ient to first account for shifts occurring in cases involving relatively little pi-bond formation, e.g., [Co(BdH)$_2$Cl$_2$].

It was suggested that a large contributing factor to the low position of the C=N band in biacetyldihydrazone is associated with the *trans* planar conformation of the molecule, which would facilitate conjugation of the NH$_2$ group and the two C=N groups. However, upon formation of a chelate ring, the ligand is required to assume a *cis* conformation. Consideration of a physical model suggested that, in the case of a *cis* conformation, not only do the two adjacent methyl groups interfere with each other, but the NH$_2$ groups press back upon the molecule. These two factors then suggest a tendency toward distortion of the planar conformation upon complexing. As a result, the interaction between the conjugated dimethine groups is decreased. Furthermore, the formation of the *cis* structure should very greatly limit the interaction of the electron pair on the NH$_2$ group with the pi electron system of the molecule. It seems quite likely that the electron pair on the NH$_2$ group is divested of its conjugative influence upon complexing even in those cases where a planar chelate ring is formed. As a consequence of these considerations, the simplest modes of coördination to metal ions should produce shifts in the position of the C=N stretching vibration toward higher frequencies. The position of the C=N absorption in the spectrum of [Co(BdH)$_2$-Cl$_2$] (1623 cm.$^{-1}$) reflects the limiting effect of converting the biacetyldihydrazone molecule from the *trans* conformation to the *cis* conformation.

The slight displacement of the C=N absorption toward higher frequencies in the spectrum of [Fe(BdH)$_3$]I$_2$ (relative to the position of this absorption in the spectrum of biacetyldihydrazone) is a consequence of two opposing effects, the displacement toward higher frequencies which results from the forced *cis* conformation (as discussed above) and the displacement toward lower frequencies which results from metal-ligand pi-bonding. The hypothetical "lowering" attributed to metal–ligand pi-bonding is 28 cm.$^{-1}$ in this case.

The limiting position of the iron(II) complex with biacetyldihydrazone (in the series of complexes above) as indicated by the infrared spectra of the several complexes provides an additional illustration of the extreme degree of pi-electron interaction between the d^6 iron(II) atom and the dimethine group, $-N=C-C=N-$.[2,3,6]

Organic Compounds of Zirconium. VII. Studies in Zirconium Salicylates

BY R. N. KAPOOR AND R. C. MEHROTRA

The reaction between zirconyl chloride and potassium salicylate has been studied by precipitation and titration (conductometric and electrometric) techniques. Further, the reactions of salicylic acid with zirconium tetrachloride and *iso*-propoxide have been studied in anhydrous benzene medium. New zirconium compounds isolated are: Zr(OPr-*iso*)$_2$(OOC·C$_6$H$_4$·O), Zr(OOC·C$_6$H$_4$O)$_2$·Pr-*iso*OH, Zr(OOC·C$_6$H$_4$·O)$_2$ and (OOC·C$_6$H$_4$·O) Zr(OOC·C$_6$H$_4$·OH)$_2$.

A detailed study of the mandelic acid derivatives of zirconium both by preparative as well as physicochemical techniques has been described in recent publications[1,2] from these Laboratories. An extension of the above studies to other α-hydroxy carboxylic (glycolic and lactic) acids revealed that the nature of conductometric and potentiometric titration curves was essentially similar to that described in the case of mandelic acid derivatives, although the products in general exhibited a much higher solubility. In view of the interesting results obtained with α-hydroxy aliphatic carboxylic acids, it was considered worthwhile to make a study of salicylates also. It has been shown in the present investigation that the reaction between zirconyl chloride and potassium salicylate in aqueous solution yielded a precipitate corresponding in analysis almost to a monosalicylate Zr(OH)$_3$ (salicylate)$_{1.1}$ of zirconium. The conductometric and electrometric titrations of zirconyl chloride and potassium salicylate gave

