methanol and in 70% ethanol the aging is much less rapid than in aqueous medium.

2. The rapid aging is to be attributed to a recrystallization of the fresh precipitate. The speed of this recrystallization and, therefore, of the aging, decreases with decreasing solubility of the lead sulfate in the particular medium.

MINNEAPOLIS, MINN. RECEIVED OCTOBER 18, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Effect of the Hydrogen Bond on the Dielectric Constants and Boiling Points of Organic Liquids

BY W. D. KUMLER

The dielectric constant of liquids is a function of the number of molecules per cc., of the dipole moment, of the electronic and atomic polarizations, of temperature, and of the interaction of the molecules with each other. If all but one of these factors can be made constant for a group of compounds, then the plot of the variable factor against the dielectric constant should be some simple curve.

The factors are eliminated or made constant as follows: temperature by taking all data at the same temperature; electronic polarization by subtracting the refractive index squared n^2 from the dielectric constant ϵ; the atomic polarization contributes so little to the dielectric constant that it may be neglected; the different number of molecules per cc. by correcting $\epsilon - n^2$ to the value it would have when there are the same number of molecules per cc. This is accomplished by use of the equation

$$(\epsilon - n^2) \text{ corrected} = (\epsilon - n^2)Md_0/dM_0$$

where M_0 is the molecular weight of the compound chosen as standard, d_0 its density, M the molecular weight of the compound being corrected and d its density. Acetone at 20° was taken as standard so $(\epsilon - n^2)$ corrected represents the dielectric constant each of these compounds would have if the contribution of the electronic polarization were eliminated and each cc. made to contain the number of molecules that exist in a cc. of acetone at 20°.

In this way the effects of all factors have been eliminated except the dipole moment and the interaction of the molecules. There has been no evidence that indicates clearly whether the interaction of molecules which causes a variation in dielectric constant is essentially of a physical or a chemical nature.[1,2] A physical interaction would be expected to be due mainly to the attractions between polar molecules, and to affect the dielectric constant in a way dependent chiefly on the dipole moments of the molecules. The quantity $\sqrt{(\epsilon - n^2) \text{ corrected}}$ would be expected to be some simple function of the dipole moments of the free molecules. On the other hand, if the interactions involve the formation of bonds, the values of $\sqrt{(\epsilon - n^2) \text{ corrected}}$ would vary greatly from this function and there would be no simple relationship between the quantity $\sqrt{(\epsilon - n^2) \text{ corrected}}$ and the dipole moments of the free molecules. Since it appeared from the equations connecting dielectric constant and dipole moment that the square root of the dielectric constant plotted against the dipole moment should give a more simple curve than the dielectric constant itself, the square root has been used.

Evidence can be obtained on this question by taking first a group of liquids in which the molecules would not be expected to form chemical bonds and plotting the square root of the dielectric constant as corrected above against the dipole moment. If this interaction is of a chemical nature, it is eliminated by the choice of liquids and the plot should be some simple curve (assuming, of course, that compounds were chosen that do not form chemical bonds).

Ten liquids of widely divergent character that would not be expected to form bonds and with dipole moments from zero to 3.91, were taken at random and $\sqrt{(\epsilon - n^2) \text{ corrected}}$ was plotted against the dipole moment μ. The compounds are benzene, ethyl ether, ethyl acetate, chloroform, ethyl iodide, ethyl bromide, acetaldehyde, acetone, acetonitrile and benzonitrile. It is seen in Fig. 1[3] that all of these ten compounds fall

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(1) Sidgwick, "The Electronic Theory of Valency," Oxford University Press, New York, 1927, p. 134.

(2) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., New York, 1931, p. 188.

(3) The dipole moment values are from Smyth's book, "Dielectric Constant and Molecular Structure," or from *Trans. Faraday Soc.*, App. I, LXXXVI, Sept. (1934). The dielectric constants and refractive indices are from the "International Critical Tables." The meas

near a straight line that passes through the origin.

