Comparison of the Complexing Processes of 1-Butyl-2-hydroxymethylimidazole and 1-Butyl-2-methylimidazole in Aqueous Solution

Barbara Barszcz and Jacek Kulig
Institute of Chemistry, Pedagogical University, 25-020 Kielce, Poland

The stability constants and structures of the complexes of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} with 1-butyl-2-methylimidazole (bmim) and 1-butyl-2-hydroxymethylimidazole (bhmim) in aqueous solution have been determined by potentiometric and spectrophotometric methods. The stability of transition-metal complexes of bhmim depends on the presence of the hydroxymethyl group the oxygen atom of which interacts with the metal ion. Cobalt(II) and Zn^{II} form both tetrahedral and octahedral species with either ligands. In the case of bhmim the additional interaction of the oxygen atom shifts the octahedron $\rightleftharpoons$ tetrahedron equilibrium in solution towards six-co-ordination.

In previous articles[1-3] we have described how an alkyl substituent situated in position 2 of the imidazole ring is a steric hindrance to complexation. It lowers complex stabilities and causes symmetry changes in the co-ordination spheres of some transition-metal cations. Recently we have found[4,5] that a CH_2OH group situated α to the donor nitrogen atom of the imidazole ring has no such steric effect. This may be explained by an additional interaction between the oxygen atom of the hydroxymethyl group and the central metal atom.

In order to confirm these observations it seemed useful to compare the stabilities and structures of complexes of two exemplary compounds in aqueous solution, namely: 1-butyl-2-methylimidazole (bmim) and 1-butyl-2-hydroxymethylimidazole (bhmim). This aim was realized by potentiometric and spectrophotometric methods. Many strongly complexing, biologically active, imidazole derivatives contain an amine or hydroxyl group in the side chain.

Experimental

Reagents and Apparatus.—The compound bmim was synthesised at the Technical University of Poznań; bhmim was obtained from Chemical Laboratory Walocha-Nowak, Kraków. The purity of both bases was monitored by chromatography. Solutions of required concentrations were prepared from weighed samples. The concentrations of solutions of nitric acid and metal nitrates used during the experiments were determined by classical analytical methods.

For the pH-metric measurements a PHM-64 pH meter (Radiometer) and GK 2321C combination electrode were used. The electrodes were calibrated by means of titration of HCl solutions of known titre with solutions of NaOH according to ref. 6. Absorption spectra were obtained on a Specord M-40 (Carl Zeiss Jena) recording spectrophotometer using 1, 0.5 and 0.2 cm quartz cuvettes.

Experimental Procedure and Calculations.—The dissociation constants of the protonated forms of the two imidazoles were derived from measurements of the pH changes during titration of the ligands with HNO_3.

The complexing reactions of bmim and bhmim with metal cations were investigated in three alternative ways: (*a*) at constant metal concentration (20, 30, 40 mmol dm^{-3}), (*b*) at constant ligand concentration and (*c*) at variable ligand and metal ion concentrations. The method of measurement and calculations were presented previously.[1,2] The stability constants of the complexes were determined numerically by minimization of the function U [equation (1)] using the

$$U = \sum_{i=1}^{N}\left(\bar{n}_{\mathrm{exptl}_i} - \bar{n}_{\mathrm{calc}_i}\right)^2 = f(\beta_1,\beta_2,\ldots,\beta_N) \quad (1)$$

$$\bar{n}_{\mathrm{calc}_i} = \frac{\sum_{n=1}^{N} n\beta_n[\mathrm{L}]_i^n}{1 + \sum_{n=1}^{N} \beta_n[\mathrm{L}]_i^n} \quad (2)$$

LETAGROP VRID program,[7] where [L] is the equilibrium ligand concentration, β_n is the stability constant of complex containing n ligands, N is the total number of complexes in the system and $\bar{n}$ is the value of the mean ligand number. The complexes of Co^{II}, Ni^{II} and Cu^{II} were also investigated by a spectral method over the visible range. Solutions for these measurements were prepared in a similar manner to those for potentiometric measurements at a fixed metal-ion concentration.

All measurements were made at a constant ionic strength (I = 0.5 mol dm^{-3} with KNO_3) and temperature (25 ± 0.1 °C).

