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Ternary Complexes in Solution. Comparison of the Coordination Tendency of Some Polybasic Oxygen Acids Toward the Binary Complexes of Cu(II) and *AMP*, *ADP* or *ATP*

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Summary. Potentiometric equilibrium measurements have been made at 25 ± 0.1 °C ($\mu = 0.1$ mol dm^{-3} KNO_3) for the interaction of adenosine-5′-mono-, -di- and -triphosphate (*AMP*, *ADP* and *ATP*) and Cu(II) with biologically important secondary ligand acids (malic, maleic, succinic, tartaric, citric and oxalic acids) in a 1:1:1 ratio and the formation of various 1:1:1 mixed ligand complex species inferred from the potentiometric *pH* titration curves. Initial estimates of the formation constants of the resulting species and the acid dissociation constants of *AMP*, *ADP*, *ATP*, and secondary ligand acid, have been refined with the SUPERQUAD computer program. In some systems $\Delta \log K$ values are positive, i.e. the ternary complexes are found to be more stable than the corresponding binary complexes. In some Cu(II) ternary systems the interligand interactions between the coordinate ligands, possibly H bond formation, have been found to be most effective in deciding the stability of the ternary complexes formed in solution. Stabilities of mixed ligand complexes increase in the order *AMP* < *ADP* < *ATP*. With respect to the secondary ligands, the formation constants of the mixed ligand complexes decrease in the order succinic > maleic > tartaric > malic > citric > oxalic acid.

Keywords. Cu(II) complexes; Polybasic oxygen acids; Ribonucleotides; Potentiometry.

Ternäre Komplexe in Lösung. Vergleich der Koordinationstendenz einiger polybasischer Sauerstoffsäuren gegenüber binären Komplexen von Cu(II) mit *AMP*, *ADP* oder *ATP*

Zusammenfassung. Es wurden potentiometrische Gleichgewichtsmessungen bei 25 ± 0.1 °C bei $\mu = 0.1$ mol dm^{-1} KNO_3 durchgeführt, um die Wechselwirkung von Adenosin-5′-mono-, -di- und triphosphat mit Cu(II) und biologisch relevanten Sekundärliganden wie Äpfel-, Malein-, Bernstein-, Wein-, Zitronen- und Oxalsäure im Verhältnis 1:1:1 festzustellen. Aus den potentiometrischen *pH*-Titrationskurven ergaben sich verschiedene 1:1:1 gemischte Ligandenkomplexe. Anfänglich abgeschätzte Komplexbildungskonstanten der Komplexe und Säuredissoziationskonstanten von *AMP*, *ADP* und *ATP* und den Sauerstoffsäuren wurden mittels des Computerprogramms SUPERQUAD verfeinert. In einigen Systemen ist $\Delta \log K$ positiv, demzufolge sind die ternären Komplexe stabiler als die korrespondierenden binären. In einigen ternären Cu(II)-Komplexen bestehen zwischen den Liganden Wechselwirkungen, vermutlich auf der Basis von stabilitätsfördernden Wasserstoffbrückenbindungen. Die Stabilitäten der gemischten Komplexe steigen in der Reihenfolge *AMP* < *ADP* < *ATP*. Bezüglich der Sekundärliganden ergibt sich für die Bildungskonstanten der

ternären Komplexe die Reihung Bersteinsäure > Maleinsäure > Weinsäure > Äpfelsäure > Zitronensäure > Oxalsaure.

Introduction

Metal ion complex formations are among the prominent interactions in nature [1–3] and the polybasic oxygen acid residues are important metabolic intermediates in biological systems, while ribonucleotides adenosine-5′-mono-, -di- and -triphosphates (*AMP*, *ADP*, and *ATP*) are equally important as substrates for many enzymic reactions [4–7]. Ternary complexes of transition divalent metal ions with *AMP*, *ADP*, and *ATP* and other secondary ligands viz. catechols, ethanolamines, 2,2′-bipyridyl, ethylene diamine, pyrocatecholate, biogenic amines, 1,10-phenanthroline, tyrosine, phenylalanine, glycine, histidine, imidazole, amonia, and aliphatic dipeptides have been investigated using several techniques [8–22] (*pH*-potentiometric, spectrophotometric and calorimetric). For an improved understanding of the driving forces leading to mixed ligand complexes of the type Cu(II)-nucleotide-polybasic carboxylic acids [Cu(II)–*NU*–*CA*], where nucleotide = *AMP*, *ADP* or *ATP* and carboxylic acid = malic, maleic, succinic, tartaric, citric or oxalic acids, have been investigated by potentiometric *pH* titrations to determine the stability constants of the complexes formed, as these systems mimic many biological reactions which may involve ribonucleotides-metal ion-metabolic intermediates interaction.

