There is a marked increase in the fraction of the total fringe displacement contributed by the moving boundary in each limb as the pH is increased, and a corresponding decrease in the contribution from the stationary boundary. These changes are sufficiently large to be evident upon visual inspection of the schlieren patterns of Fig. 2.

Finally, if the concentrations and molar refractions of the different substances present in the various phases could be determined, the refractive index changes, and from them the fringe displacements across the various boundaries, could be predicted, and compared with the experimental values. The compositions of the original solutions may be calculated with the aid of the acid dissociation constants evaluated from the titration data. The β-phase compositions then may be estimated from the original phase compositions and appropriate conductance and boundary velocity data, using strong electrolyte moving boundary theory, which holds approximately for systems of this type.[5] The molar refractions may be determined from fringe displacement measurements across boundaries involving only potassium nitrate and across the initial boundaries in the various experiments. Values predicted in this fashion for the ytterbium experiments are listed in Table I. The reasonably good agreement between the observed and predicted values provides qualitative confirmation for the correctness of the titration curve value of K for ytterbium. (The difference of about one and one-half fringes in the total fringe displacement between the pH 10 run and the other two arises from the fact that 0.102 M rather than 0.100 M potassium nitrate was used as the top solution.) The fact that the agreement for the ascending displacements is as good as that for the descending suggests that the formation of neutral complex in the ascending β-phase is not extensive.

TABLE I

INTERFERENCE FRINGE DISPLACEMENTS ACROSS BOUNDARIES FOR YTTERBIUM–HEDTA

	Fig. 2a (pH 9.0)		Fig. 2b (pH 9.8)		Fig. 2c (pH 10.0)	
	Obsd.	Pred.	Obsd.	Pred.	Obsd.	Pred.
Descending SB[a]	5.91	5.2	3.50	3.2	1.78	1.6
Descending MB[a]	3.96	4.7	6.27	6.6	6.37	6.6
Total	9.87		9.77		8.15	
Ascending SB	5.10	5.6	3.63	3.1	2.06	1.4
Ascending MB	4.75	4.3	6.14	6.6	6.14	6.8
Total	9.85		.77		8.20	

[a] SB = stationary boundary (*i.e.*, the boundary remaining near the site of the initial boundary position); MB = moving boundary.

Acknowledgments.—This research was supported by PHS research grants GMO8394-02 from the Division of General Medical Studies and A-2240 from the Division of Arthritis and Metabolic Diseases, Public Health Service.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ARIZONA, TUCSON, ARIZONA

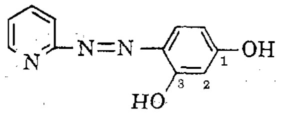
The Effect of Metal Ion Chelation on the Acid Dissociation of the Ligand 4-(2-Pyridylazo)-resorcinol

BY ALFIO CORSINI, QUINTUS FERNANDO, AND HENRY FREISER

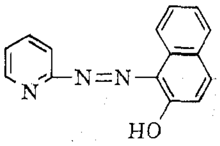
Received July 26, 1962

There has been a growing interest, recently, in the effect of metal ion chelation on the chemical properties of the ligand. Of particular interest is the effect of chelation on the acidity of ligand substituents. Investigations to date have shown, without exception, that chelation substantially increases the dissociation constants of acid substituents in the bound ligand, relative to the free ligand.[1-3]

This note is concerned with changes, caused by chelation, in the acidity of the 1-hydroxy group in 4-(2-pyridylazo)-resorcinol (PAR). The metal chelates of PAR are stable and, with the exception of the Mn(II) chelate, form at low pH.[4] These observations provided some promise that the pH range of chelate formation and of dissociation of the 1-hydroxy group in the bound ligand would not overlap appreciably.