curves (Fig. 1 and 2) similar to those described for titrations with potassium mandelate.[2] The electrometric titration of zirconyl chloride with potassium hydroxide was carried out in the presence of 1, 2 and 3 moles of potassium salicylate to estimate the extent of chelation (Fig. 3). The nature of the curves can be explained easily on the same lines as already described in the corresponding case of mandelic acid.
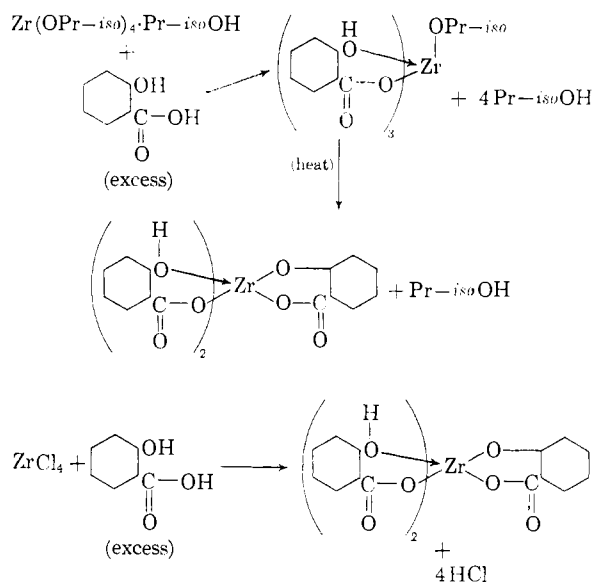
In view of the interesting results obtained on the physico-chemical studies of zirconium salicylates, it was considered of interest to study the system in non-aqueous medium also, where the complicating hydrolytic effects of water would be absent.

A preliminary reaction between zirconium isopropoxide and excess salicylic acid in benzene showed that almost all isopropylalcohol could be fractionated out azeotropically. The final zirconium compound thus formed, however, corresponded in analysis to zirconium trisalicylate only which might be represented by the first equation.
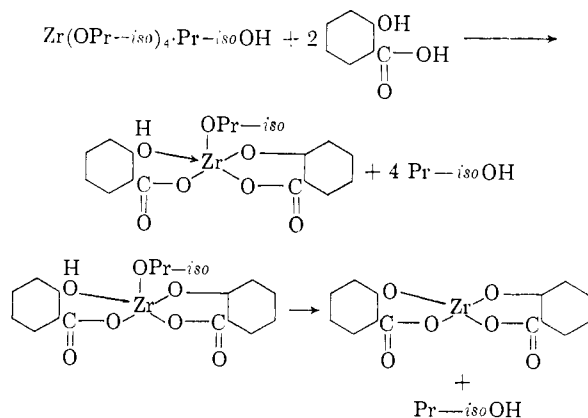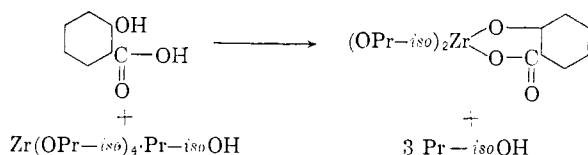
The same compound was obtained when zirconium tetrachloride in anhydrous benzene was treated with excess salicylic acid.

(1) R. N. Kapoor and R. C. Mehrotra, *J. Sci. Ind. Research (India)*, **16B**, 300, 304 (1957).

(2) R. N. Kapoor and R. C. Mehrotra, THIS JOURNAL, **80**, 3569 (1958).

$Zr(OPr-iso)_4 \cdot Pr-isoOH$
+
(excess)

$\longrightarrow$

$+ 4 Pr-isoOH$

(heat)

