Thermodynamic and Spectroscopic Studies on the Protonation and Cu^{2+} Complex Formation of a Synthetic Amino Diacid: (3-Aminopropyl)malonic Acid

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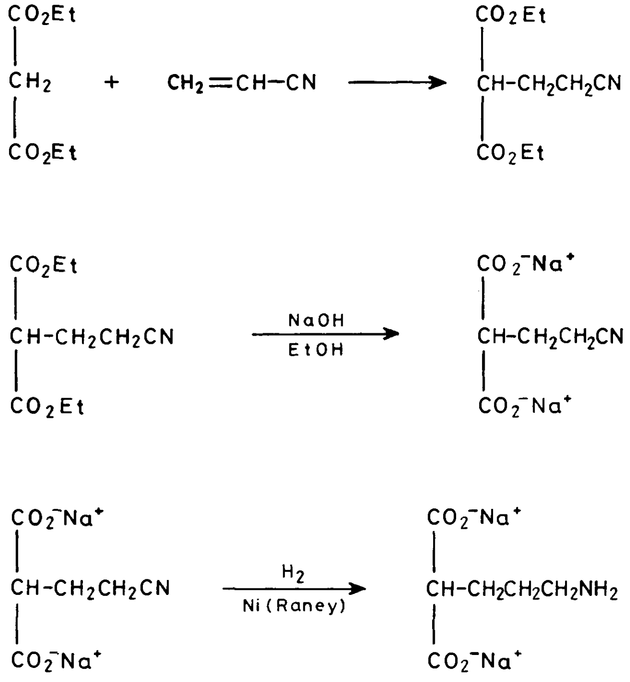
The basicity constants of (3-aminopropyl)malonate have been determined in 0.1 mol dm^{-3} NaCl at 25 °C. The structures of the different protonated forms were investigated by Fourier-transform i.r. techniques in aqueous solution and molecular mechanics. The presence of an intramolecular hydrogen bond in the diprotonated form is suggested. On the basis of the structures proposed, the heats and entropies of the protonation are discussed. Three complexes are found with Cu^{2+}, of formulae $[CuHL]^+$, $[CuH_2L_2]$, and $[Cu(HL_2)]^-$ [H_2L = (3-aminopropyl)malonic acid]. Their structures have been hypothesized on the basis of the thermodynamic and spectroscopic parameters. In all the complexes investigated the co-ordination of both CO_2^- groups is achieved.

Many papers concern the acid–base properties as well as the complexing abilities of amino acids. On the contrary there is little literature information on the amino diacids[1] if we exclude the relatively numerous studies on the two asymmetric natural glutamic and aspartic acids which behave like α-alanine in their complex formation reactions, since one carboxylic group, *i.e.* that farthest from the amino group, is rarely involved in the co-ordination.[2]

To our knowledge only one example of a symmetric amino dicarboxylic acid has been studied in aqueous solution, aminomalonic acid, of which its acid–base properties and complexing behaviour towards Hg^{2+} were investigated by Schwarzenbach and Ackermann[3] in aqueous solution. More recently (aminoalkyl)malonic acids have been synthesized and studied as a ligand towards cobalt(III) even if decarboxylation of one of the two carboxylic groups occurs under acidic conditions.[4] Our aim is to study the behaviour in solution of this relatively unexplored class of compounds, symmetric amino dicarboxylic acids, which present the properties of both amino acids and dicarboxylic acids. To this purpose, we synthesized the new amino diacid (3-aminopropyl)malonic acid (H_2apmal) and have studied its acid–base properties by potentiometry, calorimetry, Fourier-transform (F.t) i.r. spectrophotometry, and molecular mechanics.

In addition we have investigated the complexing ability of this molecule in aqueous solution towards Cu^{II} and the thermodynamic quantities compared with those obtained for a polymer[5] which contains a similar moiety in the repeating unit.



Scheme.

Experimental

Reagents.—The disodium salt of (3-aminopropyl)malonic acid was prepared as previously reported[5] by reducing disodium (2-cyanoethyl)malonate, in turn obtained by basic hydrolysis of diethyl (2-cyanoethyl)malonate. Diethyl (2-cyanoethyl)malonate was synthesized by adding diethyl malonate to acrylonitrile in the presence of sodium ethanolate. The chemical steps are summarised by the Scheme. Elemental analysis and potentiometric measurements showed a purity higher than 96%.

A CO_2-free NaOH solution was prepared, stored, and standardized as previously described.[6] Stock solutions of 0.1 mol dm^{-3} NaCl were prepared from sodium chloride (Suprapur, Merck) without further purification and used as the ionic medium for the potentiometric and calorimetric measurements.