Results and Discussion

Factors Determining the Stabilities of bmim and bhmim Complexes.—On the basis of pH-metric measurements it was possible to determine the dissociation constants of the protonated forms of bmim and bhmim over the range pH 3.5–8.5. Under these conditions the ligands bind one hydrogen ion each. The dissociation constants of the conjugate acids are 6.61×10^{-9} ($pK_a = 8.18$) and 1.00×10^{-7} mol dm^{-3} ($pK_a = 7.00$) respectively. The presence of the methyl substituent in position 2 of the imidazole ring increases the basicity because of a positive induction effect. The basicity of analogous hydroxymethyl derivatives is more than one order of magnitude smaller because of the coupling effect between one electron pair of the pyridine nitrogen atom with one pair of the oxygen atom.

The co-ordination reactions of bhmim and bmim with Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} were carried out over the range pH 3–7. On the basis of the pH measurements and acid dissociation constants of the ligands, plots of $\bar{n} = f(-\log[\mathrm{L}])$ were drawn for each investigated system. The shape of the curves (Fig. 1) is

Table 1 Stability constants of the imidazole and substituted imidazole complexes at 25 °C, ionic strength 0.5 mol dm^{-3} (KNO_3)

Ligand	pK_a	M	log β_1	log β_2	log β_3	log β_4	log β_5
Imidazole[8,9]	7.12[8]	Co^{II}	2.47	4.40	5.85	6.85	—
		Ni^{II}	3.09	5.56	7.56	9.10	—
		Cu^{II}	4.31	7.84	10.76	12.90	—
		Zn^{II}	2.56	4.89	7.16	9.19	—
1-Butylimidazole[10]	7.21	Co^{II}	2.75	4.75	6.00	6.54	—
		Ni^{II}	3.30	5.88	7.96	—	—
		Cu^{II}	4.40	8.07	11.17	13.63	—
		Zn^{II}	2.57	4.97	7.20	9.34	10.81
2-Methylimidazole[1]	8.05	Co^{II}	1.73	3.05	3.84	6.16	—
		Cu^{II}	3.35	6.38	9.23	11.92	14.45
		Zn^{II}	1.88	3.99	7.49	9.32	—
1-Butyl-2-methylimidazole	8.18	Co^{II}	1.73 ± 0.05	2.08 ± 0.10	2.76 ± 0.03	5.65 ± 0.01	—
		Ni^{II}	2.03 ± 0.01	3.49 ± 0.01	4.54 ± 0.01	5.00 ± 0.04	—
		Cu^{II}	3.74 ± 0.01	6.98 ± 0.01	9.44 ± 0.01	11.26 ± 0.01	—
		Zn^{II}	1.20 ± 0.20	4.96 ± 0.05	6.97 ± 0.02	9.73 ± 0.01	10.64 ± 0.05
1-Butyl-2-hydroxymethylimidazole	7.00	Co^{II}	2.18 ± 0.02	4.03 ± 0.02	4.67 ± 0.08	6.65 ± 0.01	—
		Ni^{II}	2.58 ± 0.01	4.67 ± 0.01	6.44 ± 0.02	7.43 ± 0.02	—
		Cu^{II}	4.11 ± 0.01	7.62 ± 0.01	10.39 ± 0.01	11.89 ± 0.02	13.18 ± 0.02
		Zn^{II}	2.22 ± 0.04	4.97 ± 0.01	6.41 ± 0.03	8.06 ± 0.01	—

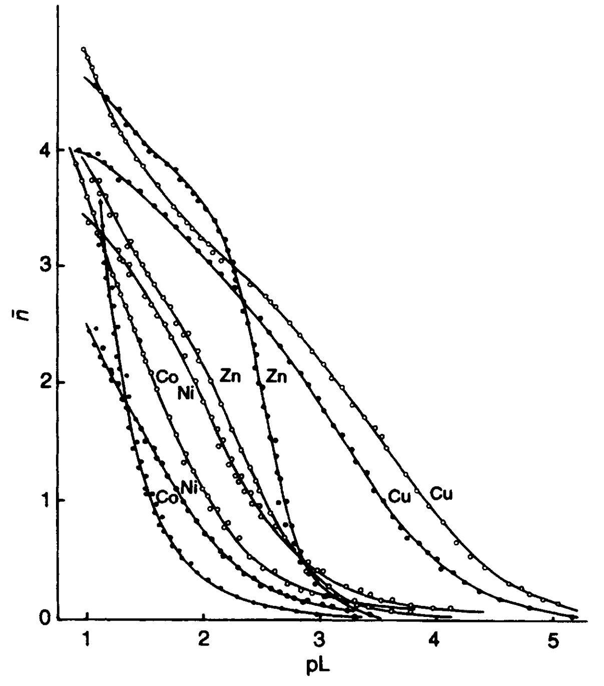

Fig. 1 Formation curves of 1-butyl-2-methylimidazole (●) and 1-butyl-2-hydroxymethylimidazole (○) complexes with Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}. The solid lines were calculated from the determined β_n values