$\downarrow$

$+ Pr-isoOH$

$ZrCl_4 + $ (excess) $\longrightarrow$

$+$
$4 HCl$

However, the experimental results of the reaction of zirconium isopropoxide with one and two moles of salicylic acid, respectively, can be explained by the equations
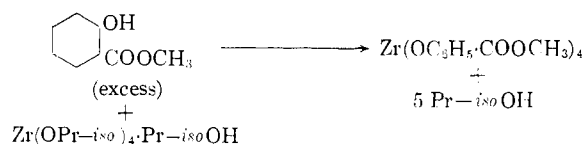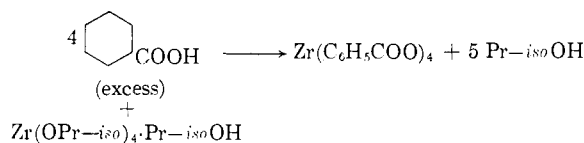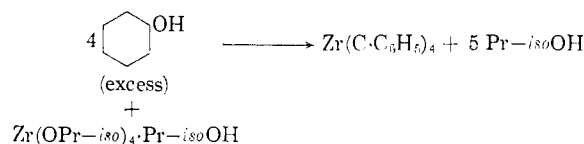
$\longrightarrow$ $(OPr-iso)_2Zr$

$+$
$Zr(OPr-iso)_4 \cdot Pr-isoOH$ $3 Pr-isoOH$

$Zr(OPr-iso)_4 \cdot Pr-isoOH + 2$ $\longrightarrow$

$H \quad OPr-iso$

$+ 4 Pr-isoOH$

$H \quad OPr-iso$

$\longrightarrow$

$+$
$Pr-isoOH$

The above results indicate that the primary tetravalency of zirconium can be satisfied by a combination of carboxylic and phenoxy oxygen atoms of the salicylic acid molecule. In earlier literature[3-5] describing the derivatives of salicylic acid with metals (beryllium, titanium and iron), only the phenoxy oxygen has been shown to be forming a primary valency bond, although different conclusions have been arrived at in a recent study of beryllium salicylates. In view of the comparative acidic character of the carboxyl and phenoxyl hydrogen atoms in salicylic acid molecule, it is to be expected that the carboxylic groups should be more reactive.

In order to compare the replaceability of isopropoxyl groups by phenoxyl and carboxyl groups, the reactions of zirconium isopropoxide with excess of phenol, benzoic acid and a mixture of the two were separately investigated. The former two reactions gave the pure tetraphenoxy and tetrabenzoate derivatives and the last one also yielded almost a tetrabenzoate product indicating the greater replacing power of the carboxylic groups. However, the reactivity of the phenoxyl group in a similar compound methyl salicylate was demonstrated by the replacement of all the isopropyl alcohol and the formation of a tetramethyl salicylate derivative, when zirconium isopropoxide was treated with excess of methyl salicylate

4 (excess) $\longrightarrow Zr(C \cdot C_6H_5)_4 + 5 Pr-isoOH$

$+$
$Zr(OPr-iso)_4 \cdot Pr-isoOH$

4 COOH (excess) $\longrightarrow Zr(C_6H_5COO)_4 + 5 Pr-isoOH$

$+$
$Zr(OPr-iso)_4 \cdot Pr-isoOH$

OH
COOCH$_3$ (excess) $\longrightarrow Zr(OC_6H_5 \cdot COOCH_3)_4$

$+$
$5 Pr-isoOH$

$+$
$Zr(OPr-iso)_4 \cdot Pr-isoOH$

Experimental

Materials.—$ZrOCl_2 \cdot 8H_2O$ was Merck G. R. Product. All other reagents employed were "Analar" grade and were purified where necessary. Zirconium isopropoxide, prepared by the method of Bradley, Mehrotra and Wardlaw,[6] was purified by repeated crystallization from isopropyl alcohol. *Anal.* Calcd. for $Zr.(OPr-iso)_4 \cdot Pr-isoOH$: Zr, 23.53; OPr-iso, 76.21. Found: Zr, 23.60; OPr-iso, 76.00.

Aqueous solutions were made up in conductivity water. Benzene was dried over metallic sodium and carefully fractionated.

Analytical Methods.—Zirconium was estimated as the oxide by the direct ignition of the compound. The alcohol content of the benzene–alcohol azeotrope was determined by an oxidimetric method[7] which could be applied directly as benzene did not reduce potassium dichromate at room temperature. Salicylic acid was estimated by testing a known weight of the sample with a measured excess of caustic soda solution and titrating the unused alkali against a standard acetic acid solution.

Conductometric and Electrometric Titrations.—The same technique was applied as described[2] earlier.

