atom can form three H-bonds with adjacent water molecules. In the condensed anions the oxygen atoms are at the vertices of MoO_6 and WO_6 octahedra which are sharing edges with one another. The possible number of H-bonds per oxygen atom in the polyanions is therefore much less. From the above ratios, equation 1, plus the crystal structures of $[Mo_7O_{24}]^{-6}$ (paramolybdate),[33] $[Mo_8O_{26}]^{-4}$ ("tetramolybdate")[33] and $[H_{10}W_{12}O_{46}]^{-10}$ (paratungstate),[34] Ottar concludes that an average of two H-bonds per oxygen atom is likely for polyanions.[35]

Although this is a plausible average value, it must be remembered that in most polyanion structures some oxygen atoms are completely shielded from contact with the solvent. Others are only slightly exposed, while a few project prominently. It is therefore to be expected that the average number of H-bonds per oxygen atom will vary considerably according to the structure of the anion.

Unfortunately, the various series of isopolyanions for which considerable diffusion data are available were not well-suited for testing Ottar's proposals. In most cases the structures of the species present in such solutions are unknown and in many instances even their formulas are as yet unclarified.

A major purpose of the present work, therefore, was to measure the diffusion coefficients for two 12-heteropoly anions of well-established formula, structure, and nearly spherical shape, in order to test the new proposals more rigorously.

For the 6-heteropoly species used, the formulas are well-known,[16,17,29] although each of those anions might contain as many as three molecules of consitutional water. It is virtually certain that every oxygen atom in these 6-heteropoly species is exposed to the solvent.

Calculation on the basis outlined above, using any of the present results, reveals an "average value" of only one H-bond per oxygen atom for any of these four heteropoly species.

The reference diffusion coefficients for simple MoO_4^{-2} and WO_4^{-2} were obtained by extrapolating to 30° the same Jander and Anderson values which Ottar used. This was done by plotting[8] $\log D/T$ *vs.* $1/(RT)^2$.

Consideration of these results, especially in conjunction with the known structures of these ions and those used by Ottar, unfortunately greatly reduces any hope that diffusion coefficients of polyanions may be correlated, even approximately, on the bases discussed above. In several respects the discrepancies run too strongly in directions opposite to those predicted. Still less is it indicated that diffusion coefficients will be of value in revealing the status of unknown polyanions in solution. More good data on species of known structure and stability might reveal some basis for correlation.

Acknowledgments.—The authors gratefully acknowledge their indebtedness for very helpful discussions with Prof. Henry Eyring, Prof. J. S. Anderson and Prof. Viktor I. Spitzyn. We are similarly indebted to Dr. B. Ottar and to Prof. Reginald Mills for helpful correspondence and advice. This research was supported by the U. S. Atomic Energy Commission, through Contract AT(30-1)-1853.

(33) I. Lindqvist, *Arkiv Kemi*, **2**, 349 (1950).

(34) I. Lindqvist, *Acta Cryst.*, **5**, 667 (1952).

(35) Unfortunately, the role of the ten constitutional hydrogen atoms in paratungstate is completely unknown[34] and was completely neglected in the calculation.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

Influence of Structure on the Stability of Some Heterocyclic Amine Chelates[1,2]

BY T. J. LANE, C.S.C. AND JOHN W. THOMPSON

RECEIVED JANUARY 28, 1960

The acid dissociation constants of 2-aminomethyl benzimidazole and analogous compounds, as well as the stability constants of the Cu(II), Co(II), Ni(II) and Zn(II) chelates, have been determined by the potentiometric titration method. The ratio of $\log K_{AV}/\log K_{RH^+}$ was used as a criterion of steric effects in planar chelates. By this method it was found that the benzene portion of benzimidazole apparently exerts little or no steric effect in chelates of the aminoalkyl derivatives. The absence of steric effects in the aminoalkyl-benzimidazoles was used to explain the apparent lack of agreement between stability constants of the benzimidazole carboxylic acids and those found for similar compounds by previous authors.