The copper(II) nitrate solution was prepared using the solid salt (C. Erba RPE grade product) and decarbonated twice with distilled water. The copper(II) content was periodically gravimetrically analyzed.

Potentiometric Measurements.—Potentiometric titrations were carried out using a Ross reference electrode (model 80-05) and a Ross glass electrode (model 81-01) connected to a PHM-84 Radiometer. The titration vessel was thermostatted at 25 °C and the solutions stirred magnetically under a CO_2-free nitrogen stream.

For each protonation constant determination, the cell was filled with *ca.* 100 cm^3 of 0.1 mol dm^{-3} NaCl containing a weighed amount of Na_2(apmal). For the titrations, the HCl or NaOH solutions were delivered from a Metrohm Multidosimat

Table 1. Experimental details for the potentiometric measurements at 25 °C in 0.1 mol dm^{-3} NaCl

Reaction	$T_L{}^a$/mmol	$T_M{}^b$/mmol	$T_{H^+}{}^c$/mmol	$C_T{}^d$/mmol dm^{-3}	pH range	Number of points
$L^{2-} + H^+$	0.3046	—	0.0	0.0980	10.74—2.85	60
	0.3852	—	0.0	0.0980	10.81—2.59	66
	0.4313	—	1.9620	−0.1188	2.28—10.52	84
$L^{2-} + Cu^{2+}$	0.5648	0.3742	1.7640	−0.1188	2.51—6.22	62
	0.3653	0.1942	1.3720	−0.1188	2.71—6.34	65
	0.3914	0.1046	1.5680	−0.1188	2.88—6.71	27

[a] T_L = Initial amount of ligand. [b] T_M = Initial amount of copper(II) ion. [c] T_{H^+} = Initial amount of hydrogen ion. [d] Titrant concentration (negative values indicate titrations with NaOH).

Table 2. Experimental details for the calorimetric measurements at 25 °C in 0.1 mol dm^{-3} NaCl

Reaction	T_L/mmol	T_M/mmol	T_{H^+}/mmol	C_T/mmol dm^{-3}	pH range	Number of points
$L^{2-} + H^+$	0.0901	—	0.0	0.0981	10.32—2.82	19
	0.2359	—	0.0	0.0980	10.64—9.80	35
	0.4027	—	0.0	0.4826	5.17—2.25	20
$L^{2-} + Cu^{2+}$	0.3896	0.0	0.4364	0.1521*	5.66—4.03	35
	0.4017	0.0	0.3552	0.1521*	6.94—6.45	28
	0.1457	0.1363	0.1015	0.1015	6.79—2.74	33

* Copper(II) nitrate titrant solution.

piston burette. For the stability constant determinations, the cell was filled with *ca.* 100 cm^3 of 0.1 mol dm^{-3} NaCl containing a known amount of the ligand and aqueous copper(II) nitrate solution, with an excess of hydrochloric acid. In this case the solutions were titrated with 0.1 mol dm^{-3} NaOH until precipitation occurred.

The data obtained were printed and stored on a floppy disk of an M 20 Olivetti computer automatically controlling the experiments by means of a Basic program.

Details of the potentiometric titrations are summarized in Table 1. The SUPERQUAD program which was used to calculate the protonation and complex formation constants has been described elsewhere.[7]

F.T.-I.r. Spectra.—Aqueous solution spectra were recorded in the range 3 000—900 cm^{-1} on a Perkin-Elmer M 1800 F.t.-i.r. spectrophotometer using a BARNES microcircle cell with ZnSe crystal. The instrument was equipped with a DTGS (deuteriated triglycine sulphate) detector and was purged with dry air. For each spectrum 100 scans were averaged with a resolution of 2 cm^{-1}.

The solutions were 4 × 10^{-2} mol dm^{-3} and the pH adjusted by adding a small amount of a 1 mol dm^{-3} HCl solution. The subtraction of water from the polymer spectrum was made with the null criterion, by trying to minimize the water band.

Theoretical Calculations.—In order to obtain a microscopic description of the solvation of the various species present in solution an energy minimization of methylmalonic acid, H_2A, and its anions, HA^- and A^{2-}, was performed. Methylmalonic acid was adopted as a model compound because i.r. and thermodynamic data suggest that an amino group on the side chain does not influence the hydration of the two carboxylic groups, thus a methyl group is sufficient to simulate the effects of the side chain on the carboxylic group surroundings. First the conformational analysis of H_2A, HA^-, and A^{2-} as isolated molecules was carried out. The calculations were performed in order to compare the conformation of each molecule in the presence and absence of solvent. Then the potential energy of three small clusters in which 16 molecules of water surround one molecule of H_2A, HA^-, or A^{2-} respectively was minimized. The whole geometry of the system was optimized using the force field by Kollman *et al.*[8] In the description of non-bonded interactions for water molecules the polar oxygen OH and hydrogen HO atom types from the force-field reference were used in the computation of the electrostatic term for water point charges on nuclei; the value of the charge on the oxygen atom, expressed as a fraction of the protonic charge, is −0.66. It derives from the experimental value of the water dipole moment.