Studies in Non-aqueous Solvents

Apparatus.—All glass apparatus with standard interchangeable joints was used throughout and special precautions were taken to exclude moisture. Fractionations were carried out in a 60 cm. column packed with Raschig rings and fitted to a total condensation variable take off stillhead.

Reaction of Zirconium Isopropoxide with Salicylic Acid.
(a) **Molar Ratio 1:4.5.**—The addition of salicylic acid (2.85 g., 0.0206 mole) to a solution of 1.82 g. of zirconium isopropoxide (0.0047 mole) in benzene (60 g.) gave a clear solution on shaking. The mixture was refluxed in a bath at 110°. The amount of isopropyl alcohol in the distillate was

(3) R. W. Ammussen and E. R. Madsen, *Z. anorg. Chem.*, **212**, 321 (1933).
(4) O. Hauser and A. levite, *Ber.*, **48**, 213 (1915); **45**, 2480 (1912).
(5) A. Rosenheim and Ichman, *Ann.*, **153**, 440 (1924).

(6) D. C. Bradley, R. C. Mehrotra and W. Wardlaw, *J. Chem. Soc.*, 2027 (1952).
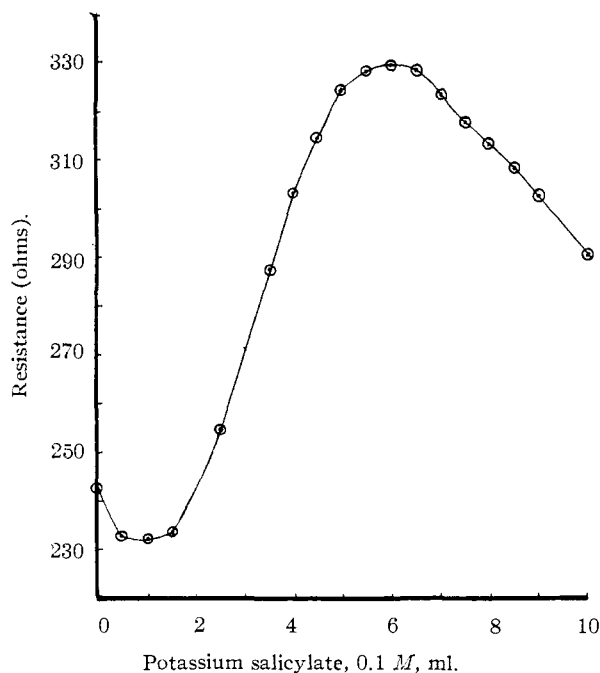(7) R. C. Mehrotra, *J. Ind. Chem. Soc.*, **30**, 588 (1953).

Fig. 1.—Conductometric titration of 50 ml. of 0.005 M zirconyl chloride with 0.1 M potassium salicylate.

1.36 g. (0.0227 mole). The residue was washed with ether and dried under reduced pressure to give a yellowish white product.

Anal. Calcd. for $(OOC \cdot C_6H_4 \cdot O)Zr(OOC \cdot C_6H_4 \cdot OH)_2$: Zr, 18.12; (HOC_6H_5COO), 81.99. Found: Zr, 18.19; (HOC_6H_4COO), 82.27.

(b) **Molar Ratio 1:1.**—A mixture of 2.44 g. of zirconium isopropoxide (0.0063 mole) dissolved in benzene (23 g.) and 0.87 g. of salicylic acid (0.0063 mole) gave a gelatinous white product on shaking. After being kept for nearly 2 hr. the volatile fractions were removed from the reaction mixture by distillation under reduced pressure (2 mm.) in a bath at 30° in the course of 2 hr. The end product was a white powder.

Anal. Calcd. for $Zr(OPr\text{-}iso)_2(O \cdot C_6H_5 \cdot COO)$: Zr, 26.41. Found: Zr, 26.51.

Molar Ratio 1:2 in Cold.—To a solution of 1.47 g. of zirconium isopropoxide (0.0038 mole) in benzene (16 g.) was added 1.04 g. of salicylic acid (0.0076 mole). After keeping overnight, the volatile fractions were removed in the usual manner under reduced pressure (2 mm.) for 2 hr. at 50°.

