Protonation of DL-4-Amino-3-Hydroxybutanoic Acid and its Complexing Capacity with Copper(II) Ions in Aqueous Solution

By **Antonio Braibanti*** and **Giovanni Mori**, Istituto di Chimica Farmaceutica, and **Francesco Dallavalle** and **Enrico Leporati**, Istituto di Chimica Generale, Università di Parma, Parma, Italy

The protonation constants of DL-4-amino-3-hydroxybutanoic acid [$H_3L^+ = H_3\overset{+}{N}\cdot CH_2\cdot CH(OH)\cdot CH_2CO_2H$], as determined potentiometrically at 25 °C and I = 0·1M-KCl, are log K_1 = 13·0 ± 0·1, log K_2 = 9·487(11), and log K_3 = 3·834(12) for the hydroxy-, amine, and carboxy-groups, respectively. From measurements of log K at different temperatures between 5 and 35 °C, values of ΔH_2, ΔS_2, ΔH_3, and ΔS_3 at 25 °C have been calculated and their sensitivity to changes in structure have been tested by comparison with appropriate compounds. With copper(II) the complexes [CuL], [Cu_2L_2], and [CuL_2^{2-}] are formed. In the first two complexes the ligand is probably tridentate, forming both five- and six-membered chelate rings, but in [CuL_2^{2-}] the second ligand molecule is bidentate through the amine and 3-hydroxyl groups.

CONTINUING our researches on the behaviour of amino-hydroxybutanoic acids, both as acids and as ligands,[1] we have now undertaken a study of DL-4-amino-3-hydroxybutanoic acid and of its complexes with bivalent metals. The problems raised by this ligand concern its capacity of binding to the metals, by analogy with 4-aminobutanoic acid, either through the amine group as in the complex di(γ-aminobutyrato)copper(II) in the solid state,[2] or by forming seven-membered chelate rings *via* amine and carboxylato-groups as suggested by previous work.[3] Moreover the compound under study contains the aminoethanol moiety, $H_2N\cdot CH_2\cdot CH(OH)$, which is capable of forming five-membered chelate rings, with or without ionisation of the hydroxy-group.[4-12] This moiety is common to several compounds of pharmaceutical and biological importance, such as ephedrine, adrenaline, noradrenaline, threonine, *etc.* DL-4-Amino-3-hydroxybutanoic acid itself is used as an anticonvulsant.

EXPERIMENTAL

Reagents and Procedure.—DL-4-Amino-3-hydroxybutanoic acid of reagent-grade purity was used without further purification after drying over P_2O_5 *in vacuo*, m.p. 217 °C (lit.,[13] 218 °C) (Found: C, 40·4; H, 7·65; N, 11·8. Calc. for $C_4H_9NO_3$: C, 40·35; H, 7·60; N, 11·75%). Standard solutions of the reagents were prepared and potentiometric measurements were made following the procedure previously described.[14] Initial amounts, pH, and n intervals are in Tables 1 and 2.

TABLE 1

Protonation-constant determinations for DL-4-amino-3-hydroxybutanoic acid at I = 0·1M-KCl