Calorimetric Measurements.—A Tronac model 1250 titration calorimeter was used as previously described.[9] A 25-cm^3 stainless steel reaction vessel and a 2.50-cm^3 Gilmont burette delivering the titrant solutions at a rate of 0.0833 cm^3 min^{-1} were used in all the runs. The water-bath temperature was kept at 25 °C accurately controlled by a precision temperature controller (PTC-40).

In order to determine the enthalpies of protonation isothermal titrations were performed by adding HCl to solutions of Na_2(apmal) in 0.1 mol dm^{-3} NaCl. Two experiments carried out using 0.1 mol dm^{-3} HCl checked the heats of reaction in the pH range where all three basic sites or only the nitrogen are being protonated. In the same way a titration using 0.5 mol dm^{-3} HCl was performed on this system in order to reach low pH values where only the carboxylate groups are generally protonated. Experimental details are summarized in Table 2. The ΔH° values were computed using the FITH program on a M 20 Olivetti computer as previously described.[9]

Two different methods have been used for determining the complex formation enthalpies isothermally. In the first, solutions of the free ligand containing a known amount of hydrogen ions were titrated with copper(II) nitrate solution until a 1:1 copper(II)–ligand molar ratio was reached. In the second method, a solution of the ligand containing known amounts of copper(II) and hydrogen ions was titrated with 0.1 mol dm^{-3} HCl. The correction for the heats of dilution were made by adding $Cu(NO_3)_2$ or HCl solutions to a 0.1 mol dm^{-3} NaCl solution.

All the experiments were controlled by a North-Star CCP 930 computer connected to the instrument and running the THERMAL program purchased by Tronac Inc. The M 20 Olivetti computer, also connected to the North-Star CCP 930, was used to calculate the enthalpies by means of the FIT program previously described.[10]

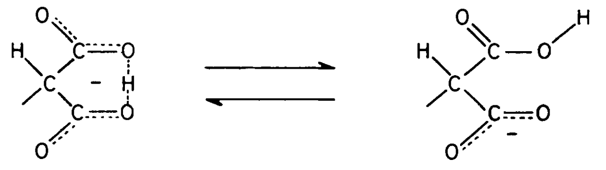
Results and Discussion

Protonation Studies in Aqueous Solution.—Basicity constants and F.t.-i.r. spectra. The stepwise protonation constants of H_2apmal (H_2L) determined on 0.1 mol dm^{-3} NaCl at 25 °C are reported in Table 3. The first protonation equilibrium refers to protonation of the most basic group, *i.e.* the primary amine site, while the second and the third equilibria refer to protonation of the carboxylate groups. As demonstrated by the log K values for the latter two, which are far from being equal, and even taking into consideration the correction due to the statistical effect, the two carboxylic groups influence each other.

The i.r. frequencies observed in the difference solution spectra at different pH values are shown in Table 4. The pH values were chosen on the basis of the log K values: at pH 9.8 the maximum percentage of HL^- (80%) and 20% of L^{2-} are present in solution; at pH 3.8 the maximum percentage of H_2L (87%) and 8% of HL^- are present; and at pH 2 both carboxylic groups are protonated as well as the primary nitrogen.

The spectrum of H_2apmal at pH 9.8 shows a strong band at 1 560 cm^{-1} which can be assigned to the asymmetric stretching of the carboxylate ion ($-CO_2^-$).[11] The band at 1 418 cm^{-1} can be attributed to the symmetric stretching (Figure 1). At pH 3.8 the spectrum shows a new band of weak intensity at 1 716 cm^{-1} which can be assigned to the C=O stretching of the carboxylic group ($-CO_2H$).[11] The band attributed to the asymmetric stretching of the carboxylate ion increases in frequency from 1 560 to 1 583 cm^{-1} and remains strong in intensity. At pH 2 both carboxylic groups are protonated, the CO_2H stretching appears as the most intense band in the spectrum, and the intensity of the band at 1 583 cm^{-1} drastically decreases.