Anal. Calcd. for $Zr(OOC \cdot C_6H_4O)_2 \cdot Pr\text{-}iso\text{-}OH$: Zr, 21.58. Found: Zr, 21.55.

The above product, when heated to about 150° under reduced pressure (1.2 mm.) for 1 hr., appeared to lose a molecule of isopropyl alcohol.

Anal. Calcd. for $Zr(OOC \cdot C_6H_4O)_2$: Zr, 25.09. Found: Zr, 24.90.

Molar Ratio 1:2 in Hot.—When a mixture of 1.78 g. of zirconium isopropoxide (0.0046 mole) in benzene (50 g.) and 1.27 g. of salicylic acid (0.0092 mole) was refluxed as above, a yellowish white product was separated out. The distillate collected in 2 hr. (about 30 ml.) contained 1.30 g. of isopropyl alcohol (0.0217 mole). Removal of the remaining benzene under a high reflux ratio gave a yellowish white solid, which was washed with benzene and dried under reduced pressure (2 mm.) for 2 hr. at 50°.

Anal. Calcd. for $Zr(OOC \cdot C_6H_4O)_2$: Zr, 25.09. Found: Zr, 24.66.

Molar Ratio 1:3.—1.75 g. of salicylic acid (0.0127 mole) was added to a benzene (20 g.) solution of zirconium isopropoxide (1.62 g., 0.0042 mole), when a clear solution was obtained on refluxing. It was kept overnight for crystallization but no insoluble mass separated out. The volatile fractions were removed in the usual manner.
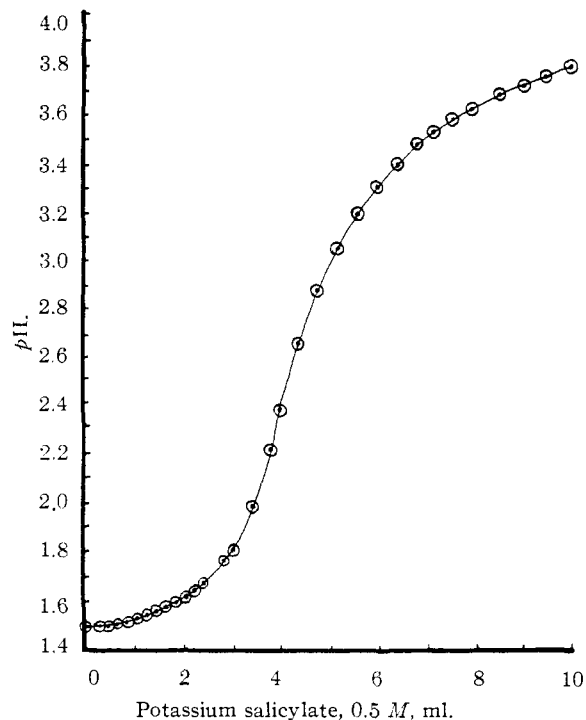

Potassium salicylate, 0.5 M, ml.

Fig. 2.—Electrometric titration of 20 ml. of 0.05 N zirconyl chloride with 0.5 M potassium salicylate.
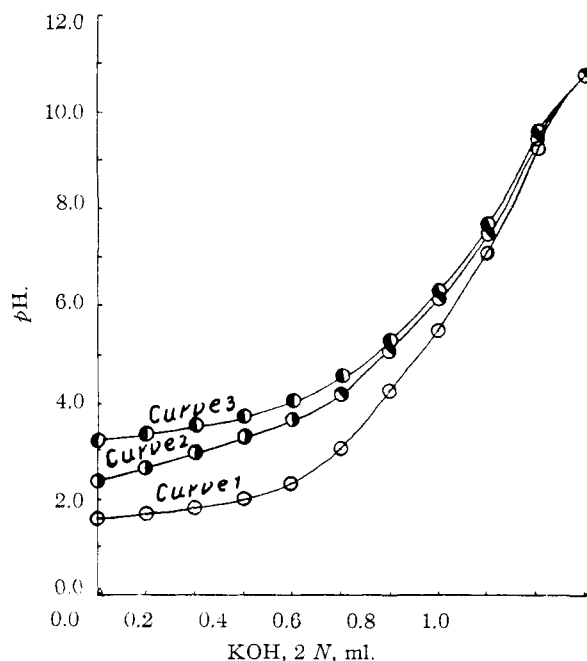

KOH, 2 N, ml.