Expt. no.	θ_c/°C	c_L/mmol	c_H/mmol	pH	$\bar{n}$ *
(1)	35	0·32550	0·65143	3·186—10·711	1·80—0·05
(2)		0·35675	0·71438	3·164—9·260	1·81—0·45
(3)		0·43232	0·86753	3·107—10·284	1·83—0·06
(4)		0·40459	0·81195	3·125—10·284	1·82—0·07
(5)	30	0·41389	0·83973	3·103—10·572	1·84—0·06
(6)		0·35398	0·77390	2·962—10·575	1·88—0·06
(7)		0·29156	0·59320	3·195—10·572	1·82—0·07
(8)		0·44062	0·88424	3·117—10·552	1·83—0·06
(9)	25	0·26997	0·80799	3·244—12·152	2·80—0·87
(10)		0·40034	1·20343	3·137—12·092	2·83—0·89
(11)		0·40739	1·22403	3·149—11·153	2·83—1·00
(12)		0·27204	0·81740	3·244—11·172	2·80—1·00
(13)		0·41632	1·25140	3·137—11·126	2·83—1·00
(14)		0·38004	1·14100	3·161—11·245	2·82—1·00
(15)	20	0·41579	0·82978	3·158—10·760	1·83—0·07
(16)		0·32286	0·74870	2·871—10·729	1·90—0·08
(17)		0·42804	0·85388	3·225—10·734	1·81—0·07
(18)		0·35459	0·70944	3·194—10·734	1·82—0·07
(19)	15	0·45684	0·92997	3·363—10·720	1·76—0·10
(20)		0·29599	0·70998	3·258—10·326	1·84—0·20
(21)		0·30699	0·70913	3·143—10·546	1·85—0·10
(22)	10	0·33090	0·66244	3·234—11·537	1·83—0·02
(23)		0·36380	0·73210	3·212—11·388	1·84—0·06
(24)		0·44899	0·90097	3·129—11·112	1·84—0·04
(25)		0·43726	0·88454	3·155—11·117	1·86—0·06
(26)	5	0·27887	0·55786	3·281—11·513	1·81—0·00
(27)		0·35968	0·71904	3·181—11·674	1·82—0·00
(28)		0·46790	0·93556	3·150—10·795	1·85—0·13
(29)		0·31442	0·62802	3·216—11·625	1·80—0·02

* $\bar{n}$ at 35, 30, 20, 15, 10, and 5 °C is based on two protonation steps.

TABLE 2

Initial amounts (mmol) and pH ranges for the DL-4-amino-3-hydroxybutanoic acid–copper(II) system at 25 °C and I = 0·1M-KCl

Expt. no.	c_L	c_M	c_H	pH
(1)	0·29465	0·29531	1·04900	2·710—7·267
(2)	0·37709	0·18939	1·13290	1·137—11·114
(3)	0·64672	0·16676	1·95570	2·972—11·040
(4)	0·29499	0·58747	1·50440	2·194—5·825
(5)	0·29557	0·09949	1·18500	2·497—11·155

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RESULTS

Protonation constants (Table 3) were determined from the formation function $\bar{n}$, and refined by the computer program GAUSS Z.[15] Titration curves of the ligand in the presence of Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} ions did not reveal appreciable complexing. Those in the presence of Cu^{2+} ions showed, after neutralisation of CO_2H, two distinct buffer zones, at pH *ca.* 5—6 and *ca.* 9—11, respectively. Assuming that the ionised 3-OH group is involved in complex formation, pH values as a function of r (r = mmol KOH added : mmol Cu^{II}) showed a reproducible inflexion at $r = 2$ (Figure 1).* Thus the first buffer zone corresponds to neutralisation of two equivalents of acid per equivalent of Cu^{2+}, attributable to the protons from $\overset{+}{N}H_3$ and OH. Mario and Bolton[7] and Näsänen *et al.*[6] found a similar situation in the system 1,3-diaminopropan-2-ol–Cu^{2+}. Only by assuming ionisation of OH were fairly good formation functions obtained (Figure 2). These suggest the existence of polynuclear complexes, although the fraction of hydrolysed copper(II) species, $[Cu_2(OH)_2]^{2+}$, will be small.[17] By excluding, according to Letter and Bauman,[12] ionisation of OH, inconsistent formation functions were obtained.

TABLE 3

Protonation constants of DL-4-amino-3-hydroxybutanoic acid at different temperatures (I = 0·1M-KCl). Standard deviations are given in parentheses

θ_c/°C	log K_2	log K_3
5	10·024 (2)	3·879 (4)
10	9·899 (7)	3·888 (11)
15	9·735 (5)	3·883 (9)
20	9·590 (7)	3·851 (12)
25 *	9·487 (11)	3·834 (12)
30	9·297 (5)	3·831 (9)
35	9·177 (2)	3·803 (4)

* The first-step protonation constant (3-hydroxy-group) is in the range 13·0 ± 0·1.

