that any changes in the orientation of the perchlorate ion would have only a very slight effect on the crystal field at the copper ion. On the other hand, a change in the orientation of the ethyl groups or more particularly a conformational change in the ring would affect the nitrogen atoms and thus be much more effective in changing the ligand field. Such conformational changes are most likely the source of the thermochromism. The elucidation of this problem will have to wait for a complete crystal structure determination.[5]

Acknowledgment.—This research was supported by the National Science Foundation. The authors wish to thank Dr. G. Newman for the infrared measurements and Dr. C. E. Pfluger for discussions about the crystal structures.

Notes

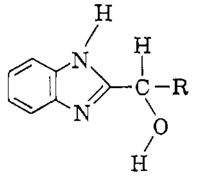
CONTRIBUTION FROM THE DEPARTMENT
OF CHEMISTRY AND RADIATION LABORATORY,[1a]
UNIVERSITY OF NOTRE DAME,
NOTRE DAME, INDIANA

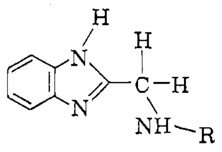
Formation Constants and Steric Factors in the Copper(II) Chelates of 2-Substituted Benzimidazoles

BY T. J. LANE, C.S.C., AND H. B. DURHAM[1b]

Received July 25, 1962

The acid dissociation constants and the stability constants for the Cu(II) chelates of 2-(α-hydroxyalkyl)-benzimidazoles (I) and of 2-(N-alkylaminomethyl)-benzimidazoles (II) (alkyl = H, CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, and n-C_5H_{11}) are presented. This preliminary study suggests that several factors are important in affecting the stability of these chelates.


I


II

Experimental

Preparation of Compounds.—2-Hydroxymethyl- and 2-(α-hydroxyethyl)-benzimidazoles were prepared according to the method of Phillips.[2] Purity was established by comparing melting points and analyses with reported values[2]; m.p.: 2-hydroxymethyl-, lit. 171–172°, obsd. 170–171°; 2-(α-hydroxyethyl)-, lit. 178–179°, obsd. 180–181°.

2-(α-Hydroxypropyl)-, 2-(α-hydroxybutyl)-, and 2-(α-hydroxyamyl)-benzimidazoles have not been reported in the literature. They were successfully prepared by the method of Phillips[2] from o-phenylenediamine (0.02 mole) in each case and (0.03 mole) of the proper acid, namely 2-hydroxybutanoic acid, 2-hydroxypentanoic acid, and 2-hydroxyhexanoic acid, respectively. After decolorization with charcoal and three recrystallizations from 50% aqueous ethanol the white crystals obtained from each of the compounds melted at 221–222°, 181–182°, and 190–191°, respectively.

Anal. Calcd. for $C_{10}H_{12}N_2O$: C, 68.2; H, 6.86; N, 15.9. Found: C, 68.1; H, 6.95; N, 15.5. *Anal.* Calcd. for $C_{11}H_{14}N_2O$: C, 69.4; H, 7.42; N, 14.7. Found: C, 69.2; H, 7.42; N, 14.5. *Anal.* Calcd. for $C_{12}H_{16}N_2O$: C, 70.6; H, 7.90; N, 13.7. Found: C, 70.5; H, 7.92; N, 13.6.

2-Aminomethylbenzimidazole was prepared by the method of Lane[3]; m.p.: lit.[3] 53°, obsd. 52–53°. The analysis agreed with theoretical values.

2-(N-Methylaminomethyl)-benzimidazole, 2-(N-ethylaminomethyl)-benzimidazole dihydrochloride, and 2-(N-butylaminomethyl)-benzimidazole were prepared according to the method of Bloom and Day[4]; m.p.: 2-(N-methylaminomethyl)-, lit.[4] 207–209° dec., obsd. 205–209° dec.; 2-(N-ethylaminomethyl)-, lit.[4] 223–225° dec., obsd. 221–225° dec.; 2-(N-butylaminomethyl)-, lit.[4] 203–204°, obsd. 204–205°. Analyses agreed with theoretical values.

2-(N-Propylaminomethyl)-benzimidazole dihydrochloride (not reported in the literature) was successfully prepared by the method of Bloom and Day[4] from propylamine (0.4 mole) and 2-chloromethylbenzimidazole (0.2 mole). The colorless prisms melted at 182–183° dec. *Anal.* Calcd. for $C_{11}H_{17}N_3Cl_2$: C, 50.4; H, 6.54; N, 16.0. Found: C, 50.4; H, 6.62; N, 16.0.