PAR



PAN

Experimental

Materials.—The preparation and purification of all the materials used in this work have been described previously.[4]

Potentiometric Measurements.—To determine the dissociation constants of the PAR chelates, titrations were conducted as follows. Fifty ml. of water, purified by passing distilled water through an ion-exchange column, 1 to 5 ml. (depending on the solubility of the PAR chelates) of a standard (0.01 M) solution of metal perchlorate, and 25 ml. of a freshly prepared standard ($\sim 10^{-3}$ M) solution of PAR in 1,4-dioxane were added to a jacketed titration vessel maintained at 25.0 ± 0.1°. A further quantity of dioxane was added to obtain, initially, a 50% v./v. aqueous dioxane solution. The quantities of metal perchlorate and PAR added were such that the metal:ligand ratio was 1:2 for Mn, Zn, Ni, and Co and 1:1 for Cu. The dissociation constants of the hydroxy groups in the reagent PAR were determined by titration in the absence of the metal ion.

A standard solution (0.01 M) of carbonate-free sodium hydroxide was added in small increments together with equal volumes of dioxane to the stirred solution. All pH measurements were made as previously described.[4]

The Ni, Co, Zn, and Mn titrations were repeated substituting the reagent PAR with 1-(2-pyridylazo)-2-naphthol (PAN).

The pK values in Table I are average values of two or three replicate titrations.

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(2) G. I. H. Hanania and D. H. Irvine, *J. Chem. Soc.*, 2745 (Part I), 2750 (Part II) (1962).

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TABLE I

ACID DISSOCIATION CONSTANTS AND FORMATION CONSTANTS OF PAR[a] CHELATES IN 50% AQUEOUS DIOXANE AT 25°

Chelate	No. of protons released on chelation	No. of titratable protons in chelate	Acid dissociation constants		Chelate formation constants[4]	
			pK_{a_1}	pK_{a_2}	$\log k_1$	$\log k_2$
Mn	~2	~2	8.8	10.3	9.7	9.2
Zn	2	2	7.7	9.3	12.4	11.1
Ni	2	2	7.7	9.2	13.2	12.8
Co	1	2	4.7	6.0	...	...
Cu	1	1	5.5	...	16.5[b]	...

[a] Acid dissociation constants of PAR: $pK' = 7.0$; $pK'' = 12.4$ [b] M. Hniličková and L. Sommer, *Collection Czech. Chem. Commun.*, **26**, 2189 (1961); the value was corrected for an arithmetical error.

Results

The potentiometric titration curves of the PAR chelates show two distinct buffer regions. The first region corresponds to the release of protons due to chelation (eq. 1). Data from this region provide the basis for chelate formation constant calculations.[4] The second buffer region is due to proton release from the hydroxy groups in the metal chelate (eq. 2 and 3). Failure to recognize the existence of the second buffer region has led to erroneous values for the chelate formation constants of PAR with several metal ions.[5]

$$2H_2A + M^{++} \xrightleftharpoons{\text{chelation}} M(HA)_2 + 2H^+ \qquad (1)$$

$$M(HA)_2 \xrightleftharpoons{K_{a_1}} M(HA)(A^-) + H^+ \qquad (2)$$

$$M(HA)(A^-) \xrightleftharpoons{K_{a_2}} MA_2^{-2} + H^+ \qquad (3)$$

The acid dissociation constants, pK_{a_1} and pK_{a_2}, of the 1-hydroxy groups in the bound ligand were determined from the data in the second buffer region.[6] These values of the acid dissociation constants together with the dissociation constants of the 1-hydroxy (pK') and 3-hydroxy (pK'') groups in the free PAR ligand are given in Table I. Despite the very weakly acidic nature of the 3-hydroxy group ($pK'' = 12.4$), its proton is released on chelation. Since chelate formation with metal ions occurs at pH values well below 7, the more acidic 1-hydroxy group ($pK' = 7.0$) is left intact.[4]

