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.

[20] Mack, THIS JOURNAL, 54, 2147 (1932).

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

[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).

precipitate was filtered off, washed with cold water and dissolved in the minimum of cold benzene. The deep red solution so obtained was treated with sufficient petroleum ether to precipitate the substance responsible for the red color. This substance, which was subjected to fractional crystallization at a later stage, was filtered off, and the orange-yellow filtrate cooled in ice with scratching. It soon deposited a yellow microcrystalline powder which was filtered off at the end of twenty minutes. Three further fractions were obtained by successive additions of petroleum ether. The first fraction was the almost pure, pale yellow, higher melting-point form of palladium bisbenzylmethylglyoxime, while the succeeding fractions were richer in the lower melting-point form. Further fractional crystallization of the latter fractions from benzene-petroleum ether solution resulted in the production of the pure, lower melting-point, more soluble compound.

After repeated recrystallization from benzene, the first pale yellow form melted at 207–208°. It is insoluble in water, slightly soluble in cold benzene, acetone and xylene, but readily soluble in bromoform and pyridine. Analyses for palladium and nitrogen were made according to the micro methods of Pregl.

Anal. α-Form. Calcd. for $Pd(C_{10}H_{11}N_2O_2)_2$: Pd, 21.82; N, 11.46; mol. wt., 489. Found: Pd, 21.7; N, 11.5; mol. wt. in bromoform, 517.

The deeper yellow β-form, which melts at 175° when plunged into a hot bath, is readily soluble in cold benzene, bromoform and acetone but insoluble in water.

Anal. β-Form. Found: Pd, 21.7; N, 11.4; mol. wt. in benzene, 478.

The mol. wt. of the β-form in bromoform was also normal.

Under the polarizing microscope acicular crystals of the α-form show positive elongation and weak double refraction, while crystals of similar habit of the β-form have negative elongation, strong double refraction, and show marked dispersion. In both forms the pleochroism is distinct and the schemes are the same. Measurement of extinction angles and other tests suggest the triclinic (or possibly monoclinic) system for both forms.[8]

Regeneration of the Glyoxime.—One-half gram of each isomer was treated in a mortar cooled in ice with 20 cc. of ice-cold acetone and 10 cc. of ice-cold potassium cyanide for one minute, filtered and treated with ice water and cold dilute acetic acid. In each case the glyoxime melted at 190° and when added back to a dilute solution of sodium chloropalladite gave a mixture of the yellow isomers which dissolved to an orange-yellow color in benzene. Microscopic examination showed both the recovered glyoximes to be identical and to belong, very probably, to the rhombic system. Both diacetyl derivatives of the recovered glyoximes prepared by acetylation in benzene solution in the presence of pyridine, crystallized in white needles melting at 79°.

Interconversion of the Isomers.—By slow melting in the usual manner the β-form could be melted at temperatures varying from 190 to 200°, according to the rate at which the temperature was raised. On recrystallizing from acetone the product of slow melting the α-form could readily be detected. Addition of the β-form to the α-form lowered the melting point of the latter, and hence variation in the melting point of the β-form may be attributed to transition of the β- to the α-form to different extents according to the rate at which the temperature is raised. The conversion of one form to the other was also achieved by allowing the β-form to stand for a few days in benzene-petroleum ether solution or by heating in xylene solution for a few minutes.

By passing dry hydrogen chloride through a dry ice-cold solution of each isomer in chloroform, what appeared from analysis to be impure specimens of $Pd(C_{10}H_{12}N_2O_2)_2Cl_2$ (A) were obtained. Attempts to purify these specimens for further identification and distinction were unsuccessful owing to the extraordinary ease with which they decompose to $Pd(C_{10}H_{12}N_2O_2)Cl_2$. Thus the idea of decomposing the dichlorides (A) with silver bromocamphorsulfonate with a view to possible resolution was abandoned.

Other Compounds of Palladium with Benzylmethylglyoxime.—Fractional crystallization of the material responsible for the deep red color of the benzene solution of the original precipitate obtained with benzylmethylglyoxime and sodium chloropalladite yielded fractions of different shades of brown and yellow and of different melting points. On analysis for palladium only, three of these fractions appeared to contain compounds in which one molecule of the glyoxime is united with one atom of palladium. Small amounts only of these fractions were available and they were probably contaminated with traces of α and β palladium bisbenzylmethylglyoxime. For instance one fraction contained 33.9% Pd, whereas $Pd(C_{10}H_{10}N_2O_2)$ requires 35.95%. Compounds of this type, that is, containing one molecule of the glyoxime, were obtained also with *syn* and *amphi* diphenylglyoxime. They were analogous to the nickel compounds formed with *amphi* glyoximes.[9] The glyoxime recovered from one of the three above fractions on microscopic examination proved to belong to the monoclinic or triclinic system. These experiments indicate that benzylmethylglyoxime is not simple as suggested by Sugden[7] but a complex mixture of some or all of its possible isomers. The nature of a fourth fraction, chocolate-brown in color and melting indefinitely between 90 and 140° and which contained as little as 23% of palladium, is not clear at present since only very small amounts of this material were available. Further investigation of this compound is being undertaken.