These results may be explained by assuming for the diprotonated (the nitrogen and one CO_2^- group) species a planar and symmetrical structure with a hydrogen bond between the COO groups (see below).[12] With this hypothesis only one stretching C=O has to be present, which can be represented by

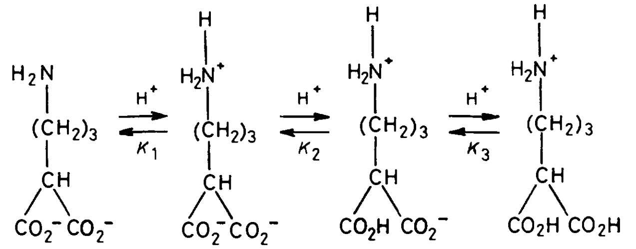


the most intense band at 1 583 cm^{-1} in the spectrum at pH 3.8. The other band at 1 716 cm^{-1}, due to the CO_2H stretching, can be explained by considering an equilibrium between the structure with an intramolecular hydrogen bond and the species without this hydrogen bond.

The shift to higher frequencies of the asymmetric stretching band on passing from pH 9.8 to 3.8 can thus be correlated with the increase in double bond character of the C=O group when the hydrogen bond is formed. This is also confirmed by the theoretical calculations and the thermodynamic changes (see later).

At pH 2 the two carboxylic groups are protonated. Thus the band at 1 720 cm^{-1} due to the CO_2H stretching is the most intense in the spectrum.

Table 3. Stepwise protonation constants of H_2apmal at 25 °C in 0.1 mol dm^{-3} NaCl



	log K*
$L^{2-} + H^+ \rightleftharpoons HL^-$	10.448(5)
$HL^- + H^+ \rightleftharpoons H_2L$	4.863(7)
$H_2L + H^+ \rightleftharpoons H_3L^+$	2.522(9)

* The values in parentheses are the estimated standard deviations of the last significant figure.

Table 4. F.t-i.r. frequencies (cm^{-1}) observed for H_2apmal in aqueous solution at different pH (the percentage of the different protonated species are given in parentheses)

pH 9.8 (80% HL^-, 20% L^{2-})	pH 3.8 (87% H_2L, 8% HL^-)	pH 2 (77% H_3L^+, 23% H_2L)
	1 716w	1 720s
1 560s	1 583s	1 583m
1 418w	1 422m	
1 360w	1 374m	1 380m
	1 267m	
	1 222m	1 215s

Theoretical Computations.—The results of optimizations on isolated molecules give nearly coplanar COO groups in H_2A and HA^-, with an intramolecular hydrogen bond forming a six-membered ring, while in A^{2-} these groups are nearly perpendicular to the plane of the three carbon atoms of the malonic acid moiety. The structures corresponding to the absolute minima found for the three molecules are illustrated in Figure 2.

If we consider the results of the calculations in the presence of water molecules, the structure of HA^- remains almost unchanged, compared to the isolated molecule, while in H_2A one of the two CO_2H groups becomes nearly perpendicular to the plane of the free molecule, showing no intramolecular hydrogen bond.

The structure of A^{2-} undergoes only minor changes upon addition of water molecules. It shows a rigid and well characterized first hydration shell, in which four water molecules form four bridges, joining pairs of oxygen atoms of the CO_2^- groups. In particular, one of the oxygen atoms is joined to the others by three water molecules: this structure can, therefore, explain the small conformational variation in A^{2-} compared to the isolated molecule.

The hydration of HA^- differs substantially from that of A^{2-}, because no bridge of water molecules joins two oxygen atoms belonging to different COO groups. Also the number of strong interactions between solute and solvent is smaller than in A^{2-}. In addition, the whole first hydration shell appears to be less ordered and rigid, because the two COO groups interact strongly only *via* the intramolecular hydrogen bond, while the interactions mediated by water molecules are less direct, involving chains of two water molecules or more. The hydration of HA^- was performed in two different ways: in the first energy minimization calculation we considered an asymmetric intramolecular hydrogen bond, with the acidic proton covalently bound to one oxygen atom, and therefore, distinct CO_2^- and CO_2H groups; in the second calculation we considered a symmetric intramolecular hydrogen bond, in which the acidic proton lies nearly 1.2 Å from the two oxygens as suggested by