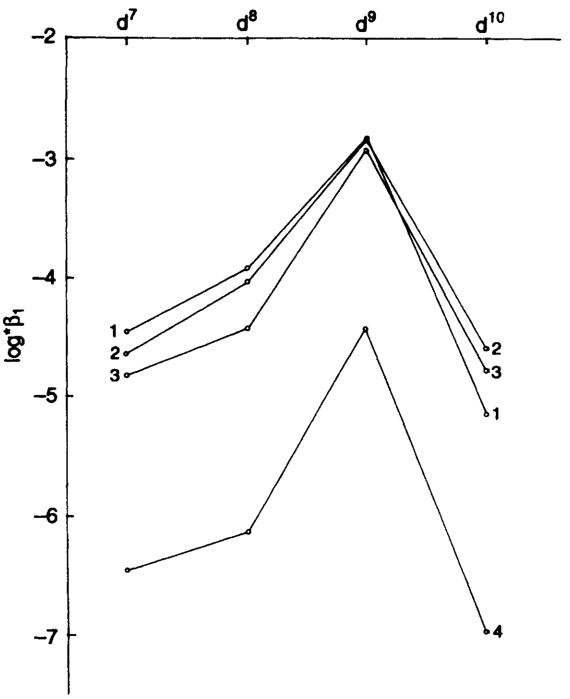

Fig. 2 Dependence of substitution constants log* β_1 on the number of d electrons of the central ion for the complexes of Co^{II} (d^7), Ni^{II} (d^8), Cu^{II} (d^9) and Zn^{II} (d^{10}) with 1-butylimidazole (1), imidazole (2), 1-butyl-2-hydroxymethylimidazole (3) and 1-butyl-2-methylimidazole (4)

in each case independent of the metal-ion concentration, which indicates the formation of only mononuclear complexes. On the basis of the $\bar{n}$ and [L] values, the stability constants (log β_n) of the complexes formed were determined (Table 1). The solid lines in Fig. 1 were drawn by use of these β_n values.

Literature data[5,11] show that the stability of the metal complexes is practically independent of the size of the alkyl substituent at position 1 (Table 1). So the stability of metal complexes with 1-alkyl-2-methylimidazoles and 1-alkyl-2-hydroxymethylimidazoles depends mostly on the substituent situated between the nitrogen atoms of the imidazole ring. As the ligand basicities differ, it is possible to use the parameter log* β_1 = log β_1 − pK_a, called the replacement constant, in order to characterize their tendency to form complexes. In Fig. 2 the values of the replacement constants are presented graphically for complexes of transition metals with imidazole and some of its derivatives. The substituents situated between the nitrogen atoms of the imidazole ring usually represent a steric hindrance to complexation.[1-3] This is also true in the case of bmim, which, in spite of its basicity (higher in comparison to imidazole), forms less-stable complexes with transition-metal cations. However, the presence of the larger hydroxymethyl substituent in position 2 doesn't decrease the complex stability, on the contrary it increases it. This is demonstrated by the values of the replacement constants for bhmim, which are similar to those for imidazole and 1-butylimidazole and higher than in the case of bmim (Fig. 2). It follows that the stability of bhmim complexes is due to the presence of the hydroxymethyl group, the oxygen atom of which interacts with the metal ion. This results in the formation of a five-membered chelate ring involving nitrogen and oxygen atoms. Quantitative analysis of the log (K_1/K_2) does not indicate the existence of typical, strong chelates in solution because the metal–oxygen bond is weak and easily broken. Formation of this chelate is not accompanied by