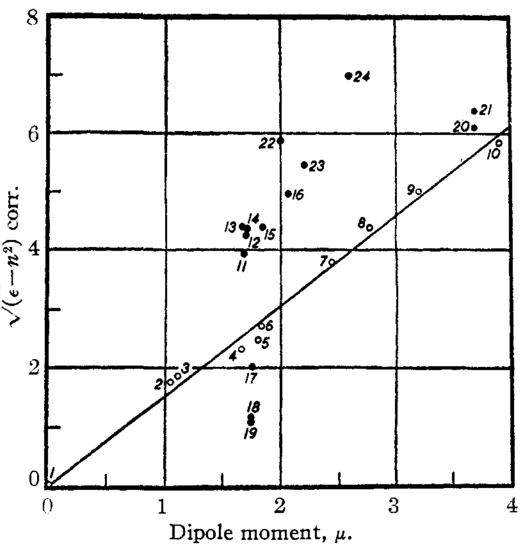

Fig. 1.—1, Benzene; 2, chloroform; 3, ethyl ether; 4, ethyl iodide; 5, ethyl acetate; 6, ethyl bromide; 7, acetaldehyde; 8, acetone; 9, acetonitrile; 10, benzonitrile; 11, methyl alcohol; 12, ethyl alcohol; 13, propyl alcohol; 14, amyl alcohol; 15, water; 16, formic acid; 17, acetic acid; 18, propionic acid; 19, butyric acid; 20, formamide; 21, acetamide; 22, hydrogen fluoride; 23, glycol; 24, hydrogen cyanide.

In Fig. 2 are plotted 26 additional liquids that are expected to be non-bond forming and again they fall near the *same* straight line. The fact that such a simple curve is obtained indicates that the choice of compounds was correct and suggests that interactions between molecules causing marked abnormalities in dielectric constant as evidenced by wide variations from this line are of a chemical nature.

To test this and at the same time the possibility of bivalent hydrogen, fourteen liquids designated by ● that would be expected to form chemical bonds are plotted in Fig. 1. The type of bond expected is the bond hypothesized by Latimer and Rodebush[4] in which two atoms are held together by hydrogen. Evidence for the existence of strong bonds of this type has been obtained only when hydrogen is connected either to fluorine, oxygen or nitrogen. Professor G. E. K. Branch has suggested to me that the conditions necessary for hydrogen bond formation may be formulated as follows: a lone pair of electrons on an atom to act as donor; hydrogen on an atom from which it is fairly easily removed as hydrogen ion; both atoms to which the hydrogen may be attached must be small. (There may be a few cases in which the last provision is not necessary.) The fourteen compounds in this second group all fulfil these conditions for hydrogen bond formation. The compounds are methyl, ethyl, propyl, butyl alcohols, formic, acetic, propionic and butyric acids, formamide, acetamide, water, glycol, hydrogen fluoride, and hydrogen cyanide. No simple curve can be drawn through these points. All of the points, with two exceptions, are far from the line about which the thirty-six liquids of Group 1 fall. The average deviation from the line of the thirty-six liquids is 0.17 and of the fourteen liquids 1.61. This indicates that the cause of the abnormalities in dielectric constant of the second group of compounds is the hydrogen bond.

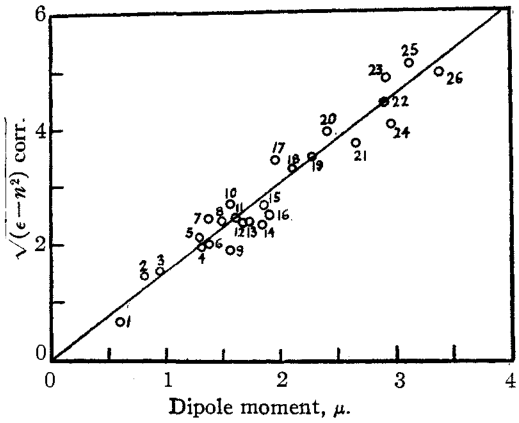

Fig. 2.—1, Thiophene; 2, triethylamine; 3, diethylamine; 4, ethylamine; 5, butylamine; 6, isopropylamine; 7, ethyl mercaptan; 8, aniline; 9, dimethylaniline; 10, diethyl sulfide; 11, sulfur dioxide; 12, methyl acetate; 13, ethyl butyrate; 14, butyl acetate; 15, propyl acetate; 16, amyl acetate; 17, ethylenediamine; 18, pyridine; 19, propyl nitrite; 20, propionaldehyde; 21, acetyl chloride; 22, ethyl nitrate; 23, ethyl acetoacetate; 24, propyl nitrate; 25, nitromethane; 26, propionitrile.