Since it is conceivable that the second step in the titration of the 1:2 PAR chelates is due to metal ion hydrolysis, the titrations were repeated for Ni, Co, Zn, and Mn using 1-(2-pyridylazo)-2-naphthol (PAN) (in which the hydroxy group *para* to the azo group is absent) in place of PAR. In the titrations of the PAN chelates the second step is absent; hence the presence of the second step in the titration of the 1:2 PAR chelates may be interpreted as dissociation of the 1-hydroxy group in the bound ligand and not metal ion hydrolysis. Only in the case of the Mn(II)–PAN titration is there a suggestion that a small, but not very significant, amount of metal ion hydrolysis has occurred. The extent of hydrolysis in the Mn(II)–PAR system would be even less than in the Mn(II)–PAN system, since the PAR chelate is more stable and forms at lower pH values.[4]

In the titration curve for Mn, the pH region in which chelation occurs overlaps that in which the dissociation of the 1-hydroxy group of the chelate occurs. This complexity must be taken into account in order to calculate the pK_{a_1} and pK_{a_2} values as well as the chelate formation constants.

On the basis of previous investigations of the stoichiometry of the Cu(II) chelates of PAR and PAN[4,7–9] the titration of the Cu(II) system was carried out at a Cu(II) to PAR ratio of 1:1. As expected, the first and second steps in the titration curve each correspond to one mole of NaOH per mole of metal ion.

In the cobalt–PAR titration, the total number of titratable protons per metal ion is three and not four as is expected for the 1:2 chelates. A similar anomaly was found in the titration of the cobalt–PAN system in which only one proton is released on the formation of the chelate which has been shown from solvent extraction studies to be a 1:2 chelate. It is not possible to distinguish the number of protons released in the chelation of cobalt with PAR from those released on subsequent ionization of H^+ from the chelate. However, if this behavior is similar to that of PAN then the cobalt chelate, like the Mn, Zn, and Ni chelates, may lose two protons. It is possible that in the formation of both the PAN and PAR cobalt chelates, an oxidation to Co(III) occurs,[10] and this oxidation might consume one proton. This would help explain the greater acidity of the 1-hydroxy groups in the cobalt–PAR chelate since it would carry a positive charge.

In the titration of the zinc and nickel chelates of PAR, two protons are released on chelation and two protons are released on the dissociation of the two 1-hydroxy groups in each chelate. The values of pK_{a_1} and pK_{a_2} for the PAR chelates are collected in Table I.

Discussion

The acid strengths of the 1-hydroxy groups in the PAR chelates increase in the order Mn(II) < Zn(II) ~ Ni(II) < Cu(II) < Co. This parallels the chelate stability order for Mn, Zn, and Ni (Table I). A similar trend has been observed previously with the chelates of 2-(2-pyridyl)-benzimidazole.[1] This acid-strengthening effect of the metal ion in PAR chelates probably is transmitted to the 1-hydroxy group *via* the bonding oxygen atom rather than through the azo group, since a study of models indicates that the azo group does not lie in the plane of the resorcinol ring in the tridentate metal–PAR chelates.[11] Hence the effect of the azo group on the 1-hydroxy group in the metal–PAR chelates is much less than that on the 1-hydroxy group of the bidentate hydrogen chelate.

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(5) W. J. Geary, G. Nickless, and F. H. Pollard, *Anal. Chim. Acta*, **27**, 71 (1962).

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In the PAR molecule, the hydrogen atom of the 3-hydroxy group is bonded to the azo group, thereby forming a planar system in which there is maximum conjugation between the azo group and the resorcinol ring. The azo group therefore can exert its large electron-withdrawing effect on the 1-hydroxy group and increase its acid strength considerably. This is demonstrated by the comparison of the pK value of the 1-hydroxy group in the free PAR molecule (7.0) with that of the 1-hydroxy group in 4-(2-pyridylazo)-1-naphthol (p$K' = 10.7$).[12] In the latter compound there is less conjugation in the system and the azo group has a relatively small electron-withdrawing effect on the 1-hydroxy group.