Fig. 3.—Electrometric titration of 20 ml. of 0.05 M zirconyl chloride with 2 N KOH in the presence of 1, 2 and 3 moles of potassium salicylate, respectively.

Anal. Calcd. for $(OOC \cdot C_6H_4O)Zr(OO \cdot C_6H_4OH)_2 \cdot Pr\text{-}isoOH$: Zr, 16.23. Found: Zr, 16.50.

When this product was heated to about 80° under reduced pressure (1.2 mm.) for an hour, it appeared to lose a molecule of isopropyl alcohol.

Anal. Calcd. for $(OOC \cdot C_6H_4O)Zr(OOC \cdot C_6H_4OH)_2$: Zr, 18.38. Found: Zr, 17.90.

Reaction of Zirconium Isopropoxide with Excess Benzoic Acid.—The addition of 1.56 g. of benzoic acid (0.0125 mole)

to a solution of 1.10 g. of zirconium isopropoxide (0.00284 mole) in benzene (40 g.) gave a white shining crystalline precipitate on shaking. After being left overnight for complete crystallization, the compound was filtered, washed with benzene (15 cc.) and dried under reduced pressure (2 mm.) at room temperature.

Anal. Calcd. for $Zr(OOC \cdot C_6H_5)_4$: Zr, 15.86; $(OOC \cdot C_6H_5)$, 84.14. Found: Zr, 15.62; $(OOC \cdot C_6H_5)$, 84.3.

Reaction of Zirconium Isopropoxide with Excess Phenol. —A solution of 2.07 g. of zirconium isopropoxide (0.0053 mole) dissolved in benzene (66 g.) and 4.0 g. of phenol (0.0426 mole) gave a clear solution on shaking. The mixture was refluxed in a bath at 110°. The amount of isopropyl alcohol in the distillate collected in 2 hr. (about 30 ml.) was 1.52 g. (0.0253 mole). Pure benzene was distilled out under a high reflux ratio. The clear solution was left overnight for crystallization. A white shining mass crystallized out. The crystals were filtered, washed with benzene and then dried as usual.

Anal. Calcd. for $Zr \cdot (C_6H_5O)_4 \cdot C_6H_5OH$: Zr, 16.25; (OC_6H_5), 83.75. Found: Zr, 16.3; (OC_6H_5), 82.06.

Reaction between Zirconium Isopropoxide with Excess Benzoic Acid and Phenol.—To a solution of 1.88 g. of phenol (0.0200 mole) and 2.44 g. of benzoic acid (0.0195 mole) in benzene (69 g.) was added 1.59 g. of zirconium isopropoxide (0.0041 mole), and a clear solution was obtained. The mixture was refluxed in a bath at 110°. The amount of isopropyl alcohol in the distillate (about 30 ml.) was 1.20 g. (0.0200 mole). Remaining benzene was distilled out under a high reflux ratio. The reaction mixture was left for crystallization, when a white mass crystallized out. The crystals were filtered, washed with dry benzene and dried in the usual manner.

Anal. Calcd. for $Zr(OOC \cdot C_6H_5)_4$: Zr, 15.86; $(OOC \cdot C_6H_5)$, 84.14. Found: Zr, 18.01; $(OOC \cdot C_6H_5)$, 81.48.

Reaction between Zirconium Tetrachloride and Salicylic Acid in Benzene.—The addition of 1.86 g. of salicylic acid (0.0135 mole) to a suspension of 0.7 g. of zirconium tetrachloride (0.00303 mole) in benzene (28 g.) gave a white precipitate on shaking. The reaction mixture was refluxed in a bath at 110° for nearly 24 hr. till the evolution of hydrogen chloride gas almost ceased. The product was filtered, washed with dry benzene and dried under reduced pressure (2 mm.) in a bath at 40° for nearly 2 hr.