Apparatus and Procedure.—The stability constants were determined by the Bjerrum method[5] of potentiometric titration in 50% v./v. dioxane–water. The titration apparatus and procedure have been described previously.[6] Titrations were carried out using ligand to metal ratios of 8:1.

The acid dissociation constants of the ligands were determined from the titration of a mixture of ligand and acid with standard sodium hydroxide.

Calculations.—The 2-(α-hydroxyalkyl)-benzimidazoles (I) contain one weakly basic ring nitrogen and one weakly acidic —OH group. The ring nitrogen picks up a proton in acid solution to give the ion, $[HN\text{-}R\text{-}OH]^+$. The acid dissociation constants can then be defined for the two ionization processes

$$[HN\text{-}R\text{-}OH]^+ \rightleftharpoons N\text{-}R\text{-}OH + H^+;\ K_{NH^+}$$

$$N\text{-}R\text{-}OH \rightleftharpoons [N\text{-}R\text{-}O]^- + H^+;\ K_{OH}$$

The 2-(N-alkylaminomethyl)-benzimidazoles (II) contain one very weakly basic nitrogen and one relatively strongly basic nitrogen. As above, the basic nitrogens pick up protons in acid solution to give a diprotonated cation, $[HN\text{-}R\text{-}NH]^{++}$, with first and second acid dissociation constants.

---

[1] (a) The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This work was also supported from research grant AM-02763-04 from the Department of Health, Education, and Welfare, Public Health Service. (b) This publication is based on a thesis submitted by H. B. Durham, in partial fulfillment of the requirements for the Ph.D. degree, to the University of Notre Dame, August, 1962. Presented at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, 1961.

(2) M. A. Phillips, *J. Chem. Soc.*, 2393 (1928).

(3) E. S. Lane, *ibid.*, 3313 (1957).

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

(5) J. Bjerrum, "Metal-Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(6) H. Freiser, R. G. Charles, and W. D. Johnston, *J. Am. Chem. Soc.*, **74**, 1383 (1952).

TABLE I

DATA FOR 2-(α-HYDROXYALKYL)-BENZIMIDAZOLES WITH Cu(II) IN 50% DIOXANE–WATER

Alkyl group	Temp., °C.	pK_{NH^+}	pK_{OH}	$\log K_1$	$2 \log K_{av}$	Est. ΔH, kcal./mole
Methyl	15	4.89	13.03	11.56	18.22	
	25	4.82	12.76	11.00	17.68	−16.7
	40	4.68	12.19	10.20	17.20	
	45	4.58	12.04	9.82	16.96	
Ethyl	15	4.88	13.06	11.80	17.70	
	25	4.82	12.77	11.43	17.34	−13.5
	40	4.66	12.27	10.80	16.88	
	45	4.59	12.05	10.50	16.72	
Propyl	15	4.89	13.07	11.69	17.92	
	25	4.82	12.77	11.24	17.60	−11.3
	40	4.68	12.26	10.52	17.20	
	45	4.60	12.06	10.38	17.06	
Butyl	15	4.88	13.07	11.47	17.86	
	25	4.80	12.77	11.05	17.54	−11.1
	40	4.68	12.30	10.47	17.20	
	45	4.58	12.06	10.28	17.02	
Amyl	15	4.88	13.07	12.07	18.20	
	25	4.80	12.77	11.45	17.86	−10.1
	40	4.66	12.30	10.75	17.56	
	45	4.58	12.06	10.58	17.40	

TABLE II

DATA FOR 2-(N-ALKYLAMINOMETHYL)-BENZIMIDAZOLES WITH Cu(II) IN 50% DIOXANE–WATER

Alkyl group	Temp., °C.	$pK_{RH_2^{++}}$	pK_{RH^+}	$\log K_1$	$\log K_2$	$2 \log K_{av}$	Est. ΔH, kcal./mole
Aminomethyl	15	2	7.34	7.59	7.26	15.00	
	25	2	7.14	7.38	6.85	14.48	−19.2
	35	2	6.86	7.18	6.66	14.06	
	45	2	6.68	6.92	6.55	13.60	
N-Methyl	15	2	7.40	7.41	4.45	10.60	
	25	2	7.32	7.30	4.38	10.28	−13.7
	35	2	7.12	6.81	4.15	10.00	
	45	2	6.97	5.83	4.00	9.66	
N-Ethyl	15	2	7.49	7.20	4.73	11.40	
	25	2	7.33	6.98	4.58	11.10	−12.8
	35	2	7.15	6.85	4.38	10.74	
	45	2	6.99	6.60	4.27	10.48	
N-Propyl	15	2	7.38	7.50	5.00	12.10	
	25	2	7.22	7.33	4.82	11.80	−11.4
	35	2	7.00	7.14	4.68	11.56	
	45	2	6.86	6.83	4.55	11.22	
N-Butyl	15	2	7.42	7.25	4.74	11.44	
	25	2	7.16	6.85	4.60	11.20	−11.6
	35	2	6.98	6.75	4.43	10.80	
	45	2	6.84	6.58	4.40	10.54	