The apparently anomalous position of the hydrogen chelate of PAR (p$K' = 7.0$) in the chelate-acidity series (Table I) may now be understood to arise from these considerations. The especially large acid-strengthening effect on the hydroxy group in the 1:1 Cu(II) chelate of PAR as well as on the hydroxy groups of the 1:2 cobalt PAR chelate may be caused by the excess positive charge on the chelates.

Acknowledgment.—The authors are grateful to the U. S. Atomic Energy Commission for financial assistance.

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CONTRIBUTION FROM THE
METCALF CHEMICAL LABORATORIES
OF BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND

Evidence for the Open Chain Structure of Ethane 1,2-Diamineborane[1]

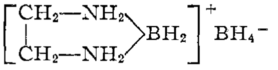
BY HENRY C. KELLY AND JOHN O. EDWARDS

Received April 12, 1962

In a previous publication,[2] various aspects of the chemistry of a white crystalline compound, obtained by the reaction of diborane with ethylenediamine, were described. This product was named ethane 1,2-diamineborane on the assumption that the structure was represented by the open chain configuration (I). In view of the fact that Parry and co-workers[3] have shown that the "diammoniate of diborane" has an ionic structure, $[(NH_3)_2BH_2]^+BH_4^-$, structure II also was considered possible.

$H_3BNH_2CH_2CH_2NH_2BH_3$

I



$$\left[\begin{array}{l}CH_2—NH_2\\ |\\ CH_2—NH_2\end{array}\!\!>BH_2\right]^+BH_4^-$$

II

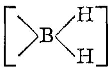
Structure I was favored on the basis of dehydrogenation data and solubility characteristics.

More recently, Goubeau and Schneider[4] reported the preparation of a compound from the reaction of ethylenediamine dihydrochloride with sodium borohydride in tetrahydrofuran. They postulated the "electrolyte" structure (II) for this product largely on the basis of its infrared spectrum.

We now report evidence which indicates that the compound prepared from diborane and ethylenediamine is identical with that obtained by the reaction of ethylenediamine dihydrochloride with sodium borohydride, and that this compound has the structure represented by configuration I.

Results and Discussion

The open chain structure of ethane 1,2-diamineborane has been confirmed by cryoscopic studies in water, and by means of the B^{11} nuclear magnetic resonance (n.m.r.) spectrum. The experimental value of 88 ± 7 molecular weight units is consistent with a monomeric species (I). The B^{11} n.m.r. spectrum, obtained in dimethoxyethane solution,[5] consists of a single boron resonance line split into a quadruplet having peaks of relative intensity 1:3:3:1. Thus, the two boron atoms are equivalent and each is bonded to three hydrogen atoms. The coupling constant of 88 c.p.s. agrees with J_{B-H} values reported for other amineboranes.[6] The B^{11} spectrum of a compound represented by structure II would consist of two boron resonance lines. One of these would be split into a triplet due to spin coupling between boron and two terminal hydrogens in the boronium species



$$\left[>B\begin{array}{l}H\\ H\end{array}\right]^+$$

The second would be split into a quintuplet due to the coupling of four hydrogen atoms with boron in the borohydride ion. The product of the ethylenediamine–diborane reaction is, clearly, ethane 1,2-diamineborane (I).

This assignment is consistent with solubility data, dehydrogenation data, and results obtained with thallium(I) salts. For example, the high solubility of ethane 1,2-diamineborane in tetrahydrofuran (46–47 g./l. of solution at 25°), 1,2-dimethoxyethane (90–91 g./l. at 27°), and bis-(2-methoxyethyl) ether (98–99 g./l. at 27°) relative to its solubility in water (8–9 g./l. at 27°) is in contrast to the solubility characteristics of the ionic compounds sodium and potassium borohydride.[7]

In addition, the liberation of two moles of hydrogen on thermal decomposition of one mole of starting material is consistent with the known dehydrogenation of

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[1] Taken from the Ph.D. thesis submitted by H. C. K. to Brown University, September, 1961.

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[7] "Sodium Borohydride, Potassium Borohydride," Metal Hydrides, Inc., Beverly, Mass., March, 1958.