Experimental Part

Adenosine-5′-monophosphoric acid disodium salt $C_{10}H_{12}N_5Na_2O_7P \cdot H_2O$ ($Na_2AMP \cdot H_2O$), adenosine-5′-diphosphoric acid disodium salt $C_{10}H_{13}N_5Na_2O_{10}P_2 \cdot 2H_2O$ ($Na_2ADP \cdot 2H_2O$) and adenosine-5′-triphosphoric acid disodium salt $C_{10}H_{14}N_5Na_2O_{13}P_3 \cdot 3H_2O$ ($Na_2ATP \cdot 3H_2O$) were purchased from Sigma Chemical Co. and were used without purification. The amounts of free phosphates initially present in the nucleotides were determined [23]. To account for this and to prepare metal ion nucleotide solutions of exactly 1:1 ratio, we also determined the molecular weight of the purchased nucleotides by potentiometric *pH* titrations. $Cu(NO_3)_2 \cdot 6H_2O$, nitric acid, NaOH and organic carboxylic acids (malic, maleic, succinic, tartaric, citric and oxalic acids) were of p.a. grade. The concentration of NaOH used for the titrations was determined with potassium hydrogen phthalate (Merck AG). The concentrations of the metal ion stock solutions were determined with *EDTA*.

Potentiometric *pH* measurements were made on solutions in a double-walled glass vessel using a Beckman model 4500 digital *pH* meter with a precision of ± 0.1 mV. The potentiometric system was connected to a glass electrode (Metrohm 1028) connected against a double junction reference electrode (Orion 9020). The titrant was delivered by an Amel 882 dispenser, readable to 1 µl. The measurement-cell was kept at a temperature constant within ± 0.1 °C and a magnetic stirrer was used. Purified nitrogen was bubbled through the solutions during titrations.

The test solution was titrated with standard CO_2-free potassium hydroxide. The electrodes were calibrated, in both the acidic and alkaline regions, by titrating 0.01 mol dm^{-3} nitric acid with standard potassium hydroxide under the same experimental conditions. Carbonate free KOH was standardized against standard potassium hydrogen phthalate by using a Gran plot.

The concentration of free hydrogen ion h, at each point of the titration is related to the measured emf, $E°$ of the cell by the Nernst equation:

$$E = E° + Q \log h, \tag{1}$$

where E° is a constant including the standard potential of the glass electrode, and Q is the slope of the glass electrode response. The value of E° for the electrode was determined from a Gran plot derived from a separate titration, using measurements in volts, of nitric acid with standard KOH solution under the same temperature and medium conditions as for the test solution titration. The data so obtained were analyzed by the non-linear least-squares computer program ESAB2M [24] to refine E° and the autoprotolysis constant of water, K_W.

In order to avoid hydrolysis prior to potentiometric measurements, samples of the nucleotides were weighed out as the solid and added to the reaction vessel just prior to the performance of the titration. The solution titrated can be represented according to the following scheme:

HNO_3(a); HNO_3 + nucleotide(b); HNO_3 + nucleotide + Cu(II)(c); HNO_3 + polybasic carboxylic acid(d); HNO_3 + polybasic carboxylic acid + Cu(II)(e); HNO_3 + nucleotide + polybasic carboxylic acid + Cu(II)(f). A constant ionic strength was obtained with 0.1 mol dm^{-3} KNO_3 and the total volume was kept constant at 50 ml.