Several studies have been made on the effect of sterically blocking groups on the stability of complexes.[3-5] Freiser and Johnston,[5] in studying the effect of methyl substitution in the 8-hydroxyquinoline molecule, found that chelates of the 2-methyl derivative were less stable than the corresponding chelates of the 4-methyl derivative and that the Ni(II) chelate of the 2-methyl compound was less stable than the corresponding Co(II) chelate. This inversion of the Ni–Co order, which Freiser attributed to steric effects, was also found with chelates of 2-(*o*-hydroxyphenyl)-benzimidazole and analogous compounds.[6] In these compounds the steric effects apparently were produced by the benzene portion of the benzimidazole molecule. Previous work on the carboxylic acid derivatives of benzimi-

(1) Presented in part before the Physical Chemistry Division of the 135th National Meeting of the A.C.S. at Boston, Mass., April, 1959.

(2) Based on a thesis submitted by John W. Thompson to the Graduate School of the University of Notre Dame in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) F. Basolo and R. K. Murmann, THIS JOURNAL, **74**, 5243 (1952); **76**, 211 (1954).

(4) F. Basolo, Y. T. Chen and R. K. Murmann, *ibid.*, **75**, 1478 (1953); **76**, 956 (1954).

(5) H. Freiser and W. D. Johnston, *Anal. Chim. Acta*, **11**, 201 (1954).

(6) H. Freiser and W. D. Johnston, *ibid.*, **11**, 201 (1954).

dazole[7] showed the normal order of chelate stability, *viz.*, Ni(II) > Co(II). If the benzene portion of the benzimidazole is actually a sterically blocking group causing an inversion in the order of Co and Ni, then this inverted order should have also been found in the benzimidazole carboxylic acids. In order to explore these effects in greater detail, it was thought appropriate to determine the extent to which the benzene portion of the benzimidazole interferes sterically with chelation.

Experimental

Apparatus and Procedure.—The apparatus, procedure and preparation of metal stock solutions have been described previously.[8]

Materials.—2-Aminomethylbenzimidazole, 2-methylaminomethylbenzimidazole and 2-(*o*-aminophenyl)-benzimidazole were prepared by standard methods.[9,10]

2-(2-Aminoethyl)-benzimidazole was prepared according to the method of Hein, *et al.*,[11] by reaction of benzoyl-β-alanine (from equimolecular quantities of benzoyl chloride and β-alanine) and *o*-phenylenediamine. The resulting product was hydrolyzed with concd. HCl to give benzoic acid and the dihydrochloride of 2-(2-aminoethyl)-benzimidazole.

2-Aminomethylpyridine, 6-methyl-2-aminomethylpyridine, 2-picolylmethylamine (Aldrich Chemical Company, Milwaukee, Wisc.) and 2-(2-aminoethyl)-pyridine (Sapon Laboratories, Valley Stream, New York) were purified by vacuum distillation. Titration data showed at least 99% purity for all the compounds studied.

Method of Calculation.—The acid dissociation constants were determined from the titration of a mixture of amine and acid with standard sodium hydroxide. The formation constants were determined from plots of $\bar{n}$ against pR. The following expressions for these terms were derived by a method similar to that given by Freiser, Charles and Johnston.[8]

$$\bar{n} \cdot T_{\mathrm{M}} = T_{\mathrm{R}} - S\left[\frac{(\mathrm{H}^+)^2 + (\mathrm{H}^+)\cdot k_2 + k_1k_2}{2(\mathrm{H}^+)^2 + (\mathrm{H}^+)\cdot k_2}\right]$$

$$R = \frac{S\cdot k_1\cdot k_2}{2(\mathrm{H}^+)^2 + (\mathrm{H}^+)}$$

where

S = $A + \mathrm{OH}^- - \mathrm{Na}^+ - \mathrm{H}^+$
T_{M} = total metal ion concentration
T_{R} = total amine concentration
A = total acid originally added
Na^+ = concentration of sodium ion from added sodium hydroxide

$$k_1 = K_{\mathrm{RH}^+} = \frac{(\mathrm{R})(\mathrm{H}^+)}{(\mathrm{RH}^+)}$$

$$k_2 = K_{\mathrm{RH_2}^{++}} = \frac{(\mathrm{RH}^+)(\mathrm{H}^+)}{(\mathrm{RH_2}^{++})}$$

The values of the temporaty constants log K_n were taken as equal to pR at the points $\bar{n} = n - 0.5$. In the case of the Cu(II) chelates, when log K_1 − log K_2 was less than 1.3 log units, true constants were calculated by the method of Rossotti and Rossotti.[12]

Results

The acid dissociation constants for the ligands are presented in Table I. The formation constants of the Cu(II), Ni(II), Co(II) and Zn(II) complexes are listed in Table II. K_3 values for Co(II) and Ni(II) with some ligands were too low to be determined. No formation constants could be calculated with 2-(*o*-aminophenyl)-benzimidazole since $\bar{n}$ values of 2.0 were obtained at the outset of the titration. Formation curves for all copper(II) complexes leveled off as $\bar{n}$ approached 2.0.