There are several factors which might account for the small displacement from the line exhibited by some of the compounds in Group 1. The inaccuracies in dipole moments as evidenced by frequently occurring differences of two- or three-

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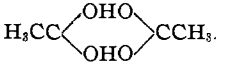
urements of the dielectric constant were all made between 17 and 21° with the exception of acetamide and sulfur dioxide. Sulfur dioxide was measured at 0° so its position on the graph is a bit high. Acetamide was measured at 83° so its position is too low. The dielectric constant of formamide was given as >84 and was taken as 84 so it also is too low. The dipole moment of the amides are from Kumler and Porter, This Journal, **56**, 2549 (1934), except formamide, which is an unpublished value (3.68) obtained by the author. If Zahn's value for formamide (3.22) had been used it would be much farther above the line.

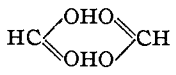
(4) Latimer and Rodebush, *ibid.*, **42**, 1419 (1920).

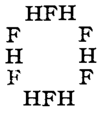
tenths of a unit when several investigators have measured the same compound are of sufficient magnitude to account for the deviation. Then some compounds might form weak bonds other than hydrogen bonds. If strong bonds of this type were formed there seems to be no *a priori* reason for assuming that they would not show the same abnormalities in the dielectric constant that are exhibited by hydrogen bonds.

Of the compounds in Group 2, acetic, propionic, and butyric acids are below the line and all other compounds above it. The compounds below the line have abnormally small dielectric constants, which suggests the formation of symmetrical association complexes having little or no dipole moment. It is known that these acids do form this type of association complex under other conditions. The molecular weight of acetic acid in benzene corresponds to double molecules.[5,6] The dipole moment of acetic acid in benzene is zero,[7] hence the double molecules must be symmetrical. The molecule most probably consists of two single molecules forming a ring with the oxygens held together by hydrogen bonds, . x-Ray data indicate[8] that the carboxyl groups of the solid higher fatty acids are together, so much the same arrangement must exist in the solid state. It is highly probable that acetic, to some extent, and propionic and butyric acids to a larger extent consist of symmetrical double molecules in the liquid state.

Formic acid is known to be associated in solution and in the vapor state[9] and presumably can form the same type of symmetrical double molecule as the other carboxylic acids, but it is evident from the position of formic acid far above the line that in liquid formic acid the molecules cannot have this symmetrical form.

Hydrogen fluoride is also known to be associated in the vapor state and in solution.[10,11] The data indicate a polymer containing six molecules of HF. A structure that has been suggested for this polymer is a six-membered ring with hydrogen bonds between the fluorine atoms. Such a polymer would have no dipole moment and a liquid made up of such molecules would have a low dielectric constant. The high dielectric constant of hydrogen fluoride as indicated by its position on the graph shows that the liquid does not consist to any appreciable extent of this symmetrical polymer. The polymer must be of the non-symmetrical, extended type that would tend to raise the dielectric constant. The value of 2 for the dipole moment of hydrogen fluoride, which was estimated by comparing values on Pauling's electronegativity scale with the dipole moments of the other hydrogen halides, gives the smallest abnormality. If a value of 0.8 is used it would be much further above the line.[12] The evidence does not show that in widely separated molecules (*i. e.*, vapor state) formic acid and hydrogen fluoride do not form symmetrical polymers





but the data do show that these structures are not present in any appreciable quantity in the liquid state.

Formamide and acetamide might be expected to form symmetrical association complexes in the liquid, but, like formic acid, they apparently do not, judging from their positions on the graph.

The three molecules, formic acid, formamide, acetamide, would have a hydrogen not involved in bond formation attached directly to the ring of the double molecule. The hydrogen atoms so attached may have something to do with the disruption of the ring. The fact that propionic and butyric acids are farther below the line than acetic suggests the larger groups may give stability to the ring by preventing neighboring molecules from coming close enough to disrupt it.

The monohydric alcohols and water are grouped closely together above the line. The dihydric alcohol glycol has an even more abnormal dielectric constant than water or the monohydric alcohols.

Hydrogen cyanide with the possible exception of hydrogen fluoride is the most abnormal compound in the group. Practically no evidence has been obtained to indicate that hydrogen attached to carbon forms hydrogen bonds. The reason for this is apparent when we consider that hydrogen attached to carbon in most compounds is not as easily removed as hydrogen ion. In hydrogen cyanide this is no longer true ($K = 1.4 \times 10^{-9}$)

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(5) Herz and Fischer, *Ber.*, **38**, 1138 (1905).

(6) Trautz and Moschel, *Z. anorg. allgem. Chem.*, **155**, 13 (1926).

(7) Ref. 1, p. 174.

(8) Müller and Shearer, *J. Chem. Soc.*, **123**, 3156 (1923).

(9) Pauling and Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

(10) Simons and Hildebrand, This Journal, **46**, 2183 (1924).