Results and Discussion

To calculate the initial estimates of the stability constants of the ternary complexes of Cu(II) with *AMP*, *ADP*, *ATP* and malic, maleic, succinic, tartaric or oxalic acid, the following equations were used:

$$\text{Cu(II)}(NU) + CA \rightleftharpoons \text{Cu(II)}(NU)(CA) \tag{2}$$

$$K^{\text{Cu(II)}(NU)}_{\text{Cu(II)}(NU)(CA)} = \frac{[\text{Cu(II)}(NU)(CA)]}{[\text{Cu(II)}(NU)][CA]} \tag{3}$$

[$\mu = 0.1$ mol dm^{-3} (KNO_3), 25 °C]

$$\text{Cu(II)} + NU \rightleftharpoons \text{Cu(II)}(NU) \tag{4}$$

$$K^{\text{Cu(II)}}_{\text{Cu(II)}(NU)} = \frac{[\text{Cu(II)}(NU)]}{[\text{Cu(II)}][NU]} \tag{5}$$

$$\text{Cu(II)} + CA \rightleftharpoons \text{Cu(II)}(CA) \tag{6}$$

$$K^{\text{Cu(II)}}_{\text{Cu(II)}(CA)} = \frac{[\text{Cu(II)}(CA)]}{[\text{Cu(II)}][CA]} \tag{7}$$

where CA = polybasic carboxylic acids (malic, maleic, succinic, tartaric, citric and oxalic acid), NU = nucleotide (*AMP*, *ADP*, and *ATP*).

It is assumed, for convenience, that complexation of the secondary ligand (CA) starts after the complete formation of the Cu(II)(NU) 1:1 complex. Thus, the overall stability constant $\beta^{\text{Cu(II)}}_{\text{Cu(II)}(NU)(CA)}$ may be represented by Eq. (8).

$$\text{Cu(II)} + NU + CA \rightleftharpoons \text{Cu(II)}(NU)(CA) \tag{8}$$

$$\beta^{\text{Cu(II)}}_{\text{Cu(II)}(NU)(CA)} = \frac{[\text{Cu(II)}(NU)(CA)]}{[\text{Cu(II)}][NU][CA]} = K^{\text{Cu(II)}(NU)}_{\text{Cu(II)}(NU)(CA)} \cdot K^{\text{Cu(II)}}_{\text{Cu(II)}(NU)} \tag{9}$$

Formation constants and protonation constants were refined with the SUPERQUAD computer program [25]. All the calculations were performed on a IBM XT 286 personal computer. The constants were refined by minimizing the error – square

sum, U, of the potentials:

$$U = \Sigma W_i \quad (E_{obs} - E_{calc})^2, \tag{10}$$

where E_{obs} and E_{calc} refer to the measured potential and that calculated from Eq. (1). The weighting factor W_i is defined as the reciprocal of the estimated variance of measurement

$$W_i = 1/\sigma^2 = 1/[\sigma^2 + (\delta E/\delta V)\sigma^2], \tag{11}$$

where σ_E and σ_V are the estimated variances of the potential and volume readings, respectively. The quality of fit was judged by the values of the sample standard deviation, S, and the goodness of fit, X^2, (Pearson's test). At $\sigma_E = 0.1$ mV (0.001 pH error) and $\sigma_V = 0.005$ ml, the values of S in different sets of titrations were between 1.0 and 1.8, and X^2 was between 12.0 and 13.0. The scatter of residuals $(E_{obs} - E_{calc})$ vs. pH was reasonably random, without any significant systematic trends, thus indicating a good fit of the experimental data.

At the experimental pH values used in the calculation in this work the interfering effects of hydroxo complexes are negligible. Thus the secondary ligand, CA, combine with the binary 1:1 Cu(II)(NU) {[Cu(II)(AMP)], [Cu(II)(ADP)$^{-1}$] and [Cu(II)(ATP)]$^{2-}$} complex in a similar manner of its interaction with aquated metal ions $[Cu(H_2O)_6]^{2+}$ in solutions. Thus the initial estimates of the stability constants of the ternary complexes formed in solution have been determined using the Rossotti and Irving formula [26]. These values were then refined using the SUPERQUAD computer program [25]. The determined acidity constants of malic, maleic, succinic, tartaric, citric, and oxalic acids and the stability constants of their binary Cu(II) complexes are in a good agreement with those found in literature [27, 28]. The two acid formation constants values for AMP, ADP, and ATP and the stability constants of their Cu(II) complexes were determined from the titration curves and the results were found to cope much with those reported in Ref. [27, 29–31].

Early workers [32–35] found pKa_1 values of 3.5–4.2 to be associated with proton ionization from the protonated forms of AMP, ADP and ATP. By analogy with aniline (protonated aniline, $pK = 4.6$) [36], it was stated by them and later workers [37, 38] that ionization is from the $C_6NH_3^+$ group. The second proton ionization was attributed to the phosphate groups.