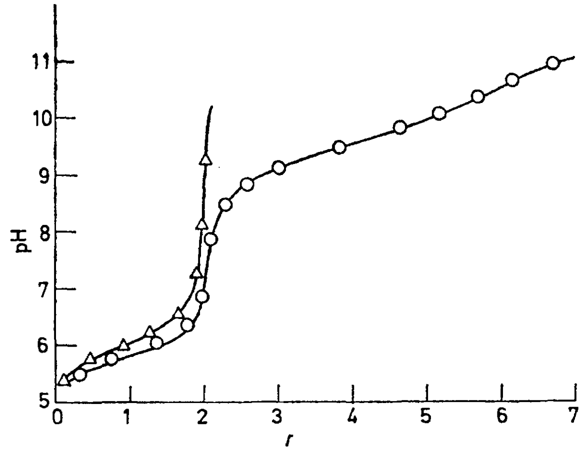

FIGURE 1 Titration curves as function of r, the ratio of mmol KOH to mmol copper(II). $c_M : c_L = 1 : 1$ (△) [experiment (1), Table 2], and 1 : 4 (○) [experiment (3)]

The arguments on which the set of complexes was chosen, namely [CuL], $[Cu_2L_2]$, $[CuL_2]^{2-}$ [$L^{2-} = H_2N{\cdot}CH_2{\cdot}CH(O^-){\cdot}CH_2CO_2^-$], *etc.* were as follows: (*i*) the $\bar{n}$ formation functions exhibited displacements for $0 \leqslant \bar{n} \leqslant 1$ dependent on the total metal concentration, thus showing the presence of binuclear complexes in this range; (*ii*) exclusion of the species [CuL] caused dramatic increases in $\Sigma\Delta^2$, the sum of the squares of the residuals (see below); (*iii*) stepwise formation constants of [CuL] and $[Cu_2L_2]$, as calculated according to Näsänen[6] from data for the first buffer zone, were not constant; and (*iv*) introduction of any other complex as $[Cu(HL)]^+$, $[Cu(HL_2)]^-$, $[Cu_2L_3]^{2-}$, $[CuL(OH)]^-$, or $[Cu_2L_2(OH)_2]^{2-}$ increased $\Sigma\Delta^2$. Although the ligand possesses an asymmetric carbon atom, complexes $[CuL_2]^{2-}$ of one kind only were considered. The complex-formation constants were refined by the MINIQUAD program of Sabatini *et al.*[18] which minimises the sum of the squares of the residuals, $\Sigma\Delta^2 = \Sigma(\Delta c_M{}^2 + \Delta c_L{}^2 + \Delta c_H{}^2)$, where c_M, c_L, and c_H are the total molar metal, ligand, and acid concentrations, respectively. All the calculations were made on the computer CDC 6600 of Consorzio Interuniversitario dell'Italia Nord-Orientale, Bologna. A complete list of the experimental data is available as Supplementary Publication No. SUP 21345 (42 pp., 1 microfiche).†

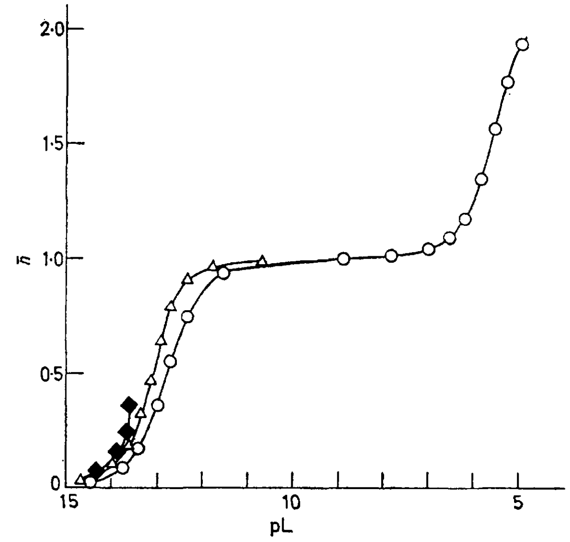

FIGURE 2 Trend of formation functions at constant total-ligand concentration (hydrolysis disregarded). $c_M : c_L = 2 : 1$ (◆) [experiment (4), Table 2], 1 : 1 (△) [(1)], and 1 : 3 (○) [(5)]

DISCUSSION

Protonation Equilibria.—The protonation constant for the 3-hydroxy-group, $RO^- + H^+ \rightleftharpoons ROH$, log K_1 = 13·0 ± 0·1, although approximate because of the high basicity, is reasonable. A value of log K_1 = 12·8 can be calculated from log K = 15·9 — 1·426σ* using values of σ* given by Barlin and Perrin.[19] The constant for the amine group, log K_2 = 9·487(11), when compared with

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* The full lines in Figure 1 were derived from the HALTAFALL program.[16]

† For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1974, Index issue.