Table I

Acid Dissociation Constants at 25° in 50% v.v. Dioxane

	$pK_{\mathrm{RH_2}^{++}}$	pK_{RH^+}
2-Aminomethylbenzimidazole	2.28	7.16
2-Aminomethylpyridine	1.78	8.18
6-Methyl-2-aminomethylpyridine	2.32	8.28
2-(2-Aminoethyl)-benzimidazole	3.49[a]	8.58[a]
2-(2-Aminoethyl)-pyridine	2.71	9.15
2-Methylaminomethylbenzimidazole	2.33[a]	7.32[a]
2-Picolylmethylamine	2.15	8.41
2-(*o*-Aminophenyl)-benzimidazole		3.84

[a] Compound run as hydrochloride.

Discussion

Acid dissociation constants in Table I show all the ligands to be diprotic with the exception of 2-(*o*-aminophenyl)-benzimidazole. Only one constant could be determined for this compound as in the case of α,α′-bipyridine and 2-pyridylbenzimida-

Table II

Chelate Stability Constants at 25° in 50% v.v. Dioxane

	log K_1	log K_2	log β_2	log K_3
2-Aminomethylbenzimidazole				
Cu(II)[a]	7.48	7.08	14.56	
Ni(II)	6.27	5.43	11.70	4.35
Co(II)	5.29	4.39	9.68	(3.60)
Zn(II)	5.80	4.72	10.52	
2-Aminomethylpyridine				
Cu(II)[a]	8.49	7.24	15.73	
Ni(II)	7.25	5.90	13.15	3.90
Co(II)	5.75	4.58	10.39	(2.80)
Zn(II)	5.57	4.27	9.84	
6-Methyl-2-aminomethylpyridine				
Cu(II)[a]	6.74	5.89	12.60	
	6.76[b]	5.80[b]		
Ni(II)	5.05	3.40	8.45	
Co(II)	4.10	(2.90)	7.00	
Zn(II)	4.30	(3.50)	(7.80)	
2-(2-Aminoethyl)-benzimidazole·2HCl				
Cu(II)	7.51	5.57	13.08	
Ni(II)	5.20	3.30	8.50	
Co(II)[c]	..	..	..	
Zn(II)	5.80	(4.05)	9.85	
2-Methylaminomethylbenzimidazole·2HCl				
Cu(II)	(7.50)	5.05	12.55	
Ni(II)	5.37	(4.00)	9.37	
Co(II)[c]	..	..	..	
Zn(II)	4.30	(3.20)	(7.50)	
2-Picolylmethylamine				
Cu(II)	(8.50)	6.10	14.60	
2-(2-Aminomethyl)-pyridine				
Cu(II)	7.45	5.45	12.90	

[a] Calculated by method of Rossotti and Rossotti. [b] Hydrochloride run as a check. [c] No values obtained before hydrolysis.

---

[7] T. J. Lane, C.S.C., and J. M. Daly, This Journal, **81**, 2953 (1959).

[8] H. Freiser, R. G. Charles and W. D. Johnston, *ibid.*, **74**, 1383 (1952).

[9] E. S. Lane, *J. Chem. Soc.*, 3313 (1957).

[10] A. Bloom and A. R. Day, *J. Org. Chem.*, **4**, 14 (1939).

[11] D. W. Hein, R. J. Alkeim and J. J. Leavitt, *ibid.*, **79**, 427 (1957).

[12] F. J. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1166 (1955).

zole, which also form only a monoprotonated species.[13,14]

Comparison of stabilities by means of the ratio log K_{AV} to log K_{RH^+} should be valid since the acid dissociation constants of the ligands are all in the same range. Bjerrum[15] used this method to compare the affinity of the ligand for hydrogen to its tendency to coördinate with metals and found that for the same metal and the same type of ligand, this ratio should be a constant. However, if steric factors affect the stability of the complex, the ratio will be decreased. Recent workers[16] have questioned the use of a method of comparison based on only one acid constant, and Fernelius and Goldberg[17] have used the sum of the acid constants to determine the extent of π-bonding in chelates of the same type as those in the present study.