The purine bases have two high electron density centers which are possible sites for metal ion chelation, viz. C_6NH_2/N_7 and N_3–N_9. Chelation of Cu^{2+} by both sites has been suggested [39–42].

Potentiometric [43, 44], ^{31}P NMR [43, 45] and aqueous solution infrared absorption data [45] confirm the binding of Cu^{2+} to the phosphate portion of AMP, ADP, and ATP. These studies are in essential agreement that Cu^{2+} binds the available phosphate group in the mono- and dinucleotides but only the α- and β-phosphates in ATP. This latter behaviour has been attributed to the square-planar stereochemical requirements of Cu^{2+}.

Based on the observed lack of reaction (from pH titration data) between Cu^{2+} and adenosine and the increased stability of Cu^{2+} complexes in the order $AMP < ADP < ATP$, the suggestion was made that Cu^{2+} did not react with the base moiety of ATP [44]. However, proton NMR studies have demonstrated binding of Cu^{2+} to the N_7 positions of the adenine base in AMP [43].

Berger and Eichhorn [47] conclude that, in general, Cu^{2+} can bind to multiple sites on the adenine base, with preference for a given site influenced by molecular associations which in the different *AMP* isomers is governed by the position of the phosphate on the ribose. In the case of 2′-*AMP* a chelate involving N_3 and a phosphate group of the same molecule is proposed. It is expected that Cu^{2+} ions would interact more strongly with the electron donor groups of the purine base of mononucleotides than they do with the phosphate groups.

Differences in the nature of binding sites for Cu^{2+} ions on purine nucleotides have been characterized by different g values and hyperfine splittings, as measured by the EPR spectra of the complexes formed under conditions close to physiological ones [48]. Thus, there is lack of agreement as to the assignment of the site of coordination. Our opinion in this point will be discussed later.

In Figs. 1–3 representative set of experimental titration curves obtained according to the sequence described in the experimental section for the different Cu(II)–*NU*–*CA* systems are displayed. It is observed that the Cu(II)–*NU* titration curves (c) diverges from the nucleotide curve (b) in the lower *pH* range ($pH \simeq 3.5$) denoting the formation of a Cu(II)–*NU* complex. Generally, the complex titration curves show an inflection after addition of two moles of base per one mole of the