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log K_1 = 10·556 for 4-aminobutanoic acid [20] shows a remarkable decrease. This is very likely due to the influence of the adjacent, slightly acidic, hydroxy-group; from the expression $\log K = 10{\cdot}15 - 3{\cdot}14\sigma^*$,[19] $\log K_2 = 9{\cdot}27$. The value of the constant for the carboxy-group, $\log K_3 = 3{\cdot}834(12)$, is slightly lower than that, 4·03,[21] for 4-aminobutanoic acid, but the trend is again in accordance with the depressing influence of the OH group. This value is in good agreement with that calculated, $\log K_3 = 3{\cdot}95$, from $\log K = 4{\cdot}76 - 0{\cdot}67\sigma^*$.[19]

The dependence of log K on temperature for two protonation steps, log K_2 and log K_3, was determined between 5 and 35 °C; for log K_1 this dependence was difficult to determine because of uncertainties implied in relation of Paoletti *et al.*[23] (ΔH_2: found, −45·6; calc., −45·3 kJ mol^{-1}). On the other hand ΔS_2, in comparison with the simple amines, is strongly increased by the presence of the carboxylato-group. In the protonation of the CO_2^- group, ΔH_3 is as low as values of other acids, while ΔS_3 is high but not as high as for simple aliphatic acids. The high values of ΔS_2 and ΔS_3 can be explained by the ordering influence of CO_2^- on the water molecules of the environment. Starting from $H_2N{\cdot}RCO_2^-$, successive addition of protons lowers the field effect of the negative charge. Therefore variations in the free-energy changes of protonation of molecules containing carboxy-groups are considerably dependent on the entropy term.

TABLE 4

Thermodynamic functions [a] ΔG (kJ mol^{-1}), ΔH (kJ mol^{-1}), ΔS (J K^{-1} mol^{-1}) for protonation of DL-4-amino-3-hydroxybutanoic acid and related compounds at 25 °C

	NH_2				CO_2^-			
Compound	log K_2	ΔG_2	ΔH_2	ΔS_2	log K_3	ΔG_3	ΔH_3	ΔS_3
4-Amino-3-hydroxybutanoic acid [b]	9·487(11)	−54·12(4)	*−45·58(62)*	*28·6(21)*	3·834(12)	−21·87(4)	*−3·28(70)*	*62·4(25)*
c	9·73	−55·52	−45·52	33·47				
Butanoic acid [d]					4·820	−27·47	2·68	101·33
2-Aminobutanoic acid	9·830 [e]	−56·02	−45·47 [e]	36·01 [e]	2·284 [d]	−13·02 [d]	*−1·26* [d]	*39·78* [d]
2-Amino-3-hydroxybutanoic acid [f]	9·096	−51·86	−42·04	33·5	2·21	−12·59	−5·69	20·9
2-Amino-4-hydroxybutanoic acid [g]	9·257	−52·77	*−45·62*	*24·7*	2·265	−12·88	*0·13*	*47·7*
4-Aminobutanoic acid	10·556 [e]	−60·16 [e]	−52·12 [e]	27·2 [e]	4·03 [d]	−22·97 [d]	*−1·67* [d]	*71·2* [d]
Acetic acid [d]					4·766	−27·16	0·08	9·69
Ammonia [e]	9·242	−52·67	−52·38	1·26				
Butylamine [e]	10·640	−60·64	−58·49	7·53				

[a] Values calculated by variation of log K at different temperatures are given in italics; estimated standard deviations are given in parentheses in units of the last digit. [b] This work. [c] Ref. 12. [d] Ref. 21. [e] Ref. 20. [f] R. M. Izatt, J. J. Christensen, and V. Kothari, *Inorg. Chem.*, 1964, **3**, 1565. [g] Ref. 1.