Discussion

Since it appears that benzylmethylglyoxime is a mixture of some or all of its four possible isomers, it remains to consider which form of the glyoxime is concerned in the formation of the two yellow isomers. In this connection it may be recalled that nickel forms a compound in which two molecules of the glyoxime are united to one atom of the nickel with the *anti* glyoximes only.[9,10] The same appears to be true of palladium. In

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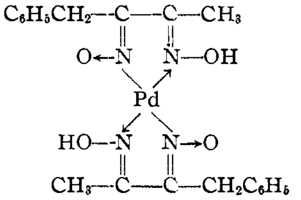
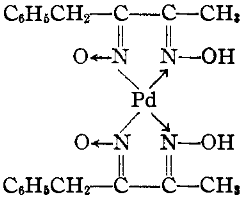
[8] We are indebted to Miss F. Quodling of the Geology Department for these data.

[9] Atack, *J. Chem. Soc.*, **103**, 1317 (1913); Hieber and Leutert, *Ber.*, **62**, 1839 (1929).

[10] Thilo, "Die Valenz der Metalle Fe, Co, Ni, Cu und ihre Verbindungen mit Dioximen," Sammlung chemischer und chemisch-technischer Vorträge, Vol. 13, p. 51.

the one case examined it was found that palladium coördinates with two molecules of *anti*-diphenylglyoxime, and with one molecule only of each of the *amphi* and *syn* forms of the glyoxime. While further examples of the formation of four-covalent inner complex compounds with palladium and *anti*-glyoximes are required to make out a more satisfactory case, it seems reasonable to assume that it is the *anti*-benzylmethylglyoxime which is concerned in the formation of the yellow isomers. That the melting points of the glyoximes recovered from each of the isomers were the same as that of the original glyoxime is considered to be due to the extreme lability of the different forms of benzylmethylglyoxime which on heating give rise to an equilibrium mixture. Further, the fact that the glyoxime recovered from each isomer when added again to sodium chloropalladite produces a mixture of the two isomers but none of the compounds containing one molecule of the glyoxime indicates that only the *anti*-glyoxime is present in the isomers. Since coördination is effected through the two nitrogen atoms, palladium forms part of a five-membered ring with the *anti*-glyoxime, and the isomers may be formulated as follows:





The experimental justification for considering each molecule of a glyoxime as occupying two coordination positions has been discussed by Pfeiffer and Richarz.[11] It is improbable that isomerism is due to a *cis–trans* distribution of the hydrogen of the hydroxyl groups since a planar or pyramidal distribution of the glyoximes about the central palladium would give rise to eight isomers of the *cis–trans* type. Moreover, it is usually considered that mobility of this hydrogen would give rise to inseparable tautomeric mixtures.[7] Nor does it seem at all probable that isomerism arises from the existence of both planar and tetrahedral configurations, since in this case four isomers should exist. There is, however, so far, nothing to indicate whether isomerism is due to a planar or pyramidal arrangement of the glyoxime about palladium. All attempts to prepare from the isomers derivatives suitable for possible resolution into optical antipodes have failed.

Summary

Two isomeric inner complex compounds of palladium with benzylmethylglyoxime have been prepared. Evidence is adduced to show that these substances are *cis* and *trans* isomers of palladium bis-*anti*-benzylmethylglyoxime.

[11] Pfeiffer and Richarz, *Ber.*, **61**, 103 (1928). See also Thilo, Ref. 10.

SYDNEY, NEW SOUTH WALES

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

Structural Changes Taking Place during the Aging of Freshly Formed Precipitates. IV. Aging of Fresh Lead Sulfate at Room Temperature in the Air-Dried State, and of Precipitates Covered with an Adsorbed Layer of Wool Violet

BY I. M. KOLTHOFF AND CHARLES ROSENBLUM

In the third paper of this series[1] it was shown that the speed of aging of fresh lead sulfate increases with the solubility in the liquid medium with which the precipitate is in contact. Since the fresh precipitate has a highly porous structure[2] the aging might be attributed to an internal recrystallization of the amicroscopic particles when the capillaries are filled with water or a dilute aqueous solution. In order to decide whether the recrystallization takes place mainly by way of the external liquid or internally, we made the following investigation in which freshly precipitated lead sulfate was made air dry and then kept for shorter or longer times at various humidities. In addition, the speed of aging was investigated after adding wool violet to the suspension of the freshly formed lead sulfate. From previous studies[3] we know that an adsorbed layer of wool violet pre-

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[1] THIS JOURNAL, **57**, 597 (1935).

[2] *Ibid.*, **56**, (a) 1264, (b) 1658 (1934).

[3] I. M. Kolthoff, W. von Fischer and Chas. Rosenblum, *ibid.*, **56**, 832 (1934).