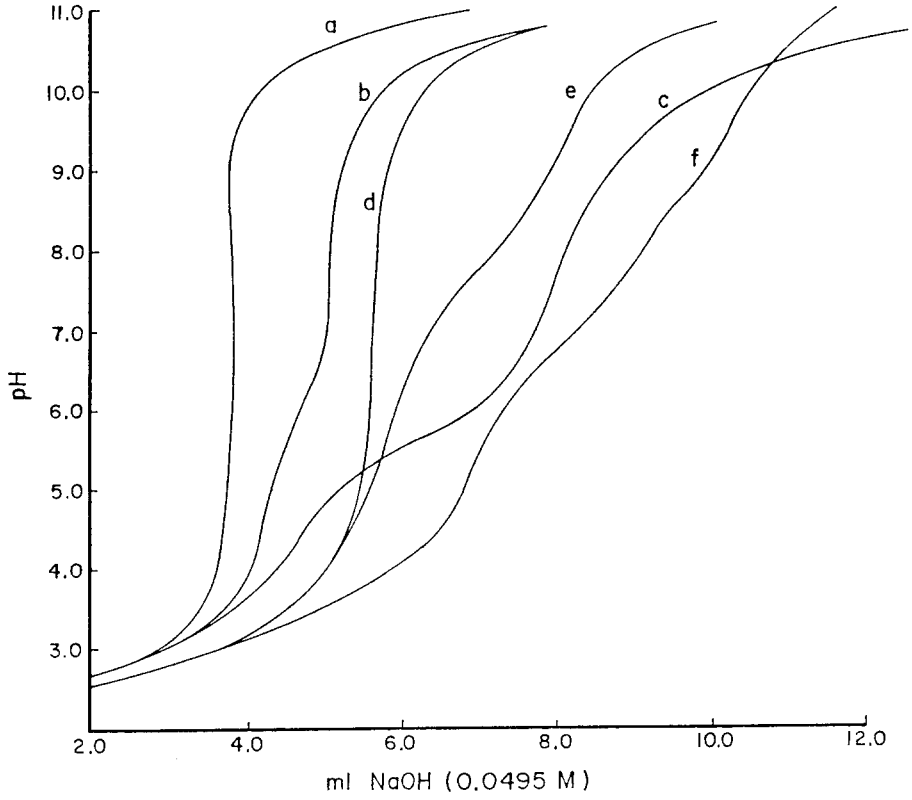

Fig. 1. Potentiometric titration curves for Cu(II)–*AMP*–oxalic acid system at 25 °C and $\mu = 0.1\,M$ KNO_3: (a) $0.0037\,M$ HNO_3; (b) solution (a) $+ 1 \times 10^{-3}\,M$ *AMP*; (c) solution (b) $+ 1 \times 10^{-3}\,M$ Cu(II); (d) solution (a) $+ 1 \times 10^{-3}\,M$ oxalic acid; (e) solution (d) $+ 1 \times 10^{-3}\,M$ Cu(II); (f) solution (e) $+ 1 \times 10^{-3}\,M$ *AMP*

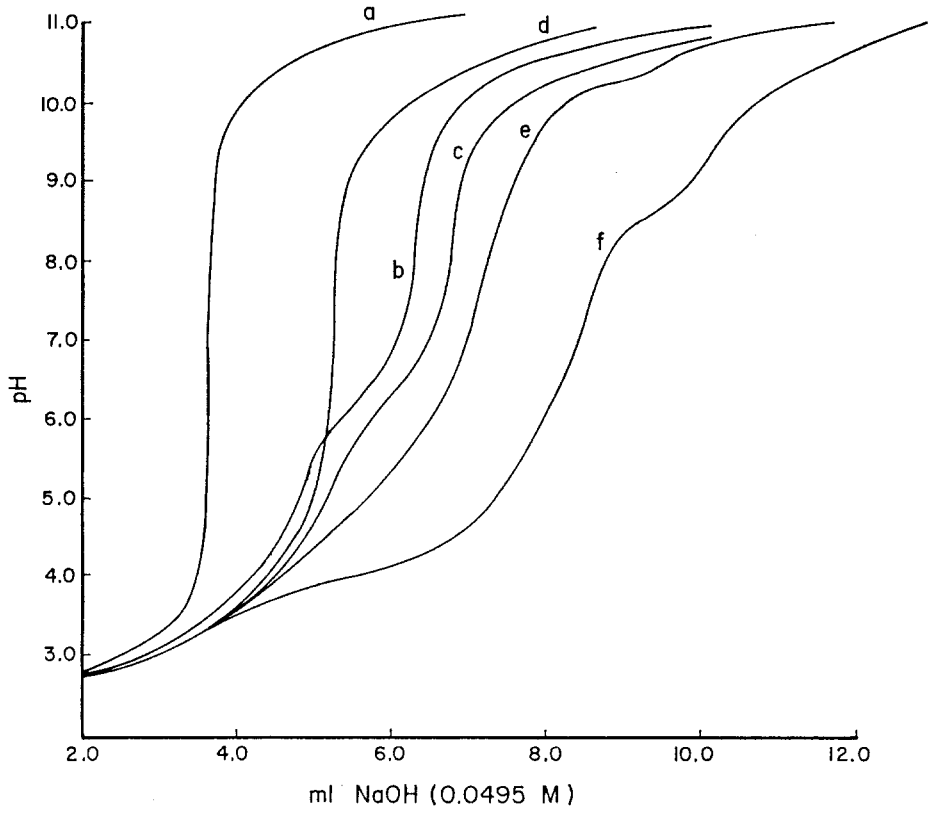

Fig. 2. Potentiometric titration curves for Cu(II)–*ADP*–malic acid system at 25 °C and $\mu = 0.1\ M$ KNO_3: (a) 0.0037 *M* HNO_3; (b) solution (a) + $1 \times 10^{-3}\ M$ *AMP*; (c) solution (b) + $1 \times 10^{-3}\ M$ Cu(II); (d) solution (a) + $1 \times 10^{-3}\ M$ malic acid; (e) solution (d) + $1 \times 10^{-3}\ M$ Cu(II); (f) solution (e) + $1 \times 10^{-3}\ M$ *ADP*

nucleotide. This indicates the simultaneous dissociation of two protons from the nucleotide. Cu(II)–*NU* are quite stable up to high *pH* values, i.e. have no tendency to form hydroxo complexes. With respect to the titration curves of the Cu(II) carboxylic acids binary complex solutions, one may deduce that these complexes begin to form at $pH > 4.0$. Generally, for all Cu(II) carboxylic acids complexes studied precipitation occurred at *pH*'s > 10.5. In all cases no calculations have been performed beyond the precipitation point, hence the hydroxospecies likely to be formed after this point could not be studied.