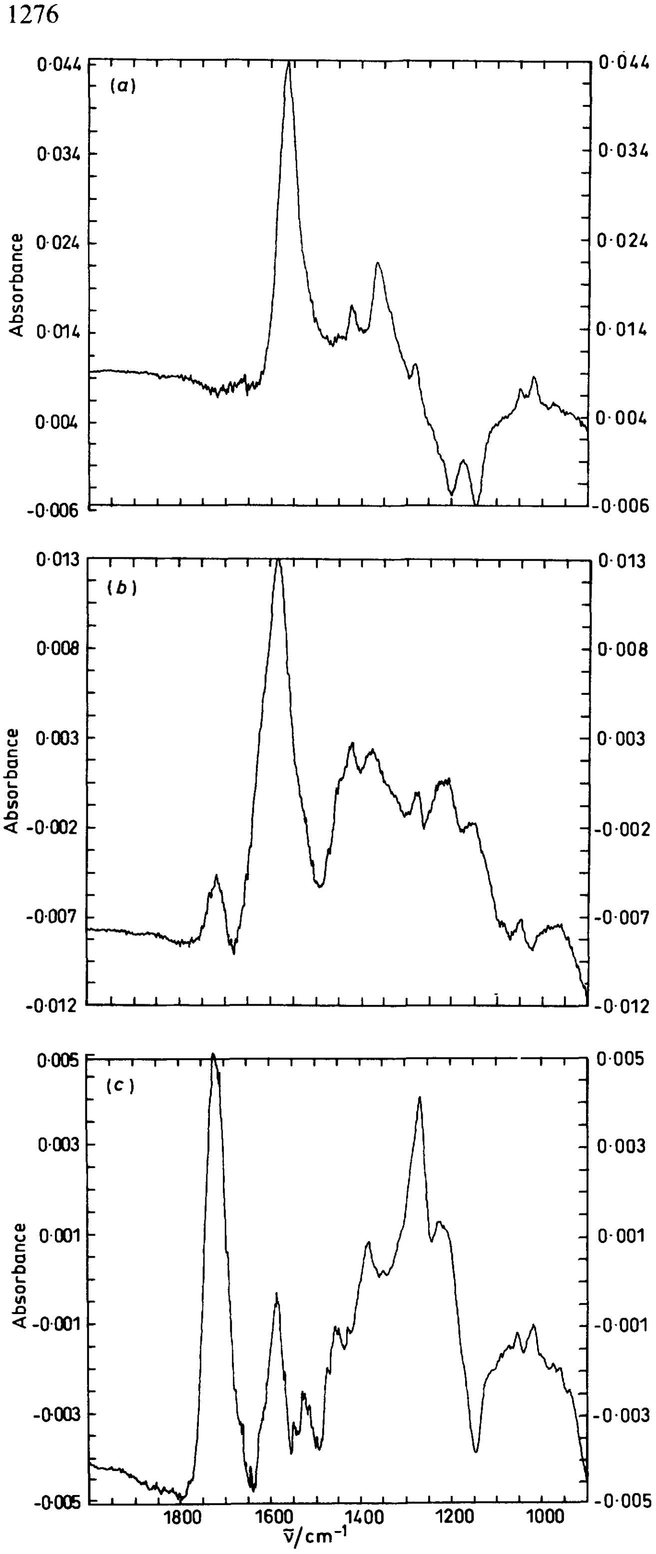


Figure 1. Difference aqueous solution F.t.-i.r. spectra of H_2apmal; (*a*) at pH 9.8, (*b*) at pH 3.8, (*c*) at pH 2

X-ray and neutron diffraction data.[13] Obviously, in the latter the intramolecular hydrogen bond is regarded as a covalent interaction on both sides of the hydrogen atom, in order to ensure its symmetry. Therefore this allows only minor stretching, bending, and torsional deformations in the six-membered ring structure. Despite this, the results of the two calculations are analogous because the asymmetrical hydrogen bond appears stable, and the structure of the solvation shell of the two systems is very similar, showing the same trend in comparison to A^{2-} hydration.

The structure of the hydration shell of H_2A is largely determined by interactions between the acidic protons and water which can break the intramolecular hydrogen bond of the isolated molecule. The non-coplanar structure of the CO_2H groups is probably due to the possibility of a best adaptation of H_2A to the tetrahedral water structure, offered by the rotation of a CO_2H group, thanks to the formation of chains of water molecules joining the carboxylic oxygens to the acidic protons of H_2A.