Using R to designate the coördinated ligands ($N-R-O^-$ and N–R–N) the formation constants[7] were determined from plots of $\bar{n}$ against pR using the method of Lane and Thompson.[8] Since the pH value at which a metal ion begins to hydrolyze sets an approximate upper limit for the calculation of formation constants, the $\bar{n}$ values in metal hydrolysis regions were obtained by extrapolation from lower values (log K_1 values could not be obtained for Ni(II), Co(II), and Zn(II) with the ligands in this study). The constants K_1 and K_2 (Tables I and II) are formation constants defined by the equations

$$M^{++} + R \longleftrightarrow MR^{++}$$

$$MR^{++} + R \longleftrightarrow MR_2^{++}$$

The values of K at four different temperatures were used to estimate the values of ΔH listed in the tables. Because of experimental problems it is recognized that the accuracy of such measurements may not be high.

Results and Discussion

Acid dissociation constants and stability data for the compounds studied are given in Tables I and II. All data show the expected temperature dependence. The equilibrium constants are concentration quotients since activity coefficients have not been taken into consideration.

Values of 2 log K_{av} for the 2-(α-hydroxyalkyl)-benzimidazole chelates decrease relative to the methyl substituent. The same effect is observed for all N-alkyl derivatives of 2-(aminomethyl)-benzimidazole. This decrease in stability is attributed to steric hindrance in which the alkyl groups prevent the most favorable

---

[7] Calculations of metal chelate stability constants were programmed in Fortran for the IBM-1620 computer. Reprints of the program and detailed experimental data have been deposited as Document Number 7462 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting $6.25 for photoprints, or $2.50 for 35-mm. microfilm. Advance payment, payable to Chief, Photoduplication Service, Library of Congress, is required.

[8] T. J. Lane and J. W. Thompson, *J. Am. Chem. Soc.*, **82**, 4179 (1960).

metal–ligand orientation. Similar phenomena were noted by Johnston and Freiser[9] and by Basolo, *et al.*[10, 11]

However, as the length of the alkyl chain increases, the chelates, in general, tend to become more stable. Approximate thermodynamic values were calculated using the temperature dependence of the equilibrium constants. These values indicate that this increase in stability is caused by an increase in entropy.

[9] W. D. Johnston and H. Freiser, *Anal. Chim. Acta*, **11**, 1 (1954).

[10] F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **74**, 5243 (1952); **76**, 211 (1954).

[11] F. Basolo, R. K. Murmann, and H. T. Chen, *ibid.*, **75**, 1478 (1953); **76**, 956 (1954).

CONTRIBUTION NO. 1173 FROM THE INSTITUTE FOR
ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

Solutions of Gallium(I) Salts in Aqueous Base[1]

BY JOHN D. CORBETT

Received July 26, 1962

The characteristic reaction of the so-called gallium dichloride with water has been known for a considerable time. With ample amounts of water a strongly reducing, flocculent, orange-brown to black precipitate is produced together with smaller amounts of hydrogen and gallium. The precipitate evolves hydrogen slowly on standing or rapidly on addition of acids with ultimate solution of the product.[2] Although the identity of this precipitate has never been carefully studied, the supposition has been made that it is gallium(II) hydroxide produced by hydrolysis of the reactant $GaCl_2$, since the empirical formula for the latter suggests a dipositive state.[3] However, subsequent studies have amply shown that the gallium dihalides are actually gallium(I)–gallium(III) salts $Ga^+(GaX_4^-)$[4–6] and that the above reaction with water is characteristic of gallium(I) since it occurs not only in the presence of the GaX_4^- anion but also with $AlCl_4^-$, $AlBr_4^-$, Br^-, and I^-.[4,7] Because of the strong reducing character of the gallium(I) oxidation state, very little information has been reported regarding its solution properties. Recently Schug and Sadowski[8] have inferred from stoichiometric evidence that hot, concentrated (11 *M*) perchloric acid reacts with metal to yield hydrogen plus the Ga^+ intermediate and that this rapidly reduces the perchlorate ion. The present paper reports some characterization of the more stable solutions obtained with gallium(I) salts in aqueous base.