the measurements at high pH. The data satisfy expression (1) with coefficients $A_2 = 4\,972{\cdot}2$, $B_2 =$

$$\log K(T) = (A/T) - B + 20 \log T \qquad (1)$$

56·732, $A_3 = 2\,761{\cdot}2$, and $B_3 = 54{\cdot}225$. From this equation, values of ΔH_2, ΔH_3, ΔS_2, and ΔS_3 at 25 °C were calculated and compared with those of other compounds (Table 4). The reliability of the data is assessed by the agreement of ΔH_2 with the result from the direct calorimetric measurements of Letter and Bauman.[12] Moreover, ΔH_2 and ΔH_3 are in the ranges of values typical for amines and acids, respectively.

The dependence of ΔG_2 and ΔG_3 on structure, which is the basis of the Barlin and Perrin equation,[19] is demonstrated by the agreement found between the observed and calculated log K values. It is interesting, however, to find out whether this dependence is due to the entropy or the enthalpy term.[20-22] A thorough examination of the data in Table 4 shows that for the amine group ΔH_2 is the major contributor to ΔG_2 and follows the values of the corresponding amines, with the structural influences of OH and CO_2^- foreseen by the

Copper(II) *Complexes*.—The equilibria and formation constants of the complexes are reported in Table 5.

TABLE 5

Equilibria and formation constants * of copper(II) complexes of DL-4-amino-3-hydroxybutanoic acid at 25 °C and I = 0·1M-KCl [$L^{2-} = H_2N{\cdot}CH_2{\cdot}CH(O^-){\cdot}CH_2CO_2^-$]

$Cu^{2+} + L^{2-} \rightleftharpoons [CuL]$	$\log \beta_{101} = 12{\cdot}961\ (43)$
$2Cu^{2+} + 2L^{2-} \rightleftharpoons [Cu_2L_2]$	$\log \beta_{202} = 28{\cdot}696\ (70)$
$Cu^{2+} + 2L^{2-} \rightleftharpoons [CuL_2]^{2-}$	$\log \beta_{102} = 18{\cdot}856\ (21)$
$2CuL \rightleftharpoons [Cu_2L_2]$	$\log K = 2{\cdot}774$
$[CuL] + L^{2-} \rightleftharpoons [CuL_2]^{2-}$	$\log K = 5{\cdot}895$
$2Cu^{2+} + 2HL^- \rightleftharpoons [Cu_2L_2] + 2H^+$	$\log K = 2{\cdot}696$

* $\beta_{pqr} = [Cu_p(H_qL_r)]/[Cu]^p[H]^q[L]^r$.

For the hydrolysed species $[Cu_2(OH)_2]^{2+}$ the stability constant from Berecki-Biedermann [17] was held constant throughout as $\beta_{22} = 2{\cdot}5 \times 10^{-11}$. A typical distribution diagram is shown in Figure 3. The [CuL] and $[Cu_2L_2]$ complexes can be assigned structures characterised by a five-membered chelate ring with amine-nitrogen and enolate-oxygen donor atoms. The carboxylato-group occupies the apical position of the co-ordination polyhedron thus forming also a six-membered ring. The

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complexes are completely different from those supposed by Letter and Bauman.[12] The dimeric complex can be compared in some respects with that given by Näsänen [6] for the equilibrium between Cu^{2+} and 1,3-diaminopropan-2-ol. The different behaviour of the two ligands may be due to the higher stability of the dimeric complex of 1,3-diaminopropan-2-ol as shown by the equilibrium constants for (2) which are log $K = 2{\cdot}696$ for DL-

$$2Cu^{2+} + 2HL^- \rightleftharpoons [CuL_2] + 2H^+ \qquad (2)$$

4-amino-3-hydroxybutanoic acid and 10·30 for 1,3-diaminopropan-2-ol.[6] In the latter system only the highly stable dimer appears, whereas in the former the lower stability of the dimer makes formation of the monomer possible too.