In Table III are listed the values of the ratio obtained using only one acid constant as well as those for the ratio log K_{AV}/(log $K_{RH_2^{++}}$ + log K_{RH^+}). According to either method it appears that steric hindrance is no greater in the planar chelates of 2-aminomethylbenzimidazole or of 2-(2-aminoethyl)-benzimidazole than in the corresponding pyridine compounds. For the N-methyl- derivatives, however, the ratio for the benzimidazole compound decreases with respect to that of the pyridine. The apparent reason is that the methyl group on the amino nitrogen can overlap with the benzene portion of the benzimidazole in a 2:1 planar chelate. The lack of steric effects in the aminoethyl- and aminomethylbenzimidazoles can be attributed to the orientation of the electrons on the 3-nitrogen away from the hydrogen in the 4-position as shown in Fig. 1. Lane, *et al.*,[18] used the same argument to explain their results for chelates of 4-hydroxybenzimidazole. Although the latter compound is more basic than the structurally similar 8-hydroxyquinoline, the stability of the chelates which it forms are of the order of 10^{10} lower than those formed by oxine. Apparently the unfavorable orientation of the electrons reduces the chelating tendency between the 3-nitrogen and the 4-oxygen.

The conclusion is that the benzene portion of the benzimidazoles does not cause any significant steric hindrance in planar chelates provided that the coördinating group in the 2-position is small, *e.g.*—CH_2NH_2, –CH_2OH, –COOH, etc. However, if a bulky group is coördinating, such as the methylaminomethyl- or the *o*-hydroxyphenyl-, this group may be sufficiently large to overlap with the hydrogen in the 4-position and thus cause steric interference.

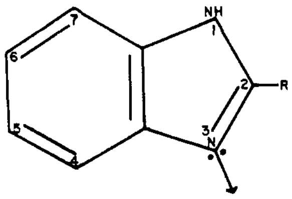

Fig. 1.—Orientation of the donor electrons on the nitrogen atom in benzimidazole.

TABLE III

RELATION OF STABILITY CONSTANTS OF Cu(II) CHELATES TO THE *pK*'S OF THE LIGANDS

	log K_{AV}/ log K_{RH^+}	log K_{AV}/ (log K_{RH^+} + log $K_{RH_2^{++}}$)
2-Aminomethylbenzimidazole	1.01	0.77
2-Aminomethylpyridine	0.96	.79
2-Aminoethylbenzimidazole	.77	.54
2-Aminoethylpyridine	.71	.54
2-Methylaminomethylbenzimidazole	.86	.65
2-Picolylmethylamine	.84	.69
6-Methyl-2-aminomethylpyridine	.76	.59

Little can be said concerning steric factors in the chelates of the other metals. In most cases the order of chelate stability was Cu > Ni > Co, Zn. There seems to be no correlation between steric effects and the position of Zn(II) in the series. In general, Zn(II) was found to be more stable than Co(II) with the benzimidazoles and less stable than Co(II) with the pyridines. These metals were not run with 2-picolylmethylamine and 2-(2-aminoethyl)-pyridine, but the results, recently obtained by Goldberg and Fernelius,[17] are in accord with this generalization. Lane and Daly[7] also noticed an enhancement of the stability of Zn(II) chelates in their study of the benzimidazolecarboxylic acid derivatives.

Acknowledgments.—The authors are grateful to Dr. J. L. Walter for many helpful suggestions. Financial aid for the work was provided by the Radiation Project of the University of Notre Dame, supported in part under U. S. Atomic Energy Commission Contract AT(11-1)-38 and from a research grant A-2763 from the Department of Health, Education and Welfare, Public Health Service.

---

[13] J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 55 (1950).

[14] T. R. Harkins and H. Freiser, THIS JOURNAL, **78**, 1143 (1956).

[15] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

[16] H. Freiser, Q. Fernando and G. Cheney, *J. Phys. Chem.*, **63**, 250 (1959).

[17] D. E. Goldberg and W. C. Fernelius, *ibid.*, **63**, 1246 (1959).

[18] T. J. Lane, A. Sam and A. Kandathil, presented before the Physical Chemistry Division of the 136th Meeting of the American Chemical Society, Atlantic City, 1959.