For the titration curves of the ternary systems Cu(II)–*NU*–*CA* one observes that the (C, F) are well separated at *pH* 4.3. This behaviour reveals that in these *pH* ranges coordination of the secondary ligand, carboxylic acid, with Cu(II)–*NU* starts.

Examination of the different formation constants values listed in Table 1 clearly reveals that the formation constant of the mixed ligand complexes increases in the order $AMP < ADP < ATP$. Though many studies in solution favoured the phosphate group rather than the base as the primary metal binding site, the simultaneous binding of Cu(II) ion to base moiety and phosphate may be reported in the mixed ligand complexes formed in the present work. Thus the Cu(II) bound

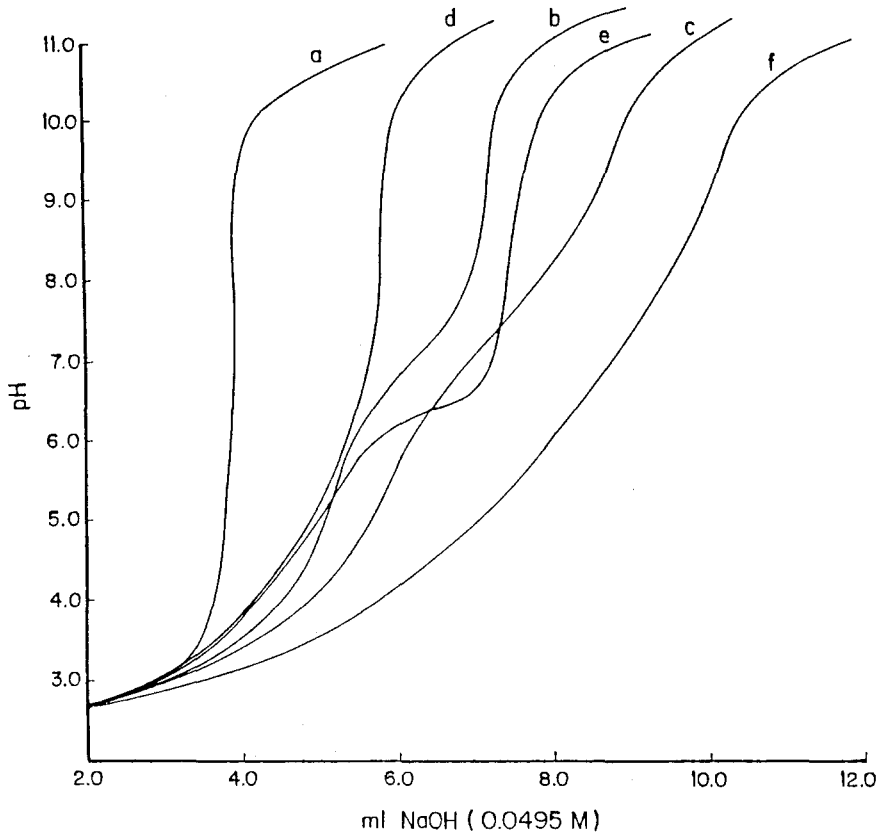

Fig. 3. Potentiometric titration curves for Cu(II)–*ATP*–succinic acid system at 25 °C and $\mu = 0.1\ M$ KNO_3: (a) 0.0037 *M* HNO_3; (b) solution (a) + $1 \times 10^{-3}\ M$ *ATP*; (c) solution (b) + $1 \times 10^{-3}\ M$ Cu(II); (d) solution (a) + $1 \times 10^{-3}\ M$ succinic acid; (e) solution (d) + $1 \times 10^{-3}\ M$ Cu(II); (f) solution (e) + $1 \times 10^{-3}\ M$ *ATP*

to the base moiety may promote intra-molecular base-phosphate interaction. Thus, the mixed ligand studied may be considered as relatively simple models from which information may be gained about the properties of nucleotides and their base moieties regarding the strength of their interactions with the important metabolic intermediates (polybasic oxygen acids) and even insight into the factors which influence this strength is thus becoming available.