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF ALKALINE SOLUTIONS OF $Ga(GaCl_4)$ AT 22–24°

NaOH, *M*	Additive, *M*	Rate constant, $sec.^{-1} \times 10^5$
0.998	...	$3.7_3 \pm 0.1$
1.99	...	$8.3_7 \pm 0.2$
1.99	0.05 Ga(III)	$8.2_1 \pm 0.1$
1.99	0.3 I^-	$8.5_4 \pm 0.1$
4.00	...	$\sim 27 \pm 9$
0.990	1.00 $NaClO_4$	$4.17_7 \pm 0.04$
0.992	2.98 $NaClO_4$	5.06 ± 0.06
1.986	2.00 $NaClO_4$	$9.9_3 \pm 0.3$
2.982	1.02 $NaClO_4$	14.7 ± 0.5

Solution of a gallium(I) salt such as Ga_2Cl_4 in aqueous NaOH gives, as with pure water, a black to dark orange precipitate, but this readily redissolves and the solution proceeds through shades of orange and yellow to colorless in a few 10-min. periods. The initially vigorous reaction, probably largely due to the hydrolysis of the $GaCl_4^-$ ion, produces some 5 to 25% (depending on sample size) of the total possible hydrogen by reduction of water and also 5 to 20% of the theoretical amount of metal through disproportionation (data for 2 *M* OH^-). It should be emphasized that separation of metal is observed *only* during the initial reaction with water. The resulting solution evolves hydrogen *homogeneously* and not from the walls of the glass container, so that the quiescent liquid becomes highly supersaturated ("pinpoint hydrogenation"). The rate of hydrogen evolution from vigorously stirred solutions 1 to 4 *M* in NaOH indicates the net reaction $[Ga^+] + 2H_2O + 2OH^- \rightarrow Ga(OH)_4^- + H_2$ is first order in gallium(I). Data obtained after the solution process appears complete were in kinetic agreement with those taken after the solution lost its light yellow to orange color 15 to 40 min. later. The rate constants obtained for solutions initially 3.5 to 10 m*M* in gallium(I) are summarized in Table I.[9] Comparison of these for solutions maintained at a fixed, total concentration of 2 or 4 *M* by $NaClO_4$ indicates that the reaction also is first order in hydroxide (0.95 to 1.0 observed) over the range studied. Gallium(III) was found to be without significant effect on the rate although at the 0.05 *M* level it virtually eliminates production of metal during the initial solution. As an indication of the stability of these solutions, the rate constant in 1.00 *M* base corresponds to a half-life of 5.2 hr. The observed linear dependence on hydroxide concentration, contrary to that for a reaction involving proton reduction, suggests that the reaction effectively takes place through an interaction of OH^- with the solvated Ga^+ ion to inductively affect transfer of the $4s^2$ electrons to water of solvation, forming hydrogen either directly (and probably intramolecularly) or *via* a hydride intermediate. Attempts

---

[1] The Lower Oxidation States of Gallium. IV. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] E. Eineck, "Das Gallium," Voss, Leipzig, 1937; Edwards Bros., Ann Arbor, Mich., 1944, p. 79.

[3] L. S. Foster, *Inorg. Syn.*, **4**, 111 (1953).

[4] J. D. Corbett and R. K. McMullan, *J. Am. Chem. Soc.*, **78**, 2906 (1956); R. K. McMullan and J. D. Corbett, *ibid.*, **80**, 4761 (1958).

[5] L. A. Woodward, G. Garton, and H. Roberts, *J. Chem. Soc.*, 3623 (1957); L. A. Woodward, N. N. Greenwood, J. R. Hall, and I. J. Worrall, *ibid.*, 1505 (1958).

[6] G. Garton and H. M. Powell, *J. Inorg. Nucl. Chem.*, **4**, 84 (1957).

[7] J. D. Corbett and A. Hershaft, *J. Am. Chem. Soc.*, **80**, 1530 (1958).

[8] K. Schug and A. Sadowski, *ibid.*, **83**, 3538 (1961).

[9] There appears to be a decrease in rate after several half-lives at the highest base concentration although this was not investigated further.