(11) Simons and Bouknight, *ibid.*, **54**, 129 (1932).

(12) Smyth and McAlpine, *J. Chem. Phys.*, **2**, 501 (1934).

and the other conditions necessary for hydrogen bond formation are also present, namely, a lone pair of electrons and small atoms. The spectrum shows that HCN is a linear molecule. With a triple bond between carbon and nitrogen the most likely position for the other pairs of electrons (either on the basis of the old idea of two faces of the tetrahedrons being in contact or on a basis of the newer quantum mechanics)[13] is on the opposite side of the nitrogen from the carbon. Thus when these molecules form hydrogen bonds they give a straight line grouping $\mathrm{HC{\equiv}NHC{\equiv}NHC{\equiv}N}$ which is the arrangement one would expect to produce the largest dielectric constant.

Effect on Boiling Point.—Several factors determine the boiling points of compounds. The most important factors are molecular weight, the kind of atoms, the dipole moment and bond formation. If we can eliminate three of these factors, then the boiling point plotted against the fourth factor should give some simple curve. Then by introducing one of the other factors we should have a measure of its influence on the boiling point by the deviation from this curve.

In the plot (Fig. 3) are six compounds containing carbon, oxygen, and hydrogen. The molecular weights of these compounds are between 58 and 60, inclusive. Four of these compounds which do not fulfil the conditions for hydrogen bond formation, namely, methyl ethyl ether, methyl formate, propionic aldehyde, and acetone fall on a straight line when their boiling points are plotted against the dipole moment. The two compounds which fulfil the conditions for hydrogen bond formation, namely, propyl alcohol and acetic acid, are far above this line. These six compounds are designated by o. The next higher homolog of each compound, designated by ●, shows the same phenomenon.

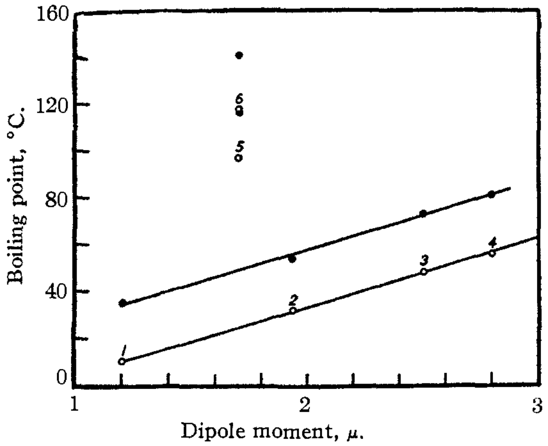

Fig. 3.—1, Methyl ethyl ether; 2, methyl formate; 3, propionaldehyde; 4, acetone; 5, propyl alcohol; 6, acetic acid.

In the amides we have a series of compounds that have very nearly the same dipole moments, the total variation being between 3.72 and 3.87. Plotting the boiling point (Fig. 4) against the molecular weight it is seen that the three compounds that do not have a hydrogen on the nitrogen, hence do not fulfil the necessary conditions for hydrogen bond formation, fall near a straight line and those fulfilling the condition are far above the line. (The average dipole moment of the points above the line is 3.76 and of those on the line 3.75.)

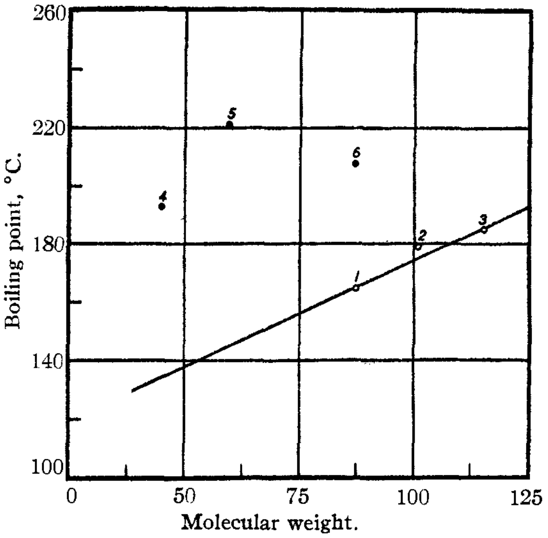

Fig. 4.—1, Dimethylacetamide; 2, methylethylacetamide; 3, diethylacetamide; 4, formamide; 5, acetamide; 6, monoethylacetamide.

The amount the boiling point is raised by the hydrogen bonds varies from 48 to 98°. The average rise for Figs. 2 and 3 is 76°.

