

64. Acidity Constants of the Thienyl- and Phenyl-Pyridines and Stability Constants of the Corresponding Copper (II) 1:1 Complexes

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Summary. The acidity constants of the six thienyl- and the three phenyl-pyridines, and the stability constants of the corresponding Cu^{2+} 1:1 complexes were determined in aqueous solution ($I = 0.1$, NaClO_4 ; 25°). The basicity of the pyridyl group is increased by a shift of a thienyl or phenyl group in the order $2 < 3 < 4$ and the influence of the 2'-thienyl group is greater than that of the 3'-thienyl group. The stability of the Cu^{2+} 1:1 complexes formed with 3- and 4-substituted pyridines is only dependent on their basicity, as is commonly observed for structurally related ligands and their complexes. Due to steric hindrance the complexes of the 2-substituted derivatives are less stable by about 1.5 log units. There is no evidence that the aromatic bonded sulfur of 2-(2'-thienyl)-pyridine participates in complex formation with Cu^{2+} , in opposition to an earlier claim [1].

In the present work the acidity constants of the six thienylpyridines (I–VI), 2-, 3-, and 4-phenylpyridine, and 2-benzylpyridine, as well as the stability constants of their Cu^{2+} 1:1 complexes were determined and compared³⁾. The published constants of pyridine, 2-, 3-, and 4-methylpyridine [1] are given with our data.

Our aim was to show, if a possible steric hindrance in α -substituted pyridines is reflected in the stability of the Cu^{2+} 1:1 complexes. If so it should be possible to deduce whether or not the aromatic bonded sulfur, as present in a sterically favoured position in 2-(2'-thienyl)-pyridine (I) participates in chelate formation.

Experimental. The six thienylpyridines [2], 2- [3], 3- [4], and 4-phenylpyridines [5] were synthesized as described. 2-Benzylpyridine was obtained from *Dr. F. Raschig GmbH*, Ludwigshafen am Rhein, Germany. All other materials were from *Fluka AG*, Buchs, Switzerland.

The apparatus and the procedure of measuring and of evaluating the experimental data are described in [1].

The acidity constants of the ligands and the stability constants of the corresponding Cu^{2+} 1:1 complexes (see Table) have been determined by potentiometric titration in aqueous solution ($I = 0.1$, NaClO_4 ; 25° for the measures with the ligands, for the Cu-complexes part of the NaClO_4 was replaced by an excess of $\text{Cu}(\text{ClO}_4)_2$ with respect to the concentration of the ligand). On titrating solutions containing only Cu^{2+} , care was taken that the stability constants were calculated only for the pH range for which hydrolysis of Cu^{2+} could be omitted.

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³⁾ In 1964 *Kahmann, Sigel & Erlenmeyer* [1] described the synthesis of a thienylpyridine to which the structure of 2-(2'-thienyl)-pyridine was assigned. By synthesizing all six possible thienylpyridines *Wynberg, van Bergen & Kellogg* [2] showed that the isomer used by *Kahmann et al.* [1] was actually 4-(2'-thienyl)-pyridine and not the believed 2-(2')-isomer. Hence, the results attributed to 2-(2'-thienyl)-pyridine (I) are actually those of 4-(2'-thienyl)-pyridine. Therefore the conclusions of *Kahmann et al.* [1] concerning the ability of aromatic bonded sulfur to participate in chelate formation need revision.

The acidity constant of 2-(2'-thienyl)-pyridine $pK_{HL}^H = 3.76 \pm 0.03$ determined by spectrophotometry was in good agreement with that determined potentiometrically.

The constants found for 4-(2'-thienyl)-pyridine agree well with those given earlier [1]³). The same is true for the spectrophotometric determination of the acidity constant of this ligand: $pK_{HL}^H = 5.58 \pm 0.02$.

