THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The Configuration of Hydrogenated Cupric Disalicylaldehyde by Means of Magnetic Measurements

BY GEORGE N. TYSON, JR., AND ROBERT E. VIVIAN

The catalytic properties of coördinated compounds of the transition elements have been well known for some time.[1] In particular, Calvin[2] has lately studied kinetics of hydrogenations using copper disalicylaldehydes and other copper compounds. In the work reported by Calvin,[2] it has been stated that the hydrogenation of cupric disalicylaldehyde results in a reduction of the compound to cuprous disalicylaldehyde. The experimental work reported in this paper requires another interpretation of the mechanism that occurs from hydrogenation of the cupric disalicylaldehyde, which satisfactorily accounts for the catalytic activity of the hydrogenated compound.

When green cupric disalicylaldehyde is dissolved in pyridine, a solution of the same color results. After hydrogenation has been effected, the solution becomes deep ruby-red. No precipitate was present, nor was the Tyndall effect evidenced with either of the solutions, and it was therefore assumed that the compounds were present in true solution. By means of magnetic susceptibility measurements, it is found that the copper is present as cupric ion in both the green and red solutions. Thus, the change in color of the solu-

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(1) Baudisch and Welo, *Chem. Rev.*, **15**, 1 (1934).
(2) M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938).

tion may logically be ascribed to a change in configuration of the cupric disalicylaldehyde molecule.

Experimental

Solutions and Hydrogenation.—The cupric disalicylaldehyde used in this investigation was previously described in detail[3]; 2.4016 g. was diluted to 100 ml. volumetrically, using triply distilled J. T. Baker and Co. C. P. grade pyridine. The solution so obtained was measured magnetically within five minutes of mixing, and again after having stood one week. In addition, the solution was hydrogenated by placing 50 ml. of solution in a 200-ml. Florence flask and evacuating to 15 mm. pressure and subsequent introduction of hydrogen into the evacuated flask, to a pressure slightly greater than atmospheric. The flask containing the hydrogen and the solution was then heated to 90° for several hours. The original solution was green and no change in color was noted in the solution in the hydrogenation apparatus unless the original green solution had developed a barely perceptible brown cast. This occurred after the solution had stood for one week. Under these conditions the solution changed to a ruby-red color on hydrogenation as described above.

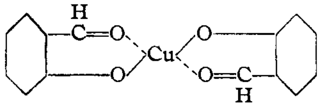
Magnetic Measurements.—The magnetic susceptibility measurements were made by the Gouy method at 22°. The susceptibilities due to the cupric disalicylaldehyde in the freshly prepared green solution (I), the green solution with slight brown cast which has stood for seven days (II), and the ruby-red solution (III) are shown in Table I. In the column listing the Bohr magnetons the calculations have been made assuming complete quenching of the orbital contribution to the magnetic moment. In the conversion of the experimental data into Bohr magnetons a correction has been made for the diamagnetism of the molecule.

TABLE I

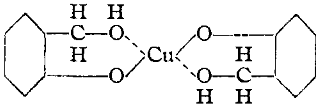
Soln.	$\chi_s \times 10^6$	$\chi_m \times 10^6$	Bohr magnetons Exptl.	Bohr magnetons Calcd.	No. of unpaired electrons
I	4.11	1256	1.9	1.73	1
II	4.11	1256	1.9	1.73	1
III	4.17	1274	1.9	1.73	1

Discussion

It is seen from Table I that the cupric disalicylaldehyde compound in solution exhibits a magnetic moment close to the theoretical value of 1.73 Bohr magnetons for one unpaired electron, regardless of whether the solution is green, green with brown cast, or red. It has been shown previously[3] that the green compound probably has a planar (*dsp*^{2} bonds) structure and the formula is written as:



It seems reasonable to assume that the planar configuration has been changed to the tetrahedral (*sp*^{3} bonds) by the introduction of hydrogen. Thus the formula of tetrahedral cupric disalicylaldehyde which has taken up hydrogen would be as follows:



This proposed formula would account for the observed uptake of hydrogen noted by Calvin,[2] but the amount of hydrogen required is greater than that needed for the conversion of cupric to cuprous ion. No reduction in copper occurs, however, as is shown in Table I. It seems reasonable to assign the change in color as due to a change in configuration in view of the work reported by Lifschitz[4] and collaborators on quadricovalent nickel complexes. These authors have reported that in the divalent nickel complexes investigated, those which exhibit diamagnetism are yellow, while if the complex is paramagnetic the color is blue. Thus, planar yellow complexes, under proper conditions, can be converted to the paramagnetic blue form, which is probably tetrahedral.