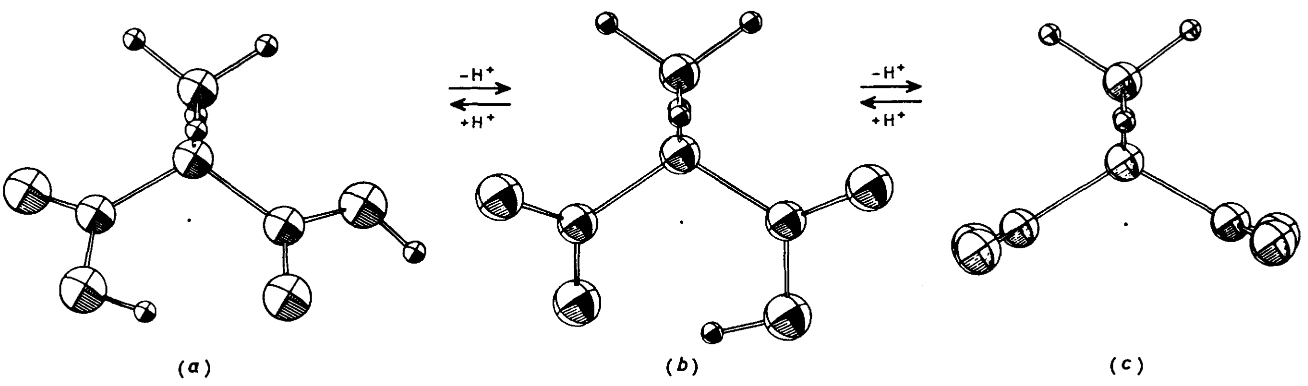
The structures of the three clusters obtained respectively for A^{2-}, HA^-, and H_2A, are shown in Figure 3. The structure related to HA^- hydration shows the result of the calculation with a symmetric hydrogen bond, while the result for the asymmetric hydrogen bond is illustrated in Figure 4. The orientation of the solute molecule of HA^- in Figure 3 differs from that chosen in the other cases in order to show the twisted structure of the hydrogen-bonded ring. The results thus obtained on the hydration of the carboxylic groups of methylmalonic acid can also be considered valid for H_2apmal, on the basis of i.r. and thermodynamic data, which strongly suggest the independence between the amino and carboxylic groups in H_2apmal.

Thermodynamic Quantities.—The thermodynamic changes related to the protonation process are reported in Table 5.

The amino group of L^{2-} is separated by a chain of four carbon atoms from the two negatively charged CO_2^- groups and therefore the thermodynamic parameters of its protonation scarcely influence the carboxylate groups. In fact the enthalpy and entropy changes are very close to those found for primary amines in simple amino acids.[11] In addition the two carboxylate groups show thermodynamic quantities similar to those found for malonate.[13]

The second equilibrium concerns the protonation of the carboxylate group. The proton is suspended between both carboxylate groups as evidenced by F.t.-i.r. and theoretical calculations. Thus a very short hydrogen bond may occur, as, for instance, in $H(RCOO)_2^-$ in the solid state,[12] or in ^-O_2C–CH_2–CO_2H, whose head is joined to the tail *via* a short (2.46 Å) hydrogen bond.[13] A similar hypothesis was also postulated for some monoprotonated dicarboxylates in aqueous solution by Rizzarelli and co-workers[14] on the basis of the thermodynamic parameters. The positive entropy contribution in the second step of protonation (Table 5) is larger than that observed in the same process with simple amino acids.[11] This is a result of the partial charge neutralization which occurs on the non-protonated CO_2^- due to the presence of the hydrogen bond, a process which provokes a further liberation of water molecules (see above theoretical calculations). The third protonation breaks the hydrogen bond thus completely neutralizing both CO_2^- groups. The entropy contribution is always positive but lower than that observed at the second step. As a consequence the enthalpy change is less endothermic.

Cu^{2+} *Complex Formation Studies.—Thermodynamic and spectroscopic data.* (3-Aminopropyl)malonate forms three complexes with Cu^{II} in aqueous solution of stoicheiometry $[CuHL]^+$, $[CuH_2L_2]$, and $[CuHL_2]^-$. This sequence is observed on increasing the pH. The relative stability constants and thermodynamic parameters are reported in Table 6. The HL^- ion forms a $[CuHL]^+$ complex with thermodynamic functions similar to those reported for the malonate ion;[15] the reaction is endothermic whereas the entropy is large and positive as occurs in Cu^{2+} complex formation with carboxylate ions. As a consequence the hydrogen ion in $[CuHL]^+$ protonates the



(*a*) (*b*) (*c*)

Figure 2. Minimum energy conformations of H_2A (*a*), HA^- (*b*), and A^{2-} (*c*)

Table 5. Thermodynamic parameters for the protonation of H_2apmal at 25 °C in 0.1 mol dm^{-3} NaCl with standard deviations in parentheses

Reaction	log *K*	$-\Delta G^{\circ}$/kJ mol^{-1}	$-\Delta H^{\circ}$/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}
$L^{2-} + H^+ \rightleftharpoons HL^-$	10.448(5)	59.61(3)	51.2(3)	28.0(8)
$HL^- + H^+ \rightleftharpoons H_2L$	4.863(7)	27.75(4)	−2.4(3)	101(1)
$H_2L + H^+ \rightleftharpoons H_3L^+$	2.522(9)	14.39(5)	−0.4(3)	50(1)