A determination of the molecular weights of different amides was made in benzene to see if the effect of hydrogen bond formation would appear in these measurements. The apparent molecular weights of these compounds are tabulated.

Mole fraction	Apparent mol. wt.	Mol. wt.
	Diethylacetamide	
0.0043	104	115
.0045	107	
.0090	107	

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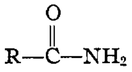
(13) Pauling, THIS JOURNAL, 53. 1367 (1931).

Mole fraction	Apparent mol. wt.	Mol. wt.
	Acetamide	
0.0116	92	59
.0111	90	
.0111	90	
.0198	107	
.0198	109	
	Monoethylacetamide	
0.0049	92	87
.0066	94	
.0134	131	
.0138	146	
.0145	150	

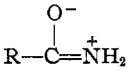
It is apparent that the effect of the hydrogen bond is present here also. The compound with no hydrogen on the nitrogen which consequently should not form hydrogen bonds has a normal molecular weight and the compounds with one and two hydrogens on the nitrogen have abnormally high molecular weights which increase with increasing concentration.

This tendency for hydrogen bond formation in unsubstituted and monosubstituted amides is connected with resonance.[14] The excited form II



$R{-}\overset{O}{\overset{\|}{C}}{-}NH_2$

I



$R{-}\overset{O^-}{\overset{|}{C}}{=}\overset{+}{N}H_2$

II

which contributes to the structure of the molecule has a plus charge on the nitrogen. This plus charge permits the hydrogen atoms to be more easily removed as hydrogen ions and thus causes them to form strong hydrogen bonds like the hydrogen atoms in ammonium hydroxide. The hydrogen atoms in amines where the plus charge is not present do not form hydrogen bonds, judging from their dielectric constants and low boiling points.

The carboxylic acids give definite evidence that the abnormality in boiling points cannot be explained on the basis of different interactions of dipoles. The dipoles of formic acid must be arranged in some fashion that greatly raises the dielectric constant and the dipoles of acetic, propionic and butyric acids in some way that lowers the dielectric constant. Yet the boiling point of formic acid is not abnormal in comparison with the other acids.

	B. p., °C.	Difference
Formic	100	
Acetic	118	18
Propionic	140	22
Butyric	162	22

In comparing the abnormalities shown by boiling points with abnormalities shown by dielectric constants it is evident that the order in the two cases is not the same. The reason for this is apparent when we consider that the corrected dielectric constant depends essentially upon the way the bonds are formed, that is, upon the configuration of the aggregates (whether they are symmetrical exclusive aggregates or unsymmetrical extended structures), and the boiling point depends chiefly upon the number and strength of bonds made to any single molecule. Thus hydrogen cyanide is more abnormal than water as far as dielectric constant is concerned, due to the straight extended structure, while water has a more abnormal boiling point than hydrogen cyanide because each water molecule can have four hydrogen bonds attached to it while each molecule of hydrogen cyanide can only have two such bonds.

The evidence indicates that liquids can be divided into two classes, those forming hydrogen bonds and those not forming such bonds. The hydrogen bond forming liquids are characterized by abnormal dielectric constants, high boiling points and high molecular weights.

Those compounds will form hydrogen bonds that have a hydrogen fairly easily removed as hydrogen ion, a lone pair of electrons and small atoms. The viewpoint has been adopted in the previous discussion that hydrogen becomes bivalent and coördinates with a second atom.[1,15,16] It is possible that the mechanism of hydrogen bond formation can be explained equally well by the theory of dipole attraction.[17,18] On the basis of this theory a much greater attraction must be accounted for in compounds with hydrogen bonds than in compounds not possessing such bonds. Sidgwick[19] pointed out that the dipole moment of the link between hydrogen and the atom to which it is attached is fairly large in most substances that form hydrogen bonds H—F(1.5–2.0?), H—O (1.6). This alone is not sufficient to account for the behavior on the dipole theory because there are links with much larger dipole moments in many compounds that do not possess hydrogen bonds. The further assumption must be made

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(14) Kumler and Porter, THIS JOURNAL, **56**, 2549 (1934).

(15) G. N. Lewis, *J. Chem. Phys.*, **1**, 24 (1933).

(16) Pauling, THIS JOURNAL, **53**, 1373 (1931).

(17) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., New York, 1931, p. 188.

(18) Martin, *Trans. Faraday Soc.*, **30**, 762 (1934).