The observed chemical behavior of the red cupric disalicylaldehyde solution is in accord with the proposed structure. Thus the planar green compound is relatively stable while the red tetrahedral complex is much less stable and is oxidized by the air to the green planar configuration. As first noted by Calvin[2] this conversion is not repeated many times before the solution changes to a brownish color which cannot be restored to either the green or red. Cupric oxide, which also has a magnetic moment due to one unpaired electron, would be a reasonable explanation for the observed change in color. No change in magnetic moment was noted when the solution became brownish. The production of the red hydrogenation catalyst is not effected by molecular hydrogen until some material other than pyridine or cupric disalicylaldehyde is produced, since an uptake of hydrogen does not occur until a brownish cast is developed in the green solution. The nature of this material is not known at the present time.

An attempt is being made currently to determine the contribution of orbital moment in the

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[3] Tyson and Adams, THIS JOURNAL, 62, 1228 (1940).

[4] Lifschitz, *et al.*, *Z. anorg. allgem. Chem.*, 242, Part 2, 97 (1939).

relatively unquenched hydrogenated configurations of cupric, as well as divalent nickel disalicylaldehyde.[5] Susceptibility measurements are also being made on phthalocyanines in an attempt to determine whether a change in configuration occurs after hydrogenation.

Summary

From magnetic measurements made on the pyridine solutions of cupric disalicylaldehyde, a mechanism of catalytic hydrogenation has been proposed. The green copper disalicylaldehyde is probably planar while in the red reduced form the aldehyde groups have been changed to alcohol groups and the configuration has become probably tetrahedral. The relatively unstable tetrahedral configuration readily reacts, losing hydrogen, and thereby reverts to the more stable planar form, with a corresponding conversion of the alcohol to aldehyde groups. The observed susceptibilities, chemical behavior, and relative stabilities of the configurations are in accord with this proposal.

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[5] See J. H. van Vleck's discussion, "The Theory of Electric and Magnetic Susceptibilities," Oxford at the Clarendon Press.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Anodic Waves Involving Electroöxidation of Mercury at the Dropping Mercury Electrode

BY I. M. KOLTHOFF AND C. S. MILLER[1]

In the present study anodic waves due to electroöxidation of mercury have been investigated. Depending on the anodic reactions in the presence of various depolarizers the equations describing the anodic waves may be different. The experiments were carried out with the manual apparatus used in most previous investigations[2] at 25.00 ± 0.05°. The drop time in general was three to four seconds.

The Anodic Wave in the Absence of Depolarizers.—When a mercury electrode is in equilibrium with the surrounding liquid its potential π is given by the expression

$$\pi = C + \frac{RT}{2F}\ln\,[\mathrm{Hg_2}^{++}]_0 = C' + \frac{RT}{2F}\ln\,[\mathrm{Hg}^{++}]_0 \qquad (1)$$

in which the subscript zero denotes the concentration (actually the activity) of the mercurous and mercuric ions at the interface of mercury and solution. Upon electroöxidation of mercury in the absence of a depolarizer the metal enters into solution practically entirely in the form of mercurous ions, the mercuric ion concentration being about one-hundredth that of the mercurous ion. The mercurous ion concentration at the surface of the dropping electrode is proportional to the current i, and hence in this case we can write instead of equation (1)

$$\pi = \pi_0 + \frac{RT}{2F}\ln i \qquad (2)$$

Since nitrate ions do not depolarize a mercury electrode, the anodic dissolution of the metal was investigated in 0.1 *N* potassium nitrate solutions. Slightly different results may be expected in acid medium in which the hydrolysis of the mercurous ions is suppressed. The "free dissolution" wave of mercury was found to start at a potential of +0.4 to +0.45 v. (*vs.* S. C. E.). Plotting the values of the potential π against log i yielded a straight line with a slope of 0.032 in good agreement with the theoretical slope of 0.030 according to equation (2). The latter equation, therefore, describes the wave of the free dissolution of mercury. It is also evident that the mercurous ions are divalent; if they were univalent a slope of 0.060 instead of 0.030 would have been found.

The Anodic Wave in the Presence of Depolarizers which Form Slightly Dissociated Soluble Compounds with Mercuric Mercury. A. Thiosulfate as Depolarizer.—The free dissolution wave of mercury starting at a potential of about +0.4 v. marks the end of the application of the dropping electrode in the positive potential region. This wave is shifted to more negative potentials in the presence of substances which have a great affinity for mercurous or mercuric ions or for both. In the presence of such depolarizers well-defined anodic waves are found

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[1] From the experimental part of a thesis submitted by Carl S. Miller to the Graduate School of the University of Minnesota in partial fulfillment of the doctor's degree (1940).

[2] I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).