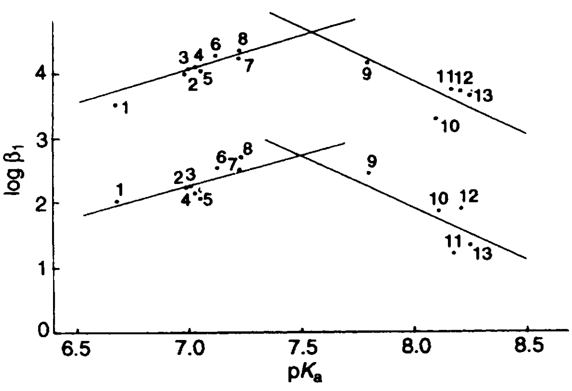

Fig. 3 The dependence log $\beta_1 = f(pK_a)$ for the complexes of Cu^{II} (○) and Zn^{II} (●) with 4(5)-hydroxymethylimidazole (1), 2-hydroxymethyl-1-methylimidazole (2), 1-butyl-2-hydroxymethylimidazole (3), 1-ethyl-2-hydroxymethylimidazole (4), 2-hydroxymethyl-1-propylimidazole (5), imidazole (6), 1-ethylimidazole (7), 1-propylimidazole (8), 4(5)-methylimidazole (9), 2-methylimidazole (10), 1-butyl-2-methylimidazole (11), 1,2-dimethylimidazole (12) and 2-methyl-1-propylimidazole (13)

loss of a proton from the hydroxymethyl group. This interpretation is in accord with other studies of complexes of hydroxymethylimidazole in solution and the solid state. Thus it was supposed that during formation of complexes of Co^{II} and Zn^{II} with 2-hydroxymethyl-1-vinylimidazole a weak chelate was formed in methanol–water solution.[12] Furthermore the structure of the complex of $CoCl_2$ with 2-hydroxymethyl-1-vinylimidazole was determined in the solid state. It was shown[13,14] that Co^{II} was bonded to two molecules of ligand, one of which was unidentate and the other bidentate (chelate).

In order to generalize the conclusions following from these investigations of the imidazole complexes, Fig. 3 presents an exemplary correlation between the values of the logarithms of the stability complexes of the first complexes of Cu^{II} and Zn^{II} and the ligand basicity. The points corresponding to log $\beta_1 = f(pK_a)$ for the chosen imidazole derivatives lie about two intersecting lines which were plotted according to linear approximation coefficients, calculated by the least-squares method. Those corresponding to imidazole and its derivative containing an alkyl substituent in position 1 or CH_2OH in position 2 are found on the line with positive slope. On the other line there are points corresponding to imidazole derivatives containing alkyl substituents situated in the position 2 or 4 and which present steric hindrance to complexation. Such a distribution of the experimental points shows that the CH_2OH group, in spite of its being at the α position, behaves differently from the alkyl groups and does not display a steric effect. Also that the OH group must be engaged in bonding to the metal ion. The stability increase caused by the chelating effect is especially notable in the case of copper(II) complexes.

Influence of the CH_3 *and* CH_2OH *Groups on the Structure of Complexes of 2-Substituted Imidazole Derivatives*.—From the shape of the formation curves (Fig. 1) and the changes in the logarithms of the formation constants of complexes of bmim and bhmim it follows that complexation occurs in different ways for each metal cation. Deviations from linearity of the dependence log $K_n = f(n - 1)$ are observed for the complexes of Co^{II} and Zn^{II} with both these ligands. From previous investigations it follows that the compounds of Co^{II} with 1-alkylimidazoles have octahedral or pseudo-octahedral symmetry.[11,15] Introduction of an additional methyl substituent at position 2 of the imidazole ring results in the case of bmim of configurational equilibria in solution of the type octahedron $\rightleftharpoons$ tetrahedron [Fig. 4(*a*)]. The change in the co-ordination symmetry of the cobalt(II) complexes is confirmed not only by a considerable bathochromic effect ($\tilde{\nu}$ = 17 500 cm^{-1}), but also the high value of the molar absorption coefficient (ε = 600 dm^3 mol^{-1} cm^{-1}). With bhmim only a small shift of the absorption spectra towards longer wavelengths ($\tilde{\nu}$ = 19 100 cm^{-1}) and a lower value of the molar absorption coefficient (ε = 60 dm^3 mol^{-1} cm^{-1}) are observed [Fig. 4(*b*)]. Similar absorption spectra were registered in the case of tetrahedral complexes of Co^{II} where the donor atom was oxygen[16,17] and with 1-alkyl-2-hydroxymethylimidazoles.[4,5] The distinct differences in the absorption spectra of the cobalt(II) complexes with both investigated ligands confirm the participation of the CH_2OH group in formation of the co-ordination bond. For both investigated ligands, particularly bmim, the establishment of the equilibrium octahedron $\rightleftharpoons$ tetrahedron upon addition of a fourth ligand favours this process.