(19) Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933, p. 166.

that due to the small size of the hydrogen these fairly large dipoles can approach very close to a large dipole in an adjacent molecule. Mack,[20] however, has given evidence that the atomic domain radius of hydrogen in other compounds (hydrocarbons) is quite large (1.29 Å.). Also it seems difficult to account for the behavior of amines and amides on the basis of the dipole theory, for although the plus charge on the nitrogen in the excited form of amides would tend to pull the electrons from the hydrogen, nevertheless, the more the electrons are displaced the more the dipole is reduced since the nitrogen is charged positively. The behavior of these compounds however is adequately explained by the other viewpoint which has been adopted.

I wish to express my thanks to Professor G. E. K. Branch for his very helpful suggestions and criticism.

Summary

A method has been devised to determine the effect of molecular interaction on the dielectric constants of liquids. Liquids that do not form bonds have normal dielectric constants, those that form hydrogen bonds have abnormal dielectric constants. The conditions necessary for hydrogen bond formation are formulated. The structures of the association complexes in the liquid state of the carboxylic acids, hydrogen fluoride and hydrogen cyanide are discussed. A scheme is used to show the effect of hydrogen bonds on the boiling points of organic liquids. It is found that such bonds raise the boiling points of the liquids considered, by an average of 76°. The molecular weights of acetamide, monoethylacetamide and diethylacetamide were measured. The connection between hydrogen bond formation and resonance in amides is discussed.

BERKELEY, CALIF. RECEIVED OCTOBER 19, 1934

(20) Mack, THIS JOURNAL, **54**, 2147 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SYDNEY]

Compounds of Palladium with Benzylmethylglyoxime

BY F. P. DWYER AND D. P. MELLOR

Wave mechanical treatment of the orientation of four electron pair bonds,[1] a number of crystal structure analyses,[2] and certain chemical evidence, seem to show that, so far at least as the stereochemistry of their four-covalent compounds is concerned, palladium, platinum and nickel have similar but unusual configurations. The isomorphism[3] of $BaPd(CN)_4 \cdot 4H_2O$, $BaPt(CN)_4 \cdot 4H_2O$ and $BaNi(CN)_4 \cdot 4H_2O$ also points to this conclusion. Except for the existence of certain types of isomerism which are probably better interpreted as arising from a pyramidal[4] arrangement of four covalent linkages the evidence is in favor of a planar disposition of the bonds. However, the chemical evidence for similarity of disposition of the bonds about each of these three atoms, whether planar or pyramidal, is incomplete, since, according to the recent investigations of Drew and his collaborators,[5] there is no evidence for the existence among the palladium ammines of *cis–trans* isomerism of the type observed with the ammines of platinum.

The following experiments show that an atom of palladium coördinates with two molecules of benzylmethylglyoxime,[6] each functioning as an unsymmetrical chelate group and what appear to be the palladium analogs of the *cis–trans* isomers of nickel benzylmethylglyoxime,[7] can be prepared readily.

Experimental

Benzylmethylglyoxime was prepared from benzylacetoacetic ester by Sugden's[7] method. A cold alcoholic solution containing 2.5 moles of benzylmethylglyoxime was added to a well-cooled 1.5% solution containing 1 mole of sodium chloropalladite. After being well shaken and allowed to stand for fifteen minutes, the resulting orange

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(1) Pauling, THIS JOURNAL, **53**, 1367 (1931).

(2) Dickinson, *ibid.*, **44**, 774, 2404 (1922); etc.

(3) Brasseur, de Rassenfosse and Piérard, *Z. Krist.*, **88**, 210 (1934).

(4) This configuration was first discussed by Grünberg, *Helv. Chim. Acta*, **14**, 455 (1931). Its existence was subsequently postulated by Rosenheim and Gerb, *Z. anorg. allgem. Chem.*, **210**, 289 (1933), in order to reconcile their resolution of four-covalent platinum and palladium with other chemical evidence relating to the orientation of chemical bonds about the atoms of these metals. See also Dwyer and Mellor, THIS JOURNAL, **56**, 1551 (1934).

(5) Drew, Pinkard, Preston and Wardlaw, *J. Chem. Soc.*, 1895 (1932). Since the completion of this work, Pinkard, Sharratt, Wardlaw and Cox, *ibid.*, 1012 (1934), have found evidence for the existence of this type of isomerism in diglycinepalladium.

(6) This compound was erroneously referred to as benzylmethyldioxime in our previous communication, THIS JOURNAL, **56**, 1551 (1934).

(7) Sugden, *J. Chem. Soc.*, 246 (1932).