The only comparable chelate complexes of aminoethanol compounds with copper(II) are those formed by 2-amino-1-phenylethanol (ape) [8] of the family of ephedrine. The first-step stability constant for 4-amino-3-hydroxybutanoic acid, log $K_1 = 12{\cdot}961$, should be compared with log $K_1 = 9{\cdot}50$ for ape, and that of the second step (log K_2 5·895) with log $K_2 = 6{\cdot}0$ for ape. The much higher stability of the first complex of the present ligand can be attributed to co-ordination of the carboxylato-group, *i.e.* the ligand is tridentate. The equality of the second formation constants for the two ligands seems to indicate that the second molecule of ligand is only bidentate.

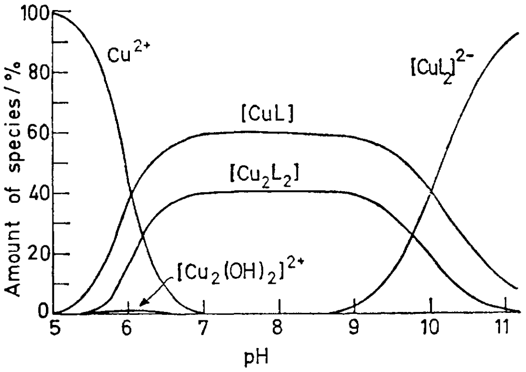

FIGURE 3 Typical distribution diagram for equilibria of Cu^{2+} with DL-4-amino-3-hydroxybutanoic acid. The percentages were calculated by the HALTAFALL program [16] from data of experiment (5) (Table 2)

Solutions of Cu^{2+} and the butanoic acid at pH $\leqslant 10$ are blue (maximum at 640 nm) and at pH >10 are purple-violet (maxima at *ca.* 630 and *ca.* 540 nm). These changes can be interpreted (Figure 3) by assigning the maximum at 640 nm to 1 : 1 and 2 : 2 complexes and that at 540 nm to the 1 : 2 complex. A similar classification can be made for the set of complexes of aminoethanols with Cu^{II} prepared by Näsänen *et al.*; solutions of 1 : 1 and 1 : 2 complexes were blue or green with maxima in the range 600—671 nm [5,6,24] and those of the 1 : 2 complex were violet with maxima in the range 520—606 nm.[25,26]

The complex-formation equilibria could also have been analysed on the basis of equation (3) suggested by Näsänen [6] for 1,3-diaminopropan-2-ol and Cu^{2+} which

$$Cu^{2+} + HL^- + H_2O \rightleftharpoons [Cu(HL)(OH)] + H^+ \quad (3)$$

is indistinguishable, from a numerical point of view, from that implying ionisation of the hydroxy-group. Such an equilibrium, however, implies ionisation of one water molecule in the co-ordination sphere of Cu^{2+}. This interpretation seems unlikely in the present case because the titration curves do not show the typical buffer zone observed at pH $\approx 7{\cdot}3$ (Martell *et al.*[27]) for other copper(II) complexes. Moreover, Näsänen has prepared the complex $[Cu_2L_2(NO_3)_2]$ $[L^- = H_2N{\cdot}CH_2{\cdot}CH(O^-){\cdot}CH_2{\cdot}NH_2]$ having the same maximum (600 nm) in the visible spectrum as that of the mother liquor (608 nm),[5] thus showing that enolate chelates of ethanolamines are possible both in the solid state and in solution.

Conclusion.—DL-4-Amino-3-hydroxybutanoic acid shows protonation constants and thermodynamic functions which parallel those of other similar compounds. With Cu^{2+} it forms the complexes [CuL], $[Cu_2L_2]$, and $[CuL_2]^{2-}$ *via* ionisation of the 3-hydroxy-group and formation of five-membered chelate rings by the aminoethanol moiety. The CO_2^- group of the first ligand molecule participates in the co-ordination in [CuL] (thus forming a six-membered chelate ring), but not that of the second L^{2-} in $[CuL_2]^{2-}$. It is remarkable that the isomers homoserine and threonine, having the same donor groups, do not show, in the presence of Cu^{2+}, ionisation of the OH group. It is likely that ionisation takes place with the assistance of both adjacent basic centres.

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