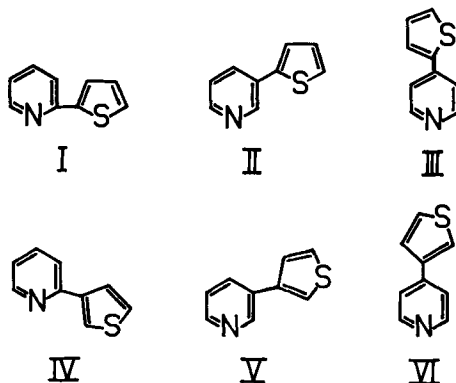


Table I

Acidity Constants, K_{HL}^H , of the Thienylpyridines, the Phenylpyridines, Pyridine, and Other Derivatives Thereof, and Stability Constants, K_{CuL}^{Cu} , of Their Corresponding Cu^{2+} 1:1 Complexes (I = 0.1, $NaClO_4$; 25°)^a)

No.	Ligand	pK'_A ^{b)}	pK_{HL}^H ^{c)}	$\log K_{CuL}^{Cu}$ ^{d)}
I	2-(2'-thienyl)-pyridine	3.775 ± 0.009	3.797 ± 0.012	~ 0.2
II	3-(2'-thienyl)-pyridine	3.794 ± 0.006	4.515 ± 0.006	2.15
III	4-(2'-thienyl)-pyridine	4.504 ± 0.027	5.591 ± 0.003	2.57
IV	2-(3'-thienyl)-pyridine	4.710 ± 0.006	4.776 ± 0.006	~ 0.7
V	3-(3'-thienyl)-pyridine	4.073 ± 0.006	4.920 ± 0.009	2.30
VI	4-(3'-thienyl)-pyridine	4.528 ± 0.012	5.712 ± 0.003	2.67
VII	2-phenylpyridine ^{e)}	4.667 ± 0.009	4.735 ± 0.009	~ 0.7
VIII	3-phenylpyridine	4.118 ± 0.012	4.924 ± 0.006	2.25
IX	4-phenylpyridine	4.430 ± 0.012	5.488 ± 0.009	2.54
X	pyridine ^{f)}		5.33	2.54
XI	2-methylpyridine ^{f)}		6.06	1.3
XII	3-methylpyridine ^{f)}		6.00	2.77
XIII	4-methylpyridine ^{f)}		6.18	2.88
XIV	2-benzylpyridine	5.148 ± 0.012	5.226 ± 0.003	~ 0.8

^a) The range of error given is three times the standard deviation. All results are the average of at least four titration curves evaluated at 15 or more pH values.

^b) Apparent acidity constant of the ligand in the presence of excess of Cu^{2+} (cf. [1]); $[Cu^{2+}]_{tot} = 3 \cdot 10^{-2} M$.

^c) $K_{HL}^H = [L][H]/[HL]$.

^d) $K_{CuL}^{Cu} = [CuL]/([Cu][L])$.

^e) Values given in [1]: $pK_{HL}^H = 4.77$; $\log K_{CuL}^{Cu} = 1.3$. The agreement between the acidity constants is good, and that between the stability constants reasonable, if one takes into account that the difference between pK_{HL}^H and pK'_A is very small.

^f) Data taken from [1].

question whether aromatic bonded sulfur may participate in complex formation. There is evidence for the participation of S in the Cu^{2+} complexes formed with 5-(2'-pyridyl)-thiazol [9] and thiophene-2-carboxylate [10]. The complexing capacities of *aliphatic* bonded sulfur in thioethers are wellknown [1] [10] [11].

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65. Utilisation d'ylides du phosphore en chimie des sucres, X¹⁾
Synthèse stéréospécifique de l'épimère en C3 du streptose et d'autres
sucres ramifiés, dérivés de désoxy-5-pentoses, à groupements
gem-hydroxy-formyle ou gem-hydroxy-hydroxyméthyle

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Summary. The synthesis of branched-chain sugars of the *gem*-hydroxy-formyl and the *gem*-hydroxy-hydroxymethyl types is described. A 5-deoxy-1,2-O-isopropylidene-furanos-3-ulose is treated with cyanomethylene-triphenyl-phosphorane, yielding the two geometrical isomers of the corresponding branched-chain unsaturated sugar. *Cis*-dihydroxylation (KMnO_4) of these cyanomethylene compounds affords stereoselectively and in high yield the *gem*-hydroxy-formyl branched chain sugars whose formyl group is on the more hindered face of the furanose ring. The hydroxymethyl analogues of the latter compounds are readily prepared by their borohydride reduction. This method constitutes a new general route to type A branched-chain sugars epimeric at the branching-point with the sugars which would have been obtained by the classical procedure involving *Grignard* reagents.

¹⁾ La référence [1] constitue la neuvième communication de cette série.

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