Anal. Calcd. for $(OOC \cdot C_6H_4O)Zr \ (OOC \cdot C_6H_4OH)_2$: Zr, 18.18; (HOC_6H_4COO), 81.99. Found: Zr, 18.28; $(HO-C_6H_4COO)$, 81.28.

Reaction between Zirconium *Iso*propoxide and Excess Methyl Salicylate in Benzene.—To a solution of 1.50 g. of zirconium *iso*propoxide (0.0038 mole) in benzene (60 g.) was added 2.93 g. of methyl salicylate (0.0193 mole), when a clear solution was obtained. The mixture was refluxed in a bath at 110°. About 40 ml. of the distillate were collected slowly between 71–80° in the course of about 3 hr. The remaining benzene was removed under a high reflux ratio and the reaction mixture (15 ml.) was left for crystallization. A shining white crystalline mass separated out. After decantation, the product was recrystallized from benzene (10 ml.). Now the crystals were separated by decantation and dried under reduced pressure (2 mm.) at a bath (50°) for nearly 2 hr. The solid has a sharp melting point of 187°.

Anal. Calcd. for $Zr \cdot (OC_6H_4CO_2CH_3)_4$: Zr, 13.11. Found: Zr, 12.93.

The Detection of a Type of Reaction Intermediate in the Combination of Metal Ions with Porphyrins

BY EVERLY B. FLEISCHER[1] AND JUI H. WANG

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A reaction intermediate in the combination of metal ions with porphyrins is detected and studied. A structure with the metal sitting-atop the flat porphyrin molecule is proposed for this intermediate compound. Spectroscopic and equilibrium data of these sitting-atop type of complexes are presented.

The metalloporphyrins, which are known to be very stable metal complexes, have been extensively studied both experimentally[2] and theoretically.[3] It has been demonstrated[4] that many metal ions in the porphyrin complex, such as Fe(II), Fe(III), Co(III), Ni(II), etc., do not undergo detectable exchange with similar ions in solution. In order to extract these transition metal ions from the metalloporphyrins, it is necessary to use concentrated hydrochloric or even sulfuric acid at high temperature. Conversely, even in basic aqueous solutions it is often necessary to heat the reaction mixture in order to introduce a transition metal ion into the porphyrin ring.[2] Based on their kinetic studies, Phillips and co-workers[5] suggested that the reaction

between zinc ion and solubilized porphyrin esters to form the corresponding metalloporphyrin takes place, as indicated in the reaction below, through a displacement rather than a dissociation type of mechanism.[6]

$$Zn^{++} + RH_2 + 2H_2O \rightleftharpoons RZn + 2H_3O^+$$
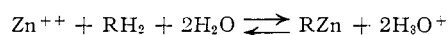
where RH_2 represents the porphyrin. We want to report some results which show not only that the reaction between metal ion and porphyrin to form metalloporphyrin takes place through a displacement mechanism but also that the metal ion first combines with the porphyrin to form a reaction intermediate which subsequently decomposes to the normal metalloporphyrin and two hydrogen ions. Our work shows that this reaction intermediate has a structure depicted in Fig. 1, with the metal ion sitting atop the flat porphyrin molecule. The

(1) National Science Foundation Predoctoral Fellow, 1959–1960.

(2) For general references, see R. Lemberg and J. W. Legge, Hematin Compounds and Bile Pigments, Interscience Publishers, Inc., New York, 1949.

(3) *Discussions Faraday Soc.*, **No. 26**, 81 (1958).

(4) S. Ruben, M. Kamen, B. Allen and P. Nahinsky, THIS JOURNAL, **64**, 2297 (1942).

(5) B. Dempsey, M. B. Lowe and J. N. Phillips, paper presented at

the Symposium on Hematin Enzymes, Canberra, Australia, Aug. 31–Sept. 4, 1959.

(6) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 91.