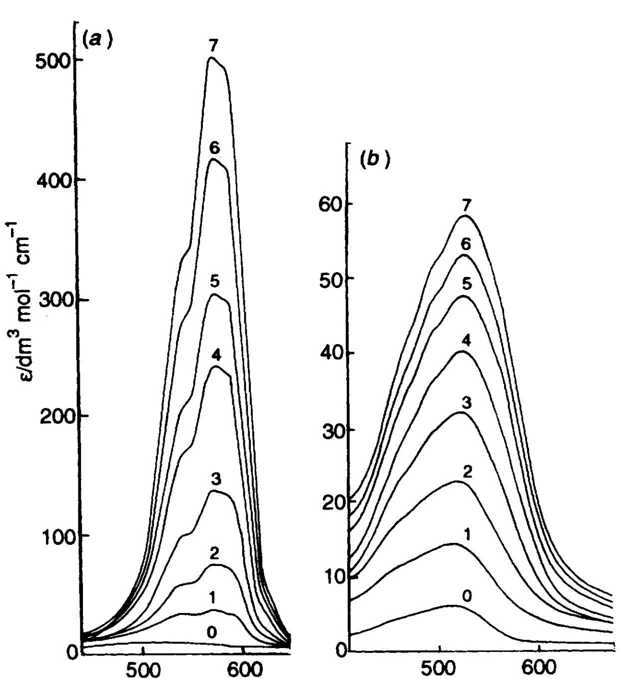

Fig. 4 Absorption spectra of cobalt(II) complexes with 1-butyl-2-methylimidazole (*a*) and 1-butyl-2-hydroxymethylimidazole (*b*) at 1 × 10^{-2} mol dm^{-3} $Co(NO_3)_2$. The bmim concentrations are 0, 0.039, 0.054, 0.088, 0.095, 0.144, 0.186 and 0.225 mol dm^{-3} fur curves 0–7 respectively. The bhmim concentrations are 0, 0.015, 0.030, 0.056, 0.082, 0.109, 0.135 and 0.161 mol dm^{-3} for curves 0–7 respectively

The shape of the formation curves for Co^{II} and Zn^{II} complexes with bmim is similar, and may point to analogous structures. The same is true of the complexes of Co^{II} and Zn^{II} with bhmim. So, in the solutions of Zn^{II}, apart from the six-co-ordinated compounds, also four-co-ordinated compounds with tetrahedral structure are present. This phenomenon was observed previously for several imidazole derivatives.[1–3] The differences in stabilities and in positions of the formation curves of the complexes of Zn^{II} with both ligands shows that the additional interaction of the oxygen atom and the metal ion shifts the octahedron $\rightleftharpoons$ tetrahedron equilibrium towards six-co-ordination. Thus $\log(K_n/K_{n+1})$ is dependent on two factors, the tendency to undergo configurational equilibria, octahedron $\rightleftharpoons$ tetrahedron, and the formation of a weak chelate.

From the absorption spectra of the complexes of Ni^{II} and Cu^{II} with bmim and bhmim it follows that in aqueous solution they have a pseudo-octahedral structure.[15,16]

Conclusion

The ligands bmim and bhmim, differing only by the substituent type at position 2 of the imidazole ring, form with metal ions complexes differing both in stability and structure. The CH_2OH group, contrary to CH_3, does not present a steric hindrance to complexation of the imidazole with transition-metal cations. It follows that there is an additional interaction of the oxygen atom with the metal ion which results in the formation of five-membered chelate rings. The chelation is reversible and diminishes with increasing ligand concentration. The presence of a CH_3 group at the α position of the imidazole ring facilitates the formation of tetrahedral complexes with Co^{II} and Zn^{II} in solution. The additional interaction of the oxygen atom shifts the octahedron $\rightleftharpoons$ tetrahedron equilibrium in the solution towards six-co-ordination.

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