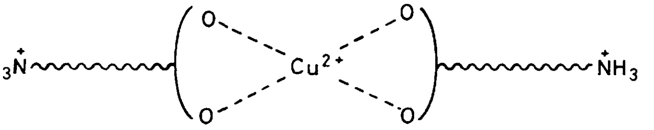
Table 6. Thermodynamic functions for the reactions of H_2apmal with Cu^{2+} at 25 °C in 0.1 mol dm^{-3} NaCl

Reaction	log β	$-\Delta G^{\circ}$/kJ mol^{-1}	$-\Delta H^{\circ}$/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}	Electronic spectrum (cm^{-1})*
$Cu^{2+} + HL^- \rightleftharpoons [CuHL]^+$	4.11(1)	23.43(4)	−11.3(8)	117(3)	13 200(18)
$[CuHL]^+ + HL^- \rightleftharpoons [CuH_2L_2]$	2.93(4)	16.74(21)	−2.1(8)	63(3)	—
$[CuHL]^+ + L^{2-} \rightleftharpoons [CuHL_2]^-$	6.62(6)	37.78(33)	~29	~21	—

* Absorption coefficient in parentheses (dm^3 mol^{-1} cm^{-1}).

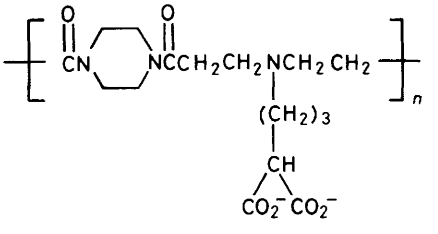
primary nitrogen atom. The similarity of the thermodynamics with those of the malonate ion also indicates that the presence of the positively charged terminal tail does not affect the thermodynamics of the complex formation of the two carboxylate ions. Also the spectroscopic parameters are indicative of a Cu^{II} complex containing a CuO'_2O_2 chromophore[15] (O′ = a carboxylate oxygen).

For $[CuH_2L_2]$ the entropy contribution is positive, but lower than that observed in $[CuHL]^+$. The thermodynamic quantities are also quite similar to those obtained for the bis malonate complex of Cu^{II}.[15] Thus the Cu^{II} ion is co-ordinated by four carboxylate anions, the whole complex being formally neutralized by two positive charges on the nitrogen atoms, as shown below. This particular zwitterionic complex can orientate a larger number of water molecules than a real neutral complex.



The final complex, $[CuHL_2]^-$, is formed at high pH. Unfortunately it was not possible to determine accurately the ΔH° due to the small quantity of the complex present in solution at each Cu:L ratio. However its stability constant is much larger than that observed for $[CuH_2L_2]$ and its heat decidedly exothermic. Similar thermodynamic values have been found for the bis aspartate and glutamate complexes of Cu^{II}.[2a,c] The latter two ligands co-ordinate through NH_2 and a carboxylate group; therefore $[CuHL_2]^-$ appears to complex with two CO_2^- groups, belonging to HL^-, and one CO_2^- group and the NH_2 group of L^{2-}. This hypothesis is rather hazardous when considering the dimension of the chelate ring which would be formed. In the literature some examples of complexes with such large chelate rings are reported with Cu^{II}.[16] This type of complex indicates that only the presence of the proton on the NH_3^+ group would prevent its co-ordination, which is favoured over carboxylate co-ordination, despite the dimension of the chelate ring formed.

At this point we can compare the co-ordinating ability of H_2apmal with that of a polymer, shown below, containing the same ligand moiety in the repeating unit. As previously reported,[5] the polymer is unable to form stable Cu^{2+} complexes in aqueous solution, even though the Cu^{2+} complexes of H_2apmal involve the co-ordination of two carboxylate groups which are similar to those present in the polymer.



Looking at the simple $[Cu(HL)]^+$ complex (HL^- = repeating monoanionic unit of polymer), the most favoured to be formed by the polymer for the absence of steric hindrance, it is only formally charged. The positive charge lies on the nitrogen atom which is far from the uncharged $Cu(O_2C-)_2$ group. The presence of the charge does not influence the thermodynamic or spectroscopic parameters of the complex but aids its solubility. Complexation with the polymer as the ligand is therefore