With respect to the secondary ligands, the formation constants of the mixed ligand complexes decrease in the following order: succinic > maleic > tartaric > malic > citric > oxalic. This behavior can be interpreted in terms of the basicities ($\Sigma pKa_1 + pKa_2$) of the secondary ligand carboxylic acids used. It is well known that the increases in basicity of a ligand increases the stability of its metal complexes.

$\Delta \log K$, defined by Eq. (12), is a measure of the stability of the ternary complexes with respect to the binary complexes,

$$\Delta \log K = \log K^{\mathrm{Cu(II)}(NU)}_{\mathrm{Cu(II)}(NU)(CA)} - \log K^{\mathrm{Cu(II)}}_{\mathrm{Cu(II)}(NU)} \tag{12}$$

In the case of Cu(II)–*NU*–*CA* systems, $\Delta \log K$ is found to be slightly positive or

Table 1. Formation constant values for the binary Cu(II)-nucleotide or -carboxylic acid complexes and those for the mixed ligand complexes Cu(II)-nucleotide-carboxylic acid at 25 °C and $\mu = 0.1$ mol dm^{-3} KNO_3

Ligand	$\log K^{Cu(II)}_{Cu(II)(Nucleotide)}$ or $\log K^{Cu(II)}_{Cu(II)(CA)}$	$\log K^{Cu(II)(AMP)}_{Cu(II)(AMP)(CA)}$	$\log K^{Cu(II)(ADP)}_{Cu(II)(ADP)(CA)}$	$\log K^{Cu(II)(ATP)}_{Cu(II)(ATP)(CA)}$	$\log \beta^{Cu(II)}_{Cu(II)(AMP)(CA)}$	$\log \beta^{Cu(II)}_{Cu(II)(ADP)(CA)}$	$\log \beta^{Cu(II)}_{Cu(II)(ATP)(CA)}$	$\Delta \log K_1$	$\Delta \log K_2$	$\Delta \log K_3$
AMP	5.402 ± 0.03	–	–	–	–	–	–	–	–	–
ADP	5.869 ± 0.03	–	–	–	–	–	–	–	–	–
ATP	6.080 ± 0.03	–	–	–	–	–	–	–	–	–
Oxalic acid	6.400 ± 0.02	6.169 ± 0.030	6.320 ± 0.03	7.068 ± 0.03	11.571	12.589	13.166	−0.231	−0.080	+0.686
Succinic acid	5.768 ± 0.03	5.740 ± 0.02	6.273 ± 0.04	6.723 ± 0.04	11.342	12.442	12.803	−0.028	+0.505	+0.955
Tartaric acid	4.992 ± 0.02	5.635 ± 0.04	6.138 ± 0.02	6.612 ± 0.04	11.237	12.207	12.692	+0.643	+0.503	+1.620
Malic acid	4.788 ± 0.02	5.552 ± 0.04	5.942 ± 0.03	6.363 ± 0.03	10.954	11.811	12.443	+0.764	+0.390	+1.575
Maleic acid	4.694 ± 0.04	5.326 ± 0.02	5.748 ± 0.03	6.282 ± 0.04	10.728	11.617	12.362	+0.632	+1.054	+1.588
Citric acid	4.532 ± 0.02	5.290 ± 0.03	5.520 ± 0.02	6.202 ± 0.04	10.692	11.389	12.282	+0.758	+0.988	+1.670

$\Delta \log K_1 = \log K^{Cu(II)(AMP)}_{Cu(II)(AMP)(CA)} - \log K^{Cu(II)}_{Cu(II)(CA)}$

$\Delta \log K_2 = \log K^{Cu(II)(ADP)}_{Cu(II)(ADP)(CA)} - \log K^{Cu(II)}_{Cu(II)(CA)}$

$\Delta \log K_3 = \log K^{Cu(II)(ATP)}_{Cu(II)(ATP)(CA)} - \log K^{Cu(II)}_{Cu(II)(CA)}$

negative (Table 1) in accordance with statistical expectations [49]. Some of the $\Delta \log K$ values for Cu(II)–*AMP–CA* systems are negative in accordance with statistical considerations [44] where the statistical, steric, and electrostatic factors result in a lower stability constant for the 1:1:1 metal/ligand complexes as compared with those for the binary systems. The higher stability constant of Cu(II)–*ATP–CA* ternary complexes compared with the binary systems may be attributed to the interligand interactions or some cooperativity between the coordinate ligands, possibly H-bond formation.

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