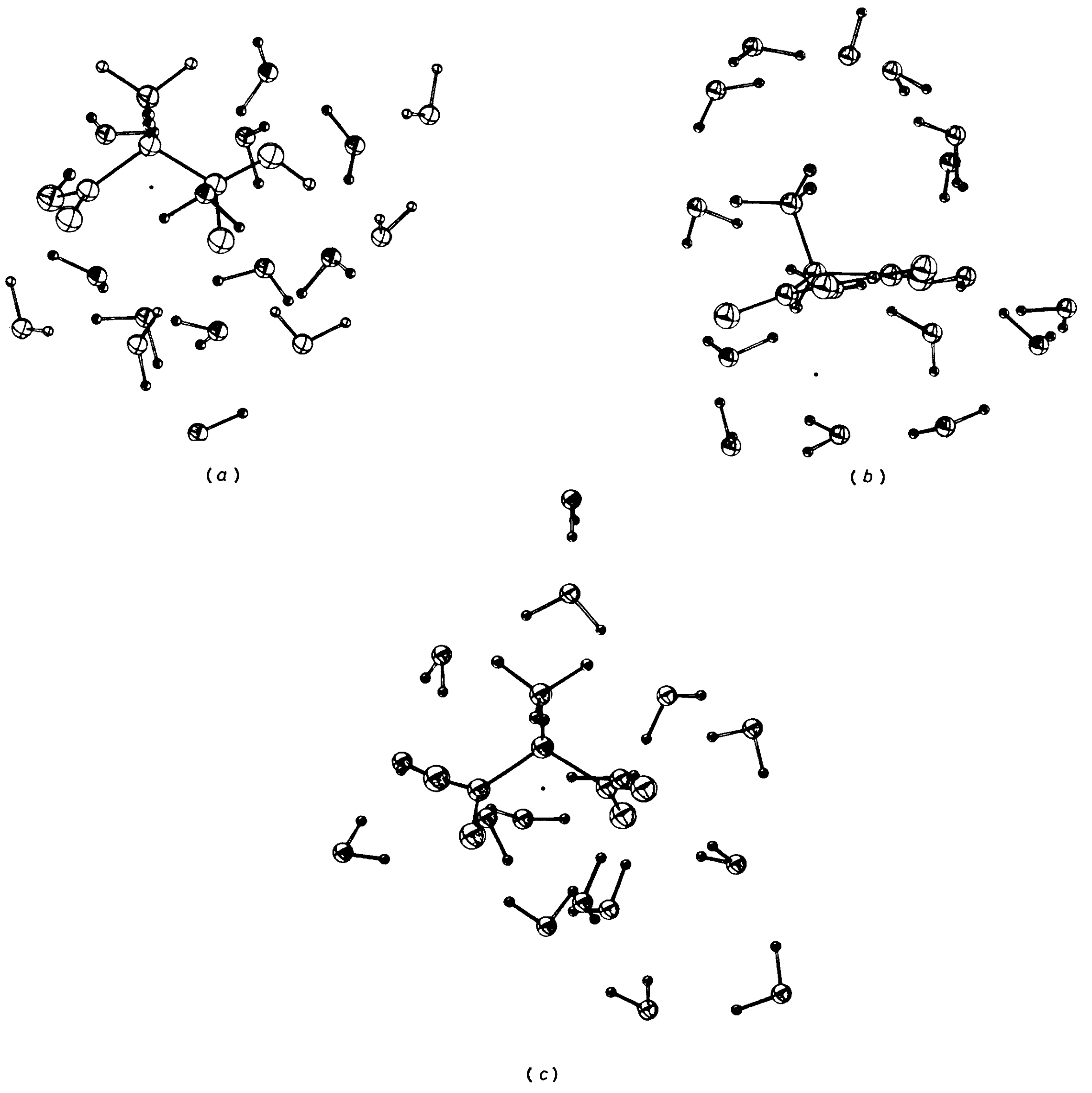


Figure 3. Minimum energy structures of $H_2A + 16\ H_2O$ (*a*), $HA^- + 16\ H_2O$ (symmetric hydrogen bond) (*b*), and $A^{2-} + 16\ H_2O$ (*c*) systems

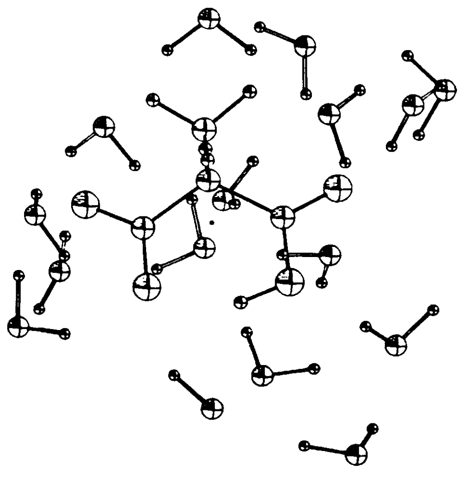


Figure 4. Minimum energy structure of $HA^- + 16\ H_2O$ (asymmetric hydrogen bond) system

prevented because the surroundings are scarcely hydrophilic while the tertiary nitrogen atom of the chain is protonated at lower pH than the primary one. The retardation in the protonation determines the instability of the complex in aqueous solution.

Acknowledgements

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